Synthesis of [2.2](3,6)-Phenanthrenophanediene

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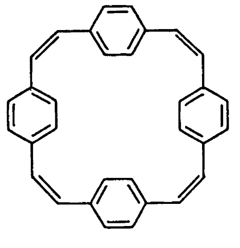
Several large ring compounds of fused benzene, thiophene and furan rings have been synthesized. Dopper and Wynberg[1] have suggested and defined the name circulenes for a special class of such compounds. Coronene or [6]circulene is a well-known member of this class. Like coronene,[2] tetraoxo[8]circulene[3] and some thia-[7]circulenes[4] seem to be planar molecules. A non-planar circulene is also known; corannulene or [5]circulene is bowl-shaped because of the short periphery.[5] On the other hand, [7]circulene and [8]circulene should have long peripheries and thus be expected to form saddle-shaped molecules.

We now report an attempted synthesis of [8]-circulene by photochemical ring closures of [2.2.2.2]paracyclophanetetraenes which can be conveniently prepared by Wittig reactions.[6]



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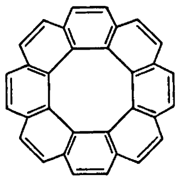

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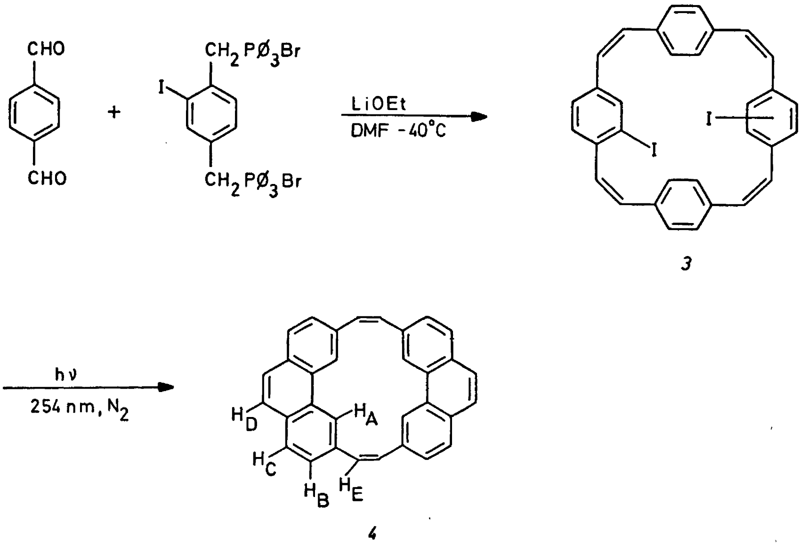
Results and discussion. The photolysis of [2.2.2.2]paracyclophanetetraene *1* in the presence of iodine and air gave no [8]circulene *2*. Instead, products from the oxidation of double bonds were observed.

Iodo-substituents in [2.2.2.2]paracyclophanetetranes might favour photochemical ring closures under an inert atmosphere to avoid photo-oxidation of strained double bonds. Such a cyclophane *3* was prepared by a Wittig reaction between terephthalaldehyde and the bis-triphenylphosphonium salt from α,α'-dibromo-2-iodo-*p*-xylene (Scheme 1).

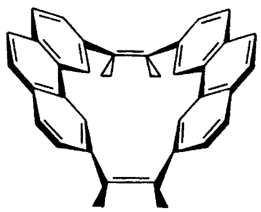
Photolysis of di-iodo[2.2.2.2]paracyclophanetetraene *3* under nitrogen gave a 15 % yield of [2.2](3,6)phenanthrenophanediene *4*. The cyclophane *4* has four internal hydrogens which show a large chemical shift δ 9.46 whereas the outer protons show somewhat smaller chemical shifts than the same protons in phenanthrene.[7] This could be due to a small paramagnetic ring current over the entire molecule as in [4n]annulenes[8] indicating a relatively planar structure with π-electron delocalisation.

However, the UV spectrum of cyclophane *4* is very similar to that of phenanthrene, and the molar extinction coefficient is twice as large which may indicate that the two phenanthrene parts of [2.2](3,6)phenanthrenophanediene *4* are almost perpendicular *5* with no significant π-electron interaction as inspection of simple molecular models of the compound shows.

[2.2](3,6)Phenanthrenophanediene *4* was irradiated under various conditions. In the absence of air the compound is relatively stable and decomposes slowly. In the presence of air



Scheme 1.



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the compound decomposes to give a complex mixture of aromatic aldehydes, showing the ease of photo-oxidation of strained double bonds. No [8]circulene *2* has yet been observed among the reaction products.

Clearly photo-oxidation must be suppressed in order to prepare [8]circulenes by photolysis of suitable [2.2.2.2]cyclophanetetraenes. One possibility is to photocyclize tetraiodo[2.2.2.2]paracyclophanetetraene under an inert atmosphere, another interesting possibility is to photocyclize [2.2.2.2]cyclophanetetraenes with two or more thiophene or furan rings to obtain hetero[8]circulenes with less steric strain in reaction intermediates and products. These routes to [8]circulenes are now being tried.

Experimental. Mass spectra were recorded on an AEI MS 902, UV spectra on a Beckman DK 2, IR spectra on a Beckman IR 9 and NMR spectra on a Bruker WH 270. Photochemical experiments were run in a Rayonet reactor RPR-100 with low pressure mercury lamps (254 nm).

*Bistriphenylphosphonium salt of α,α′-dibromo-2-iodo-*p*-xylene.* 2-Iodo-*p*-xylene (0.1 mol), recrystallized *N*-bromosuccinimide (0.22 mol) and dibenzoyl peroxide (0.1 g) were refluxed in dry redistilled carbon tetrachloride (500 ml) for 24 h. The hot solution was filtered to remove succinimide. α,α′-Dibromo-2-iodo-*p*-xylene precipitated from the cooled filtrate (10.2 g, 26 %, m.p. 114 – 16 °C). The crude product was refluxed in dry dimethyl formamide (200 ml) with triphenylphosphine (57.8 g) overnight. The white crystals formed were collected, washed with ethanol and dried in a vacuum at 110 °C. The yield was 90 %. (Found: C 57.7; H 4.12; Br 17.6; I 13.2; P 6.65. Calc. for $C_{44}H_{37}Br_2IP_2$: C 57.9; H 4.10; Br 17.5; I 13.9; P 6.60).

4,20(21)-Di-iodo[2.2.2.2]paracyclophanetetraene 3. Terephthalaldehyde (10 mmol) and the bistriphenylphosphonium salt from α,α′-dibromo-2-iodo-*p*-xylene (10 mmol) were stirred in dry dimethylformamide (500 ml) under nitrogen. The mixture was kept at – 40 °C in a thermostated bath. A freshly prepared solution of lithium ethoxide in ethanol (*ca.* 0.3 M) was added dropwise to allow for consumption of the coloured ylid between successive additions. The addition required 10 h. When no colour change was observed on addition of the base the reaction mixture was diluted with water (*ca.* 500 ml) and extracted with diethyl ether (3 × 500 ml). The combined ether solution was washed with water several times, dried over sodium sulfate and the solvent distilled off. The yellow residue was chromatographed on silica gel with dichloromethane as eluent. The first yellow fraction gave yellow needles (0.33 g, 10 %) melting at 221 – 224 °C after recrystallisation from carbon tetrachloride. (Found: C 58.3; H 3.36; I 38.4. Calc. for $C_{32}H_{22}I_2$: C 58.2; H 3.35; I 38.4). IR: 1585 cm^{-1}(m), 1418 (s), 1028 (s), 895 (s), 840 (s). UV: 302 nm, log $\varepsilon = 4.71$. MS: *m/e* 660 (M$^+$, 100 %), 532 (8), 406 (50), 405 (12), 404 (10). NMR: δ 7.75 (~1, broad s, protons adjacent to iodine), 7.29 – 7.27 (2, m, protons *meta* and *para* to iodine), 7.18 – 7.13 (4, m, aromatic protons), 6.53 – 6.37 (4, m, olefinic protons).

A second yellow fraction from the chromatography gave a yellow residue (< 1 %). The mass spectrum was consistent with a tri-iodo-[2.2.2.2.2.2]paracyclophanehexaene (*m/e* 990, M$^+$, 45 %).

[2.2](3,6)Phenanthrenophanediene 4. Cyclophane *3* (0.1 mmol, 66 mg) was dissolved in benzene (150 ml, spectroscopic grade) and nitrogen was bubbled through the solution for 1 h. The water-cooled solution was then irradiated for 3 h. The solvent was distilled off and the residue purified by chromatography on silica gel with carbon tetrachloride as eluent. The second fraction gave almost white crystals of [2.2](3,6)phenanthrenophanediene *4* (6 mg, 15 %, m.p. 321 – 323 °C) after recrystallization from ethanol. (Abs. mass: Found 404.154 ± 0.003. Calc. for $C_{32}H_{20}$ 404.156). IR: 1603 cm^{-1} (m), 1235 (m), 1150 (m), 910 (s), 878 (s), 850 (s), 839 (s), 740 (s) and 657 (s). UV: 250 nm, log $\varepsilon = 5.11$. NMR: δ 9.45 (4, broad s, H_A), 7.71 (4, d, H_C), 7.58 (4, s, H_D), 7.41 (4, broad d, H_B, $J_{BC} = 8.0$ Hz) and 7.23 (4, s, H_E). MS: *m/e* singly charged ions; 405 (35), 404 (100), 403 (8), 402 (12), 401 (8), 400 (10), 399 (5), 398 (8), 387 (9), 374 (6), doubly charged ions; 202.5 (6), 202 (22), 201.5 (10), 201 (20), 200.5 (10), 200 (20), 199.5 (7), 199 (15), 193.5 (12), 187 (14).

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Preparation and Relative Configurations of Some 2,2′-Spirobiindanes

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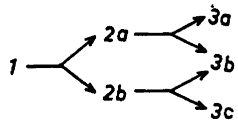
Stepwise reduction of 2,2′-spirobi[2*H*-indene]-1,1′(3*H*,3′*H*)-dione (*1*) according to Scheme 1 gives two diastereomeric monohydroxy ketones (*2a,b*) and three diastereomeric dihydroxy compounds (*3a,b,c*); formulae, see Fig. 1 and Table 1.



Scheme 1.

The monohydroxy ketone (*2b*) and the dihydroxy compound (*3b*) were previously prepared[1] by reduction of *1* with lithium tri-*t*-butoxyaluminium hydride [LiAl(O-*t*-Bu)$_3$H] and lithium aluminium hydride, respectively, in tetrahydrofuran (THF).

In continuation of these experiments, *1* was reduced with excess of LiAl(O-*t*-Bu)$_3$H in THF. The product was a mixture of the epimeric dihydroxy compounds (*3a*) and (*3b*) of which *3a* was isolated in 60 – 65 % yield.

Reduction of *2b* with LiAl(O-*t*-Bu)$_3$H in THF afforded a mixture of preferentially *3b* and *3c*.

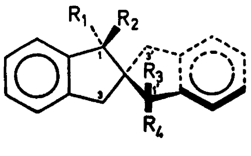


Fig. 1.

Table 1. ^{1}H NMR data[a] for some 2,2′-spirobiindane derivatives in DMSO-d_6 solution.

Signal	δ[b]	δ_{AB}[c]	J_{AB}/Hz[c]
4,[2] $R^1=R^2=R^3=R^4=H$			
CH_2	2.89		
5,[2] $R^1,R^2= \,=O$; $R^3=R^4=H$			
H(1′) = H(3′)	3.08	0.39	15.5
H(3)	3.18		
6, $R^1=R^2=H$; $R^3,R^4=H,OH$			
H(1)[d]	2.85	f	f
H(1′) (H)	4.78	0.60	6.0
(OH)	5.38		
H(3′)[d]	2.86	f	f
H(3)	2.93	0.83	16.0
2a, $R^1,R^2= \,=O$; $R^3,R^4=OH,H$			
(H1′) (H)	5.01	0.42	6.5
(OH)	5.43		
H(3′)	3.12	0.44	16.0
H(3)	3.23	0.08	17.9
2b, $R^1,R^2= \,=O$; $R^3,R^4=H,OH$			
H(1′) (H)	5.33	0.45	6.3
(OH)	5.78		
H(3′)	3.03	0.32	15.4
H(3)	3.21	0.92	17.3
3a, $R^1,R^2=H,OH$; $R^3,R^4=OH,H$			
H(1) = H(1′) (H)	4.99	0.43	4.2
(OH)	5.42		
H(3) = H(3′)	2.73	0.62	15.5
3b, $R^1,R^2=H,OH$; $R^3,R^4=H,OH$			
H(1)[e] (H)	4.59	0.55	6.5
(OH)	5.14		
H(1′)[e] (H)	5.27	0.48	6.5
(OH)	4.79		
H(3)	3.00	0.90	16.0
H(3′)	2.77	f	f
3c, $R^1,R^2=OH,H$; $R^3,R^4=H,OH$			
H(1) = H(1′) (H)	5.01	0.46	6.2
(OH)	5.47		
H(3) = H(3′)	2.79	0.81	15.6

[a] The spectra were recorded at 60 MHz except for compound *2a* which was recorded at 100 MHz. TMS was used as internal reference. [b] For the methylene groups the quoted values are the arithmetic means of the chemical shifts of the A and B protons. [c] δ_{AB} and J_{AB} are the differences in chemical shift between protons A and B, and the corresponding coupling constants, respectively. [d,e] Assignments may be reversed. [f] Not calculated because of lack of fine structure.