[2.1.1]Metacyclophane[1]

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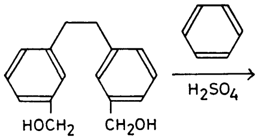
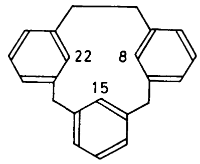
Recently interest has been shown in the chemistry of multi-benzene cyclophanes.[2] We wish to report the preparation and conformational studies of [2.1.1]metacyclophane. The compound was obtained *via* new cycloalkylation, in which a benzene molecule was incorporated in the cyclic system as a *m*-phenylene unit.

Slow addition of a benzene solution containing 3,3′-bis(hydroxymethyl)bibenzyl[3] to concentrated sulfuric acid at room temperature in course of 20 hr produced a mixture of hydrocarbons from which 22.8% of bis-phenylation product, 3,3′-dibenzylbibenzyl, and a crystalline material having a formula $C_{22}H_{20}$ was isolated by column chromatography on Florisil (eluted by *n*-hexane-benzene).





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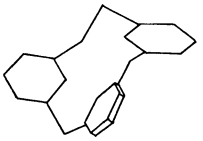

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The C_{22} hydrocarbon was obtained as colorless needles, mp 130—132°C, in 17% yield. Found: C, 92.74; H, 7.14%. Calcd for $C_{22}H_{20}$: C, 92.21; H, 7.09%. Spectral data suggested a cyclic structure in which benzene was cycloalkylated by diol. It showed a parent peak at *m/e* 284 together with abundant $P-91$, $P-106$ and $P-119$ peaks. Convincing evidence for the suggested structure was obtained by NMR spectra, which showed singlets at δ 2.78 (ethylene) and 3.60 (methylene) and three groups of absorption for the arylprotons at δ 6.27 (2H), 6.49 (1H), and 6.90 (9H). The upfield shift of two-proton and one-proton aryl signals which can be assigned to $C_{8,22}$ and C_{15} protons, respectively, suggests a metacyclophane structure. They appeared as triplets with $J=1.74$ Hz (*m*-coupling) by irradiating the benzyl methylene signal at 3.60.

The upfield shift of inner aryl protons favors the stepped conformation Ia (C_2 symmetry) over a folded one (C_s symmetry), in which two benzene rings take an overlapping arrangement. This was also supported by the UV spectrum determined in *n*-hexane, which showed benzenoid bands at 250 (ε 726), 265 (787), 270 (626) and 274 mμ (537). The absorption curve is quite similar to the overlapping spectra of *m*-xylene and diphenylmethane.

Comparison of the UV spectrum of I with that of [2.2]metacyclophane[4] reveals that anomalies associated with bent benzene structure and transannular electron interaction found in the latter compound no longer prevail, suggesting that the 13-membered ring would be quite free to undergo conformational changes. This was further confirmed by low temperature NMR spectroscopy, which showed that both the methylene and ethylene signals stayed singlets over a wide range of temperature. They showed slight broadening only at low temperatures, the half-height width being doubled at −100°C.

Attempts to obtain [1.1.1]metacyclophane by a similar reaction of bis(3-hydroxymethylphenyl)methane failed and gave only bis-phenylation product in 60% yield. Similarly the treatment of 1,2-bis(hydroxymethyl)benzene under the same conditions gave *o*-dibenzylbenzene in 64% yield.

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