Gaseous Bivalent Boron Cations: Stability and Structure

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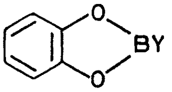
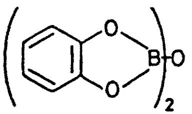
Summary Experimental evidence for the instability of five-membered cyclic borenium ions supports the view that for such ions a linear structure is probably the most stable.

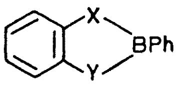
THE structure of ions in the gas phase is a topic of longstanding concern in several fields of chemistry. We report some observations concerning the stabilities of borenium ions (BX_2^+) and the structural implications of these observations.

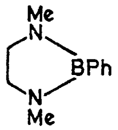
From a recent tabulation of heats of formation of gaseous ions[1] the following thermodynamic stability order can be derived: $B(OMe)_2^{\dotplus} \gg BF_2^{\dotplus} > MeBF^+ > BCl_2^{\dotplus} \geqslant BEt_2^{\dotplus} > BMe_2^{\dotplus} \simeq BBr_2^{\dotplus} > BH_2^+$. It is apparent that borenium ions are stabilized by substituents bearing lone pairs. A further demonstration of this stability is found in numerous reported mass spectra in which borenium ions are abundant; examples include the alkyl borates,[2] boron halides,[3] boron–boron bonded compounds such as $(Me_2N)_2B–B(NMe_2)_2$,[4] and dimethylboronic acid anhydride.[5]

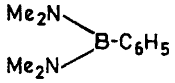
We now report that when potential borenium ions are encompassed in five-membered rings, the mass spectra are devoid of these ions.† For example, the spectrum of compound (I) did not include a $M^{+\cdot} - C_6H_5\cdot$ ion (the ion of 1·5% relative abundance observed at this nominal mass was shown by exact mass measurement to be the ^{10}B isotope of the $M^{\dotplus} - C_6H_4$ fragment), even though this ion might have been expected to have been rather well stabilized. To establish the generality of this result, we obtained the mass spectra of compounds (II)—(IX);‡[6] in no case was an ion of more than 1% relative abundance observed at the nominal mass of the borenium ion. The compounds


(I) Y=Ph
(II) Y=Cl
(III) Y=Et
(IV) Y=OH


(V)


(VI) X=Y=NH
(VII) X=NH, Y=O
(VIII) X=NH, Y=S


(IX)


(X)

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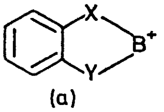
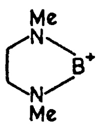
† This is true of all the compounds mentioned here, but it is not implied that such ions can never be formed. There are two examples in the literature where such ions are apparently formed, albeit in very low abundance: (a) M. F. Lappert and J. Horner, *J. Chem. Soc.* (*A*), 1969, 173; (b) C. J. W. Brooks, B. S. Middelditch, and G. M. Anthony, *Org. Mass Spectrometry*, 1969, **2**, 1023. In contrast to the five-membered cyclic compounds, six-membered heteroaromatic boron compounds [R. C. Dougherty, *Tetrahedron*, 1968, **24**, 6755], including boroxines [E. W. Post, R. G. Cooks, and J. C. Kotz, *Inorg. Chem.*, in the press] and borazines [W. Snedden, *Adv. Mass Spectrometry*, 1961, **2**, 456], sometimes give abundant ions by loss of the substituent from boron; we have no simple explanation for this difference from the five-membered cyclic compounds.

‡ Complete spectra of the compounds discussed in this study are available on request. Spectra were obtained on an AEI MS9 spectrometer at 70 and 20 ev.

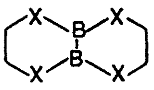
examined were chosen to optimize the possibility of generating the cyclic borenium ions, a requirement that dictated the inclusion of the B–Cl bond in compound (II) (good leaving radical) and the B–alkyl bond in (III) (weaker B–C bond). The non-observation of borenium ions is not due to ready competitive fragmentations; the spectra are generally extremely simple with the molecular ions constituting the base peaks, while those fragment ions which do occur are mostly due to simple ring cleavages. Low electron energy spectra showed that the absence of borenium ions could not be explained by their removal by further fragmentation. Furthermore, the absence of these ions could not be ascribed to any special molecular ion stability due to an aromatic backbone; neither (VI) nor the non-aromatic compound (IX) showed loss of $C_6H_5\cdot$, whereas the $M^{+\cdot} - C_6H_5\cdot$ ion had a relative abundance of 25% in the 70ev spectrum of compound (X). (The most prominent fragment ion in this spectrum was the alternative borenium ion, $Me_2N{-}B^+{-}C_6H_5$, 97% relative abundance. Phenylboronic acid, an oxygen analogue of compound (X), exhibited analogous borenium ions in its mass spectrum.[7]) It is particularly noteworthy that homolysis of the boron-carbon bond in (I) occurs with charge retention by the phenyl fragment; in compounds (I) and (III) the charge may be retained by the boron-containing fragment only if hydrogen transfer accompanies the bond scission. We therefore conclude that the cyclic borenium ions (a) and (b) are thermodynamically unstable relative to their non-cyclic analogues.

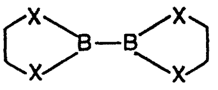

(a)
X and Y = O, NH, NMe, or S


(b)

Using well-known arguments,[8] ions of the type $BX_2^{+\cdot}$ (X = halogen, OR, NR_2, *etc.*) are predicted to be thermodynamically most stable when linear. In fact, an MO calculation predicts $BF_2^{+\cdot}$ to be *ca.* 30 kcal more stable when the F–B–F angle is 180° than when it is 120°, a not surprising result considering that $BF_2^{+\cdot}$ is isoelectronic with CO_2.§ However, while abundant experimental evidence supports the fact that 16 valence electron AB_2 molecules are linear, experimental evidence for the structures of gaseous ions is very limited.¶ Our observation that non-cyclic borenium ions are thermodynamically more stable than their five-membered cyclic analogues may be taken as experimental evidence that such non-cyclic ions are probably linear.

A further result of our observations is that they cast doubt on the validity of the arguments recently used in assigning structure (XI) rather than (XII) to a series of $B_2(X_2C_2H_4)_2$ compounds,[4] since the assumption that the bicyclic structure (XII) would give abundant borenium ions is now questionable. Finally, the recently noted stability of the $(C_2H_4O_2)BPh$ molecular ion is explained as a general phenomenon.[9]


(XI) X=O, S, or NMe


(XII) X=O, S, or NMe

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§ The calculation was performed according to the CNDO procedure of Pople using the program provided by the Quantum Chemistry Program Exchange. A B–F bond length of 1·38 Å was used. The increase in internal energy on bending a linear borenium ion should be smaller for nitrogen substituents (one lone pair) than for oxygen or halogen substituents. This makes our comparison of the spectra of compounds (IX) and (X) even more appropriate as they provide an extreme example of the sensitivity of mass spectra to differences in internal energies of ions.

¶ Electronic spectra of certain triatomic ions have been used to demonstrate their linear (CO_2^+ and CS_2^+) or non-linear (N_2O^+) structures. G. Herzberg, "Molecular Spectra and Molecular Structure, III, Electronic Spectra and Electronic Structures of Polyatomic Molecules," Van Nostrand, Princeton, New Jersey, 1966, pp. 499—507.

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[6] Prepared using literature procedures, see M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 1958, 3076; J. A. Blau, W. Gerrard, M. F. Lappert, B. Z. Mountfield, and H. Pyszora, *ibid.*, 1960, 380; K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, 1962, **1**, 738.
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[9] R. H. Cragg and J. F. J. Todd, *Chem. Comm.*, 1970, 386.