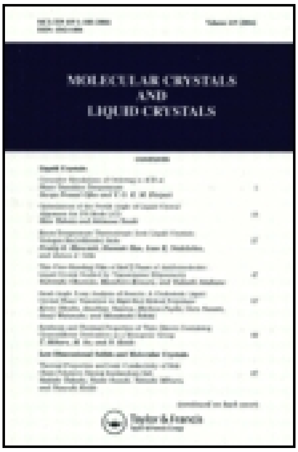

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Ab Initio Computational Study of the C-H...Donor and C-H...Anion Contact Interactions in Organic Donor Salts

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AB INITIO COMPUTATIONAL STUDY OF THE C-H···DONOR AND C-H···ANION CONTACT INTERACTIONS IN ORGANIC DONOR SALTS

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Abstract By performing ab initio SCF-MO/MP2 calculations on simple model systems, we have examined the energetics of the π-framework bending and the six-membered ring conformational change in BEDT-TTF, the chalcogen···chalcogen contact interactions, the C-H···donor contact interactions, and the C-H···anion contact interactions. Our study shows that the chalcogen···chalcogen interactions are repulsive while the C-H···donor and C-H···anion interactions are attractive. The energy required for the π-framework bending and the six-membered ring conformational change is provided by the C-H···donor and C-H anion interactions. These attractive interactions involving the C-H bonds are important factors governing the packing patterns of donor-molecule layers and hence the electronic properties of organic donor salts.

INTRODUCTION

With a number of monovalent anions X^-, organic donor molecules BEDT-TTF (**1a**), BEDO-TTF (**1b**), and their analogs form charge-transfer salts with a layered structure, in which layers of donor molecules alternate with layers of anions[1]. The electronic properties of these donor molecule salts depend upon the packing patterns of their donor molecule layers, which are primarily governed by donor···donor and

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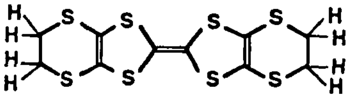
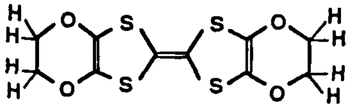


BEDT-TTF

1a



BEDO-TTF

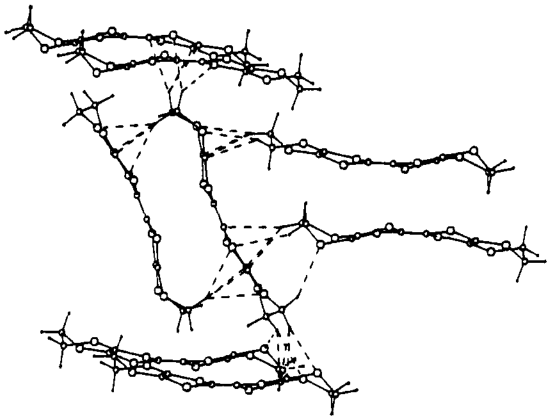
1b

donor···anion interactions involving the C-H bonds of the donor molecules[2]. These 'weak hydrogen bonding' C-H···donor and C-H···anion interactions provide a key to understanding various physical properties of organic donor molecule salts[2]. Examples include the anion- and pressure-dependence of the superconducting transition temperature T_c of β-(BEDT-TTF)$_2$X ($X^- = I_3^-$, AuI_2^-, IBr_2^-)[3,4], the thermal conversion of α-(BEDT-TTF)$_2$I$_3$ to α_t-(BEDT-TTF)$_2$I$_3$[5], that of δ-(BEDT-TTF)$_2$AuBr$_2$ to α'-(BEDT-TTF)$_2$AuBr$_2$[6], the presence of two different C-C-H bending modes in the polarized reflectance spectrum of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$[7], the differences in the structural properties of κ-phase organic donor salts[8-10], the similarity in the donor-layer packing patterns of BEDO-TTF salts[2,11], and the π-framework bending of donor molecules in their neutral solids but its absence in their charge-transfer salts[2]. In the present work, we examine the nature of the C-H···donor and C-H···anion contact interactions and related questions by performing ab initio SCF-MO and second-order Moller Plesset (MP2) calculations on appropriate model molecular systems.

IMPORTANT STRUCTURAL CHARACTERISTICS OF DONOR MOLECULES

We now describe several important structural features of neutral donor molecule solids and charge-transfer salts that will be studied in the next section. These structural characteristics are related to the C-H···donor and C-H···anion interaction and are crucial for understanding the crystal packing patterns of organic donor molecule salts.

Diagram **2** shows a perspective view of how the donor molecules are packed in neutral BEDT-TTF solid[2]. It is noted from **2** that (a) the C-H bonds of a donor molecule make short C-H···S and C-H···C(sp^2) contacts (shown by dashed lines) with adjacent donor molecules, (b) the π-framework of BEDT-TTF is bent as shown in **3** ($\theta \cong 15°$), and (c) one six-membered ring of BEDT-TTF has a staggered conformation (**4a**) while the other ring has a conformation similar to the eclipsed one (**4d**).



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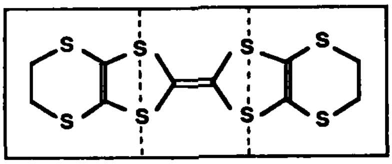
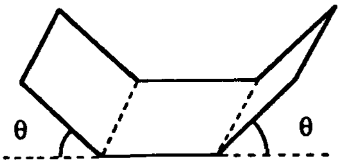
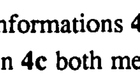


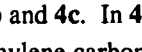
3a



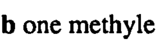
3b



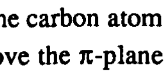
4a



4b



4c

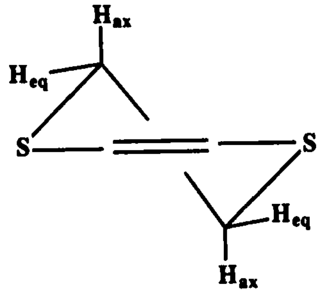


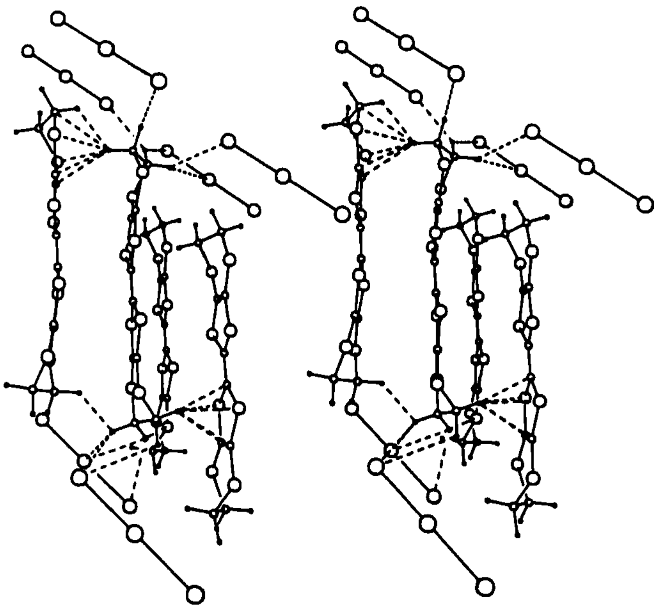
4d

The six-membered ring conformation **4a** is converted to **4d** via the intermediate conformations **4b** and **4c**. In **4b** one methylene carbon atom is on the π-plane, while in **4c** both methylene carbon atoms are above the π-plane with the height of one carbon half that of the other carbon. When a methylene group is above the π-plane, one C-H bond of the methylene group is approximately perpendicular to the π-plane ($C\text{-}H_{ax}$ bond) while the other C-H bond is approximately parallel to the π-plane ($C\text{-}H_{eq}$ bond) (see **5**).

Diagram **6** shows a stereodiagram of how the BEDT-TTF molecules of β*-$(BEDT\text{-}TTF)_2I_3$ (i.e., β-$(BEDT\text{-}TTF)_2I_3$ with $T_c \cong 8K$ under pressure greater than 0.5 kbar[3, 12]) make short C-H···donor and C-H···anion contacts. We note from **6** that (a) the π-framework of BEDT-TTF is nearly flat, (b) each donor molecule has

5



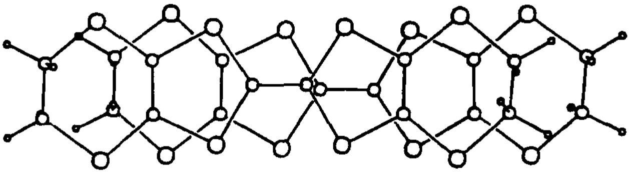


6

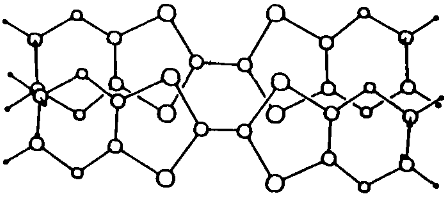
the six-membered ring conformations **4a** and **4b**, and (c) the C-H bonds of BEDT-TTF make short C-H···S, C-H···C(sp^2), and C-H···H contacts with the adjacent donor molecules and also make short C-H···I contacts with the anions I_3^-. Two C-H_{ax} bonds of each donor molecule are positioned on top of the five- and six-membered rings of the adjacent donor molecules.

In a 'donor molecule dimer' of β^*-(BEDT-TTF)$_2$I$_3$, the molecules are slipped along the direction parallel to the donor molecule central C=C bond, as shown by a projection view **7a**. In contrast, the molecules in a donor stack of (BEDO-TTF)$_2$AuBr$_2$ are slipped along the direction perpendicular to the donor central C=C bond, as shown by a projection view **7b**[2, 11]. The latter slipping

7a

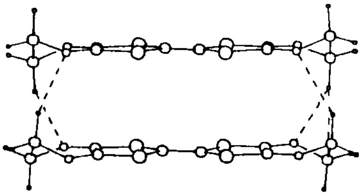


7b

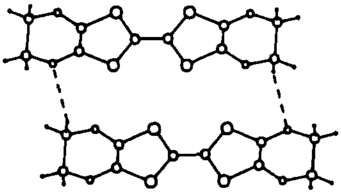


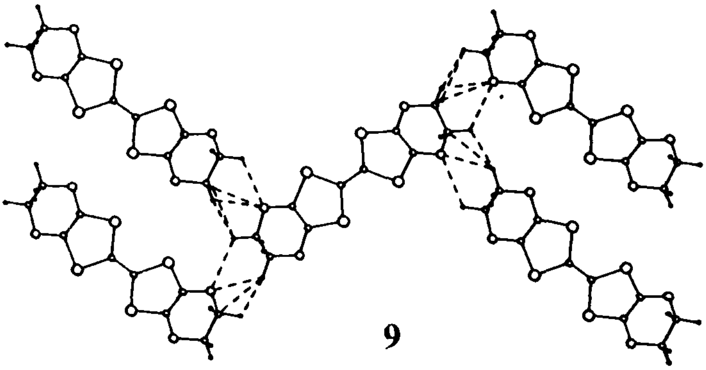
allows the donor molecules in $(BEDO\text{-}TTF)_2AuBr_2$ to make short C-H···O contacts both within each donor stack (**8a**) and between adjacent donor stacks (**8b**). The difference between the donor molecules BEDT-TTF and BEDO-TTF is also apparent in the structural behaviors of their neutral solids. A layer of BEDO-TTF molecules in neutral BEDO-TTF solid is depicted in **9**, which shows that the donor molecules make optimum use of the C-H···O contacts[2]. Neutral BEDO-TTF molecules have a bent π-framework, which leads to short C-H···O, C-H···S, and C-H···C(sp^2) contacts between layers of donor molecules.

8a



8b





9

As described above, important structural properties of the donor molecules BEDT-TTF and BEDO-TTF are their π-framework bending and their six-membered ring conformation. In the next section, we examine how these variables are affected by the C-H···donor and C-H···anion interactions by carrying out ab initio SCF-MO/MP2 calculations.

COMPUTATIONAL METHODS

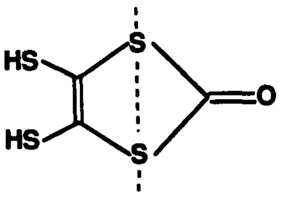
The ab initio SCF-MO/MP2 calculations described in the present work are carried out by using GAUSSIAN 86[13] and PSHONDO[14] programs. Unless stated otherwise, the atomic orbital basis sets used in our calculations are as follows: The C, O, S, and H atoms were represented by the 3-21 G basis set. For the Se, Te, Cl, Br and I atoms, the core electrons were represented by the pseudopotentials of Wadt and Hay[15] in GAUSSIAN 86 calculations and by those of Barthelat and Durand[16] in PSHONDO calculations, while the valence electrons were described by a [2s, 2p] basis orbitals contracted from (3s, 3p) in both GAUSSIAN 86 and PSHONDO calculations.

RESULTS AND DISCUSSION

A. π-FRAMEWORK BENDING

The donor molecule BEDT-TTF is large for ab initio calculations, so we examine the energetics of its π-framework bending by performing ab initio SCF-MO calculations on the model systems **10** and **11** as a function of the bending angle θ. The geometry of **11** was taken from the structure of neutral BEDT-TTF by replacing the C(sp^2)-S bonds of the six-membered rings with C-H bonds (1.08 Å). The geometry of **10** was also taken from neutral BEDT-TTF by replacing the central C=C bond with a C=O bond (1.215 Å) and by replacing the S-C (sp^3) bonds of the six-membered ring with S-H bonds (1.340 Å). The energies of **10** and **11**, with respect to those for θ=0°, are summarized in Table 1. Also listed in Table 1 are the

10



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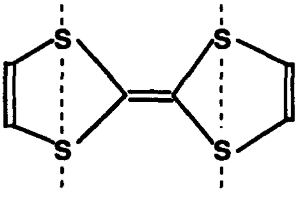


energies of **10**, and **11**, neutral BEDT-TTF (**3a**), and BEDT-TTF$^+$ cation (**3a**$^+$) calculated by the semiempirical MNDO SCF-MO method[17].

TABLE 1. Relative energies (kcal/mol) of the molecules **10**, **11**, **3a**, and **3a**$^+$ calculated as a function of the π-framework bending angle θ (degrees) by using the ab initio SCF-MO (with the 3-21G basis set) and the MNDO SCF-MO methods

θ	ab initio SCF-MO		MNDO SCF-MO			
	10	**11**	**10**	**11**	**3a**	**3a**$^+$
0	0.00	0.00	0.00	0.00	0.00	0.00
5	0.16	-	0.12	-	0.19	0.46
10	0.65	-	0.49	-	0.78	1.85
15	1.45	0.92	1.97	1.80	1.81	4.21

Table 1 shows that BEDT-TTF is most stable when its π-framework is flat (θ=0°), but the potential surface for the π-framework bending is very soft. When BEDT-TTF is oxidized, the bending potential becomes stiffer. These findings are consistent with the observation that the π-frameworks of BEDT-TTF and BEDO-TTF are bent in their neutral solids but flat in their charge-transfer salts. The π-framework bending of the donor molecules in their neutral solids must be caused by external forces associated with short intermolecular contacts.

B. SIX-MEMBERED RING CONFORMATION

Based on steric considerations, the staggered conformation **4a** is expected to be the most stable one among the conformations **4a**-**4d** of the six-membered ring. However, ring conformations other than **4a** are found experimentally as described in the previous section. Thus we examine the relative energies of the six-membered ring conformations **4a**-**4d** by carrying out ab initio SCF-MO/MP2 calculations on the model **12**. In order to continuously vary the conformation of **12** from **4a** to **4d**, we performed molecular mechanics calculations on **12** using the MMP2 (85) program[18] as function of the two methylene carbon atom heights from the π-plane.

These MMP2 (85) calculations show that the conformation **4a** is the only energy minimum on the potential energy surface. Ab initio SCF-MO/MP2 calculations were performed for the conformations **4a-4d** using their geometrics determined by the MMP2 (85) calculations. As summarized in Table 2, our ab initio calculations show that the staggered conformation **4a** is the most stable one among **4a-4d** in agreement with the MMP2 (85) results, and that a conformational change away from **4a** does not require much energy as long as it avoids the fuly eclipsed conformation **4d.** (The latter has not been experimentally observed so far.) As discussed in the previous section, six-membered ring conformations other than **4a** are found experimentally. The occurrence of such conformations must arise from external forces associated with short intermolecular contacts, as in the case of the π-framework bending.

12

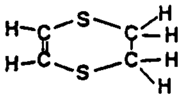


TABLE 2. Relative energies of the six-membered ring conformations **4a** - **4d** calculated by the ab initio SCF-MO/MP2 method using the 3-21G basis set

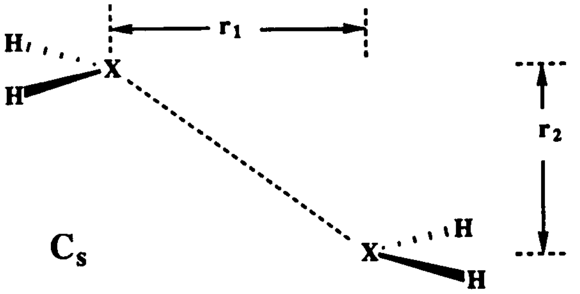
Conformation	Relative energy (kcal/mol)
4a	0.00
4b	0.61
4c	2.94
4d	5.67

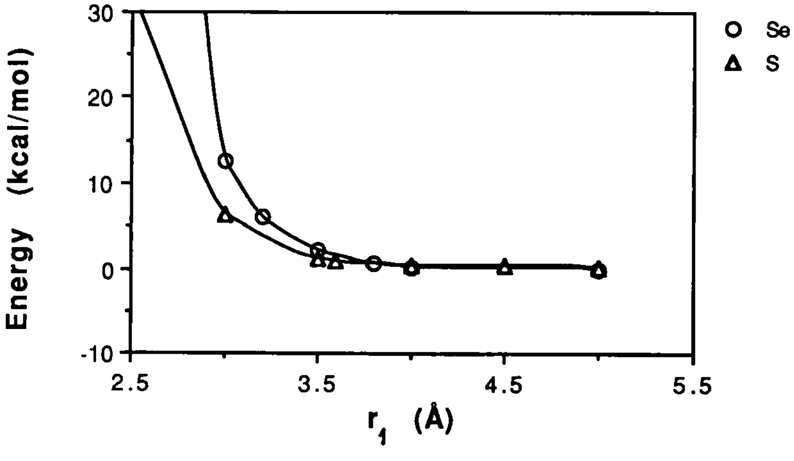
Diagrams **2** and **6** show that the short intermolecular contacts of importance are donor···donor and donor···anion contacts involving the C-H bonds. Though not shown in these diagrams, there exist short S···S contacts (shorter than the van der Waals radii sum of 3.60Å) between the donor molecules. In the following, therefore, we examine the nature of these S···S, C-H···donor, and C-H···anion contact interactions.

C. S···S AND Se···Se INTERACTIONS

To examine the nature of the S···S contact interactions, we carry out ab initio SCF-MO/MP2 calculations on the $H_2S \cdots SH_2$ dimer as a function of the r_1 and r_2 distances defined in **13**, where two H_2S molecules are arranged to have a D_{2h} point group symmetry. Our calculations employed the experimental geometry of H_2S (H-S = 1.3455 Å, <HSH = 93.3°) and the 3-21 G* basis set. The potential energy surface of $H_2S \cdots SH_2$, calculated at the SCF-MO/MP2 level as a function of r_1 and r_2, shows that the $H_2S \cdots SH_2$ interaction is always repulsive, although the potential energy surface is soft in the vicinity of the van der Waals S···S contact distance. Diagram **14** shows the potential energy curve for the colinear approach of $H_2S \cdots SH_2$ (i.e., $r_2 = 0$). With respect to the dissociation limit, the $H_2S \cdots SH_2$ dimer is less stable by 0.85 kcal/mol at $r_1 = 3.60$ Å and $r_2 = 0$.

13





14

For the purpose of comparison, we also examined the potential energy surface of $H_2Se\cdots SeH_2$ dimer (see **13**) by using the experimental geometry of H_2Se (H-Se = 1.47 Å, < HSeH = 91.0°) and the 3-21G* basis set for H and the same quality basis set for the valence orbitals of Se (built from the contracted [2s, 2p] set of Wadt and Hay[15] by adding one set of d-functions with exponent 0.38). Just as in the case of $H_2S\cdots SH_2$, the potential energy of the $H_2Se\cdots SeH_2$ interaction is repulsive, although it is soft in the vicinity of the van der Waals Se···Se contact distance (3.80 Å). The potential energy curve for the colinear approach of $H_2Se\cdots SeH_2$ (i.e., $r_2 = 0$) is also shown in **14**. Compared with the dissociation limit, the $H_2Se\cdots SeH_2$ dimer is less stable by 0.66 kcal/mol at $r_1 = 3.80$ Å and $r_2 = 0$.

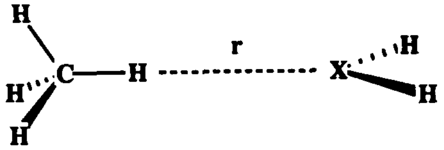
Our ab initio calculations on $H_2X\cdots XH_2$ (X = S, Se) strongly suggest that the X···X interactions are repulsive in nature but are soft in the region of the van der Waals X···X contact distance. Therefore, the occurrence of short X···X contacts in organic donor salts must originate mainly from some other types of attractive intermolecular interactions. As will be described in the following, such attractive forces are provided by the C-H···donor and C-H···anion contacts.

D. C-H···DONOR INTERACTIONS

As described in the previous section, short C-H···donor contacts can be grouped into three classes: (a) the C-H···heteroatom contacts (e.g., C-H···O, C-H···S), (b) the C-H···C(sp^2) contact, and (c) the C-H···H-C contact. To investigate the nature of these interactions, we carry out ab initio SCF-MO/MP2 calculations on the model systems **15a-15c**. A C-H···heteroatom interaction between CH_4 and XH_2 (X = O, S, Se, Te) is shown in **15a** where one C-H bond of CH_4 approaches the σ-lone pair orbital of XH_2 in a colinear fashion while keeping the C_s symmetry for $H_3C-H\cdots XH_2$. A C-H···C(sp^2) interaction between CH_4 and $CH_2 = CH_2$ is depicted in **15b** where one C-H bond of CH_4 approaches the p-orbital of one double-bond carbon atom colinearly with the C_s symmetry for $H_3C-H\cdots CH_2=CH_2$. Diagram **15c** represents a C-H···H interaction between two CH_4 molecules, in which the C-H bonds associated with the C-H···H contact are colinear with the D_{3h} symmetry for $H_3C-H\cdots H-CH_3$.

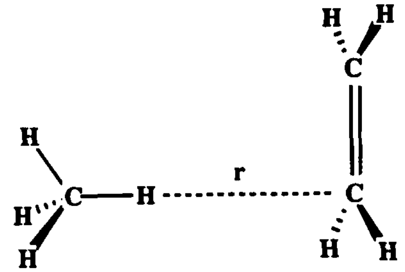
In our ab initio calculations on the models **15a-15c**, which were carried out as a function of the contact distance r, the geometries of the molecular fragments and the overall symmetries of the composite systems were kept constant (i.e., C-H = 1.091 Å and <HCH = 109.47° for CH_4; O-H = 0.9584 Å and <HOH = 104.45° for

15a



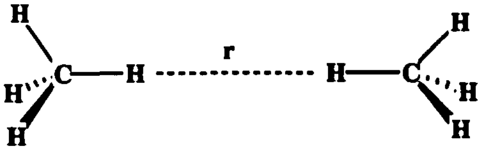
C_s

15b



C_s

15c



D_{3h}

H_2O, S-H = 1.3455 Å and <HSH = 93.3° for H_2S, Se-H = 1.470 Å and <HSeH = 91.0° for H_2Se, Te-H = 1.6539 Å and <HTeH = 90.4° for H_2Te; C-H = 1.076 Å, C-C = 1.330 Å, and <HCC = 121.7° for $CH_2 = CH_2$). Our ab initio SCF-MO/MP2 calculations on the model systems were carried out using the 3-21G as well as the more extensive basis sets 6-311G** and 6-311 + G** [13]. Table 3 summarizes the results of our calculations where r_{opt} (Å) is the calculated optimum contact distance and ΔE (kcal/mol) is the dissociation energy calculated at r_{opt}. In sharp contrast to the case of the S···S and Se···Se interactions between donor molecules, all donor···donor interactions involving the C-H bonds are attractive. These C-H···donor intractions are comparable in magnitude to the energies required for the π-framework bending or the six-membered ring conformation change. Since the donor molecules have numerous C-H···donor contacts per molecule in the neutral solids and charge-transfer salts of BEDT-TTF and BEDO-TTF, the stabilization energy resulting from these C-H···donor contacts is expected to be greater than the destabilization energy associated with the donor π-framework bending, the adoption of higher energy six-membered ring conformations, and the repulsive S···S contacts.

TABLE 3. Optimum contact distances r_{opt} (Å) and dissociation energies ΔE (kcal/mol) of the various C-H ··· donor contacts calculated by the ab initio SCF-MO/MP2 method using the 3-21G, 6-311G** and 6-311+G** basis sets

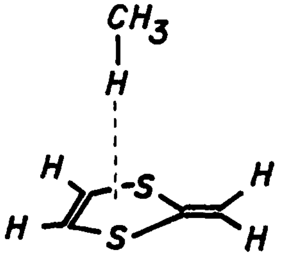
Contacts	3-21G		6-311G** / 6-311+G**	
	r_{opt}	ΔE	r_{opt}	ΔE
C-H ··· O	2.23	3.05	2.58^a	1.48^a
			2.70^b	1.08^b
C-H ··· S	3.05	0.52	3.96^a	0.48^a
C-H ··· Se	3.45	0.28	4.34^a	0.26^a
C-H ··· Te	3.75	0.27	---	---
C-H ··· C(sp^2)	3.09	0.93	3.22^b	0.58^b
C-H ··· H	2.39	0.54	2.74^b	0.20^b

[a] 6-311G** [b] 6-311+G**

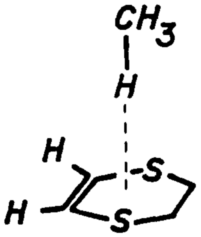
Table 3 shows that the C-H···X (X = O, S, Se, Te) interaction energies decrease in the order C-H···O > C-H···S > C-H···Se > C-H···Te, which follows the electronegativity ordering of the X atoms. This trend in the C-H···X (X = O, S, Se, Te) interaction energies explains why in a donor layer of neutral BEDO-TTF solids the molecules make optimum use of C-H···O contacts and also why the BEDO-TTF salts $(BEDO\text{-}TTF)_2X$ ($X^- = AuBr_2^-$, ClO_4^-) have a donor packing arrangement in which the donor molecules have optimum use of C-H···O contacts within a donor stack as well as between adjacent donor stacks [2]. According to the ΔE values obtained from the extensive basis sets 6-311G** and 6-311 + G**, the C-H···C(sp^2) and C-H···H interactions are similar in magnitude to the C-H···S and C-H···Se interactions, respectively. Compared with the 3-21G basis set results, the extensive basis sets provide smaller ΔE and longer r_{opt} values. Currently, we are studying how the ΔE and r_{opt} values are affected by further increasing the basis set quality.

It was noted from **6** that, in β*-(BEDT-TTF)$_2$I$_3$, two C-H$_{ax}$ bonds of the donor molecule are positioned on top of the five- and six-membered rings of the adjacent donor molecules. These C-H$_{ax}$ bonds therefore make several C-H···C(sp^2), C-H···S, and C-H···H contacts. To examine the overall interaction energies of these C-H···ring contacts, we performed ab initio SCF-MO/MP2 calculations on model **16** for the C-H$_{ax}$···five-membered ring interaction and model **17** for the C-H$_{ax}$···six-membered ring interaction. In **16** and **17** the geometries of the five- and six-membered rings were taken from the structure of β*-(BEDT-TTF)$_2$I$_3$ except that the C(sp^2)-S bonds are replaced by C-H bonds (1.08 Å), while one of the C-H bonds of CH$_4$ is positioned just as the C-H$_{ax}$ bond is found in β*-(BEDT-TTF)$_2$I$_3$. Our calculations reveal that, with respect to the dissociation limit, the C-H···five- and the C-H···six-membered ring interactions are more stable by 0.06 and 0.82 kcal/mol, respectively. The calculated energy minima for **16** and **17** are found when the CH$_4$ molecules are moved away from the rings along the directions of the C-H$_{ax}$ bonds. At the calculated optimum positions of CH$_4$ molecules, the interaction energies for the C-H···five- and the C-H···six-membered ring contacts are 1.35 and 1.22 kcal/mol, respectively. Therefore, the nature of the C-H···ring interactions is attractive, which is reasonable because they consist of attractive C-H···donor interactions such as C-H···C(sp^2), C-H···S, and C-H···H.

16



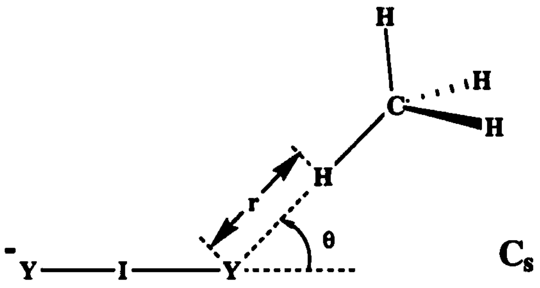
17



E. C-H···ANION INTERACTIONS

To probe the nature of the donor···anion contact interactions associated with the C-H bonds, we perfomed ab initio SCF-MO/MP2 calculations on the model systems H$_3$C-H···Y-I-Y$^-$(Y=I, Br, Cl) shown in **18**, where one C-H bond of CH$_4$ approaches the end halogen atom of Y-I-Y$^-$ anion with the C$_s$ symmetry for H$_3$C-H···Y-I-Y$^-$. In our ab initio calculations on H$_3$C-H···Y-I-Y$^-$ as a function of the contact distance r and the contact angle θ (see **18**), the geometries of CH$_4$ and Y-I-

18



Y^- were kept constant (i.e., the geometry of CH_4 is the same as described in the previous seciton, and the Y-I-Y^- anion geometries were taken from the calculated optimum values[19]: I - I = 2.995 Å , I - Br = 2.7705 Å, and I - Cl = 2.598 Å).

According to our preliminary ab initio SCF-MO calculations[20] on H_3C-H···Y-I-Y^- using PSHONDO program (the double zeta quality basis set augmented with a set of s and p diffuse functions and a set of d-polarization functions on I, Br, Cl, and C and the double zeta quality basis set augmented with a set of p-polarization functions on H), the optimum θ values are 79.0°, 69.2°, and 0.0° for Y = I, Br, and Cl, respectively. In our ab initio SCF-MO/MP2 calculations on H_3C-H···Y-I-Y^- using GAUSSIAN 86 program, we adopted these θ values and optimized only the C-H···Y contact distance r by using the 3-21+G** basis set for CH_4. For the halogen atoms I, Br and Cl, we employed the [2s, 2p] basis contracted from (3s, 3p)[15] augmented with a set of diffuse s and p functions (exponents of 0.020344, 0.05 and 0.049 for I, Br, and Cl, respectively) and a set of d-polarization functions (exponents of 0.25, 0.371, and 0.58 for I, Br, and Cl respectivley). These basis sets of the halogen atoms are similar in quality to those used for C and H.

Our ab initio SCF-MO/MP2 results on H_3C-H···Y-I-Y^- are summarized in Table 4, where r_{opt} (Å) is the calculated optimum H···Y distance and ΔE (kcal/mol) is the dissociation energy calculated at r_{opt}. Note from Table 4 that the nature of the C-H···anion contact interactions is, as expected, attractive. The magnitudes of these C-H···anion interactions are somewhat greater than that of the C-H···O interaction (calculated with the similar quality basis set, 6-311 + G**), the strongest C-H···donor interaction in Table 3. Thus the C-H···anion contacts are energetically more favorable than the C-H···donor contacts. This finding, plus the fact that the π-framework bending of the donor molecules becomes stiffer upon partial oxidation, accounts for the nearly planar π-frameworks of the donor molecules in the charge-transfer salts of BEDT-TTF and BEDO-TTF. Examination of the crystal structures of α-(BEDT-TTF)$_2$I$_3$ and β*-(BEDT-TTF)$_2$I$_3$ reveals[5] that each donor molecule on

TABLE 4. Optimum contact distances r_{opt} (Å) and dissociation energy ΔE (kcal/mol) of the various C-H ··· anion contacts calculated by the ab initio SCF-MO/MP2 method

Contacts	r_{opt}	ΔE
H_3C-H ··· $I\text{-}I\text{-}I^-$	3.50	1.13
H_3C-H ··· $Br\text{-}I\text{-}Br^-$	3.14	1.27
H_3C-H ··· $Cl\text{-}I\text{-}Cl^-$	2.85	1.58

average has more C-H···anion contacts in β*-(BEDT-TTF)$_2$I$_3$ than in α-(BEDT-TTF)$_2$I$_3$. Likewise, each donor molecule on average has more C-H···anion contacts in α'-(BEDT-TTF)$_2$AuBr$_2$ than in δ-(BEDT-TTF)$_2$AuBr$_2$[6]. Consequently, the thermal conversion of α-(BEDT-TTF)$_2$I$_3$ to α_t-(BEDT-TTF)$_2$I$_3$ (which is believed to be quite similar in structure to β*-(BEDT-TTF)$_2$I$_3$) and that of δ-(BEDT-TTF)$_2$AuBr$_2$ to α'-(BEDT-TTF)$_2$AuBr$_2$[5,6] are consistent with the finding that the C-H···anion contacts are energetically more favorable than the C-H···donor contacts.

CONCLUDING REMARKS

Important structural parameters of an organic donor molecule such as BEDT-TTF and its analogs are the π-framework bending and the six-membered ring conformation. According to the present study, the π-framework of a donor molecule is most stable when flat but the π-framework bending potential is very soft. The conformation of the six-membered ring is most stable when staggered (**4a**) but the potential surface for the ring conformational change is very soft. Therefore, the occurrence of the π-framework bending and the adoption of a ring conformation other than the staggered one originate from the external forces associated with the short intermolecular contacts less than the van der Waals radii sums.

Short intermolecular contacts in neutral solids and charge-transfer salts of organic donor molecules can be grouped into three classes: (a) the chalcogen···chalcogen (e.g., S···S, Se···Se), (b) the C-H···donor, and (c) the C-H···anion contacts. Our ab initio SCF-MO/MP2 calculations reveal that the chalcogen···chalcogen contact interactions are repulsive although the potential surfaces for the interactions are very soft in the vicinity of their van der Waals contact distances. It is the C-H···donor (e.g., C-H···heteroatom, C-H···C(sp^2), and C-H···H) and the C-H···anion contacts that lead to attractive interactions and therefore provide the energy needed for the π-framework bending in the neutral donor solids and the donor molecule six-membered ring conformational changes. Therefore the packing patterns of donor-molecule layers of organic donor salts are largely a consequence of making optimum use of the attractive C-H···donor and C-H···anion contact interactions. Since the electronic properties of organic donor salts are primarily determined by the packing patterns of their donor molecule layers, it is essential to accurately describe the C-H···donor and C-H···anion interactions in order to develop a more complete understanding of these novel materials.

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