CNDO/2 Calculations of Some Carboranes[1a]

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Abstract: CNDO/2 calculations have been performed on the isomers of the carboranes $C_2B_3H_5$, $C_2B_4H_6$, $C_2B_5H_7$, and $C_2B_{10}H_{12}$. The relative stabilities of the various isomers of each carborane, their molecular structure, charge densities, and dipole moments have been calculated. The results are discussed.

The carboranes constitute a large and unusual class of compounds of which many of the possible members have now been synthesized and characterized. They are particularly interesting in that they frequently contain carbon atoms which are in valence situations with a formal coordination that is greater than four. As is true of the more thoroughly studied boron hydrides, hydrogen is frequently found in a bridging position. However, carboranes of the homologous series $C_2B_nH_{n+2}$ have no bridge hydrogens and are distinctly more chemically inert than the corresponding boron hydrides. The entire field of carborane chemistry has recently been exhaustively reviewed by Williams.[2]

In view of the great interest in carborane chemistry in recent years and its peculiar valence characteristics, we have undertaken a molecular orbital study of the structure and bonding in these compounds which we report here. Since most of the members of the homologous carborane series $C_2B_nH_{n+2}$ have been prepared and a large body of their experimental properties is available, we have limited our considerations to the members of this series. As a result of this concentration, we have available ample information against which to check the results of our theoretical work and are able to roughly define the limits of reliability of the theory. We therefore have a guide as to the reliability of predictions with respect to compounds which have not yet been found.

Of primary interest to the chemist is the question of the relative stabilities of the possible isomers with a given empirical formula. Our calculations include an attempt to estimate the relative stabilities of these isomers, and these results lead to some conclusions as to which of the possible isomers are likely to be the most stable thermodynamically and which are unlikely to be prepared.

Any theoretical treatment which attempts to arrive at a prediction of the relative stabilities of a group of related molecules must face the question of whether the theoretical energies to be compared should be calculated at the molecule's *experimental* equilibrium geometry or at its *calculated* equilibrium geometry. There is a paucity of geometrical information on a number of the molecules which we consider, and since the theory, as will be shown below, is quite successful in the prediction of geometry in those cases where the geometry is known, we have chosen the latter course. We have, therefore, calculated the most stable geometry of these compounds. An examination of these results led us to some conclusions as to the distribution of electronic charge in these molecules, and these are discussed in section II.

At elevated temperatures, some of the carborane isomers are known to rearrange to others under fairly mild conditions,[3,4] and it is of interest to examine some of the proposed reaction paths with respect to their energies of activation. These results are presented in section III.

It is also known that in many cases, substituents have marked effects upon the properties and stabilities of the basic carborane structure. We have, therefore, carried out a few calculations on substituted carboranes in an attempt to examine the effects of substituents in some detail. These are reported in section IV.

The program of investigation which has just been outlined requires a considerable number of calculations on fairly large molecules. Therefore, semiempirical molecular orbital methods are indicated. The carboranes are, by normal valence standards, electron deficient, so that a considerable asymmetry is to be expected in the electronic charge distribution. It would appear to be necessary to utilize a theory which includes the elements of electronic interaction in an explicit fashion. Our calculations have been carried out in the CNDO/2 approximation,[5-7] which satisfies these criteria. Details of the method and its capabilities may be found in the original papers and in a recent review by Jaffé.[8] The parametrization is the same as that used in ref 7.

I. Calculations of Equilibrium Geometries and Relative Stabilities of Carboranes

CNDO/2 MO calculations were carried out for all the possible isomers of four members of the homologous series $C_2B_nH_{n+2}$: $C_2B_3H_5$, $C_2B_4H_6$, $C_2B_5H_7$, and $C_2B_{10}H_{12}$. The geometric arrangement of each compound and the labeling convention used are illustrated in Figure 1.

To optimize the molecular structure, the bond lengths and bond angles of each isomer were varied to

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[1] This work was supported in part by the Air Force Office of Scientific Research under Grant No. 849-67 extended to R. A. B.; (b) Alfred P. Sloan Research Fellow.

[2] R. E. Williams in "Progress in Boron Chemistry," Vol. II, Pergamon Press, Oxford, 1969, Chapter 2.

[3] (a) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964); (b) R. M. Salinger and C. L. Frye, *ibid.*, **4**, 1815 (1965).

[4] S. Papetti and T. L. Heying, *J. Amer. Chem. Soc.*, **86**, 2295 (1964).

[5] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

[6] J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965).

[7] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[8] H. H. Jaffé, *Accounts Chem. Res.*, **2**, 136 (1969).

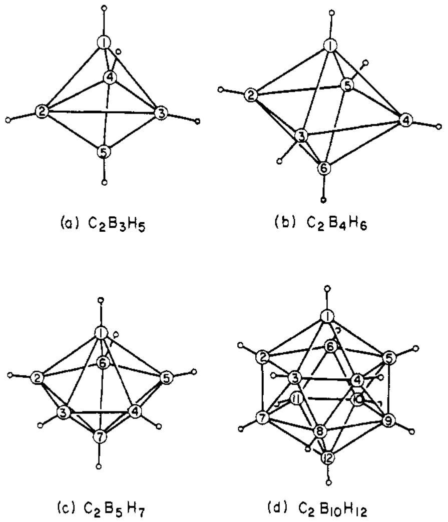
Table I. Bond Lengths[a] Calculated for Carboranes[b]

		Trigonal Bipyramids		
1,5-$C_2B_3H_5$		2,3-$C_2B_3H_5$		1,2-$C_2B_3H_5$
C–B 1.57		C–C 1.60		C–C 1.49
B–B 1.76 (1.84 and 1.87)[c]		C(2)–B(4) 1.71		C(1)–B(3) 1.57
		C(2)–B(1) 1.57		C(2)–B(5) 1.57
		B(1)–B(4) 1.60		C(2)–B(3) 1.70
				B(3)–B(5) 1.61
				B(3)–B(4) 1.77
Octahedrons				Icosahedron
1,6-$C_2B_4H_6$		2,3-$C_2B_4H_6$		1,12-$C_2B_{10}H_{12}$
C–B 1.64		C–C 1.54 (1.54)[e]		C(1)–B(2) 1.70
B–B 1.68 (1.68 and 1.70)[d]		C(2)–B(5) 1.65 (1.60)		B(2)–B(7) 1.77
		C(2)–B(1) 1.64 (1.63)		B(2)–B(3) 1.74
		B(1)–B(4) 1.69 (1.72)		
		B(4)–B(5) 1.70 (1.75)		
		Pentagonal Bipyramids		
1,2-$C_2B_5H_7$		1,7-$C_2B_5H_7$	2,3-$C_2B_5H_7$	2,4-$C_2B_5H_7$
C–C 1.63		C–B 1.71	C(2)–C(3) 1.49	C(2)–B(1) 1.72 (1.71)[f]
C(1)–B(3) 1.68	B(3)–B(4) 1.62	B–B 1.61	C(2)–B(1) 1.71	C(2)–B(3) 1.58 (1.55)
C(1)–B(4) 1.72	B(4)–B(5) 1.63		C(2)–B(6) 1.58	C(2)–B(6) 1.58 (1.56)
C(2)–B(3) 1.57	B(3)–B(7) 1.73		B(1)–B(4) 1.75	B(1)–B(3) 1.74 (1.82)
C(2)–B(7) 1.72	B(4)–B(7) 1.77		B(1)–B(5) 1.76	B(1)–B(5) 1.75 (1.82)
			B(4)–B(5) 1.65	B(5)–B(6) 1.66 (1.65)

[a] All lengths are given in Å. [b] The available experimental values are in parentheses after the calculated values. [c] From B–methyl derivative: L. Li and R. A. Beaudet, in preparation. [d] From B–Cl derivative: C. McKown and R. A. Beaudet, in preparation. [e] R. A. Beaudet and R. L. Poynter, in preparation. [f] R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, **43**, 2166 (1965).

attain a minimum in the total molecular energy. The following assumptions were made in obtaining the optimum structures. First, some molecular symmetries have been assumed. For the known compounds, these symmetries, with one exception, are those which have been experimentally determined. For example, 1,5-$C_2B_3H_5$ has D_{3h} symmetry, and there are only four independent structural parameters, the bond lengths C–B, B–B, B–H, and C–H. However, in 1,2-$C_2B_5H_7$, although the plane of symmetry in the base no longer exists, the pentagonal base was assumed to be planar to simplify the variational procedure. Secondly, since the variation of the hydrogen parameters would be a tedious and time consuming task, the B–H and C–H bond lengths were fixed at 1.20 and 1.10 Å, respectively. This is partially justified by the fact that terminal hydrogen bond lengths have never been determined experimentally to be very different from these values. Furthermore, in the optimization of the structure of pentaborane as described later in this section, the terminal B–H bonds were predicted by the CNDO/2 theory to be very close to 1.20 Å. Thirdly, the B–H and the C–H bonds were oriented to bisect the exterior angles of the polyhedrons. The sensitivity of the results to changes in hydrogen bond orientations was tested in the following manner. In 2,3-$C_2B_4H_6$, instead of bisecting the exterior angles of the trapezium, the B(5)–H and C(2)–H bonds were each bent 5° toward the other as were the B(4)–H and C(3)–H bonds. The change in the total molecular energy was only 2 kcal/mol. The dipole moment was changed by 1%, while changes in the charge distribution were insignificant.

The remaining structural parameters were varied in the following manner. Either the experimental structure or an intuitively estimated structure was used as the starting point. Each independent bond length was varied in turn to obtain the partial derivatives of the total molecular energy. The next estimate of the equilibrium structure was then determined by extrapolation and the procedure was repeated until a minimum in the total molecular energy was obtained. The bond lengths were optimized to better than ±0.01 Å in all cases.



(a) $C_2B_3H_5$ (b) $C_2B_4H_6$

(c) $C_2B_5H_7$ (d) $C_2B_{10}H_{12}$

Figure 1. Geometries of the carboranes.

The calculated structures are in satisfactory agreement with the experimental structures. The results are given in Table I. Comparing the experimental and the calculated values for 2,4-$C_2B_5H_7$, the CNDO calculations predict the observed short B(5)–B(6), C(2)–B(6), and C(2)–B(3) bonds, and the observed long B(1)–B(3) and B(1)–B(5) bonds. However, in all cases the length of the B–B bonds is underestimated. Hence, while the long B–B bonds are greater than 1.8 Å, the predicted values are 1.75 Å. For 2,3-$C_2B_4H_6$, a pure single bond is predicted for the C–C bond, 1.54 Å, as observed, and the relative lengths of the B–B bonds are essentially correct, but the absolute values are again underestimated. The trigonal bipyramid, 1,5-$C_2B_3H_5$, differs

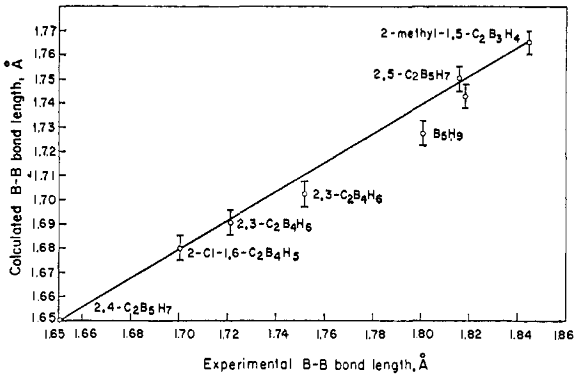


Figure 2. Calculated B–B bond lengths.

from the other carboranes because the molecular bonding can be explained completely by classical valence theory without the use of three-center bonds and delocalization. This can be viewed as a bicyclic system involving C–B–C bonds and no B–B bonding. The experimental B–B bond lengths of 1.87 and 1.85 Å in $2\text{-}CH_3\text{-}1,5\text{-}C_2B_3H_4$ reflect this weak bonding.[9]

The underestimation of the B–B bond lengths is nicely illustrated by the plot of observed *vs.* calculated B–B bond lengths. As can be seen in Figure 2, there is a linear relationship between the observed and calculated B–B bond lengths, but the calculation systematically underestimates these numbers.

The success in the geometry predictions parallels similar success for a boron hydride. As a preliminary test for the ability of the CNDO theory to predict the geometry of molecules with highly delocalized electrons, the structure of pentaborane was completely optimized and compared with the microwave results.[10] The only assumption made in the calculation was that the molecule retained C_{4v} symmetry. The agreement in the comparison was excellent. The apex to base B–B bond was predicted to be 1.68 Å (experimental value, 1.687 Å). The base B–B bonds length was somewhat underestimated as 1.73 Å (experimental value, 1.80 Å). The terminal hydrogen bond lengths were predicted to be 1.19 and 1.20 Å for the apex boron and the base borons, respectively. The bridge hydrogen bond lengths were predicted to be 1.36 Å (experimental value, 1.35 Å). The base B–H (terminal) bonds were predicted to bend upward from the base by 6° (experimental value, 3° upward) while the bridge hydrogens were predicted to bend downward by 57° (experimental value, 56° downward).

The total molecular energies of all the carboranes that were calculated are given in Table II, for both a standard set of geometric parameters and the optimized structures. For clarity, the energies of the isomers of each carborane are compared to that of the most stable isomer, and the total energy of each of these isomers is given in the footnote.

It is interesting to compare our results to the known relative stabilities of the geometric isomers. It is reasonable to assume, when only one isomer of a given carborane has been prepared, that it is thermodynamically the most stable. For $C_2B_4H_6$ and $C_2B_{10}H_{12}$, all the isomers have been prepared. Though little is known quantitatively about the thermodynamic properties of these compounds, $2,3\text{-}C_2B_4H_6$ isomerizes completely to $1,6\text{-}C_2B_4H_6$ when kept in a sealed tube overnight at 250°.[3a] Also $1,2\text{-}C_2B_{10}H_{12}$ isomerizes to $1,7\text{-}C_2B_{10}H_{12}$ at 450°;[3b] this in turn isomerizes to $1,12\text{-}C_2B_{10}H_{12}$ at 630°.[4] Hence, we do know the relative ordering of stability for these compounds.

Table II. The Calculated Energies of the Carboranes

Isomers	CNDO/2 calculation with standard bond lengths,[a] kcal/mol	CNDO/2 calculation with optimized structures, kcal/mol
	Trigonal Bipyramids	
$1,5\text{-}C_2B_3H_5$	144.5[b]	0.0
$1,2\text{-}C_2B_3H_5$	156.2	10.7
$2,3\text{-}C_2B_3H_5$	170.6	45.6
	Octahedrons	
$1,6\text{-}C_2B_4H_6$	81.3	13.6
$2,3\text{-}C_2B_4H_6$	81.7	0.0
	Pentagonal Bipyramids	
$2,3\text{-}C_2B_5H_7$	133.1	0.0
$2,4\text{-}C_2B_5H_7$	117.3	7.1
$1,2\text{-}C_2B_5H_7$	160.3	52.7
$1,7\text{-}C_2B_5H_7$	190.5	106.1
	Icosahedrons	
$1,12\text{-}C_2B_{10}H_{12}$	14.5	0.0
$1,7\text{-}C_2B_{10}H_{12}$	19.7	
$1,2\text{-}C_2B_{10}H_{12}$	34.1	

[a] The energies in this column were calculated assuming all B–B, B–C, and C–C bonds were 1.75 Å. All C–H and B–H bonds were assumed to be 1.10 and 1.20 Å long, respectively, and were assumed to bisect the exterior polyhedral angles. [b] The standard energies used are: $1,5\text{-}C_2B_3H_5$, −3624.9; $2,3\text{-}C_2B_4H_6$, −4571.0; $2,3\text{-}C_2B_5H_7$, −5495.7; and $1,12\text{-}C_2B_{10}H_{12}$, −10,196.3 kcal/mol. It should be noted that these energies are on an arbitrary energy scale and cannot be used for comparison with any experimental quantity.

The CNDO calculations do predict the proper stability for $C_2B_{10}H_{12}$, but not for $C_2B_4H_6$. In the latter case, the energy difference is 13.6 kcal/mol in favor of the 2,4 isomer. From this discrepancy the errors in the total energy differences can be estimated to be approximately ±20 kcal/mol, although it must be realized that the total zero-point vibrational energies of these molecules will be of the order of 70 kcal/mol, and the uncertainty in the difference between this quantity for various isomers is a failing which is inherent to any calculations carried out within the Born–Oppenheimer approximation. On closer examination, this discrepancy can be ascribed to the overestimation of the strength of the B–B bond, a feature which is consistent with the short lengths calculated for these bonds. The energy of the isomer with the most B–B bonds is lowered relative to the others, owing to the additional bond stability. Hence, since the *cis* isomer of $C_2B_4H_6$ has five B–B bonds while the *trans* isomer has only four, the stability of the *cis* form is exaggerated relative to the *trans*.

Despite this effect, some general predictions can still be made about the relative stabilities of the carborane isomers. It is unlikely that $2,3\text{-}C_2B_3H_5$, $1,2\text{-}C_2B_5H_7$, and $1,7\text{-}C_2B_5H_7$ are thermodynamically stable, though they may be kinetically stable. Their formation may be encouraged by a high-temperature technique such as pyrolysis followed by rapid thermal quenching. This is in agreement with experiment, since only the 2,4 isomer of $C_2B_5H_7$ and the 1,5 isomer of $C_2B_3H_5$ have

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(9) L. Li and R. A. Beaudet, in preparation.

(10) H. J. Hrostowski and R. J. Myers, *J. Chem. Phys.*, **22**, 262 (1954).

Table III. Dipole Moments[a]

	Calcd	Obsd
1,2-$C_2B_3H_5$	3.80	
2,3-$C_2B_3H_5$	2.74	
2,3-$C_2B_4H_6$	4.35	1.50[b]
2,3-$C_2B_5H_7$	6.21	
2,6-$C_2B_5H_7$	2.36	1.32[c]
1,2-$C_2B_5H_7$	4.94	
1,7-$C_2B_{10}H_{12}$	5.29	2.78[d]
1,2-$C_2B_{10}H_{12}$	8.50	4.31[d]

[a] Only molecules with nonzero dipole moments have been included. All calculations are at optimized geometries except 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$, where standard geometries are used. [b] See footnote *e* of Table I. [c] See footnote *f* of Table I. [d] R. Maruca, H. Schroeder, and A. W. Laubengayer, *Inorg. Chem.*, **6**, 572 (1967).

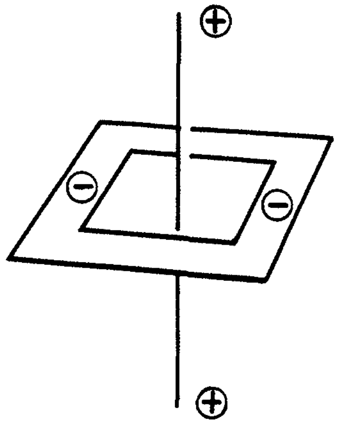


Figure 3. Schematic net charge distribution in 1,6-$C_2B_4H_6$.

been prepared. On the other hand, 1,2-$C_2B_3H_5$ and 2,3-$C_2B_5H_7$ may very well be stable enough to be prepared, particularly if they are stabilized by substituents. As a matter of fact, Grimes[11] has reported the identification of the dimethyl derivative of 1,2-$C_2B_3H_5$. This derivative has been shown by nmr to be either the 1,3- or the 2,3-dimethyl derivative.

The differences in bond energies between the isomers seem to be intricately related to the number of B–B and B–C bonds and the coordination number of the carbon atoms. A few qualitative conclusions can be made about the effect on the energy of changing the carbon coordination number. For $C_2B_5H_7$, the first two isomers in the table have two carbons in equatorial positions where the site coordination number is five, while the third moves one carbon to the apex with a coordination number of six. In the last isomer, the second carbon is moved to the other apex position. Changing the carbon coordination number from five to six increases the molecular energy by 50 kcal/mol in an additive fashion. Comparing the trigonal bipyramids, the results are not so clear, but one may estimate that the difference in energy between a four-coordinated and a five-coordinated carbon is between 10 and 35 kcal/mol. The change in the carbon coordination number seems to have the largest single effect on the relative stabilities of isomers in keeping with the inorganic chemist's intuitive rule that carbon seeks the position of least coordination. In the icosahedral isomers carbon is six coordinate in all isomers, and these forms are therefore rather close together in energy.

As can be seen from comparison of the calculated energies of the carboranes in Table II, the large difference in the energies calculated at standard bond lengths relative to those calculated at the optimized lengths underlines the danger in drawing thermodynamic conclusions from energies calculated at arbitrary geometries

The dipole moments of the carboranes have also been calculated and are listed in Table III. In the CNDO treatment, the total dipole moment ($\mu = \langle\psi|\hat{r}|\psi\rangle$) is the sum of two terms.[6]

$$\mu_Z = \sum_{\mathrm{A}}^{\mathrm{ATOMS}} \{(Z_\mathrm{A} - P_\mathrm{AA})z_\mathrm{A} - P_{2s(\mathrm{A}),\,2p_z(\mathrm{A})}\langle\phi_{2s(\mathrm{A})} z \phi_{2p_z(\mathrm{A})}\rangle\}$$

The first term represents a contribution from the net atomic charge densities, while in the last term, the atomic polarization is represented by the mixing of $2s_\mathrm{A}$ and $2p_\mathrm{A}$ orbitals.

As can be seen from Table III, the calculated values are roughly twice as large as the experimental.

It should be noted that our calculations employ only a minimal basis set of 2s and 2p orbitals on boron and carbon. The 3d orbitals of carbon and boron are very high in energy and would be expected to contribute a rather small amount of d character to the orbitals if they were included in the basis set. A very small admixture of d-orbital character, while producing an insignificant change in the net atomic charge distribution, can, however, change the value of the calculated dipole moment greatly.[12]

II. Net Charge Distributions

As is shown in Table IV, the principal conclusion which may be drawn from the calculated charge densities is that the carbon atoms tend to donate charge into the electron-deficient boron atom systems. In general, the higher the coordination number of carbon, the more electropositive it is calculated to be. Thus, the six-coordinate carbons in 1,7-$C_2B_{10}H_{12}$ and 1,7-$C_2B_5H_7$ are found to bear charges of +0.18 and +0.29, respectively. In Figure 3, we give a schematic display of the charge distribution in 1,6-$C_2B_4H_6$, a highly symmetric molecule. As shown in the diagram, this molecule has a sheet of negative charge in the boron plane and a "pipe" of positive charge perpendicular to this plane. This molecule would therefore be expected to have an extremely large electric quadrupole moment.

The tendency of carbon to donate charge into the boron system is contrary to the trend which would be predicted from the fundamental electronegativity of carbon. The electronegativity which must be considered, however, is that not of the carbon atom in its ground state, but that of carbon in the highly unusual valence state which corresponds to its situation in these molecules. In view of the fact that the calculated electric dipole moments of these molecules are uniformly too high, a result which is unusual for the CNDO/2 method, which usually is capable of quite reasonable predictions of this quantity,[13] it is difficult to know to

(11) R. N. Grimes, *J. Amer. Chem. Soc.*, **88**, 1895 (1966).

(12) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

Table IV. Net Atomic Charges in Carboranes[a],[b]

Trigonal Bipyramids		
$1,5\text{-}C_2B_3H_5$[a]		
C(1), C(5)	0.02	(0.04)
All B	0.04	(−0.07)
$2,3\text{-}C_2B_3H_5$		
C(2), C(3)	0.15	(0.06)
B(1), B(5)	−0.10	(−0.05)
B(4)	−0.09	(0.00)
$1,2\text{-}C_2B_3H_5$		
C(1)	0.20	(0.04)
C(2)	0.01	(0.04)
B(3), B(4)	−0.02	(−0.05)
B(5)	−0.10	(−0.06)
Octahedrons		
$1,6\text{-}C_2B_4H_6$		
C(1), C(6)	0.14	(0.03)
All B	−0.02	(−0.06)
$2,3\text{-}C_2B_4H_6$		
C(2), C(3)	0.14	(0.03)
B(1), B(6)	−0.02	(−0.07)
B(4), B(5)	−0.02	(−0.07)
Pentagonal Bipyramids		
$1,2\text{-}C_2B_5H_7$		
C(1)	0.30	(0.01)
C(2)	0.10	(0.06)
B(3), B(6)	−0.04	(−0.06)
B(4), B(5)	−0.09	(−0.05)
B(7)	0.10	(−0.10)
$1,7\text{-}C_2B_5H_7$		
C_1, C_7	0.29	(0.01)
All B	−0.08	(−0.04)
$2,3\text{-}C_2B_5H_7$		
C(2), C(3)	0.14	(0.04)
B(4), B(6)	−0.04	(−0.07)
B(1), B(7)	0.11	(−0.10)
B(5)	−0.09	(−0.06)
$2,4\text{-}C_2B_5H_7$		
C_2, C_4	0.09	(0.04)
B(5), B(6)	−0.05	(−0.07)
B(1), B(7)	0.11	(−0.09)
B(3)	−0.01	(−0.07)
Icosahedrons		
$1,2\text{-}C_2B_{10}H_{12}$		
C(1), C(2)	0.18	(0.06)
B(3), B(6)	0.05	(−0.07)
B(4), B(5) B(7)	0.03	(−0.08)
B(8), B(10)	0.01	(−0.08)
B(9), B(12)	0.02	(−0.09)
$1,7\text{-}C_2B_{10}H_{12}$		
C(1), C(7)	0.18	(0.05)
B(2), B(3)	0.04	(−0.07)
B(5), B(12)	0.04	(−0.08)
B(4), B(6) B(8), B(11)	0.03	(−0.08)
B(9), B(10)	0.01	(−0.08)
$1,12\text{-}C_2B_{10}H_{12}$		
C(1), C(12)	0.20	(0.04)
All B	0.03	(−0.07)

[a] All calculations are at optimized geometries except $1,2\text{-}C_2B_{10}H_{12}$ and $1,7\text{-}C_2B_{10}H_{12}$, where standard geometries are used. Number in parentheses is the charge on the hydrogen bonded to the named atom. [b] See Figure 1 for numbering system.

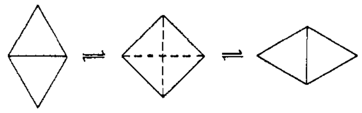
what degree the calculated charge distribution reflects the true situation in the molecule. Epstein, Koetzle, Stevens, and Lipscomb[14] have recently carried out all-electron rigorous SCF LCAO MO calculations on both the 1,2 and 1,6 isomers of $C_2B_4H_6$. They find the carbon atoms to be negative in these molecules. They, however, employ the Mulliken population analysis, since the normalization of their wave function includes the overlap matrix. We, on the other hand, use an orthonormal basis set and draw our conclusions from the charge-density and bond-order matrices. As is well known, the Mulliken population analysis evenly divides the overlap density between the two bonded atoms. It may, therefore, give a somewhat distorted picture of the density to be assigned to each atom if the density in the center of the bond is polarized toward one or the other of the bonded atoms. The situation is, therefore, unclear with respect to both of these types of calculation. One notes, however, that the dipole moment calculated by these authors for the $1,2\text{-}C_2B_4H_6$ molecule, while also much too large, has its positive end at the carbon atoms. In addition, the charge-density contour maps shown by them do appear to show polarization of the carbon atoms toward the boron structure.

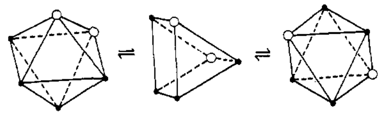
It would seem probable that the positive charge on the carbon atoms is overestimated in our calculations, but that the qualitative effect does exist.

III. Transition-State Study

Lipscomb has proposed that carboranes isomerize by intramolecular polyhedral rearrangements.[15] This mechanism involves the formation of a transition state where four of the atoms in the compound are arranged in a square configuration, as shown in Figure 4a. This intermediate state is formed by a lengthening and weakening of the diagonal B(1)–B(3) bond, with the subsequent formation of the B(2)–B(4) bond. This method is generally known as a "dsd" rearrangement. To test the feasibility of this mechanism, the molecular energy of the transition state in the square configuration was calculated to estimate the heat of activation of the mechanism.

For proper comparison with the stable forms of the isomers the structure of the square transition state should be optimized for minimum energy under the constraint that the reacting fragment of the compound remains in a square configuration. To make the problem tractable, a carborane with a high degree of symmetry and, therefore, a small number of variable


(a) Single dsd rearrangement


(b) D_{3h} intermediate
(3 simultaneous dsd rearrangements)

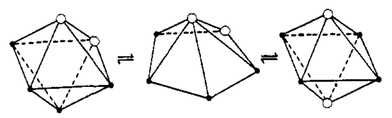

(c) C_{5v} intermediate

Figure 4. Possible rearrangement mechanics for $C_2B_4H_6$.

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(13) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

(14) I. R. Epstein, T. F. Koetzle, R. M. Stevens, and W. N. Lipscomb, *ibid.*, in press.

(15) W. N. Lipscomb, *Science*, **153**, 373 (1966).

structural parameters was required. Also, the carborane had to have two known geometrical isomers which rearrange readily. Since only one form of $C_2B_3H_5$ is presently known, $C_2B_4H_6$ was selected. Both the *cis* and *trans* isomers have been synthesized. Also, the *cis* isomer is known to convert completely to the *trans* at 250° overnight.[3a] The *trans* form, therefore, must be thermodynamically more stable than the *cis* form. The only simple aesthetic mechanism for this molecular isomerization involves three simultaneous dsd arrangements as depicted in Figure 4. Essentially, the reaction mechanism consists of the relative rotation of two opposite triangular faces of the octahedron. Hence, the transition state is a trigonal prism. The structure of this intermediate was optimized with the restriction that it remain a trigonal prism. The molecular energy could then be compared with those of the two stable isomers. The activation energy necessary to carry out this mechanism was determined to be about 300 kcal/mol. Using the simple relationship for the rate constant, $k = s \exp(-E_a/kT)$, k is readily calculated to be 10^{-112} sec^{-1} at 250° if $s = 10^{13}$ sec^{-1}. This cannot account in any way for the observed rate of isomerization. Even if the energy of activation is lowered by 50%, the rate is still too slow. Thus, we are forced to conclude that the dsd mechanism does not seem probable in this case.

We have also explored a second mechanism for this isomerization. The transition state involves the formation of a pentagonal pyramid by moving one apex boron into the four-membered ring between the *cis* carbon atoms. When a different boron atom fills the apex position, the *trans* form is obtained, as can be seen from Figure 4. We have calculated the molecular energy of the pentagonal bipyramid to be about 350 kcal/mol more than that of the stable isomers. Hence, this pathway also seems to be unlikely.

We must conclude that there is no simple path for the isomerization of $C_2B_4H_6$. Since the potential hypersurface of this reaction involves many independent parameters, it is very likely that other more complex but less energetic paths exist on its multidimensional potential surface.

IV. Substituent Effects

In view of the marked effects of substituents upon the stability of carboranes, we have carried out calculations on Cl, F, and CH_3 derivatives of 1,6-$C_2B_4H_6$. The CNDO/2 method is, within the limits previously discussed, capable of estimating the relative stabilities of different geometric arrangements of the same atoms, but is not capable of such comparisons between molecules containing different atoms. We, therefore, give only the effect of substituents upon the net charge densities in the molecule. The shifts in charge in the molecular framework, taken relative to 1,6-$C_2B_4H_6$ itself, are given in Table V.

The first conclusion that can be drawn from these calculations is that the principal manner in which the substituent affects the molecule is through a simple inductive effect, the effect on the boron to which the substituent in bonded being much larger than that on any other atom. If the transfer of charge about the structural framework of the molecule is taken as a measure of the existence of resonance, a view that can, for instance, be taken in benzene, then one must draw the conclusion that resonance plays a minor role in the bonding of this molecule.

Table V. Effect of Substituents on Net Charge Densities in 1,6-$C_2B_4H_6$[a]

Substituent[b]	Cl	F	CH_3
C(1)	−0.005	−0.033	−0.013
C(6)	−0.005	−0.033	−0.015
B(2)	0.105	0.272	0.044
B(3)	−0.001	−0.034	−0.006
B(4)	0.005	0.004	−0.002
B(5)	0.001	0.034	0.006
H (Cl)	0.011	0.010	0.000
H (C6)	0.011	0.010	0.000
H (B3)	0.011	0.013	0.001
H (B4)	0.009	0.006	−0.001
H (B5)	0.011	0.013	0.001

[a] All charge densities are listed as shifts relative to the charge densities in 1,6-$C_2B_4H_6$ given in Table IV. The substituent is bonded to B(2). [b] B–Cl is taken as 1.83, B–F as 1.33, and C–B as 1.63 Å. The CH_3 group is taken as tetrahedral with a C–H distance of 1.10 Å and one methyl hydrogen is taken as parallel to the C–C axis of the molecule. All other geometric parameters are as in 1,6-$C_2B_4H_6$.

The second conclusion is that the substituent acts to relieve the positive charges on the carbons which are in a pentavalent situation in this molecule. This effect is one mechanism through which additional stability could be achieved.

V. Conclusions

Whenever theoretical molecular orbital calculations are performed on large chemical systems, one must always face a compromise between expensive, rigorous calculations or less expensive, less accurate techniques. Each has its role. The more accurate SCF LCAO MO calculations furnish more reliable molecular wave functions, but the semiempirical methods such as CNDO/2 lend themselves to repeated use for optimizing structures, estimating relative energies, etc. From our work the CNDO/2 method does seem accurate enough to predict rough trends in relative stabilities, charge densities, and accurate structures of carboranes.

Although the compounds are sometimes thought of as possessing "aromaticity," there is little evidence to this effect.

Bonding does occur in an intricate fashion, but this is no reason to believe that aromatic resonance effects are present. Substituents may stabilize some carboranes because they relieve the electron deficiency on the carborane.

Also, the shortcomings of this technique should be reemphasized. As we have previously remarked, it is essential for valid comparison that the structures be optimized to the lowest total molecular energies before comparisons are made. This is particularly true when comparisons are being made between known and unknown compounds.

Certainly, small differences in numbers should not be believed, although the gross trends would appear valid.

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Thermodynamics of Proton Ionization in Dilute Aqueous Solution. XIII. $\Delta G°$ (pK), $\Delta H°$, and $\Delta S°$ Values for Proton Ionization from Several Methyl- and Ethyl-Substituted Aliphatic Carboxylic Acids at 10, 25, and 40°[1a]

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Contribution from the Departments of Chemical Engineering and Chemistry, and Contribution No. 2 from the Center for Thermochemical Studies, Brigham Young University, Provo, Utah 84601. *Received December 16, 1969*

Abstract: A calorimetric study has been made of proton ionization in dilute aqueous solution from aliphatic carboxylic acids at 10, 25, and 40° (13 acids) and at 25° (3 acids). Values of $\Delta S°$ are calculated by combining the resulting $\Delta H°$ values with $\Delta G°$ values obtained from the literature or determined from potentiometric or calorimetric measurements. The trends in $\Delta G°$, $\Delta H°$, and $\Delta S°$ are described by an electrostatic model, and deviations from this model are taken as a measure of nonelectrostatic substituent effects for carboxylic acids.

This study was undertaken as part[2] of a program to determine the thermodynamic quantities associated with proton ionization from a variety of donor atom types in aqueous solution. Previously, the effects of polar substituents (Cl, Br, etc.)[3] and of a protonated amino group[4] on the magnitudes of the thermodynamic quantities for proton ionization from the –COOH group were reported. The present study provides an extension of these investigations to include methyl and ethyl substituents.

Experimental Section

Materials. The following compounds were obtained in the best grade available from the indicated sources: Baker, Baker grade 2,2-dimethylpropanoic acid, 2-methylpropanoic acid, 2-methylpentanoic acid, 3-methylpentanoic acid, 2-methylpentanoic acid, hexanoic acid; Eastman, White Label octanoic acid; Eastman, practical 2-ethylbutanoic acid, 3-methylbutanoic acid; Aldrich Chemical Corp., heptanoic acid, pentanoic acid, 2-propylpentanoic acid; Chemical Procurement, Inc., 2,2-dimethylbutanoic acid.

All acids were fractionally distilled under reduced pressure. They were then treated with slightly less than a stoichiometric amount of sodium hydroxide (Baker, Analyzed Reagent, carbonate free, 50% solution). The resultant solutions of the salts were washed with benzene and ether, the water was slowly evaporated, and ethanol was added until the solutions became slightly turbid. Following precipitation and separation from the cooled solutions, the salts were recrystallized twice from an alcohol–water solution and dried under vacuum. Standardized solutions of perchloric acid (Baker and Adamson) or imidazole (Eastman) were used as titrants in both the potentiometric and calorimetric determinations.

Procedure. The titration calorimeter used in this study has been described.[5,6] This calorimeter makes possible the measurement of heats of 1–10 cal with a precision of 0.1% or 0.02 cal, whichever is greater. Solutions of the sodium salts of the methyl- and ethyl-substituted carboxylic acids were titrated with perchloric acid solutions at 10, 25, and 40°. At least five calorimetric titrations were made for each acid with ionic strength, $\mu < 0.02$.

The pK values were either taken from the literature or determined using (1) a potentiometric titration method[7] or (2) in the case of 2,2-dimethylbutanoic acid, a calorimetric titration procedure[6,8] using an imidazole solution as titrant.[9,10]

Calculations. The general method used to calculate ΔH values from the thermometric titration data has been described.[6,8,11] Values for the heats of dilution of $HClO_4$ were determined calorimetrically at 10, 25, and 40°. Values for the heat of ionization of water at 10 and 40° were determined by us[12] to be 14.216 and 12.62 kcal/mol, respectively, and that at 25°, 13.335 kcal/mol, was taken from the literature.[13] At the low ionic strength ($\mu < 0.02$) used in the calorimetric determinations, ΔH values do not vary significantly with μ;[3] therefore, they were assumed to be equal to $\Delta H°$ values. The standard state to which $\Delta H°$ refers is defined to be an ideal 1 *M* solution behaving as an infinitely dilute solution. The calculations were aided by a P. E. Liberscope L-3055 computer.

Results

In Table I are presented the pK, $\Delta G°$, $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ values determined in this study together with

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(1) (a) Presented in part at the Northwest Regional Meeting of the American Chemical Society, Salt Lake City, Utah, June 12–13, 1969. Supported by U. S. Public Health Service Grant No. RG09430-08 from the National Institutes of Health. (b) Supported by Public Health Service Research Career Development Award No. 1-K3-GM-24, 361-02. (c) Supported by Public Health Service Research Career Development Award No. 1-K3-GM-35,250-02. (d) Deceased.

(2) Part XI: J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc., A*, 1212 (1969).

(3) J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Amer. Chem. Soc.*, **89**, 213 (1967).

(4) J. J. Christensen, J. L. Oscarson, and R. M. Izatt, *ibid.*, **90**, 5949 (1968).

(5) J. J. Christensen, R. M. Izatt, and L. D. Hansen, *Rev. Sci. Instrum.*, **36**, 779 (1965).

(6) L. D. Hansen, Ph.D. Dissertation, Brigham Young University, Provo, Utah, 1965; *cf. Diss. Abstr.*, **26**, 65-14556 (1965).

(7) L. D. Hansen, J. A. Partridge, R. M. Izatt, and J. J. Christensen, *Inorg. Chem.*, **5**, 569 (1966).

(8) J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. A. Partridge, *J. Phys. Chem.*, **70**, 2003 (1966).

(9) J. J. Christensen, D. P. Wrathall, J. O. Oscarson, and R. M. Izatt, *Anal. Chem.*, **40**, 1713 (1968).

(10) J. J. Christensen, D. P. Wrathall, and R. M. Izatt, *ibid.*, **40**, 175 (1968).

(11) J. J. Christensen and R. M. Izatt, *J. Phys. Chem.*, **66**, 1030 (1962).

(12) Unpublished data, this laboratory.

(13) J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, **67**, 2605 (1963).