1979, *101*, 6142].

(25) The reversible reduction potentials of TCNE and $IrCl_6^{2-}$ in acetonitrile are 0.46 and 0.67 V vs. SHE, respectively.[10b,12] For TCNE, $\Delta G = \mathcal{F}(E^\circ_{RM} - 0.46) + w_p$; for $IrCl_6^{2-}$, $\Delta G = \mathcal{F}(E^\circ_{RM} - 0.67) + w_p$ where $E^\circ_{RM} + w_p/\mathcal{F}$ is obtained from Table VIII. The work term is assumed to be the same.

(26) The reorganization energy $\lambda = (\lambda_{11} + \lambda_{22})/2$, where λ_{11} is related to the self-exchange reaction of $RM/RM^{+\cdot}$ and λ_{22} to that of $FeL_3^{3+,2+}$, $TCNE/TCNE^{-\cdot}$, or $IrCl_6^{2-,3-}$.[1] When λ_{22} for FeL_3^{3+} is taken as zero,[1c] the corrected reorganization energy is $\lambda = 41 + \lambda_{22}/2$. The solid line for $\Delta G^{\ddagger}$ is recalculated from eq 12 using λ_{22}(TCNE) and $\lambda_{22}(IrCl_6^{2-})$ of 8.3 and 26 kcal mol^{-1}, respectively.

(27) Equation 12, originally derived for the region of weak overlap, has been applied to reactions with considerable resonance splitting such as inner-sphere electron transfers, proton transfers, and atom transfers in which the meanings of the terms are modified.[28]

(28) (a) Sutin, N. *Annu. Rev. Phys. Chem.* **1966,** *17*, 154. (b) Haim, A.; Sutin, N. *J. Am. Chem. Soc.* **1966,** *88*, 434. (c) Patel, R. C.; Endicott, J. F. *Ibid.* **1968,** *90*, 6364. (d) Linck, R. G. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1971**, *9*, 303. (e) Fan, F. F.; Gould, E. S. *Inorg. Chem.* **1974,** *13*, 2647. (f) Linck, R. G. *Surv. Prog. Chem.* **1976,** *7*, 89. (g) Durham, B.; Endicott, J. F.; Wong, C. L.; Rillema, D. P. *J. Am. Chem. Soc.* **1979,** *101*, 847. (h) Kresge, A. J. In "Proton Transfer Reactions", Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975; p 179 ff.

(29) (a) The importance of the work term has been noted in outer-sphere cross reactions with ions of opposite charges [Haim, A.; Sutin, N. *Inorg. Chem.* **1976,** *15*, 476]. (b) Steric effects may also affect the reorganization energies but are not included in this qualitative discussion (however, see Figure 9).

(30) Foster, R. In ref 10a, Vol. 2, p 107.

(31) Tamres, M.; Strong, R. L. In "Molecular Association", Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2.

(32) Importantly, the comparative definition of ΔE in eq 17 minimizes solvation terms by cancellation. Thus it can be used directly for the work term in the free-energy change for inner-sphere electron transfer. (In contrast, the *absolute* value of the interaction energy ω in the vertically excited CT state differs from the work term w_p in thermal ion pairs since the latter includes a significant contribution from solvation, whereas ω does not.)

(33) Excluding vibronic states, the principal difference between these ion pairs lies in the mean separation parameters, $r^{\ddagger}$ and r_{DA}, for the thermal and photochemical processes, respectively. [For potential-energy diagrams illustrating the relationship between the thermal ($r^{\ddagger}$) and photochemical (r_{DA}) processes in CT interactions, see ref 17.] Thus, it is implicit in this treatment that as a result of steric effects the *relative change* of the mean separation in the CT excited state is the same as that in the thermal ion pair.

(34) The Brønsted slope $\alpha = 1$ corresponds to a slope of 9.4 in the plot of log k vs. I_D, since $I_D = 1.8\Delta G +$ constant (ref 12).

(35) It is remarkable that ΔE obtained for TCNE can be applied to $IrCl_6^{2-}$. The selectivities in Table III suggest that the ion pairs are similar, which may account for its success.

(36) Marcus, R. A. *J. Phys. Chem.* **1968,** *72*, 891.

(37) Since the microscopic reverse represents a diffusion-controlled electron transfer, in qualitative terms eq 20 and 22 can be related to the Hammond postulate for endothermic processes.

(38) In order to present the inner-sphere slope (*b*) for TCNE and $IrCl_6^{2-}$ in Figure 9, C in eq 20 was taken as -11.6 kcal mol^{-1}, which is the difference between $\Delta G^{\ddagger} = 21.6$ kcal mol^{-1} and $\Delta G = 33.2$ kcal mol^{-1} for Me_4Sn and TCNE, respectively, since $\Delta G^{\ddagger}$ cannot be smaller than ΔG. For Me_4Sn and $IrCl_6^{2-}$, the difference is 7.6 kcal mol^{-1} (i.e., $\Delta G^{\ddagger} - \Delta G = 20.8 - 28.4$). In computing curve (*b*), λ was taken as 20 kcal mol^{-1}. After the Brønsted slope of eq 12 exceeded unity, eq 22 was used. (See comments by Scandola and Balzani.[24c]) Compare also Efrima, S.; Bixon, M. *Chem. Phys.* **1976,** *13*, 447.

(39) Since the outer-sphere work term for FeL_3^{3+} in eq 20 is taken to be nil,[1c] ΔG in Figure 3 is relabeled as ΔG° here.

(40) The value of Δw_p chosen is a minimum value corresponding roughly to C in eq 20.[36] The actual difference between the outer-sphere and inner-sphere correlations in Figure 9 will be larger, i.e., the latter will be shifted to the right. Although it can be larger, the actual value of Δw_p will not affect the general discussion in Figure 9 relating to the shift from the outer-sphere correlation to the inner-sphere correlations in curves (*a*) and (*b*) by changing the magnitudes of w_p and λ_{RM}.

(41) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.*, accepted for publication.

Isomers of *closo*-Dicarbapentaborane(5) and Their Methyl and Fluoro Derivatives. A Theoretical Study

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Abstract: Relative energies have been calculated using the partial retention of diatomic differential overlap (PRDDO), STO-3G, and 4-31G methods for $(CH)_2(BH)_3$, $(CH)_2(BH)_2BCH_3$, and $(CH)_2(BF)_3$ in the isomeric 1,5-trigonal bipyramidal (I), 1,2-planar (II), 1,2-trigonal bipyramidal (III), 2,3-square planar (IV), 1,3-planar (V), and 2,3-trigonal bipyramidal (VI) geometries, optimized at the PRDDO level. The 1,5-TBP form is considerably more stable than the other structures for $C_2B_3H_5$ and for $(CH)_2(BH)_2BCH_3$, although the 1,2-planar isomer is almost as stable as the 1,5-TBP for $(CH)_2(BF)_3$. The planar, "classical" forms are comparable in energies to the 1,2-TBP and the other nonclassical isomers of $C_2B_3H_5$ and $(CH)_2(BH)_2BCH_3$. Localized molecular orbitals are examined, and some isomerization pathways are discussed among these isomers.

The term "superaromatic" has been used[2a] to characterize the relative unreactivity, stability, and symmetrical bonding patterns in the *closo*-carboranes $C_2B_{n-2}H_n$ and their isoelectronic dianions $B_nH_n^{2-}$. These polyhedral species undergo isomerizations which are still under active study.[2b,3] For $n = 5$ only the 1,5-trigonal bipyramidal $C_2B_3H_5$ has been isolated,[4] although C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$, 3,4,5-$(CH_3)_3$-1,2-$C_2B_3H_2$, C,3,4,5-$(CH_3)_4$-1,2-C_2B_3H, and C′,3,4,5-$(CH_3)_4$-1,2-C_2B_3H have also been obtained.[5] One question which we study here is whether there is some special thermodynamic stability or lack of reactivity associated with methylation. These observations and questions will lead us to reexamine the nonclassical three center bond structures relative to the classical structures having formally trigonal boron atoms in the smallest known, probably most anomalous member of the *closo*-carboranes. Furthermore, we shall find that methyl substitution for H does not confer unusual stability, but that fluorine substitution does drastically favor "classical" structures. The question of energy wells high above the most stable isomer of $C_2B_3H_5$ will arise for trigonal-bipyramidal 1,2-$C_2B_3H_5$. Finally, numerous plausible (but not all possible) isomerization pathways will be examined.

Some limited theoretical aspects of the complex structural chemistry of this system have been discussed previously.[6-10] Our preliminary results[11] have introduced the concept of the classical to nonclassical to classical conversion in isomerization of carboranes and boron hydride anions, and have indicated circumstances in which halogen substitution might favor "classical" structures. Examples of the halogen effect previously known are B_2H_6 vs. BF_3 or B_2F_4, of *nido*-$C_4B_2H_6$[12] vs. planar $(CH)_4(BF)_2$,[13] of $B_8H_8^{2-}$ vs. B_8Cl_8, and of nonexistent B_4H_4 vs. known B_4Cl_4.

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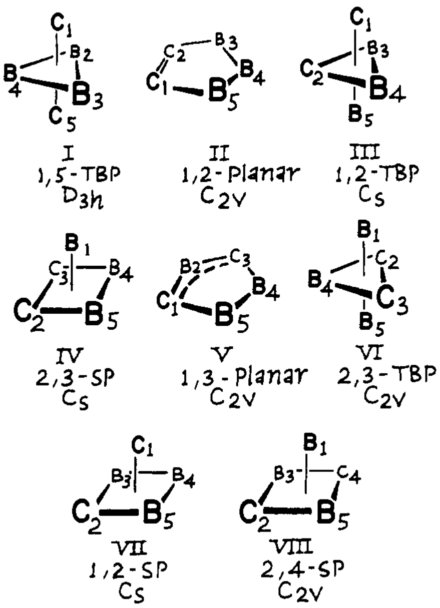


Figure 1. Structures and framework atom numbering schemes for the $C_2B_3H_5$ isomers. Hydrogen atoms have been omitted for clarity.

Computational Methods

Calculations on all of the reported structures were performed by the method of the partial retention of diatomic differential overlap (PRDDO)[14,15] using the Pople exponent set for all atoms.[16,17] PRDDO is an efficient nonempirical molecular orbital method designed to approximate an ab initio minimum basis set calculation. The geometries of the parent carborane structures I-VI (see Figure 1) were optimized at the PRDDO level by the cyclic variation of all parameters (except C-H and B-H distances), consistent with the overall symmetry of the molecular point group indicated in the figure, until convergence was achieved. The C-H and B-H bond lengths were held constant at standard values of 2.061 and 2.249 au, respectively. Partial optimizations of the square-pyramid (SP) structures VII and VIII were also performed. Ab initio calculations employing the PRDDO-determined geometries were then carried out for structures I-VI at the minimal basis STO-3G[17,18] and at the extended basis 4-31G[19] levels using the program GAUSSIAN 70.[20]

The configurations of all of the possible mono-*B*-methyl derivatives of carborane isomers I-VI were computed by optimization of the PRDDO energy upon variation of the methyl-group position about the appropriate previously optimized $C_2B_3H_4$ skeleton. A tetrahedral methyl group with a C-H bond length of 2.059 au was assumed. STO-3G calculations were then performed on the optimized methyl derivative structures.

The geometries of the per-*B*-fluoro ($C_2H_2B_3F_3$) derivatives of compounds I-VI were constructed by replacing the hydrogens bonded to boron in the PRDDO optimized structures by fluorine atoms directed along the former B-H bond vectors but held at a standard B-F distance of 2.494 au. No ab initio calculations were performed on the $C_2H_2B_3F_3$ isomers, but test calculations on selected mono-*B*-fluoro systems by the PRDDO and STO-3G methods yielded estimates of the energy change upon fluorination that were of comparable magnitudes. For example, the energy defined as $(E_{\mathrm{IIF}} - E_{\mathrm{IF}}) - (E_{\mathrm{IIH}} - E_{\mathrm{IH}})$ is −19.1 kcal/mol for PRDDO and −12.2 kcal/mol for STO-3G, where E_{IIF} refers to the energy of the planar 4-F-1,2-$C_2B_3H_4$, E_{IF} to the B-fluorinated 1,5-TBP, and E_{IIH} and E_{IH} to unfluorinated II and I. For the trigonal-bipyramidal 5-F-1,2-$C_2B_3H_4$ the energy $(E_{\mathrm{IIIF}} - E_{\mathrm{IF}}) - (E_{\mathrm{IIIH}} - E_{\mathrm{IH}})$ is 7.8 kcal/mol for PRDDO and 8.6 kcal/mol for STO-3G.

Table I. Relative PRDDO, STO-3G, and 4-31G Energies of the $C_2B_3H_5$ Isomers

	isomer	PRDDO	STO-3G	4-31G
		rel energies[a,b]		
(I)	1,5-TBP	0.0	0.0	0.0
(II)	1,2-planar	+48.3	+67.1	+37.2
(III)	1,2-TBP	+53.9	+56.7	+49.8
(IV)	2,3-SP	+69.8	+76.3	+61.7
(V)	1,3-planar	+73.0	+92.2	+56.3
(VI)	2,3-TBP	+83.9	+86.6	+80.5

[a] Energies in kcal/mol. [b] The relative energies are the total electronic energies for each isomer minus the total energy of the 1,5-TBP isomer. Total energies for structure I are −152.5656, −150.8402 and −152.4375 au at the PRDDO, STO-3G, and 4-31G levels, respectively.

Table II. Selected Structural Parameters of the Optimized Geometries of the $C_2B_3H_5$ Isomers

		bond lengths[a]		angles[b,c]	
(I)	1,5-TBP	r(C-B)	2.878	∠CBC	89.57
		r(B-B)	3.538		
(II)	1,2-planar	r(C=C)	2.542	∠CCB	113.85
		r(C-B)	2.889	∠CBB	105.15
		r(B-B)	3.139	∠BBB	102.00
(III)	1,2-TBP	r(C-C)	2.953		
		r(C1-B3)	2.807		
		r(C2-B3)	3.515		
		r(C2-B5)	2.769		
		r(B3-B4)	3.541		
		r(B3-B5)	3.161		
(IV)	2,3-SP	r(C-C)	2.807		
		r(C-B1)	3.117		
		r(C2-B4)	2.710		
		r(B1-B4)	3.137		
		r(B4-B5)	3.809		
(V)	1,3-planar	r(C-C)	4.674	∠BCB	108.50
		r(C-B2)	2.844	∠CBC	110.52
		r(C-B4)	2.867	∠BBC	106.25
		r(B4-B5)	3.070		
(VI)	2,3-TBP	r(C-C)	3.222		
		r(C-B1)	2.863		
		r(C-B4)	3.319		
		r(B1-B4)	3.061		

[a] Bond lengths in au. [b] Angles in degrees. [c] Angles are omitted for the nonclassical isomers, for which the number of distinct bond angles between the framework atoms is large.

Localized molecular orbitals (LMOs) for all of the examined structures were found by transforming the PRDDO canonical molecular orbitals so that the sum of the LMO centroid distances from an arbitrary molecular origin was maximized according to the criterion of Boys.[21,22]

Parent Carboranes $C_2B_3H_5$

The energies of the $C_2B_3H_5$ isomers are reported in Table I and the optimized structural parameters are collected in Table II. The agreement among the energies calculated by the PRDDO, STO-3G, and 4-31G methods is only moderately good. For example, inversions of the energy ordering occur for structures II and III and for structures V and VI at the STO-3G level and for compounds IV and V at the 4-31G level relative to PRDDO. For the three lowest energy isomers of greatest interest in this study, PRDDO fortuitously approximates more closely the 4-31G than the STO-3G results.

Our findings are in good agreement with other theoretical and experimental work in the few cases where direct and detailed comparisons are possible. Fitzpatrick and Fanning,[8] in the only ab initio study to date reporting energy differences between two $C_2B_3H_5$ isomers, find the 1,2-TBP structure (III) 61 kcal/mol higher in energy than the 1,5-TBP (I), based on optimized geometries and energies at the STO-3G levels. This

Table III. Comparison of the Theoretical and Experimental Bond Lengths[a] of 1,5-TBP $C_2B_3H_5$ (1)

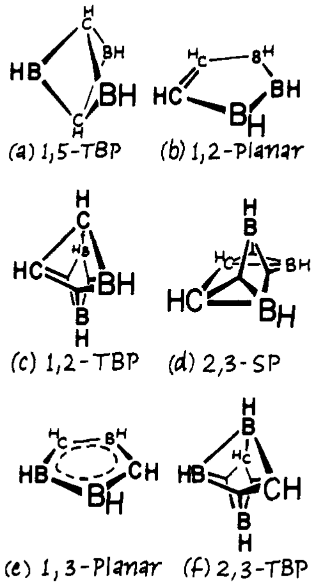
bond	PRDDO	STO-3G[b]	exptl[c]
C-B	1.523	1.537	1.556
B-B	1.872	1.871	1.853

[a] Bond lengths in ångstroms. [b] References 8. [c] Reference 23.

is close to our STO-3G energy gap between these structures of 57 kcal/mol. Experimental structural parameters are available for the 1,5-TBP isomer only from a gas-phase electron-diffraction study.[23] The PRDDO values for the B-C and B-B bond lengths (Table III) closely match both the experimental and STO-3G results for this molecule. Thus, PRDDO is shown to be an appropriate and accurate method for the determination of the molecular structures of the $C_2B_3H_5$ isomers and similar compounds.

Single-atom properties and bond properties are obtained from an analysis of the optimal PRDDO wave function. Valencies, degrees of bonding, and atomic charges are calculated according to the method of Armstrong, Perkins, and Stewart.[24] These charges seem more chemically reasonable than those derived from a standard Mulliken analysis,[25] although the qualitative trends are very similar. The concept of group charge, the sum of the charge of each framework carbon or boron atom and its terminally bonded hydrogen, or other atom, has been previously introduced to provide a measure of the electronic environment about each heavy-atom site, and to serve as one index of susceptibility to electrophilic or nucleophilic attack.[9] Our calculated group charges are in accord with the empirical observation that the carbon sites tend to be positively charged in most known carboranes.[2b]

The 1,5-TPB structure (I) is the only known unsubstituted $C_2B_3H_5$ isomer and is readily produced in electron-discharge reactions of boron hydrides with acetylenes, along with other small carboranes.[4,26,27] As shown in Table I, all of the computational methods employed in this study indicate that I is considerably more stable than the other structures considered. The bonding in this 1,5-TBP isomer is unusual for a carborane possessing a polyhedral geometry, in that a localization of the molecular wave function yields what appears to be a classically bonded network of purely two-center linkages, with carbon and boron assuming close to the expected sp^3 and sp^2 hybridizations, respectively (see Figure 2a). Accordingly, this is the only molecule among the structures I-VI for which the group charges follow normal electronegativity trends and place negative charge at the carbon sites. This charge distribution, unusual for carboranes, has been observed in prior theoretical studies.[8,9] The chemical studies that have been performed on the 1,5-TBP indicate that the boron atoms are the reactive sites, subject to chlorination by Cl_2 to give $C_2B_3H_4Cl$ with a B-Cl bond,[28,29] substitution of a methyl group for a B-bonded hydrogen atom using $B(CH_3)_3$,[29] and dimerization through boron with the loss of a molecule of hydrogen.[28] The adduct $C_2B_3H_5{\cdot}N(CH_3)_3$ is also known,[28] but the C_2B_3 unit is probably not closo as was assumed earlier,[28] but nido: this molecule is isoelectronic with $B_5H_8^-$. These examples suggest that the effects of any charge differences existing between boron and carbon atoms in the carborane are superseded by the presence of largely vacant orbitals on boron. The excess orbital on boron also gives rise to a small but significant degree of boron-boron bonding interaction, as shown by a B-B bond order of 0.252 and a bond length of 3.538 au, far shorter than normal nonbonding distances in carboranes and well within the range of reported B-B bond lengths. These weaker interactions have led to a description of such bonding as being "semiclassical" in nature,[30] intermediate between classical and nonclassical. The short C-B bonds, and the interactions between the coplanar boron atoms, help to explain the stability of the 1,5-TBP relative to other $C_2B_3H_5$ isomers, its existence in monomeric form, and its highly compressed structure, with a calculated CBC angle of 89.57° (the experimental value is 93.16°[23]).



(a) 1,5-TBP (b) 1,2-Planar (c) 1,2-TBP (d) 2,3-SP (e) 1,3-Planar (f) 2,3-TBP

Figure 2. Representations of the Boys localized molecular orbitals for the $C_2B_3H_5$ isomers.

The relative energies of the 1,2-planar (II) and 1,2-TBP (III) geometries are not given unequivocally by the methods used in this study. Surprisingly, although PRDDO and STO-3G predict opposite energetic orderings for these two isomers, the more accurate 4-31G calculation yields a not insignificant 12.6 kcal/mol energy difference between II and III, with the classical II found to be more stable. However, an unambiguous interpretation of these results is complicated by the fact that, from studies of the dimerization of borane[31] and of BeH_2,[32] and of the structures of the $C_2H_3^+$ and $C_2H_5^+$ ions,[33] it has been observed that electron correlation effects not accounted for in this study tend to stabilize molecules exhibiting three-center bonding more than those with only classical bonds. Thus, while the extended basis 4-31G calculation prefers the planar isomer, more elaborate calculations including configuration interaction would likely reduce the energy spacing between II and III, perhaps reversing the ordering.

Neither the 1,2-planar or 1,2-TBP $C_2B_3H_5$ has been detected experimentally. Their absence from the products of electrical discharge reactions that produce the 1,5-TBP and other small carboranes causes one to suspect that they may be reactive or unstable species. However, the methods of product analysis typically used in studies of small carborane formation are frequently those incapable of distinguishing among different isomeric forms, such as mass spectroscopy.[34] No concerted experimental effort has been mounted to detect and isolate possible isomers of $C_2B_3H_5$. The hydroboration of propyne by 1,5-$C_2B_3H_5$ to yield 1,5-$C_2B_3H_4C_3H_5$ has been described,[28] and intramolecular hydroboration has been suggested in the acetylene-pentaborane(9) reaction.[35] Clearly, detailed mechanistic studies are needed. Two dimethyl derivatives of $C_2B_3H_5$ have been observed, one corresponding to a methylated I and a second that, on the basis of NMR[3] and chemical-derivative evidence,[4,5] has been assigned as a substituted 1,2-TBP (III) structure. However, the cause of the enhanced stability of the methylated compounds is unclear, although it may be related to a reduced tendency for hydroboration and other reactions. Our further discussion will suggest that there is little thermodynamic stability due to methylation in these compounds. A concrete result is that classical structures such as II, previously not considered to be energetically feasible for molecules such as the boron hydrides and carboranes, are demonstrated to be potentially of great importance as intermediates in the rearrangements and reactions of nonclassical molecules, if not as ground-state structures.[11]

The bonding in II is purely classical in nature. Only two-center single bonds and a carbon-carbon double bond exist; the nonbonded interactions of the sort found in I are absent. All of the heavy atoms exhibit approximately sp^2 hybridization, and there is little charge separation. The unexpected stability of this geometry may be explained by the delocalization of electrons in the π bond between carbon atoms to partially populate (0.129 electron at B3) the p orbitals perpendicular to the molecular plane. The corresponding $p_\perp$ orbital of the unique boron atom, however, remains essentially vacant (0.031 electron at B4) and would be a likely site for chemical reactivity.

Although, as noted above, 1,2-planar $C_2B_3H_5$ has yet to be isolated as such, the structure does exist both as a monometallic complex[36] and as the central ring of a triple-decker sandwich complex[36-39] with transition metals. The metals probably stabilize the planar carborane by donating electrons to populate the near-vacant boron $p_\perp$ orbitals. X-ray structures[40] of the sandwich complexes reveal short carbon-carbon distances indicative of a bond order substantially greater than unity. The 1,2-planar atomic array also occurs as the equatorial plane of the *closo*-carborane 2,3-$C_2B_5H_7$.[2b]

Analysis of the wave function computed for the 1,2-TBP (III) reveals it to be a clearly nonclassical molecule employing all carbon and boron valence orbitals to a significant extent. Extrapolating from the known structures of other carboranes, one would expect the polyhedral III to be preferred over the planar II, but several unusual features of the bonding of the 1,2-TBP may contribute to its relative instability. Compared to the classical 1,2-planar isomer there is considerable separation of charge, placing excess positive charge on C2 and negative charge on B5. Fractional bonds do exist between most of the atom pairs, although the carbon-carbon interaction, that was close to a full double bond in II, is less than a full single bond in III. The weakening of this energetically important bond may help to destabilize III relative to II. However, we remind the reader that correlation corrections may tend to favor III more than II. The LMOs of III, drawn in Figure 2c, reveal an unusual mixture of two-center bonds (those involving C1) and three-center bonds (those involving B5) among the first-row atoms. The two-center C-C and C-B bonds occur between traditional sp^3-hybridized centers. The three-center BBB bond incorporates between sp^2 and sp^3 orbitals from each of the boron atoms and has a nearly symmetric electronic population from each center. The C2-B3-B5 and C2-B4-B5 bonds are atypical in that, while orbitals hybridized between sp^2 and sp^3 are contributed by the carbon and equatorial boron atoms, axial boron orbital has greater p character ($sp^{4.2}$). Nevertheless, the electronic population in the bond from each atomic center, with 0.96, 0.66, and 0.37 electron from C2, B5, and B4, respectively, is not what would be predicted for an open three-center bond centered at B5, for which a one electron contribution from B5 and a one-half electron contribution from C2 and B3 would be expected.[41] This asymmetric three-center linkage is unusual, and the overall localized bonding in III might well be described as half classical and half nonclassical in nature.

The next less stable $C_2B_3H_5$ isomer after III at the 4-31G level is the 1,3-planar structure (V), lower in energy than the 2,3-SP (IV) by 5.4 kcal/mol. This energy ordering is reversed in the PRDDO and STO-3G calculations. This molecule represents another possible geometry employing a classical bonding scheme for $C_2B_3H_5$, and, like the 1,2-planar structure (II), it is seen to be energetically comparable with or preferred to other polyhedral bonding schemes such as IV or VI. Thus, it is of potential importance as an intermediate in the reactions of carboranes. The heavy-atom framework of V is connected by five two-center B-C or B-B bonds formed from hybrid orbitals with somewhat greater s character than the idealized sp^2 mixing (Figure 2e). There also exists an additional π-bonding MO, which, even after localization, contains significant contributions from all five of the ring atoms. This LMO is comprised almost exclusively of the carbon and boron atomic p orbitals perpendicular to the ring. These p orbitals are populated by 0.527 electron for C1 and C3, 0.500 electron for B2, and 0.223 electron for B4 and B5. Hence, no nearly vacant atomic orbitals exist in this structure. The double bond of II is no longer present in V, but the compensating effect of the partial population of all p orbitals leaves V proximal in energy to II. The highest occupied molecular orbital (HOMO) at −8.3 eV is higher in energy in V than in the other $C_2B_3H_5$ isomers, and the lowest unoccupied molecular orbital (LUMO) is exceptionally low in energy, only +1.67 eV; therefore, V might be expected to be a highly reactive molecule. While the parent compound V has yet to be reported, 1,3-planar $C_2B_3H_5$ does occur as the central ring in "triple-decker sandwich" transition-metal complexes such as $(C_5H_5)Co(C_2B_3H_5)Co(C_5H_5)$, where it is pentacoordinated by π orbitals to both metal atoms.[36-39] The delocalized π electrons and small HOMO-LUMO gap, both noted above, make V a strong π-bonding ligand, especially where complexation with two transition-metal atoms may serve to complete the population of the partial vacancies in those p orbitals that are perpendicular to the ring. The structural unit V also occurs as a coplanar fragment in the carborane 2,4-$C_2B_5H_7$.[2b,3]

Table IV. Relative PRDDO, STO-3G, and 4-31G/STO-3G Energies of the Mono-*B*-methyl Derivatives of the $C_2B_3H_5$ Isomers

isomer	site of methylation	rel energies[a] PRDDO[b]	STO-3G[b]	4-31G/STO-3G[c]
(I) 1,5-TBP		0.0	0.0	0.0
(II) 1,2-planar	B3	+46.1	+67.3	+37.4
	B4	+45.9	+67.1	+37.2
(III) 1,2-TBP	B3	+54.6	+57.5	+50.6
	B5	+56.3	+59.3	+52.4
(IV) 2,3-SP	B1	+73.3	+78.8	+64.2
	B4	+68.4	+75.9	+61.3
(V) 1,3-planar	B2	+73.9	+94.5	+58.6
	B4	+71.4	+92.8	+56.9
(VI) 2,3-TBP	B1	+88.1	+88.6	+82.5
	B4	+88.8	+89.9	+83.8

[a] Energies in kcal/mol. [b] Total energies for each isomer minus the total PRDDO or STO-3G energy for the B-CH_3-1,5-TBP isomer of −191.5732 and −189.4345 au, respectively. [c] The relative energies of the unsubstituted carboranes at the 4-31G level plus the difference in STO-3G energies between the methylated and parent compounds.

Structure IV is the only one of the three possible square-pyramidal (SP) geometries IV, VII, and VIII found to be energetically comparable to the other planar or polyhedral isomers, perhaps because this is the only SP structure that preserves a strong carbon-carbon interaction. The LMOs for the 2,3-SP, illustrated in Figure 2d, reveal a largely nonclassical bonding array, consisting of a strong C-C bond and two-center C-B bonds with the basal boron atoms and three three-center bonds involving the apical boron. The BBB bond is symmetrically populated by two-thirds electron from each B atom, although the contributing atomic orbital of the apical boron has greater p character. The BCB bond involves greater contributions from the apical boron and, especially, from the carbon atom than from the basal boron. Moroever, the hybridized orbital of carbon in this bond has very high p character. These bonds therefore appear to be closer to the idealized open three-center bond rather than the closed. All atomic orbitals are occupied to a significant extent in this structure.

The localized structure for the 2,3-TBP (VI) (Figure 2f) is surprising in that no two-center C-C bond exists. The low C-C bond order of 0.506 in VI may explain the preference for the 1,2-TBP structure. The LMOs do not possess the full symmetry of the molecular point group. One of the axial boron atoms forms two-center bonds to the equatorial atoms while the other axial boron is involved in three-center bonding to the equatorial plane. This half classical, half nonclassical array of bonds also occurs in the LMOs of III. The three-center BCB bonds are also similar to those found in III, in the sense that the carbon atom contributes more to the electronic population of the bond, while the boron hybrid orbital has greater p character. This pattern also occurs in the CBC bond in VI.

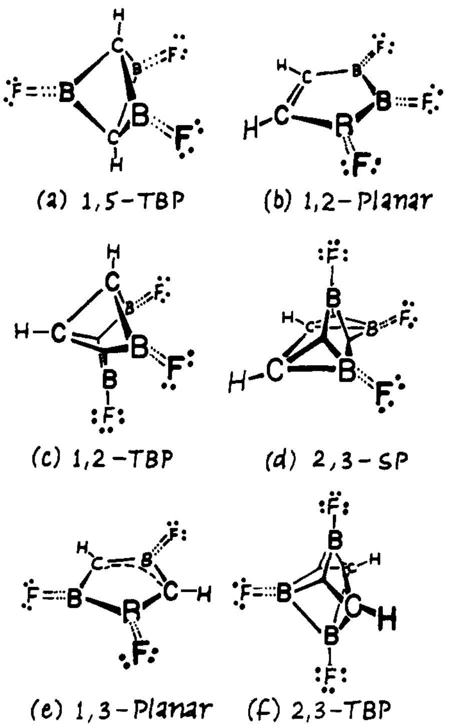
Although our preliminary calculations revealed that the 1,2-SP (VII) is energetically unfavorable relative to the other isomers studied, this structure is greatly stabilized by the addition of bridging hydrogens between the basal boron atoms (B3-B4 and B4-B5), yielding the stable carborane 1,2-$C_2B_3H_7$.[42,43]

B-Methyl Derivatives of $C_2B_3H_5$

The PRDDO and STO-3G energies for the monomethyl derivatives of $C_2B_3H_5$, in which the methyl group replaces a terminal hydrogen atom attached to boron, are collected in Table IV. For structures II-VI two symmetry-distinct B atoms exist. Calculations have therefore been performed for both possible isomers. The column labeled 4-31G/STO-3G contains our best estimate of the relative energies of the methyl derivatives, obtained by correcting the 4-31G relative energies of I-VI for the parent $C_2B_3H_5$ molecules by adding to them the change in energy upon methylation at the STO-3G level, found by calculating the difference between the STO-3G relative energies for the substituted and unsubstituted compounds.

A comparison of Tables I and IV shows that only very small energetic changes are introduced by methylation. The largest changes in relative stability are only about 5.0 kcal/mol at either the PRDDO or STO-3G levels and many of the shifts are negligible. Surprisingly, methylation almost always increases the energy separations between I and the other isomers II-VI. Only the B4-methylated 2,3-SP(IV) is stabilized relative to the 4-31G energy of the unsubstituted carboranes. The gross electronic structures of the methylated carboranes are also very similar to those of the parent compounds, as almost no changes are detected in the LMOs of the corresponding methylated and unmethylated isomers. In general, methylation tends to shift the group charges of the framework boron atoms to more positive values, especially for the boron directly bonded to the methyl group. The carbon atom group charges become more negative, in some cases changing from an overall positive to a negative charge. For example, the group charges of the CH, BH, and BCH_3 moieties of the 1,5-TBP are −0.195, +0.109, and +0.172 electron, respectively, in contrast to the parent compound, which has CH and BH group charges of −0.046 and +0.031 electron. It appears that, while a local shift of,charge from boron to carbon in a B-CH_3 bond occurs, the BCH_3 group as a whole does donate some additional electron to the carbon atoms of the polyhedral framework.

It was previously noted that, although both PRDDO and 4-31G calculations predict structure II to be more stable than III for unsubstituted $C_2B_3H_5$, a second carborane isomer other than the 1,5-TBP has been detected only in dimethylated form, for which strong experimental evidence[3,27] exists supporting the structural assignment of a 1,2-TBP geometry methylated both at carbon and at B3. Both thermodyanmic[23] and kinetic[21] effects have been postulated to explain the existence of this isomer only in methylated form. Our results show that mono-B-methylation appears to destabilize slightly the 1,2-TBP (III) as compared to both the 1,5-TBP (I) and 1,2-planar (II) geometries. Thus, only a very small electronic effect exists, and we are left with kinetic stability arguments and reactivity as possible explanations of the experimental facts.


(a) 1,5-TBP (b) 1,2-Planar

(c) 1,2-TBP (d) 2,3-SP

(e) 1,3-Planar (f) 2,3-TBP

Figure 3. Representations of the Boys localized molecular orbitals for the *B*-fluoro-$C_2H_2B_3F_3$ isomers.

Methylation also fails to stabilize the classical structures to any appreciable extent, but it does increase slightly the partially vacant $p_\perp$ orbital population. Hence, only slight increases in π-electron donation to B atoms are detected. Also, structure I undergoes a small increase in back-donation to the polyhedral framework at the site of methylation, effectively nullifying any decrease in relative energies. While small stabilizing effects are calculated by PRDDO for B3- or B4-methyl II and for B4-methyl V, STO-3G predicts small increases in relative energy for all of the classical isomers.

B-Fluoro Derivatives of $C_2B_3H_5$

The relative ineffectiveness of a methyl group in donating negative charge to the electron-deficient polyhedra and in populating the vacant p orbitals of the classical structures led us to perform PRDDO calculations on carboranes I-VI for which B-H bonds have been replaced by B-F bonds. It has long been postulated, based on qualitative theoretical reasoning, that the B-X bonds in boron halides possess "partial double bond character" in which halogen lone pair electrons are donated to the boron atom and partially populate otherwise vacant p orbitals.[44] More recently, highly polarized BF double and triple bonds have been reported in the localizations of ab initio and PRDDO wave functions for boron halides such as BF, BF_3, BH_2F, and B_4F_4.[45,46] As is expected for LMOs generated by the Boys criterion, the multiple bonds appear as pairs or triads of identical bent τ bonds, a description of bonding essentially equivalent to σ,π multiple bond LMOs. As may be seen from an examination of the LMO structures for $C_2H_2B_3F_3$ depicted in Figure 3, all of these geometries yield at least one polarized B:::=F bond, which we draw using the notation of ref 46.

Multiple bonds of this type play an important role in determining the relative stabilities of these isomers. The energetic ordering of the $C_2H_2B_3F_3$ isomers (Table V) is significantly different from those found for the parent or methylated car-

Table V. PRDDO Estimates of the Relative Energies of the *B*-Fluoro Isomers $C_2H_2B_3F_3$

isomer		rel energy[a,b]	ΔE[c]
(I)	1,5-TBP	0.0	0.0
(II)	1,2-planar	+1.8	−46.5
(III)	1,2-TBP	+71.4	+17.5
(IV)	2,3-SP	+79.0	+9.3
(V)	1,3-planar	+45.5	−27.5
(VI)	2,3-TBP	+124.4	+38.6

[a] Relative energies in kcal/mol. [b] Total PRDDO energy for I is −447.9128 au. [c] The difference between the $C_2H_2B_3F_3$ and $C_2B_3H_5$ relative energies for each isomer.

boranes. The 1,2-planar isomer (II) is now only 1.8 kcal/mol higher in energy than I. Even though PRDDO had tended to overestimate the stability of II when compared to the STO-3G or 4-31G calculations, it is clear that the clsssical *B*-fluoro 1,2-planar isomer is energetically competitive with the 1,5-TBP (I). In addition, the 1,3-planar isomer (V) is now clearly more stable than either III or IV. These results are in accord with experimental[13] and theoretical[11] work on other carborane systems, where B-fluorination has been shown to favor planar or classical geometries.

From the differences between the relative energies of the $C_2H_2B_3F_3$ and $C_2B_3H_5$ structures listed in Table V, it is seen that all of the classical structures are stabilized and nonclassical structures destabilized relative to I. It seems most likely that fluorination stabilized the classical structures II and V the most and the nonclassical isomers III, IV, and VI least, with the "semiclassical" I being stabilized to an intermediate extent. This pattern is borne out by the fluorine valencies and bond orders, greater for BF than for BH, and by the LMO networks (Figure 3). Using an arbitrary criterion that considers an atomic center involved in a localized bond if it contributes at least 0.2 electron to the LMO, we see that the classical II and V and the semiclassical I all possess three polarized B:::=F bonds, while III and IV have only two B:::=F linkages. The 2,3-TBP isomer, which exhibits the greatest increase in relative energy upon fluorination, retains only a single B:::=F bond. This ordering corresponds to that expected from a comparison of the B-F bond orders among the different structures.

The B:::=F bonds are far from full classical double bonds, as indicated by the low bond orders, ranging between 1.204 and 1.342, and by low fluorine valencies. The LMOs for the B-F τ bonds are unsymmetrically populated: about 1.6 electrons of the two-electron bond are donated by the fluorine atom. They also involve unusually large contributions from atomic p orbitals, especially on fluorine. The small atomic charges on fluorine, far smaller than the electronegativity differences between B and F would lead one to expect, underscore the donor-receptor nature of the B:::=F bond. Electronic charge is donated from boron to fluorine in a σ-type bond and is back-donated from fluorine to boron via interactions principally involving atomic p orbitals. By this mechanism, the boron $p_\perp$ orbitals of the planar structures are effectively populated, considerably more than in the methylated and unsubstituted carboranes.

Nevertheless, the bonding among the framework carbon and boron atoms in the B-fluorinated $C_2H_2B_3F_3$ isomers is very similar to the patterns found for the parent compounds. In general, the boron orbitals involved in two- or three-center framework bonding in the fluorinated derivatives have a somewhat higher percentage of s character, which compensates for the greater p character in the terminal B-F bonds, although the 2,3-TBP structure (VI) is an exception to this rule. The atomic centers involved in each localized bond and the fractional contribution of each center to the population of each LMO are very nearly the same in the fluorinated and unfluorinated molecules (Figures 2 and 3). Only one significant difference exists in the framework LMO structures. The five-center π orbital of the unfluorinated 1,3-planar isomer becomes truncated to a three-center CBC π bond in the fluorinated V, reflecting the higher $p_\perp$ population at B4 and B5. The group charges for the *B*-fluoro structures indicate that carbon atoms on fluorinated structures I-IV bear negative charges, while only the carbons of I for (unfluorinated) $C_2B_3H_5$ had negative group charges. Thus, B-fluorination places more negative charge on carbon atoms, normally more electronegative than boron atoms, and also gives rise to somewhat more saturated valencies. In these senses, the bonding in these *B*-fluoro compounds is slightly more "classical" than it is in the corresponding nonfluorinated members of this series.

Interconversions of the Isomers of $C_2B_3H_5$

The method of linear synchronous transits[47] has been employed in a preliminary study of some of the reaction pathways among isomers of $C_2B_3H_5$. The isomerizations of V to I, VIII to I, IV to II, IV to III, and VII to III occur without barriers. Only isomers I, II, III, and possibly VI lie in stable or metastable local energy minima, the other structures being optimal only with respect to molecular deformations preserving the overall molecular symmetry. Extensive orthogonal optimizations[47] on the pathway from III to II reduced the barrier from 70 to 25 kcal/mol. No low-barrier process was found for transformation of either II or III to I. However, further studies are needed to clarify these pathways. We expect that correlation corrections will stabilize I and III relative to II, and hence a low barrier for conversion of II to III may eventually be found to account for the absence of II from the experimental literature. The clearest predictions so far, then, are that compound III, trigonal-bipyramidal 1,2-$C_2B_3H_5$, should be found, and that the observed methyl derivatives of III are not significantly more stable than the parent 1,2-$C_2B_3H_5$ with respect to rearrangements. Hence, attention may therefore be given to other aspects of the chemistry of formation or further reaction of 1,2-$C_2B_3H_5$ in order to explain its absence, while its methylated derivatives are observed.

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Supplementary Material Available: Tables of the calculated boron and carbon single atom and bond properties in the $C_2B_3H_5$ isomers, the percent of delocalization of the $C_2B_3H_5$ LMOs, the $p_\perp$ orbital populations for the substituted and unsubstituted classical isomers, and of the fluorine and the carbon and boron atom environments and properties of the *B*-fluoro $C_2H_2B_3F_3$ isomers (Tables VI-XI) (6 pages). Ordering information is given on any current masthead page.

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Electronegativities of the Elements from Simple Xα Theory

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Abstract: Electronegativities are calculated by a simple Xα method for the elements up to atomic number 54, employing a transition-state method devised for the purpose. Electron affinities also are determined.

I. Method

One might expect to find it in the literature, but we cannot: It is elementary to calculate electronegativities of the elements by the spin-independent Xα theory, and the values of electronegativities so obtained agree with values obtained by other means.

Electronegativity, χ, is, in the first instance, a quantitative property of an atom (or molecule), the negative of the slope of the ground-state electronic energy as a function of the number of electrons. This is the negative of the chemical potential, μ, of the density functional theory of Hohenberg and Kohn.[1,2]

$$\chi = -\mu = -(\partial E/\partial N)_v \qquad (1)$$

Equivalently, it is the corresponding quantity in the first-order density-matrix functional theory that derives from Hohenberg-Kohn theory.[3]

From the point of view of conventional wave function theory, the determination of an electronegativity of a system of interest must be carried out by determination of the energy from the principle $\delta[\langle\psi|H|\psi\rangle - E\langle\psi|\psi\rangle] = 0$, for the system and two or more of its positive and/or negative ions. Numerical differentiation of the resultant E vs. N data then gives μ. In principle there is no objection to this procedure, but its computational difficulty and lack of physical perspicuity have meant that it has never been fully implemented.

Density functional theory provides a more attractive route to the electronegativity. The reason is twofold. First, the variational principle in the theory contains the electronegativity: $\delta[E[\rho] - \mu N[\rho]] = 0$. Secondly, the theory allows for the number of particles to be varied continuously, so that the differentiation in eq 1 can be carried out explicitly. While nonintegral numbers of electrons do not occur in nature, the concept of nonintegral populations of electrons on atoms in molecules long has been generally accepted as valid and useful in chemistry. It is natural in density functional theory.

In the present paper we present results of systematic calculations of electronegativities of atoms by a known density-functional technique: the spin nonpolarized Xα transition-state method.[4,5] This method entails the self-consistent solution of

$$\left[-\frac{1}{2}\nabla_1^2 + V_{\text{eff}}\right]\phi_i(1) = \epsilon_i\phi_i(1) \qquad (2)$$

where

$$V_{\text{eff}} = -\frac{Z}{r_1} + \int \frac{\rho(2)}{r_{12}}\,\mathrm{d}\tau_2 - 3\alpha\left(\frac{3}{8\pi}\right)^{1/3}\rho^{1/3} \qquad (3)$$

and

$$\rho(1) = \sum_i n_i|\phi_i(1)|^2 \qquad (4)$$

The ground-state energy is then determined from

$$E[\rho] = \sum_i n_i\epsilon_i - J[\rho] + K_{\text{X}\alpha}[\rho] \qquad (5)$$

Differentiation of eq 5 by the occupation number n_i yields[4,5]

$$(\partial E/\partial n_i)_{n_j} = \epsilon_i \qquad (6)$$

This formula is the key formula for our application.

In the simple Xα model just outlined, for an ordinary atom or ion, orbitals contain integral numbers of electrons, and E

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