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Lithium-Induced Cyclization of Tetrabenzocyclyne. A Novel Zipper Reaction of Cyclic *o*-Ethynylbenzenes

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Abstract: Reacting lithium with 1,2:5,6:9,10:13,14-Tetrabenzo-3,7,11,15-tetradehydro[16]annulene (tetrabenzocyclyne, QBC) in THF gives the meso and *d,l*-pair of 9,18-bis(trimethylsilyl)diindeno[2,3-*g*:2′,3′-*p*]chrysene. The X-ray crystal structures of these compounds show them to be ribbon oligomers with two helical interactions correlated with two chiral centers.

Introduction

The design and synthesis of ribbon and ladder oligomers and polymers with extended π-electron conjugation are topics of fundamental and practical interest.[1] Such systems show considerable promise as conducting and nonlinear optical materials because of their π-electron conjugation, environmental stability, high mechanical strength, and enhanced laser damage threshold. The most serious problem associated with such applications is that of poor solubility.[1] We predict that helical or twisted aromatic ribbon polymers, in which the helical axes extend down the aromatic chains, will have lower lattice energies and therefore higher solubilities than planar systems of comparable molecular weight. Helical and twisted polycyclic aromatic hydrocarbons have been synthetic targets for studies of aromaticity[2] and stereochemistry[3] and for the synthesis of chiral organometallic compounds.[4] Double helicenes[5] and some overcrowded *ortho*-annulated benzenoid systems[6] have been described as containing "two coils of angular condensed benzene rings".[5g] Two helicenes each having an incorporated chiral center have been reported.[7] Here we report a lithium-induced zipper reaction of cyclic *o*-ethynylbenzenes that offers a route to helical ribbon oligomers and may be applicable to the synthesis of helical ribbon polymers from *o*-ethynylbenzene polymers. Included in this report is the crystallographic characterization of the *d,l*-pair and meso isomers of an *ortho*-annulated benzenoid hydrocarbon incorporating two chiral centers and two helical axes.

Diphenylacetylene is known to undergo reductive dimerization when reacted with lithium.[8] In this process it is believed that two

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[•] Abstract published in *Advance ACS Abstracts*, March 1, 1994.

[1] (a) Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater.* **1990**, *2*, 649–659. (b) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23–38.

[2] (a) Randic, M.; Gimarc, B. M.; Trinajstic, N. *Croat. Chem. Acta* **1986**, *59* (2), 345–358. (b) Randic, M.; Gimarc, B. M.; Nikoki, S.; Trinajstic, N. *Gazz. Chim. Ital.* **1989**, *119* (1), 1–11.

[3] (a) Krow, G. *Top. Stereochem.* **1970**, *5*, 31–68. (b) Nakazaki, M. *Top. Stereochem.* **1984**, *15*, 199–251. (c) Laarhoven, W. H.; Prinsen, W. J. C. *Top. Curr. Chem.* **1984**, *125*, 63–130.

[4] (a) Katz, T. J.; Sudhakar, A.; Yang, B.; Nowick, J. S. *J. Macromol. Sci., Chem.* **1989**, *A26* (243), 309–326. (b) Dewan, J. C. *Organometallics* **1983**, 2, 83–88.

[5] (a) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652–5653. (b) Laarhoven, W. H.; Cuppen, Th. J. H. M.; Nivard, R. J. F. *Tetrahedron* **1974**, *30*, 3343–3347. (c) Martin, R. H.; Eyndela, Ch.; Defay, N. *Tetrahedron* **1974**, *30*, 3339–3342. (d) Sudhakar, A.; Katz, T. J. *Tetrahedron Lett.* **1986**, *27*, 2231–2234. (e) Laarhoven, W. H.; Cuppen, Th. H. J. M. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 553–562. (f) Laarhoven, W. H.; Cuppen, Th. H. J. M. *Tetrahedron Lett.* **1971**, 163–164. (g) Laarhoven, W. H.; De Jong, M. H. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 651–657.

[6] (a) Broene, R. D.; Diederich, F. *Tetrahedron Lett.* **1991**, *32* (39), 5227–5230. (b) Herbstein, F. H. *Acta Crystallogr.* **1979**, *B35*, 1661–1670 and references therein.

[7] (a) Imajo, S.; Shingu, K.; Kuritani, H.; Kato, A. *Tetrahedron Lett.* **1981**, *22*, 107–110. (b) Van Meerssche, M.; Declercq, J. P.; Germain, G.; Soubrier-Payen, B.; Lindner, H. J.; Kitschke, B. *Bull. Soc. Chim. Belg.* **1984**, *93* (6), 445–448.

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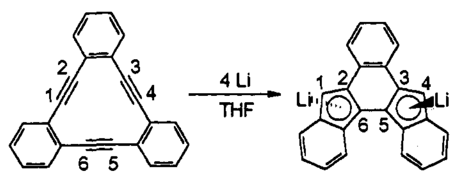
radical anions of diphenylacetylene couple. In our laboratory it has been shown that 1,2:5,6:9,10-tribenzo-3,7,11-tridehydro[12]-annulene (tribenzocyclyne, TBC) undergoes reductive cyclization with 4 mol equiv of lithium to form a dilithium dianion **1** (reaction 1).[9] These results prompted investigation of the effect of lithium on larger cyclyne systems such as 1,2:5,6:9,10:13,14-tetrabenzo-3,7,11,15-tetradehydro[16]annulene (tetrabenzocyclyne, QBC).[10]



TBC 1 (1)

Experimental Section

Manipulations were carried out under argon using standard Schlenk techniques. Trimethylsilyl chloride was distilled from Na$_2$CO$_3$, and THF was distilled from Na and benzophenone. QBC was synthesized by the Stephens–Castro coupling of copper(I) 2-(iodophenyl)acetylide.[10] A 60-mL flask was charged with QBC (0.25 g, 0.62 mmol) and an excess of lithium powder (0.035 g, 5.04 mmol, Aldrich) while in a drybox. THF (20 mL) was added to the flask, and the resulting solution was stirred and occasionally agitated at room temperature for 18 h. In the course of the reaction, the color of the reaction mixture turned from yellow to brilliant green, and finally to a red-brown solution. The reaction mixture was filtered, and trimethylsilyl chloride (5.0 mL, 39.5 mmol) was added. Stirring was continued for another 6 h before the solvent and excess trimethylsilyl chloride were removed in vacuo. In air the products were eluted with 1:4 methylene chloride:hexanes on a 40-μm silica gel column to give the *d,l*-pair and meso isomers of 9,18-bis(trimethylsilyl)diindeno-[2,3-*g*:2′,3′-*p*]chrysene, **2** and **3** (Figure 1), in isolated yields of 38.2% (0.131 g) and 16.4% (0.056 g), respectively. Spectra of **2**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.07 (s, 18 H), 4.59 (s, 2 H), 7.18 (m, 4 H), 7.47 (t, 2 H), 7.60 (m, 4 H), 8.04 (d, 2 H), 8.10 (d, 2 H), 8.92 (d, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ −1.6, 44.8, 123.2, 123.3, 124.0, 124.1, 124.5, 125.4, 125.8, 127.2, 128.6, 128.7, 128.9, 133.1, 143.3, 144.6, 147.6; ^{13}C NMR (75 MHz, C$_6$D$_6$) δ −1.7, 45.0, 123.7, 123.8, 124.4, 124.7, 124.9, 126.0, 127.9, 129.2, 129.4, 129.5, 133.8, 143.9, 145.2, 147.7; MS (EI) m/z 548 (M$^+$), 475 (M$^+$ − SiMe$_3$), 460 (M$^+$ − SiMe$_3$ − Me), 402 (M$^+$ − 2SiMe$_3$), 73 (SiMe$_3^+$); UV–Vis (CH$_2$Cl$_2$) λ_{max}(log ϵ) 425.4 (3.47), 403.2 (3.42), 327.2 (4.44), 311.8 (4.48), 277.8 (4.41), 230.6 (4.44). Spectra of **3**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.00 (s, 18 H), 4.64 (s, 2 H), 7.43 (m, 4 H), 7.61 (m, 6 H), 8.07 (d, 2 H), 8.18 (d, 2 H), 8.95 (d, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ −1.8, 44.3, 123.4, 123.5, 123.8, 124.0, 124.6, 125.8, 126.2, 127.0, 128.4, 129.0, 129.6, 129.7, 132.9, 142.7, 147.3; MS (EI) m/z 548 (M$^+$), 475 (M$^+$ − SiMe$_3$), 460 (M$^+$ − SiMe$_3$ − Me), 402 (M$^+$ − 2SiMe$_3$), 73 (SiMe$_3^+$).

X-ray Crystallographic Analyses. Crystals of **2** and **3** were obtained by slow concentration of the elution solvent mixture. These crystals were mounted on glass fibers and their unit cells determined using 15 photographic data. Unit cell dimensions were refined using an additional 25 reflections with $20.0° \le 2\theta \le 30.0°$. Data were collected using Mo Kα (λ = 0.710 73 Å) radiation on a Syntex P2$_1$ diffractometer at 294 and 133 K for **2** and **3**, respectively. Data were corrected for Lorentz and polarization effects. Compound **2** was solved in $P\bar{1}$ with a = 10.648(2) Å, b = 14.432(3) Å, c = 20.382(4) Å, α = 98.88(3)°, β = 92.14(3)°, γ = 95.69(3)°, V = 3074.7(11) Å^3, and Z = 4. Compound **3** showed mirror diffraction symmetry along the b axis and systematic absences agreeing with $C2/c$ or Cc (hkl, $h + k = 2n + 1$; $h0l$, $h,l = 2n + 1$; $0kl$, $k = 2n + 1$; $hk0$, $h + k = 2n + 1$; $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$). The structure of **3** was successfully refined in $C2/c$ with a = 20.402(4) Å, b = 10.555(2) Å, c = 13.609(3) Å, β = 94.38(3)°, V = 2922.1(10) Å^3, and Z = 4. For both models, Si and C positions were determined by direct methods with some outlying C and H positions being determined by successive difference Fourier syntheses (Siemens SHELXTL PLUS).[11] Full-matrix least-squares refinement was used to refine the models with Si and C atoms being refined anisotropically. For compound **2**, H atoms were refined using a riding model with the exception of the methyl hydrogens which were placed in calculated positions. All H atoms in **2** were given a fixed isotropic thermal parameter of 80 Å^2. For **3**, all H atoms were refined isotropically with the methyl H atoms being refined with a common isotropic thermal parameter. For **2**, refinement on 3894 unique reflections with $|F_o| \ge 4.0\sigma(|F_o|)$ from 3.5 to 45° in 2θ converged to R = 4.56% and R_w = 5.64%; all unique data (8044) gave R = 9.70% and R_w = 6.69%. For **3**, refinement on 1551 unique reflections with $|F_o| \ge 2.0\sigma(|F_o|)$ from 3.5 to 45° in 2θ converged to R = 5.10% and R_w = 5.09%; all unique data (1922) gave R = 6.65% and R_w = 5.26%.

Results and Discussion

In an effort to elucidate the reaction of lithium with cyclic *o*-ethynylbenzene systems, QBC (0.62 mmol) was reacted with an excess of lithium (5.04 mmol) in THF at room temperature followed by the addition of trimethylsilyl chloride (39.5 mmol) and workup. This resulted in the formation of the *d,l*-pair and meso isomers of 9,18-bis(trimethylsilyl)diindeno[2,3-*g*:2′,3′-*p*]-chrysene, **2** and **3** (Figure 1), in isolated yields of 38.2% (0.131 g) and 16.4% (0.056 g), respectively.

Our current working hypothesis for the mechanism of this reaction is that a *trans* radical anion (**4**) is produced upon reduction of one of the alkynes (Scheme 1). Molecular models suggest that the *trans* radical anion (**4**) will interact with the next alkyne in the chain to form a five-membered ring and a new radical (**5**). On the basis of molecular models, the radical (**5**) is best situated to interact with an alkyne across what was once the central cavity of QBC to form a six-membered ring and a new radical (**6**). Mechanistically the reaction is completed with the coincident formation of six- and five-membered rings, radical trapping with Li, and a 2-fold reduction. It is not clear at what stage protonation takes place. THF is known to be a source of protons in other reactions.[12]

The crystal structures of **2** and **3** show helical geometries which arise in part from steric interactions of hydrogens on rings H and F with those of rings A and G, respectively (for ring labeling see Scheme 1). The closest, average hydrogen–hydrogen interaction is 2.218 Å for both independent molecules in the asymmetric unit of **2**, and the closest interaction is 2.226 Å for **3**. The pitch of the helical interaction[13] measured between rings H and A, or F and G, is 40.9° for **3** and an average of 46.0° for **2**. In the meso compound, **3**, the two helical interactions have opposing P and M helicity[14,15] and are related by an inversion center. In **2**, the two helical interactions complement one another (P,P or M,M), making the overall structure spiral with the same pitch and direction (P or M) around a third chiral axis. This third chiral axis lies midway between and perpendicular to the first two helical axes and passes between C23 and C24, C1 and C17, and C7 and C8.

In **2** and **3**, a correlation can be drawn between the chirality of an sp^3 center of a five-membered ring and the helicity of the

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(8) (a) Smith, L. I.; Hoehn, H. H. *J. Am. Chem. Soc.* **1941**, *63*, 1184–1187. (b) Dadely, D. A.; Evanes, A. G. *J. Chem. Soc. B* **1968**, 107–111. (c) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 2268–2275. (e) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *Trans. Faraday Soc.* **1971**, *67* (3), 768–771.

(9) (a) Youngs, W. J.; Djebli, A.; Tessier, C. A. *Organometallics* **1991**, *10*, 2089–2090. (b) Malaba, D.; Chen, L.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1992**, *11*, 1007–1009. (c) Malaba, D.; Djebli, A.; Chen, L.; Zarate, E. A.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1993**, *12*, 1266–1276.

(10) Solooki, D.; Ferarra, J. D.; Malaba, D.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J. *Inorg. Synth.* in press.

(11) Siemens Analytical Instruments, Inc., Madison, WI, 1990.

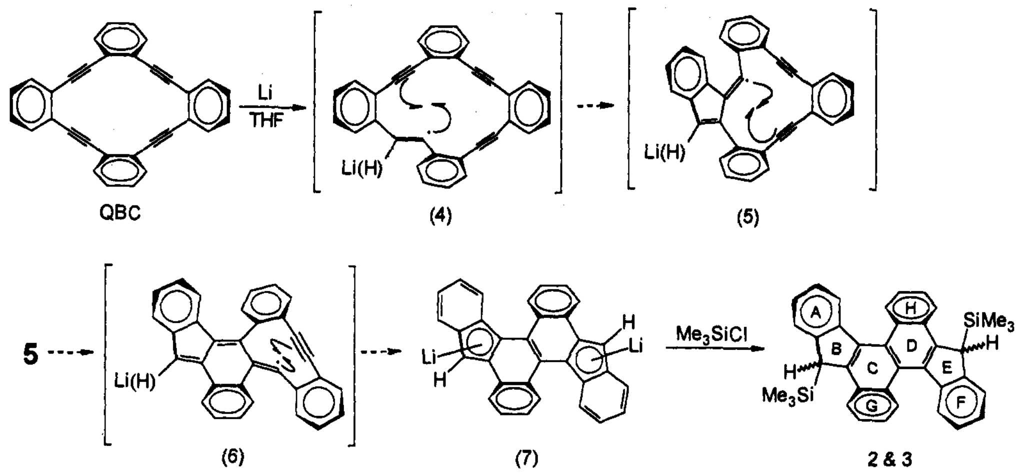
(12) (a) Reference 9c contains d_8-THF studies. (b) Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972–989. (c) Wen, J. Q.; Grutzner, J. B. *J. Org. Chem.* **1986**, *51*, 4220–4224. (d) Brandsma, L.; Hommes, H.; Verkruijsse, H. C.; de Jong, R. L. P. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 226–230. (e) Jung, M. E.; Blum, R. B. *Tetrahedron Lett.* **1977**, *43*, 3791–3794. (f) Hauptmann, H.; Mader, M. *Tetrahedron Lett.* **1980**, *21*, 897–898.

(13) Angles between rings were calculated as the angles between the normals to the least-squares planes of the rings.

(14) (a) Prelog, V.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 567–583. (b) Alternatively, the authors of ref 14a note that P helices can be described as R stereogenic units and M as S.

(15) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5* (4), 385–415.

Scheme 1



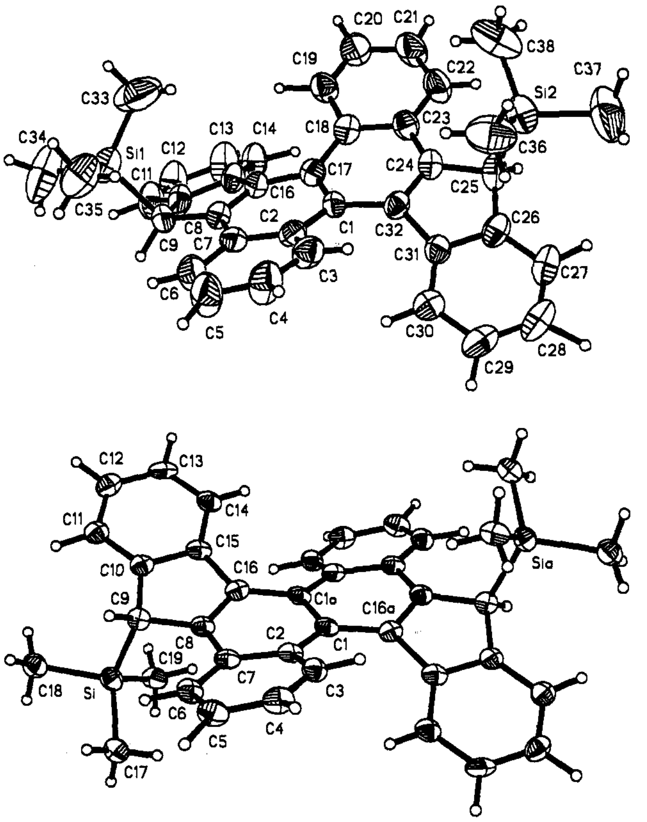


Figure 1. Thermal ellipsoid plots of one of the *d,l*-pairs, **2** (S,P,S,P (top) and R,M,R,M), and the meso compound **3** (R,M,S,P (bottom)) drawn at 50% probability.

coil containing the same five-membered ring. S centers are associated with P helical axes and R with M.

Rings C and D are common to two of the helical interactions. This and the positioning of the trimethylsilyl groups *cis* or *trans*[16] have a marked effect on the twisting of the central chrysene defined by rings C, D, H, and G of both **2** and **3**. This twisting of the central chrysene in **2** (*cis*) is demonstrated by a 32.7° torsion angle between rings H and G. The progression of this twist in **2** can be followed by the angles made by rings B (6.0°, 9.8°), C (18.1°, 26.7°), D (34.6°, 43.6°), E (46.7°, 59.2°), and F (51.3°, 68.8°) relative to ring A.[16] This effect is more pronounced in the second molecule of the asymmetric unit of **2** (second angles). All C–C bond distances and C–C–C bond angles in both independent molecules of **2** are within 1% probability of being the same on the basis of the differences between corresponding bond lengths being less than 2.58σ_{dif}.[17] An undulation of the central chrysene is observed in **3** (*trans*) with C3, C4, and C16 displaced 0.2020, 0.1831, and 0.3540 Å above and C6 and C7 displaced 0.1939 and 0.1336 Å below its least-squares plane. This undulating of carbons in and out of the least-squares plane of the central chrysene in **3** is continued down the chrysene backbone as related by the inversion center. A significant alternation of bond lengths conforming to the resonance form shown in Scheme 1 is observed in rings C and D of both **2** and **3**.

We are currently investigating reductive, intramolecular cyclization of larger cyclic *o*-ethynylbenzene systems[18] and linear *ortho*-ene–yne systems with prospects of forming helical ribbon oligomers and polymers. These nonplanar systems should have enhanced solubilities in comparison with planar aromatic chains of comparable molecular weight. The synthesis of main-group and transition-metal complexes of **2** and **3** is underway.

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Supplementary Material Available: Tables of data collection and structure solution details, bond distances and angles, atomic coordinates, and thermal parameters (21 pages); listings of structure factor amplitudes (23 pages). This material is contained in many 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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(16) *Cis* or *trans* assignment made relative to the least-squares plane of the fused ring portion of the molecule.

(17) Stout, G. H.; Jensen, L. H. *X-ray Structure Determination*, 2nd ed.; John Wiley and Sons: New York, 1989; pp 404–405.

(18) (a) Solooki, D.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J.; See, R. F.; Churchill, M. R.; Ferrara, J. D. *J. Organomet. Chem.*, in press. (b) Baldwin, K. P.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J. *Synlett* **1993**, 853–854.