Synthesis and Photoinduced cis–trans Isomerization of Diaryl Enediyne Chromophores

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The photochemical and thermal isomerization of diarylenes, such as stilbenes, is a well-known process that has been used to design photochromic materials and molecular switches. By the formal insertion of two acetylenic units into the olefin-arene bond, diarylenes are expanded to 1,6-diaryl 3-ene-1,5-diynes, a chromophore with altered properties. Only one example of this interesting class of compounds has hitherto been described. We report here a new and general synthetic route to cis-diaryl enediynes and the first investigations of their photophysical properties.

The palladium-catalyzed two-fold coupling of various iodoarenes (2a–g) with the parent enediyne 1 at room temperature gave the diaryl enediynes cis-3a–g in one step. The isolated yields are summarized in Table 1. In all cases complete retention of the cis-configuration of the enediyne was observed. However, the corresponding bromoarenes react sluggishly and do not give the desired products.

The UV spectra of all diaryl enediynes show the expected strong absorption bands between 300 and 400 nm and the compounds cis-3a–g isomerize rapidly to a cis–trans mixture when solutions are exposed to sunlight or irradiated with low intensity UV light at 366 nm. In the photostationary state, a nearly equal mixture of both isomers is present as a consequence of the similar absorption spectra of the cis- and trans-compounds. The isomers of 3a, 3c, and 3e were separated by column chromatography and irradiated individually, leading to the original equilibrium mixtures. Assignment of the stereochemistry was based on the respective 13C satellite proton NMR constants. If the irradiation is interrupted before the photostationary equilibrium is reached, the ratio of both isomers remains constant, even when the solutions are heated to 80 °C for several hours. The clean isomerization process was followed by 1H NMR for 3e and the obtained kinetic data agree with the equations for a reversible equilibrium.

The photoinduced isomerization at 366 nm depends on the interaction of the π-systems of the aromatic rings and the central double bond. Although 3g shows strong absorption bands up to 450 nm, it does not isomerize if irradiated with UV light of low intensity. A rapid deactivation process or the insufficient coplanarity of the π-systems, because of the steric demand of the 9-anthracene groups, might prohibit the photoisomerization process. Stilbenes and azobenzenes have already been used to construct photoswitchable supramolecular host guests.

However, diaryl enediynes cannot be switched photochemically because of the similar absorption spectra of their cis- and trans-isomers, but their rigid geometry and photochemical properties make them useful as molecular hinges that are unlocked by light. The application of diaryl enediynes as molecular control elements of conformational mobility will be the subject of further research.

X-ray Crystallographic Analysis. The structure of 3f2NaPF6·2CH3CN was determined by X-ray crystallography and confirms the nearly planar arrangement of the enediyne moiety and the aromatic rings, with torsion angles of 1.6° and 5.2°. The benzo-crown ethers and sodium ions are stacked in columns, while the alternating enediyne moieties form a central cavity as shown in Figure 1.

Table 1. Palladium-Catalyzed Coupling Reaction of Iodoarenes with cis-Hexa-1,5-diyne-3-ene (1) to Diaryl Enediynes

<table>
<thead>
<tr>
<th>Ar-I</th>
<th>Ar</th>
<th>product</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>Ph</td>
<td>3a</td>
<td>23</td>
</tr>
<tr>
<td>2b</td>
<td>4-N02-C6H4</td>
<td>3b</td>
<td>42</td>
</tr>
<tr>
<td>2c</td>
<td>4-MeO-C6H4</td>
<td>3c</td>
<td>38</td>
</tr>
<tr>
<td>2d</td>
<td>1-naphthalene</td>
<td>3d</td>
<td>68</td>
</tr>
<tr>
<td>2e</td>
<td>9-phenanthrene</td>
<td>3e</td>
<td>53</td>
</tr>
<tr>
<td>2f</td>
<td>4-benzo-18-crown-5</td>
<td>3f</td>
<td>65</td>
</tr>
<tr>
<td>2g</td>
<td>9-anthracene</td>
<td>3g</td>
<td>46</td>
</tr>
</tbody>
</table>

cis-1,6-Bis(p-methoxyphenyl)hexa-1,5-diyne-3-ene (3c):
eluent PE:EE (10:1), \( R_F = 0.46 \), 38%, white solid, mp 145 °C; ¹H-NMR \( \delta = 3.81 \) (s, 6 H), 6.03 (s, 2 H), 6.85 and 7.45 (AB-system, \( J = 8.9 \) Hz, 8 H); ¹³C-NMR \( \delta = 55.28 \) (+), 86.43 (C_qua), 97.51 (C_qua), 114.04 (+), 115.34 (C_qua), 118.71 (+), 133.16 (+), 159.87 (C_qua); IR (KBr) 2177, 1749 cm⁻¹; MS EI 288 (M⁻, 100). Anal. Calcd for C₃₆H₂₄O₃: C, 83.34; H, 5.73.

cis-1,6-Bis(1-naphthyl)hexa-1,5-diyne-3-ene (3d):
eluent PE:EE (20:1), \( R_F = 0.52 \), 68%, pale yellow solid, mp 142 °C; ¹H-NMR \( \delta = 6.40 \) (s, 2 H), 7.26 (m, 2 H), 7.48 (m, 4 H), 7.86 (m, 6 H), 8.59 (d, \( J = 8.9 \) Hz, 2 H); ¹³C-NMR \( \delta = 92.57 \) (C_qua), 96.02 (C_qua), 119.63 (+), 120.74 (C_qua), 125.25 (+), 125.52 (+), 127.07 (+), 128.24 (+), 129.32 (+), 131.58 (+), 133.16 (C_qua), 133.26 (C_qua); IR (KBr) 2171, 772 cm⁻¹; MS EI 328 (M⁺, 100). Anal. Calcd for C₂₆H₂₂: C, 83.34; H, 5.73.

Experimental Section

Melting points were taken on a hot-plate microscope apparatus and are not corrected. NMR spectra were recorded at 200 MHz (¹H) and 50 MHz (¹³C) in chloroform-d solutions unless otherwise stated. The multiplicity of the ¹H signals was determined with the DEPT technique and quoted as (+) for CH₂ or CH or (-) for CH₃ and (C_qua) for quarternary carbons. PE indicates petroleum ether of a boiling range 60-70 °C. EE indicates ethyl acetate. 2d and 2g were prepared from the corresponding bromides.1° 2f was prepared from benzo-18-crown-5 according to a literature procedure.15

General Procedure for the Coupling Reaction of cis-Hexa-1,5-diyne-3-ene (1) with Iodoarenes: A volume of 8.3 mL of a 0.12 M solution of 1 (1.0 mol) in pentane were added to a mixture of 2 mmol of the iodoarene, 3 mmol of n-butylamine, and 2.5 mL of acetonitrile. The reaction mixture was stirred at room temperature for 3 h, quenched with 2 mL of saturated NH₄Cl solution, diluted with 50 mL of dichloromethane, washed with water (2 x 30 mL), dried over MgSO₄, and evaporated in vacuo. The crude products were chromatographed on silica gel (230-400 mesh).

cis-1,6-Bis(p-nitrophenyl)hexa-1,5-diyne-3-ene (3b):
eluent PE:EE (5:1), \( R_F = 0.45 \), 42%, yellow solid, mp 150 °C dec; ¹H-NMR \( \delta = 6.16 \) (s, 2 H), 7.56 and 8.16 (AB-system, \( J = 9.0 \) Hz, 8 H); ¹³C-NMR \( \delta = 91.52 \) (C_qua), 96.07 (C_qua), 120.54 (+), 128.82 (+), 129.55 (C_qua), 132.58 (+), 147.44 (C_qua); IR (KBr) 2179, 2197, 1341 cm⁻¹; MS EI 318 (M⁺, 100). Anal. Calcd for C₂₄H₁₈N₂O₂: C, 76.93; H, 3.37; N, 8.80. Found: C, 76.19; H, 3.17; N, 8.74.

Notes