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Structures and Energetics Study of Tetrathiafulvalene-Based Donors of Organic Superconductors

Ersan Demiralp and William A. Goddard, III*

Materials and Process Simulation Center, Beckman Institute (139-74), Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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The donors of the best organic superconductors are all based on organic donor molecules (X) containing a core of tetrathiafulvalene (TTF) or a Se-substituted derivative. In this paper, we present ab initio quantum mechanical calculations (HF, MP2, and DFT using the 6-31G** basis) for the optimized structures and other properties of TTF-based organic donors X and X^+. We find that X^+ is planar but that X deforms to a boat structure. The cases in which the boat is most stabilized with respect to the planar conformation are observed to be superconductors.

1.0. Introduction

Most organic superconductors involve a tetrathiafulvalene (TTF)-like donor as in Figure 1 coupled with appropriate acceptors.[1] Bis(ethylenedithio)tetrathiafulvalene (denoted as BEDT-TTF or ET, see Figure 1b) is the best donor for these organic superconductors. The superconducting transition temperatures (T_c) have improved slowly over the year, now ranging up to 12.8 K.[1] This progress has been impeded because it is not understood how superconductivity is related to fundamental structural quantities.

The electronic structures of the molecular crystals involving these ET donors show a wide variety of electronic behavior leading to semiconductors, metals, or superconductors,[1−3] depending on the anion and the packing. For metallic behavior of ET salts, the intermolecular S···S contacts seem important.[3] Hence, the conformations and packing of these donors play an important role in determining the electronic behavior of these materials.

We have shown[4,5] that the donors (X) for organic superconductors all lead to a distorted boat conformation (see Figure 2) for the neutral X but a planar conformation for the ion X^+. The organic superconductors tend to have about half the X oxidized to X^+, with a dynamic average of $X^{+1/2}$. As an electron hops from X to X^+, the original X distorts from boat to planar while the original X^+ distorts from planar to boat. Thus conduction in this system leads to a coupling between charge-transfer and the boat deformation phonon modes. We have suggested that this electron−phonon coupling is responsible for the superconductivity.[4,5] Indeed the best organic superconductors have the largest stabilization of the boat deformation for neutral X.[4] This suggests a criterion for determining new classes of donors and suggests new TTF-based donors[4] (see Figure 1b).

In this paper, we report structures and other properties of these TTF-based organic donors that may be useful in establishing the relation between boat distortions and superconductivity.

2.0. Calculational Details

We used ab initio quantum mechanics[6,13,14] to examine the structures of donors in both the oxidized (X^+) and neutral (X) states. The methods used include Hartree−Fock (HF), second-order Moller−Plesset (MP2) perturbation theory, and density functional theory (DFT). We used the Becke 1988 exchange functional and the Perdew gradient corrected correlated correlation functionals.[6] The changes in the properties of these molecules upon chemical modification (structure, ionization potential, shape and energy of the molecular orbitals) are important for understanding the electronic and crystal structures of materials containing these organic donors. We used the 6-31G** basis for all atoms except for Se and Te where we used the Hay−Wadt effective core potential with the LAV2P basis.

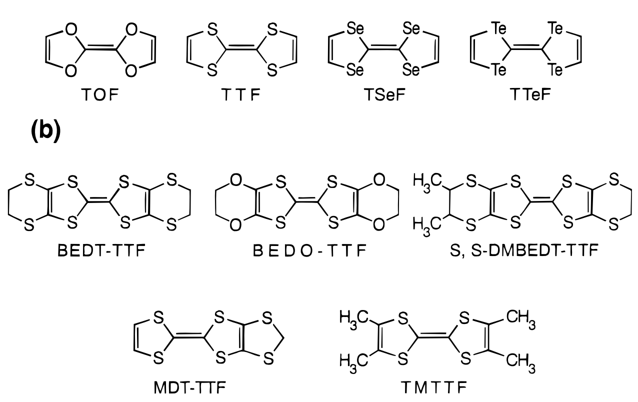

Figure 1. (a) Parent TTF-like donors. (b) Modified TTF-like donors of organic superconductors.

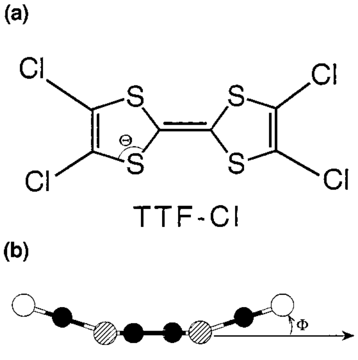

Figure 2. (a) Top view of the optimum boat structure for TTF−Cl. The optimum angle is Θ = 92.99° from MP2 calculation. (b) Side view of the optimum boat structure for TTF−Cl. The optimum angle is Φ = 24.4° from MP2 calculation. The bend is along the S−S axis on each side. Here C is a solid circle, S is a crosshatched circle, and Cl is an open circle.

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* To whom correspondence should be addressed.

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TABLE 1: HF Energies for Organic Donors. All Results Are for the Optimized Geometries (Neutral and Cation) from HF Calculations (See Figure 1 for Structures)

			X			X^+		
species[f]	conformation	symmetry[g]	total (H)	HOMO (eV)	LUMO (eV)	total (H)	HOMO (eV)	LUMO (eV)
TTF−H	planar	D_{2h}	−1819.5165	−6.806	3.070	−1819.3026	−11.641	−4.768
−F	boat	C_{2v}[a]	−2214.8467	−7.833	1.853	−2214.5967	−12.513	−5.752
−Cl	boat	C_{2v}[a]	−3655.0704	−7.807	1.988	−3654.8279	−12.143	−5.397
TSeF−H[h]	planar	D_{2h}	−265.4650	−7.099	2.060	−265.2339	−11.747	−5.330
−Cl	boat	C_{2v}	−2098.1371	−8.024	1.034	−2097.8796	−12.210	−5.902
TTeF−H[h]	boat	C_{2v}	−260.7927	−6.884	0.958	na[e]	na[e]	na[e]
−Cl	boat	C_{2v}	−2093.4755	−7.767	0.036	−2093.2228	−11.653	−5.917
TOF−H	planar	D_{2h}	−528.8507	−6.940	5.278	−528.6526	−12.948	−3.676
−Cl	planar	D_{2h}	−2364.4078	−7.952	4.329	−2364.1781	−13.160	−4.291
TMTTF	boat	C_{2v}[a]	−1975.6844	−6.579	3.151	−1975.4826	−11.092	−4.342
BEDT-TTF[b]	boat	C_2	−3563.3607	−7.073	2.748	−3563.1476	−10.929	−4.541
BEDO-TTF[c]	boat	C_2	−2272.7063	−6.791	2.798	−2272.4959	−11.071	−4.612
MDT-TTF	boat	C_1[d]	−2652.3944	−7.055	2.816	−2652.1756	−11.299	−4.833
S,S-DMBEDT-TTF	boat	C_1[d]	−3641.4361	−7.022	2.811	na[e]	na[e]	na[e]

[a] There is only one negative curvature from the Hessian matrix for the planar conformation, indicating that the only stable structure is boat. [b] The staggered conformation of the ethylenes for the two six-membered rings is used. There is also an eclipsed conformation of the ethylene with C_s symmetry. This has an energy 0.000 005 2 Hartrees = 0.000 14 eV = 0.0032 kcal/mol lower than that of the staggered conformation (see ref 5). [c] BEDO is BEDT but with S replaced by O in the hexagon rings. The staggered ethylene conformation is used. We expect that the staggered and eclipsed conformations of BEDO-TTF should be essentially degenerate as for BEDT-TTF, but we did not study the eclipsed conformation for BEDO-TTF. [d] Molecule is asymmetric (see Figure 1b). [e] Not yet calculated. [f] For TOF, TTF, TSeF, and TTeF, the substitutions replace all four H atoms with the corresponding substituents. [g] Symmetry of the neutral molecule. [h] Hay-Wadt effective core potential with LAV2P basis is used for Se and Te atoms.

TABLE 2: The Deformation Angle (Φ, See Figure 2), the Pentagon Ring Angle C−X−C (Θ, Where X = O, S, Se, Te), the Energy Difference between Boat and Planar Structures (ΔE_{boat}), and the Lowest Boat Deformation Vibrational Frequency (ν_{boat}) for Various TTF-Based Organic Donors. All Results Are from HF Calculations

species	substitutions[a]	Φ[b] (deg)	Θ[b] (deg)	ΔE_{boat} (kcal/mol)	ν_{boat} (cm^{-1})
TTF		0.0	95.09	+0.332[c]	17.7
	F	11.3	93.49	−0.046	18.6
	Cl	14.3	94.48	−0.135	18.1
TSeF		0.0	93.22	POS[g]	na[f]
	Cl	15.5	94.52	−0.132	na[f]
TTeF		10.1	91.66	NEG[e]	na[f]
	Cl	18.8	91.35	NEG[e]	na[f]
TOF		0.0	105.01	POS[g]	76.1
	Cl	0.0	104.78	POS[g]	29.7
TMTTF		5.8	96.23	−0.004	10.3
BEDT-TTF		21.1	94.56	−0.654	19.5
BEDO-TTF		8.6	93.74	−0.017	10.5
MDT-TTF		21.5 (7.6)[d]	93.30 (94.99)	NEG[e]	29.8
S,S-DMBEDT-TTF		21.9 (21.5)[d]	94.40 (94.55)	NEG[e]	na[f]

[a] For TOF, TTF, TSeF, and TTeF, all substitutions replace H atoms with the corresponding substituents. [b] For ET-derived molecules with C_2 symmetry, Φ and Θ are the average angles on both sides of central plane. [c] To obtain the positive ΔE_{boat} we started with the optimized planar and boat structures containing Cl and replaced each Cl with H as the appropriate distance. [d] For these asymmetric molecules, Φ and Θ are the average angles of left and right angles for each part of the molecule. [e] NEG indicates that starting with C_2 (or C_{2v}) symmetry, the structure optimizes to a boat structure; hence, the energy of the boat structure is lower than planar structure. However, we did not separately optimize the planar structure to obtain ΔE_{boat}. [f] Frequencies are not yet calculated. [g] POS indicates that, starting with C_2 (or C_{2v}) symmetry, the structure optimizes to a planar structure with D_2 (or D_{2h}) symmetry; hence, the energy of the boat structure is higher than planar structure.

3.0. Results

3.1. Structures. It is often assumed that the TTF region of the TTF-related donors for organic superconductors are flat.[7] Some deviations from planarity have been suggested by the X-ray structure for the neutral ET crystal.[8] We find that X^+ always has a planar TTF region but that the neutral is distorted into a boat form as in Figure 2 (for TTF−Cl) or a chair form with equivalent energy.[4,5]

Figure 2b shows the side view of the boat structures for TTF−Cl, which has C_{2v} symmetry. For ET molecules the ethylene of the six-membered rings must be nonplanar (to avoid eclipsed CH bonds). This leads to a staggered conformation with C_2 symmetry and an eclipsed conformation with C_s symmetry. These two conformations have almost same energy. Thus, at the HF level the eclipsed conformation is lower by 0.000 005 2 Hartrees = 0.000 14 eV = 0.0032 kcal/mol).[5] In this paper we consider only the staggered conformation (with C_2 symmetry). The boat distortion of the staggered conformation leads to a degenerate pair of chiral molecules.

3.2. Energetics. Table 1 compares the molecular symmetries and total energies along with the orbital energies of the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) from HF calculations. The deformation angle (Φ), the C−X−C angle (Θ) in the pentagon ring, and the energy difference between boat and planar structures (ΔE_{boat}) are reported in Table 2. In Table 3, we present the molecular symmetries and total energies along with the HOMO and LUMO energies of the key molecules from DFT and MP2 calculations for understanding of the boat deformations. Table 4 compares for several systems the deformation angles (Φ) and the energy difference between boat and planar structures (ΔE_{boat}) from HF, DFT, and MP2 calculations. We find that HF, DFT,

TABLE 3: Total Energies, HOMO, and LUMO for the Neutral Organic Donors from DFT and MP2 Calculations

species		calculation	conformation	symmetry[g]	total energy (hartrees)	HOMO (eV)	LUMO (eV)	Φ (deg)	Θ (deg)
TTF−H	X	DFT	planar	D_{2h}	−1823.855 824	−3.874	−1.863	0.0	94.91
			boat	C_{2v}	−1823.856 232	−4.010	−1.784	15.6	94.30
		MP2	planar	D_{2h}	−1820.801 222	−6.630	3.091	0.0	94.62
			boat	C_{2v}	−1820.802 093	−6.839	3.205	18.5	93.81
TTF−Cl	X	DFT	planar	D_{2h}	−3662.329 658	−4.566	−2.899	0.0	94.64
			boat	C_{2v}	−3662.331 436	−4.818	−2.751	22.5	93.43
		MP2	planar	D_{2h}	−3656.865 360	−7.512	1.959	0.0	94.36
			boat	C_{2v}	−3656.867 702	−7.845	2.145	24.4	92.99
	X^+	DFT	planar[a]	D_{2h}	−3662.088 527	−8.840	−8.545	0.0	95.61
TOF−Cl	X	DFT	planar	D_{2h}	−2370.296 153	−4.116	−1.188	0.0	103.59
		MP2	planar	D_{2h}	−2366.387 927	−8.056	4.032	0.0	103.41
BEDT-TTF	X	DFT	planar	D_2	−3571.558 993	−3.816	−2.193	0.0	95.28
			boat	C_2	−3571.566 182	−4.180	−1.913	27.9	93.34
	X^+	DFT	planar[a]	D_2	−3571.351 750	−7.666	−5.900	0.0	96.21

[a] Starting from the initial boat structure, the planar structure was obtained for the optimum structure.

TABLE 4: The Deformation Angle (Φ, See Figure 2) and the Energy Difference between Boat and Planar Structures (ΔE_{boat}) for TTF, TTF−Cl, TOF−Cl, and BEDT-TTF from HF, DFT, and MP2 Calculations

	HF		DFT		MP2	
species	Φ (deg)	ΔE_{boat} (kcal/mol)	Φ (deg)	ΔE_{boat} (kcal/mol)	Φ (deg)	ΔE_{boat} (kcal/mol)
TTF	0.0	POS[a]	15.6	−0.256	18.5	−0.547
TOF−Cl	0.0	POS	0.0	POS	0.0	POS
TTF−Cl	14.3	−0.135	22.5	−1.116	24.4	−1.470
BEDT-TTF	21.1	−0.654	27.9	−4.511	na[b]	na[b]

[a] POS indicates that the energy of the boat structure is higher than planar structure. [b] Not yet calculated.

and MP2 give similar trends for the boat deformation, with electron correlation favoring the boat structures. Thus, for TTF, HF calculations lead to a planar geometry (D_{2h} symmetry) whereas DFT and MP2 calculations lead to the boat structure (C_{2v} symmetry). HF, DFT, and MP2 all lead to a planar structure for TOF−Cl (with oxygens in the pentagon ring).

The energy difference between the stable boat mode and optimized planar structure leads to a double-well potential along the boat coordinate, with a maximum barrier of 0.03−0.2 eV for ET (see Table 4).

3.3. Origin of the Boat Distortion. At the HF level the parent TTF molecule is planar, but all the TTF-based neutral molecules deform to a boat conformation when H in TTF is replaced with F, Cl, or bulky (CH_3) groups. Similarly, substituting Se for S to form TSeF leads to a planar structure, but again neutral molecules with similar substitutions for H are boat-like.[4] However, with Te substitutions for S, both TTeF and TTeF−Cl lead to boat structures. On the other hand, substituting S for O to form TOF leads to planar structures for all similar substitutions of H.[4] With LMP2 and DFT we find that all neutral structures except TOF-based molecules distort to the boat form but that the bulky substituents lead to larger distortions.

The propensity for distortion is easily understood. S, Se, and Te have a strong preference for 90° bond angles (thus, H_2S has 92.1°, H_2Se has 90.6°, and H_2Te has 90.2°[9]] while O prefers a value near 105° (H_2O has 104.5°). (These preferences in bond angles are well understood.[10]) As a result, the five-membered rings in the TTF-like molecules have similar values: The average angles are 105.0° for O in TOF, 95.1° for S in TTF, 93.2° for Se in TSeF, and 91.7° for Te in TTeF. Since the average angle for a planar five-membered ring must be 108°, S, Se, and Te lead to large strains to obtain the small bond angle. By allowing a nonplanar distortion of the five-membered rings, the angle at the S, Se, and Te is allowed to be ∼92°−95° without inducing strain into the rest of the five-membered ring. The strain in the five-membered ring is the highest for Te, hence TTeF distorts to a boat even in the HF description. For S and Se, it is only when a bulky ligand is attached (providing steric interactions to increase the strain) that the TTF-like moiety snaps to a strongly distorted structure.

TABLE 5: Ionization Potentials (eV) for Organic Donors. All Results Are from HF Calculations

species	substitutions[a]	$X^+ - X$ (eV)	KT (eV)	expt[a] (eV)
TTF		5.821	6.806	6.7,[b] 6.4[c]
	F	6.803	7.833	na[d]
	Cl	6.599	7.807	na[d]
TSeF		6.289	7.099	6.68[c]
	Cl	7.005	8.024	na[d]
TTeF		na[e]	6.884	na[d]
	Cl	6.876	7.767	na[d]
TOF		5.389	6.940	na[d]
	Cl	6.249	7.952	na[d]
TMTTF		5.491	6.579	6.03[c]
BEDT-TTF		5.799	7.073	6.7,[b] 6.21[c]
BEDO-TTF		5.725	6.791	6.46[b]
MDT-TTF		5.954	7.055	na[d]
S,S-DMBEDT-TTF		na[e]	7.022	na[d]

[a] For TOF, TTF, TSeF, and TTeF, all substitutions replace H atoms with the corresponding substituents. [b] Data from ref 11. [c] Data from ref 12. [d] No experimental data available. [e] Not yet calculated.

Ionizing the molecules leads to a strong preference for planarity that overcomes these strain effects, leading to a planar molecule for all cases. Thus, the C−X−C angle (Θ) in the pentagon ring is the key factor in determining the boat deformation (Φ). However, there is no linear relation between Θ and Φ because the pentagonal ring relaxes upon distorting to the boat and because the attached ligands also affect the amount of the distortion.

3.4. Ionization Potential. The total energy and orbital energies from HF calculations are shown in Table 1. Two ways of estimating ionization potentials (IP) are by the difference in energy and by Koopmans' theorem.

(i) ΔE is based on the total energy differences of neutral and cation molecules. Since the correlation error is smaller for the positive ion than the neutral, this usually leads to too small an IP.

(ii*)* Koopmans' theorem (KT) is based on the orbital energy of the HOMO level. This assumes that the orbitals do not relax upon ionization and hence usually leads to too large a value.

Table 5 shows that the available experimental gas-phase IPs are between these estimates, as expected. The average of the

ΔE and KT values, which often gives a good estimate for the IP, leads to the order

$$\text{BEDT-TTF}(6.44\text{ eV}) > \text{TTF}(6.31\text{ eV}) > \text{BEDO-TTF }(6.26\text{ eV})$$

This is consistent with some gas-phase experimental results[11]

$$\text{BEDT-TTF} \approx \text{TTF}(6.7\text{ eV}) > \text{BEDO-TTF}(6.46\text{ eV})$$

but different from others[12] (see Table 5)

$$\text{TTF}(6.4\text{ eV}) > \text{BEDT-TTF}(6.21\text{ eV})$$

The IPs are very close so that the relative donor abilities are affected by the molecular environment.[11] Thus, the oxidation potentials in solution are ordered BEDT-TTF > BEDO-TTF > TTF, which differs from the order of the gas-phase first IP. Such polarization effects should also be important in crystals. Hence, the structures and packing will influence the charge-transfer properties of the salts of TTF-based donors. This is responsible for the remarkable variety of electronic properties in the molecular crystals based on TTF donors.

4.0. Discussion

These calculations show that the donors (X) for organic superconductors all lead to a distorted boat conformation for the neutral X but a planar conformation for the ion X^+. We have suggested that this electron−phonon coupling is responsible for the superconductivity.[4,5] Thus, as the electron hops to (or from) a site, it tends to distort the molecule to be less (or more) planar. This leads to a coupling between charge carriers and phonons that we believe provides the attractive pairing of superconductors.

The boat deformation of the donor lowers the symmetry, allowing both IR and Raman to be active for some vibrational modes of these molecules. This allows the electrons to couple several vibrational modes which would be forbidden for the more symmetric planar donor molecules. This may play a role in the mechanism of superconductors for these organic systems.

5.0. Summary

The ab initio calculations show that TTF-based molecules lead to a planar conformation for X^+ but a distorted boat conformation for neutral X. This leads to a coupling of charge transfer with the boat deformation modes of these molecules which we believe is at the heart of the superconducting properties. The strains on the pentagon ring of fulvalene, especially on Θ (the ring angle C−X−C), are the key factors for the boat deformation. The boat deformation and ionization potentials are strongly affected by the ligands, leading to dramatic changes in the crystal and electronic properties of molecular crystals based on TTF-based molecules. By synthesizing appropriate donor−acceptor systems, it might be possible to adjust these structural properties and the coupling of distortion with transient electrons so as to optimize superconducting properties.

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