

to compensate for the decreased effective electronegativity of the carbon cores in b^{2-} , do not show degeneracy of the highest occupied π orbital. Also, bond length measurements indicate biphenylene is essentially devoid of cyclobutadiene character.²²

Further evidence inferring b^{2-} does not derive special stability from being a closed shell $4n + 2$ π -electron molecule is obtained from the proton magnetic resonance spectrum of b^{2-} . The chemical shift difference between the centers of b^0 and b^{2-} patterns indicates that partitioning of electron density in the dianion²³ between C-1-C-8 and C-9-C-12 is essentially identical with that determined for b^{-} by electron spin resonance.^{24,25} The electron distribution in this latter species was best explained by assuming unequal bond lengths in the 4-C ring, *i.e.*, C-C of 9-10 and 11-12 are long,²⁵ thus indicating a lack of aromaticity for these species.

The effects of factors influencing disproportionation of polyacene radical anions are under investigation, as is the analysis of b^{2-} and other dianion p.m.r. spectra.

(22) T. C. W. Mak and J. Trotter, *Proc. Chem. Soc.*, 161 (1961).

(23) Using the equation $\Delta\delta = 10.7\rho$ [T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 96 (1963)].

(24) C. A. McDowell and K. F. Paulus, *ibid.*, **40**, 828 (1962).

(25) A. Carrington and J. Dos Santos-Veiga, *Mol. Phys.*, **5**, 285 (1962).

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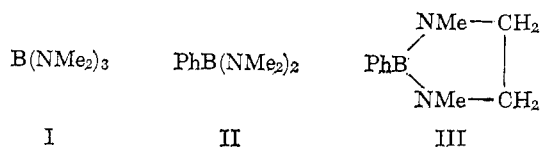
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Doubly Charged Ions in the Mass Spectra of Some Organoboron Derivatives¹

Sir:

We wish to report the appearance of very intense peaks, due to doubly charged ions, in the mass spectra of tris(dimethylamino)borane (I), bis(dimethylamino)phenylborane (II), and 1,3-dimethyl-2-phenyl-1,3,2-diazaborolidine (III).



The intensities of peaks due to doubly charged ions in the mass spectra of organic compounds rarely exceed 1-2% of the base peak intensity.² If the molecule, or part of it, is aromatic or heteroaromatic, the ability of the molecule, or some of its fragments, to sustain two positive charges can be considerably increased.³ Mass spectra of substituted indoles² and of some alkaloids³ show abundant peaks due to doubly charged ions, some of which correspond to 10% or more of the base peak intensity. The presence of abundant double charged ions in the mass spectrum of a compound is invariably connected with the presence of aromatic rings or high unsaturation in the molecule.³

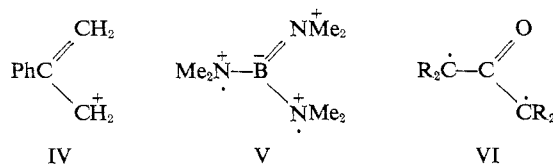
(1) This work was supported by the Atomic Energy Commission through Contract Number AT-(40-1)-3207.

(2) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, p. 344, 401.

(3) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 158.

The boron amides were prepared by standard methods: I, b.p. 33° (5.5 mm.), lit.⁴ 43° (12 mm.), n_D^{25} 1.4450; II, b.p. 56° (0.5 mm.), lit.⁵ 59° (3 mm.), n_D^{25} 1.5155; III, b.p. 66.5° (0.5 mm.), lit.⁵ 73° (3 mm.), n_D^{25} 1.5350. The mass spectra were measured by Mr. F. C. Maseles in the Mass Spectrometry Laboratory of The University of Texas, using a Consolidated Electroynamics Corp. Type 21-103C mass spectrometer with an ionization potential of 70 v. and 50- μ a. current. The doubly charged ions could be identified by the presence of peaks corresponding to half-integral mass number, either for the ¹⁰B or ¹¹B isotopic species. The total contributions of doubly charged species to the mass spectra of I, II, and III were 6.6, 6.15, and 11.1% Σ_{50} , respectively. The largest peaks for doubly charged ions corresponded in each case to ions derived from the parent molecules by loss of two electrons. The appearance potentials for the relevant peaks in the spectra of I and III were found to be 21 ± 1 and 23.5 ± 1 e.v., respectively, using xenon calibration. Although the facilities available to us did not permit these to be measured with any great accuracy, the results are sufficient to indicate that the species involved have high energies and must almost certainly be doubly charged. At the same time these values are considerably less than those commonly observed³ for multiple ion formation, a further indication of the unusual stability of the dipositive ions in our case.

Previous compounds yielding abundant dipositive ions have invariably been aromatic³; in this case aromaticity is clearly not a factor, given that I and II form a comparable percentage of such ions. The ready formation of dipositive ions at relatively low ionizing potentials indicates clearly that the ions are unusually stable. This is not surprising in the case of II and III, which are isoconjugate with the stable β -phenylallyl-carbonium ion IV. The case of V is interesting; this is isoconjugate with the "nonclassical" system VI, which was postulated⁶ some time ago by Burr and Dewar on the basis of MO calculations to be an intermediate in the Favorskii reaction, a conclusion later confirmed experimentally by Fort.⁷



The ease with which V was formed in the mass spectrometer suggests that it might conceivably be isolable in the form of stable salts; however, treatment of I with antimony pentachloride led to decomposition.

(4) H. A. Skinner and N. B. Smith, *J. Chem. Soc.*, 4025 (1953).

(5) K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962).

(6) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

(7) A. W. Fort, *J. Am. Chem. Soc.*, **84**, 4979 (1962). Fort represented the intermediate in terms of resonance theory, a formulation which is equivalent to, but much less satisfactory than, the earlier MO representation used by Burr and Dewar.⁶

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