# Stability of Triphenylborthiin $(PhBS)_3$

By Richard H. Cragg* and Alan F. Weston

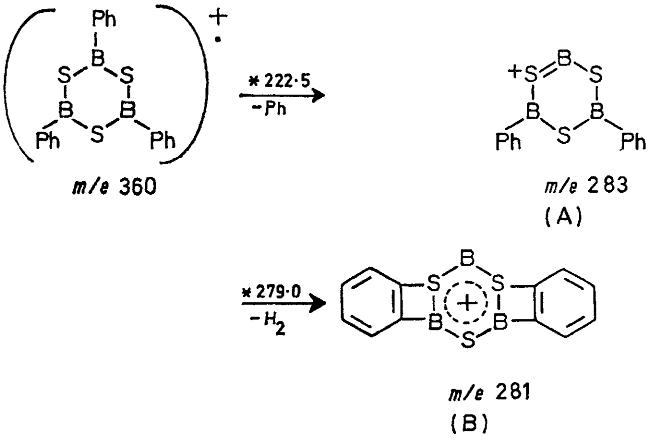
(*The Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent*)

*Summary* A comparison of the mass spectrum of triphenylborthiin with that of 2,4,6-triphenyl-1,3,5-trithian shows triphenylborthiin to have considerable stability which could possibly be due to charge delocalisation in the borthiin ring.

Although there have been many reports concerned with charge delocalisation in compounds containing boron–nitrogen and boron–oxygen bonds, in the case of compounds containing boron–sulphur bonds this effect has been thought, by comparison, to be small. For example trisdimethylaminoborane and trimethoxyborane do not form 1:1 complexes with bases such as pyridine. In contrast trismethylthioborane forms a stable complex.[1]

In our extensive studies into the mass spectra of organoboranes we were surprised to find that triphenylborthiin was particularly stable towards fragmentation under electron impact and its stability was comparable with that of triphenylboroxine.[2] The parent ion (*m/e* 360) accounted for 28·5% of the total ionisation and a doubly-charged ion was also observed, at *m/e* 160 (4%). The spectrum was devoid of ions of the type $(PhBS)_2$ and (PhBS); instead one observed the loss of a phenyl radical to give ion (**A**) followed by the loss of neutral hydrogen to give an ion at *m/e* 281 which we assign to structure (**B**) similar to that assigned to tri-*N*-phenylborazine fragments by Snedden.[3] A fragmentation pattern *via* loss of hydrogen radical followed by loss of benzene as a neutral species was also observed. The spectrum was also devoid of low *m/e* boron-containing ions.

In contrast the mass spectrum of the hydrocarbon analogue 2,4,6-triphenyl-1,3,5--trithian, determined under the same conditions as that for triphenylborthiin, showed a strong fragmentation route *via* the $\frac{2}{3}\,P^+$ and $\frac{1}{3}\,P^+$ ions; the lower ions were of high abundance, and the parent ion accounted for only 0·7% of the total ionisation. A common argument concerning six-membered ring systems has been that strong parent ions accompanied by few fragment ions implies possible aromaticity in the system. *E.g.*, Biemann[4] states that the stability of the molecular ion is increased by the presence in the molecule of π-electron systems from which the loss of one electron is more easily accommodated than from a σ-bond and similar comments on the stabilisation of a positive charge by an aromatic nucleus[5,6] and π-electron systems[7] have been made. Similar arguments have also been used to demonstrate that borazines are less aromatic than their benzene analogues.[3,8] If this is the case then the mass spectral results support the suggestion that the stability of triphenylborthiin can be attributed to charge delocalisation in the borthiin ring whilst the hydrocarbon analogue has little or no aromatic



character. The lack of fragmentation of triphenylborthiin and the strength of the parent ion peak could possibly be associated with the stability of the parent ion compared with the original molecule, *i.e.*, charge delocalisation occurring in the electron-deficient species. However this is not likely since substitution of phenyl by bromine, MeS, and MeO reduced the stability of the parent ions considerably, the parent ions accounting for 28·6, 5·5, 13·2, and 1·1%, respectively, of the total ionisation.

(*Received*, 8*th October* 1973; *Com.* 1383.)

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