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MASS SPECTRA OF HETEROAROMATIC BORON COMPOUNDS

INTERPRETATION OF β-CLEAVAGE REACTIONS USING THE PMO METHOD

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Abstract—Low and high resolution fragmentation patterns for derivatives of 10,9-borazarophenanthrene, 2,1-borazaronaphthalene and 4,3-borazaroisoquinoline are reported. The spectra are qualitatively similar to the parent aromatic systems, however, if one heteroatom is eliminated the boron atom usually remains with the charged particle. Application of the PMO method[1] to the interpretation of β-cleavage reactions in heteroaromatic systems has been reviewed. The PMO approach is shown to give a sound qualitative account of the observed β-cleavage reactions.

INTRODUCTION

THE borazarenes[2] offer many unique opportunities for studies of the relative importance of molecular structure and atom electronegativity in determining the physical properties and chemical reactivity of molecules. A typical heteroaromatic B—N system, 12,11-borazarophenanthrene[3] (I) may be viewed as a phenanthrene system in which there has been a 12,11-nuclear proton shift. The reciprocal changes in atomic charge at two sites in the molecular backbone should be small perturbations when compared to the total π-energy of the system. A careful comparison of the properties and reactivity of heteroaromatic B—N systems with their isolectronic hydrocarbon analogues should provide a susbstantial amount of information about the effects of these small electronic perturbations. The reactions of gas phase ions are particularly well suited for this kind of comparison because of the lack of differential solvent effects in gas phase systems. A logical first step for the comparison of gas phase reactivity involves the study of EI fragmentation patterns for a suitable series of compounds. This paper reports the results of a preliminary study along these lines.

RESULTS

Tables 1 and 2 indicate respectively the structures and mass spectra of the borazaro compounds we have investigated. The compounds fall conveniently into three groups, namely, derivatives of borazarophenanthrene, borazaronaphthalene and borazaroisoquinoline.

In the fragmentation schemes which follow, strong arrows indicate transitions for which metastable ions could be found, presumed transitions are indicated by dashed arrows. We have no direct evidence concerning the structures of the ions in these spectra, hence the structures presented in the following fragmentation schemes were drawn by observing the following considerations. The structures of the ions in all cases meet the usual requirements of valence. Hydrogen atoms were presumed to

TABLE 1. STRUCTURE OF THE BORAZARENES INVESTIGATED

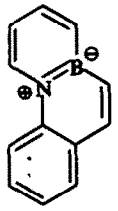
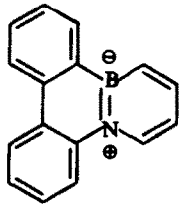
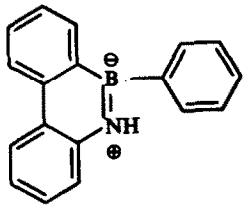
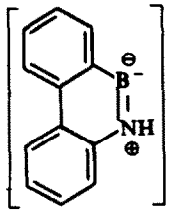
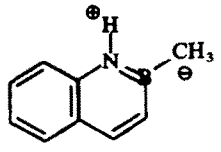
		Ref.
Borazarophenanthrenes		
I.		3
	12,11-borazarophenanthrene	
II.		4
	14,13-borazarotriphenylene	
III.		5
	10,-phenyl-10,9-borazarophenanthrene	
IV.		6
	bis-10,9-borazarophenanthryl ether	
Borazaronaphthalenes		
V.		5
	2-methyl-2,1-borazaronaphthalene	

TABLE 1—*continued*

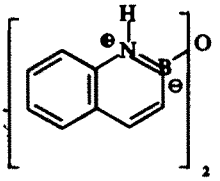
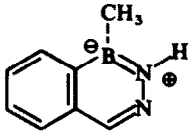
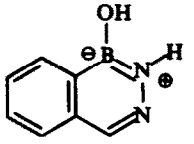
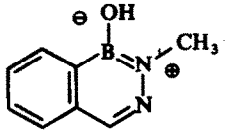
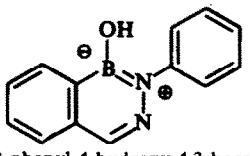
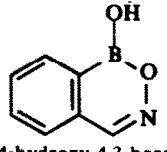
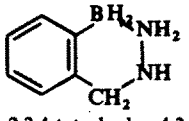
		Ref.
Borazarophenanthrenes—continued		
VI.	 bis-2,1-borazaro-2-naphthyl ether	7
Borazaroisoquinolines		
VII.	 4-methyl-4,3-borazaroisoquinoline	8
VIII.	 4-hydroxy-4,3-borazaroisoquinoline	8
IX.	 3-methyl-4-hydroxy-4,3-borazaroisoquinoline	9
X.	 3-phenyl-4-hydroxy-4,3-borazaroisoquinoline	9
XI.	 4-hydroxy-4,3-boroxaroisoquinoline	10
XII.	 1,2,3,4-tetrahydro-4,3-borazaroisoquinoline	9

TABLE 2. PRINCIPAL PEAKS IN THE MASS SPECTRA OF THE BORAZARENES

Peaks are listed in order of decreasing mass to charge ratio with intensities in parentheses expressed as a percentage of the most intense peak. The heteroatom content of ions, for which atomic compositions were determined by mass measurement, is listed following the intensity. Hydrocarbon ions are indicated by the letter C. Multiplets are listed in order of decreasing intensity. Atomic compositions of doubly charged ions are followed by (D). Spectra that are not graphically recorded in the text are presented in full, otherwise only the mass measured ions are listed here. Ions with intensity less than 1% of the base peak, and all ions below *m/e* 70 have been omitted. The very prominent metastable ions (m*) are listed separately along with the probable transition.

I. 179(100)^{11}BN; 178(30)^{10}BN, ^{11}BN; 152(9)^{11}BN, ^{10}BN; 100(4)^{11}B; 99(^{11}B, ^{10}B); m*: 129·6 (178 → 152)

II 229(100)^{11}BN; 228(30)·^{0}BN, ^{11}BN; 202(6)^{11}BN; 201(4)^{10}BN, ^{11}BN; 179(18)^{11}BN; 177(4)^{11}BN; 153(3)C, ^{10}BN; 151(2)C, ^{11}B; 150(2)^{11}B, ^{10}C; 114·5(11)^{11}BN(D); 89·5(1)^{1}BN(D); m*: 179·9 (229 → 203); 178·2 (229 → 202)

III. 255(100)^{11}BN; 225(1)^{11}B, ^{11}BN; 177(18)^{11}BN; 152(2)C; 151(3)^{11}B, C; 150(4)^{11}B^{10}B, C; m*: 122·8 (255 → 177).

IV. 372(100)^{11}B$_2$N$_2$O; 357(1)^{11}B$_2$N$_2$O; 356(1)^{11}B$_2$N$_2$O; 344(1)^{11}B$_2$N$_2$O; 343(1)^{11}B^{10}BN$_2$O; 195(14)^{11}BNO; 186(5)^{11}B$_2$N$_2$O(D); 152(2)C; 151(2)^{11}B, C; 150(2)^{11}B; m*: 160·7 (195 → 177); 318·1 (372 → 344).

V. 144(15); 143(100)^{11}BN; 142(44)^{10}BN, ^{11}BN; 141(5) 140(4); 139(2); 129(5); 128(56)^{11}BN, ^{11}B; 127(15); (126(2); 117(3)^{11}BN; 116(9)^{11}BN; 115(8)^{11}BN, ^{10}BN; 114(5); 113(3); 112(1); 102(4); 101(10)^{11}B; 100(4)^{10}B, ^{11}B; 99(1); 91(1); 90(2); 89(5)^{11}B, BN, C; 88(3); 87(3): 86(1); 85(1); 77(3)C; 76(4); 75(6); 74(4); 73(1); 71·5(7); 71(3); 70·5(5); 70(2); m*: 114·6 (143 → 128); 78·1 (128 → 100).

VI. 274(2); 273(18); 272(100)^{11} B$_2$N$_2$O; 271(87); 270(44); 269(15); 268(4); 257(2); 253(2); 244(1); 243(1); 242(1); 154(1); 146(1); 145(9)^{11}BNO; 144(3); 143(2); 136·5(2); 136(14)^{11}B$_2$N$_2$O(D); 135·5(15) ^{11}B$_2$N$_2$O, ^{10}B^{11}BN$_2$O(D); 135(19^{10}B^{11}BN$_2$O, ^{10}B$_2$N$_2$O(D); 134·5(8); 134(2); 129(3); 128·5(1); 128(19)^{11}BN; 127(9); 126(3); 123(2); 122·5(1); 122(1); 121·5(2); 121(1); 118(1); 117(10)^{11}BN, ^{11}BO; 116(2); 115(1); 103(1); 102(4); 101(10)^{11}B, ^{10}B; 100(7); 99(2); 91(3); 90(4); 89(3); 79(1); 78(11); 77(7); 76(5); 74(4); 73(1); m* 79·7 (128 → 101); 78·7 (127 → 100).

VII. VV(100)^{11}BN$_2$; 143(24)^{10}BN$_2$; 129(26)^{11}BN$_2$; 116(7)^{11}BN; 102(10)^{11}BN; 89(4)^{11}B, C; m*: 115·6 (144 → 129); 80·7 (129 → 102); 93·4 (144 → 116); 68·3 (116 → 89).

VIII. 147(8); 146(100)^{11}BN$_2$O; 145(30)^{10}BN$_2$O, ^{11}BN$_2$O; 144(2); 119(11)^{11}BNO; 118(7); 117(22)^{11}BO, ^{10}BO; 116(5)^{11}BN, ^{10}BO; 105(2); 104(2); 103(5); 102(1); 92(5) 91(8)^{11}BN, C, ^{11}BN$_2$, ^{11}BO; 90(4); 89(3); 78(1); 77(5); 76(6); 75(2); 74(2); 73(2); m*: 97 (146 → 119; 92·2 (146 → 116); 73·2 (145 → 103); 71·4 (116 → 91).

X. 163(2); 162(2); 161(10); 160(100^{11}BN$_2$O; 159(82)^{11}BN$_2$O, ^{10}BN$_2$O; 158(16); 157(1); 151(2); 148(6); 147(32); 146(44); 145(81)^{11}BN$_2$O; 144(25); 143(11)^{11}BN$_2$; 142(3); 141(4); 134(1); 133(15); 132(44)^{11}BNO; 131(31)^{10}BNO; 130(13); 129(11); 128(4); 127(1); 123(1); 122(1); 120(1); 119(3); 118(25); 117(31)^{11}BO; 116(78)^{11}BN, ^{10}BO; 115(25); 114(14); 113(4); 112(1); 107(1); 106(8); 105(12)^{11}BO; 104(31); 103(22); 102(9); 101(8); 100(5); 99(2); 92(11); 91(72)C, ^{11}BO; 90(10); 89(22)^{11}B, C; 88(12); 87(15); 86(5); 85(4); 84(1); 80(2); 79(4); 78(9); 77(24C. ^{11}B); 76(15); 75(12); 74(8); 73(3); 72(4); 71(18); 70(8); m*: 131·4 (160 → 145); 109·6 (159 → 132).

X. 224(2); 223(15); 222(100)^{11}BN$_2$O; 221(67)^{10}BN$_2$O, ^{11}BN$_2$O; 220(16); 205(1); 204(2)^{11}BN$_2$; 203(2)^{11}BN$_2$, ^{10}BN$_2$; 199(2); 195(2); 194(3); 193(4)^{11}BNO; 192(1); 178(2)^{11}BN; 178(1); 177(1); 176(1); 168(1); 167(4)N; 166(1); 165(1); 152(1); 151(1); 150(1); 141(1); 132(1); 131(2); 130(2); 129(1); 119(5); 118(4); 117(3); 116(2); 115(2); 111·5(1); 111(4)^{11}BN(D); 110·5(3); 110(1); 105(1); 104(6); 103(6)N; 102(2); 96·5(1); 96(1); 93(10); 92(5); 91(6); 90(1); 89(1); 83(1); 78(3); 77(13); 76(2); 75(1); m*: 187·5 (222 → 204); 186·5 (221 → 203); 170·3 (221 → 194); 169·3 (220 → 193); 143·8 (194 → 167).

TABLE 2—*continued*

XI. 148(8); 147(100)$^{11}BNO_2$; 146(24)$^{10}BNO_2$; 133(1); 130(2); 129(2); 128(1); 122(1); 121(1); 120(4); 119(2); 118(1); 117(16)^{11}BO; 116(4); 105(3); 104(7); 103(62)^{11}BO; 102(4); 92(1); 91(2); 90(1); 89(1); 78(3); 77(7); 76(43); 75(7); 74(4); m*: 72·2 (147 → 103).

XII. 134(4); 133(52)$^{11}BN_2$; 132(24); 131(24)$^{11}BN_2$; 130(8); 129(6); 128(2); 119(4); 118(6); 117(27); 116(44); 115(16); 114(4); 107(3); 106(12); 105(4); 104(31)^{11}BN; 103(12); 102(5); 101(4); 100(2); 93(2); 92(18); 91(100)C, ^{11}BN; 90(6); 89(12); 88(4); 87(6); 86(2); 85(2); 79(4); 78(7); 77(16); 76(11); 75(8); 74(6); 73(3); m*: 62·3 (133 → 91).

be mobile.[11] Open chain structures were drawn by analogy with hydrocarbon ions,[12] in the open chain structures the molecular backbone was not rearranged. Only one resonance structure was drawn for each ion, all of which will be resonance stabilized. Many of the structures below are highly speculative and are presented primarily for bookkeeping purposes. Appearance potentials and deuterium labeling studies are clearly needed to define the respective ion structures and clarify the analogy between the hydrocarbon and B—N systems.

DISCUSSION

Borazarophenanthrenes. The resemblance between the fragmentation patterns of 12,11-borazarophenanthrene, phenanthrene (PH)[12,13] and diphenylacetylene[12,13] (DPA) dan be seen in Fig. 1. The fraction of the ion current that corresponds to unipositive fragment ions is roughly equivalent for diphenylacetylene and 12,11-borazarophenanthrene; both show more unipositive fragmentation than phenanthrene. The intensity of the doubly charged spectrum decreases in the order phenanthrene, diphenylacetylene and 12,11-borazarophenanthrene. The differences in the extent of unipositive fragmentation are not, however, sufficient to account for the differences in the doubly charged spectrum. That is, the decrease in the intensity of the doubly charged spectrum of I and DPA as compared to PH cannot be due only to instability of the double ions of the former towards fragmentation such as:

$$M_1^{+2} \rightarrow M_2^{+\cdot} + M_3^{+\cdot} \quad (1)$$

or

$$M_1^{+2} \rightarrow M_2^{+} + M_3^{+\cdot} + M_4^{\cdot} \quad (2)$$

In fact the total ionization for the three compounds decreases as PH > DPA > I (Σ_{50} normalized to base peak = 100 was 391, 360 and 278 respectively). This means that the cross section for double ionization must decrease in the same sense.

Although the 12,11-borazarophenanthrene shows slightly more fragmentation and less double ionization than phenanthrene, the differences between the two spectra are quantitative rather than qualitative, especially when one considers the shifts due to the nuclidic masses of B and N. Regardless of whether the *m/e* 152 ion of the hydrocarbons is an excited unipositive *o*-biphenylene[13,14], a unipositive phenylbenzyne[11a] or an open chain[12] ion, it seems very likely that the $C_{10}H_8{}^{11}BN$ ion at *m/e* 153 in the mass spectrum of I has a similar structure to its hydrocarbon analogue. If the *m/e* 151 ion in the hydrocarbons is indeed open chain,[12] the similarity between C=C and $\overset{\oplus}{B} = \overset{\oplus}{N}$ units in the same hydrocarbon structure is remarkably close.

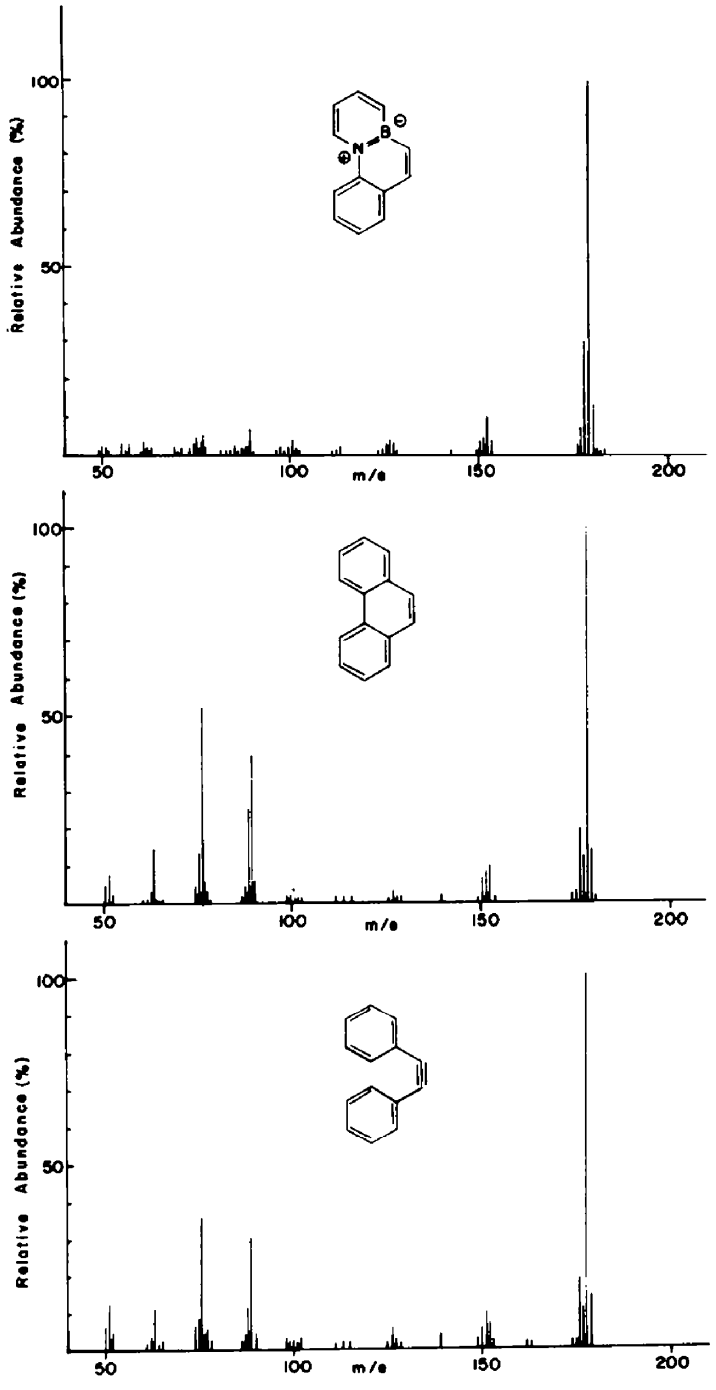
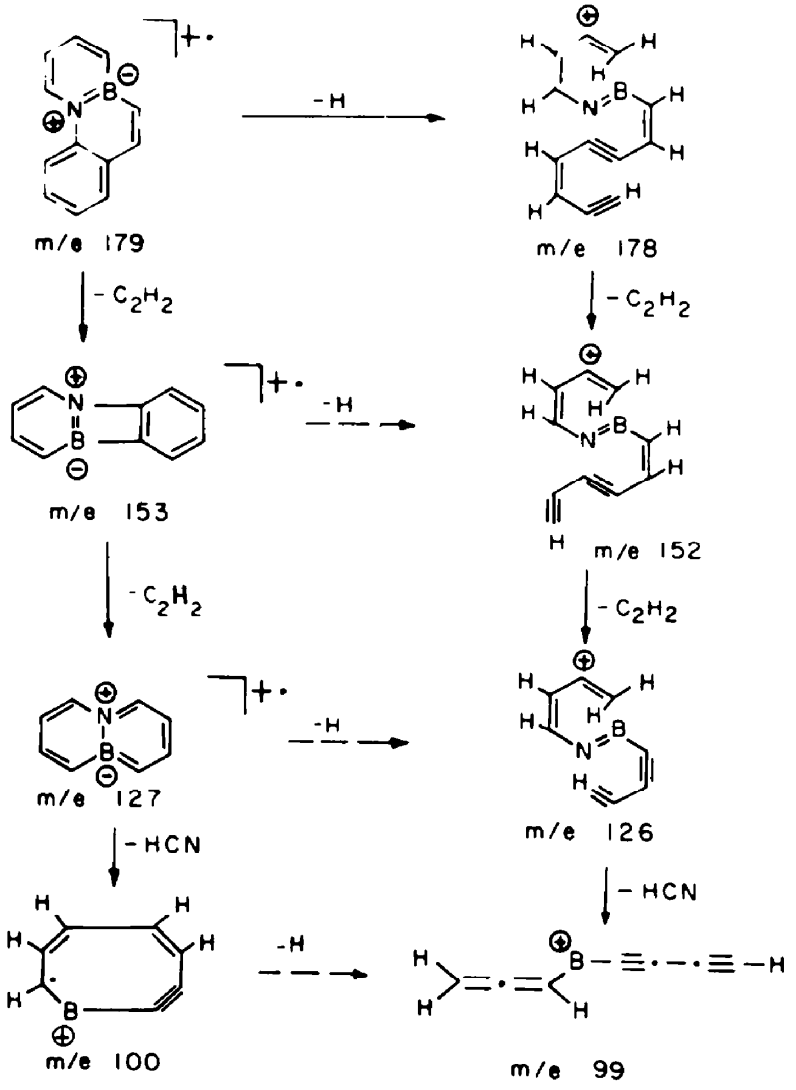


FIG. 1 Low Resolution mass spectra of 12,11-borazarophenanthrene, I, phenanthrene[14,15] and diphenylacetylene[14,15]

Scheme I provides a rationalization for the fragmentation of 12,11-borazarophenanthrene. The interesting points in the spectrum of this compound are (1) neither the boron nor the nitrogen atom has a pronounced directive influence on the fragmentation and (2) when one of the two heteroatoms is eliminated the boron remains with the charged particle. The first of these conclusions suggests that the orbital framework can be more important in directing the fragmentation of a hydrocarbon than the electronegativity of the individual atoms. The second observation is likely to be general for boron systems because of the lack of highly stable boron-carbon neutrals, that would correspond to HCN or C_2H_2 for example, and the relative stability of $R_2B^{\oplus}$.

SCHEME I Fragmentation paths for unipositive 12,11-borazarophenanthrene, 1.



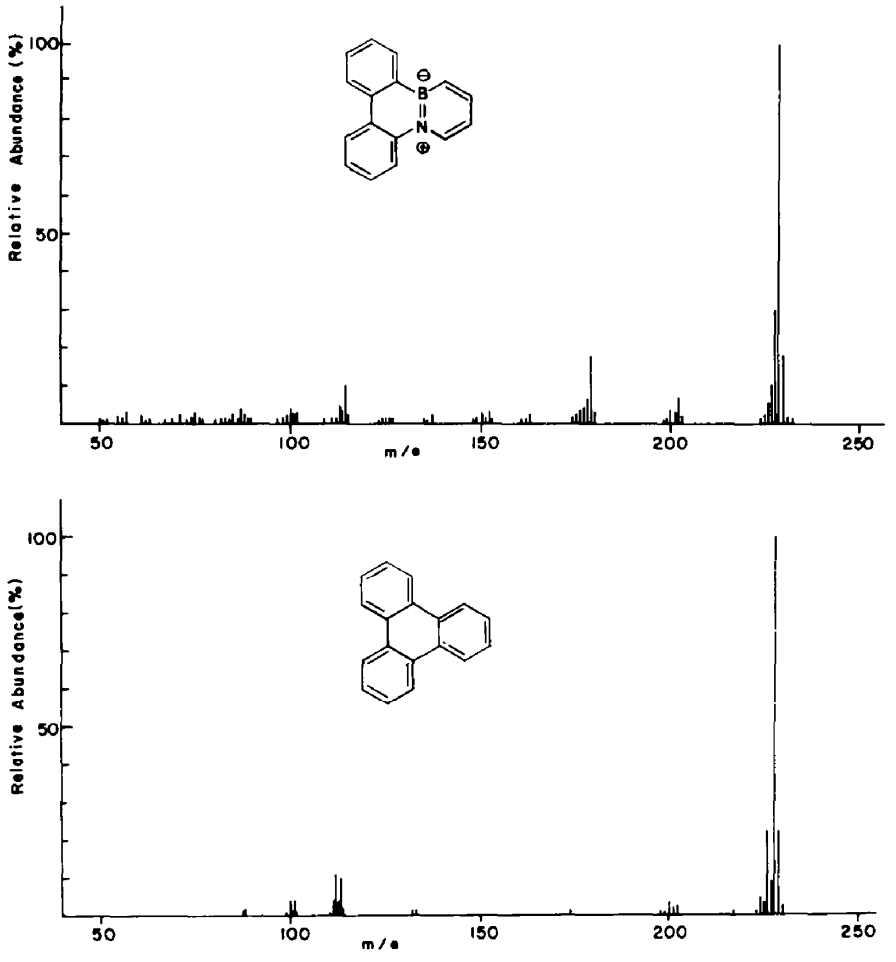


FIG. 2 Low resolution mass spectra of 14,13-borazarotriphenylene, II, and triphenylene[17]

In contrast with 12,11-borazarophenanthrene, the mass spectrum of 14,13-borazarotriphenylene does not, at first glance, appear to be very similar to its hydrocarbon analogue[15] (Fig. 2). The hydrocarbon and the heterocycle both give corresponding ions for loss of C_2 neutrals, and their doubly ionized spectrum is similar in intensity and distribution (triphenylene does show a significantly more intense $(M\text{-}2)^{+2}$ ion and fewer doubly charged ions in the *m/e* 89 region than its borazaro analogue). The rest of the fragmentation patterns show little correspondence. The two major groups of ions at *m/e* 179 and *m/e* 150 in 14,13-borazarotriphenylene have no analogues in the hydrocarbon spectrum. It seems very probable that the *m/e* 179 ion from II corresponds to unipositive 10,9-borazarophenanthrene (Scheme II), which is related to 14,13-borazarotriphenylene by hydrogen migration and loss of diacetylene. The *m/e* 152, 150 ions would be expected (see below) in the spectrum of 10,9-borazarophenanthrene, as would the double ions in the region of *m/e* 89.

If one subtracts these ions from the borazarotriphenylene mass spectrum, the resemblance between the remainder of the spectrum and that of triphenylene is quite remarkable. Introduction of a B═N couple into triphenylene destroys the 3-fold symmetry of the molecule in addition to decreasing the π-bond strength at positions 13 and 14. The loss of diacetylene in the spectrum of II is understandable on this basis.

The fragmentation of 10-phenyl-10,9-borazarophenanthrene, III, (Fig. 3) is highly consistent with that of II and other phenanthrene related compounds.[13] The relatively high intensity of the (M-2) ion in the spectrum of III could be related to the formation of a dibenzo-borazarobiphenylene ion through condensation of the phenyl ring with the nitrogen at position 9. The ion cluster at *m/e* 225 (double ions at *m/e* 112.5) presumably comes from further decomposition of these (M-2), (M-3) ions, as the appearance of both groups of ions is unique in this series. The intense ion at *m/e* 177 and the *m/e* 152 ion that is produced from it appear to be characteristic of the 10,9-borazarophenanthrenes.

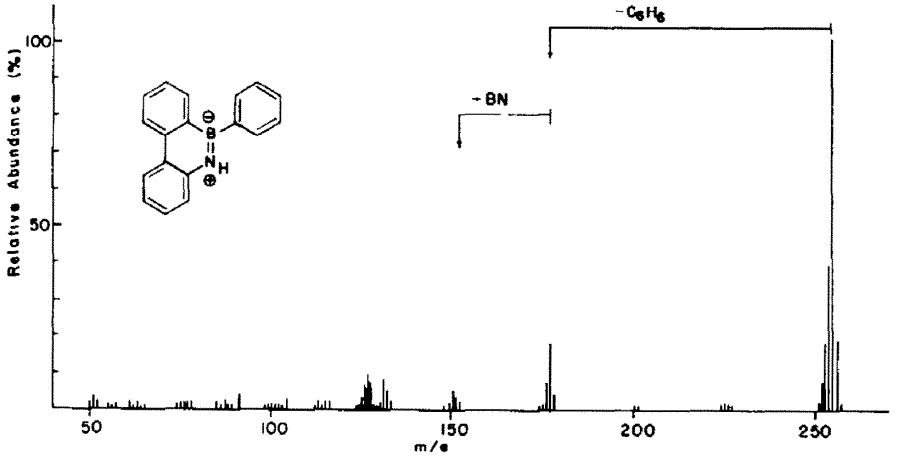
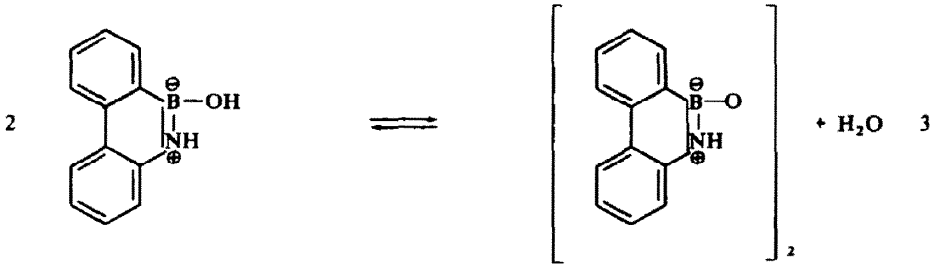


FIG. 3 Low resolution mass spectrum of 10-phenyl-10,9-borazarophenanthrene, III

Analysis of the fragmentation of IV (Fig. 4) is complicated by the fact that the B-oxides of the borazarenes are known to participate in the following equilibrium: The intense *m/e* 195 ion in the spectrum of IV could have been caused by an elimination similar to the loss of C_6H_6 from the molecule ion of III; however, it seems likely that



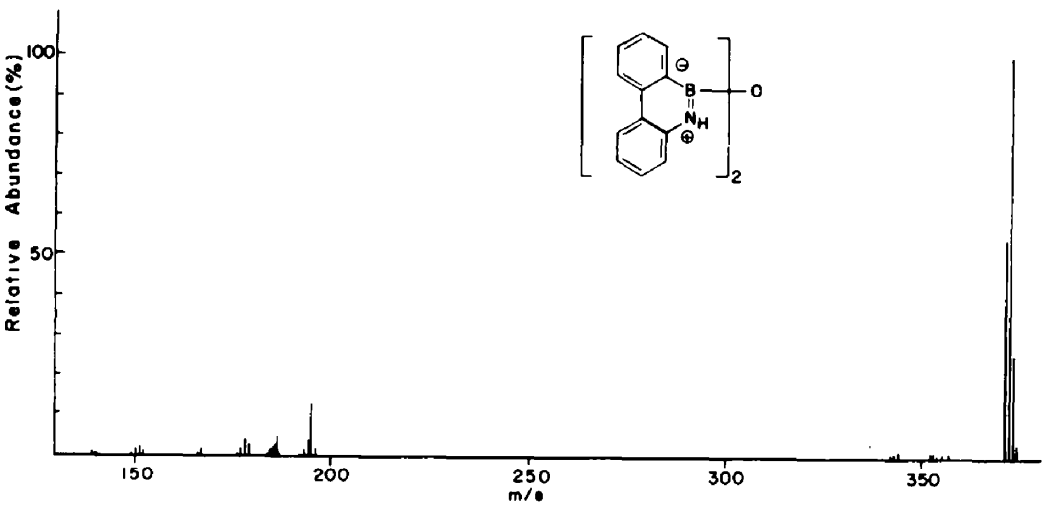


FIG. 4 Low resolution mass spectrum of bis-10,9-borazaro-10-phenanthryl ether, IV

at least part of the current at *m/e* 195, 177 and smaller masses is due to the hydrated form of IV. The (M—CH_3) and (M—C_2H_4) ions in the spectrum of IV may have arisen from decomposition of doubly charged ions,[16] as we observed no normal mestables for these transitions and there were very diffuse metastable peaks well above the parent mass.

Borazaronaphthalenes. The nuclear proton shift that converts naphthalene into 2,1-borazaronaphthalene also destroys the electronic symmetry of the molecule and should substantially complicate the fragmentation. Neither of the compounds in the 2,1-borazaronaphthalene series provide the basis for a clear analogy between the fragmentation of the heterocycle and the parent hydrocarbon system. The spectrum of 2-methyl-2,1-borazaronaphthalene (V, Table 2) is considerably more complex than that of 2-methylnaphthalene.[17]

Scheme III deals with the major fragmentation reactions in 2-methyl-2,1-borazaronaphthalene. The most remarkable difference between the mass spectra of normal and 2,1-borazaro-2-methylnaphthalene is the very prominent (56%) loss of methyl from the latter molecule ion. This reaction reflects the relatively low stability of carbon-boron single bonds. The borazaro-compounds also show substantially less β-cleavage (M-1) than the hydrocarbon. The PMO method[1,18] can provide an immediate rationalization for the latter difference in reactivity.

We have previously shown that the change in energy on β-cleavage in a radical cation is given by:

$$\Delta E = \Delta E\pi^{\oplus} + \Delta E_{\sigma} + (W_{ArCH_2\odot} - W_{ArCH_2R}) \tag{4}$$

The last term can be treated as a constant, particularly for systems of the same size. The change in σ-energy will be approximately equal for β-hydrogen cleavage in the hydro-carbon and heteroaromatic systems.

In the Hückel approximation the π-electron energy is given by:

$$E\pi^{\oplus} = \Sigma q_i \alpha_i + 2 \sum_{i>j} \sum P_{ij} \beta_{ij} \tag{5}$$

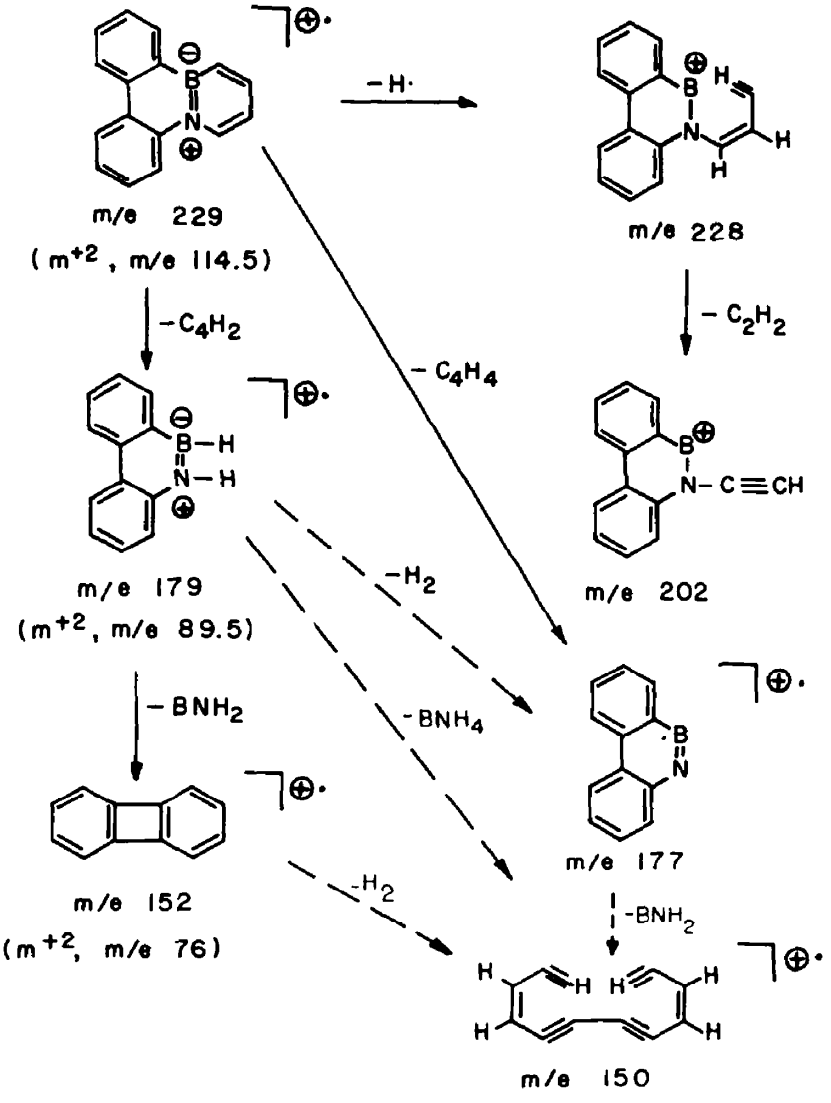
where q_i is the charge at atom i, α_i is the coulomb integral, P_{ij} is the i-j π-bond order and β_{ij} is the resonance integral. In the PMO treatment[18] α_c is assumed to be zero, so the coulomb term does not enter expressions for $\Delta E\pi$ in hydrocarbon systems. The coulomb term is only important for heteroatoms, and in the PMO formalism α_i is approximated by $\delta\alpha_i$.

$$\delta\alpha_i = \alpha_i - \alpha_c \tag{6}$$

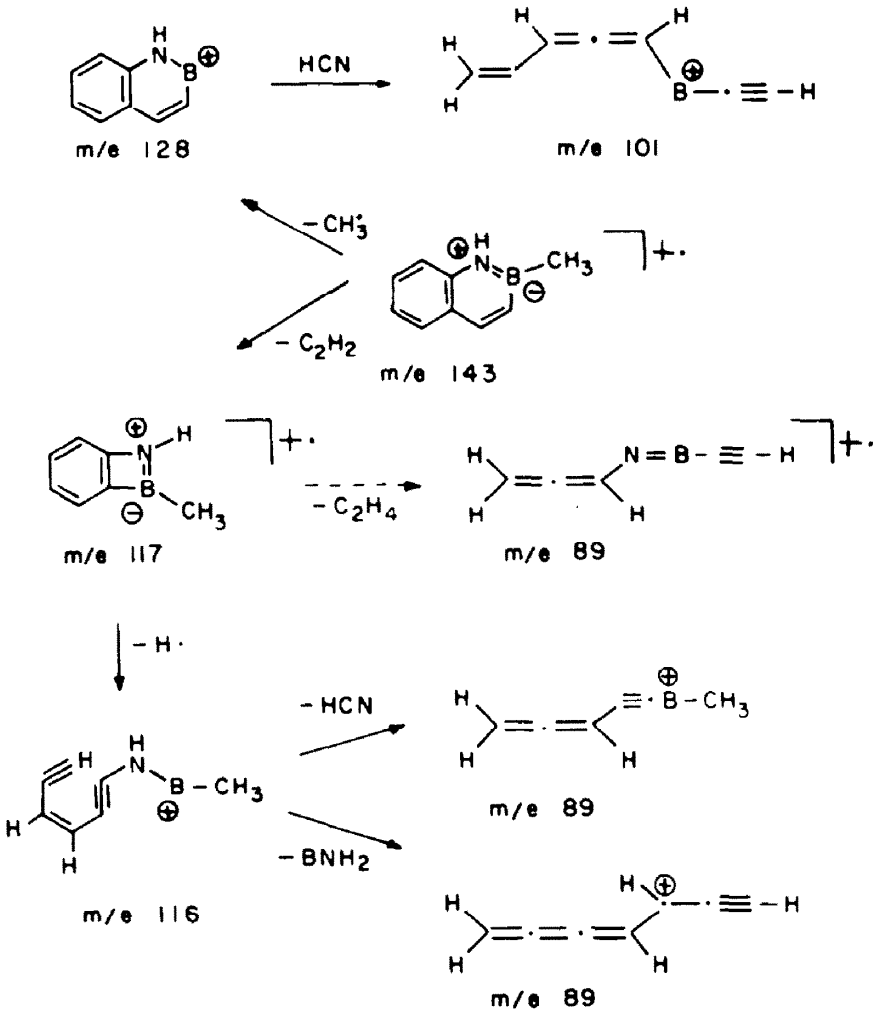
The charge density at atom i in AH systems is unity. In odd alternate cations the charge density is given by[18]:

$$q_i = 1 - a_{oi}^2 \tag{7}$$

SCHEME II Fragmentation paths for unipositive 14,13-borazarotriphenylene, II.



SCHEME III Fragmentation paths for unipositive 2-methyl-2,1-borazaronaphthalene, V.



where a_{oi} is the NBMO coefficient at atom i. The coulomb part of $\Delta E\pi^{\oplus}$, $\Delta E\pi_{-\alpha\oplus}$ is then given by:

$$\Delta E\pi_{-\alpha\oplus} = \sum_i - a_{oi}^2\, \delta\alpha_i \tag{8}$$

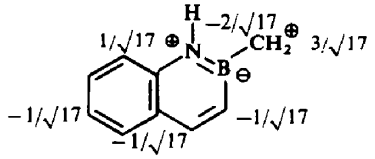
It has been previously shown that the resonance term in $\Delta E\pi$, for β-cleavage, is given by[1]:

$$\Delta E\pi\beta_{\oplus} = 2(1 - a_{or})\,\beta \tag{9}$$

The change in energy for β-cleavage in a general (heteroatomic) case is now given by:

$$\Delta E = \sum_i -a_{oi}^2\, \delta\alpha_i + 2(1 - a_{or})\,\beta + \text{constants.} \tag{10}$$

The NBMO coefficients in the 2,1-borazaro-2-naphthyl cation (XIII) are given in the figure:

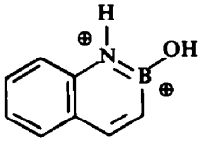


These coefficients were obtained very easily using the Longuette-Higgins procedure.[1,18] When we compare 2-methylnaphthalene to 2-methyl-2,1-borazaronaphthalene, the energy factor which favors β-cleavage in the hydrocarbon over β-cleavage in the heteroatomic system is at least:

$$\Delta E = -4/17\,\delta\alpha_N \tag{11}$$

which is a substantial positive term. The relatively low abundance of (M-1) ions in 2-methyl-2,1-borazaronaphthalene can be rationalized on this basis.

Interpretation of the mass spectrum of bis-2,1-borazaro-2-naphthyl ether (VI) is complicated by the problem of the hydration equilibrium (see above). This compound shows considerably more fragmentation than the β-methyl derivative (Σ_{50} normalized to base peak = 100 was 520 and 221 respectively), the equilibrium above is probably involved in this apparent increase. The major groups of ions observed in the spectrum of 2-methyl-2,1-borazaronaphthalene (Scheme III) are also prominent in the spectrum of VI. The substantially lower intensity of the *m/e* 128 ion (which includes a contribution from a doubly charged ion) is concordant with the strength of the B—O bond as compared to the B—C bond. The intense (M-2) ion at *m/e* 270 (44%) bears additional comment. It seems very likely that this ion is formed with participation of the two borazaronaphthyl rings. The relative abundance of the *m/e* 144, 145 ions (respectively 3 and 9%) should reflect the $^{11}B/(^{10}B$ and 145-H) ratio for the hydrated form of VI (VIa):

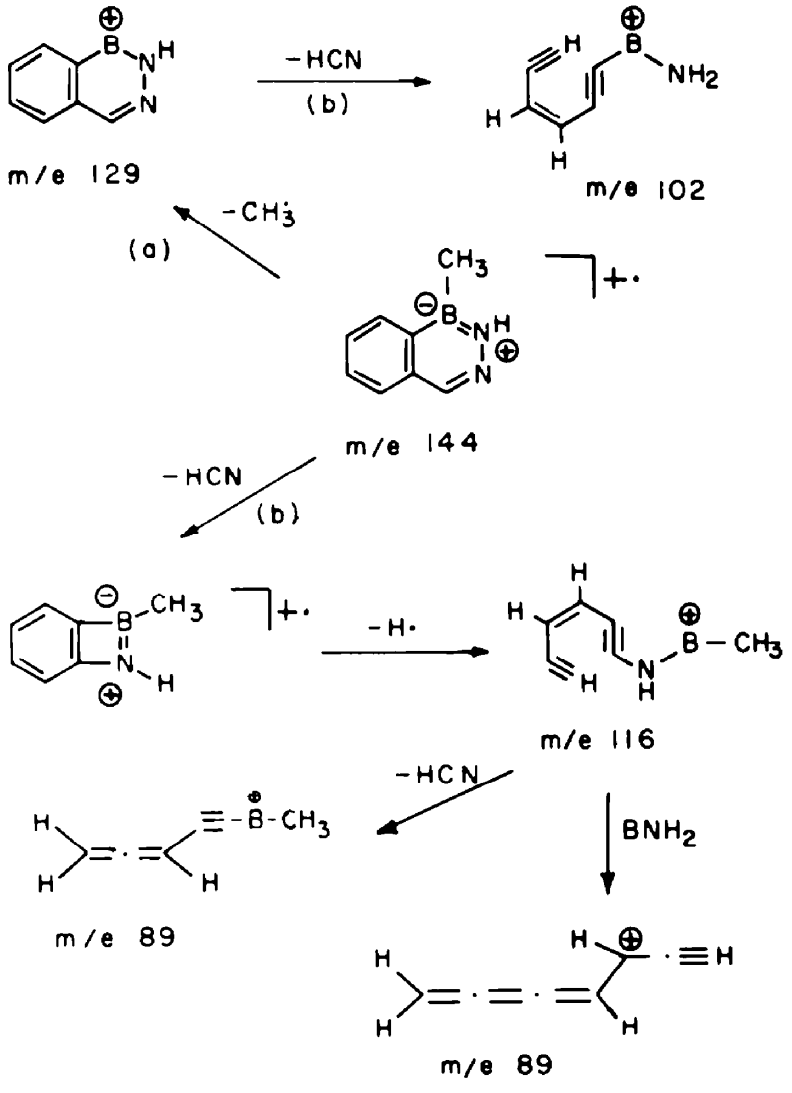


VIa

If the *m/e* 270 ion were formed by loss of a hydrogen atom from separate residues the ratio of *m/e* 270 to *m/e* 272 should be similar to the ratio of *m/e* 144 to *m/e* 145 for the hydrated form. This is clearly not the case.

Borazaroisoquinolines. The fragmentation patterns of all of the 4,3-borazaroisoquinolines in this group show many common features, and they will be discussed with reference to the spectrum of 4-methyl-4,3-borazaroisoquinoline (VII, Scheme IV). The fragmentation of VII was qualitatively similar to that of 3-methylquinoline[16] (Fig. 5). By analogy[19] 4-methylisoquinoline should show similar fragmentation to

SCHEME IV Fragmentation paths for unipositive 4-methyl-4,3-borazaroisoquinoline, VII.



the present model. There are three major differences between the two spectra (1) β-cleavage in the borazaro compound has been completely suppressed. The 143/144 ratio in the spectrum of VII is the same as that required by the $^{10}B/^{11}B$ isotope ratio (19·91/80·09), whereas the *m/e* 142 peak from 3-methylquinoline arises exclusively from β-cleavage.[19] The suppression of β-cleavage by an atom with higher electronegativity than carbon, which occupies a starred position with respect to the cleavage site, was dealt with above for 2-methyl-2,1-borazaronapththalene. Similar phenomena have been observed in the spectra of the alkyl quinolines.[19] (2) The fragment which in sum corresponds to loss of H_2CN from the molecule ion is much

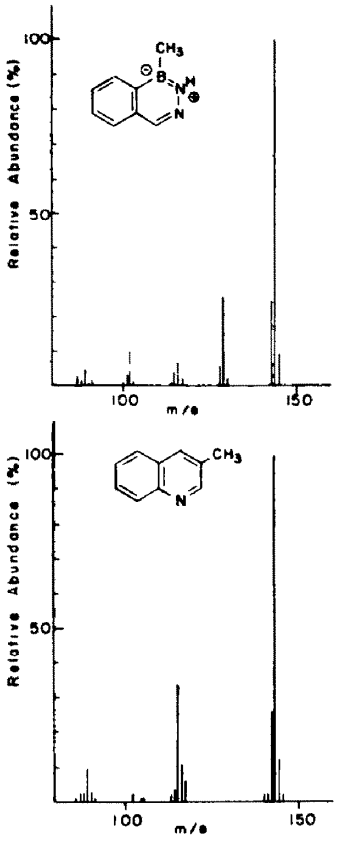


FIG 5 Low resolution mass spectrum of 4-methyl-4,3-borazaroisoquinoline VII, and 3-methylquinoline

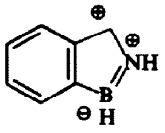
more intense in the spectrum of 3-methylquinoline than in the spectrum of 4-methyl-4,3-borazaroisoquinoline (respectively 35% and 7%). This is no doubt related to the differences in β-cleavage and the formation of benzoazatropylium type cations which subsequently lose HCN. (3) The (M-15) ion and the (M-43) ions which arise by methyl cleavage, and elimination of HCN are much more prominent in the spectrum of 4-methyl-4,3-borazaroisoquinoline than in the spectrum of 3-methylquinoline. The difference between the B—C and C—C bond strength no doubt accounts for the large change in intensities.

In view of the modility of hydrogen atoms on aromatic ions[11, 12, 13], it is interesting that we did not observe any ions in the mass spectra of the 4,3-borazaroisoquinolines that could be attributed to the loss of N_2 neutrals, as in the mass spectra of other diazines.[20] This observation again indicates the analogy between C=C and $\overset{\ominus}{B}=\overset{\oplus}{N}$ systems, and supports the observation that the 4,3-borazaroisoquinolines are indeed aromatic.[9]

All of the other spectra in this group had significant ions for cleavage of the exocyclic bond to boron (process IV(a)). In the spectrum of 3-phenyl-4-hydroxy-4,3-borazaroisoquinoline, X, the major cleavage of this type appears to have involved

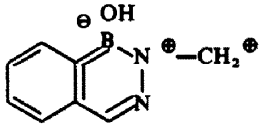
loss of water with possible cyclic condensation as in the spectrum of the β-phenyl derivative of 10,9-borazarophenanthrene, III. All of the spectra showed significant ions from loss of HCN as a neutral (process IV(b)). Loss of HCN is the most significant fragmentation process in quinoline and isoquinoline ions,[19] so in this respect the analogy holds quite well.

The relatively intense *m/e* 116 ^{11}BN and *m/e* 117 ^{11}BO ions in this group of spectra probably represent relatively stable ionic structures as they consistently appear even in structurally dissimilar compounds. It seems likely that these ions have a common structure with those observed in the spectra of the 2,-1-borazaronaphthalene. We have drawn hypothetical open chain structures by analogy with some hydrocarbon ions;[11] the 3,2-borazaroindenyl cation XIV would possibly be a more likely *m/e* 116 ^{11}BN ion structure among the many possibilities.



XIV

The very high abundance of (M-1) ions in the spectrum of 4-hydroxy-3-methyl-4,3-borazaroisoquinoline, IX, (60% after roughly accounting for the ^{11}B/^{10}B isotope ratio), no doubt reflects the stability of the borazaro-N-benzyl type cation IXa.



IXa

The NBMO coefficients for the β-naphthyl system have been given above. In this case the coulomb term for β-cleavage strongly favors the reaction. If we allow that $\delta\alpha_N$ and $\delta\alpha_B$ will be of the same magnitude and different in sign the coulomb term for β-cleavage in this case is given by:

$$\Delta E\pi_{-\alpha\oplus} = -3/17\,\delta\alpha_B \tag{12}$$

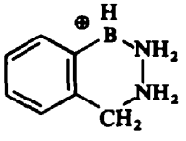
The increase of almost a factor of 2 in β-cleavage as compared to the methylquinoline model system[19] is easily rationalized on this basis. 4-hydroxy-3-methyl-4,3-borazaroisoquinoline, IX, also gave an intense ion for loss of methyl. This α-cleavage reaction again reflects the lability of exocyclic bonds to heteroatoms. The ion at *m/e* 177 (13%) in the spectrum of 4-hydroxy-3-phenyl-4,3-borazaroisoquinoline X, demonstrates the same phenomena. In this case the charge was retained by the phenyl residue from α-cleavage. The spectrum of X also shows increased fragmentation similar to that observed in 10-phenyl-10,9-borazarophenanthrene (III).

The successive loss of two molecules of HCN in the mass spectrum of 4-hydroxy-3-methyl-4,3-borazaroisoquinoline, IX, may reflect the formation of a borazaro-

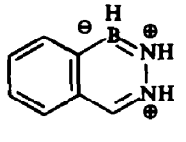
benzoazatropylium cation during or subsequent to β-cleavage. The two reactions (m/e 159 $\xrightarrow{-HCN}$ m/e 132 $\xrightarrow{-HCN}$ m/e 105) are clearly analogous to the loss of HCN in alkyl isoquinoline mass spectra in which benzoazatropylium ions are clearly indicated.[19]

4-hydroxy-4,3-borazaroisoquinoline, XI, which is considerably less aromatic than its aza-analogue,[2] showed surprisingly little fragmentation on electron impact. The prominent fragments m/e 117 ^{11}BO and m/e 103 ^{11}BO are directly analogous to the m/e 116 and m/e 102 ions in the 4-hydroxy-4,3-borazaroisoquinoline, VIII, mass spectra.

The mass spectra of tetrahydro-4,3-borazaroisoquinoline, XII, shows several interesting features which are germane to the fragmentation of other borazaro heterocycles. Unlike the fully conjugated systems (I-XI) in which the parent ion was the base peak in the spectrum, tetrahydro-4,3-borazaroisoquinoline did not show a significant parent ion; however, there were abundant framents corresponding to (M-1), XIIa, and (M-3), XIIb, ions. The M-3 ion is probably the protonated parent, 4-3-borazaroisoquinoline. The prominence of this ion suggests that the borazaro π-electron system has a reasonably high resonance energy. The abundant fragments



XIIa



XIIb

at m/e 116 (see Scheme IV) and m/e 104 (m/e 131 $\xrightarrow{-HCN}$ m/e 104) are completely in accord with the fragmentation of the other borazaroisoquinolines. The fact that m/e 91 C was the base peak in this spectrum (m/e 131 $\xrightarrow{-BN_2H_3}$ m/e 191) is quite interesting, in that it confirms the ready mobility of hydrogen atoms on these π-electron systems.

CONCLUSIONS

The mass spectra of heteroaromatic boron compounds can be easily interpreted in terms of the spectra of their hydrocarbon analogues which points to the similarity of $\overset{\ominus}{B}{=}\overset{\oplus}{N}$ and C=C units in aromatic structures. When one heteroatom is eliminated, the boron usually remains with the charged particle. The importance of α-cleavage of the exocyclic hydrocarbon groups attached to boron or nitrogen is substantially increased over the hydrocarbon analogues. The large differences in the amount of β-cleavage for alkyl residues attached to boron or nitrogen may be qualitatively accounted for by a PMO analysis.

EXPERIMENTAL

The preparation and physical properties of the compounds studied have been described in detail.[3-10] All samples were of analytical purity. Low resolution mass spectra were determined by use of the Associated Electrical Industries MS-902 direct inlet system with the following routine parameters: source temperature 220°; source pressure 3×10^{-7} to 2×10^{-6} torr; emission 70 eV, electron trap current 500 μ, source slit 3/1000 inch, collector slit 5/1000 inch. Mass measurements were obtained by use of the MS-902 Nier peak matching system using perfluorotri-n-butylamine as primary standard. Resolving power was set to

15,000 before mass measurement was attempted. The reported elemental compositions agreed with the measured mass within 5 ppm. Weak metastable transitions were observed by increasing the source temperature (and thus pressure) and fully opening the source and collector slits.

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