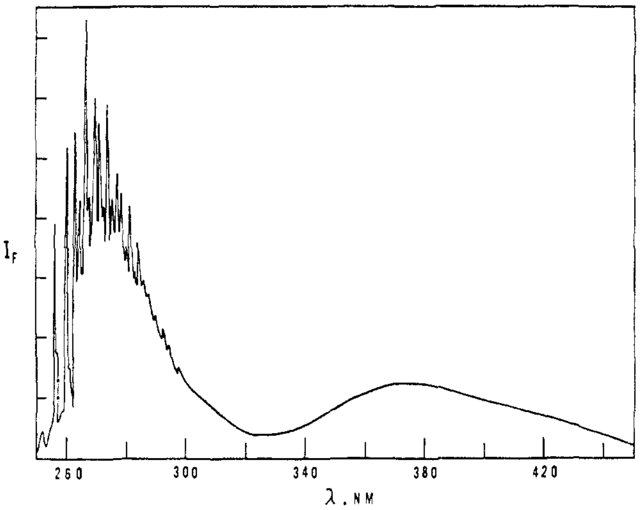


Figure 2. Uncorrected emission spectrum of ABCO vapor at 24° in the presence of 7 cm of *n*-hexane vapor.

excimer. At 24°, the vapor pressure of ABCO is approximately 2 Torr[13] (1.1×10^{-4} *M*), and thus the relative amount of excimer formed appears to be similar to that in the solution phase at this concentration. Fluorescence from ABCO vapor in equilibrium with solid ABCO which is kept at 0° (vapor pressure *ca.* 0.3 Torr[13]) was too faint to detect with the fluorimeter used; however, the time dependence of the (total) emission was easily measured[14] and found to follow a single exponential decay. The emission reached maximum intensity instantaneously with respect to the lamp flash.

Emission from ABCO microcrystals was examined at 25° and found to resemble that of the ABCO excimer fluorescence. Thus, a blue-violet emission was observed with λ_{max} at 3490 Å.

The emission spectrum of the related cage amine 1-azabicyclo[3.3.3]undecane (ABCU)[16] was studied and found to be independent of concentration. This amine showed only monomer fluorescence.[17] From lifetime measurements, however, it was determined that ABCU undergoes self-quenching at the diffusion-controlled rate in *n*-hexane at 24°. The fluorescence spectra of 1,4-diazabicyclo[2.2.2]octane (DABCO) and triethylamine were also found to be concentration independent in the same solvent.[8,18] DABCO's fluorescence lifetime was invariant with concentration between 10^{-4} and 10^{-2} *M* while triethylamine was found to undergo self-quenching at nearly the diffusion-controlled rate.

Another cage amine, 1-azaadamantane[19] (1-AA, II),

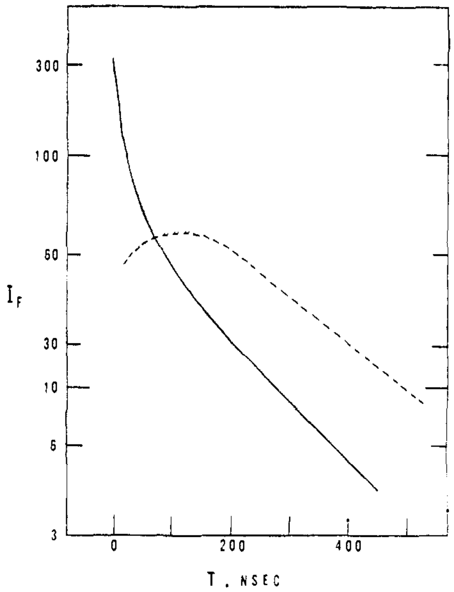
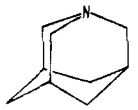


Figure 3. Time dependence of the emission from ABCO vapor at 24°: (——) total emission observed; (– – –) emission isolated with a Corning 0-52 filter. Fluorescence intensity units are arbitrary for each decay curve.



II

was observed to have the same type of concentration-dependent luminescent properties in *n*-hexane as ABCO. For 1-AA, λ_{max} (monomer) is 2860 Å. Preliminary data imply that the ABCO and 1-AA excimers have similar enthalpies, but the former appears to have a larger $\Delta G°$. Results of further studies relating to thermodynamic and structural properties of saturated amine excimers will be reported separately.

Acknowledgment. The donors of the Petroleum Research Fund administered by the American Chemical Society, Research Corporation, and The Society of the Sigma Xi have provided grants for partial support of this work. E. M. is indebted to the National Science Foundation for an Undergraduate Research Participation Summer Fellowship. Many helpful discussions with Dr. E. A. Chandross are gratefully acknowledged.

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(13) H. C. Brown and S. Sujushi, *J. Amer. Chem. Soc.*, **70**, 2878 (1948).

(14) The time-correlated single-photon technique was employed for all lifetime measurements. The apparatus which is similar to one previously described[15] will be mentioned in detail elsewhere.

(15) A. M. Halpern and W. R. Ware, *J. Chem. Phys.*, **53**, 1969 (1970).

(16) This compound, also called manxine, was provided as ABCU·HCl through the courtesy of Professor N. J. Leonard and Dr. J. C. Coll.

(17) Results of photophysical and spectroscopic studies of ABCU will be reported shortly; however, see N. J. Leonard, J. C. Coll, A. H.-J. Wang, R. J. Missavage, and I. C. Paul, *J. Amer. Chem. Soc.*, **93**, 4628 (1971).

(18) The fluorescence spectrum and lifetime of DABCO have been reported: A. M. Halpern, *Chem. Phys. Lett.*, **6**, 296 (1970); see also A. M. Halpern and R. M. Danziger, *ibid.*, **16**, 72 (1972).

(19) 1-AA was kindly provided by Professor W. N. Speckamp.

(20) National Science Foundation Undergraduate Research Participant, summer, 1971.

Crystal Structure of the Biscarborane Complex $Co[(B_{10}C_2H_{10})_2]_2^-$

Sir:

The reaction of 2,2′-dilithiobiscarborane with various anhydrous metal salts has produced[1] a series of transition metal biscarborane complexes of general

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(1) D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 3194 (1970); **93**, 873 (1971).

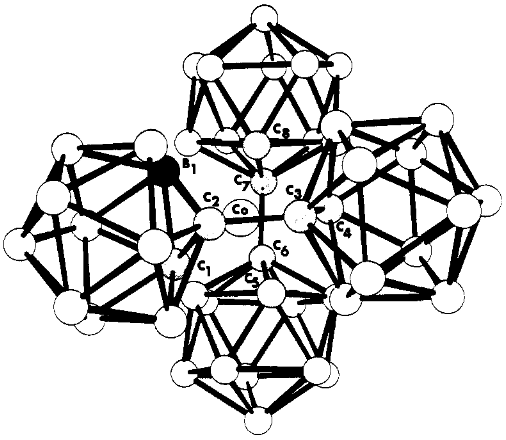

Figure 1. The structure of the $Co[(B_{10}C_2H_{10})_2]_2^-$ anion.

formula $M[(B_{10}C_2H_{10})_2]_2^{n-}$. We have examined the structure of one of these compounds, the tetraethylammonium salt of the Co(III) derivative, and have found that the coordination about the cobalt atom consists of four Co–C σ bonds and one Co–H–B bridge bond.

Crystal data for $[(C_2H_5)_4N]^+\{Co[(B_{10}C_2H_{10})_2]_2\}^-$: space group $P2_1/c$ (monoclinic); a = 14.85 (1) Å, b = 18.66 (2) Å, c = 15.54 (1) Å, β = 95.6 (1)°, V = 4321 Å^3; ρ_{calcd} (based on Z = 4) = 1.16 g/cm^3, ρ_{obsd} = 1.15 g/cm^3. One quadrant of data was collected on an automated Nonius CAD-3 diffractometer with Mo Kα radiation up to a limit of 50° in 2θ. The structure was solved using heavy-atom methods. Fractional occupancy factors had to be assigned to the methylene carbon atoms of the cation, which were found to be disordered. The structure was refined with block-diagonal least-squares techniques (only nonhydrogen atoms were included at this point) to an R factor of 10.0% for the 2643 independent nonzero reflections.[2]

The geometry of the $Co[(B_{10}C_2H_{10})_2]_2^-$ anion is shown in Figure 1. It is found that the four carborane icosahedra are tetrahedrally arranged about the cobalt atom. Although this result would normally imply that the four bonding carbon atoms are also tetrahedrally arranged about the cobalt atom, a closer examination of the structure revealed that this is not the case. Severe distortions from tetrahedral symmetry[3] become apparent when the C–M–C angles are calculated; for example, the angle (C_1–Co–C_8) is 150.4°. At this point, it was noticed that one of the boron atoms (B_1) is rather close (2.29 Å) to the cobalt atom. This observation suggests that the possible existence of a B–H–M bridge as found in $(Ph_3P)_2Cu(B_3H_8)$[4] and $[(CH_3)_4N][(CO)_4Cr(B_3H_8)]$.[5]

From a series of difference Fourier maps, the positions of all 40 hydrogen atoms in the anion[6] were unambiguously determined. One of the hydrogen atoms

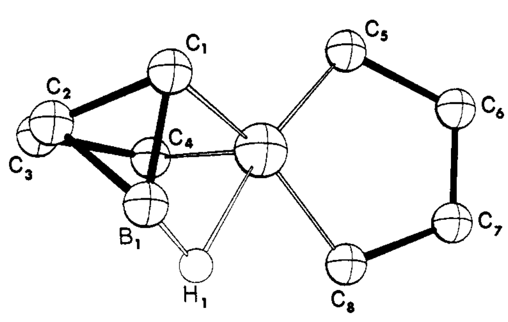

Figure 2. The coordination about the cobalt atom, simplified to show only the atoms in the immediate vicinity of the cobalt atom.

(H_1 in Figure 2) is indeed located at a position expected for a B–H–M bridge bond. Further least-squares refinement[7] (now including the H atom positions) reduced the R factor to the final value of 7.9%. Copies of the final atomic parameters and the observed and calculated structure factor tables are available.[8]

The bonding about the Co atom (see Figure 2) thus consists of four Co–C σ bonds and one Co–H–B bridge bond arranged in what might be described as a badly distorted square pyramid. The atom C_4 forms the apex of this square pyramid, while the basal plane is defined by the atoms C_1, C_5, C_8, and H_1 (coplanar within 0.12 Å); the Co atom is situated about 0.22 Å from this plane. The distances and angles associated with these atoms are given in Table I. The Co–H_1 distance of 1.82 (7) Å agrees very well with the Cu–H distances of 1.84 (5) and 1.85 (5) Å found in $(Ph_3P)_2Cu(B_3H_8)$[4] and the Cr–H distance of 1.78 (6) Å found in $[(CH_3)_4N][(CO)_4CrB_3H_8]$.[5]

Table I. Selected Distances and Angles in $Co[(B_{10}C_2H_{10})_2]_2^-$

	(a) Bond Lengths (Å)		
Co–C_1	2.05 (1)	B_1–H_1	1.11 (7)
Co–C_4	1.95 (1)	C_1–C_2	1.64 (2)
Co–C_5	1.95 (1)	C_2–C_3	1.51 (2)
Co–C_8	2.00 (1)	C_3–C_4	1.72 (2)
Co–H_1	1.82 (7)	C_5–C_6	1.71 (2)
B_1–C_1	1.62 (2)	C_6–C_7	1.53 (2)
B_1–C_2	1.66 (2)	C_7–C_8	1.65 (2)
	(b) Bond Angles (deg)		
C_1–Co–C_4	92.7 (5)	Co–C_1–C_2	101.9 (7)
C_1–Co–C_5	109.9 (5)	Co–C_4–C_3	107.2 (7)
C_1–Co–C_8	150.4 (5)	Co–C_5–C_6	106.0 (7)
C_4–Co–C_5	100.2 (5)	Co–C_8–C_7	110.3 (8)
C_4–Co–C_8	102.8 (5)	C_1–C_2–C_3	113.1 (9)
C_5–Co–C_8	92.2 (5)	C_2–C_3–C_4	111.1 (9)
H_1–Co–C_1	72 (2)	C_5–C_6–C_7	114.4 (9)
H_1–Co–C_4	87 (2)	C_6–C_7–C_8	111.0 (9)
H_1–Co–C_5	172 (2)	B_1–C_2–C_3	115.5 (9)
H_1–Co–C_8	84 (2)	H_1–B_1–C_1	112 (4)
Co–H_1–B_1	100 (5)	H_1–B_1–C_2	118 (4)

Of all the biscarborane complexes reported by Owen and Hawthorne, the Co(III) derivative is unique in that

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(2) All the major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. R. E. Marsh's group at the California Institute of Technology.

(3) This distortion is clearly displayed (see Figure 1) in the conformations of the $\underline{\mathrm{CoCCCC}}$ rings, which are expected to be planar. Note that $C_1C_2C_3C_4$ is severely bent (dihedral angle 30°) while $C_5C_6C_7C_8$ is reasonably planar.

(4) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

(5) L. J. Guggenberger, *ibid.*, **9**, 367 (1970).

(6) No serious attempt was made to locate the hydrogen atoms of the cation because of the disorder of methylene groups.

(7) The hydrogen temperature factors were held constant at 5 Å^2 in this refinement.

(8) Listings of the final atomic parameters (Table II) and the observed and calculated structure factors (Table III) will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N. W., Washington, D. C. 20036, by referring to code number JACS-72-8274. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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).

Acknowledgment. We thank Professor M. F. Hawthorne and Dr. A. Owen of the University of California at Los Angeles for supplying the crystals used in this work. We are also grateful to the Petroleum Research Fund (administered by the American Chemical Society; Grant No. 2059-G3) and the Research Corporation for supporting this research, to the Computer Center of the University of Southern California for making available its IBM 360/65 computer, and to the National Science Foundation for the purchase of the diffractometer. Special thanks are due to Professor Anton B. Burg of this department for valuable discussions.

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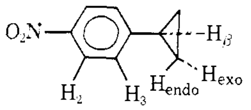
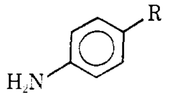
Pseudocontact and Contact Shifts for 4-Aminophenylcyclopropane Derivatives. Signs for the Long-Range Electron Paramagnetic Resonance Coupling Constants[1]

Sir:

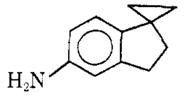
Interesting problems are posed by the epr coupling constants, a_{endo} and a_{exo}, for the cyclopropyl protons in the cyclopropylcarbinyl radical and its derivatives.[2] These constants are larger for the anion radical of 4-



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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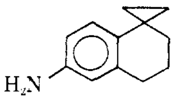

7

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.

(2) (a) G. A. Russell and H. Malkus, *J. Amer. Chem. Soc.*, **89**, 160 (1967); (b) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1877, 1879 (1969); (c) N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, and J. Zoeller, Jr., *ibid.*, **91**, 6666 (1969); (d) L. M. Stock and P. E. Young, *ibid.*, **94**, 7686 (1972).

(3) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **90**, 4201 (1968).

(4) (a) Z. Luz, *J. Chem. Phys.*, **48**, 4186 (1968); (b) M. Barfield, *J. Phys. Chem.*, **74**, 621 (1970).

(5) (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, **92**, 1267 (1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *ibid.*, **93**, 3922 (1971); (c) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Jap.*, **43**, 379 (1970).

(6) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).