Inorganica Chimica Acta, 18 (1976) 13–18

The Electronic Structures of Bis(carbonyl)diborane(4), Triborane(7) Carbonyl and Their Parent Boranes Diborane(4) and Triborane(7)

D. R. ARMSTRONG
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland, U.K.
Received August 2, 1975

The electronic structure of bis(carbonyl)diborane(4), $B_2H_4(CO)_2$, triborane(7) carbonyl, B_3H_7CO, and their parent boranes have been examined by a non-empirical molecular orbital technique. It is found that the carbonyl groups are weakly bound to the borane portion. The staggered form of $B_2H_4(CO)_2$ is calculated to be more stable than the eclipsed configuration by 74 kJ mol^{-1}. The structure of B_2H_4 is computed to be two BH_2 groups in a staggered conformation joined by a boron-boron bond. The following optimised bond lengths, B–B = 1.683 A, B–H = 1.202 A nm, and bond angle ∠HBH = 116.2° are obtained. The energy of rotation about the boron–boron bond in B_2H_4 is 57.2 kJ mol^{-1} and optimisation of the geometry of the eclipsed configuration reduces this energy barrier by 6.3 kJ mol^{-1}. The electronic situation within the B_3 rings of B_3H_7CO and B_3H_7 is discussed. The presence of the carbonyl group only marginally alters the bonding within the BBB triangle which consists of a distorted three-centre bond. The bridging hydrogen atom which almost lies in the same plane as the three boron atoms interacts with the inplane orbitals of two of the boron atoms and hence deforms the electronic situation within the ring.

Introduction

The borane carbonyls have been regarded for many years as synthetically useful molecules within the sphere of preparative boron chemistry.[1–6] Carbon monoxide is a weak nucleophile and the borane carbonyls are easily decomposed into the parent borane and carbon monoxide. The facile production of reactive borane fragments establishes the borane carbonyls as useful precursors of some less stable boranes. Formerly, borane carbonyl, BH_3CO, was the subject of experimental and theoretical probings.[3,7–11] Latterly, however, the higher borane carbonyls have commanded more attention in experimental investigations.[6,12–14] It is the purpose of this paper to augment the results of these examinations by presenting the electronic structures of two higher borane carbonyls, bis(carbonyl)diborane(4), $B_2H_4(CO)_2$ and triborane(7) carbonyl, B_3H_7CO, plus the electronic structures of the parent boranes diborane(4) and triborane(7). $B_2H_4(CO)_2$ has a particularly interesting structure, similar to that of 1,2-substituted ethane, with the carbonyl groups possessing a staggered conformation with respect to each other.[14] The influence of the carbon monoxide groups is such that hydrogen bridging bonds are not necessary to ensure stability. As the groups are not free-rotating, an energy barrier to rotation about the boron–boron bond is indicated. This is a rare occurrence and therefore worthy of investigation. The parent borane, B_2H_4 is almost certain to be present in interborane conversions.[14] The extremely reactive nature of B_2H_4, however, precludes the transaction of a successful structural determination. Hence this presents an opportunity for theoretical techniques to provide information about the molecular framework which would be difficult to obtain by other methods.

B_3H_7CO is an example of a reactive borane stabilised by a carbonyl group.[12,13] Moreover, the parent borane is a ring compound and it is of interest to discover if this will affect the pattern of carbonyl donation.

Method

All the calculations were performed within a non-empirical LCAO–MO–SCF framework. A double-zeta basis set was employed in which the atomic orbitals were represented by two simulated Slater orbitals consisting of a linear combination of four Gaussian functions.[16] The orbital exponents were extracted from the work of Clementi[17] while the molecular geometries of the borane carbonyls were constructed from information given in references 13 to 15.

Results and Discussion

Prior to detailed analysis of the structures of each carbonyl and parent borane, it is perhaps instructive to obtain a general picture of the structures of the

TABLE I. The Electronic Populations of the Borane Carbonyls and Their Parent Boranes.

	BH_3CO	$B_2H_4(CO)_2$		B_3H_7CO	BH_3	B_2H_4	B_3H_7	CO
		Staggered	Eclipsed					
Electron Densities								
B_1 *s*	2.976	2.859	2.893	2.898	3.053	3.000	2.897	–
p	2.290	2.336	2.263	2.455	1.917	2.036	2.078	–
total	5.266	5.195	5.156	5.353	4.970	5.036	4.975	–
B_2 B_3 *s*	–	2.859	2.893	2.955	–	3.000	2.973	–
p	–	2.336	2.263	2.105	–	2.036	2.153	–
total	–	5.195	5.156	5.060	–	5.036	5.126	–
C *s*	3.236	3.205	3.192	3.167	–	–	–	3.755
p	2.214	2.236	2.316	2.197	–	–	–	1.783
total	5.450	5.441	5.508	5.364	–	–	–	5.538
O *s*	3.960	3.960	3.963	3.961	–	–	–	3.934
p	4.456	4.466	4.461	4.456	–	–	–	4.528
total	8.416	8.426	8.424	8.417	–	–	–	8.462
H_1	0.956	0.969	0.956	0.920	1.010	0.982	0.947	–
H_2	0.956	0.969	0.956	0.920	1.010	0.982	0.947	–
H_3	0.956	0.969	0.956	0.982	1.010	0.982	0.959	–
H_4	–	0.969	0.956	0.954	–	0.982	0.959	–
H_5	–	–	–	1.033	–	–	1.039	–
H_6	–	–	–	0.982	–	–	0.959	–
H_7	–	–	–	0.954	–	–	0.959	–
Overlap Populations								
B_1–B_2	–	0.710	0.664	0.287	–	0.848	0.333	–
B_2–B_3	–	–	–	0.063	–	–	0.119	–
B_1–C	–0.198	0.002	–0.143	–0.205	–	–	–	–
C–O	1.121	1.110	1.092	1.126	–	–	–	0.743
B_1–H_1	0.863	0.872	0.811	0.853	0.825	0.815	0.826	–
B_2–H_3	–	0.872	0.811	0.916	–	0.815	0.900	–
B_2–H_4	–	0.872	0.811	0.916	–	0.815	0.900	–
B_2–H_5	–	–	–	0.428	–	–	0.412	–

carbonyls. The gross atomic and overlap populations of $B_2H_4(CO)_2$, B_3H_7CO and BH_3CO are presented in Table I. It can be seen that the electron donation from the carbonyl moiety amounts to 0.133 electrons for the mono and diborane carbonyls while it is 0.219 electrons for the triborane carbonyl. Comparison with the electronic pattern of CO reveals that the source of donation within the CO molecule is the carbon 2*s* orbital. However complexing produces a concomitant movement of electronic charge to the *p*-orbitals of carbon. The oxygen atom of the carbon monoxide is comparatively unaffected by complexing as this produces a slight increase in the *s*-orbital population and, coupled with a decrease in the *p*-orbital population, results in an overall diminution in the electron density of the oxygen atom. The B–C bond populations disclose the weak nature of the carbonyl–borane link and account for its labile nature. Inspection of the three donor–acceptor bonds indicates that B_3H_7CO should be the most unstable while the B–C bonds of $B_2H_4(CO)_2$ should be the least prone to scission. Experimentally it is found that B_3H_7CO is liable to decompose into $B_2H_4(CO)_2$ and so confirms the relative values of the B–C bond populations.[14] An interesting feature of the three borane carbonyl molecules is the increase in the C–O bond population upon complexing. This is perhaps an important factor in the complexing nature of the CO reagent. The largest increase occurs for B_3H_7CO and this is slightly greater than that obtained for BH_3CO. The order of stabilities of the various borane–carbonyl bonds can be obtained by inspection of the electronic energies of carbonylation defined as the difference between the electronic energy of the borane carbonyl and the sum of the corresponding energies of the parent borane and carbon monoxide. These energies are for BH_3CO –23.71 kJ mol^{-1}, $B_2H_4(CO)_2$ +2.13 kJ mol^{-1} and B_3H_7CO +38.78 kJ mol^{-1}. BH_3 shows the greatest gain in stability while B_3H_7 is the borane least stabilised by CO. It should be noted that only the electronic energy term has been used here. Inclusion of other energy terms which constitute the free energy of reaction will merely alter the absolute values of the energy differences and leave the order unchanged.

TABLE II. Energies of the Staggered and Eclipsed Configuration of $B_2H_4(CO)_2$ (in au).

	Staggered	Eclipsed	ΔE (Stag.–Eclp.)
Electronic Energy	–446.60299	–461.56175	+14.95876
Nuclear Energy	170.28983	185.27692	–14.98709
Total Energy	–276.31316	–276.28483	–0.02833

The Electronic Structure and Energies of $B_2H_4(CO)_2$ and B_2H_4

The energies of the staggered and eclipsed conformers of $B_2H_4(CO)_2$ are presented in Table II. It can be seen that the staggered configuration is more stable by 74 kJ mol^{-1}. This arises from the difference in the nuclear energy terms having a larger value than the disparity between the electronic energies. In other words, the electronic energy term is not stabilised as much as the nuclear energy term is destabilised during rotation to the eclipsed configuration. The electronic populations of the two conformers were inspected (Table I) for reasons for the relatively destabilised energy of the eclipsed configuration. The electron donation of the carbonyl groups is lower in the eclipsed configuration while the electron drift from the hydrogen atoms is slightly higher for the eclipsed rotamer, producing in total, a smaller negative charge on the boron atoms. The overlap population data establish that the B–B bond order decreases upon rotation to the eclipsed configuration. Detailed analysis of this overlap bond population reveals that it is the σ- and π-B_p–B_p components which are smaller in the eclipsed configuration. The reduction in the σ-bond population probably originates from the smaller electron donation present in the eclipsed form while the smaller π-bond population is undoubtedly related to the greater antibonding long-range interactions along the B–B bond which are found in the eclipsed configuration. The highest bonding orbital of $B_2H_4(CO)_2$ has an energy –0.416 au and is largely composed of the B–B σ-bond. The lowest vacant orbital of this molecule is largely localised about the carbonyl group. Hence electrophilic reagents are likely to react along the central bond while nucleophiles will attack the substituents.

The Electronic Structure of B_2H_4

As there is no available information appertaining to the structure of B_2H_4 it was necessary to procure an energy optimised geometry. Four possible models were chosen (Figure 1) and the structural parameters which produced the lowest energy were obtained. The optimised geometry and energy of models A–D are presented in Table III. Models A and B were formulated so that no hydrogen-bridge bonding was present between the boron atoms, while models C and D contained two and four hydrogen-bridging bonds, respectively. It was found that models C and D are considerably less stable than models A and B which contain no hydrogen-bridge bonding. Comparison of the latter two models reveals that the eclipsed, *i.e.*, planar model A is less stable than model B which has a staggered conformation.

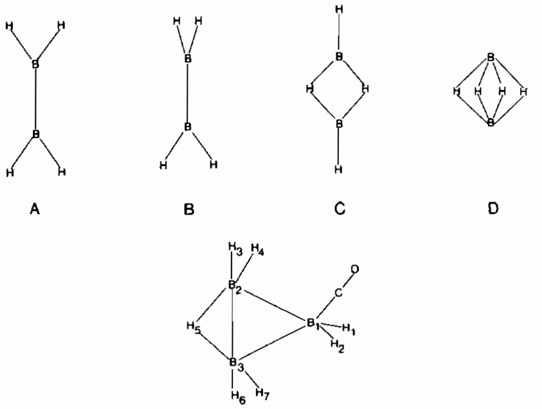

Figure 1. Geometrical structure of models A–D of Diborane(4) and the numbering system used in Triborane(7) Carbonyl.

Models A and B

It is of value to discuss these two models together as they are closely related. Model B is more stable than model A because, although it possesses a larger nuclear energy term, it is also endowed with a much more negative electronic energy. The electronic populations of Table III indicate that in both models the boron atoms bear a slightly negative charge. From the overlap population data we can ascertain that the planar B_2H_4 molecule possesses a weaker B–B bond and stronger B–H bonds than the staggered configuration. The boron–boron bond in both geometries is essentially composed of *pσ–pσ* and *s–pσ* bonding components. The π-bonding portion makes a small positive contribution to the B–B bond population of the staggered configuration, whereas it is an antibonding component of the bond population of the planar species.

From the tabulated structural parameters of models A and B it is observed that rotation from a staggered to a planar configuration induces an increase in the B–B bond length, while other geometrical features are virtually unaltered. It is of interest to collate these figures with comparable experimentally observed dis-

TABLE III. The Electronic Energies and Populations of the Various Models of B_2H_4.

	Model A	Model B	Model C	Model D
Energies (in au)				
Electronic Energy	–72.95215	–73.49320	–76.03191	–72.60558
Nuclear Energy	21.48410	22.00617	24.65480	21.52185
Total Energy	–51.46805	–51.48703	–51.37711	–51.08373
Structure				
B–B (A)	1.775	1.683	1.528	2.343
B–H (A)	1.199	1.202	1.172	–
B–H_{br} (A)	–	–	1.296	1.531
∠HBH	116.2°	116.2°	–	–
∠BH_{br}B	–	–	72.2°	99.8°
Populations				
B s	3.028	3.000	2.780	3.868
p	1.977	2.036	2.369	1.221
total	5.005	5.036	5.149	5.089
H	0.998	0.982	0.912	–
H_{br}	–	–	0.939	0.955
Overlap Populations				
B–B	0.715	0.848	1.093	–0.782
B–H	0.838	0.815	0.798	–
B–H_{br}	–	–	0.374	0.222

tances and angles. The B–B bond distances in B_2F_4, B_2Cl_4, B_2H_6 and $B_2H_4(CO)_2$ are of the same order as those calculated in the two models A and B.[14, 15, 18, 19] The ∠H_tBH_t bond angle and B–H_t bond lengths in B_2H_6 are 121.0° and 1.200 A, respectively,[19] which are also not too dissimilar from the calculated geometrical values.

The energy of rotation about the B–B bond in diborane(4) can be calculated from the energies given in Table III. This rotational energy, 50.99 kJ mol^{-1}, includes a relaxation energy term which is the contribution due to permitting the bond lengths and angles of the eclipsed model adopt their optimum values rather than retain those of the staggered configuration. A direct rotational energy resulting from the use of constant bond lengths and angles in the eclipsed and staggered conformations is calculated to be 57.25 kJ mol^{-1}. From these values it can be seen that the relaxation energy contribution, 6.26 kJ mol^{-1}, is small compared to the energy of direct rotation. By inspection of the direct rotational energies of B_2H_4 and $B_2H_4(CO)_2$, we can observe that the presence of extra substituents not unnaturally increases the barrier to rotation about the B–B bond.

We can now summarise the changes in the electronic structure of diborane(4) which occur upon carbonylation. Complexing increases the electron density of the boron atoms and decreases the population of the hydrogen 1*s* orbitals. The B–B bond population is smaller, while the B–H bond is more heavily populated upon the introduction of carbon monoxide. These changes are consistent with the corresponding geometrical transformations which involve a lengthening of the B–B bond, a shortening of the B–H bond and an increase in the number of groups interacting with a boron atom.

The preference of B_2H_4 for the staggered configuration is in contrast to ethylene and aminoborane, which opt for a planar geometry.[15, 20] This structural difference emanates from the presence of two extra electrons in the latter molecules. These occupy a π orbital which thereby confers extra stability to the planar conformation. Calculations were performed on $B_2H_4^{2-}$, using the structural parameters of model B, in order to demonstrate the effect of two additional electrons on the choice of geometry. It was found that the eclipsed, *i.e.* planar, form of $B_2H_4^{2-}$ is more stable. Moreover, when further calculations were carried out to obtain the optimised B–B bond length of both rotamers, it was discovered that the staggered rotamer is an unstable species whose energy becomes more stable as the B–B bond lengthens and in the limit approaches the energy of two BH_2^- species. Conversely, the planar form is able to accommodate the additional two electrons which occupy the π orbital. Furthermore, the optimum B–B bond length (1.604 A) is much smaller than the corresponding distance in the neutral molecule for either configuration. It is undoubtedly the formation of the π bond which causes the contraction of the B–B bond.

We can use the foregoing information to explain the relatively small energy barrier to rotation about the boron–boron bond of the diboron tetrahalides.[21,22] The planar conformation of these molecules will possess a partial π bond between the boron atoms. This π bond, which originates from the conjugation of the boron–halogen π-bonding system, will preferentially stabilise the planar form of the tetrahalide species and hence reduce the energy difference between the two conformers.

Model C

Inspection of the optimised geometry values of the four models presented in Table III reveals that model C has the smallest B–B, B–H_t and B–H_{br} bond distance. It is not surprising, therefore, that the nuclear repulsion energy is large while the overlap populations are high. The bonding in this structure consists of strong boron–hydrogen bonds in addition to a heavily populated boron–boron bond.

Reorganisation of the optimised structure of B_2H_4 to the geometry of model C requires 288.4 kJ mol^{-1}, which is perhaps too excessive for model C to be considered an easily obtainable intermediate. The bonding situations of the two geometries are so different, however, that it is possible for the hydrogen-bridged structure to be obtained in a reaction and not necessarily rearrange to the geometry of model B.

Model D

The comparatively high energy of this model precludes the formation of this geometry even as a high energetic intermediate. It can be deduced from the overlap populations that there is no B–B bond while the bonding electrons are associated with the B–H–B bridging system. The electron distribution of the boron atom is worthy of attention due to an uncharacteristically large *2s* density and a low *2p* population. The former arises from a valence orbital of B_2H_4 consisting of a linear combination of boron *2s* orbitals. The participation of the boron *p* orbitals within the bonding scheme is minimal resulting in a boron $p\pi$ population of only 0.34 electrons.

Comparison of the structures of models C and D with the geometry of diborane(6)[19] is worthy of comment. The B–B and B–H_{br} bond distances (17.62 nm and 13.20 nm, respectively) of B_2H_6 are intermediate between the values of the two models, with a closer agreement to model C. It is interesting to note that the B–B bond lengths of model A and B_2H_6 are similar. The gross features of the bonding in B_2H_6, as indicated by the overlap population values, consist of strong boron–hydrogen bonds plus a weak boron–boron bond. This differs, therefore, from model C, due to the presence of a second B–H_t bond and a weaker B–B bond. However, the total overlap bond populations about the boron atom in both compounds are remarkably similar (2.67 and 2.64 for B_2H_6 and B_2H_4, respectively). It is not too difficult to perceive that B_2H_4, with a geometry of model C, could be a degradation product of diborane(6) if the hydrogen bridge bonds are not broken in the process.

Electronic Structure of B_3H_7 and B_3H_7CO

The structure of B_3H_7 is also unknown. The number of structural parameters present in this borane precludes a complete geometrical optimisation by energy minimisation techniques. It was therefore assumed that B_3H_7 had the same overall geometry as the triborane portion of B_3H_7CO except for the $H_1B_1H_2$ portion. Calculations were performed in which the $H_1B_1H_2$ fraction was positioned (i) in the same plane as the BBB triangle (ii) perpendicular to the triangle and (iii) in the same conformation as found in B_3H_7CO. It is found that the most stable geometry about the B_1 atom occurs when the BH_2 unit is coplanar with the BBB triangle. Rotation of the BH_2 moiety to the perpendicular position produces an energy destabilisation of 75.6 kJ mol^{-1} while reorganisation of the borane into a configuration appropriate for complexing with a carbonyl group requires 9.76 kJ mol^{-1}. This latter value is low compared to the reorganisation energy of borane[10], which involves the transformation of three boron-hydrogen bonds.

Comparison of the electronic populations of B_3H_7 and B_3H_7CO presented in Table I reveals that carbonylation increases the electron density of the boron atom B_1. It is the *p* orbital which is perpendicular to the triangular boron plane which especially benefits by complexing, with an increase in electron density from 0.024 to 0.441. The hydrogen atoms bonded to B_1, however, incur a loss of electron density upon the formation of B_3H_7CO. This is in contrast to the gain in electron density experienced by a terminal hydrogen atom of B_2 and B_3, *i.e.,* H_3 and H_6. The overlap population data indicate that the triangular framework boron–boron populations are significantly reduced by combination with carbon monoxide. The π component of the B_1–B_2 bond is 0.013 and –0.008 for B_3H_7 and B_3H_7CO, respectively, indicating that the interaction between the boron atoms is strictly in the BBB plane. Also of interest is the value of the bond population between atoms B_2 and H_1 (and the corresponding B_2–H_2 bond) – for B_3H_7 this totals 0.020, while for B_3H_7CO we obtain 0.043. The latter is not an insignificant quantity and hence, with a stronger donor ligand, it could well be envisaged that the B–B bonds of the triangular structure could become further depleted with an additional increase in these hydrogen bridging bonds.

The electronic situation within the BBB triangle is best illustrated by an electron density plot. It is found that the electron topography in the plane of the boron atoms is only slightly altered by the presence of a carbonyl group. Inspection of the accompanying electron density grid at the midpoint of both the B–B and the bridging B–H bonds shows that B_3H_7CO has marginally less electron density at these positions than the parent borane. This corroborates the overlap population data, which also suggested that the stability of the triangular boron system is reduced by the coordination of the carbon monoxide. The electron density contours of the triangular BBB plane of B_3H_7CO are presented in Figure 2. The contour pattern fails to indicate the presence of strong boron–boron bonding. Instead, the bonding within the plane is dominated by the orbitals of B_1 as the in-plane orbitals of B_2 and B_3 are also involved in bonding to the bridging hydrogen and so their contribution to the electronic population of the BBB triangle is less. Therefore, the bonding within this area can be described as a distorted three-centre bond. The position of minimum electron density within the triangle, M, is marked on Figure 2 and is clearly closer to the boron atoms B_2 and B_3.

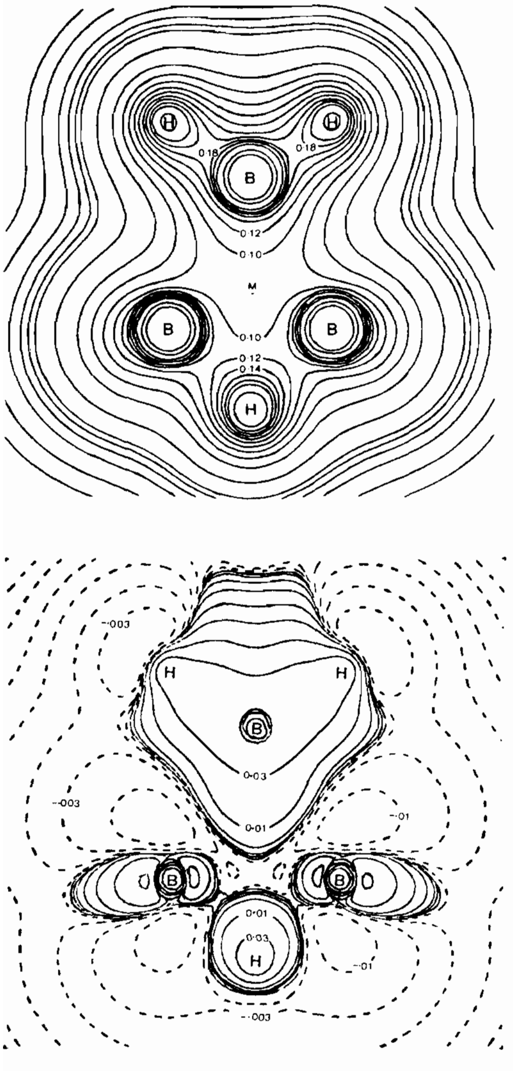

Figure 2. Electron density contours for B_3H_7CO, a section containing the BBB triangle. (a) Total electron density contours; (b) electron density difference contour. The broken lines indicate negative electron density differences while unbroken lines represent positive electron density differences.

In the formation of B_3H_7CO we can conclude that the coordination of the carbonyl moiety only marginally affects the bonding situation within the ring system. The CO bonds to the weakly electropositive boron atom of B_3H_7 and donates electrons into the π orbital of this boron atom. This decreases the π bonding within the BBB domain and augments the population of the boron–hydrogen bonds emanating from the coordinating boron.

References

1 G.T. Ter Haar, Sr. M.A. Fleming and R.W. Parry, *J. Am. Chem. Soc., 84,* 1767 (1962).
2 J.R. Spielman and A.B. Burg, *Inorg. Chem., 2,* 1139 (1963).
3 J.C. Carter and R.W. Parry, *J. Am. Chem. Soc., 87,* 2354 (1965).
4 J. Grotewold, E.A. Lissi and A.E. Villa, *J. Chem. Soc. A, 8,* 1034 (1966).
5 A.D. Norman and R. Schaeffer, *J. Am. Chem. Soc., 88,* 1143 (1966).
6 R. Schaeffer and E. Walter, *Inorg. Chem., 12,* 2209 (1973).
7 R.W. Parry, C.E. Nordman, J.C. Carter and G.T. Ter Haar, *Advan. Chem. Soc., 42,* 302 (1964).
8 A.B. Burg and H.I. Schlesinger, *J. Am. Chem. Soc., 59,* 780 (1937).
9 W. Gordy, H. Ring and A.B. Burg, *Phys. Rev., 75,* 208 (1949).
10 D.R. Armstrong and P.G. Perkins, *J. Chem. Soc. A,* 1044 (1969).
11 Y.C. Fu and G.R. Hill, *J. Am. Chem. Soc., 84,* 353 (1962).
12 R.T. Paine and R.W. Parry, *Inorg. Chem., 11,* 268 (1972).
13 J.D. Glore, J.W. Rathke and R. Schaeffer, *Inorg. Chem., 12,* 2175 (1963).
14 J. Rathke and R. Schaeffer, *Inorg. Chem., 13,* 760 (1974).
15 *'Interatomic Distances in Molecules and Ions', Chemical Society (London), Special Publication No. 11* (1958).
16 R.F. Stewart, *J. Chem. Phys., 52,* 431 (1970).
17 E. Clementi, *J. Chem. Phys., 40,* 1944 (1964).
18 R.R. Ryan and K. Hedberg, *J. Chem. Phys., 50,* 4986 (1969).
19 W.J. Lafferty, *J. Mol. Spectroscopy, 33,* 345 (1970).
20 D.R. Armstrong, B.J. Duke and P.G. Perkins, *J. Chem. Soc. A,* 2566 (1969).
21 R.R. Ryan and K. Hedberg, *J. Chem. Phys., 50,* 4986 (1969).
22 J.R. Duvig, J.W. Thompson, J.D. Witt and J.D. Odom, *J. Chem. Phys., 58,* 5339 (1973).