Molecular Geometry and Electronic Structure of Carbon Trioxide[1]

John F. Olsen[2] and Louis Burnelle

Contribution from the Department of Chemistry, New York University, New York, New York 10003. *Received June 9, 1969*

Abstract: The extended Hückel and INDO methods have been applied to various molecular geometries of CO_3 (pyramidal, symmetric trigonal, and Y-shaped). Both methods predict the Y-shaped structure (of C_{2v} symmetry) to be favored in the ground state, in agreement with infrared observations. The electronic ground state of the molecule is $^1A_1$, correlating with $^1E'$ in D_{3h} symmetry, so that the adoption of the C_{2v} symmetry can be related to the Jahn–Teller effect. The low value predicted by the INDO method for the unique OCO angle (65°), as well as the results of the electron-population analysis, strongly suggest a closed-ring structure for the compound, with a carbonyl bond.

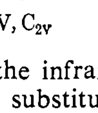
Carbon trioxide, CO_3, has recently been isolated and identified by Moll, Clutter, and Thompson,[3] using a matrix isolation technique. This unusual oxide of carbon was first postulated by Katakis and Taube[4] as a kinetic intermediate in the reaction of oxygen atoms and CO_2. Carbon trioxide is, to our knowledge, the first reported 22-valence electron AB_3-type molecule. AB_3 molecules containing 24, 25, or 26 valence electrons are of course well known,[5] *e.g.* NO_3^-, CO_3^{2-}, ClO_3, and IO_3^-. These AB_3 molecules have planar or pyramidal structures in their ground electronic states.[5] At present, only spectrally detectable quantities of CO_3 have been prepared and the most important method of preparation of the compound is probably the photolysis of solid CO_2 at 77°K using a xenon resonance lamp.[6] The most probable reactions leading to the production of CO_3 are[6]

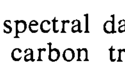
$$CO_2 \xrightarrow{h\nu} CO_2^* \longrightarrow CO + O\ (^1D)$$

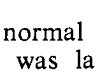
$$CO_2 + O\ (^1D) \longrightarrow CO_3$$

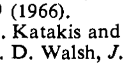
where CO_2^* represents an electronically excited CO_2 molecule.

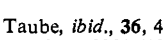
Moll, *et al.*,[3] have considered structures I–VI as reasonable for a species resulting from the reaction of an oxygen atom with a CO_2 molecule. However, the analysis[3] of the infrared spectral data of normal and isotopically substituted carbon trioxide was largely in favor of a planar C_{2v} molecule, namely III.

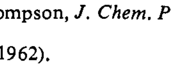

I, D_{3h}


II, C_{3v}


III, C_{2v}


IV, C_{2v}


V, $C_{\infty v}$


VI, C_s

We wish to present herein the results of some extended Hückel[7] (XHMO) and some INDO[8] molecular orbital calculations on CO_3. The computational details have been presented elsewhere[7,8] and will not be given herein. The calculations have been carried out by assuming the three bond lengths equal to 1.20 Å throughout.

Results and Discussion

The major part of this study is focused primarily on the D_{3h}, C_{3v}, and C_{2v} symmetry species of CO_3. All of these species are related *via* an angular displacement of the internal coordinates and they presumably result from the reaction of a singlet oxygen atom with a CO_2 molecule at the carbon center of the latter.[3,6] The other species that are possible for CO_3 (IV–VI) apparently result from the interaction of a singlet oxygen with an oxygen center of the CO_2 molecule.[3,6] Extensive bond-length minimization procedures would be necessary to find the most stable structure for these latter species. We have elected not to undertake in this work any absolute minimization, especially in view of the fact that the computational methods used are not to be trusted, in general, for their bond-length information.[8,9] The computational methods do generate accurate information when only bond-angle variations are considered, however.[9,10] Consequently, we have assumed as a first approximation that the D_{3h} species of CO_3 can be related to the C_{3v} and the C_{2v} species by means of bond-angle variations only, leaving all CO bond lengths fixed at 1.20 Å.

The XHMO calculations predict the two highest energy electrons of D_{3h} CO_3 to reside in a degenerate molecular orbital, namely 3e′. According to the extended Hückel method, a distortion to a pyramidal C_{3v} species is not predicted to occur. Thus, when the bond angle is 105° the C_{3v} structure lies 2.14 eV higher in energy than the D_{3h} configuration; for a bond angle of 90° it lies 7.03 eV higher than the latter. On the other hand, as will be seen shortly, the XHMO method predicts that an in-plane distortion of CO_3 leading to a C_{2v} symmetry species is very favorable. We illustrate in Figure 1 the XHMO orbital-energy correlation diagram for CO_3. It gives the orbital energies *vs.* an in-plane OCO angular distortion.

---

[1] Work supported by the U. S. Army Research Office (Durham).
[2] Address correspondence to: Department of Chemistry, Staten Island Community College, Staten Island, N. Y. 10301.
[3] N. G. Moll, D. R. Clutter, and W. E. Thompson, *J. Chem. Phys.*, **45**, 4469 (1966).
[4] D. Katakis and H. Taube, *ibid.*, **36**, 416 (1962).
[5] A. D. Walsh, *J. Chem. Soc.*, 2301 (1953).
[6] K. V. Krishnamurty, *J. Chem. Educ.*, **44**, 594 (1967).
[7] J. F. Olsen and L. Burnelle, *J. Phys. Chem.*, **73**, 2298 (1969).
[8] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
[9] L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, **71**, 1060 (1967).
[10] J. A. Pople, D. L. Beveridge, and N. S. Ostlund, *Intern. J. Quant. Chem.*, **1**, 293 (1967).

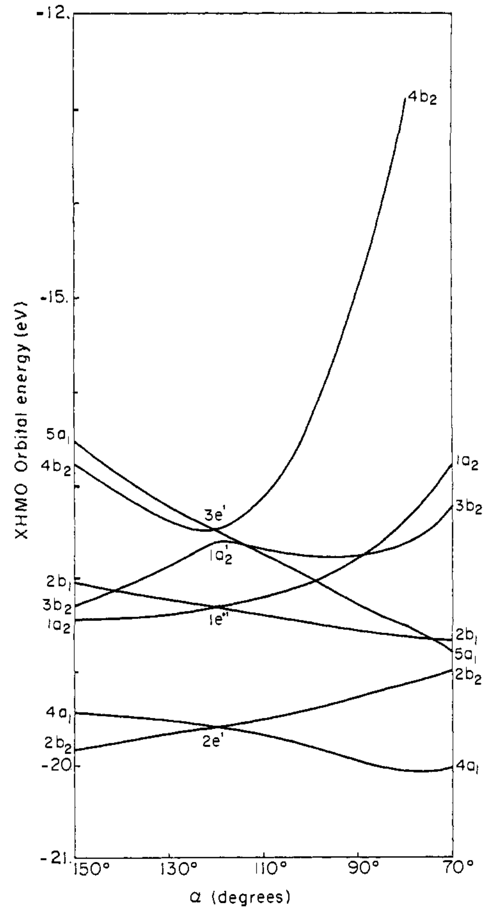


Figure 1. XHMO orbital energy diagram of CO_3, as a function of the unique OCO angle α.

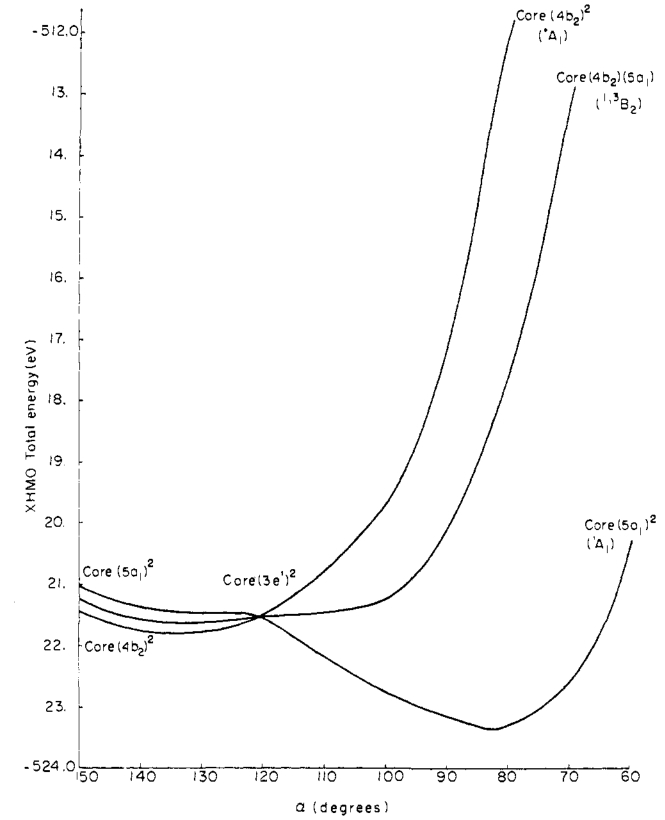


Figure 2. Energies of the lower configurations of CO_3 as a function of in-plane bending.

(The abscissa is the unique OCO angle, which is labeled α.) It is essentially a Walsh[5] correlation diagram for AB_3 molecules, although Walsh in constructing diagrams for AB_3 systems considered only the out-of-plane distortion leading to a pyramidal structure. For clarity, the five lowest and the four highest energy molecular orbitals have been omitted from Figure 1. Of the two components of the degenerate 3e′ molecular orbital, the $4b_2$ level is seen to rise sharply as α decreases from 120°, due to the repulsive interaction with the $3b_2$ molecular orbital (this is an application of the noncrossing rule). The other component, namely $5a_1$, is seen, on the other hand, to sharply stabilize at low values of α. It is primarily this stabilization of the $5a_1$ molecular orbital that accounts for the low calculated unique equilibrium angle in CO_3 (*vide infra*).

The configuration $(3e')^2$ gives rise to three electronic states, namely $^3A_2'$, $^1E'$, and $^1A_1'$. They most probably lie in the order given here, the triplet being the lowest. Since the extended Hückel method does not take the interelectronic repulsion explicitly into account, it cannot make a distinction between the three states, which are predicted to coincide. As the molecule distorts to C_{2v} symmetry, the splitting of the 3e′ orbital enables the extended Hückel method to distinguish three states, corresponding respectively to the three configurations $(5a_1)^2$, $(5a_1)(4b_2)$, and $(4b_2)^2$ (outside a core). Their energies *vs.* the unique OCO angle α are plotted in Figure 2. The energy of the $(5a_1)^2$ configuration exhibits a very deep minimum in the vicinity of $\alpha = 82°$, that of $(4b_2)^2$ a shallow minimum around 135°. The state associated with $(5a_1)(4b_2)$ has a shallow minimum near 130°. As a matter of fact, this is actually a mixture of singlet and triplet states and in the case where the splitting of the degenerate orbital is small, it may happen that the triplet is actually the ground state. However, in CO_3 the splitting is remarkably large (4.95 eV) at the equilibrium angle predicted for the $(5a_1)^2$ configuration, so that on the basis of the extended Hückel results one can predict that the ground state of CO_3 is $^1A_1$ (correlating with $^1E'$ in D_{3h} symmetry). Its electronic configuration is predicted to be $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2(4a_1)^2(2b_2)^2(2b_1)^2(5a_1)^2(3b_2)^2(1a_2)^2$: $^1A_1$.

For values of α larger than 120°, the splitting of the 3e′ orbital is considerably smaller. At the angle minimizing the energy of the $(4b_2)(5a_1)$ configuration, the splitting amounts to 0.15 eV only. Under those conditions it is most probable that the triplet is actually the lowest state for these values of the angle. In a study on methylenes, Hoffmann[11] has proposed a criterion according to which the triplet state is the lowest when the splitting is less than 1.5 eV. Even if we do not know the form the criterion should take in CO_3, in the case under discussion the splitting is so small that there is little doubt that our conclusion is valid. According to Hund's rule, the triplet must be the lowest state for the symmetric trigonal arrangement of the molecule. One may thus deduce that the curve of the triplet ($^3B_2$, correlating with $^3A_2'$ in D_{3h} symmetry) intersects the curve of the ground state ($^1A_1$) for α smaller than 120° and remains the lowest state for larger values of α.

---

[11] R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968); R. Hoffmann, *ibid.*, **90**, 1475 (1968).

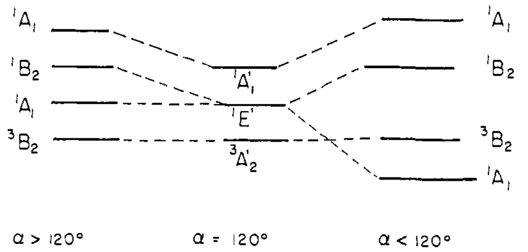


Figure 3. Schematic diagram of the lowest states of CO_3.

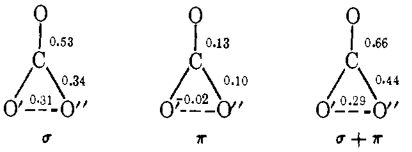
A very approximate diagram for the states associated with the electronic configuration $(3e')^2$ is presented in Figure 3. The geometry adopted by the triplet is hard to predict from the extended Hückel results; we will see that the application of the INDO method brings useful information on this state. It is also to be noted that, for small values of α, the crossings of various orbital energy levels (see Figure 1) must cause a number of excited states to lie between the levels indicated on the diagrams. We have simplified the discussion by ignoring these various excited states.

The distortion of the $^1E'$ state of CO_3 may be viewed as a manifestation of the Jahn–Teller effect,[12] in the sense that we observe an instability of the degenerate electronic state with respect to a nontotally symmetric displacement of the nuclei. In the mathematical formulation of their theorem, Jahn and Teller consider the removal of the degeneracy by the effect of normal coordinates; the distortion we have introduced cannot be associated with a normal mode of vibration, but it could be approximated by an expansion in terms of several coordinates.

We have applied the INDO procedure to the lowest singlet ($^1A_1$–$^1E'$) as well as to the lowest triplet ($^3B_2$–$^3A'_2$) of the system. The single determinantal wave function we have used for the singlet is not adequate in the vicinity of $\alpha = 120°$ because of the important configuration interaction which must manifest itself in that region. For the trigonal arrangement of the bonds the wave function does not transform according to an irreducible representation of D_{3h}, but according to a representation of a subgroup of D_{3h}, namely C_{2v}. The equilibrium angle of the singlet state is predicted to be 65°, somewhat smaller than the extended Hückel value. This low value of the angle strongly suggests a closed-ring structure for the compound. It will be seen that this point is consistent with the results of the electron-population analysis. It is of interest to note that cyclopropanone, which is isoelectronic with CO_3, exists in the gas phase in the closed-ring form,[13] and that the angle corresponding to α has been found equal to 64.5° in this molecule.[14] The curve of the triplet is very shallow over the range covered by α in the calculations. It shows a minimum at 71°, lying some 4.7 eV above the singlet state. The two curves intersect each other in the region between 90 and 100° and the triplet remains below the singlet for larger values of α, as suggested by the extended Hückel results. The empirical criterion employed in the XHMO method is thus substantiated by the INDO results.

It is encouraging to note that both methods used in this work point to a C_{2v} structure for the molecule, in agreement with the infrared characterization of Moll, *et al.*[3] The following ground-state electronic configuration of CO_3 results from the INDO calculations: $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(5a_1)^2(2b_1)^2(1a_2)^2(3b_2)^2$: $^1A_1$. There are seen to be some inversions of the individual molecular orbitals in the INDO picture compared with the ordering resulting from the XHMO calculations. The differences are primarily due to the overstabilization of the π-molecular orbitals by the INDO method.[7]

Further information on the electronic structure of the compound is provided by the results of the Mulliken population analysis.[15] The extended Hückel wave function yields the following overlap populations (at the calculated equilibrium bond angle)



The populations associated with the unique CO bond are very close to those calculated for the corresponding bond in formaldehyde (σ, 0.51; π, 0.15). This bond thus appears to be essentially of the carbonyl type, according to the XHMO theory. This is consistent with the findings of Moll, *et al.*,[3] who identify the carbonyl stretch with an intense infrared band they observe at 2045 cm^{-1}.

In spite of the fact that we have used three equal bond lengths in the calculations, the overlap populations of the two equivalent CO bonds are definitely smaller. Furthermore, the sizable positive overlap population between the two symmetry-equivalent oxygens reveals the presence of a formal bond between these two atoms.

In the INDO method, since the basis set is assumed to be orthogonal, the populations are directly obtained from the first-order density matrix, the elements of which are given by

$$P_{\mu\nu} = \sum_i^{\text{occ}} N_i C_{i\mu} C_{i\nu}$$

where N_i is the orbital occupation number, the $C_{i\mu}$'s are the LCAO expansion coefficients in MO i, and the summation extends over all occupied MO's. The on-diagonal matrix elements ($P_{\mu\mu}$) represent the orbital charge density, while the off-diagonal elements ($P_{\mu\nu}$) represent orbital bond orders. These orbital bond orders can be taken as an indication of the degree of bonding between two atomic orbitals. The atomic charge densities are easily obtained as follows

$$P_{AA} = \sum_\mu^A P_{\mu\mu}$$

where the summation is over all atomic orbitals on atom A.

In order to have an idea of the type of bonding present in CO_3 we have taken the license of calculating a quantity called the total bond order defined as

$$P_{AB} = \sum_\mu^A \sum_\nu^B P_{\mu\nu}$$

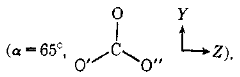
---

[12] H. A. Jahn and E. Teller, *Proc. Roy. Soc.*, **161A**, 220 (1937).

[13] J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, 90, 1072 (1968).

[14] J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *ibid.*, **91**, 1896 (1969).

[15] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

Table I. INDO First-Order Density Matrix for CO_3 ($\alpha = 65°$, ).

Atom	Orbital	C				O				O′			
		2s	$2p_x$	$2p_y$	$2p_z$	2s	$2p_x$	$2p_y$	$2p_z$	2s	$2p_x$	$2p_y$	$2p_z$
C	2s	0.946	0	0.136	0	0.278	0	−0.650	0	0.256	0	0.389	0.151
	$2p_x$	0	0.726	0	0	0	0.774	0	0	0	0.404	0	0
	$2p_y$	0.136	0	0.759	0	0.397	0	−0.573	0	−0.283	0	−0.295	−0.227
	$2p_z$	0	0	0	0.830	0	0	0	0.399	−0.253	0	−0.580	0.079
O	2s					1.774	0	0.404	0	0.021	0	−0.016	0.034
	$2p_x$					0	1.530	0	0	0	−0.245	0	0
	$2p_y$					0.404	0	1.246	0	0.024	0	0.109	−0.019
	$2p_z$					0	0	0	1.864	0.082	0	0.198	−0.038
O′	2s									1.728	0	−0.267	0.210
	$2p_x$									0	1.872	0	0
	$2p_y$									−0.267	0	1.520	−0.050
	$2p_z$									−0.368	0	−0.050	1.042
O″	2s									0.046	0	−0.022	−0.210
	$2p_x$									0	−0.128	0	0
	$2p_y$									−0.022	0	0.095	0.144
	$2p_z$									0.210	0	−0.144	−0.844

where P_{AB} is the total bond order between the atoms in question. Some caution must be exercised when summing the $P_{\mu\nu}$ terms, so as to ensure that bonding effects always give positive contributions to the total bond order. This is due to the constraints imposed on some orbital bond order terms by the choice of coordinate axes,[16] *i.e.*, some $P_{\mu\nu}$ terms necessarily appear antibonding whereas in fact they contribute a positive bonding effect. Consequently, in taking the summation over all pairs of σ atomic orbitals (π orbitals offer no difficulty), we have made the appropriate changes of sign. In addition, we have only carried out this procedure for the unique CO bond and the O′O″ bond since it was too difficult to decide whether a given $P_{\mu\nu}$ for the CO′ (or CO″) bond was in fact bonding or antibonding (the axes chosen were oriented as indicated in Table I).

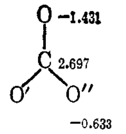
Table I records the INDO charge density–bond order matrix for CO_3 at its equilibrium angle. The following total bond orders are then obtained from the matrix elements of Table I

	CO	O′O″
σ	2.30	1.40
π	0.77	−0.13
$\sigma + \pi$	3.07	1.27

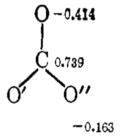
Applying the same procedure to the CNDO/2 wave function of formaldehyde gives a CO total bond order of 3.17 (σ, 2.18; π, 0.99). These quantities are seen to be remarkably similar to the ones found for the unique bond of CO_3. Thus the INDO method confirms the existence of a unique CO bond quite similar to a carbonyl bond. In addition, as seen from Table I, the INDO π-bond order is much larger for the unique CO bond (0.77) than it is for either of the two symmetry equivalent CO bonds (0.40). This appears to be a more logical picture than the one resulting from the XHMO treatment.

The quantity $P_{O'O''}{}^{\sigma}$ was obtained by neglecting the matrix elements $P_{s'y''}$ and $P_{z'y''}$. There is seen to be a moderately strong σ bond between the two symmetry equivalent oxygen atoms. This σ bond, as seen from Table I, is primarily due to the $2p_z$ atomic orbitals on each oxygen atom. There is also seen to be a weak π-antibonding effect. Both the INDO and the XHMO methods are in agreement as to the existence of a formal σ bond between the two equivalent oxygens, with a small π-antibonding character.

Both methods give a positive charge on carbon, and a negative charge on the carbonyl oxygen which is larger than on the other two. The computed values are

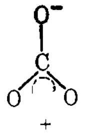


XHMO



INDO

As might be expected, the XHMO charges are grossly exaggerated in comparison to the SCF results. A look at Table I reveals that the unique oxygen atom is the only atom carrying an excess of negative charge in the π framework. Consequently, we could write the following structure for CO_3 in the π framework



A similar structure has been proposed by Turro, *et al.*,[17] for the reactions of cyclopropanone and its derivatives.

While this work was in progress, a paper on the electronic structure of CO_3 has appeared by Gimarc and Chou.[18] These workers carried out extended Hückel calculations on various geometries of CO_3, and the results obtained were similar to ours, namely a *Y-shaped* molecule was found to be the most stable structure. However, apparently due to their choice of parameters their ordering of the one-electron levels is somewhat different from ours. This is notably apparent at the trigonal arrangement (D_{3h}) where they find the 3e′ level below the $1a_2{}'$ level. Consequently, in the trigonal arrangement, according to their results, the molecule is not orbitally degenerate, and a Jahn–Teller distortion is not *a priori* predicted to occur. These workers have

---

(16) J. A. Pople and G. A. Segal, *J, Chem, Phys.*, **43**, S136 (1965).

(17) N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *J. Amer. Chem. Soc.*, **91**, 2283 (1969), and references cited therein.

(18) B. M. Gimarc and T. S. Chou, *J. Chem. Phys.*, **49**, 4043 (1968).

also calculated CO_3 in which the unique CO bond length was 1.15 Å and the symmetry equivalent bond lengths were 1.40 Å (Moll's[3] parameters). The unique angle found by Gimarc and Chou occurred around 90°. We have also carried out INDO calculations for this CO_3 species with the results that the unique angle occurs in the vicinity of 60–55°, again consistent with a closed-ring structure for this compound.

Conclusions

The two quantum-mechanical methods used in this work confirm the deductions of Moll, *et al.*,[3] that the CO_3 molecule belongs to the C_{2v}-point group, although we have not investigated the stability of species IV–VI. On the basis of our calculations, one can relate the adoption of the C_{2v} structure to the Jahn–Teller effect; the trigonal (D_{3h}) arrangement is unstable because the singlet wave function is degenerate.

The bond populations provided by both methods suggest a closed-ring structure for the compound, similar to the one found experimentally for cyclopropanone.[13,14] The equilibrium bond angle calculated by the XHMO method appears somewhat large for such a structure, whereas the INDO angle is more reasonable; it is possible that the use of two different bond lengths for the two types of CO bonds would reduce the discrepancy between the two methods on this point.

Acknowledgments. A grant of computer time at the Courant Institute Computation Center of New York University is gratefully acknowledged. We also wish to express our sincere thanks to Dr. D. L. Beveridge for making available to us his INDO program.

Chelate Adducts of a Difunctional Lewis Acid. 1,2-Bis(difluoroboryl)ethane. III[1,2]

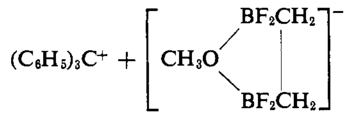
Michael J. Biallas

Contribution from the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115. *Received June 23, 1969*

Abstract: Chelate adducts are formed when $F_2BCH_2CH_2BF_2$ reacts either with triphenylmethylamines in CH_2Cl_2 or with 1,3,5-cycloheptatrienyl-7 methyl ether; *e.g.*, see eq 5. Unchelated 1:1 adducts are formed when $F_2BCH_2CH_2BF_2$ reacts with triphenylmethylamines in a nonpolar solvent or with 1,3,5-cycloheptatrienyl-7-N,N-dimethylamine; *e.g.*, see eq 3.

The difunctional Lewis acid 1,2-bis(difluoroboryl)ethane reacts with triphenylmethyl ethers to produce "chelated" 1:1 adducts.[1] In these reactions a C–O bond is cleaved in order to form (a) a resonance-stabilized organic cation, and (b) an anion which has two boron atoms coordinated to a single oxygen atom. For example

$(C_6H_5)_3COCH_3 + BF_2CH_2CH_2BF_2 \longrightarrow$


(1)

The generality of this reaction has now been evaluated by examining the reactions of 1,2-bis(difluoroboryl)ethane with triphenylmethylamines, 1,3,5-cycloheptatrienyl-7 methyl ether, and 1,3,5-cycloheptatrienyl-7-N,N-dimethylamine. This group of Lewis bases allows variation in the identity of both organic cation and the donor atom.

Experimental Section

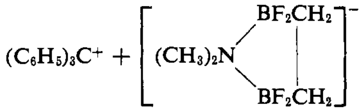
Materials. The following compounds were prepared according to procedures given in the literature: triphenylmethylamine, mp 103° (lit.[3] 103°); N,N-dimethyltriphenylmethylamine (*via* an analogous procedure) (*Anal.* Calcd: C, 87.76; H, 7.37, N, 4.87. Found: C, 87.67; H, 7.37; N, 4.52); 1,3,5-cycloheptatrienyl-7 methyl ether,[4] and 1,3,5-cycloheptatrienyl-7-N,N-dimethylamine,[5] (the latter two compounds were characterized *via* nmr[6]). All solvents were stored over molecular sieves and distilled before use.

Techniques. Most of the compounds used in these studies were air sensitive, so manipulations were performed on a vacuum line or in a glove bag. Tared samples of each donor were dissolved in the chosen solvent, and a known amount of the difunctional Lewis acid was added by means of a calibrated bulb. Solution mixing was done by a solenoid stirrer. After completion of the reaction, solvent and excess acid (if any) were removed and analyzed. Visible and ir spectra of the adducts (all were solids) were obtained as both hydrocarbon and halocarbon mulls on a Cary Model 14 and a Beckman IR-12 instrument, respectively. C, H, and N analyses were obtained on a Perkin-Elmer 240 analyzer, and nmr spectra were obtained on a Varian A-60 spectrometer.

Results and Discussion

Triphenylmethylamines. A chelate adduct is obtained exclusively when N,N-dimethyltriphenylmethylamine reacts with 1,2-bis(difluoroboryl)ethane in methylene chloride solvent, *i.e.*

$(C_6H_5)_3CN(CH_3)_2 + BF_2CH_2CH_2BF_2 \xrightarrow{CH_2Cl_2}$


(2)

---

[1] Part II: D. F. Shriver and M. J. Biallas, *J. Amer. Chem. Soc.*, **89**, 1078 (1967).

[2] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., Spring 1969.

[3] C. A. Krause and R. Rosen, *J. Amer. Chem. Soc.*, **47**, 2739 (1925).

[4] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[5] W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957).

[6] G. W. Borden, O. L. Chapman, R. Swindell, and T. Tezuka, *ibid.*, **89**, 2979 (1967).