

Strength and Directionality of the S...S Intermolecular Interactions Present in TTF-Based Molecular Crystals. A Combined Statistical and Ab Initio Study

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Abstract: The strength and directionality of the S...S interactions have been evaluated by combining the results from the statistical analysis of neutral and charge-transfer molecular crystals of the tetrathiafulvalene (TTF) family with those from Møller–Plesset (MP2) calculations on model systems. The model systems have been designed to represent the environment of the S...S interactions in these crystals. Our statistical analysis of the geometrical distribution of the S...S contacts in these crystals

suggests that they are attractive and that there is a maximum probability for collinear S...S orientations. Small differences are found between the neutral and charge-transfer distributions. MP2 computations on the H₂S dimer and functionalized XYS dimers oriented to

present short S...S contacts show that the S...S interactions are attractive and quite anisotropic. Their strength depends significantly on the X and Y functional groups and can be of the order of $-1.5 \text{ kcal mol}^{-1}$ for the $\pi-\pi$ interactions between the five-membered rings of the TTF molecule. Consequently, S...S interactions should contribute significantly to the cohesive energy of TTF-based crystals.

Keywords: ab initio calculations • conducting materials • crystal engineering • S...S noncovalent interactions • stacking interactions

Introduction

The packing of a molecular crystal is a compromise that involves all the intermolecular interactions between the molecules in that crystal.^[1] The stronger energetic interactions can force a change in the optimum energy conformation of weaker ones, if the number or strength of the stronger interactions is increased by this process. Consequently, although the geometrical distribution of the molecules in the packing is at a minimum for the total interaction energy, this does not necessarily imply that each interaction is in its minimum energy geometry. Therefore, knowing the strength of the intermolecular interactions presumed to dominate the packing is very helpful for qualitative rationalization. Traditionally, the dominating interactions are identified by looking at the shortest intermolecular contacts present in the crystal, supposedly the strongest ones,^[1c] although there are exceptions to this rule.^[2]

The rationalization of the crystal packing is relevant because it determines the crystal electronic structure^[3] and, therefore, the ability of the material to become a conductor or superconductor,^[4] to name but two properties of potential

interest. It is experimentally known that different crystal packings of the same molecule sometimes results in different electrical and magnetic properties.^[3] Therefore, for a proper understanding and control of these properties in molecular crystals it is necessary to understand the key factors that determine their crystal packing and their influence on the electronic structure. This implies a good knowledge of the strength and directionality of the shortest intermolecular interactions present in the crystal of interest.

Among the molecular crystals, some of the most studied are those with conducting and superconducting properties.^[4] Most of these crystals are charge-transfer solids with a donor molecule D that donates some of its electrons to an acceptor molecule A, which then becomes negatively charged. In many of these crystals, D is a derivative of the tetrathiafulvalene (TTF) molecule (Figure 1a), in which some of the TTF external H atoms have been substituted by various types of functional groups. One example is the BEDT-TTF (BEDT = bis(ethylenedithio)tetrathiafulvalene) molecule, one of the donors that gives D_nA_m crystals with superconducting properties. The connection between packing and the conducting properties of these crystals is well known. However, the factors controlling their packing are not fully understood yet,^[4] a major drawback for the design of new crystals with these properties.

The analysis of the molecular conducting and superconducting crystals shows the existence of many short contacts of the S...S type, together with short C(spⁿ)–H...S ($n = 1, 3$)

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contacts;^[4] this suggests a key role of these two types of contacts in the packing of these crystals. While the nature, strength, and anisotropy of the second type of contacts has been studied in detail by accurate ab initio methods,^[5] knowledge of the strength and directionality of the S...S contacts is limited. Most of this information was obtained from statistical analysis on selected subsets of the Cambridge Structural Database (CSD).^[6] This information allowed us to obtain a first characterization of the S...S properties in the form of an isotropic atom–atom potential, whose minimum

Abstract in Catalan: *En aquest treball s'ha investigat la força i direccionalitat de les interaccions S...S en cristalls orgànics moleculars de la família del tetratiofulvalè (TTF). La metodologia emprada consisteix en una anàlisi estadística de la distribució geomètrica dels contactes S...S en cristalls neutres i sals de transferència de càrrega, combinada amb càlculs ab initio Møller–Plesset (MP2) en sistemes senzills que modelen l'entorn de les interaccions S...S en els esmentats cristalls. Els resultats de l'anàlisi estadística ens suggereixen que les interaccions S...S són atractives, alhora que apareix un màxim de probabilitat per interaccions col·lineals. Val a dir que es troben petites diferències entre les distribucions corresponents a cristalls neutres i les corresponents a les sals. Pel que fa als càlculs MP2, aquests s'han realitzat en el dímer d'H₂S i en dímers funcionalitzats de fórmula (XYS)₂, orientats de manera que presentin contactes S...S. Els resultats obtinguts posen de manifest que les interaccions S...S són atractives i força anisotròpiques. L'energia d'interacció presenta una forta dependència amb el tipus de substituents X,Y i, en el cas d'interaccions π–π que s'estableixin entre els anells de cinc membres de la molècula de TTF, pot arribar a –1.5 kcal mol⁻¹. Tot això ens porta a la conclusió que les interaccions S...S contribueixen significativament a l'energia de cohesió dels cristalls derivats del TTF.*

Abstract in Spanish: *La fuerza y direccionalidad de las interacciones S...S se ha estudiado combinando, por una parte los resultados del análisis estadístico de cristales neutros y de transferencia de carga de moléculas de la familia de los tetratiofulvalenos (TTF), y por otra cálculos Møller–Plesset (MP2) de sistemas modelo diseñados para representar el entorno de las interacciones S...S en dichos cristales. Nuestro estudio estadístico de la distribución geométrica de los contactos S...S en esos cristales, sugiere que son atractivos y con probabilidad máxima para orientaciones colineales. Las diferencias entre las distribuciones de los cristales neutros y de transferencia de carga son pequeñas. Cálculos MP2 sobre el dímero del H₂S y dímeros XYs orientados de tal forma que presenten contactos cortos S...S, muestran que las interacciones S...S son atractivas y bastante anisotrópicas. Su fuerza depende significativamente del grupo X e Y empleado, pudiendo ser del orden de –1.5 kcal mol⁻¹ para las interacciones π–π existentes entre dos anillos de cinco de la molécula de TTF. Por lo tanto, las interacciones S...S deberían contribuir de forma significativa a la energía de cohesión de los cristales de la familia del TTF.*

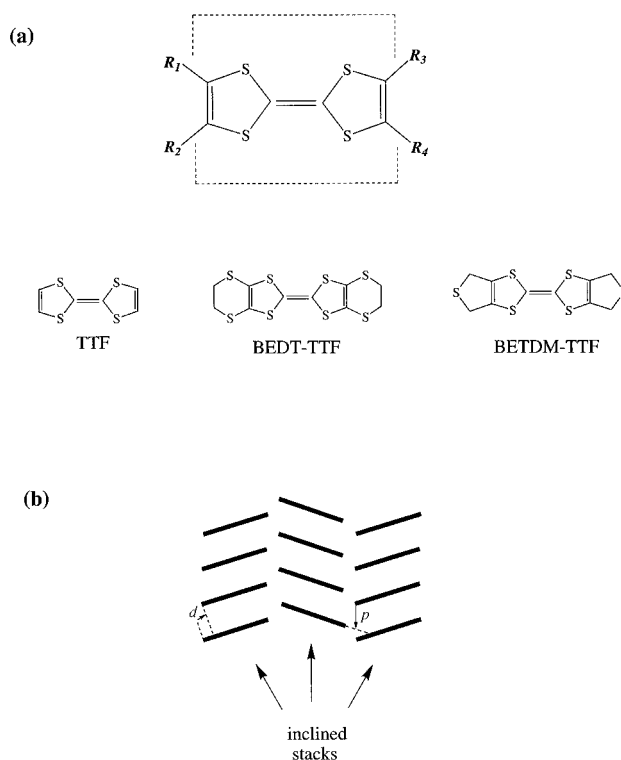


Figure 1. a) General form of the TTF-based family of molecules with some specific examples. b) Most usual packing found in the TTF-based crystals.

lies at 3.83 Å and its minimum energy is –0.44 kcal mol⁻¹.^[7d] However, different subsets provided slightly different angular distributions.^[7a–c] Consequently, we decided to perform a detailed statistical analysis on the geometrical distribution of the short S...S contacts found in the TTF-based crystals present in the CSD.

The results from the statistical analysis of the crystal packing give averaged information on the nature of the S...S interactions. To gain more detailed knowledge, one can carry out complementary ab initio computations on these interactions. Therefore, as a result of the longstanding interest of our group in the nature, strength, and directionality of the intermolecular interactions in organic conductors and superconductors,^[5, 8] we decided to extend these studies to the S...S intermolecular interactions found in the crystals of organic conductors and superconductors of the TTF family.^[4] This requires the use of model systems selected to mimic the local electronic structure and geometry of the S...S contacts found in the neutral and charge-transfer TTF-based crystals. A B3LYP/6–31 + G(d,p) Mulliken population analysis^[9] on the TTF⁻, TTF⁺, and TTF²⁺-isolated D donor showed that the net charge is delocalized over the whole donor. The net charge on the S atom is 0.02 e in the neutral molecule, which becomes 0.19 e and 0.30 e in the +1 and +2 cations, respectively. This fact combined with the small amount of charge transfer suggests that the S...S interactions found within the donor stacks of the D_nA_m charge-transfer salts should be similar to those found in the packing of their D neutral precursors. This is probably the reason for the similar packing found for D in some neutral TTF-based crystals and in their D_nA_m charge-

transfer crystals, which involve small acceptors.^[10] In the light of these facts, it seems natural to use neutral model dimers as starting models in our study of the intermolecular S...S interactions.

To obtain a general picture of the nature of the S...S interactions found in the TTF-based neutral and charge-transfer crystals, we proceeded in the following way: first, we performed a statistical analysis on the TTF-based neutral and charge-transfer crystals in the CSD database.^[6] This determined the main features of their packing and the preferred geometrical position of these contacts, which were required to select the representative model systems used in our ab initio computations. Then, we carried out Møller–Plesset computations with extended basis sets on the model systems. We studied the nature of the S...S interaction in the H₂S dimer and then we analyzed how these results were modified when the H₂S hydrogens were substituted by functional groups of different size and electronegativity, such as methyl (–CH₃), ethylenyl (–CH=CH₂), and formyl (–CH=O) groups. Lastly, we studied the S...S interaction in the environment of the five-membered ring of the TTF molecule. In this form, we determined the impact of the chemical environment on the strength and directionality of the S...S interactions.

Results and Discussion

Statistical analysis of the geometrical arrangement of the S...S contacts in TTF-based crystals: We began our study by searching on the CSD database to find all purely organic neutral and charge-transfer molecular crystals with a functionalized TTF molecule (Figure 1). This search resulted in 102 neutral TTF-based crystals and 280 charge-transfer crystals, a set large enough to allow a meaningful statistical analysis of the S...S orientations. A visual inspection of these crystals showed that one of the most common packing motifs is one in which the TTF-based molecules are piled up to form inclined stacks, whose molecules are laterally displaced by a value d (Figure 1b). These stacks are repeated along the long or short molecular axis (Figure 1b) with a p vertical displacement between the adjacent planes (defined as the distance between the extreme of one plane and the prolongation of the closest plane in the adjacent stack along the stack-packing direction). In this type of geometrical arrangement, the shortest S...S contacts are expected to be found between S atoms of neighboring molecules of the same stack or between S atoms of one stack and those of the adjacent stack. The other general packing motif is a T-shaped one, which is similar to that found in benzene, although in this case it sometimes involves individual molecules, whereas in other cases, like in the BEDT-TTF neutral crystal,^[10] it involves pairs of molecules. From the point of view of the geometrical distribution of the S...S contacts, the two motifs are not so different, as in both cases for one atom the shortest contacts are nearly perpendicular to the plane of the other molecule. There are also cases in which none of these motifs are found.

As we wanted to test the influence of the possible charge transfer on the S...S preferred orientations, we built two separate subsets, one with the neutral precursors and the

other with the charge-transfer TTF-based crystals. In each subset, we selected, for a geometrical study, all the S...S contacts whose S–S bond lengths were smaller than 4.5 Å. This is a bond length slightly larger than the sum of the isotropic van der Waals radii of sulfur.^[11] There were 1287 S...S contacts which fulfilled that criterion in the neutral subset and 6690 in the charge-transfer subset. The geometry of these contacts was analyzed by using the geometrical parameters defined in Figure 2. Six parameters are generally

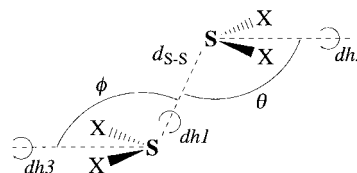


Figure 2. Geometrical parameters used to define the relative position of two H₂S molecules.

needed to describe the relative orientation in the space of two identical X₂S molecules whose geometry is frozen: the S...S bond length (d_{S-S}), the angles between the C_{2v} axis of each fragment and the intermolecular S...S bond (here called ϕ and θ), and three torsional angles that define the relative orientation between the two X₂S planes ($dh1$, $dh2$, and $dh3$). When a Y atom in each fragment substitutes one of the X atoms, the C_{2v} axis is lost, but one can still use the axis that passes through the middle of the $\angle XSY$ angle in the plane of the XY molecule. By using these parameters, the shortest S...S contacts within the same stack or between adjacent stacks are characterized by the following values for the angles: the intra-stack contacts have θ and ϕ angles in the 90–140° range (a value of 90° corresponds to the case of $d=0$ lateral displacement). The inter-stack contacts are mostly in the 140–180° range (the last value for $p=0$ vertical displacements). Notice that the range of definition for the ϕ and θ angles is 0–180°, while the dihedrals have a 0–360° range.

Figure 3 shows the histograms for the neutral subset that give the number of S...S contacts for each value of the geometrical parameters. The same results are collected in Figure 4 for the charge-transfer subset. The distribution of contacts along the d_{S-S} length (Figures 3a and 4a) is similar in both subsets and has an inverted V shape. In the neutral subset, the maximum is located at 3.93 Å with a median at 3.932 Å. The equivalent values for the charge-transfer subset are shifted towards shorter lengths, at 3.78 and 3.881 Å, respectively. This 0.05 Å shift could result from the increase in the strength of the S...S interactions due to the small depopulation of the antibonding orbitals caused by the charge donation.^[12] However, it is difficult to know the size of the charge transfer in many of these crystals. Besides, as the charge transfer increases there are new C–H^{δ+}...X^{δ-} interactions between the donor and the acceptor^[4, 13] in addition to the S...S ones. On the other hand, the packing of the neutral crystals is a compromise between the S...S interactions and the competing C–H...S ones.^[14] Notice also that both d_{S-S} distributions are similar to those found by Gavezzotti et al.^[7d] in a much broader subset of crystals. Therefore, the S...S interactions in TTF-based crystals can be modeled by the

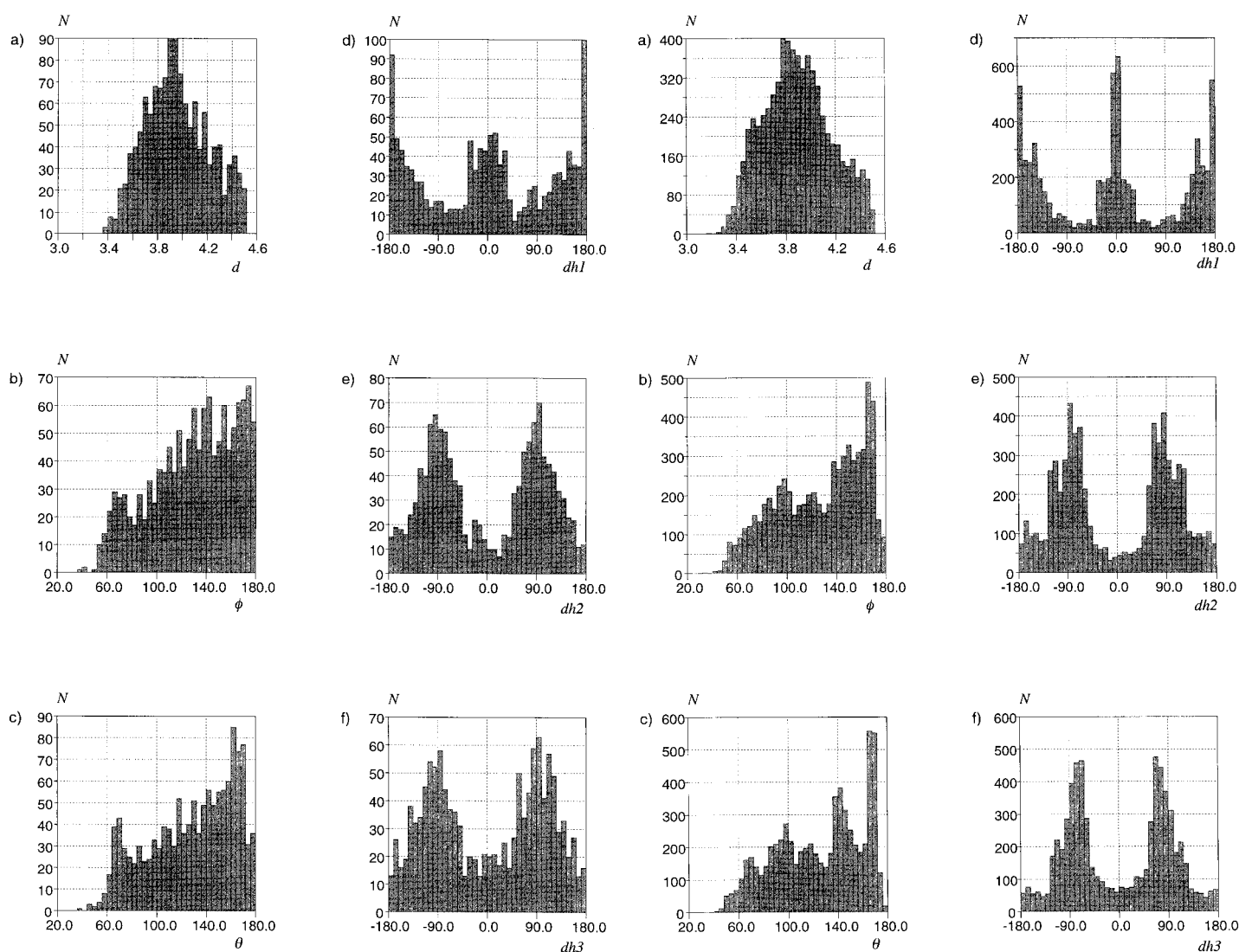


Figure 3. Distribution of the values of the geometrical parameters, defined in Figure 2, within the TTF-based neutral crystals. In the left column, the d_{S-S} , ϕ , and θ distributions are represented (a–c, respectively). In the right column, the data for the $dh1$, $dh2$, and $dh3$ dihedral angles are given, (d–f respectively). The distribution of ϕ and θ angles has been normalized by the solid-angle correction (conical correction).

same atom–atom potential that was introduced by these authors, that is, one with a minimum at $d_{S-S} = 3.93$ Å and a well depth of -0.44 kcal mol $^{-1}$.^[7d]

The angular distributions of the θ and ϕ angles (Figures 3b, 3c, 4b, and 4c) show a trend towards collinear angles in all four cases, although the maximum is around 170° in all these cases (the θ and ϕ histograms have been cone-corrected). The shape of the neutral and charge-transfer subsets is not the same, and the most striking difference is the number and importance of the local maxima. Also notice that the angular distribution is not the same as those reported in other studies;^[7a–c] this shows the influence of the type of subset in statistical packing analysis of $S \cdots S$ contacts. The absence of a maximum around 90° reflects the existence of $d \neq 0$ lateral displacements between consecutive planes of the stack. The maximum around 170° can be obtained if coplanarity is achieved between adjacent stacks ($p = 0$ and the adjacent

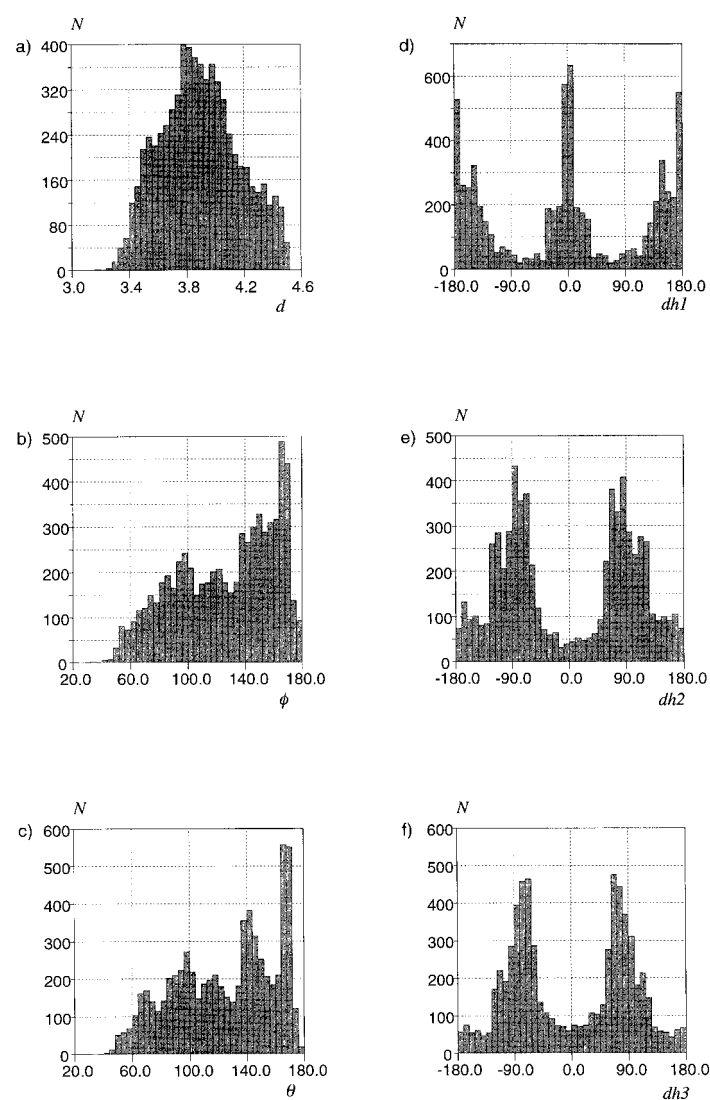


Figure 4. The same as Figure 3 for the TTF-based charge-transfer crystals.

stacks in Figure 1 are parallel, thus imposing $\theta = \phi = 180^\circ$), or when the p vertical displacement is zero and either θ or ϕ is 180° while the other parameter has a different value. The second case—the most probable one—is like the one depicted in Figure 1b. It can also be found for T-shaped motifs when the angle between the two molecules is 90° and the plane of one molecule hits the other molecule on top of one S atom (a fact quite common due to the $C-H \cdots S$ interactions between these two planes).^[10, 13]

The distribution of the dihedral angles in the $0-360^\circ$ range shows a sharp maximum for $dh1$ at 0° and 180° (Figures 3d and 4d), while that for the $dh2$ and $dh3$ parameters presents a sharp maximum at 90° (Figures 3e, 3f, 4e, and 4f). The results for these dihedral angles are consistent with the most probable arrangement discussed in the previous paragraph (Figure 1b). The shortest $S \cdots S$ contacts are between adjacent parallel stacks ($dh3 = 90^\circ$), such as the two XYS fragments that point in the same direction ($dh1 = 0^\circ$ for contacts within the same stack) or in opposite directions ($dh1 = 180^\circ$ for contacts between adjacent stacks). The d lateral displacements are, in most of the cases, along the short or long

molecular axis (this explains the $dh_2 = 90^\circ$). It is also consistent with T-shaped motifs under the conditions indicated above, but in this instance only contacts between the perpendicular molecules are made.

The packing pattern shown in Figure 1b is the average of different situations, and not all the crystals pack in this form. Both subsets show a similar tendency to pack in parallel planes. It is also worth pointing out here that other statistical studies carried out with different subsets of the CSD crystals did not find the same preferred orientations.^[7c] This fact reflects the presence of more than one class of packing patterns, the proportion of which in each analysis was different.

Ab initio study of the S...S contacts using model systems: The results of the previous section do not give a clear understanding of the nature of the S...S interactions in the TTF-based molecular crystals. As a result, we decided to carry out ab initio computations on some representative model dimers, which have the geometry and environment of the S...S contacts found in these crystals. We selected as model dimers the H₂S dimer, as the simplest test example, and XY S dimers, in which X and Y can go from an H atom to methyl (–CH₃), ethylenyl (–CH=CH₂), and formyl (–CH=O) groups. We also selected, as a representative case of the environment of the S atom in the TTF molecule, one of the five-membered rings of the TTF molecule (Figure 1) and substituted the central TTF double bond with a C=O bond. These dimers were oriented in such a way that the shortest contacts were always the S...S interactions.

Computational details: To compute the strength and directionality of the S...S interaction in the dimer systems, we had to select a method capable of giving a uniform precision for the calculation of the interaction energy of the dimers. It is well known that van der Waals interactions can be adequately described at the second order Møller–Plesset (MP2) level when an extended basis set is used, although a fourth order expansion (MP4) is required for very accurate results.^[15] However, given the size of some of our model dimers we used the MP2 method, after evaluating the importance of the MP4–MP2 difference on the smallest dimer.

To find the basis set required to describe the S...S interaction with enough precision, we computed the H₂S dimer interaction energy using various basis sets of increasing quality, with and without correction of the basis set superposition error (BSSE).^[15c, 16] Deliberately, we have selected the same basis sets for evaluation that were employed in a similar test on hydrogen-bonded dimers.^[17] These basis sets were built using totally different criteria and can be grouped into three classes.

- 1) The standard group, made up of Pople's standard basis sets, as the 6–31++G(d,p).^[18]
- 2) The correlation-consistent group, made up of part of the newly designed Dunning's basis set.^[19]
- 3) The extended group formed by LS(3d,2p) and LS(3d2f,3p2d), in which the LS part is the near-Hartree–Fock limit basis set of Lee and Schaeffer for the H atoms^[20] and the [11s8p] contraction of Partridge's

(11s8p) for the S atom.^[21] The (3d,2p) and (3d2f,3p2d) polarization part is taken from the polarization part of the correlation-consistent basis using the procedure explained in reference [17].

We have also included in the last group some of the standard basis sets, in which the polarization part was substituted by a (3d2f,3p2d) or (4d3f,4p3d) polarization set that were also from the correlation-consistent basis. In these computations, the geometry of the XY S...SXY' dimer was kept fixed at the intramolecular coordinates of $r_{SH} = 1.346 \text{ \AA}$ and $\angle HSH = 93.3^\circ$. The H atoms pointed outwards to allow a short S...S contact and to preserve the overall D_{2d} symmetry, and the plane of one XY S molecule was rotated 90° relative to the other. The intermolecular S...S bond length is optimized in each basis set.

The results of these calculations are summarized in Table 1. A graphical representation of Table 1 values (not plotted here) shows that the BSSE-corrected and uncorrected inter-

Table 1. Basis-set dependence of the BSSE-corrected interaction energy [kcal mol⁻¹] for the H₂S dimer at the D_{2d} geometry indicated in the text. The HF (ΔE_{cp}^{HF}) and MP2 (ΔE_{cp}^{MP2}) values are given, together with the size of the basis set (N) and, in parenthesis, the BSSE [kcal mol⁻¹].

	N	ΔE_{cp}^{HF} (BSSE)	ΔE_{cp}^{MP2} (BSSE)
6–31++G(d,p)	70	0.60 (0.07)	0.26 (0.91)
6–31++G(2d,2p)	94	0.50 (0.05)	–0.16 (0.28)
6–311G(2d,2p)	98	0.53 (0.12)	–0.19 (0.35)
6–311G(2df,2pd)	132	0.49 (0.15)	–0.21 (0.33)
6–311G(3df,3pd)	154	0.54 (0.11)	–0.42 (0.44)
6–311++G(2d,2p)	110	0.55 (0.05)	–0.21 (0.32)
6–311++G(2df,2pd)	144	0.57 (0.07)	–0.23 (0.30)
6–311++G(3df,3pd)	166	0.56 (0.07)	–0.41 (0.40)
6–311++G(3d,3p)	132	0.55 (0.06)	–0.38 (0.41)
cc-pVDZ	56	0.42 (0.10)	0.13 (0.15)
aug-cc-pVDZ	90	0.57 (0.04)	–0.33 (0.31)
cc-pVTZ	124	0.47 (0.02)	–0.22 (0.08)
aug-cc-pVTZ	192	0.58 (0.01)	–0.48 (0.46)
6–31++G(3d2f,3p2d)	180	1.03 (0.06)	–0.43 (0.36)
6–311++G(3d2f,3p2d)	200	0.58 (0.09)	–0.51 (0.34)
6–311++G(4d3f,4p3d)	256	0.76 (0.09)	–0.52 (0.21)
LS(3d,2p)	160	0.54 (0.00)	–0.33 (0.13)
LS(3d2f,3p2d)	240	0.58 (0.00)	–0.52 (0.19)

action energies follow a pattern similar to that found in the first and second row hydrogen-bonded dimers,^[17] that is, the BSSE-corrected interaction energy computed at the MP2 level approaches an asymptotic limit as the basis set quality increases. The four largest basis sets, the aug-cc-pVTZ, 6–311++G(3d2f,3p2d), 6–311++G(3d2f,3p2d), and LS(3d2f,3p2d) basis sets, give the same BSSE-corrected interaction energy within a 0.04 kcal mol⁻¹ deviation. The corresponding BSSE-uncorrected values for the same basis sets have a much larger deviation (0.31 kcal mol⁻¹). The 6–311G(3df,3pd) basis set gives also reasonable results and its quality is dependent on the polarization set (notice the decrease from the 3df to the 2df sets). The cc-pVTZ gives interaction energies of the order of the 6–311++G(2d,2p) basis set, while the cc-pVDZ and 6–31++G(d,p) basis sets are clearly too small to describe the energy of the S...S interaction. We note also the smaller oscillation with the basis

set size of the BSSE-uncorrected values relative to the uncorrected results.

In the light of the results in Table 1, we decided to select the 6-311++G(3d2f,3p2d) basis set for the H₂S dimer computations. We were now able to test the impact of the MP2 or MP4 methods on the S...S strength by computing the BSSE-corrected interaction energy for the H₂S dimer at its optimum MP2/6-311++G(3d2f,3p2d) S...S bond length. The 6-311++G(3d2f,3p2d) MP2, MP3, and MP4 BSSE-corrected energies are -0.51, -0.34, and -0.43 kcal mol⁻¹, respectively (the Hartree-Fock value is 0.58). The BSSE errors are 0.34, 0.23, and 0.24 kcal mol⁻¹ for the same methods (0.09 kcal mol⁻¹ in the HF computation). Therefore, it seems that the MP2 computations give a reasonable estimate of the S...S strength. All the calculations have been done using the GAUSSIAN-94 package,^[22] and the core electrons in the MP n calculations are "frozen".

The S...S interaction in the H₂S dimer: The anisotropy of the S...S interaction was first investigated with the six conformations of the H₂S dimer shown in Figure 5. These were selected from representative cases of the S...S geometrical orientations found in the previous statistical analysis of the packing

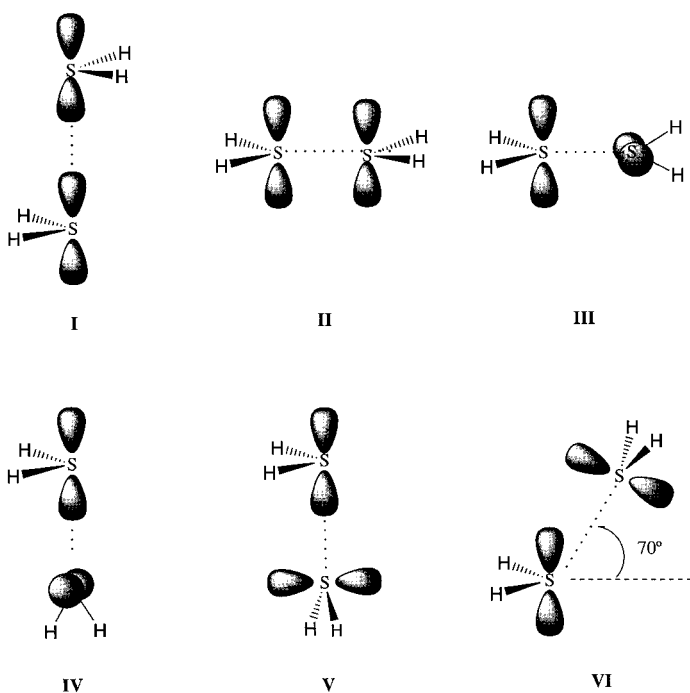


Figure 5. Conformations of the H₂S...SH₂ dimers considered in our calculations (the π lone-pair electrons on each S atom are indicated).

of the neutral and charge-transfer crystals as well as in some interesting extreme cases. For each conformation of Figure 5, we have drawn the position of the π lone-pair electrons located on the S atom (the σ sp² lone pair located along the fragment C_{2v} axis is not plotted here, in order to simplify the drawings). Conformation I represents the π - π interaction found within the stacks, conformations II and III represent two extreme cases of the σ - σ interaction, conformations IV and V are two cases of σ - π interaction, and conformation VI,

an intermediate case, corresponds to the most preferred geometrical approach between divalent sulfur found in earlier statistical studies.^[7b] We did not fully optimize the geometry of the fragments in these computations because one always obtains a hydrogen-bonded minimum for a S-H...S bond.^[23]

The dependence of the MP2/6-311++G(3d2f,3p2d) interaction energy on the S...S bond length is shown in Figure 6 for all six conformations. In all cases, the HF curves represent repulsion and the MP2 curves always have a minimum,

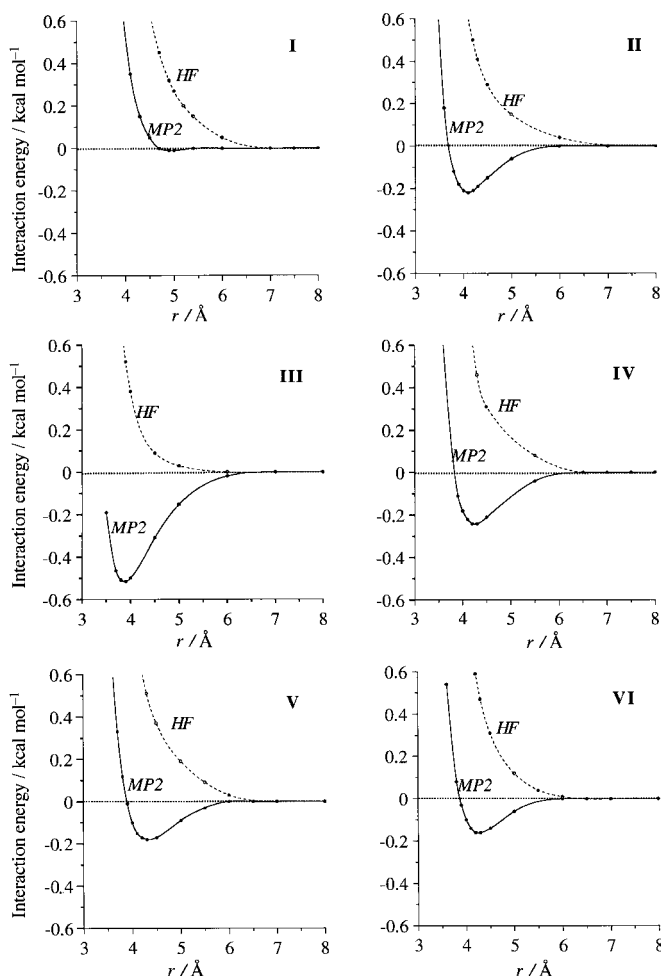


Figure 6. Variation with the S...S bond length (r) of the BSSE-corrected interaction energy computed at the Hartree-Fock and MP2 levels. All calculations are performed with the 6-311++G(3d2f,3p2d) basis set.

although conformation I is only slightly stable. Therefore, the dispersion contribution plays an essential role in making these S...S attractive and is large enough to compensate the repulsive electrostatic contribution of two opposing dipoles. Such a large dispersion contribution is associated with the large polarizability of the H₂S molecule (twice that for the water molecule).^[24] This is supported by the absence of minima in the potential energy curves computed for the H₂O dimer for the same six conformations as in Figure 5 at the MP2/6-311++G(3d2f,3p2d) level. This same conclusion is reached when a separate intermolecular perturbation theory computation of the energetic components of the interaction energy is carried out with the IMPT method.^[25]

The value of the MP2 interaction energy at the minimum of each curve increases in the order (kcal mol⁻¹): **I** (−0.05) < **VI** (−0.16) < **V** (−0.18) < **II** (−0.22) < **IV** (−0.24) < **III** (−0.51). Consequently, the S...S interaction in the H₂S dimer is anisotropic. This anisotropy is parallel to the form of the repulsive Hartree–Fock contribution, which is caused mainly by the dipole–dipole repulsion, while the correlation contribution is nearly isotropic. Thus it is not surprising that the energetic ordering of the six conformations can be rationalized by using qualitative electrostatic arguments based on the repulsion among the dipole and/or quadrupole moment of the interacting molecules (a simple dipole–dipole interaction does not explain some aspects, for instance, it would predict that collinear σ – σ approaches **II** and **III** are the most disfavored. However, this can be explained by the role of the quadrupole moment on the S...S interaction). It is also interesting to note that the most stable conformation (**III**) has a similar strength to that for the weakest C(sp³)–H...S^[5] and C(sp³)–H...O bonds.^[26] However, the optimum S...S intermolecular bond length from 3.9 Å to 4.2 Å (Figure 6) is larger than those of these two bonds (3.0–3.2 Å).^[5] The average shape of the potential energy curves in Figure 6 is very similar to the empirical isotropic intermolecular potential proposed by Gavezzotti et al. ($r_{\min} = 3.83$ Å, $E_{\min} = -0.44$ kcal mol⁻¹).^[7d]

Effect of neighboring substituent groups: The previous computations describe the properties of the S...S interactions for the simplest model dimer. However, as mentioned above, the charge distribution on the sulfur atoms of the H₂S dimer is not the same as the one found for the TTF molecule, in which there are functional groups attached to the S atom that induce charge donation, charge withdrawing, or charge delocalization, for instance. Therefore, it is important to evaluate the effect induced by these groups on the strength and/or directionality of the S...S interaction in some representative cases.

We selected the groups to study by looking at the structures of TTF-based molecules found in the CSD database. We found that there are two types of S atoms: the inner S atoms, which are always present as part of the five-membered rings of the TTF molecule, and the outer ones, which are found in molecules like BEDT-TTF (Figure 1a). The inner ones have substituted ethyl groups on both sides. The outer S atoms have substituted ethyl groups on one side and a variety of groups on the other one. Therefore, we have chosen to study the following groups: the methyl group (−CH₃), which is present in the external part of the BEDT-TTF molecule, the ethylenyl group (−HC=CH₂), which is found attached to the inner S atoms of all TTF-based molecules, and the formyl (−CH=O) group, which is also present in many cases. These groups were attached in the positions of the H₂S hydrogens to obtain a XYX...SX'Y' model dimer. We also decided to use a model representative for the environment of the TTF five-membered ring. This model was built by substituting one of the two five-membered rings of the TTF molecule and by changing the dangling C=C bond to a C=O bond. This allows the evaluation of the effect of delocalizing the S charge in the five-membered ring.

The selected functional groups were combined to obtain the model dimers shown in Figure 7. For these dimers, the interaction energy was computed for the geometry of conformations **I** and **II** and for models of the π – π and σ – σ S...S contacts found within the donor stacks and between nearby stacks (see the statistical analysis section). These

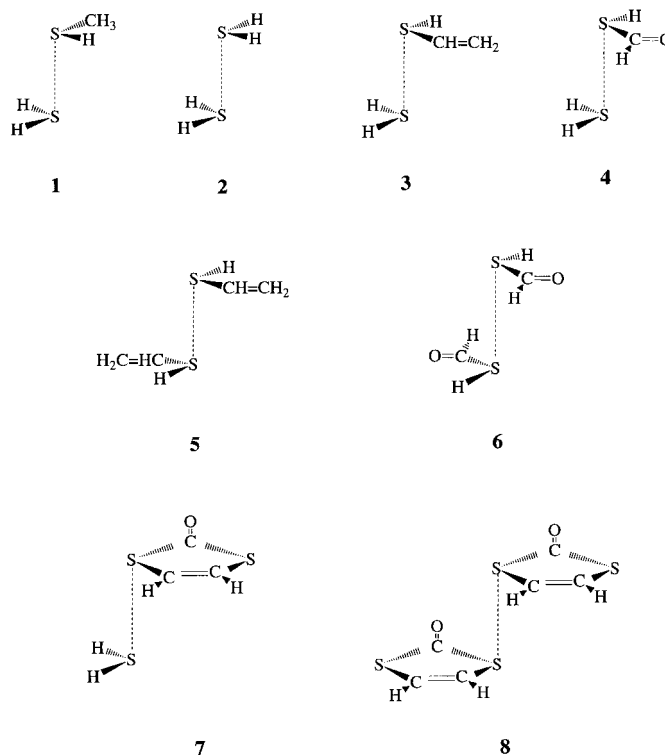


Figure 7. Model dimers employed to compute the substituent effect. Only the π – π conformers are shown ($\phi = 90^\circ$). The σ – σ conformers are similar but with $\phi = 180^\circ$ (see conformation **II** in Figure 5).

orientations are the most relevant ones in the TTF-based crystals, since they largely determine the conducting properties of these crystals (they are responsible for the presence of a sizable HOMO band dispersion and, consequently, for the possible conductivity associated with that dispersion).^[4] The S...S bond length was fixed at 4 Å, which is the average value of this parameter in the H₂S-dimer potential energy curves of Figure 6. The structure of each fragment in these computations was optimized at the HF/6–31 + G(d) level and was kept fixed during these dimer computations.

A first evaluation of the inductive effect generated by the selected functional groups can be obtained by comparing the MP2/6–31 + G(d) values of the BSSE-corrected interaction energy for all the model dimers (Table 2). Notice that although the values of the BSSE-corrected interaction energy computed at MP2/6–31 + G(d) are less attractive than those obtained with larger basis sets (see Table 1), the relative stability of the model dimers can still be determined. We recomputed the BSSE-corrected interaction energy for the smaller four model dimers in Figure 7 at the MP2/6–31 ++ G(2d,2p) and MP2/6–31 ++ G(3d2f,3p2d) levels, and the interaction energy in all dimers decreased by a nearly constant value in the four cases [the average decrease between the

Table 2. BSSE-corrected interaction energy [kcal mol^{-1}] computed at the MP2/6-31 + G(d) level for the model dimers of Figure 7 in their (π - π) and (σ - σ) conformations.

	$E(\pi-\pi)$	$E(\sigma-\sigma)$
1	1.04	0.79
2	1.27	0.65
3	0.84	0.58
4	0.20	0.20
5	0.37	0.49
6	0.37	0.43
7	-0.12	-0.08
8	-0.59	0.18

MP2/6-31 + G(d) and MP2/6-31 ++ G(3d2f,3p2d) values is $0.82 \text{ kcal mol}^{-1}$ for the π - π conformations and $0.95 \text{ kcal mol}^{-1}$ for the σ - σ conformations].^[27] When this averaged value is added to the largest model dimers, one obtains the BSSE-corrected energies plotted in Figure 8. They show a clear inductive effect that is stronger in the π - π conformations. Each set of interaction energies can be roughly fitted to a straight line of negative slope, which reflects an increase in the S...S interaction with the charge-withdrawing capability from the substituent.

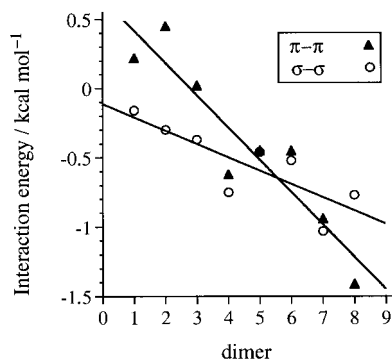


Figure 8. Variation of the BSSE-corrected interaction energy with the model system. The first four values are computed MP2/6-311 ++ G(3d2f,3d2d) results, while the remaining ones are estimated values (see text). Filled triangles refer to the π - π conformation, while open circles are for the σ - σ conformation.

The previous results indicated that the analysis of the TTF-based crystals should enable one to distinguish between S...S interactions made by the five-membered rings and those from the other S atoms, as the interactions in the five-membered rings are generally stronger. It is also interesting to note the higher stability of the π - π conformation for the larger substituents and, in particular, for model dimer 8. This implies that from the point of view of the S...S interactions the TTF molecules should have a preference for forming π - π stacks instead σ - σ planes. The stacks can then aggregate by means of their σ - σ interactions, which are not used in the formation of the π - π stacks. Notice, however, that there are also other short contacts, like the C-H...S ones, which can contribute significantly to the resulting preferred orientation, because the strength of the S...S interaction is in many cases similar to that reported in the literature for the $\text{C}(\text{sp}^n)\text{-H}\cdots\text{S}$ ($n = 1, 2, 3$) hydrogen bonds.^[5]

We also performed a potential energy scan for the pathway from conformation **I** to **II**. This was done for the $\text{H}_2\text{S}\cdots\text{SH}_2$ and $\text{H}_2\text{S}\cdots\text{SH-CH=CH}_2$ model dimers at the MP2/6-311 ++ G(3d2f,3p2d) level, by changing the angle ϕ (Figure 2) and by forcing the two fragments to lie in parallel planes. The two energy curves are parallel with two minimum arrangements at $\phi = 90^\circ$ and 180° ; the second one is more stable and has low-energy angular motions along ϕ . In between them, there is a maximum at $\phi = 110^\circ$, which is $0.2 \text{ kcal mol}^{-1}$ above the energy of the $\phi = 90^\circ$ conformation. Therefore, if no other contacts were present between the molecules involved in the S...S interaction, the packing of TTF-based molecules should follow, statistically, a pattern parallel to that found in the potential energy scan. However, this is not the case for the angular distributions shown in Figures 3 and 4, as they have a preference for the 180° orientations, but no maximum at 90° . This is probably due to the influence of the $\text{C}(\text{sp}^n)\text{-H}\cdots\text{S}$ ($n = 1, 2, 3$) hydrogen bonds in the packing; these have a similar amount of energy to that for the S...S interactions.^[5] It can be also due to the existence of the outer S atoms. As Figure 8 indicates, the anisotropy of the S...S interaction depends on the substituents attached to the S atom (compare the left and right parts of Figure 8 with the central part of that figure). The external S atoms of the BEDT-TTF have a methyl group on one side and an ethylenyl group on the other. The first has a preference for σ - σ contacts, while the second does not have such a clear preference. When these preferences are considered in addition to that shown by the inner S atoms, the overall result is difficult to predict and will depend on the external substituents. Therefore, it is not unusual that when we perform a statistical analysis on many crystals we find no parallelism with the shape of the potential energy scan on a $\text{XYS}\cdots\text{SX}'\text{Y}'$ dimer.

Conclusion

The main conclusion of our study is that S...S interactions are attractive in character, that is, they have a minimum in their potential energy curve for all orientations explored. Notice, however, that at short S...S bond lengths, 3 \AA for instance, all the curves represent repulsion. Furthermore, the strength and anisotropy of the S...S interactions can be modeled by changing the environment of the S atoms that are directly involved in the interaction. When the S atoms are those in the inner part of the TTF-based molecules, the interaction strength can be of the order of $-1.5 \text{ kcal mol}^{-1}$ (a bit more if the S...S bond length is the optimum one for the model dimer). There is a preference for the π - π stacked conformations over the σ - σ ones; this is particularly pronounced in the five-membered ring of the TTF molecule. Sulfur atoms attached to $\text{C}(\text{sp}^3)$ give rise to the weakest S...S interactions. The strength of the S...S interaction is similar to that reported in the literature for the $\text{C}(\text{sp}^n)\text{-H}\cdots\text{S}$ ($n = 1, 2, 3$) hydrogen bonds.^[5] Therefore, one should expect that the packing of the TTF-based neutral and charge-transfer molecular crystals is a compromise between the S...S and $\text{C}(\text{sp}^n)\text{-H}\cdots\text{S}$ competing interactions. Once a proper knowledge of the strength and directionality of the second type of interactions is obtained,

along with an estimate of the substituent effects, it will be possible to use the data for the rationalization of the crystal packing of TTF-based neutral and charge-transfer molecular crystals. Work in this direction is under way in our laboratory.

We have also performed a statistical analysis of the geometrical arrangement of the shortest S...S contacts found in neutral crystals of TTF-based molecules and in their associated charge-transfer crystals. Most of the S...S contacts in the neutral crystals lie in the 3.4–4.3 Å range, with a maximum at 3.93 Å. For the charge-transfer crystals, we obtained a similar distribution of the S...S contacts in the space, but with slightly shorter bond lengths. These distributions are similar to those found in a much broader subset of crystals.^[7d] This similarity suggests that the S...S interactions in TTF-based crystals could be modeled by the same atom–atom potential obtained by the inversion of the bond-length distribution of the broader subset; this is attractive and has a minimum at 3.93 Å and a well depth of 0.44 kcal mol⁻¹. However, our ab initio data also indicate that the S...S interactions can be as strong as –1.5 kcal mol⁻¹ if the proper substituents are selected. They also show that with some substituents the S...S interactions can be far from isotropic. These findings could be useful in formulating a more refined S...S potential.

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