it is the only one whose B^{11} nmr spectrum shows a doublet at extraordinarily low field [chemical shift -103.8 ppm relative to $BF_3 \cdot O(C_2H_5)_2$]. This doublet, of intensity 2 (out of a total integrated intensity of 10), was assigned by the authors to the two borons in each icosahedron which are simultaneously bonded to two carbon atoms. The very low chemical shift of this doublet was rationalized by postulating that these boron atoms are within bonding distance of the cobalt atom and are thus experiencing the electron-withdrawing effect of the metal atom. Our result is certainly consistent with this idea. Although in the solid state only one of eight such boron atoms is actually hydrogen-bridge bonded to the cobalt atom, in solution one evidently observes a time-averaged effect whereby each of the eight boron atoms (accounting for one-fifth of all boron atoms) feels the presence of the metal atom equally.

The observed geometry can also provide a rationalization for the magnetic properties of this compound. The observed diamagnetism[1] of this d^6 complex is undoubtedly due to its very low symmetry (C_s, or, more properly, C_1).

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Richard A. Love, Robert Bau*
Department of Chemistry, University of Southern California
Los Angeles, California 90007
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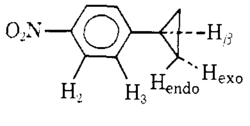
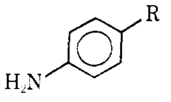
Pseudocontact and Contact Shifts for 4-Aminophenylcyclopropane Derivatives. Signs for the Long-Range Electron Paramagnetic Resonance Coupling Constants[1]

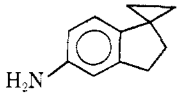
Sir:

Interesting problems are posed by the epr coupling constants, a_{endo} and a_{exo}, for the cyclopropyl protons in the cyclopropylcarbinyl radical and its derivatives.[2] These constants are larger for the anion radical of 4-nitrophenylcyclopropane than for comparable acyclic molecules.[2d] Thus, a_{endo} and a_{exo} are equal for 4-nitrophenylcyclopropane, 5-nitrospiro[cyclopropane-1,1′-indan], and 6-nitrospiro[cyclopropane-1,1′-tetralin] anion radicals. For radicals in the bisected conformation, the INDO model[3] suggests that a_{endo} and a_{exo} have approximately equal magnitude, but that a_{endo} is negative while a_{exo} is positive.[2d] The predictions of spin polarization theories based on parameters for strain-free molecules are very different.[4] The Luz formulation[4a] suggests that these constants are both negative, whereas the Barfield formulation[4b] suggests that they are both positive. To investigate this problem, we used the method developed by Morishima and Yonezawa[5] to determine the signs of these constants through the contact shifts resulting from the interaction of nickel acetylacetonate with aminophenylcyclopropane derivatives, **5–7**. These compounds were studied because the cyclopropyl group is constrained to the bisected form enabling an unambiguous test of theory.





1, R = CH_3
2, R = CH_2CH_3
3, R = $CH(CH_3)_2$
4, R = $C(CH_3)_3$
5, R = $CH(CH_2)_2$



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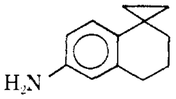

7

The methylene proton resonances in **5–7** are not readily identified. The endo and exo protons of **5** appear in two multiplets centered at δ 0.62 and 0.79, respectively. The same protons of **6** yield a singlet ($\Delta\nu_{1/2}$ = 1.8 Hz) at δ 0.81. For **7**, these multiplets are at δ 0.72 and 0.83. To assign these signals, we measured the pseudocontact shifts experienced by the amines **1–7** in the presence of $Pr(fod)_3$.[6] The pseudocontact shifts are illustrated in Figure 1 and summarized in Table I.

Our observations for *p*-toluidine agree with previous results.[5c] The fixed geometric relationship between the

Table I. Pseudocontact Chemical Shifts for Aniline Derivatives

	Relative pseudocontact shift[a]			
Amine	H_2	H_3	H_β	H_γ
1	1.00	0.28	0.14	
2	1.00	0.30	0.14	0.11
3	1.00	0.29	0.13	0.11
4	1.00	0.28		0.11
5	1.00	0.30		0.14 (endo)[b] 0.08 (exo)[c]
6	1.00	0.34		0.15 (endo)[c] 0.09 (exo)[b]
7	1.00	0.38		0.13 (endo)[c] 0.08 (exo)[b]

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

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

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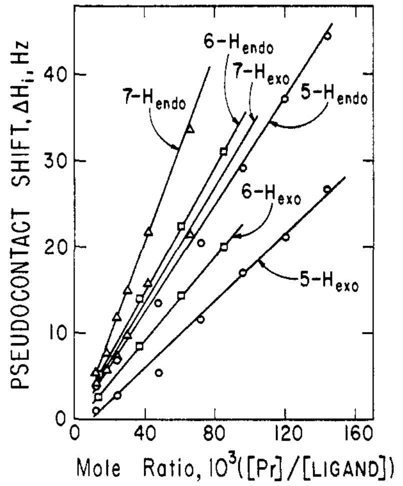

Figure 1. The dependence of the pseudocontact chemical shifts, in hertz, of the cyclopropane protons in amines **5–7** on the metal/ligand mole ratio is illustrated.

amino group and the methylene protons in **6** and **7** enables the assignment of the signal experiencing the larger pseudocontact shift to the endo protons and the less shifted signal to the exo protons of the cyclopropane ring as shown in Table I.

The contact chemical shifts were measured in chloroform solution,[7] with a low nickel acetylacetonate/amine ratio,[5b] and relative to internal tetramethylsilane. The observations for the endo and exo protons of **5–7** are illustrated in Figure 2 and the results are summarized in Table II.

Table II. Relative Contact Chemical Shifts for Aniline Derivatives

Amine	Relative contact shift[a]			
	H_2	H_3	H_β	H_γ
1	1.00	−0.47	−1.08	
2	1.00	−0.45	−0.82	−0.007
3	1.00	−0.43	−0.45	−0.036
4	1.00	−0.46		−0.039
5	1.00	−0.42	−0.34	0.048 (endo) −0.034 (exo)
6	1.00	−0.45		0.090 (endo) −0.120 (exo)
7	1.00	−0.45		0.079 (endo) −0.095 (exo)

[a] The relative contact shift, $\Delta H_i/\Delta H_2$. The contact shift for the ortho proton is positive in each case.

The contact shifts for the ortho protons (positive), the meta protons (negative), and the β protons (negative) are in complete accord with prior sign determinations with a negative sign for the epr coupling constant a_2 and positive signs for a_3 and a_β.[8] The shifts for the γ protons of the alkyl groups in **2–4** are small and negative, indicative of positive a_γ values. In contrast, both positive and negative contact shifts are observed for the γ methylene protons of the cyclopropyl ring. The shifts for the endo protons of **5** and **7** are positive, whereas the shifts for the exo protons are negative.

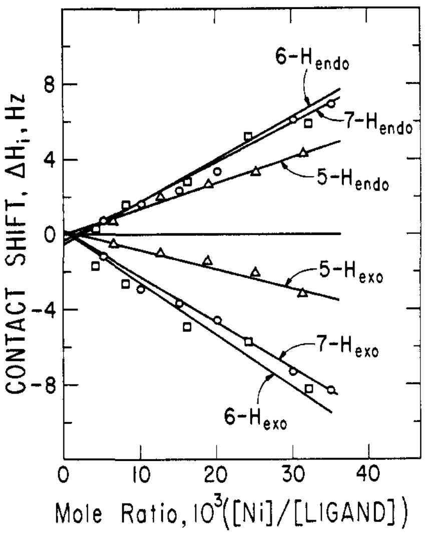

Figure 2. The dependence of the contact chemical shifts, in hertz, of the cyclopropane protons in amines **5–7** on the metal/ligand mole ratio is illustrated.

The nickel reagent also separates the singlet of **6** into an upfield and a downfield component. To assign these resonance signals, we added incremental amounts of nickel acetylacetonate to a solution of **6** and the rare earth pseudocontact shift reagent. The resonances of the methylene protons remained sharp indicating that fast exchange was realized. As the nickel reagent was added, the upfield (endo) signal of **6** shifted further upfield while the downfield (exo) signal shifted further downfield. The results for **5–7** establish that a_{endo} and a_{exo} differ only modestly in magnitude, but that a_{endo} is negative and a_{exo} is positive.

These findings are consistent with the spin density distribution in strained bicyclic molecules observed by Morishima and Yonezawa[5b] and by Rassat and his group.[9] We note that the spin polarization models apparently have limited utility compared with the INDO model. Our observations concerning the spin density distribution in the unstrained isopropyl group as well as the strained cyclopropyl group agree well with the predictions of the latter theory.[10]

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(11) Fannie and John Hertz Foundation Fellow at the University of Chicago.

Leon M. Stock,* Michael R. Wasielewski[11]
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

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5 *vs.* 4a Addition to Isoalloxazines

Sir:

It has been suggested, as a general concept, that flavin-mediated oxidation reactions should be considered to occur *via* the formation of covalent intermediates.[1,2] The most important question as to the

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