New strained and chiral aromatic molecules

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Abstract: Substantial improvements in the synthesis of heterocyclic [2.2]meta-cyclophanes allow the preparation of new chiral medium membered ring skeletons. The enantiomers of triple layered and diagonally hetero-substituted cyclophanes have been separated chromatographically. Relationships between X-ray-structural results and the circular dichroism curves of the new phanes are studied.

There is a structural relation between "helicenes" and "phanes" with respect to overlapping aromatic rings as shown in the following scheme:

[7]helicene  helically wound cyclophanes

In order to maintain the chirality of the (open chained) helicenes, bridges must be introduced, leading to cyclophane ring structures 1). The smallest helical molecules of this type consist of only two benzene rings and two bridges. Whilst [2.2]metacyclophane (1) is achiral, the introduction of hetero atoms leads to chiral hetera[2.2]metacyclophanes like 2, 3 and 4, 5 which we described some time ago 2):

\[
1 \quad 2: X=O \quad 4: X=O, Y=S \\
3: X=S \quad 5: X=NTos, Y=S
\]

Recently we succeeded in synthesizing the phanes 6 and 7, in which the heteroatoms are placed diagonally in the bridges and which also proved to be chiral 3). The geometries of several of these phanes have been determined in detail by X-ray crystallography. The molecules are fixed in a step-type anti-conformation:
The barriers of racemisation were determined and are in the range of 130 - 140 kJ/mole. Interestingly, the racemisation barrier of the new oxa[2.2]naphthalenophane \( \text{8} \) was found to be as high (137 kJ/mole \( \approx \) 32.6 kcal/mole) as that of the corresponding oxa[2.2]metacyclopahne \( \text{2} \) (132 kJ/mole) \(^4\). Of course there are four intraannular hydrogen atoms in \( \text{8} \) and only two in \( \text{2} \), but the ring system is larger in \( \text{8} \) and ring strain can be distributed over more atoms. The c.d. curves for the enantiomers of \( \text{8} \) are shown in Fig.1.

Newer results presented in the lecture comprise the syntheses of the first heterocyclic and chiral triple layered metacyclopahnes like \( \text{9} \) \(^5\), new helical naphthaleno- and pyrenophanes \(^5\) and highly strained chiral [2.2]phanes \( \text{10} \) bearing intraannular substituents (R) for the first time \(^6\):

Some of these chiral molecules seem to be well suited for studying structure/chiroptic-correlations.

REFERENCES
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