# A Synthetic Equivalent for [2.2]Paracyclophane-1,9-diyne: Octaphenyl-1:2,9:10-dibenzo[2.2]paracyclophane-1,9-diene and Its Reduction to the Hexaanion**
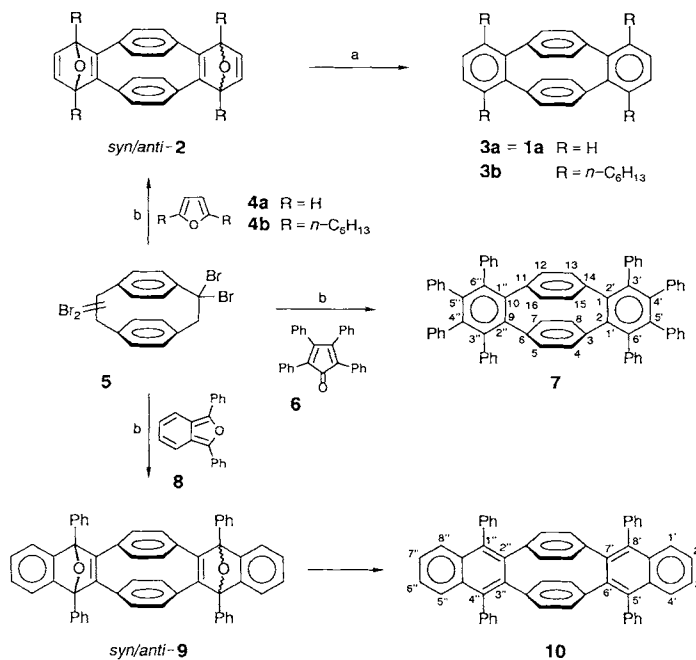
By *Armin de Meijere,* *Jürgen Heinze, Klaus Meerholz, Oliver Reiser,* and *Burkhard König*

Dedicated to Professor Marit Traetteberg on the occasion of her 60th birthday

The synthesis of unusual molecules that are not naturally occurring is not just a challenge, but often an opportunity to discover new properties and phenomena. 1:2,9:10-Dibenzo[2.2]paracyclophane-1,9-diene (1 a), first synthesized by Wong,[1] contains two biphenyl units that are nonconjugated in the classical sense because the phenyl rings are mutually orthogonal. Reduction of 1 a with alkali metals gives a radical anion, 1 a•⊖, whose unpaired electron resides in the phane benzene rings.[2] The tetraphenyl derivative 1 b, which we synthesized,[3] behaves differently; the first two additional electrons reside in the lateral *ortho*-terphenyl units.[4] Compound 1 c can be reversibly reduced to the tetraanion.[5] Thus, octaphenyl-1:2,9:10-dibenzo[2.2]paracyclophane-1,9-diene (7), described here, was expected to extend this trend still further.

1a R = H
1b R = C₆H₅
1c R = *p*-C₆H₄C(CH₃)₃
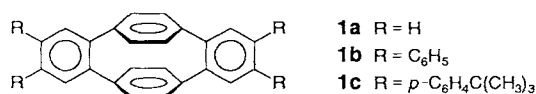
The synthesis of 1 a developed by Wong[1] starts with 9,9-dibromo-1:2-benzo[2.2]paracyclophan-1-ene, which is obtained in five steps from *o*-terphenyl in only poor yield (0.3 %). This route is therefore hardly suitable for a synthesis of 1 a in preparative quantities. However, we found that the concept of double dehydrobromination of a geminal dibromide can be applied to the isomeric mixture of 1,1,9,9- and 1,1,10,10-tetrabromo[2.2]paracyclophane (5), easily obtained in large amounts (90% yield) from commercially available [2.2]paracyclophane.[6] In this way, not only 1 a but also a series of interesting derivatives, such as 3 b, 7, and 10, are now readily available for the first time in large amounts. Treatment of 5 with potassium *tert*-butoxide in tetrahydrofuran (THF) results, via fourfold dehydrobromination, in the stepwise formation of a triple bond in each bridge of [2.2]paracyclophane. In the presence of furan (4 a), the highly strained alkynes are immediately trapped and afford the two diastereomeric bis-endoxides *syn/anti*-2 a (23 % yield) in a ratio of about 1:1 (Scheme 1). The bis-endoxides *syn/anti*-2 a[7] undergo facile deoxygenation upon treatment with low-valent titanium (TiCl₄/LiAlH₄) to give 3 a (= 1 a) (75%). Dibenzo[2.2]paracyclophanediene (1 a) can thus be prepared in three steps in gram amounts from [2.2]para-

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Scheme 1. a) TiCl₄/LiAlH₄, NEt₃, THF, room temperature 0.5 h; b) KO*t*Bu/THF, 22 °C, 4–5 h.

cyclophane. Use of 2,5-disubstituted furans 4 b[8] as trapping agents in this sequence leads, via the corresponding bis-endoxides 2 b,[7] to 3′,6′,3″,6″-tetrasubstituted dibenzo-[2.2]paracyclophanedienes such as 3 b.[7]

Analogously, reaction with 2,5-diphenylisobenzofuran (8) affords the dibenzo bis-endoxides *syn/anti*-9, which are deoxygenated by TiCl₄/LiAlH₄ to give dinaphtho[2.2]paracyclophane-1,9-diene (10).[7] Dropwise addition of a solution of potassium *tert*-butoxide in THF to a mixture of 5 and tetraphenylcyclopentadienone (tetracyclone, 6) furnishes octaphenyldibenzo[2.2]paracyclophanediene (7)[7] in a yield of 69%. The high efficiency with which the ring-strained alkyne generated here is trapped by tetracyclone (6), a diene with inverse electron demand, is also known for other highly strained cycloalkynes.[9]

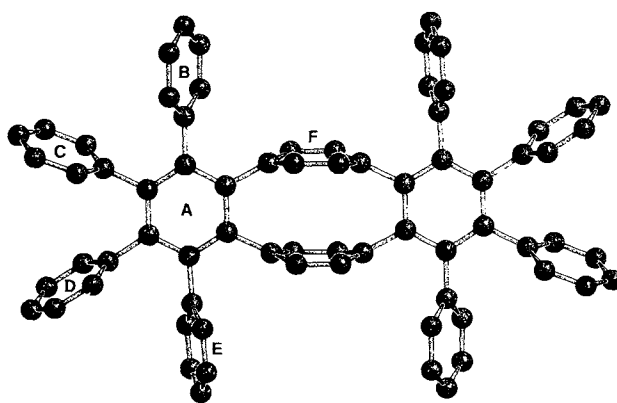Compound 7 has a centrosymmetric structure in the crystal (Fig. 1). The interplanar angles in each of the four

Fig. 1. Molecular structure of 7 (SCHAKAL drawing) [11]. Triclinic crystals of space group P1̄, Z = 1, unit cell a = 612.3(7), b = 1137(1), c = 1878(3) pm, α = 79.1(1), β = 86.79(9), γ = 81.4(1)°, ϱ_calcd = 1.12 g cm⁻³, 3959 evaluated reflections with 2θ ≤ 65°, Cu_Kα, R_w = 6.8%. C1-C2 142.7(5), C1-C14 150.2(5), C2-C3 149.8(5) pm; average CC bond length in ring A: 140.1(5), B: 137.6(6), C: 137.5(6), D: 136.1(8), E: 137.1(7), F: 139.1(5) pm; bond angles C14-C1-C2 117.0(1), C1-C2-C3 116.3(2)°; interplanar angles A/B: 63, A/C: 70, A/D: 78, A/E: 81°.

biphenyl units formed by the two lateral benzene rings and their four phenyl substituents increase sequentially from 63.2° to 81.4°, presumably owing to intermolecular effects in the crystal. The same phenomenon has also been observed for hexaphenylbenzene,[10] for which the average value of the interplanar angle (67.2°) is slightly, but significantly, smaller than that in **7** (average value 73.2°). The geometry of the central framework in **7** corresponds to that in the parent compound **1a**.[12]

Whereas **1a** can be reduced to a dianion in two steps and the tetraphenyl derivative **1c** can be reduced to a tetraanion in four steps,[5] the cyclovoltammogram of the octaphenyl derivative **7**[13] shows three reversible two-electron reduction waves at $E^0 = -2.61, -2.76$, and -3.13 V versus Ag/AgCl. Only a few examples of reversibly formed hexaanions have been reported so far.[14] As expected, the reduction potentials of **7** are all more positive than those of hexaphenylbenzene, which is reduced in three steps at $E^0 = -2.73, -3.10$, and -3.23 V to only a trianion. Even in **1c**, the potential differences between mono- and dianion formation and tri- and tetraanion formation (70 and 85 mV, respectively) are very small owing to the weak interaction between the two substituted, lateral benzene rings.[5] It is not surprising, therefore, that formal 2e processes with $\Delta E^0 < 50$ mV are observed for **7**, which has still larger conjugated systems. Also noteworthy is the formation of the hexaanion over an extremely small potential range ($\Delta E^0 = 0.52$ V). Compound **7** is thus an efficient storer of charge, since Coulomb repulsions between the six excess charges are minimized by the unusual structure.

[1] a) H. N. C. Wong, C. W. Chan, J. Am. Chem. Soc. 107 (1985) 4790; b) H.-N. C. Wong, C. W. Chan, ibid. 110 (1988) 463.

[2] F. Gerson, W. B. Martin Jr., H. N. C. Wong, C. W. Chan, Helv. Chim. Acta 70 (1987) 79.

[3] A. de Meijere, S. Reichow, O. Reiser, Angew. Chem. 98 (1987) 1285; Angew. Chem. Int. Ed. Engl. 26 (1987) 1277.

[4] F. Gerson, A. de Meijere, O. Reiser, B. König, T. Wellauer, J. Am. Chem. Soc. 112 (1990) 6827.

[5] A. de Meijere, J. Heinze, K. Meerholz, O. Reiser, B. König, unpublished results.

[6] M. Stöbbe, O. Reiser, R. Näder, A. de Meijere, Chem. Ber. 120 (1987) 1667.

[7] All new compounds were fully characterized by spectroscopic methods (IR, 1H NMR, 13C NMR, MS, UV) and elemental analysis. The assignment of 13C NMR data was aided by spectra recorded with the DEPT protocol; (+) and (−) designate tertiary/primary and secondary carbon atoms, respectively. Representative data for **2a**: 1H NMR (250 MHz; CDCl3): $\delta = 5.69$ (br. s, 4H, 3'(6',3'',6'')-H), 6.14 and 6.17 (each dd, 4H, $^3J = 8.0$ Hz, $^4J = 1.9$ Hz), 7.45 (br. s, 4H, 4'(5',4'',5'')-H). 13C NMR (63 MHz; CDCl3): $\delta = 85.26$ (+, C-3'(6',3'',6'')), 127.90 and 130.71 (+, phane -C6H4), 136.21 (C_quat), 145.04 (+; C-4'(5',4'',5'')), 160.51 (C_quat). MS (70 eV): m/z 336 ($M^\oplus$, 100%). **3b**: 1H NMR (250 MHz; CDCl3): $\delta = 0.85$ (t, 12H, CH2-CH3), 1.2–1.8 (m, 32H, -CH2-); 2.79 (t, 8H, aryl-CH2-), 6.65 (s, 8H, phane-C6H4), 7.28 (s, 4H, 4'(5',4'',5'')-H). 13C NMR (63 MHz, CDCl3): $\delta = 14.03$ (+, CH3), 22.61, 29.32, 31.63, 31.82 and 35.00 (-, -CH2-), 127.51 and 132.23 (+, arene-C), 136.44, 139.95 and 144.24 (C_quat; arene-C). MS (70 eV): m/z 640 ($M^\oplus$, 100%). **7**: 1H NMR: (400 MHz, CDCl3): $\delta = 6.62$ (s, 8H, phane-C6H4), 6.85, 6.94 and 7.10 (m, 24/8/8 H, phenyl-H). 13C NMR: (63 MHz, CDCl3): $\delta = 125.05, 125.52, 126.35, 126.73, 130.64, 131.12$ and 132.30 (+), 138.22, 139.46, 139.94, 140.37, 140.98 and 143.31 (C_quat). MS (70 eV): m/z 913 ($M^\oplus + 1$, 77%); 912 ($M^\oplus$, 10), 456 ($M^{2\oplus}$, 2). **10**: 1H NMR (250 MHz, CDCl3): $\delta = 6.42$ (s, 8H, phane-C6H4), 7.24–7.40 (br. m, 24H, phenyl-H and naphtho-H), 7.50 (m, 4H, naphtho-H). 13C NMR (63 MHz, CDCl3): $\delta = 126.06, 126.89$,

127.06, 127.98, 130.98, 130.69 and 132.77 (+), 131.93, 135.96, 139.34, 139.94 and 141.33 (C_quat). MS (70 eV): m/z 708 ($M^\oplus$, 100%), 354 ($M^{2\oplus}$, 6).

[8] Cf. a) V. Ramanathan, R. Levine, J. Org. Chem. 27 (1962) 1216; b) G. Büchi, H. Wuest, ibid. 31 (1966) 975.

[9] Vgl. a) H. Meier, T. Molz, U. Merkele, T. Echter, M. Lorch, Liebigs Ann. Chem. 1982, 914; b) A. Hohmann, A. Krebs, unpublished results; c) A. Hohmann, Dissertation, Universität Hamburg 1985.

[10] J. C. J. Bart, Acta Crystallogr. Sect. B 24 (1968) 1277.

[11] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaft-lich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-54703, the names of the authors, and the journal citation.

[12] H. N. C. Wong, C. W. Chan, T. C. W. Mak, Acta Crystallogr. Sect. C 42 (1986) 703.

[13] Recorded with a scan rate of between 10 and 100 mVs⁻¹ at −65 °C in dimethylamine/tetrahydrofuran 1:1, electrolyte 0.1 M tetrabutylammonium bromide.

[14] a) J. Heinze, Angew. Chem. 96 (1984) 823; Angew. Chem. Int. Ed. Engl. 23 (1984) 821; b) R. Cosmo, C. Kantz, K. Meerholz, J. Heinze, K. Müllen, Angew. Chem. 101 (1989) 638; Angew. Chem. Int. Ed. Engl. 28 (1989) 604.

[Cu₄(ddtp)₂Br₄], a Unique Tetranuclear Copper(I) Complex with Bridging Thioethers and Bridging Bromides **

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The ligand 1,5-bis(3',5'-dimethylpyrazolyl)-3-thiapentane (ddtp), which has three potential donor atoms, forms coordination compounds with a 1:1 stoichiometry, namely M(ddtp)X₂, with divalent first row transition metals and anions.[1] In contrast, when reacting CuBr₂ with ddtp in warm ethanol/acetone in air,[2] the solution decolorizes almost immediately. On cooling, colorless air-stable crystals of stoichiometry Cu₂(ddtp)Br₂ separate. Apparently a reduction to a Cu¹ species has occurred. Cu¹¹ compounds exhibit a d-d transition band in the VIS-NIR region and usually give rise to an EPR signal. Both phenomena were absent in the resulting ddtp copper bromide compound. The same compound was also prepared by reacting ddtp with CuBr in a nitrogen atmosphere,[3] as confirmed by a comparison of IR spectra and X-ray powder patterns.

ddtp
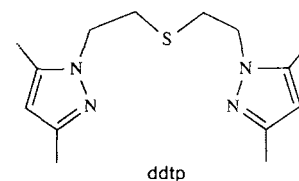
Single-crystal X-ray structure analysis[4] shows that each copper ion resides in a distorted tetrahedral environment provided by a nitrogen, a bridging thioether and two bridging bromides (see Fig. 1). Two copper ions are linked by two bromides forming a Cu₂Br₂ fragment. The Cu···Cu distance

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