demonstrated by comparison of its electronic spectrum (Figure 3) with that of BChl$\cdot^{-}$. Noteworthy similarities are bleaching of the intense ir band, uv band(s) shifting to higher energies, and appearance of an absorption with vibrational structure in the region 800–1100 nm. Furthermore, both spectra agree well with the general features of metallotetrahydroporphyrin anion radical spectra calculated with π-electron closed-shell[23] or open-shell SCF theories.[8] For example, open-shell computations give the following transition energies (dipole oscillator strengths) to compare with experimental findings: 1020 nm (0.17), 710 (0.09), 565 (0.002), 520 (0.15), 339 (0.85), 325 (0.87), 312 (2.09).

The hfs observed in the epr spectrum of ZnTPBC$\cdot^{-}$ and selectively deuterated compounds (Figure 2e) permits the following assignments (see Figure 3 for numbering): four β-pyrrole protons, $a_{H_7} = 1.80$ G; eight CH_2 protons, $a_{H_2} = 0.70$ G; two nitrogen nuclei, $a_N = 2.88$ G, and an additional splitting of $a_H \sim 0.1$ G due to phenyl protons. Hyperfine constants calculated from SCF–MO spin densities and McConnell relationships are $a_{H_7} = 1.62$ G, $a_{H_2} = 0.62$, $a_{N_{21}} = 2.72$, and $a_{N_{22}} = 0.42$. On this basis the experimental nitrogen splitting is assigned to N_{21}.

Although its identity remains uncertain, some properties presently attributed to the primary acceptor are readily distinguished from those found for BChl$\cdot^{-}$. Thus, the acceptor has an epr signal[13,15] at $g = 2.005$ with a line width of 7–8 G, and no hfs (*vs.* $g = 2.0028$, 10-G line width, and 12 resolved lines); a possible optical absorption[12,14,17] at *ca.* 430–455 nm with no significant absorption from 900 to 1100 nm (*vs.* no increase in absorption at 450 nm but characteristic ir absorption); and a midpoint potential[13,24–26] of -0.05 to -0.20 V (*vs.* $E_{1/2} = -0.84$ V *vs.* SHE). In contrast to the favorable comparison of properties of oxidized Chl or BChl with photooxidized reaction centers[4,6,7,27,28] which has led to the identification of Chl$\cdot^{+}$ and BChl$\cdot^{+}$ in photosynthesis, one must conclude on the basis of properties presently assigned to the primary acceptor that this species is not BChl.

However, the possibility of a reactive BChl$\cdot^{-}$ serving as a precursor to the observed electron acceptors is not excluded. Our findings suggest that flash spectroscopy with rapid time resolution could well include the 900–1100-nm region where BChl$\cdot^{-}$ has a characteristic absorption.

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Stereochemical Dependence of the Sign and Magnitude of Coupling Constants on Geometry in ^{15}N (*E*)- and (*Z*)-Aldimines

Sir:

A growing body of evidence[1] has indicated that both the magnitude and the sign of nuclear spin coupling constants are affected by the relative stereochemistry of proximate lone pairs of electrons on atoms such as nitrogen and phosphorus. The particular spin system of interest here is that between hydrogen and nitrogen-15 across a carbon–nitrogen double bond (H—C=^{15}N—). Thus, hydrazones,[2] imines,[3,4] oximes,[5,6] and aza aromatic systems[5b,6,7] show larger ^{2}J(H—C=^{15}N—) couplings when the hydrogen is cis ($\sim$14 to 16 Hz) rather than trans ($\sim$2 to 5 Hz except for aza aromatic systems) to the nitrogen lone pair. Unfortunately, in each of these investigations either the stereochemistry of the molecule or the absolute sign of the coupling constant was not known with certainty, or only one of the two possible geometric isomers was examined. The most definitive study was that of Crepaux and Lehn[5a] on ^{15}*N*-formaldoxime; in this case, the signs of $^{2}K_{(H-C={}^{15}N)}$ (*K* defined in ref 14) for the two nonequivalent hydrogens attached to carbon were demonstrated to be opposite. The absolute sign of the larger ^{2}K (lone pair cis to hydrogen) was assumed positive based on the sign determined for H—C=^{15}N in ^{15}*N*-quinoline.[5b] We now report the first unequivocal assignment of both the sign and magnitude of the ^{2}J(H—C=^{15}N) coupling for an (*E*)- and (*Z*)-*N*-alkylaldimine.

N-Alkylaldimines were chosen for this study for several reasons: (i) systems with a heteroatom bearing a long pair (*e.g.*, oximes) on the atom attached to nitrogen were avoided in view of possible complications due to the additional lone pair, (ii) the *Z* isomers of *N*-arylaldimines were known to have lifetimes so short[8]

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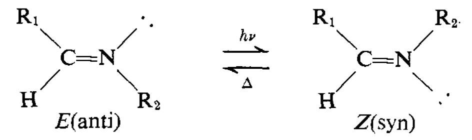
Table I. Photoisomerism of *N*-Alkylaldimines[a]



	Compound	% *Z* isomer[b]	δ(*Z*)-*N*-alkyl	δ(*E*)-*N*-alkyl)
1	R_1 = 9-anthryl R_2 = *tert*-butyl	<1, 70–80	0.98	1.54
2	R_1 = 9-anthryl R_2 = methyl	5, 70–80	3.02	3.77
3	R_1 = naphthyl R_2 = methyl	<1, 50–60[c]	3.18	3.56
4	R_1 = phenyl R_2 = methyl	<1, 50–60[c]	3.43	3.45

[a] Samples (~20 mg) were irradiated (solutions in 0.5 ml of tetradeuteriomethanol containing a trace of sodium methoxide) in standard nmr tubes with a focused, medium pressure, 700-W mercury lamp for 30–45 min at $-77°$. Chemical shifts (ppm) were measured relative to internal TMS. [b] The first number designates the % *Z* isomer at equilibrium (25°), while the second number indicates % *Z* isomer present after irradiation at $-77°$. [c] Benzophenone (~10 mg) as photosensitizer was present in sample.

Table II. Coupling Constants in *N*-Alkylaldimines[a]

Compound	$^2J(H—C{=}^{15}N)$[b]		$^2K(H—C{=}^{15}N)$[b]		$^4J(H—C{=}N—CH_3)$		$^2J(^{15}NCH_3)$	
	E	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*
1	+3.8	−10.0	−3.1	+8.2			(2.0)[c]	(2.2)[c]
2	+3.4	−9.8	−2.8	+8.1	1.6	2.2	0.8	0.6
3	+3.6	−10.4	−3.0	+8.5	1.6	2.3	0.7	0.6
4	+3.7	−10.0	−3.0	+8.2	1.7	2.2	0.8	0.7

[a] Couplings were measured in tetradeuteriomethanol at $-40°$; for **1** couplings were measured in hexadeuteriobenzene at 10°. [b] Absolute signs were determined only for compound **1** while those for compounds **2–4** were assigned by analogy. The values of J and K are in Hz and 10^{20} cm^{-3}, respectively. [c] These values are for $^3J(^{15}NCCH_3)$ and are entered here for convenience.

that a sign determination would be precluded, and (iii) the recent observation of the first (*Z*)-*N*-alkylaldimine (**2**), present at equilibrium[9] to the extent of 5–10% with its *E* isomer, indicated that both geometric isomers could be examined in this system. Since solutions of *N*-alkylaldimines generally do not contain significant amounts of the thermodynamically less stable *Z* isomer (Table I), a method was sought to enhance and maintain this isomer for sufficient time to permit investigation by nmr. Photoinduced isomerization about the carbon–nitrogen double bond[8] proved satisfactory. Direct irradiation of **1** and **2** in deuteriomethanol at room temperature showed substantial enhancement in the amounts of the *Z* isomers which had half-lives of ~260 min at 29° and ~130 min at 33°, respectively.[10] For compounds **3** and **4** with 1-naphthyl and phenyl substituents instead of 9-anthryl (**1** and **2**), the presence of a photosensitizer, benzophenone, and reduced temperature ($-77°$) were required to obtain solutions enhanced in the *Z* isomer. Equilibration of the *E* and *Z* isomers is remarkably sensitive to acid catalysis. Thus, a trace of sodium deuteriomethoxide was added to all solutions before photolysis. The structures generated during photolysis were established as the *Z* isomers by their nmr spectra[9] and by their spontaneous reversion to more stable *E* isomers.

For spectral studies, compounds enriched 98% in ^{15}N were prepared as previously described.[11] The magnitude of $^2J(H—C{=}^{15}N)$ was ~10 Hz for *Z* isomers and 3.4–3.8 Hz for the *E* isomers (Table II), values consistent with those cited above for related molecules. The proximity of the ^{13}C satellites to other portions of the spectrum required the preparation of **1** enriched[12] both in ^{15}N and ^{13}C in order to determine absolute signs of couplings. Additionally, hexadeuteriobenzene was required as solvent to prevent coincidence of signals. Both the photolysis and the recording of spectra for **1** were done at 10°. The absolute signs of the reduced coupling constants (K) for the *E* and *Z* isomers of **1** were deduced from $\{^{13}C\}$–H and $\{^{15}N\}$–H spin tickling experiments by the conventional method.[13] The *tert*-butyl group was concomitantly decoupled from ^{15}N during the course of these experiments in order that the spectra remain interpretable. Absolute values of the reduced coupling constants[14] $^1K(H–^{13}C)$, $^1K(^{13}C{=}^{15}N)$, and $^2K(H—C{=}^{15}N)$ are +53.3, +16.3, and −3.1 for the *E* isomer and +58.6, +16.3, and +8.2 for the *Z* isomer, assuming $^1K(H—^{13}C)$ to be positive. Thus, the cis geometry between hydrogen and the lone pair of electrons on nitrogen (*Z* isomer) results in a large positive contribution to K, a result consistent with "through space" coupling.[15] As might be anticipated, the values of $^1K(^{13}C{=}^{15}N)$ are identical in sign (positive) and magnitude for the two isomers. To date, the only negative $^1K(^{13}C{=}^{15}N)$ definitely established was in an oxaziridine.[1c]

Determination both of sign and magnitude of coupling for this series of geometric isomers should permit refined molecular orbital calculations[16] for compounds containing the $H—C{=}^{15}N$ spin system. In addition, the consistency of the magnitude of $^2J(H—C{=}^{15}N)$ for the *E* and *Z* isomers provides a means of assigning relative stereochemistry in aldimines. The effect of a large positive contribution to K when hydrogen is cis to a

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(15) For a general discussion of "through space" coupling, see M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969).

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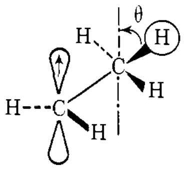
Pseudocontact and Contact Shifts for 6-Aminobenzobicyclo[2.2.2]octene and 2-Aminotriptycene. The Sign of B_0[1]

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 ρ_C^π 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	$H_{\beta1}$	$H_{\beta2}$
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 $H_{\beta2}$, Table I. Tori and his associates similarly assigned the upfield signal of the β protons of **4** to $H_{\beta1}$.[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 $H_{\beta2}$ (negative $a_{\beta2}$) and the downfield shifts for $H_{\beta1}$ (positive $a_{\beta1}$) 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 $H_{\beta1}$ and $H_{\beta2}$ are constrained to

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