Ab Initio and Semiempirical Electronic Structural Studies on Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET)

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We report electronic structure calculations for the organic molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET), associated with the highest T_c organic superconductors. The experimental structures exhibit considerable disorder in the outer rings and concomitant uncertainty in the structures. We find that Hartree–Fock (6-31G** basis set) calculations leads to results within 0.01 Å and 1° of experiment for the ordered regions allowing us to predict structures for the disordered regions expected to have this accuracy. We report optimized geometries and atomic charges for ET, ET+, and ET+1/2 that should be useful for atomistic simulations.

1.0. Introduction

Since 1980 the T_c of quasi one-dimensional and two-dimensional organic superconductors has improved from[1] 1.4 to[16] 12.8 K. The best systems involve bis(ethylenedithio)-tetrathiafulvalene (denoted as BEDT-TTF or ET), shown in Figure 1, complexed to appropriate electron acceptors. Such systems show a variety of electronic behaviors (semiconducting metallic, superconducting), but it is not understood how the superconductivity is related to the structure, composition, electronic states, or vibrational states. We are carrying out a series of theoretical studies aimed at establishing a basis for such an understanding. In carrying out these studies we found a disturbing variation in experimental structures from various sources. Since structure is the starting point for many of our studies, we optimized the structures for both neutral and cationic ET molecules using both the *ab initio* Hartree–Fock (HF) method (with the 6-31G** basis set)[4] and the semiempirical modified neglect of differential overlap (MNDO) method.[5]

The best organic superconductors have the composition $(ET)_m X_n$, where X is an electron acceptor.[2,3] In most such crystals there are ET_2^+ dimers, but some crystals have ET+. Consequently, we report properties (structure, electronic levels, atomic charges) for ET, ET+, and ET+1/2. By comparing theory and experiment, we were able to extract composite best structures.

2.0. Calculations

Using the HF method with a 6-31G** basis set, we optimized the structures of ET and ET+ using D_2 symmetry.[4] With MNDO[5] we also optimized the structures of ET and ET+. [The MNDO program would optimize the structure only if the molecule was distorted to C_1 symmetry. This led to deviations from the strict D_2 symmetry (less than 0.001 Å for distances and less than 0.05° for angles for the neutral case, less than 0.005 Å for distances and less than 0.5° for angles for the cation case).]

3.0. Structural Results

3.1. Neutral ET. The crystal structure of neutral ET was reported by Kobayashi *et al.*[3] The monoclinic unit cell has four
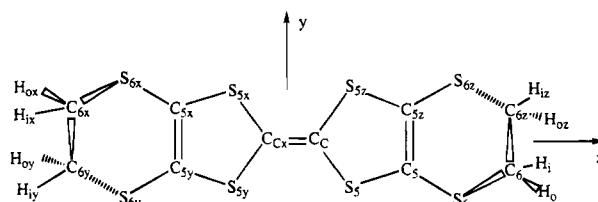
Figure 1. ET molecule, bis(ethylenedithio)tetrathiafulvalene (D_2 symmetry).

molecules grouped into two dimers. Such dimer structures are observed in most crystals containing ET molecules. The structural studies show a planar geometry (D_{2h} symmetry) for the central TTF-like region; however, the terminal CH_2CH_2 groups are nonplanar, leading to distortion and (probably) disorder.

The *ab initio* calculations show the terminal CH_2CH_2 groups as out-of-plane but opposite in phase (D_2 symmetry). However the in-phase structure (C_{2h} symmetry) has essentially the same energy (with MNDO the C_{2h} structure is 0.26 kcal/mol less stable than the D_2 one). Thus at room temperature, crystals are expected to have a mixture of conformations, leading to disorder and poor structural parameters, particularly for the terminal groups.

With D_2 symmetry there are only seven independent atoms: C_C (central double-bonded carbon), S_5 (S in a five-membered ring), C_5 (double-bonded C in a five-membered ring), S_6 (S in a six-membered ring), C_6 (single-bonded C in a six-membered ring), H_o (H bonded to C_6 but out of plane, axial), H_i (H bonded to C_6 but nearly in the plane, equatorial). The other atoms are obtained from rotations about the x, y, or z axes.

From Table 1 we see that the HF bond distances are within about 0.015 Å of experiment while MNDO is within about 0.06 Å. The bond angles also agree well, with errors of about 1° for HF and about 3° for MNDO. In these comparisons with experiment, we do not use the experimental positions for the terminal CH_2CH_2 groups, since they are disordered (thus the experimental C_6-C_6 bond distance of 1.46 Å is clearly low by 0.07 Å). As a result the experimental data on the out-of-plane distortions are not reliable. The HF calculations show that the C_6 carbons are out-of-plane by about 15° ($C_6-S_6-C_6-C_{5z}$ torsion), however the S_6 sulfurs remain in the plane [$(C_C-S_5-C_5-S_6) = -179.3°$].
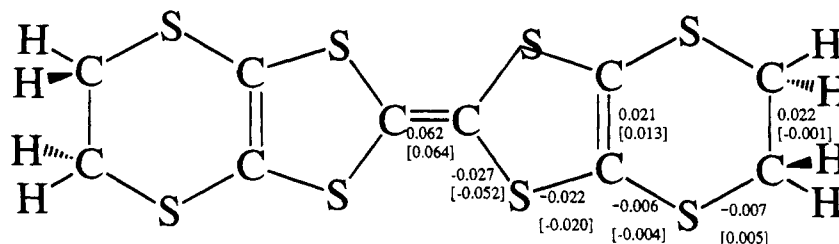
Figure 2. Distance changes upon ionization: experiment and [theory].
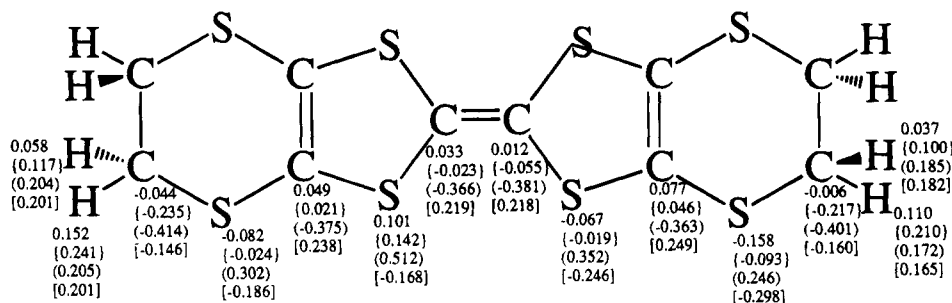
Figure 3. Calculated charges for ET (right side) and ET$^+$ (left side). For each atom the top entry is PDQ (Gaussian) and the next is PDQ (PS-GVB), followed by Mulliken and QEq.

TABLE 1: Structural Parameters for Neutral ET from Theory (HF and MNDO) and Experiment (Ref 3; See Figure 1 for Notation)

	number	Xtal	HF/6-31G**	MNDO
a. Bond Distances (Å)				
$C_C=C_{Cx}$	1	1.319	1.326	1.356
C_C-S_5	4	1.758	1.773	1.695
S_5-C_5	4	1.754	1.771	1.688
$C_5=C_{5z}$	2	1.332	1.322	1.367
C_5-S_6	4	1.742	1.769	1.670
S_6-C_6	4	1.802	1.812	1.737
C_6-C_{6z}	2	$(1.462)^a$	1.524	1.530
C_6-H_i	4		1.084	1.112
C_6-H_o	4		1.081	1.112
RMS error		0.00	0.017	0.063
b. Bond Angles (deg)				
$C_C-C_C-S_5$	4	123.2	123.22	123.38
$C_C-S_5-C_5$	4	94.5	95.57	97.66
$S_5-C_5-C_{5z}$	4	117.3	117.65	115.72
$C_{5z}-C_5-S_6$	4	126.6	128.68	127.19
$C_5-S_6-C_6$	4	100.8	100.86	106.35
$S_6-C_6-C_{6z}$	4	$(116.8)^a$	112.93	115.91
$C_{6z}-C_6-H_i$	4		109.89	109.43
$C_{6z}-C_6-H_o$	4		110.91	109.97
RMS error		0.00	1.06	2.96

^{a} Crystallographic value is not accurate and was not included in the RMS error calculation.

TABLE 2: Structural Parameters of ET$^+$ from Theory (HF and MNDO) and Experiment [ϵ-(ET)PF$_6$ from Ref 6a and δ-(ET)PF$_6$ from Ref 6b]^a

	number	ϵ-(ET)PF$_6$	δ-(ET)PF$_6$	HF/6-31G**	MNDO
a. Bond Distances (Å)					
$C_C=C_{Cx}$	1	1.396	1.381	1.389	1.398
C_C-S_5	4	1.715	1.721	1.721	1.672
S_5-C_5	4	1.743	1.732	1.751	1.676
C_5-C_{5z}	2	1.353	1.351	1.336	1.389
C_5-S_6	4	1.727	1.736	1.765	1.663
S_6-C_6	2	1.761	1.809	1.816	1.741
C_6-C_{6z}	4	$(1.32)^b$	$(1.484)^b$	1.523	1.529
C_6-H_i	4			1.083	1.112
C_6-H_o	4			1.080	1.112
RMS error		0.024	0.00	0.017	0.059
b. Bond Angles (deg)					
$C_C-C_C-S_5$	4	122.1	122.5	122.76	122.65
$C_C-S_5-C_5$	4	95.8	95.9	96.33	97.47
$S_5-C_5-C_{5z}$	4	116.3	116.6	116.42	115.17
$C_{5z}-C_5-S_6$	4	127.3	126.9	128.83	126.95
$C_5-S_6-C_6$	4	116.4	100.6	100.50	106.54
$S_6-C_6-C_{6z}$	4	$(126.9)^b$	$(115.0)^b$	112.68	115.69
$C_{6z}-C_6-H_i$	4			109.74	109.54
$C_{6z}-C_6-H_o$	4			111.46	110.34
RMS error		2.5	0.0	0.9	2.8

^{a} See Figure 1 for notation. It appears that δ-(ET)PF$_6$ is more accurate. ^{b} Crystallographic value is not accurate and was not included in the RMS error calculation.

Both theory and experiment show the S_6-C_6 bond to be significantly longer than S_6-C_5 (by 0.04–0.06 Å), indicating partial double-bond character for bonding of S_6 to $C_5=C_{5z}$.

3.2. ET$^+$. There are two crystal structures[6] with essentially a full positive charge on ET, ϵ-(ET)PF$_6$ and δ-(ET)PF$_6$. We carried out a full self-consistent optimization of the structure for ET$^+$ with both HF(6-31G**) and MNDO. The structural parameters are compared with experiment in Table 2. Again there is excellent agreement between HF and experiment for the ordered region. Of the experimental results, the structure for ϵ-(ET)PF$_6$ seems less reliable, since the value obtained for the C_6-C_{6z} bond is 1.32 Å (rather than the expected value of 1.53 Å). The δ-(ET)PF$_6$ crystal leads to $R(C_6-C_{6z}) = 1.484$ Å, short but in agreement with the structural data for the neutral compound. Thus we consider the δ crystal results as the standard. Comparing ET and ET$^+$, we see that the structure changes occur only within the TTF portion, as indicated in

Figure 2. This suggests that ionization involves primarily the central C=C bond followed by some delocalization of the S_5 π orbital onto C_C and some delocalization of the $C_5=C_{5z}$ bond onto S_5.

3.3. ET$^{+1/2}$. The best organic superconductors have an average charge of +0.5 on each ET. Examples include two important κ phase crystals {κ-(ET)$_2$Cu(NCS)$_2$ and κ-(ET)$_2$Cu[N(CN)$_2$]Br} and β-(ET)$_2$I$_3$.[9–11] In Table 3 we compare the average of the calculated structures for ET and ET$^+$ with the average structural parameters. The five-membered rings from all three crystal structures agree well with the theory (error of 0.01 Å for HF); however, the six-membered rings disagree substantially. Thus the C_5-S_6 distances of the two κ crystals have values of 1.744 and 1.749 Å while β-(ET)$_2$I$_3$ has 1.712 Å. The experimental studies of ET lead to 1.742 Å while ET$^+$ of δ-(ET)PF$_6$ leads to 1.736 Å. Thus we assume that there is some

Electronic Structural Studies on BEDT-TTF

J. Phys. Chem., Vol. 98, No. 39, 1994 **9783**

TABLE 3: Structural Parameters for ET$^{1/2}$ (See Figure 1 for Notation) from Theory (the Theory Values (HF and MNDO) Use the Average from ET and ET$^+$) and Experiment (the Experimental Structures (Refs 9–11) Are X1 = κ-(ET)$_2$Cu(NCS)$_2$, X2 = κ-(ET)$_2$Cu[N(CN)$_2$]Br, and X3 = β-(ET)$_2$I$_3$)^a

	no.	X1	X2	X3	av exp^b	HF/6-31G** ^{c}	MNDO^c
			a. Bond Distances (Å)				
C_C—C_{Cx}	1	1.364	1.360	1.363	1.350	1.358	1.378
C_C—S_5	4	1.742	1.741	1.733	1.740	1.747	1.699
S_5—C_5	4	1.758	1.751	1.770	1.743	1.761	1.680
C_5—C_{5z}	2	1.339	1.343	1.360	1.342	1.329	1.374
C_5—S_6	4	1.744	1.749	1.712	1.739	1.767	1.670
S_5—C_6	4	1.740	1.811	1.810	1.806	1.814	1.738
C_6—C_{6z}	2	(1.522)^d	(1.485)^d	(1.304)^d	(1.473)^d	1.524	1.530
C_6—H_i	4					1.084	1.112
C_6—H_o	4					1.081	1.112
RMS error		0.033	0.0	0.020	0.007	0.011	0.063
			b. Bond Angles (deg)				
C_C—C_C—S_5	4	123.00	122.41	122.39	122.8	122.99	123.18
C_C—S_5—C_5	4	96.22	95.14	95.78	95.2	95.95	97.70
S_5—C_5—C_{5z}	4	116.75	117.13	116.36	117.0	117.04	115.49
C_{5z}—C_5—S_6	4	127.66	128.85	128.93	126.8	128.76	127.13
C_5—C_6—C_6	4	102.78	100.86	100.61	100.7	100.68	106.32
S_6—C_6—C_{6z}	4	(115.56)^d	(115.10)^d	(123.46)^d	115.7	112.80	115.82
C_{6z}—C_6—H_i	4					111.191	110.06
C_{6z}—C_6—H_o	4					109.20	109.46
RMS error		1.16	0.0	0.43	0.9	0.46	2.92

^{a} It appears that X2 is the most consistent. ^{b} From neutral ET and δ-(ET)$^+$(PF$_6$)$^-$ crystals. ^{c} Average of the optimized ET and ET$^+$ structures. ^{d} Crystallographic value is not accurate and not included in the RMS error calculation.

TABLE 4: Torsion Angles (deg) from Theory (HF and MNDO) for ET and ET$^+$ (See Figure 1)

		ET		ET$^+$	
	no.	HF/6-31G**	MNDO	HF/6-31G**	MNDO
S_5—C_C—C_{Cx}—S_{5x}	2	180.00	180.00	180.00	179.80
S_5—C_C—C_{Cx}—S_{5y}	2	−0.33	0.26	−0.91	−2.07
C_{Cx}=C_C—S_5—C_5	4	180.00	−179.86	179.91	−179.84
C_C—S_5—C_5=C_{5z}	4	0.04	−0.49	0.30	−1.07
C_C—S_5—C_5—S_6	4	−179.30	−179.70	−179.03	179.29
C_6—S_6—C_5=C_{5z}	4	14.84	12.23	15.01	11.25
C_5—S_6—C_6—C_{6z}	4	−49.27	−39.51	−49.31	−39.84
S_6—C_6—C_{6z}—S_{6z}	2	72.27	56.32	72.50	57.12
S_6—C_6—C_{6z}—H_{iz}	4	−171.56	175.26	−171.99	175.57
S_6—C_6—C_{6z}—H_{ox}	4	−51.65	−67.95	−51.76	−67.13
H_{oz}—C_{6z}—C_6—H_i	2	64.52	50.98	63.74	51.42
H_{iz}—C_{6z}—C_6—H_o	2	64.52	50.98	63.74	51.24

problem with the value 1.712 Å for β-(ET)$_2$I$_3$. Also for the S_6—C_6 distance, the value of 1.740 Å for κ-(ET)$_2$Cu(NCS)$_2$ differs substantially from all others (1.811 Å for the other κ structure, 1.810 Å for β(ET)$_2$I$_3$, 1.809 Å for δ-(ET)PF$_6$, and 1.802 Å for neutral ET). As a result only the κ-ET$_2$Cu[N(CN)$_2$]-Br structure seems to be without problems, and we will use it for all comparisons. Comparing the crystal structure for ET$^{+1/2}$ and the average experimental values for ET and ET$^+$ (see Table 3), we find excellent agreement (C_C=C_{Cx} longer by 0.01 Å, S_5—C_5 longer by 0.008 Å). This justifies the use of the average values from the theory.

Comparing the theoretical values with experiment for ET$^{+1/2}$, we also find excellent agreement: bonds distance within 0.02 Å for HF and 0.08 Å for MNDO, bond angles within 0.9° for HF and 5.6° for MNDO. The HF and MNDO calculated torsion angles are listed in Table 4.

4.0. Charges

Considerations of molecular packing and vibrational frequencies require an accurate description of the charges. There are two popular ways to evaluate charges from electronic wave functions. Mulliken charges are based on the MO coefficients. Potential derived charges (PDQ) are based on the electric field derived from the HF density.[15] A set of atomic charges is obtained that reproduces the same electric field outside the van
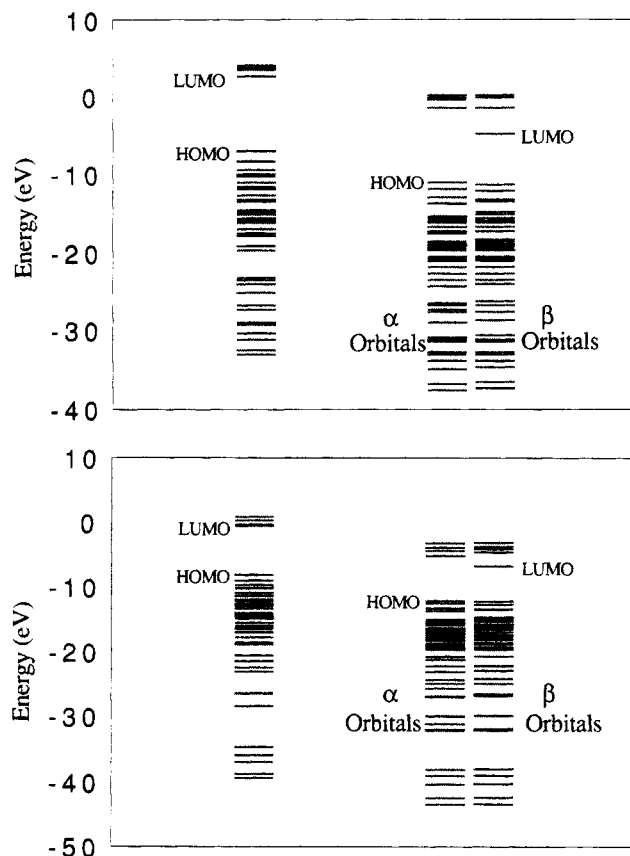
Figure 4. Molecular orbital energy levels for ET (left) and ET$^+$ (right) from (a, top) HF/(6-31G**) and (b, bottom) MNDO calculations.

der Waals radii. Since these charges will be used to predict packing energies and geometries in the crystal, the PDQ should be more useful. In addition we have applied an empirical method, charge equilibration[14] (denoted as QEq), which is based only on atomic parameters.

PDQ were calculated using both the CHELPG model of GAUSSIAN 92 and the PDQ module of the PS-GVB[20] program. (For the latter, the point charges fit not only the potential but

TABLE 5: Energies for HF and MNDO Calculations

	ET		ET$^+$	
	HF/6-31G**	MNDO[a]	HF/6-31G**	MNDO[a]
total energy (hartree)	−3563.3597	−118.4398	−3563.1476	−118.1670
orbital energies (eV)				
HOMO	−6.86794	−8.09285	−10.92928	−12.05553
LUMO	2.61286	−0.51878	−4.54049	−6.71122
ionization potential (eV)				
ET$^+$ − ET (total energy difference)	5.77	7.42		
Koopmans theorem	6.87	8.09		
experiment[b]	6.21	6.21		

[a] For MNDO, total energy is the sum of the electronic energy of valence electrons and core−core repulsions. [b] Reference 13.
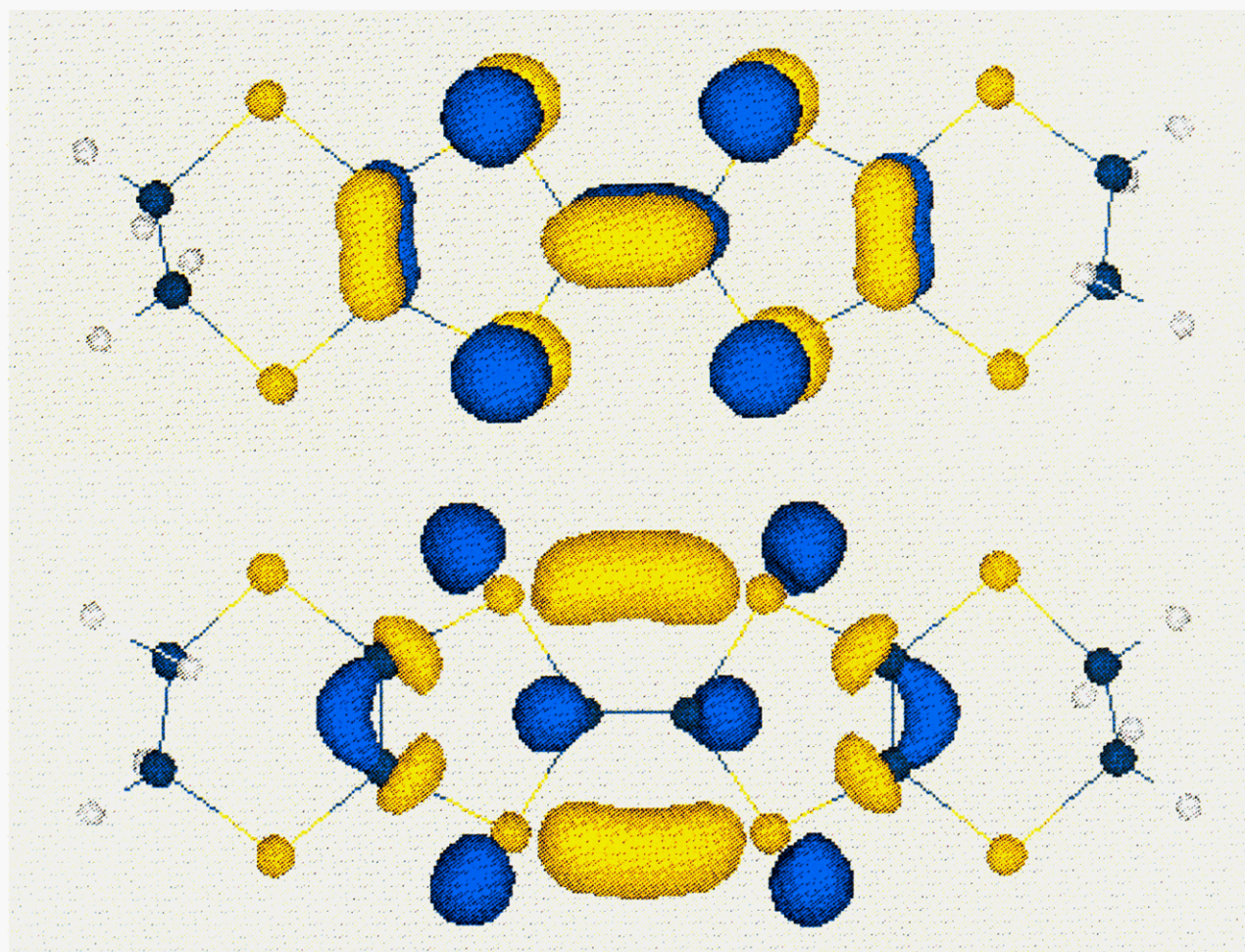
Figure 5. (a, top) HOMO and (b, bottom) LUMO orbitals of the neutral ET molecule from HF calculations.

also the *ab initio* dipole and quadrupole moments.) There seems to be a numerical problem with GAUSSIAN 92, since the calculated charges do not reflect the D_2 symmetry of the molecule and of the wave function. The largest error is ∼0.02. These numerical problems are probably related to the numerical grid used in the program. We symmetry averaged the GAUSSIAN 92 results to obtain the values in Figure 3 (top line for each atom). PS-GVB leads to symmetry consistent results without averaging (Figure 3, second line for each atom).

The main charge density is around the central part of the molecule. This result is consistent with the STM experiment on κ-(ET)$_2$Cu(NCS)$_2$.[12] The change between ET and ET$^+$ suggests that, during the electron transfer between ET molecules, the vibrational modes of the central part of ET (center carbons and sulfurs on the pentagon ring) may couple with the electrons. However, recent isotope experiments exclude the importance

of these kinds of couplings for the superconductivity of organic superconductors.[17,18]

5.0. Ionization Potential

The orbital energies from HF and MNDO calculations on ET and ET$^+$ are shown in Figure 4 and Table 5, and the HOMO and LUMO orbitals from HF are plotted in Figure 5, parts a and b, respectively. The experimental gas-phase ionization potential is 6.21 eV.[13] Comparing the total energies from the HF calculations on the ion and neutral leads to IP = 5.77 eV whereas the orbital energy of the neutral (Koopmans theorem) leads to IP = 6.87 eV. This is typical; the correlation error is smaller for the positive ion, leading to too small an IP. Koopmans theorem assumes that the orbitals do not relax upon ionization, leading to too large a value. The average value of 6.32 eV is in good agreement with experiment. From MNDO,

Electronic Structural Studies on BEDT-TTF

J. Phys. Chem., Vol. 98, No. 39, 1994 **9785**

the total energies lead to an IP = 7.42 eV, whereas the orbital energy leads to an IP = 8.09 eV.

6.0. Conclusion

The structures from HF calculations (6-31G** basis) are in excellent agreement (0.01 Å and 1°) with the experimental data on the ordered regions of ET, ET$^+$, and ET$^{+1/2}$. Thus one may use the HF structures to obtain the full set of structural parameters. The atomic charges should be useful in molecular dynamics simulations.

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