cycles (annelation, homoconjugation); in practice, however, it will be far simpler to make use of the annelated aromatic framework as parent system.
(43) It should be noted, that by starting from the annelated derivative we lose the "self-consistency" between bond order and resonance integral,[8] and comparisons within the system (which assume a constant β and $\delta\beta$) will be somewhat less reliable.[8]
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Molecular Orbital Studies of Electron Donor–Acceptor Complexes. I. Carbonyl Cyanide–ROR and Tetracyanoethylene–ROR Complexes

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Abstract: Ab initio molecular orbital methods are used to study the ground and the charge-transfer states of the weak electron donor-acceptor complexes: carbonyl cyanide-ROR and tetracyanoethylene-ROR where water is used in most calculations as a model for the ether. Modes of approach of the water upon the acceptor molecules were investigated and results of geometries and interaction energies are in reasonable agreement with experiment. The decomposition of interaction energies into components and the comparison with simple electrostatic models indicate that for the complexes studied, the electrostatic energy is the predominant term in their stabilization.

I. Introduction

The origin of the attractive forces responsible for the intermolecular binding of two molecules has been sought for some time. Although the majority of effort has been directed toward the understanding of hydrogen-bonded systems,[1] another area of current interest is that of so-called "charge-transfer" complexes.[2] The ground state wave function for such a complex between a donor molecule D and an acceptor molecule A is traditionally expressed as

$$\Psi_{\mathrm{DA}}{}^{\mathrm{GS}} \approx a\psi(\mathrm{D}, \mathrm{A}) + b\psi(\mathrm{D}^+\text{–}\mathrm{A}^-)$$

a sum of a no-bond resonance structure $\psi(\mathrm{D,A})$ and a dative resonance structure $\psi(\mathrm{D}^+\text{–}\mathrm{A}^-)$ corresponding to an ionic plus a covalent bond. The amount of charge transfer is judged by the relative values of the coefficients *a* and *b*: the larger *b*, the greater the contribution of $\psi(\mathrm{D}^+\text{–}\mathrm{A}^-)$ and hence more charge transfer. A "charge-transfer" band is sometimes seen in the electronic absorption spectrum arising from the transition from the ground state to the charge-transfer state with approximate wave function

$$\Psi_{\mathrm{DA}}{}^{\mathrm{CT}} \approx -b\psi(\mathrm{D}, \mathrm{A}) + a\psi(\mathrm{D}^+\text{–}\mathrm{A}^-)$$

An example of such a band is apparent in the spectrum of the much-studied benzene–iodine system. In the charge-transfer state the predominant resonance structure is the dative one in which an electron has been transferred from the electron donor to the acceptor.

The amount of charge transfer in the ground state of both strong and weak "charge-transfer" complexes has received much attention in the chemical literature. Although a large charge-transfer effect is usually conceded for strong complexes, there has been considerable discussion concerning the origin of the attractive forces in weak "charge-transfer" complexes. Through the efforts of many workers (e.g., Hanna, who showed that the quadrupole-induced dipole forces are of considerable importance in complexes between benzene and halogens[3]), electrostatic forces are presently believed to be the predominant factor in the intermolecular binding in weak "charge-transfer" complexes. For this reason the term "charge-transfer complex" is in disfavor with the preferred expression being "electron donor–acceptor complex".[2a]

In the present work we report the results of an ab initio molecular orbital study of two weak "charge-transfer" complexes in an attempt to further elucidate the intermolecular binding in these systems. The first system, for which a preliminary report has appeared previously,[4] is carbonyl cyanide–ROR, an example of an nπ complex. The second is another nπ complex, tetracyanoethylene–ROR. In most of our calculations we employ water as a model for the ether moiety in order to make the complexes of a size amenable to ab initio methods at a reasonable computational expense.[5] Another reason for the choice of the carbonyl cyanide–ROR

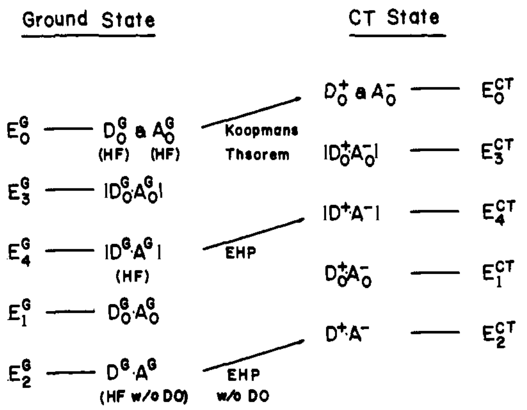

Figure 1. Wave functions and associated energies used in the energy decomposition analysis. (HF) indicates the Roothaan procedure is used. w/o DO means the differential overlap between AO's belonging to different molecules is neglected, and EHP with an arrow indicates an EHP calculation is performed starting from the MO's from the wave function at the tail and resulting in EHP MO's for the state at the arrow's point.

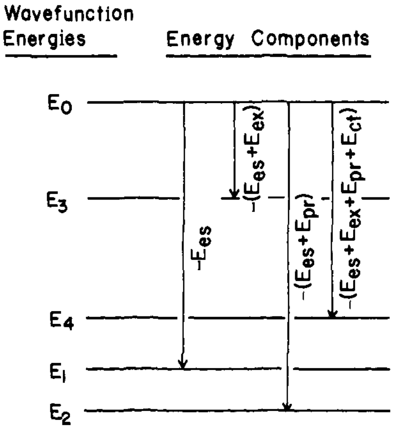

Figure 2. Relationship between the five wave function energies and the component energy terms: electrostatic (E_{es}), exchange (E_{ex}), polarization and resonance (E_{pr}), and charge transfer (E_{ct}).

system is the availability of gas phase experimental results by Prochorow and Tramer[6a] and by Fueno and Yonezawa[6b] on intermolecular complexes involving carbonyl cyanide as the electron acceptor. In this work we investigate the complexes in their ground and charge-transfer states and examine their stabilization energies in terms of an energy decomposition analysis developed by Morokuma and first applied to the formaldehyde-water hydrogen-bonded system.[7] We thus obtain the stabilization energy in electrostatic, exchange, polarization and resonance, and charge-transfer energy terms. Furthermore, we determine the equilibrium geometries of both the ground and charge-transfer states. Although we cannot give predictions with general applicability to all charge-transfer complexes. our study suggests points which are probably shared by most weak "charge-transfer" complexes.

Only a few other ab initio studies of donor-acceptor complexes have been published.[8] Basch[8a] studied the very weak complex between a silver ion and ethylene in the ground state. Electronic structures of isolated electron donors and acceptors, such as tetracyanoquinodimethane,[9] have also been studied in connection with their behaviors in forming molecular complexes.

II. Computational Methods

A. SCF Procedures and Basis Sets. We use single determinant LCAO-SCF-MO theory. For closed shell ground-state calculations we employ Roothaan's procedure,[10] and for the charge-transfer state (and other excited states) the electron hole potential (EHP) method of Morokuma and Iwata is used.[11] Two basis sets are employed: the minimal (1s on H; 1s, 2s, $2p_x$, $2p_y$, $2p_z$ on C, N, and O) STO-3G set of Hehre, Stewart, and Pople[12] and the split-valence 4-31G set of Ditchfield, Hehre, and Pople,[13] both sets using the suggested standard scale factors. In the 4-31G basis the valence shells are split into inner and outer parts giving added flexibility over the smaller minimal set. However, the computational expense is also greater. Thus, 4-31G calculations are performed only at selected points on the STO-3G potential surface.

B. Energy Decomposition Analysis. Although calculation of the stabilization energy of a complex, the difference between the sum of the energies of the donor and acceptor and the energy of the complex, allows one to determine the most stable geometry of the complex as well as giving the total interaction energy, for a better understanding of the origin of such stabilization it is often useful to decompose this total stabilization energy into components.[7] Electrostatic E_{es}, polarization and resonance E_{pr}, exchange E_{ex}, and charge-transfer energy E_{ct} terms whose sum equals the total stabilization energy ΔE give one a detailed account of the molecular interaction. Such terms have been traditionally determined by means of perturbation theory, usually with some confusion as to the terms' precise definitions. We use a method due to Morokuma in which wave functions and corresponding energies, easily calculated within the molecular orbital framework, give precise definitions to the energy components mentioned above. These energies and associated wave functions have been given previously and will not be discussed in detail here.[7] Figure 1 presents a schematic representation of these associated energies and wave functions where a zero subscript on the D or A indicates the isolated molecule wave function, no subscript denotes the wave function of the molecule optimized in the presence of the other species, and the vertical lines indicate an antisymmetrized product. The reference state for the charge-transfer state has energy equal to the sum of the isolated donor cation (D_0^+) and isolated acceptor anion (A_0^-) energies. These isolated wave functions in the EHP approximation reduce to Koopmans' theorem[14] results. The energies of the wave functions yield the component energy terms as shown in Figure 2. Note that the sign of these energy terms as well as of the total stabilization energy is such that a positive value denotes attraction while a negative value indicates repulsion.

C. Electrostatic Potential. The electrostatic potential between a unit positive charge at $\mathbf{x}_B$ and a molecule whose electron distribution is represented by the one-electron density $\rho(\mathbf{x})$ is given by

$$\Phi(\mathbf{x}_B) = -\int \frac{\rho(\mathbf{x})}{|\mathbf{x} - \mathbf{x}_B|}\,d\mathbf{x} + \sum_A \frac{Z_A}{|\mathbf{x}_A - \mathbf{x}_B|} \qquad (1)$$

where the sum in the second term is over all atoms in the molecules where Z_A is the atomic number and $\mathbf{x}_A$ the nuclear coordinates of atom A. In the LCAO approximation the first term in eq 1, the electron term, is

$$-\int \frac{\rho(\mathbf{x})}{|\mathbf{x} - \mathbf{x}_B|}\,d\mathbf{x} = -\mathrm{tr}(\boldsymbol{PV}) \qquad (2)$$

where $\boldsymbol{P}$ is the bond-order matrix which has elements

$$P_{rs} = \sum_k \nu_k c_{kr} c_{ks} \qquad (3)$$

where ν_k is the occupation number of orbital k, and in the single determinant approximation is 2 (doubly occupied), 1 (half-occupied), or 0 (unoccupied). The matrix $\boldsymbol{V}$, the one-electron potential integrals, has elements of the form

$$V_{rs} = \int \chi_r \frac{1}{|\mathbf{x} - \mathbf{x}_B|} \chi_s \, d\mathbf{x} \tag{4}$$

where the χ's are atomic orbital basis functions. Equation 1 thus becomes

$$\Phi(\mathbf{x}_B) = -\sum_{r,s} P_{rs} V_{rs} + \sum_A \frac{Z_A}{|\mathbf{x}_A - \mathbf{x}_B|} \tag{5}$$

Calculation of Φ at many different points allows the construction of a contour map, thus indicating probable points of attack assuming an electrostatic interaction.

D. Programs. The programming system GAUSSIAN 70 was used for standard integral evaluation and the ground-state SCF calculations.[15] The EHP method, energy decomposition analysis, and electrostatic potential were programmed by the authors and Dr. Suehiro Iwata.

III. Geometries and Modes of Approach

Throughout all calculations presented here, the monomer geometries were fixed and only variations in the relative orientations of the two species in the complex were examined. For water[16] and tetracyanoethylene (TCNE)[17] experimental geometries were used.

$$H_2O\ (C_{2v}):\ r_{OH} = 0.957\ \text{Å} \qquad \angle HOH = 104.5°$$

$$\begin{aligned} \text{TCNE}\ (D_{2h}):\ & r_{C=C} = 1.357\ \text{Å} && r_{C-C} = 1.435\ \text{Å} \\ & r_{CN} = 1.162\ \text{Å} && \angle C{-}C{=}C = 121.1° \\ & \angle CCN = 180° \end{aligned}$$

Since the experimental structure of carbonyl cyanide is not available, experimental parameters from formaldehyde[18] and TCNE were employed.

$$\begin{aligned} (CN)_2CO\ (C_{2v}):\ & r_{CO} = 1.203\ \text{Å} && r_{CC} = 1.435\ \text{Å} \\ & r_{CN} = 1.162\ \text{Å} && \angle CCO = 121.1° \\ & \angle CCN = 180° \end{aligned}$$

The constraint of rigid monomers in the complex calculations is not expected to cause much of an error for the ground-state calculations as complete geometry optimization of weak hydrogen-bonded systems such as the water dimer shows little monomer deformation.[1,19] In the charge-transfer state, however, deformations are likely to occur and will be discussed in detail in a later section.

In our study of the two complexes water was used as a model for an ether except for one calculation for verification which is to be discussed later. Consequently, orientations were not studied which, although perhaps favorable for water, are obviously not sensible when the water hydrogens are replaced by methyl or larger groups. For the carbonyl cyanide-water complex we confined ourselves to the modes of approach indicated in Figure 3. Solid circles represent points of approach from above the CC plane as shown in the inset. The water hydrogens are directed away from carbonyl cyanide, and the imaginary line connecting these water hydrogens is parallel to the ···C=O or C—C≡N axes for approaches above these axes or their extensions. As will be shown later, there is little energy difference between rotational orientations of H_2O about its C_{2v} axis so that our choice causes little error in energy quantities. Approaches of H_2O within the carbonyl cyanide plane are shown by arrows in Figure 3. Again, rotation of H_2O about its C_{2v} axis (so that the H's move out of the CC plane) causes only very small energy differences which may be ignored.

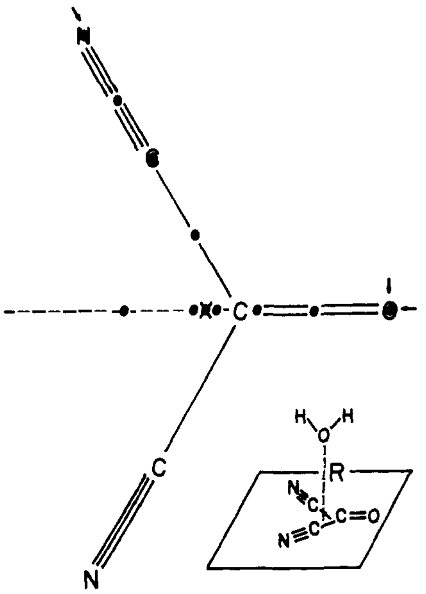

Figure 3. Modes of approach examined for the $(CH)_2CO$-H_2O complex. Closed circles represent approach from above the plane as shown in the inset: arrows refer to planar approaches. The X marks the ground-state favored approach.

Table I. Monomer Energies and Dipole Moments[a]

	STO-3G		4-31G	
Molecule	E_T	μ	E_T	μ
H_2O	−74.96293	1.73[b]	−75.90740	2.61[b]
H_2O^+	−74.57166[c]		−75.40787[c]	
$(CN)_2CO$	−293.43510	1.00	−296.84525	0.19
$(CN)_2CO^-$	−293.30663[c]		−296.85735[c]	
TCNE	−439.24987	0.		
$TCNE^-$	−439.18937[c]			

[a] Energies are given in hartrees (1 hartree = 627.5 kcal/mol). Dipole moments are in debyes. [b] Experimental value: 1.846 (G. Birnbaum and S. K. Chatterjie, *J. Appl. Phys.*, 23, 220 (1952). [c] Energies are calculated from the neutral molecular via Koopmans' theorem.

On the basis of electrostatic potential maps of TCNE and TCNE anion and consideration of the success of electrostatic potential maps in predicting the favorable modes of approach in the carbonyl cyanide-H_2O case, the only approach considered for TCNE-H_2O in both ground and charge-transfer states was water attacking from above the TCNE plane onto the midpoint of the carbon-carbon double bond. The imaginary line connecting the H_2O hydrogens was again parallel to the C=C axis with the H's directed away from TCNE.

IV. Results

A. Isolated Molecules $(CN)_2CO$ and TCNE. To aid in subsequent discussion, some properties of monomers important to our study are presented. Table I gives energy quantities and dipole moments for these species and Figure 4 presents excess atomic charges based on the Mulliken population analysis. Figure 4 also includes populations of formaldehyde and ethylene for comparative purposes. As seen in the atomic charges of formaldehyde and carbonyl cyanide, the cyano groups act as π donors and σ acceptors with a net electron-withdrawing effect leading to an increased positive charge on the central carbon atom. These charges are responsible for the red shift in the singlet n → π^* absorption

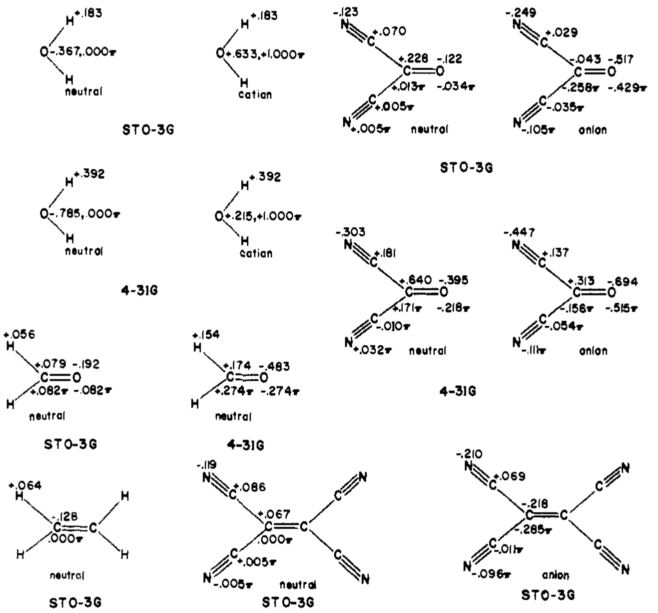

Figure 4. Excess atomic charges for isolated species. Values designated π are π orbital charges, others are total charges. Cation and anion wave functions were obtained from the neutral species via Koopmans' theorem. The geometry used for ethylene is the experimental one taken from K. Kuchitsu, *J. Chem. Phys.*, **44**, 906 (1966).

which is observed both theoretically and experimentally. (The theoretical red shifts[20] are 4401 and 710 cm^{-1} for the STO-3G and 4-31G basis sets, respectively, whereas the experimental value[21] is 4638 cm^{-1}.) The STO-3G basis set tends to underestimate the polarity of a molecule, while the 4-31G basis set tends to overestimate, as is clearly seen in Figure 4. This is reflected in the calculated dipole moments of H_2O, with the experimental value falling between the two (Table I). For carbonyl cyanide the calculated dipole moment for the 4-31G basis is smaller than for the STO-3G basis, due to accidental cancellation of large opposing CO and CN moments. Carrying out calculations both with 4-31G and STO-3G basis sets is desirable, because two results are expected to sandwich the true electrostatic interaction energy.

B. $(CN)_2CO\cdots ROR$ Ground State. Calculations were carried out for all modes of approach indicated in Figure 3 at various intermolecular separations of carbonyl cyanide and H_2O. Planar approaches are found to be unfavorable: either there is electrostatic repulsion or else the exchange repulsion more than offsets a small electrostatic attraction. Thus, planar approaches were not considered further for the ground state. Slices of the potential surface for vertical approaches with the stabilization energy, ΔE, plotted as a function of the vertical distance R and a coordinate reflecting the point of approach above the $\cdots C{=}O$ or $C{-}C{\equiv}N$ axes are shown in Figures 5 and 6, respectively. It can be seen that the ground-state minimum structure is one in which the intermolecular separation between the carbonyl cyanide plane and the oxygen atom of the H_2O molecule is 2.7 Å and that the approach is above a point of the extension of the C=O axis 0.3 Å from the central carbon atom (the point marked with an X in Figure 3). The stabilization energy for this structure is 3.5 kcal/mol and is decomposed into energy components as indicated in Table II. This table also shows the energy decomposition analysis results for intermolecular separations other than 2.7 Å and indicates results of similar analyses on the charge-transfer states resulting from vertical transitions.

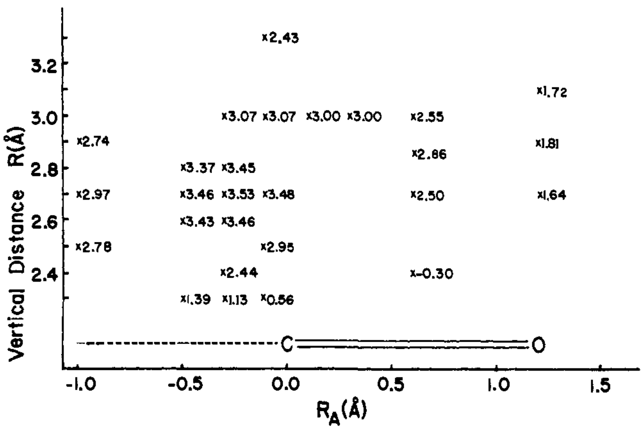

Figure 5. Interaction energy in kcal/mol as a function of the vertical distance R between H_2O and the $(CH)_2CO$ plane (R is depicted in the inset of Figure 3) and R_A, a measure of the approach on the C=O axis and its extension.

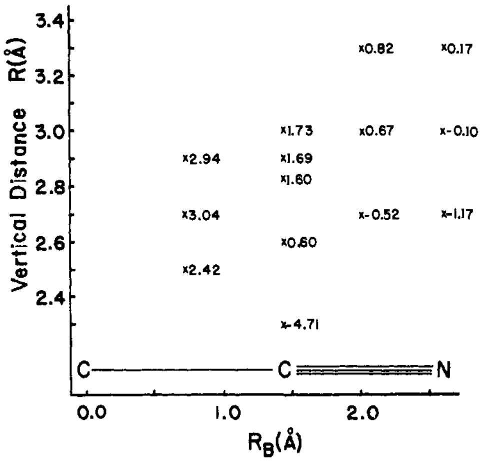

Figure 6. Interaction energy in kcal/mol as a function of the vertical distance R between H_2O and the $(CN)_2CO$ plane (R is depicted in the inset of Figure 3) and R_B, a measure of the approach on the C—C≡N axis.

As can be seen from Table II, the dominant energy term for the ground-state theoretical equilibrium structure is E_{es} with a value of 4.2 kcal/mol compared to values with magnitudes much less for E_{ex}, E_{pr}, and E_{ct}. Thus, our calculations indicate that the ground-state molecular interaction is predominantly electrostatic in nature. The charge-transfer energy term, E_{ct}, is only 1.1 kcal/mol, reflecting a transfer of only 0.005 electron from the donor to the acceptor as shown by the atomic charges for the complex in Figure 7. A comparison of Figures 4 and 7 reveals that this fractional part of an electron is removed from the water σ electron system and is distributed fairly evenly between the σ and π systems of a carbonyl cyanide. (In this geometry the highest occupied, nonbonding orbital $1b_1$ of water is forbidden by symmetry from donating electrons to the carbonyl cyanide π^* orbital.) The polarization term, E_{pr}, contributes little to the attractive interaction, and the exchange term, E_{ex}, is repulsive with magnitude 2.0 kcal/mol at this geometry.

It is of interest, since the interaction is essentially an electrostatic one, to determine whether simple electrostatic arguments are capable of predicting the correct mode of approach or whether other effects such as charge transfer make such methods unreliable. Qualitative examination of the electron populations in Figure 4 suggests that the nega-

Table II. Energy Decomposition Analysis for the Carbonyl Cyanide–Water Complex for Ground-State Least-Energy Approach (R_A = −0.3 Å) (kcal/mol), STO-3G Basis

Ground state	R, Å 2.0	2.4	2.6	2.7	2.8	3.0
ΔE	−9.57	2.44	3.46	3.53	3.45	3.07
E_{es}	17.2	6.6	4.8	4.2	3.8	3.1
E_{ex}	−42.2	−8.0	−3.2	−2.0	−1.3	−0.5
E_{pr}	0.9	0.4	0.3	0.2	0.2	0.1
E_{ct}	14.5	3.4	1.6	1.1	0.7	0.3
Singlet CT state						
ΔE	68.32	87.80	88.08	87.22	86.00	82.95
E_{es}	110.5	93.0	88.2	86.1	84.2	80.7
E_{ex}	−52.4	−10.3	−4.2	−2.7	−1.7	−0.6
E_{pr}	6.8	4.4	3.7	3.4	3.1	2.7
E_{ct}	3.4	0.6	0.4	0.4	0.3	0.2

Table III. Ground-State Energy Decomposition Analysis for the Carbonyl Cyanide–Water Complex for Least-Energy Approach (R_A = −0.3 Å) (kcal/mol), 4-31G Basis

Ground state	R, Å 2.4	2.7	3.0	3.3
ΔE	7.01	8.02	7.00	5.52
E_{es}	16.2	9.7	6.6	4.8
E_{ex}	−14.1	−4.4	−1.3	−0.4
E_{pr}	1.8	1.0	0.6	0.3
E_{ct}	3.2	1.8	1.2	0.7

tively charged oxygen atom of water seeks to approach a region of positive charge, which exists in carbonyl cyanide's triangle of carbon atoms. Thus, this simple model is consistent with our MO calculations. More quantitatively, the electrostatic potential map of Figure 8 representing a map of a plane 2.7 Å above the carbonyl cyanide plane also predicts an approach in the region of the carbon triangle. Thus, the electrostatic models, although not yielding good energy quantities, do yield the proper orientation of the carbonyl cyanide–H_2O ground-state complex.

Because of the computational expense of the 4-31G basis set it was not possible to do as exhaustive a search as was done with the STO-3G basis. Thus, it was assumed that the point of attack is the same as predicted by STO-3G. The stabilization energy was studied as a function of intermolecular separation with energy decomposition results as shown in Table III. The most favorable intermolecular distance remains at 2.7 Å but the stabilization energy is over twice that predicted by the STO-3G basis. This energy is again due primarily to an electrostatic interaction and as such suffers from the 4-31G basis set's tendency to overestimate charge effects. Greater net charges (see Figure 4) create greater bond dipoles whose interactions generate a greater electrostatic interaction energy.

C. $(CN)_2CO$. . .ROR Charge-Transfer State. The best stabilization energy for the charge-transfer state of the carbonyl cyanide–H_2O complex at the STO-3G level results from a planar approach of water to the carbonyl oxygen, the line of approach being perpendicular to the C=O axis with one H atom extended toward the N of one of the CN groups. This stabilization is 96 kcal/mol for an O–O distance of 2.5 Å. However, this is probably partly due to a hydrogen-bond interaction between HO of water and N of carbonyl cyanide. The N···H distance is only 1.99 Å, less than the sum of the covalent radii, a distance not suitable for replacement of hydrogen by a methyl group. A calculation with the hydrogen closest to the nitrogen atom replaced by a methyl group yields a repulsive interaction with ΔE = −20 kcal/mol due to a dramatic increase in the exchange

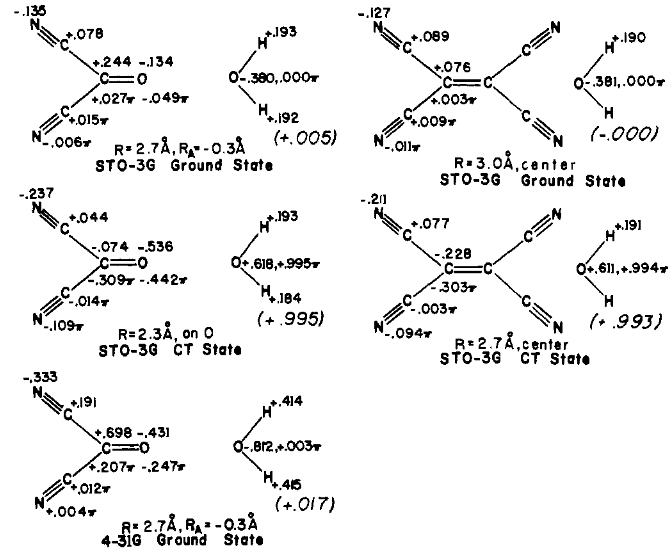

Figure 7. Excess atomic charges of the molecular complexes in their respective calculated equilibrium geometries. The environments of the H_2O hydrogens are different in the $(CN)_2CO$–H_2O complexes and the hydrogens drawn lower in the figure are those closer to the carbonyl oxygen for the ground states and closer to the carbonyl carbon for the CT state. The number in parentheses is the total charge on H_2O in the complex.

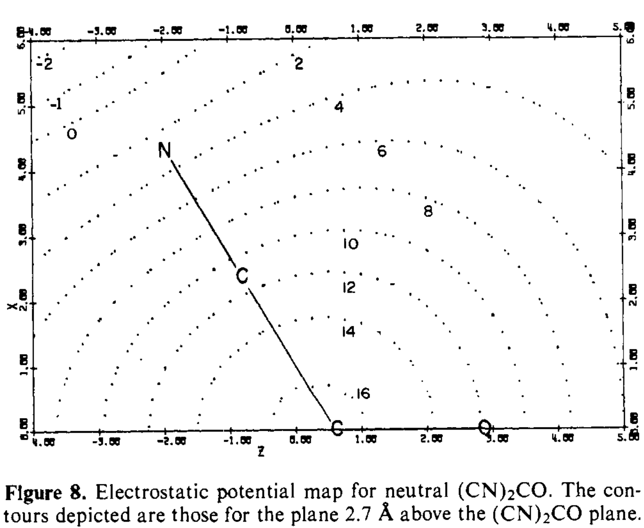

Figure 8. Electrostatic potential map for neutral $(CN)_2CO$. The contours depicted are those for the plane 2.7 Å above the $(CN)_2CO$ plane. Contour energies are in kcal/mol; the distance scale is in Bohr units (1 Bohr = 0.529 Å). The origin of the coordinate system is the location of the least-energy approach in the SCF calculation of the ground state. STO-3G basis set.

Table IV. Energy Decomposition Analysis for the Carbonyl Cyanide–Water Complex for Approach on Oxygen Atom (kcal/mol), STO-3G Basis[a]

	R, Å						
Ground state	1.9	2.1	2.3	2.5	2.7	2.9	3.1
ΔE	−24.02	−9.01	−2.07	0.73	1.64	1.81	1.72
E_{es}	10.9	5.5	3.5	2.7	2.2	1.9	1.7
E_{ex}	−43.9	−17.9	−7.0	−2.6	−0.9	−0.3	−0.1
E_{pr}	0.8	0.5	0.3	0.2	0.2	0.1	0.1
E_{ct}	8.2	2.8	1.1	0.4	0.2	0.1	0.0
Singlet CT state							
ΔE	75?	85?	93.83	92.26	88.84	84.95	81.77
E_{es}			95.8	90.6	86.2	82.2	78.7
E_{ex}			−7.0	−2.6	−0.9	−0.3	−0.1
E_{pr}			5.0	4.2	3.6	3.0	2.6
E_{ct}			0.0	0.1	0.1	0.0	0.0

[a] The numbers with question marks are somewhat unreliable due to convergence difficulties.

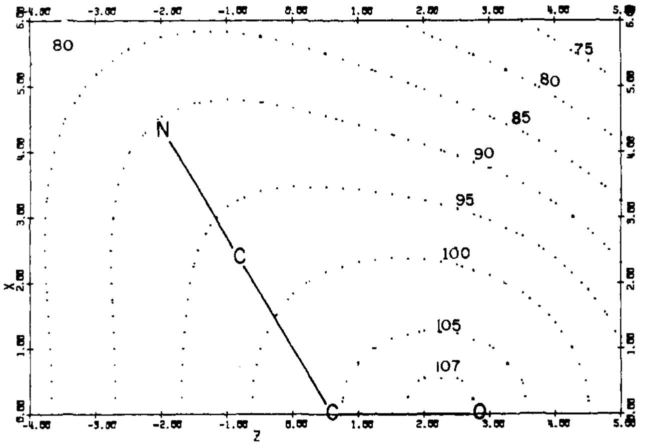

Figure 9. Electrostatic potential map for the $(CN)_2CO$ anion. The contours depicted are those for the plane 2.3 Å above the $(CN)_2CO$ plane. See Figure 8 for units and scales.

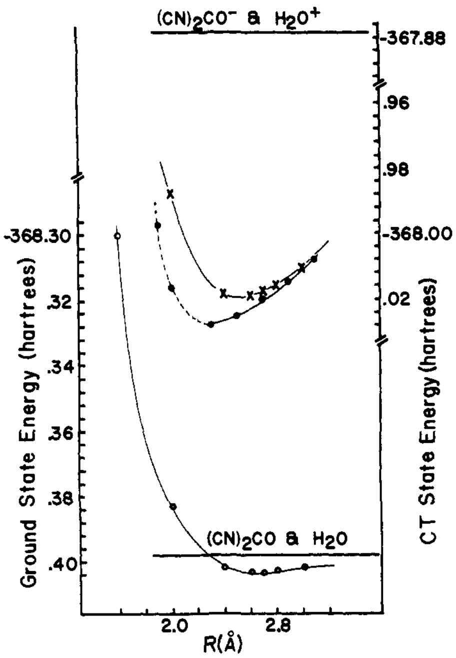

Figure 10. STO-3G potential curves for the $(CN)_2CO–H_2O$ complex as a function of the intermolecular separation R: (○) ground state, (×) CT state from vertical transitions at $R_A = -0.3$ Å, (●) CT state on the carbonyl oxygen. The broken line portion is not very reliable due to the existence of a nearby state of the same symmetry.

repulsion (E_{es} = 157 kcal/mol, E_{ex} = −212 kcal/mol). Thus, the planar approach is not suitable for interaction with an ether. The STO-3G structure with the greatest stabilization energy which can be used as a model for the ether interaction is a geometry resulting from the approach of H_2O above the carbonyl oxygen at an intermolecular separation of 2.3 Å. Energy decomposition results for this mode of approach at various intermolecular distances are listed in Table IV. Since the charge-transfer state results from the transfer of an electron from water to carbonyl cyanide, i.e., a state formed from species of opposite charge, it is to be expected that this interaction is predominantly an electrostatic one. The charge-transfer energy term is small, as is seen in Table IV, but Figures 4 and 7 indicate that there is back transfer of 0.005 electron from the carbonyl cyanide anion to the water cation. As expected this back donation goes into the water π system which became vacant in H_2O^+.

As in the case of the ground state, simple electrostatic theories predict the same approach as determined from our more extensive calculations. The atomic populations in Figure 4 indicate a large positive charge on the oxygen atom of the water cation, which would approach the large negative charge of the carbonyl oxygen of carbonyl cyanide anion. In Figure 9 an electrostatic potential map in the plane 2.3 Å above the carbonyl cyanide plane predicts approach above the carbonyl oxygen. The only mode of approach studied with the 4-31G basis is that found to be best by the smaller STO-3G basis set, i.e., the approach on the carbonyl oxygen from above as a function of the intermolecular distance. However, due to a near degeneracy of the charge-transfer excitation with an intramolecular transition of carbonyl cyanide, the resulting EHP wave functions are mixtures of two states. The results, therefore, are not completely reliable but they suggest a $\Delta E \sim 85$ kcal/mol at $R \sim 2.5$ Å.

The results for the ground and charge-transfer states of the carbonyl cyanide–H_2O complex are summarized as potential energy curves in Figures 10 and 11 for the STO-3G and 4-31G bases, respectively.

D. TCNE–ROR. Because of the success of the electrostatic potential maps in predicting the mode of approach in the carbonyl cyanide–H_2O complex, maps were obtained for both the neutral tetracyanoethylene and its anion. These maps predict that the mode of approach is from above the C–C double bond. STO-3G ground and charge-transfer state calculations were performed for this approach as a function of the intermolecular distance. The energy decomposition analysis results and potential curves are shown in

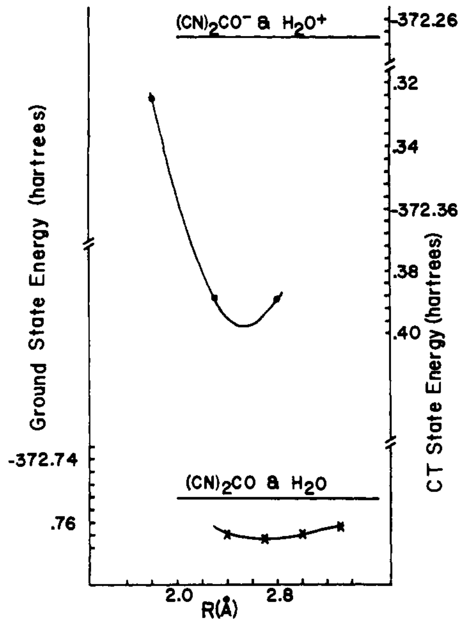

Figure 11. 4-31G potential curves for the $(CN)_2CO-H_2O$ complex as a function of the intermolecular separation R: (×) ground state, (●) CT state on the carbonyl oxygen.

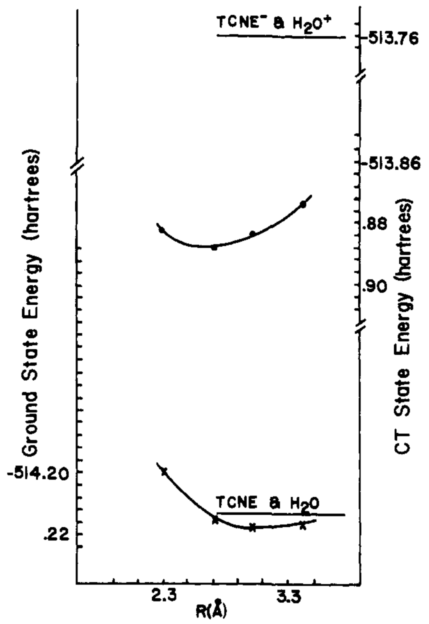

Figure 12. STO-3G potential curves for the $TCNE-H_2O$ complex as a function of the intermolecular separation R: (×) ground state, (●) CT state.

Table V and Figure 12, respectively. As in the carbonyl cyanide-H_2O case the predominant energy term for both states is the electrostatic one.

IV. Discussion

Our stabilization energies of 3.5 kcal/mol and 8.0 kcal/mol for $(CN)_2CO \cdots H_2O$ at the STO-3G and 4-31G basis set levels, respectively, bracket the experimental gas phase value of 4.4 kcal/mol for carbonyl cyanide-diethyl ether obtained by Fueno and Yonezawa.[6b] The theoretical results may also be roughly compared to the experimental gas phase potential curves for $(CN)_2CO \cdots$toluene by Prochorow and Tramer (PT).[6a] Our STO-3G stabilization energies of 3.5 kcal/mol and 93.8 kcal/mol for the ground and CT states, respectively, may be compared to their values of 5.1 and 115 kcal/mol. PT's experimental difference in intermolecular separations for the two states is 0.4 Å, the same value as we obtain from our STO-3G calculations although the absolute distances are shorter theoretically than experimentally estimated. In addition, the experimental observation that at the equilibrium separation of the CT state the ground state curve is repulsive is also shown by the STO-3G calculations. The 4-31G basis fails to reproduce the latter two experimental results, perhaps due to the unreliable CT state calculations.

Gas phase experimental results are not available for the TCNE-ether complex. However, Kroll has obtained a ΔE of 7.4 kcal/mol for TCNE-p-xylene.[22] Our $TCNE-H_2O$ results are very similar to those for $(CN)_2CO-H_2O$ with stabilization energies of similar magnitude. The difference of intermolecular separations for the two states is 0.3 Å. However, unlike the STO-3G calculations on carbonyl cyanide-H_2O, at the equilibrium separation of the charge-transfer state of $TCNE-H_2O$ the ground-state potential curve is attractive.

Table V. Energy Decomposition Analysis for the $TCNE-H_2O$ Complex at Various Separations (kcal/mol), STO-3G Basis

	R, Å			
Ground state	2.3	2.7	3.0	3.4
ΔE	−7.56	1.99	3.04	2.70
E_{es}	8.0	4.5	3.5	2.7
E_{ex}	−17.3	−3.0	−0.7	−0.1
E_{pr}	0.5	0.2	0.2	0.1
E_{ct}	1.3	0.3	0.1	0.0
Singlet CT state				
ΔE	76.43	80.11	76.89	71.39
E_{es}	86.9	78.0	73.4	68.4
E_{ex}	−18.0	−3.1	−0.7	−0.1
E_{pr}	6.8	5.1	4.1	3.1
E_{ct}	0.6	0.2	0.1	0.0

In our calculations we have assumed that the monomers which interact to form a complex do not deform during complex formation. Studies have shown this assumption to be reasonable for weak ground-state hydrogen-bonded systems[19] and it is probably valid in the present case. However, the situation of the CT state is likely to be different. The pertinent species to consider for this excited state are the water cation and the anion of the acceptor molecule. H_2O^+ has been shown theoretically to have a larger valence angle and a longer OH bond length than the neutral molecule,[23] and the anions of $(CN)_2CO$ and TCNE are likely to have a longer C=O or C=C bond length and possibly an out-of-plane bending of the cyano groups. Prochorow, Tramer, and Wierzchowski have determined experimentally that carbonyl cyanide remains planar in its n → π^* excited state which suggests that the anion may also be planar.[24] It is not obvious what effect better geometries would have on the calculated stabilization energies for the CT state since the energies of the separated species would be lowered as well as the energies of the complexes. We have not tested this behavior.

We have, however, tested the other assumption made with regard to the complex geometry, i.e., the rotational orientation of the H_2O molecule. A 90° rotation about the H_2O C_{2v} axis for the ground-state equilibrium structure of $(CN)_2CO \cdots H_2O$ reported above results in an energy lowering of only 0.04 kcal/mol. Since the EHP procedure converges more easily with the parallel orientation, we chose that for all calculations. The error is felt to be negligible for calculated separation distances and stabilization energies.

We have not carried out total optimization of relative orientations and positions between a donor and an acceptor.

Some qualitative discussions, however, may be given. The relative geometry optimization for the H_2CO–H_2O hydrogen-bonded complex with the STO-3G (4-31G, in parentheses) basis set gives the hydrogen-bond energy of 3.5 (6.3) kcal/mol. Since the negative charge on the carbonyl oxygen of carbonyl cyanide is only 64 (82)% of formaldehyde, the hydrogen-bond energy for carbonyl cyanide–H_2O with an OH approaching to the carbonyl oxygen can be estimated to be about $2._2(5._1)$ kcal/mol. This is substantially smaller than the stabilization energy 3.5 (8.0) kcal/mol of the complex found in the present paper, suggesting carbonyl cyanide with H_2O would form a donor–acceptor complex rather than a hydrogen-bonded complex. For the ground-state donor–acceptor complex, the *perpendicular* approach of H_2O to the carbonyl cyanide plane with the H atoms pointed away from the latter was assumed throughout the paper. This may not be the most favorable approach. For instance, possibly more favorable is an approach of H_2O to the CCC triangle of carbonyl cyanide with the H_2O plane *parallel* to the $(CO)_2CN$ plane or perhaps somewhat inclined so as to favor additional hydrogen bonding to the cyanogen N atoms. For the carbonyl cyanide–ether complex, the unavailability of such hydrogen bonding and the steric hindrance by the alkyl groups will favor a more perpendicular orientation.

Since dispersion energy is not included in an SCF treatment, this term is not included in our energy decomposition analysis. Whether or not such a term makes a significant contribution to the total stabilization is now under investigation using a second-order perturbation approach and will be reported in a subsequent publication.[25]

V. Summary

Our calculations have shown the electrostatic interaction to be the predominant term in the stabilization of the model complexes considered, in agreement with currently held views of forces involved in weak "charge-transfer" complexes. Furthermore, our quantitative results are in reasonable agreement with experiment. Although accurate calculations are required for quantitative comparisons, electrostatic potential maps appear to be capable of predicting the proper mode of approach between the polar components of the molecular complexes.

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(21) Excitation energies used to determine the red shift are 23,550 cm^{-1} from J. Prochorow, A. Tramer, and K. L. Wierzchowski, *J. Mol. Spectrosc.*, **19**, 45 (1966), for carbonyl cyanide and 28,188 cm^{-1} from G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966, p 612, for H_2CO.
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