# Correspondence

## Pitfalls in the Interpretation of the Mass Spectra of Polyisotopic Molecules

*Sir*:

In a recent paper, Melcher, *et al.*,[1] have pointed out that the parent ion cluster in the mass spectra of borazine and some substituted borazines is distorted from that expected on the basis of the natural abundances of the isotopes concerned. By means of computer deconvolution, they determined the contribution to the polyisotopic cluster of both the parent ion P and the P – H ion. Significant arguments on the lability of the substituents are then based on the relative intensities of the derived P – H contributions. However, it is apparent from Melcher's paper that, for borazine, the only compound for which actual experimental data are given, the P and P – H contributions cannot account for *m/e* 76 (9.3%) and *m/e* 75 (4.1%).

We have, using the same data, calculated the contributions to the parent ion cluster, allowing for loss of more than one hydrogen. Our calculated fit is compared to that of Melcher in Table I. For the contribution from the parent ion, $(HNBH)_3\cdot^+$, the difference in the values obtained between partial and full treatment of the data is relatively small. The P – H contribution, however, decreases to such an extent (70.6-57.3%) that without a similar treatment for all of the compounds reported, some of the conclusions may be erroneous.[2]

Since no other experimental data are given by Melcher, we have measured the mass spectra for some of the other compounds reported. In Table II it can be seen that the relative contributions to the parent ion cluster for ions having lost more than one hydrogen is variable, being greatest for the unsubstituted borazine. It is interesting to note that $(MeNBF)_3$ appears to show contributions from P – H and P – 3H, but not P – 2H, while the loss of 2H is favored over the loss of H from the parent ion of $(HNBCl)_3$.

Melcher noted that for P – Z ions (Z = methyl, halogen or phenyl), overlapping isotope patterns do not arise, and deconvoluting procedures need not be applied. However, this treatment does not take into account the P – HZ contributions. Serious errors may be introduced into the values obtained for the P – Z contributions if the P – HZ were not identical in all instances.

**Table I.** Contributions to the Parent Ion Cluster in the Mass Spectrum of Borazine

| | Rel intens | | |
|---|---|---|---|
| *m/e* | P + (P – H)[a] | P + (P – *n*H); *n* = 1-6[b] | Obsd[c] |
| 75 | 0.0 | 4.1 | 4.1 |
| 76 | 0.0 | 9.3 | 9.3 |
| 77 | 1.1 | 13.3 | 13.3 |
| 78 | 14.0 | 23.2 | 23.2 |
| 79 | 61.5 | 64.8 | 64.8 |
| 80 | 100.0 | 100.0 | 100.0 |
| 81 | 32.9 | 35.5 | 35.5 |
| 82 | 0.4 | 0.4 | 0.0 |

[a] Reference 1; P = 29.4%, P – H = 70.6%. [b] Our computer fit of the observed data shows the following relative contributions: P = 26.5%, P – H = 57.3%, P – 2H = 3.2%, P – 3H = 4.8%, P – 4H = 5.3%, P – 5H = 2.4%, P – 6H = 0.4%. [c] Reference 1.

**Table II.** Comparison of Contributing Ions to the Parent Ion Cluster of Some Borazines

| | Rel abundances | | | | | | |
|---|---|---|---|---|---|---|---|
| | Our work (AEI MS-30) | | | | | Melcher, *et al.*[1] | |
| Compd | P | P – H | P – 2H | P – 3H[a] | Rel dev | P | P – H |
| $(MeNBH)_3$ | 24.9 | 75.1 | | | 1.33 | 21.3 | 78.7 |
| | 24.9 | 71.0 | 1.8 | 2.3 | 0.16 | | |
| $(MeNBF)_3$ | 20.9 | 79.1 | | | 2.14 | 22.5 | 77.5 |
| | 20.5 | 75.3 | 0.0 | 4.2 | 1.29 | | |
| $(HNBCl)_3$ | 97.7 | 2.3 | | | 0.85 | 97.3 | 2.7 |
| | 97.1 | 0.8 | 2.1 | 0.0 | 0.67 | | |

[a] Contributions for P – 4H, P – 5H, and P – 6H were negligible for the above compounds.

The above examples illustrate the problems of beginning the deconvolution of polyisotopic mass spectra but not carrying the deconvolution through to its natural conclusion. The partial deconvolution may lead to as serious an error as ignoring the overlapping ions completely.

**Registry No.** Borazine, 6569-51-3; $(MeNBH)_3$, 1004-35-9; $(MeNBF)_3$, 13722-15-1; $(HNBCl)_3$, 933-18-6.

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[1] L. A. Melcher, J. L. Adcock, G. A. Anderson, and J. J. Lagowski, *Inorg. Chem.*, 12, 601 (1973).

[2] Communication with Professors Lagowski and Melcher reveal that they had considered a more complete deconvolution. Examination of their data shows that full deconvolution, although changing the numbers, does not materially affect their conclusions.