The InfraRed Spectra of Borine Carbonyl and Tetramethyldiborane

R. D. Cowan

The frequencies of the principal bands occurring in the range 900–2700 cm^{-1} are shown in Table I, which includes the most recent data on B_2H_6 for comparison.[1,2] The frequencies in class (a) are attributed to B-H deformations, and those in class (c) to ordinary B-H stretching modes. The presence of strong absorption around 1500 and 2000 cm^{-1} in the Be and Al compounds is very strong evidence that these molecules have bridged structures, as suggested already by one of us.[3] In these two molecules there are two groups of frequencies in the range (b); by analogy with diborane, these are probably associated with motion of the bridge hydrogen atoms parallel and perpendicular to the bridge axis, respectively. However, when we pass to the more ionic lithium and sodium borohydrides, these frequencies respectively degenerate into bending and stretching frequencies of the BH_4^- ion.

The B-H stretching frequencies in class (c) are probably associated with terminal BH_2 groups in the Al and Be compounds, but until detailed assignments can be made it would probably be wiser not to draw conclusions as to the relative force constants in these molecules.

Our warmest thanks are due Professor R. S. Mulliken for constant encouragement and help in many ways.

[1] W. C. Price, J. Chem. Phys. 16, 894 (1948).
[2] T. F. Anderson and A. B. Burg, J. Chem. Phys. 6, 586 (1938).
[3] H. C. Longuet-Higgins, J. Chem. Soc., 139 (1946).

The Infra-Red Spectra of Borine Carbonyl and Tetramethyldiborane*

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THE infra-red spectra of borine carbonyl and of tetramethyldiborane have been obtained in the interval 2 to 25 microns with a Perkin-Elmer spectrometer.

In the spectrum of borine carbonyl (H_3BCO) the coarse structures of two bands (a strong one at 2440 and a weak one at 810 cm^{-1}) have been resolved. In each case the structure is typical of perpendicular-type bands of a symmetric-top molecule, and successive maxima show a distinct intensity alternation of the type strong, weak, weak, strong, . . . which is to be expected in the case of a threefold symmetry axis. These results thus indicate a molecular structure with symmetry C_{3v}, in agreement with Bauer's electron-diffraction results[1] and with the conclusions of Gordy, Ring, and Burg[2] from microwave rotation spectra. The spacing between adjacent Q-maxima of the perpendicular bands is 6.7 cm^{-1} in the case of the 2440-cm^{-1} band and 3.1 cm^{-1} for the 810-cm^{-1} band. Because of the large but uncertain amount of Coriolis coupling which is present, it is difficult to compare these values with the value 8.2 cm^{-1} to be expected from Bauer's data in the absence of such coupling. The band at 2440 cm^{-1} can be ascribed to the degenerate B−H stretching vibration, and a

very strong parallel band at 2164 cm^{-1} is due probably to the corresponding symmetrical vibration.

The spectrum of tetramethyldiborane provides further evidence in support of the bridge structure for diborane (B_2H_6). The complete absence of other than weak bands at frequencies greater than 1700 cm^{-1} indicates there are no B−H bonds of the type which gives rise to the very strong bands at 2522 and 2614 cm^{-1} in diborane;[3] trimethyldiborane, which was also investigated, has, on the other hand, a single strong band at 2509 cm^{-1}. The strongest band in the tetramethyldiborane spectrum lies at 1602 cm^{-1} and is almost certainly the analog of the bridge-hydrogen band of diborane at 1604 cm^{-1}.[3] A weak band at 1968 cm^{-1} may similarly correspond to the bridge-hydrogen band of B_2H_6 at 1984 cm^{-1}. The analog of the third bridge-hydrogen vibration (probably 1283 cm^{-1} in diborane), if present, is probably obscured by numerous strong methyl bands in the interval 900 to 1400 cm^{-1}.

Detailed reports on these spectra and on those of boric acid and dimethyl boric acid will be published later.

[1] S. H. Bauer, J. Am. Chem. Soc. 59, 1804 (1937).
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Infra-Red Absorption Spectra of Organic Compounds

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THE infra-red absorption spectra of some derivatives of methane, ethane, and benzene have been measured in the region from 22 to 39μ. The method of measurement in this spectral region has been previously described.[1] All the compounds were measured in the liquid state and the cells were from 0.2 to 1.6 mm in thickness. The observed bands, all of medium or of low intensity, are listed in Table I. The wave numbers listed for the regions of maximum absorption are accurate to about ±2 cm^{-1}. The accuracy is sufficient for survey work. One source of error arises from changes in the temperature of the prism. The temperature coefficient of the index of refraction for the TlBr-I prism is −0.00016 as measured in the visible region. Changes in refractive index of these crystals over a period of time have also been observed. Hyde[2] has reported changes in the index of refraction of 0.0048 over a period of a few months. For work of high accuracy the instrument should be calibrated before and after each substance is measured. Methods of annealing recently developed by the Engineer Research and Development Laboratories give promise of producing more stable prisms than those which have been available.

Most of the compounds listed in Table I have been measured in the NaCl and KBr regions. Many bands appear in the region of wave-lengths from 2 to 22μ. Carbon tetrachloride in cell thicknesses of 1.0 mm has been investigated with a KBr prism. Bands have been found at 17.59, 18.82, 20.73, and 22.43μ. These have all been interpreted in

TABLE I. List of observed bands.

Substance	Wave-length (μ)	Wave number (cm⁻¹)
Chlorodibromomethane	26.2	381
	35.8	279
Dichlorobromomethane	22.9	437
	26.2	381
	30.3	330
Dichlorodibromomethane	22.6	442
	25.2	397
	26.7	375
	28.4	351
Trichlorobromomethane	23.8	420
	28.4	351
	34.0	294
Ethylene chloride	24.3	412
	36.7	272
Ethylene bromide	24.9	402
	28.1	355
s-Tetrachloroethane	28.4	352
	30.7	326
	34.5	290
Ethylcyclopentane	23.6	424
	25.4	393
cis-1,3-Dimethylcyclopentane	23.5	426
Methylcyclohexane	22.6	442
	24.7	405
1-Methyl-2-ethylbenzene	22.1	452
	22.9	437
	31.1	322
1-Methyl-3-ethylbenzene	22.9	437
1-Methyl-4-ethylbenzene	27.3	366
	32.5	308
2-Methyl-2-phenylpropane	25.3	395
	32.5	308
Chlorobenzene	23.9	418
	33.8	296
Bromobenzene	31.9	313
Iodobenzene	22.3	448
o-Dichlorobenzene	22.9	437
	29.8	335
1,2,4-Trichlorobenzene	22.8	438
	25.2	397
	32.6	307
p-Chlorobenzotrifluoride	24.4	409
	26.0	385
	31.9	313
	33.1	302
	36.5	274
o-Bromoanisole	22.9	437
	30.3	330
	35.7	280
p-Bromoanisole	30.7	326
	37.9	264
α-Bromonaphthalene	24.9	402
	33.5	298
Diethyl ether	22.7	440
	26.7	374

accordance with the known energy level scheme for CCl₄, and include the difference bands at 20.73 and 22.43μ, predicted by Herzberg as of sufficient intensity for observation. A detailed report is in preparation.

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Structure—Optical Studies. II. Aqueous Dispersion of Polyvinyl Borate— Iodine and Its Heat of Formation

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A QUEOUS dispersions of polyvinyl borate (PVB), formed by mixing dilute polyvinyl alcohol (PVA) with boric acid solution, react to iodine in the same way as do amylose solutions by giving a blue color due to a strong absorption band in the near red. If the boric acid is omitted from the reaction mixture, no blue color results because of complete dissociation of the blue PVA-iodine compound at the dilutions in question. The wave-length of maximum absorption for PVB-iodine solution is 670 mmu, while that of soluble starch-iodine is only 590 mmu under parallel conditions; that reported[1] for amylose-iodine is 628 mmu. The absorption bands of these compounds are symmetrical and are similar to each other in height and half-width. The triple color reaction of boric acid, PVA, and iodine, by reason of its marked specificity, has analytical possibilities for the detection or determination of any one of its three components, more especially the latter two. Colloidal polyvinyl phenylborate, made in the same way and having similar properties, does not give a color reaction with iodine under similar conditions. When bromine is added to rather concentrated soluble starch or PVB solutions, we observe a distinct color change from yellow to orange or red but have failed to measure an intense absorption band here; the spectrophotometric data suggest extensive dissociation of such compounds in solution.

(With E. Emerson.) We find unexpectedly large heats are evolved when one mole of halogen (iodine or bromine) is added to an excess of organic polymer in aqueous dispersion under conditions to give as complete formation of addition compound as possible. Our results, which we did not reproduce to better than 10 percent, are summarized as the starred figures in Table I, together with data from the literature.[2] All values here are in kcal. per mole of halogen and refer to the halogens in their standard (condensed) states. While the complexity of the colloidal systems (lines 2 and 3 of Table I) prevents a detailed interpretation of these figures taken by themselves, they suggest that the energy of formation of these compounds from halogen molecules is an appreciable fraction of the energy of formation of the molecules from neutral atoms, and is considerably greater than the heat of formation of simple crystalline trihalides from the crystalline halides (last line of Table I). It would be of considerable interest to know the heat of formation of the present dry addition compounds from the dry reactants, which is in principle determinable.

These findings are of interest in connection with the x-ray diffraction results reported in Paper I of this series.[3] With the polymers there listed as showing the characteristic interferences of linear polyiodine we should have included the poorly crystalline polyvinyl silicate, made by esterifying PVA; we have since added the crystalline polymer known commercially as Terylene. Solid, oriented iodine-bearing polyvinyl silicates and borates have been described

TABLE I. Thermochemistry of halogens.

	Iodine	Bromine
Heat of formation from atoms	51	54
Heat of addition to PVB	20*	12.5*
Heat of addition to potato starch	10*	7*
Heat of solution in various solvents	−6 to 6*†	−1 to 3
Heat of addition to ionic halides to give trihalides	0,8(K, Cs)	5(NH₄)

* New results.
† From measured heat of solution of 6.35 g (0.025 mole) I₂ in 180 cc EtOH containing 3.6 g (0.025 mole) NH₄I.