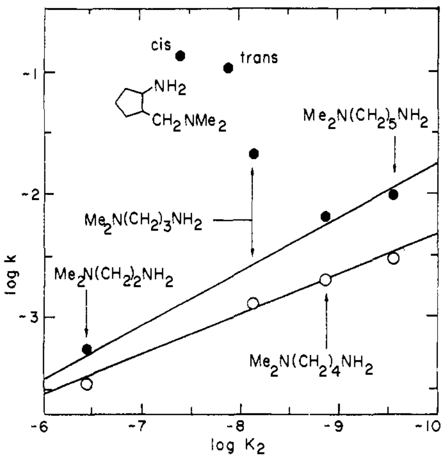
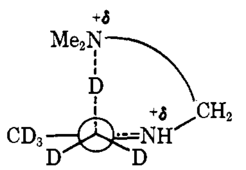


Figure 1. Brønsted plot for the dedeuteration of isobutyraldehyde-*2-d* (open symbols) and acetone-d_6 (solid symbols). K_2 is the acidity constant for the loss of one proton from the diprotonated diamine and k is the apparent second-order rate constant (in M^{-1} sec^{-1}) for catalysis by the monoprotonated diamine in water at 35°.

tonically with the basicity of the catalyst, but in the case of acetone-d_6, 3-dimethylaminopropylamine is seen to be about seven times as reactive as would be expected from the results obtained with the other ω-dimethylaminoalkylamines, whose points approximate a line roughly parallel to the one described by the points for the dedeuteration of isobutyraldehyde-*2-d*. Further observations, that the reaction in the presence of 3-dimethylaminopropylamine at a given pH is first order in amine and that a marked rate maximum in a pH-rate plot is found for 3-dimethylaminopropylamine but not for the other three ω-dimethylaminoalkylamines, add to the evidence that the monoprotonated form of 3-dimethylaminopropylamine is a bifunctional catalyst for the dedeuteration of acetone-d_6, whereas the other monoprotonated ω-dimethylaminoalkylamines are much poorer bifunctional catalysts, at best.

It therefore appears that in this series the optimum cyclic transition state contains an eight-membered ring,[6] a fact most reasonably interpreted in terms of stereoelectronic effects. Since the carbon-deuterium bond being broken should be in a plane nearly perpendicular to the plane of the iminium double bond[4] and since the C–D–N grouping should preferentially be linear,[7] the cyclic transition state should have a structure like that shown in Newman projection **2**. Molecular models show that although four carbon



2

atoms between the two nitrogen atoms of the catalyst are required to construct **2** with a linear C–D–N grouping, C–D–N angles of about 150° can be obtained with only three carbon atoms between the two nitrogens. Apparently, the advantage that 4-dimethylaminobutylamine may derive from having a linear C–D–N grouping in its transition state is more than offset by the disadvantages of having a longer polymethylene chain between the two functional groups.

In the case of 3-dimethylaminopropylamine each of the two plausible models of the transition state has carbon atoms 1 and 2 eclipsed. As seen in Figure 1, the 2-(dimethylaminomethyl)cyclopentylamines, in which such eclipsing is more or less frozen into the molecule, are considerably better catalysts than any of the acyclic diamines studied. The cis isomer is about 100 times as active as would be expected from the best straight line through the three points for ω-dimethylaminoalkylamines that were not shown to be bifunctional catalysts.

With each of the three bifunctional catalysts the dedeuteration of acetone-d_6 gave acetone-d_5, -d_4, and -d_3 (but not -d_2, -d_1, or -d_0) directly from the beginning of the reaction, whereas with the other catalysts the less deuterated species were formed consecutively with no appreciable amount of d_3, for example, being formed until much larger amounts of d_4 had been formed. This shows that the iminium ions formed from the bifunctional catalysts lose deuterium (from the trideuteriomethyl group cis to the ω-dimethylaminoalkyl group) and hydrolyze to acetone at comparable rates.

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Beryllium Borohydride Structure in the Solid Phase

Sir:

Both bent[1-4] and linear[5,6] structures for BBeB in $Be(BH_4)_2$ have been suggested, with a variety of arrangements for bonds toward hydrogen atoms. Indirect evidence from the crystallographic diffraction pattern led to the conclusion[7] that the solid phase consisted of discrete molecules. Our solution of this structure from a single crystal establishes that the solid consists of helical polymers, having a chemical repeat shown in Figure 1 and a crystallographic polymeric unit shown in Figure 2.

In agreement with the earlier study[7] the space group is $I4_1cd$. Cell parameters are $a = 13.62 \pm 0.01$ and $c = 9.10 \pm 0.01$ Å, and the assumption of 16 formula weights in the unit cell gives a reasonable calculated density of 0.609 g cm^{-3}. The structure was solved from its symmetry minimum function[8,9] and its Patterson function. Some 276 diffraction maxima, measured at 5° with the use of Cu Kα radiation and a Picker automated diffractometer, have yielded a value of R (de-

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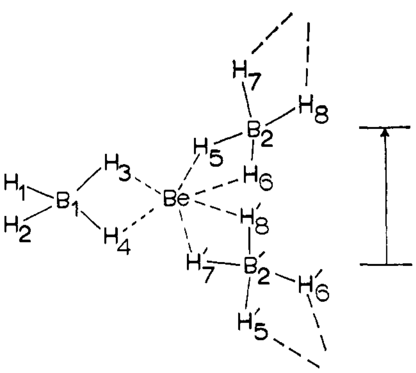
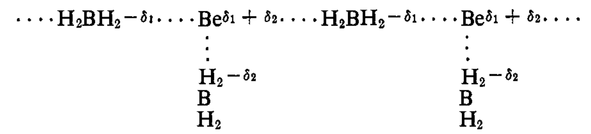


Figure 1. Schematic representation of the $Be(BH_4)_2$ structure, which can also be represented as



$$\cdots\cdot H_2\underset{\underset{H_2}{\overset{\vdots}{\underset{B}{H_2{}^{-\delta_2}}}}}{BH_2{}^{-\delta_1}}\cdots\cdot Be^{\delta_1+\delta_2}\cdots\cdot H_2\underset{\underset{H_2}{\overset{\vdots}{\underset{B}{H_2{}^{-\delta_2}}}}}{BH_2{}^{-\delta_1}}\cdots\cdot Be^{\delta_1+\delta_2}\cdots\cdot$$

The arrow indicates the chemical repeat.

fined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0.045. Atomic coordinates are listed in Table I. Probable standard deviations are 0.01 Å for Be and B distances, and 0.03 Å for distances from these atoms to hydrogen. However, these distances to hydrogen are subject to an anomalous shortening of about 0.1 Å, because of the use of spherical atoms in the refinement (0.08 Å)[10] and because of the neglect of torsional oscillation (usually about 0.02 Å).

Table I. Coordinates for the $Be(BH_4)_2$ Crystal Structure

	x	y	z
Be	0.200	0.087	−0.003
B_1	0.164	−0.049	0.006
B_2	0.139	0.194	0.118
H_1	0.095	−0.067	0.070
H_2	0.220	−0.101	−0.048
H_3	0.207	−0.002	0.098
H_4	0.143	0.009	−0.091
H_5	0.105	0.157	0.027
H_6	0.211	0.163	0.137
H_7	0.145	0.273	0.099
H_8	0.090	0.185	0.224

Distances B_1–Be = 1.92, B_2–Be = 2.00, and B_2'–Be = 2.03 Å are comparable with 1.94 Å, the sum of covalent radii.[11] Other distances are from B_1 to H_1 (1.13 Å), H_2 (1.16 Å), H_3 (1.20 Å), and H_4 (1.21 Å); from B_2 to H_5 (1.07 Å), H_6 (1.09 Å), H_7 (1.11 Å), H_8 (1.18 Å); and from Be to H_3 (1.53 Å), H_4 (1.55 Å), H_5 (1.63 Å), H_6 (1.65 Å), H_7' (1.61 Å), and H_8' (1.59 Å). For comparison we note that BH_4^- has a B–H internuclear distance of 1.255 ± 0.02 Å in the alkali borohydrides,[12] and that the Be···H···Be bridge distance of 1.4 Å has been found in $NaO(C_2H_5)_2\cdot(C_2H_5)_4Be_2H_2$.[13] Only B_1–H_1 and B_1–H_2 are not involved in some degree of bonding to Be. Possibly this $BH_4\cdots$ Be interaction (for boron B_1) has some geometrical features which may be related to the unknown structure of $Be(BH_4)_2$ in the gas phase. However, the nature of bonding, *e.g.*, whether it is predominantly covalent or ionic and whether it occurs primarily between Be and B or through hydrogen bridges, must await detailed theoretical and other experimental studies.

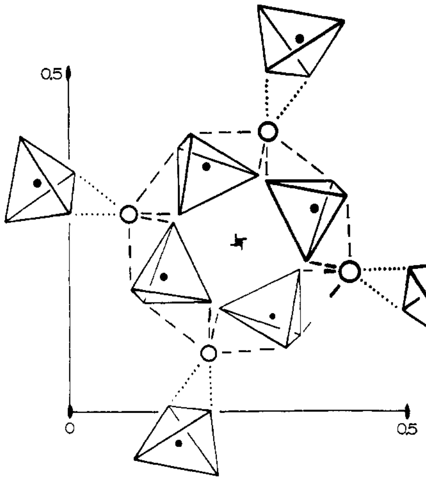


Figure 2. Portion of the unit cell, showing one helical polymeric chain around a 4_1 axis and projected along the c axis. Hydrogen arrangements are tetrahedral around B (●), and trigonal prismatic around Be (○). B–H distances are 1.14 (away from Be) and 1.20 Å (toward Be) for B_1, and 1.11 Å for the BH_4 unit within the helix. The average dotted Be···H distance is 1.54 Å, and the average dashed Be— — —H distance 1.63 Å. See text for accuracy and probable systematically short values of these distances.

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Carbonium Ion Photochemistry. The Photoisomerization of Protonated Eucarvone[1]

Sir:

The distribution of products obtained upon irradiation of eucarvone has been shown[2] to be remarkably solvent dependent. In order to assess the importance of protonated excited states and ionic intermediates, which have been invoked[2,3] in these reactions, we have investigated the photochemistry of protonated eucarvone (**1**). We wish to report that this homolog of the protonated cyclohexa-2,4-dienones[4] undergoes a superficially similar photoisomer-

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[1] Research supported by the National Research Council of Canada.

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