

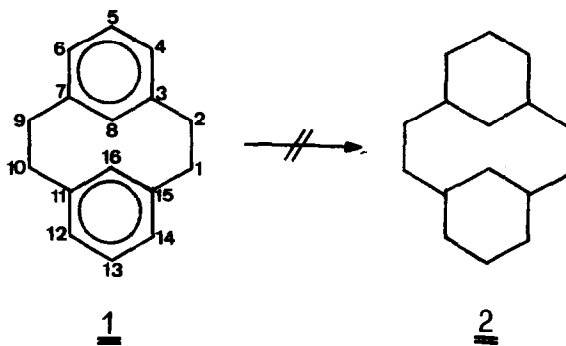
THE STRUCTURE OF THE HYDROGENATION PRODUCT OF [2.2]METACYCLOPHANE

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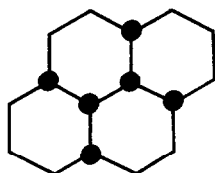
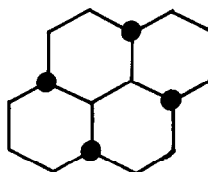
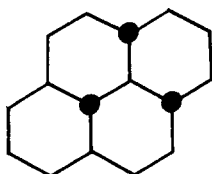
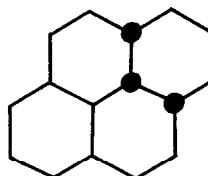
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In 1961, Allinger, Da Rooze and Hermann investigated the hydrogenation of [2.2]metacyclophane (1) and assigned to the product obtained (m.p. 174°) - more or less tentatively - the structure of a dodecahydro[2.2]metacyclophane (2)¹. In the course of our studies on the stereochemistry of chiral [2.2]metacyclophanes² we gained evidence that during the hydrogenation of 1 (with PtO₂ in acetic acid at 25° and atmospheric pressure) intramolecular cyclization between the positions 8 and 16 occurs to give a hexadecahydropyrene: the molecular ion peak in the mass spectrum of the hydrogenation product appears at m/e = 218, whereas 2 has a molecular weight of 220; moreover, the fragmentation pattern is typical for a perhydropyrene. No olefinic protons were detectable in the NMR spectrum. Consequently, the proposed structure 2¹ is incorrect and has to be revised.



Furthermore we have determined the configuration of this hexadecahydro-pyrene of m.p. 174° - one of the fourteen possible configurational isomers (excluding enantiomers of chiral species) - to correspond to stereoformula 6. So far, only one isomer (*viz.* 5, m.p. 103°) was described; its structure had been proposed on the basis of stability arguments deduced from equilibrium experiments³.

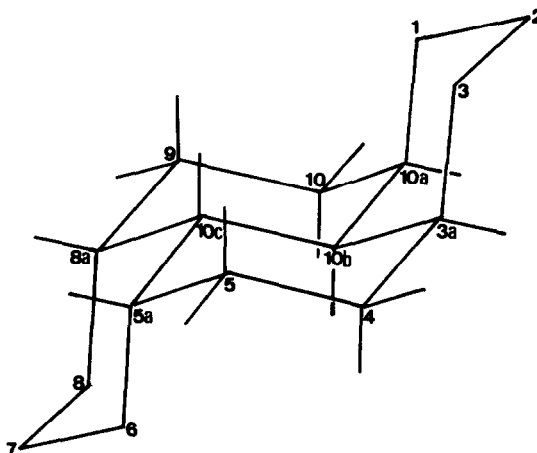
Our assumption in favour of a highly symmetric and rather rigid molecule - based on its high m.p. of 174° - was confirmed by the ^{13}C NMR spectrum; the ^1H decoupled spectrum exhibits five individual signals consistent with either C_{2v} or C_{2h} symmetry. The following structures are in accord with these symmetry requirements. 3 and 4 (C_{2v}) or 5 and 6 (C_{2h}).

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The final assignment of the correct configuration 6 was established by ^1H NMR studies at 100 MHz comparing the spectra of the perhydroproduct and of a selectively deuterated hydro-pyrene (at positions 3a, 5a, 8a and 10a) which was obtained from [2.2]metacyclophane (1) by catalytic "hydrogenation" in a deuterium atmosphere:

1. The protons at C-4, C-5 and C-9, C-10, resp., give rise to a partial spectrum of the AA'BB' type, just weakly perturbed by the protons at C-3a, C-5a and C-8a, C-10a, resp., which implies a dihedral angle of appr. 60 deg.

2. The same holds for the dihedral angle between these protons and those at C-10b and C-10c, resp.: the sharp singlet (protons at C-10b and C-10c) in the spectrum of the deuterated compound becomes slightly broadened in the hydrogenated product 6.



6

The perhydrophyrene 6 is made up of four fused cyclohexane rings in the chair conformation. A very remarkable feature of the hydrogenation of 1 to 6 is the preservation of symmetry (C_{2h}) as well as of topology.

Detailed papers on the deuteration experiments, the mechanism of the catalytic hydrogenation of 1 (including the structures of partially hydrogenated intermediates) as well as on the NMR analysis of 6 are in preparation.

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