

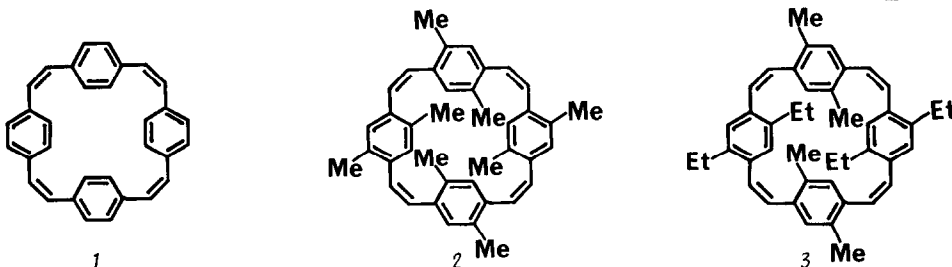
CORRELATED FLIPPING OF FOUR BENZENE RINGS IN
SUBSTITUTED [2.2.2.2]PARACYCLOPHANETETRAENES

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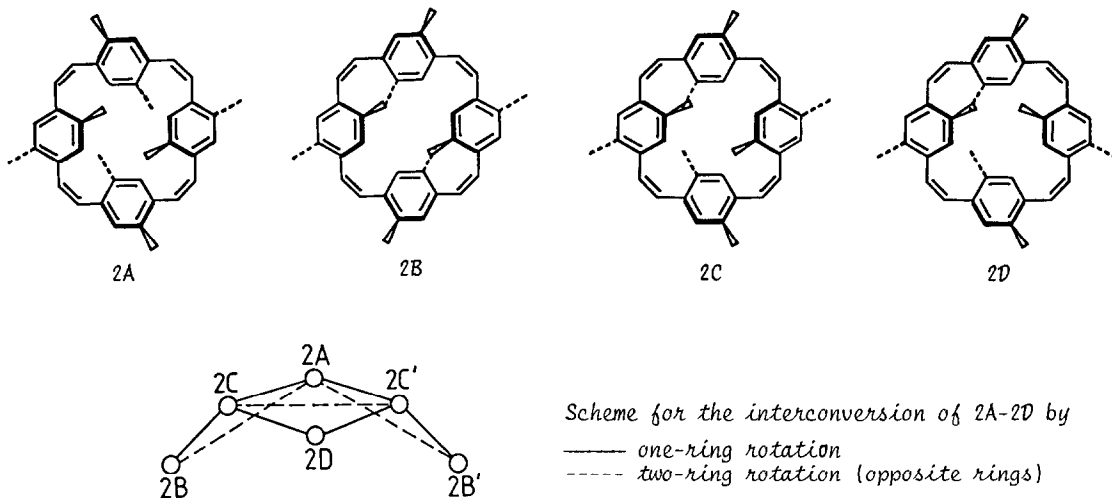
Abstract: Dynamic NMR spectroscopy and molecular mechanics calculations show that the flipping of the four benzene rings in certain substituted [2.2.2.2]paracyclophanetetraenes occurs in a correlated fashion.

The correlated rotation and flipping of benzene rings in, for example, tri- and tetra-aryl methanes can be conveniently studied by NMR spectroscopy and the results have contributed significantly to the understanding of dynamic processes in small crowded molecules.¹ The restricted rotation of the arene rings is most often due to severe steric crowding which confines the internal motion of the molecule to a relatively narrow, steep-sided, reaction path on the energy surface. In contrast, for compounds such as styrene and stilbene, with conjugated phenyl groups and olefinic double bonds, the relative energies of the various conformers are determined primarily by electronic factors, *i.e.* by the degree of π -electron delocalisation. However, the barriers to phenyl rotation in compounds such as stilbene are low enough to escape detection by presently available DNMR techniques, and the conformational interconversion of unsymmetrically substituted stilbenes most probably occurs by stepwise processes rather than *via* the correlated motion of both benzene rings. A recent investigation of triarylethylenes has shown the complexity and stereochemical consequences of restricted and correlated rotation and flip of the aromatic rings,² a major problem being discrimination between processes involving ring rotation and ring flip.³ We now present DNMR evidence, in a related case, for a correlated four-fold ring flip which can be observed separately, and distinguished, from processes involving ring rotation. The model compounds are macrocycles containing *cis*-stilbene units substituted with methyl- or ethyl groups, *viz.* [2.2.2.2] (2,5-dimethyl)paracyclophanetetraene, **2**, and a tetraethyltetramethyl [2.2.2.2]paracyclophanetetraene, **3**.



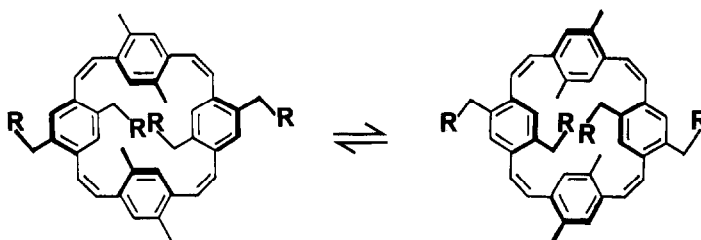
The unsubstituted [2.2.2.2]paracyclophanetetraene, 1, shows a simple ^1H NMR spectrum consistent with rapid rotation or flipping³ of the benzene rings down to -100°C .⁴ In the anion radical⁵ as well as the dianion and tetra-anion⁶ of 1 the rotation/flipping of the benzene rings is slowed to the extent that internal and external hydrogens can be distinguished at low temperature. Both the neutral compound and the charged derivatives maintain rather planar, sterically similar, conformations and the increased barriers in the charged species can be ascribed to electronic effects (*i.e.* loss of π -electron delocalisation as the phenyl groups rotate out of conjugation).

We have recently found that, in solution at room temperature, [2.2.2.2]-(2,5-dimethyl)paracyclophanetetraene, 2, exists mainly as one conformer, 2A, out of four reasonable conformers 2A-2D.⁷ This conclusion is supported by molecular mechanics calculations (Allinger's MMP2-scheme) which show that steric interactions between the methyl groups prevent the molecules becoming planar, and thus decrease the stabilising delocalisation of the π -electrons over the entire macrocyclic perimeter. The steric interactions between both adjacent and opposite methyl groups are minimised in conformer 2A, which represents a delicate balance between steric and electronic factors.



The ^1H NMR spectrum (270 MHz, CD_2Cl_2) of 2 shows only three sharp singlets (δ 6.90, 8H; 6.57, 8H; 1.97, 24H) at room temperature. On cooling the sample the signals first broaden and then reappear, below -70°C , as two singlets ($\Delta\delta$ 0.77) for the methyl protons, two singlets ($\Delta\delta$ 0.35) for the aromatic protons and an AB-pattern for the olefinic protons. The large chemical shift difference for the equally intense methyl singlets is better explained by a slowed dynamic process within one conformer, 2A, than by the slow interconversion of conformers 2A and 2B which would then have to be present in exactly the same amounts. (Isomers 2C and 2D should give more than one methyl proton signal each.) It should be noted that two rotamers are observed for 2,2',5,5'-tetramethyl[2.2.2.2]paracyclophanetetraene and these interconvert

only slowly at room temperature via rotation of the methyl-substituted benzene rings.⁴ The $\Delta\delta$ value for the methyl is small (0.05) and the two isomers are present in roughly a 2:1 ratio at room temperature. We thus conclude that the low temperature process in 2 is the correlated flipping of the four benzene rings as depicted below. The barrier to this process is calculated from the coalescence temperature and the chemical shift difference at slow exchange to be 10 kcal mol^{-1} . Inspection of CPK models reveals that the presence of the eight methyl groups obliges the flipping of the aromatic rings to occur in a correlated fashion. Three of the aromatic rings must be brought out of conjugation with the bridging vinylene groups before the fourth can flip. The other three rings can then follow and reattain their positions with maximum π -electron delocalisation. The hypothetical conformation of 1 with all four benzene rings orthogonal to the plane of the vinylene bridges is calculated (MMP2) to lie 20 kcal mol^{-1} above the ground state conformation, and this should represent an upper limit to the barrier in 2.



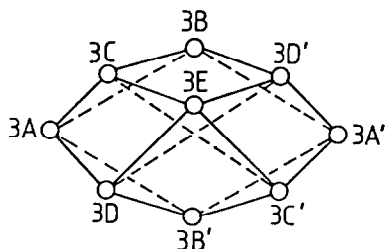
2A $R=H$ (S_4 -symmetry)

3A $R=CH_3$ (C_2 -symmetry)

Fourfold flip of the aromatic rings in 2A and 3A

Further support for the four-fold flip was obtained from analysis of the variable temperature ^1H NMR spectra of the tetraethyltetramethyl[2.2.2.2]-paracyclophanetetraene 3.⁷ In this less symmetrical cyclophane with five different conformers 3A-3E, benzene ring rotation will ultimately interconvert the mirror image forms (see scheme below) whereas a four-fold ring flip leads to an identical conformation in which inner and outer protons have exchanged sites. Thus the barrier to enantiomerisation is caused by hindered rotation whereas the barrier to exchange of inner and outer sites is caused by a hindered four-ring flip. At temperatures higher than 70°C the ^1H NMR spectrum of 3 shows the expected pattern of a triplet and a quartet for the ethyl groups, singlets for the methyls and the two types of aromatic protons, and an AB-pattern for the olefinic protons. On cooling the sample, the spectrum changes and the methylene proton quartet broadens and reappears at -20°C as two complex patterns which on decoupling of the neighbouring methyl protons collapse to an AB-pattern with $J_{\text{gem}}=15 \text{ Hz}$. All other signals remain essentially unchanged. This behaviour is consistent only with slow rotation

of the aromatic rings, *i.e.* a slow enantiomerisation process. The barrier was calculated from the coalescence temperature (32°C) of the decoupled spectra to 15 kcal mol^{-1} which is slightly lower than that in the tetramethyl derivative mentioned above ($16.5\text{ kcal mol}^{-1}$). The latter process must be a one-ring rotation whereas the former may be either a one- or a two-ring rotation (see scheme below).



Scheme for the interconversion of the five conformers 3A-3E and their enantiomers by
 ——— one-ring rotation
 - - - - - two-ring rotation (opposite rings)

The temperature dependence of the NMR spectrum of **3** shows that only one rotamer (**3A**) of the five possible is present in significant amounts at normal temperatures. On further cooling of **3**, the ^1H NMR spectrum changes rapidly and all peaks broaden and reappear as two new sets of peaks at -80°C (except for the signals for the olefinic protons). The barrier was calculated to 10 kcal mol^{-1} , from the chemical shift difference at low temperature and the coalescence temperatures for four pair of signals.

Conclusion. In suitably substituted macrocycles built from *cis*-stilbene units a correlated flip of four benzene rings has been observed by DNMR-techniques. The barrier to flip (10 kcal mol^{-1}) and the barrier to rotation (15 kcal mol^{-1}) of the aromatic rings can be measured separately in **3**. The former is believed to be essentially due to loss of π -electron delocalisation rather than due to steric crowding in the transition state.

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References and notes

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3. For a definition of rotation and flip see ref. 1 and 2. In [2.2.2.2]paracyclophanetetraenes rotation means that the plane of the aromatic ring passes the plane of the olefinic bridges whereas flip means that the plane of the aromatic ring passes a plane perpendicular to that of the four olefinic bridges.
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