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Charge-Transfer Complexes. NH_3–F_2, NH_3–Cl_2, NH_3–ClF, $N(CH_3)_3$–F_2, $N(CH_3)_3$–Cl_2, and $N(CH_3)_3$–ClF

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Abstract: Nonempirical electronic structure theory has been applied to several charge-transfer complexes, which involve ammonia and trimethylamine as electron donors, and molecular fluorine, chlorine, and ClF as electron acceptors. The self-consistent field calculations employed both minimum and double-ζ basis sets of contracted Gaussian functions. For NH_3–F_2 and NH_3-ClF, the importance of d functions on the N, F, and Cl atoms was investigated. In several cases the minimum basis results do not appear reliable. With the geometries of the donor and acceptor molecules fixed from experiment, the equilibrium geometries of the charge-transfer complexes were predicted. N–X (X = nearest halogen atom) distances are 3.08 Å (NH_3–F_2), 2.93 Å (NH_3–Cl_2), and 2.65 Å (NH_3–ClF), while the predicted binding energies are 0.6 kcal (NH_3–F_2), 2.4 kcal (NH_3–Cl_2), and 7.7 kcal (NH_3–ClF). NH_3–FCl is predicted to be bound by less than 0.1 kcal/mol. The most intriguing prediction is that the binding energies of the ammonia complexes are greater than those of the corresponding trimethylamine complexes. Although this prediction is in distinct disagreement with accepted chemical intuition, it is consistent with Mulliken populations, which suggest a significantly greater "negative charge" on the ammonia N atom than that for trimethylamine. Further, the dipole moment of NH_3 is significantly larger than that of $N(CH_3)_3$.

The term "charge-transfer complex" was introduced by Mulliken[2a] in 1950 in his explanation of the observation by Benesi and Hildebrand[2b] of a new absorption band in a solution of benzene and iodine dissolved in *n*-heptane. The observed band did not appear in the spectra of either C_6H_6 or I_2. Mulliken stated that the color of such organic molecular complexes "may be due to an intermolecular charge-transfer process during light absorption". These early experimental and theoretical investigations signaled the beginning of a period of intense interest[3-9] in the properties of donor-acceptor complexes, and this interest continues to accelerate. A particularly visible example of current interest is the complex between tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ).[10] TTF-TCNQ behaves like a one-dimensional metal at room temperature and has rekindled hopes for the eventual discovery of a practical organic superconductor.

A particularly thorny question concerns the relative importance of charge-transfer and classical electrostatic forces in the ground state of complexes such as C_6H_6–I_2. While Mulliken's early work[1,11] successfully exploited the charge-transfer model, more recent work by Hanna[12] and by Stiles[13] has emphasized the electrostatic considerations, e.g., the quadrupole-induced dipole interaction in C_6H_6–I_2. In their most recent paper on the subject, Mulliken and Person[14] conclude that electrostatic forces are likely to dominate the bonding only for the weakest donor-acceptor complexes. In this regard it should be noted that the quantitative energy decomposition scheme recently proposed by Morokuma[15] might be valuable in resolving the above controversy.

Perhaps surprisingly, there have been very few ab initio theoretical studies reported on charge-transfer complexes. An early study, that of Clementi[16] on the NH_3·HCl complex, suggested a large binding energy (19.5 kcal/mol relative to the separated molecules) and a considerable similarity with the idealized ionic $NH_4^+Cl^-$ model. Another molecular complex that has been studied ab initio is BH_3–NH_3, which Veillard and Palke find[17] to have a rotational barrier comparable to ethane.

In the present paper we report the first ab initio calculations on charge-transfer complexes involving halogen molecules. Halogen molecules are obvious candidates in this regard because of their substantial electron affinities:[18] F_2 (3.08 ± 0.10 eV), Cl_2 (2.38 ± 0.10 eV), Br_2 (2.51 ± 0.10 eV), and I_2 (2.58 ± 0.10 eV). Although known to be substantial, the experimentally determined electron affinities of the interhalogen diatomics are less certain:[19] FCl (~2.7 eV).

Our natural inclination was to study the classic benzene-halogen systems. And, in fact, nonempirical studies employing a minimum basis set were completed for C_6H_6–F_2 and C_6H_6–Cl_2. For axial (C_{6v}) approaches the predicted equilibrium distances from the center of the benzene ring to the nearest halogen atom were 3.63 Å (C_6H_6–F_2) and 4.18 Å (C_6H_6–Cl_2). However, the binding energies relative to the infinitely separated molecules were calculated to be only 0.03 and 0.06 kcal/mol. Since the uncertainty in the theo-

Table I. Experimental Binding Energies[20] of Several Amine–Iodine Charge-Transfer Complexes

Electron donor	Ionization potential, eV	ΔH, kcal/mol
NH_3	10.15	-4.8
$NH_2(CH_3)$	8.97	-7.1
$NH_2(C_2H_5)$	8.86	-7.4
$NH(CH_3)_2$	8.24	-9.8
$NH(C_2H_5)_2$	8.01	-9.7
$N(CH_3)_3$	7.82	-12.1
$N(C_2H_5)_3$	7.50	-12.0

Table II. Theoretical Predictions of the Structures, Dissociation Energies (ΔE), and Dipole Moments (μ) of Several Amine–Halogen Molecular Complexes[a]

Complex	R(N–X), Å	E, hartrees	ΔE, kcal/mol	μ, D
H_3N–F_2				
MBS	2.81	−251.4209	0.43	1.93
DZ	3.08	−254.8845	0.60	2.68
Extended	3.08	−254.8884	0.62	2.68
Polarized	3.04	−254.9338	0.79	2.27
H_3N–Cl_2				
MBS	2.95	−964.5674	1.09	2.33
DZ	2.93	−975.1008	2.38	3.41
H_3N–FCl				
MBS	2.71	−607.9855	0.93	2.52
DZ	Repulsive potential curve[b]			
H_3N–ClF				
MBS	3.32	−607.9843	0.17	1.45
DZ	2.65	−615.0190	7.66	5.06
Polarized	2.62	−615.0866	7.42	4.49
$(CH_3)_3N$–F_2				
MBS	2.84	−367.1551	0.32	1.12
$(CH_3)_3N$–Cl_2				
MBS	3.01	−1080.3015	0.83	1.46
$(CH_3)_3N$–FCl				
MBS	2.76	−723.7195	0.70	1.71
$(CH_3)_3N$–ClF				
MBS	3.39	−723.7186	0.12	0.63

[a] Here X signifies the halogen atom closest to the nitrogen nucleus. Several types of basis sets were used in these self-consistent field calculations, including minimum basis sets (MBS) and double-ζ (DZ) sets. [b] At R(N–X) = 2.71 Å, the interaction is repulsive by 4.35 kcal/mol.

retical method used is at least 1 kcal/mol, the value of the calculations is severely limited, except to establish that the attractions are indeed rather weak. For C_6H_6-F_2, several other orientations of approach were also considered, but most proved to be repulsive.

Given this unsatisfactory initial experience, a decision was made to pursue a series of more strongly bound charge-transfer complexes. A review of the literature[3-9] suggested the amine-halogen complexes as an important series of model compounds with the desired property. Particularly important in this regard is the work of Nagakura and coworkers[20,21] on amine-iodine complexes in solution (usually *n*-heptane). Their experimental ΔH values are summarized in Table I, which also gives the ionization potentials of the electron-donor amines. There we see that the binding energies vary from 4.8 kcal/mol for ammonia to 12.1 kcal/mol for trimethylamine. This is of course consistent with the chemical intuition that the methyl group is a much better electron-donating group than hydrogen. Nagakura's ΔH values also reflect the expected (in terms of Mulliken's charge-transfer model) inverse relationship with the amine ionization potentials.

The molecules investigated in our theoretical study were derived from all possible combinations of NH_3 and $N(CH_3)_3$ with F_2, Cl_2, and FCl. From Nagakura's experiments one expects these charge-transfer complexes to have dissociation energies of the order of 5 kcal/mol. This conclusion is supported by the semiempirical calculations of Carreira and Person,[22] who predict NH_3-F_2 and NH_3-Cl_2 to be bound by 10 and 22 kcal/mol, respectively. Hence these molecules should lend themselves to meaningful study by a priori quantum mechanical methods. The goal of the present research, then, is to begin to understand, in a systematic way, the electronic structure of model charge-transfer complexes. As will be seen, at least one of the trends predicted here theoretically is quite contrary to accepted chemical intuition and the experimental data presented in Table I.

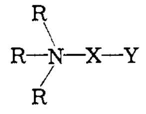
Theoretical Details

All results were obtained at the single configuration self-consistent field (SCF) level of theory. The interactions under study are of strength comparable to hydrogen bonds, and hence one expects SCF theory to be adequate in this regard.[23] Two types of basis sets were generally used. The first of these was a three-Gaussian expansion of a minimum basis set of Slater functions.[24] Second, Dunning's double-ζ basis sets[25,26] for H, C, N, F, and Cl were used. Our general philosophy was to compare the results obtained using the two basis sets on the smaller complexes, and then use the differences to estimate uncertainties likely for the larger complexes, where only the minimum basis set was used.

All calculations were carried out on the Berkeley Datacraft 6024/4 minicomputer. Two computer programs were used, GAUSSIAN 70[27] and the Cal Tech-Ohio State-Berkeley version of POLYATOM.[28] For the largest complex considered, C_6H_6-Cl_2, 1 hr of minicomputer time was required for a complete calculation at a single geometry, using GAUSSIAN 70.

Throughout, the NH_3, $N(CH_3)_3$, F_2, Cl_2, and FCl molecules were fixed at their experimentally determined equilibrium geometries. For ammonia, an N-H bond distance of 1.0124 Å and H-N-H bond angle of 106.67° were used.[29] For trimethylamine the geometry of Wollrab and Laurie[30] was used and we note that the nuclear repulsion energy at this geometry is +138.98685 hartrees. For F_2, Cl_2, and ClF, bond distances of 1.417, 1.988, and 1.628 Å were assumed.[31]

For all of the complexes except NH_3-F_2, a C_{3v} geometry was assumed, of the general type



(1)

For NH_3-F_2, excursions about the C_{3v} potential minimum were considered but shown to be higher in total energy than the assumed orientation. Thus it seems likely that the equilibrium geometry of NR_3-XY charge-transfer complexes is the one generally postulated.

Binding Energies and Geometrical Structures

Our principal results are summarized in Table II. Let us first turn to the binding energies, in particular those of NH_3-F_2 and NH_3-Cl_2. For these two complexes the minimum basis and double-ζ results are in qualitative agreement. Both basis sets predict NH_3-Cl_2 to be the more strongly bound, a result consistent with the greater polarizability of Cl_2. In both cases the more flexible DZ basis yields a deeper potential well. For the F_2 complex, the MBS and DZ binding energies differ by only 0.17 kcal/mol, while the analogous difference is much greater, 1.29 kcal/mol, for NH_3-Cl_2.

Since it is quite important to establish whether significant differences occur when the basis set is extended beyond

Table III. Mulliken Populations and Dipole Moments for the Polar Molecules Employed as Electron Donors and Electron Acceptors[d]

ClF	Cl	F	μ(theory)	μ(exptl)
s	5.95 (5.96)	3.98 (4.00)		
p	11.03 (10.67)	5.05 (5.37)		
Total	16.98 (16.63)	9.02 (9.37)	−0.50 (+1.60)	+0.88[a]

NH_3	N	H(3)	μ(theory)	μ(exptl)
s	3.59 (3.68)	0.84 (0.71)		
p	3.88 (4.20)			
Total	7.47 (7.88)	0.84 (0.71)	1.79 (2.34)	1.47[b]

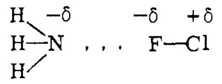
$N(CH_3)_3$	N	C	$H_a(6)$	$H_s(3)$	μ(theory)	μ(exptl)
s	3.52 (3.58)	3.16 (3.42)	0.93 (0.81)	0.96 (0.85)		
p	3.75 (3.69)	2.92 (3.02)				
Total	7.27 (7.27)	6.08 (6.44)	0.93 (0.81)	0.96 (0.85)	1.01 (1.15)	0.61[c]

[a] D. A. Gilbert, A. Roberts, and P. A. Griswold, *Phys. Rev.*, 76, 1723 (1949). [b] D. K. Coles, W. E. Good, J. K. Bragg, and A. H. Sharbaugh, *ibid.*, 82, 877 (1951). [c] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, 28, 572 (1958). [d] The minimum basis results are presented first, with the double-ζ results in parentheses.

the DZ level, two larger basis sets were used for the NH_3-F_2 complex. The first, labeled "extended" in Table II, employs a more flexible set of p functions on the N and F atoms. Instead of the (9s 5p/4s 2p) contraction used in the DZ studies, a (9s 5p/4s 3p) set was adopted, again following Dunning's suggestions.[25] As seen in Table II, this extended basis increases the binding energy by only 0.02 kcal/mol relative to the DZ result.

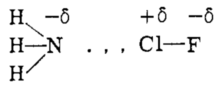
The entry labeled "polarized" in Table II uses a (9s 5p 1d/4s 2p 1d) basis on the N and F atoms. That is, d functions have been added to the heavy atom DZ basis sets. The d functions have a more profound effect on the binding energy, increasing it by 0.19 kcal/mol relative to the DZ results. However, this difference is of a quantitative rather than qualitative nature, and tends to support our use of the DZ basis in general. Further support of this conclusion is given by the NH_3-ClF results obtained with a comparable polarized basis.

The first serious clash between the MBS and DZ results occurs for the NH_3-FCl complex. There the smaller basis yields a substantial binding energy (0.93 kcal/mol), while the larger suggests no attraction at all in the expected region, r(N-F) varying from 2 to 5 Å. Simple chemical reasoning suggests that the NH_3-ClF attraction should be stronger than that for NH_3-FCl, since the "repulsive"



(2)

interaction is clearly less favorable than the "attractive"



(3)

interaction. However, the use of the word "repulsive" to describe the NH_3-FCl interaction does not preclude the possibility that this complex might be bound, for example, by 1 kcal/mol. Nevertheless, considering the tests on NH_3-F_2 using larger basis sets, we conclude that the double-ζ results for NH_3-FCl are reliable.

The MBS and DZ results again disagree for NH_3-ClF, with the small basis yielding only a small attraction (0.17 kcal/mol) and the larger basis predicting a strongly bound (7.66 kcal/mol) charge-transfer complex. At this point, chemical intuition clearly favors the double-ζ results, in that they predict (3) to be significantly lower in energy than (2). Further, the DZ ordering of binding energies

$$NH_3\text{–}ClF > NH_3\text{–}Cl_2 > NH_3\text{–}F_2 \tag{4}$$

is reasonable, although the fact that the ClF complex is more than three times more strongly bound than the Cl_2 complex would have been quite difficult to guess. However, in light of the additional NH_3-ClF calculations carried out with the polarized basis, this conclusion seems quite reliably established.

There is a simple explanation of the apparently spurious MBS results for the interaction between ammonia and chlorine monofluoride. It is, as seen in Table III, that the MBS predicts the wrong sign for the dipole moment of ClF. This error makes the reasoning in (2) and (3) incorrect and yields the otherwise confusing prediction that NH_3-FCl is more strongly bound than NH_3-ClF. To test if this dipole moment prediction were due to the approximation of each Slater function by a linear combination of three Gaussians, additional computations were performed. However, using four- and five-Gaussian expansions,[24] dipole moments of 0.44 and 0.43 D (Cl^-F^+) were obtained. We conclude that a minimum basis is inadequate for the theoretical study of the interaction of ClF with amines.

Since the trimethylamine complexes have been studied using only the MBS, only qualitative conclusions may be made. Note, as expected, that the erroneous dipole moment of ClF results in the spurious prediction that $(CH_3)_3N$-FCl is more strongly bound than $(CH_3)_3N$-ClF. However, the F_2 and Cl_2 complexes should exhibit no such problems, although a DZ or larger basis would be expected to yield larger binding energies.

The key result concerning the trimethylamine complexes is that *all four have smaller binding energies than the corresponding ammonia complexes*. This result is certainly in conflict with chemical reasoning, which holds that methyl is superior to hydrogen as an electron-donating group. This in turn should result in the nitrogen atom being more negatively "charged" in $(CH_3)_3N$ than in H_3N and hence in a more effective charge-transfer interaction. Even more important, the theoretical predictions clash with the experimental binding energies of Nagakura and coworkers,[20,21] illustrated in Table I. It should be noted, however, that the theoretical differences between the NH_3 and $N(CH_3)_3$ complexes are of a much smaller magnitude than those obtained from experiment.

The validity of simple chemical reasoning may be challenged in light of Table III. There it is seen that both MBS and DZ calculations predict nitrogen to have a more negative charge in NH_3 than in $N(CH_3)_3$. Further, this ab initio conclusion is supported by experiment in that the dipole moment of ammonia is 1.47 D, while that of trimethylamine is much less, 0.61 D.

Table IV. Mulliken Populations for Several Amine–Halogen Molecular Complexes[a]

		Amine			Halogen			
	Basis set	H	C	N	F$_a$	F$_b$	Cl$_a$	Cl$_b$
H_3N-F_2	MBS	0.84		7.47	8.98	9.02		
	DZ	0.70		7.89	8.96	9.04		
	Polarized	0.68		7.96	8.97	9.03		
H_3N-Cl_2	MBS	0.84		7.47			16.97	17.04
	DZ	0.69		7.91			16.92	17.09
H_3N-FCl	MBS	0.84		7.47	9.00			17.00
	DZ	Repulsive potential curve						
H_3N-ClF	MBS	0.84		7.47		9.04	16.96	
	DZ	0.68		7.94		9.44	16.58	
	Polarized	0.66		8.01		9.36	16.67	
$(CH_3)_3N-F_2$	MBS	0.96, 0.93	6.08	7.27	8.99	9.01		
$(CH_3)_3N-Cl_2$	MBS	0.96, 0.93	6.08	7.27			16.98	17.03
$(CH_3)_3N-FCl$	MBS	0.96, 0.93	6.08	7.27	9.01			16.99
$(CH_3)_3N-ClF$	MBS	0.96, 0.93	6.08	7.27		9.04	16.97	

[a] The subscript a refers to the halogen atom closest to the nitrogen atom.

It should be emphasized that the present study does not positively establish that the NH$_3$ complexes are the more strongly bound. The referee has noted that with *different donors* involved, relative errors of the order of 1 kcal/mol are not out of the question. Additional studies using larger basis sets would certainly help clarify this point.

If the present ab initio binding energies do predict the correct ordering of the ammonia complexes relative to the trimethylamine complexes, there is perhaps only one plausible explanation of the experimental results summarized in Table I. This is that the theoretical results are appropriate only to the gas phase, and that gas-phase charge-transfer complex binding energies are inherently different from solution ΔH values of the type reported by Nagakura. This in turn would mean that solvent effects dominate the binding energies of such molecular complexes in solution. This conclusion is quite reminiscent to some of those arrived at by ion cyclotron resonance (ICR) experimentalists concerning acidities and basicities of species in solution and the gas phase.[32] To take the example closest to the systems studied here, it has long been known[33] that the proton-acceptor abilities of amines in solution are in the order

$$NH_3 < RNH_2 = R_2NH > R_3N$$

In the gas phase, however, the order of basicity is now known to be[34]

$$NH_3 < RNH_2 < R_2NH < R_3N$$

The predicted intermolecular separations R(N–X) are easily correlated with the binding energies ΔE. That is, the stronger the charge-transfer complex, the shorter is the N–X equilibrium separation. For NH$_3$–ClF, the N–Cl distance is quite short, 2.65 Å, while for NH$_3$–F$_2$, a N–F distance of 3.08 Å was predicted with the larger DZ basis. Incidentally, both the "extended" and "polarized" basis sets yield similar structures for NH$_3$–F$_2$, allowing us to put a reasonable degree of trust in the DZ geometry predictions. As with the binding energy, the very poor MBS result for the structure of NH$_3$–ClF may be attributed to the failure of the MBS to correctly predict the sign of the dipole moment of ClF.

Dipole Moments and Electronic Structure Considerations

For charge-transfer complexes, a particularly significant observable is the dipole moment. More specifically the difference $\Delta\mu$ between the dipole moment of the complex and that of the separated donor and acceptor molecules is of considerable importance. The binding energy of a charge-transfer complex may be thought of as arising from the superposition of a number of interactions,[35] including permanent multipole–permanent multipole, permanent multipole–induced multipole, dispersion, charge transfer, and short-range repulsion interactions. Of these, only the second and fourth will lead, in a qualitative picture, to a dipole moment in excess of the vector sum of the donor and acceptor dipoles. Thus, when both the binding energy and dipole moment of a molecular complex are known, it may be possible to make qualitative conclusions concerning the nature of the interaction.

Table III indicates that the DZ dipole moments of both NH$_3$ and FCl are predicted to be significantly larger than experiment. However, the *difference* in the dipole moment brought about by the formation of the charge-transfer complex should be predicted in a qualitatively reasonable way. Comparison of Tables II and III shows that for NH$_3$–F$_2$ and NH$_3$–Cl$_2$ these $\Delta\mu$ values are 0.34 and 1.07 D from double-ζ calculations. The minimum basis set predicts the dipole moment enhancements to be less, 0.14 and 0.54 D. In both calculations, however, the $\Delta\mu$ value is roughly three times greater for NH$_3$–Cl$_2$ than for NH$_3$–F$_2$. When d functions on N are added to the basis set, the SCF dipole moment for NH$_3$ is reduced by 0.37 D to 1.97 D. Table II in turn shows that the NH$_3$–F$_2$ dipole is reduced by 0.41 D, a nearly comparable amount. Thus, the dipole moment enhancement remains 0.3 D to one significant figure.

The basis set including d functions yielded an SCF dipole moment of 1.35 D for ClF. However, the $\Delta\mu$ value obtained with the polarized basis set is 1.17 D, quite close to the 1.12 D obtained with the double-ζ set. Thus we find the interesting result that the $\Delta\mu$ values for NH$_3$–Cl$_2$ and NH$_3$–ClF are quite comparable.

For the N(CH$_3$)$_3$ complexes, $\Delta\mu$'s have been obtained from the minimum basis calculations. Although the ClF complex results are not meaningful, those for N(CH$_3$)$_3$–F$_2$ (0.11 D) and N(CH$_3$)$_3$–Cl$_2$ (0.45 D) should be. Comparison with the minimum basis results for NH$_3$–F$_2$ and NH$_3$–Cl$_2$ shows that the trimethylamine complex $\Delta\mu$'s are smaller, consistent with the prediction that the N(CH$_3$)$_3$ complexes have smaller binding energies. Thus our unconventional ordering of the NH$_3$ and N(CH$_3$)$_3$ complexes is supported by the $\Delta\mu$ results.

Another measure of the electronic structure changes

Table V. Valence Orbital Energies for Amine–Halogen Molecular Complexes[a]

Symmetry type	NH_3–F_2	NH_3–ClF	NH_3–Cl_2
a_1	−1.752 ($2\sigma_g$ −1.777)	−1.603 (5σ −1.649)	−1.219 ($4\sigma_g$ −1.244)
a_1	−1.478 ($2\sigma_u$ −1.504)	−1.184 ($2a_1$ −1.151)	−1.164 ($2a_1$ −1.151)
a_1	−1.154 ($2a_1$ −1.151)	−1.076 (6σ −1.115)	−0.996 ($4\sigma_u$ −1.024)
e	−0.791 ($1\pi_u$ −0.817)	−0.682 (2π −0.728)	−0.642 (1e −0.629)
a_1	−0.714 ($3\sigma_g$ −0.741)	−0.646 (7σ −0.679)	−0.558 ($5\sigma_g$ −0.584)
e	−0.651 ($1\pi_g$ −0.677)	−0.660 (1e −0.629)	−0.552 ($2\pi_u$ −0.578)
e	−0.632 (1e −0.629)	−0.465 (3π −0.504)	−0.430 ($2\pi_g$ −0.456)
a_1	−0.422 ($3a_1$ −0.419)	−0.453 ($3a_1$ −0.419)	−0.430 ($3a_1$ −0.419)

[a] Results presented here were obtained using the double-ζ basis. In parentheses are the orbital energies of the isolated NH_3, F_2, Cl_2, and ClF molecules.

upon complex formation is the Mulliken population analysis.[36] Table IV summarizes the Mulliken analyses for the systems studied here. Comparison with Table III would seem to imply that permanent multipole-induced multipole effects are larger than actual charge transfer from amine to halogen. Considering the DZ results for NH_3-F_2, it is seen that to within our round-off criterion of 0.01 "electron", there is *no* transfer of charge from NH_3 to F_2. A small shift within the ammonia molecule occurs, with 0.01 being transferred from the hydrogens to the N atom. However, there is a sizable separation of charge (0.08 "electron") induced in the F_2 molecule, presumably by the dipole moment of NH_3. The same effect is seen to a greater degree in the NH_3-Cl_2 system. There 0.01 is transferred to the Cl_2 molecule, in which a charge separation of 0.17 is induced. The effect within the NH_3 molecule is also much larger, and the enhancement of the ammonia dipole moment may be credited to the quadrupole moment of Cl_2.

The Mulliken populations for NH_3-ClF cannot be analyzed in quite as transparent a manner, as Table III shows ClF to have considerable charge separation (0.74 "electron") by itself. In the complex, this separation becomes 0.86 electron, implying that a charge separation of 0.12 electron is induced by the ammonia molecule. Also in NH_3-ClF, 0.02 electron is actually "transferred" from NH_3 to ClF. Quotation marks are used here and elsewhere to emphasize that such statements are based on the Mulliken analysis, which is necessarily arbitrary and of primary value for comparative rather than absolute purposes. For NH_3-ClF, the electronic rearrangement (transfer of 0.06 electron from the hydrogens to N) in ammonia is twice as large as was the case for NH_3-Cl_2. This is an expected result in light of the sizable dipole moment of ClF.

Our overall conclusion is that "charge transfer" per se appears to be less important in these molecular complexes than are classical electrostatic considerations. The fact that the NH_3-ClF binding is three times stronger than that for NH_3-Cl_2 seems best understood in terms of the dipole-dipole attraction. We come to this conclusion since both the $\Delta\mu$ values and the induced charge separations (from Mulliken populations) for NH_3-ClF and NH_3-Cl_2 are comparable. Further, a simple classical calculation shows the dipole-dipole attraction between NH_3 and ClF to be of the order of 2 kcal/mol. However, we should point out that, although the magnitudes are small, twice as much Mulliken population is transferred from NH_3 to ClF than from NH_3 to Cl_2. Also it may be worth noting that this "charge transfer" occurs over a somewhat longer distance than does the charge separation induced in the halogen molecules. Our interpretation of the forces involved in these amine-halogen complexes is strikingly similar to that of Fleming and Hanna,[37] based on their NQR study of the pyridine-ICl complex.

Finally, in Table V we report orbital energies for the complexes studied with the double-ζ basis. Perhaps the most interesting point to be made concerning these data is that the orbital energies differ from those of the separated molecules to a degree roughly porportional to the binding energies. Consider as an example the orbitals corresponding to the ammonia 1e orbital. For NH_3-F_2 the complex orbital energy, −0.632 hartree, is 0.003 hartree lower than that of isolated NH_3. For NH_3-Cl_2 and NH_3-ClF the analogous differences are progressively larger, 0.013 and 0.031 hartree. Similar trends can be seen for the other orbitals.

As each molecular complex is formed, the donor (NH_3) orbital energies are lowered, while those of the acceptor halogen are raised. As seen in Table V, this general rule is followed for every orbital of the three complexes. This trend is perhaps most apparent for the NH_3-Cl_2 complex. For the separated molecules the $3a_1$ orbital of NH_3 lies 0.37 hartree above the $2\pi_g$ orbital of Cl_2. However, for the molecular complex these two orbitals become nearly degenerate, their energies lying within 0.001 hartree of each other. Thus the donor and acceptor one-electron energy levels tend to become equalized upon formation of the molecular complex.

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Electronic Structure of Dicarbonyls. The Ground State of Glyoxal[1a]

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Abstract: The ground electronic state of the simplest α-dicarbonyl, glyoxal, $(CHO)_2$, has been studied by ab initio self-consistent field (SCF) methods using a double-ζ basis set of contracted Gaussian functions. The internal rotation potential curve was determined by optimizing the five structural parameters in the cis and trans forms and three intermediate geometries. The cis-trans energy separation was found to be 5.9 kcal/mol with the trans being the lower form. The internal rotation barrier was 7.5 kcal/mol with respect to the trans minimum, and the potential maximum occurs at an angle of about 102° away from the trans planar form. The energy ordering of the highest occupied molecular orbitals was determined to be n, π, n, and π, in order of increasing Koopmans theorem ionization potential. The close correspondence of these orbitals with those of two interacting CO molecules made possible generalizations of ground electronic state structure of α-dicarbonyls and some predictions concerning excited electronic states.

The reactivity, photochemistry, photophysics, and other properties of carbonyl-containing molecules have made them the subject of a wide variety of experimental studies. It is clear that such properties are intrinsically related to molecular electronic structure. Of particular interest in large or complex systems is determining the effect of localized CO electronic structure so as to facilitate prediction of the chemistry or properties of such systems. With existing theoretical descriptions of the electronic structures of simple carbonyl molecules, such as carbon monoxide[2-8] and formaldehyde,[9-16] a direct approach to this problem would be the theoretical study of a series of systems of more than one carbonyl. And an obvious beginning point is the simplest dicarbonyl, glyoxal.

Glyoxal has been an interesting molecule in photochemistry and spectroscopic studies since the early photolysis experiments of Norrish and Griffiths.[17] Their work and that of others[18,19] showed the dissociation products of glyoxal to be CO, formaldehyde, and hydrogen molecules. While the production of formaldehyde involves excited electronic states,[20,21] it appears hydrogen is formed from vibrationally excited ground electronic state molecules.[22] Spectroscopic work has shown the structure of the major form of glyoxal to be planar trans.[23,24] In 1970, *cis*-glyoxal was identified by high-resolution visible spectroscopy[25,26] and its planar structure was confirmed by microwave experiments.[27] No gauche forms have been detected.

The structure and properties of glyoxal depend largely on the valence molecular orbitals (MO's). Within the paradigm of carbonyl chemistry, these are expected to correlate with oxygen nonbonding orbitals and CO π orbitals. Since only a few excited states of glyoxal have been identified,[23,24,26,28] photoelectron spectroscopy along with semiempirical and ab initio calculations have been used to study the valence molecular orbitals. However, the results have not been entirely consistent.

Turner's assignment of the photoelectron spectrum of glyoxal[29] ordered the valence molecular orbitals as n_a, n_b, π_b, and π_a in order of increasing ionization potential (a and b subscripts denote C_2 rotational symmetry). The spectra also indicated the level separations were of about the same magnitude. This seems in agreement with CNDO calculations[30] showing the n_a-n_b splitting of otherwise degenerate noninteracting orbitals to be due to a through-bond interaction with the carbons. The acceptance of this description of the valence molecular orbitals has limited the search for excited states to $n \rightarrow \pi^*$ excitations, with the $\pi \rightarrow \pi^*$ states presumed to be much higher in energy. Qualitative interpretations concerning the O-C-C-O skeleton of biacetyl[31] and CNDO/CI calculations[32,33] of α-dicarbonyls have given generally the same ordering with some differences in the n_a-n_b separation. Also, minimum basis ab initio calculations[34] on the negative ion, $(CHO)_2^-$, have agreed with this ordering, though with some σ MO's located energetically among the n and π MO's.

The first work inconsistent with this MO scheme was the semi-empirical study of Kato et al.[35] They found the valence molecular orbitals to be ordered n_a, π_b, n_b, σ_a, π_a in the trans form and n_a, π_a, n_b, σ_a, π_b in the cis form. The separation of the highest π and lowest n for both forms