A Novel Titanium-induced Aromatic Dicarbonyl Coupling. Synthesis of a Chiral Strained Polynuclear Aromatic Hydrocarbon

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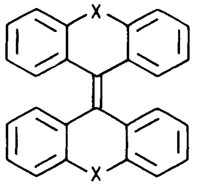
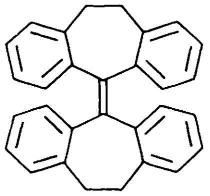
The titanium-induced coupling of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**3**) gave 10,10′,11,11′-tetrahydro-5,5′-bis(5*H*-dibenzo[*a*,*d*]cycloheptenyl) (**5**) and the chiral bridged diphenylanthracene (**4**), which was resolved and has a racemization barrier of ~23 kcal/mol (1 cal = 4.184 J); the crystal structure of (**4**) has been determined.

Overcrowded bistricyclic ethylenes (**1**) with six-membered central rings (X = CO, O, or NMe)[1,2] undergo fast thermal *E*,*Z* isomerizations.[3] This was attributed to the ground-state destabilization due to steric strain in the *anti*-folded conformation of (**1**).[3] In an attempted one-flask synthesis of (**2**) [≡ (**1**, X = CH_2CH_2)], the titanium-induced dicarbonyl coupling reaction[4] of (**3**) was applied. We report a novel aromatization coupling of (**3**) leading to the chiral strained bridged diphenylanthracene (**4**), a homologue of rubicene.[5]

Treatment of (**3**) with a low-valent titanium reagent [$TiCl_4$, Zn, tetrahydrofuran (THF), argon, pyridine; the Mukaiyama–Lenoir variation[6] of the McMurry reaction[4]] gave after



(1)



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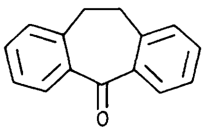

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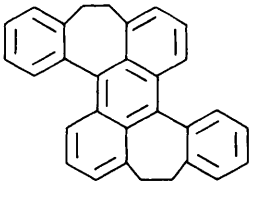

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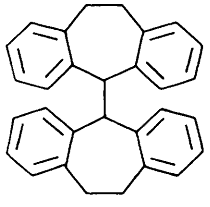

(5)

work-up a mixture of dimeric products, but no (2).[7] Column chromatography (silica gel; heptane–CH_2Cl_2, 4:1) afforded two major products: the dimeric (5), m.p. 271—272 °C, 33% yield (lit.[8,9] m.p. 271.5—272.5, 275—276 °C) and a $C_{30}H_{22}$ hydrocarbon (m/z 382, M^+, 100%).† Purification by sublimation (150—180 °C at 0.01 mmHg) gave (4) as red crystals (yellow powder, fluorescent in solution), m.p. 253 °C, in 26% yield, with 15 distinct ^{13}C n.m.r. signals,‡ consistent with C_2 symmetry.

The structure of (4) (Figure 1) was determined by X-ray crystallography.§ Compound (4) is a strained, doubly bridged 9,10-diphenylanthracene. The following dihedral angles (°) between the planes of the aromatic rings may be noted: A–B 9.2, A–C 12.5, A–D 53.0, A–E 53.1, B–D 44.4, C–E 41.0.[10] Compound (4) adopts the chiral *syn*-conformation (CH_2CH_2 bridges *syn*) rather than the achiral *anti*-conformation. The anthracene and dibenzocycloheptene moieties adopt a bowl-shaped conformation (∠B–C 21.6°), and S-shaped conformations, respectively.

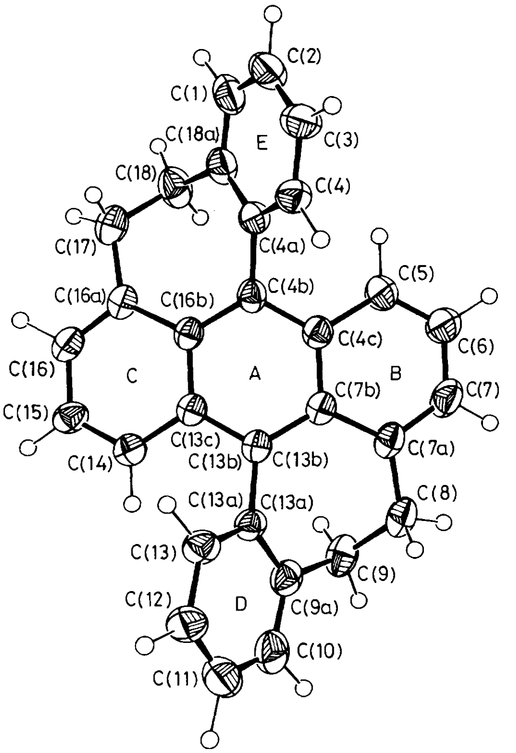

Figure 1. ORTEP drawing of molecule (4).

When (4) (in EtOH) was subjected to low-pressure liquid chromatography on swollen, microcrystalline triacetylcellulose,[11] complete enantiomer resolution (α 2.7) occurred in one cycle. The c.d. spectrum of the solution containing the first eluted (−)-enantiomer was recorded immediately after the chromatography, and slow racemization was observed. Monitoring the c.d. intensity of a strong band at 221 nm in a thermostated cell gave $k_{rac} \times 10^5 = 7.85$, 56.0, and 298 s^{-1} at +19.3, +34.5, and +50.0 °C, corresponding to free activation energies for inversion of (4) of 23.0, 23.0, and 23.2 kcal/mol (1 cal = 4.184 J). The inversion barrier could also be estimated by dynamic ^1H n.m.r. spectroscopy. The resonance of the CH_2CH_2 bridge protons appears as an ABCD system at ambient temperature and should under conditions of fast inversion give an AA'BB' system. In the intermediate rate range a merging of one of the shifts at δ 3.50 with the one at δ 2.94 should occur. An experiment with (4) in benzophenone solution revealed no coalescence of these multiplets even at +200 °C (300 MHz); however, a 5.2 Hz selective broadening of the bridge proton resonance lines could be observed at +160 ± 4 °C. Assuming the validity of the relation $k_{inv.} = \pi W$,[12] where W is the exchange broadening near the slow exchange limit, we find $k_{inv.} = 16\ s^{-1}$ and $\Delta G^{\ddagger}_{inv.} = 23.2 \pm 0.2$ kcal/mol, in good agreement with the results from the c.d. measurements.

A likely racemization–inversion mechanism would involve a centrosymmetric achiral *anti* form as high energy intermediate. In a critical step one of the CH_2CH_2 bridges passes through an eclipsed arrangement whereafter the attached ring D in a more or less coupled movement goes through the plane of the anthracene ring C. This is followed by the passage of

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† Two additional products were separated: an unidentified yellow fluorescent compound (R_f, silica; C_5H_{12}–CH_2Cl_2, 4:1, 0.33) and $(pyridine)_2ZnCl_2$, m.p. 201 °C.

‡ ^1H N.m.r. (300 MHz): δ ($CDCl_3$) 7.71 (d of d, J 8.8 and 0.9 Hz, 2H), 7.35 (m, 4H), 7.23 (m, 4H), 7.12 (d of d, J 8.8 and 5.3 Hz, 2H), 7.08 (d, br., J 7.1 Hz, 2H), 3.51 (m, 6H), and 2.97 (m, 2H); ^{13}C n.m.r. (50.29 MHz): δ ($CDCl_3$) 143.04 (s), 139.60 (s), 137.00 (s), 135.38 (s), 135.07 (d, J 163 Hz), 133.12 (s), 129.01 (s), 127.81 (d, J 162 Hz), 127.44 (d, J 157 Hz), 126.49 (d, J 158 Hz), 126.24 (d, J 164 Hz), 125.19 (d, J 164 Hz), 123.34 (d, J 164 Hz), 40.72 (t, J 128.7 Hz), and 33.06 (t, J 129.4 Hz); u.v. in EtOH: $\lambda_{max.}$/nm (ε) 195.5 (88 000), 275 (78 700), 396.5 (7 000), 416 (12 300), and 439 (12 500).

§ *Crystal data:* $C_{30}H_{22}$, monoclinic, space group $P2_1/c$, $a = 7.736(1)$, $b = 10.965(2)$, $c = 23.242(3)$ Å, $\beta = 93.96(1)°$, $U = 1966.8(7)$ Å^3, $Z = 4$, $D_c = 1.292\ g\ cm^{-3}$, $R = 0.0416$, $R_w = 0.0562$. Enraf–Nonius CAD-4 diffractometer; 3501 reflections measured, 2653 with $I \geqslant 2\sigma(I)$ used in the refinement. Programs: MULTAN-78; SHELX-76. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ring E through the plane of ring B and of the other CH_2CH_2 bridge through an eclipsed arrangement to give the enantiomeric configuration.

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