Tetrahedron Letters, Vol. 34, No. 37, pp. 5889-5892, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Orthogonal Connection of Acenes via Two-Fold Diels-Alder Reactions

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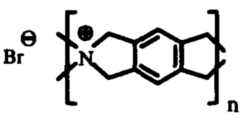
Abstract: Novel bis-acenes are described whose acene subunits are held in an almost orthogonal geometry by silicon-spiro centers. The synthesis involves Diels-Alder active bis-dienes with orthogonal five-membered rings.

Intramolecular energy and electron transfer mechanisms depend sensitively on the geometry of the unsaturated subunits.[1] An electronic "decoupling" of the electroactive centers can be achieved when they are placed in an orthogonal arrangement. This situation prevails in bi- and polyaryls[2] with strong steric inhibition of resonance, which may even exhibit high-spin character in the case of the charged derivatives, or in compounds such as spiroionenes 1[3] containing rigid connection of the subunits by spirocenters.



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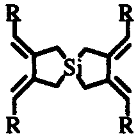
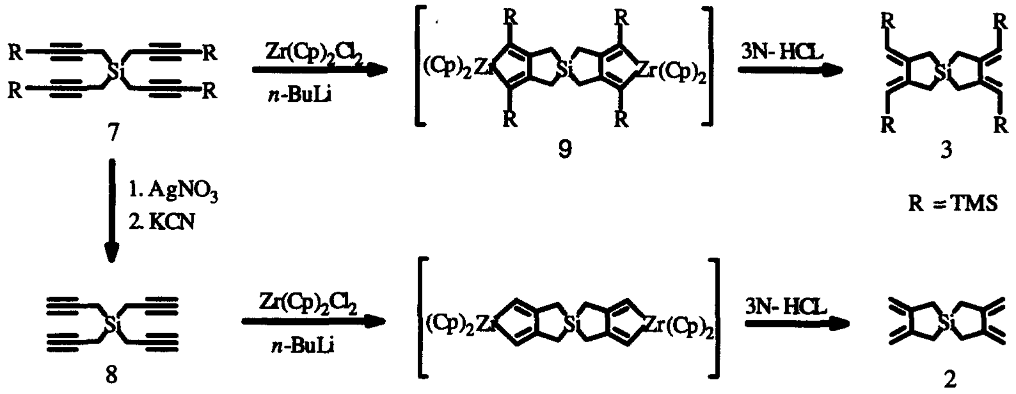


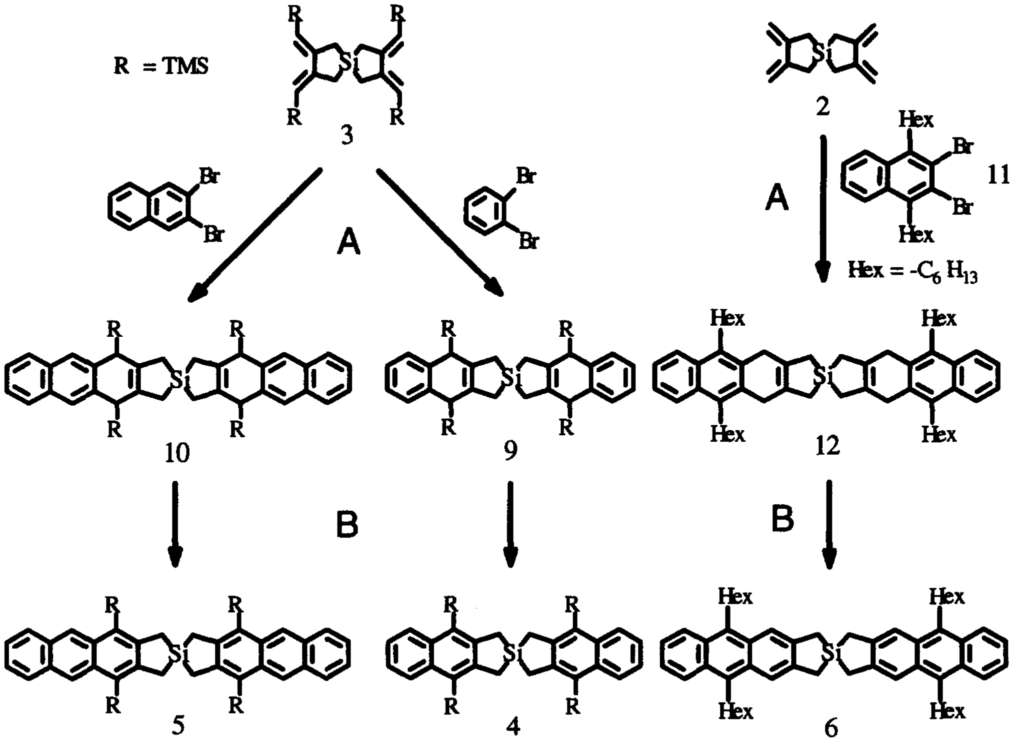
R = TMS 3
R = H 2

The concept proposed herein achieves an almost orthogonal arrangement of acenes such as naphthalene and anthracene via two-fold Diels-Alder reaction. The two novel tetraenes 2 and 3 serve as bis-diene functions for the cycloaddition, and the geometry is controlled by the silicon-spiro center common to the two five-membered rings. In order to achieve information on the electronic interaction of the π-units[4], the resulting bis-acenes 4, 5 and 6 were submitted to chemical and electrochemical reduction under cyclovoltammetric and EPR-spectroscopic control.

The tetraalkyne 7 is known to form the bis-zirconium complex 9[5] (Scheme 1). Using 9 as starting material, the new tetraene 3 can be obtained by acid hydrolysis with 3N-HCl. Furthermore, the TMS groups of 7 can be cleaved with $AgNO_3$ and KCN producing the new tetraalkyne 8 in 45% yield, without affecting the silicon-spiro center. The cyclization step, which proves successful in the synthesis of 3, has so far failed with unsubstituted tetraalkynes such as 8[5] (Table 2). Surprisingly enough, however, 8 reacts with zirconocene dichloride and *n*-butyllithium in THF at -78 °C to afford tetraene 2 (10%). Compounds 2 and 3 can then be used in a series of Diels-Alder cycloadditions with arynes (Scheme 1). They appear as appropiate dienophiles not only due to their high reactivity, but also due to the facile one-step aromatization under formation of 4, 5 and 6 (Table 2).



Scheme 1:



A = *n*-BuLi, toluene, -20°C B = chloranil, benzene, 90°C

Scheme 2:

The Diels-Alder reaction of tetraene **3** with two equivalents of benzyne, generated from 1,2-dibromobenzene and *n*-butyllithium, provides compound **9** in 45% yield. **9** can, in turn, be aromatized with chloranil in refluxing benzene to produce the bis-naphthalene species **4** (92%) (Scheme 2). The spiro-bridged bis-anthracene **5** is obtained in a similar fashion. The dienophile, in this case liberated from 2,3-dibromonaphthalene,[6] is treated with **3** to form **10** (38%), which is dehydrogenated to **5** in 50% yield (Scheme 2). On exposure to light and air , the TMS substituted bis-anthracene **5** in solution is transformed within seconds into the corresponding 9,10-bis-endoperoxide. Therefore, in order to stabilize the molecule, we thought to introduce two *n*-hexyl side-chains in the 9,10-positions of the anthracene units. For this purpose 2,3-dibromo-1,4-di-*n*-hexylnaphthalene (**11**) was synthesized[7] and reacted with the unsubstituted tetraene **2** affording **12** in a 40% yield. The following aromatization of **12** results in the formation of bis-anthracene **6** in 91% yield, owing its enhanced stability (as compared to **5**) to the hexyl substituents at the anthracene system. The stability of **6** allows easy handling and spectroscopic examination. Upon crystallization from ethanol, single crystals of **4** can be obtained. The crystal structure of **4** is shown in figure 1.[8] The two planes formed by the silicon-spiro center and the methylene groups are almost orthogonal to each other at an angle of 98°. On the other hand, the crystal of **4** exhibits an envelope conformation of the sila-cyclopentene units, which results in a deviation from orthogonality of the two naphthalenes of 46°. In solution, however, the methylene protons are isochronic so that, within the time-scale of the nmr experiment, orthogonality of the naphthalene units can be assumed.

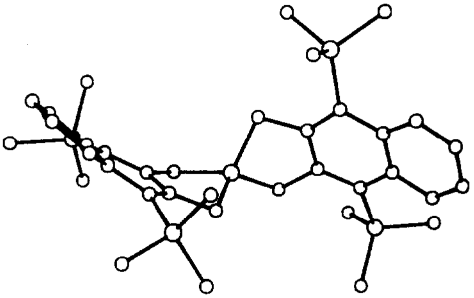


Figure 1 : Compound **4**.

Cyclovoltammetric investigations of **6** reveal that both anthracene units are electronically independent. This is concluded from the following potentials for reduction and oxidation steps: $E^{1}1/2 = -2.30$ V, $E^{2}1/2 = -2.41$ V and $E^{1,2}1/2 = 0.82$ V[9], since these potentials are in good agreement with the values determined for a single anthracene electrophor.[10]

The radical anions of **4**, **5** and **6**, generated in THF solution with potassium at 10^{-4} mbar, can be characterized by means of EPR and ENDOR spectroscopy (Table 1). The proton hyperfine couplings determined from the ENDOR spectrum of $\mathbf{4}^{\cdot-}$/ K^{+} are significantly diminished as compared to those of a single naphthalene unit. Indeed, in order to obtain a satisfactory simulation of the EPR spectrum of $\mathbf{4}^{\cdot-}$ it is necessary to consider the protons of *both* naphthalene units. We conclude from this that, within the time-scale of the experiment, the spin density is delocalized over the *whole* molecule. Further reduction of **4** leads to a dianion for which ESR measurements exclude a high-spin state.

Table 1: Coupling constants a_H in *mT* and number of protons *n* in the radical anions of **4** and **6** (ENDOR- and EPR-measurements at 220 K, solvent: THF)

4:

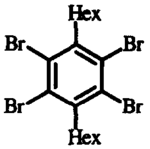
H-position	2.3	5.8	6.7	TMS
a_H [mT]	0.143	0.273	0.117	0.0116
n	8	4	4	36

6:

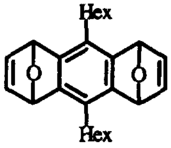
H-position	1.4	5.8	6.7 and 2.3	n-hexyl
a_H [mT]	0.309	0.239	0.143	0.219 / 0.024
n	2	2	6	8

A completely different result is obtained for the monoradical anions of **5** and **6** (Table 1). The spin density is localized on one single anthracene unit, and an electron-hopping process is not detectable within the EPR time-scale. In contrast to **5**, compound **6** forms a dianion with a high-spin state. From the zero-field splitting (D = 3.0 mT) we estimate the average distance between the unpaired electrons as 9.5 Å, which corresponds nicely to the distance between the central rings of the two anthracene units.

A synthesis involving the tetraenes **2** and **3** as bifunctional monomers (AA-type) together with bis-dienophiles (BB-type) should lead to polymers in which π-systems are connected orthogonally as well as being equidistantly separated. Repetitive Diels-Alder reactions with arynes such derived from **13** and bis-epoxyanthracenes such as **14** have already been carried out by us.[11] Polymerization reactions involving **2** and **3** will be published elsewhere.



13



14

Table 2:

Analytical data for **2, 3, 4, 5, 6** und **8** (nmr spectra recorded in $CDCl_3$ at 200 MHz (^1H), 50 MHz (^{13}C) and 30°C):
2 : MS (EI 70eV): m/z 188.1 (M^+) ; ^1H-NMR : d = 5.25, (s, 4 H); 4.80, (s, 4 H); 1.82, (s, 8 H); ^{13}C-NMR : C-quart.: 149.8, C-sec.: 109.1, 21.0.
3 : MS (EI 70eV): m/z 476.6 (M^+) ; ^1H-NMR : d = 0.15 (s, 36 H); 1.82, (s, 8 H); 5.95, (s, 4 H); ^{13}C-NMR : C-quart.: 160.0; C-tert.: 123.0; C-sec.: 20.0; C-prim.: 0.1.
4 : MS (EI 70eV): m/z 624.1 (M^+) ; ^1H-NMR : d = 8.4 und 8.2, (AA' BB', 8 H); 2.55, (s, 8 H); 0.58, (s, 36 H); ^{13}C-NMR : C-quart.: 147.3, 138.1, 137.0; C-tert.: 129.2, 124.1; C-sec.: 22.2; C-prim.: 4.2.
5 : MS (EI 70eV): m/z 724.4 (M^+) ; ^1H-NMR : d = 8.7, (s, 4 H); 7.95 und 7.4, (AA' BB', 8 H); 2.55, (s, 8 H); 0.6, (s, 36 H); ^{13}C-NMR : C-quart.: 147.8, 137.5, 135.6, 130.5; C-tert.: 128.4, 127.2, 125.5; C-sec.: 22.2; C-prim.: 4.1.
6 : MS (EI 70eV): m/z 772.3 (M^+) ; ^1H-NMR : d = 8.3 und 7.45, (AA' BB', 4 H); 8.2, (s, 4 H); 3.6, (t, 8 H); 2.65, (s, 8 H); 0.95, (t, 12 H); ^{13}C-NMR : C-quart.: 140.0, 133.2, 129.5, 129.4; C-tert.: 125.6, 124.8, 124.2; C-sec.: 32.3, 31.9, 30.6, 28.7, 23.2, 19.9; C-prim.: 14.6.
8 : MS (EI 70eV): m/z 182.9 (M^+) ; ^1H-NMR : δ = 1.97, (s, 12 H); (both protons are isochronic); ^{13}C-NMR : C-quart.: 80.0; C-tert.: 69.0; C-sec.: 0.15.

References and notes:

1. M. Baumgarten, W. Huber, K. Müllen, *Adv. in Phys. Org.Chem.* **1993**, 28, 1.
2. M. Baumgarten, U. Müller, A. Bohnen, K. Müllen, *Angew. Chem.* Int. Ed. Engl. **1992**, 31, 448.
3. K. Müllen, J. Lex, R. C. Schulz, F. Walter, *Polymer Bull.* **1990**, 24, 2132.
4. R. Hoffmann, A. Imamura, W. J. Hehre, *J. Am. Chem. Soc.* **1968**, 90, 1499; R. Gleiter, *Angew. Chem.* Int. Ed. Engl. **1974**, 13, 696; H. E. Simmons, T. Fukunaga, *J. Am. Chem. Soc.* **1967**, 89, 5208; R. Hoffmann, A. Imamura, G. D. Zeiss, *ibid.* **1967**, 89, 5215.
5. J.M. Tour, R. Wu, J.S. Schumm, *J. Am. Chem. Soc.* **1990**, 112, 5662.E. Negishi, S.J. Holmes, J.M. Tour, J.A. Miller, F.E. Cederbaum, D.R. Swanson, T. Takahashi, *J. Am. Chem. Soc.* **1989**, 111, 3336.
6. H. Hart, A. Bashir-Hashemi, J. Luo, M. A. Meador, *Tetrahedron* **1986**, 42, 1641.
7. The synthesis proceeds as in ref. 6, but starting with 1,2,4,5-tetrabromo-1,4-di-*n*-hexylbenzene prepared according to: K. Blatter, A. D. Schlüter, *Chem. Ber.* **1989**, 122, 1351.
8. Atomic coordinates, bond lengths, angles and thermal parameters of 4 have been deposited at the Cambridge Cristallographic Data Centre.
9. Oxidation in CH_2Cl_2, reduction in THF, salt : n-Bu_4NPF_6, gold-electrode, silver-wire as reference, redox-potentials of reversible pairs in V vs. saturated calomel-electrode (ferrocene-calibration 310 mV), scan-speed v = 100mV s^{-1}.
10. M. Dietrich, J. Heinze, *J. Am. Chem. Soc.* **1990**, 112, 5142; A. Bohnen, H. J. Räder, K. Müllen, *Synth. Met.* **1992**, 47, 37.
11. T. Horn, U. Scherf, S. Wegener, K. Müllen, *Polymer Preprints* **1992**, 33, 190.

(Received in Germany 18 June 1993; accepted 19 July 1993)