

An Ab Initio Molecular Orbital Calculation on Aromatic-tetracyanoethylene Charge Transfer Complexes

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Introduction

One of the first steps in carrying out a MO calculation is to choose a set of atomic orbitals, a basis set, that is thought to best describe the bonding in the complex. The molecular orbital wavefunctions are then approximated by taking a linear combination of the atomic orbitals in the basis set.

$$\psi_i = \sum C_{ik} X_k \quad (\text{LCAO})$$

where

$$\begin{aligned} \psi_i &= \text{molecular orbital wave functions} \\ C_{ik} &= \text{atomic orbital mixing coefficients (eigenvectors)} \\ X_k &= \text{atomic orbital wave functions} \end{aligned}$$

The best molecular orbital wavefunctions are determined by minimizing the energy with respect to the atomic orbital mixing coefficients. This minimizing process, variational theory, results in the formation of n equations and n unknowns.

$$C_{ik} (H_{jk} + E_i S_{jk}) = 0$$

where

$$\begin{aligned} H_{jk} &= \int X_j H X_k dt \\ S_{jk} &= \int X_j X_k dt \end{aligned}$$

In order for the above system of equations to have solutions other than the mixing coefficients being equal to zero, the so called secular determinant must be zero.

$$\det(H_{jk} + E_i S_{jk}) = 0$$

A number of methods are used to evaluate the integrals in the secular determinant. Huckel theory assigns alpha to H_{jj} , beta to H_{jk} , zero to S_{jk} when j is not equal to k , and 1 to S_{jk} when j is equal to k , and the energies are determined in terms of these parameters (2). Semiempirical methods use experimental data, VOIE, to approximate the H_{jj} , and a number of other approximate methods to determine S_{jk} and H_{jk} (2). The ab initio method used in the Gaussian 80, G80, program evaluates the integrals without the use of experimental data.

The G80 program is based on the Hartree Fock method (3). The Hartree Fock operator that is used to determine the MO wavefunctions is also dependent on the MO wavefunction. This operator-wavefunction dependence, therefore, requires an iterative process for the Hartree Fock type calculation. A set of MO wavefunction must be guessed, and the Hartree Fock operator evaluated. The Hartree Fock operator is then used to determine a new set of MO wavefunctions and their energies. This new set of MO wavefunctions, called the first improved set, is then used to calculate a new Hartree Fock operator and a second improved set of MO wavefunctions. This process is continued until a consistent set of wavefunctions and energies are obtained, a self consistent field.

Calculations

The origin of the G80 program is J. Pople, et al. at Carnegie-Mellon University; however, the program has gone through some evolution. The version used in this calculation is the result of the work done by U.C. Singh and P.A. Kollman at the University of California-San Francisco. The major program input parameters for the calculation are the nature basis set and the coordinates of each atom. The G80 program offers several basis set options (minimal option, extended option, and the option to enter functions from outside the program). A minimal basis set containing core and valence Slater type gaussian atomic orbital functions (STO-NG) on each atom was chosen for this calculation. Table 1 summarizes the basis set. The gaussian nature of the atomic orbital functions allows the program to compute the two electron multicenter integrals with greater ease (4). The coordinates of each atom were calculated from standard bond length and angles (1).

TABLE 1. Gaussian 80 Limited Basis Set (STO-3G)

Number of Atoms in the Complex	22
Number of Electrons in the Complex	106
Number of Atomic Orbitals in the Basis Set:	
6 benzene carbons (1S, 2S, 2PX, 2PY, 2PZ)	$6 \times 5 = 30$
6 benzene Hydrogens (1S)	$6 \times 1 = 6$
6 TCNE carbons (1S, 2S, 2PX, 2PY, 2PZ)	$6 \times 5 = 30$
4 TCNE nitrogens (1S, 2S, 2PX, 2PY, 2PZ)	$4 \times 5 = 20$
Total Atomic Orbitals in the Basis Set	86

Results and Discussion

The tetracyanoethylene-benzene charge-transfer complex is described in the literature as a coplaner sandwich type complex formed through the donation of the pi electron density of the benzene to the pi antibonding orbitals of the tetracyanoethylene (3). The complex contains 22 atoms and 106 electrons. The G80 calculations were carried out for both the triplet and the singlet states of the complex at various benzene tetracyanoethylene intermolecular distances. The results reported in this paper are for the intermolecular distance, 2.27 angstrom, that yielded agreement between $E(\text{total, triplet}) - E(\text{total, singlet})$ and the uv charge transfer band at 385 nm. This method of determining the intermolecular distance is an over simplification of the problem; however, the intermolecular distance determined in this manner is near the value previously reported (1). A study using the extended basis set and the coordinate optimization options is now underway.

The approximate nature of each molecular orbital was determined by examining the magnitudes of the eigenvectors for each AO in each MO. Figure 1 gives the energies in Hartree units and the approximate description of seventy of the eighty-six molecular orbitals generated by the eighty-six AO basis set. The first sixteen molecular orbitals were determined to be primarily nonbonding S type orbitals and were omitted from the diagram for clarity. For the singlet state, the first fifty-three molecular orbitals (total electrons / 2) are doubly populated with electrons, and molecular orbital number 54 will be the unoccupied orbital with the lowest energy. Figure 1 shows that there is a significant break in energy between the populated MO 53 (Energy of 53 < 0) and the unoccupied MO 54 (Energy of 54 > 0). It should also be noted that highest energy occupied and lowest energy unoccupied molecular orbitals are pi in nature. Finally, examination of the eigenvectors for molecular orbitals 54 and above shows more antibonding character than those molecular orbitals 53 and below.

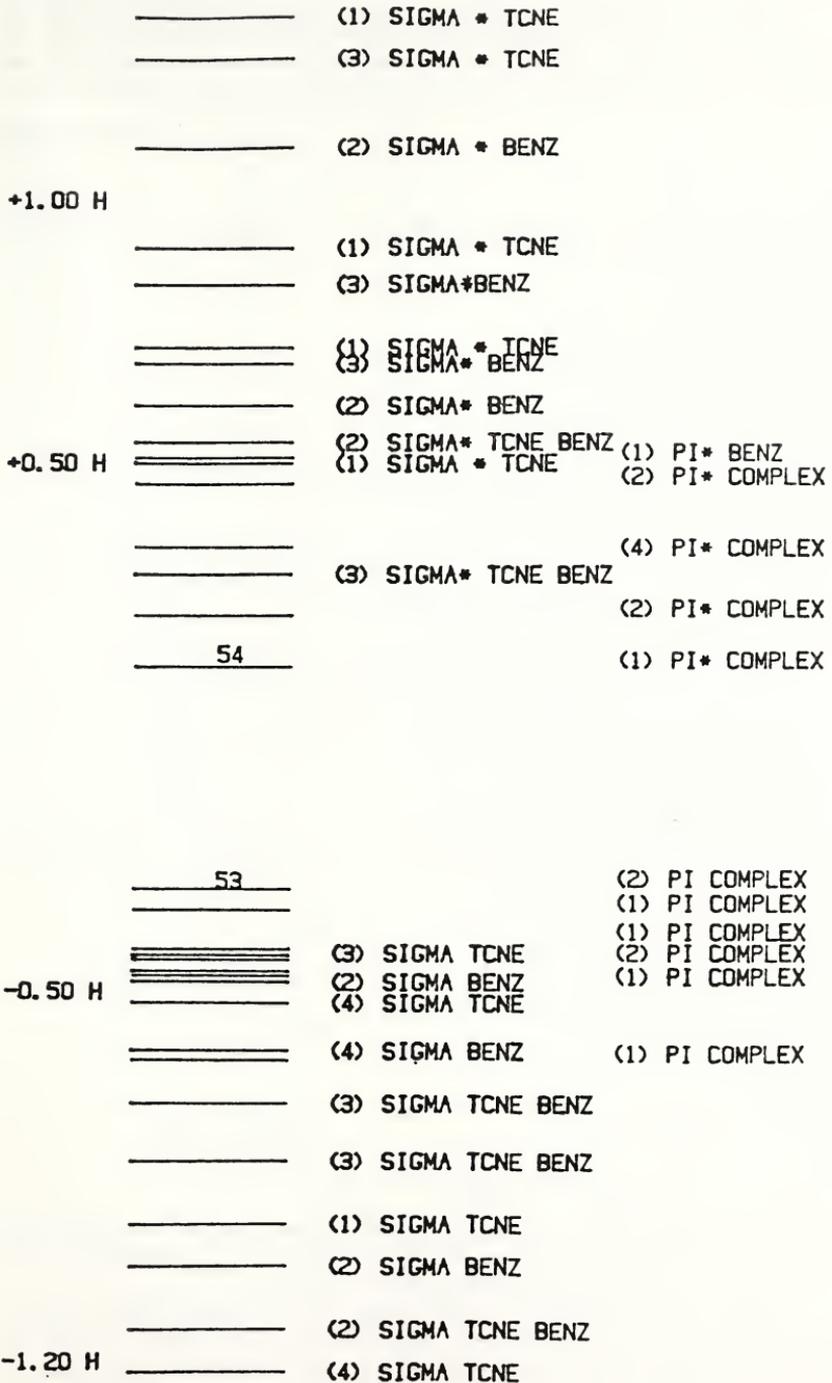


FIGURE 1. G80 MO Energy Level Diagram

Figure 2 is a MO energy level diagram of the pi molecular orbitals near the occupied-unoccupied interface for both the triplet and singlet state. This diagram gives the G80 calculation's description of the singlet to triplet electronic transition. Table 2 lists the eigenvectors for MO 51 and MO 54 which are involved in the singlet to triplet transition.

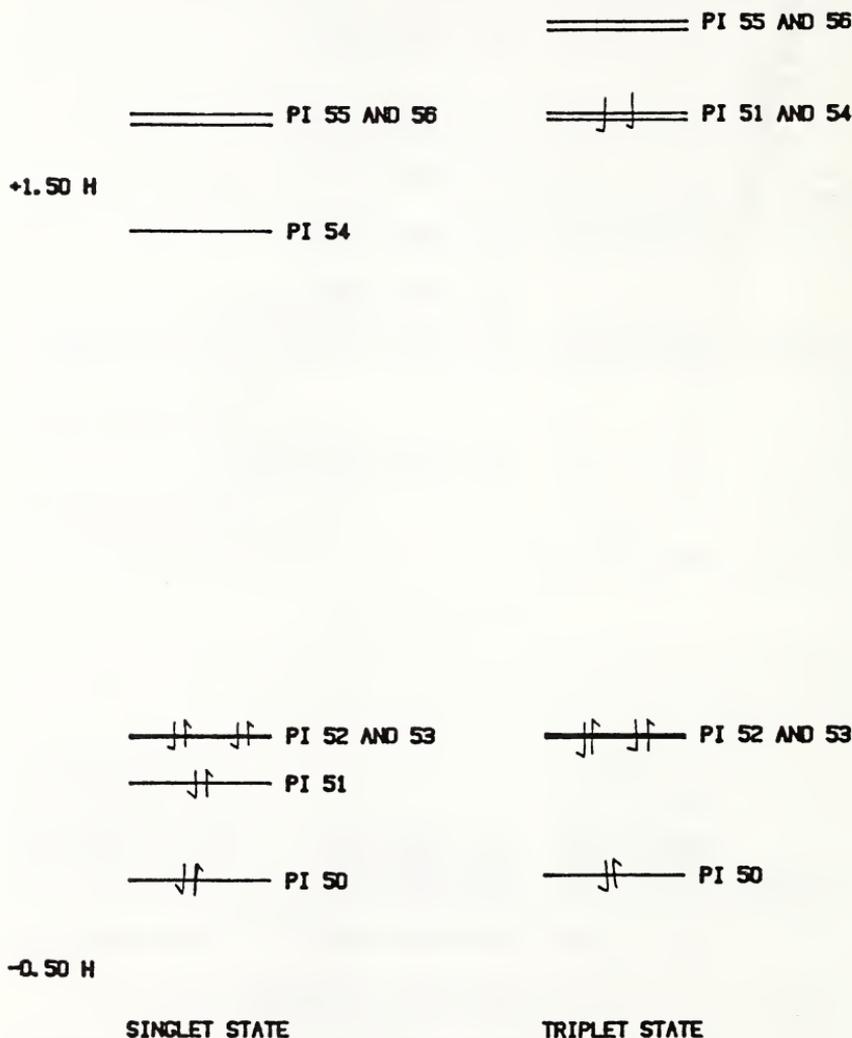


FIGURE 2. Pi MO Energy Level Diagram

The atom numbering system for these eigenvectors is given in Figure 3. Drawings of MO 51 and MO 54 based on these eigenvectors are shown in Figure 4. These calculation results say that the lowest energy electronic transition is pi to pi*.

The results of the Mulliken population analysis for the singlet state are listed in Table 3. The column labeled total charge is the G80 calculation's assignment of the electron density to each atom in the complex. The numbers in the net charge column are the difference in total charge and the normal valence state of the atom (C-6, H-1, N-7). It is interesting to note that the sum of net charges on benzene and tetracyanoethylene

TABLE 2. Eigenvectors for 2PZ (π type) Atomic Orbitals (singlet)

Atom		MO # 51	MO # 54
Benzene	C1	0.064	-0.183
Benzene	C2	0.106	-0.103
Benzene	C3	0.106	0.103
Benzene	C4	0.064	0.183
Benzene	C5	0.106	0.103
Benzene	C6	0.106	-0.103
TCNE	C13	0.496	0.591
TCNE	C14	0.496	-0.591
TCNE	C15	-0.142	-0.153
TCNE	C16	-0.142	-0.153
TCNE	N17	-0.276	0.282
TCNE	N18	-0.276	0.282
TCNE	C19	-0.142	0.153
TCNE	C20	-0.142	0.153
TCNE	N21	-0.276	-0.282
TCNE	N22	-0.276	-0.282

indicates a transfer of 0.173 electrons from benzene donor to the tetracyanoethylene acceptor. Clearly, the results of this study are consistent with the accepted notion that a charge transfer complex is formed between these two compounds.

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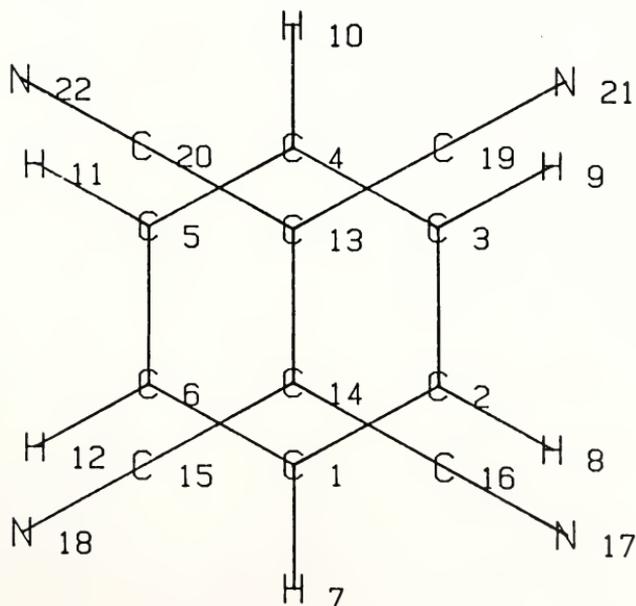
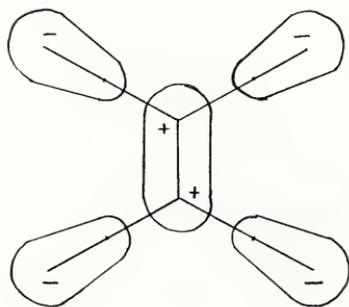


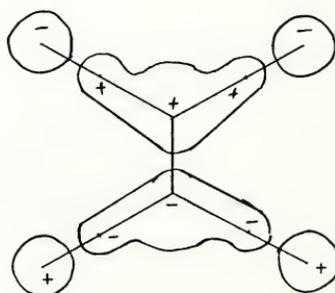
FIGURE 3. Atom Numbering System

TABLE 3. Atomic Charge from Population Analysis (Singlet State)

Atom		Total Charge	Net Charge
Benzene	C1	6.0578	-0.0578
Benzene	C2	6.0656	-0.0656
Benzene	C3	6.0656	-0.0656
Benzene	C4	6.0578	-0.0578
Benzene	C5	6.0656	-0.0656
Benzene	C6	6.0656	-0.0656
Hydrogen	H7	0.9118	0.0882
Hydrogen	H8	0.9063	0.0937
Hydrogen	H9	0.9063	0.0937
Hydrogen	H10	0.9118	0.0882
Hydrogen	H11	0.9063	0.0937
Hydrogen	H12	0.9063	0.0937
		Total	0.173
TCNE	C13	5.9463	0.0537
TCNE	C14	5.9463	0.0537
TCNE	C15	5.9135	0.0865
TCNE	C16	5.9135	0.0865
TCNE	N17	7.1566	-0.1566
TCNE	N18	7.1566	-0.1566
TCNE	C19	5.9135	0.0865
TCNE	C20	5.9135	0.0865
TCNE	N21	7.1566	-0.1566
TCNE	N22	7.1566	-0.1566
		Total	-0.173



MO # 51



MO # 54

FIGURE 4. MO Drawings

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