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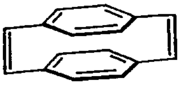
ELECTROCYCLIC RING CLOSURE OF [2.2.6]PARACYCLOPHANEPENTAENE. STRUCTURE AND DYNAMIC STEREOCHEMISTRY OF THE PRODUCT

David Tanner, Olof Wennerström and Thomas Olsson

Department of Organic Chemistry, Chalmers University of Technology
and University of Göteborg, S-412 96 Göteborg, Sweden.

The structure and dynamic stereochemistry of a novel paracyclophane formed by electrocyclic ring closure of a hexatriene-bridged precursor are described.

The $[2_n]$paracyclophane-enes, exemplified by compounds 1-3 below, form an intriguing class of compounds possessing often unusual steric and electronic properties.[1]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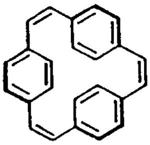
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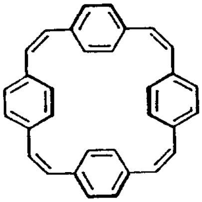
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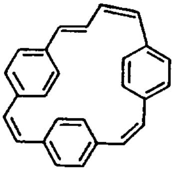
The major topics of structural interest have included the distribution of molecular strain (as manifested in the deformation of benzene rings) and the barrier to rotation or flipping of the aromatic moieties - points which are well illustrated by the homologous series depicted above. Cyclophanes 1 and 3 differ radically, as the compressed, stacked, geometry of the former[2] results in boat-shaped benzene rings and prevents their rotation, while the latter is relatively planar and conjugated with little *steric* hindrance to the flipping of the benzene rings.[3,4] Indeed, 3 is sufficiently planar to allow formation of a perimeter-conjugated, highly diatropic, dianion[5] in which the accentuated desire for planarity and increased barrier to phenyl rotation are due to *electronic* factors. Cyclophanes of type 2 occupy the middle ground between these extremes, a recent X-ray crystallographic molecular mechanics investigation[6] revealing an asymmetric, non-planar structure for 2 and suggesting a "low"[6] barrier to the rotation of the benzene rings. In an elegant demonstration, Boekelheide[7] showed that 2 is capable of complete photocyclisation to a diatropic bridged [18] annulene species.

Our own current interest in perimeter-conjugated cyclophanes and their dianions led us to attempt the synthesis of the series of compounds 2, 4, and 5 by a short synthetic route which we have recently developed[8].



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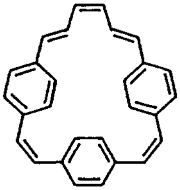

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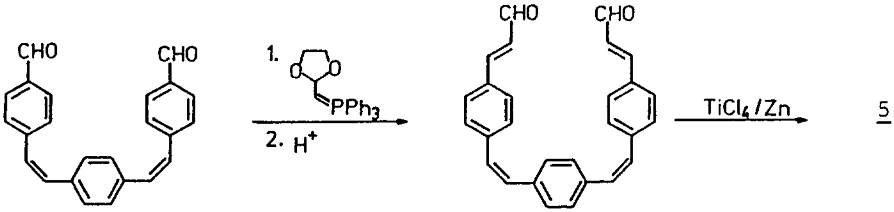
The syntheses of 2 and 4 were straightforward, providing a much simpler and improved route[7] to 2 and allowing a study of the reduction of 4 to its diatropic dianion[9]. The projected route to 5 is shown below:

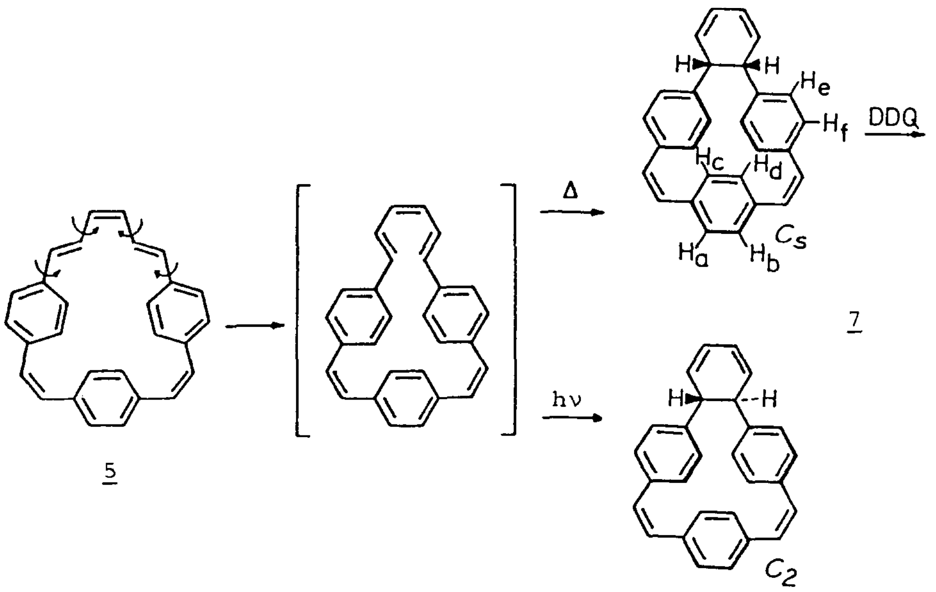


(ref. 10)

6

Dialdehyde 6, ^{1}H NMR: δ 6.55 (2H,d,J_{cis}= 12 Hz), 6.64 (2H,d, 12 Hz), 6.65 (2H,dd, 8, 16 Hz), 7.13 (4H,s), 7.31 and 7.42 (8H,*AA'BB'*m, 8Hz), 7.40 (2H,d, 16 Hz), 9.68 (2H,d, 8 Hz).

Intramolecular reductive coupling[8] of 6 gave a 70% yield of a single product as a yellow semi-crystalline solid. (Abs. mass 358.172, calc. for $C_{28}H_{22}$ 358.172). However, the room-temperature 270 MHz ^{1}H NMR spectrum of the new compound in various solvents was not that expected for structure 5, consisting of both sharp and broad peaks in the aromatic region, an unexpectedly complex olefinic region, and a narrow multiplet around δ 3.9 coupled to some of the olefinic protons. The data are better accommodated by structure 7, derived from 5 *via* electrocyclic ring closure of the *s-cis,s-cis* conformer of the hexatriene bridge. The *cis* isomer of 7 would derive from a thermal (disrotatory) process, the *trans* isomer from a photochemical (conrotatory) one.



As well as the intrinsic interest of the unexpected ring closure reaction, the actual course of events also provides (albeit serendipitously) an excellent stereochemical probe for ^{1}H NMR studies of the barrier to rotation of the benzene rings in 7. If this process could be slowed sufficiently, both *cis*-7 (C_s symmetry) and *trans*-7 (C_2) - in their respective "frozen" conformations would allow differentiation between the "halves" of the benzene ring opposite to the cyclohexadiene unit. This is not possible for 2 since the solution-phase symmetry is too high, but it seems reasonable to assume that the barrier to phenyl rotation in 2 should be of the same order of magnitude as that for rotation of the above-mentioned benzene ring in 7. Such a freezing-out process would simultaneously allow a direct assignment of the stereochemistry at the bridging single bond of the cyclohexadiene unit, since the protons H_a and H_b would be chemically equivalent in the "frozen" *cis* isomer (mirror plane symmetry, J_{ab} apparently zero) while in the "frozen" *trans* isomer (twofold proper axis) J_{ab} should be 8-9 Hz in magnitude.

That the peak-broadening observed in the room-temperature NMR spectra was indeed due to the dynamic processes referred to above was shown by the sharpening of these peaks upon warming the sample, all spectral changes being reversible. Thus in DMSO-d_6 solution at 388K, for example, all the signals were sharp and the spectral pattern was that expected for structure 7: δ 3.96 (2H, m), 5.86 (2H, m), 6.08 (2H,m), 6.66 and 6.75 (8H, *AA'BB'*m, J = 9 Hz), 6.78 (4H, s), 6.83 (2H, d, J_{cis}= 12 Hz), 6.89 (2H, d, 12 Hz). Upon cooling the sample, the signals due to protons of type H_e and H_f broadened first, indicating slowed rotation of the relevant benzene rings. Further cooling resulted in a resharpening of these peaks to a complex *ABCD*-type pattern (163K, CD_2Cl_2). The signals due to H_a, H_b, H_c and H_d

(a sharp singlet at elevated temperatures) broadened more slowly as the temperature was lowered and finally resharpened to appear at 163K as two apparent "singlets", only slightly broadened, at δ 7.00 and 6.53 (each 2H). The appearance of the well-resolved low-temperature spectrum is thus consistent only with the *cis* isomer of 7, H_a and H_b being chemically equivalent (as are H_c and H_d) and the slight residual broadening of their respective signals being primarily due to small *meta* couplings of the type J_{ac}. The electrocyclic ring closure is thus shown to be a thermal (disrotatory) process. An estimation of the barrier to rotation of the "unique" benzene ring in 7 ($\Delta\nu$ = 70 Hz, coalescence temperature *ca.* 250K) gives a value of *ca.* 50 kJ mol^{-1}.

Further studies of such dynamic processes in analogues of 2 incorporating a variety of naphthalene units are currently in progress.

Finally, chemical proof of the structure of 7 was provided by smooth DDQ oxidation to the terphenylparacyclophanediene 8, the structure of which was confirmed by high-resolution MS (Abs. mass 356.156, calc. for $C_{28}H_{20}$ 356.157) and 270 MHz ^1H NMR ($CDCl_3$), δ 6.81 (8H, m), 6.84 (4H, s), 6.91 (4H, *AB*m, J_{cis}= 12 Hz), 7.37 (4H, *AA'BB'*m).

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