

Studies in Mass Spectrometry. Singly- and Doubly-charged Molecular Ions; Stability and Abundance

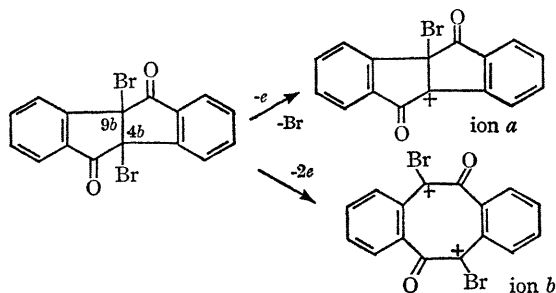
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Summary The first case of a doubly-charged molecular ion of higher abundance than that of the singly-charged one is reported and discussed.

THE abundance of doubly-charged ions formed under electron impact is usually low.¹ If the molecule is aromatic or heteroaromatic and if it does not contain bonds which can undergo rupture with great ease, its ability to sustain two positive charges is considerably increased.¹ This is also true for some diamminoboranes, which exhibit relatively abundant doubly-charged parent ions.²

The existence of a doubly-charged molecular ion of higher abundance than that of the singly-charged parent ion has, however, not yet been demonstrated.† The



highest $M^{2+}:M^+$ abundance ratio reported to date was observed in the case of hexabenzocoronene, where it is 0.6 at 70 eV.³

The relative electronic transition probabilities for multiply-charged parent ions are always lower than those

of the singly-charged ones⁸ and their ionization potentials are always higher. Therefore, a doubly-charged molecular ion M^{2+} cannot be expected to be more abundant than the singly-charged M^+ unless it is *much more stable*, i.e. decomposes to a much smaller extent. Such cases are evidently quite rare and none have been reported so far.

We report the first case of a doubly-charged parent ion which is more abundant than the singly-charged one at 70 eV.

4b,9b-Dibromo-4b,5,9b,10-tetrahydroindeno[2,1-a]inden-5,10-dione, ‡ (I), exhibited a molecular ion of extremely low abundance ($<10^{-4}$ of the most intense ion; m/e 390, 392, and 394, containing ^{79}Br ^{79}Br , ^{79}Br ^{81}Br , and ^{81}Br ^{81}Br , respectively). The most abundant fragment-ion was formed by the loss of a bromine atom (m/e 311 and 313; base peak). The doubly charged parent ion M^{2+} (m/e 195, 196, and 197) was *more than 200 times more abundant* than M^+ in this case (1.3% of the base peak).

We attribute the difference in the abundance of the singly- and doubly-charged parent ions to the difference in their relative stabilities. While the singly-charged parent ion M^+ is stabilised by the loss of a bromine atom, forming an even-electron benzylic cation *a* (or an isomer⁹ thereof), the doubly-charged molecular ion M^{2+} can be stabilised by the cleavage§ of the 4b-9b bond, forming an isomerised even-electron⁵ parent ion *b* (or an isomer⁹ thereof), in which the two positive charges are localised at separated favourable positions.^{4,5,10} The positive charge on the carbon atom attached to each of the bromine atoms is expected to increase the stability of the C-Br bond and thus stabilise the doubly-charged molecular ion. In fact the $[M-\text{Br}]^{2+}$ ion is of very low abundance. The ratio of abundances $[M-\text{Br}]^{2+}:[M]^{2+}$ is 0.13 while $[M-\text{Br}]^+:[M]^+$ is more than 10,000.

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† Doubly-charged *fragment ions* of higher abundance than that of the corresponding singly-charged fragments are rather common.^{1,4-6} In the case of bisbenzylisoquinoline alkaloids⁶ and some thiophen analogues of porphyrins⁷ doubly-charged *fragment ions* have been reported to be the most abundant in the mass spectra.

‡ Prepared by bromination of 4b,5,9b,10-tetrahydroindeno[2,1-a]inden-5,10-dione (R. B. Davis, *J. Amer. Chem. Soc.*, 1958, **80**, 1752; A. C. Cope and S. W. Fenton, *ibid.*, 1951, **73**, 1668). M.p. 204–206° (ethanol). Satisfactory elemental analysis, i.r. and n.m.r. spectra were obtained.

§ Beynon¹¹ suggested an open-chain structure with maximum charge separation for the doubly-charged parent ion of benzene.

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⁴ S. Meyerson, J. Puskas, and E. K. Fields, *Chem. Comm.*, 1969, 347.

⁵ F. W. McLafferty and M. M. Bursey, *Chem. Comm.*, 1967, 533.

⁶ M. Shamma, R. S. Dudock, M. P. Cava, K. V. Rao, D. R. Dalton, D. C. DeJongh, and S. R. Shrader, *Chem. Comm.*, 1966, 7; J. Baldas, Q. N. Porter, J. R. C. Bick, and M. J. Vernengo, *Tetrahedron Letters*, 1966, 2059; D. C. DeJongh, S. R. Shrader, and M. P. Cava, *J. Amer. Chem. Soc.*, 1966, **88**, 1052.

⁷ M. Ahmed and O. Meth-Cohn, *Tetrahedron Letters*, 1969, 1493.

⁸ R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice Hall, New Jersey, 1965, p. 130, and references cited therein.

⁹ S. Meyerson, H. Hart, and L. C. Leitch, *J. Amer. Chem. Soc.*, 1968, **90**, 3419 and references cited therein.

¹⁰ A. Mandelbaum and D. Ginsburg, *Israel J. Chem.*, 1966, **4**, 149; J. Sharvit and A. Mandelbaum, unpublished results.

¹¹ J. H. Beynon and A. E. Fontaine, *Chem. Comm.*, 1966, 717.