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[6]METACYCLOPHANE AND RELATED COMPOUNDS

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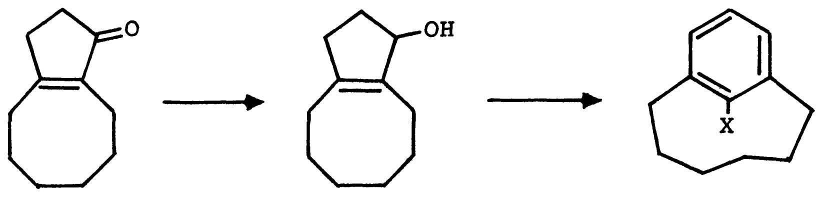
The title phane (IV) with the shortest aliphatic bridge among [n]metacyclophanes has been obtained from the enone I. The PMR spectra indicate the pseudorotation of the hexamethylene chain occurring with abnormally high energy barrier of 11.1 kcal/mol at -31.5°C for IV and 12.4 kcal/mol at -4.5°C for its 12-bromo derivative (III).

We wish to report the preparation of the highly strained metacyclophanes III-V according to the scheme as indicated below and also to refer to the conformational change as investigated by PMR temperature dependence.

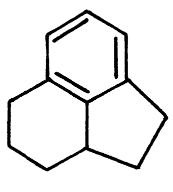
Condensation of cyclooctanone with diethyl succinate, followed by treatment with polyphosphoric acid and hydrobromic acid, gave the cyclopentenone I (28%, bp 96-101°C/ 4 mmHg, IR: 1694, 1646 cm^{-1}, m/e 164),1) which was reduced to II (91%, bp 95°C/0.3 mmHg, IR: 3320 cm^{-1})1) by means of lithium aluminum hydride. Treatment of II with $CHBr_3$-tert-BuOK gave a dibromocarbene adduct, which was thermolyzed (170-180°C/0.1 mmHg) without isolation to afford 12-bromo[6]metacyclophane (III) (25%, bp 97°C/0.18 mmHg, IR: 3063, 3044, 1562 cm^{-1}, m/e 238, 240).1) Lithiation of III (n-BuLi) and subsequent quenching (water) gave [6]metacyclophane (IV) (63%, bp 120°C/5 mmHg, IR: 3098, 3055, 3034, 1608, 1585 cm^{-1}, m/e 160)1) along with a transannular product (VI)2) (22%). Quenching with deuterium oxide gave V (61%, IR: 2268 cm^{-1}) and VI (15%). Irradiation of III (ethanol solution, 200-W high-pressure Hg arc, Pyrex filter, 3.5 hr) also gave VI (66%).3)

The PMR spectra4) of III and IV at room temperature (Fig 1.) clearly indicated the nonequivalence of benzylic methylene protons. In order to explain the observations we propose that the hexamethylene chain of IV resides in the one side of the aromatic ring and the flipping of the chain to the both sides does not occur. This is in contrast with the heptamethylene homolog5) and 2,5-dithia[6]metacyclophane.6) The temperature dependence of the PMR of IV is given in Fig 2. The multiplet (2H) at a relatively high field (δ 0.35) disappeared at -31.5°C and a new signal (1H)



I II III IV V

X = Br H D



VI

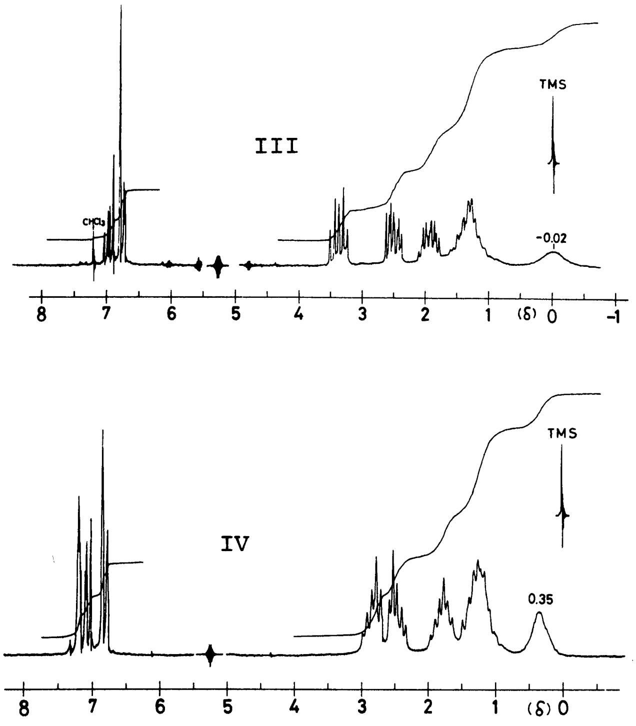


Fig. 1. PMR of III and IV. (100 MHz, $CDCl_3$, 31.5°C)

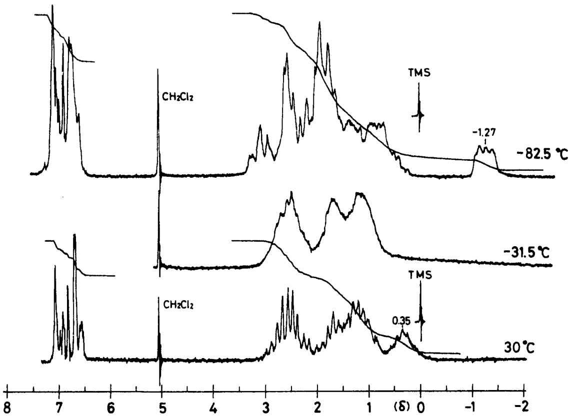
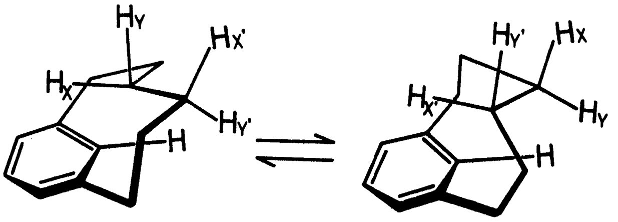


Fig. 2. PMR of IV, Temp. Dependence. (60 MHz, Freon 11)



IVa IVb

reappeared at δ -1.27 at a sufficiently low temperature (-82.5°C). The temperature dependence can be understood by assuming that IV exists in two conformers IVa and IVb, and at room temperature a rapid equilibrium between them is established by pseudorotation. The energy barrier of the pseudorotation in IV was estimated to be 11.1 kcal/mol (at Tc -31.5°C), and a higher value of 12.4 kcal/mol (at Tc -4.5°C) was obtained for the 12-bromo derivative (III). The relatively large barriers may be ascribed to the compressed structure. A fairly large valence angle expansion of the hexamethylene C-C bond angles is possibly required for the pseudorotation, which has otherwise to occur too close to the π electron cloud of the benzene ring.

Footnotes and References

1) All the new compounds gave the satisfactory analyses. All the IR refer to neat liquids and bp's to the bath temperatures.
2) The authentic sample was prepared by Clemmensen reduction of 2a,3,4,5-tetrahydroacenaphthen-1-one (J. v. Braun and J. Reutter, Ber., **59**, 1922 (1926)).
3) The transannular photocyclization is characteristic to the compressed systems, for example, see: W. E. Parham, D. R. Johnson, and C. T. Hughes, J. Org. Chem., **35**, 1048 (1970); see also: T. Hiyama, S. Fujita, and H. Nozaki, Bull. Chem. Soc., Japan, **44**, 3222 (1971).
4) The aromatic signals appeared at a field 0.1-0.3 ppm higher than those of [7]metacyclophanes. This indicates that the benzene nucleus is more strained than that of the heptamethylene homologs. As to the similar discussion, see ref. 5.
5) S. Fujita, S. Hirano, and H. Nozaki, Tetrahedron Letters, 403 (1972).
6) F. Vögtle, Tetrahedron, **25**, 3231 (1969).

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