The Dipole Moment and Infrared Spectrum of Beryllium Borohydride

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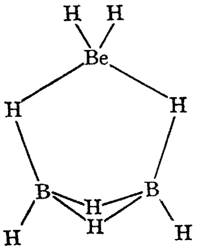
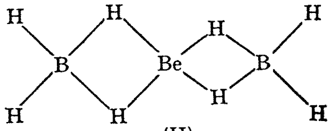
PARTICULAR interest in BeB_2H_8 stems from a recent electron diffraction study[1] which suggests that the structure has a C_{2v} configuration (I). Earlier electron diffraction data[2] and i.r. results[3] were interpreted in terms of a D_{2d} structure (II). Subsequent theoretical calculations on both structures also favour the D_{2d} configuration.[4,5]

(I)





(II)

We have re-examined the i.r. spectrum and have measured the dipole moment of BeB_2H_8. We report the symmetry of the molecule.

The dipole moment measurement was frustrated by decomposition of gaseous BeB_2H_8 above 35° in the dielectric cell, possibly due to a catalytic effect by the metal electrodes. Although this prohibited a temperature-dependence study of the molar polarization P, we measured an absolute value of $P = 105 \pm 40$ c.c./mole at 25°. Coupled with our estimate of the electronic contribution to the molar polarization of 20 ± 5 c.c./mole, we obtain a value of $2 \cdot 1 \pm 0 \cdot 5$ D for the dipole moment. Clearly structure (II) is unacceptable.

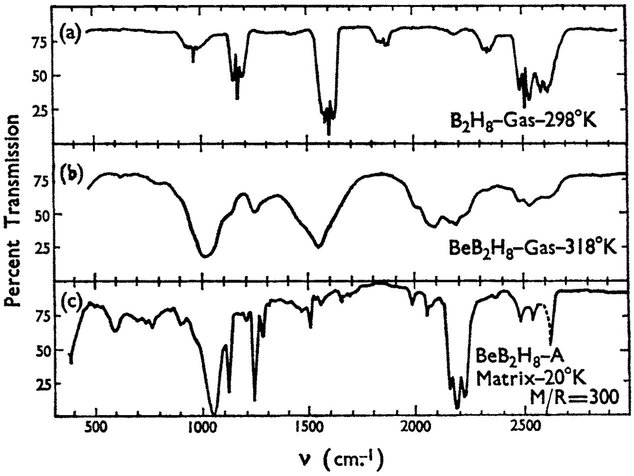


FIGURE. *I.r. spectra of* B_2H_6 *and* BeB_2H_8.

Further evidence for this is given by the i.r. spectrum (Figure). Identical gas-phase spectra were obtained with inert BaF_2, $AgCl_2$, and quartz windows, thus eliminating the window-reaction problem.[3]

A D_{2d} configuration of BeB_2H_8 would be a symmetric top molecule, as is B_2H_6 to a good approximation. Hence the parallel vibrational modes should show characteristic *PQR* rotational structure. Such structure is apparent in the B_2H_6 spectrum at 2525, 1606, and 1177 cm.$^{-1}$; however, it is absent in the BeB_2H_8 spectrum, a result best explained if the molecule has C_{2v} symmetry and hence is an asymmetric top. In addition, calculations of the rotational constants of both structures of BeB_2H_8 lead us to expect resolvable *Q*-branches in the perpendicular modes for (II) but not for (I). Such branches are resolved for B_2H_6 (*e.g.*, mode at 2612 cm.$^{-1}$) but the highest available resolution (0·5 cm.$^{-1}$) reveals no structure in the BeB_2H_8 absorptions.

The sharp matrix spectra indicate that none of the overlapping gas-phase absorptions are rotational side bands. Thus, the large number of i.r. absorptions (more than 20 in the matrix) is also an argument against (II) since this structure would have 12 active modes *vs.* 23 for (I).

The striking drop in intensity of the 1550 and 2075 cm.$^{-1}$ gas-phase bands upon matrix isolation is ascribed to an effect such as has been reported for other molecules [AlF_3, NF_2, NO_2, CuF_2, and $Cu(NO_3)_2$],[6,7] which orient with the molecular plane parallel to the substrate. By symmetry, a similar orientation of the BeB_2 plane in BeB_2H_8 necessitates assignment of one of the 2075 and 1550 cm.$^{-1}$ absorptions to the BeH antisymmetric stretch. The long BeH bond-length reported for (I) (1·65 Å) suggest assignment of the lower frequency.

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