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Molecular Structure and Internal Rotation in Tetramethyldiborane. An Electron Diffraction Study[1,2]

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The structure of gaseous $(CH_3)_2BH_2B(CH_3)_2$ was reinvestigated by electron diffraction. Mean (r_g) internuclear distances and approximate standard errors determined from the radial distribution function are B–C = 1.590 ± 0.003 Å, B–B = 1.840 ± 0.010 Å, C–H = 1.119 ± 0.004 Å, and $B–H_b$ = 1.364 ± 0.045 Å. The derived BBC and BCH angles, uncorrected for "shrinkage effects," are 120.0 ± 1.3° and 112 ± 2°, respectively. Root-mean-square amplitudes of vibration are also reported. Methyl groups are staggered with respect to the bonds radiating from boron atoms, and the barrier to rotation is approximately 1 kcal/mole. A brief comparison of structural parameters is made with corresponding boranes and hydrocarbons, and alternative interpretations of trends are discussed.

Introduction

An investigation of tetramethyldiborane (TMDB) was initiated as part of a program to study changes in bond length with changes in coordination number. The investigation was performed concurrently with structural analyses of trimethylborane, diborane, and deuteriodiborane, the results of which have already been published.[4,5] A preliminary report of the internal rotation in TMDB has also appeared.[6]

Experimental Section

A sample of vacuum-distilled tetramethyldiborane was maintained at −196° prior to use in order to minimize decomposition. Shortly before injection into the electron diffraction camera the sample was evacuated for 20 min at −78° to remove the more volatile products of decomposition. Diffraction patterns were then taken with the compound at −11°. This temperature corresponds to a vapor pressure of about 26 torr.

Procedures for obtaining diffraction patterns and the apparatus and methods for converting measurements into leveled experimental intensities have been described elsewhere.[5,7-9] An analysis of the leveled experimental intensities was carried out using the conventional radial distribution method.[7] The experimental radial distribution function f(r) is illustrated in Figure 1. Experimental intensities and background functions are shown in Figure 2.[10] The uncertainties were derived by least squares and by trial and error. In most cases the trial-and-error uncertainties were appreciably larger and were adopted because they seemed more reasonable.

Results

Mean bond lengths and amplitudes of vibration determined for TMDB are listed in Table I where they are compared with corresponding results for $B(CH_3)_3$ and B_2H_6. The structural parameters are in remarkably close agreement with those previously derived for TMDB by Jones, Hedberg, and Schomaker,[11] who used the old "visual method" of electron diffraction. Indeed, the agreement is considerably closer than customarily expected from the uncertainties of the visual method and attests to the exceptional skill of the aforementioned investigators.

The distribution of internuclear distances in the 3–5.5-Å region of the radial distribution function f(r) indicates that the methyl groups have staggered conformations with respect to the B–C and B–H bond lines radiating from the boron atoms. Presumably, then, the leading term representing the potential energy function for restricted rotation is $V_0(1 - \cos 3\theta)/2$. In view of the relatively low barrier anticipated for the molecule and consistent with the diffuseness of the outer region of the f(r) curve, the classical probability distribution function $P(\theta) = P_0 \exp[-V(\theta)/RT]$ was adopted in calculations of synthetic radial distribution functions. Radial distribution functions calculated for several different barriers are compared with the experimental f(r)[12] in Figure 3. The best fit between experimental and calculated curves was obtained for V_0 equal to about 1 kcal/mole.

Discussion

A comparison of internuclear distances listed in Table I reveals two significant differences between corresponding bonds in the boranes. The B–C bond is 0.012 ± 0.003 Å longer in TMDB than in $B(CH_3)_3$, and the B–B distance is 0.065 ± 0.01 Å longer in TMDB than in B_2H_6. Both of these changes are in the direction expected on the basis of hyperconjugation theory. In $B(CH_3)_3$ the p_π orbital of boron is unoc-

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[1] Contribution No. 2182. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] Based on a dissertation by B. L. Carroll to the Graduate School, Iowa State University, in partial fulfillment of the requirement for the degree of Doctor of Philosophy, 1963.

[3] Author to whom correspondence concerning reprints should be addressed at the Department of Chemistry, University of Michigan, Ann Arbor, Mich. 48104.

[4] L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, **42**, 3076 (1965).

[5] L. S. Bartell and B. L. Carroll, *ibid.*, **42**, 1135 (1965).

[6] L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Letters*, **13**, 705 (1964).

[7] R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).

[8] S. Shibata, L. S. Bartell, and R. M. Gavin, Jr., *ibid.*, **41**, 717 (1964).

[9] S. Shibata and L. S. Bartell, *ibid.*, **42**, 1147 (1965).

[10] Numerical electron intensity data have been deposited as Document No. 9729 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[11] M. E. Jones, K. Hedberg, and V. Schomaker, 2nd International Congress on Crystallography, Stockholm, Sweden, 1951.

[12] Note that the experimental f(r) curve depends mildly upon the parameters of the calculated f(r) since it is based on calculated intensity values in the experimentally inaccessible low-angle range. In each comparison of f(r) in Figure 3 the experimental curve is self-consistent with the calculated curve.

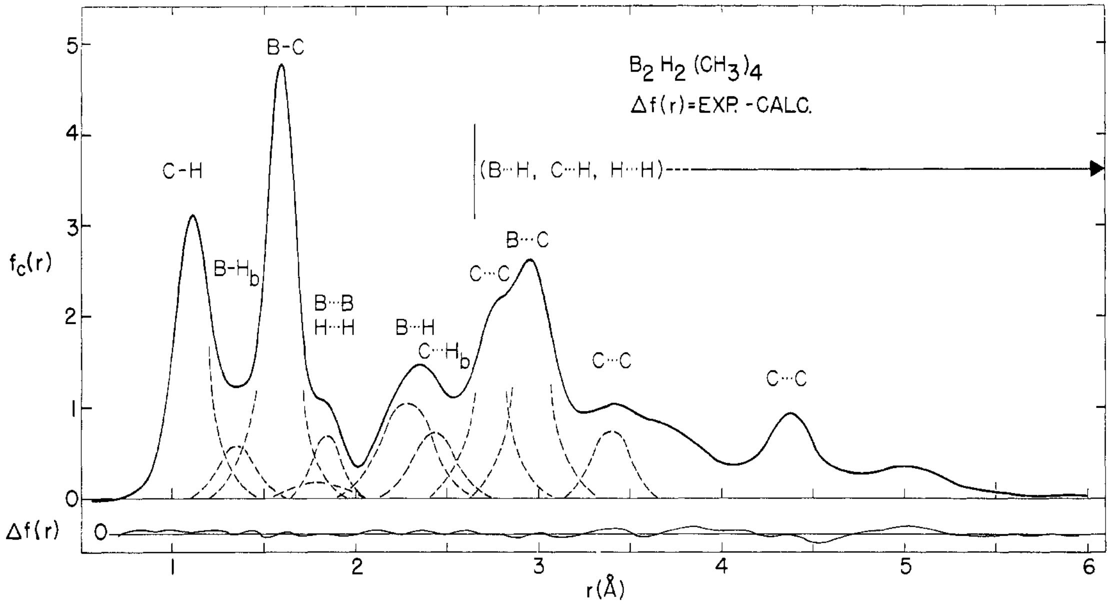

Figure 1.—Experimental radial distribution function for $B_2H_2(CH_3)_4$. The lower curve is a plot of the difference between the experimental and calculated radial distribution functions.

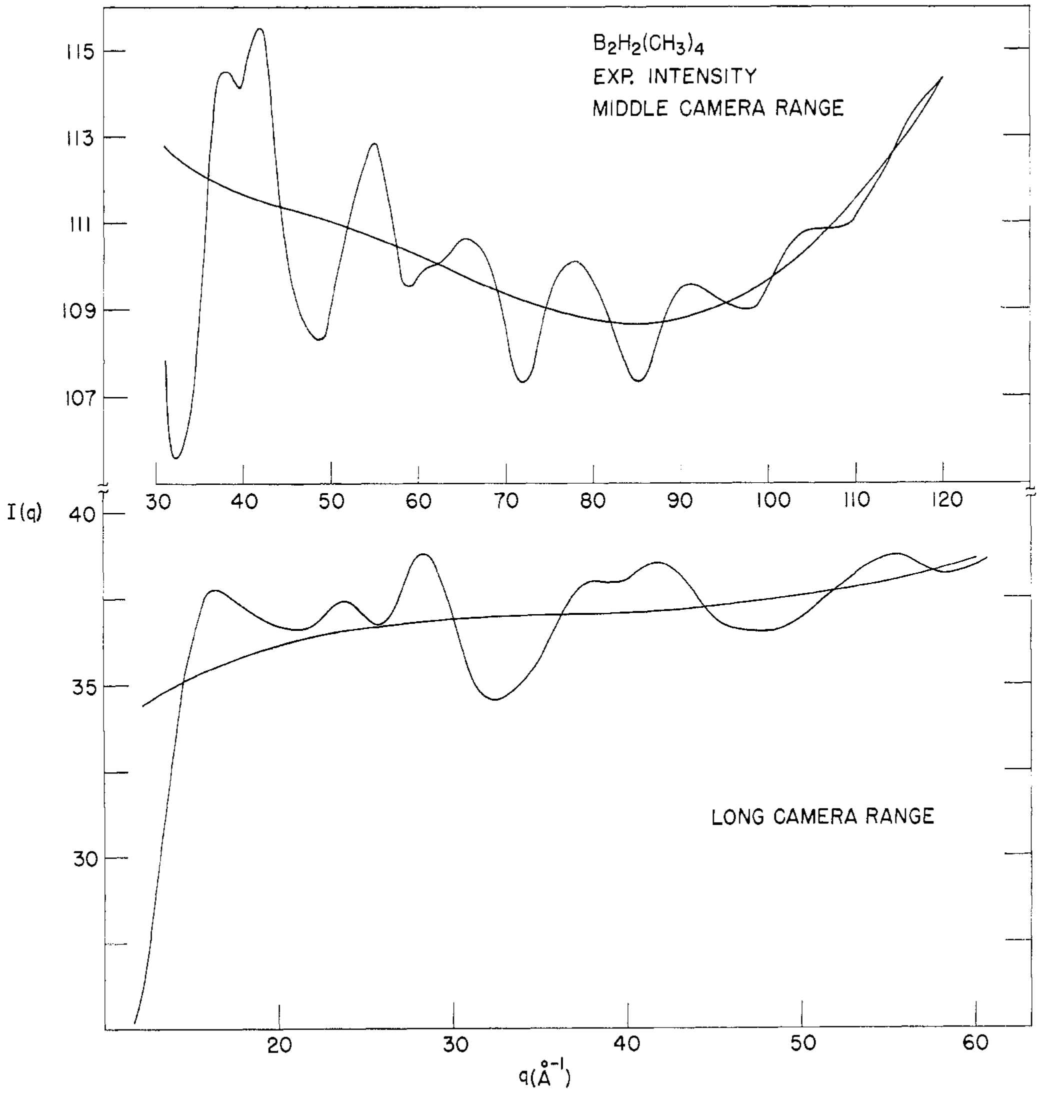

Figure 2.—Experimental total intensity and background functions for $B_2H_2(CH_3)_4$.

TABLE I

STRUCTURAL PARAMETERS FOR $B_2H_2(CH_3)_4$ AND RELATED COMPOUNDS

Mean distance, r_g, Å	$B_2H_2(CH_3)_4$[a]	$B(CH_3)_3$[b]	B_2H_6[c]
BC	1.590 ± 0.003	1.578 ± 0.001	
BB	1.840 ± 0.010		1.775 ± 0.004
CH	1.119 ± 0.004	1.114 ± 0.002	
BH_b	1.364 ± 0.045		$1.339\begin{cases}+0.002\\-0.006\end{cases}$
Mean amplitude, l_g, Å			
BC	0.057 ± 0.004	0.054 ± 0.001	
BB	0.067 ± 0.012		0.061 ± 0.002
CH	0.086 ± 0.006	0.081 ± 0.002	
BH_b	0.086[e]		0.086 ± 0.009
Mean angles,[d] deg			
CBC	120.0 ± 2.6	119.4 ± 0.3	
H_bBH_b	95 ± 5		97.0 ± 0.3
BCH	112 ± 2	111.9 ± 0.2	

[a] Standard errors were estimated by the techniques discussed in ref 5. [b] Reference 4. [c] Reference 5. [d] Not corrected for Bastiansen–Morino shrinkage effect. [e] Assumed to be same as in B_2H_6.

cupied except by methyl electron delocalization, a circumstance which invites hyperconjugative shortening of the B–C bond.[13] In TMDB, on the other hand, the corresponding boron p orbital is engaged actively in the bridge bonding and, hence, is not as readily available for interaction with the methyl groups. Nevertheless, there is no reason to believe that there is a complete absence of π character in the B–C bonds of TMDB. This π delocalization should lengthen the B–B distance, for if the capacity of the boron p orbital is dissipated hyperconjugatively, the effectiveness of the BHB bridge bonds is sacrificed in proportion. A similar sacrifice in B_2H_6 is negligible since the π character of the B–H terminal bonds must be very small.

The magnitudes of the small B–C and large B–B shifts do not lend confidence in the hyperconjugation argument. In olefins a C=C lengthening analogous to the B=B lengthening in TMDB is not observed when vinyl hydrogens are replaced by methyl groups. Of course, not even in hydrocarbon molecules is there compelling evidence for hyperconjugation in ground-state properties. It is now well known that shifts commonly rationalized in terms of hyperconjugation can also be accounted for by alternative steric[14] or hybridization[15] arguments. That the same situation prevails in the present cases is suggested by the parallels portrayed in Figure 4.

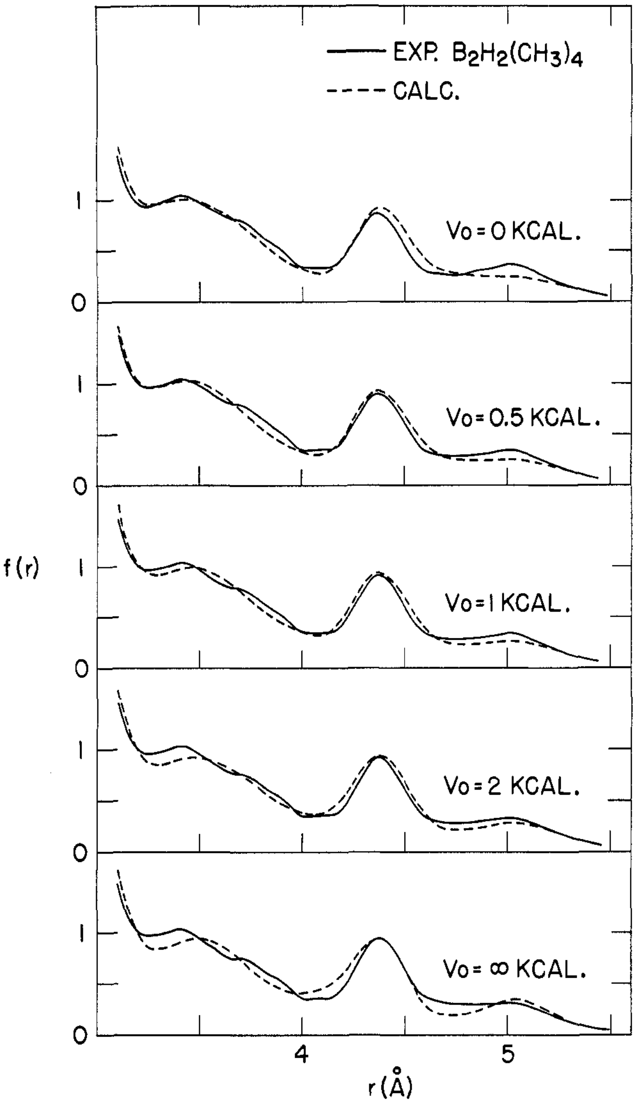

Figure 3.—Radial distribution curves for region sensitive to methyl group orientation. Dashed lines represent synthetic curves calculated for various hindering potentials; solid lines represent experimental data.

Decreasing the coordination number about a central atom decreases the number of nonbonded repulsions between its ligands and tends to shorten the bonds to the ligands. The change from $H_3C{-}B\begin{smallmatrix}\diagup H\\ -H\\ \diagdown C\end{smallmatrix}$ (in TMDB) to $H_3C{-}B{<}\begin{smallmatrix}C\\ C\end{smallmatrix}$ (in trimethylborane) is effectively less than from $H_3C{-}C\begin{smallmatrix}\diagup H\\ -H\\ \diagdown C\end{smallmatrix}$ (in propane) to $H_3C{-}C\begin{smallmatrix}\diagup\!\!\diagup C\\ \diagdown C\end{smallmatrix}$ (in isobutylene) since the TMDB bridge bonds are "electron deficient." This is consistent with the smaller shift in C–B length than in C–C.

The effect on the B–B length of replacing terminal hydrogens by methyls strikingly parallels the corresponding effect exhibited for hydrocarbons in Figure 4. Few workers would attribute the effect in hydrocarbons to hyperconjugation. The effect in hydrocarbons is,

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(13) Note, however, as pointed out in ref 4, that the B–C bond length in $B(CH_3)_3$ manifests no shortening with respect to the Schomaker–Stevenson–Pauling reference value (L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 228) to confirm hyperconjugative interaction. Perhaps this negative result is due as much to the difficulty in establishing a suitable "pure single bond" B–B reference length as it is to an absence of hyperconjugation. Note, also, that the reference single bond B–C length quoted as 1.52 Å in ref 4 should have read 1.54 Å.

(14) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960); *Tetrahedron*, **17**, 177 (1962).

(15) M. J. S. Dewar and H. N. Schmeising, *ibid.*, **5**, 166 (1959); **11**, 96 (1960); M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962.

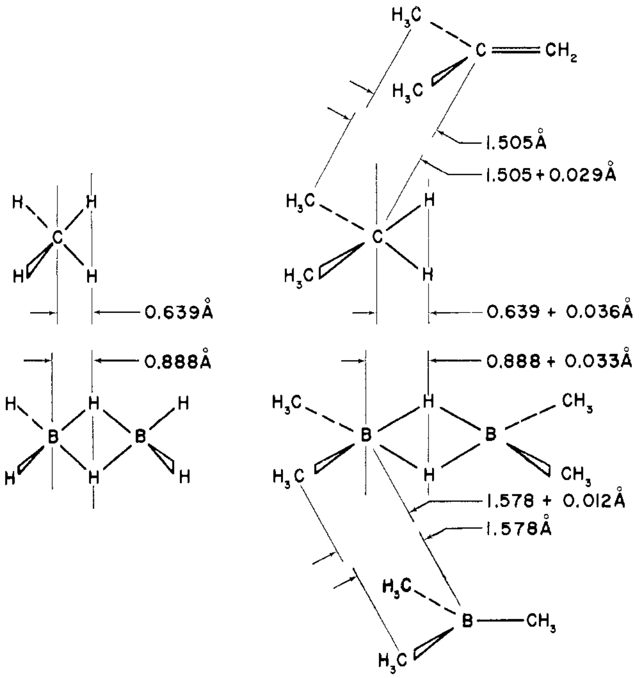
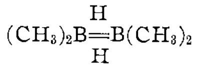


Figure 4.—Comparison of related structural parameters in boranes and hydrocarbons.

however, in excellent accord with calculations[16] based on a model force field in which it is assumed that all C–H bonds are identical except for steric environment (a fact which by no means proves that the effect is steric). Those who favor hybridization arguments could undoubtedly piece together a self-consistent picture notwithstanding the scant evidence provided by the borane bond angles.

Although it is fair to advance interpretations alternative to the popular hyperconjugative one, it is unwise to overstress the analogies depicted in Figure 4. This need for caution becomes evident on examination of the barriers to rotation where TMDB rather than $B(CH_3)_3$ is seen to be related to the model compound $(CH_3)_2C{=}CH_2$. Clearly, hyperconjugation is not involved in threefold barriers, for $B(CH_3)_3$ has nearly free rotation of its methyl groups[4] consistent with the symmetry-imposed exclusion of a threefold potential energy component. In TMDB the symmetry is broken and a threefold contribution is allowed for methyl rotations. It is probably significant that the barrier turns out to be approximately the same as in $(CH_3)_2C{=}O$, for it takes little reflection to recognize the similarity between the electron density distributions in



$$(CH_3)_2B\overset{H}{\underset{H}{=}}B(CH_3)_2$$

and $(CH_3)_2C{=}O$. For the sake of argument we have applied Hoffmann's extended Hückel MO treatment[17] to TMDB and acetone. In both cases the stable conformations were those observed experimentally. Moreover, the magnitude of the barrier calculated for acetone was correct. By contrast, the TMDB barrier was almost an order of magnitude higher than that inferred from the electron diffraction analysis, partly, perhaps, because of the excessive repulsions between hydrogens which seem characteristic of the Hoffmann program.

In summary, the results of the present study are not inconsistent with long-held views of bonding in small molecules. Unfortunately, however, the same impasses which are encountered in interpreting details of hydrocarbon structures are also encountered here. These serve to remind us of the superficiality of our present qualitative interpretational schemes.

Acknowledgments.—We wish to express our garitude to Dr. C. W. Heitsch for donating the sample of tetramethyldiborane. We are also indebted to Lockheed Electronics Co. and their technical publications staff for assistance in preparing the final document.

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(16) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, in press.

(17) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179 (1962); R. Hoffmann, *ibid.*, **39**, 1397 (1963).

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The Reactions of 1-Isopropenylcarborane with Dinitrogen Tetroxide, Tetrafluorohydrazine, and Bromine

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The preparation of several new compounds by reaction of 1-isopropenylcarborane with N_2O_4, N_2F_4, and Br_2 is reported. Derivatives of some of these compounds have been made. The susceptibility of the alkenyl group to radical attack is discussed as well as its inert nature with respect to ionic additions. Some physical properties of the new compounds are reported.

The reactions of vinyl groups adjacent to a carborane nucleus have not been extensively studied. Cohen, *et al.*,[1] synthesized 1-isopropenylcarborane (I) and reported some of its reactions. These authors found that the alkenyl group could be hydrogenated and also that oxidation could be achieved though the product was not

(1) M. M. Fein, J. Robinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 111 (1963).