the observed interconversions among 5-chloro-*m*-, chloro-*p*-, and 4-chloro-*m*-carboranes. A distribution matrix based upon mechanism b (Table II) does reproduce the intermediate yields as well as the final yields, but we cannot be sure that this mechanism is unique and we comment that triangle rotations are required to be less frequent relative to cuboctahedral rearrangements than they are in the 9-Br-*o* rearrangement in order to avoid a quasi steady state among 4-Cl-*m*, 5-Cl-*m*, and 9-Cl-*m* isomers.

Table II. Predicted Initial Product Distributions for the Cuboctahedral (a), Cuboctahedral with Triangle Rotations (b), Pentagonal Pyramidal Rotation (c), and Triangle Rotation (d) Mechanisms

	Product				
	2-Cl-*m*	4-Cl-*m*	5-Cl-*m*	9-Cl-*m*	Cl-*p*
			Mechanism a		
From 2-Cl-*m*	0.75	0.25	0	0	0
4-Cl-*m*	0.125	0.75	0	0.125	0
5-Cl-*m*	0	0	1.0	0	0
9-Cl-*m*	0	0.25	0	0.75	0
Cl-*p*	0	0	0	0	1.0
			Mechanism b[a]		
From 2-Cl-*m*	0.744	0.254	0	0.002	0
4-Cl-*m*	0.116	0.713	0.028	0.116	0.027[b]
5-Cl-*m*	0	0.031	0.932	0.01	0.027[b]
9-Cl-*m*	0.002	0.252	0.01	0.737	0
Cl-*p*	0	0.01[b]	0.01[b]	0	0.98
			Mechanism c		
From 2-Cl-*m*	0.5	0.167	0	0	0.333
4-Cl-*m*	0.083	0.417	0.167	0	0.333
5-Cl-*m*	0	0.333	0.167	0.167	0.333
9-Cl-*m*	0	0	0.167	0.5	0.333
Cl-*p*	0.167	0.333	0.167	0.167	0.167
			Mechanism d		
From 2-Cl-*m*	0.625	0.25	0	0	0.125
4-Cl-*m*	0.125	0.5	0.125	0.125	0.125
5-Cl-*m*	0	0.25	0.5	0.125	0.125
9-Cl-*m*	0	0.25	0.125	0.5	0.125
Cl-*p*	0.111	0.222	0.111	0.111	0.444

[a] B_3 and B_2C triangle rotations assumed to be equally probable.
[b] Adjusted to fit only the experimental final ratio of *para* to the sum of 4-Cl-*m* and 5-Cl-*m* (48:36).

Other mechanisms based either upon mutual rotations of two pentagonal pyramids[9] (Table IIc) or rotation by 120° of a triangular face in the icosahedron[10] (Table IId) fail to give the trends shown in the data. Assuming equal probability for all mutual rotations, the major faults are predictions of equal rates of conversion of each *meta* isomer to the *para* isomer, random return rates from *para* to a statistical distribution of *meta* isomers, large 4-Cl-*m* to 5-Cl-*m* to 9-Cl-*m* interconversions, and lack of account of the initial distributions. In addition, the rotating pentagon mechanism does not provide for 4-Cl-*m* to 9-Cl-*m* interconversions. No reasonable restrictions or modifications of these mechanisms could be devised to reduce substantially the strong tendency toward randomization which is not in accord with the experimental results.

The bromo- and iodo-*m*-carboranes decompose in this temperature range,[11] but further studies with dichloro derivatives and evaluation of thermodynamic and kinetic quantities are in progress.

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H. V. Hart, W. N. Lipscomb
Harvard University
Cambridge, Massachusetts 02138

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[11] In the above experiments decomposition products (almost exclusively polymeric) averaged about 25% of the total.

Polarized Infrared Spectroscopy of Molecules Oriented in a Nematic Liquid Crystal. Application to $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$[1]

Sir:

Recent work in our laboratory has demonstrated that polarizations of electronic absorption bands can be obtained by orienting the molecule of interest in a nematic liquid crystal host.[2] We now wish to report that this new technique is useful for measuring the polarizations of absorption bands in the infrared region. The present communication describes the application of the method to obtain the first polarization data for infrared bands of binuclear metal carbonyls.

The compounds studied were the decacarbonyldimetal(0) complexes of Mn and Re; $Mo(CO)_6$ was included for reference. Solutions were prepared by dissolving approximately 1 mg of solute in 100 mg of the nematic phase of *p*-(*p*′-ethoxybenzoxy)phenyl butyl carbonate. Infrared spectra were taken at room temperature with a Perkin-Elmer 225 grating spectrophotometer equipped with wire grid polarizing optics. The cells consisted of two barium fluoride plates held in a stainless steel body and separated by a 0.0025-cm Teflon spacer. Uniform orientation of the nematic phase was achieved by rubbing the BaF_2 plates in one direction before introducing the sample. As was shown earlier,[2] this procedure is sufficient to produce uniform alignment of the nematic molecules in the direction of rubbing.

Figure 1 shows the polarized spectra of the liquid crystal solvent; it is apparent that many of the bands are strongly polarized. In the region where terminal C≡O stretching frequencies occur (2200–1900 cm^{-1}), absorption by the nematic solvent is not very significant, amounting in our cell to an absorbance of 0.15 or less when the electric vector is parallel to the long-axis orientation of the liquid crystal molecules. Thus, it is convenient to use this particular liquid crystal to study the polarizations of C≡O stretching bands.

Figure 2 gives the polarized spectra for $Re_2(CO)_{10}$ in the region 2100–1900 cm^{-1}. The spectra show that the

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[1] This research was supported by the National Science Foundation.

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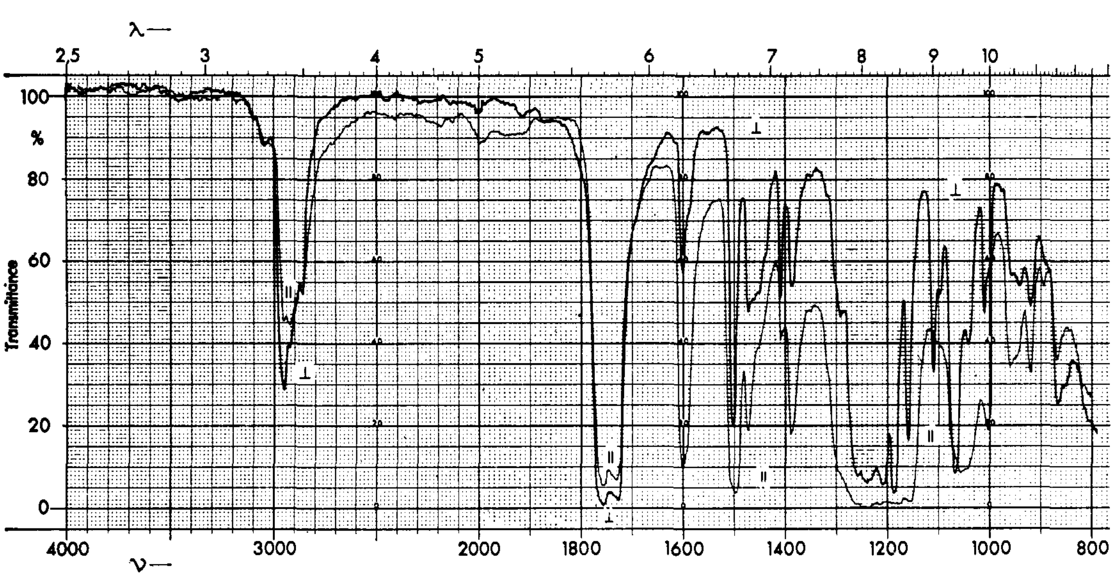

Figure 1. Polarized infrared spectra of p-(p'-ethoxybenzoxy)phenyl butyl carbonate in a "supercooled" nematic state at ambient temperature. The spectra are for the electric vector of light polarized parallel and perpendicular to the long axis of the molecule.

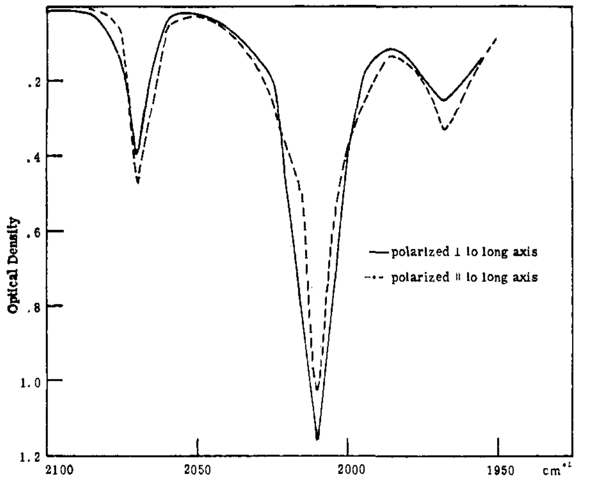

Figure 2. Polarized infrared spectra of a 2.7×10^{-2} M nematic solution of $Re_2(CO)_{10}$. The spectra are corrected for background absorption by the nematic solvent.

absorbance of the intense 2010-cm^{-1} band measured perpendicular to the long-axis orientation of the solvent molecules ($A_\perp$) is significantly greater than that measured parallel ($A_\parallel$). For the other two bands, however, $A_\parallel$ is greater than $A_\perp$. The experimental data for $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ are summarized in Table I.

The polarization data lead to unambiguous assignments for the three C≡O stretching bands and as a bonus also independently determine the orientation of the D_{4d}[3,4] $M_2(CO)_{10}$ molecules in the nematic host. For molecules with axial symmetry, the quantity $(A_\parallel - A_\perp)$ is related to the optical density along molecule fixed axes as shown in eq 1.[5] The z direction is along the fourfold symmetry axis of the molecule and $x(y)$ is perpendicular to this. S_{zz} describes the average orientation of the solute molecules and is defined as

$$(A_\parallel - A_\perp) = S_{zz}(A_z - A_{x,y}) \qquad (1)$$

$$S_{zz} = \frac{1}{2}\langle 3 \cos^2 \theta - 1\rangle_{\text{average}} \qquad (2)$$

where θ is the angle that the symmetry axis makes with the long axis of the liquid crystal. For parallel orientation S_{zz} is positive, while for perpendicular alignment it takes negative values.[6]

There are three infrared-allowed normal modes which correspond to C≡O stretching in $M_2(CO)_{10}$ molecules of D_{4d} symmetry, two of B_2 symmetry, and one of E_1 symmetry; the B_2 modes should be parallel polarized ($A_z > A_{x,y} = 0$), whereas E_1 should be perpendicularly polarized ($A_{x,y} > A_z = 0$). Since symmetry requires that $(A_z - A_{x,y})$ be positive for two of the three C≡O stretching fundamentals, the fact that we find that $(A_\parallel - A_\perp)$ is positive for two observed bands establishes them as the B_2 transitions and determines that S_{zz} is

Table I. Polarized Infrared Absorption Data for Decacarbonyldimetal(0) Complexes in Liquid Crystal Solvent

Complex		Band[a] aB$_2$	E$_1$	bB$_2$
$Mn_2(CO)_{10}$	$\bar{\nu}$, cm^{-1}	2045	2009	1980
	$A_\parallel$	0.62	0.81	0.21
	$A_\perp$	0.54	0.92	0.19
	$(A_\parallel - A_\perp)$	0.08	−0.11	0.02
$Re_2(CO)_{10}$	$\bar{\nu}$, cm^{-1}	2070	2010	1967
	$A_\parallel$	0.47	1.03	0.33
	$A_\perp$	0.39	1.16	0.25
	$(A_\parallel - A_\perp)$	0.08	−0.13	0.08

[a] Band positions differ slightly from ref 7 because of the different solvent medium employed. Absorbance is given in arbitrary units. The experimental error in determining the quantity $(A_\parallel - A_\perp)$ is not greater than 15%.

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(6) For an octahedral molecule no orientation is expected and thus S_{zz} and $(A_\parallel - A_\perp)$ should equal zero. We have measured $(A_\parallel - A_\perp)$ for the 1981-cm^{-1} band in $Mo(CO)_6$ and found it to be zero, as predicted.

positive. Furthermore, the perpendicularly polarized band must be assigned as the E_1 fundamental. Thus our experiment rigorously establishes an interpretation of the $M_2(CO)_{10}$ spectra proposed by Flitcroft, Huggins, and Kaesz[7] on the basis of intensities and force constant calculations.

The infrared data provide strong support for the generalization[2] from nmr experiments[8] and polarized electronic spectroscopy[2] that *solute molecules with a long axis tend to align with that axis parallel to the long axis of the liquid crystal molecules.* For $Mn_2(CO)_{10}$, where we have determined that S_{zz} is positive, the distance across the molecule along the z axis is 1.5 times longer than the distance across the x axis.[4]

Because of experimental difficulties inherent in single crystal methods, relatively few infrared band polarizations have been determined. The technique described in this communication should facilitate such polarization studies and allow more band assignments to be placed on a firm basis.

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Gerald P. Ceasar,[9] Robert A. Levenson, Harry B. Gray
Contribution No. 3778
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109

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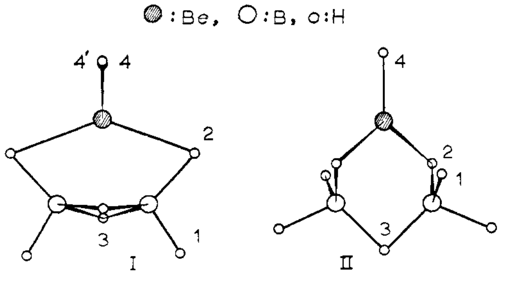
The Structure of Beryllium Borohydride

Sir:

A recent electron diffraction study[1] has disproved the classical structure for beryllium borohydride and proposed structure I as being consistent with the data. Subsequent calculations for this structure[2,3] indicate rather weak bonding interactions between the BeH_2 and "diborane" moieties. For this reason, as well as the disturbingly long beryllium–hydrogen bonds, 1.60 and 1.85 Å respectively for terminal and bridge hydrogens, we question the validity of I. We propose that the true structure is II based largely on infrared and mass spectral data.



A special gas cell, with modified, inert windows, had to be constructed for the infrared study owing to the rapid reaction of this compound with KBr plates. The earlier study[4] did not take this into account, and some of the reported bands are definitely due to this reaction. The gas-phase infrared spectra of both BeB_2H_8 and BeB_2D_8 consist of 22 bands in the 4000–400-cm^{-1} region. At this time we wish to demonstrate only the presence of BH_2 and the absence of BH terminal groupings. Studies of several boron hydride compounds indicate very sharp differentiation between these modes.[5]

Bands at 2630, 2531, 1017, and 974 cm^{-1} (shifting to 1910, 1816, 860, and 698 cm^{-1} respectively, in BeB_2D_8) clearly correspond to BH_2 terminal group frequencies. In diborane the analogous absorptions appear at 2612, 2525, 1035, and 974 cm^{-1} (shifting to 1985, 1840, 860, and 720 cm^{-1}, respectively, in B_2D_6). In borane compounds containing only BH terminal bonds, the last two bands are absent and there is only one BH stretching frequency. All known compounds containing BH terminal bonds have an absorption in the 890–910-cm^{-1} region. The absence of absorption in this region in BeB_2H_8 therefore indicates the absence of BH terminal bonds.[4] These arguments are consistent for II but not for I.

The mass spectra of both BeB_2H_8 and BeB_2D_8 were recorded at 80° using ionizing voltages of 70 and 15 eV. Typical ions present at 70 eV include Be^+, $^{10}B^+$, BeH^+, $^{11}B^+$, BH_2^+, $BeBH_2^+$, $B_2H_2^+$, $B_2H_5^+$, $BeB_2H_2^+$, $BeB_2H_4^+$ (the most abundant species), $BeB_2H_6^+$, $BeB_2H_8^+$. At 15 eV the relative abundances of larger fragments (*e.g.*, $BeB_2H_8^+$) increase relative to smaller fragments and the Be^+, $^{10}B^+$, BeH^+, $^{11}B^+$, and BH_2^+ ions no longer are present. No peaks were observed beyond the mass corresponding to the monomeric parent ions. Several metastable peaks were observed in BeB_2H_8 and BeB_2D_8, which correspond to the following reactions

$$Be^{10}B^{11}BD_7^+ \longrightarrow Be^{10}B^{11}BD_5^+ + D_2 \quad (m^* = 36.38)$$

$$BeB_2D_6^+ \longrightarrow BeB_2D_4^+ + D_2 \quad (m^* = 35.39)$$

$$Be^{10}B^{11}BD_6^+ \longrightarrow Be^{10}B^{11}BD_4^+ + D_2 \quad (m^* = 34.45)$$

$$BeB_2D_5^+ \longrightarrow BeB_2D_3^+ + D_2 \quad (m^* = 33.48)$$

These data show that the beryllium atom is strongly bonded within the compound. The predominance of the $BeB_2H_4^+$ ion at 70 eV indicates an especial stability for this grouping which is the "core" of II. Structure I, on the other hand, contains very long, and therefore weak, Be–H–B bonds which would result in a quite different mass spectrum.

The chemical reactivity of BeB_2H_8 is also more compatible with II. Several isolatable 1:1 adducts with bases such as trimethylphosphine have been reported.[6] Such adducts could be easily formed by bonding through the vacant p orbital on the sp^2-hybridized beryllium in II, but would necessitate bond breaking in I. The trimethylphosphine adduct absorbs a second mole of base to ultimately form trimethylphosphine borane and a viscous liquid characterized to be polymeric beryllium hydride.[6] Examination of structure II reveals a more convenient path for attack of the borons than is present in I.

We have constructed a model of II and calculated a radial distribution curve which is in satisfactory agree-

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