Photo-electron Spectrum of Trivinylboron

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Summary Comparison of the photo-electron spectra of trivinylboron and triethylboron suggests there is only limited conjugation in the former.

RESULTS from spectroscopy and the chemical behaviour of trivinylboron compounds, $(R^1R^2C{=}CR^3)_3B$, have been interpreted[1] as implying a planar structure for these molecules in which a vacant $p\pi$-orbital of sp^2-hybridized boron conjugates with the π-orbitals of the vinyl groups. Extensive molecular orbital calculations have been carried out using a similar model.[2] Examination of the u.v. and n.m.r. spectra of methylvinylboranes was judged to provide evidence for only partial conjugation in which the σ-bonding orbitals on boron are intermediate between sp^2 and sp^3 hybrids and the vacancy available for π-donation is therefore intermediate between pure $p\pi$ and sp^3 hybrids.[3] Such a non-planar structure for trivinylboron would imply limited conjugation through boron.

The photo-electron spectra of trivinylboron, triethylboron, trimethylboron, and propene were obtained on a Perkin–Elmer PS-16 spectrometer using irradiation from the 21·21 eV helium line. The principal adiabatic ionization potentials are listed in the Table together with those of ethane and ethylene.[4]

If the spectrum of triethylboron is compared with that of trivinylboron, the first ionization potentials are close together and the first ionization band is a broad, structureless envelope with two maxima similar to those found for other symmetrical molecules and generally ascribed to Jahn–Teller effects.[5] The second ionization band in trivinylboron begins at 10·7 eV unlike that of triethylboron starting at 11·5 eV. These second ionization potentials show many similarities to ethylene and ethane, respectively. The ethylene band starting at 10·51 eV shows vibrational structure with ν_2 1230 (totally symmetric C=C stretch), ν_4 430 (C=C twisting), and ν_3 1370 cm^{-1} (totally symmetric C–H deformation); in trivinylboron, the second ionization band beginning at 10·7 eV shows structure with ν_2 1210 and ν_4 484 cm^{-1} [the C=C stretching frequencies in ethylene and trivinylboron are at 1623 (Raman) and 1610 cm^{-1}, respectively].[1,6] The second ionization band in triethylboron beginning at 11·5 eV with C–H deformation bands at 1170 cm^{-1} is quite similar to the first ionization band in ethane starting at 11·56 eV with deformation bands at 1170 cm^{-1}. Since the first ionization potentials of triethylboron and trivinylboron are very similar and, in the remainder of their spectra, each substance exhibits similarities to the spectra of ethane and ethylene, respectively, we conclude that the first band represents ionization from essentially a B–C σ-bond and that there is only a small amount of conjugation through boron in trivinylboron.

Trimethylboron has a first ionization potential at 10·4 eV which is 0·8 eV greater than that of triethylboron; the change in the ionization level of the B–C bond in changing from trimethyl- to triethyl-boron is in keeping with the increased electron-donating nature of ethyl compared to methyl. Similarly, the first ionization potential of propene is 0·5 eV less than that of ethylene.

If boron in trivinylboron is sp^2-hybridized, the above results suggest that the vinyl groups are twisted out of plane leading to reduced conjugation. Dreiding models indicate there would be non-bonding interaction between the hydrogens on adjacent vinyl groups in a completely planar structure (internuclear distance approximately

1·9 Å). Alternatively, the carbon atoms attached to boron may not be completely sp^2-hybridized even in a planar structure and lead to a low level of conjugation (quasi-allenic). If boron is in a hybrid state between sp^2 and sp^3 with a pyramidal structure[3] this could also account for the small amount of conjugation observed. Other chemical and spectroscopic information to be reported shortly also supports the conclusion that there is only limited conjugation through boron in the trivinylborons.

Ionization potentials (eV) from bands found: photo-electron spectra[a]

Triethylboron	Trivinylboron	Ethylene	Ethane	Propene	Trimethylboron
9·6 (broad band with maxima at 10·2, 10·6)	9·7 (broad band with maxima at 10·0, 10·2)	—	—	—	10·4 broad band with maxima at 10·9, 11·5
11·5 extending to *ca.* 14. C–H sym. def., 1170 cm^{-1}	10·7 extending to *ca.* 12·1. ν_2 1210, ν_4 484 cm^{-1}	10·51 extending to *ca.* 11. ν_2 1230, ν_4 430, ν_3 1370 cm^{-1}	11·56 extending to *ca.* 14. C–H def., 1170 cm^{-1}	10·0 extending to *ca.* 10·8. ν_2 1370, ν_4 438 cm^{-1}	12·6—16·5 with maxima at 13·3, 14·5.
Approx. 14—16·5 (no structure)	12·7 extending to *ca.* 14·5 (no structure)	12·38 (no structure)	14·7 extending to *ca.* 16·5 (no structure)	—	—
	Approx. 14·5—17 (no structure)	14·47 C–H stretch, 1700 cm^{-1}			
		15·68 C–H def., 1340 cm^{-1}			

[a] The vibration frequencies are estimated to ±50 cm^{-1}.

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