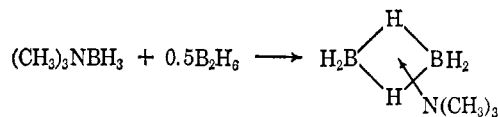


Thermodynamic data available for a number of years also speak against structure II. Consider the reaction



The heat of formation of $(\text{CH}_3)_3\text{NBH}_3$ in solution from diborane and trimethylamine is about -22 kcal/mole.⁴ From a thermochemical cycle it can be seen that for the reaction to be exothermic, the heat of formation of structure II would have to exceed that of $(\text{CH}_3)_3\text{NBH}_3$. We doubt that such an amount of energy is available from interaction of a vacant nonbonding orbital with an electron donor as Eastham² envisions.

Even the direct reaction of diborane with an amine offers little hope of preparing and identifying structure II. It is well known that such a reaction will produce either a simple adduct, LBH_3 , or an analog of the diammoniate of diborane, $\text{BH}_2\text{L}_2^+\text{BH}_4^-$, at temperatures as low as -78° . Only on rare occasions, under extremely mild conditions of reaction, has a metastable intermediate species been suggested.⁵ Such conditions were used by Rathjens and Pitzer to study, calorimetrically, solutions of diborane in ammonia.⁶ Freezing point depression studies showed it to be molecular containing two boron atoms per mole. It was not $\text{H}_2\text{B}(\text{NH}_3)_2^+\text{BH}_4^-$, but it must have been the precursor to this compound.⁷ While there is no direct information to distinguish the material studied by Rathjens and Pitzer⁶ as either structure I or structure II, we believe that the measured heat of reaction between diborane and ammonia to form this two boron atom species (-16 kcal/mole) suggests that structure I was formed.

The principal experimental argument on which structure II is based rests in the claim² that the boron-11 nmr spectrum assigned to structure I¹ is "virtually superimposable on the first boron-11 nmr spectrum published 12 years ago by Ogg."⁸ It should be recognized, however, that Ogg's spectrum was taken at 6 Mc while our spectrum was taken at 19.25 Mc. There is in fact a marked difference between the spectra in methylene chloride at 19.25 Mc.¹ The diborane spectrum consists of nine well-resolved lines (a triplet of triplets), in contrast to the relatively poorly resolved septet assigned to structure I.

Eastham² has generalized structure II, suggesting that all compounds which were formerly considered to be singly bridged analogs of structure I are in fact intact diborane molecules with the ligand attached symmetrically. In the case of B_2H_7^- , the boron-11 nmr spectrum is not ambiguous; the only reasonable interpretation favors a single hydrogen bridge, $\text{H}_3\text{B}-\text{H}-\text{BH}_3^-$.⁹ If there is a problem with the boron-11 spectrum assigned to structure I,¹ it probably arises from a complicating exchange process; we are looking into this possibility.

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S. G. Shore, C. L. Hall

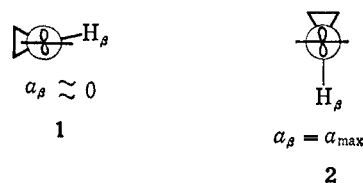
Evans Laboratory of Chemistry
The Ohio State University, Columbus, Ohio

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Preferred "Symmetrical" Cyclopropyl Conformations in Hydrocarbon Anion Radicals

Sir:

Much interest has recently focused on the conformations of cyclopropyl rings joined to potentially conjugating centers. "Bisected" cyclopropyl conformations (**1**) appear to have been established as absolute conformational energy minima for the dimethylcyclopropylcarbinyl cation,¹ cyclopropylcarboxaldehyde,² cyclopropyl methyl ketone,³ cyclopropylcarbinyl chloride,⁴ phenylcyclopropane,⁵ vinylcyclopropane,⁶ and cyclopropylsemidiones.⁷ It therefore seems desirable to call attention to two species, both hydrocarbon anion radicals, in which the "symmetrical" conformation (**2**) of cyclopropyl is preferred over the "bisected" conformation.



Equation 1 is generally accepted as approximating the conformational dependence of the hyperfine splitting constant, a_β , of a hydrogen β to a carbon 2p orbital having spin density ρ_i ; θ represents the angle between the β C-H bond and the relevant p orbital.⁸

$$a_\beta = \rho_i a_{\max} \cos^2 \theta \quad (1)$$

Thus **1** should be characterized by $a_\beta \approx 0$ and **2** by $a_\beta = a_{\max}$. Although a_{\max} is not directly measurable, $a_\beta(\text{CH}_3) = 0.5a_{\max}$ by application of (1). Thus, $C(R) = a_\beta(R)/a_\beta(\text{CH}_3)$ is a measure of the predominance of form **1** or **2**; specifically, if $C(R) < 1$, **1** is preferred; if $C(R) > 1$, **2** is preferred. The range of $C(R)$ is $0 < C(R) < 2$.⁹ Table I gives values of $C(R)$ for various 9-substituted anthracene and 1,4-disubstituted naphthalene anion radicals. In both cases the symmetrical cyclopropyl form is favored. These appear to be the first reported instances of preferred symmetrical cyclopropyl conformations. In all other cases previously studied, q_i , the excess charge density present in the relevant p orbital, is zero or positive.¹⁰ Thus it is reasonable to assume that the change in the conformational preference

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(9) The approximation is made that all β C-H bonds have approximately equal a_{\max} .

(10) Even in the semidione anion radical systems q_i is calculated (HMO) to be positive ($\sim +0.10$).

of cyclopropyl may be related to the change in sign of q_i . Either torsional or conjugative effects could account for this. If it is correct to assume internuclear, as opposed to bent, cyclopropyl bonds, torsional effects should clearly favor **2**. Thus, where conjugative effects are small, as they might be in an anionic species, the resultant could favor **2**. The interesting possibility that anionic cyclopropyl conjugation has a different conformational preference than cationic conjugation also deserves serious consideration. It should be recalled that the Walsh model of cyclopropane has a quasi-cyclopropenyl system internal to the ring which could be more effective at accepting an electron pair than the external (to the ring) p system, which is so adept at electron-pair donation. Delocalization into the former would require the symmetrical conformation **2** observed for the anion radicals. Steric effects seem to be ruled out by the fact that $C(R)$ is approximately the same in both anion radicals cited, whereas steric repulsions should be more pronounced in the 9 position of anthracene than in the 1 position of naphthalene.

In contrast to the anion radical, and as expected, 9-cyclopropylanthracene's cation radical has $C(R) = 0.6$, *i.e.*, favoring the bisected form.

We have calculated the energy difference, ΔE_{SB} , between the symmetrical and bisected conformations by using eq 2, which embodies eq 1 and the integrated

$$C(R) = \frac{a_{\beta}(R)}{a_{\beta}(CH_3)} = \frac{\int_0^{\pi/2} e^{-\Delta E \cos^2 \theta / RT} \cos^2 \theta d\theta}{\frac{1}{2} \int_0^{\pi/2} e^{-\Delta E \cos^2 \theta / RT} d\theta} \quad (2)$$

Boltzmann equation. The conjugational (or torsional) energy was assumed to be of the form $E = \Delta E_{SB} \cos^2 \theta$. Integrating (2) for various values of ΔE_{SB} at the temperatures of interest gives $C(R)$, which can be compared with the experimental value. For both anion radicals $\Delta E_{SB} = -0.9$ kcal. This value is essentially unaffected if a potential of the form $E = \Delta E_{SB} \cos \theta$ is assumed. The 9-cyclopropylanthracene cation radical yields $\Delta E_{SB} = +1.0$ kcal. Thus the anion and cation radicals of 9-cyclopropylanthracene have ΔE_{SB} values which are nearly equal in magnitude but of opposite sign.¹¹

Table I

Substrate ^a	Charge type	α_{β}	α_{γ}	$C(R)$
9-Methylanthracene (1)	Anion radical	4.27		1.00
9-Ethylanthracene (2)	Anion radical	2.5		0.59
9-Isopropylanthracene (3)	Anion radical	0.62		0.14
9-Cyclopropylanthracene (4)	Anion radical	6.64	0.17	1.55
1,4-Dimethylnaphthalene (5)	Anion radical	3.26		1.00
1,4-Dicyclopropylnaphthalene (6)	Anion radical	4.77	0.17	1.46
9-Methylanthracene (7)	Cation radical	7.79		1.00
9-Ethylanthracene (8)	Cation radical	3.6	0.3	0.46
9-Isopropylanthracene (9)	Cation radical	1.6	0.16	0.20
9-Cyclopropylanthracene (10)	Cation radical	4.8	0.26	0.62

^a The anion radicals were generated using sodium or potassium in THF and the spectra recorded at -50 to -70° . The cation radicals were generated using concentrated sulfuric acid and the spectra recorded at ambient temperatures.

(11) The q_i at the 9 position of anthracene is calculated (HMO) to be $\sim \pm 0.19$ in the cation and anion radicals ($\rho_i = 0.19$).

Work is in progress to distinguish between torsional and conjugative effects as the cause of symmetrical cyclopropyl conformations in anionic species.

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N. L. Bauld, R. Gordon, J. Zoeller, Jr.

Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

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Mechanism of Photochemical Alcohol Addition to α,β -Unsaturated Ketones

Sir:

Many examples of photochemical solvent addition to α,β -unsaturated carbonyls have been reported,^{1,2} but few have been concerned with the stereochemistry³ and none with the mechanism of the reaction. We report here the more germane aspects of the mechanism of alcohol addition to 1-acetylcyclohexene (I). The reaction occurs readily with methanol, ethanol, and *t*-butyl alcohol in the condensed phase to give mixtures of *cis* and *trans* adducts (II-IV) in yields and with compositions shown.⁴ Reactions were carried only to 35-55% conversion to minimize secondary photochemical reactions (fragmentation) of the photoadducts which occur more efficiently than the photoaddition itself.⁵ The predominance of *cis* product in each mixture clearly indicates that the stereochemistry of products is kinetically rather than thermodynamically dictated. A parallel is noted in the stereochemistry of enol ketonization which appears to be governed by the direction of approach of the proton donor.^{6,7} Evidence for the intermediacy of enols in the I \rightarrow IV addition was obtained both by oxygenation studies and by direct observation.

The irradiation of an oxygen-saturated solution of I in *t*-butyl alcohol followed by hydrogenation of hydroperoxide intermediates afforded V (15%),⁸ VI (40%), and VII (14%).⁴ Very interesting results were obtained from experiments involving irradiation followed by oxygenation in the dark. No V was formed, and the *trans*:*cis* ratio of alcohols (VI and VII) dropped to 40:60 as the ketonization reaction became competitive. It is thus clear that two enols are produced and

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(4) All new compounds have expected spectral properties and gave correct analytical data. Stereochemical assignments are based on unambiguous independent syntheses and/or *cis-trans* equilibration studies.

(5) This was demonstrated in experiments using pure IV. The light-absorption properties of I are such as to "protect" IV during the early stages of photoaddition. The use of a filter would be expected to permit higher conversions of I to IV.

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