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Synthesis and Photoinduced *cis−trans* Isomerization of Diaryl Enediyne Chromophores

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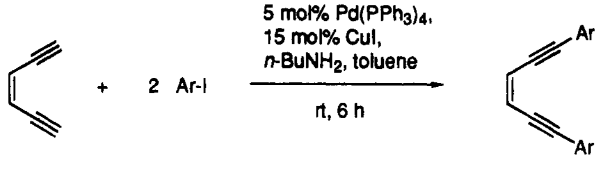
The photochemical and thermal isomerization of diarylethenes, such as stilbenes, is a well-known process that has been used to design photochromic materials[1] and molecular switches.[2] By the formal insertion of two acetylenic units into the olefin-arene bond, diarylethenes are expanded to 1,6-diaryl 3-ene-1,5-diynes, a chromophore with altered properties. Only one example of this interesting class of compounds has hitherto been described.[3] 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[4] of various iodoarenes (**2a−g**) with the parent enediyne **1**[5] 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.[6] 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 individualy, leading to the original equilibrium mixtures. Assignment of the stereochemistry was based on the respective $^3J_{cis}$ (**3c**: 10.7 Hz) and $^3J_{trans}$ (**3c**: 15.9 Hz) coupling constants obtained from the ^{13}C satellite proton NMR spectra. 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 ^{1}H NMR for **3e** and the obtained kinetic data agree with the equations for a reversible equlibrium.[7]

Scheme 1

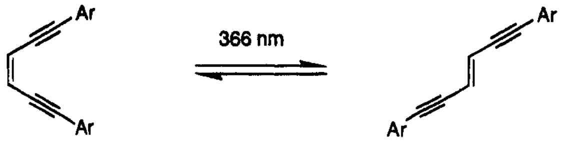


1 2 3

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

Ar−I	Ar	product	yield (%)
2a	Ph	**3a**[3]	23
2b	4-NO_2-$C_6H_4^-$	**3b**	42
2c	4-MeO-$C_6H_4^-$	**3c**	38
2d	1-naphthalene	**3d**	68
2e	9-phenanthrene	**3e**	53
2f	4-benzo-18-crown-5	**3f**	65
2g	9-anthracene	**3g**	46

Scheme 2



cis-**3** *trans*-**3**

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[8] 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 guest systems.[2] 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.[9] The structure of **3f**·$2NaPF_6$·$2CH_3CN$ 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.

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(1) Satil, J.; Sun, Y.-P.; Rau, H. In *Photochromism;* Dürr, H., Boas-Laurent, H., Eds.; Elsevier: New York, 1990; p 64.

(2) Vögtle, F. *Supramolecular Chemistry;* J. Wiley & Sons: New York, 1991; pp 206−229.

(3) Vollhardt, K. P. C.; Winn, L. S. *Tetrahedron Lett.* **1985**, *26*, 709−712.

(4) (a) Hagihara, N; Takahashi, S.; Kuroyama, Y.; Sonogashira, K. *Synthesis* **1980**, 627−630. (b) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138−2152.

(5) (a) Rato, G.; Linstrumelle, G. *Tetrahedron Lett.* **1981**, *22*, 315−318. (b) Linstrumelle, G.; Guillerm, D. *Tetrahedron Lett.* **1985**, *26*, 3811−3812. (c) Alami, M.; Crousse, B.; Linstrumelle, G. *Tetrahedron Lett.* **1994**, *35*, 3543−3544.

(6) For a recent example of an acid-catalyzed *cis−trans* isomerization of enediynes see: Anthony, J.; Knobler, C. B.; Diederich, F. *Angew. Chem.* **1993**, *105*, 437−440. *Angew. Chem Int. Ed. Engl.* **1993**, *32*, 406−409.

(7) Connors, K. A. *Chemical Kinetics*; VCH: Weinheim, 1990; p 60.

(8) Photoproducts from anthracene dimerization could not be detected. The formation of an eximer could be excluded due to the absence of the eximer fluorescence band in the fluorescence spectra of **3g**. However, the excited molecule might be rapidly deactivated *via* torsional vibrations.

(9) The authors have deposited atomic coordinates for **3f**·$2NaPF_6$·$2CH_3CN$ with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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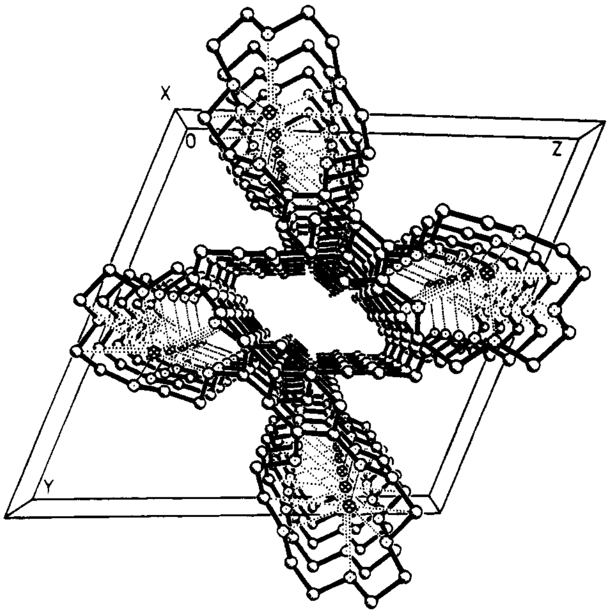

Figure 1. Packing diagram for 3f·2NaPF$_6$·2CH$_3$CN.

Crystal data: $C_{38}H_{46}F_{12}N_2Na_2O_{10}P_2$, triclinic, space group $P\bar{1}$, a = 930.7(3), b = 1645.4(4), c = 1658.0(3) pm, α = 111.12(2), β = 102.63(2), γ = 90.97(2)°, V = 2.2983(1) nm^3, Z = 2, μ = 0.218 mm^{-1}, T = 143 K, D_x = 1.484 mg/m^3, $F(000)$ = 1056. A total of 8102 intensities (8090 unique) were measured to 2θ 50° with Mo K$_\alpha$ radiation. The final $wR(F^2)$ for all reflections was 0.1995, with a conventional $R(F)$ of 0.042, for 595 parameters. Diffractometer: Stoe STADI-4. Refinement program: SHELXL-93 (G. M. Sheldrick, Univ. of Göttingen).

Experimental Section

Melting points were taken on a hot-plate microscope apparatus and are not corrected. NMR spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}C) in chloroform-*d* solutions unless otherwise stated. The multiplicity of the ^{13}C signals was determined with the DEPT technique and quoted as: (+) for CH$_3$ or CH, (−) for CH$_2$ and (C$_{quart.}$) 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.[10] **2f** was prepared from benzo-18-crown-5 according to a literature procedure.[11]

General Procedure for the Coupling Reaction of *cis*-Hexa-1,5-diyn-3-ene (1) with Iodoarenes. A volume of 8.3 mL of a 0.12 M solution of **1** (1.0 mmol) in pentane were added to a mixture of 2 mmol of the iodoarene, 3 mmol of *n*-butylamine, 58 mg (5 mol %) of Pd(PPh$_3$)$_4$, and 29 mg (15 mol %) of CuI in 20 mL of dry toluene. The reaction mixture was stirred at room temperature for 6 h, quenched with 2 mL of saturated NH$_4$Cl solution, diluted with 50 mL of dichloromethane, washed with water (2 × 30 mL), dried over MgSO$_4$, and evaporated *in vacuo*. The crude products were chromatographed on silica gel (230−400 mesh).

***cis*-1,6-Bis(*p*-nitrophenyl)hexa-1,5-diyn-3-ene (3b):** eluent PE:EE (5:1), R_f = 0.45, 42%, yellow solid, mp 160 °C dec; ^{1}H-NMR δ 6.16 (s, 2 H), 7.56 and 8.16 (AB-system ^3J = 9.0 Hz, 8 H); ^{13}C-NMR: δ 91.52 (C$_{quart.}$), 96.07 (C$_{quart.}$), 120.54 (+), 123.82 (+), 129.55 (C$_{quart.}$), 132.39 (+), 147.44 (C$_{quart.}$); IR (KBr) 2179, 2197, 1341 cm^{-1}; MS EI 318 (M$^+$, 100). Anal. Calcd for $C_{18}H_{10}N_2O_4$: C, 67.93; H, 3.17; N, 8.80. Found: C, 68.19; H, 3.17; N, 8.74.

***cis*-1,6-Bis(*p*-methoxyphenyl)hexa-1,5-diyn-3-ene (3c):** eluent PE:EE (10:1), R_f = 0.46, 38%, white solid, mp 145 °C dec; ^{1}H-NMR δ 3.81 (s, 6 H), 6.03 (s, 2 H), 6.85 and 7.45 (AB-system, ^3J = 8.9 Hz, 8 H); ^{13}C-NMR δ 55.28 (+), 86.43 (C$_{quart.}$), 97.51 (C$_{quart.}$), 114.04 (+), 115.34 (C$_{quart.}$), 118.71 (+), 133.16 (+), 159.87 (C$_{quart.}$); IR (KBr) 2177, 2192 cm^{-1}; MS EI 288 (M$^+$, 100). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.00; H, 5.73.

***cis*-1,6-Bis(1-naphthalenyl)hexa-1,5-diyn-3-ene (3d):** eluent PE:EE (20:1), R_f = 0.62, 68%, pale yellow solid, mp 142 °C; ^{1}H-NMR δ 6.40 (s, 2 H), 7.26 (m, 2 H), 7.48 (m, 4 H), 7.86 (m, 6 H), 8.59 (d, ^3J = 8.9 Hz, 2 H); ^{13}C-NMR δ 92.57 (C$_{quart.}$), 96.02 (C$_{quart.}$), 119.63 (+), 120.74 (C$_{quart.}$), 125.25 (+), 126.52 (+), 127.07 (+), 128.24 (+), 129.32 (+), 131.09 (+), 133.16 (C$_{quart.}$), 133.26 (C$_{quart.}$); IR (KBr) 2171, 772 cm^{-1}; MS EI 328 (M$^+$, 100). Anal. Calcd for $C_{26}H_{16}$: C, 95.04; H, 4.91. Found: C, 95.17; H, 4.96.

***cis*-1,6-Bis(9-phenanthrenyl)hexa-1,5-diyn-3-ene (3e):** eluent PE:EE (5:1), R_f = 0.54, 53%, pale yellow solid, mp 140 °C dec; ^{1}H-NMR δ 6.38 (s, 2 H), 7.34 (m, 2 H), 7.70 (m, 8 H), 8.10 (s, 2 H), 8.66 (m, 6 H); ^{13}C-NMR δ 92.14 (C$_{quart.}$), 96.70 (C$_{quart.}$), 119.71 (+), 122.64 (+), 126.95 (+), 127.09 (+), 127.18 (+), 127.29 (+), 127.67 (+), 128.67 (+), 130.01 (C$_{quart.}$), 130.59 (C$_{quart.}$), 131.14 (C$_{quart.}$), 132.67 (+); IR (KBr) 2174 cm^{-1}; MS EI 428 (M$^+$, 1); 177 (100). Anal. Calcd for $C_{34}H_{20}$: C, 95.30; H, 4.70. Found: C, 95.28; H, 4.67.

***cis*-1,6-Bis(4′-benzo-18-crown-5)hexa-1,5-diyn-3-ene (3f):** eluent CH$_2$Cl$_2$:methanol (10:1), R_f = 0.45, 65%, slow solidifying clear oil; ^{1}H-NMR δ 3.73−4.13 (m, 32 H), 6.02 (s, 2 H), 6.77 (d, ^3J = 8.3 Hz, 2 H), 6.92 (s, 2 H), 7.07 (d, ^3J = 8.3 Hz), 2 H); ^{13}C-NMR δ 68.30 (−), 68.89 (−), 69.96 (−), 70.65 (−), 86.65 (C$_{quart.}$), 97.78 (C$_{quart.}$), 112.92 (+), 115.69 (C$_{quart.}$), 116.78 (+), 119.24 (+), 125.28 (+), 148.26 (C$_{quart.}$), 149.56 (C$_{quart.}$); IR (KBr) 2177 cm^{-1}; MS EI 608 (m$^+$, 100).

***cis*-1,6-Bis(4′-benzo-18-crown-5)hexa-1,5-diyn-3-ene Bis(sodium hexafluorophosphate) (3f·2NaPF$_6$).** A mixture of 50 mg (0.082 mmol) of **3f** and 34 mg (0.2 mmol) of NaPF$_6$ in 10 mL of acetonitrile was stirred for 6 h at rt under nitrogen. The solvent was removed *in vacuo*, the solid residue extracted with dichloromethane, and the filtrate evaporated to yield 70 mg (90%) **3f**·2NaPF$_6$, as a white solid, mp 117 °C. Crystals were obtained by slow diffusion of diethyl ether into an acetonitrile solution of **3f**·2NaPF$_6$: ^{1}H-NMR (DMSO-d_6) δ 3.60−4.09 (m, 32 H), 6.24 (s, 2 H), 6.98 (d, ^3J = 8.3 Hz, 2 H), 7.03 (d, ^4J = 1.9 Hz, 2 H), 7.08 (dd, ^3J = 8.3 Hz, ^4J = 1.9 Hz, 2 H); ^{13}C-NMR (DMSO-d_6) δ 68.22 (+), 68.31 (+), 68.55 (+), 69.52 (+), 69.56 (+), 70.36 (+), 86.66 (C$_{quart.}$), 97.78 (C$_{quart.}$), 113.46 (−), 114.40 (C$_{quart.}$), 116.02 (−), 119.42 (−), 124.99 (−), 148.26 (C$_{quart.}$), 149.61 (C$_{quart.}$); IR (KBr) 2928, 2194, 1512, 843 cm^{-1}; MS FAB 799 (M$^+$ − PF$_6$, 38); 631 (M$^+$ − NaPF$_6$, 40), 154 (100). Anal. Calcd for $C_{38}H_{46}N_2Na_2O_{10}P_2F_{12}$: C, 44.45; H, 4.52; N, 2.73. Found: C, 44.73; H, 4.65; N, 2.40.

***cis*-1,6-Bis(9-anthracenyl)hexa-1,5-diyn-3-ene (3g):** eluent PE:EE:triethylamine (10:1:0.2), R_f = 0.47, 46%, orange red solid, mp 175 °C dec; ^{1}H-NMR δ 6.41 (s, 2 H), 6.90 (m, 4 H), 7.18 (m, 4 H), 7.80 (m$_d$, 4 H), 8.26 (s, 2 H), 8.49 (m$_d$, 4 H); ^{13}C-NMR: δ 94.92 (C$_{quart.}$), 98.94 (C$_{quart.}$), 116.97 (C$_{quart.}$), 119.57 (+), 125.70 (+), 126.71 (+), 127.08 (+), 128.30 (+), 128.47 (+), 131.08 (C$_{quart.}$), 132.82 (C$_{quart.}$); IR (KBr) 2167, 2184 cm^{-1}; MS EI 428 (M$^+$, 0.5), 304 (100). Anal. Calcd for $C_{34}H_{20}$: C, 95.30; H, 4.70. Found: C, 94.80; H, 4.69.

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Supplementary Material Available: UV/vis absorptions of **3b−g**, ORTEP drawing of **3f**·(NaPF$_6$)$_2$·2CH$_3$CN, ^{1}H NMR spectra of *cis*-**3e** and a -ln[c − c^e/c^o − c^e] vs time graph of *cis*-**3e** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[10] (a) Suzuki, H.; Kondo, A.; Inouye, M. *Synthesis* **1986**, 121−122. (b) Suzuki, H.; Padmanabhan, S.; Inouye, M.; Ogawa, T. *Synthesis* **1989**, 468−471.

[11] Hyde, E. M.; Shaw, B. L.; Shepherd, I. *J. Chem. Soc., Dalton Trans.* **1978**, 1697−1705.