

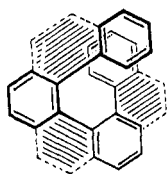
## New strained and chiral aromatic molecules

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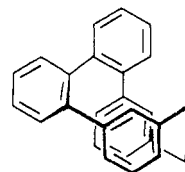
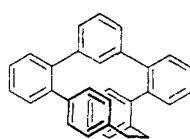
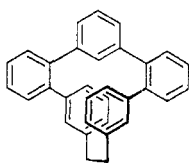
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**Abstract:** Substantial improvements in the synthesis of heterocyclic [2.2]meta-cyclophanes allow the preparation of new chiral medium membered ring skeletons. The enantiomers of triple layered and diagonally hetero-substituted cyclophanes have been 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:



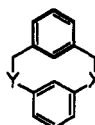
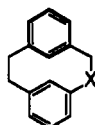
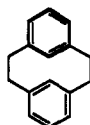
[7]helicene



helically wound cyclophanes

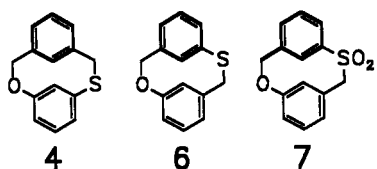
In order to maintain the chirality of the (open chained) helicenes, bridges must be introduced, leading to cyclophane ring structures <sup>1)</sup>.

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 hetero[2.2]metacyclophanes like 2, 3 and 4, 5 which we described some time ago <sup>2)</sup>:



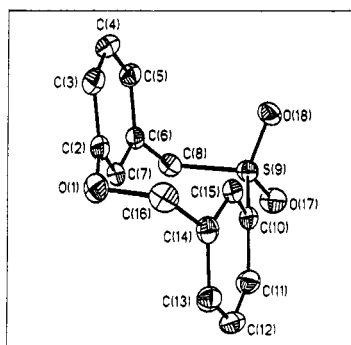
1    2: X=O    4: X=O, Y=S  
3: X=S    5: X=NTos, Y=S

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 <sup>3)</sup>. 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 **8** was found to be as high (137 kJ/mole  $\cong$  32.6 kcal/mole) as that of the corresponding oxa[2.2]metacyclophane **2** (132 kJ/mole)<sup>4</sup>.

Of course there are four intraannular hydrogen atoms in **8** and only two in **2**, but the ring system is larger in **8** and ring strain can be distributed over more atoms. The c.d. curves for the enantiomers of **8** are shown in Fig.1.



geometry of **7**

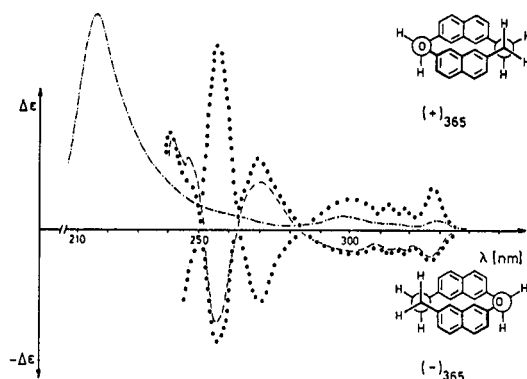
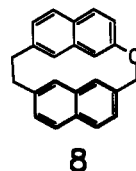
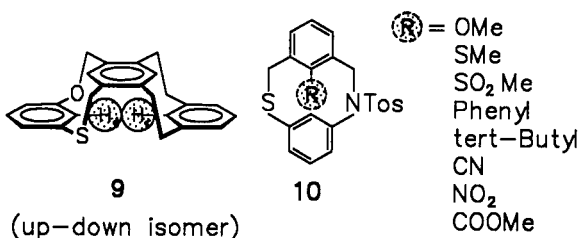


Fig.1. Circular dichroism curves of the enantiomers (···) and u.v. curve (- - -) of **8**

Newer results presented in the lecture comprise the syntheses of the first heterocyclic and chiral triple layered metacyclophanes like **9**<sup>5</sup>, new helical naphthaleno- and pyrenophanes<sup>5</sup> and highly strained chiral [2.2]phanes **10** bearing intraannular substituents (R) for the first time<sup>6</sup>:



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

#### REFERENCES

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