resonances of the *R*-pn group are constant for the two species, it is reasonable to assign the same overall configuration to both. On the basis of arguments presented above concerning the starting carbonate complex, this should be the Δ configuration. Further support for the Δ configuration can be derived from the relative positions of the methyl protons of the lactic acid. For the Δ configuration, molecular models indicate that more steric compression of the methyl protons is experienced for coordinated *S*(+)-lactate. Hence these should have resonances at lower field[14] as was found to be the case.

Further evidence for the Δ configuration comes from the CD spectrum. The *S*(+)-lactate complex has a large negative band in the region of the $A_{1g} \rightarrow T_{1g}$ transition and is similar to that of Δ-[Co(*R*-pn)$_2$CO$_3$]$^+$ reported earlier[4] and that of Δ-[Co(en)$_2$(*S*(+)-lactate)]$^+$.[1] The *R*-lactate compound has a CD sign pattern similar to that found earlier[1] for Δ-[Co(en)$_2$(*R*(−)-lactate)]$^+$ but the relative intensities differ quite markedly. However, since the sign patterns of the individual transitions are identical, it would appear that both of the isolated lactate species indeed have the Δ configuration.

The difference in CD spectra therefore appears to arise from a very significant contribution from the vicinal effect, and as is shown for the *R*(−)-lactate complex, the vicinal effect predominates over the configurational effect in its contribution to the observed CD spectrum. The contribution from vicinal effects should exhibit CD spectra similar in shape to those determined for the analogous ethylenediamine systems.[1] However, there will be differences, other than sign for the two acids since the conformational preferences of the other rings present have a very marked effect on the vicinal CD intensity. This was quite evident for the [Co(en)$_2$(lactate)]$^+$ complexes where the vicinal CD intensity was an order of magnitude greater than that of [Co(NH$_3$)$_4$(lactate)]$^+$. The coordinated *R*-pn ligands have an even greater conformational preference and hence the enhanced vicinal effect could be related to this. Moreover, the two acids would not necessarily have the same vicinal effect in terms of absolute magnitude since the relationship of the coordinated acid to the other ligands is not enantiomeric as it is in other systems studied. The vicinal CD appears to be strongest for the *R*-lactate ion and this is consistent with predictions from conformational arguments. For Δ-[Co(*R*-pn)$_2$(*R*(−)-lactate)]$^+$ all three chelate rings would have the same configuration and would be coordinated with the λ conformation. The C-C bonds of the chelate would thus have the lel arrangement[7] and the CD due to the vicinal effect of all ligands would enhance each other.

The findings of our study are significant in that an example has been found in which the vicinal contribution to the optical activity outweighs the configurational contribution. Further studies are now in progress to determine reasons for such a situation.

Registry No. [Co(*R*-pn)$_2$(*R*(−)-lactate)]ClO$_4$, 39208-10-1; [Co(*R*-pn)$_2$(*S*(+)-lactate)]ClO$_4$, 39208-11-2; [Co(*R*-pn)$_2$CO$_3$]ClO$_4$, 36545-34-3.

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Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Molecular Orbital Descriptions of the Bonding in Bis(amino)diborane(4) and (Amino)vinylborane as Theoretical Models for Photochemical Reactivity

Anthony K. Uriarte and Kenneth G. Hancock*

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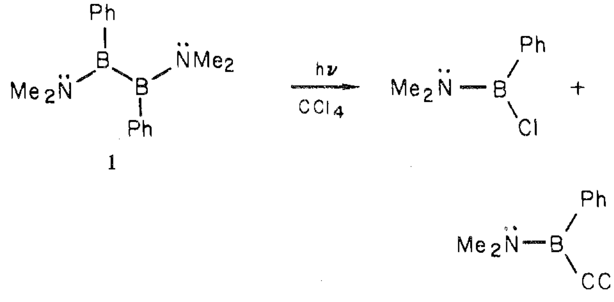
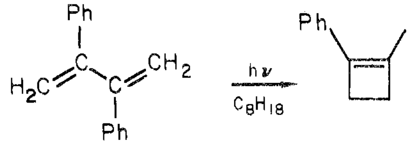
We recently reported that the photochemistry of 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) (1) was best rationalized in terms of photolytic boron-boron homolysis as the primary process.[1] The contrast between this reaction and the photochemical electrocyclic ring closure of the isoelectronic 2,3-diphenyl-1,3-butadiene[2] (2), while thermodynamically reasonable, is nevertheless striking. In order to gain further insight into the causes for the diverging excited-state properties of the bis(amino)diborane(4) and butadiene systems, a theoretical investigation of the electronic structure of the >N̈-B-B-N̈< chromophore seemed desirable. Several theoretical studies of the closely related tetrakis(amino)diborane(4) (3) system have appeared,[3] but these are not sufficient since the photochemistry of tetrakis(dimethylamino)diborane(4) and bis(amino)diborane(4) systems are significantly different.[4]



1



2

$(Me_2\ddot{N})_2B-B(\ddot{N}Me_2)_2$ $H_2\ddot{N}-BH-BH-\ddot{N}H_2$ $CH_2{=}CH-BH-\ddot{N}H_2$
3 4 5

Accordingly, two systems—bis(amino)diborane(4) (4) and (amino)vinylborane (5)—were chosen so as to note any trends in the electronic redistribution as one and then two aminoboryl moieties are substituted for the vinyl linkages in butadiene. Two all-valence-electron semiempirical solutions to the Schrodinger equation were employed: (a) extended Huckel theory, iterated to self-consistent charge (EHT-SCC);[5] and (b) the intermediate neglect of differential overlap (INDO) approximation.[6] Although both offer economic advantages over *ab initio* methods, INDO in particular has

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(1) K. G. Hancock and A. K. Uriarte, *J. Amer. Chem. Soc.*, 92, 6374 (1970).

(2) E. H. White and J. P. Anhalt, *Tetrahedron Lett.*, 3937 (1965).

(3) (a) P. G. Perkins and D. H. Wall, *J. Chem. Soc. A*, 1207 (1966); (b) N. C. Baird and M. A. Whitehead, *Can. J. Chem.*, 45, 2059 (1967).

(4) K. G. Hancock, A. K. Uriarte, and D. A. Dickinson, submitted for publication.

(5) R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963).

(6) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967).

not seen extensive application to molecules of the organo- and aminoborane classes. Simple Huckel[7] and extended Huckel calculations for **4**[3b,8] and simple Huckel calculations for substituted **5**[9] have been reported; however, such calculations were repeated (with somewhat different parameterization) as a portion of the EHT-SCC treatment and to facilitate comparison of results from π-only and all-valence-electron calculations. Pariser-Parr-Pople self-consistent field calculations with configuration interaction (SCF-CI) were also cursorily examined.[10,11]

Experimental Section

Calculations were carried out on a CDC 6400 computer at the University of California, using versions of Fortran IV programs written by U. Mueller-Westerhoff, E. Levine, J. Pople, and D. Beveridge. Nuclear magnetic resonance spectra were recorded on Varian A-60A and Jeolco JNM-100 instruments, ultraviolet absorption spectra on a Cary 15 spectrometer, and infrared spectra on a Beckman IR-8.

Computational Parameters and Methods. A strong proclivity of 4 and 5 to polymerization[12] has heretofore prevented both isolation and the acquisition of precise molecular geometry data. Nor have X-ray or electron diffraction structure determinations been reported for substituted bis(amino)diborane(4) or (amino)vinylborane systems. Geometries have therefore been estimated from precise structure determinations on closely related aminoboranes;[13,14] energy minimization with respect to optimized geometry was not attempted.

Both molecules **4** and **5** were assumed planar, with 120° bond angles, consistent with recent X-ray structures on substituted aminoboranes.[13,14] The s-trans conformation has been shown to be favored in (amino)vinylboranes,[15] and this geometry was therefore adopted for calculations on both **4** and **5**. The interatomic distances employed and their sources were as follows: (a) 1.38 Å for the BN bond, from electron diffraction data on (dimethylamino)dichloroborane;[13] (b) 1.70 Å for the BB bond, from SCF-π calculations on tetrakis(dimethylamino)diborane(4);[3a] (c) 1.55 Å for the BC bond, 1.35 Å for the C=C bond and 1.09 Å for the CH bond, from SCF-π calculations on vinylboranes;[16] (d) 1.19 Å for the BH and 1.01 Å for the NH bonds, from *ab initio* calculations on aminoborane.[17]

Input parameters for the extended Huckel treatment were the basis set of 1s for H and 2s and 2p Slater orbitals for B, C, and N[18] and VSIP's for the Coulomb integrals.[19] In the iterative modification to self-consistent charge,[20,21] diagonal matrix elements were modified by total atomic charge, including a damping parameter λ to facilitate convergence, at each iteration according to the equation $H_{ii}^{n+1} = (1 - \lambda)H_{ii}^{n} + \lambda(H^{\circ}_{ii} + q_i\Delta H_{ii})$. The ΔH proportionality constants were theoretically calculated.[19,22] Off-diagonal Hamiltonian matrix elements were approximated by the Wolfsberg-Helmholtz equation,[23] $H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$, where K was chosen to equal 1.75 as a compromise value to improve correlation with experimental data.[5] Overlap integrals S_{ij} were calculated from Slater orbitals. Parameters employed in the semiempirical INDO method[6] were included directly in the program, which is described in the recent Pople-Beveridge monograph.[24] Input parameters and sources for SHMO and SCF-CI π-electron calculations are included in the tables of results.[11]

Results[11]

Tabulations of pertinent calculated molecular parameters are recorded elsewhere.[11,25] Explicit inclusion of valence σ electrons in MO descriptions of **4** and **5** markedly affects certain molecular parameters, *e.g.*, atomic charges and energy level ordering.

Most striking is the relative energy ordering of the molecular orbitals in **4** and **5**. Examination of the INDO and EHT eigenvectors of the highest occupied molecular orbital (HOMO), ϵ_{11}, for the bis(amino)diborane(4) system **4** reveals that it is a σ-type orbital with a_g symmetry, primarily comprised of the two boron $2p_x$ atomic orbitals. The highest filled orbital of the π type is ϵ_{10}, localized primarily on the nitrogen atoms, possessing b_g symmetry, and lying *ca.* 3 eV lower in energy than the HOMO ϵ_{11}. The lowest vacant molecular orbital (LVMO) is ϵ_{12}, a π-type orbital of a_u symmetry, largely made up of the boron $2p_z$ atomic orbitals. The first predicted electronic transition, then, is the symmetry-allowed $A_u \leftarrow A_g$ σ-π* excitation. The first symmetry-allowed π-π* transition is the $B_u \leftarrow A_g$ charge-transfer excitation, predicted to occur at 205 nm.

Both EHT-SCC and INDO calculations for (amino)vinylborane (**5**) predict near degeneracy ($\Delta_{\sigma,\pi}$ *ca.* 0.2 eV) of the two highest occupied levels—one of π symmetry and the other a σ type, heavily localized between the CB bond. Only the precise ordering is reversed in the two calculations. Lack of symmetry in **5** would make both π-π* and σ-π* excitations at *ca.* 350 nm allowed.

Comparison of EHT-SCC and INDO results with π-electron computations[11] suggests the latter not only give inadequate qualitative description of charge distributions but also fail to recognize potentially important occupied σ MO's of high energy. The INDO-EHT density matrix analyses find considerable electron density on B hydrogens in both **4** and **5**, while the N hydrogens are predicted to be substantially electron deficient. Such predictions are borne out experimentally in the proton nmr spectrum of 1,2-bis(dimethylamino)-1,2-diethyldiborane(4) (**6**).[26] Decreased electron density is reflected in deshielding and a downfield chemical shift of the *N*-methyl resonances from δ 2.1 in dimethylamine to δ 2.9 and 3.1 in the diborane(4) **6**. The high calculated electron density around the B hydrogens in **4** and **5** is compatible with the upfield shift of the B methylenes (δ 0.85) in **6** relative to normal hydrocarbon values.

Discussion

Several aspects of the photochemistry of bis(amino)diborane(4) (**4**) and (amino)vinylborane (**5**) systems may be

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(7) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(8) R. Hoffmann, *J. Chem. Phys.*, 40, 2474 (1964).

(9) M. R. Chakrabarty, C. C. Thompson, Jr., and W. S. Brey, Jr., *Inorg. Chem.*, 6, 518 (1967).

(10) R. L. Flurry, Jr., "Molecular Orbital Theories of Bonding in Organic Molecules," Marcel Dekker, New York, N. Y., 1968.

(11) The less realistic SHMO and SCF-CI calculations are not discussed here. Partial tables (Tables I-IV) of orbital energies, atomic charges, and other pertinent molecular parameters from SHMO, SCF-CI, EHT-SCC, and INDO calculations will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1428.

(12) K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer-Verlag, Berlin, 1965.

(13) F. B. Clippard and L. S. Bartell, *Inorg. Chem.*, 9, 2439 (1970).

(14) G. J. Bullen and N. H. Clark, *J. Chem. Soc. A*, 992 (1970).

(15) K. N. Scott and W. S. Brey, Jr., *Inorg. Chem.*, 8, 1703 (1969).

(16) P. G. Perkins and D. R. Armstrong, *Theor. Chim. Acta*, 4, 352 (1966).

(17) D. R. Armstrong, B. J. Duke, and P. G. Perkins, *J. Chem. Soc. A*, 2566 (1969).

(18) (a) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 38, 2686 (1963); (b) S. Aung, R. M. Pitzer, and S. I. Chan, *J. Chem. Phys.*, 49, 2071 (1968).

(19) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, 3, 458 (1965).

(20) B. J. Duke, *Theor. Chim. Acta*, 9, 260 (1968).

(21) R. Rein, N. Fukuda, H. Win, G. A. Clarke, and F. E. Harris, *J. Chem. Phys.*, 45, 4743 (1966).

(22) D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, 44, 1865 (1965).

(23) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, 20, 837 (1952).

(24) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(25) A. K. Uriarte, Ph.D. Thesis, University of California, Davis, Calif., 1972.

(26) K. G. Hancock and A. K. Uriarte, experimental observations.

rationalized in terms of the EHT-INDO semiempirical theoretical models.

π Bonding and π-Electron Delocalization. Semiempirical molecular orbital descriptions of **4** and **5** at all levels predict substantial BN double-bond character (0.20 BN overlap population by EHT for **4**, 0.18 for **5**),[11] but scant BB π bonding in **4** (0.01) relative to the CB π bonding counterpart in **5** (0.12).[11] Observable physicochemical effects of these bonding variations are seen in the infrared, nmr, and electronic spectra. In the infrared, ν_{BN} is *ca.* 1500 cm^{-1} for 1,2-bis(dimethylamino)-1,2-dialkyldiboranes(4)[26] and *ca.* 1430 cm^{-1} in (amino)vinylboranes,[27] in good correlation with calculated π-bond orders.[9] Substantial BN double-bond character in **4** is also reflected by hindered rotation about the BN bonds in diboranes(4): 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) (**1**) shows no coalescence of magnetically nonequivalent N methyls even at 120°.[26] The blue shift predicted to occur in the electronic absorption spectrum because of diminished π delocalization as $\mathrm{N}\overset{\rightharpoonup}{=}\mathrm{B}$ bonds replace C=C moieties of butadiene has a counterpart in fact. Experimentally determined ultraviolet absorption spectra for alkyl-substituted bis(amino)diborane(4) systems exhibit their major λ_{max} below 200 nm.[26] The observed λ_{max} for (dimethylamino)vinylborane is 223 nm[27] and for tetraalkylbutadienes is *ca.* 235 nm. Lack of experimental data precludes a test of the predicted oscillator strengths.

Energy Level Ordering, Electronic Transitions, and Photochemical Excited States. Perhaps the most important distinction of the all-valence-electron calculations is that both EHT and INDO methods predict an inversion in the ordering of the two highest filled molecular orbitals, one σ and one π type, to accompany the stepwise replacement of C=C units in butadiene by $\mathrm{N}\overset{\rightharpoonup}{=}\mathrm{B}$ linkages (Figure 1). Thus, the HOMO in butadiene is π_2, lying some 3.5 eV above the highest filled σ orbital, according to EHT computations.[5] Both EHT and INDO predict near degeneracy of the highest occupied σ and π MO's in **5**, and an inversion for **4**, in which the σ HOMO ϵ_{11} lies 3.1 eV above the highest filled π orbital ϵ_{10}. This correlation is illustrated in Figure 1.

The prediction of a σ HOMO in **4** is not yet verified but could clearly exert a profound effect on the photochemistry of bis(amino)diborane(4) systems. In the absence of detailed excited-state calculations, some insight may be gained by analysis of the virtual orbitals of the ground state.

Eigenvectors obtained from both EHT and INDO computations on **4** show that the σ HOMO ϵ_{11} is essentially a description of the boron-boron σ bond. The π^* LVMO ϵ_{12} has very slightly larger contributions from boron $2p_z$ orbitals, suggesting that a σ-π^* state would have increased electron density about boron atoms, but probably a considerable net diminution of boron-boron bonding since the π-bonding overlap is less effective than the σ-bonding overlap. A σ-π^* excited state could therefore reasonably account for the observed facile boron-boron photohomolysis in the bis(amino)diborane(4) system. In contrast, the eigenvectors of the highest filled π orbital ϵ_{10} suggest a slight increase in boron-boron bonding would be expected in the lowest π-π^* excited state of **4**, similar to that postulated for 1,3-butadiene.[28] It must be conceded, however, that excited-state arguments based on properties of ground-state virtual orbitals are tenuous, despite their successful application elsewhere.[29]

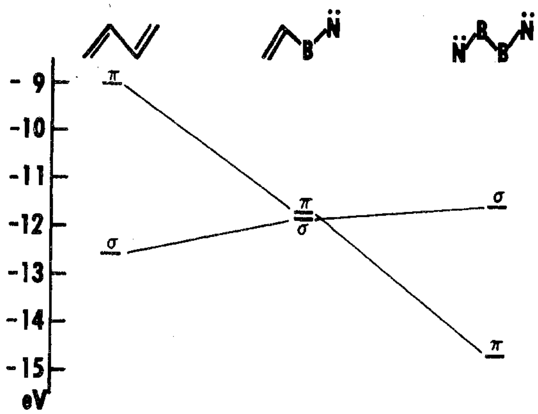

Figure 1. EHT-MO correlation diagram for the two highest filled molecular orbitals in 1,3-butadiene, (amino)vinylborane, and bis(amino)diborane(4).

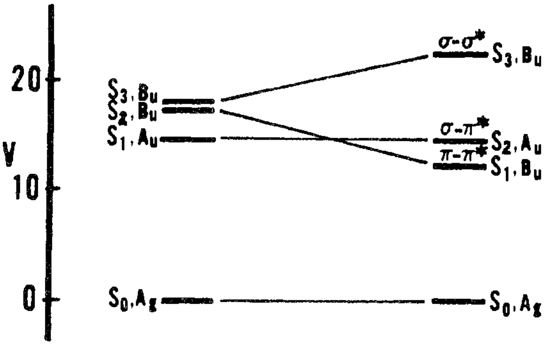

Figure 2. Configuration interaction of the upper B$_u$ excited states (INDO calculations) of bis(amino)diborane(4).

Population of the σ-π^* excited state by direct excitation is symmetry allowed. Nevertheless, electronic absorption spectra of substituted bis(amino)diboranes(4) in concentrated solutions exhibit no long-wavelength absorption,[26] but this does not rule out the photochemical reaction possibility of initial excitation to $S_2(\pi$-$\pi^*)$ followed by internal conversion to the lower σ-π^* S_1 state or by intersystem crossing to a σ-π^* T_1 state.

Although both all-valence-electron calculations predict a σ-π^* S_1 state, the symmetries and energies of several upper excited states (Figure 2) are such that configuration interaction is a realistic possibility. Thus the INDO calculation of a σ-π^* S_1 state (A_u symmetry) some 15 eV above the ground state S_0 (A_g) also predicts that S_2 and S_3 would be 17.7-eV π-π^* and 18.2-eV σ-σ^* states, respectively, both of B_u symmetry, and suitable for configuration interaction. It is entirely conceivable that such mixing of the two upper excited states could cause a crossing in which the B_u π-π^* state would drop below the A_u σ-π^* state and thus become S_1 (Figure 2). Experiments designed to test these theoretical possibilities are in progress.

Registry No. Bis(amino)diborane(4), 18447-56-8; (amino)vinylborane, 39023-05-7.

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[27] K. Niedenzu, J. W. Dawson, G. A. Neece, W. Sawodny, D. R. Squire, and W. Weber, *Inorg. Chem.*, **5**, 2161 (1966).

[28] G. O. Schenk, *Angew. Chem.*, **73**, 413 (1961).

[29] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2046, 2511 (1965), and succeeding papers.

Jr., and Dr. P. Owens are gratefully acknowledged. In addition, A. K. U. expresses appreciation for an NSF traineeship, 1969-1972.

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

Photoelectron Spectroscopy of Tin Compounds

P. A. Grutsch,[1] M. V. Zeller, and T. P. Fehlner*

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Photoelectron spectroscopy of core electrons is a technique capable of yielding information pertinent to the study of chemical bonds in that the binding energy of an inner shell electron is characteristic of both its elemental identity and the chemical environment of the atom.[2] As the sensitivity of the binding energy to valence state depends on the element, the first objective of this work was to determine this sensitivity for tin core electrons. It should be noted that some tin binding energies have already been interpreted in terms of a specific oxidation state.[3] In addition, the tin nucleus is amenable to the Mossbauer technique and communications reporting relationships between isomer shifts and core electron binding energies for some Sn(IV) compounds and some Fe(II) compounds appeared during the course of this work.[4,5] Our second objective was to investigate the existence of such a correlation for selected complexes of tin(IV) chloride. Finally, the differences in binding energies between coordinated and uncoordinated ligand atoms have been used to support arguments concerning π back-bonding in some coordination compounds.[6,7] As such an interaction can also be important in coordination to tin, another objective of this work was to investigate the changes in core electron binding energies of a variety of ligand atoms upon coordination to tin.

Experimental Section

This work was carried out on a Varian IEE-15 spectrometer employing an electrostatic electron analyzer and controlled by a Varian 260/i digital computer. Powdered samples, mounted with double-faced tape on cylindrical aluminum holders, were bombarded with either Al $K\alpha_{1,2}$ or Mg $K\alpha_{1,2}$ X-rays with energies of 1.487 and 1.254 keV, respectively. Three samples were investigated with both sources and the measured binding energies were found to be independent of the X-ray source. Instrument resolution at an analyzer energy of 100 eV corresponded to a 1.9-eV peak width at half-height for the carbon 1s electrons from a graphite standard. Other typical line widths were as follows: Sn 4d, 2.5 eV; Sn 3d, 2.2 eV; P 2p, 2.5 eV; Au 4f, 1.9 eV; N 1s, 2.2 eV; S 2p, 3.3 eV; O 1s, 3.2 eV. All compounds were run at least once with a gold standard deposited on the mounted sample under vacuum conditions and most were examined on at least two separate occasions with this standard. Several compounds were examined as many as eight separate times over the course of 1 year. The standard deviation for these measurements was typically 0.3 eV and, although the reproducibility was much better for many samples, we have taken this as a measure of the precision of all the determinations.

To support the standardization technique, we have measured the phosphorus 2p binding energies in three compounds that have been examined in other laboratories. Our results and those reported by others[8,9] are compared in Table I. With one exception, the agreement between our values and those reported by other laboratories using phenyl carbon as an internal standard is good. As the absolute binding energy for the Au $4f_{5/2}$ line was not determined, the values in the tables are only relative.

Most compounds were also run without deposited gold and the relative binding energies of the core electrons of the various atoms present were independent of the presence of gold. In measuring the binding energies, the reference line was always measured before and after the lines of interest. Instrument drift was rarely observed but when it was the determination was discarded.

The Sn(IV) compounds examined were gifts of Professor Columba Curran and Drs. Data Naik and Merle Arnold. The preparations and characterizations have been reported elsewhere.[10-17] Selected compounds were rechecked for purity by elemental analysis or by infrared spectroscopy. The Sn(II) compounds were commercial samples as were the free ligands.

Results and Discussion

Chemical Shift. The observed binding energies for the Sn (4d) and ($3d_{5/2}$) electrons for a variety of tin compounds are presented in Table II. The agreement between the chemical shifts for the two levels measured is good. For the compounds measured the values span a mere 2 eV although charges (q, Table II) estimated using Pauling's electronegativities[2] span about 3 units. Clearly the tin core electron binding energies are fairly insensitive to their chemical environment. This behavior can be understood in that the change in binding energy with reference to a standard is roughly proportional to the change in atomic charge. The constant of proportionality is in turn inversely proportional to atomic radius.[2,9,18,19] Thus as the radii of tin are fairly large,[20] the insensitivity of the core electron binding energies of tin to chemical environment is reasonable. Unfortunately, this technique will not be extremely useful in examining the bonding of tin compounds. Thus the tin binding energies in platinum-tin cluster compounds[3] do not allow one to distinguish unambiguously the Sn(IV) oxidation state from that of Sn(II).

In the tin(IV) chloride and bromide complexes, the binding energies of the Cl 2p electrons and Br 3d electrons

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[1] National Science Foundation Undergraduate Research Participant.

[2] (a) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Karlsson, I. Lindgren, and B. Lindberg, "ESCA: Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, 1967; (b) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. P. Werme, R. Manne, and Y. Bear, "ESCA: Applied to Free Molecules," North-Holland, Amsterdam, 1969.

[3] G. W. Parshall, *Inorg. Chem.*, 11, 433 (1972).

[4] M. Barber, P. Swift, D. Cunningham, and M. J. Frazer, *Chem. Commun.*, 1338 (1970).

[5] I. Adams, J. M. Thomas, G. M. Bancroft, K. D. Butler, and M. Barber, *Chem. Commun.*, 751 (1972).

[6] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 8, 2642 (1969).

[7] J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge, and M. M. Jones, *Inorg. Chem.*, 9, 2374 (1970).

[8] W. E. Morgan, W. J. Stec, R. G. Albridge, and J. R. Van Wazer, *Inorg. Chem.*, 10, 926 (1971).

[9] M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, 74, 1116 (1970).

[10] M. A. Mullins and C. Curran, *Inorg. Chem.*, 7, 2584 (1968).

[11] C. Curran and M. A. Doskey, *Inorg. Chim. Acta*, 3, 169 (1969).

[12] M. A. Mullins and C. Curran, *Inorg. Chem.*, 6, 2017 (1967).

[13] J. Philip, M. A. Mullins, and C. Curran, *Inorg. Chem.*, 7, 1895 (1968).

[14] J. Philip, Ph.D. Thesis, University of Notre Dame, 1965.

[15] W. W. Welna, Ph.D. Thesis, University of Notre Dame, 1968.

[16] M. A. Mullins, Ph.D. Thesis, University of Notre Dame, 1968.

[17] M. Arnold, Ph.D. Thesis, University of Notre Dame, 1971.

[18] U. Gelius, P. F. Heden, J. Hedman, B. J. Linberg, R. Manne, R. Nordberg, C. Nordling, and K. Siegbahn, *Phys. Scr.*, 2, 70 (1970).

[19] J. C. Carver, G. K. Schweitzer, and T. A. Carlson, *J. Chem. Phys.*, 57, 973 (1972).

[20] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 25, 925 (1969).