

## Microwave Spectra of Bromodiborane and Vinyl Bromide

C. D. Cornwell

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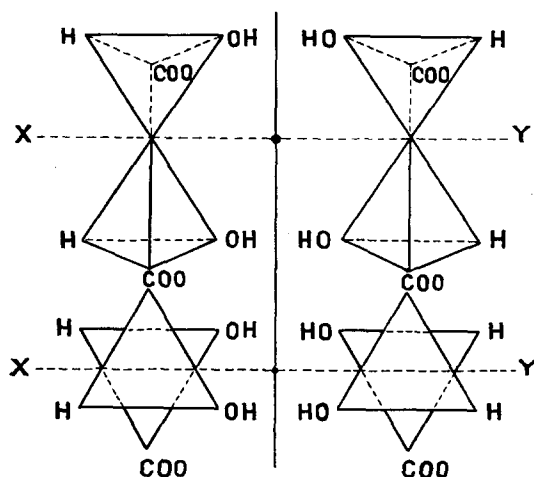


Fig. 1

Fig. 2

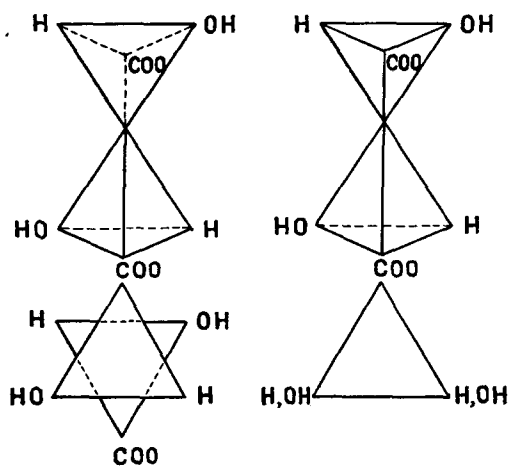


Fig. 3

Fig. 4

With our hypothesis, the *d*-tartaric ion is shown in Fig. 1 and *l*-tartaric ion in Fig. 2 or inversely, but without any possible choice. We call again attention to the fact that this configuration is in accordance with the crystal structure as determined by x-rays.<sup>3</sup> On the other hand, the mesotartaric ion is represented by Fig. 3. In all cases, the horizontal projection is a hexagon.

We would like to point out that the *d*- (or *l*-) tartaric ion possesses but one binary axis *XY* located in the plane of the paper. Thence, a few molecular vibrations are forbidden in infra-red absorption; this fact explains the very complicated spectra we recorded. Moreover, a good agreement was found between infra-red bands and Raman lines. The mesotartaric ion possesses only one center of symmetry; thus, one-half of the fundamental vibrations is inactive in absorption; accordingly, the infra-red spectrum has been simplified and we may notice an alternance between absorption and diffusion spectra; the racemic ion is then formed as a *compound* (not a mixture) of a dextro and laevo-ion. The whole assembly possesses but one center of symmetry, and in accordance with the selection rules, the racemic differs from the mesotartaric ion only by the fact that an assembly of two ions is concerned. If racemates were formed by simple juxtaposition of a *d*- and *l*-ion, we would find exactly the same number of infra-red band in the active and racemic forms, but experiments show that it is not the case.

If Fischer's convention be kept (with the carboxylic groups either ahead or behind the plane determined by hydrogen and OH-groups), the meso-tartaric ion should be shown as in Fig. 4; but this picture is false since there is no element of symmetry to explain a decrease of the recorded infra-red bands with regard to those of the active tartrates.

<sup>1</sup> E. E. Turner and K. Lonsdale, *J. Chem. Phys.* **18**, 156 (1950).

<sup>2</sup> C. Duval and J. Lecomte, *Comptes Rendus* **219**, 483 (1944); Communication à la Société Chimique de France, January 26, 1945; *Bull. Soc. Chim.* **19**, 477 (1946); Communication à la Société de Minéralogie, April 12, 1945; *Bull. Soc. franç. Min.* **69**, 56 (1946).

<sup>3</sup> Bevers and Stern, *Nature* **162**, 864 (1948).

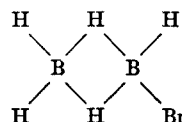
## Microwave Spectra of Bromodiborane and Vinyl Bromide\*

C. D. CORNWELL\*\*

Mallinckrodt Chemical Laboratory, Harvard University,  
Cambridge, Massachusetts

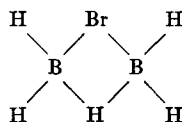
June 1, 1950

SIXTY-EIGHT lines have been observed in the microwave spectrum of bromodiborane ( $B_2H_5Br$ ). By assuming a configuration



with the ring plane normal to the plane of symmetry, it is possible to assign forty-five lines as various bromine nuclear quadrupole multiplets of  $J=2 \rightarrow 3$  and  $J=3 \rightarrow 4$  transitions. Twenty-nine lines (belonging to the most abundant isotopic species, with both boron atoms having weight eleven) are fitted with six independent parameters. Lines were found for each of the four isotopic species with mixed boron weights expected for a structure in which the boron atoms are not symmetrically located (see Table I). The aplanarity, which is clearly observable ( $I_A + I_B - I_C = 4.1 \pm 0.8$  in atomic units) corresponds to a separation of the bridge hydrogen atoms of  $2.0 \pm 0.2$  Å. This and the parameters of Tables I and II reproduce the observed frequencies with an average error of 0.2 megacycle. A structural determination is now in progress. No fine structure attributable to boron quadrupolar effects was resolved.

In order to consider the possibility of a structure with the bromine atom in the bridge,



the frequencies to be expected for this configuration were calculated. They could not be made to conform to the observed spectrum for any reasonable  $\angle B-Br-B$  or  $B-Br$  distance. Now was the observed boron isotopic pattern compatible with a structure of

TABLE I. Rotational parameters of  $B_2H_5Br$ .\*

Isotopic species	$b-c$	$b+c$	$I_B$	$I_C$
11-11-79	$228.17 \pm 0.06$	$6511.13 \pm 0.10$	$149.989 \pm 0.004$	$160.883 \pm 0.004$
11-11-81	$225.80 \pm 0.06$	$6475.70 \pm 0.10$	$150.835 \pm 0.004$	$161.734 \pm 0.004$
10-11-79	$245.30 \pm 0.06$	$6802.13 \pm 0.10$	$143.431 \pm 0.004$	$154.163 \pm 0.004$
10-11-81		$6766.4 \pm 0.2$		
11-10-79	$222.57 \pm 0.06$	$6574.67 \pm 0.2$	$148.710 \pm 0.008$	$159.131 \pm 0.008$
11-10-81	$220.1 \pm 0.2$	$6539.8 \pm 0.2$	$149.53 \pm 0.01$	$159.95 \pm 0.01$

\* Isotopic weights are for the atoms B-B-Br reading from left to right in the structural formula given.  $b$  and  $c$  are the two smaller reciprocal moments of inertia in megacycles,  $I_B$  and  $I_C$  the corresponding moments in atomic units. Probable errors are given.

TABLE II. Nuclear quadrupole coupling constants in  $B_2H_5Br$  and  $C_2H_5Br$ .

Molecule	$eQV_{aa}^*$
$B_2H_5Br^{79}$	293 mc
$B_2H_5Br^{81}$	244
$C_2H_5Br^{79}$	479
$C_2H_5Br^{81}$	399

\*  $V_{aa}$  is the component along the principal axis of least moment of the molecular electric field gradient at the bromine nucleus,  $Q$  the electric quadrupole moment of the bromine nucleus. A ratio  $Q^{79}/Q^{81}=1.20$  was assumed. Probable error is 5 mc.

TABLE III. Rotational parameters of  $C_2H_5Br$ .\*

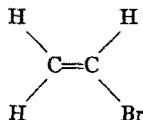
Isotopic species	$b-c$	$b+c$	$I_B$	$I_C$
$C_2H_5Br^{79}$	$299.3 \pm 0.2$	$8025.2 \pm 0.2$	$121.43 \pm 0.01$	$130.83 \pm 0.01$
$C_2H_5Br^{81}$	296.1	7979.9	122.14	131.55

\* See Table I for definitions of parameters.

this symmetry, which has only two molecular species with mixed boron isotopes.

The bromodiborane was prepared by the reaction of bromine with diborane.<sup>1</sup> The melting point and vapor pressure of the product agreed with the reported values. Although it decomposes at room temperature, it was found to be quite stable at  $-78^\circ C$  and hence all distillation paths and the absorption cell were packed in dry ice. The decomposition yields diborane and boron tribromide, which do not have microwave spectra. Di- and tribromodiborane are far less stable than bromodiborane and further more their lines could hardly be mistaken for those of the latter since the bromine isotopic pattern, which is striking because the two isotopes have equal abundances, would be different.

For the purpose of comparison with bromodiborane as well as on its own merits the structure of vinyl bromide



is of interest. Ten lines in its microwave spectrum have been assigned as  $J=2 \rightarrow 3$  transitions. They are fitted with a maximum deviation of 0.5 megacycle by the parameters of Tables II and III. The few observable Stark effects of corresponding lines of this molecule and bromodiborane are qualitatively similar. A structural determination is planned for vinyl bromide also.

The author is grateful to Professor E. B. Wilson, Jr. for his encouragement and advice and to Dr. C. A. Brown for helpful suggestions concerning the preparation and handling of bromodiborane.

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\*\* Socony-Vacuum Oil Company Research Fellow.

<sup>1</sup> A. Stock, *Hydrides of Boron and Silicon* (Cornell University Press, Ithaca, New York, 1933), p. 117.

### Low Frequency Raman Spectrum of a Benzene Single Crystal

A. FRUHLING

Laboratoire de Physique, Ecole Normale Supérieure, Paris, France  
June 16, 1950

M<sup>AIR</sup> and Hornig<sup>1</sup> have reported recently that they have been able to detect by means of the infra-red combination lines the low frequency lines of solid benzene.

In this range, however, the Raman effect yields better results as these lines are not forbidden. Following the fragmentary results of several workers,<sup>2-4</sup> I have carried out a detailed experi-

mental study of benzene, using all possible orientations of incident and scattered light vectors with respect to the axes of the single crystal, and given an interpretation of my results.<sup>5</sup>

There are four lines emitted, all very strong, with the respective frequencies 35, 63, 69 and  $105 \text{ cm}^{-1}$  at  $0^\circ C$ ; the first and third are finer than the other.

These lines arise from rotatory oscillations of the whole molecules.<sup>6,7</sup>

Assuming that the ellipsoid of polarizabilities of the molecule does not get distorted during these oscillations, the theoretical form of the polarizability tensor of the unit cell can be determined. Comparison with the experimental result then shows that the 63 and  $105 \text{ cm}^{-1}$  lines arise from rotatory oscillations around the two axes of inertia situated in the plane of the molecule. Only two out of the four possible couplings (the unit cell of benzene contains four molecules<sup>8</sup> are shown to exist by the theory, but the corresponding frequencies are not separated experimentally.

The same perfectly symmetrical polarization characteristics are found for the 35 and  $69 \text{ cm}^{-1}$  lines. I would suggest that they take their origin in oscillations around the sixfold axis, together with strong distortions of the ellipsoid of polarizabilities due to the large mobility of the  $\pi$ -electrons. This would precisely give the observed type of polarization.

The corresponding coupling can be determined through examination of a model of the crystal: the intermolecular forces act essentially between the nearest hydrogen atoms, and the estimated value of the force constant between these atoms belonging to two neighboring molecules is  $4.10^8$  dyne/cm.

The study of the two couplings for the oscillations around the other axes, using this numerical value, shows that the corresponding lines cannot be resolved experimentally.

The low frequency lines depend strongly on temperature, especially the first and third ones. They become at  $-37^\circ C$ : 45, 69, 78,  $112 \text{ cm}^{-1}$  and at  $-85^\circ C$ : 53, 74, (?),  $117 \text{ cm}^{-1}$ .

The effect of pressure (700 atmos. applied) is to increase the frequencies by five percent, in agreement with London's dispersion formula.

The oscillation hypothesis is confirmed by the study of a crystal of diphenyl.

Finally, the results concerning diphenylmethane, diphenylether (structure unknown) and anthracene show that for aromatic compounds with one, two or three rings, the restoring torques  $C$  for low frequency lines is related to the melting point  $T_f$  according to the formula  $C = A(T_f - T_0)$ , where  $A$  and  $T_0$  are constants.

<sup>1</sup> R. D. Mair and F. D. Hornig, *J. Chem. Phys.* **17**, 1236 (1949).

<sup>2</sup> E. Gross and M. Vuks, *J. de phys. et rad.* **7**, 113 (1936).

<sup>3</sup> S. C. Sirkar, *Ind. J. Phys.* **10**, 109 (1936); **10**, 189 (1936).

<sup>4</sup> A. Fruhling, *Diplôme d'Etudes Supérieures*, Paris, 1944. A. Kastler

and A. Fruhling, *Comptes Rendus* **218**, 993 (1944).

<sup>5</sup> A. Fruhling, *J. de phys. et rad.* **9**, 88 (1948). State Doctorate Thesis

to be published in *Ann. de Physique*.

<sup>6</sup> A. Kastler and A. Rousset, *J. de phys. et rad.* **2**, 49 (1941).

<sup>7</sup> T. M. K. Nedungadi, *Proc. Ind. Acad. Sci.* **A13**, 161 (1941); **A15**, 376

(1942).

<sup>8</sup> E. G. Cox, *Proc. Roy. Soc.* **135A**, 491 (1932).

### Carrier-Free Radioisotopes from Cyclotron Targets. X. Preparation and Isolation of $Mg^{27}$ from Aluminum\*

HERMAN R. HAYMOND, JOHN Z. BOWERS, WARREN M. GARRISON,  
AND JOSEPH G. HAMILTON

Crocker Laboratory, Radiation Laboratory, and Divisions of Medical Physics,  
Experimental Medicine, and Radiology; University of California,  
Berkeley and San Francisco, California

May 8, 1950

THE  $10.2\text{-min. } Mg^{27}$  was produced from aluminum by the nuclear reaction  $Al^{27}(d, 2p)Mg^{27}$  using the 20-Mev deuteron beam of the 60-in. cyclotron at the Crocker Laboratory. With deuterons of this energy, 14.8 hr.  $Na^{24}$  is also produced in comparable yield by the reaction,  $Al^{27}(d, \alpha p)Na^{24}$ . Other possible<sup>1</sup> concurrent reactions produce radioisotopes having half-lives of