proximate lone pair of electrons has now been established for aldimines and oxaziridines.[1c] In all likelihood, this is also the case for formaldoxime and is probably a general phenomenon. We are presently examining the barrier to interconversion in *N*-alkylaldimines and will present these results, along with the details of the tickling experiments, separately.

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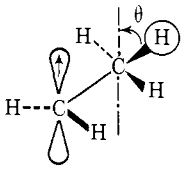
Pseudocontact and Contact Shifts for 6-Aminobenzobicyclo[2.2.2]octene and 2-Aminotriptycene. The Sign of B_0[1]

Sir:

The conformational preferences of radicals may be



studied *via* their β-proton epr coupling constants.[2] These constants are related to the average dihedral angle $\langle\theta\rangle$ through eq 1 where $\rho_C{}^{\pi}$ is the p orbital

$$a_\beta = \rho_C{}^{\pi}(B_0 + B_2\langle\cos^2\theta\rangle) \qquad (1)$$

spin density, and B_0 and B_2 are constants near 0 and 50 G, respectively.[2] For anion radicals with structural constraints which require θ to be 90°, a_β is very small, suggesting that $|B_0/B_2|$ is no more than 0.03.[3] Consequently, the B_0 term is often neglected in the conformational analyses.[2] Recently, studies of a_β have been undertaken to assess rotational barriers and to detect structural changes in substituted ethyl radicals, *e.g.*, 2-chloroethyl[4] or cyclopropylcarbinyl.[5] To illustrate, a_β for cyclopropylcarbinyl radical is smaller than estimated by the usual B_2 constant. One interpretation attributes the small a_β to a negative B_0 with B_0/B_2 about -0.04.[5a] Another view adopts the positive B_0 and B_2 values suggested by the INDO model[6] and identifies the decrease in a_β with a structural change.[5b] Knowledge of the sign and magnitude of B_0 is central to an evaluation of these explanations and to a more secure basis for the discussion of β-proton constants. Theory has provided divergent answers, the INDO model[6] suggests that B_0 is positive with $B_0/B_2 = 0.04$ whereas another analysis[7] infers that B_0 is negative with $B_0/B_2 = -0.02$. To resolve this problem, we have estimated the sign and magnitude of B_0 by study of the contact shifts resulting from the interaction of nickel acetylacetonate with xylidine derivatives,[8] **1**–**4**, including **2** and **3** in which θ is 90°.

For **2** the bridgehead proton resonances at 270 MHz appear as two broad singlets centered at δ 2.803 and 2.835. For **3**, these resonances are somewhat narrower singlets centered at δ 5.236 and 5.270. To assign these resonances we measured the pseudocontact shifts experienced by **1**–**3** in the presence of Pr(fod)$_3$,[9] Table I.

Table I. Pseudocontact Chemical Shifts for 3,4-Xylidine Derivatives

Amine	Relative pseudocontact shift[a]			
	H_2	H_3	$H_{\beta 1}$	$H_{\beta 2}$
1	1.00	0.30	0.168	0.178
2	1.00	0.33	0.215[b]	0.232[c]
3	1.00	0.38	0.161[b]	0.176[c]

[a] The relative pseudocontact shifts, $\Delta H_i/\Delta H_2$. The pseudocontact shift for the ortho proton is positive in each case. [b] The upfield signal of the methine hydrogen atoms at 270 MHz. [c] The downfield signal of the methine hydrogen atoms at 270 MHz.

The fixed geometric relationship between the amino group and the β protons of **2** and **3** allows the assignment of the signal experiencing the larger pseudocontact shift to $H_{\beta 2}$, Table I. Tori and his associates similarly assigned the upfield signal of the β protons of **4** to $H_{\beta 1}$.[10]

Contact shifts, ΔH_i, measured in the usual way,[8,11] are presented relative to the shift, ΔH_2, for the ortho proton, **1**-**4**. The observations for all the aromatic protons are in accord with previous work[8,11,12] with positive shifts for the ortho protons (negative a_2) and negative shifts for the meta protons (positive a_3) indicative of positive spin density at the 2 and 4 positions and negative spin density at the 3 position. The upfield shifts for $H_{\beta 2}$ (negative $a_{\beta 2}$) and the downfield shifts for $H_{\beta 1}$ (positive $a_{\beta 1}$) observed for **1** and **4** are also in accord with earlier studies and reflect the dominance of the $B_2\langle\cos^2\theta\rangle$ term when $\theta < 90°$. On the other hand, in **2** and **3**, where $H_{\beta 1}$ and $H_{\beta 2}$ are constrained to

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(1) This research was supported by the National Science Foundation.

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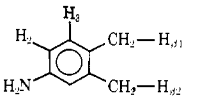
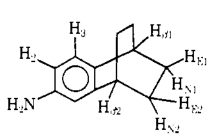
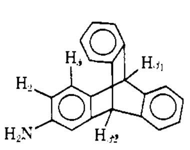
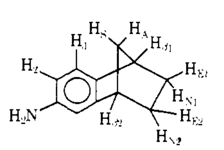








1		**2**				**3**		**4**[10]			
Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$
2	1.00	2	1.00	E1	−0.331	2	1.00	2	1.00	E1	−0.325
3	−0.49	3	−0.46	E2	0.080	3	−0.44	3	−0.40	E2	0.082
β1	−1.155	β1	0.069	N1	0.029	β1	0.055	β1	−0.156	N1	0.015
β2	0.391	β2	−0.048	N2	−0.033	β2	−0.033	β2	0.075	N2	0.0
										S	0.013
										A	−0.096

the nodal plane, the nickel reagent shifts the resonance of $H_{\beta1}$ upfield and that of $H_{\beta2}$ downfield. Thus, $a_{\beta1}$ is negative and $a_{\beta2}$ is positive. The contact shifts for the endo and exo protons of **2** are similar to the results for the heptane derivative, **4**.[10]

Values of B_0/B_2 may be assessed for $H_{\beta1}$ and $H_{\beta2}$ in both **2** and **3** using eq 2 (see Table II)

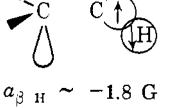
$$\frac{B_0}{B_2} = \frac{1}{2}\left[\frac{\Delta H_{\beta\text{-CH}_3}/\Delta H_2}{\Delta H_{\beta\text{-H}}/\Delta H_2} - 1\right]^{-1} \tag{2}$$

Table II. Values of B_0/B_2 Calculated from Equation 2

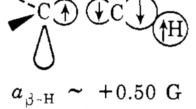
Amine	B_0/B_2 $H_{\beta1}$	$H_{\beta2}$
2	−0.028	−0.055
3	−0.023	−0.039

where $\Delta H_{\beta\text{-CH}_3}/\Delta H_2$ and $\Delta H_{\beta\text{-H}}/\Delta H_2$ are the contact shifts for the β protons relative to the shifts for the ortho protons. This analysis assumes that the distribution of spin density in the aromatic nuclei of **1–4** is sensibly constant and that $\langle\theta\rangle$ is 90° for $H_{\beta1}$ and $H_{\beta2}$ in the bicyclic molecules **2** and **3** and 45° for the freely rotating methyl groups in the xylene.[13]

The values of B_0/B_2 range from −0.023 to −0.055, with $|B_0/B_2|$ somewhat smaller for the triptycene **3**.[14] With B_2 about 50 G, these observations indicate that B_0 is about −1.5 G for protons constrained to the nodal plane. This finding conflicts with the predictions of the INDO model, but agrees with the analysis presented by Colpa and de Boer.[7] They propose than spin delocalization occurs most effectively *via* valence bond structure IA with a lesser role for IB. The importance of IA



$a_{\beta\text{ H}} \sim -1.8$ G
IA



$a_{\beta\text{-H}} \sim +0.50$ G
IB

may be enhanced by electronegative substituents with a decrease in a_β, for example in a 2-haloethyl radical.[15] In summary, we find B_0 is small, negative, probably only modestly influenced by hybridization changes, and presumably dependent on the dihedral angle.[5a]

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[13] Several approaches can be used to estimate B_0/B_2. All analyses, however, yield similar results.

[14] The change may reflect the change in hybridization of the exocyclic carbon bonding orbital from 25% s character in **2** to 28% s character in **3**.

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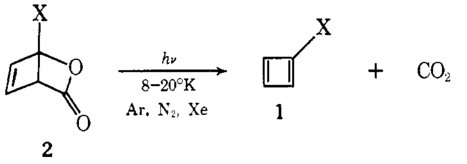
Cyclobutadiene. II. On the Geometry of the Matrix-Isolated Species

Sir:

Lin and Krantz[1] recently provided the first physical evidence for the structure of cyclobutadiene (**1a**) (the object of an intensive search since Kekulé's abortive attempt 100 years ago)[2–11] generated as a primary prod-



a, X = H
b, X = D

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[7] For discussions of cyclobutadiene as an antiaromatic prototype, see R. Breslow, *Sci. Amer.*, **227**, 32 (1972); *Pure Appl. Chem.*, **28**, 111 (1971), and references therein.

[8] For stable cyclobutadienes see R. Gompper and G. Seybold, *Angew. Chem.*, **80**, 804 (1968); H. Kimling and A. Krebs, *Angew. Chem.*, **84**, 952 (1972).

[9] Professor O. L. Chapman has recently obtained similar results from the irradiation of α-pyrone confirming the previously published report of Lin and Krantz.[1]

[10] For reviews of cyclobutadiene, see (a) W. Baker and J. F. W. McOmie in "Non-Benzoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., Chapter II, 1959; (b) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **1**, 519 (1962); (c) G. Subrahonanyam, *J. Sci. Ind. Res.*, **26**, 158 (1967); (d) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

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