Ring Current Calculations and Proton Nuclear Magnetic Resonance Chemical Shifts in 2,3-Dicarbahexaborane-8 and some Derivatives

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BY employing a classical free electron model[1] for 2,3-dicarbahexaborane-8 ($C_2B_4H_8$), it is possible to account for the relative chemical shifts in the proton n.m.r. spectra of apical and basal boron-attached hydrogens and also of methyl hydrogens of the *B*-methyl derivatives.[2] (Table).

The apical boron in $C_2B_4H_8$ appears to have a slight positive charge relative to the basal boron atoms[3] which makes it difficult to account for the observed upfield shift of the apical substituents on the basis of inductive effects alone. Further, an upper limit 0·2 p.p.m. can be assigned to the magnitude of inductive effects on the boron-attached methyl hydrogens.[4] Contributions of this kind are also assumed to be comparatively small, and opposite in sign to that of the observed shift, for the boron-attached hydrogens of the parent system. To calculate $\Delta\tau$ values from ring-current contributions alone the following model is adopted.

The structural parameters are obtained from the *X*-ray studies[3] on the parent compound and the 2,3-dimethyl derivative. It is convenient to think of the pentagonal pyramidal framework of carbon and boron atoms as approximating a cone. The geometric centre of the slightly irregular pentagonal basal plane gives a weighted "radius" of 1·37 Å. A distance of 1·1 Å from the basal plane to the apex is used. For the *B*-methyl derivatives a methyl C–B bond distance of 1·56 Å and C–H of 1·1 Å (bond angle 109°) are assumed.[5] Finally, the six "delocalized" electrons bonding the apex to the pentagonal base are treated in a manner similar to the free electron approach used for benzene.[1a]†

Assuming the ring current to be at the basal plane $\Delta\tau_{calc}$ values are, not surprisingly, slightly high: for the methyl and boron-attached hydrogens, $\Delta\tau_{calc}$ 2·3 and 5·9 p.p.m., respectively. A better correlation between $\Delta\tau_{calc}$ and $\Delta\tau_{exp}$ is obtained for both the methyl and boron-attached hydrogens when the ring current loop is placed parallel to the base and about the conical centroid (0·32 Å from the base) of the model. The radius of this ring is 0·97 Å. This seems a more realistic position to place the ring current since the maximum density of the electrons in question is effectively near a weighted midway position between the basal plane and the apex.

From the close agreement of $\Delta\tau_{calc}$ and $\Delta\tau_{exp}$

Ring current contributions to the $C_2B_4H_8$ *proton chemical shifts*

Compound	Nucleus	$\Delta\tau_{exp}$[a]	$\Delta\tau_{calc}$[a]
2,3-$C_2B_4H_8$	boron-attached terminal H	4·5 p.p.m.[b]	4·0 p.p.m.
2,3-Dimethyl-2,3-dicarbahexaborane-8	boron-attached terminal H	4·1[c]	
B-Methyl-2,3-dicarbahexaborane-8	boron-attached methyl H	1·1	1·2
B,2,3-Trimethyl-2,3-dicarbahexaborane-8	boron-attached methyl H	1·2	

[a] $\Delta\tau_{exp}$ (and $\Delta\tau_{calc}$) = $\delta'_{base} - \delta'_{apex}$. For example, δ'_{apex} of *B*-methyl-2,3-dicarbahexaborane-8 is measured using 1-methyl-2,3-dicarbahexaborane; and, δ'_{base} is measured using both 4- and 5-methyl-2,3-dicarbahexaborane. No distinction is made between the two different (4,5) basal positions. Both in the parent molecule and the *B*-methyl derivatives the chemical-shift difference between the 4 and 5 positions is too small to be measured. Although the above chemical shifts were not measured at infinite dilutions, mixtures of the appropriate *B*-methyl isomers were used for the chemical shift comparisons reported here.

[b] T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, 1964, **3**, 1686.

[c] T. Onak, F. J. Gerhart, and R. E. Williams, *J. Amer. Chem. Soc.*, 1963, **85**, 3378.

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† The method for a single current loop[1a] was employed. The offered corrections [1b,c] to the original set of data and formulae[1a] are somewhat ambiguous. The expression given for H'_{eff} in ref. 1a should be multiplied by $4\pi k$ as mentioned in ref. 1c; however, a numerical result derived from an evaluation of H'_{eff} by using B_0 values in ref. 1a should be multiplied by 4π only.

values (Table) it is clear that ring current contributions can be of use in predicting the proton chemical shifts in the $C_2B_4H_8$ pyramid.

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[1] Ring currents have been used in many instances to satisfactorily predict chemical shifts in aromatic compounds.[1a–d] Although this approach has been subject to some scrutiny,[1e] such a system is considered empirically valid and useful as long as the limitations are realized. (a) J. S. Waugh and R. Fessenden, *J. Amer. Chem. Soc.*, 1957, **79**, 846; (b) (correction to 1a), *J. Amer. Chem. Soc.*, 1958, **80**, 6697. (c) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012; (d) see also numerous references in the two volumes entitled "High Resolution Nuclear Magnetic Resonance Spectroscopy," J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon Press, 1966; (e) J. I. Musher, *J. Chem. Phys.*, 1965, **43**, 4081; *Adv. Magnetic Resonance*, 1966, **2**, 177.

[2] The preparation of these compounds will be discussed in detail elsewhere, T. Onak, D. Marynick, P. Mattschei, and G. Dunks. Essentially, the procedure parallels the earlier study of T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, 1964, **3**, 1686.

[3] W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1963, **85**, 2331; *Inorg. Chem.*, 1964, **3**, 1666.

[4] *Cf.* apical- and basal-attached methyl hydrogen resonance positions for methylpentaboranes, T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, 1967, **6**, 1476. Various estimates for the charge distribution of pentaborane are summarized by W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, 1963, p. 110.

[5] The adopted values appear quite reasonable when compared to related systems: T. Onak, L. B. Friedman, J. H. Hartsuck, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1966, **88**, 3439; L. B. Friedman and W. N. Lipscomb, *Inorg. Chem.*, 1966, **5**, 1752.