Molecular Switches Based on Dihydroazulene/Vinylheptafulvene Photochromism

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Contents

Abbreviations

a	absorption
abs.	absolute
br s	broad singlet
CAS	Chemical Abstracts
DDQ	4,5-dichloro-1,2-dicyanobenzoquinone
DHA	dihydroazulene
EtOAc	ethyl acetate
EI-MS	electron ionisation – mass spectrum
Φ	quantum yield
EtOH	ethanol
h	hour
HOMO	highest occupied molecular orbital
HRMS	high resolution mass spectrum
IR	Infrared spectroscopy/-spectrum
λ_{em}	emission wavelength
λ_{ex}	excitation wavelength
λ_{max}	absorption maximum
LDA	lifetime distribution analysis
LE	locally excited
LUMO	lowest unoccupied molecular orbital
M	molar
m.p.	melting point
MeOH	methanol
min.	minute
ms	millisecond
NMR	nuclear magnetic resonance-spectroscopy/-spectrum
PE	petrol ether 40/60
Ref.	reference
RT	room temperature
TFA	trifluoroacetic acid
TLC	thin layer chromatogram
TMS	tetramethylsilane
UV/vis	Ultraviolet /visible-spectroscopy/spectrum
VHF	vinylheptafulvene

1. Introduction

Modern society depends on an increasing demand and access of information, e.g. on the technology for handling, processing and storage of it. The modern computers are based on electronic devices (transistors). More powerful and faster computers are necessary to handle the increasing volumes of information. Miniaturisation of computing chips has to be developed. It has been predicted by Gordon Moore in 1965 that the exponential growth in the number of transistors per integrated circuit and the number of devices per chip will doubling every 18-24 month.[1] But the physical limit will be reached in the next decade. In order to handle the increasing amount of data in the future non-electrical types are under discussion, among which are "photonic gates" computer systems or reaction-diffusion devices which are mimicking the organization in the brain. Molecular systems are the basic elements of each kind of information processing system.[2]

Molecular switches have at least two stable states that are reversibly interchangeable by photonic, electrochemical or thermal activation.[3,4] By definite external stimulus the molecule quantitatively transforms into another state. This stimulus depends on the structure of the molecule and could be an electron,[5] a proton,[6] an ion[7] or a photon, in case of a photochromic switch. An output or a signal, response from the switching molecule, can be fluorescence,[8] phosphorescence, change of absorption, redox potential, circular dichroism, charge transfer, or polymer conductivity.[9]

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[1] G.E. Moore, *Electronics*, **1965**, 38, 114-17.

[2] K.-P. Zauner, *Crit. Rev. in Sol. St. and Mat. Sc*., **2005**, 30, 33-69.

[3] a) *Molecular Switches*; B.L. Feringa, Ed.; Wiley-VCH: Weinheim, **2001**;

b) Photochromism: Memories and Switches, Special issue of *Chem. Rev*., **2000**, *100*, 1683-1890.

[4] a) F.M. Raymo, *Adv. Mater*., **2002**, 14, 401;

b) F.M. Raymo, M. Tomasulo, *Chem. Soc. Rev.,* 34, **2005**, 327-336.

[5] a) Y.-Y. Luk, N.L. Abbott, *Science*, **2003**, 301, 623-6;

b) H. Tseng, S.A. Vignon, P.C. Celestre, J. Perkins, J.O. Jeppesen. A. Di Fabio, R. Ballardini, M.T. Gandolfi, M. Venturi, V. Balzani, J.F. Stoddart, *Chem. Eur. J.*, **2004**, 10, 155-172.

[6] a) X. Guo, D. Zhang, D. Zhu, *Adv. Mater.* **2004**, 16, 125-130;

b) K. Rurack, M. Kollmannsberger, J. Daub, *Angew. Chem. Int. Ed.* **2001**, 40, 385-387.

[7] K. Rurack, A. Koval'chuck, J.L. Bricks, J.L. Slominskii, *J. Am. Chem. Soc*., **2001**, 123, 6205-06.

[8] K. Rurack, *Spectrochimica Acta Part A*, 57, **2001**, 2161-2195.

[9] a) J. Daub, C. Fischer, J. Salbeck, K. Ulrich, *Adv. Mater*. **1990**, 8, 266;

b) J. Daub, M. Beck, A. Knorr, U. Spreitzer, *Pure Appl. Chem*. **1996**, 68 (7), 1399;

c) N. Robertson, C.A. McGowan, *Chem. Soc. Rev*., **2003**, 32, 96-103.

The range of application of these molecules might be quite wide: from the optical storage systems, that are already widely used by almost every computer user and not yet well developed molecular logical schemes for biological and medicine purposes (drug delivery systems,[10] biosensors). Some of optical molecular switches are based on the photochromic dyes that are well known from Nature; some are based on new principles.

1.1 Photochromism in Nature

Solar light is the key factor for the growth and development of living organisms. Incoming solar energy is transformed into chemical energy or is the signal mediator for sensory processes. One of the most significant processes is the process of vision.[11] On Earth, the ambient light, provided by the Sun is crucial for competition and surviving not only for plants and phototrophic organisms, but even for insects and mammals (e.g. circadian clock circuits).[12]

Rhodopsin is a protein in the membrane of the photoreceptor cell in the retina of the eye. The 11-*cis*-retinal chromophore lies in a pocket of the protein and is isomerized to all-*trans* retinal when light is absorbed, Scheme 1.1. The isomerisation of retinal leads to a change of the shape of rhodopsin which triggers a cascade of reactions leading to a nerve impulse which is transmitted to the brain by the optical nerve. The chromophore, rhodopsin, is bounded to a protein via a lysine through a protonated Schiff base, Scheme 1.1.

c) H. Spreitzer, J. Daub, *Liebigs Ann.* **1995**, 1637-1641.

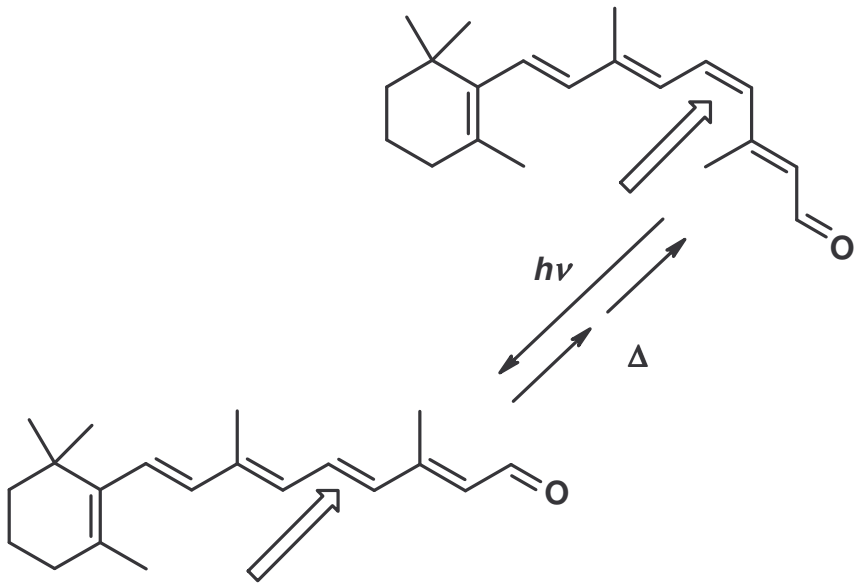
d) H. Spreitzer, J. Daub, *Chem. Eur. J*. **1996**, 2 (9), 1150.

e) L. Gobbi, P. Seiler, F. Diederich, V. Gramlich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **2001**, 84, 743-777.

[10] N.S. Bodor, *Chemical Aspects of Drug Delivery Systems;* D.R. Karsa, R.A. Stephenson, Eds; Royal Society of Chemistry: London, **1996**.

[11] R.R. Rando, *Angew. Chem*. **1990**, 102, 507-526.

[12] K.J. Hellingwerf, *J. Photochem. Photobiol. B: Biol*. 54, **2000**, 94-102.



Scheme 1.1: Retinal, the chromophore of rhodopsin protein.[13]

The control of plant development by light, independent of photogenesis is called *photomorphogenesis.* There are diverse photomorphogenetic responses such as the synthesis of chlorophyll, the transport of sucrose and many others.[14] The signals for photomorphogenetic have in common that initiation occurs at one wavelength and may be inhibited by another one. The photoreversibility is found to be due to phytochrome[15, 16] a molecule isolated from higher plants. Phytochrome is a biliprotein, the chromophore absorbing light is a single open-chain conjugated tetrapyrrole, called phytochromobilin. The physiologically inactive form of the phytochrome (P_r) under red light changes configuration (isomerization around the C_{15}-C_{16} bond occurs)[17]; so that the physiologically active form P_{fr} is formed, Scheme 1.2. This form isomerises into original by irradiation in near-IR range.

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[13] Here and later the arrow shows the bond which is isomerising.

[14] a) W. Haupt, *Phil. Trans. R. Soc. Lond.*, B 303, **1983**, 476;

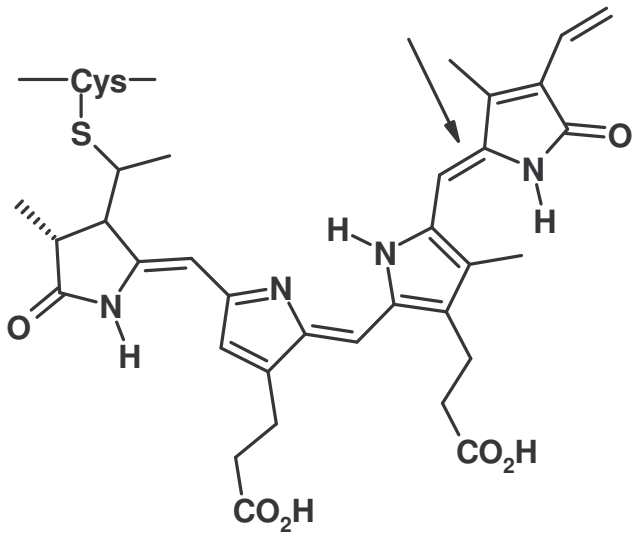
b) H. Senger, W. Schmidt in R.E. Kendrick and G.H.M. Kronenberg (Eds.), *Photomorphogenesis in Plants*, Nijhoff, Dordrecht, **1986**, 137-183.

[15] a) S.E. Braslavsky, *Phytochrome* in *Photochromism: Molecules and Systems*, H. Dürr, H. Bouas-Laurent, Elsevier, New York, **1990**, 738-755.

[16] a) M. Ni, J.M. Tepperman, P.H. Quail, *Nature* **1999**, 400, 781-784;

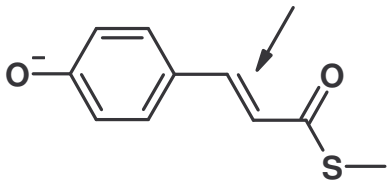
b) P.H. Quail, M.T. Boylan, B.M. Parks, T.W. Short, Y. Xu, D. Wagner, *Science*, **1995**, 268, 675-680.

[17] G.H.M. Kroneneberg and R.E. Kkendrick in R.E. Kkendrick and G.H.M. Kroneneberg (Eds.), *Photomorphogenesis in Plants,* Nijhoff, Dordrecht, **1986**, 99-114.



Scheme 1.2: Structure of the Pr form of phytochromobilin (The arrow shows the double bond (C_{15}-C_{16}) which is isomerising upon irradiation).

Other example of photochromic protein is the Photoactive Yellow Protein (PYP). PYP is the primary photoreceptor for the negative phototactic response of *Halorhodospira halophila*. Blue light induces a *trans*-to-*cis* isomerization of a double bond in the covalently bound *p*-coumaric acid chromophore, Scheme 1.3. In the resulting metastable state, a change in the protonation state of the chromophore triggers major conformational changes in the protein which give rise to signal transduction.[18]



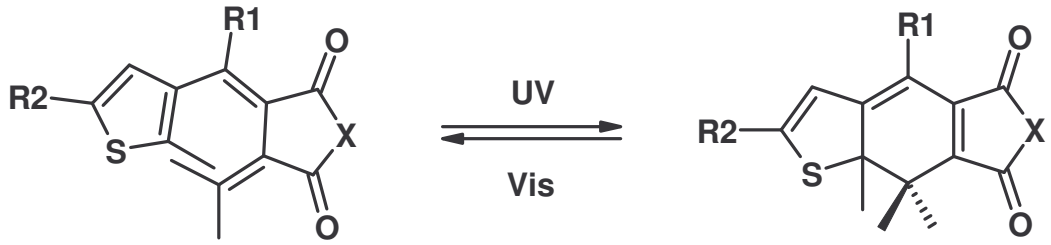
Scheme 1.3: Chromophore of PYP: p-coumaric acid derivative.

[18] G. Groenhof, M. Bouxin-Cademartory, B. Hess, S.P. de Visser, H. J. C. Berendsen, M. Olivucci, A. E. Mark and M.A. Robb, *J. Am. Chem. Soc.,* **2004**, 126, 4228-33.

1.2 Artificial molecular switches

Not only nature based photochromic systems are known but artificial as well. Several examples of such systems are shown. For example well-known diarylethenes,[19] fulgides or *cis – trans* isomerization of azobenzene.[20] Many of these systems have been studied and used for developing of molecular devices.

Fulgides[21] (bismethylenesuccinic anhydrides) have at least one annulated aromatic ring, Scheme 1.4. They were synthesised first by Stobbe.[22] Upon irradiation colourless (or slightly coloured) isomer of fulgide that incorporates a 1,3,5 – hexatriene moiety, transforms by electrocyclic reaction into an isomer with deep colour. The process obeys the Woodward–Hoffmann rules and the rearrangement occurs in the conrotatory way.



Scheme 1.4: Fulgides.

[19] M. Irie (Guest Ed.), *Chem. Rev., Photochromism: Memories and Switches* **2000**, 100, 1683-1890.

[20] B. L. Feringa, R. A. van Delden, N. Koumura and E. M. Geertsema, *Chem. Rev*. **2000**, 100, 1789-1816.

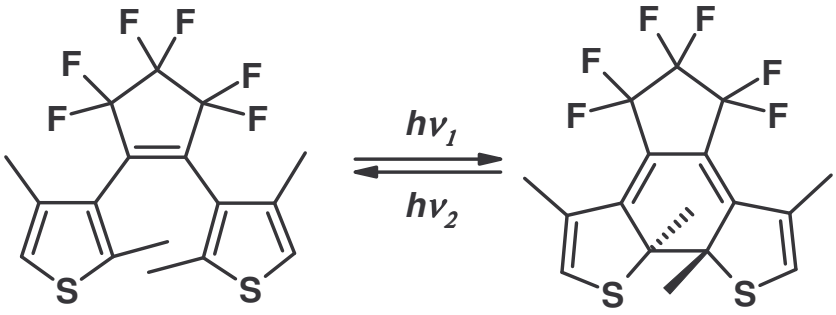
[21] J. Whittall in *Photochromism: Molecules and Systems*; (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **1990**, 467-92.

[22] a) H. Stobbe, *Ber*. **1905**, 38, 3673-82;

b) H. Stobbe, *Ann*. **1911**, 380, 1-129;

c) H. Stobbe, *Ber*. **1905**, 40, 3372-82.

Dithienylethene (DTE) / dihydrothienobenzothiophene (DHB) photochromism is established by two photochemical reactions and represents a six-electron rearrangement.[23] A reversible pericyclic reaction can take place in these compounds as irradiation with UV light of the colourless open form leads to the closed (coloured) form, which can undergo ring-opening again with visible light, Scheme 1.5.[24] The conrotatory ring closure by irradiation of a symmetric dithienylethene generates the C2-symmetric closed forms (S,S)- and (R,R).[25] Upon ring-opening, the stereochemical information is however lost.



Scheme 1.5: Diarylethene photochromism

[23] a) M. Irie, K. Sayo, *J. Phys. Chem*, **1992**, 96, 7671.

b) M. Irie, *Pure Appl. Chem*. **1996**, 68, 1367.

c) M. Irie, K. Sakemura, M. Okinaka, K. Uchida, *J. Org. Chem*. **1995**, 60, 8305;

d) M. Irie, T. Eriguchi, T. Takada, K. Uchida, *Tetrahedron* **1997**, 53, 12 263;

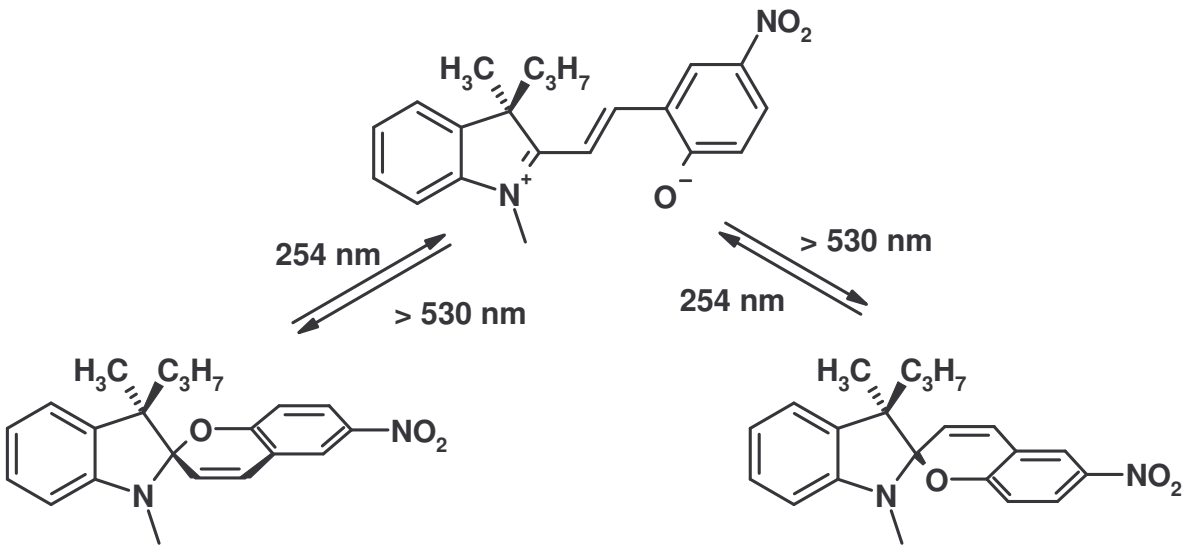
e) M. Irie, K. Uchida, *Bull. Chem. Soc. Jpn*. **1998**, 71, 985.

[24] a) M. Irie, S. Nakamura, *J. Org. Chem*. **1988**, 53, 6136;

b) O. Miyatake, K. Uchida, T. Eriguchi, *J. Am. Chem. Soc.* **1994**, 116, 9894.

[25] T. Yamaguchi, K. Uchida, M. Irie, *J. Am. Chem. Soc*. **1997**, 119, 6066.

The photochromic (and thermochromic) behaviour of spiropyrans is due to the interconversion of the closed spiropyran form and the open merocyanine dye, Scheme 1.6.[26] Hirshberg proposed that the photochromism of spiropyrans could form the basis for a photochemical[27] memory device. UV irradiation leads to the open form, which reverts to the closed form either thermally or by irradiation with visible light. The spiro carbon atom is a stereogenic centre in the spiropyrans, but as a consequence of the achiral nature of the merocyanine form, the photochromic process will always lead to racemization. When a chiral substituent remote from the spiro centre was present, diastereoisomers of spiropyrans could be isolated.



Scheme 1.6: Spiropyrans

Chiroptical switches are based on so-called sterically overcrowded alkenes, Scheme 1.7.[28] The molecules consist of an unsymmetrical upper part (tetrahydrophenanthrene or 2,3-dihydronaphtho-

[26] a) R.C. Bertelson In *Photochromism in Techniques in Chemistry*; G.H. Brown, Ed.; Wiley-Interscience: New York, **1971**; Vol. 3, Chapter 3;

b) L. Eggers, V. Bush, *Angew. Chem. Int. Ed. Engl.*, **1997**, 36, 881;

c) A. Miyashita, A. Iwamoto, T. Kuwayama, H. Shitara, Y. Aoki, M. Hirano, H. Nohira, *Chem. Lett.,* **1997**, 965;

d) V.I. Minkin, *Chem. Rev.* **2004,** *104,* 2751-2776.

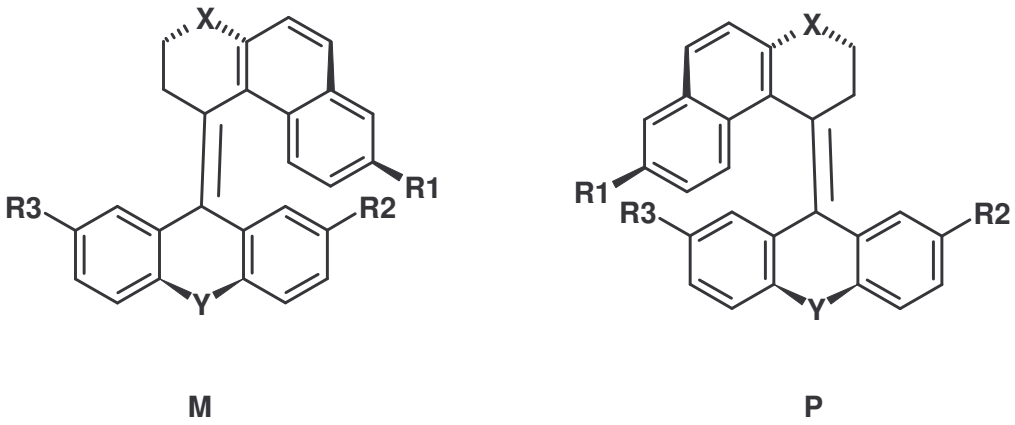
[27] a)Y. Hirshberg, *J.Am.Chem.Soc*. **1956**, 78, 2304;

b) Y. Hirshberg, *New Scientist,* **1960**, 7, 1243.

[28] a) B.L. Feringa, N.P.M. Huck, A.M. Schoevaars, *Adv. Mater*.**1996**, 8, 681;

b) J. Sandstrom, In *Topics in Stereochemistry*; N.L. Allinger, E.L. Eliel, S.H. Wilen, Eds.; Wiley: New York, **1983**; 14, 160.

thiopyran) connected via a double bond to a symmetric (or unsymmetrical, depends on substituents) lower part (xanthene, thioxanthene, fluorene). To avoid unfavourable sterical interactions around the central olefinic bond, the molecules are forced to adopt a helical shape. The chirality in these inherently dissymmetric alkenes denoted M and P for left and right-handed helices respectively.



Scheme 1.7: Overcrowded alkenes.

The tetrahydrophenanthrene-type upper part is bulky enough to inhibit fast racemization by movement of the aromatic moieties of the upper and lower halves through the mean plane of the molecules, but there is sufficient conformational flexibility in the upper and lower halves to prevent excessive distortion of the central olefinic bond[29], which could lead to rapid racemization.

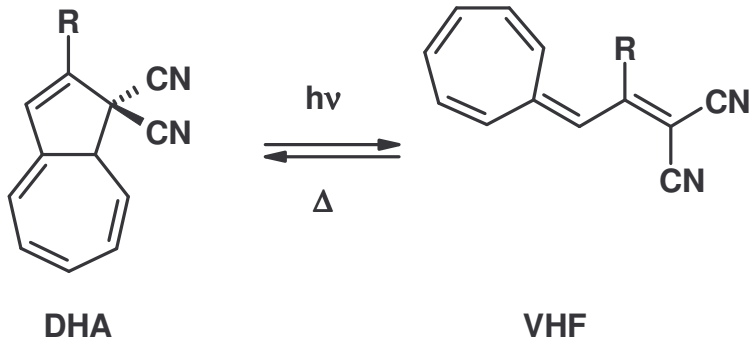
[29] a) B.L. Feringa, H. Wynberg, *J. Am. Chem. Soc*. **1977**, 99, 602.

b) W.F. Jager, B. de Lange, A.M. Schoevaars, B.L. Feringa, *Tetrahedron: Asymmetry,* **1993**, 4, 1481.

1.3 Dihydroazulene/Vinylheptafulvene

1.3.1 Introduction to DHA/VHF photochromic system

DHA (dihydroazulene, closed form) under photoirradiation with UV light isomerizes through 10-electron retrocyclization to VHF (vinylheptafulvene, opened form). It is accompanied by a colour change from yellow to red (aryl-substituted derivatives). The photoinduced reaction of DHA to VHF and subsequent thermal back reaction (VHF → DHA) has been reported for the first time in 1984,[30,31] Scheme 1.8. Dihydroazulene/vinylheptafulvene derivatives are a promising family of photochromic compounds to develop ultrafast molecular devices. They fulfil requirements such as a very high quantum yield of conversion, a large shift of the absorption band on going from DHA to VHF, and a singlet state strictly one-way photoreaction path allowing a high fatigue resistance that make them interesting to use for developing and studying molecular switches.[32]



Scheme 1.8: The photochromism of DHA/VHF system

The photochromism of 1,1-dicyano-2-(4-cyanophenyl)-1,8a-dihydroazulene (CN-DHA) derivative has been well studied.[33] After excitation around 360 nm in the S_0–S_1 absorption band, CN-DHA

[30] J. Daub, T. Knöchel, A. Mannschreck, *Angew. Chem*, **1984**, 96, 980-981.

[31] J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz, *Chem. Ber*. **1986**, 119, 2631.

[32] a)T. Mrozek, J. Daub, A. Ajayagosh, In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinhein, **2001**;
b) J. Daub, T. Mrozek, A. Ajayaghosh, *Mol. Cryst. Liq. Cryst*. **2000**, 344, 41-50.

[33] V. De Waele, U. Schmidhammer, T. Mrozek, J. Daub, E. Riedle, *J. Am. Chem. Soc*. **2002**, 124, 2438.

undergoes a photoconversion to the CN-VHF conformer[34], which absorbs around 480 nm, Scheme 1.9. X-ray analysis showed that the s-*trans* conformation of CN-VHF (CN-VHF-s-*trans*) identified as the stable photoproduct.[31] In the dark at room temperature CN-VHF-s-*trans* thermally converts to the CN-DHA form with half-life around one hour. The photochromism from DHA to s-*trans*-DHA involves two structural mechanisms: the first one is ring opening which leads to s-*cis*-VHF form and the second one is s-*cis* – s-*trans* isomerisation of VHF.[35] It has been shown that this isomerization is slower by several orders of magnitude than the ring opening itself.[33]

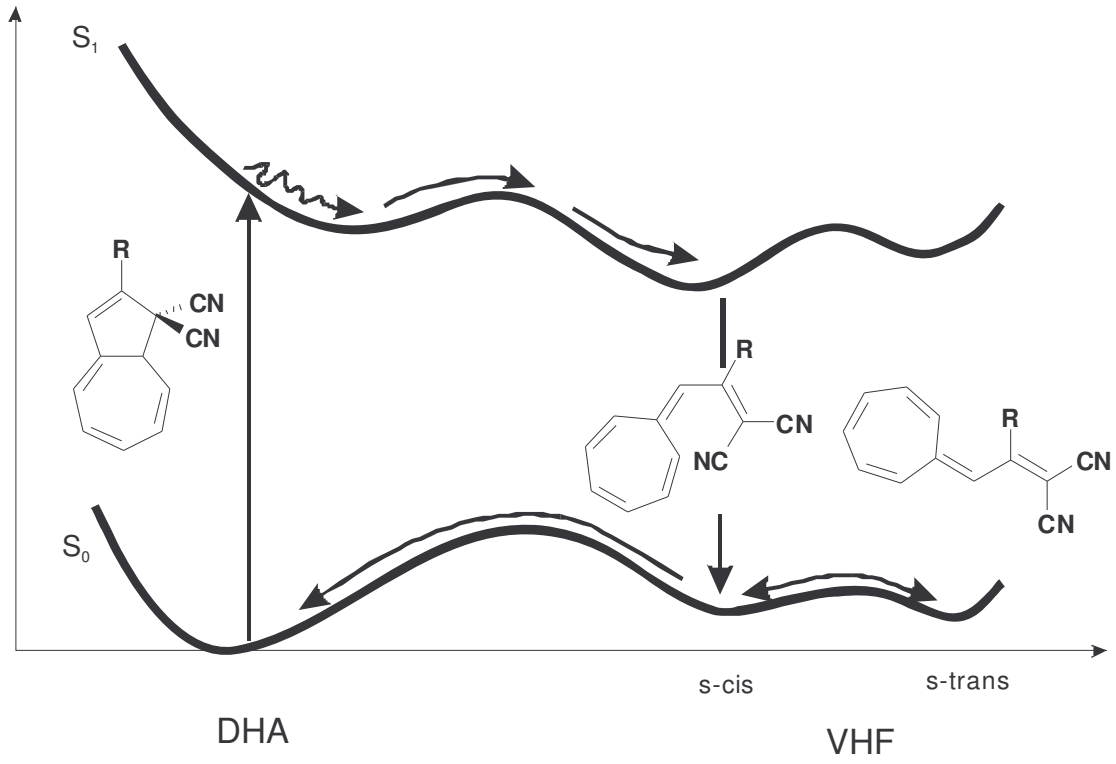


Figure 1.1: Schematic representation of the reaction profiles of the photochemical pathway DHA→VHF and the thermal pathway VHF→DHA.[32a]

Taking in account of the data from photophysical and photochemical investigations of switching behaviour of various DHA/VHF derivatives,[9c, 34, 36] a qualitative energetic profile of the DHA/VHF couple was depicted, Figure 1.1.

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[34] H. Görner, C. Fischer, S. Gierisch, J. Daub, *J. Phys. Chem.* **1993**, 97, 4110.

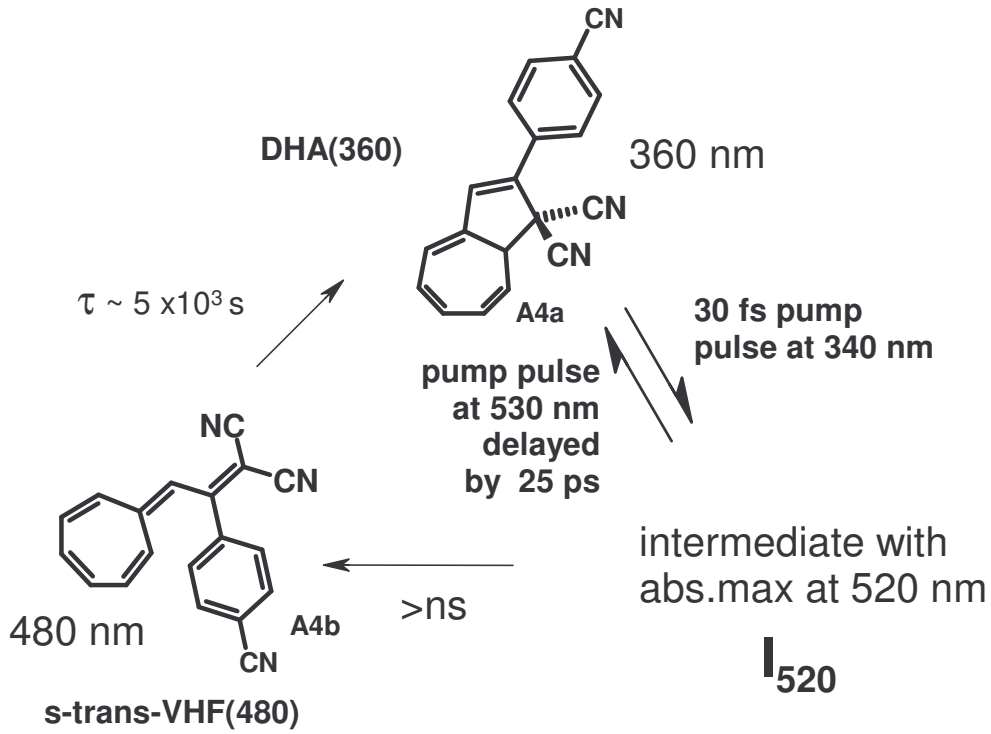
[35] s-*cis* and s-*trans* isomers are stereoisomers which differ in the stereochemistry of the exocyclic C–C single bond of the VHF form.

[36] a) H. Görner, C. Fischer, J. Daub, *J. Photochem. and Photobiol., A: Chemistry,* **1995**, 85, 217-124;

b) M. Komma, *Diploma-thesis*, University of Regensburg, **1996**.

Upon irradiation of DHA at around 360 nm ring in 1ps a strong absorption occurs between 485 and 568 nm with a time constant of 13 ps and decreases with the same time constant at 610 nm and above. As neither **A4a** and **A4b**-*s-trans* (see Scheme 1.9) nor **A4b**-*s-cis*[33] in the electronic ground state absorb at 610 nm or above nor do they emit in this spectral range after excitation at 360 nm. The time constant of 13 ps has been assigned to the internal conversion to the ground state **A4b**-*s-cis* which is then followed by the rearrangement to the final *trans*- conformer within 10 μs.[37,38]

In a two-pulse experiment the first pulse at 340 nm triggers the photoconversion of **A4a** while the second pump pulse at 530 nm delayed by 25 ps from the first pulse excited the **A4b**-*cis* isomer.[33] That experiment has shown in comparing with a one pulse experiment much less *s-trans*-VHF presented as product of photoreaction.



Scheme 1.9: Photochromism of dihydroazulene/vinylheptafulvene system A4.

Behaviour of the photochemical reaction strongly depends on the structure of system that has been shown by femtosecond-resolved transient absorption spectroscopy.[33,38] For the DHA → VHF photo process in case of **CP-DHA** the quantum yield of photoreaction is nearly unity.

[37] U. Schmidhammer, V. De Waele, G. Buntinx, E. Riedle, Springer Series in Chem. Phys., **2005**, 79, 465-467.

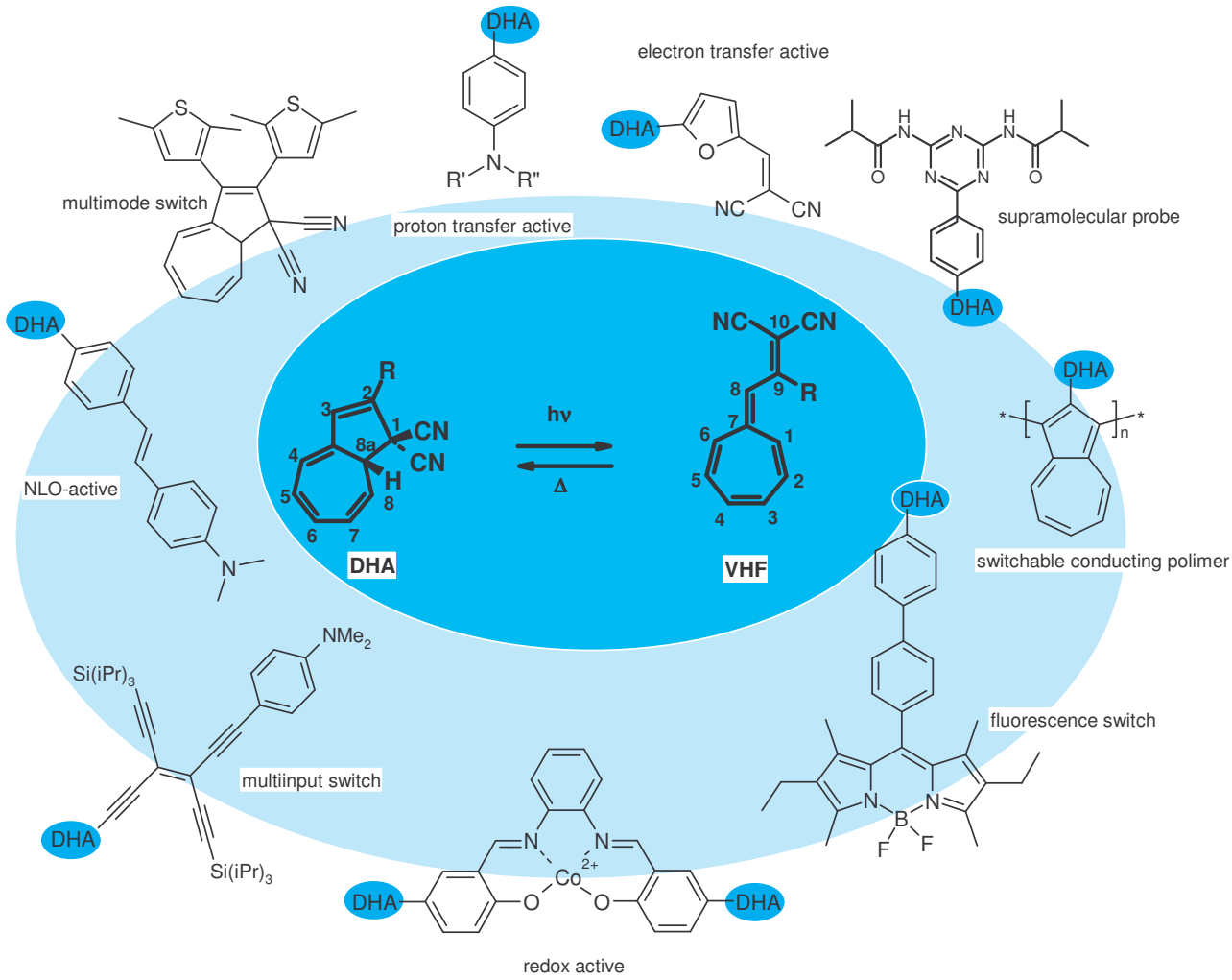
[38] V. De Waele, M. Beutter, U. Schmidhammer, E. Riedle, J. Daub, *Chem. Phys. Lett.* **2004,** 390, 328–334.

The speed of the thermal back reaction depends on solvent polarity (more polar – faster reaction) and the substitution of phenyl ring. Irradiation of DHA leads to a Frank-Condon state (^{1}DHA*) from that in 600 fs at RT the molecule transforms to VHF-*cis* and in ms range to VHF-*trans*.
DHAs are weakly fluorescent at room temperature and have quantum yields 0.15 – 0.9 in glass.[39] In the usual case (for example CN-DHA) the dominant photochemical process is the formation of the s-*trans*-VHF isomer. VHF exists as s-*trans* form in solid but in solution it transforms to the thermodynamically more stable DHA by a thermal process.

1.3.2 DHA/VHF based molecular switches

The photochemical ring opening from nearly colourless DHA to coloured VHF gives noticeable changes in the electronic structure of molecule. The alternant conjugated π-system of DHA converts in the non-alternant VHF system. The cyano groups come into conjugation with π-system of VHF. This influences the electronic properties of substituent at C-9 of VHF. This photochromic rearrangement which leads to the significant change in electronic structure of the system could be used for the photoswitching of various electronic properties (for example fluorescence, optical nonlinearity, redox potential, etc.), Scheme 1.10.

[39] J. Ern, M. Petermann, T. Mrozek, J. Daub, K. Kuldova, C. Kryschi, *Chem. Phys*. **2000**, 259, 331-337.



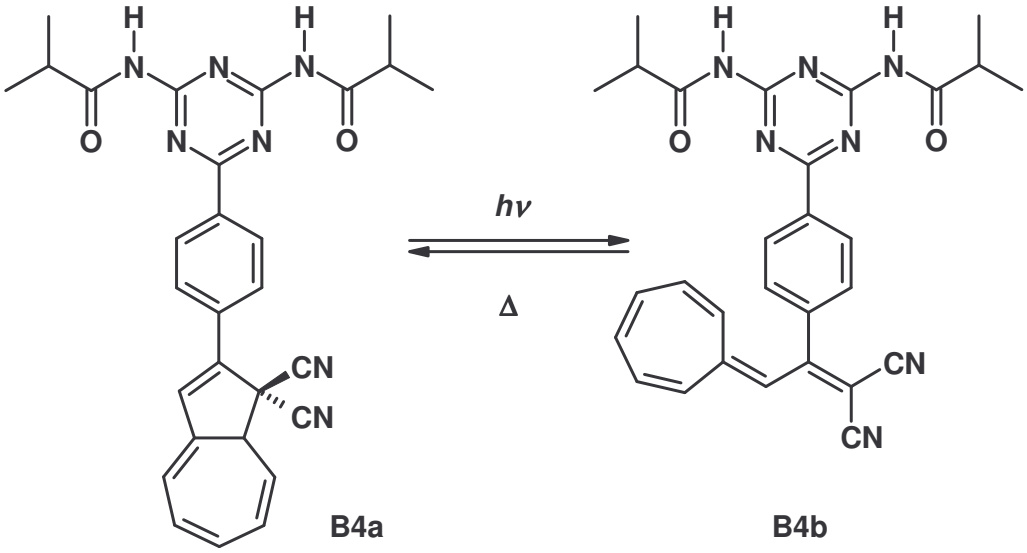
Scheme 1.10: examples of optoelectronic molecular switching systems based on DHA/VHF photochromism.

The diamidotriazine derivative of DHA, **B4** is interesting from the point of view of probing supramolecular interaction,[40] Scheme 1.11. The diamidotriazine moiety is complementary to uracil (A-D-A motif)[41] and creates three hydrogen bonds, Scheme 1.12.

[40] C. Trieflinger, *Dissertation*, University of Regensburg, **2004**.

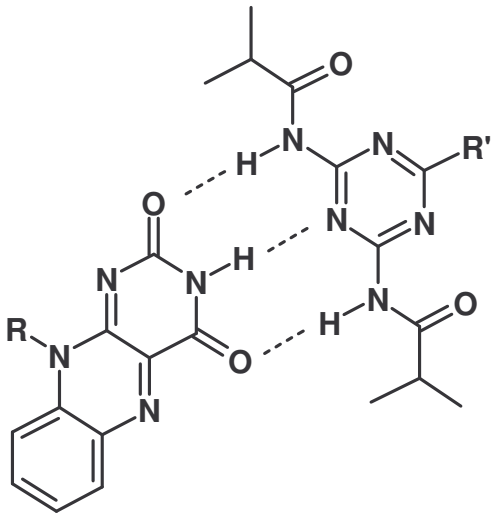
[41] a) A.O. Cuello, C.M. McIntosh, V. Rotello, *J. Am.Chem Soc*., **2000**, 123, 3517-3521;

b) E. Breinlinger, A. Niemz, V. Rotello, *J. Am.Chem Soc*., **1995**, 117, 5379-5380.



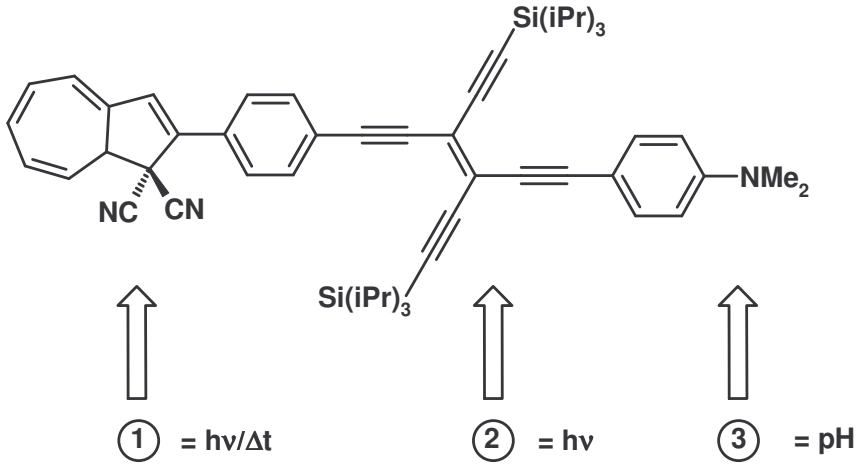
Scheme 1.11: Photochromism of dihydroazulene/ diamidotriazine system B4.

Changes in the electronic structure of molecule due to a photochromic rearrangement in case of **B4** should influence the complexing properties of the diamidotriazine moiety (Indeed, constant of complexing changes, but not so significantly). This system is the good example of photochromically controlled supramolecular interaction.



Scheme 1.12: Isoalloxazin - diamidotriazine hydrogen bonding.

Several multimode photochromic systems based on dihydroazulene are known.[42,43] Diederich and co-workers have published results[43] about composing system based on DHA/VHF photochromism with a three-way molecular switch. This system might be controlled by several different types of input: pH, light, and heat. All three subunits are individually addressable and can undergo individual, reversible switching cycles, Scheme 1.13.



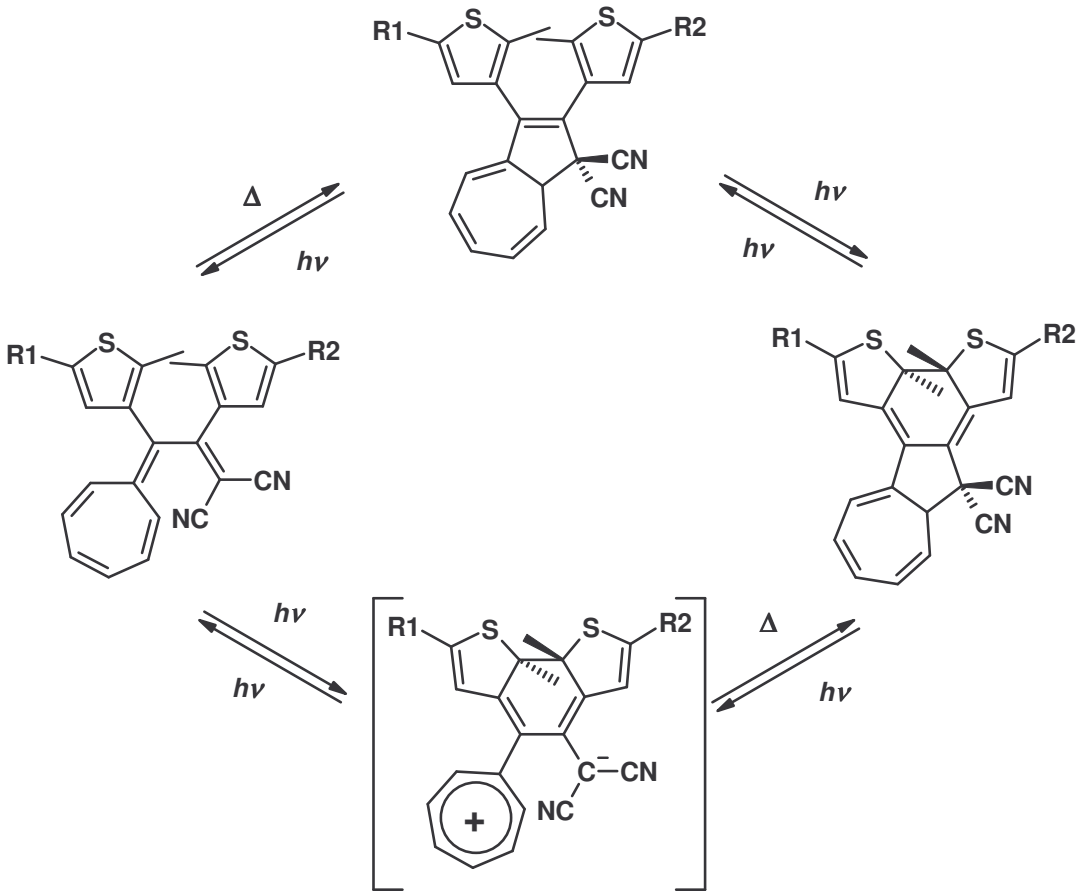
Scheme 1.13: Multi-addressable system with different input types.

The system could undergo three possible switching processes (see Scheme 1.13): first, with emission by λ_{em} = 411 nm the photochromic ring opening reaction of DHA to VHF and thermal back reaction; second, *cis-trans* photoisomerisation (λ_{em} = 464 nm and λ_{em} = 396 nm); third, reversible protonation/deprotonation processes. Although this molecule could adopt theoretically eight interconvertible states, only six where detected.

[42] J. Achatz, C. Fischer, J. Salbeck, J. Daub, *J. Chem. Soc., Chem, Comm.*, **1991**, 504-507.

[43] a) L. Gobbi, P. Seiler, F. Diederich, *Angew. Chem., Int. Ed.*, **1999**, 38, 674-677;

b) L. Gobbi, P. Seiler, F. Diederich, V. Gramlich, C. Boudon, J.-P. Giesselbrecht, M. Gross, *Helv. Chim. Acta*, **2001**, 84, 743-777.



Scheme 1.14: Cyclic multistate switching of DHA/DTE system

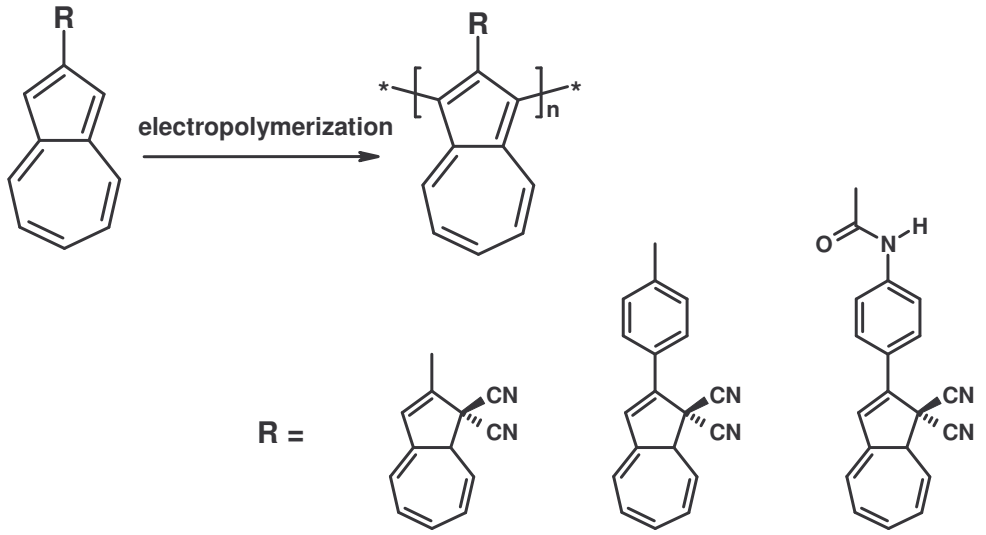
Fusion of different photochromic systems makes it possible to create a multimode molecular reversible switching system. Cyclic four-stage process has been achieved by using DHA and dithienylethene (DTE) moiety,[44] Scheme 1.14.

To create multifold switching in the macromolecular system azulene derivatives have been used. By the electropolymerization of 1,3 – unsubstituted azulenes this system have been created, Scheme 1.15. [45]

[44] a) T. Mrozek, H. Görner, J. Daub, *Chem. Commun.*, **1999**, 1487–1488;

b) T. Mrozek, H. Görner, J. Daub, *Chem. Eur. J.* **2001**, 7, 1028-1040.

[45] P.A. Bross, A. Mirlach, J. Salbeck, J. Daub, *Dechema-Monographien,* **1990**, 121, 375-382.



Scheme 1.15: DHA/azulene conjugates.

It was found that polymers based on directly and through phenyl-spacer bound DHA to azulene moiety are non-photochromic at room temperature. Because of strong coupling of subunits photophysical deactivation processes might quench photoinduced ring-opening. Using of another spacer (amide-link) gave photochemical response.[46]

A light-controlled fluorescence switches have been provided by boron-dipyrromethene dyes as fluorescent sensors and the photochromic DHA/VHF as photonic switching device, Scheme 1.16.[40]

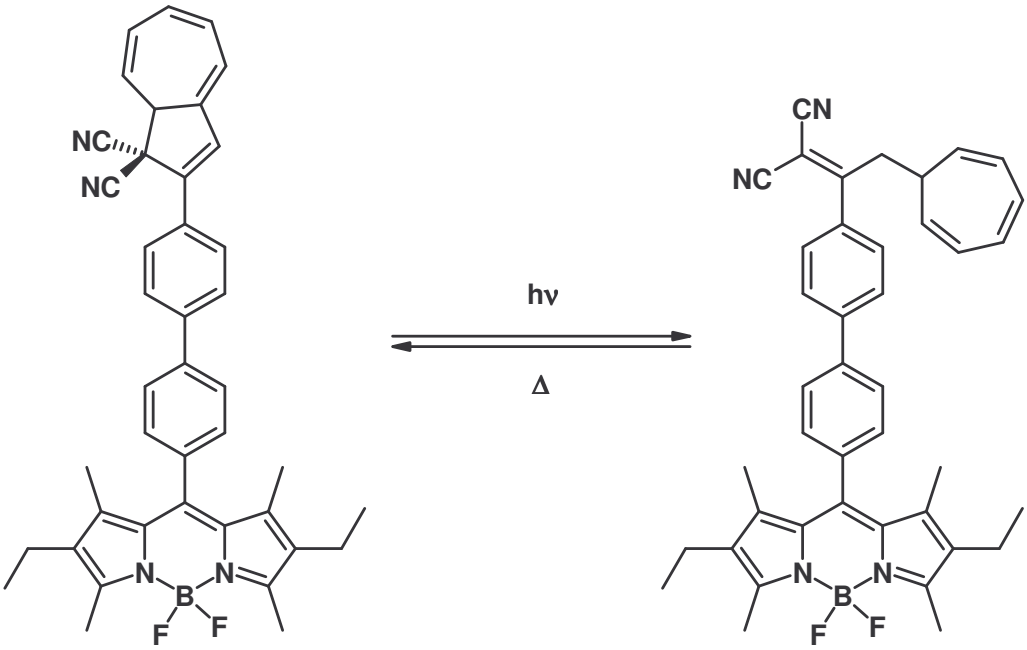
[46] a) J. Daub, M. Feuerer, A. Mirlach, J. Salbeck, *Synthetic Metals*, **1991**, 41-43, 1551-1555;

b) A. Mirlach, M. Feuerer, J. Daub, *Adv. Mater*., **1993**, 5, 450-453;

c) W. Schuhmann, J. Huber, A. Mirlach, J. Daub, *Adv. Mater*., **1993**, 5, 124-126;

d) M. Porsch, G. Sigl-Seifert, J. Daub, *Adv. Mater*., **1997**, 9, 635-639;

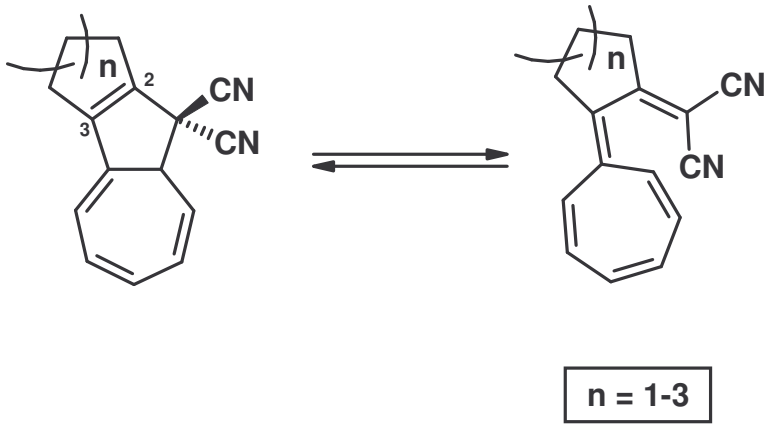
e) F.X. Redl, O. Köthe, K. Röckl, W. Bauer, J. Daub*, Macromol. Chem. Phys*., **2000**, 201, 2091-2100.



Scheme 1.16: Fluorescent switch

1.3.3 Sterically constrained photochromic DHA systems

The photochemical ring-opening reaction is well studied compared to the thermal back reaction. This reaction proceeds in the dark by the ground-state reaction pathway. As it had been noticed before, the open form, vinylheptafulvene is more stable in the s-*trans* conformation. The thermal back reaction passes through the s-*cis* conformation of VHF, which is less stable than s-*trans*. To study this process in detail some modification of the initial molecule should be made. Thus, connecting positions C2 and C3 of DHA with a flexible enough bridge still will allow this system to undergo a photochemical ring-opening reaction, but s-*cis*–s-*trans* rotation will be hindered or blocked. Several systems of such type are known already, Scheme 1.17.



Scheme 1.17: Sterically hindered system.

1,2,3,8a-Tetrahydro-cyclopenta[a]azulene-9,9-dicarbonitrile (Scheme 1.17, n=1, **CP-DHA**) undergoes a photochemical ring-opening reaction with a quantum yield of nearly unity to the corresponding vinylheptafulvene, **CP-VHF**. Back reaction **CP-VHF** → **CP-DHA** at room temperature shows a lifetime of **CP-VHF** of more than 6 h.[39]

For 1,3,4,9a-tetrahydro-2H-benzo[a]azulene-10,10-dicarbonitrile (**CHex-DHA**, n=2)[47] and tricyclo[8.5.0.0*2,8*]pentadeca-1(10),2,4,6-tetraene-9,9-dicarbonitrile, Scheme 1.17 (**CHept-DHA**, n=3)[48] the timescale of thermal back reactions differs from that of **CP-VHF**. In case of **CP-DHA** the thermal back reaction is quite similar to usual the DHA systems. Surprisingly, **CHex-DHA** has totally different time regime in contrast to **CP-DHA**, and the product of the photochemical reaction, **CHex-VHF** has a drastically smaller lifetime at room temperature and could be detected only in non-polar solvents and clearly seen under lower temperature. **CHept-DHA** shows similar to **CHex-DHA** behaviour with a slightly slower thermal back reaction.

For the system **CP-DHA/VHF,** Boggio-Pasqua et al.[49] proposed a model of photoreaction and thermal back reaction based on quantum mechanical calculations, Figure 1.2. The complete active space-self consistent field (CASSCF) has been used. To reduce calculation time costs smaller models were used.

[47] S. Gierisch und J. Daub, *Chem. Ber.*, **1989**, 122, 69-75.

[48] T. Mrozek, *Diploma Thesis*, Universität Regensburg, **1997**.

[49] M. Boggio-Pasqua, M.J. Bearpark, P.A. Hunt, and M.A. Robb, *J. Am. Chem. Soc*. **2002**, 124, 1456-1470.

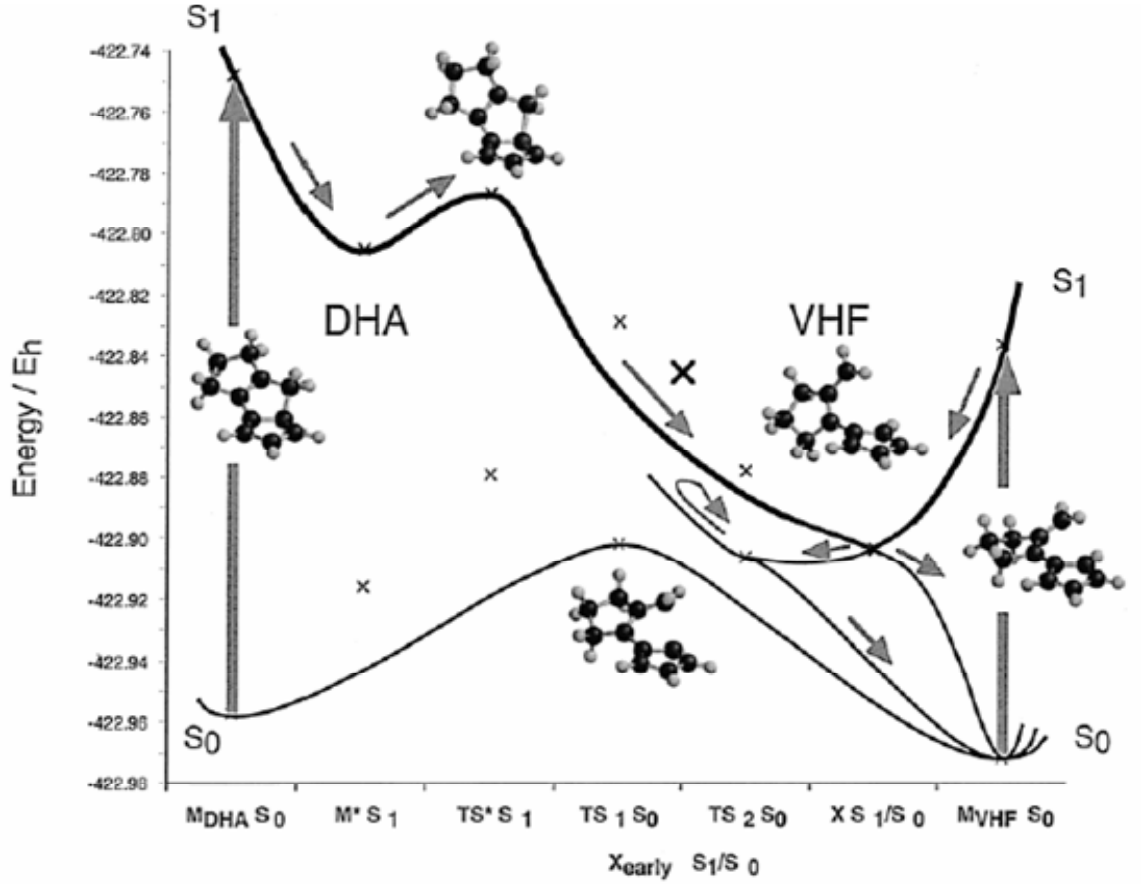
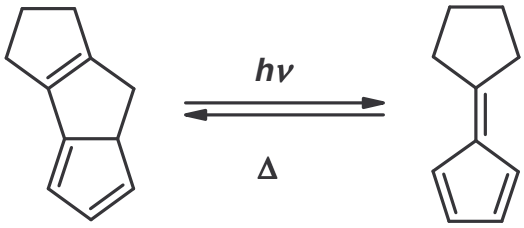


Figure 1.2: Reaction paths on S_0 and S_1 potential energy surfaces of DHA/VHF.[49]



Scheme 1.18: Model system used.[49]

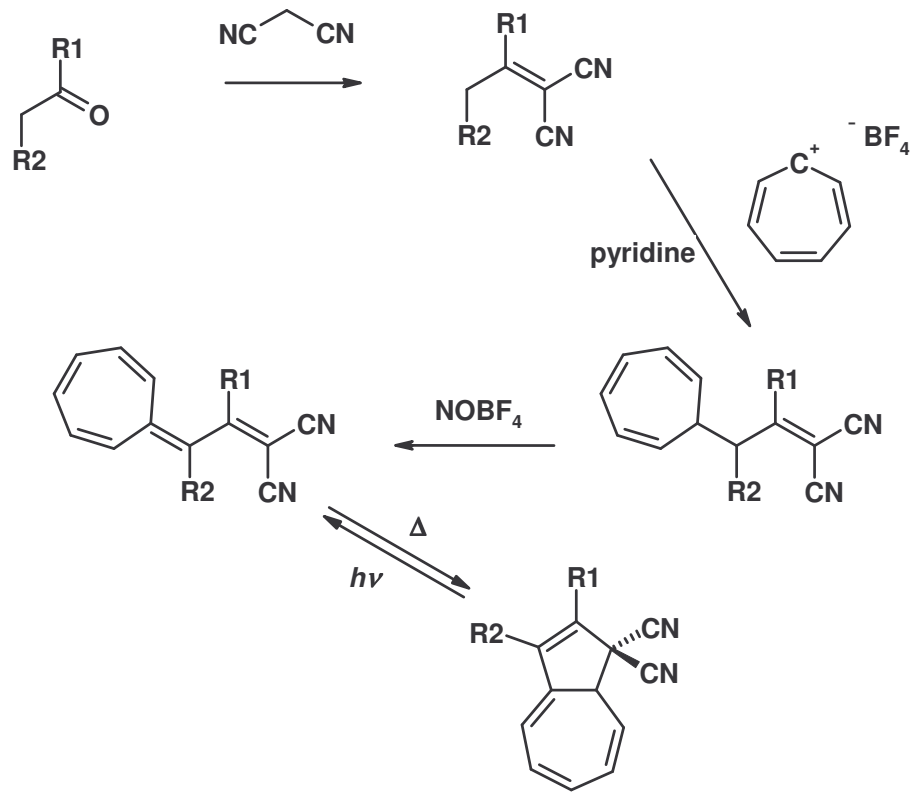
By quantum mechanical calculations have been found the existence of a conical intersection on photochemical reaction pathway from **CP-DHA** to **CP-VHF**, while VHF-like structure is not a real S_1 minimum but a crossing between the excited- and ground-state potential energy surfaces.[50]

[50] J. Ern, M. Petermann, T. Mrozek, J. Daub, K. Kuldova, C. Kryschi, *Chem. Phys*. **2000**, 259, 331-337.

2 Syntheses

2.1 General methods of synthesis of dihydroazulenes

DHAs are alternant π-systems that could be obtained in different ways: by bond formation between dicyanoethylene derivatives with tropylium tetrafluoroborate followed by dehydrogenation leading to the formation of the non-alternant VHF, which thermally rearranges to the corresponding DHA, Scheme 2.1.[51] As a variant of this synthetic strategy might be used the reaction of tropylium fluoroborate with corresponding carbonyl compound followed by treatment with malonodinitrile (Knoevenagel reaction), Scheme 2.1.

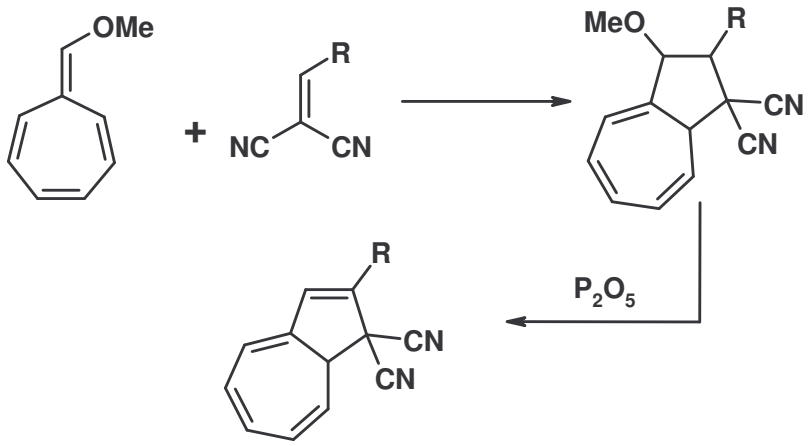


Scheme 2.1: Synthesis of DHA by VHF route

[51] a) T. Mrozek, H. Görner, J. Daub, *Chem. Commun.,* **1999**, 1487-88.

b) S. Gierisch, J. Daub, *Chem. Ber.,* **1989**, 122, 69-75.

Another described synthetic route is the [2+8] cycloaddition of 8-methoxyheptafulvene to dicyanoethylenes and following elimination of methanol[52], Scheme 2.2.



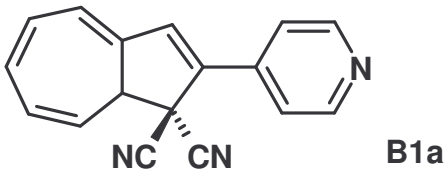
Scheme 2.2: Synthesis of DHA with methoxyheptafulvene as intermediate

Usage of the first way gives the possibility to create systems substituted in 2, 3 positions while the second, older way gives only mono-substituted in the 2 position of DHA.

2.1.1 Some aspects of 4-pyridyl-DHA synthesis:

Dimerization of 2-(1-pyridin-4-yl-ethylidene)-malononitrile (2-amino-6-methyl-4,6-di-pyridin-4-yl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile)

The first step of dihydroazulene **B1** synthetic pathway is Knoevenagel reaction of malonodinitrile with 1-pyridine-4-yl-ethanone. As a main product of reaction, Scheme 2.3, some side product has been achieved, Scheme 2.5. Further studies confirm this finding.



B1a

[52] a) J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz, *Chem. Ber.,* **1986**, 119, 2631-46.

b) J. Daub, T. Knöchel, A. Mannschreck, *Angew. Chem.,* **1984**, 96, 980-981.

B1-1

Scheme 2.3: Synthesis of 2-(1-pyridin-4-yl-ethylidene)-malononitrile.

The first difference observed in the properties of **B3** is that unlike the other substances, homologous to **B1-1** (other aryl-substituent instead of pyridine) it is a solid powder in contrast to viscous substances usually achieved in the first step. The spectroscopic studies showed that the achieved product differs from **B1-1**.

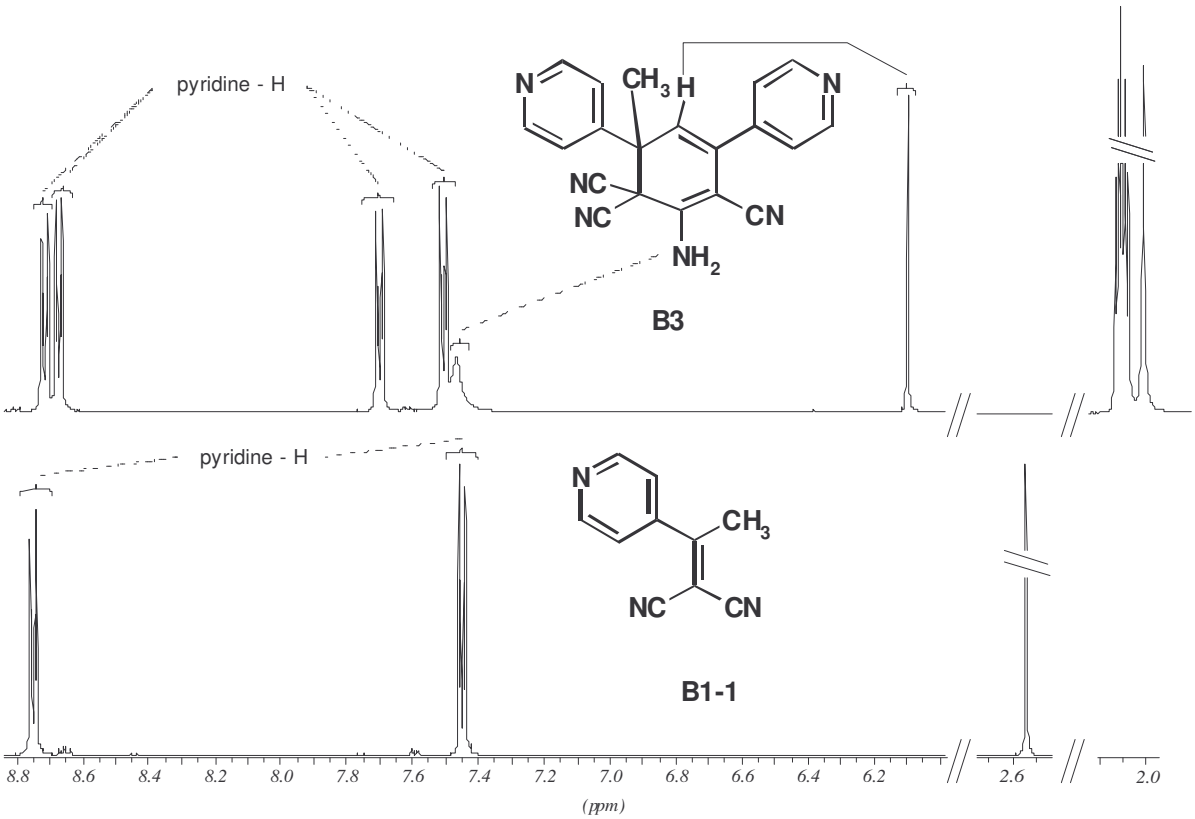
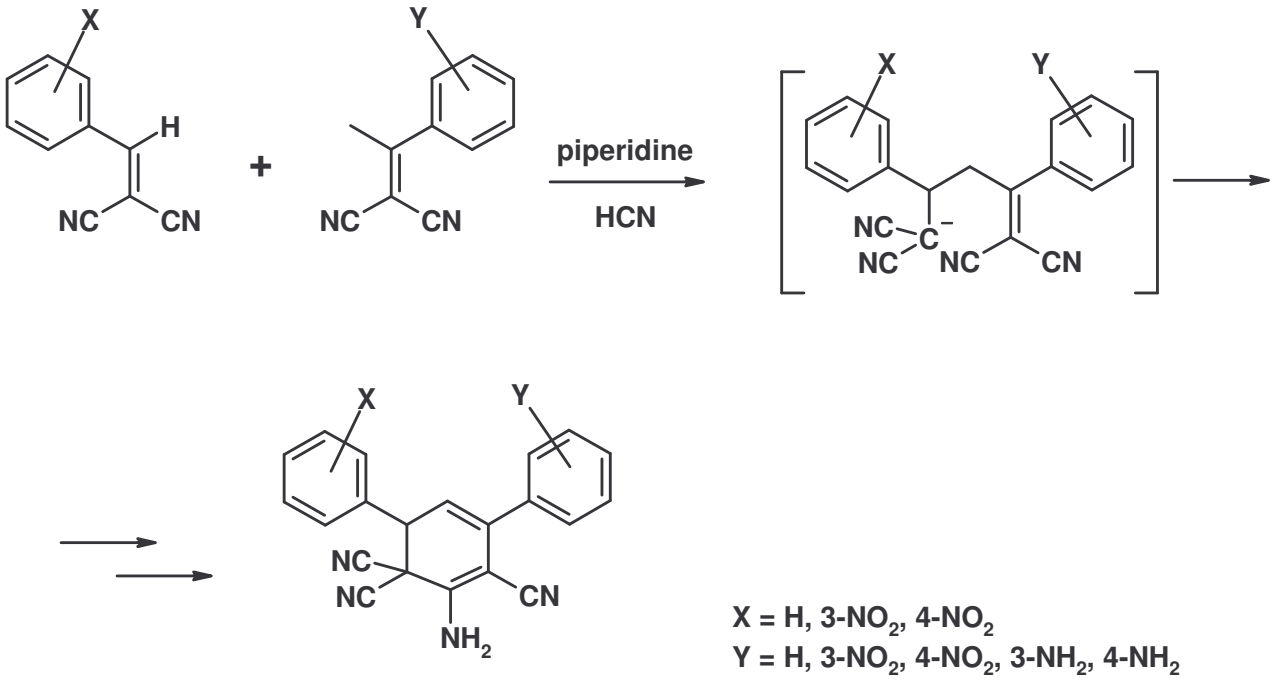


Figure 2.1: Comparing of ^{1}H-NMR spectra of B1-1 and B3.[53]

[53] ^{1}H-NMR spectrum of **B1-1** have been measured in acetone-d_6; spectrum of **B3** – in CD_3CN.

^{1}H-NMR spectrum of **B3**[54], Figure 2.1, showed that the number of proton peaks does not correspond to the **B1-1** compound. The singlet of three protons (2.01 ppm) and the singlet of one proton (6.09 ppm) are the signals of protons of two pyridine rings, and a broad peak that changes its position in different environments could be assigned to the -NH_2 group[55].

A possible pathway of the side reaction might be similar to that on Scheme 2.4[56]. Here the first step is the Michael addition of the anion generated from ethylidenemalonodinitrile to benzylidenemalonodinitrile. The addition is followed by the Thorpe's cyclization of the Michael adduct to the cyclohexadiene product.



Scheme 2.4: Reaction scheme of ylidenemalonodinitriles.[57]

In case of **B1-1** the reaction is self-catalyzed, Scheme 2.5. The reaction has been tested in different solvents (benzene, EtOH) and without (neat). As a main product **B3** compound has been observed. In some cases a minor fraction of **B1-1** has been achieved, but usual workup procedure of this

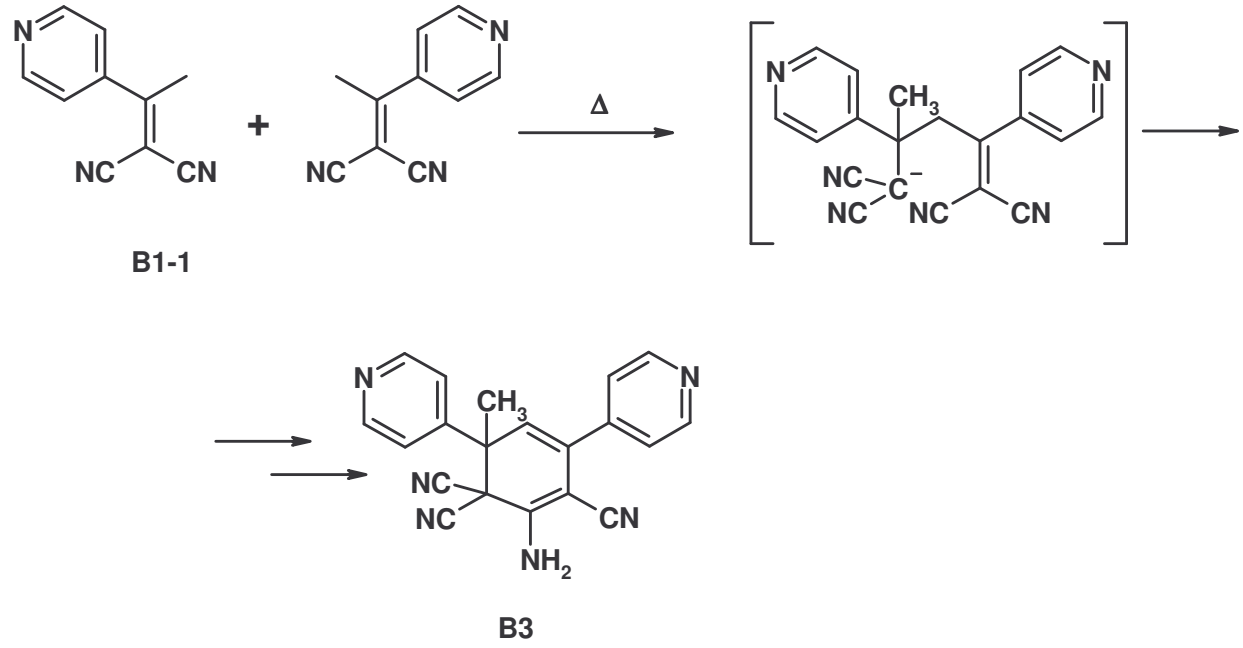
[54] ^{1}H-NMR (300 MHz, CD_3CN): δ = 2.01 (s, 3H,), 6.09 (s, 1H), 7.48 (br s, 2H), 7.51 (AABB, 2H), 7.70 (AABB, 2H), 8.67 (aabb, 2H), 8.72 (aabb, 2H).

[55] NMR spectra of **B3** (2-Amino-6-methyl-4,6-di-pyridin-4-yl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile) were measured in acetone-d_6 if other is not noted.

[56] K. Gewald, W. Schill, *J. Prakt. Chem*, **1971**, 313, 678-685.

[57] P. Milart, J. Wilamowski, J.J. Sepioł, *Tetrahedron*, **1998**, 54, 15643-56.

reaction, treatment with elevated temperature (concentrating of solution) or storing at RT leads to **B3**.

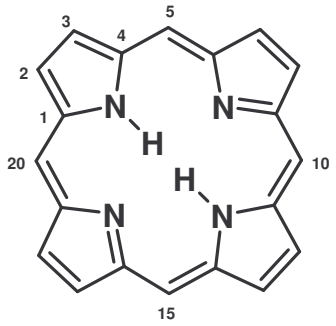


Scheme 2.5: Assumed side reaction of B3.

In case of Milart *et al.*[57] the reaction is catalyzed by base (piperidine). The self-catalyzed reaction of 2-(1-pyridin-4-yl-ethylidene)-malononitrile could be explained by the presence of pyridine moiety that catalyzes Michael addition.

2.2 Syntheses of porphyrins

Porphyrin—tetrapyrrolic macrocycle, Scheme 2.6, is widely found in Nature and is involved in a number of important biological functions. It is being used in many applications such as dyes, catalyst for numerous reactions, photoconducting agents in energy transfer and light-harvesting systems.[58]



Scheme 2.6: Porphyrin structure.

There are many strategies to create the required porphyrin structures[59]. The simplest variant is to create a porphyrin core with four similar substituents[60,61] Scheme 2.7:

[58] a) R.W. Wagner, J.S. Lindsey, J. Seth, V. Palaniappan, and D.F. Bocian, *J. Am. Chem. Soc*. **1996**, 118, 3996-3997;

b) L. Yu, J.S. Lindsey, *J. Org. Chem*. **2001**, 66, 7402-7419;

c) M.S. Vollmer, F.Würthner, F. Effenberger, P. Emele, D.U. Meyer, T. Stümpfig, H. Port and H.C. Wolf, *Chem. Eur. J*., **1998**, 4, 260-269;

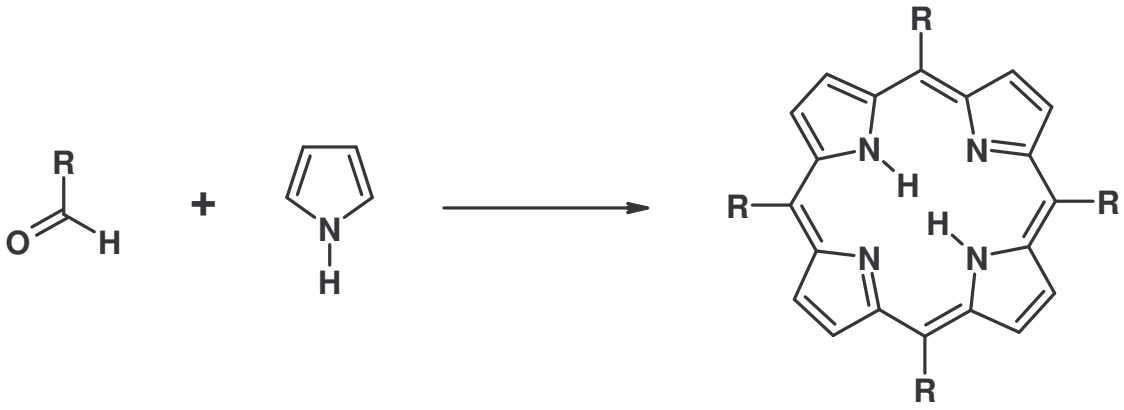
d) L. Giribabu et al., *Angew. Chem*. **2001**, 19, 113.

[59] a)J.S. Lindsey in *The Porphyrin Handbook*; K.M. Kadish, K.M. Smith, R. Guilard, Eds.; Academic Press: San Diego, CA, **2000**, 1, 45-118;

b) J.S. Lindsey, In *Metalloporphyrin-Catalyzed Oxidations*; F. Montanari, L. Casella, Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, **1994**; 49-86.

[60] Here and later the substituent means 5-, 10-, 15-, and 20- substituents of porphyrin if other is not mentioned.

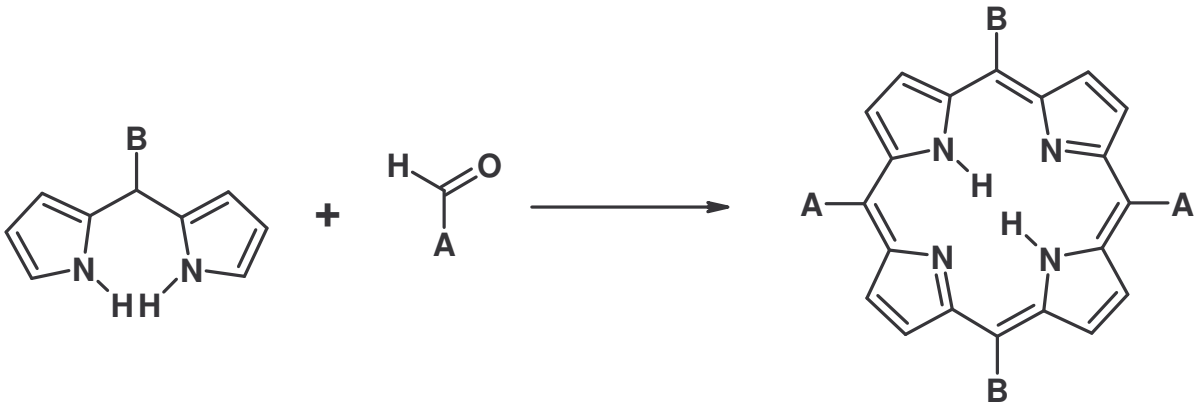
[61] To describe synthetic strategies of different porphyrins the system have been proposed by Lindsey et al. is used: different substituents at 5, 10, 15, and 20 position of porphyrin marked with different capital characters A-D.



Scheme 2.7: Synthesis of AAAA porphyrin.

2.2.1 Synthesis of porphyrin with different substituents

To create an ABAB system a strategy one can use to couple the dipyrrylmethane with substituent B and an aldehyde with A one[62], Scheme 2.8:

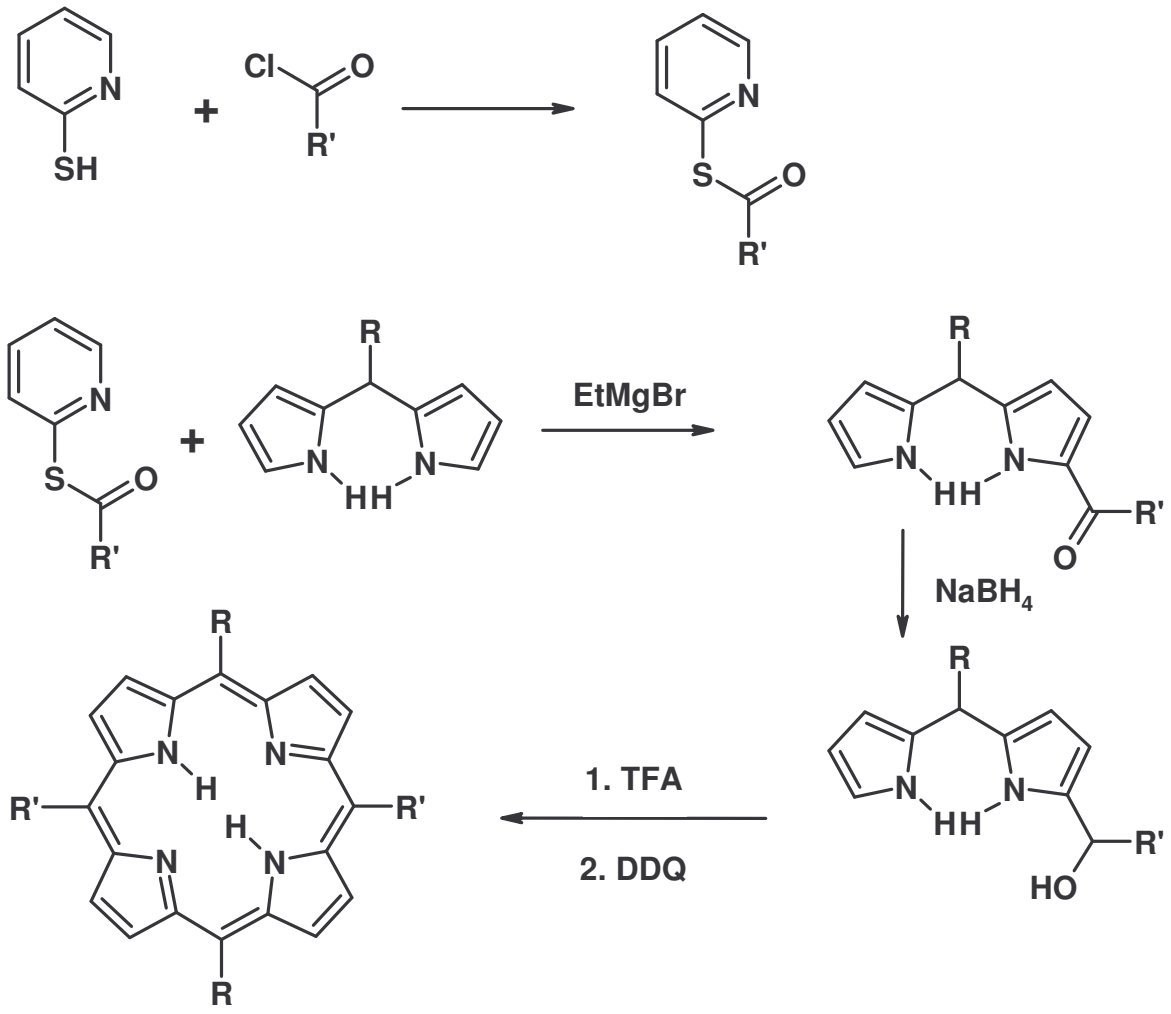


Scheme 2.8: Synthesis of ABAB porphyrin.

To improve the yield of this reaction Lindsey *et al*. proposed a modified way[63] shown on the Scheme 2.9:

[62] H.L. Anderson*, Tetrahedron Lett.*, **1992**, 33, 1101-1104.

[63] P.D. Rao, B.J. Littler, G.R. Geier III, J.S. Lindsey, *J. Org. Chem.* **2000,** 65*,* 1084-1092.



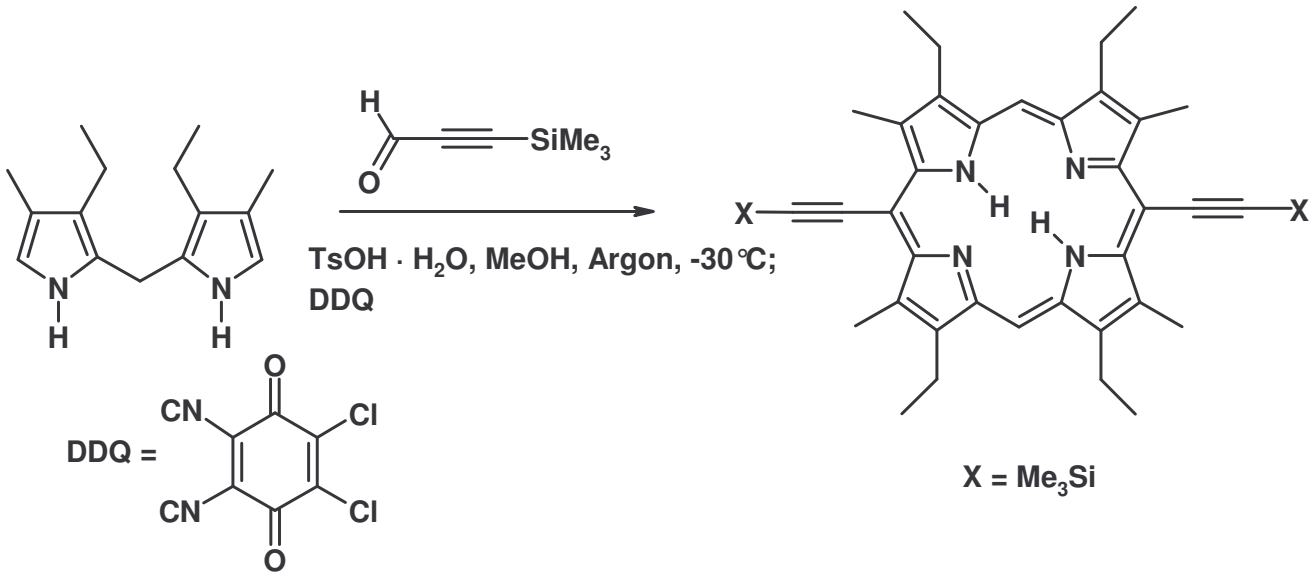
Scheme 2.9: Improved synthesis of ABAB porphyrin.

To create more complex unsymmetrical derivatives of porphyrin several approaches are described: the first way—using of the mixture of different aldehydes and the second one—step-by-step synthesis, proposed by the Lindsey's group.[64] This method avoids statistical reactions, employs minimal chromatography, and affords up to gram quantities of regioisomerically pure porphyrins bearing predesignated patterns of up to four different *meso* substituents. The methodology is based upon the availability of multigram quantities of dipyrromethanes.

[64] P.D. Rao, S. Dhanalekshmi, B.J. Littler and J.S. Lindsey, J. Org. Chem. **2000**, 65, 7323-7344.

2.2.2 Synthesis of a porphyrin with Gunter's conditions[65]:

Synthesis of a porphyrin with *meso*-alkynyl substituents has been done by treatment of dipyrrilmethane with trimetylsilylpropynal according to H. Anderson[65] using Gunter's conditions.[66] Trimethylsilylpropynal was added to the solution of dipyrrilmethane and *p*-toluenesulfonic acid monohydrate in methanol under nitrogen at -30°C, and treated with DDQ, Scheme 2.10.



Scheme 2.10: Synthesis of porphyrin with Gunter's conditions.

2.2.3 Synthesis of porphyrin building units

As it has been mentioned before, porphyrin is a tetrapyrrolic macrocycle. To create porphyrins with different substituents a number of pyrroles, dipyrrylmethanes, aldehydes and their precursors were synthesised and used.

[65] H.L. Anderson, *Tetrahedron Letters*, **1992**, 33(8), 1101-1104.

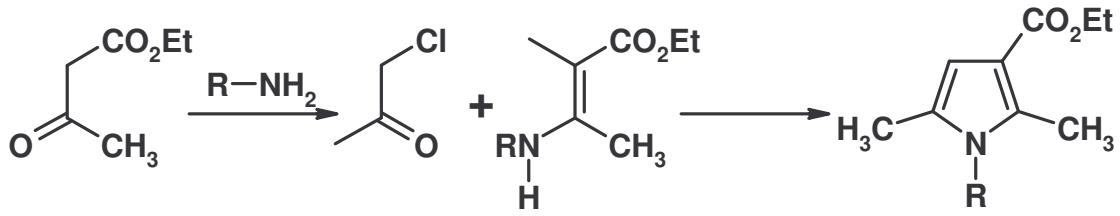
[66] M.J. Gunter, L.N. Mander, *J. Org. Chem.*, **1981**, 46, 4792.

2.2.3.1 Synthesis of pyrrole (4-ethyl-3,5-dimethyl-1H-pyrrole-2-carboxylic acid ethyl ester)

Pyrrole is a main basic unit of the porphyrin cycle. There are many methods for the synthesis of different pyrroles. The most important synthetic methods are to create a pyrrole ring with substituents, which after can be eliminated or modified afterwards. Here are some main methods to create pyrrole; the one used will be discussed later on. Modification of 4 and 5-positions of pyrrole gives higher solubility of the porphyrin.

Hantzsch pyrrole synthesis[67]

This method is based on the condensation of α-halogeneketones with β-ketoesters and ammonia or an amine.[68] The scheme of reaction, Scheme 2.11, shows how the intermediate aminocrotonic ester undergoes β-alkylation, as it usually does with enamines.



Scheme 2.11: Hantzsch synthesis of pyrrole

Knorr pyrrole synthesis[69]

This reaction and its modifications are the most used method of the pyrrole synthesis.[70] The reaction is based on the formation of pyrrole derivatives by condensation of already prepared α-

[67] A. Hantzsch, *Ber.,* **1890,** 23, 1474.

[68] a) R. Elderfield, T. N. Dodd, Jr., *Heterocyclic Compounds* **1950**, 1, 132;

b) A. H. Corwin, *ibid.* 290; M. W. Roomi, S. F. MacDonald, *Can. J. Chem.* **1970**, 48, 1689;

c) K. Kirschke *et al., J. Prakt. Chem.,* **1990**, 332, 143;

d) A. W. Trautwein *et al., Bioorg. Med. Chem. Lett.,* **1998**, 8, 2381.

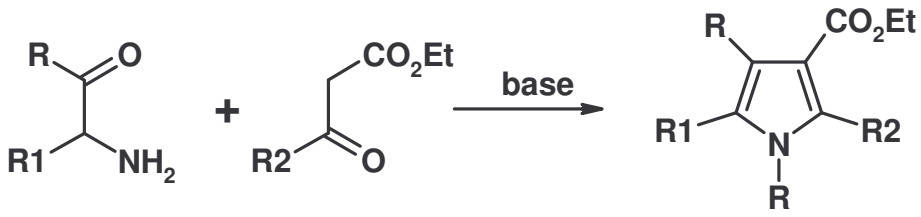
[69] a) L. Knorr, *Ber.,* **1884**, 17, 1635;

b) L. Knorr, *Ann..* **1886**, 236, 290;

c) L. Knorr, H. Lange, *Ber.,* **1902**, 35, 2998.

[70] a) E. Fabiano, B. T. Golding, *J. Chem. Soc. Perkin Trans. I* **1991,** 3371;

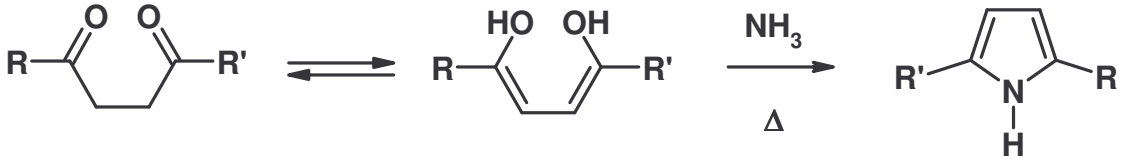
amino ketones or generated *in situ* from isonitrosoketones with carbonyl compounds containing an active α-methylene groups, Scheme 2.12:



Scheme 2.12: Knorr synthesis.

Paal-Knorr pyrrole synthesis.[71]

This method relies on the formation of pyrroles via cyclization of 1,4-dicarbonyl compounds with ammonia or primary amines, Scheme 2.13:[72]



Scheme 2.13: Paal-Knorr pyrrole synthesis.

b) A. Alberola, A.G. Ortega, M.L. Sadaba, C. Sanudo*, Tetrahedron,* **1999**, 55, 6555-6566;

c) P. E. Harrington, M. A. Tius, *Org. Lett.,* **1999**, 1, 649.

[71] C. Paal, *Ber.,* **1885**, 18, 367.

[72] a) S.-X. Yu, P. W. Le Quesne, *Tetr. Let.,* **1995**, 36, 6205;

b) R. Ballini, L. Barboni, G. Bosica, M. Petrini, *Synlett,* **2000**, 3, 391-393;

c) S. E. Korostova, A.I. Mikhaleva, A.M. Vasil'tsov, B.A. Trofimov, *Russ. J. Org. Chem.,* **1998**, 34, 1691-1714.

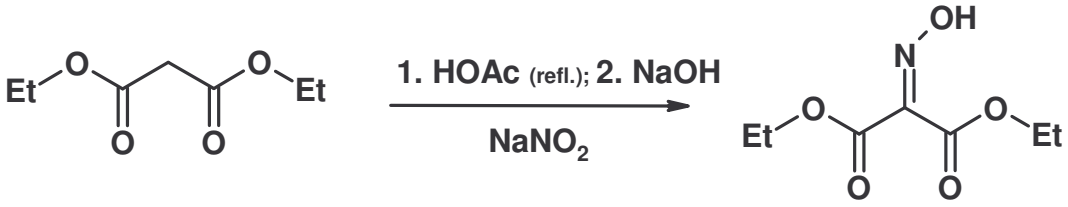
2.2.3.1.1 Synthesis of 3-ethyl-2,4-pentanedion[73]:

3-Ethyl-2,4-pentanedion has been achieved by the reaction of acetylacetone with ethyliodide in anhydrous acetone, Scheme 2.14.

Scheme 2.14: Synthesis of 3-ethyl-2,4-pentanedion.

2.2.3.1.2 Synthesis of diethyloximinomalonate[74]:

Diethyloximinomalonate was obtained by treatment of diethyl malonate in glacial acetic acid/sodium hydroxide with aqueous solution of sodium nitrite, Scheme 2.15:



Scheme 2.15: Synthesis of diethyloximinomalonate.

2.2.3.1.3 Synthesis of 2-carboxyethyl-3,5-dimethyl-4-ethylpyrrole:

This pyrrole was created by two methods:

The first one is the modified Knorr reaction at Kleinspehn's conditions. The diethyloximinomalonate reacts with 3-ethylpentane-2,4-dione in the presence of zinc powder[75], Scheme 2.16:

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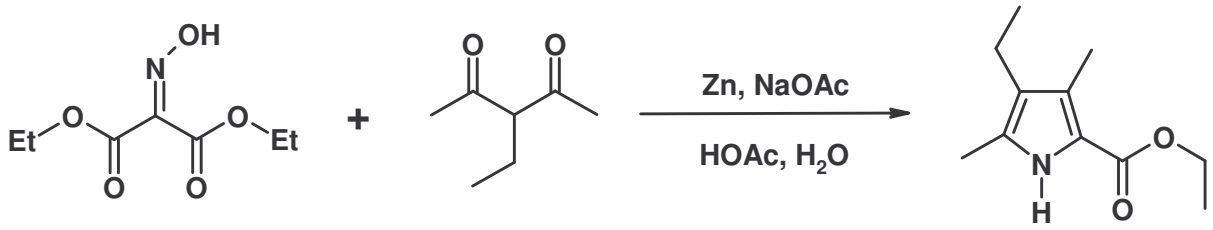
[73] K.V. Auwers and H. Jacobsen, *Liebigs Ann. Chem.*, **1921**, 426, 227.

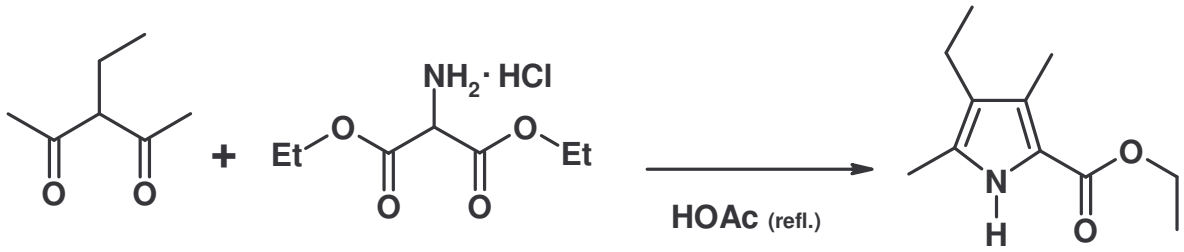
[74] J.B. Paine III, D. Dolphin, *J. Org. Chem.* **1985**, 50, 5598-5604 .

[75] G.G. Kleinspehn, *J. Am. Chem. Soc.*, **1955**, 77, 1546 - 1548.



Scheme 2.16: Synthesis of 2-carboxyethyl-3,5-dimethyl-1H-pyrrole-2-carboxylic acid ethyl ester.

By the second synthetic route 2-carboxyethyl-3,5-dimethyl-4-ethylpyrrole was synthesised by reaction of 3-ethyl-2,4-pentanedion with diethylaminomalonate[74], Scheme 2.17:



Scheme 2.17: Synthesis of -ethyl-3,5-dimethyl-1H-pyrrole-2-carboxylic acid ethyl ester, second method.

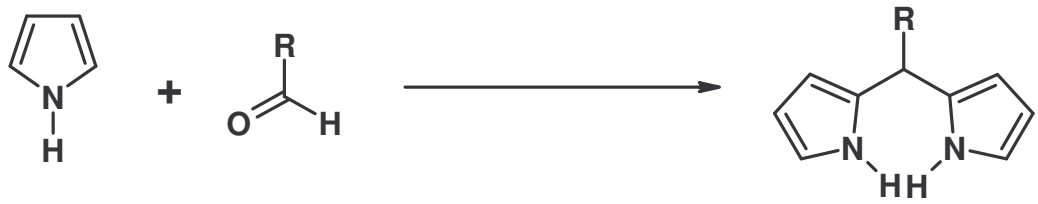
Comparing this two methods' yields and purity it has been found that the first method[75] gave a crude product with better quality.

2.2.3.2 Syntheses of dipyrrylmethanes

Dipyrrylmethanes occupy a central place in porphyrin chemistry. They possess exceedingly high reactivity. Dipyrrylmethanes are main building blocks for *trans*-A_2B_2 system.[76]
The synthesis of dipyrrylmethanes can be achieved via the one-pot reaction of an aldehyde with an excess pyrrole.[77 - 78] The synthetic method has generally employed TFA as the acid catalyst and

[76] a) D.S. Sharada, A.Z. Muresan, K. Muthukumaran, J.S. Lindsey, *J. Org. Chem.*, **2005**, 70(9), 3500-3510;
b) N.Zh. Mamardashvili, O. A. Golubchikov, *Rus. Chem. Rev.*, **2000**, 69 (4), 307 – 323.
[77] C.-H. Lee, J.S. Lindsey, *Tetrahedron* **1994**, *50*, 11427-11440.

workup via chromatography and Kugelrohr distillation.[78] Recently it was found by Lindsey's group that milder acids could be employed in conjunction with a more simple purification procedure via direct crystallization.[78, 79]



Scheme 2.18: General synthetic scheme of dipyrrylmethane.

Syntheses of dipyrrylmethanes catalyzed by $InCl_3$, $MgBr_2$ in pyrrole as solvent (ca. 100 equiv to aldehyde) gave products in a good yield, depending on the substituent in the aldehyde, Scheme 2.18.[79]

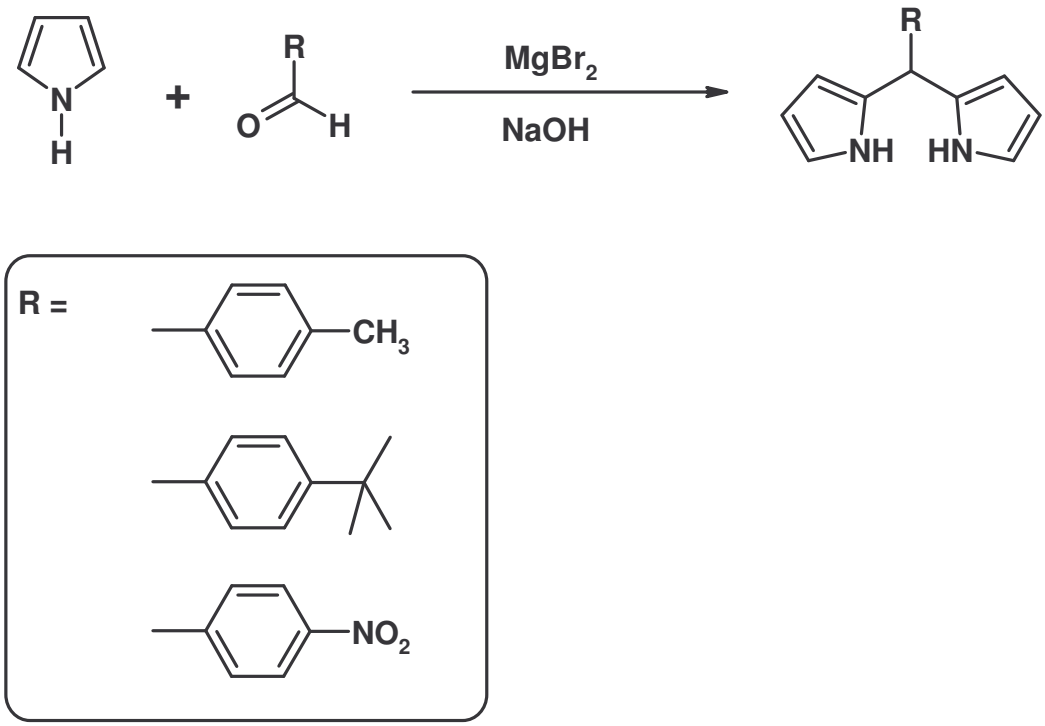
2.2.3.2.1 Syntheses of dipyrrylmethanes from 1-H pyrrole

For syntheses of dipyrrylmethanes form 1-H pyrrole conditions that have been proposed by Lindsey's group were used.[79] Pyrrole (100-fold excess, serves as a solvent) and an aldehyde were treated with $MgBr_2$, and then reaction was quenched with NaOH, Scheme 2.19.

[78] B.J. Littler, M.A. Miller, C.-H. Hung, R.W. Wagner, D.F. O'Shea, P.D. Boyle, J.S. Lindsey, *J. Org. Chem.* **1999**, *64*, 1391-1396.

[79] a) Z. Liu, A.A. Yasseri, R.S. Loewe, A.B. Lysenko, V.L. Malinovskii, Q. Zhao, S. Surthi, Q. Li, V. Misra, J.S. Lindsey, and D.F. Bocian, *J. Org. Chem*, **2004**, *69*, 5568-5577;

b) J.K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise, and J.S. Lindsey, *Org. Proc. Res. & Dev*., **2003**, *7,* 799-812.

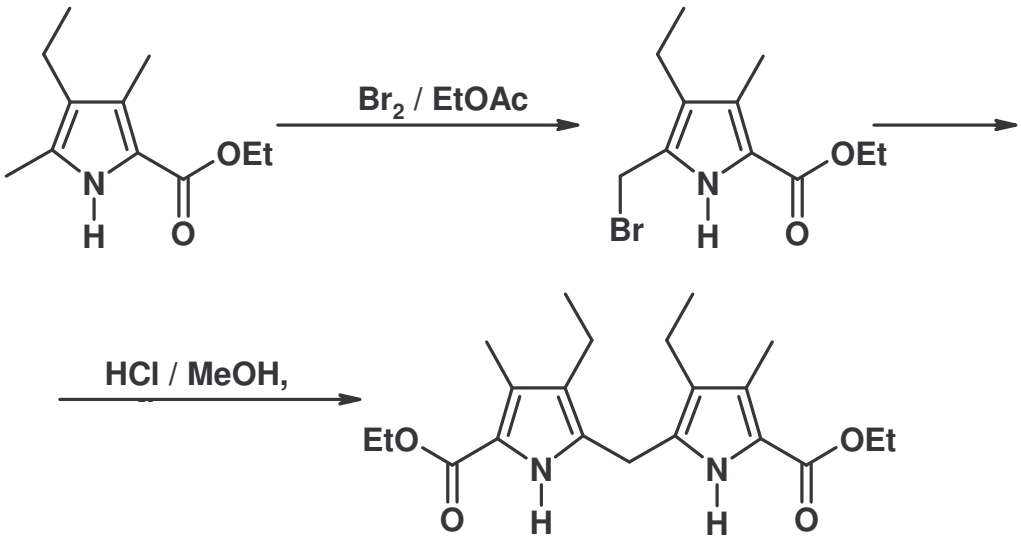


Scheme 2.19: Synthesis of 5-(4-*tert*-butylphenyl)dipyrrylmethane and 5-(p-tolyl)dipyrrylmethane.

2.2.3.2.2 Synthesis of 3,3'-diethyl-4,4'-dimethyl-5,5'-bis-(ethoxycarbonyl)-2,2'-dipyrryl-methane[80]:

Bromination of the α-methyl group of the pyrrole with subsequent condensation of 5-bromomethyl-4-ethyl-2-ethoxycarbonyl-3-methylpyrrole in methanol in the presence of acid results in the 5,5'-diethoxycarbonyl derivative, Scheme 2.20.

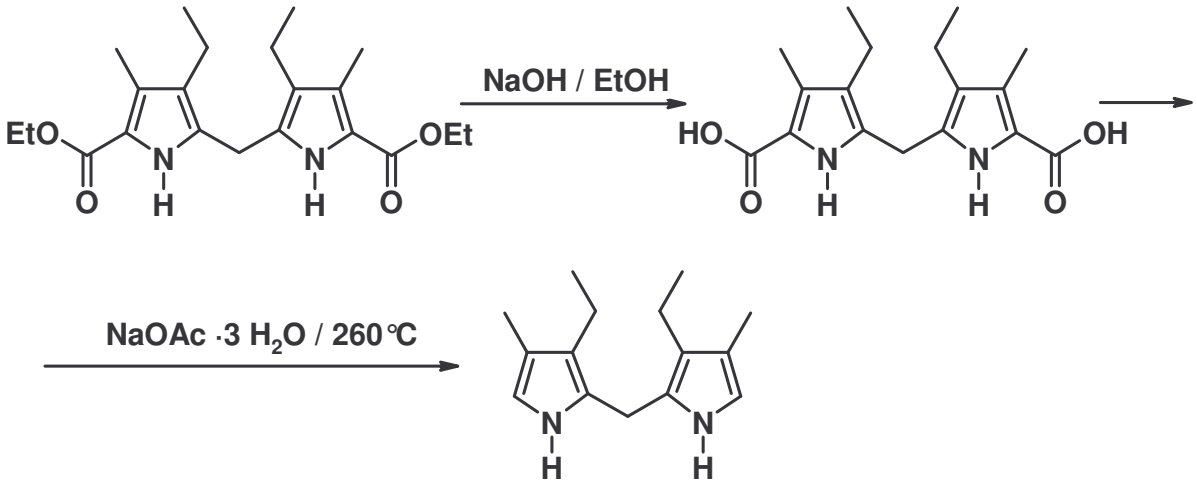
[80] M.T. Huggins, A.K. Tipton, Q. Chen, D.A. Lightner, *Monatsh. Chemie*, **2000**, 131, 825-838.



Scheme 2.20: Synthesis of 3,3'-diethyl-4,4'-dimethyl-5,5'-bis-(ethoxycarbonyl)-2,2'-dipyrryl-methane.

2.2.3.2.3 Decarboxylation of bis-(ethoxycarbonyl)-2,2'-dipyrryl-methane

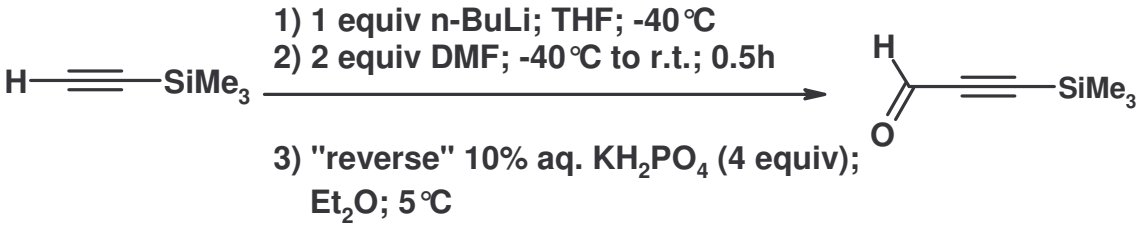
The easy saponification of bis-(ethoxycarbonyl)-2,2'-dipyrryl-methane giving high yield of the dicarboxylic acid was followed by decarboxylation. Dicarboxylic acid undergoes a smooth loss of CO_2 in molten sodium acetate trihydrate [80], Scheme 2.21:



Scheme 2.21: Decarboxylation of dipyrrylmethane.

2.2.3.3 Synthesis of trimethylsilylpropynal

The formylation of lithium acetylide with DMF led to acetylenic aldehyde in a good yield. The reaction was finished by a reverse quenching into a phosphate buffer (10% aqueous KH_2PO_4 ,4 equiv)[81], Scheme 2.22:



Scheme 2.22: Synthesis of trimethylsilylpropynal.

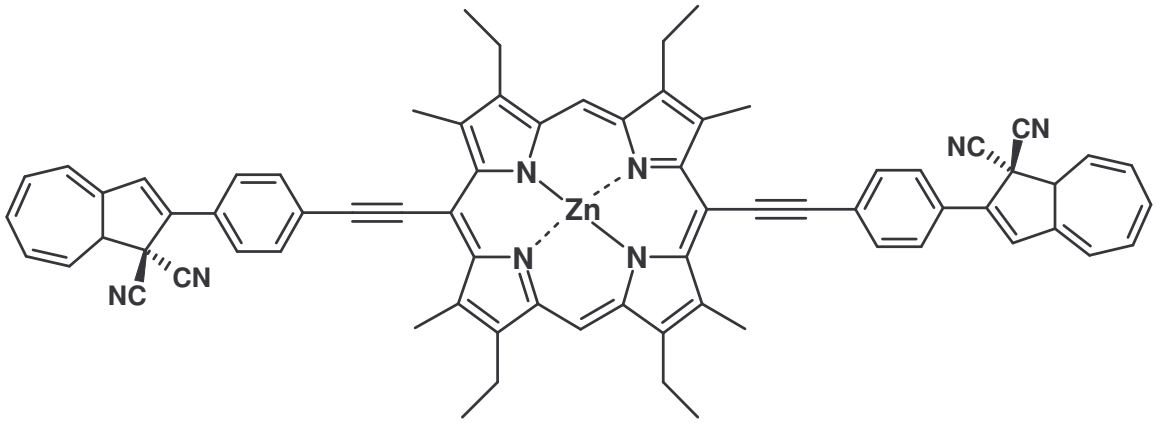
2.3 Synthesis of porphyrin conjugates

An integrated chemical system consists of photosensitive switchable subunits and a receptor/transformer unit; it is able to give an analytical response (change in fluorescence band and intensity, electrochemical potentials etc.), Scheme 2.23. The approach used here employs the photochromism of a photosensitive switching unit dihydroazulene/vinylheptafulvene (DHA/VHF) covalently bound to a zinc-coordinated porphyrin serving as a molecular receptor. Features of DHA/VHF give possibilities to use them for creating of ultrafast logic functions.[82, 83]

[81] M. Journet, D. Cai, L.M. DiMichele and R.D. Larsen, *Tetrahedron Letters*, **1998**, 39, 6427-6428.

[82] J. Daub, T. Mrozek, and A. Ajayaghosh, *Mol. Cryst. Liq. Cryst.*, **2000**, 344, 41.

[83] V. De Waele, U. Schmidhammer, T. Mrozek, J. Daub and E. Riedle*, J. Am. Chem. Soc.,* **2002**, 124, 2438.



Scheme 2.23: Dihydroazulene – porphyrin conjugate.

2.3.1 Coupling of the photochromic and porphyrin subunits, Sonogashira coupling[84]

Carbon-carbon bond forming reactions are the key steps in many organic syntheses.[85] Alkynes are outstanding building blocks for unsaturated molecular scaffolds because of their rigid structure and conjugated π-system. They are a common motif in drugs, for example, in some antibiotics and the contraceptives. Their high-energy structure makes alkynes an attractive functional group for further transformations in different synthetic routes.[86] Various frequently used cross-coupling reactions are mediated by palladium catalysts, Scheme 2.24.[87]

---

[84] a) K. Sonogashira, Y. Tohda, N. Hagihara, *Tetr. Lett*. **1975**, 4467;

b) Sonogashira in 'Metal-catalyzed Cross-coupling Reactions', Eds. F. Diederich, P.J. Stang, Wiley-VCH, Weinheim **1998**, 203-269;

c) L. Gobbi, P. Seiler, F. Diederich, *Angew. Chem., Int. Ed. Engl*., **1999**, 38, 674-677;

d) L. Gobbi, P. Seiler, F. Diederich, V. Gramlich, C. Boudon, J.-P. Giesselbrecht, M. Gross, *Helv. Chim. Acta*, **2001**, 84, 743-777.

[85] Modern Acetylene Chemistry (Eds.: P. J. Stang, F. Diederich), VCH, Weinheim, **1995**;

b) (b) K.C. Nicolaou, E.J. Sorensen, Classics in Total Synthesis, VCH, Weinheim, **1996**.

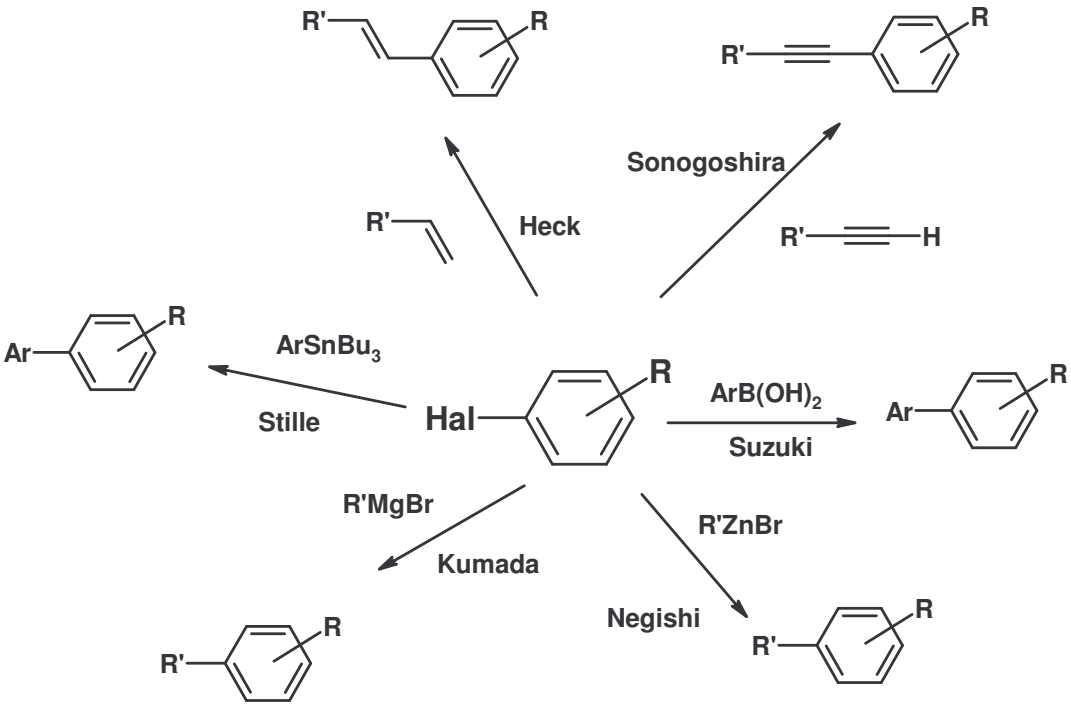
[86] a) A. Elangovan, Y.-H. Wang, T.-I. Ho, *Org. Lett.*, **2003**, *5*, 1841-1844;

b) R. A. Batey, M. Shen, A. J. Lough, *Org. Lett.*, **2002**, 1411-1414;

c) R.R. Tykwinski*, Angew. Chem. Int. Ed.,* **2003**, 42, 1566 – 1568.

[87] a) J. Tsuji, Palladium Reagents and Catalysts, Wiley, Chichester, **1995**;

b) R.F. Heck, Palladium Reagents in Organic Synthesis, VCH, Weinheim, **1996**.



Scheme 2.24: Palladium catalyzed cross-coupling reactions.

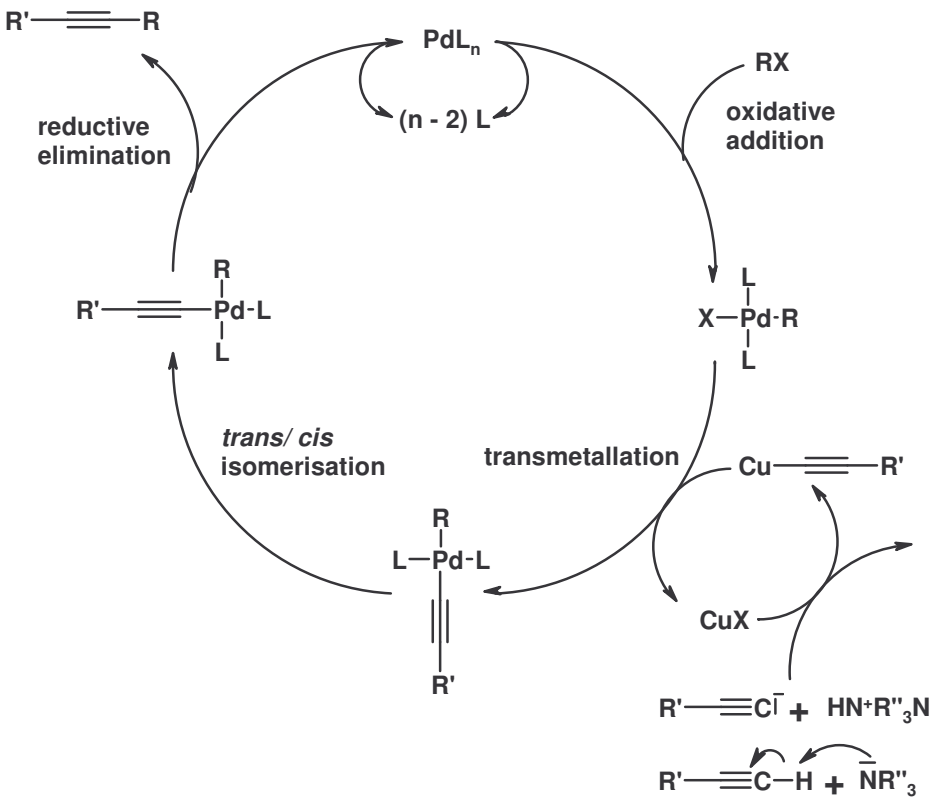
Sonogashira cross-coupling of terminal alkynes with aryl and vinyl halides has many applications. A variety of arylhalides including electron-deficient heteroaryl chlorides has been employed in palladium-catalyzed coupling reactions with terminal alkynes to afford versatile precursors for the formation of fused aromatic heterocycles, whereas the coupling of less reactive electron-rich aryl chlorides remains challenging.[88] Typically, the Sonogashira reaction requires inert and anhydrous reaction conditions. Scheme 2.25 represents the schematic view of Sonogashira coupling mechanism.

[88] a) A. N. Thadani and V. H. Rawal, *Org. Lett.*, **2002**, 4, 4321–4323;

b) G. Hilt, T. J. Korn and K. I. Smolko, *Synlett*, **2003**, 241–243;

c) A. Kollhofer, T. Pullmann and H. Plenio, *Angew. Chem., Int.Ed.*, **2003**, 42, 1056–1058;

d) S. Ma, H. Ren and Q. Wei, *J. Am. Chem.Soc.*, **2003**, 125, 4817–4830.



Scheme 2.25: Mechanism of Sonogashira Coupling.

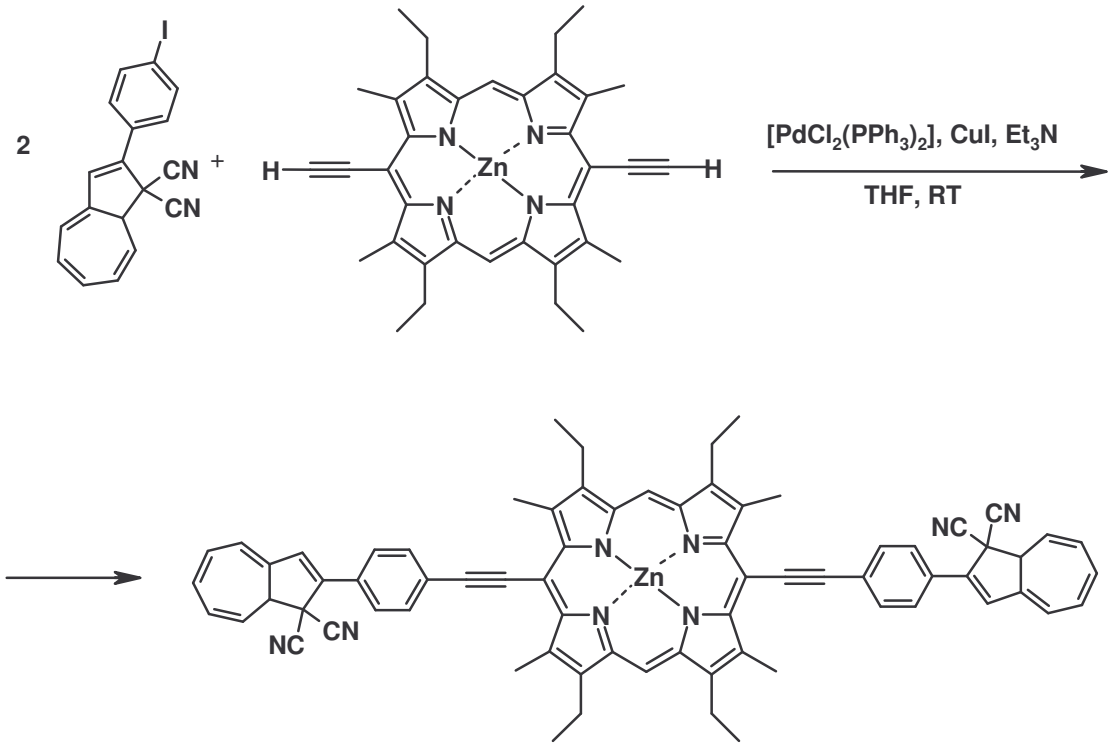
2.4 Porphyrin/DHA conjugates' incomplete studies

The Sonogashira coupling has been carried out with zinc porphyrin **C6** which carries two terminal alkyne groups and iodine derivative of dihydroazulene **D1**[89]**.** The reaction has been done in THF at room temperature with triethylamine as base and [$PdCl_2(Ph_3P)_2$] as catalyst, Scheme 2.26.

[89] a) T. Mrozek, *Dissertation*, Regensburg, **2001**.

b) J. Daub, G. Hirmer, L. Jakob, G. Maas, W. Pickl, E. Pirzer, K.M. Rapp, *Chem. Ber.*, **1985**, 118,1836;

c) S. Gierisch, J. Daub, *Chem. Ber.*, **1989**, 122, 69.



Scheme 2.26: Synthesis of porphyrin - dihydroazules conjugated system, Sonogashira coupling

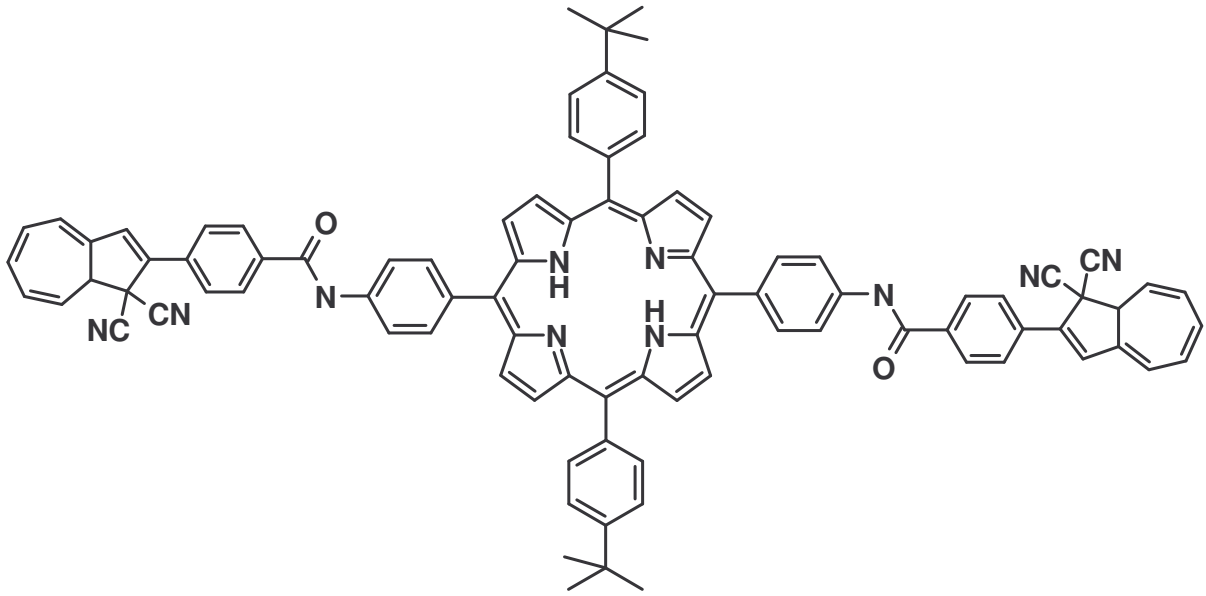
The side product of this coupling reaction was 1-cyanoazulene derivative, Scheme 2.27:

Scheme 2.27: Side reaction of dihydroazulene

To avoid reaction of porphyrin **C6** hydrogens at C-10 and C-20 atoms, derivatives **C3** and **C4** have been synthesised. These porphyrins have *t*-Bu-phenyl groups at the noted positions.

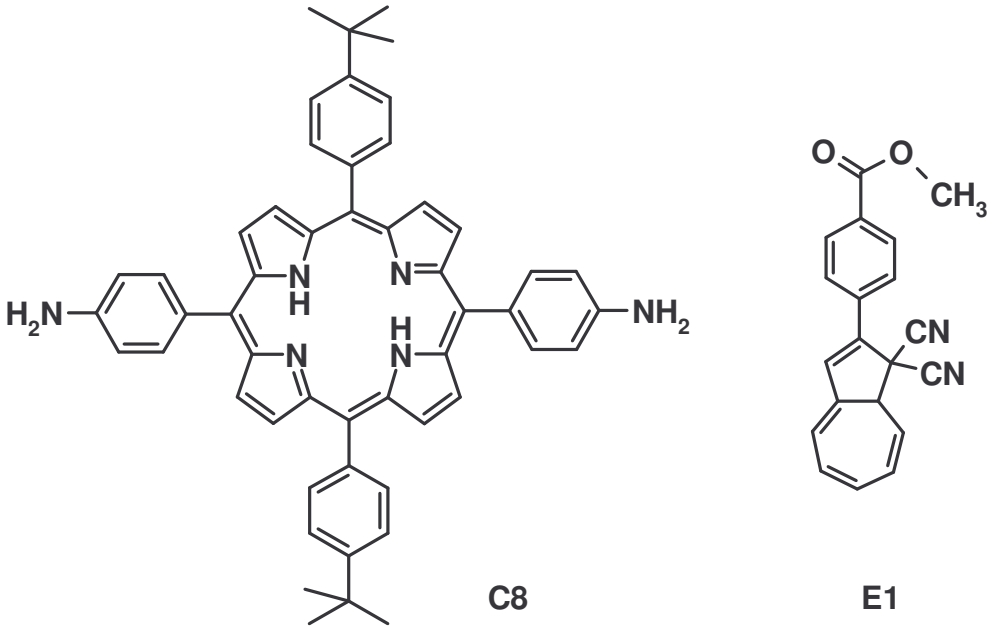
The most significant amount of monocyanoazulene has been noticed when tetrahydrofurane has been used. Diisopropylamine has been used as a base and then changed to stronger triethylamine. Product formation in the reaction with presence of diisopropylamine has been detected by mass spectra.

Another approach has been started to create a similar system connected by peptide bonds, Scheme 2.28.



Scheme 2.28: Porphyrin - dihydroazules conjugated system.

The porphyrin **C8** and DHA **E1,** the precursor of carboxylic acid derivative **E2,** have been synthesised, Scheme 2.29.



Scheme 2.29: Porhyrin C8 and digydroazulene E1.

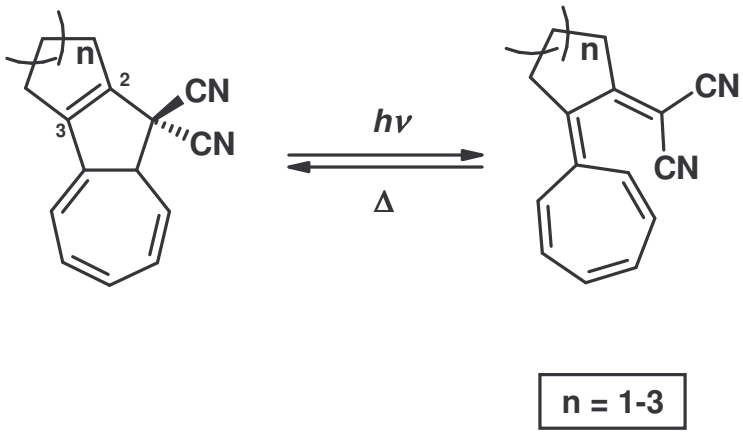
3 Sterically constrained dihydroazulene systems

3.1 Introduction

Attention is paid to studying the photochromism of dihydroazulene that undergoes upon irradiation with UV light a ring opening that leading to the corresponding vinylheptafulvene. Previous studies include theoretical and experimental findings in order to elucidate some aspects of the reaction mechanism. [90, 91]

The thermal back reaction from VHF to DHA hasn't been yet studied in great detail. An important aspect of the ground state back reaction of VHF to DHA is the assumption that the vinylheptafulvene occupies a s-*cis* – s-*trans* VHF interconvertible equilibrium. The idea behind present studies is to get more information about the influence of the vinylheptafulvene form on the thermal back reaction.

There are several constrained DHA/VHF systems already known, Scheme 3.1.

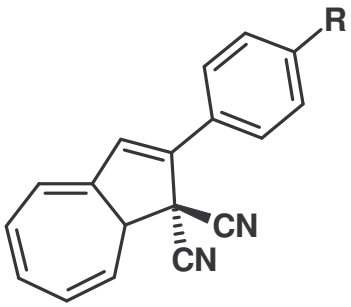


Scheme 3.1: Sterically constrained photochromes

[90] a) V. De Waele, U. Schmidhammer, T. Mrozek, J. Daub, E. Riedle, *J. Am. Chem. Soc.,* **2002**, 124, 2438;
b) V. De Waele, M. Beutter, U. Schmidhammer, E. Riedle, J. Daub, *Chem. Phys. Lett.* **2004**, 390, 328–334.

[91] M. Boggio-Pasqua, M.J. Bearpark, P.A. Hunt, and M.A. Robb, *J. Am. Chem. Soc*. **2002**, 124, 1456-1470.

1,2,3,8a-Tetrahydro-cyclopenta[a]azulene-9,9-dicarbonitrile (**CP-DHA**, n = 1) undergoes photochemical ring opening reaction to the vinylheptafulvene with a quantum yield almost one, Scheme 3.1. The thermal back reaction of **CP-VHF** has a lifetime of more than 6 h at RT. This timescale is common also for other non-constrained dihydroazulene derivatives such as **A2** – **A4**, Scheme 3.2, etc.[92] Nevertheless, in case of **CHex-DHA** (n = 2) properties of photoproduct **CHex-VHF** are significantly different.[93] The thermal back reaction at RT is takes place in a scale of seconds measured by steady state spectroscopy at -60 °C in ethanol.



	R
A2	-H
A3	$-CH_3$
A4	-CN

Scheme 3.2: Structures of phenyl derivatives of dihydroazulene

CHept-DHA (Scheme 3.1, n = 3) shows similar to **CHex-DHA** behaviour with a slightly slower thermal back reaction speed.[95]

In case of normal DHA derivative, like **A4,** the irradiation starts photoisomerisation reaction, which leads first to *cis*-VHF isomer and then to more stable energetically *trans*-VHF. [93,94,95]

The molecule might be imagined as **A2** with additional linking backbone between phenyl ring and C-3 atom of dihydroazulene moiety. This approximation gives possibility to compare influence of stabilization of vinylheptafulvene in s-*trans* conformation with analogous system that can't be stabilized and study behaviour of VHF in *cis* conformation only, Scheme 3.3.

[92] a) J. Daub, C. Fischer, S. Gierisch, and J. Sixt, *Mol. Cryst. Liq. Cryst*., **1992**, 217, 177-185;

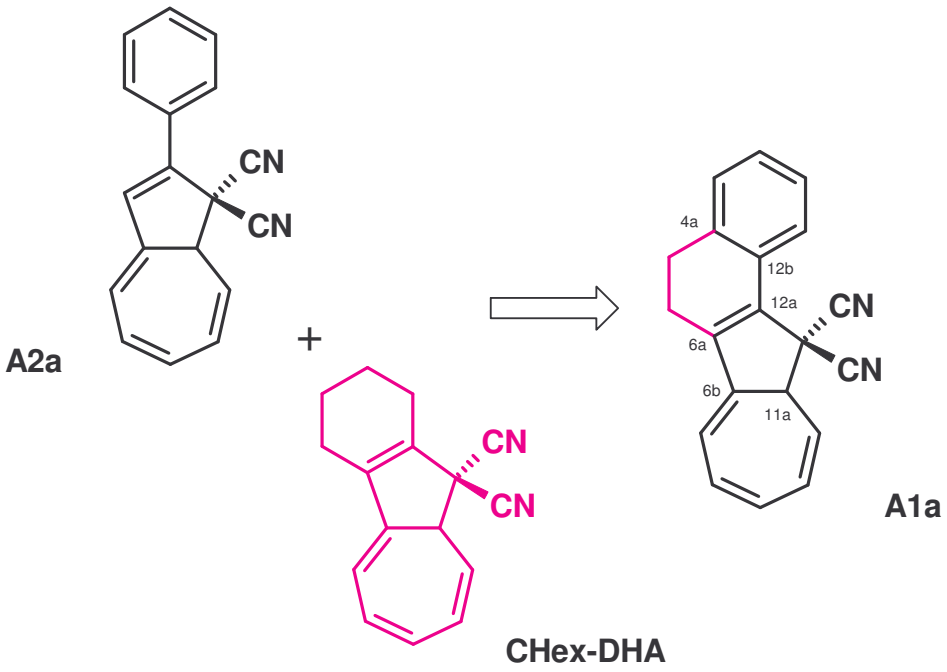
b) H. Görner, J. Daub, C. Fischer, S. Gierisch, *J. Phys. Chem.* **1993**, 97, 4110-17;

c) H. Görner, C. Fischer, J. Daub, *J. Photochem. and Photobiol., A: Chemistry,* 85, **1995**, 217-124.

[93] S. Gierisch, J. Daub, *Chem. Ber.*, **1989**, 122, 69-75.

[94] J. Ern, M. Petermann, T. Mrozek, J. Daub, K. Kuldova, C. Kryschi, *Chem. Phys*. **2000**, 259, 331-337.

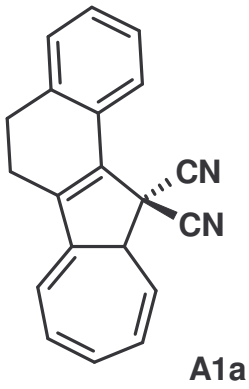
[95] T. Mrozek, *Diploma Thesis*, Universität Regensburg, **1997**.



Scheme 3.3: Structure of 5,11a-dihydro-6H-naphtho[2,1-a]azulene-12,12-dicarbonitrile.

The system **A1,** 5,11a-dihydro-6H-naphtho[2,1-a]azulene-12,12-dicarbonitrile have been made. It might be described like fusion of **A2** and CHex-DHA systems. The difference from **A2** is the $–CH_2-CH_2–$ bridge between phenyl and C3 atom of dihydroazulene. This backbone is flexible enough for vinylheptafulvene formation but does not allow *cis – trans* conversion of VHF.

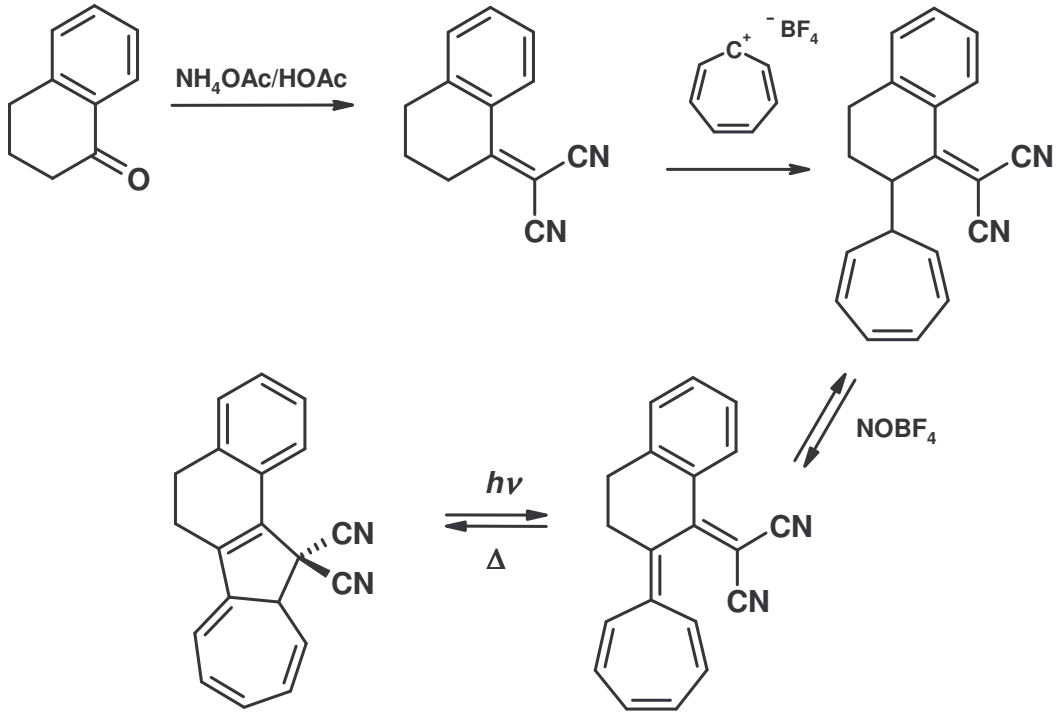
The difference from CHex-DHA is the phenyl ring and so additional double bond in six-membered ring system which makes it less flexible.



Scheme 3.4: Structure of the sterically constrained dihydroazulene A1a.

3.2 Synthesis of bridged dihydroazulene

Synthesis of this DHA is analogous to common synthetic pathway described in chapter 2.1. First step is Knoevenagel reaction of α-tetralon (3,4-dihydro-2H-naphthalen-1-one) with malononitrile catalyzed by ammonium acetate in glacial acetic acid. Next step is the reaction with tropilium tetrafluoroborate catalyzed by base. Obtained product treated with nitrosyl tetrafluoroborate gives the corresponding vinylheptafulvene that quickly thermally converts to dihydroazulene - 5,11a-dihydro-6H-naphtho[2,1-a]azulene-12,12-dicarbonitrile, Scheme 3.5.



Scheme 3.5: Synthetic pathway of bridged Ar-DHA

3.3 Spectroscopic data of A1a and photochromic behaviour

A1a shows similar absorption for DHA derivatives (for example p-CN-DHA[96]), the absorption maximum of **A1a** is at about 363 nm the extinction coefficient is 19300 $M^{-1}cm^{-1}$ in cyclohexane, Figure 3.1.

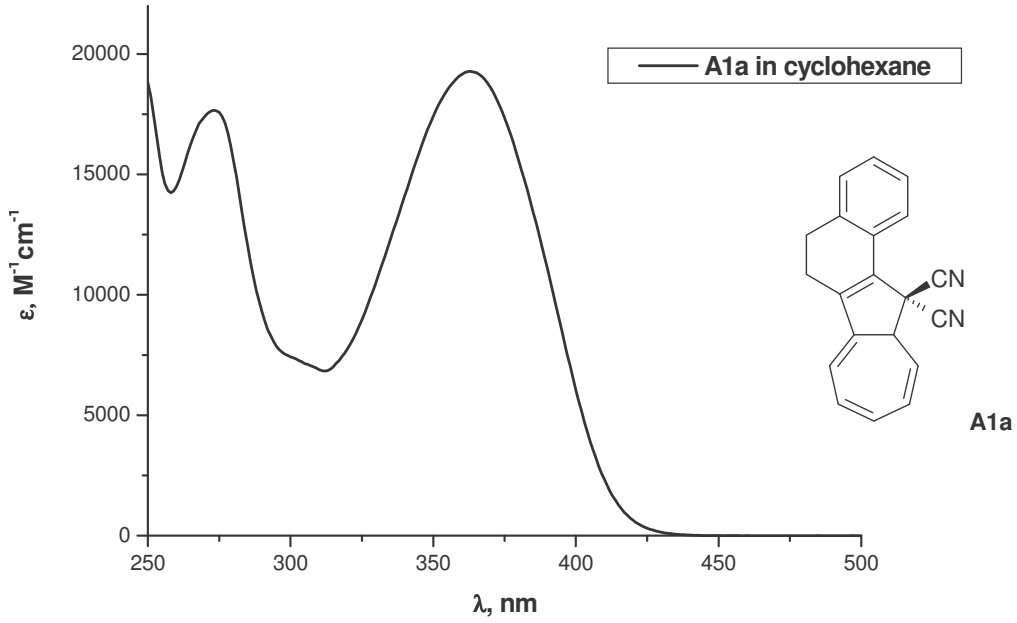


Figure 3.1: Absorption spectrum of A1a in cyclohexane.

Irradiation of the sample in CH_3CN with UV lamp λ_{ex} = 366nm at RT showed no photochromic reaction at second timescale. As it is known the rate of the thermal back reaction depends on solvent polarity (more polar – faster reaction) and substitution of phenyl ring.[97] Therefore the solvent have been changed to less polar, cyclohexane. These changes gave possibility to observe at room temperature photochromic behaviour of solution but for really short time.

Afterwards the solution in cyclohexane has been irradiated in 10mm cell for ca. 10 minutes with the UV lamp, λ_{ex} = 366nm, Figure 3.2. The colour of the solution changed to slightly red but disappears in few seconds, right after irradiation have been stopped. In all other cases, when more polar solvents where used (CH_2Cl_2, DMSO, CH_3CN) the product of photochromic reaction couldn't be noticed.

[96] V. De Waele, U. Schmidhammer, T. Mrozek, J. Daub and E. Riedle, *J.Am.Chem.Soc.,* **2002**, 124, 2438-2439.

[97] T. Mrozek, J. Daub, A. Ajayagosh, In *Molecular Switches*; B. L Feringa, Ed.; Wiley-VCH: Weinhein, **2001.**

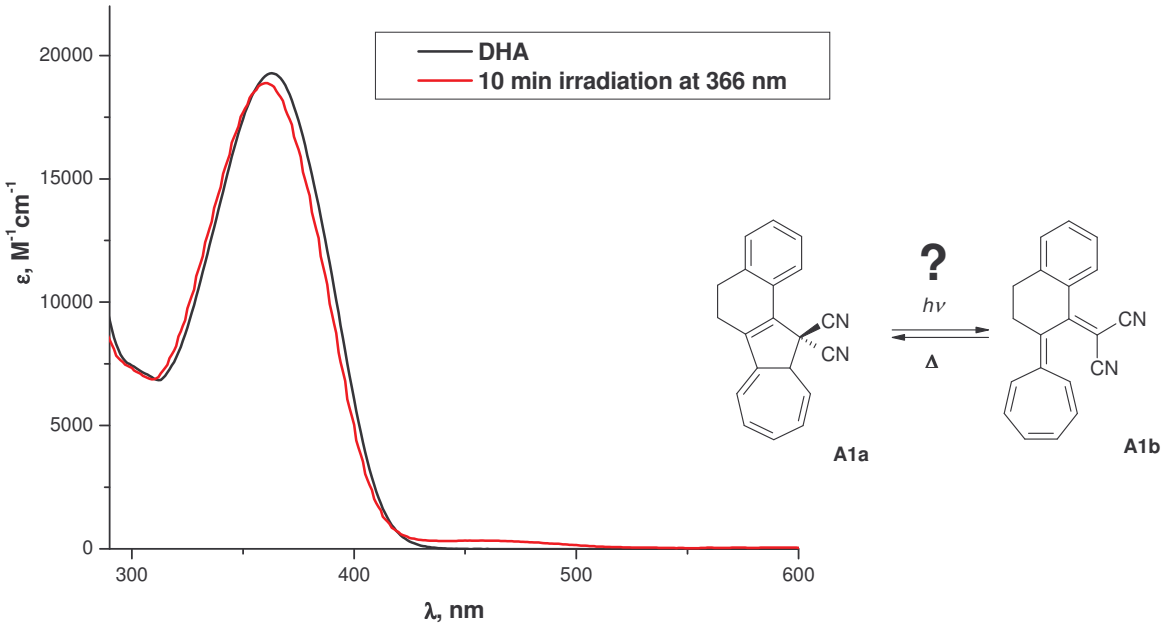


Figure 3.2: Absorption spectra of A1a in cyclohexane before and after irradiation at λ_{ex} = 366 nm for ca. 10 minutes.

Photochromism of DHAs could be clearly seen under lower temperature.[93] The solution of **A1a** in CH_3CN has been frozen in liquid nitrogen and irradiated with UV light λ_{ex} = 366nm. The probe solution changed its colour from slightly yellowish to reddish. During the solution warming the decolouration occurs that is the sign of thermal back reaction. Irradiation with UV light λ_{ex} = 254 nm (ca. 15 minutes) provides formation of non-photochromic product detected by UV spectroscopy.

3.4 Discussion

3.4.1 Photochromism of sterically constrained systems

As have been mentioned already **A1** might be imagined as **A2** with additional linking backbone between phenyl ring and C-3 atom of dihydroazulene. On the assumption of similar electronic influence onto dihydroazulene moiety one can propose quite similar photochromic properties of **A1** and **A2**. The ethyl bridge between phenyl ring and C-3 atom is quite flexible to give molecule undergo normal photoinitiated reaction.

Quantum yields of VHF formation for **A2** and **A3** are 0.55 respectively 0.5 in acetone. For aryl-DHA systems have been proposed energetic diagram, Figure 3.3. After excitation around 360 nm in the S_0–S_1 absorption band, **C4a** undergoes a photoconversion to the **C4b** conformer.[98]

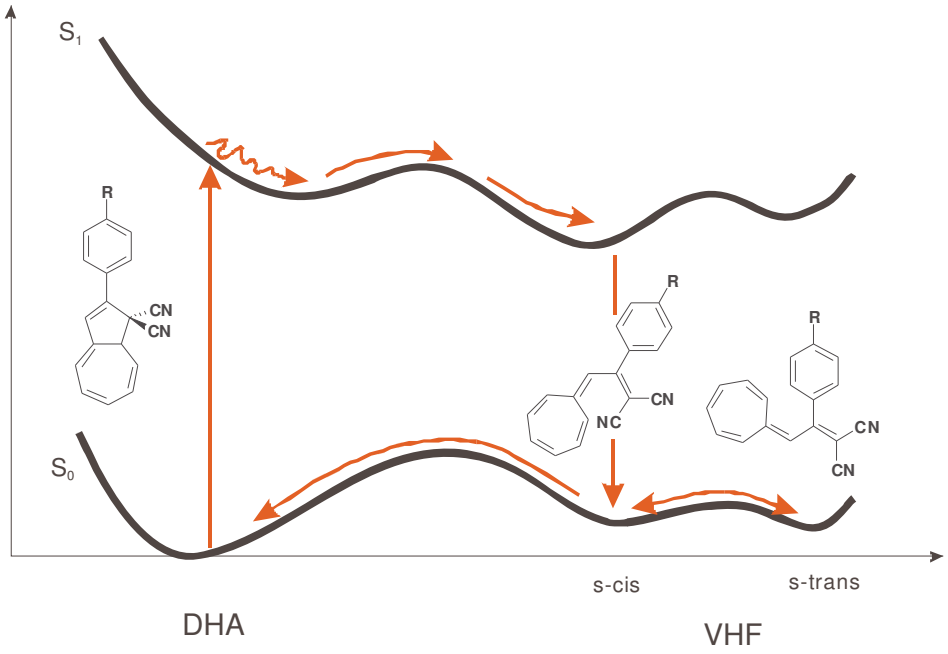


Figure 3.3: Schematic representation of the reaction profiles of the photochemical pathway DHA→VHF and the thermal pathway VHF→DHA.

As a member of the DHA-family **CP-DHA** is unique in its photochemical performance and it is also surprisingly that **CHex-DHA** behave as a usual DHA-family member.[93] **CP-DHA** undergoes photochemical reaction from DHA to VHF with quantum yield almost one and forms vinylheptafulvene within 1.2 ps.[94] The speed of this reaction has been attributed to a conical intersection between the ground and first excited states, Figure 3.4.

[98] H. Görner, C. Fischer, S. Gierisch, J. Daub, *J. Phys. Chem.* **1993**, 97, 4110.

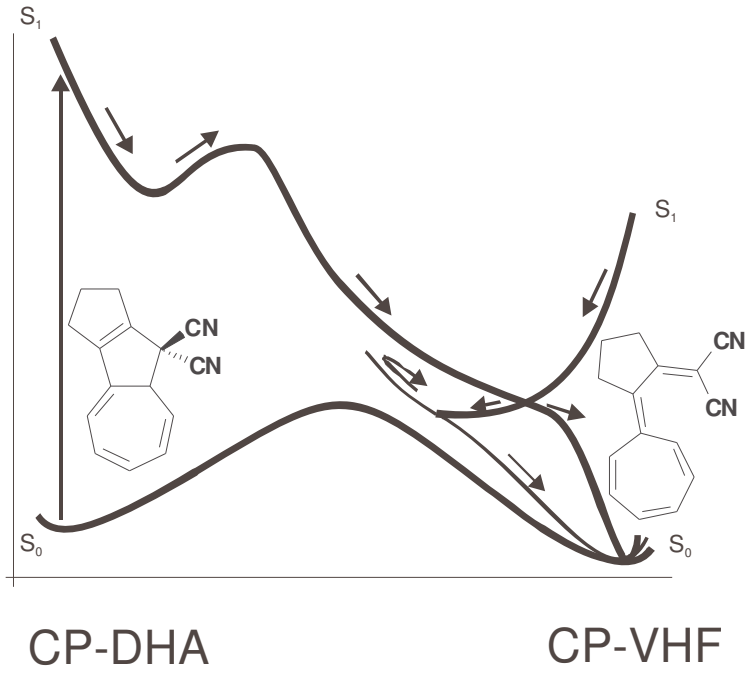


Figure 3.4: S_1 and S_0 potential energy surfaces of CP-DHA/VHF based on calculations and experiment.[94, 99]

One can imagine that the scheme of photochromic reaction **CHex-DHA** to **CHex-VHF** will be similar to **A2**-**A4**, Figure 3.5.

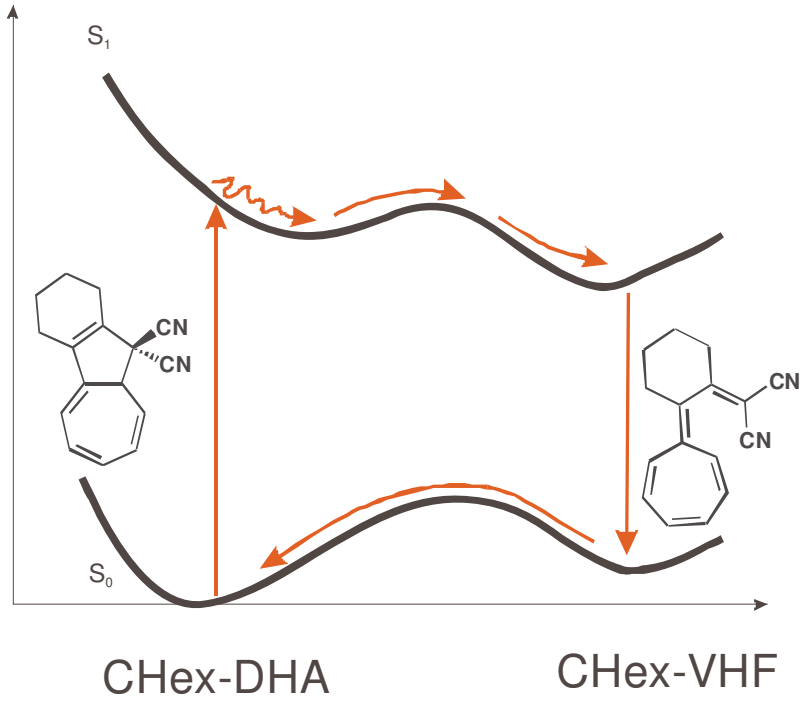


Figure 3.5: S_1 and S_0 potential energy surfaces of sterically constrained DHA/VHF suggested by experiment.

[99] M. Boggio-Pasqua, M.J. Bearpark, P.A. Hunt, and M.A. Robb, *J. Am. Chem. Soc*. **2002**, 124, 1456-1470.

It might be assumed that photochromic reaction of **A1** should be similar to **CHex-DHA** and **A2**-**A4** systems, than the S_1 reaction pathway for **A1** will look like for **CHex-DHA** one, Figure 3.5.

3.4.2 Thermal back reaction of sterically constrained systems

Known systems **CP-DHA**, **CHex-DHA** and **CHept-DHA** show different rates of VHF to DHA thermal back reaction.

In case of **CP-VHF** at room temperature it has a lifetime of more than 6 h.[94] But this is the only example of sterically constrained dihydroazulene systems that consistent with results obtained from other experiments.[98] Other systems show totally different behaviour from the point of view of thermal back reaction. **CHex-VHF** has drastically smaller lifetime in comparison to other vinylheptafulvenes. At room temperature it could be detected only in non-polar solvents and clearly seen under lower temperature. **CHept-DHA** shows similar to **CHex-DHA** behaviour with a slightly slower thermal back reaction speed.

According experimental result achieved for **A1** system that showed extremely fast thermal back reaction. Unlike photochromic reaction where **A1** could be compared with **A2**-**A4** in case of thermal reaction of vinylheptafulvene it shows comparable properties to **CHex- and CHept-DHA/VHF** sterically constrained system.[90-92, 95, 100]

Preliminary studies with cooperation of Riedle group in Munich showed that the results of measuring **A1a** are consistent with obtained for **C4a** and CP-DHA.[90,94,96] The thermal back reaction have been resolved at 22°C in cyclohexane and CH_3CN. The lifetimes of vinylheptafulvene **A1b** are 1.12 s in cyclohexane and 0.09 s in CH_3CN.

Several factors should be discussed that are important for description of thermal back reaction VHF→DHA and influence the rate of this reaction:

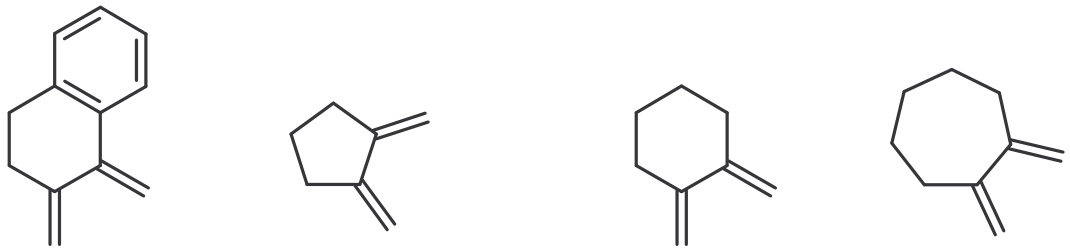
- Stabilization by transformation of VHF from s-*cis* conformation to more energetically favourable s-*trans* conformation
- Structural aspects of constrained systems
- Energetics of s-*cis*-VHF→DHA process, value of energy barrier of process

[100] T. Mrozek, *Dissertation*, Universität Regensburg, **2000.**

Stabilization due to s-*cis* – s-*trans* conformation have been proposed before and described several times. The stability of s-*trans* form is postulated. It is not possible in case of discussed systems. This option is prohibited by structure of molecules.

If not to take into account **CP-DHA** system, introduction of hindrance to DHA/VHF system destabilizes its open form. The **CP-DHA** case might be explained from the point of view of geometrical properties and will be discussed later.

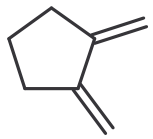
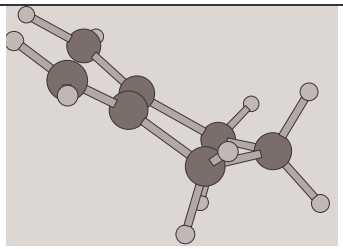
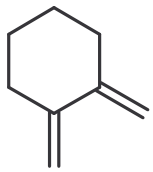
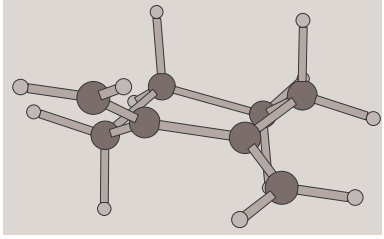
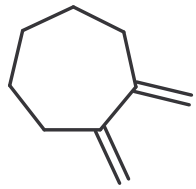
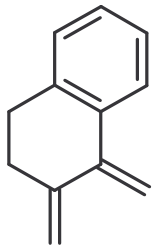
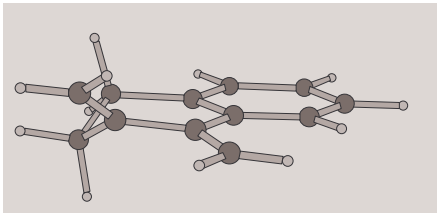
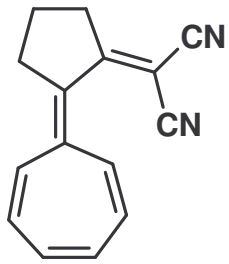
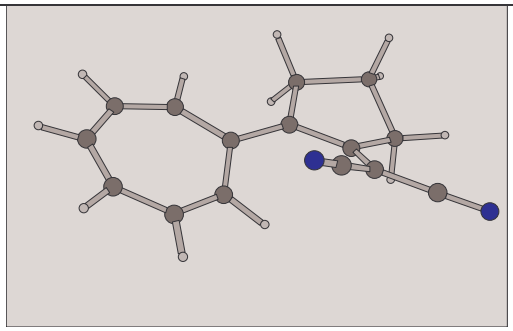
Sterical hindrance due to different linking pattern might play a great role in molecule open form stabilization. But by this factor it is harder to explain why system with less flexible 5-membered ring is more stable than 6-membered. The answer might be comparing of geometry of cyclic fragments in molecule with geometry of similar model compounds that are free from hindrances caused by interaction of heptafulvene and dicyanoethylene fragments. For described systems **CP-**, **CHex-** , **CHept-VHF**, and **A1b** this model compounds could be proposed, Scheme 3.6.



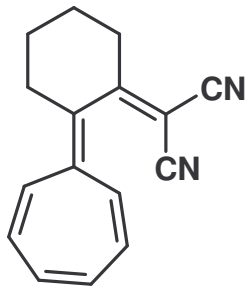
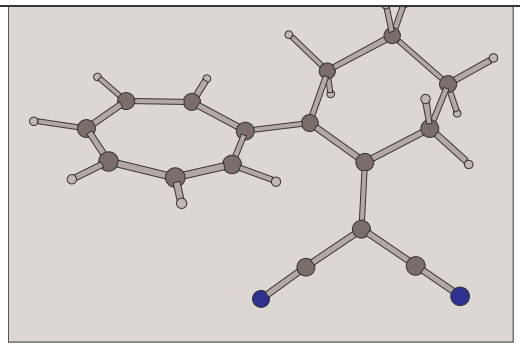
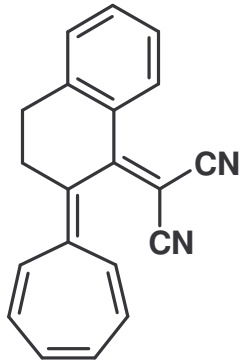
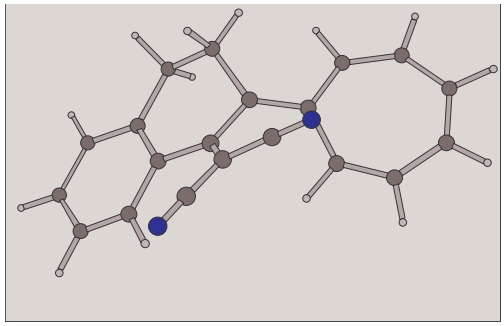
Scheme 3.6: Model compound of constrained systems.

All vinylheptafulvenes and corresponding model compounds were calculated with Gaussian 98W. By DFT method B3LYP/6-31Gd for all structures optimized geometries were found. Calculated data presented below:

Table 3.1: Calculated structures of constrained systems and corresponding model compounds.

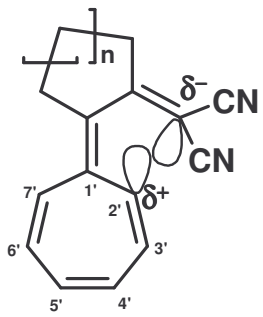
Structure	Calculated structure[101]	C=C-C=C angle
		0.00
		32.69
		47.64
		39.02
		30.52

[101] Calculated structures are visualized with *MOLVIEW 3.0.*

		42.43
		60.45

Comparison of model systems with corresponding VHFs shows only higher geometrical changes in CP-system due to hindrances caused by overlapping of cyano- and tropilium substituents. Also clear that larger ring systems are more flexible in comparing to five-membered. It might be assumed that the geometrical perturbations upon thermal reaction should be smaller for bigger ring systems and have lower energy barrier. Also should be noticed that partial charges of methylene and 2' carbon atom of tropilium moiety are comparable for all observed systems and might be assumed that they are not play a great role in such a big differences of thermal back reaction rates.

Taking into account results of time measurements of the thermal back reactions of vinylheptafulvenes described before and geometrical structures of calculated open forms might be proposed such a explaining of this reaction.



Scheme 3.7: Vinylheptafulvene with showed positions of orbitals that form σ – bond.

Thermal back reaction proceeds on ground state reaction pathway and according to frontier orbital theory leads to bond formation between 2' carbon atom of heptafulvene moiety and methylene atom and requires disrotatory motion.

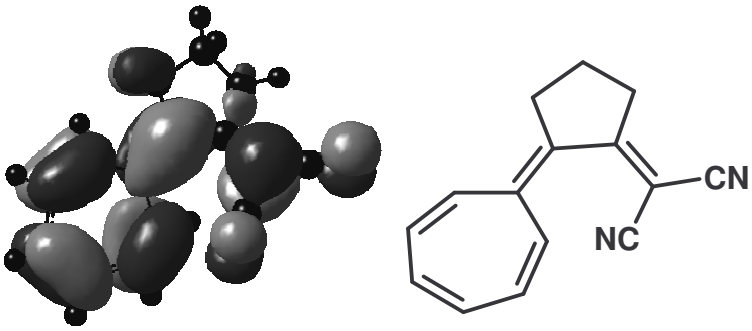
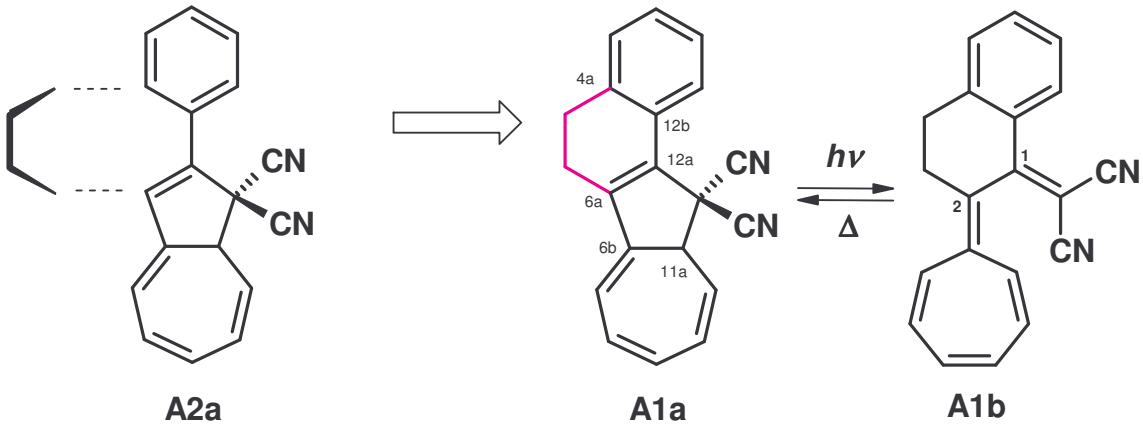


Figure 3.6: Higher occupied molecular orbital (HOMO) orbitals of CP-VHF.

Taking in account previous assumption it might be conclude that thermal back reaction rate will depends mostly on geometrical changes needed for thermal rearrangement and this rearrangements in most rigid CP-VHF system should be largest.

3.5 Conclusions

Annulation of **A2a** as indicated in Scheme 3.8 has a two-fold effect on the structure and dynamics of the DHA/VHF system. At first, the rotation around C_{12a}-C_{12b} in **A1a** is restricted and second, the rotation around C_1-C_2 bond in **A1b** is blocked.



Scheme 3.8: Structure of dihydroazulenes A1a and A2.

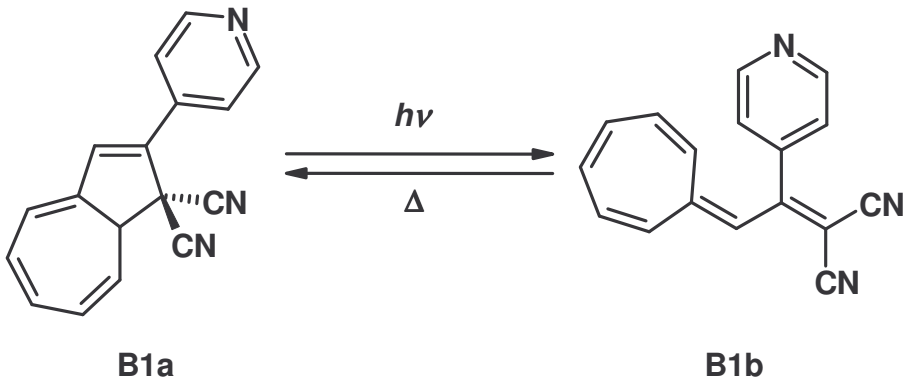
Six-ring annulation as shown in **A1** leads to an increase of the rate of the thermal back reaction (VHF → DHA) and as a consequence the photochromism cannot be observed at room temperature under the normal experimental conditions. However, lowering the temperature the colouring occurs on irradiating the DHA form.

Future photophysical investigations, especially by the resolved methods will provide more information on the excited states of this sterically restricted system.

4 Receptor functionalized chromophores

4.1 Introduction

The compounds 2-pyridin-4-yl-8aH-azulene-1,1-dicarbonitrile **B1a** and 2-pyridin-3-yl-8aH-azulene-1,1-dicarbonitrile **B2a** were synthesised to create a photochromic system, based on dihydroazulene/vinylheptafulvene and pyridine moiety which serves as a binding/receptor site for probing intermolecular interactions, Scheme 4.1.[102,103] Complexing function of pyridine and its derivatives is well known in biological systems and artificial assembles as well.



Scheme 4.1: Photochromic reaction of B1a to B1b.

In this chapter, the influence of the non-covalent bonding on photochromic behaviour of DHA/VHF is discussed.[104] The pyridine used as a complexation site.[105] Heterocyclic ligands such as pyridine

[102] a) *Molecular Switches*; B.L. Feringa, Ed.; Wiley-VCH: Weinhein, **2001**;

b) Photochromism: Memories and Switches, Special issue of *Chem. Rev*., **2000**, *100*, 1683-1890.

c) Photochromism: Molecules and Systems (Revised Edition), H. Dürr, H. Bouas-Laurent, Elsevier, Amsterdam, **2003**.

[103] a) F.M. Raymo, M. Tomasulo, *Chem. Soc. Rev*., **2005**, 34, 327-336;

b) F.M. Raymo, *Adv. Mater*., **2002**, 14, 401.

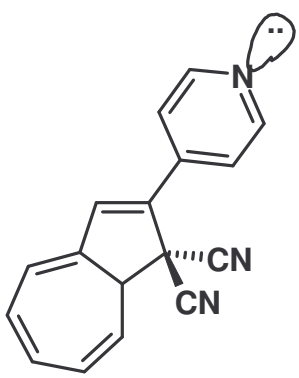
[104] a) L. Biczók and H. Linschitz, *J. Phys. Chem. A*; **2001**; 105, 11051;

b) K. Sebok-Nagy and L. Biczók, *Photochem. Photobiol. Sci*. **2004**, 3, 389.

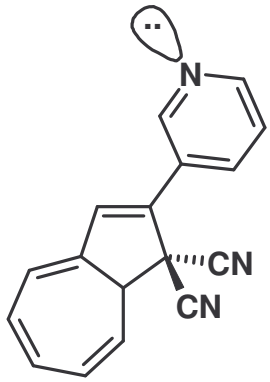
[105] a) F. Deng, A.C. Testa, *J. Photochem. Photobiol. A: Chem.* **1998**, *112*, 191;

b) F. Deng, J. Kubin, A.C. Testa, *J. Photochem. Photobiol. A: Chem.* **1998**, *118*, 1.

and related molecules are good ligands due to the presence of a localized lone pair on a nitrogen atom of the aromatic ring.[106]



B1a



B2a

It is evident that any heterocyclic nitrogen atom can act with a non-conjugated lone pair as a donor atom toward protons and metal ions only if sterical effect of the substituent does not hinder the coordination. Pyridine itself is the best-known heterocyclic nitrogen ligand and its coordination chemistry has been studied in great details, as well as its derivatives bearing non-coordinating substituents.[107]

They have become essential in many fields, such as supramolecular chemistry[108], transition metal chemistry[109], optoelectronic[110], and pharmaceutical chemistry.[111]

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[106] J. Reedijk, in Comprehensive Coordination Chemistry (Eds.: G.Wilkinson, R. D. Gillard, J. A. McCleverty) Vol.2, 73-98, Pergamon Press, **1987**.

[107] For the physical properties: a) A. R. Katritzky (ed.), "Advanced in Heterocyclic Chemistry", Academic, New York, Vol.6, 229, **1963**.

b) A. R. Katritzky and C. W. Rees (eds.), "Comprehensive Heterocyclic Chemistry", Pergamon, Oxford, **1984**.

[108] a) G. Hanan, U. Schubert, D. Volkmer, E. Rivie`re, J.-M. Lehn, N. Kyritaska, J. Fischer, *Can. J. Chem.* **1997**, *75*, 169-182;

b) E. C. Constable in *Progress in Inorganic Chemistry*, (Ed.: K. D. Karlin), Wiley, **1994**, *42*, 67.

[109] a) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85-277;

b) C. Bolm, M. Zehnder, D. Bur, *Angew. Chem.* **1990**, *102*, 206-208;

c) G. R. Newkome, *Chem. Rev.* **1993**, *93*, 2067-2089;

d) C. Kaes, A. Katz, M. W. Hosseini, *Chem. Rev.,* **2000**, *100*, 3553-3590.

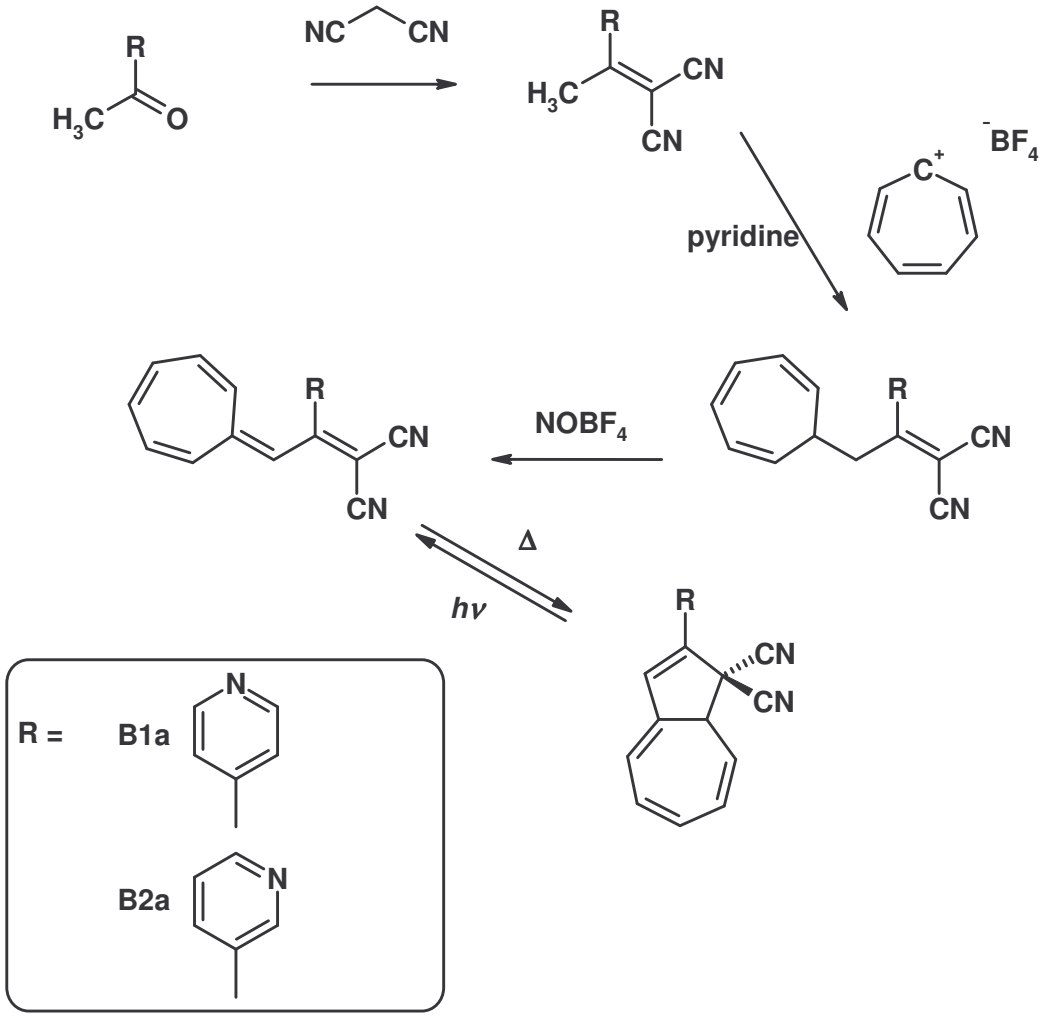
[110] H. Le Bozec, T. Renouard, *Eur. J. Inorg. Chem.* **2000**, *2*, 229-239.

[111] A. Godard, F. Marsais, N. Plé, F. Trécourt, A. Turck, G. Quéguiner, *Heterocycles* **1995**, *40*, 1055-1091.

To elucidate the influence of complexation on photochromic/spectral properties of the DHA/VHF systems **B1a** and **B2a** compounds were synthesised.

4.2 Syntheses of B1a and B2a

The syntheses[112,113] of pyridyl DHAs have the same way as the common synthesis of aryl derivatives of dihydroazulenes:



Scheme 4.2: Common synthetic pathway towards pyridyl-DHAs, B1a and B2a.

[112] a) T. Mrozek, H. Görner, J. Daub, *Chem. Commun.,* **1999**, 1487-88.

b) S. Gierisch, J. Daub, *Chem. Ber.,* **1989**, 122, 69-75.

[113] a) J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz, *Chem. Ber.,* **1986**, 119, 2631-46.

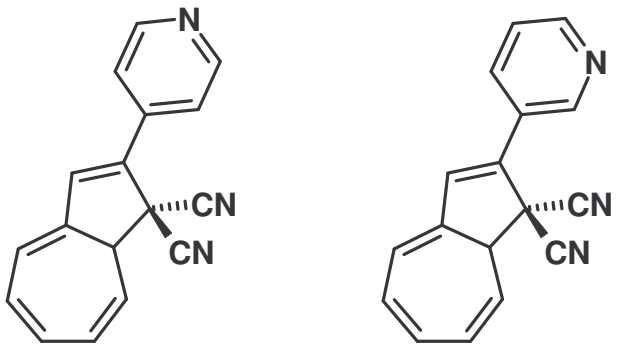
b) J. Daub, T. Knöchel, A. Mannschreck, *Angew. Chem.,* **1984**, 96, 980-981.

On Scheme 4.2 the common synthetic route for pyridyl-DHAs is shown. The first step is Knoevenagel reaction of the corresponding pyridyl ketone with malonodinitrile. This reaction is followed by the bond formation between the obtained dicyanoethylene derivatives with tropylium tetrafluoroborate. The last step of this synthetic route is dehydrogenation of the corresponding 2-(2-cyclohepta-2,4,6-trienyl-1-pyridinyl-ethylidene)-malononitrile with nitrosyl tetrafluoroborate and leads to the formation of the non-alternant VHF, which thermally rearranges to the corresponding DHA.

Some aspects of this synthesis have been already discussed in the synthesis part (chapter 2). Most differences in the syntheses, working up and handling of these compounds are due to common properties of pyridine derivatives.[114] For example self-catalyzed side reaction in case of 2-(1-pyridin-4-yl-ethylidene)-malononitrile discussed in synthesis, chapter 2.1.1.

4.3 Molecular structure and spectroscopic data of pyridine substituted DHA

In this chapter, spectroscopic properties of chromophore-receptor **B1** and **B2** units are elucidated, Scheme 4.3. Optical properties for initial dihydroazulene forms are described, as well as for open vinylheptafulvene forms.



B1a **B2a**

Scheme 4.3: Structures of dihydroazulenes B1a and B2a.

[114] a) Chemistry of Heterocyclic Compounds, Vol. 15, Part 1 (Ed. A. Weissberger), Wiley-Interscience, New York, **1961**;

b) T. Eicher, S. Hauptmann, The Chemistry of Heterocycles, Wiley-VCH, **2003**.

4.3.1 ^{1}H-NMR spectra

Dihydroazulene, closed form, under photoirradiation with UV light $\lambda_{ex.}$ = 366 nm isomerizes through 10-electron retrocyclization to vinylheptafulvene, opened form, Figure 4.1.[115, 116]

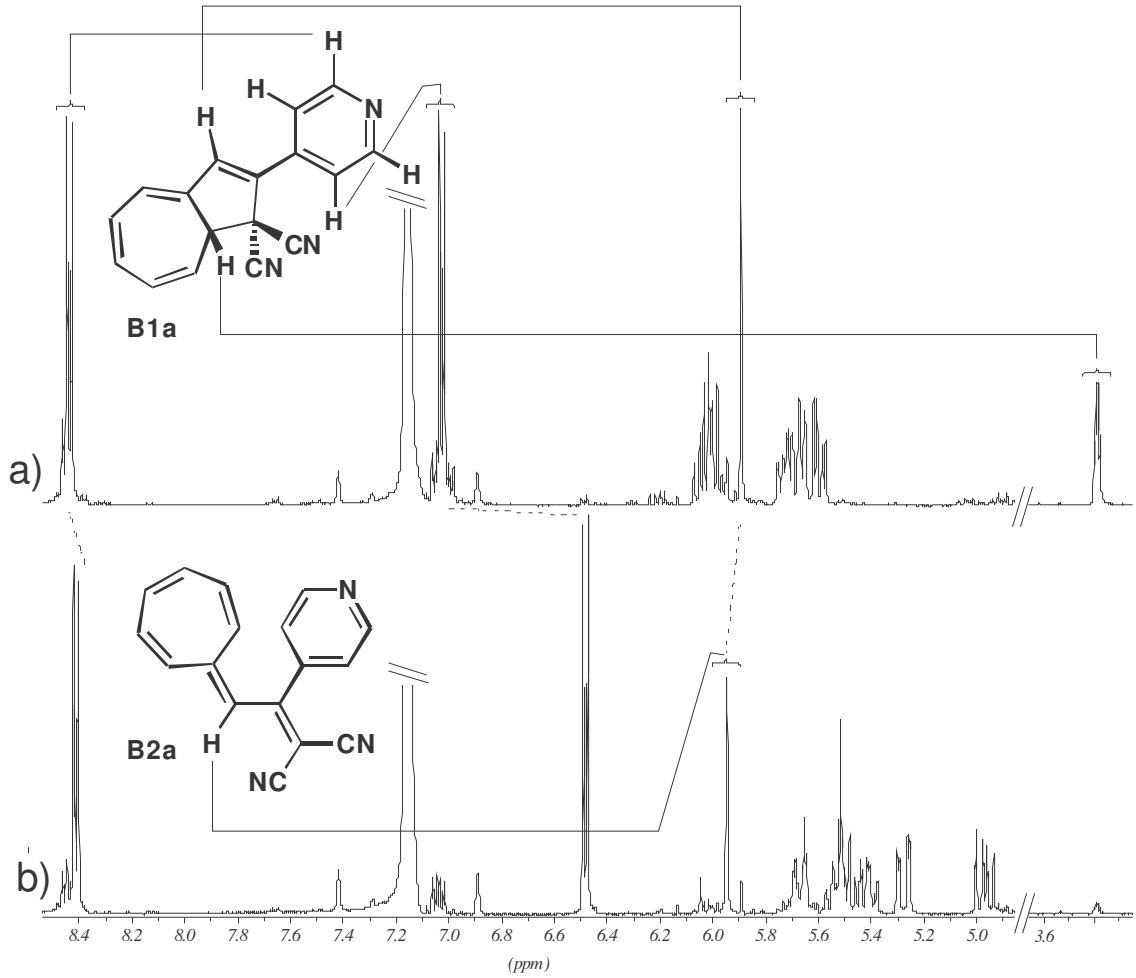


Figure 4.1: Part of ^{1}H-NMR spectra of DHA, a) before and VHF, b) after irradiation.[117]

The photochromism from DHA to s-*trans*-DHA involves two structural mechanisms: the first one is the ring opening which leads to s-*cis*-VHF form and the second one is s-*cis* – s-*trans* isomerisation

[115] J. Daub, T. Knöchel, A. Mannschreck, *Angew. Chem*, **1984**, 96, 980-981.

[116] J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz, *Chem. Ber*. **1986**, 119, 2631.

[117] D_6H_6 solution **B1a** have been irradiated for ca. 45 min in NMR tube with light λ = 366 nm.

of VHF.[118] It has been shown that this isomerization is slower by several orders of magnitude than the ring opening itself.[119]

The photochromic rearrangement leads to the significant change in the electronic structure of the system. Two electron-withdrawing cyano-groups come into conjugation with π-system of VHF that provides stronger acceptor character to nonalternant conjugated π-system of vinylheptafulvene. This specially influences the functional groups at C-2 position which is a pyridine ring in our case.[120]
^{1}H-NMR spectra of **B1a** and **B1b** clearly show changes of the system caused by photochromic reaction, Figure 4.1. Shifts of pyridine ring protons: $H_{A,A'}$ – from 8.44 in **B1a** to 8.41 in **B1b** – 0.03 ppm shift; for $H_{B,B'}$ – from 7.03 to 6.48 ppm - 0.55 ppm shift. Changes of dihydroazulene to vinylheptafulvene moiety spectra are similar to other Ar-DHAs.[121]

4.3.2 Absorption properties of pyridyl – DHAs

The absorption spectra of **B1** and **B2** are similar to those of other dihydroazulenes (for example **A4**[119]). The photochemically induced rearrangement of DHA to VHF is accompanied by change of colour: from yellow DHA to reddish VHF as a result of the decreasing absorption band around 350-360 nm for **B1a** and **B2a** and a new long wavelength absorption band forming around 480 nm.

The absorption maximum of **B1a** is about at 357 nm in CH_3CN, Figure 4.2 with molar extinction coefficient of 11900 $M^{-1}cm^{-1}$. [122]

[118] s-cis and s-trans are stereoisomers which differ in the stoichiometry of the exocyclic C–C single bond of the VHF form.

[119] V. De Waele, U. Schmidhammer, T. Mrozek, J. Daub, E. Riedle, *J. Am. Chem. Soc*. **2002**, 124, 2438-2439.

[120] J. Daub, C. Fischer, S. Gierisch, and J. Sixt, *Mol. Cryst. Liq. Cryst*., **1992**, 217, 177-185.

[121] S. Gierisch, *Dissertation*, Universität Regensburg **1989**.

[122] All characteristic absorption and VHF lifetime data collected in Table 4.2.

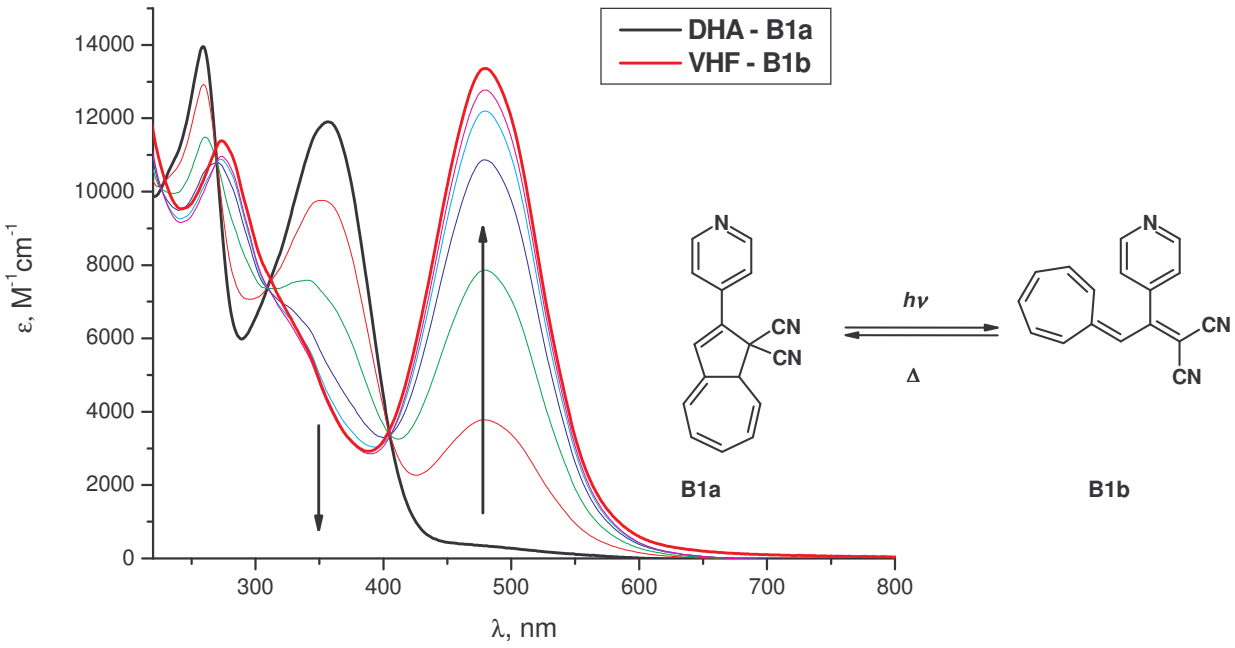


Figure 4.2: Absorption spectra of B1a and B1b in CH_3CN.

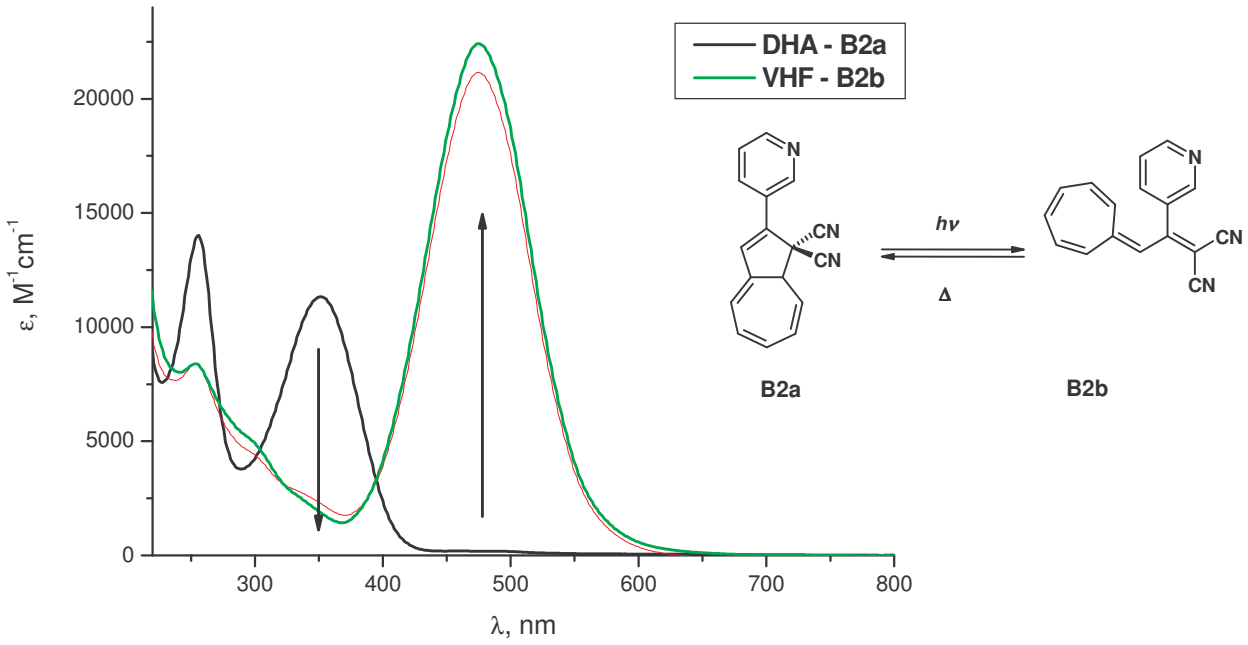


Figure 4.3: Absorption spectra of B2a and B2b in CH_3CN.

In case of **B2a**, the maximum of absorption is at 351 nm in CH_3CN and the molar extinction coefficient is 11300 $M^{-1}cm^{-1}$, Figure 4.3.

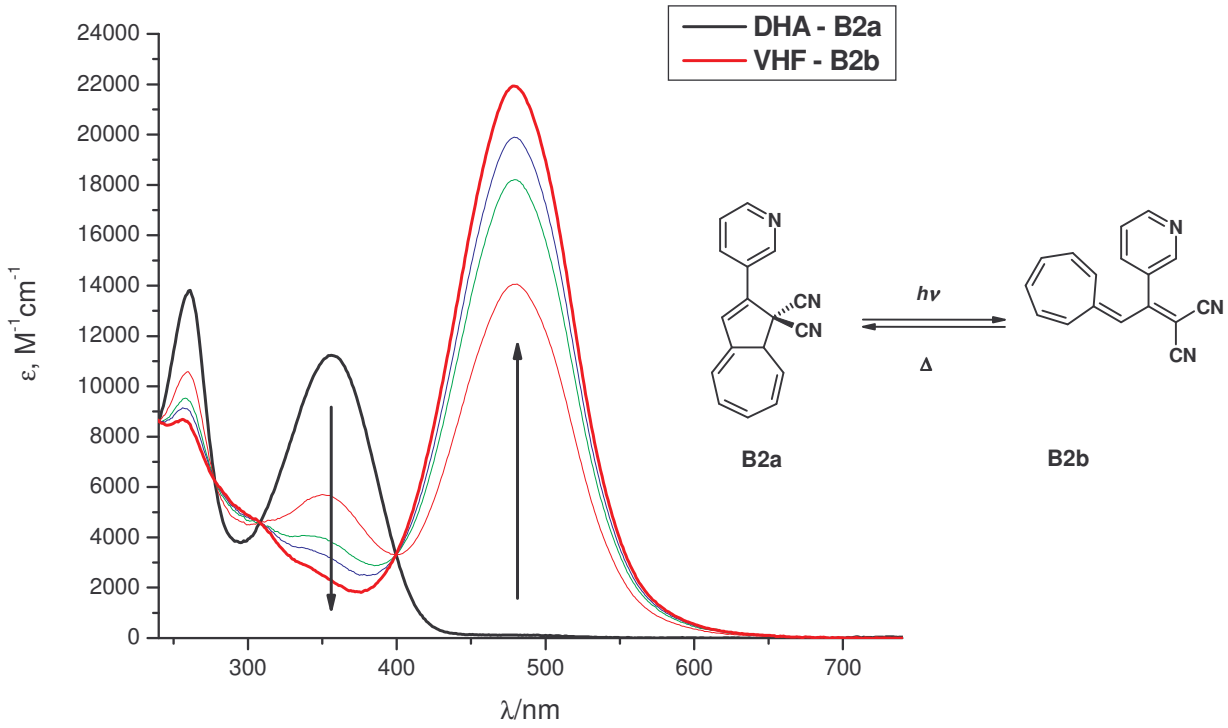


Figure 4.4: Absorption spectra of B2a and B2b in CH_2Cl_2.

Irradiation of DHA solution by 366 nm provides the photoconversion to VHF, Figure 4.2 and Figure 4.4, **B1b** and **B2b** respectively. Upon UV photolysis of **B1a** the spectra show isosbestic points which indicates that side product formation plays no role. The vinylheptafulvene **B1b** has the maximum of absorption at 480 nm in CH_3CN (ε = 13400 $M^{-1}cm^{-1}$) and for **B2b** 480 nm in CH_2Cl_2 (ε = 22400 $M^{-1}cm^{-1}$).

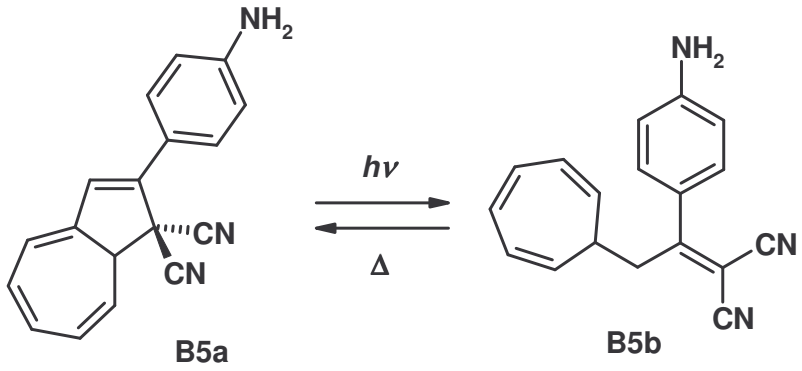
4.4 Impact of protonation on the spectral properties

Studies of the influence of the protonation onto **B1** and **B2** dihydroazulene/vinylheptafulvene forms were carried out. The results of the obtained spectral data expose the impact of protonation of the pyridine-based derivatives with trifluoroacetic acid.

Dihydroazulenes show no significant spectral changes towards substituent pattern or solvent polarity. Also protonation of DHA for example p-amino-phenyl derivative, **B5a**, Scheme 4.4 has no significant influence on spectral properties.[123]

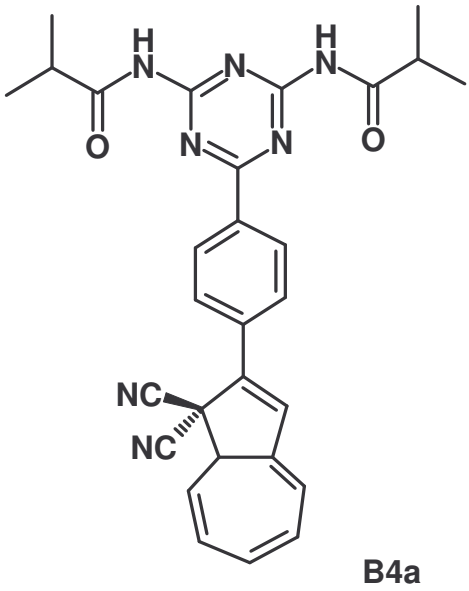
[123] H. Görner, J. Daub, C. Fischer, S. Gierisch, *J. Phys. Chem.* **1993**, 97, 4110-17

However, vinylheptafulvene is more sensitive to protonation due to more polar character of VHF. The polar solvent and stronger electron acceptor substituent cause faster thermal back reaction.[124]



Scheme 4.4: p-Amino-phenyl DHA.

Nevertheless, there is a known example of significant changes of properties of the DHA derivative. In case of 2,6-diamidotriazine dihydroazulene[125] (**B4a**) protonation showed great changes of both spectral data and photochromic behaviour.



[124] a) L.Gobbi, P. Seiler, F. Diederich, Angew. Chemie, Int. Ed., **1999**, 38, 674-678,

b) J. Daub, C. Fischer, S. Gierisch, J. Sixt, Mol. Cryst. Liq. Cryst., **1992**, 217, 177-185,

c) S. Gierisch, *Dissertation*, Universität Regensburg **1989**.

[125] C. Trieflinger, *Dissertation*, Universität Regensburg **2004**.

4.4.1 ^{1}H-NMR studies of protonation

^{1}H-NMR spectra of **B1a** and protonated form **B1aH$^+$** showed significant changes of the chemical shifts of the **B1a** protons, Figure 4.5.

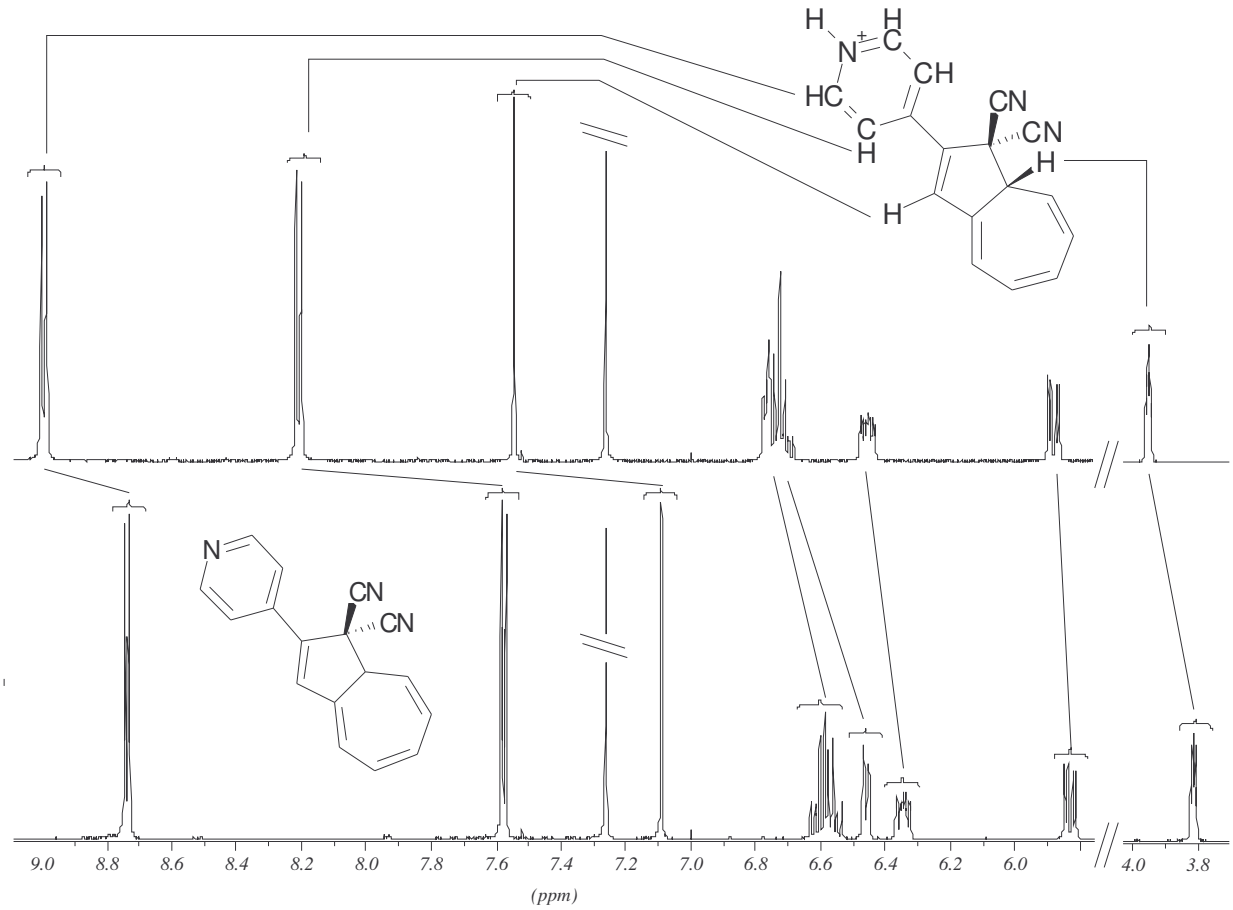


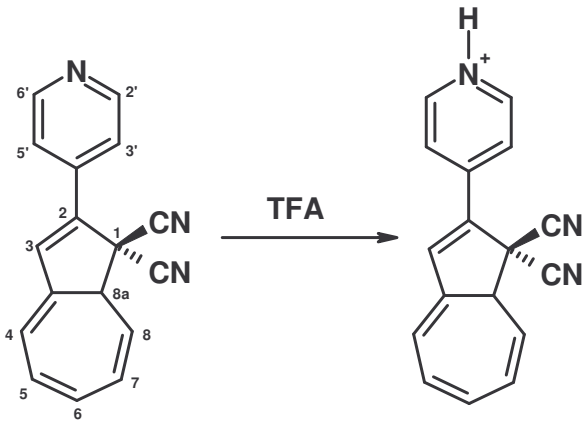
Figure 4.5: ^{1}H-NMR spectra of free B1a and protonated B1aH$^+$ in $CDCl_3$/TMS.

The spectra were measured in $CDCl_3$ solution at 400 MHz.[126] Addition of trifluoroacetic acid (ca. 38.5 fold excess) to the solution of **B1a** in $CDCl_3$ gave noticeable shift of protons to weak field, Table 4.1.

[126] Avance 400 (^{1}H: 400,1MHz), measuring temperature: 26°C

Table 4.1: ^{1}H-NMR data of free B1a and protonated B1aH$^+$ in $CDCl_3$.[127]

H	B1a	B1aH$^+$	Δδ
8a	3.81	3.95	0.14
8	5.83	5.88	0.05
7	6.35	6.45	0.10
4	6.47	6.72	0.25
6	6.55	6.70	0.15
5	6.61	6.76	0.15
3	7.11	7.54	0.43
2',6'	7.59	8.21	0.62
3',5'	8.75	9.00	0.25



The data presented at Table 4.1 show shift of protons to weak field and it is clear indication of some losses of electron density of hydrogen atoms not only at pyridine ring but by dihydroazulene moiety as consequence of interaction of pyridine ring with dihydroazulene part of molecule.

4.4.2 Influence of protonation on the electronic spectra: absorption

Addition of trifluoroacetic acid (TFA) in excess to **B4a** gave bathochromic shift from 379 nm to 434 nm; for **B4b** the shift is from 480 to 517 nm.

Protonation of **B1a** and **B2a** by TFA gave similar reaction as for **B4a**. The maximum absorption band for **B2a** has the bathochromic shift from 360 to 412 nm, Figure 4.6. In case of **B4a,** the shift is from 357 to 379 nm. The position of absorption maximum does not depend on the amount of added TFA. The protonation is reversible and addition of base shows the return of absorption maximum to initial state, Figure 4.6, dashed line. By the addition of triethylamine it is possible to get the initial spectra back; this shows the reversibility of the protonation of the pyridine derivatives **B1a** and **B2a**.

Similarly, the protonation of **B1b** and **B2b** by addition of TFA gave a bathochromic shift from 480 nm to 519 nm for **B1b** and 480 nm to 504 nm for **B2b**, Figure 4.7.

[127] 1.7 mg of **B1a** in 0.8 ml of $CDCl_3$/TMS; for **B1aH$^+$** spectrum – added 20 μl of trifluoroacetic acid to the previous solution.

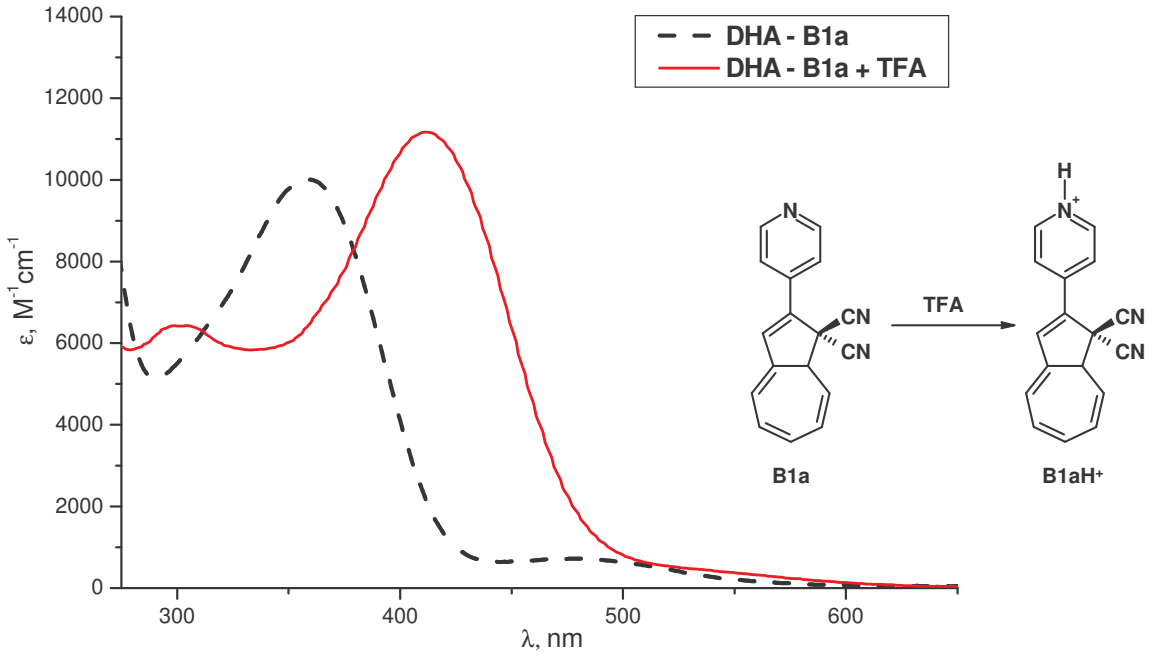


Figure 4.6: Absorption spectra of B1a and $B1aH^+$ (with addition of TFA) in CH_2Cl_2 ($c=5.44\cdot10^{-5}$ M).

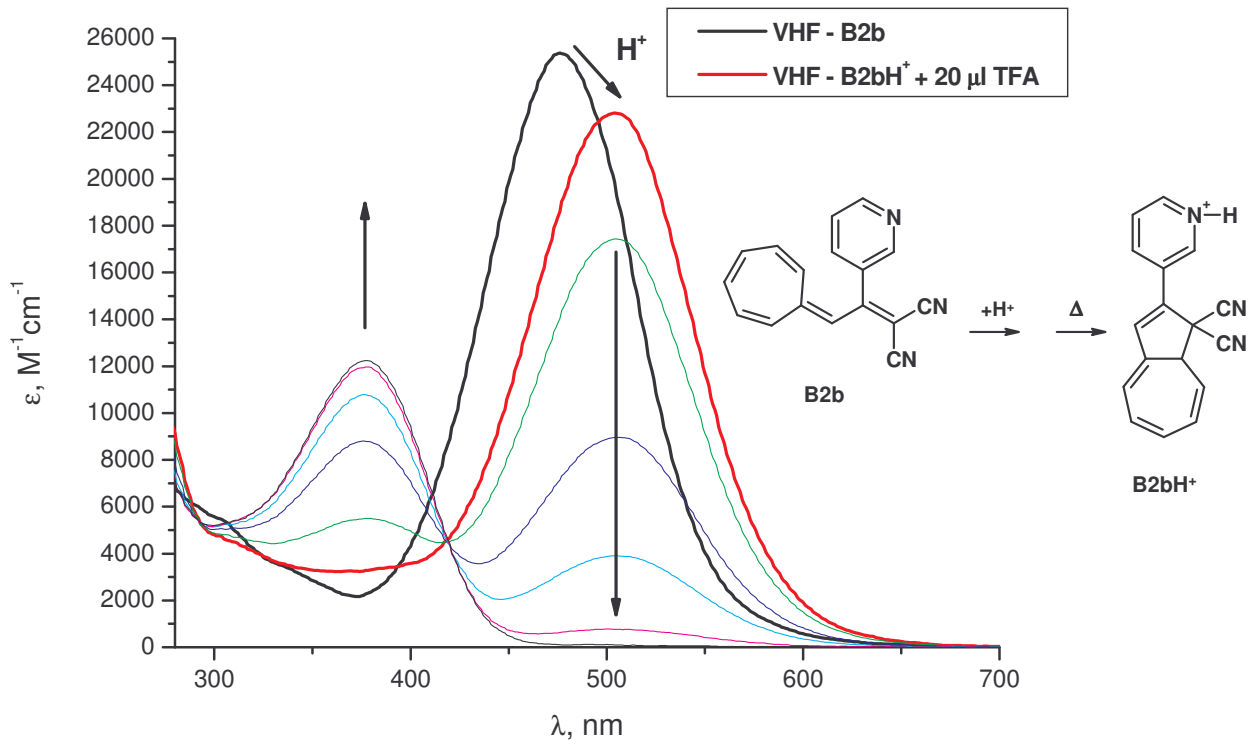


Figure 4.7: Thermal back reaction of $B2bH^+$ ($c = 4.66\cdot10^{-5}$ M) to $B2aH^+$ in 2.5 ml of CH_3CN.

4.4.3 Impact of protonation on the electronic spectra: emission

The fluorescence of pyridyl-DHA in comparison to other aryl-DHAs is weak.[128] With the addition of TFA, Figure 4.8, the emission increases. The emission maximum of the protonated **B1a** peaks at 450 nm, and of the protonated **B2a** at 485 nm. Excitation of **B1a** at 412 nm shows maximum absorption of protonated DHA **B1aH$^+$** at 506 nm. In the last case the emission increases by the addition of TFA but smaller than in case of irradiation at 366 nm, Figure 4.8. The fluorescence signals of **B1a** and **B2a** are weak, whereas no emission has been found for the VHF form.

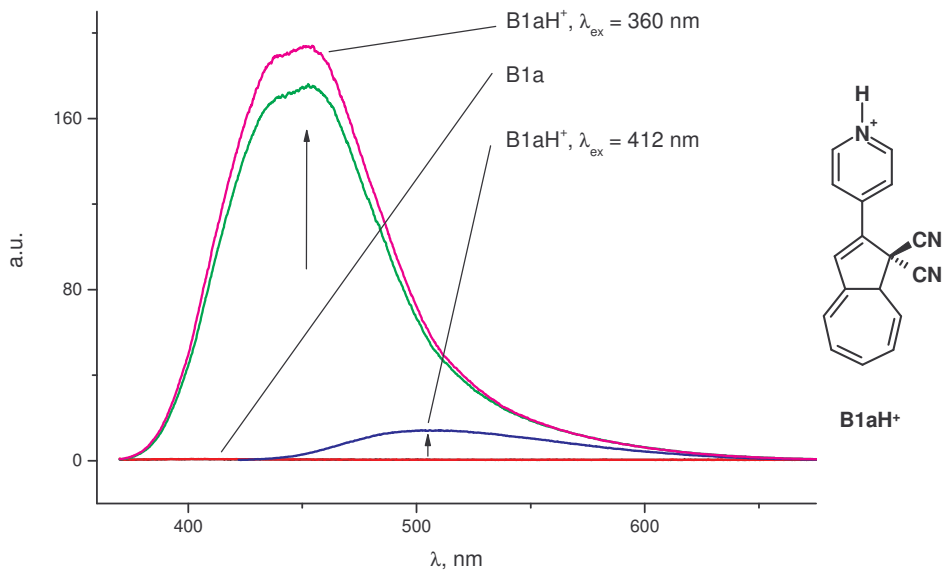


Figure 4.8: Changing of emission spectrum of B1a (c = 3.9•10^{-5}M) in CH_3CN by addition of TFA (30 µl), λ_{ex} = 360 nm, 412 nm.

[128] H. Goerner, C. Fischer, S. Gierisch, J. Daub, *J.Phys.Chem.* **1993**, 97, 4110-4117s.

4.5 Effect of protonation on dynamics of the pyridyl-DHA-VHF photochromism: forward and back reaction

In this part the rate of thermal back reaction were studied. The effect of the protonation on the dynamics of the pyridine – DHA/VHF isomerisation is shown. Some aspects of the forward and the back reactions are elucidated.

4.5.1 Calculation of half-life of thermal back reaction, DHA – VHF

This method has been used to calculate all rates of thermal back reaction of vinylheptafulvenes to corresponding dihydroazulenes. Protonated vinylheptafulvenes were achieved by protonation of corresponding VHFs.

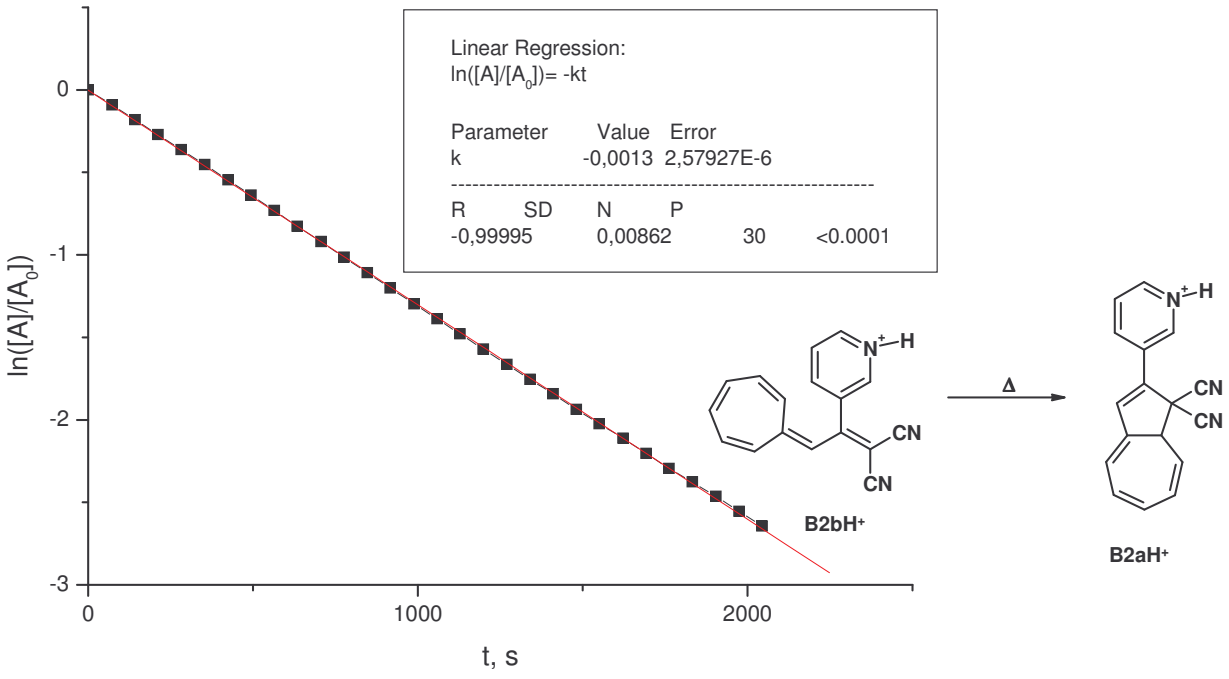


Figure 4.9: The determination of the rate constant of thermal back reaction of B2bH$^+$ by changes of absorption maximum at λ_{abs} = 501 nm in CH_3CN.

The first step is transformation of the corresponding dihydroazulene with a common laboratory UV lamp, λ_{ex} = 366 nm and following addition of TFA to the spectroscopic cell (only for experiments where decay time of protonated vinylheptafulvenes were studied), Figure 4.9.

Right after irradiation and addition of TFA (for cases where protonated forms of pyridine – vinylheptafulvenes were studied) series of absorption spectra were measured. Using this data maximum absorption of vinylheptafulvene was plotted versus measured time. This data was fitted by monoexponential decay. Achieved coefficient, k – decay rate constant was used to calculate half-life of thermal back reaction according the following equation:

$$(4.1)\quad kt_{1/2} = -\ln\left(\frac{\frac{1}{2}[A]_0}{[A]_0}\right) = -\ln\frac{1}{2} = \ln 2\,,$$

$t_{½}$: the time for [A] to decrease from $[A]_0$ to ½$[A]_0$;
A_0: concentration of measured compound in the time $t = 0$;
k: is the rate constant of decay expressed in units of inverse time.

The half-life ($t_{½}$) is the time it takes for half the molecules to decay. The half-life and the decay rate constant are related by this equation:

$$(4.2)\quad t_{1/2} = \frac{\ln(2)}{k}.$$ [129]

4.5.2 Pyridyl-DHA/VHF photochromism: forward and back reaction. Influence of protonation

As it has been mentioned before compounds **B1**, **B2** and **B4** have a bathochromic shift of the maximum absorption (λ_{max}) upon protonation. This is not the only change of the properties. The lifetime of the thermal back reaction from VHF to DHA decreases dramatically for **B4** from ca. 250 to ca. 5 min. It has been postulated that the main reason of these changes is due to the protonation of triazine.[125] The same protonation effect should also apply for the **B1** and **B2** systems. The difference between these substances is described below.

[129] P. W. Atkins "Physical Chemistry" 5th edition, Oxford University Press, Oxford, **1995**.

Irradiation of protonated DHAs **B1aH$^+$** and **B2aH$^+$** with λ_{ex} = 366 nm shows slightly different results: in case of the 4-substituted **B1aH$^+$,** continuous irradiation gave low intensity of absorption maximum band of **B1bH$^+$** at 519 nm. Irradiation of protonated 3-derivative shows higher rate of photochromic reaction of protonated compound **B2aH$^+$** to **B2bH$^+$**. The protonated **B1bH$^+$** were irradiated with UV lamp with $\lambda_{ex.}$ = 366 nm during 30 s, Figure 4.10.

At room temperature the half-life of the thermal back reaction, VHF→DHA for **B1b** to **B1a** is about 80 min, for **B2b** to **B2a** – 97 min.[130] Upon the protonation the rate of thermal back reaction is much higher as for non-protonated species: the half-life of **B1bH$^+$** decreases to 1.89 min and of **B2bH$^+$** to 9.03 min.

All obtained spectroscopic data is collected in the Table 4.2.

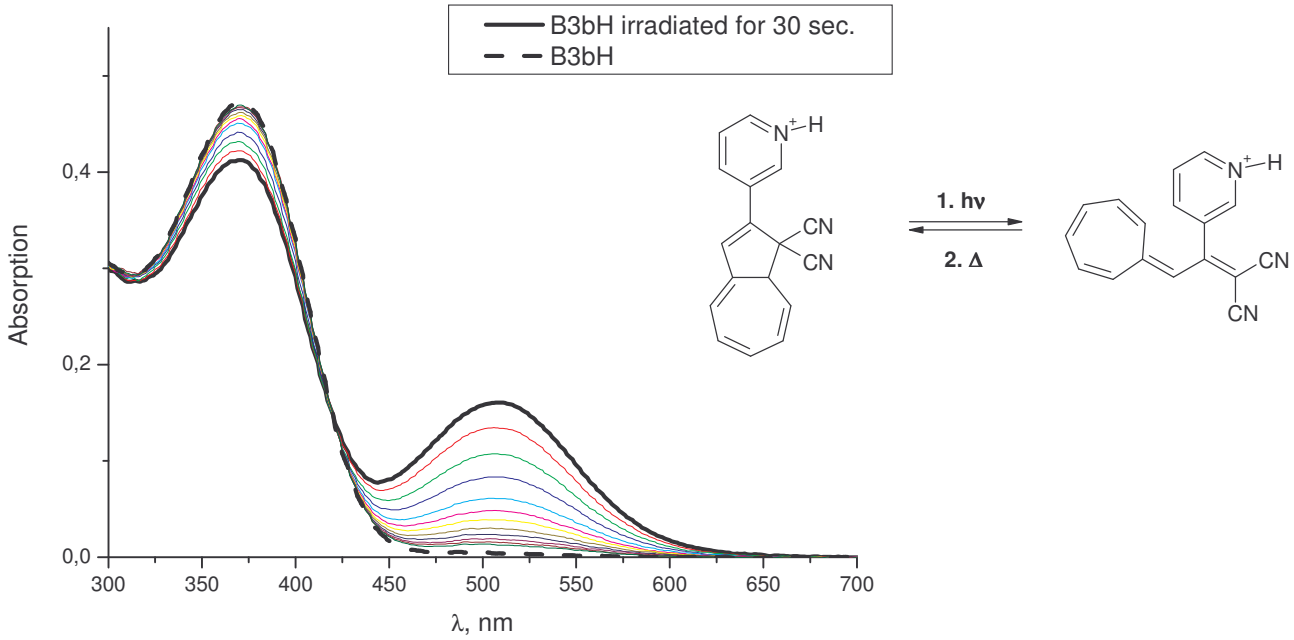


Figure 4.10: Spectrum of irradiated B2aH$^+$ by λ = 366 nm during 30 second in CH_2Cl_2.[131]

The lower rate of the photochromic reaction of the protonated species might be interpreted by higher influence of 4-pyridyl substituent on the electronic structure of vinylheptafulvene moiety in comparison with 3-pyridyl one. The influence of protonation is elucidated in the discussion part.

[130] Experiments for measuring the half-life of the thermal back reaction have been done in CH_3CN.

[131] Thermal back reaction of **B2b** was measured in CH_3CN, for complete data set see Table 4.2.

Here the main spectroscopic data and the half-life of the thermal back reaction data are presented. For comparison the data of **B4** are included: [132]

Table 4.2: Experimental data of DHAs and VHFs: characteristic absorption maxima, effect of TFA on absorption and thermal back reaction half-life $t_{1/2}$ (min).

		solvent	Absorption maximum [nm]		$t_{1/2}$ [min]	
				+ TFA		+ TFA
DHAs	**B1a**	Toluene	**360**	**410**		
		CH_2Cl_2	**360**	**406**		
		CH_3CN	**357**			
	B2a	CH_2Cl_2	**357**	**380**		
		CH_3CN	**351**	**369**		
	B4a		379	434		
VHFs	**B1b**	Toluene	**472**	**515**	**425.4**	**1.68**
		CH_2Cl_2	**480**	**519**	**79.8**	**1.89**
		CH_3CN	**480**			
	B2b	CH_2Cl_2	**480**	**504**		**4.72**
		CH_3CN	**475**	**501**	**96.61**	**9.03**
	B4b		480	517	254	5.75

It is clearly shown that the difference in behaviour of 3- and 4- substituted derivatives related to a different influence of pyridine ring and directly pyridine is protonated by treatment of TFA: in case of 4-pyridyl- substituted dihydroazulene pyridine has more influence on molecule, electron-withdrawing influence is higher than in 3-pyridyl-substituted. Upon protonation, electron deficiency of a pyridyl group has even higher influence than in 4-substituted case. This could be clearly seen from spectral/timing behaviour, Table 4.2.

The obtained protonated vinylheptafulvenes **B1bH$^+$** and **B2bH$^+$** are thermally less stable than the corresponding **B1b** and **B2b**. The thermal back reaction of VHF-H$^+$ to DHA-H$^+$ occur in minutes range distinctly faster as for non-protonated species.

Observed changes of absorption could be explained by higher electron deficiency of protonated pyridine rings which interferences with the π-system of dihydroazulene.

[132] C. Trieflinger, *Dissertation*, Universität Regensburg **2004**.

4.6 Discussion

4.6.1 Photochromic reaction. Changes upon protonation

The photochromic reaction of DHA in general proceeds after excitation of the S_0-S_1around 360 nm, the molecule undergoes a photoconversion to the VHF form[133], which usually absorbs around 480 nm.[119] Both compounds **B1** and **B2** have the same photochromic behaviour under normal conditions as other DHAs.[133] Nevertheless unlike **A4** the protonation of **B1**, **B2** and **B4** change significantly the chemical and photophysical properties which are absorption, emission, photochromism, and rate of thermal back reaction.

The photochromic reaction of protonated DHAs **B1aH$^+$** and **B2aH$^+$** irradiated at λ_{ex} = 366 nm has different result on the second or minute timescale. Dihydroazulene **B1aH$^+$** under continuous irradiation gave low intensity of the absorption maximum of **B1bH$^+$** at 519 nm; more extended irradiation causes decomposition of the compound. In contrast to **B1aH$^+$** the irradiation of **B2aH$^+$** behaves different at this timescale: irradiated at λ_{ex} = 366 nm **B2aH$^+$** for 30 minutes gave some photoproduct **B2bH$^+$** and then by thermal back reaction returned to initial **B2aH$^+$**. This experiment is illustrated in Figure 4.10.

Protonation of **B1**, **B2** and **B4** shows a decrease of the rate of the photochemical forward reaction and an increase of the rate of the thermal back reaction. A comparison of the half-life of the thermal back reaction of the protonated and non-protonated species is shown in Table 4.2. The fluorescence of the protonated species increases significantly as it has been mentioned before, Figure 4.8.

The results of the studies on the influence of the protonation onto the emission of the DHA species confirm previous considerations that the protonation of the pyridyl derivatives increases the energy barrier on the S_1 energy surface.[134] Also it is assumed that the heterolytic ring opening occurs on the excited state reaction pathway, Figure 4.11. Which again indicates the ring opening process on the S_1 energy surface follows a heterocyclic pathway under the formation of dipolar (charge-separated) intermediate.

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[133] H. Görner, J. Daub, C. Fischer, S. Gierisch, *J. Phys. Chem.* **1993**, 97, 4110-4117.

[134] J. Daub, C. Trieflinger, O. Kushnir, R. Prochàzka, *Mol. Cryst. Liq. Cryst*, **2005**, 430, 115-122.

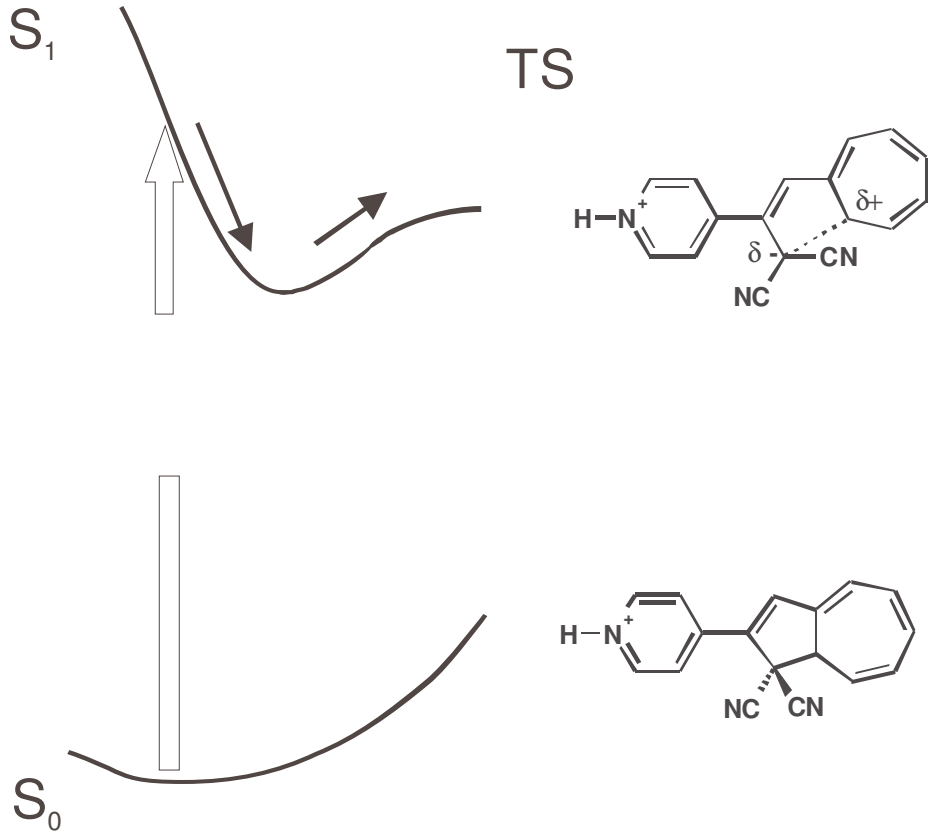
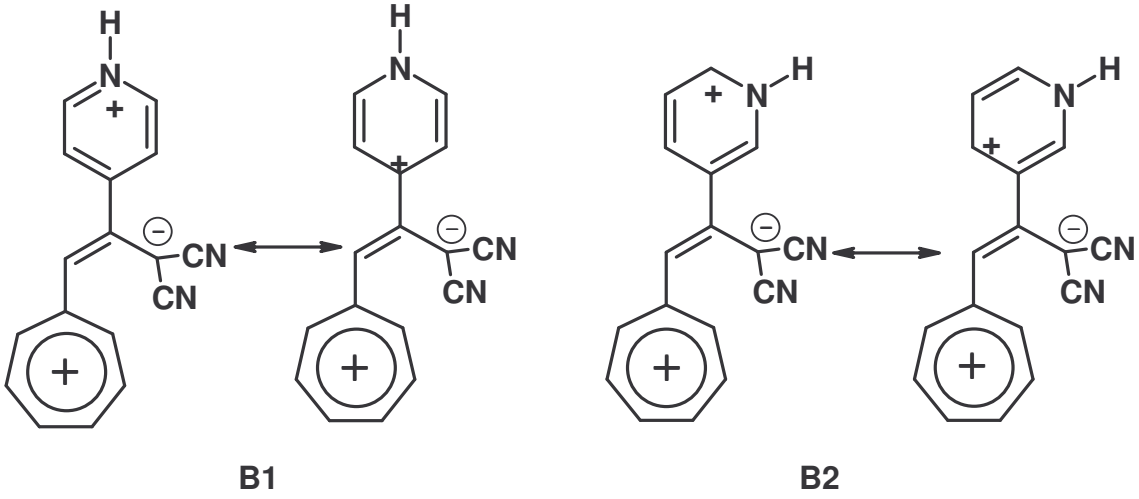


Figure 4.11: Ring opening on the excited state energy surface, schematic representation.

The rate of the fluorescence quantum yield increases as a consequence of the decrease of the photochemical ring-opening; the rate of the back reaction increases what is observed for protonated species **B1aH$^+$** and **B2aH$^+$**. The photochemical forward reaction is also "ground-state quenched" by the fast thermal back reaction.

According to assumption of a heterolytic ring opening on the excited state reaction pathway several structure of representations of the intermediates can be, Scheme 4.5:



Scheme 4.5: Possible structures of photochemical reaction intermediates.

The destabilising effect has stronger influence in case of protonated 4-pyridyl derivative, **B1** Scheme 4.5. In case of 3-pyridyl **B2** this influence is smaller.

This difference in behaviour of protonated species might be explained from the point of positive charge delocalization in the pyridine ring. In consideration of structures of resonance stabilization of protonated derivatives with 3- and 4- substituent might be concluded that in the case of 4-pyridyl derivative the influence of electron deficient aromatic ring is much higher than in case of 3-pyridyl one.

4.6.2 Thermal ground state reaction, changes upon protonation

DHAs undergo an efficient photoreaction towards the corresponding VHFs. Unlike the DHAs the VHFs are not emitting and photochemically inactive. In solution s-*cis* and s-*trans* VHFs are in equilibrium but higher a concentration of more thermodynamically favourable s-*trans* is assumed.[135] In the crystalline form the s-*trans* conformer is found exclusively.[136] In the dark at RT VHF-s-*trans* thermally converts to the DHA form, Figure 4.12.

[135] T. Mrozek, J. Daub, A. Ajayagosh, In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinhein, **2001**.

[136] a) J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas, U. Seitz, *Chem. Ber*. **1986**, 119, 2631;

b) S. Gierisch, W. Bauer, T. Burgemeister, J. Daub, *Chem. Ber*., **1989**, 122, 2341-2349.

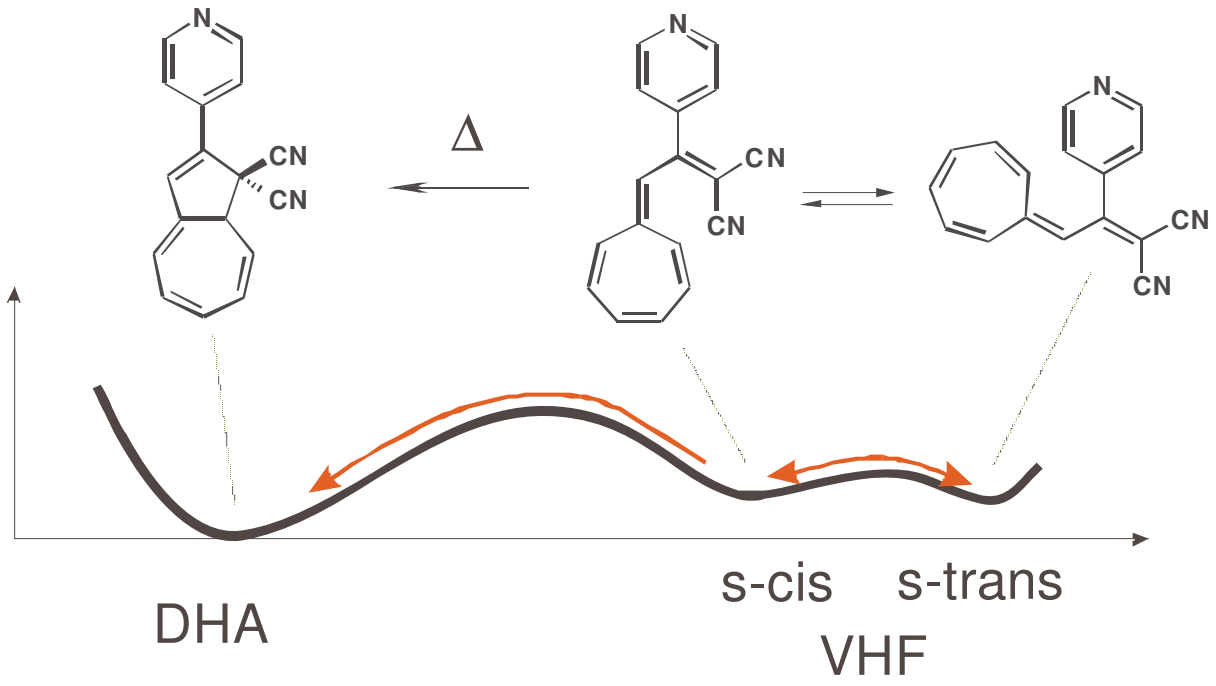
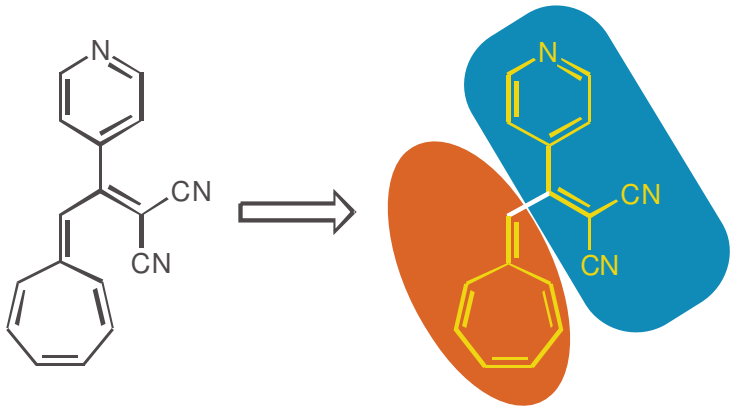


Figure 4.12: Schematic representation of the reaction profile of the thermal pathway VHF → DHA.

As indicated before upon the protonation the rate of the thermal back reaction of **B1**, **B2**, and **B4** increases significantly, Table 4.2.

To elucidate the changes of the electronic properties upon protonation the s-*cis*-VHF system is discussed and some simplifications were made to clarify description of the observed system.

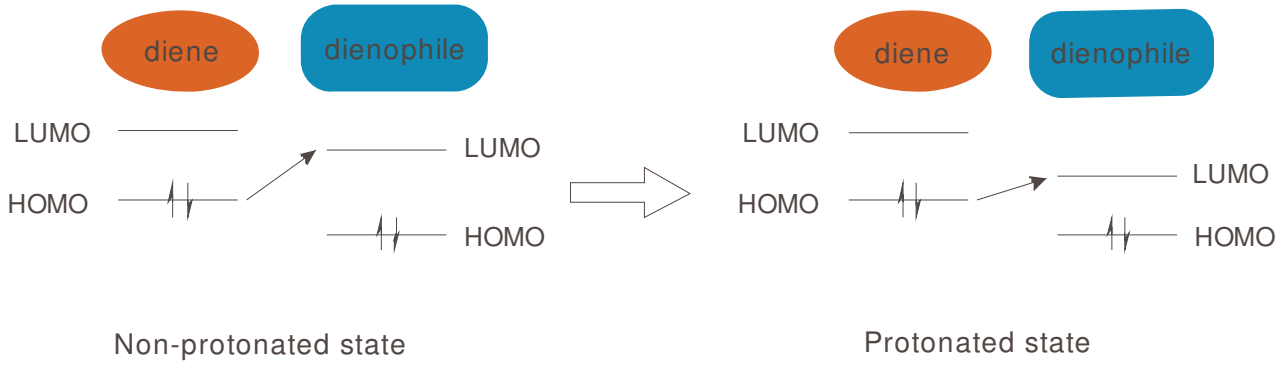
Let's assume that in case of thermal reaction of s-*cis* VHF we have [8π + 2π] cycloaddition, the dienophile - 2-pyridin-4-ylmethylene-malononitrile (rectangular area) part and as tetraene – heptafulvene part (oval area), Scheme 4.6.



Scheme 4.6: Schematic representation of VHF molecule for cycloaddition approach for thermal back reaction mechanism.

Due to this assumption we could consider thermal back reaction as cycloaddition reaction keeping in mind that both parts are connected but are not planar in s-*cis* case due to some sterical hindrance. The reaction proceeds with forming of new five-membered ring. In our case we have quite efficient electron-attracting groups on the dienophile: two cyano- and one pyridyl. Thermal reaction rate of non-protonated compounds is comparable with CN-DHA one. But upon protonation of pyridine ring electron-attracting ability of protonated pyridyl substituent is highly increased.

It is known that the cycloaddition reaction more rapid and efficient when the dienophile contains one or more electron-attracting groups. In the case of the diene, reactivity is increased by electron-releasing substituent.[137] The reactivity in non- and protonated can be understood on the basis of frontier orbital theory. In our case the frontier orbitals will be the diene HOMO and the dienophile LUMO, Scheme 4.7.



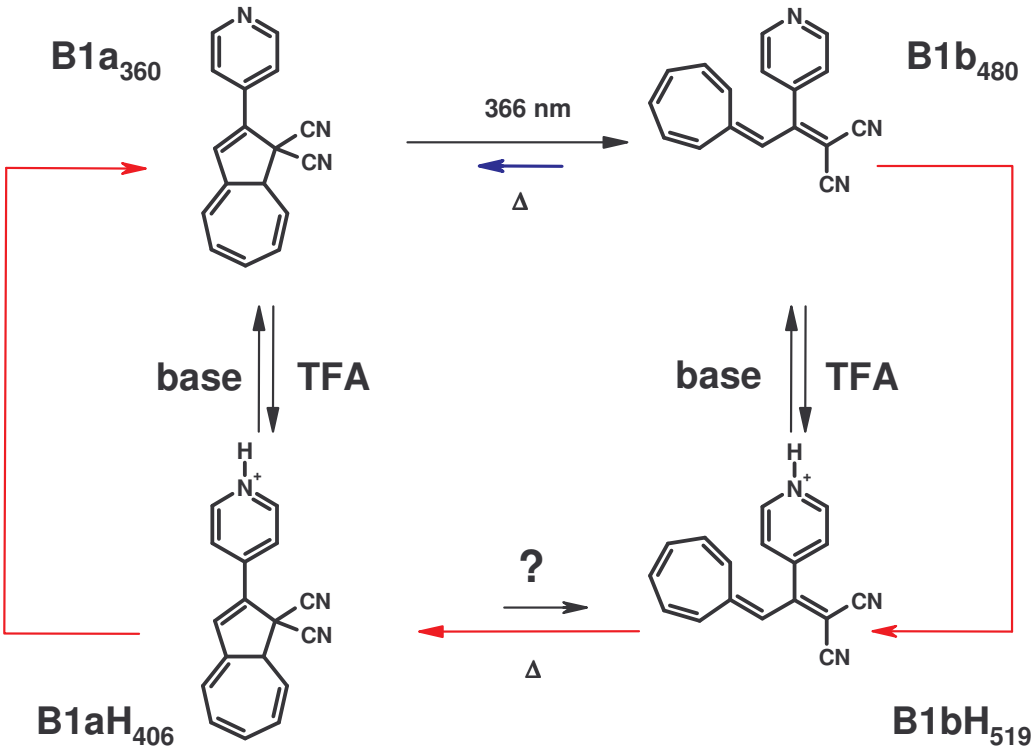
Scheme 4.7: Frontier orbital interactions in cycloaddition approach for thermal back reaction mechanism.

The protonation of pyridine makes the electron-attracting ability of dienophile higher and in turn lowers its orbitals. This leads to stronger interaction of diene's LUMO and dienophile's HOMO orbitals and correspondingly to higher rate of reaction in case of protonated species.

[137] C. Rücker, D. Lang, J. Sauer, H. Friege, and R. Sustmann, *Chem. Ber.*, **1980**, 113, 1663.

4.6.3 Multimode switching system

Summarising all the properties of the pyridyl derivatives **B1** and **B2** discussed before gives interesting result from the point of view of multi-input, multi-state system. This system has two types of input: light and proton. The summary of the observed data presented on Scheme 4.8:

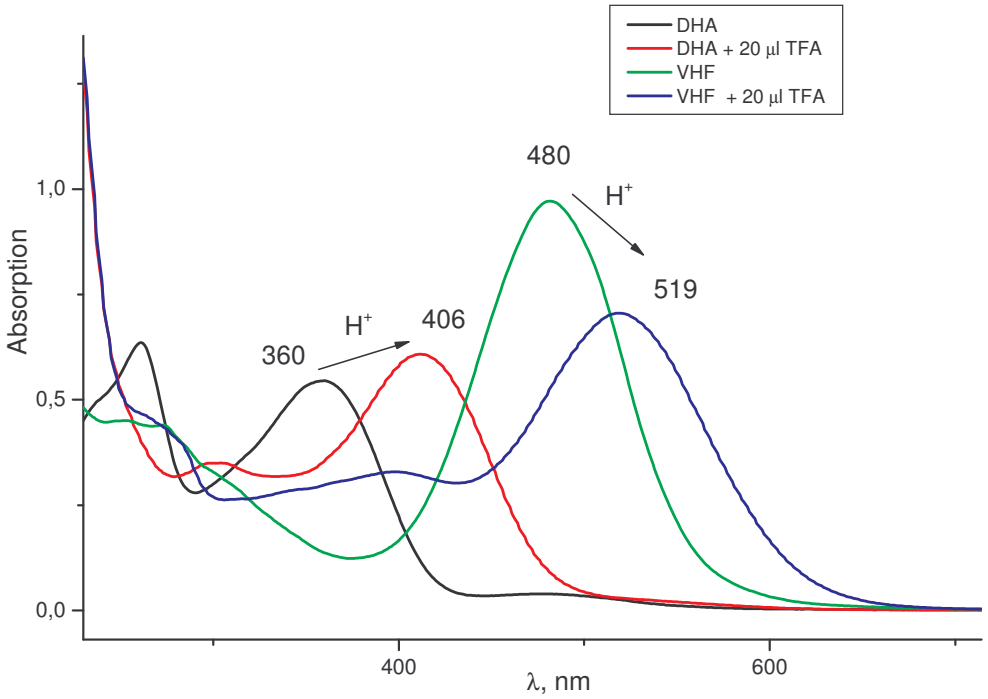


Scheme 4.8: Scheme of possible states of B1 with photons and protons as input signal.

Usual DHA/VHF photochromic/ thermal back reaction introduced by **B1a**$_{360}$ and **B1b**$_{480}$: irradiation of **B1a**$_{360}$ at 366 nm gives **B1b**$_{480}$ as a product of photoreaction. Thermal back reaction at room temperature gives **B1a** form within ca. 80 minutes. **B1a**$_{360}$ and **B1b**$_{480}$ might be protonated with TFA to **B1aH**$^{+}_{406}$ and **B1bH**$^{+}_{519}$. With addition of TFA to **B1b**$_{480}$ rate of thermal back reaction of **B1bH**$^{+}_{519}$ to **B1aH**$^{+}_{412}$ increases in comparison to **B1b**$_{480}$ → **B1a**$_{360}$, 42 times faster – 1.89 minutes. Addition of base to protonated species **B1aH**$^{+}_{406}$ and **B1bH**$^{+}_{519}$ converts them to **B1a**$_{360}$ and **B1b**$_{480}$ respectively.

Irradiation of **B1aH**$^{+}_{406}$ with continuous light initiates photoreaction but at room temperature and in a timescale of seconds only traces of photoproduct **B1bH**$^{+}_{519}$ were found. It is not clear yet what type of process increase its rate upon protonation: faster back reaction process in compare to non-protonated reaction, **B1b**$_{480}$ → **B1a**$_{360}$ or as it has been mentioned before increasing of the energy

barrier on the excited state reaction pathway. Last process leads to increasing of emission process as a product of excitation; it could be clearly seen from Figure 4.8. This question might be explained by similar studies for **B1a** – **B1b** system: irradiation of **B2aH**$^+$ with λ_{ex} = 366 nm during ca. 30 seconds showed much higher concentration of protonated photoproduct, **B2bH**$^+$ compared to corresponding **B1bH**$^+$, Figure 4.10.



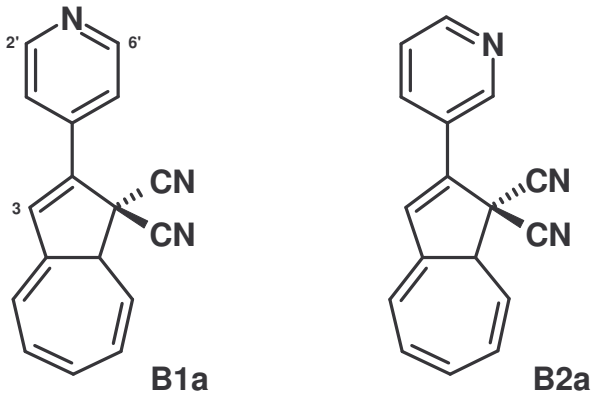
Scheme 4.9: Four States. Absorption spectrum of B1a and protonated B1aH$^+$ by addition TFA, B1b and B1bH$^+$.

It has been shown that **B1a** exists in several states that could be selectively achieved and clearly spectroscopically identified either by absorption or emission. Scheme 4.9 shows that it is possible to distinguish clearly all four states of the system.

In comparison to **B1a**, **B2a** has a slightly different behaviour in the second/minute timescale. The irradiation of protonated DHA **B2aH**$^+$ with 366 nm in contrast to **B1aH**$^+$ shows a rise of the 504 nm absorption band corresponding to **B2bH**$^+$. The thermal back reaction of protonated VHF in case of **B2** is slower, that allows detecting quantitative amount of a protonated photoproduct.

4.7 Conclusions

Dihydroazulenes **B1a** and **B2a** are photochromic compounds that upon photoirradiation transform to the open form – vinylheptafulvene, **B1b** and **B2b,** respectively. The thermal back reaction at room temperature goes with a half-life of about 80 min for **B1b,** and 97 min for **B2b**.



Protonation of **B1** and **B2** changes significantly the chemical and photophysical properties:

- ^{1}H-NMR: The protons 2'-, 6'-, and 3-H of **B1** are shifted significantly to lower field. The same effect, however less pronounced, is also found for the pyridine derivative **B2**
- The absorption maxima of both DHA and VHF forms show a bathochromic shift due to a decrease of the HOMO-LUMO gap
- the rate of the thermal back reaction of the protonated form of VHF increases significantly
- the emission (fluorescence) of DHA increases
- the rate of the photochemical reaction decreases due to a rise of the energy barrier on the S_1 energy surface
- the appearance of the photochromism at room temperature is reduced as a result of the increased rate of the thermal back reaction and the lower quantum yield of the photoreaction.

Comparing the constitutional isomers **B1** and **B2** shows that in case of **B2** the effect of protonation is weaker. Continuous irradiation of $\mathbf{B1aH^+}$ gave a less intense absorption of $\mathbf{B1bH^+}$ (Figure 4.10).

Under the same conditions **B2aH$^+$** leads to a higher concentration of the protonated photoproduct, **B2bH$^+$**.

In summary, the multi functionality of the pyridine substituted DHAs **B1** and **B2** as are photochromism, receptor properties, emission and absorption changes makes them to interesting "two-mode input/multi-output" systems, which are important for using molecular switches for digital processing and communication.

It is also important to note that the multi-mode switching may be further extended via transition metal complexation which expands the potential of application towards molecular sensing and supramolecular architecture.

5 Porphyrin conjugates

5.1 Introduction

Electron and photon processing at the molecular and supramolecular level are of great interest in the last decade; the development of molecular based information processing devices increased.[138,139] Electronic communications of these devices on molecular level are based on electron and energy transfer processes. To manage this communication, build-up logical schemes, on-off switching of these processes by external triggering processes photochromic units could be used.[140,141] Electronic changes in the photochromic unit upon light irradiation such as π-conjugation, redox potential, absorption and emission spectra could be used to switch the electronic transfer pathways. Usability of systems containing photochromic units in information readout processes highly depends on ease of identifying all photochromic states.

Dihydroazulenes/vinylheptafulvenes are promising photochromic compounds for developing of ultrafast switching logic systems.[142] Photoinitiated transformation DHA to VHF causes noticeable changes in electronic structure of molecule.[143] They fulfil requirements such as a very high quantum

[138] a) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**;

b) A.J. Myles, N.R. Branda, *Adv. Funct. Mater*, **2002**, 12, 167-173;

c) C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, **2000**, 408, 541–548.

[139] C.M. Drain1, I. Goldberg, I. Sylvain, A. Falber*, Top. Curr. Chem*., **2005**, 245, 55–88.

[140] a) A. J. Myles, N. R. Branda, *J. Am. Chem. Soc.*, **2001**, 123, 177–178;

b) M. Raymo, *Adv. Mater*., **2002**, 14, 401;

c) J.L. Bahr, G. Kodis, L. de la Garza, S. Lin, A.L. Moore, T.A. Moore, D. Gust, *J. Am. Chem. Soc.*, **2001**, 123, 7124–7133;

d) P. A. Liddell, G. Kodis, A. L. Moore, T. A. Moore and D. Gust, *J. Am. Chem. Soc.*, **2002**, 124, 7668–7669;

e) Y. Terazono, G. Kodis, J. Andreasson, G. Jeong, A. Brune, T. Hartmann, H. Durr, A. L. Moore, T.A. Moore and D. Gust, *J. Phys. Chem. B*, **2004**, 108, 1812–1814.

[141] a) A.J. Myles, B. Gorodetsky, N.R. Branda, *Adv. Mater*, **2004**, 16, 922-925;

b) A. Osuka,, D. Fujikane, H. Shinmori, S. Kobatake, M. Irie, *J. Org. Chem*. **2001**, 66, 3913-3923;

c) J. Otsuki, A. Suka, K. Yamazaki? H. Abe, Y. Araki, O. Ito, Chem. Comm., **2004**, 1290-1291.

[142] a) V. De Waele, U. Schmidhammer, T. Mrozek, J. Daub, E. Riedle, *J. Am. Chem. Soc*. **2002**, 124, 2438;

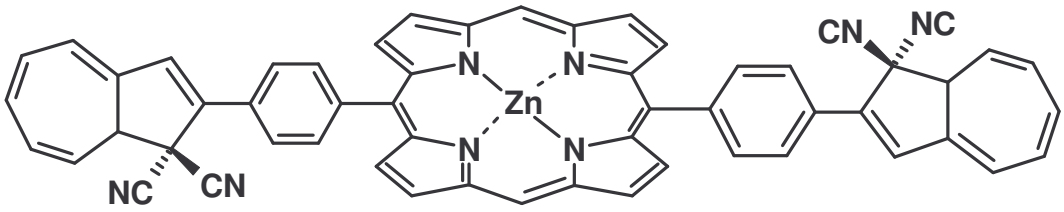
b) V. De Waele, M. Beutter, U. Schmidhammer, E. Riedle, J. Daub*, Chem. Phys. Lett.* **2004,** 390, 328–334.

[143] T. Mrozek, J. Daub, A. Ajayagosh, In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinhein, **2001**.

yield of conversion, a large shift of the absorption band on going from DHA to VHF, and a singlet state strictly one-way photoreaction path, a high fatigue resistance. [142,144]

Porphyrins are attractive building blocks; they are providing rich redox-, and photo- properties into system in which they are incorporated. A lot of different covalent and non-covalent interactions are used to create different systems, including artificial photoactive molecular devices.[145]

Integrated chemical system consists of photosensitive switchable subunits and a receptor/transformer unit, able to give an analytical response (change in fluorescence band and intensity, electrochemical potentials, etc.). The approach used here employs photochromism of a photosensitive switching unit dihydroazulene/vinylheptafulvene (DHA/VHF), covalently bound to a zinc-coordinated porphyrin as molecular receptor is used. The system consists of linear interaction of two photochromic subunits through bridging and suitable for signal conversion and transduction. The bridge in case of a porphyrin could be not only a simple mediating π-conjugated system but due to properties of porphyrin to incorporate different metals inside the core it could also be used to vary the photochromic unit-unit interaction. Incorporation of Zn(II) gives ability to have influence onto system due to intermolecular coordination. Features of DHA/VHF give possibilities to use them for creating of ultrafast logic functions.[142-144]



Scheme 5.1: Multi-input DHA/porphyrin molecular system.

[144] J. Daub, T. Mrozek, A. Ajayaghosh, *Mol. Cryst. Liq. Cryst*. **2000**, 344, 41-50.

[145] a) R.W. Wagner, J. Seth, S.I. Yang, D. Kim, D.F. Bocian, D. Holten and J.S. Lindsey, *J. Org. Chem.*, **1998**, 63, 5042;

b) R.W. Wagner, J.S. Lindsey, J. Seth, V. Palaniappan, and D.F. Bocian, *J. Am. Chem. Soc*. **1996**, 118, 3996-3997;

c) J.S. Lindsey in *The Porphyrin Handbook*; K.M. Kadish, K.M. Smith, R. Guilard, Eds.; Academic Press: San Diego, CA, **2000**; Vol. 1, pp 45-118;

d) D. Gust, T.A. Moore in *The Porphyrin Handbook*; K.M. Kadish, K.M. Smith, R. Guilard, Eds.; Academic Press: San Diego, CA, **2000**; Vol. 1, pp 153-190;

This molecular system is of interest in various directions, Scheme 5.2:

• as an integrated chemical systems with photosensitive switchable subunits and a receptor/transformer unit ready to respond towards intermolecular bonding

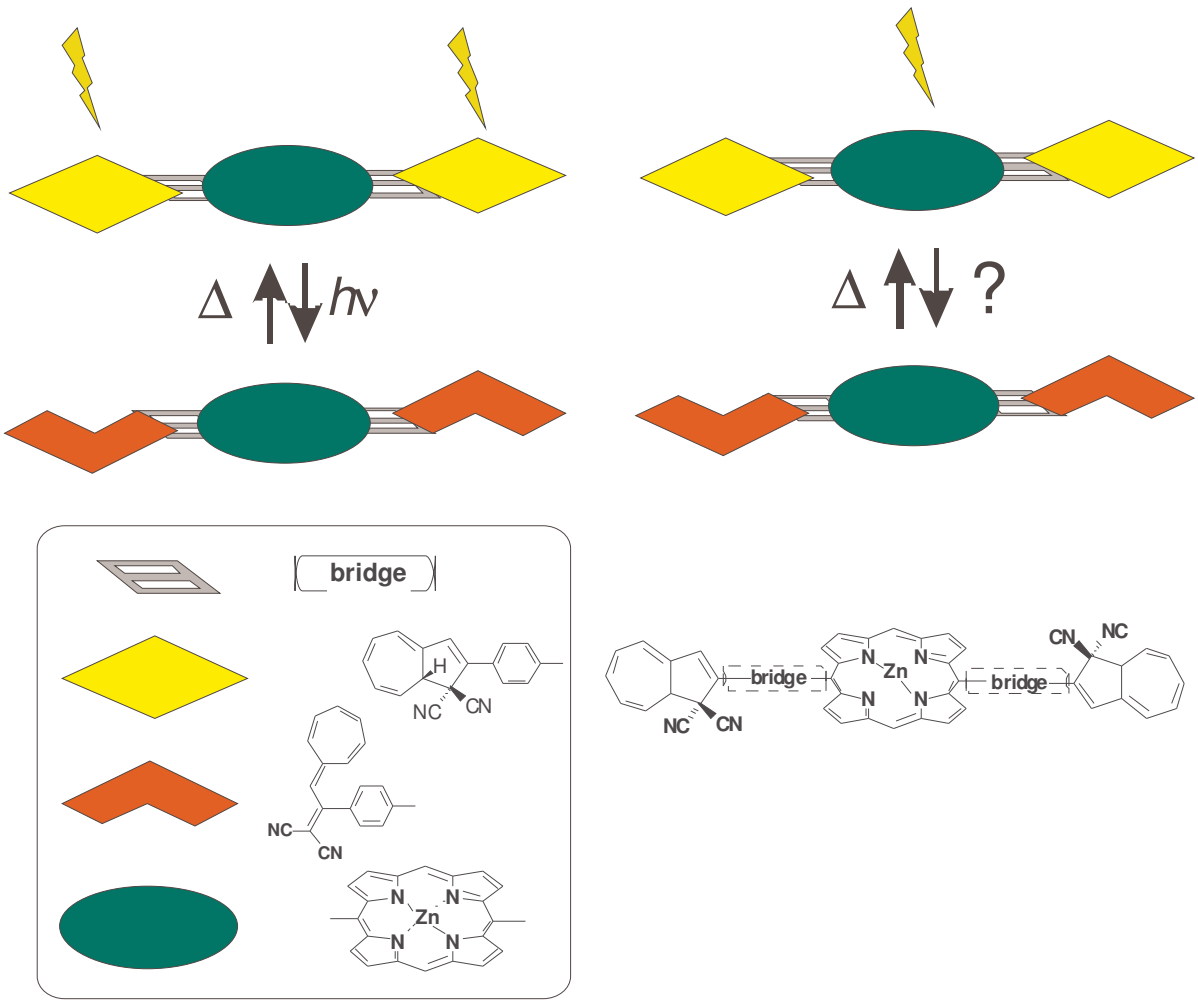
• as a photosensitive switching unit - dihydroazulene /vinylheptafulvene (DHA/VHF)

• for signal conversion and transduction towards intermolecular coordination

• to analyze the interference of two dihydroazulene groups by the spectral properties of the conjugated molecules

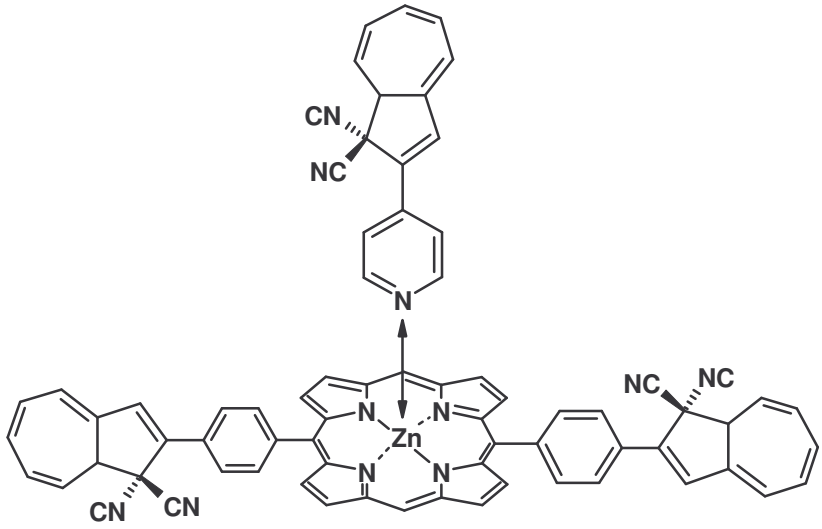
• for sensing properties of the entire system due to changes of photochromic behaviour of dihydroazulene subunits depending upon the complexation by the receptor part.

Scheme 5.2 shows a schematic representation. The scheme on the left shows influence of photoisomerisation of the photochromic units onto complexation properties of zinc porphyrin. The scheme on the right shows possible influence of the porphyrin irradiation onto the photochromic subunits.



Scheme 5.2: Light induced interaction of subunits

An extension of this work could be a two-dimensional photoswitchable system. The application of a pyridyl-modified dihydroazulenes as a ligand to the core metal atom of the porphyrin would provide an additional input mediating the coupling between the two photochromic units, Scheme 5.3.



Scheme 5.3: Dihydroazulene-porphyrin supramolecular aggregation.

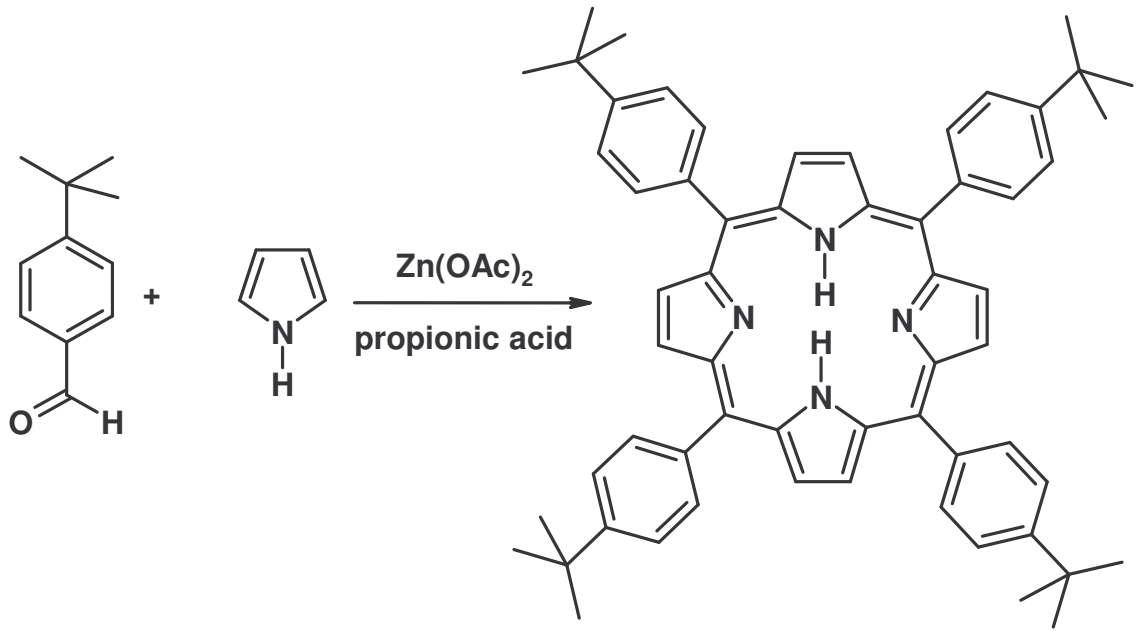
5.2 Syntheses of porphyrins

Some aspects of the porphyrin synthesis were discussed already in the chapter 2.2. 5,10,15,20 – Tetra-(4-tert-butylphenyl)-porphyrin has been synthesised according to the straightforward strategy[146] - synthesis of a porphyrin with a four similar substituents, A_4 strategy, Scheme 5.4.[147]

[146] a)J.S. Lindsey in *The Porphyrin Handbook*; K.M. Kadish, K.M. Smith, R. Guilard, Eds.; Academic Press: San Diego, CA, **2000**; Vol. 1, pp 45-118;

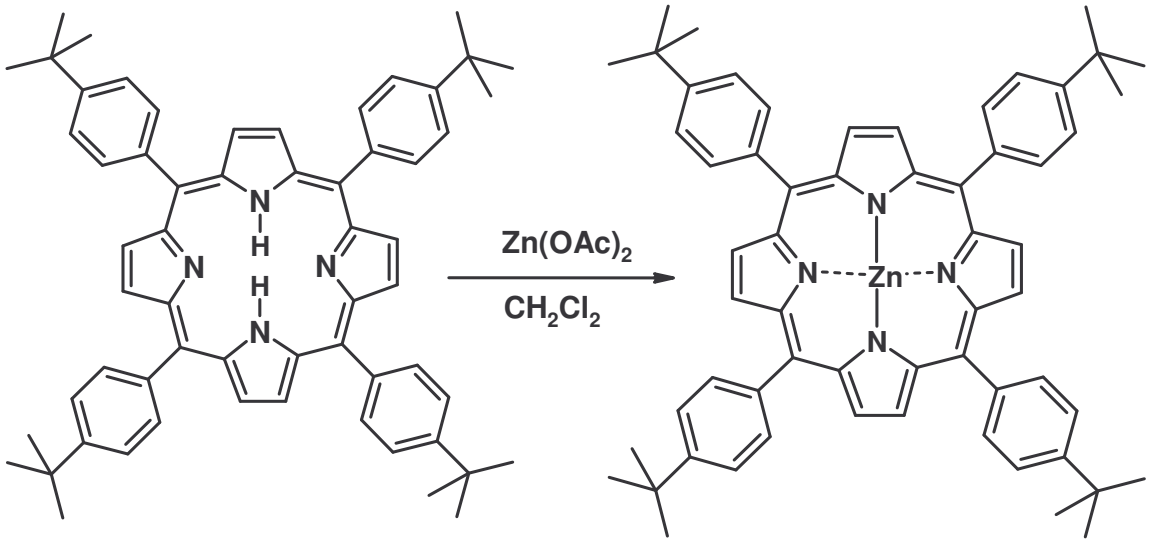
b) Lindsey, J. S. In *Metalloporphyrin-Catalyzed Oxidations*; Montanari, F., Casella, L. Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, **1994**; pp 49-86.

[147] S. Matile, N. Berova, K. Nakanishi, J. Fleischhauer, and R.W. Woody, *J. Am. Chem. Soc.*, **1996**, 118, 5198 - 5206.



Scheme 5.4: Synthesis of 5,10,15,20 – tetra-(4-tert-butylphenyl)-porphyrin, C1.

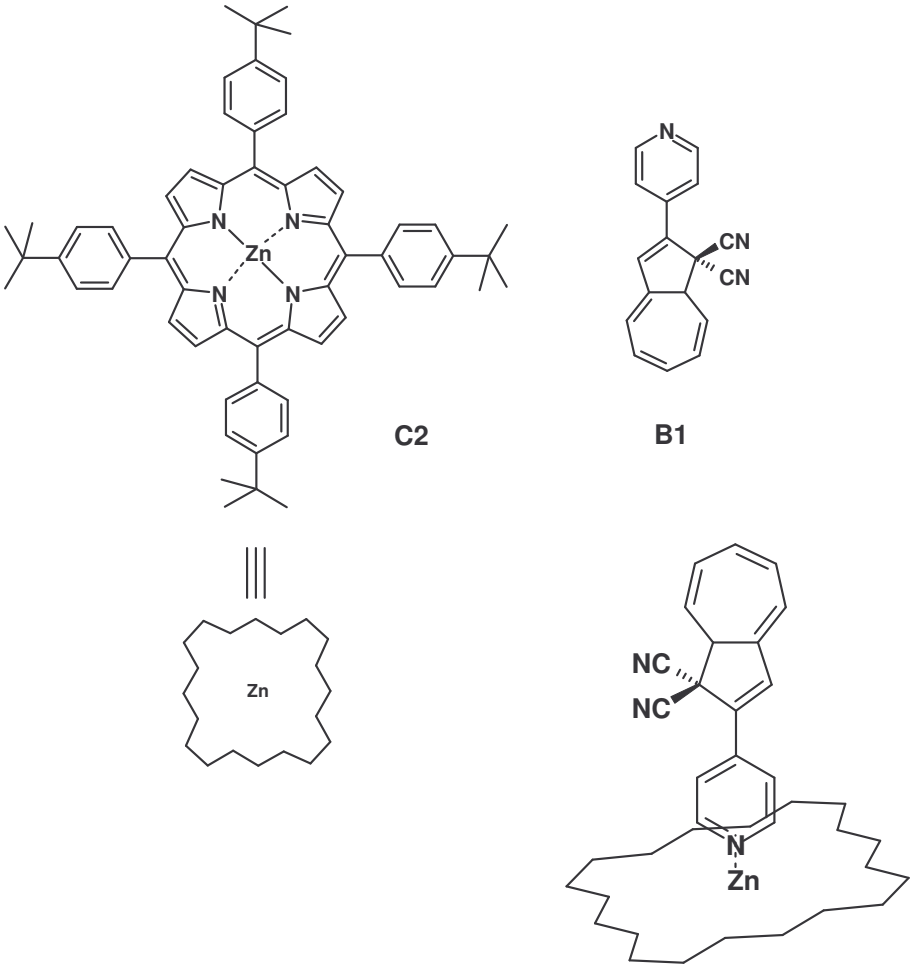
Zinc contained porphyrin have been achieved by a treating of 5,10,15,20 – tetra-(4-tert-butylphenyl)-porphyrin with methanol saturated solution of zinc acetate in gently boiling methylene chloride.



Scheme 5.5: Synthesis of zinc porphyrin C2.

5.3 ^{1}H-NMR studies of complexation and photoexcitation

^{1}H-NMR measurements were used to study the complexation properties of pyridyl-dihydroazulenes, **B1, B2** as ligands and **C2** as host. Spectra of free ligand/host molecules were done in benzene-d6 as non-polar solvent and chloroform-d1, Scheme 5.6. Complexation properties, binding constants, photochromic properties of the ligand in complex, were carried out.



Scheme 5.6: Zn-tetra-t-butylphenyl porphyrin and 2-pyridin-4-yl-8aH-azulene-1,1-dicarbonitrile. Complexation geometry of dihydroazulene and Zn porphyrin.

According to the literature zinc porphyrin make a complex with 1:1 stoichiometry.[148] Zinc porphyrins show no tendency to add a sixth ligand at axial position. The lack of formation of six-

[148] a) W.R. Scheidt, M.E. Kastner, K. Hatano, *Inorg. Chem*., **1978**, 17, 706-710;

b) J.R. Miller, G.D. Dorough, *J. Am. Chem. Soc*., **1952**, 74, 3977;

c) C.H. Kirksey, P. Hambright, C.B. Storm, *Inorg. Chem*., **1969**, 8, 2141.

coordinate derivative has been interpreted in terms of the stereochemical constrains of the porphyrin core.[149]

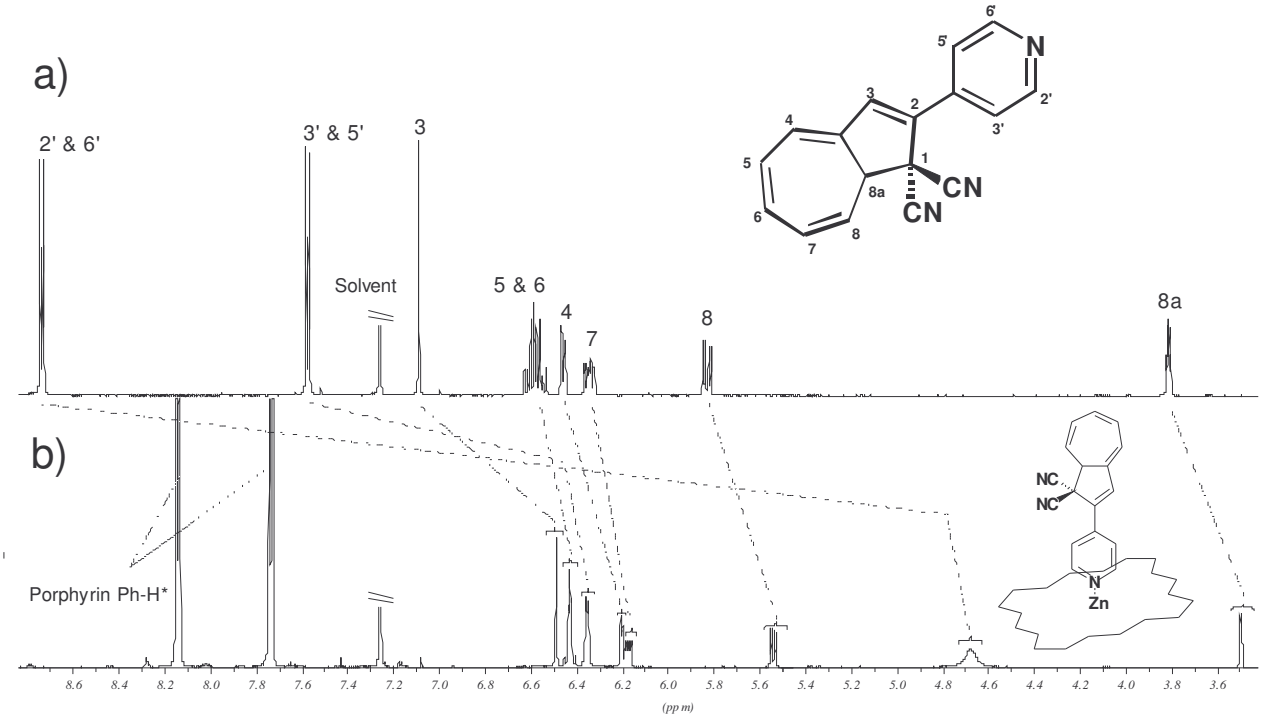


Figure 5.1: ^{1}H-NMR spectra in $CDCl_3$: a) B1a DHA; b) C2 and B1a DHA complexation.[150] On spectrum b) the ratio [DHA]/[Porphyrin] = 0.84.

Preliminary ^{1}H-NMR studies of **C2/B1** showed high influence of complexation on spectra of **B1**, Figure 5.1. Especially it could be noticed by significant upfield shift of 2' and 6' **B1** protons' signals that is more than 4 ppm. Such large shift explained by shielding that causes the porphyrin ring.[151]

[149] D.M. Collins, J.L. Hoard*, J. Am. Chem. Soc.*, **1970**, 92, 3761.

[150] Porphyrin aromatic proton signals on spectrum b) are not showed completely due to high intensity; also other signals of porphyrin are not showed.

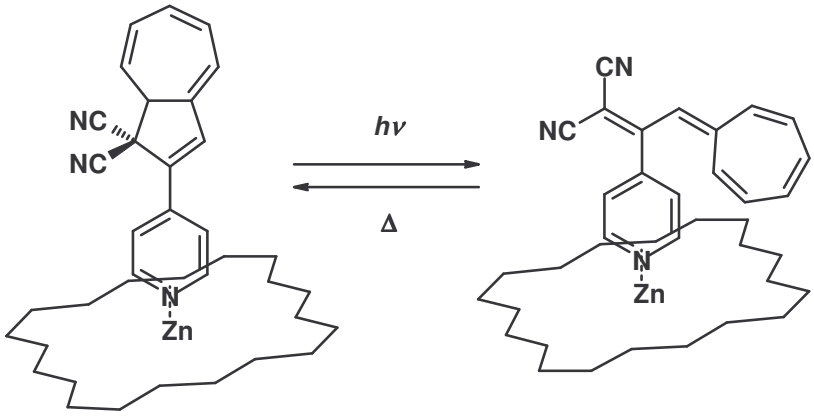
[151] a) H. M. McConnell, *J. Chem. Phys.*, **1957**, 27, 226;

b) J. A. Pople, *J. Chem. Phys.*, **1956**, 24, 1111.

5.4 Photochromic properties of dihydroazulene/porphyrin complex, ^{1}H-NMR

The main part of complex studies is to examine the photochemical properties of the dihydroazulene under these conditions. The protonation studies were carried out for **B1** and **B2** and showed some noticeable results[152] and further investigations of complexation properties are of great interest.

Irradiation of **B1/C2** solution in $CDCl_3$, Scheme 5.7, by light $\lambda_{ex.}$ = 366 nm during 1.5 min in the NMR tube showed nearly no photoreaction of dihydroazulene. ^{1}H-NMR spectrum shows only minor changes caused by photoreaction. The sample has been irradiated with UV lamp with the same excitation wavelength for ca. 45 min. The changes in spectrum could be clearly seen on Figure 5.2.



Scheme 5.7: Irradiation of zinc porphyrin – DHA complex.

Figure 5.2 shows protons of pyridine ring in **B1/C2** complex are overlapping with: 3,5 – pyr-H at 7.72 ppm with Ph-H of porphyrin, and 2,6 – pyr-H at 7.26 ppm with solvent peak.

To understand spectra of **B1/C2** complex let's take a look on changes upon photochromism in individual spectra of **B1**, Figure 4.1. The decreasing amount of dihydroazulene upon irradiation could be clearly noticed in its ^{1}H-NMR spectrum checking integral of 8a-H proton at 3.39 ppm, Figure 4.1.[153]

Upon irradiation the photochemical ring opening from DHA to VHF gives noticeable changes in electronic structure of molecule.[154] This should have influence on binding strength. These changes

[152] See chapter 4.3.2.

[153] S. Gierisch, *Dissertation*, University of Regensburg, **1989**.

[154] a) Look chapter 1.3.1;

b) T. Mrozek, J. Daub, A. Ajayagosh, In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinhein, **2001**.

are noticeable by shifts of aromatic protons of **B1** upon photoisomerisation: in individual compound signals are shifted for 3'and 5' - protons of pyridine ring, from 7.02 for DHA to 6.48 ppm for VHF; for 2'and 6' - protons of pyridine ring, from 8.43 for DHA to 8.42 ppm for VHF.

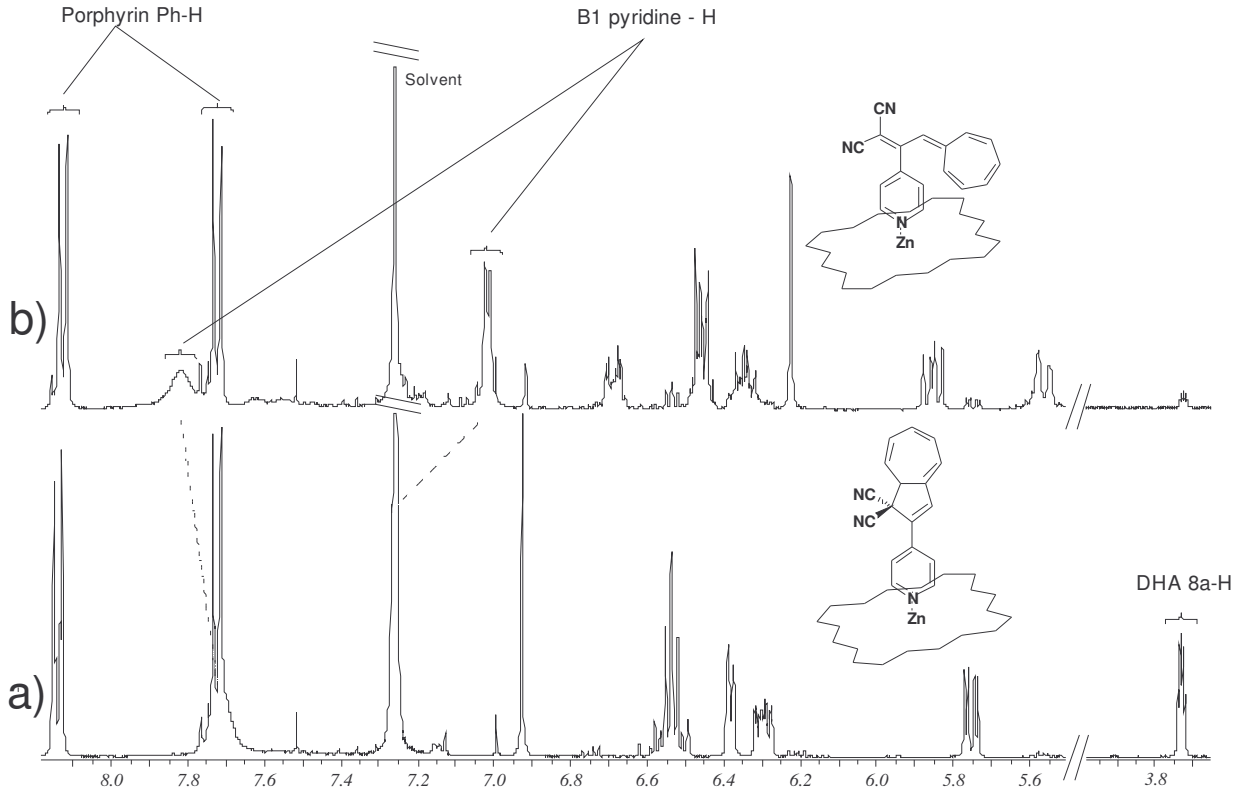


Figure 5.2: ^{1}H-NMR spectra of C2 and B1 complex before, a) and after, b) irradiation.[155]

In case of **B1/C2** complex these protons are shifted already in DHA form due to complexation with zinc atom in porphyrin and anisotropy caused by porphyrin ring. Upon irradiation signals of pyridine protons 3'and 5' are shifted upfield from 7.26 for DHA to 7.02 ppm for VHF; for 2'and 6' - downfield from 7.71 for DHA to 7.82 ppm for VHF.

[155] $CDCl_3$ solution a) have been irradiated for ca. 26 min in quartz NMR tube with light λ = 366 nm.

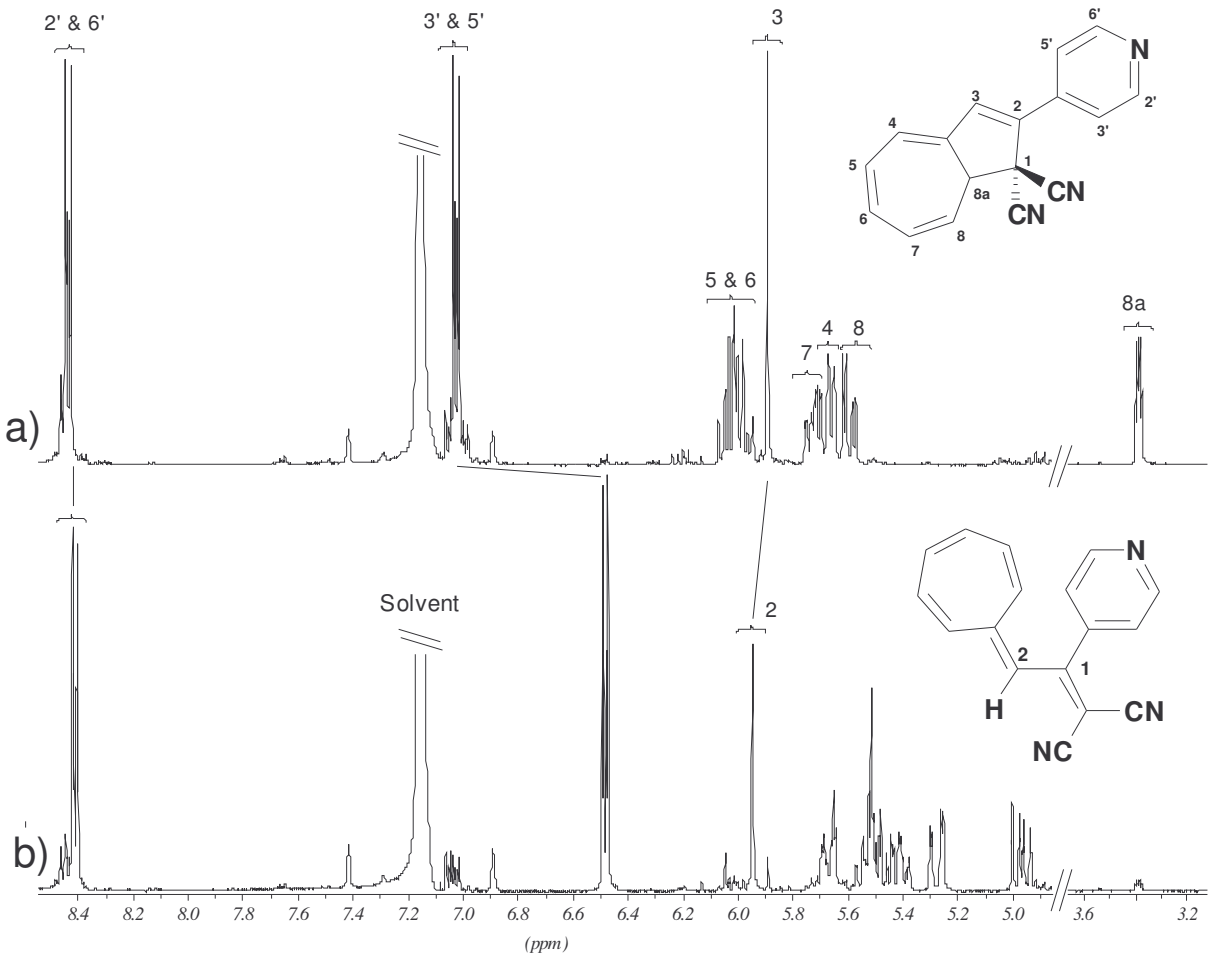


Figure 5.3: ^{1}H-NMR spectra of B1a and B1b after irradiation.[156]

5.5 UV-vis studies of dihydroazulene B1/porphyrin C2 complex

The absorption spectrum of the B1/C2 complex is a superposition of the **C2** and the **B1** spectra, Figure 5.4. The absorption maximum of **B1a** is about at 360 nm in toluene with molar extinction coefficient 11900 $M^{-1}cm^{-1}$, porphyrin's Soret band at 424 nm with molar absorption coefficient $267 \cdot 10^{3}$ $M^{-1}cm^{-1}$and Q-bands at 550, 589 and 630 nm.

[156] D_6H_6 solution a) have been irradiated for ca. 45 min in NMR tube with light λ = 366 nm. DHA spectrum contains some peaks of VHF and vice versa.

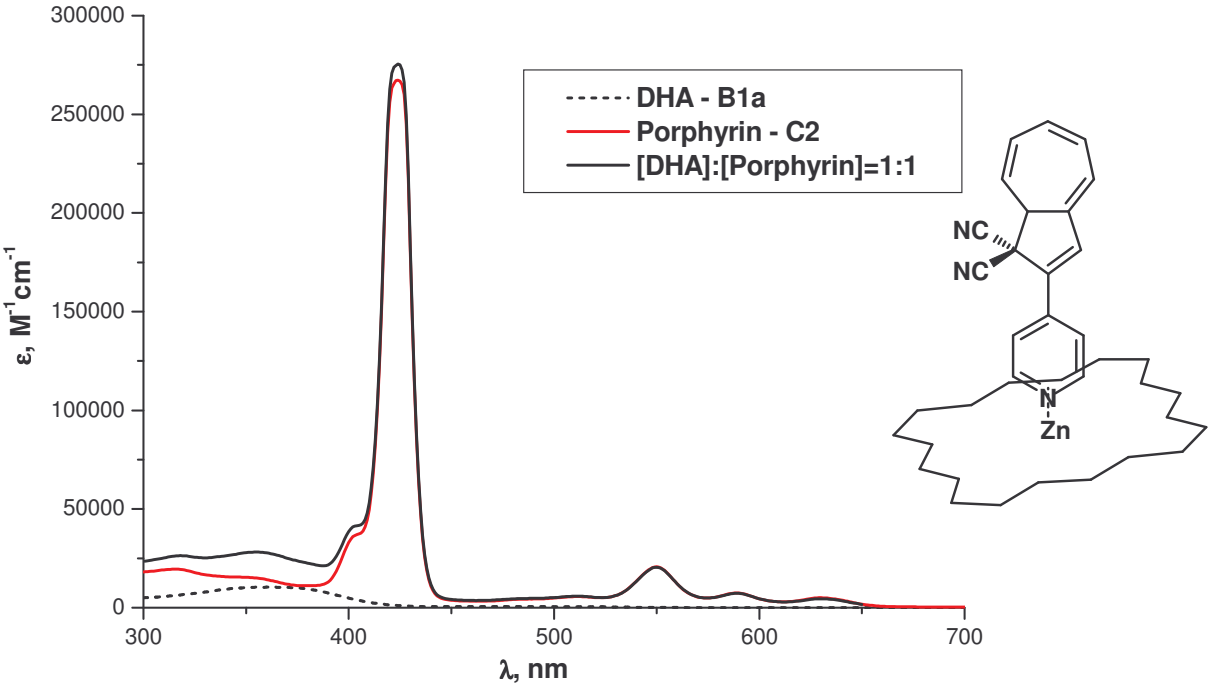


Figure 5.4: Absorption spectra of B1a, C2 and their complex with ratio 1:1 in toluene.

Irradiation of **B1a/C2** complex with λ_{ex} = 366 nm during ca. 1.5 minute causes the appearance of absorption band of **B1b/C2** at 475 nm which corresponds to the long-wavelength absorption band of VHF, Figure 5.5.

5.6 Thermal back reaction of B1b/C2 complex

According to previous findings about protonation of **B1** and **B2** the rate of thermal back reaction upon protonation is strongly increases. Also depending on the polarity of the solution the changing of reaction rate changes; polar solvent cause a faster thermal back reaction.[157] For less polar solvents this difference is higher, Table 4.2.

These measurements were carried out in toluene. This solvent has been chosen due to lower polarity in comparison with used for previous studies of **B1** and **B2** dichloromethane and acetonitrile. It should be mentioned that solvent polarity influences complex stability.[158] These complexes are more stable in less polar solvents.

[157] a) L.Gobbi, P. Seiler, F. Diederich, *Angew. Chemie, Int. Ed.,* **1999**, 38, 674-678,

b) J. Daub, C. Fischer, S. Gierisch, J. Sixt, *Mol. Cryst. Liq. Cryst.,* **1992**, 217, 177-185.

[158] S.J. Cole, G.C. Curthoys, E.A. Magnusson, J.N. Phillips, *Inorg. Chem*., **1972,** 11, 1024-1028.

To study the half-life of thermal back reaction the solution of **B1** and porphyrin have been prepared with a ratio of 1:1 (concentration of substances, $c = 5 \cdot 10^{-5}$ M).[159]

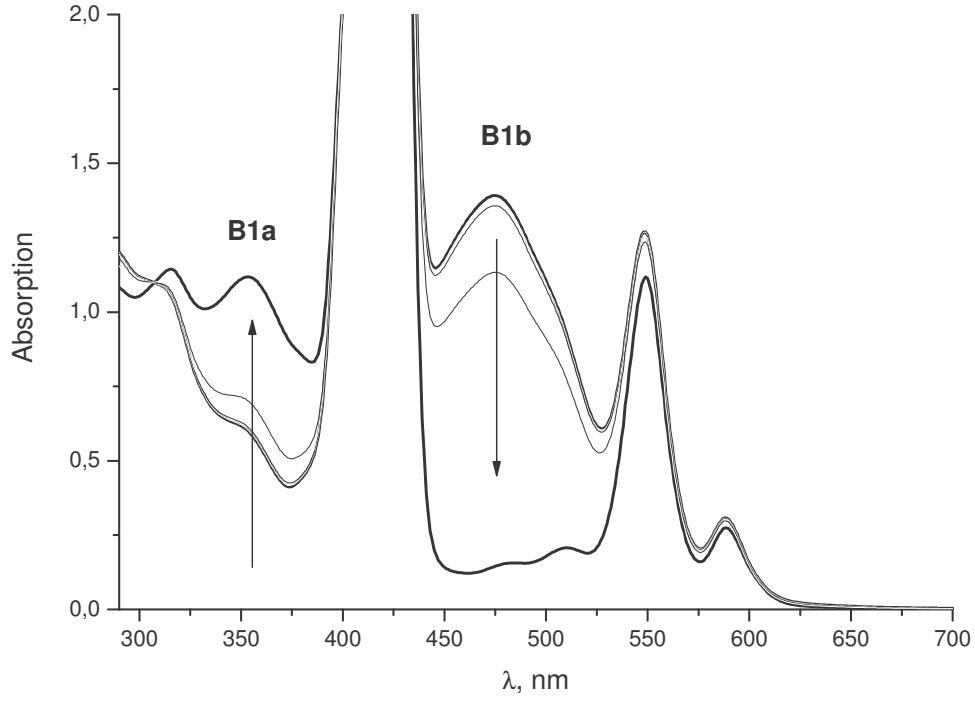


Figure 5.5: Thermal back reaction of B1b/porphyrin, ratio 1:1, ($c = 5 \cdot 10^{-5}$ M) in 2.5 ml of toluene.

Irradiation of **B1a/C2** complex with λ_{ex} = 366 nm during ca. 1.5 minutes behave similar to free **B1** The absorption band of the VHF isomer (**B1b/C2)** appears at 475 nm.

At room temperature half-life of the thermal back reaction, VHF→DHA for **B1b** to **B1a** – 425.4 minutes in toluene, for **B1b/C2** to **B1a/C2** is about 473.55 minutes. Surprisingly, the rate of thermal back reaction is higher as for **B1** in the coordinated state: half-life increases in contrast that has been found for protonated species. Half-life of the thermal back reaction for $\mathbf{B1bH^+}$ to $\mathbf{B1aH^+}$ is about 1.68 minute at room temperature!

All obtained spectroscopic data is collected in Table 5.1.

[159] For calculation of half-life of the thermal back reaction, DHA – VHF see Chapter 4.5.1.

Table 5.1: Characteristic absorption maxima, thermal back reaction half-life $t_{1/2}$ (min) in toluene

	Absorption maximum **[nm]**		**$t_{1/2}$ [min]**
	DHA	**VHF**	
B1	360	472	**425.4**
B1H$^+$	410	515	**1.68**
B1/C2	357	475	**473.55**

The higher half-life of the VHF in the coordinated state could be explained by additional sterical hindrances that occur upon complexation of DHA to porphyrin: it might be assumed that **B1b** in the complex has a slightly higher barrier between *s-trans* and *s-cis* forms.[160]

5.7 ^{1}H-NMR titration, complex stability constant

All titration studies of **B1/C2** complex were made in $CDCl_3$ due to solubility aspects. It has been already mentioned that solvent polarity influences complex stability[158] but the limitation due to solubility of porphyrin in non-polar solvents effected the solvent selection.

All protons of DHA exhibit upfield-shifted signals in ^{1}H-NMR spectra. Especially ortho- and meta-protons show significant shifts that could be interpreted by shielding of porphyrin; these hydrogen atoms are situated deep within porphyrin's shielding and experience the greatest anisotropic effect. It could be conclude that complexation occurs.

The stability constants of complex between **B1** and **C2** were achieved by variation of **C2** concentration (c = 0.0039 M – 0.0013 M) and constant concentration of **B1** (c = 0.0033 M).The resulting data, Figure 5.6, shows shift of **B1** protons vs. concentrations ratio of **B1** and **C2**.

It have been calculated according Benesi – Hildebrand equation[161] (5-1) using data from plot, Figure 5.7, where reciprocal value of difference between observed shift of proton in complex and in free compound, **B1** is plotted versus reciprocal value of **C2** concentration, Figure 5.7.

[160] T. Mrozek, J. Daub, A. Ajayagosh, In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinhein, **2001**.

[161] a) H.A. Benesi, J.H. Hildebrand*, J. Am. Chem. Soc*., **1949**, 71, 2703;

b) M.W. Hanna, A.L. Ashbaugh, *J. Phys. Chem*., **1964**, 68, 811.

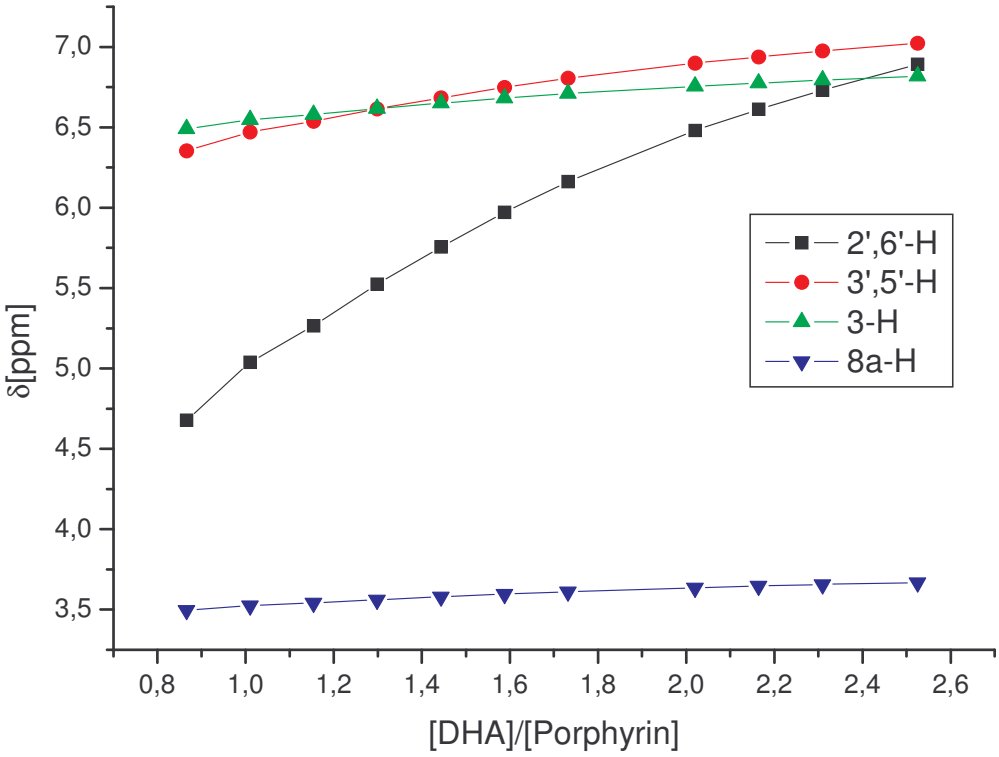


Figure 5.6: Concentration dependence of ^{1}H-NMR shifts of DHA protons upon complexation with C2 in $CDCl_3$.

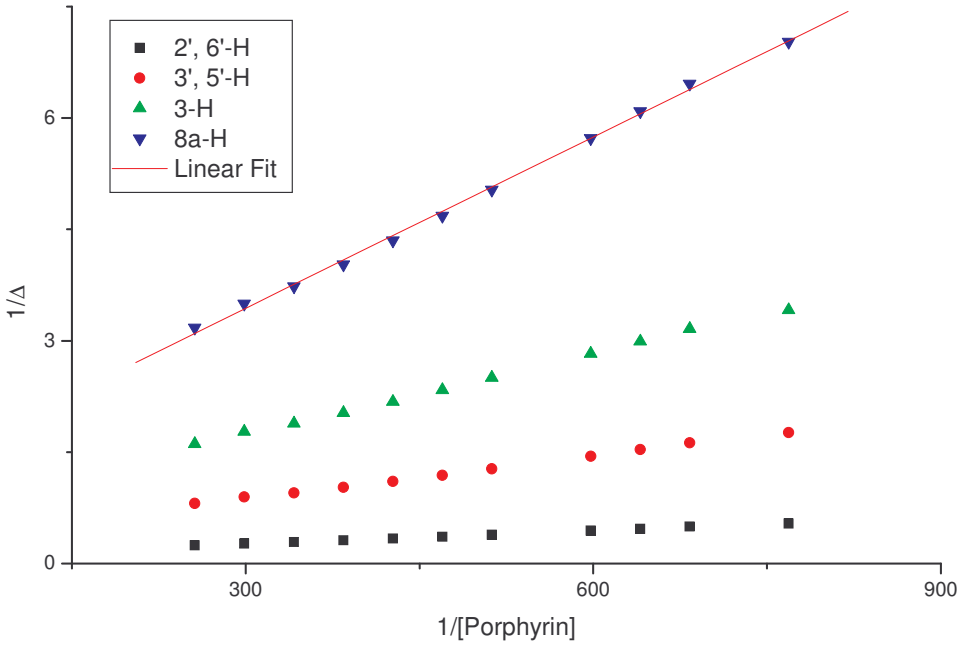


Figure 5.7: Benesi – Hildebrand plot; linear fit of 2' and 6' protons of B1.

(5-1)

$$\frac{1}{\Delta} = \frac{1}{\Delta_0 K[C2]} + \frac{1}{\Delta_0} \ ,$$

Benesi – Hildebrand equation, where:

$\Delta = \delta_{DHA} - \delta_{obs}$,

δ_{DHA} – the proton shift of free DHA

$\delta_{obs.}$ - the observed chemical shift of B1 proton in the equilibrium solution

$\Delta_0 = \delta_{DHA} - \delta_{complx}$,

$\delta_{complx.}$ – proton shift of the pure complex

[C2] – concentration of porphyrin

K – stability constant.

Linear character of Benesi – Hildebrand plot, Figure 5.7, is indication of complex formation with stoichiometry 1:1.

Table 5.2: Results of NMR titrations of C2 and B1 in $CDCl_3$.

	K (M^{-1})	**$\delta_{complx.}$ (ppm)**	**R**
B1/C2	147	7.87	0.9990

5.8 UV-vis spectroscopic studies, titration

Experiments were carried out in toluene. But the concentrations of **C2** and **B1** (10^{-6} – 10^{-5}) are too low to get data about complexation strength. The most significant changes are observed for the Q-bands of the porphyrin.

5.9 Emission studies

A solution of porphyrin **C2** in toluene have been prepared (c = $5.05 \cdot 10^{-6}$ M). Dihydroazulene **B1** has been added to this solution, to get ratios of **B1a/C2** from 1:5 to 20:1, Figure 5.8. Excitation of **B1a/C2** at 424 nm shows two emission maximum at 596 and 646 nm.

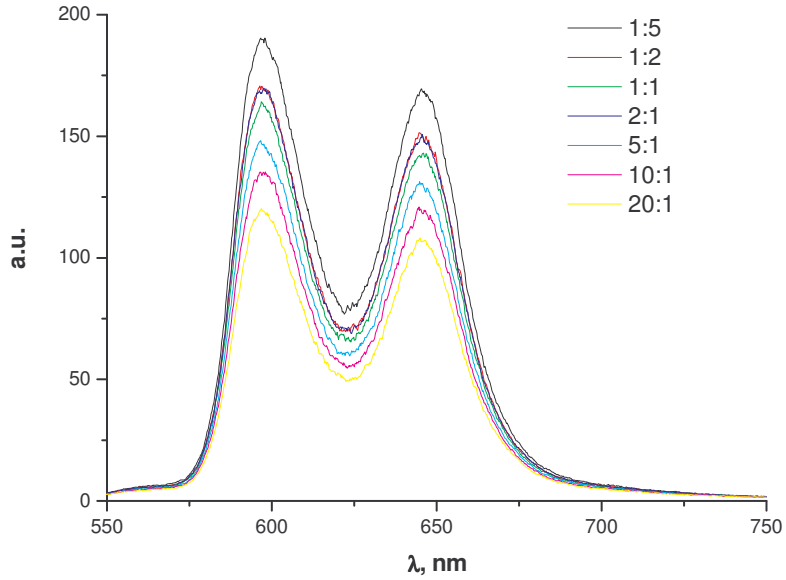


Figure 5.8: Emission spectra of B1a/C2 complex in toluene, λ_{ex} = 424 nm.

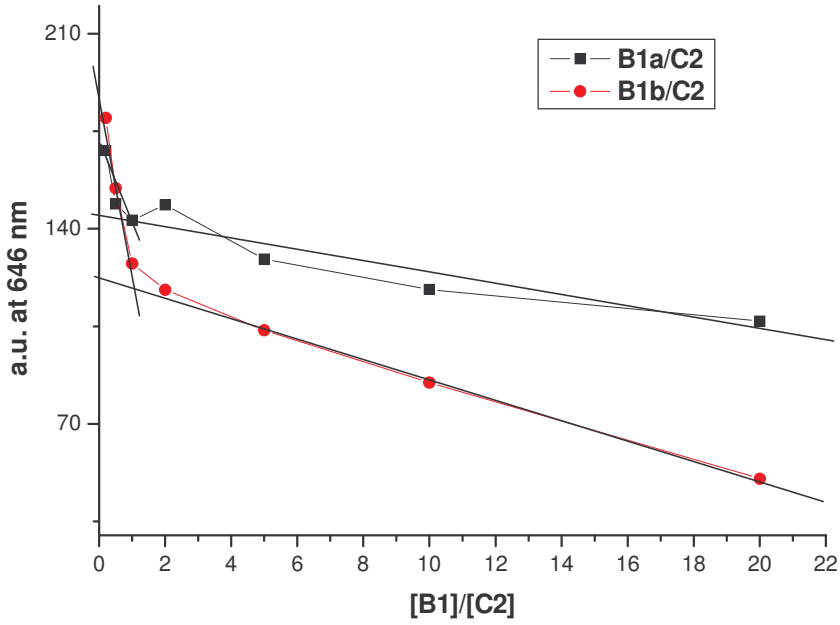


Figure 5.9: Mol ratio plot 1:1 complexation of C2 (c = $5.05 \cdot 10^{-5}$M) with B1a and B1b in toluene.

Also same studies were carried out for irradiated solution of **B1b/C2** complex, Figure 5.9. For every measurement the sample has been irradiated with low intensity lamp by light $\lambda_{ex.}$ = 366 nm during 30 seconds.

The stoichiometry of porphyrin / dihydroazulene complex has been achieved with mole ratio method.[162] Achieved data confirm findings done by ^{1}H-NMR studies. The ratio of ligand:host is 1:1.

5.10 Conclusion and outlook

Pyridine substituted dihydroazulene **B1** and Zn-porphyrin **C2** form a complex of the stoichiometry 1:1. This follows from ^{1}H-NMR titration studies and data analysis by the Benesi-Hildebrand approach.

The interaction of the pyridine nitrogen with the Zn-porphyrin depends on the state of the DHA/VHF equilibrium. The electron attracting VHF form decreases the electron density at the pyridine nitrogen and presumably reduces the strength of complexation. The thermal back reaction VHF $\rightarrow$ DHA is slower in the coordination complex.

Preliminary studies on the synthesis of a wire-type DHA-Porphyrin-DHA triad are reported. It is hypothesised that this triad may be used as a gated molecular switch. Furthermore by using the molecular subunits described in this work a supramolecular and multiadressible molecular switch is designed. These molecular units are of interest for molecular information processing.

[162] a) Comprehensive supramolecular chemistry, J.-M. Lehn, Ed.; H. Tsukube, H. Furuta, A. Odani, Y. Takeda, Y. Kudo, Y. Inoue, Y. Liu, H. Sakamoto, K. Kimura, 8, 425-482, Elsevier, UK, **1996**;

b) A.S. Meyer, Jr., and G.H. Ayres, *J. Am. Chem. Soc*. **1957**, 79, 49-53;

c) B.J. Whitlock, and H.W. Whitlock, *J. Am. Chem. Soc*. **1990**, 112, 3910.

5.11 Appendix

5.11.1 Development of formula (5-1)

K – stability constant

[C2] – equilibrium concentration of free **C2**

[B1] – equilibrium concentration of free **B1**

[B1-C2] – equilibrium concentration of **B1/C2** complex

$[B1^0]$ – total concentration of **B1**

$[C2^0]$ – total concentration of **C2**

$\delta_{obs.}$ - the observed chemical shift of **B1** proton in the equilibrium solution

$\delta_{complx.}$ – proton shift of the pure complex

δ_{DHA} – the proton shift of free **B1**

N – mole fraction

(2) $K = \dfrac{[B1-C2]}{[B1][C2]}$

(3) $\delta_{obs} = N_{DHA}\delta_{DHA} + N_{compl}\delta_{compl}$

(4) $N_{DHA} = \dfrac{[B1]}{[B1]+[B1-C2]}$

(5) $N_{compl} = \dfrac{[B1-C2]}{[B1]+[B1-C2]}$

(6) $N_{DHA} + N_{compl} = 1$

(7) $\delta_{obs} = \delta_{DHA} + \dfrac{[B1-C2]}{[B1]+[B1-C2]}(\delta_{compl} - \delta_{DHA})$

(8) $[B1^0] = [B1]+[B1-C2]$

(9) $[C2^0] = [C2]+[B1-C2]$

(10) $[B1-C2] = \dfrac{[B1^0](\delta_{obs} - \delta_{DHA})}{(\delta_{compl} - \delta_{DHA})} = [B1^0]\left(\dfrac{\Delta}{\Delta_0}\right)$

(11) $\Delta = \delta_{DHA} - \delta_{obs}$

(12) $\Delta_0 = \delta_{DHA} - \delta_{complx}$

$$(13)\ [B1^0] = \frac{[B1-C2]}{K[C2]} + [B1-C2] = [B1-C2]\left(\frac{1}{K[C2]} + 1\right)$$

$$(1)\ \frac{1}{\Delta} = \frac{1}{\Delta_0 K[C2]} + \frac{1}{\Delta_0}$$

6 Experimental part

6.1 General

6.1.1 Spectroscopy

6.1.1.1 IR-spectroscopy

Bio-Rad FT-IR spectrometer FTS 155.

Intensive signal peaks are marked with bold font.

6.1.1.2 NMR – spectroscopy

- Brucker AC-250 (^{1}H: 250.1 MHz, ^{13}C: 62.9 MHz), measuring temperature: 24 °C.
- Brucker ARX-400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz), measuring temperature: 21 °C.
- Avance 300 (^{1}H: 300,1MHz, ^{13}C: 75,5MHz), measuring temperature: 26°C
- Avance 400 (^{1}H: 400,1MHz, ^{13}C: 100,6MHz), measuring temperature: 26°C
- Avance 600 (^{1}H: 600,1MHz, ^{13}C: 150,9MHz), measuring temperature: 26°C

The chemical shifts are indicated in δ-values (ppm) relative to TMS as internal standard. The evaluation takes place so far possible according to first order.

Data format: Chemical shift (multiplicity, number of protons, coupling constant, allocation).
Abbreviations: s = singlet, bs = broad singlet, d = doublet, dd = doublet of the doublets, t = triplet, q = quartet, m = multiplet, p = pseudo -.

Accuracy of the indication: chemical shift: 0,01ppm with ^{1}H-nmr, 0,1ppm with ^{13}C-nmr; coupling constant: 0,1Hz.

The used solvent is noted with the spectra in each case.

6.1.1.3 UV/Vis spectroscopy

Perkin-Elmer Lambda 9 UV/Vis/NIR-Spectrophotometer.

1 and 0.1 cm quartz cuvettes of the company Hellma and Uvasol solvent of the companies Acros and Aldrich were used.
Data format: λ_{max} in nm (ε)

6.1.1.4 Fluorescence spectroscopy

F-4500 Hitachi Fluorescence-Spectrophotometer.

1 cm quartz cuvette of the company Hellma and Uvasol solvent of the companies Acros and Aldrich were used. If it not noticed, excited with longest wave absorption band. The concentration of the measuring solution lies within the range of 10^{-6}M.

6.1.1.5 Mass spectra

- Varian CH-5 (EI)
- Finnigan MAT 95 (FAB and FD)
- Finnigan MAT SSQ 7000 (ESI)

With FAB xenon serves as ionization gas. The matrix is specified in each case.

6.1.1.6 Solvents

Solvents for the spectroscopic measurements were of spectroscopic purity grade, unless other specified.

6.1.2 Analytics

6.1.2.1 Melting point

Microscope heating table Reichert Thermovar.

Melting points are uncorrected.

6.1.2.2 Elemental analysis

Micro-analytical laboratory, Institute of Chemistry and Pharmacology, University of Regensburg

6.1.3 Synthesis

6.1.3.1 Column chromatography

Silicagel Merck Geduran SI 60.
Column chromatography was performed in glass columns filled with silica or alumina. To obtain more regularly structured column, solvent mixture (in each case corresponding starting mixture) was flowed through the column several times, until all absorbed gases and possible impurities were removed. The procedure was performed without any additional pressure; eluent expense 2-10ml per minute, depending on the exact case. The regenerated solvent was not put into the chromatographic cycle to avoid impurities.

6.1.3.2 Thin layer chromatography

Aluminium foils Merck 60 F_{254} silicagel, layer thickness 0.2mm.
TLC (Thin Layer Chromatography) has been made in a chromatographic chamber at normal conditions. For the exact eluent composition see corresponding synthetic description.

6.1.3.3 Crystallization

For crystallization, the product usually was dissolved in a minimal volume of appropriate solvent (chosen before crystallization if not described or tested before) and filtered still hot to avoid beginning of crystallization on undissolved particles, such as dust etc. Then the filtered solution was slowly cooled to room temperature and filtered. In some cases, when yield was too low, the solution was further cooled in refrigerator and filtered once again.

6.1.3.4 Reagents and Solvent

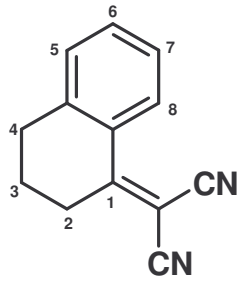
Solvents and reagents used for synthesis were of reagent grade purity and used as received, unless specified. All chemicals were purchased from Sigma-Aldrich, Merck or Acros.

6.1.4 Layout

This work has been created in Microsoft Office – Microsoft Word - writing and editing. Chemical formulas and schemes were created with ISIS/Draw and Corel Draw. Spectral graphics were created and edited with Origin.

6.2 Synthesis of dihydroazulenes

6.2.1 2-(3,4-Dihydro-2H-naphthalen-1-ylidene)-malononitrile[163], A1-1



$C_{13}H_{10}N_2$: 194.24

CAS-Nr.: [2510-03-4]

1 Equivalent of 2-(3, 4-dihydro-2H-naphthalen-1-ylidene)-malononitrile and 1.5 equivalent of malononitrile were dissolved in 35 ml of benzene in 3-neck flask equipped with Dean-Stark trap and condenser. When it started boiling 6 ml of catalytic solution (NH_4OAc/HOAc (glacial) – 1 g in 3 ml) was added. Mixture was refluxed and stirred for 7 hours. The reaction mixture was washed with water, water fractions were washed with benzene (3x50ml). Organic fractions were collected and dried with Na_2SO_4 and after were evaporated and chromatographed (SiO_2/CH_2Cl_2).

Yield: 2.02 g (83.7 %)

IR (KBr): $\tilde{\nu}$ = 2964, 2937, 2895, 2223, 1602, 1567, 1528, 1478, 1455, 1335, 1312, 1247, 1196, 1096, 946, 915, 876, 849, 768, 737, 672, 641, 533 cm^{-1};

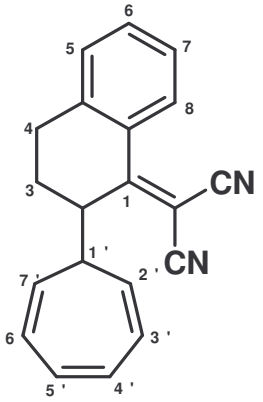
^{1}H-NMR (300 MHz, CD_3CN): δ= 2.01 (m, 2H, 3-H), 2.90 (t, 2H, 4-H), 3.03 (dd, 2H, 2-H), 7.29 (m, 1H, 5-H), 7.35 (m, 1H, 6-H), 7.50 (m, 1H, 7-H), 8.21 (m, 1H, 8-H);

MS (EI, 70 eV): m/z (%) = 194.1 (100) [M^+];

Elemental analysis	C	H	N
calculated	80.39	5.19	14.42
found	80.46	5.25	14.68

[163] D. T. Mowry, *J. Am. Chem. Soc.,* **1945**, 67, 1050 – 1051.

6.2.2 2-(2-Cyclohepta-2, 4, 6-trienyl-3, 4-dihydro-2H-naphthalen-1-ylidene)-malononitrile, A1-2



$C_{20}H_{16}N_2$: 284.36

2-(3,4-Dihydro-2H-naphthalen-1-ylidene)-malononitrile (1 g, 5.15 mmol) and tropilium tetrafluoroborate (0.56 g, 6.18 mmol, 1.2 equivalent) dissolved in 25 ml acetonitrile. After compounds were completely dissolved solution of pyridine 0.5 ml in 15 ml acetonitrile has being added during 15 minutes. After 2 hours of stirring at RT 0.5 ml of pyridine in 15 ml acetonitrile were added and stirred overnight. TLC showed nearly complete conversion of precursor. 2 Equivalents of aqueous solution of HCl (1M) have been added. Separated, organic layer washed with water, dried with Na_2SO_4 and chromatographed (SiO_2 / EtOAc/PE 40-60 1:4). The product came as a 2nd band, 1st – disubstituted.

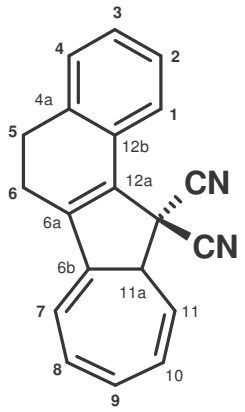
Yield: 0.91g (62%) white solid

IR (KBr): $\tilde{\nu}$ = 3026, 2933, 2860, 2223, 1602, 1571, 1555, 1525, 1478, 1451, 1436, 1324, 841, 772, 737, 718, 699, 594 cm^{-1};

^{1}H-NMR (300 MHz, CD_3CN): δ = 2.05 (m, 2H, 3-H), 2.39 (m, 1H, 1'-H), 2.92 (dd, 2H, 4-H), 3.48 (m, 2H, 2-H), 5.23 (m, 2H, 2', 7'-H), 6.27 (m, 2H, 3', 6'-H), 6.62 (m, 2H, 4', 5'-H), 7.21 (m, 1H, 5-H), 7.30 (m, 1H, 6-H), 7.46 (m, 1H, 7-H), 7.99 (m, 1H, 8-H);

MS (PI-EI, 70 eV): m/z (%) = 283.1 (2.24) [$M-H^+$], 91 (100) [$C_7H_7^+$]

6.2.3 5,11a-Dihydro-6H-naphtho[2,1-a]azulene-12,12-dicarbonitrile, A1



$C_{20}H_{14}N_2$: 282.35

2-(2-Cyclohepta-2, 4, 6-trienyl-3, 4-dihydro-2H-naphthalen-1-ylidene)-malononitrile 0.5 g (1.76 mmol) dissolved in 30 ml acetonitrile (abs) in 100 ml 3-neck flask (dried and flushed with nitrogen). Cooled solution to -20 °C. Added 1.2 equivalent of nitrosyl tetrafluoroborate. Stirred at -10 ÷ -20°C for 3 hour. Added 30 ml absolute dichloromethane and 2 equivalents of pyridine. Stirred for 10 minutes. Washed with 40 ml of water, dried with Na_2SO_4 (kept all the time in darkness). Chromatographed (SiO_2 / CH_2Cl_2/PE 40-60 2:1).

Yield: 0.27 g (55%, yellow solid)

m.p.: 173 °C

^{1}H-NMR (300 MHz, CD_3CN): δ = 2,59 (m, 2H, 6-H), 2,98 (t, 2H, 5-H), 3,77 (m, 1H, 11a-H), 5,84 (m, 1H, 11-H), 6,26 (m, 1H, 7-H), 6,31 (m, 1H, 10-H), 6,49 (m, 1H, 9-H), 6,61 (m, 1H, 8-H), 7,24 (m, 1H, 4-H), 7,28 (m, 1H, 3-H), 7,34 (m, 1H, 2-H), 7,66 (m, 1H, 1-H) ppm.

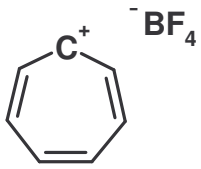
IR (KBr): $\tilde{\nu}$ = 3025, 2968, 2929, 2856, **2281**, 1736, 1655, 1559, 1543, 1509, 1458, 1385, 1266, 1112, 1030, 899, 768, 671, 582 cm^{-1}

MS (EI, 70 eV): m/z (%) = 282 (100) [M^+];

HRMS: (EI, 70 eV): calc.: 282.1157, found: 282.11569

Elemental analysis	**C**	**H**	**N**
calculated	**85.08**	**5.00**	**9.92**
found	**84.57**	**5.02**	**9.76**

6.2.4 Tropilium tetrafluoroborate, A2



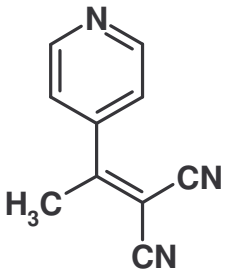
CAS-Nr.: [27081-10-3]

Reference: according to lit.[164]

^{1}H-NMR (300 MHz, $(CD_3)_2SO$): δ = 9.34 (s, 7H).

6.2.5 Synthesis of 2-Pyridin-4-yl-8aH-azulene-1,1-dicarbonitrile:

2-(1-Pyridin-4-yl-ethylidene)-malononitrile, B1-1



$C_{10}H_7N_3$: 169.19

To 3-neck flask with Dean-Stark trap added methyl 4-pyridyl ketone 1.26 g (10.40 mmol) in 60 ml benzene and heated up to gently boiling. Added 1g of NH_4OAc in 3 ml glacial HOAc and after 1.3 g (19.68 mmol) malononitrile. Stirring for 3.5 hours (t_{bath} ca. 100°C). Washed with aqueous solution of $NaHCO_3$ (saturated) *(Caution! foam)*. Organic phase separated, water phase washed 2x50ml benzene. Organic fractions collected and dried with Na_2SO_4. Evaporated main part of benzene (*except heating!*) and chromatographed (EtOAc/SiO_2). Concentrated and dried with vacuum. Transferred to next reaction immediately.

Yield: 1.5g (85%)

[164] D.W. Wiley, B.C. McKusick, *Org. Synth.* **1963**, 43, 101-104.

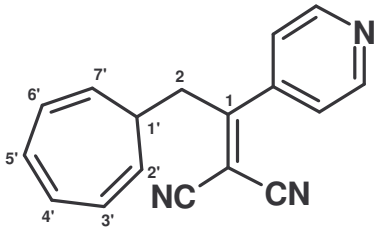
m.p.: decomposition

DC-Rf (EtOAc): 0.45

IR (KBr): $\tilde{\nu}$ = 3053, 2983, 2960, 2929, 2204, 1945, 1733, 1660, 1598, 1575, 1413, 1393, 1374, 1250, 1162, 1100, 1073, 1046, 1000, 892, 818, 664 cm^{-1};

^{1}H-NMR (300 MHz, CD_3CN): δ= 2.57 (s, 3H, Me), 7.46 (B,B', 2H, Pyr-H), 8.91 (A,A', 2H, Pyr-H);

6.2.6 2-(2-Cyclohepta-2,4,6-trienyl-1-pyridin-4-yl-ethylidene)-malononitrile, B1-2



$C_{17}H_{13}N_3$: 259.31

2-(1-Pyridin-4-yl-ethylidene)-malononitrile, **B1-1** 1.5 g (8.87 mmol, 2 equivalents) immediately after purifying dissolved in 75 ml CH_3CN and added 0.78 g (4.38 mmol) tropilium tetrafluoroborate. Bubbled reaction mixture with N_2 for 15 min, stirred for 48 hours. Filtered, evaporated and chromatographed (EtOAc:CH_2Cl_2 = 1:1).

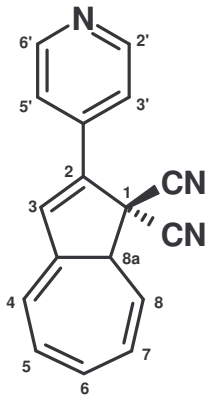
Yield: 0.85g (74.9 %)

DC-Rf (EtOAc): 0.75

MS (EI, 70 eV): m/z (%) = 259 (1) [M^+], 91 (100) [$C_7H_7^+$];

^{1}H-NMR (300 MHz, CD_3CN): δ= 1.98 (m, 1H, 1'-H), 3.14 (d, 2H, 2-H), 5.15 (dd, 2H, 2', 7'-H), 6.23 (m, 2H, 3', 6'-H), 6.63 (m, 2H, 4', 5'-H), 7.24 (B,B', 2H, Pyr-H), 8.79 (A,A', 2H, Pyr-H)

6.2.7 2-Pyridin-4-yl-8aH-azulene-1,1-dicarbonitrile, B1



$C_{17}H_{11}N_3$: 257.30

2-(2-Cyclohepta-2,4,6-trienyl-1-pyridin-4-yl-ethylidene)-malononitrile 0.45 g (1.76 mmol) dissolved in 30 ml acetonitrile (abs.) in 100 ml 3-neck flask (dried and flushed with nitrogen). Cooled solution to -20 °C. 1.2 Equivalent of nitrosyl tetrafluoroborate added and stirred at -10 ÷ -20°C for 2 hour. 30 ml absolute dichloromethane and 2 equivalents of pyridine added and stirred for 10 minutes; washed with 40 ml of water, dried with Na_2SO_4 (kept all the time in darkness). Chromatographed (SiO_2 / EtOAc : CH_2Cl_2 = 1:1).

Yield: 0.17g (37.8%)

m.p.: 104-106 °C

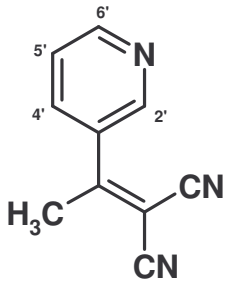
IR (KBr): $\tilde{\nu}$ = 3034, 2246, 2227, **1594**, 1532, **1420**, 1231, 996, 826, 814, **699**, 672, 536

^{1}H-NMR (300 MHz, CDCl3)**:** δ = 3,81 (m, 1H, 8a-H), 5,83 (m, 1H, 8-H), 6,35 (m, 1H, 7-H), 6,47 (m, 1H, 4-H), 6,56 (m, 1H, 6-H), 6,62 (m, 1H, 5-H), 7,11 (s, 1H, 3-H), 7,59 (m, 2H, 3'&5' pyr-H), 8,75 (m, 2H, 2'&6' pyr-H)

MS (EI, 70 eV): m/z (%) = 257.1 (100) [M^+];

Elemental analysis	**C**	**H**	**N**
calculated	**79.36**	**4.31**	**16.33**
found	**78.74**	**4.28**	**16.61**

6.2.8 2-(1-Pyridin-3-yl-ethylidene)-malononitrile, B2-1



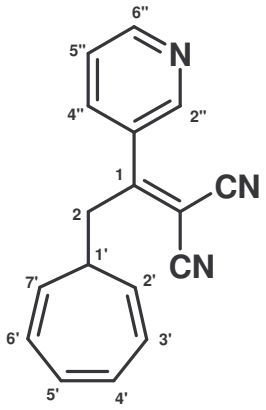
$C_{10}H_7N_3$: 169.19

To a gently boiling solution of methyl 3-pyridyl ketone (2.5ml, 18.61 mmol) in 60 ml added malononitrile (4.7g, 71.1 mmol). To the reaction mixture 9 ml (¼ of full portion) of catalyst (1g of NH_4OAc in 3ml glacial HOAc) added. The rest of catalyst added in the same portions every ½ hour. Stirring for 2 hours (t_{bath} ca. 100°C). Washed with water 2x100ml. Organic phase separated, water phase washed 3x50ml benzene. Organic fractions collected and dried with Na_2SO_4. Evaporated main part of benzene (*except heating!*) and chromatographed (EtOAc/SiO_2). Concentrated and dried with vacuum.

Yield: 3.91 g (81%)
m.p.: decomposition
DC-Rf (EtOAc): 0.45
IR (KBr): $\tilde{\nu}$ = 3049, 2968, 2929, 2215, 1656, 1544, 1478, 1420, 1193, 1131, 1100, 1027, 810, 749, 710, 629 cm^{-1};
^{1}H-NMR (300 MHz, CD_3CN): δ= 2.68 (s, 3H, -C<u>H</u>$_3$), 7.48 (m, 1H, 5'-H), 7.91 (d, 1H, 4'-H), 8.78 (d, 1H, 6'-H), 8.80 (s, 1H, 2'-H);
MS (EI, 70 eV): m/z (%) = 169.1 (100) [M^+];

Elemental analysis	C	H	N
calculated	70.99	4.17	24.84
found	70.37	4.42	25.28

6.2.9 2-(2-Cyclohepta-2, 4, 6-trienyl-1-pyridin-3-yl-ethylidene)-malononitrile, B2-2



$C_{17}H_{13}N_3$: 259.31

2-(1-Pyridin-3-yl-ethylidene)-malononitrile 1.2 g (10 mmol) dissolved in 60 ml CH_3CN and added 1.44 g (8.1 mmol) tropilium tetrafluoroborate. Added 1 ml pyridine and stirred for 48 h at RT. Filtered, evaporated and chromatographed (EtOAc : PE 40-60 = 1:1).

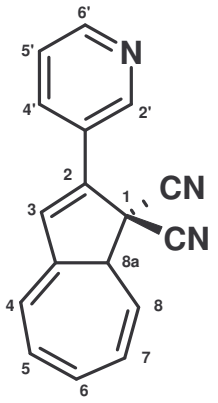
Yield: 1,29g (62 %, yellow-brown viscous)

IR (film) $\tilde{\nu}$ = 3022, 2929, 2856, 2231, 1733, 1586, 1413, 1247, 1046, 1023, 810, 749, 706 cm^{-1};

^{1}H-NMR (300 MHz, CD_3CN): δ = 2.00 (m, 1H, 1'-H), 3.20 (d, 2H, 2-H), 5.15 (dd, 2H, 2', 7'-H), 6.22 (m, 2H, 3', 6'-H), 6.62 (t, 2H, 4', 5'-H), 7,45 (m, 1H, 5" pyr-H), 7,76 (d, 1H, 4" pyr-H), 8,65 (d, 1H, 6" pyr-H), 8,76 (s, 1H, 2" pyr-H) ppm;

MS (EI, 70 eV): m/z (%) = 258.1 (2.80) [ΔH], 91 (100) [$C_7H_7^+$]

6.2.10 2-Pyridin-3-yl-8aH-azulene-1,1-dicarbonitrile, B2



$C_{17}H_{11}N_3$: 257.30

2-(2-Cyclohepta-2,4,6-trienyl-1-pyridin-3-yl-ethylidene)-malononitrile 0.5 g (1.93 mmol) dissolved in 30 ml acetonitrile (abs) in 100 ml 3-neck flask (dried and flushed with nitrogen). Solution cooled to -25 °C. Two equivalent of nitrosyl tetrafluoroborate added to reaction mixture and stirred at -10 ÷ -20°C for 2 hour. 50 ml absolute dichloromethane and 0.2 ml of pyridine added and stirred for 10 minutes; washed with 40 ml of water, dried with Na_2SO_4 (kept all the time in darkness). Chromatographed (SiO_2 / EtOAc : CH_2Cl_2 = 1:1).

Yield: 0.33 g (67%, brown solid)

m.p.: 115-117°C

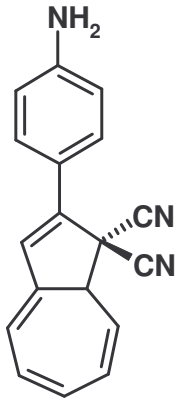
^{1}H-NMR (300 MHz, CDCl3) δ= 3,81 (m, 1H, 8a-H), 5,82 (m, 1H, 8-H), 6,33 (m, 1H, 7-H), 6,41 (d, 1H, 4-H), 6,52 (m, 1H, 6-H), 6,60 (m, 1H, 5-H), 6,99 (s, 1H, 3-H), 7,47 (m, 1H, 5'-H), 8,08 (d, 1H, 4'-H), 8,66 (d, 1H, 6'-H), 8,98 (s, 1H, 2'-H) ppm;

IR (KBr) $\tilde{\nu}$ = 3034, 2926, 2856, 2250, 1586, 1563, 1490, 1416, 1193, 1019, 915, 903, 814, 807, 764, 702 /cm^{-1}

MS (EI, 70 eV): m/z (%) = 256.1 (100) [M^+]

Elemental analysis	**C**	**H**	**N**
calculated	**79.36**	**4.31**	**16.33**
found	**78.72**	**4.52**	**16.68**

6.2.11 2-(4-Amino-phenyl)-8aH-azulene-1,1-dicarbonitrile, B5

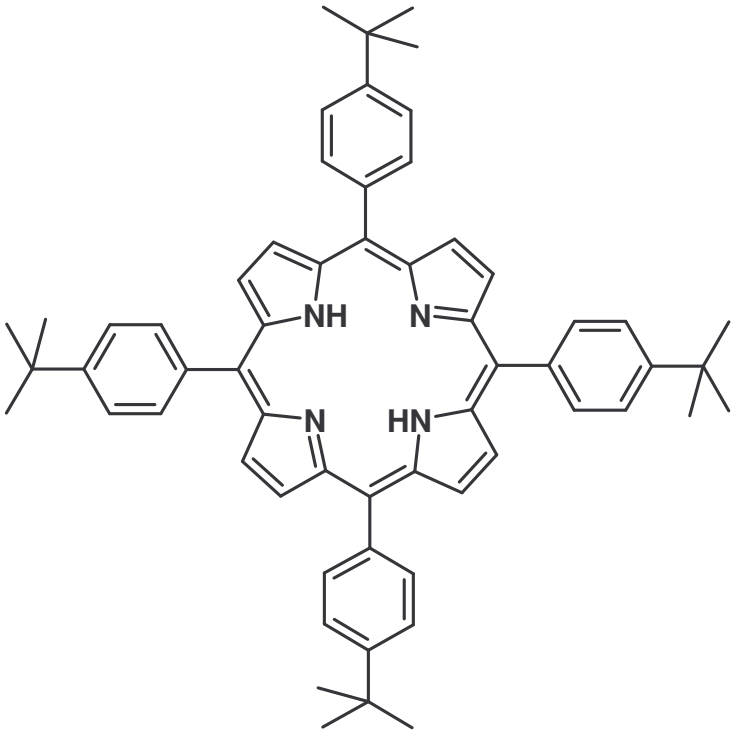


CAS-Nr.: [102780-27-8]

Reference: according to lit.[165]

6.3 Syntheses of porphyrins

6. 3.1 5,10,15,20 – tetra-(4-tert-butylphenyl)-porphyrin, C1



CAS-Nr.: [110452-48-7]

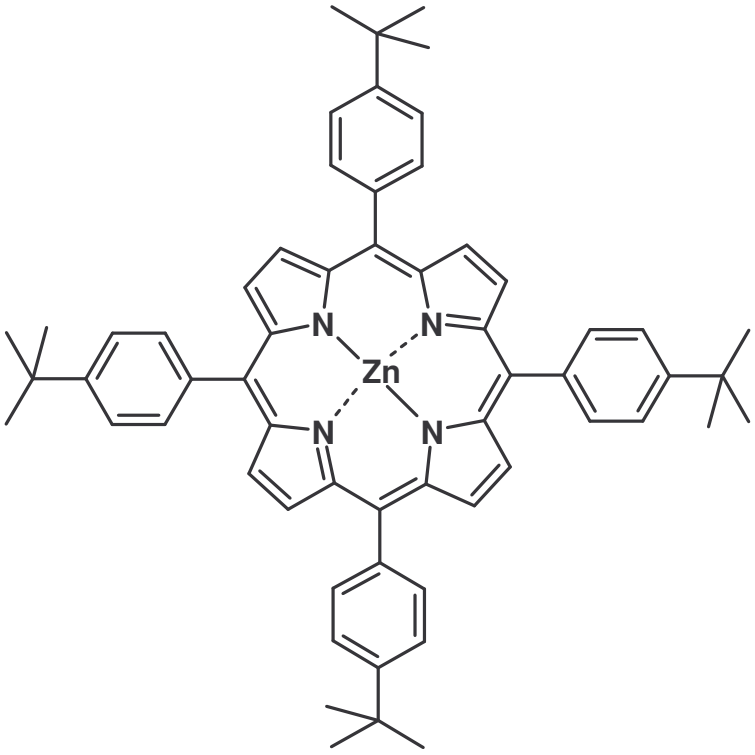
[165] J. Daub, S. Gierisch, U. Klement, T Knoechel, G. Maas, U. Seitz, *Chem. Ber*. **1986**, 119, 2631-2646.

Reference: analogous to lit.[166]

Notice: The product contains some Zn porphyrin. For cases where Zn porphyrin was the main target mixed product further metallation were done. For other cases zinc has been removed from the porphyrin core with trifluoroacetic acid.[167]

Yield: 17.35 %

6.3.2 Zn - 5,10,15,20 – tetra-(4-tert-butylphenyl)-porphyrin, C2



CAS-Nr.: [118589-15-4]

To a solution of acid porphyrin in dichloromethane was added a saturated solution of zinc(II) acetate in methanol. Heated to gently boiling and stirred for ca. 2 hours. After finishing the reaction mixture has been washed with water and dried with Na_2SO_4.

MS (DCM/MeOH + 0.10% TFA) 959.6 (100) [M+CH_3COO^-]

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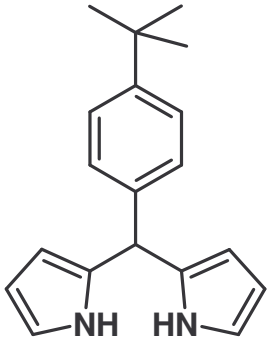
[166] S. Matile, N. Berova, K. Nakanishi, J. Fleischhauer, and R.W. Woody, *J. Am. Chem. Soc.*, **1996**, 118, 5198 - 5206.

[167] R.W. Wagner, T.E. Johnson, J.S. Lindsey, *J. Am. Chem. Soc.*, **1996**, 118, 11166-11180.

Elemental analysis	C	H	N
calculated	79.85	6.70	6.21
found	79.66	6.82	6.10

6.3.3 5-(4-*tert*-Butylphenyl)dipyrrylmethane, C3-1



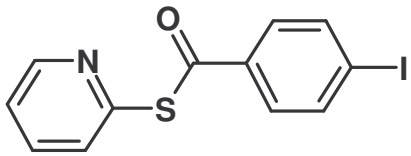
CAS-Nr.: [167482-98-6]

Reference: analogous to lit.[168]

m.p.: 160 °C

^{1}H-NMR (300 MHz, CD_3CN): δ = 1.30 (s, 9 H), 5.45 (s, 1 H), 5.94 (m, 2 H), 6.15 (q, J = 2.9 Hz, 2 H), 6.68 (m, 2 H), 7.14 (m, 2 H), 7.33 (m, 2 H), 7.90 (br s, 2 H).

6.3.4 4-Iodo-thiobenzoic acid S-pyridin-2-yl ester, C3-2



CAS-Nr.: [262267-33-4]

Reference: according to lit.[169]

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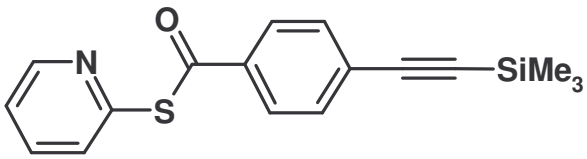
[168] Z. Liu, A.A. Yasseri, R.S. Loewe, A.B. Lysenko, V.L. Malinovskii, Q. Zhao, S. Surthi, Q. Li, V. Misra, J.S. Lindsey, and D.F. Bocian, *J. Org. Chem*, **2004**, 69, 5568-5577.

[169] P.D. Rao, B.J. Littler, G.R.III Geier,; J.S. Lindsey, *J. Org. Chem.,* **2000**, 65, 1084-1092.

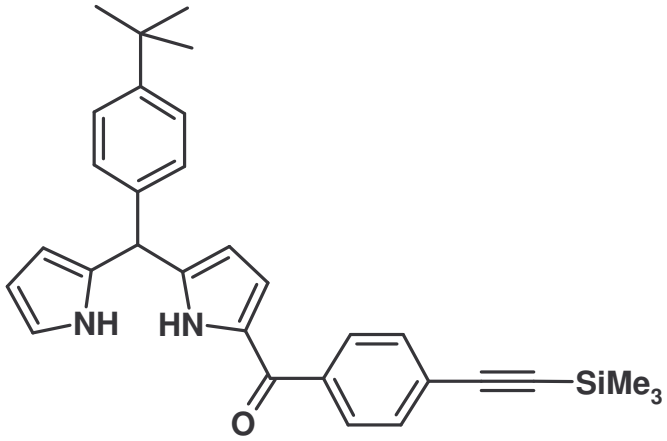
6.3.5 4-Trimethylsilanylethynyl-thiobenzoic acid S-pyridin-2-yl ester, C3-3



CAS-Nr.: [262267-34-5]

Reference: according to lit.[169]

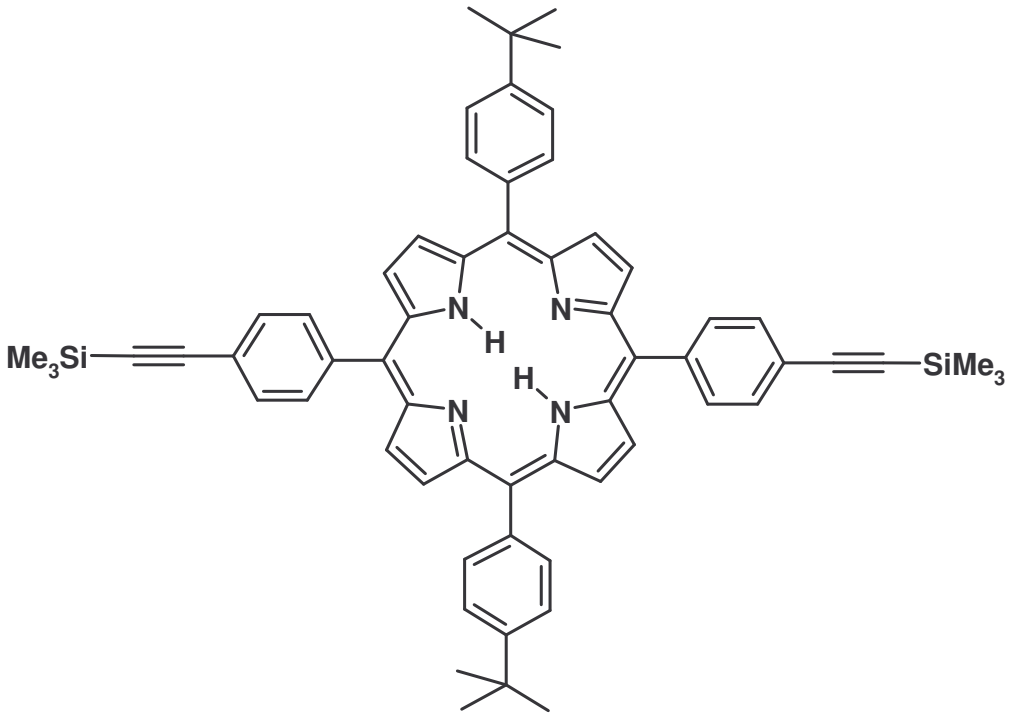
6.3.6 {5-[(4-tert-Butyl-phenyl)-(1H-pyrrol-2-yl)-methyl]-1H-pyrrol-2-yl}-(4-trimethylsilanyl-ethynyl-phenyl)-methanone, C3-4



CAS-Nr.: [262267-49-2]

Reference: according to lit.[169]

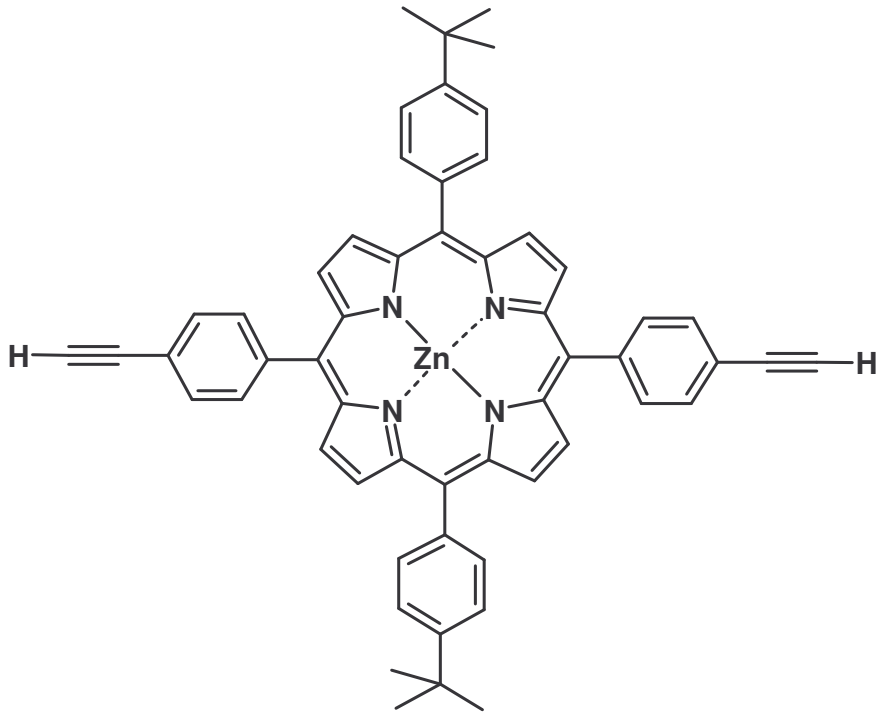
6.3.7 5,15-Bis-(4-tert-butyl-phenyl)-10,20-bis-(4-trimethylsilanylethynyl-phenyl)-porphyrin, C3



CAS-Nr.: [630401-62-6]

Reference: according to lit.[169, 170]

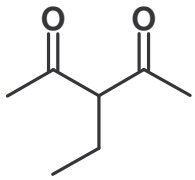
6.3.8 Zn-5,15-Bis-(4-tert-butyl-phenyl)-10,20-bis-(4-ethynyl-phenyl)-porphyrin, C4



CAS-Nr.: [632301-78-1]

Reference: according to lit.[169, 170]

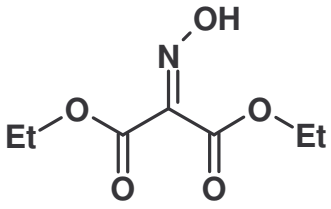
6.3.9 3-Ethyl-2,4-pentanedion, C5-1



CAS-Nr.: [1540-34-7]

Reference: according to lit.[171]

6.3.10 Diethyloximinomalonate, C5-2



CAS-Nr.: [6829-41-0]

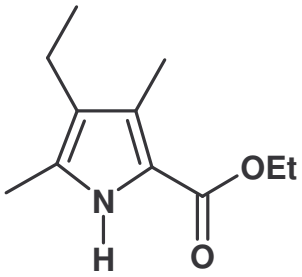
Reference: according to lit. [172]

[170] K. Tomizaki, L. Yu, L. Wei, D.F. Bocian, J.S. Lindsey, *J. Org. Chem*., **2003**, 68, 8199-8207.

[171] K.V. Auwers and H. Jacobsen, *Liebigs Ann. Chem*., **1921**, 426, 227.

[172] J.B. Paine III, D. Dolphin, *J. Org. Chem*. **1985**, 50, 5598-5604 .

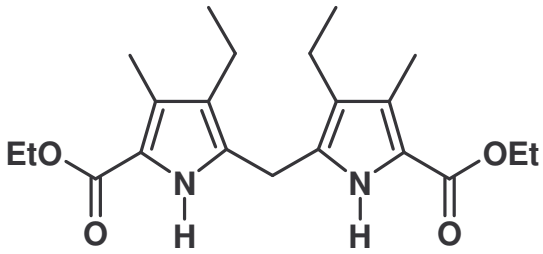
6.3.11 2-Carboxyethyl-3,5-dimethyl-4-ethylpyrrole, C5-3



CAS-Nr.: [2199-47-5]

Reference: according to lit. [173]

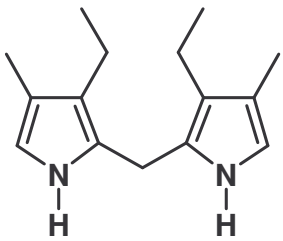
6.3.12 3,3'-Diethyl-4,4'-dimethyl-5,5'-bis-(ethoxycarbonyl)-2,2'-dipyrryl-methane, C5-4



CAS-Nr.: [6305-93-7]

Reference: analogous to lit.[174]

6.3.13 3,3'-Diethyl-4,4'-dimethyl-2,2'-dipyrryl-methane, C5-5



CAS-Nr.: [92415-30-0]

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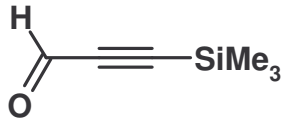
[173] D.P. Shrout, D.A. Lightner, *Synthesis* **1990**, 1062.

[174] M.T. Huggins, A.K. Tipton, Q. Chen, D.A. Lightner, *Monatsh. Chemie*, **2000**, 131, 825-838.

Reference: analogous to lit.[80]

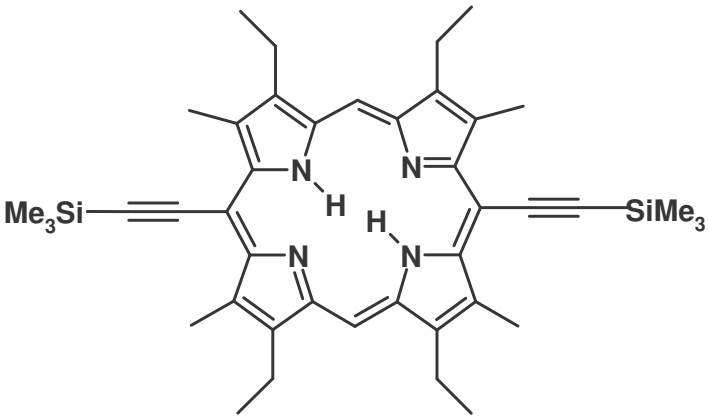
6.3.14 Trimethylsilanyl-propynal, C5-6



CAS-Nr.: [2975-46-4]

Reference: according to lit. [175]

6.3.15 2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis[(trimethylsilyl)ethynyl]-21H,23H-porphine, C5



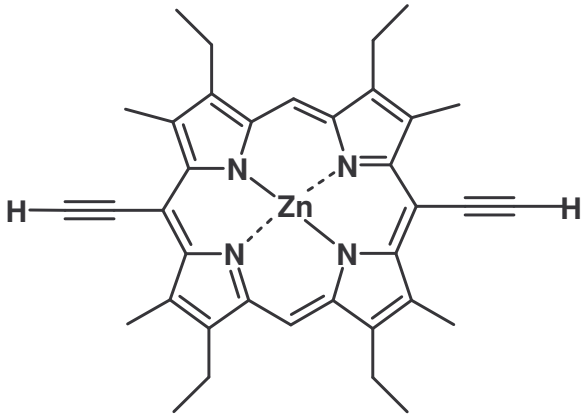
CAS-Nr.: [140683-91-6]

Reference: according to lit.[176]

[175] M. Journet, D. Cai, L.M. DiMichele and R.D. Larsen, *Tetrahedron Letters*, **1998**, 39, 6427-6428.

[176] H.L. Anderson, *Tetrahedron Letters*, **1992**, 33(8),1101-1104.

6.3.16 2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis[(trimethylsilyl)ethynyl]-21H,23H-porphine, C6

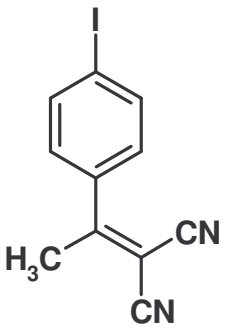


CAS-Nr.: [140707-97-7]

Reference: according to lit.[176]

6.4 Syntheses of dihydroazulene/porphyrin conjugates

6.4.1 2-[1-(4-Iodo-phenyl)-ethylidene]-malononitrile, D1-1

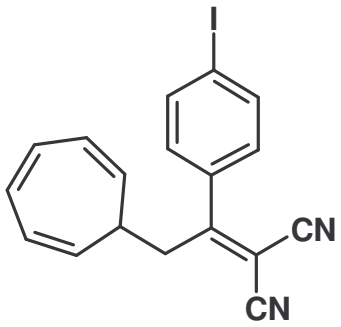


CAS-Nr.: [351459-69-3]

Reference: according to lit. [177]

[177] T. Mrozek, *Dissertation*, University of Regensburg, **2000**.

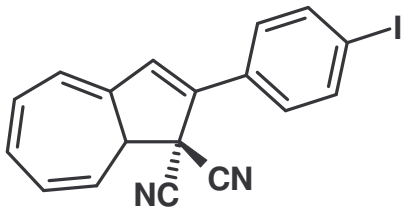
6.4.2 2-[2-Cyclohepta-2,4,6-trienyl-1-(4-iodo-phenyl)-ethylidene]-malononitrile, D1-2



CAS-Nr.: [351459-67-1]

Reference: according to lit.[177]

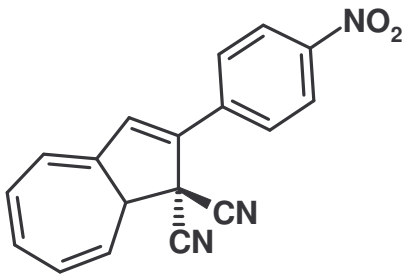
6.4.3 2-(4-Iodo-phenyl)-8aH-azulene-1,1-dicarbonitrile, D1



CAS-Nr.: [298212-99-4]

Reference: according to lit.[177]

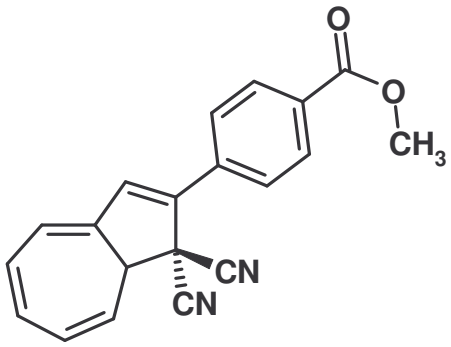
6.4.4 2-(4-Nitro-phenyl)-8aH-azulene-1,1-dicarbonitrile, D2



CAS-Nr.: [94111-20-3]

Reference: according to lit.[177, 165]

6.4.5 4-(1,1-Dicyano-1,8a-dihydro-azulen-2-yl)-benzoic acid methyl ester, E1



CAS-Nr.: [102780-11-0]

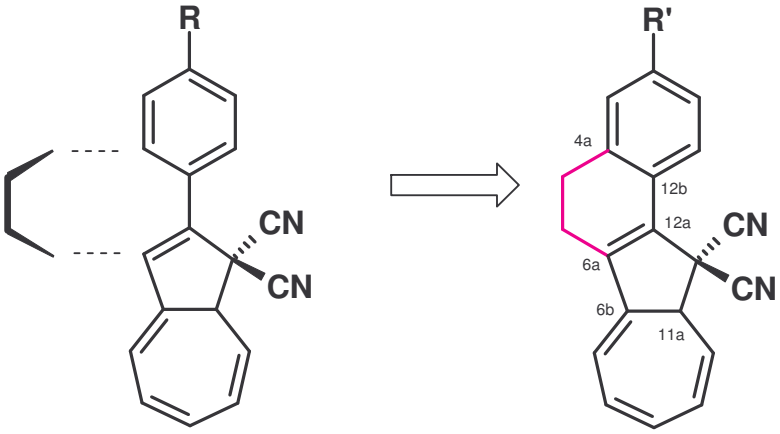
Reference: according to lit. [177, 165]

7 Summary

This work reports on the synthesis of new dihydroazulene/vinylheptafulvene systems and on the study of their photochromic and physical properties. Main emphasis is given to multiple addressable systems in order to control of different properties of the molecules such as emission, absorption and the rate of thermal reaction as a response on blue light irradiation, protonation, and complexation.

Chapter 3: Sterically constrained dihydroazulene systems:

The phenyl-dihydroazulene **A2a** have been modified to prevent s-*cis*-s-*trans* isomerisation. Have been found that six-ring annulation as shown in **A1a** leads to an increase of the rate of the thermal back reaction (VHF → DHA) and as a consequence the photochromism cannot be observed at room temperature under the normal experimental conditions. Lowering the temperature the colouring occurs on irradiating the DHA form.



	R
A2a	-H
A4a	-CN

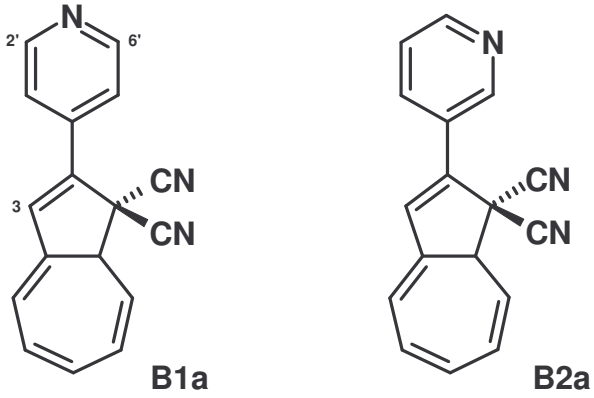
	R
A1a	-H

Chapter 4: Receptor functionalized chromophores:

The photochromic behaviour of **B1a** and **B2a** has been investigated. The protonation changes significantly their chemical and photophysical properties, such as the rate of the photochemical and thermal back reactions, the absorption and emission, the appearance of the photochromism at room temperature, and the quantum yield of photoreaction.

It has been shown that the multi functionality of the pyridine substituted DHAs **B1a** and **B2a** as are photochromism, receptor properties, emission and absorption changes makes them to interesting "two-mode input/multi-output" systems, which are important for using molecular switches for digital processing and communication.

The multi-mode switching may be further extended via transition metal complexation which expands the potential of application towards molecular sensing and supramolecular architecture



Chapter 5: Porphyrin conjugates:

It has been shown that the pyridine substituted dihydroazulene **B1a** and Zn-porphyrin **C2** form a complex of the stoichiometry 1:1. This follows from ^{1}H-NMR titration studies and data analysis by the Benesi-Hildebrand approach.

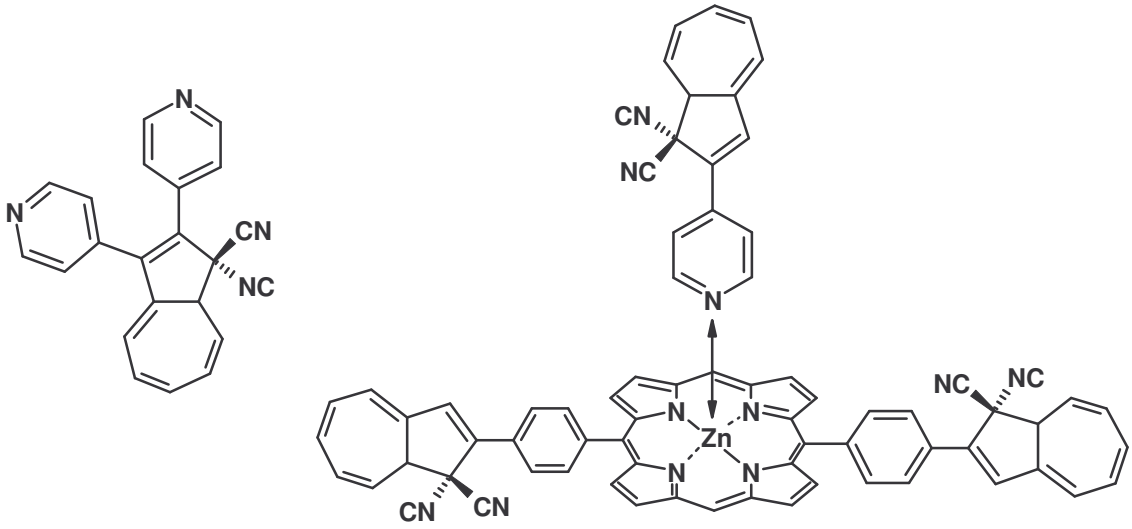
The interaction of the pyridine nitrogen with the Zn-porphyrin depends on the state of the DHA/VHF equilibrium. The electron attracting VHF form decreases the electron density at the pyridine nitrogen and presumably reduces the strength of complexation. The thermal back reaction VHF $\rightarrow$ DHA is slower in the coordination complex.

Preliminary studies on the synthesis of a wire-type DHA-Porphyrin-DHA triad are reported. It is hypothesised that this triad may be used as a gated molecular switch. Furthermore by using the molecular subunits described in this work a supramolecular and multiadressible molecular switch is designed. These molecular units are of interest for molecular information processing.

Extension of this work might be the synthesis of annulated cyano-phenyl-DHA **A4** to compare with well-studied **A4** by the time-resolved laser spectroscopy.[178]

The receptor topic could be extended to a photochromic system with two coordination sites (See formula below, left part).

Porphyrin conjugates might be extended towards two-dimensional photosensitive systems containing two covalently bound photochromic units bridged by a metal porphyrin. The interaction between the chromophores would be mediated by the photochromic switch coordinated to the metal porphyrin (See formula below, right part).

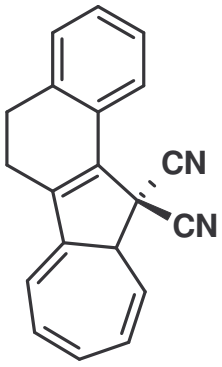


[178] V. De Waele, U. Schmidhammer, T. Mrozek, J. Daub, E. Riedle, *J. Am. Chem. Soc*. **2002**, 124, 2438-2439.

8 List of formulas

Notes:

1. Some compounds are named according to nicknames found in published work. This may help to understand the described systems easier: **CP-DHA**, **CHex-DHA**, **CHept-DHA**.
2. The nomenclature of the DHA/VHF systems is as follows: Behind the capital letter and the number that describe the individual compound additional characters are used. Lower case characters **a** and **b** denote DHA and VHF form, respectively. Symbol $\mathbf{H^+}$ is used for the protonated form. For example $\mathbf{B1aH^+}$.
3. Intermediates have an additional number after the index character of the full compound. For example **B1-1**.



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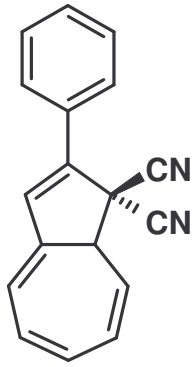

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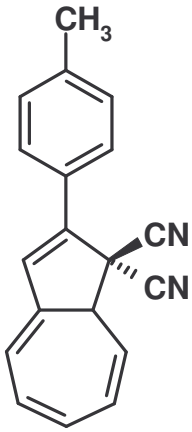

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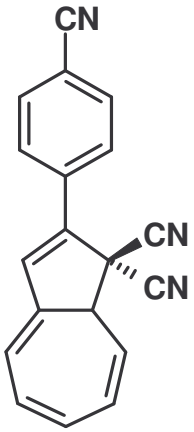
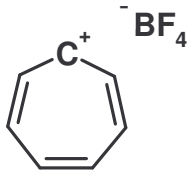
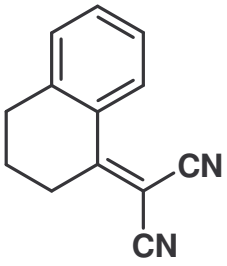


A4



A5



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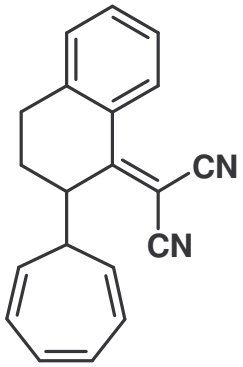

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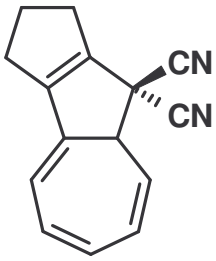
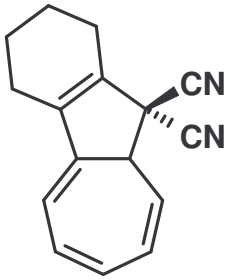
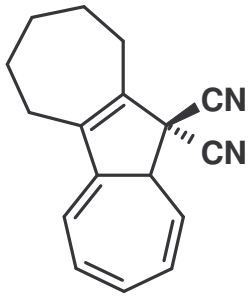


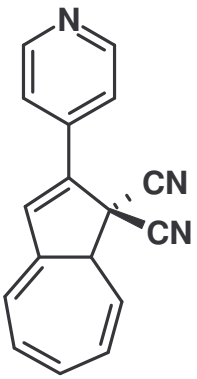
CP-DHA



CHex-DHA



CHept-DHA



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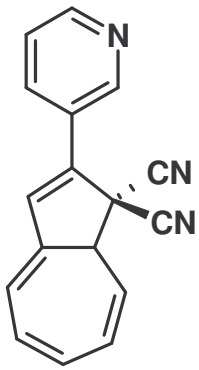
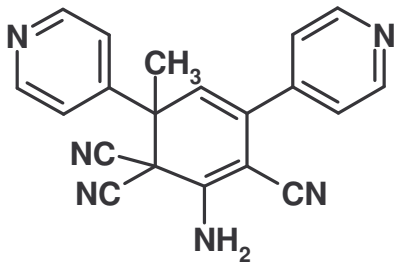


B2



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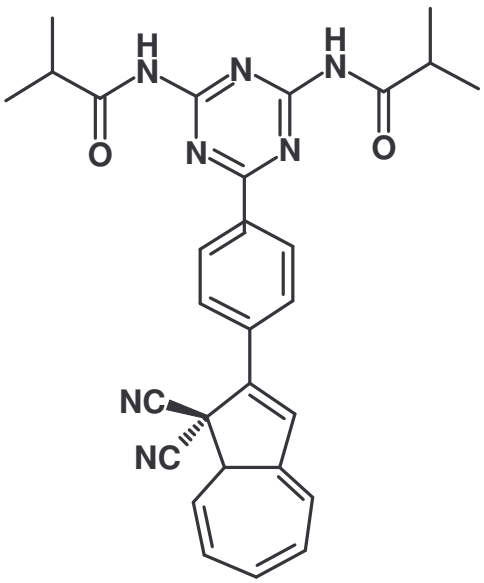

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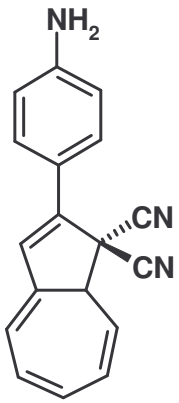

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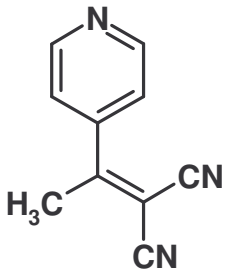

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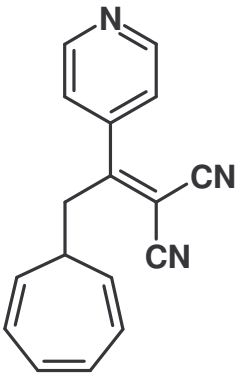

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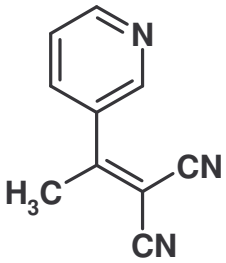

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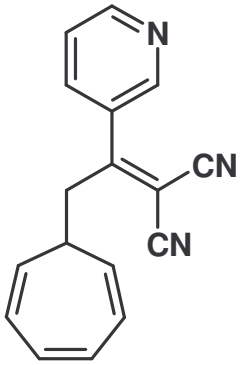

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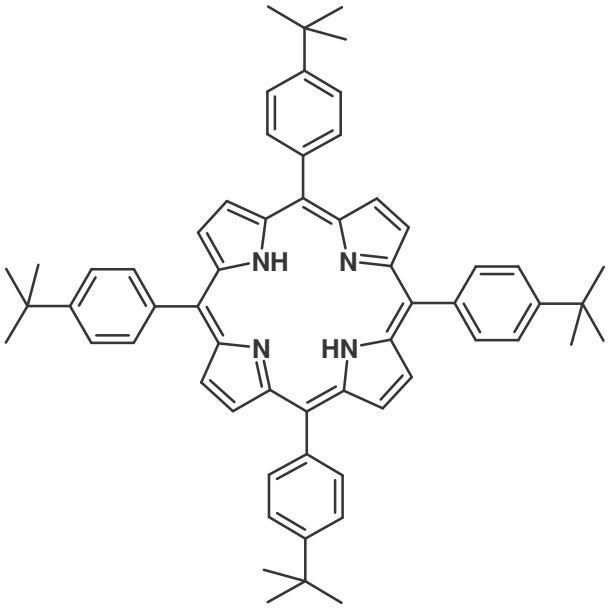

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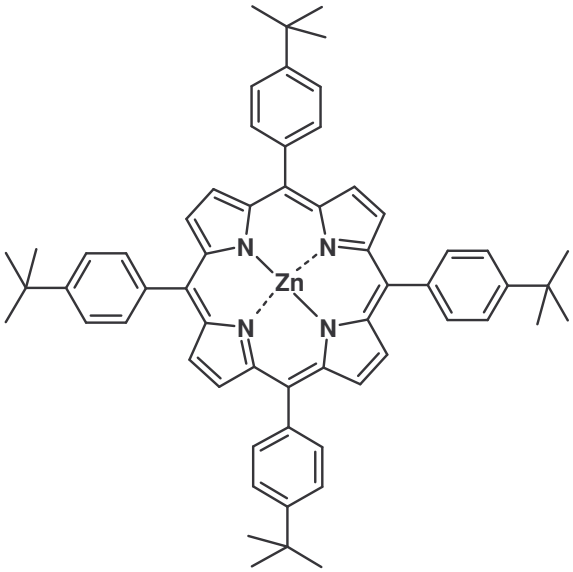

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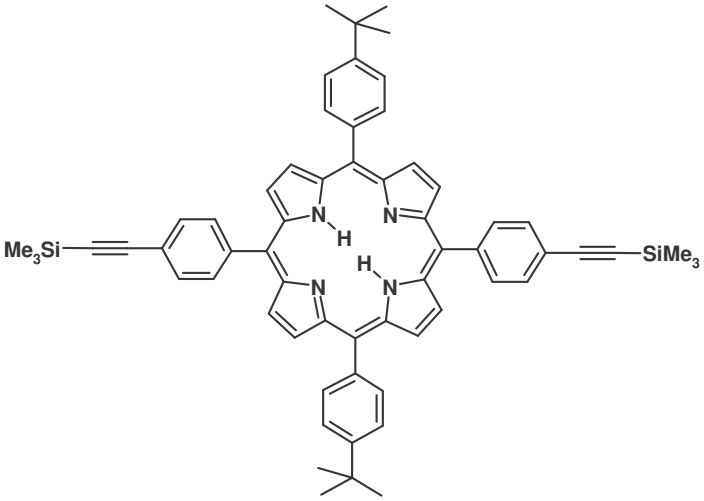

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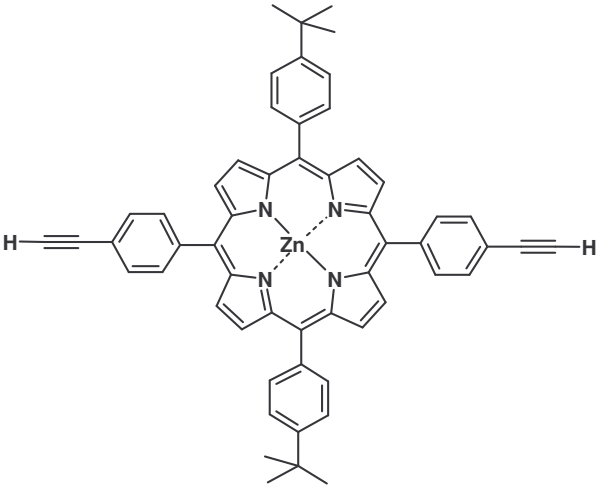

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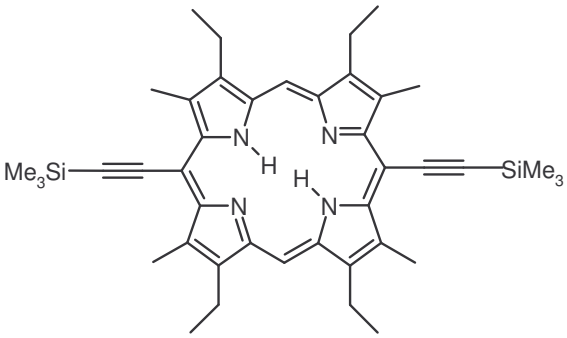

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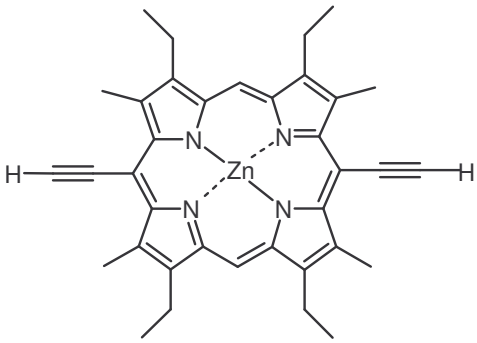

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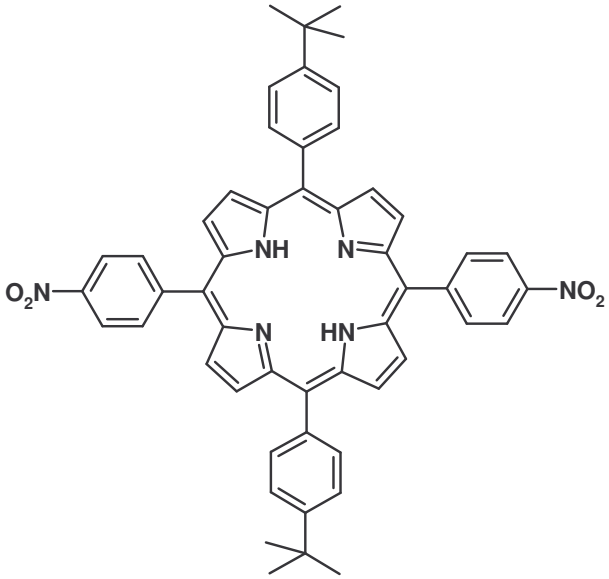

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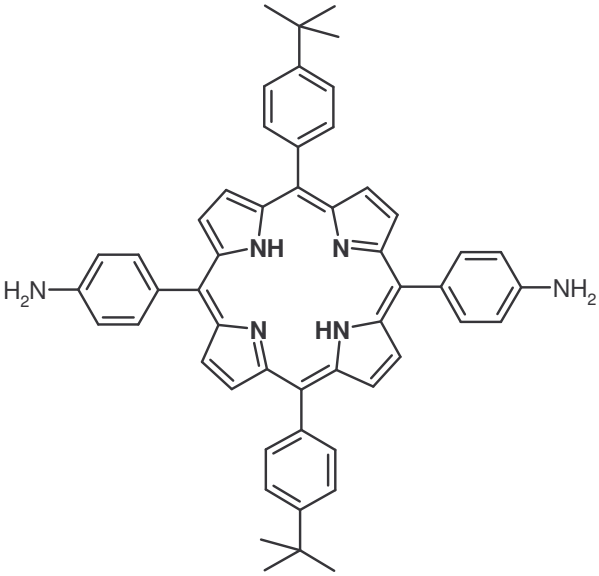

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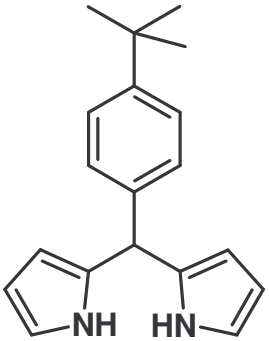

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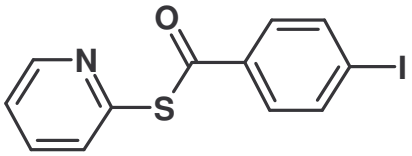

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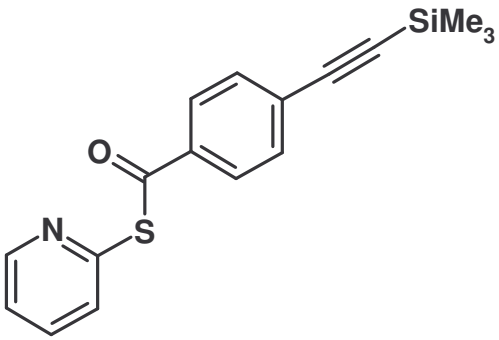

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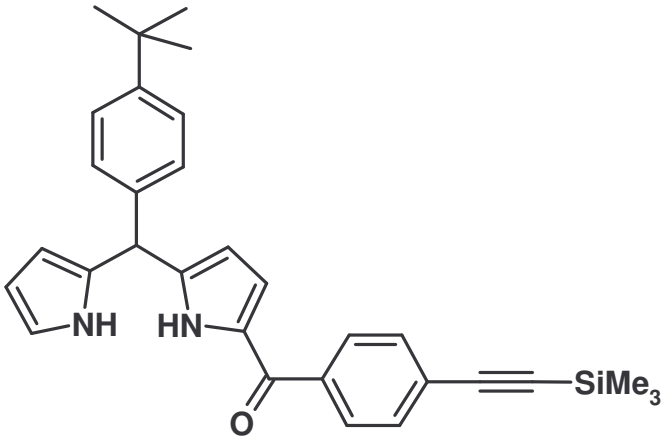
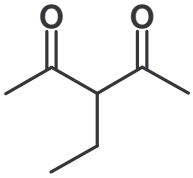


C3-4



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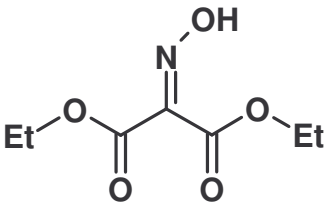

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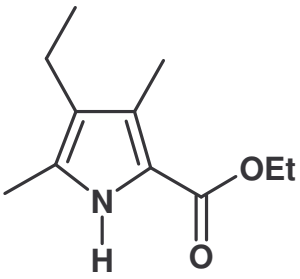

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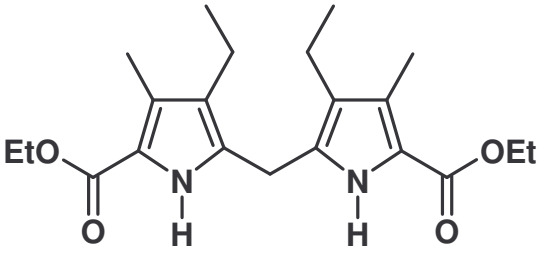

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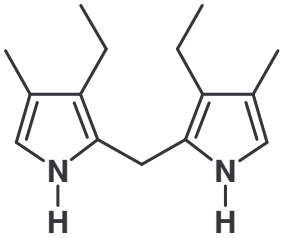

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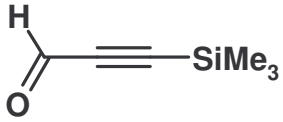

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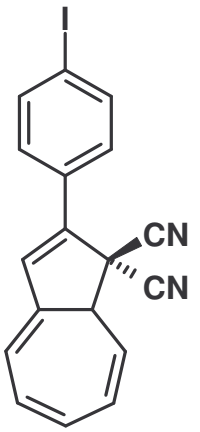

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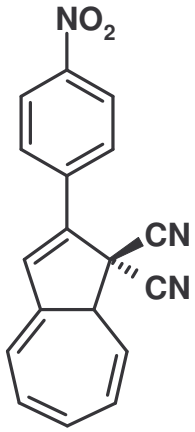
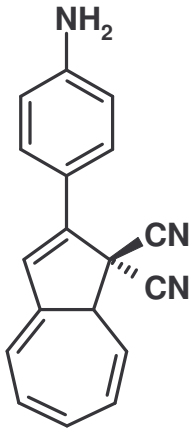


D2



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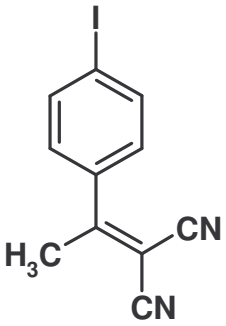

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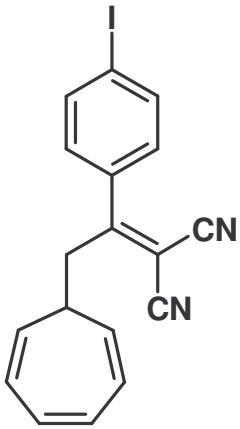
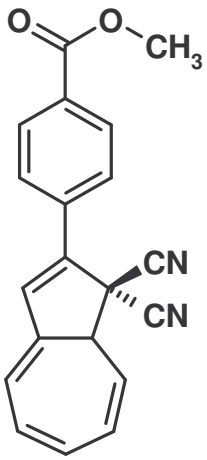


D1-2



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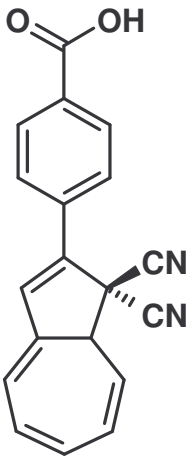

E2

Appendix

Publications

- *Mimicking the dye processes of sensory photoreceptors.* J. Daub, C. Trieflinger, O. Kushnir, R. Procházka, *Mol. Cryst. Liq. Cryst.* **2005**, 430, 115-122.

Conferences and Presentations

- Summer School of Graduate College: „ Sensory photoreceptors in natural and artificial systems“, University Regensburg, presentation, Nove Hrady, Czech Republic, 2002
- 53rd Annual Meeting of the International Society of Electrochemistry, poster presentation, Düsseldorf, 2002
- Summer School of Graduate College: „ Sensory photoreceptors in natural and artificial systems“, University Regensburg. Presentation: *„Multimode Switching Based on Porphyrin/dihydro-azulene System - Towards Artificial Sensory Photoreceptors“*, Frauenchiemsee, 2003
- 8th Conference on Methods and Applications of Fluorescence; poster presentation, Prague, Czech Republic, 2003
- Summer School of Graduate College: „ Sensory photoreceptors in natural and artificial systems“, University Regensburg, presentation, Regen, 2004
- 4th International Symposium on Photochromism, poster presentation, Arcachon, France, 2004.

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I would like to thank all the people who took a part in my work, gave help or support, and without whom the presented work would have been not possible in the present way; among them:

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