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METHANO-BRIDGED HETEROHELICENES.

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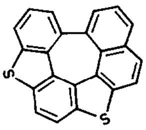
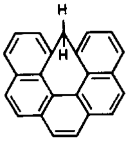
There is accumulating evidence[1], that aromatic systems, especially polycondensed aromatics, can exhibit conformational flexibility and should not be considered as rigid frameworks This flexibility is important for the helicenes, whose racemisation provides a quantitive tool for examining this phenomenon.

It occurred to us, that helicenes of varying conformation could be obtained by attaching alkano- (or other) bridges of varying length to suitable parts of the helical molecule[2]

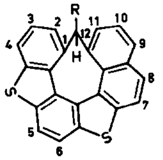
As can be seen by inspecting structures I, II, III and IV it seems likely that the aromatic system is planar in I proceeding to a "buckled" conformation in III Martin[3] recently reported the isolation of II in a review article, while compound I was prepared in this laboratory[4]



I



II



III R=H

IV R=CH_3

This paper deals with synthesis and structure proof of the two methano-bridged heterohelicenes III and IV. It is interesting to note that III and IV, when non-planar are asymmetric molecules, whereas II has probably at least one mirror plane and would be non-resolvable in that case

Simple models indicate a structure as shown in figure A for the methano-bridged heterohelicene III

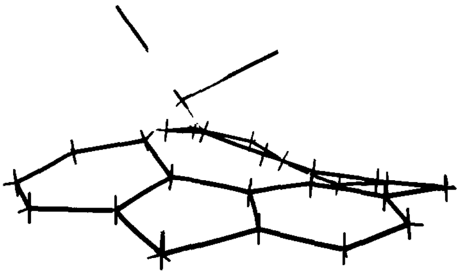
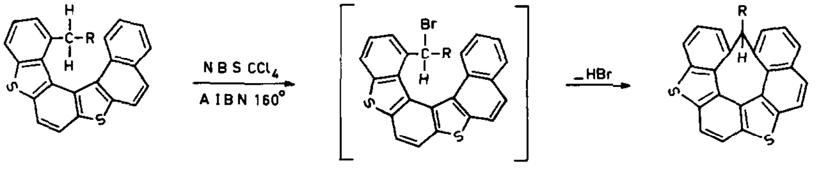


Figure A

Synthesis A solution of the 1-alkylheterohelicenes V and VI[5] in carbontetrachloride, containing one equivalent of N-bromosuccinimide and a trace of azoisobutyronitrile was stirred and placed in a preheated oilbath (160°) The mixture was maintained at this temperature for 20 minutes The 1-bromoalkylheterohelicenes VII and VIII, likely intermediates, could not be isolated. Instead evolution of hydrogen bromide occurred and the the methano-bridged compounds were isolated.



V $R=H$
VI $R=CH_3$

VII $R=H$
VIII $R=CH_3$

III $R=H$
IV $R=CH_3$

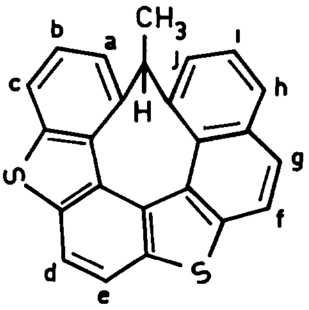
The yield of III was 35% Chromatography on alumina using benzene as eluens and extensive recrystallisation from benzene was needed to remove traces of bromine containing aromatic impuritie Although compound III (m p. 209-211°C) could not be obtained analytically pure, a correct exact mass was obtained.

The yield of IV was 76% An analytically pure sample of IV, m p 272-274°C, was obtained by extensive recrystallisation from benzene

The P.M R spectra The two aliphatic bridge-head protons of compound III show up as two doublets at δ· 3 90 p p m and δ. 5 09 p p m (J = 12Hz) This fact by itself is virtually conclusive evidence for the non-planarity of compound III We assigned the proton at δ 3.90 p p m as outside and the proton at δ. 5.09 p p.m as placed inside the inner core of the compound III, on the basis of deshielding effects of the aromatics and the spectral data of 1,1-diphenylethane (δ_H 4 05 p.p m , δ_{CH_3}. 1 58 p p.m).

For compound IV two configurations for the bridged carbon atom are possible the one with the methyl group situated above the inner core of the compound and the other one with the hydrogen in that position. A careful inspection of the P.M.R. spectrum of the crude reaction mixture revealed only one sharp doublet for the methyl (δ 1 62 p.p.m.) and a quartet for the hydrogen (δ 5 77 p p m), coupling constant 7 Hz, pointing to the presence of one isomer only Using the same criteria as above the configuration of IV is that one with the hydrogen atom over the inner core of the molecule, while the methyl group is on the outside

Table I P M R. data of aromatic protons of IV.*



	δ ppm		Hz.
H_a	7 50	J_{ab}	7 5
H_b	7 37	J_{ac}	1 1
H_c	7 53	J_{bc}	7 9
H_d	7.62	J_{de}	8 4
H_e	7.88	J_{fg}	8 6
H_f	7 62	J_{gh}	0 5
H_g	7 46	J_{hi}	8.0
H_h	7.55	J_{hj}	1 3
H_i	7.36	J_{ij}	7 3
H_j	7.62		

* a) solution in carbondisulfide,
b) chemical shifts in δ ppm

Proof for the fact that the methano-bridges were attached to the carbon atoms 1 and 12 of the molecule IV was given by the 100 Mc-spectrum, using INDOR techniques The coupling constants and the chemical shifts were obtained by the use of the iterative computer programme LAME The results as compiled in Table I show that there is no para coupling in the ABC systems, providing the structure as is given in IV

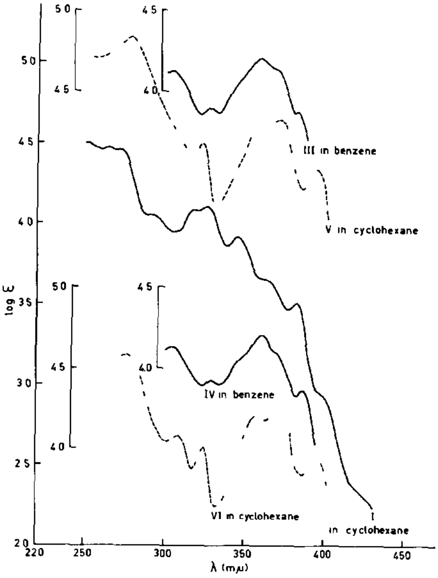


Fig. B The U V spectra

In the U V spectra of III and IV blue shifts of the α-bands (± 8 mμ) are observed, When compared with the corresponding bands of the alkylheterohelicenes (see fig B).

In contrast compound I has a red shift for the α-band. This might also indicate the non-planarity of the compounds III and IV.

Conclusion. The ease of ring closure from one deformated aromatic (e g V) to another bend molecule (e.g III) is further support for the idea, that aromatic rings may show surprising flexibility. An attempt to resolve these bridged-helicenes would be worthwhile

Acknowledgement We thank Dr. J H Dopper for stimulating discussions and Dr. J H Wieringa for his help in the interpretation of the P M R. spectra

References.

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