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$[2_6]$PARACYCLOPHANEHEXAENES

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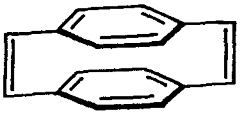
Three stereoisomers of $[2_6]$paracyclophanehexaene, 4, 5, and 6 have been synthesised and their photo-induced interconversions investigated.

For the series of $[2_n]$paracyclophane-enes 1 - 3, increasing n from two (1) to four (3) greatly reduces molecular rigidity and strain energy, allowing the π system to adopt a more planar geometry.



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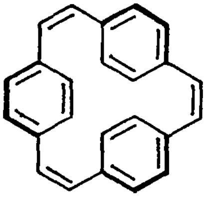

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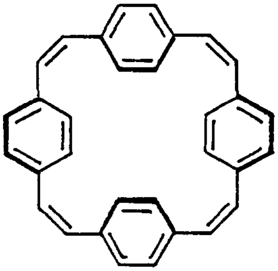

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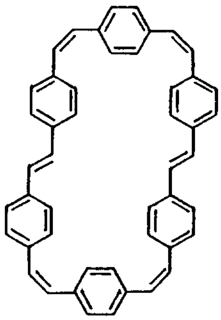
In cyclophanediene 1 the benzene rings and olefinic bridges are mutually perpendicular[1] and in 2 they are close to perpendicular,[2] but in tetraene 3 the average twist angle is reduced[3] to *ca.* 35°. As a consequence, cyclophane 3 undergoes reduction to a stable, annulene-like dianion. This dianion contains a formal perimeter of 26 π electrons and its ^{1}H NMR spectrum shows a shift difference of approximately 16 ppm between inner and outer aromatic protons due to a large induced diamagnetic ring current effect.[4] In the $[2_n]$paracyclophane-enes with n > 4, which may be relatively planar and strain-free with extensive conjugation, configurational isomerism at the olefinic bridges becomes possible, resulting in a greater variety of possible structures and conformations.

Recently,[5] we reported the synthesis and properties of a cis,cis,trans,cis,cis,trans- or Z,Z,E,Z,Z,E isomer of $[2_6]$paracyclophanehexaene, 4. We have now prepared two new symmetrical isomers of this cyclophane, namely, the Z,E,Z,E,Z,E isomer,5 and the Z,Z,Z,Z,Z,Z isomer,6.



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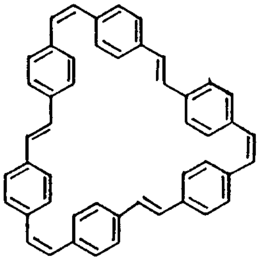

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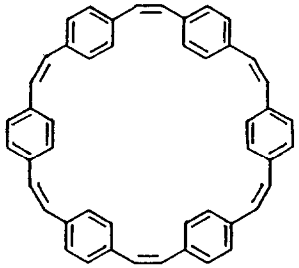

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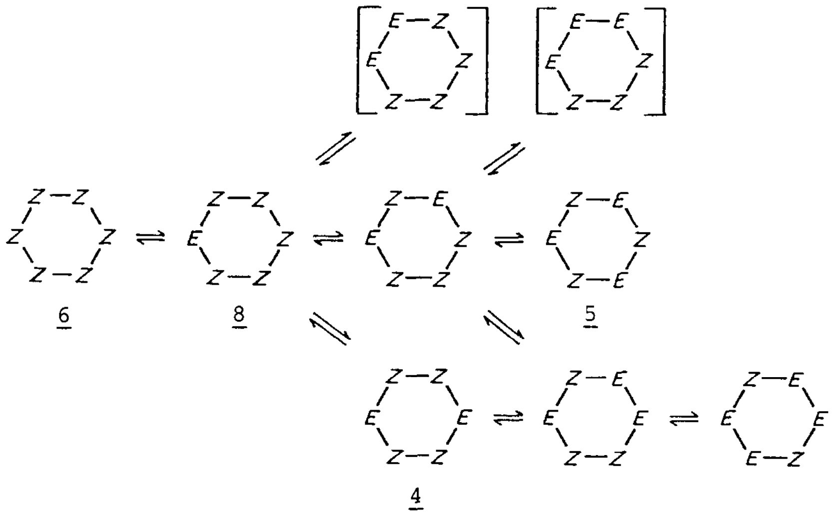
A cis-selective three-fold Wittig reaction of an aromatic monoaldehyde-monophosphonium salt has been used recently to synthesise $[2_3]$metacyclophanetriene.[6] The cyclophane 5 was synthesised by the same method from E-4,4'-stilbenedicarbaldehyde *via* partial reduction ($NaBH_4$) to 4'-(hydroxymethyl)-stilbene-4-carbaldehyde which, after purification, was converted (HBr) to the corresponding bromomethyl-aldehyde, treatment of which with triphenylphosphine in warm DMF gave the desired phosphonium salt. The salt was stirred under nitrogen at -40°C in dry DMF and lithium ethoxide in ethanol added dropwise during 4h. After the usual work-up and purification,[6] cyclophane 5 was obtained in 8.6% yield. MS: 612 (M^{+}, 100%); abs. mass 612.280, calc. for $C_{48}H_{36}$ 612.282. The high symmetry of 5 is revealed by its ^{1}H NMR spectrum which consists of two singlets (δ 6.71 and 6.97) for the olefinic protons and an *AA'BB'*-type pattern (δ 7.02 and 7.28) for the aromatic protons.

The Z,Z,Z,Z,Z,Z-isomer, 6, was prepared by partial catalytic hydrogenation of cyclophane 7[5] (Lindlar catalyst, room temp., atm. pressure, darkness) and, although extremely light-sensitive, could be obtained free from isomers by rapid chromatography. MS: 612 (M^{+}, 100%); abs. mass 612.277, calc. for $C_{48}H_{36}$ 612.282. The all-Z geometry follows from the extremely simple ^{1}H NMR spectrum (two sharp singlets at δ 6.52 and 7.04, ratio 1:2). Inspection of CPK models reveals clearly that cyclophane 4 can be more planar than 5, which in turn can be more planar than 6. This is consistent with UV data (ethanol): 4 (λ_{max} 342 nm, $\log\varepsilon$ 4.99), 5 (332, 4.80; 290 sh, 4.37 and 243 sh, 4.29), 6 (319, 4.41 and 242, 4.49). Detailed interpretation of the UV data is complicated by the different symmetries and the large number of possible conformations.

Irradiation of 4 (254 nm) results in slow formation of 5 and a final equilibrium mixture of 4 and 5 (ratio *ca.* 1:2) accompanied by some decomposition. No other isomers or reaction products could be detected during the photoisomerisation ($<$ 5% by ^{1}H NMR at 270 MHz) and essentially the same mixture was obtained upon irradiation of 5 under identical conditions.

This facile photo-induced interconversion of isomers 4 and 5 requires a change of configuration at at least three double bonds. If the isomerisation



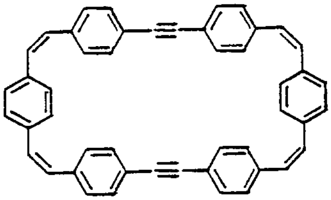
Scheme 1

Interconversion scheme for isomers 4, 5 and 6 of $[2_6]$*paracyclophanehexaene. Highly strained isomers have been omitted or placed in brackets.*

is a stepwise process involving one inversion of double-bond configuration *per* photon, then a minimum of two intermediates is necessary for each of the routes depicted in Scheme 1, and it follows that the less symmetrical intermediates must be much more photosensitive than both 4 and 5, otherwise these intermediates would be detectable by NMR techniques. There is, however, the intriguing alternative possibility that the photo-interconversion of 4 and 5 occurs *directly* in the excited state without recourse to ground-state intermediates, thus requiring only one photon *per* interconversion. In this respect, isomer 6 provides an interesting additional entry into Scheme 1. Irradiation of 6 under the same conditions as above leads to rapid formation of a mixture of 4 and 5 (initial ratio *ca.* 2:3) which upon prolonged irradiation slowly changes towards the equilibrium mixture, with no intermediates being detected by ^{1}H NMR (< 5%). This observation supports the idea that the overall isomerisation occurs directly without the intervention of ground-state intermediates, but a more quantitative investigation is required to prove (or disprove) this interesting possibility. Furthermore, the key intermediate 8 should be prepared and its photoisomerisation studied.

The relative ground-state energies of 4, 5, and 6 could be partly elucidated by separate treatment with a small amount of iodine in the dark. Periodic NMR analysis revealed that neither 4 nor 5 changed (some decomposition only) upon prolonged exposure to iodine, while 6 was converted slowly to isomer 5 only, the NMR spectrum of the reaction mixture showing additional signals which suggested the possible intermediacy of isomer 8.

The excited-state geometry of simple olefins has been studied extensively, both experimentally and theoretically, and it has become clear that, *inter alia*, non-planar structures are important[7]. However, large $[2_n]$paracyclophane-enes show large Stokes shifts[8], and it is tempting to speculate that this is due to *increased* planarity in the excited state as compared to the ground state. Such planar structures are indeed believed to be of importance in the dianions of this class of cyclophanes[9], simple Hückel calculations (assuming planar geometries) revealing the same bond orders for both the dianions and the first excited state in which the formal double bonds of the olefinic bridges are weakened and the single bonds strengthened[9]. The valence isomer represented by the Kekulé structure 4' is of no significance as regards the ground state, but may well be of more importance for the properties of the first excited state.



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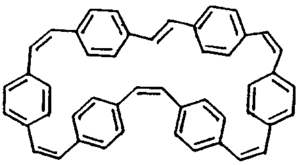

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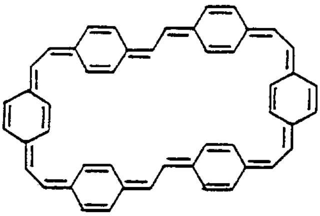

4'

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