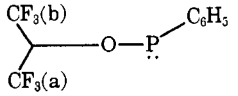
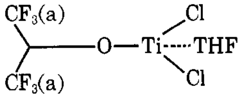
peaks) of equal area centered at ϕ values of (a) 65.4 and (b) 66.8. Coupling with phosphorus was apparent. The pmr spectrum had τ values centered at 2.65 and 2.24. Ir (cm^{-1}): 1590–1440 (w–m) (C_6H_5), 1300–1200 (vs), (C–F), 1160 (sh), 1100 (s), 1075 (vs), 1035 (w), 1005 (ms), 975 (sh), 950 (vs), 885 (s), 810 (s), 775 (ms), 755 (s), 715 (vs), 710 (w, sh), 695 (ms). The pertinent mass spectral peaks are $C_4F_5^+$ (>100), $C_6H_5^+$ (100), CF_2^+ (70), $C_6H_4P^+$ (61), CF_3^+ (69), $C_6H_5PF^+$ (57), $C_{12}F_{11}H_5PO_2^+$ (55), $C_6H_5P^+$ (28), PO^+ (15), $C_{11}F_9PO_2^+$ (6), $C_{12}F_{12}H_2PO_2^+$ (3), and $C_{12}F_{12}H_5PO_2^+$ (1). This substance was assigned the conformation



VIII

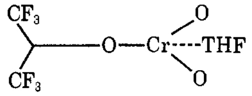
2,2-Dichloro-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxatitanolane Tetrahydrofuranate, $[(CF_3)_2CO]_2TiCl_2\cdot THF$ (IX).—Thirty grams (0.0867 mol) of I and 50 ml of dried CCl_4 were placed in a 125-ml flask in the drybox. A slurry formed which was magnetically stirred with vigor as 16.4 g (0.0867 mol) of $TiCl_4$ was added dropwise over a 15-min period. Then all solids had dissolved. Five minutes later a white precipitate formed with the evolution of heat. Two hours later the mixture was filtered yielding 6.5 g of LiCl solid and a light yellow filtrate which was stripped of CCl_4 leaving a pale yellow crystalline solid. The yellow solid was recrystallized from hot CCl_4 and was recovered as almost colorless needle-shaped crystals which melted between 70.5 and 72.5°. They amounted to 28.2 g or a yield of not less than 72%. *Anal.* Calcd for $C_{10}F_{12}TiO_3Cl_2H_8$: C, 16.60; H, 1.53; F, 43.59; Ti, 9.18. Found: C, 17.16; H, 1.40; F, 41.94; Ti, 9.14. The ^{19}F nmr spectrum was a sharp singlet at a ϕ value of 67.6. The pmr spectrum of a sample dissolved in CCl_4 was two multiplets whose τ values were not shifted on addition of several drops of pure THF. Ir (cm^{-1}) in KBr: 1540 (w), 1500–1190 (s, br), 1150 (m), 1110 (s), 1035 (w), 895 (ms), 955 (w), 930 (ms), 880 (ms), 830 (ms), 770 (s), 750 (s), 730 (ms), 720 (s), 705 (s).

The heaviest positive ion observed in the mass spectrum was 345 (mol wt 523 with THF, 451 unsolvated). Excluding most Cl and Ti isotopic effects the pertinent fragments are CF_3^+ (100), $C_4H_8O^+$ (85), $C_4H_7O^+$ (79), CF_3CO^+ (60), $TiCl_2^+$ (30), $TiCl^+$ (16), Ti^+ (12 + 12), CF_2^+ (12), Cl^+ (12), CO^+ (9), and $C_6F_{11}TiO^+$ (7). This substance is assigned the conformation shown above.



IX

2,2-Dioxo-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxachromatolene Tetrahydrofuranate, $[(CF_3)_2CO]_2CrO_2\cdot THF$ (X).—Twenty grams (0.0578 mol) of I was stirred in 100 ml of dried CCl_4 in a 250-ml flask in a drybox. Nine grams (0.0578 mol) of CrO_2Cl_2 dissolved in 15 ml of dried CCl_4 was added to the slurry dropwise over a 20-min period. The slurry dissolved and shortly thereafter an apparent white precipitate formed with the evolution of heat. As the mixture was stirred for 2 hr, it slowly turned dark green and more "white" solid formed. The mixture was vacuum stripped of CCl_4. The very dark, almost black, solid residue was extracted for 20 hr in a Soxhlet extractor with dry CCl_4. The residue was an off-white solid, mainly LiCl, and amounted to 3.4 g. The extract was very dark blue. The solvent was stripped away leaving a blue-black solid amounting to 22.8 g. This was recrystallized from boiling CCl_4 and dried *in vacuo*. This purified residue amounting to 17.4 g, a yield of at least 74%, melted between 152.0 and 152.5°. *Anal.* Calcd for $C_{10}F_{12}H_8CrO_5$: C, 24.59; H, 1.64, F, 46.72; Cr, 9.83. Found: C, 25.07; H, 1.65; F, 46.28; Cr, 9.58. The pmr spectrum was exactly the same as that observed for IX. The ^{19}F nmr spectrum consisted of a single paramagnetically broadened peak centered at a ϕ value of 62.7. Ir (cm^{-1}) (KBr pellet): broad weak peak centered at 1625, 1300–1175 (s) (C–F), 1070 (s), 1035 (w), 1020 (w), 980 (w), 940 (ms), 870 (ms), 760 (m), 750 (m), 735 (m), 715 (m), 700 (m). No fragment heavier than 223 (mol wt 488 or 416) was observed in the mass spectrum. The more prominent peaks are CF_3^+ (100), $C_4H_8O^+$ (90), $C_4H_7O^+$ (82), CO^+ (54), CF_3CO^+ (39), CF^+ (29), CF_3COCr^+ (25), CF_2^+ (12), $C_2F_3CrO_4^+$ (2), and $C_5F_5CrO^+$ (2). This substance is assigned the conformation



X

Acknowledgment.—The authors are indebted to Dr. W. S. Brey of our department and Professor R. E. Richards of Cambridge University, a visiting professor, for their helpful discussion pertinent to the ^{19}F nmr interpretations.

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Approximate Wave Functions for Carboranes Parametrized from Self-Consistent Field Model Calculations

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Molecular orbitals have been obtained by a nonempirical method for carboranes in the series $B_nC_2H_{n+2}$, using parameters from minimum basis set SCF calculations for $B_4C_2H_6$. Molecular energies, ionization potentials, charge distributions, and dipole moments have been calculated, and certain predictions made concerning *relative* reactivities of B atoms within each of these molecules.

In the past, the carboranes have been the subject of many theoretical studies utilizing molecular orbitals (MO) expressed as a linear combination of atomic orbitals (LCAO). Approximate wave functions have been calculated by both the extended Hückel method[2] and the nonempirical molecular orbital (NEMO)

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(1) NIH Predoctoral Fellow, 1967–1969.

(2) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962).

method,[3,4] in which matrix elements are transferred from self-consistent field (SCF) results on small related molecules. All 1s orbitals are included specifically, and overlap and kinetic energy integrals are calculated exactly.

SCF results have recently been reported for the two isomers of $B_4C_2H_6$.[5] These are the first SCF calculations to become available for a compound containing both B and C atoms. Here we use these results for the $B_4C_2H_6$ isomers as a model in the calculation of new NEMO wave functions for several other carboranes. We also discuss the accuracy to which the NEMO method is capable of reproducing the SCF results for these $B_4C_2H_6$ isomers. Of course, some sizable errors do arise in the NEMO results, but in spite of these errors the new wave functions show improvement over those from previous studies[6,7] in which parameters were taken from SCF results for boron hydrides[8,9] for B and from C_2H_6[8,10] for C.

Calculations

Calculations were performed using Newton, Boer, and Lipscomb's NEMO program[4] for the IBM 7094 computer. One isomer of each of the seven carboranes studied is shown in Figure 1, from which H atoms are omitted for the sake of clarity. The assumed molecular symmetries and coordinates for unique atoms are given in Table I. These geometries, several of which are newly available, were obtained from microwave spectroscopic studies for 1,5-$B_3C_2H_5$,[11] 1,2- and 1,6-$B_4C_2H_6$,[12] and 2,4-$B_5C_2H_7$.[13] The distorted icosahedra of the three $B_{10}C_2H_{12}$ isomers were constructed to have B–B and B–C bond lengths of 1.77 and 1.72 Å, respectively. These are average values from X-ray diffraction studies of four halogenated derivatives of the 1,2 isomer.[14,15] Coordinates for 1,7-$B_6C_2H_8$, 1,6-$B_7C_2H_9$, and 1,6-$B_8C_2H_{10}$ were taken from X-ray structures of their dimethyl derivatives[7] without imposing any additional molecular symmetry and are not shown in Table I. In all of the above molecules, H atoms were placed to give bond lengths of 1.196 Å for B–H and 1.102 Å for C–H.[16]

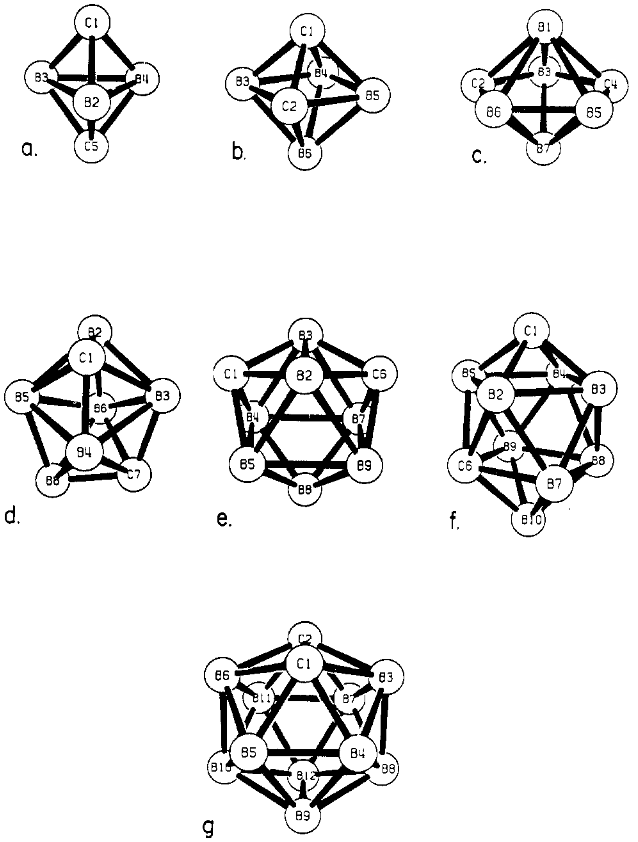

Figure 1.—Carborane geometries: (a) 1,5-$B_3C_2H_5$, (b) 1,2-$B_4C_2H_6$, (c) 2,4-$B_5C_2H_7$, (d) 1,7-$B_6C_2H_8$, (e) 1,6-$B_7C_2H_9$, (f) 1,6-$B_8C_2H_{10}$, (g) 1,2-$B_{10}C_2H_{12}$.

A fundamental assumption behind the NEMO method is the transferability of diagonal elements (α) of the F matrix between related molecules. In Table II we give values of α from the SCF model calculations[5] for the $B_4C_2H_6$ isomers, and we also include the exponents of the minimum Slater basis set for these SCF wave functions. It is encouraging to note that corresponding α's from the two isomers agree to within 0.03 au. Also, the two unique B atoms of the asymmetric 1,2 isomer are remarkably similar: their α's differ by less than 0.03 au. On the other hand, large anisotropies are observed in all 2p orbitals. For example, in symmetric 1,6-$B_4C_2H_6$, the 2p orbital on B perpendicular to the plane of the four B atoms ($2p_z$) has $\alpha = -0.511$ au, while the two 2p orbitals in the plane have α's of -0.171 and -0.185 au. A serious error in our method results from our present requirement that the same α be employed for the three 2p orbitals on each center. These α's are to be used to generate matrix elements for atoms in molecules of different geometry and are therefore required to be invariant under transformations among the 2p orbitals of the basis set. Methods for transferring anisotropic atoms or of allowing the local environment to generate anisotropy in these α's have not been introduced into our present programs.

The off-diagonal elements of the potential energy

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(10) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

(11) R. A. Beaudet, private communication, Sept 22, 1969. Only the B atoms were located in a study of 2-CH_3-1,5-$B_3C_2H_4$; the C atoms were placed to give a B–C bond distance of 1.58 Å.

(12) The geometries are those used in the SCF model calculations of ref 5, except for the inclusion of a revised geometry for the 1,6 isomer based upon a recent microwave study of 2-Cl-1,6-$B_4C_2H_5$.[11]

(13) R. A. Beaudet and R. L. Poynter, *J. Amer. Chem. Soc.*, **86**, 1258 (1964).

(14) (a) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1673 (1964); (b) *ibid.*, **5**, 1471, 1478, 1483 (1966).

(15) D. Voet and W. N. Lipscomb, *ibid.*, **3**, 1679 (1964).

(16) Sources for these distances are given in ref 7c.

TABLE I

COORDINATES OF UNIQUE ATOMS FOR CARBORANES (IN Å)

	Assumed symmetry[a]	Atom	x	y	z
1,5-$B_3C_2H_5$	D_{3h}	C1	0.0	0.0	1.159
		B2	1.074	0.0	0.0
		H1	0.0	0.0	2.261
		H2	2.270	0.0	0.0
1,2-$B_4C_2H_6$	C_{2v}	C1	0.770	0.0	0.760
		B3	0.0	1.218	0.0
		B4	0.876	0.0	−0.844
		H1	1.555	0.0	1.534
		H3	0.0	2.414	0.0
		H4	1.737	0.0	−1.674
1,6-$B_4C_2H_6$[b]	D_{4h}	C1	0.0	0.0	1.053
		B2	1.228	0.0	0.0
		H1	0.0	0.0	2.155
		H2	2.424	0.0	0.0
1,6-$B_4C_2H_6$[c]	D_{4h}	C1	0.0	0.0	1.026
		B2	1.195	0.0	0.0
		H1	0.0	0.0	2.128
		H2	2.391	0.0	0.0
2,4-$B_5C_2H_7$	C_{2v}	B1	1.154	0.0	0.135
		C2	0.0	−1.210	0.328
		B3	0.0	0.0	1.388
		B5	0.0	0.825	−1.120
		H1	2.342	0.0	0.273
		H2	0.0	−2.264	0.649
		H3	0.0	0.0	2.584
		H5	0.0	1.554	−2.069
1,2-$B_{10}C_2H_{12}$	C_{2v}	C1	0.0	0.833	−1.348
		B3	1.432	0.0	−0.885
		B4	0.885	1.432	0.0
		B8	1.432	0.0	0.885
		B9	0.0	0.885	1.432
		H1	0.0	1.412	−2.285
		H3	2.449	0.0	−1.514
		H4	1.514	2.449	0.0
		H8	2.449	0.0	1.514
		H9	0.0	1.514	2.449
1,7-$B_{10}C_2H_{12}$	C_{2v}	C1	0.0	1.348	−0.833
		B2	0.885	0.0	−1.432
		B4	−1.432	0.885	0.0
		B5	0.0	1.432	0.885
		B9	−0.885	0.0	1.432
		H1	0.0	2.285	−1.412
		H2	1.514	0.0	−2.449
		H4	−2.449	1.514	0.0
		H5	0.0	2.449	1.514
		H9	−1.514	0.0	2.449
1,12-$B_{10}C_2H_{12}$	D_{5d}	C1	0.0	0.0	1.584
		B2	1.506	0.0	0.753
		H1	0.0	0.0	2.686
		H2	2.576	0.0	1.288

[a] The symmetry axis is along z. [b] Geometry used in the SCF calculations in ref 5. [c] Revised geometry.

term in the NEMO Hamiltonian are obtained according to a modified Mulliken approximation[17]

$$U_{ij} = K_{ij}S_{ij}(U_{ii} + U_{jj})/2 \tag{1}$$

In Table III we give Mulliken coefficients K_{ij}, which have been calculated by substituting into eq 1 values of overlap and potential energy integrals, S_{ij} and U_{ij}, all taken from the SCF results for $B_4C_2H_6$.[5] Also shown are values of the zero-overlap parameter K^{ZO}. One-center 2s–2p elements, which correspond to a vanishing overlap integral, are evaluated as

TABLE II

EXPONENTS AND α's

Orbital[a]	Exponent	α, au 1,2-$B_4C_2H_6$	 1,6-$B_4C_2H_6$
(C−)H1s	1.160	−0.560	−0.543
(1B−)H1s	1.147	−0.445	
(2B−)H1s	1.147	−0.457	−0.459
C1s	5.680	−11.269	−11.241
C2s	1.730	−1.643	−1.619
C2p	1.760	−0.405	−0.378
1B1s	4.680	−7.551	
1B2s	1.443	−1.171	
1B2p	1.477	−0.261	
2B1s	4.680	−7.569	−7.573
2B2s	1.443	−1.195	−1.195
2B2p	1.477	−0.288	−0.289

[a] 1B and 2B denote B atoms bonded to one and two C atoms, respectively. In the 1,6 isomer, all four B atoms are equivalent.

TABLE III

MULLIKEN COEFFICIENTS

		1,2-$B_4C_2H_6$ 1B–1B[a]	1,6-$B_4C_2H_6$ B–C[b]	 B–B
One-center	K_{1s-2s}	0.66	0.66	0.66
Two-center	K_{1s-1s}	1.0[c]	1.0[c]	1.0[c]
	K_{1s-2s}	0.79	0.79	0.79
	K_{1s-2p}	0.80	0.80	0.80
	K_{1s-H}	0.81	0.83	0.81
	K_{2s-2s}	1.07	1.04	1.08
	K_{2s-2p}	1.11	1.07	1.12
	K_{2s-H}	1.02	1.04	1.02
	$K_{2p-2p,\sigma}$	1.10	1.06	1.14
	$K_{2p-2p,\pi}$	1.10	0.99	1.11
	K_{2p-H}	0.89	0.91	0.88
	K_{H-H}	0.96	0.99	0.95
Zero overlap	K^{ZO}	0.41	0.36	0.35

[a] For the interaction between B atoms bonded to one C. [b] Interactions involving H taken from C–H; one-center K_{1s-2s} and K^{ZO} taken from C. [c] Set at 1.0; the overlap is too small to obtain meaningful results from eq 1.

$$U_{2s-2p} = K^{ZO} \sum_k S_{2sk}S_{2pk}\alpha_k \tag{2}$$

where the summation runs over basis orbitals.[18] Table III gives three sets of K_{ij} and K^{ZO}, one from the asymmetric and two from the symmetric isomer. The agreement among them is quite good. In order to maintain consistency all of our NEMO calculations were performed using input parameters taken from the asymmetric isomer, with the exception of calculations on symmetric $B_4C_2H_6$ itself, in which we used α's and K's (B–C interaction) from that isomer.

One limitation of the NEMO method is its failure to give either total molecular energy or the energy of atomization directly. Here we have used the approximate relations for these energies in terms of eigenvalues obtained by Boer, Newton, and Lipscomb[19]

$$E_{tot} = (\sum \epsilon_i{}^m + \sum E_i{}^a)/2 \tag{3}$$

$$A = (\sum \epsilon_i{}^m - \sum \epsilon_i{}^a)/2 \tag{4}$$

Sums are taken over all electrons i, and ϵ_i and E_i are

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[17] R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949).

[18] For a more detailed discussion of eq 2, see ref 4.

[19] F. P. Boer, M. D. Newton, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2361 (1966).

TABLE IV

ENERGIES AND IONIZATION POTENTIALS (IN AU)

		$-{}^1/_2\Sigma_i\epsilon_i{}^m$	$-A$	$-E_{tot}$	T	$-IP$
1,2-$B_4C_2H_6$	I	60.871	1.363	177.601	178.005	0.364
	II	61.321	1.811	178.047	177.413	0.420
	III	61.463	1.953	178.189	178.187	0.423
1,6-$B_4C_2H_6$ (SCF geometry)	I	60.852	1.387	177.625	178.006	0.340
	II	61.139	1.629	177.865	178.018	0.444
	III	61.249	1.739	177.975	178.528	0.429
1,6-$B_4C_2H_6$ (revised geometry)	II	61.017	1.507	177.743	178.405	0.431
	III	61.126	1.616	177.852	178.769	0.413
1,5-$B_3C_2H_5$	II	52.740	1.792	153.030	152.826	0.459
	III	52.842	1.894	153.132	153.402	0.484
2,4-$B_5C_2H_7$	II	70.080	2.008	203.242	202.952	0.396
	III	70.227	2.155	203.389	203.728	0.392
1,7-$B_6C_2H_8$	II	78.693	0.059	228.291	228.161	0.384
	III	78.850	0.216	228.448	228.998	0.385
1,6-$B_7C_2H_9$	II	87.454	2.258	253.488	253.172	0.396
	III	87.617	2.421	253.651	254.079	0.401
1,6-$B_8C_2H_{10}$	II	96.159	2.401	278.629	278.234	0.399
	III	96.337	2.579	278.807	279.233	0.407
1,2-$B_{10}C_2H_{12}$	II	113.562	2.680	328.904	328.094	0.376
	III	113.755	2.873	329.097	329.240	0.382
1,7-$B_{10}C_2H_{12}$	II	113.589	2.707	328.931	328.296	0.375
	III	113.781	2.899	329.123	329.430	0.380
1,12-$B_{10}C_2H_{12}$	II	113.464	2.582	328.806	328.311	0.368
	III	113.654	2.772	328.996	329.435	0.372

molecular (m) or atomic (a) orbital eigenvalues and core (kinetic plus electron–nuclear attraction) energies, respectively. Atomic parameters were taken from Clementi's best single-ζ atoms.[20] The major assumption leading to eq 3 and 4 is that the internuclear repulsion cancels against half of the difference between molecular and atomic core energies. The SCF results for $B_4C_2H_6$[5] show that this cancellation holds within 0.05 au for both isomers.

Results

Results of our carborane LCAO–MO studies are outlined in Tables IV–VI. Energies are given in Table IV, net Mulliken atomic[21] and framework charges in Table V, and nonzero dipole moments, calculated according to Ruedenberg's origin-invariant method of partitioning,[22] in Table VI. Throughout, calculation I refers to the SCF results of ref 5, while calculation II is the NEMO method with one-center 2s–2p zero-overlap elements included. Calculation III neglects zero-overlap elements ($K^{ZO} = 0$) but is otherwise the same as calculation II.

A. $B_4C_2H_6$.—Until very recently, no experimentally determined geometry was available for 1,6-$B_4C_2H_6$. The SCF calculation[5] used an approximate geometry based upon average bond distances taken from the 1,2 isomer. In order to estimate the resulting errors, we have included here NEMO results for a new geometry determined by microwave spectroscopy.[12] For both calculations II and III, the charge distribution (Table V) obtained from the revised geometry for 1,6-$B_4C_2H_6$ is quite similar to that obtained from the geometry assumed for the SCF calculation. For example, the net Mulliken charges differ by only about 0.03 electron. The total energy (Table IV) increases by 0.12 au in going from the SCF to the revised geometry. This small change is in the opposite direction from that expected, but may be associated with the limitation to a minimum basis set. Hence, optimizations based upon our approximate NEMO total energies would probably be unreliable. However, our calculations do show that the SCF wave function for symmetric $B_4C_2H_6$ is not likely to be in serious error due to choice of geometry.

A detailed comparison (not shown) of NEMO and SCF eigenvalues for $B_4C_2H_6$ indicates differences of up to 0.14 au (symmetric isomer) or 0.19 au (asymmetric isomer) in the energies of corresponding MO's as well as some inversions in the order of eigenvalues which are similar in energy.[23] These changes produce sizable deviations between the SCF and NEMO methods in the molecular energies of Table IV. Similar differences were observed in B_4H_{10}, B_5H_9, and B_5H_{11},[9] although better agreement was obtained for the smaller boron hydrides BH_3 and B_2H_6.[19] Finally, we note that the NEMO results appear to satisfy the virial theorem almost as well as do those from the SCF calculations.

The Mulliken atomic charges (Table V) obtained by the NEMO method for $B_4C_2H_6$ do not agree well with those from the SCF method. The NEMO charge distribution is sensitive to the choice of K^{ZO}. As had previously been observed in boron hydrides,[19] the effect of including zero-overlap elements is to transfer charge out to the terminal H atoms. Framework charges (Table V) tend to show less dependence on K^{ZO} than do atomic charges and may be a more reliable index for comparison of nonequivalent B atoms in these systems. In asymmetric $B_4C_2H_6$, B4 (bonded to one C atom) is predicted to be more negative than B3 (bonded to two C's) in all three calculations. Turning to the calculated dipole moments for this isomer given in Table VI, we note that, as usual, the charge separation is exaggerated in the NEMO results as compared with the SCF results. The direction of the dipole is, however, the same in both methods.

The most important source of the differences between the NEMO and SCF results for both $B_4C_2H_6$ isomers is probably to be found in NEMO's failure to account for anisotropies in the 2p orbitals, as noted above. One other possible source of error may lie in the neglect of one-center 2p–2p zero-overlap elements. In the SCF Hamiltonian for the asymmetric isomer, these elements are as large as 0.16 au, or roughly the same size as the 2s–2p zero-overlap elements which are included in calculation II.

B. Other Carboranes.—It is difficult to judge our NEMO results for carboranes other than $B_4C_2H_6$, because there are so few experimentally measured quantities available for comparison. Among the energies and ionization potentials (Table IV), the extremely low energy of atomization calculated for 1,7-$B_6C_2H_8$ may be significant. From the calculated total energies for

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(20) (a) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963). (b) Sums of eigenvalues and core energies calculated using Clementi's exponents are ${}^1/_2\Sigma\epsilon_i{}^a(H) = -0.250$, ${}^1/_2\Sigma\epsilon_i{}^a(B) = -8.312$, ${}^1/_2\Sigma\epsilon_i{}^a(C) = -12.381$, ${}^1/_2\Sigma E_i{}^a(H) = -0.250$, ${}^1/_2\Sigma E_i{}^a(B) = -16.186$, and ${}^1/_2\Sigma E_i{}^a(C) = -25.241$ au.

(21) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(22) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

(23) In the case of the 1,6 isomer, these discussions and those which follow refer only to results based on the geometry assumed for the SCF calculation.

TABLE V

CHARGE DISTRIBUTIONS

		Net Mulliken charge			Framework charge[a]		
	Atom	I	II	III	I	II	III
1,2-$B_4C_2H_6$	C1	−0.08	0.25	−0.02	−0.01	0.13	0.07
	B3	0.09	0.31	−0.05	0.01	0.00	−0.01
	B4	0.08	0.21	−0.05	0.00	−0.13	−0.06
	H1	0.07	−0.11	0.09			
	H3	−0.07	−0.31	0.04			
	H4	−0.08	−0.34	−0.01			
1,6-$B_4C_2H_6$ (SCF geometry)	C1	−0.10	0.05	−0.13	−0.05	−0.05	−0.06
	B2	0.10	0.28	−0.04	0.03	0.02	0.03
	H1	0.05	−0.10	0.07			
	H2	−0.07	−0.25	0.07			
1,6-$B_4C_2H_6$ (revised geometry)	C1		0.05	−0.14		−0.09	−0.09
	B2		0.34	0.00		0.05	0.05
	H1		−0.14	0.05			
	H2		−0.29	0.05			
1,5-$B_3C_2H_5$	C1		−0.15	−0.30		−0.20	−0.18
	B2		0.40	0.03		0.14	0.12
	H1		−0.05	0.12			
	H2		−0.26	0.09			
2,4-$B_5C_2H_7$	B1		0.38	0.03		0.04	0.02
	C2		0.03	−0.18		−0.05	−0.09
	B3		0.45	0.09		0.12	0.11
	B5		0.25	0.02		−0.05	0.00
	(B–)H_{av}		−0.32	0.00			
	H2		−0.08	0.08			
1,7-$B_6C_2H_8$	C1		−0.02	−0.22		−0.09	−0.13
	B2		0.35	0.09		0.03	0.07
	B3		0.44	0.12		0.11	0.09
	B5		0.28	0.03		−0.05	−0.03
	H1		−0.07	0.09			
	(B–)H_{av}		−0.33	−0.03			
1,6-$B_7C_2H_9$	C1		0.02	−0.17		−0.03	−0.07
	B2		0.46	0.14		0.15	0.13
	B4		0.30	0.04		0.01	0.01
	B8		0.00	−0.15		−0.27	−0.17
	H1		−0.05	0.10			
	(B–)H_{av}		−0.29	−0.02			
1,6-$B_8C_2H_{10}$	C1		−0.02	−0.22		−0.08	−0.12
	B2		0.41	0.12		0.11	0.10
	B3		0.36	0.10		0.05	0.05
	C6		0.05	−0.14		0.03	−0.05
	B7		0.27	0.03		0.00	0.01
	B8		0.06	−0.12		−0.22	−0.16
	B10		0.27	0.02		−0.04	0.00
	(C–)H_{av}		−0.04	0.10			
	[B–)H_{av}		−0.29	−0.03			
1,2-$B_{10}C_2H_{12}$	C1		0.25	0.07		0.22	0.17
	B3		0.36	0.10		0.07	0.07
	B4		0.32	0.08		0.02	0.03
	B8		0.13	−0.08		−0.16	−0.14
	B9		0.12	−0.09		−0.17	−0.16
	H1		−0.03	0.09			
	(B–)H_{av}		−0.29	−0.05			
1,7-$B_{10}C_2H_{12}$	C1		0.06	−0.10		0.04	−0.01
	B2		0.38	0.12		0.09	0.10
	B4		0.32	0.08		0.02	0.03
	B5		0.31	0.07		0.01	0.02
	B9		0.10	−0.10		−0.19	−0.16
	H1		−0.02	0.09			
	(B–)H_{av}		−0.29	−0.05			
1,12-$B_{10}C_2H_{12}$	C1		0.04	−0.13		0.02	−0.05
	B2		0.29	0.06		0.00	0.01
	H1		−0.02	0.09			
	H2		−0.30	−0.05			

[a] Defined as the sum of the atomic charges for a B–H or C–H unit.

TABLE VI

DIPOLE MOMENTS (IN DEBYES)

		μ_{exptl}	$\mu_{\text{total}}{}^a$	$\mu_{\text{classical}}$	μ_{atomic}	μ_{bond}
1,2-$B_4C_2H_6$	I		2.95	1.15	1.49	0.32
	II		5.46	3.88	0.51	1.07
	III		4.50	1.77	1.79	0.94
2,4-$B_5C_2H_7$	II		2.18	1.49	0.30	0.39
	III		2.21	0.94	0.97	0.29
1,7-$B_6C_2H_8$	II		2.68	1.69	0.34	0.65
	III		2.42	0.60	1.27	0.56
1,6-$B_7C_2H_9$	II		5.05	4.23	0.29	0.53
	III		4.64	2.83	1.31	0.51
1,6-$B_8C_2H_{10}$	II		4.31	3.14	0.49	0.72
	III		4.46	2.22	1.64	0.61
1,2-$B_{10}C_2H_{12}$	II	4.31	11.47	9.90	0.66	0.91
	III		10.75	7.92	1.81	1.02
1,7-$B_{10}C_2H_{12}$	II	2.78	6.94	5.84	0.53	0.58
	III		6.58	4.67	1.22	0.69

[a] Calculated as $\int \psi \vec{r} \psi \, d\tau$.

$B_{10}C_2H_{12}$ we might predict the meta (or 1,7) isomer to be most stable, followed by the ortho (1,2) and para (1,12) isomers, in that order. However, these predictions are in contradiction with experiments, which show the para isomer to be comparable in stability to the meta isomer.[24] Thus, the total energies obtained from our NEMO results are clearly not accurate enough reliably to predict the small differences between isomers.

Some consistent trends do emerge from the atomic and framework charges of Table V. In each molecule, B atoms become more positive as the number of C atoms to which they are bonded increases. From this order of charges, which was also found in earlier NEMO studies,[7] we predict the most reactive B atoms in electrophilic substitution to be those furthest removed from C. Conversely, the B atoms bonded to two C's should be most susceptible to nucleophilic attack. These predictions agree with the observed positions of Friedel–Crafts bromination in 1,2-$B_{10}C_2H_{12}$[14b,25] and in 1,7-$B_{10}C_2H_{12}$.[26] On the other hand, our results show no generally valid relationship between the charges of four- and five-coordinated B's bonded to the same number of C atoms.[27] We have also calculated Mulliken overlap populations[21] (not shown) for all pairs of atoms in the molecules studied. Here we merely note that the extremely low overlap populations (0.10 in calculation II and 0.17 in calculation III) obtained for the B–B bond in 1,5-$B_3C_2H_5$, in addition to the long distance (1.86 Å),[11] indicate very weak bonding in the plane of the three B atoms in this molecule. When a more normal B–B distance of 1.74 Å was used, the B–B overlap populations increased only slightly to 0.11 and 0.20 in calculations II and III, respectively.

The dipole moments of Table VI are probably all about 2.5 times too large, as are those for 1,2- and 1,7-$B_{10}C_2H_{12}$, which have been measured experimentally.[28] In every case, the direction of the dipole makes the side of the molecule containing the C atoms positive. Although the total dipoles from calculations II and III agree to 10%, the partitioning into classical (point charge), atomic, and bond terms again illustrates the sensitivity of charge distributions to zero-overlap elements.

In conclusion, we look forward to future measurements of ionization potentials, energies of atomization, dipole moments, and reactivities for carboranes, with the hope that our MO results may prove useful in correlating this experimental information.

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