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Synthesis and Characterisation of [2.2](5,13)Dibenzo[*c*;1]chrysenophane

Hiroshi Matsubara,* Mitsunobu Osatani, Koji Yano, Tomohiro Adachi and Koji Yamamoto*

Department of Chemistry, College of Integrated Arts and Sciences, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

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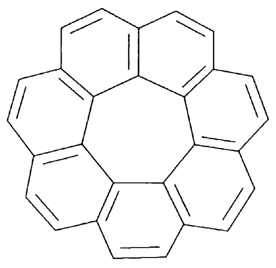
High-dilution coupling of 5,13-bis(bromomethyl)dibenzo[*c*;1]chrysene (**7**) and 5,13-bis(sulfanylmethyl)dibenzo[*c*;1]-chrysene **8** afforded the dithia derivative **9** which was converted, *via* the disulfone **10**, into an unusually strained compound, [2.2](5,13)dibenzo[*c*;1]chrysenophane **5**.

We have been interested in the synthetic studies of non-planar polycyclic aromatic molecules, and previous papers from our laboratory describe the synthesis of [7]circulene **1**[5] with twisted saddle-shaped geometry. An obvious extension of our interests in these non-planar polycyclic aromatic molecules led us to investigate the synthesis of 8-shaped closed circulene **3**, a new type of circulene shaped like a figure of eight, and this contribution is concerned with the synthesis of [2.2](5,13)dibenzo[*c*;1]chrysenophane **5** with external framework of **3**.



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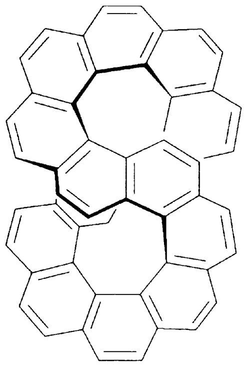

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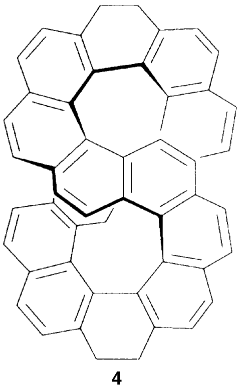

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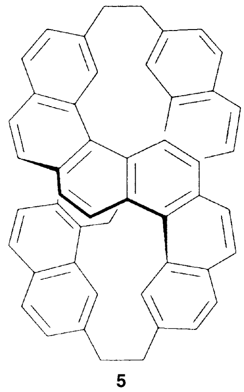

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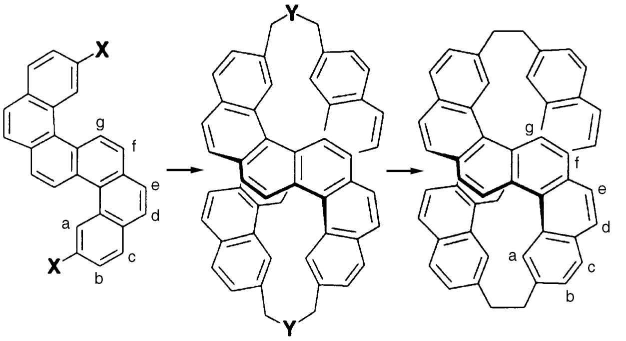
NBS bromination of 5,13-dimethyldibenzo[*c*;1]chrysene **6**[7] afforded the bromomethyl derivative **7** which was transformed into the dithio **8** by sulfenylization with thiourea. The coupling of dibromide **7** and dithiol **8** was carried out in DMF with caesium carbonate to give the dithiacyclophane **9** (19% yield).



6 X = CH_3
7 X = CH_2Br
8 X = CH_2SH

9 Y = S
10 Y = SO_2

5

Oxidation of **9** with *m*-chloroperbenzoic acid gave the disulfone **10** whose pyrolysis at 550 °C (0.01 Torr) produced the cyclophane **5**, as pale yellow prisms, mp $>$ 300 °C (32% yield from **9**). Its structure was characterised by elemental analysis, spectroscopic measurements and X-ray crystallographic analysis. Finally, we attempted the preparation of tetrahydro-8-shaped [14]circulene **4** from **5**. Dehydrogenation of **5** by 5% Pd/C at 300–350 °C or flash vacuum pyrolysis[8] at 1000–1200 °C/10^{-3} Torr) was unsuccessful, invariably giving a polymer as a product.

The ^{1}H NMR data of the layered cyclophane **5** are characterised by magnetic anisotropic effect of the adjacent aromatic rings. The remarkable upfield shift of aromatic protons of H_f and H_g in **5**, δ (ppm) 7.06 and δ 8.22, compared with the corresponding ones of the reference compound **6**, δ 7.93 and δ 9.12, clearly indicates a obliquely stacking structure of **5**.

The transannular π-electron interactions of layered cyclophane **5** can be best understood by electronic spectroscopy. The compound **5** demonstrates a common spectral characteristic of layered cyclophanes, *i.e.* bathochromism, hyperchromism, and broadening.[9] The longest wavelength band at **5** (350 nm) shows a remarkable bathochromic shift (12 nm), when compared with that of the reference compound **6**, demonstrating that the transition associated the longest wavelength band of 2,7-dimethyldibenzochrysene chromophore is affected by the transannular interaction between two bibenzochrysenes. The strong transannular π-electron interaction of **5** was also confirmed by its fluorescence spectrum compared with the monomer emission of **6** in 1,4-dioxane. The large redshift (22 nm) of the emission band of **5** (442 nm) indicates the strong π–π interaction that stabilises the intramolecular excimer state.[10]

The molecular structure of **5** was determined by single-crystal X-ray diffraction, and is shown in Fig. 1. The bridging ethylene bonds are torsional to avoid the eclipsing form. The dibenzochrysene rings are bent into a twist form to disperse a strain throughout the fused system and the

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*To receive any correspondence.

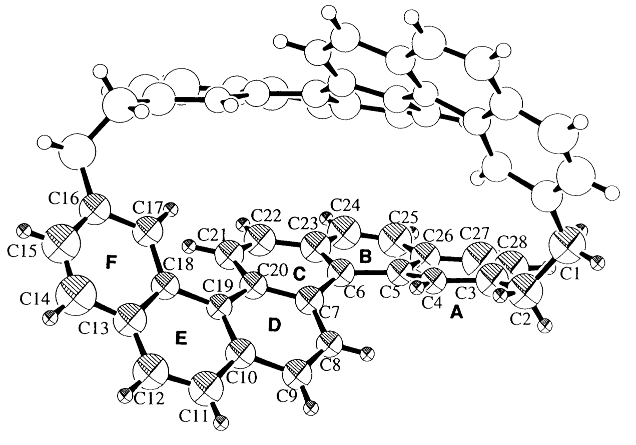

Fig. 1 X-Ray crystal structure of **5**

nearest nonbonded atomc distances between the neighbouring aromatic rings are situated in 3.3 Å. The largest dihedral angle between a mean plane *C* and a mean plane *D* is 18.2° so that a considerable strain exists in the structure.

Crystal data for **5**: $C_{56}H_{36}\cdot C_6H_6$; $M_r = 787.01$; monoclinic; space group $P2/n$ (no. 13); $a = 11.748(3)$, $b = 12.460(5)$, $c = 14.789(2)$ Å; $\beta = 108.31°$; $V = 2055.3(9)$ Å^3; $Z = 2$, $D_c = 1.272$ g cm^{-3}; $F(000) = 828$; $\mu(\mathrm{MoK}\alpha) = 0.72$ cm^{-1}. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromatized MoKα radiation ($\lambda = 0.71069$ Å). The structure was solved by a direct method (SIR92).[12] The final R value was 0.077 ($R_w = 0.069$).

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Techniques used: IR, ^{1}H NMR, mass spectrometry, elemental analysis, TLC, UV, fluorescence emission and X-ray diffraction

References: 12

Table 1: Spectral data for **5** and **6**

Table 2: Dihedal angles in **5**

Figures: 1

Appendix: X-Ray structure determination for **5**: experimental details, final atomic coordinates and B_{iso}, bond lengths, bond angles, torsion angles, selected non-bonded distances and least-square planes

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