TABLE I

CHARACTERIZATION DATA OF THE PHOSPHINE SELENIDES

Compound	Yield, %	Mp, °C[a]	P=Se infrared band, cm^{-1} [9]	% C		% H		% Se	
				Calcd	Found[b]	Calcd	Found[b]	Calcd	Found[b]
$(p\text{-}CH_3C_6H_4)_3PSe$[c]	95	198–198.5[d]	544	65.80	65.56	5.52	5.45	20.60	20.81
$(m\text{-}CH_3C_6H_4)_3PSe$[c]	94	139–140	574	65.80	65.57	5.52	5.50	20.60	20.36
$(CH_3)_2NCH_2CH_2CH_2P(Se)(C_6H_5)_2$[c]	87	90–91	532	58.29	58.52	6.33	6.50	22.54	22.30
$(C_6H_5)_2P(Se)CH_2CH_2P(Se)(C_6H_5)_2$[e]	84	194–195	539	56.13	56.37	4.35	4.42	28.39	28.09
$(C_6H_5)_2P(Se)CH_2CH{=}CH_2$[c]	89	78–79	[f]	59.03	58.99	4.95	5.13	25.87	25.62

[a] Uncorrected melting point (generally the crude melting point) was only 1–3° lower than that of the pure compound. [b] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. [c] Recrystallized from absolute ethanol. [d] Lit. 193° [A. Michaelis, *Ann.*, **315**, 43 (1901)]. [e] Recrystallized from 1-butanol. [f] Indeterminate due to other strong absorptions.

was washed with 300 ml of distilled water to remove the potassium cyanide, then with 10 ml of cold absolute ethanol, and finally with anhydrous ethyl ether. The crude product, after drying for 12 hr over P_4O_{10} *in vacuo*, melted at 183–186° and weighed 16.4 g (yield 96%). Small white crystals of analytical purity were obtained after one recrystallization from absolute ethanol, mp 187–188° (lit. 184–186°,[6] 187–188°[7]). The P=Se stretching frequency was assigned at 562 cm^{-1} (Nujol mull) (lit.[8] 560 cm^{-1}).[9]

Anal. Calcd for $C_{18}H_{15}PSe$: C, 63.35; H, 4.43; Se, 23.11. Found: C, 63.36; H, 4.45; Se, 23.00.

Preparation of Other Arylphosphine Selenides.—Table I lists the characterization data of the phosphine selenides which were prepared by the above procedure.

Discussion

The reaction of arylphosphines and alkyl–arylphosphines with potassium selenocyanate rapidly provides solid phosphine selenides of high purity. For example, triphenylphosphine and *o*- and *m*-tolylphosphines give 94–96% yields of products which melt within 1–3° of the pure compound. The ease with which the reaction is accomplished and the product isolated, and the high purity of the resulting material, make this reaction particularly advantageous for preparations of selenide derivatives of solid phosphines.[10]

An important advantage of this synthesis is that the investigator handles solid, relatively nonodorous selenium compounds throughout. Three arylphosphine selenides and three aryl–alkylphosphine selenides were prepared readily by this reaction. No trialkylphosphines were employed because of the odor and handling problems associated with the low molecular weight liquid alkylphosphine selenides.

The reaction of potassium selenocyanate with triphenylarsine failed to produce triphenylarsine selenide; triphenylarsine was recovered nearly quantitatively. Although triphenylarsine selenide has been reported,[11] it was not characterized. Recently, Zingaro and Merijanian[12] failed to prepare $(C_6H_5)_3AsSe$ by the reported procedure, owing probably to the inherent instability of the compound.

One very interesting aspect of the reaction between tertiary phosphines and KSeCN is that the analogous reaction with KSCN[13] or KOCN does not yield tertiary phosphine sulfides or phosphine oxides, respectively. This difference in reactivity and the mechanism of the KSeCN reaction will be investigated further.

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(6) A. Michaelis and H. Soden, *Ann.*, **229**, 295 (1885).

(7) C. Screttas and A. F. Isbell, *J. Org. Chem.*, **27**, 2573 (1962).

(8) R. A. Zingaro, *Inorg. Chem.*, **2**, 192 (1963).

(9) The strong to very strong P=Se stretching frequencies were determined in Nujol mulls with a Beckman IR-9 high-resolution infrared spectrometer by comparing the spectrum of each compound with that of the parent phosphine.

(10) Phosphines which are oxidized by air must be protected with a nitrogen atmosphere during the initial phase of the synthesis.

(11) N. N. Mel'nikov and M. S. Rokitskaya, *J. Gen. Chem. USSR*, **8**, 834 (1938); *Chem. Abstr.*, **33**, 1267^5 (1939).

(12) R. A. Zingaro and A. Merijanian, *Inorg. Chem.*, **3**, 580 (1964).

(13) P. D. Bartlett and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 2513 (1958).

Correspondence

Energy States of the Tetrachloroplatinate(II) Ion[1]

Sir:

The polarized spectra of single K_2PtCl_4 crystals at 15°K in the visible and ultraviolet regions were recently reported from this laboratory.[2] In this work the locations of the band maxima were compared with energy states calculated by means of strong-field matrix elements for the d^8 configuration with square-planar geometry published earlier.[3] Perumareddi[4] recently called our attention to some errors among these matrix elements. Consequently, elements in the two tables of both the strong-field and weak-field matrices[3] have been redetermined and tested by the transformation matrices of the weak-field to strong-field basis functions. Corrections, which were found for the earlier paper, are included in the Appendix.

The energy levels for the square-planar d^8 system have now been recalculated with the revised set of matrix elements and the parameters of the previous

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1858.

(2) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **4**, 1682 (1965).

(3) R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *ibid.*, **1**, 441 (1962).

(4) J. R. Perumareddi, private communication.

TABLE I

OBSERVED BANDS (CM^{-1}) IN THE SPECTRUM OF K_2PtCl_4 CRYSTALS AT 15°K AND CALCULATED ENERGY LEVELS OF THE EXCITED STATES FOR ALTERNATIVES A AND B

	Calcd energies of states[2] and major singlet eigenvector component	Obsd absorption bands, K_2PtCl_4, 15°K (molar extinction coef in parentheses)		Calcd energies and major singlet eigenvector component	
		xy (⊥)	*z* (‖)	Alternative A	Alternative B
	46,268 $\Gamma_3(2)$, 0.84			>42,000	>41,000
	36,412 $\Gamma_5(4)$, 0.33				
	36,043 $\Gamma_4(2)$			35,278 $\Gamma_3(2)$, 0.95	
	29,203 $\Gamma_5(3)$, 0.91	29,200^{b} (37)	29,800^{b} (55)	29,592 $\Gamma_5(4)$, 0.81	29,929 $\Gamma_5(4)$, 0.88
					29,684 $\Gamma_3(2)$, 0.83
	26,332 $\Gamma_2(2)$, 0.96	26,300^{a} (28)		27,232 $\Gamma_4(2)$	26,736 $\Gamma_2(2)$, 0.93
				26,352 $\Gamma_2(2)$, 0.96	25,990 $\Gamma_4(2)$
		24,000^{a} (7)	24,100^{a} (3)	24,204 $\Gamma_5(3)$, 0.53	24,109 $\Gamma_5(3)$, 0.19
					23,676 $\Gamma_1(3)$, 0.29
	21,905 $\Gamma_1(3)$, 0.20				
	21,500 $\Gamma_5(2)$, 0.06				
				22,057 $\Gamma_1(3)$, 0.23	20,692 $\Gamma_3(1)$, 0.51
	21,318 $\Gamma_3(1)$, 0.12	20,900 (9)	20,600 (10)	20,783 $\Gamma_5(2)$, 0.28	19,621 $\Gamma_5(2)$, 0.37
	20,901 $\Gamma_4(1)$			19,565 $\Gamma_3(1)$, 0.23	18,152 $\Gamma_2(1)$, 0.34
	18,396 $\Gamma_5(1)$, 0.13		19,000	18,223 $\Gamma_4(1)$	17,440 $\Gamma_1(2)$, 0.05
	17,766 $\Gamma_2(1)$, 0.26	18,000 (2)	17,000 (<1)	16,836 $\Gamma_5(1)$, 0.12	16,797 $\Gamma_5(1)$, 0.08
	17,107 $\Gamma_1(2)$, 0.01			16,137 $\Gamma_2(1)$, 0.25	16,647 $\Gamma_4(1)$
				15,676 $\Gamma_1(2)$, 0.44	
	0 $\Gamma_1(1)$, 0.97			0 $\Gamma_1(1)$, 0.96	0 $\Gamma_1(1)$, 0.97
Parameters, cm^{-1}					
α	1,300			1,500	1,700
F_2	1,200			1,000	820
F_4	65			65	54
$\Delta_3(e_g)$	33,700			30,200	30,500
$\Delta_2(a_{1g})$	51,000			38,300	30,200
$\Delta_1(b_{2g})$	26,300			26,100	25,700

[a] Strong vibrational structure. [b] No detectable vibrational structure.

study for $PtCl_4^{2-}$. These calculated states are included in Table I. The observed band centers and intensities for 15°K from the earlier work[2] are also included in Table I. The symmetry representation in the Γ notation employed earlier[2,3] for each calculated energy state is included in Table I. This is the representation for the total wave function, involving both the orbital and spin parts.[3] Because spin–orbit coupling mixes singlet and triplet states, the spin-forbidden bands can be considered to gain intensity from the singlet character mixed into each state. Such intensity will come from the singlet ground state $^1(b_{1g}, b_{1g})$ in the Γ_1 states, and the one-electron-transfer states, *i.e.*, $^1(b_{1g}, b_{2g})$ in Γ_2, $^1(b_{1g}, a_{1g})$ in Γ_3, and $^1(b_{1g}, e_g)$ in Γ_5. The normalized eigenvector component for each of these states measures the contribution of these singlet states, and this quantity has been included after the representation for each of the calculated energy levels in Table I. The intensity of a transition should be strongly related to this number. Thus, transitions to Γ_4 states which do not include any one-electron-transition states should be very weak. However, intensity for all states is gained from the triplet character of the ground state and perhaps to a smaller degree from mixing of the two-electron states as well.

With the corrected matrix elements, the separation of the two Γ_1 states arising from $^3A_{2g}$ and ^3E_g under spin–orbit coupling is much smaller than was indicated before. Therefore, it is not possible to assign the transition at 24,000 cm^{-1} to a single Γ_1 state which has split away from other members of the "spin-forbidden" states below 21,500 cm^{-1}.

The vibronic model for $PtCl_4^{2-}$ requires that transitions to Γ_2 and Γ_4 states be polarized in the *x,y* direction, whereas transitions to Γ_1, Γ_3, and Γ_5 can occur with both *x,y* and *z* polarization. With its polarization and intensity, the band at 26,400 cm^{-1} unquestionably appears to be associated with a Γ_2 state, comprising primarily the $^1A_{2g}$. The intensity and the nature of the magnetic circular dichroism[5] associated with the band at 30,300 cm^{-1} of solutions imply that a Γ_5 (primarily, ^1E_g) state is associated with the absorption peak at 29,200 to 29,800 cm^{-1}.

To account for the band at 24,000 cm^{-1} as a d–d transition, it has been necessary to reduce Δ_2 considerably and thus bring the one-electron energy of the a_{1g} (d_{z^2}) orbital to a much lower value. Two possible alternatives, labeled A and B, are shown in Table I for which the electron–electron interaction parameters, F_2 and F_4, and the spin–orbit coupling parameters have been modified within reasonable limits, as indicated in Table I, to improve the fit between calculated energy levels and the observed bands. The correlation of the calcu-

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(5) D. S. Martin, Jr., J. G. Foss, M. E. McCarville, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **5**, 491 (1966).

lated states under these two alternatives with zero spin–orbit coupling states of the square-planar symmetry, D_{4h}, and the tetrahedral symmetry, T_d, of ligands is shown in Figure 1.

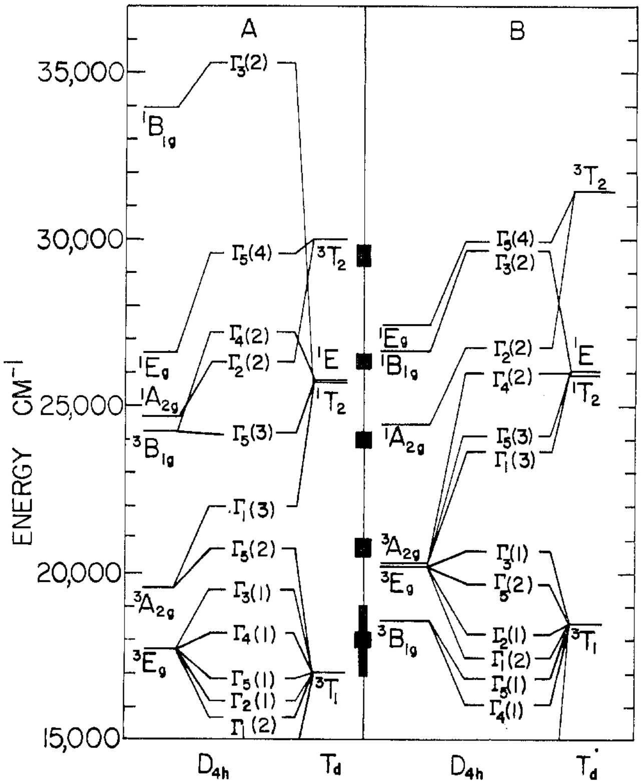

Figure 1.—Calculated energy levels for $PtCl_4^{2-}$ ion from the two alternative sets of parameters in Table I. Observed bands are indicated on the center line. The T_d states were calculated with the F_2 and F_4 values of the D_{4h} states and a Δ_t of 14,000 cm^{-1}.

Both alternatives place calculated transitions near the observed band centers of the single-crystal spectra which are indicated along the center line of Figure 1. In alternative A the transition at 24,000 cm^{-1} is assigned at $\Gamma_5(3)$ which arises from $^3B_{1g}$. The $\Gamma_3(2)$, consisting primarily of $^1B_{1g}$, falls at 35,300 cm^{-1}. It was not possible to change the parameters in order to raise this state and still obtain agreement with the other states. The crystal spectra indicate that such an additional primarily spin-allowed transition must lie no lower than 36,000 cm^{-1} which is on the edge of a charge-transfer band. A band has been observed at 36,500 cm^{-1} in a reflectance spectrum of K_2PtCl_4 crystals by Day, *et al.*[6] The calculation of 35,300 cm^{-1} is therefore in poor agreement with these observations. This alternative also places the $\Gamma_1(3)$ state with moderate singlet character at 22,000 cm^{-1} where no band can be observed. The high intensity of the absorption observed at 20,600–20,900 cm^{-1} does not appear to be consistent with the low singlet character of the states in comparison with the states at about 16,000 and 24,000 cm^{-1}. Also, the strong x,y polarization at 18,000 cm^{-1}, due to a Γ_4 state, and relative weak one at 15,700 cm^{-1}, due to a Γ_2 state with a relatively high singlet character, seem inconsistent. The Γ_2 state at 26,400 and Γ_4 at 27,200 cm^{-1} account for the strong, completely polarized band at 26,300 cm^{-1} although the transition to the Γ_4 may be very weak. Alternative B possesses the highest spin–orbit coupling parameters of the three transition schemes considered in Table I. The $\Gamma_3(2)$ state, primarily $^1B_{1g}$, is placed so low that it becomes nearly accidentally degenerate with the degenerate $\Gamma_5(4)$ pair of states, and only a single band can be resolved in the vicinity of 29,000 to 30,000 cm^{-1}. Such a feature would account for the considerable separation of the peaks in x,y and z polarizations. Again, the band at 26,300 cm^{-1} is primarily due to the $\Gamma_2(2)$ state with a nearby Γ_4 state which should be reached by a transition of low intensity. The 24,000-cm^{-1} band arises from the $\Gamma_5(3)$ and $\Gamma_1(3)$ states. The high intensity of the 20,600–20,800-cm^{-1} band is then attributable to the moderate singlet character for the $\Gamma_3(1)$ at 20,700 cm^{-1}. The intensity of the x,y-polarized band at 18,000 cm^{-1} is consistent with the $\Gamma_2(1)$, and much lower intensities are predicted for transitions at longer wavelengths with no band center below 16,640 cm^{-1}. The fit of the transition energies and intensities to the crystal spectra appears rather satisfactory even if not exact. One shortcoming is that the scheme does not account for the band at 36,500 cm^{-1} in the reflectance spectra,[6] which also appears in solution spectra at 37,900 cm^{-1} with an extinction coefficient extimated to be 250 cm^{-1} M^{-1} by Chatt, *et al.*[7] Such a band may possibly arise from a spin-forbidden charge transfer. The F_2 and F_4 parameters are about 0.6 to 0.7 times the free Pt atom values[8] with an F_2/F_4 ratio of 15 compared to 14 for the free atom. As predicted by McClure,[9] the spin–orbit coupling is somewhat smaller than the value of 2040 cm^{-1} deduced from the free-atom spectrum. In all, the transition scheme under alternative B is believed the more suitable, although alternative A is not completely excluded. The correlation of the square-planar D_{4h} states with the tetrahedral T_d under alternative B, shown in Figure 1, is still consistent with the earlier proposal[2] that the principal transitions with strongly resolved vibrational structure at 26,300 and 24,000 cm^{-1} correlate with T_d states of considerably higher energy whereas the transitions with little or no detectable fine structure correlate with similar or lower energies in T_d.

With alternative B, the d_{z^2}, d_{xz}, and d_{yz} orbitals all have very nearly the same energy. Such an arrangement cannot result from a point charge or dipole crystal field.[3] Therefore, a molecular orbital model will be required for its description.

Appendix

The matrix elements indicated below replace those for the d^8 configuration in a square-planar crystal field published previously.[3]

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[6] P. Day, A. F. Orchard, A. J. Thompson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).

[7] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

[8] C. Moore "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1958.

[9] D. S. McClure, *Solid State Phys.*, **9**, 399 (1959).

Weak-field matrix elements

Γ_1 representation

$(9|8) = (\sqrt{2}/5)(-2Q_2 + Q_1 + Q_0)$

$(8|3) = (-\sqrt{210}/5)\alpha$

$(9|4) = (2\sqrt{6})\alpha$

Γ_4 representation

$(6|5) = (\sqrt{14}/70)(2Q_2 - 2Q_0 + 10B_{2-2})$

Γ_5 representation

$(3|1) = (-\sqrt{42}/7)B_{2-2}$

Strong-field matrix elements

Γ_1 representation

$(9|8) = -2\alpha - 3F_2 + 15F_4$

$(5|4) = 2i\alpha$

$(7|4) = \sqrt{6}\alpha$

$(8|4) = -\sqrt{2}\alpha$

$(9|4) = \sqrt{2}\alpha$

Γ_4 representation

$(3|1) = \sqrt{2}\alpha$

$(4|2) = -\sqrt{2}\alpha$

Γ_5 representation

$(10|9) = 6F_2 - 30F_4$

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RECEIVED FEBRUARY 11, 1966

Comments on the Inductive Rule in Carboranes. Charge Distributions in $B_8C_2H_{10}$ Isomers

Sir:

All known positions of halogen substitution[1] on o-$B_{10}C_2H_{12}$ follow a simple inductive rule[2] relating to ground-state charge distribution in this carborane: substitution occurs first on those B atoms which are furthest from C. More sophisticated molecular orbital studies[1,3] of o-$B_{10}C_2H_{12}$ give the same predictions, if ambiguities in total charges are resolved by favoring the more polarizable charges. Thus, this apparent domination of the transition state by the ground-state charge distribution of the parent carborane may be useful as a starting point for studies of more complex reactions, where steric, multiple-step kinetic and other effects may also be important. Here, we wish to record (Table I) both molecular orbital charge distributions and a simple development of the inductive rule for the various isomers (Figure 1) of $B_8C_2H_{10}$, in view of the earlier success with o-$B_{10}C_2H_{12}$ and of the recent preparation in quantity of two isomers[4] of this formerly mass spectroscopic[5] species.

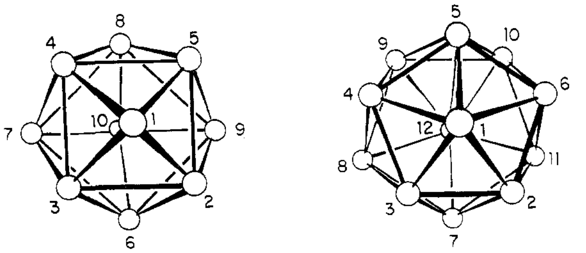

Figure 1.—Numbering convention for the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ polyhedra.

TABLE I

FRAMEWORK (BH UNIT) CHARGES FOR $B_8C_2H_{10}$ ISOMERS[a,e]

NEMO[c]	EH[d]	I[a]	NEMO	EH	I
1,2[b] Isomer			1,6 Isomer		
3 (0.18)	3 (0.14)	3	2 (0.14)	2 (0.17)	2
4 (−0.12)	4 (0.04)	4	4 (0.00)	7 (0.04)	4
6 (−0.03)	6 (0.03)	6	7 (−0.04)	4 (0.03)	7
7 (−0.21)	7 (−0.11)	7	10 (−0.16)	10 (0.02)	10
10 (−0.38)	10 (−0.14)	10	8 (−0.24)	8 (−0.11)	8
2,3 Isomer			2,4 Isomer		
6 (0.12)	6 (0.14)	6	3 (0.12)	3 (0.16)	3
1 (0.03)	1 (0.11)	1	1 (−0.01)	1 (0.14)	1
7 (−0.03)	4 (0.04)	4	6 (−0.04)	6 (0.02)	6
4 (−0.06)	7 (0.02)	7	10 (−0.41)	10 (−0.20)	10
8 (−0.20)	8 (−0.10)	8			
10 (−0.43)	10 (−0.19)	10			
2,6 Isomer			2,7 Isomer		
3 (0.12)	3 (0.13)	3	3 (0.11)	3 (0.16)	3
5 (−0.03)	5 (0.04)	5	5 (−0.04)	5 (0.02)	5
1 (−0.17)	1 (−0.03)	1	4 (−0.07)	4 (0.01)	1
4 (−0.23)	4 (−0.12)	4	1 (−0.18)	1 (−0.03)	4

[a] Total charges are given in parentheses. The inductive order *I* probably favors the higher energy, more polarizable molecular orbitals. The criteria are that B's bonded to two C's are most positive, those bonded to no C's are most negative, and, where these factors are equal, the apex B is more negative than equatorial B. Differences in charges less than about 0.05 are not regarded as significant. [b] Positions of C atoms identify the isomers. [c] Nonempirical molecular orbital method.[6] [d] Extended Hückel method.[3] [e] All calculations here are based upon the geometry of the $B_{10}H_{10}^{2-}$ ion. Similar NEMO calculations for all puckered geometries in which C–C distances and B–C distances are appropriately shorter than B–B distances indicate no change in the order of atom types, except for interchange of B-1 and B-6 of the 2,4 isomer.

Calculations by the nonempirical molecular orbital method,[6] based upon self-consistent field (minimum basis set) molecular parameters from B_2H_6 and C_2H_6, confirm the order of charges B-9 (−0.25), B-4 (−0.03), B-5 (−0.02), and B-2 (0.15) predicted earlier in Hückel calculations on m-$B_{10}C_2H_{12}$. Application of the simple inductive rule shows that in m-$B_{10}C_2H_{12}$ only atoms 9 and 10 are bonded to no C atoms, while atoms 2 and 3 are bonded to two C atoms. Atoms of types 4 and 5 are each bonded to one C atom, but 4 is slightly closer than 5 to the other C atom; however, this simple rule may neglect an undiscovered *trans* effect of C-7 on B-5, for which no evidence presently exists. It is to be noted that MO theory gives four most negative B atoms in o-$B_{10}C_2H_{12}$, but only two (9 and 10) in m-$B_{10}C_2H_{12}$.

Predictions for the $B_8C_2H_{10}$ isomers (Table I) are somewhat more risky than for the icosahedral carboranes, because of the important difference in polyhedral coordination of the two types of positions (Figure 1). For example, in the $B_{10}H_{10}^{2-}$ ion[7] the B_5 units of C_{4v} symmetry have a B (apex)–B (basal) distance of

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(1) J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Am. Chem. Soc.*, **88**, 628 (1966).

(2) W. N. Lipscomb, American Chemical Society Western Regional Meeting, Nov 18–20, 1965, Los Angeles, Calif. See also H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

(3) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962); **37**, 520 (1962). In the present calculations, H atoms are included explicitly; see *ibid.*, **37**, 2872 (1962).

(4) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 609 (1966).

(5) I. Shapiro, *Talanta*, **11**, 211 (1964).

(6) M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **53**, 1089 (1965); also M. D. Newton, F. P. Boer, and W. N. Lipscomb, to be published.

(7) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).