A SCC MO Calculation on the Tetracyanoethylene-benzene Complex

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Introduction

The tetracyanoethylene-benzene charge transfer complex is formed through the interaction of the pi electron density of the benzene and the pi antibonding orbitals of the tetracyanoethylene. Two sandwich type structures of the complex have been proposed in the literature (2) and are shown in Figure 1. Molecular orbital calculations
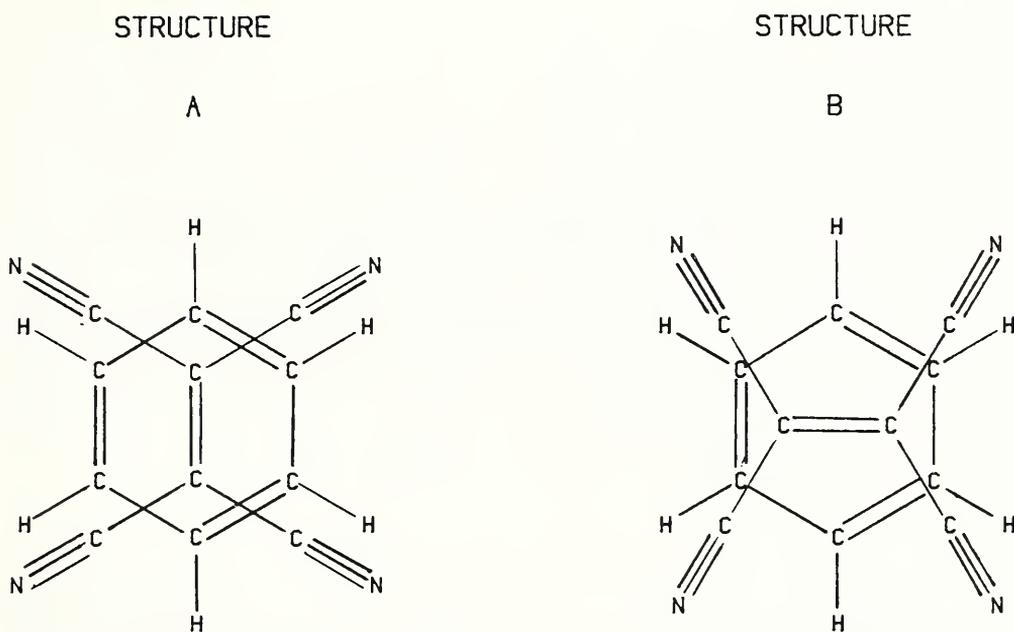
STRUCTURE

A

STRUCTURE

B

FIGURE 1.   Proposed Structures of Benzene-Tetracyanoethylene Complex.

can be used to determine the nature and energy of the absorption which results from complex formation. If the calculations are carried out as a function of the benzene-tetracyanoethylene intermolecular distance, the intermolecular distance that yields the best agreement with the observed charge transfer energy can be obtained.

Calculations

The MO calculations were carried out on a VAX 11/780 computer. The necessary input data for the SCC MO program are given in Table 1. The atomic coordinates are calculated from standard bond lengths and bond angles. These molecular parameters are also listed in Table 1.

The SCC MO calculations require the evaluation of overlap integrals, coulomb integrals, and resonance integrals. These integrals are the elements of the secular determinant. Calculation of the overlap integrals, S_{ij}, using Slater type atomic orbitals, the effective nuclear charge, and the atomic coordinates have been described in the literature (1). Valence orbital ionization energies, VOIE, are used to approximate the coulomb

TABLE 1.   Input Data for the SCC MO Program

1. Total Number of Atoms in the Complex (22)
2. Atomic Number of Each Atom
3. Valence Shell Atomic Orbitals (Carbon and Nitrogen—2s, $2p_x$, $2p_y$, $2p_z$; Hydrogen - 1s)
4. Total Number of Valence Electrons (74)
5. Charge on Each Atom
6. Electron Population in Each Atomic Orbital
7. Coordinates for Each Atom*

* Bond Type	Length (angstroms)	Angle (Deg.)
Benzene C-C	1.390	
Benzene C-H	1.085	
TCNE C=C	1.336	
TCNE C≡C	1.157	
TCNE C-C	1.450	
Benzene C-C-C		120
Benzene C-C-H		120
TCNE C=C-C		120
TCNE C-C≡N		180

integrals, H_{ij} (1). The Wolfsberg-Helmholtz approximation is used to determine the resonance integrals, H_{ij} (1). The secular determinant is then solved from these values of S_{ij}, H_{ii}, H_{ij} to obtain two sets of MO mixing coefficients (Eigenvectors) and MO energies (eigenvalues).

The eigenvectors resulting from the calculation are used in a Mulliken population analysis to calculate new atomic charges for each atom in the complex. These new atomic charges, output atomic charges, are compared to the input atomic charges. If the input and the output charges are different, the difference times 0.1 is used as a new input charge; and the calculation is recycled until the input and output atomic charges converge and self consistent charges on the atoms are obtained.

Results and Discussion

The benzene-tetracyanoethylene complex has 74 valence electrons and 70 valence atomic orbitals in its basis set. This basis set and collection of valence electrons will yield 70 molecular orbitals with the first 37 molecular orbitals being doubly populated with electrons. The 38th molecular orbital is the lowest unoccupied molecular orbital. The lowest energy electronic transition, the charge transfer band, will then occur between the 37th MO and the 38th MO.

Examination of the eigenvectors for molecular orbitals 37 and 38 show that all of the atomic orbital coefficients are near zero except those for the pi 2p type atomic orbitals. This indicates that molecular orbitals 37 and 38 are primarily pi type molecular orbitals. The values of the eigenvectors of the pi 2p atomic orbitals for molecular orbitals 37 and 38 are listed in Table 2. The atom numbering system is given in Figure 2 and 3 for each proposed structure. Further examination of the eigenvectors show that MO 37 is bonding for benzene (C2-C3 and C5-C6), bonding for tetracyanoethylene (CN groups), and bonding for the complex for both structures. Molecular orbital 38, however, is antibonding for the tetracyanoethylene part of the complex for both structures. Finally, it can be noted that the eigenvectors indicate more electron density, larger values for the eigenvectors, on the tetracyanoethylene for MO 38 than for MO 37 in both structures. In summary, the analysis of the eigenvectors for MO 37, highest occupied, and MO 38, lowest empty, supports the notion of an electronic transition, charge transfer, from a benzene pi bonding MO to a tetracyanoethylene pi antibonding MO as a description of the charge transfer band.

TABLE 2. Pi AO Eigenvectors for the Benzene—Tetracyanoethylene Complex

Atom Number*		Structure A		Structure B	
		MO37	MO38	MO37	MO38
Benzene	C-1	0	0	0	0
Benzene	C-2	−.36	.38	−.32	−.25
Benzene	C-3	−.36	−.38	−.32	−.25
Benzene	C-4	0	0	0	0
Benzene	C-5	.36	−.38	.32	.25
Benzene	C-6	.36	.38	.32	.25
TCNE	C-7	0	0	.07	.47
TCNE	C-8	0	0	−.07	−.47
TCNE	C-9	.13	−.21	.14	.22
TCNE	C-10	−.13	.21	.14	.22
TCNE	C-11	−.13	−.21	−.14	−.22
TCNE	C-12	.13	.21	−.14	−.22
TCNE	N-13	−.29	−.35	.32	−.30
TCNE	N-14	.29	.35	.32	−.30
TCNE	N-15	−.29	.35	−.32	.30
TCNE	N-16	.29	−.35	−.32	.30

*Refers to the numbering system in figures 2 and 3

Table 3 shows the energy difference of MO 38 and MO 37, energy of the charge transfer band, as a function of the benzene-tetracyanoethylene intermolecular distance. Figures 4 and 5 are plots of this data for each proposed structure. The plots for both structures show minimum near the observed charge transfer absorption energy for an intermolecular distance of 2 angstroms, structure A—386 nm, 2.04 A; structure B—389 nm, 2.09 A.
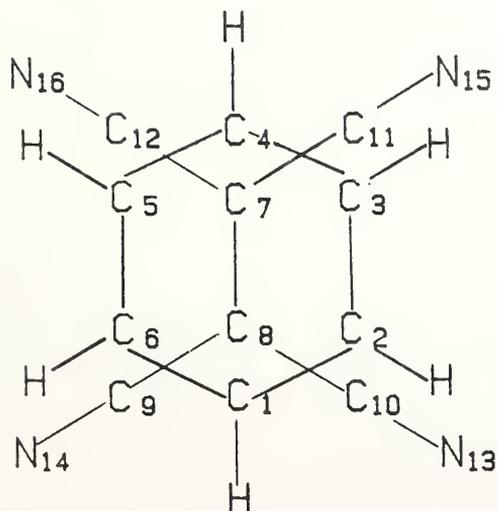
STRUCTURE A

STRUCTURE B

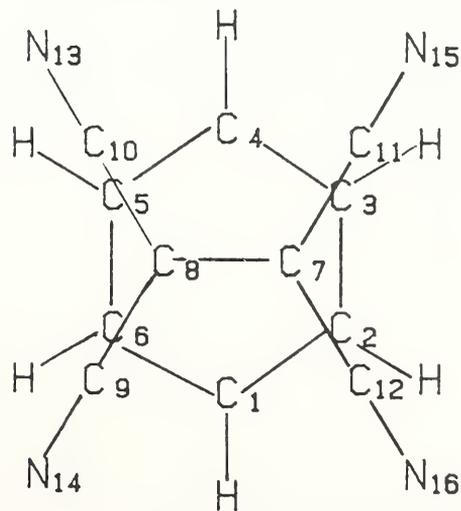FIGURE 2. Atom Numbering System for Eigenvector Analysis in Table 2.

FIGURE 3. Atom Numbering System for Eigenvector Analysis in Table 2.

TABLE 3.   E(MO 38) − E(MO 37) versus the Benzene-Tetracyanoethylene Intermolecular Distance

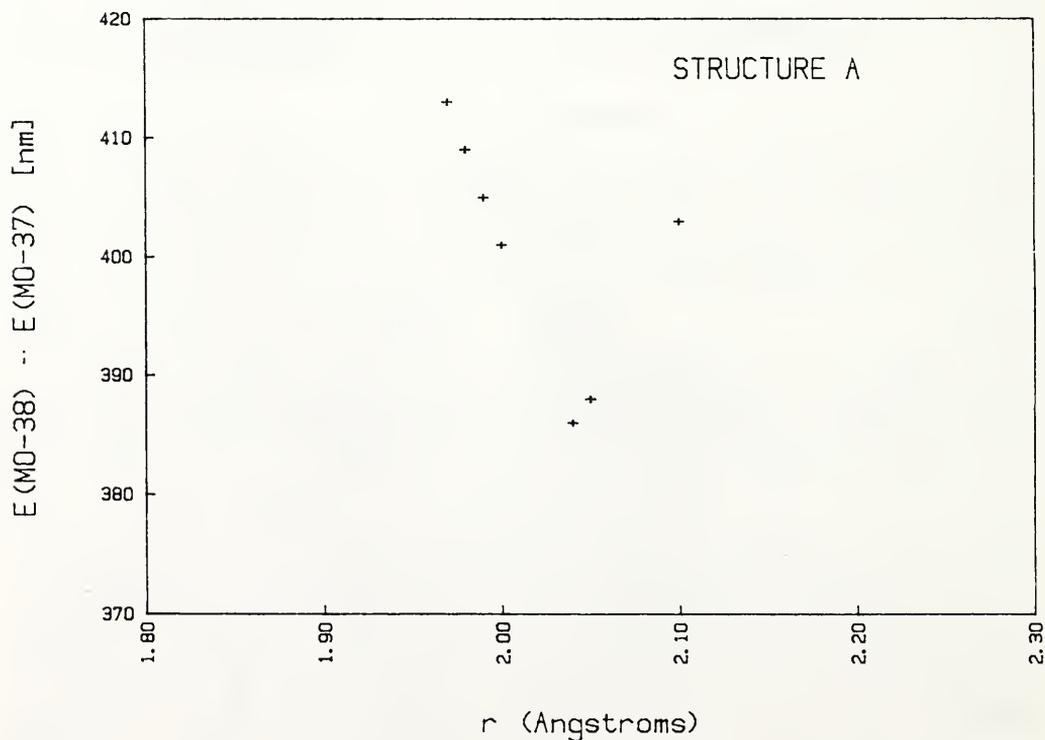| Structure A	
r (angstroms)	E(MO-38) − E(MO-37) [nm]
1.97	413
1.98	409
1.99	405
2.00	401
2.04	386
2.05	388
2.10	403
Structure B	
r (angstroms)	E(MO-38) - E(MO-37) [nm]
2.03	409
2.04	406
2.05	402
2.06	398
2.07	395
2.08	391
2.09	389
2.10	392
2.12	398

FIGURE 4.   Charge Transfer Band Energy vs Benzene—TCNE Intermolecular Distance.
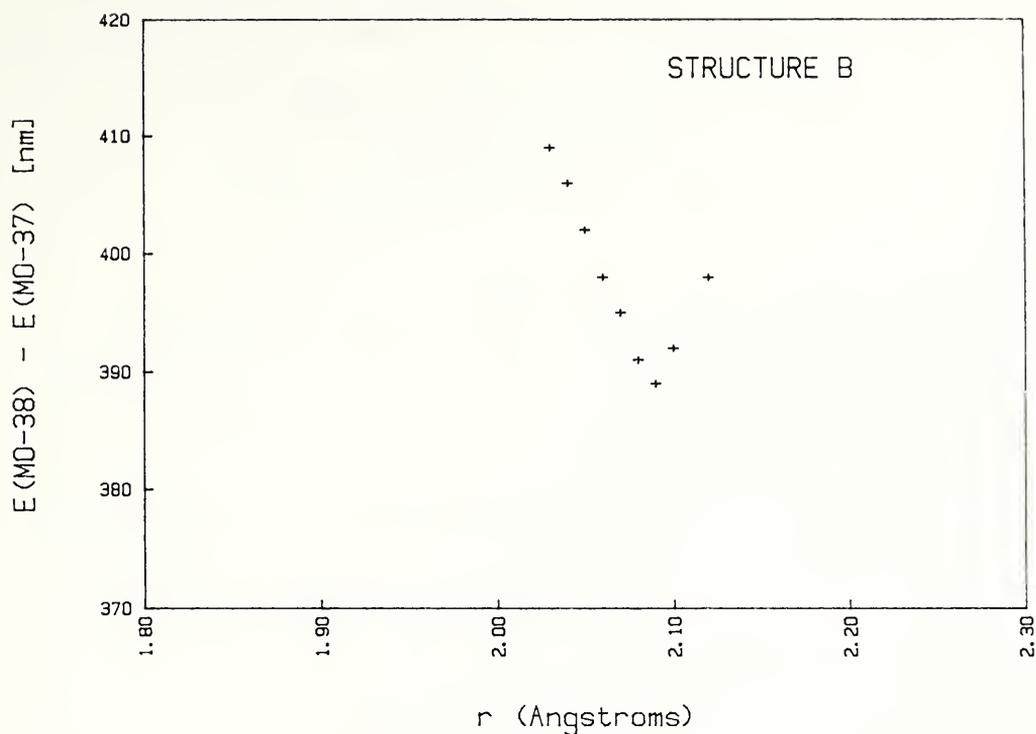
FIGURE 5. Charge Transfer Band Energy vs Benzene—TCNE Intermolecular Distance.

Acknowledgments

Literature Cited

1. McGlynn, S.P., L.G. Vanquickenborne, M. Kinoshita, and D.G. Carrol, 1972, Introduction to Applied Quantum Chemistry, Holt Rinehart Winston, New York, N.Y., 48, 97-140.
2. Mobley, M.J., K.E. Rieckhoff, and E.M. Voight, 1978, Spectroscopic Studies on the Conformations of Electron Donor Acceptor Complexes of Tetra-cyanoethylene, J. Physical Chem., 82, 2005-2012.