entirely to the optimum affinity of cyclohexaamylose for the activated complex. This is equivalent to saying that, in the ground state, a portion of the free energy gained from association of cyclohexaamylose with **1** is used to impose the orientational restriction, thereby decreasing the stability of the inclusion complex by an amount equal to the rate acceleration.

In conclusion, orientational catalysis by cyclohexaamylose supports the suggestion that binding forces between an enzyme and its substrate can be used to overcome part of the free-energy barrier to activation.[8] The cyclohexaamylose-induced rate acceleration, however, is much smaller than rate accelerations which can be achieved by converting intermolecular to intramolecular reactions.[9] Consequently, when the reacting groups in an intramolecular reaction can assume a mutually favorable orientation without introducing strain elsewhere in the system, the imposition of rigid orientational restrictions apparently leads to only a small additional rate acceleration.

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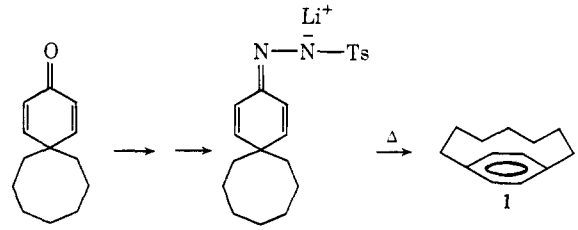
[7]Paracyclophane[1]

Sir:

The smallest known [*m*]paracyclophane[2] is the $m = 8$ isomer, first described over 11 years ago.[3] The synthesis of [8]paracyclophane was an indirect one and not obviously extended to the lower homologs.[4] A more conventional ring contraction route succeeded in providing [8]paracyclophanecarboxylic acid,[5,6] but [7]paracyclophane (**1**) has evaded synthesis for over a decade.[4]

We report here a simple, one-step synthesis of **1** and a few of the properties of this smallest of the known [*m*]paracyclophanes.

Our route was suggested by the observation that 4,4-dimethylcyclohexadienylidene[7] rearranged to *p*-xylene on generation in the gas phase.[8] Accordingly, we synthesized[9] spiro[5.7]trideca-1,4-dien-3-one (**2**) and converted it to the lithium salt of the corresponding tosylhydrazone. Flash pyrolysis of this material at 360–380° (0.1 Torr) gave a material which was resolved by gas chromatography into two peaks in the ratio 1.4/1. The yield was approximately 20%.[11] The first product was a mixture of 1-phenylheptane and 7-phenylheptene-1 (nmr analysis), and the second was the anticipated **1**.



2 1

A precise mass measurement established the formula as $C_{13}H_{18}$ (calcd, 174.14084; found, 174.14078). The nmr spectrum, which closely resembled that of [9]paracyclophane[12] (CCl_4, singlet, τ 2.93, 4 H; triplet, τ 7.36, 4 H, $J = 6.5$ Hz; sym mult, τ 8.5–9.5, 8 H; sym mult, τ 10.3–10.9, 2 H), is consistent only with **1**. Benzocyclononene is eliminated by a comparison of nmr spectra,[13] and one would not expect a singlet for the aromatic protons of [7]metacyclophane.[14] Further, the ultraviolet spectrum reported for [8]metacyclophane (266 nm, log ϵ 2.4)[15] does not compare well with that of **1**.

The ultraviolet spectrum of **1** (EtOH, nm (log ϵ), 216 (4), 245 (4), 283 (3)), does match well with that predicted by Allinger and coworkers,[4,5] 210 (4), 247 (3), 288 (2), and thus the aromatic ring is probably substantially deformed. A precise determination of the amount of bending must await the determination of the structure of **1** or a derivative, however.

Speculation on the mechanism of formation of **1** is premature, but leading possibilities include direct ring migration or carbon–carbon insertion to give a bridged Dewar benzene that subsequently opens to **1**.

(1) Support for this work by the National Science Foundation through Grant GP-30797X and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged (5528 ACl,4).
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Electron Nuclear Double Resonance of Bacteriochlorophyll Free Radical *in Vitro* and *in Vivo*[1]

Sir:

This is a preliminary account of the first electron nuclear double resonance (endor)[2] studies of bacterio-

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.
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