

# Synthesis and Photocyclization of [2.0.2.0]-, [2.2.2.0]- and [2.2.2.2]Cyclophanediene

BENGT THULIN and OLOF WENNERSTRÖM

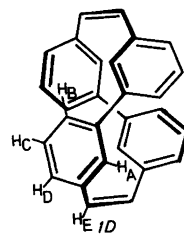
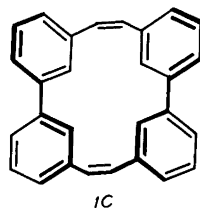
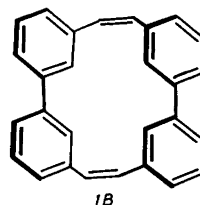
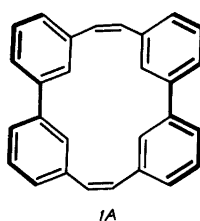
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Three cyclophanes, [2.0.2.0]-, [2.2.2.0]- and [2.2.2.2]cyclophanediene, *1*, *5* and *6*, respectively, have been prepared by double Wittig reactions. On irradiation under oxidative conditions, cyclophanes *1* and *6* give bi-4,5-phenanthrylene, *2*, and [2.2](3,6)-phenanthreneophane, *7*, respectively. On further oxidation of *2*, dibenzo[*def*,-*pqr*]cyclobutanol[*jkl*]tetraphenylene, *4*, is formed.

During the last few years we have investigated the application of multiple Wittig reactions to the synthesis of cyclophanes with unsaturated bridges,<sup>1</sup> some of the products being potential precursors for circulenes and other topologically interesting compounds. In this paper, we describe the preparation and attempted photocyclization of three cyclophanediene. The conformations of the cyclophanes are discussed briefly in relation to the photocyclizations. Part of this work has been reported in a short communication.<sup>2</sup>

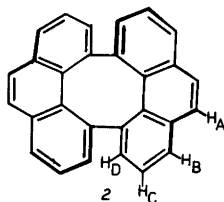
## RESULTS AND DISCUSSION

[2.0.2.0]Metacyclophanediene, *1*, can be prepared in 4 % yield from biphenyl-3,3'-dialdehyde and the bis triphenylphosphonium salt from 3,3'-bis(bromomethyl)biphenyl by a double Wittig reaction at -40 °C.<sup>2</sup> An alternative but longer synthetic route *via* the dithiacyclophane and ring contraction rearrangements has been described by Leach and Reiss.<sup>3</sup> The structure of the cyclophane follows from its <sup>1</sup>H NMR, UV and MS. The conformation of *1* is of interest when



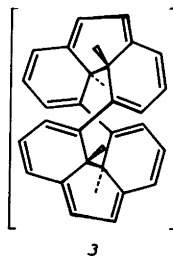
discussing its photocyclization. Four symmetrical conformations, *1A*–*1D*, can readily be envisaged. Leach and Reiss considered the *syn* conformation *1A* to be the preferred one. Of the four symmetrical conformations, *1A* and *1B* contain relatively planar biphenyl units. In *1A*, the bridging double bonds are almost orthogonal to the  $\pi$ -systems of the biphenyls, while conformer *1B* is sterically rather strained, as apparent by inspection of molecular models (CPK). Conformer *1B*, however, allows for a delocalized  $\pi$ -system. Conformer *1C* is rigid with almost orthogonal  $\pi$ -systems, while conformer *1D* is much less rigid, resembling two *cis*-stilbenes linked together to form a ring, and has the symmetry of a two-bladed propeller (*D*<sub>2</sub>). From the <sup>1</sup>H NMR spectrum of *1*

it is not possible to discriminate between the four conformers *1A–1D*. Although the internal aromatic protons appear at unusually low field ( $\delta$  7.61) this shift can be attributed either to proximity effects in *1A* or *1C* or to deshielding effects from neighbouring phenyl rings in *1B* or *1D*. However, the UV spectrum of *1* is similar to that of *cis*-stilbene, with almost double the  $\epsilon$ -value (see Experimental) which is to be expected only for conformer *1D*.

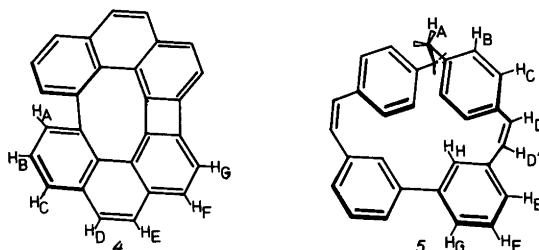


Irradiation of cyclophane *1* under oxidative conditions gave bi-4,5-phenanthrylene, *2*, (or dibenzo[*def,pqr*]tetraphenylene) in 65 % yield. The product must be rather strained and the two twisted phenanthrene (or 3 helicene) units could be almost orthogonal giving the molecule a propeller-shaped structure ( $D_2$ -symmetry) similar to that of its precursor. This proposal is supported by the UV spectrum of *2* which closely resembles that of phenanthrene. A recent X-ray investigation of *2* shows that the internal deformations of the two phenanthrene subunits are similar to those found in helicenes and that the angle between the two phenanthrene moieties is  $69^\circ$ .<sup>4</sup> The  $^1\text{H}$  NMR spectrum of *2* is also similar to that of phenanthrene except for the signal from the  $\text{H}_\text{D}$ -protons which is shifted upfield by 0.98 ppm. This shift is probably due to shielding by the opposite phenanthrene unit in the severely twisted structure.

It is conceivable that irradiation of cyclophane *1* under nonoxidative conditions (degassed solution, nitrogen atmosphere) would lead to two successive photocyclizations to give a product with two dihydrophenanthrene units linked together to form a ring. Such an unstable intermediate, ideally with  $D_2$ -symmetry, could be considered as a bridged [24]annulene, *3*. However, we have not been able to detect such an intermediate on irradiation of *1*. Instead, we observed a slow decomposition of the starting material and initially some *cis-trans* isomerization (NMR evidence only).



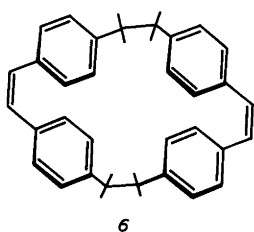
Oxidation of *2* in a melt of sodium chloride and aluminium trichloride<sup>5</sup> gave *4*, dibenzo[*def,pqr*]-cyclobutano[*jkl*]tetraphenylene, the structure of which was determined by  $^1\text{H}$  NMR and MS (see Experimental). The NMR spectrum of *4* resembles those of the dehydrohelicenes prepared by Wynberg and co-workers.<sup>6</sup> The MS of *4* is very simple, showing  $\text{M}^+$  and  $\text{M}^{2+}$  and almost no fragmentation, which reflects the stability of the compound. Further oxidation of *4* to the fully ring-closed derivative was unsuccessful. In contrast to that of *4* the MS of *1* and *2* showed not only strong molecular ions but the successive loss of six and two mass units, respectively, interpreted as being due to ring closure reactions. The same ring closures could be achieved by irradiation and oxidation. Thus, there seems to be a close parallel between facile ring-closure reactions in the mass spectrometer and chemically-induced reactions in these compounds.



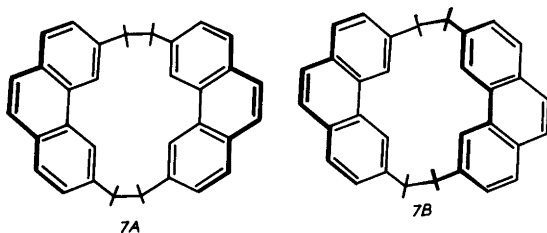
In order to increase the flexibility of the cyclophanediene and its ring-closed derivatives, we prepared a new cyclophane in which one of the biphenyl units in *1* had been replaced by a bibenzyl unit. The bis(triphenylphosphonium) salt from 3,3'-bis(bromomethyl)biphenyl was reacted with bibenzyl-4,4'-dialdehyde under the standard conditions to give [2.2.2.0]metapara-cyclophanediene, *5*, in 4 % yield after chromatography. To our surprise, irradiation of *5* in various solvents under oxidative conditions gave

no ring closed product. Instead, slow decomposition of the starting material and, possibly, *cis-trans* isomerization was observed. It is difficult to rationalize the failure of the photocyclization as being due to unfavourable geometry in the ground state. Although no certain conclusions about the ground state geometry can be drawn from available data, there seems to be little steric hindrance in a conformation with two *cis*-stilbene units (from CPK models). Thus, since the UV spectrum of **5** is consistent with such a conformation, we are left with the speculation that unfavourable steric effects in the excited state prevent the photocyclization reaction.<sup>7</sup>

An even more flexible cyclophanediene, *cis,cis*-[2.2.2.2]paracyclophanediene, **6**, can be prepared by a double Wittig reaction from bibenzyl-4,4'-dialdehyde and the bis(triphenylphosphonium) salt from 4,4'-bis(bromomethyl)-bibenzyl. The same cyclophane has also been prepared by preparative electrolysis at constant potential of [2.2.2.2]paracyclophanetetraene<sup>8</sup>



and by light-induced isomerization of the *trans-trans* isomer of [2.2.2.2]paracyclophanediene.<sup>9</sup> We have also reported on the conformations and dynamic processes in the *cis,cis* isomer of [2.2.2.2]paracyclophanediene, **6**, elsewhere.<sup>10</sup> As expected, the cyclophanediene **6** readily undergoes photocyclizations under oxidative conditions to give [2.2](3,6)phenanthrenophane, **7**, which can also be prepared by catalytic hydrogenation of [2.2](3,6)phenanthrenophanediene.<sup>11</sup> The cyclophane **7** is rather rigid and



should adopt a *syn*, **7A**, or *anti*, **7B**, conformation. The downfield shift of the methylene protons in **7** ( $\delta$  3.62) as compared to those observed in a series of similar cyclophanes with ethylene bridges<sup>10</sup> is best explained by assuming the *syn* conformation to be lowest in energy. If so, exchange of the "outer" and "inner" methylene protons in **7** to give a singlet in the NMR spectrum, requires a rapid inversion process *via* the *anti* conformation.

## EXPERIMENTAL

<sup>1</sup>H NMR spectra were recorded on a Bruker WH 270 instrument using CDCl<sub>3</sub> as solvent and TMS as internal standard. Mass spectra were run on an AEI MS 902 spectrometer and UV spectra (in cyclohexane unless otherwise stated) on a Beckman DK-2A instrument. Melting points were determined on a Reichert hot stage apparatus. The photochemical experiments were carried out using a Rayonet reactor with light of maximum intensity at 254 nm and 300 nm.

*The bis(triphenylphosphonium) salt from 3,3'-bis(bromomethyl)biphenyl.* 3,3'-Dimethylbiphenyl (0.05 mol), recrystallized *N*-bromosuccinimide (0.11 mol) and dibenzoylperoxide, as initiator, were refluxed for 24 h in dry, redistilled, tetrachloromethane. The hot solution was filtered to remove succinimide, and 3,3'-bis(bromomethyl)biphenyl precipitated from the cooled filtrate (38 %, m.p. 114–115 °C, NMR:  $\delta$  7.6–7.3 (8H, m), 4.54 (4H, s)). The product was then heated in dry DMF with two equivalents of triphenylphosphine for 10 h. On cooling of the reaction mixture, the white crystalline phosphonium salt precipitated. This was collected, washed with dry ether, and dried *in vacuo* before use.

*The bis(triphenylphosphonium) salt from 4,4'-bis(bromomethyl)biphenyl* was prepared from 4,4'-bibenzylidicarbalddehyde. Reduction of the dialdehyde with LiAlH<sub>4</sub> gave the hydroxymethyl compound which was converted to the corresponding bromomethyl compound by treatment with HBr in acetic acid. The bis(bromomethyl) compound was then heated with two equivalents of triphenylphosphine in dry DMF for 12 h, and the reaction mixture cooled. The precipitated bisphosphonium salt was collected, washed with ether, and dried *in vacuo* before use.

*3,3'-Biphenyldicarbalddehyde.* The crude 3,3'-bis(dibromomethyl)biphenyl prepared by four-fold NBS bromination of 3,3'-dimethylbiphenyl was refluxed in a mixture of water-ethanol (1:1) for 24 h. The solution was then stirred overnight

with sodium bisulfite and then extracted with chloroform several times. The aqueous layers were collected and acidified with sulfuric acid. After the gas evolution had ceased, the mixture was extracted with chloroform. The solvent was then distilled off giving 3,3'-biphenyldicarbaldehyde in 60 % yield (m.p. 83–85 °C). NMR:  $\delta$  10.2 (2H, s), 8.3–7.5 (8H, m). MS:  $m/e$  210 ( $M^+$ , 100 %), 209 (93), 182 (11), 181 (23).

The Wittig reactions were performed as previously described and the products were separated and isolated by the standard procedure.<sup>1</sup>

[2.0.2.0]Metacyclophanediene 1. 3,3'-Biphenyldicarbaldehyde (3 mmol) and the bis(triphenylphosphonium) salt from 3,3'-bis(bromomethyl)biphenyl (3 mmol) were reacted under the standard conditions to give cyclophane 1, in 4 % yield, (m.p. 114–115 °C). NMR:  $\delta$  7.61 ( $H_A$ , t,  $J_{AB}=J_{AD}=1.5$ ), 7.31 ( $H_C$ , t,  $J_{BC}=J_{CD}=7.5$ ), 7.18 ( $H_B$  or  $H_C$ , d of t), 7.11 ( $H_B$  or  $H_D$ , d of t) and 6.60 ( $H_E$ , s). MS:  $m/e$  356 ( $M^+$ , 100 %), 355 (6), 354 (5), 353 (6), 352 (6), 351 (6), 350 (6), 340 (8), 339 (9), 182 (11), 178 (9), 176 (10), 175 (9), 169.5 (12), 168.5 (13). Abs.mass; 356.156 $\pm$ 0.003; calc. for  $C_{28}H_{20}$  356.156. UV:  $\lambda_{max}$  282 nm,  $\epsilon=19$  500.

[2.2.2.0]Metaparacyclophanediene 5. 4,4'-Bibenzylaldehyde (3 mmol) and the bis(triphenylphosphonium) salt from 3,3'-bis(bromomethyl)biphenyl were reacted under the standard conditions to give cyclophane 5, in 4 % yield (m.p. 192 °C). NMR:  $\delta$  7.36 ( $H_F$ , t,  $J_{EF}=J_{FG}=7.5$  Hz), 7.19 ( $H_E$ ,  $H_G$ ,  $H_H$ , m), 6.81, 6.68 ( $H_B$  and  $H_C$ , d,  $J_{BC}=8$  Hz), 6.64, 6.47 ( $H_D$  and  $H_D'$ , d,  $J_{DD'}=12$ ) and 2.87 ( $H_A$ , s). MS:  $m/e$  384 ( $M^+$ , 100 %), 383 (3), 192 (26), 91 (15). Abs.mass 384.187 $\pm$ 0.003; calc. for  $C_{30}H_{24}$  384.187. UV: 262 nm,  $\epsilon=24$  200.

[2.2.2.2]Paracyclophanediene 6. Bibenzyl-4,4'-dialdehyde (5 mmol) and the bis(triphenylphosphonium) salt from 4,4'-bis(bromomethyl)biphenyl (5 mmol) were reacted under the standard conditions to give cyclophane 6 (156.5 mg, 15.2 %, m.p. 137–139 °C). NMR:  $\delta$  7.00 and 6.73 (16 H, d, aromatic protons), 6.53 (4 H, s, olefinic protons), and 2.84 (8 H, s, methylene protons). MS (68 eV):  $m/e$  412 ( $M^+$ , 100 %), 207 (20, 206 (80), 205 (18), and 191 (14). Abs.mass 412.222 $\pm$ 0.005; calc. for  $C_{32}H_{28}$  412.219. UV (ethanol): 265 nm,  $\epsilon=23$  600.

Bi-4,5-phenanthrylene 2. The cyclophanediene 1 was dissolved together with iodine in cyclohexane and irradiated for 24 h. The reaction products were separated by column chromatography on silica gel with tetrachloromethane as eluant, giving 2 in 65 % yield (m.p. 262–263 °C). NMR:  $\delta$  7.80 ( $H_B$ , d, of d,  $J_{BC}=J_{CD}=7.5$ ), 7.66 ( $H_A$ , s),

7.40 ( $H_C$ , t), 6.63 ( $H_D$ , d of d,  $J_{BD}=1.4$ ). MS:  $m/e$  352 ( $M^+$ , 67 %), 351 (80), 350 (100), 349 (13), 348 (27), 176 (7), 175.5 (13), 175 (47), 174.5 (7), 174 (27). Abs.mass 352.126 $\pm$ 0.003; calc. for  $C_{28}H_{16}$  352.125. UV: 253 nm,  $\epsilon=100$  000.

Dibenzo[def,pqr]cyclobutano[jkl]tetraphenylene 4. To a mixture of 2 (8 mg) and sodium chloride (30 mg) was added powdered aluminium chloride (60 mg) and the compounds were mixed quickly.<sup>5</sup> The reaction vessel was fitted with a drying tube and placed in a preheated oil bath at 140 °C. As soon as the melt was completed (10 min) it was hydrolyzed with water (20 ml). The water phase was extracted with chloroform several times and the combined organic phases evaporated to dryness. The residue was chromatographed on silica gel with chloroform as eluant giving 4 in 40 % yield (m.p. 330 °C decomp.). NMR:  $\delta$  9.34 ( $H_G$  or  $H_F$ , d,  $J_{FG}=8.5$ ), 9.15 ( $H_A$  or  $H_C$ , d of t,  $J_{BC}$  or  $J_{AB}=7.5$ ), 8.52 ( $H_G$  or  $H_F$ , d), 8.27 ( $H_A$  or  $H_C$ , d of t), 8.23 ( $H_D$  and  $H_E$ , AB-quartet,  $J_{DE}=8$ ) and 8.13 ( $H_B$ , t). MS:  $m/e$  350 ( $M^+$ , 37 %), 348 (7), 175 (16), 123 (15), 109 (24). Abs.mass 350.109 $\pm$ 0.003; calc. for  $C_{28}H_{14}$  350.109.

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