A New Polymorphic Modification of Tetrathiafulvalene. Crystal Structure, Lattice Energy and Intermolecular Interactions[†]

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The molecular and crystal structure of the previously unknown modification of 2,2'-bi-1,3-dithiole (tetrathiafulvalene or TTF) has been determined by X-ray diffraction. The crystal is triclinic, at 298 K, a = 8.379(2), b = 12.906(3), c = 8.145(2) Å, α = 98.91(3), β = 96.62(3), γ = 100.44(3)°, V = 846.4(4), Z = 4, space group $P\bar{1}$. The molecular geometrical parameters of this modification (TTF2) do not differ from those found for the known modification (TTF1). However, the crystal structures are rather different. Only infinite chains formed by intermolecular interactions between S atoms of the closest molecules have been found in TTF2, in contrast to TTF1 monoclinic modification (space group $P2_1/c$), in which all molecules of the cell are stacked along the short b axis. The two structures have been used as the basis for a reexamination of the idea of a van der Waals radius for sulfur and the comparison and evaluation of various atom⋯atom potential energy forms and parameters which include interactions involving sulfur atoms.

Introduction

In an oft-quoted pseudoaphorism, McCrone suggested that virtually "every compound has different polymorphic forms... [and] the number of forms for a given compound is proportional to the time and energy spent in research on that compound".[1] While a great deal of time and energy have been spent studying tetrathiafulvalene (TTF) since its discovery in 1972, only one polymorph has been reported to date.[2] The combined experience of many people who deal with crystals and crystal growing is that polymorphic forms are more often than not discovered via a combination of serendipity and careful observation, rather than as a result of systematic searches and variation of experimental conditions.[3,4] In view of the fact that this issue of *Chemistry of Materials* is dedicated to the memory of M. C. Etter, it is fitting to mention here one case, the formation of crystalline complex of a cyanine dye molecule and an oxonol dye molecule, in which her systematic search for polymorphs and solvates did lead to a large number of identified and characterized different phases.[5]

Tetrathiafulvalene (TTF) is arguably the prototypical π-electron donor, and together with its derivatives, has

TTF
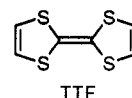
been widely used in the formation of charge transfer complexes and salts, especially those with potential as organic conductors and superconductors.[6] Recently, in the course of preparing tellurium derivatives of TTF[7] according to Scheme 1, we recovered one brown crystal of a material, which turned out to be a new polymorph of TTF, referred to herein as TTF2. The existence of two polymorphic structures of this symmetric prototypical molecule presents an excellent opportunity to examine in detail the nature and relative importance of various intermolecular interactions, especially those of the S⋯S

(1) McCrone, W. C. In *Physics and Chemistry of the Organic Solid State*; Fox, D., Labes, M. M., Weissberger, A., Eds.; Interscience: New York, 1963; Vol. 1, p 725.

(2) Cooper, W. F.; Kenny, N. C.; Edmonds, J. W.; Nagel, A.; Wudl, F.; Coppens, P. *J. Chem. Soc., Chem. Commun.* **1971**, 889. Cooper, W. F.; Edmonds, J. W.; Wudl, F.; Coppens, P. *Cryst. Struct. Commun.* **1974**, *3*, 23.

(3) There are some notable exceptions to this generalization, namely the school of M. Kuhnert-Brandstatter and A. Burger in Innsbruck and of course W. McCrone himself, who make extensive use of the polarizing microscope and the hot stage to search for the existence of polymorphs [see, for instance: Kuhnert-Brandstatter, M. *Thermomicroscopy Analysis of Pharmaceuticals*; Pergamon Press: New York, 1971]. While these methods are extremely useful in identifying the existence of polymorphs, most laboratory and industrial procedures for obtaining organic crystals still involve crystallizations from solutions. Under these conditions a much narrower thermodynamic range is generally covered, resulting in the generation, and hence the discovery, of many fewer polymorphic forms.
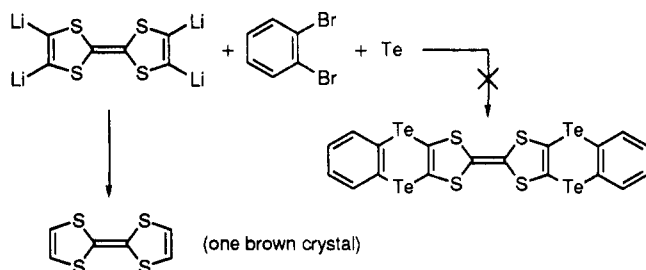
(4) The lack of careful observation or suitable analytical techniques where no polymorphic forms are expected is also remarkable. For instance, it has been shown that the recently discovered polymorphs (more correctly allotropes of carbon) C_{60} and C_{70} fullerenes may be obtained from the soot generated in carbon arc lamps. Hundreds of thousands of such lamps existed around the world a century ago, and not a single scientist thought, or had the proper means, to analyze the soot for anything but "carbon black". Over the period during which such arcs were used for public lighting literally tons of fullerenes must have been produced without having been discovered.

(5) Etter, M. C.; Kress, T. B.; Bernstein, J.; Cash, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 6921.

(6) See, for instance: Bechgaard, K. In *Studies in Physical and Theoretical Chemistry*; Pierrot, M., Ed.; Elsevier: Amsterdam, 1990; Vol. 69, "Structure and Properties of Molecular Crystals", Chapter 5, p 235.

(7) Shahal, L. Ph.D. Thesis, Ben-Gurion University of the Negev, Beer Sheva, 1993.

A New Polymorphic Modification of TTF

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Scheme 1

(one brown crystal)

type considered to be of importance in determining the conductivity properties in the whole family of conductors based on TTF. In addition, such a polymorphic system provides an almost ideal testing ground for the efficacy of potential forms and potential parameters used in atom···atom lattice energy calculations, and the results of those tests are presented here as well. Finally, since the crystal structure of TTF2 contains some unusual crystallographic aspects, we report on its determination and analysis in some detail.

Experimental Section

Preparation of TTF2. In the course of the workup at the end of the attempted preparation shown in Scheme 1, the organic phase was separated from the aqueous phase, and the former was evaporated to dryness under vacuum, leaving an oily mass which contained large amounts of *o*-bromobenzene. The vessel containing the oil was put in the refrigerator for 3–4 days, after which there appeared one large crystal. Since the crystal was brown, it was thought to contain tellurium. Rather than subject this small amount of material to an analysis requiring dissolution or grinding, it was subjected to a crystal structure analysis and proved to a second polymorph of TTF. The desired product was not obtained, and attempts by other routes to prepare it have not been successful.

Crystal Structure Determination of TTF2. $C_6H_4S_4$, triclinic, space group $P\bar{1}$, at 298 K: $a = 8.379(2)$, $b = 12.906(3)$, $c = 8.145(2)$ Å, $\alpha = 98.91(3)$, $\beta = 96.62(3)$, $\gamma = 100.44(3)°$, $V = 846.4(4)$, $Z = 4$, $\rho = 1.603$ Mg m^{-3}, μ(Mo Kα) = 1.039 mm^{-1}, $F(000)$ = 416. 1885 unique reflections with $F_o > 4\sigma(F_o)$ were used out of a total of 2181 independent reflections collected with a Philips PW1100 diffractometer (Mo Kα = 0.710 69 Å, graphite monochromator, $\omega/2\theta$ scan, $2\theta < 45°$). The structure was solved by direct methods and refined by a full-matrix least-squares procedure using SHELX-86 and SHELX-76, respectively,[8] to R = 0.038, R_w = 0.055, GOF = 1.81. SCHAKAL92[9] was used for the graphic representations. Other details are given in Table 1. The final coordinates are given in Table 2. Tables of bond lengths, bond angles, and temperature factors have been deposited.

While the structure solution was quite routine, the crystal structure has a number of unusual properties. The first of these is the fact that the asymmetric unit in the triclinic $P\bar{1}$ cell is composed of the halves of four molecules, each one lying about a center of symmetry, to complete the four molecules in the unit cell. Such cases are quite rare, and a number of those reported recently (often resulting from "black-box" solution space-group assignment and structure solution) have been shown to be incorrect.[10] Hence, considerable effort was expended in verifying the correctness of this assignment. It is worthy of note that these programs all give the corrected cells reported by Marsh.[11]

While cell reduction algorithms are by no means new,[12] the past few years have witnessed the development of increasingly

(8) Sheldrick, G. M. SHELX86, a Crystallographic Structure Solution Package; SHELX76, a Crystallographic Structure Solution and Refinement Program; University of Gottingen: Gottingen, 1986.

(9) Keller, E. SCHAKAL92, A Molecular and Crystallographic Plotting Package, Crystallographic Institute, University of Freiburg, 1993.

(10) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1983**, *B39*, 280; **1988**, *B44*, 77.

(11) Marsh, R. E. *Acta Crystallogr.* **1986**, *C42*, 511; **1989**, *C45*, 347; **1990**, *C46*, 1761; **1989**, *C45*, 2029.

Table 1. Details of Data Collection, Structure Solution and Refinement for TTF2

empirical formula	$C_6H_4S_4$
color	brown
crystal size (mm)	0.31 × 0.21 × 0.2
scan speed	variable 2.00–29.30°/min in ω
scan range	(ω) 1.8°
background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
standard reflections	3 measured every 100 reflections
index ranges	$-9 < h < 8, -13 < k < 13, 0 < l < 8$

Solution and Refinement	
program packages used	Shelx-76, Shelx-86[8]
structure solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$
no. of parameters refined	181
final R indices	$R = 0.0379, R_w = 0.0555$
final R indices (all data)	$R = 0.0536, R_w = 0.1958$
goodness-of-fit	1.81
largest and mean Δ/σ	0.001, 0.000
data-to-parameter ratio	10.4:1
largest difference peak	0.22 e Å^{-3}
largest difference hole	-0.25 e Å^{-3}

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	y	z	U(eq)^a
S(1)	5268(1)	8393(1)	$-1136(2)$	74(1)
S(2)	7540(1)	10167(1)	1164(2)	79(1)
S(3)	6161(2)	5027(1)	7567(1)	81(1)
S(4)	3820(2)	3358(1)	5134(1)	75(1)
S(5)	8982(2)	5480(1)	2294(1)	77(1)
S(6)	9447(1)	3386(1)	603(2)	71(1)
S(7)	319(1)	8337(1)	4464(1)	69(1)
S(8)	2340(1)	10377(1)	4059(2)	74(1)
C(1)	7233(5)	8224(4)	$-511(6)$	75(2)
C(2)	8241(5)	9008(4)	514(5)	72(2)
C(3)	5576(4)	9699(3)	9(4)	53(1)
C(4)	5436(5)	3834(3)	8190(5)	73(2)
C(5)	4404(5)	3085(3)	7116(5)	71(2)
C(6)	4996(4)	4669(3)	5553(4)	52(1)
C(7)	8502(6)	4398(4)	3281(6)	83(2)
C(8)	8689(5)	3465(4)	2513(6)	80(2)
C(9)	9678(4)	4769(3)	598(4)	53(1)
C(10)	2174(6)	8303(4)	3756(6)	82(2)
C(11)	3065(6)	9211(4)	3571(6)	84(2)
C(12)	550(4)	9735(3)	4702(4)	51(1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

sophisticated programs for checking space-group assignments, and the presence of unrecognized symmetry elements, including centering.[13] We have applied three of these programs to the cell of TTF2. All of them produced results indicating that the reported cell is the correct one. No other solution was produced.

Additional examples of cases such as the current one, in which the asymmetric unit is comprised of the halves of even *two* crystallographically independent molecules (each full molecule being generated by an inversion center) cannot be readily identified automatically with the current software of the Cambridge Structural Database. The ZPRIME parameter, which is extremely useful for identifying structures with multiple molecules in the asymmetric unit, would in the present case simply

(12) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1952; Vol. I, pp 530–533.

(13) For instance, the following are now available: (a) BLAF: Macicek, J. Bulgarian Academy of Sciences, Sofia, Bulgaria, 1991. (b) NIST*LATTICE: Karen, V. L. Reactor Radiation Division, U.S. National Institute of Standards and Technology, Gaithersburg, MD 20899, 1991. (c) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578, based on the algorithm of LePage, Y. *J. Appl. Crystallogr.* **1982**, *15*, 255.

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Table 3. Some Representative Examples of Structures in Which the Asymmetric Unit Is Comprised of Molecules Lying in Both a General Position and on a Symmetry Element

compound	space group	Z	ZPRIME	contents of asymmetric unit	ref
9-cyanoanthracene dimer	$P\bar{1}$	4	2.0	$1 + 2 \times {}^1/_2$	a
2,5-dimethylhexane-2,5-diol	$P2_1/c$	6	1.5	$1 + {}^1/_2$	b
biphenylene	$P2_1/a$	6	1.5	$1 + {}^1/_2$	c
anthanthrone	$P2_1/c$	8	2.0	$1 + 2 \times {}^1/_2$	d
hexafluorobenzene	$P2_1/n$	6	1.5	$1 + {}^1/_2$	e
pinnacol	$C2/c$	16	2.0	$1 + 2 \times {}^1/_2$	f
2,3-dimethylthiirene	$A2/a$	12	1.5	$1 + {}^1/_2$	g

a Theocharis, C. R.; Jones, W. *J. Chem. Soc., Chem. Commun.* 1984, 369. *b* Helmholdt, R. B.; Reynaens, H. *Acta Crystallogr.* 1976, *B32*, 2243. *c* Fawcett, J. K.; Trotter, J. *Acta Crystallogr.* 1966, *20*, 87. *d* Edwards, I. A. S.; Stadler, H. P. *Acta Crystallogr.* 1971, *B27*, 946. *e* Boden, N.; Davis, P. P.; Stam, C. H.; Wesselink, G. A. *Mol. Phys.* 1973, *25*, 81. *f* Jeffrey, G. A.; Robbins, A. *Acta Crystallogr.* 1978, *B34*, 3817. *g* Ammon, H. L.; Fallon, L.; Planstas, L. A. *Acta Crystallogr.* 1976, *B32*, 2171.

give a value of 2 and would not hint at the fact that there are four half molecules in the asymmetric unit. While we are not aware of another example of a structure in which the asymmetric unit contains four half molecules, one classic case in which there are two crystallographically independent half molecules in the asymmetric unit is the pair of isostructural stilbene and azobenzene structures[14] which, however, are monoclinic $P2_1/a$, so the problem of unidentified symmetry elements does not exist. By examination of the individual cases for which ZPRIME > 1 in the three most commonly encountered centrosymmetric space groups ($P\bar{1}$, $P2_1/c$, $C2/c$),[15] we have identified a selection of additional examples (Table 3), including some in which the asymmetric unit consists of a whole molecule plus one or two halves of molecules, e.g., $(1 + {}^1/_2)$ or $(1 + 2 \times {}^1/_2)$ molecules in the asymmetric unit that result in a ZPRIME of 1.5 or 2.0, respectively. We have not found any other structures similar to TTF2, in which the asymmetric unit is comprised of the halves of four molecules, each lying at an inversion center.

Packing calculations were carried out with the widely used PCK83 program of Williams.[16,17] The majority of calculations using this program have been carried out on hydrocarbons or hydrocarbon compounds containing only first-row elements as additional substituents. Since the available parameters for sulfur have not been widely tested, either individually or in combination with other widely used parameters, we have employed three different sets of parameters in these calculations (Table 4). First, we have set all C–H bonds to 1.08 Å[18] and used the standard Williams hydrocarbon C, H potentials.[17] Second, we have employed the full set of Mirsky potentials for C and H and S,[19] The third set of potentials was taken from the recently published list of improved potentials for PCK83 (Buckingham potential form) by Filippini and Gavezzotti[20] that is based on a statistical analysis of intermolecular contacts found in a large sampling of crystal structures in the Cambridge Structural Database.[21] Although they appear to be quite similar, the two sulfur potentials (Figure 1) differ slightly both in the position and depth of the energy minimum, and it was of interest to examine whether these

Table 4. Atom–Atom Potential Parameters in the Form $U = B \exp(-\alpha R_{ij}) - A R^{ij-6}$ with A in kJ/mol Å⁻⁶, B in kJ/mol, and α in Å⁻¹

interaction	A	B	α	D_6	ϵ	parameter set
H···H	136.40	11 970.5	3.74	3.311	−0.0534	W^a
C···H	576.90	66 527.8	3.67	3.606	−0.1434	
C···C	2439.40	369 737.0	3.60	3.898	−0.3978	
C···S^d	4893.10	602 946.2	3.545	3.894	−0.7937	
S···S	9815.70	983 240.0	3.49	3.889	−1.5836	
S···H^d	1157.10	108 489.9	3.615	3.592	−0.2898	
H···H	121.30	20 501.6	4.29	2.794	−0.1273	M^b
C···H	493.70	77 822.4	3.94	3.297	−0.2067	
C···C	1761.50	299 574.4	3.68	3.805	−0.3319	
C···S	3543.80	415 889.6	3.54	3.876	−0.5880	
S···S	9815.70	983 240.0	3.49	3.889	−1.5836	
S···H	1091.20	141 978.8	3.89	3.275	−0.468	
H···H	109.20	24 158.4	4.01	3.363	−0.0419	F/G^c
C···H	472.80	120 792.1	4.10	3.295	−0.2054	
C···C	2418.40	226 145.2	3.47	3.891	−0.3874	
C···S	6292.70	529 108.6	3.41	3.958	−0.9090	
S···S	10757.10	1 087 672.6	3.52	3.831	−1.8891	
S···H	1167.30	268 571.0	4.03	3.351	−0.4578	

a Average values with S···S of M set. *b* Williams potentials.[17] *c* Mirsky potentials.[19] *d* Filippini/Gavezzotti potentials.[20]
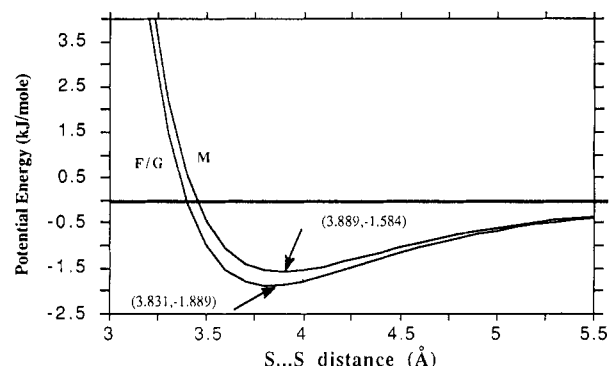
Figure 1. Nonbonded S···S potential functions used in the lattice energy calculations. "F/G" refers to the potential of ref 20, while "M" is that of ref 19. The first entry in parentheses is the S···S distance at the energy minimum, which is the second entry.

rather small differences would influence the results or the interpretation of them.

Comparison of Molecular Structures

While TTF is a rigid molecule and large variations in the features are not expected,[22] it is of interest to examine the internal consistency of the results obtained for the four independent molecules and to compare those features with those of TTF1. The average values of the bond lengths and angles are given in Figure 2. Virtually none of the out-of-plane deformation found recently in di-TTF derivatives linked by tellurium[23] is found in any of the four molecules, the largest deviation from the least-squares plane in TTF2 being 0.031 Å. On the other hand it is noteworthy that a recent electron diffraction study of TTF indicated that in the gas phase the TTF molecule not centrosymmetric but rather is distorted into a boat

(14) Hoekstra, A.; Meertens, P.; Vos, A. *Acta Crystallogr.* 1975, *B31*, 2813. Brown, *Acta Crystallogr.* 1966, *31*, 146.

(15) Donohue, J. *Acta Crystallogr.* 1985, *A41*, 203.

(16) Williams, D. E. *PCK83*, QCPE Program 548, Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, IN.

(17) Williams, D. E. *Acta Crystallogr.* 1984, *B40*, 404.

(18) Allen, F. H.; Kennard, O.; Watson, D.; Brammer, L.; Orpen, G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* 1987, S1.

(19) Mirsky, K. V. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, M., van Komingsveld, M., Bassi, G. C., Eds.; Delft University Press: Twente, 1978; pp 169–182.

(20) Filippini, G.; Gavezzotti, A. *Acta Crystallogr.* 1993, *B49*, 868.

(21) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; MacRae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Inf. Comput. Sci.* 1991, *31*, 187.

(22) A noteworthy exception in the present context is the pair of polymorphic structure of tetramethylthiotetrathifulvalene. In the triclinic form [Endres, E. *Z. Naturforsch.* 1986, *41*, 1351] the molecule lies on a crystallographic inversion center and is essentially planar. In the monoclinic form [Katayama, C.; Honda, M.; Kumagai, H.; Tanaka, J.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* 1985, *58*, 2272] the molecule lies on a general position and adopts a boat conformation due to dihedral angels about the transannular S···S axes of 23.7° and 19.3°.

(23) Martin, J. D.; Canadell, E.; Becker, J. Y.; Bernstein, J. *Chem. Mater.* 1993, *5*, 1199.
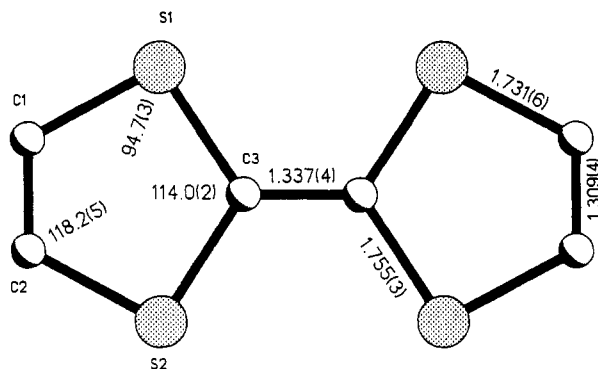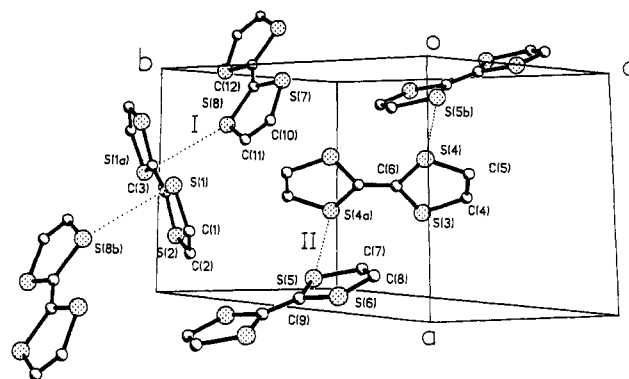
Figure 2. Molecular structure of TTF2 showing the values of the bond lengths (angstroms) and bond angles (degree) averaged over the four independent (half) molecules in the asymmetric unit. The numbers in parentheses represent the esd of the average value.

Figure 3. Partial view of the experimentally determined crystal structure of TTF2, showing the relationships between the four different molecules in the unit cell (each lying on the inversion center), and the formation of chains. The two S···S intermolecular distances <3.70 Å are indicated: I: S8···S1a $(1 - x, 2 - y, - z)$, 3.65 Å. II: S5···S4a $(1 - x, 1 - y, 1 - z)$, 3.69 Å.

conformation as manifested in dihedral angles of 13.5° about transannular S···S axes.[24] In the TTF1 structure this angle is equal to 2.1°, in equal but opposite directions, consistent with the molecule lying on a center of symmetry. For the four molecules in TTF2 the distortion was found to be in the range 1.2–4.1°.

Packing and Intermolecular Interactions, Including a Brief Reconsideration of the Significance of a van der Waals Radius

The crystal packing of TTF and its derivatives is of particular interest, because many of the unique properties observed for ion-radical salts and charge-transfer complexes of these compounds (e.g., electrical conductivity and superconductivity) stem from the arrangement of molecules in the crystal. In particular, molecules in this family tend to form networks of intermolecular S···S contacts, which have been considered an important structural element in facilitating electrical conductivity.[25,26] The crystal structures of the two polymorphic modifications of TTF are clearly different (Figures 3 and 4). The TTF1 crystal has a short *b* axis, and consequently all the molecules in the cell are stacked along this axis. The distance between parallel planar molecules of a stack is 3.63 Å, and the two symmetry-related S atoms have two contacts of 3.41 and 3.58 Å with S atoms of molecules in another stack (Figure 4a), which are shorter than twice the van der Waals radius of sulfur (3.6 or 3.7 Å, depending on the value chosen for the van der Waals radius[27,28]). This additional interaction leads to the two-dimensional network shown in Figure 4b.

The structure of TTF2, on the other hand, is probably best characterized as being composed of two chains of molecules, each chain consisting of alternating crystallographically independent molecules. The first chain contains the TTF molecules with S(1) and S(2) alternating with that containing S(7) and S(8), while the second chain contains the TTF units with S(3) and S(4) alternating
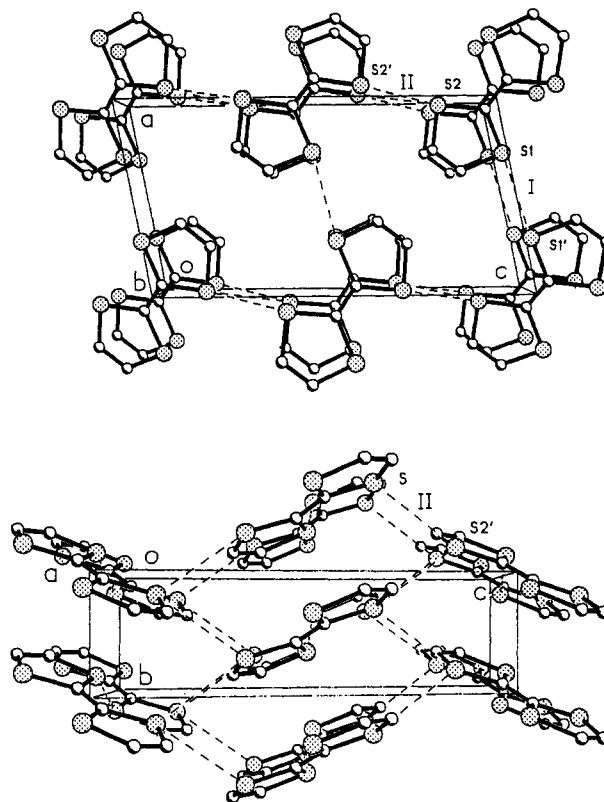
Figure 4. Two views of the experimentally determined crystal structure of TTF1. (a) View on the *ac* plane. (b) View on the *bc* plane. The intermolecular S···S contacts less than 3.7 Å are indicated: I: S1···S1' $(1 - x, - y, - z)$, 3.41 Å. II: S2···S2' $(- x, 0.5 + y, 0.5 - z)$, 3.58 Å.

with that containing S(5) and S(6). We are inclined to call these "chains" rather than stacks, since the angles between the planes of alternating molecules (defined as C(1)–C(2)–C(3) ∧ C(10)–C(11)–C(12) and C(4)–C(5)–C(6) ∧ C(7)–C(8)–C(9) are 50.8° and 56.1°, respectively. In contrast to the crystal structure of TTF1, the structure of TTF2 cannot be characterized by a small number of particularly short S···S intermolecular distances less than 3.9 Å. As can be seen in Table 5, there are no fewer than eight intermolecular distances varying almost continuously over the range 3.65–3.90 Å.

This observation raises some fundamental questions about the nature of the van der Waals radius and its use in understanding the "important" or "dominant" interac-

(24) Hargittai, I.; Brunvoll, J.; Kolonits, M.; Khodorkovsky, V. *Angew. Chem., Int. Ed. Engl.*, in press.

(25) Wudl, F. *Acct. Chem. Res.* **1984**, *17*, 227.

(26) Williams, J.; Beno, M. A.; Wang, H. H.; Leung, P. C. W.; Enge, Y. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.* **1984**, *17*, 227. Williams, Schultz, A. J.; Geiser, U.; Carlson, K. D.; Kini, A. M. J.; Wang, H. H.; Kwok, W.-K.; Whangbo, M. H.; Schirber, J. E. *Science* **1991**, *252*, 1501.

(27) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(28) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

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Table 5. Summary of S···S Intermolecular Distances before and after Lattice Energy Minimization for TTF1 and TTF2

TTF1

atom I	atom II	symmetry operation[a]	X-ray[b]	distances in Å F/G	W	M	interaction no. (Figure 5)
S1	S1	I 0 1 0		3.63	3.76	3.64	IV
S1	S1A[c]	I -1 0 0	3.41		3.50		I
S2	S2	II 0 -1 0	3.58	3.51	3.52	3.52	II
S1	S2A[c]	I 0 -1 0		3.59	3.86	3.67	III
S2	S2	I 0 1 0		3.63	3.76	3.64	IV

TTF2

atom I	atom II	symmetry operation[d]	X-ray	distances in Å F/G	W	M	interaction no. (Figure 6)
S1A[c]	S4	I 0 -1 0	3.90	3.59	3.66	3.60	I
S1A[c]	S8	I 0 0 0	3.65	3.63	3.67	3.66	V
S2A[c]	S7	I 0 0 1	3.84	3.73	3.78	3.76	VI
S2A[c]	S8	I 0 0 0				3.89	
S2A[c]	S8	I 0 0 1		3.89	3.90	3.85	
S3	S6A[c]	I 0 0 -1	3.88	3.72	3.78	3.79	VII
S4A[c]	S5	I 0 0 0	3.67	3.64	3.66	3.66	IV
S4A[c]	S7	I -1 0 0	3.82	3.57	3.60	3.58	II
S4	S8	I 0 1 0	3.75	3.63	3.83	3.72	VIII
S5	S7	I -1 0 0	3.74	3.59	3.79	3.66	III

[a] For symmetry operations the roman numeral indicates either I: x, y, z or II: $-x, 0.5 + y, 0.5 - z$. The following three numbers indicate translations along the a, b, and c unit-cell axes, respectively. [b] For X-ray column distances equal to or less than 3.9 Å are listed. [c] The "A" designator indicates the atom generated through the inversion center. [d] For symmetry operations the roman numeral indicates either I: x, y, z. The following three numbers indicate translations along the a, b, and c unit-cell axes, respectively.

tions in molecular crystals. To the best of our knowledge, the idea of a van der Waals radius originated with Pauling,[28] and it represents a *characteristic, average value* for the closest intermolecular approach of two atoms in a variety of crystal structures. All two-body interactions can be described by some potential energy curve similar to those in Figure 1, and the implication of this definition is that the sum of the van der Waals radii is, or is very close to, the minimum energy value for that interaction. By the very nature of a potential energy curve, both shorter and longer values may very well represent higher energies, unless, of course, interactions other than those of the van der Waals type are being considered.

It is common practice in discussing the crystal structures of organic materials to tabulate and note the intermolecular distances that are shorter than the sum of the van der Waals radii for the two atoms in question. In the age of automation of crystal structure analysis, such a tabulation is a trivial matter. Analysis of the resulting data then forms the basis for the understanding of the "important" interactions in a particular crystal structure—indeed, in whole classes of crystals structures. A case in point is the family of compounds based on TTF and its derivatives.[25,26]

We believe that the definition of a van der Waals radius is still somewhat uncertain and arbitrary. Moreover, the *automatic* tabulation of "short" intermolecular distances based on van der Waals radii and the subsequent attribution of particular significance to the resulting "interactions" contains the ingredients on which misunderstandings and incorrect models and theories can be based, and if practiced at all, should be done so with caution. This idea is not new; the origin and use of the van der Waals radius has been recently reviewed and critically analyzed by Zefirov and Zorkii,[29] and they have expressed many of the ideas presented here. The danger of using a van der Waals radius as a criterion for defining hydrogen bonds was stated quite

clearly by Jeffrey and Saenger[30] in rejecting a strict geometric definition of hydrogen bonds, in particular the donor···acceptor or H···acceptor distance. Moreover, such notions were crucial in Etter's emphasis on focusing on and defining the *patterns* of hydrogen bonds and hydrogen-bond networks, rather than the strict geometric or symmetry relations of individual hydrogen bonds.[31]

The structure of TTF2 is a perfect case in point. The blind use of, say 1.85 Å as the van der Waals radius of sulfur (i.e. Pauling's value) would have led to the "recognition" of two "important" interactions in the structure. Are the two "interactions" of 3.74 and 3.75 Å so much less important that they can be ignored? Examination of any potential energy curve for the van der Waals S···S interaction (for example, see Figure 1) indicates that the energy is not changing rapidly at this distance. And why should these four distances, say, be chosen as "important", when there are four more very similar ones, with correspondingly similar (albeit lower, according to these potential energy curves) energies of interaction?

There is no simple formula for resolving this dilemma. Each structure must be examined carefully to determine the nature and relative importance of the intermolecular interactions. In TTF1 there are very clearly two short intermolecular S···S distances (Figure 4), and these can indeed be attributed to the dominant interactions with a fair degree of confidence. In TTF2 the S···S distances (X-ray column in Table 5) are spread over a distance continuum, and considerable caution must be exercised in attributing more or less particular significance to any one or even any small number of "interactions". For instance, three of the distances are greater than the minimum in F/G potential curve of Figure 1, and one is longer than the M potential curve in Figure 1. Depending on the curvature of those curves, these longer distances could, in fact, correspond to lower energies than some of the shorter distances.

Lattice Energy Calculations

Polymorphic systems provide unique opportunities for comparing and testing the parameters used in atom-atom potential energy calculations.[32-34] The only variable between polymorphs in the structural one, thus eliminating considerations of electronic, substitutional, and other variables. The relative stability of different polymorphic forms of a substance are generally known, even from considerations of crystallization conditions,[35] history of appearance,[36] etc., and this information may be used for the qualitative comparison with the relative stabilities obtained from the computed energies. In the present case, the fact that TTF2 did not appear for 20 years, and the unusual conditions under which it did appear, suggest that it is the less stable form. Also, it has been shown that in polymorphic systems the more dense polymorph is gener-

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ally the more stable form.[37] The calculated density of TTF1 is 1.679 and that of TTF2 1.603 Mg m^{-3}, which again is consistent with the proposition that TTF1 is the more stable polymorph. The best measure of the validity of computational procedures and parameters is the comparison with experimentally determined sublimation energy, but the number of cases in which the sublimation energy is available for different polymorphs of a particular substance is very limited.[38] However, it is possible to make a rough estimate of the expected energies of different polymorphs, since the energy differences among polymorphs of organic compounds usually do not exceed 10–12 kJ mol^{-1}.[39] Thus, knowledge of the sublimation energy of one polymorph (usually the most stable one) does provide at least a semiquantitative basis for comparison with the other polymorphic structure(s).

TTF is also a particularly suitable molecule for the comparative calculations of polymorphic structures. In addition to its importance as a π-electron donor in charge-transfer complexes and salts, it has become one of the archetypical molecules of organic chemistry. Its high molecular symmetry (mmm, D_{2h}) means that all four sulfur atoms are chemically equivalent, as are the four hydrogens, the four carbons to which they are bonded, and the two central carbon atoms. It is thus relatively easy to isolate and analyze the particular intermolecular interactions which are principally responsible for the packing patterns in the different polymorphic structures. Because of this high chemical symmetry on the molecular level, there is a very limited number of types of intermolecular interactions, which considerably simplifies the analysis of the packing energies and the energetic comparison of the two structures. This polymorphic system also provides a fertile testing ground and fairly stringent requirements for the parameters used in the lattice energy calculations, since we can require all of them to indicate that TTF1 is the more stable polymorph with a sublimation energy that approximates the experimental value, while the calculated lattice energy for TTF2 should be higher by no more than approximately 10 kJ-mol^{-1}.[39]

We will examine simultaneously the packing patterns and packing energy of the two forms of TTF. The packing of TTF1 is shown in Figure 4. The view down the *b* axis (Figure 4a) highlights the presence of plane-to-plane stacks with a repeat of 4.023 Å. Neighboring stacks are related by the glide operation in $P2_1/c$, as can be seen clearly from Figure 4b. Short intermolecular S···S distances have long been recognized as important factors in determining the structures of TTF and its derivatives.[25,26] The two short distances of this type which dominate the structure of TTF1 generate a three-dimensional network. Qualitative observations of this type have traditionally led to the conclusion that these short distances represent the dominant interactions in stabilizing the crystal structure. With the increasing sophistication of computational methods for calculating the energetics of crystal structures, such correlations can be put to quantitative test.

The results of the lattice energy calculations on TTF1, using the methods and parameters described in the

Table 6

(a) Results of Lattice Energy
Minimizations on the Two Forms of TTF

potential	form 1			form 2			
	E_i	E_f	R	E_i	E_f	R	$\Delta E^{a,b}$
W	−102.4	−105.9	51.7	−92.0	−96.6	70.5	9.3
M	−93.2	−102.4	404	−86.5	−94.9	117	7.5
F/G	−114.6	−123.4	589	−105.6	−112.4	109	11.0

(b) Cell Parameters and Shifts at Covergence for the
Three Parameter Sets of the Two Forms of TTF

potential	W	M	F/G	X-ray
		Form I		
a (Å)	7.418	8.306	8.514	7.364
b (Å)	3.764	3.635	3.627	4.023
c (Å)	14.115	12.432	12.252	13.922
β (deg)	100.20	102.95	102.18	101.42
Δa (Å)	0.054	0.942	1.150	
Δb (Å)	−0.259	−0.388	−0.396	
Δc (Å)	0.193	−1.490	−1.670	
$\Delta \beta$ (deg)	−1.22	1.53	1.49	
		Form II		
a (Å)	8.232	8.078	8.221	8.379
b (Å)	13.048	12.782	12.865	12.906
c (Å)	7.791	7.653	7.733	8.145
α (deg)	100.70	99.47	100.94	98.91
β (deg)	95.75	97.14	94.98	96.62
γ (deg)	101.89	101.07	103.04	100.44
Δa (Å)	−0.147	−0.301	−0.158	
Δb (Å)	0.142	−0.124	−0.041	
Δc (Å)	−0.354	−0.492	−0.412	
Δa (deg)	1.79	0.56	2.03	
$\Delta \beta$ (deg)	−0.87	0.52	−1.64	
$\Delta \gamma$ (deg)	1.45	0.63	2.60	

^{a} Energy in kJ mol^{-1}. ^{b} E_i and E_f indicate initial and final energies.

Experimental Section, are summarized in Table 6. The lattice energy minimizes quite smoothly, and for all three sets of potential parameters the commonly known TTF1 calculates as the lower energy form, consistent with our earlier qualitative observations. Two values for ΔH_s have been reported: 92 ± 6.3 and 95.3 ± 1 kJ mol^{-1}.[40,41] While none of the computed values agrees precisely with either of the two experimental values, it is encouraging that all three give quite similar energy differences between the two forms and that these are within the expected range for such values. The closest match is for the *M* parameter set. This strengthens a point that we have been making for some time about these calculations—namely, that there can be quite large variations in absolute energies for different parameter sets, but *differences* in energies, which are of particular interest in regard to polymorphic systems, appear to be less sensitive to the potential function and parameters used.[42]

We note that for the *F/G* and *M* potentials the "*R* factor", which is a measure of the changes between the initial and minimized structures, is quite large (normal values are <100).[42] This indicates that there have been considerable, and perhaps significant, changes in the structure as a result of the minimization. The structure resulting from the minimization is shown in Figure 5. For all three minimizations there are now three S···S intermolecular distances less than 3.80 Å, and these are the three largest contributors to the minimized lattice energy (Table 7). In general, in molecular crystals which are dominated by van

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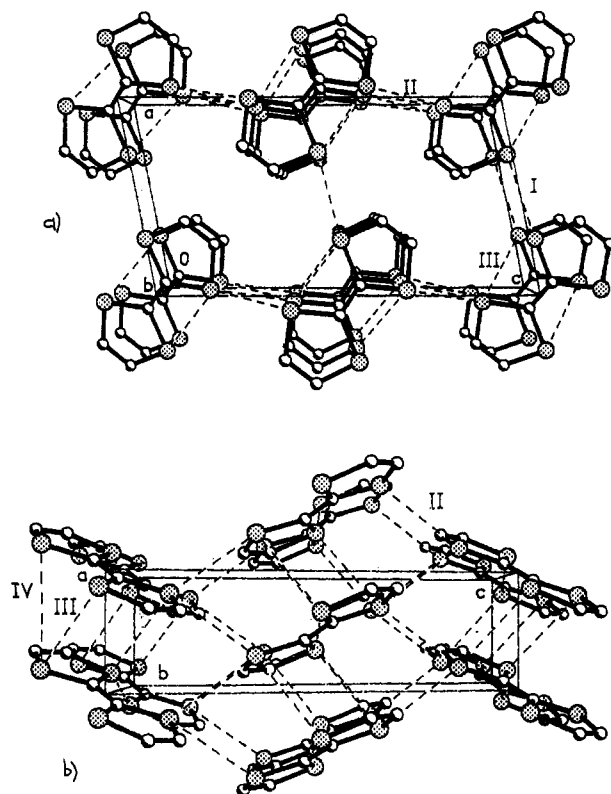
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Figure 5. Two views of the crystal structure of TTF1 after lattice energy minimization: (a) View on the ac plane. (b) View on the bc plane. The intermolecular S···S distances indicated are discussed in the text and are given in Table 7. To minimize confusion only one interaction of the types S1···S1 (x, $1 + y$, z) and S2···S2 (x, $1 + y$, z) is shown (IV).

Table 7. Summary of Specific S···S Interactions for TTF1[a,b]

| rank | potential function | | |
	W^c	M^d	F/G^e
1	−0.48	−0.62	−1.06
	S1···S1	S2···S2	S2···S2
	I −1 0 0	II 0 −1 0	II 0 −1 0
	3.501	3.520	3.509
2	−0.64	−1.21	−1.50
	S2···S2	S1···S1	S1A^f···S2
	II 0 1 0	I 0 1 0	II 0 −1 0
	3.523	3.635	3.594
3	−1.51	−1.32	−1.62
	S1···S1	S1A^f···S2	S1···S1
	I 0 1 0	II 0 −1 0	I 0 1 0
	3.764	3.669	3.627

[a] Down the columns entries are given in order of increasing distance. Each entry contains, respectively, the energy of the specific interaction (in kJ mol⁻¹), the atom pair involved in the interaction, the symmetry operation generating the atom pair interaction,[b] and the distance (in angstroms) between the two atoms in the pair. [b] For symmetry operations the roman numeral indicates either I: x, y, z or II: $-x$, $0.5+y$, $0.5 - z$. The following three numbers indicate translations along the a, b, and c unit-cell axes, respectively. [c] Williams potentials.[17] [d] Mirsky potentials.[19] [e] Filippini/Gavezzotti potentials.[20] [f] The "A" designator indicates the atom generated through the inversion center.

der Waals interactions (i.e., in the absence of hydrogen bonds or stronger intermolecular interactions) the crystal structure is stabilized by the cooperative effect of many small contributions to the lattice energy.[43] In the present case the dominance of these three interactions simply reinforces the historically intuitive recognition by chemists and crystallographers of the dominance of S···S interactions in determining the packing of these structures.
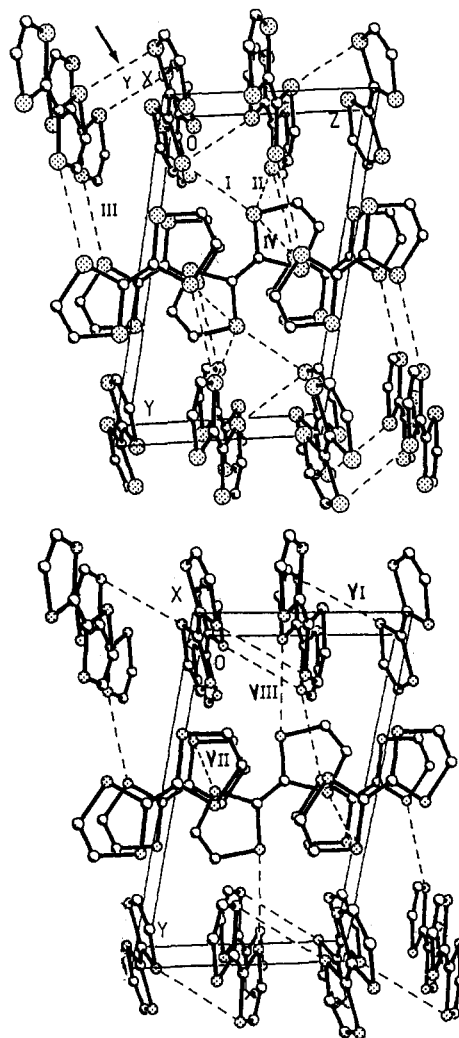
Table 8. Summary of Specific S···S Interactions of TTF2[a]

| rank | potential function | | |
	W^c	M^d	F/G^e
1	−0.97	−1.08	−1.40
	S7···S4A	S7···S4A	S7^f···S4A
	I −1 0 0	I −1 0 0	I −1 0 0
	3.579	3.602	3.570
2	−1.05	−1.28	−1.48
	S4^f···S1A	S4···S1A	S7···S5
	I 0 −1 0	I 0 −1 0	I −1 0 0
	3.595	3.656	3.587
3	−1.28	−1.28	−1.50
	S5···S7	S5···S4A	S4···S1A
	I −1 0 0	I 0 0 0	I 0 −1 0
	3.655	3.656	3.593
4	−1.29	−1.33	−1.63
	S5···S4A	S8···S1A	S8A···S4A
	I 0 0 0	I 0 0 0	I −1 0 0
	3.659	3.671	3.631
5	−1.30	−1.53	−1.66
	S8^f···S1A	S3···S6A	S5···S4A
	I 0 0 0	I 0 0 −1	I 0 0 0
	3.660	3.776	3.639

[a] Down the columns entries are given in order of increasing distance. Each entry contains, respectively, the energy of the specific interaction (in kJ mol⁻¹), the atom pair involved in the interaction, the symmetry operation generating the atom pair interaction,[b] and the distance (in angstroms) between the two atoms in the pair. [b] For symmetry operations the roman numeral I indicates x, y, z. The following three numbers indicate translations along the a, b, and c unit-cell axes, respectively. [c] Williams potentials.[18] [d] Mirsky potentials.[19] [e] Filippini/Gavezzotti potentials.[18] [f] The "A" designator indicates the atom generated through the inversion center.

However, in the process of minimizing the lattice energy, the crystal structure of TTF1 has been shifted to maximize the interactions along the c axis and to decrease the contribution of the interaction along the a axis present in the experimentally determined structure. The short b axis has been reduced further, leading to an increase in the plane-to-plane stacking interactions (Table 6). While this result may appear surprising at first, upon consideration it is totally consistent with the computational process. The algorithm for minimizing the lattice energy attempts to adjust the crystal structure to bring the maximum number of interactions to the lowest possible energy. Both S···S potential energy curves employed in this case (Figure 1) have energy minima at distances which are *greater* than the two shortest contacts in the experimental crystal structure. Hence the minimization procedure will *lengthen* those two interactions and shorten others which exceed 3.83 or 3.89 Å in the experimental structure. In the M and F/G minimizations, the number of interactions and the corresponding energy can be maximized by lengthening the a axis and reducing that interaction, while at the same time decreasing the lateral interactions along the c axis and the interactions along the stack, which is exactly what happens.

While the use of lattice energy calculations is becoming increasingly common as a means for investigating and understanding the structure of organic crystals, the analysis of the results of such calculations is often limited to a comparison of the initial and final energies. In light of the significant changes in the nature and number of the interactions that stabilize the crystal structure as a result of the minimization, this procedure is not sufficient, and it is clearly necessary to examine carefully the crystal

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Figure 6. Two views of the crystal structure of TTF2 after lattice energy minimization. Both are views on the *bc* plane but indicate different intermolecular S⋯S distances described in the text and listed in Table 8.

structures as well. In the case in point the procedure indeed leads to a reasonable energy, but not a necessarily representative structure. The source of the discrepancy is the S⋯S potential.

Similar results, but manifested in a different way, are obtained for TTF2.[44] The S⋯S intermolecular distances <3.90 Å which have been discussed earlier for the experimentally determined structure are shown in Figure 6 and listed in Tables 6 and 7. The changes in the order of the interactions (as determined by the energy contribution and corresponding to the distance) are dependent on the potentials used in the calculation. Hence, in this case, as opposed to that of TTF1, in terms of the *kinds* of interactions, the calculated structure accords with that of the experimental one; however, their relative importance changes as a result of the energy minimization. In addition,

for the *F/G* potential only, two additional (S(2)⋯S(8)) distances <3.90 Å appear in the list.

The structural differences between the experimental crystal structure and that following the minimization are visibly imperceptible. In either case, it is still clear that the S⋯S interactions are those which dominate the structure. Which are the "truly important" ones seems to be impossible to determine at this stage. As opposed to TTF1, where a few short intermolecular distances dominate the structure, TTF2 is a structure in which it does seem clear, however, that many nearly energetically equivalent S⋯S interactions serve to stabilize the crystal structure. Many TTF derivatives crystallize with plane-to-plane stacking which involves S⋯S distances of the magnitude of those observed here.[42] Also, transverse interactions are observed, leading to the formation of sheets. The geometry of nonbonded contacts to divalent sulfur has been surveyed, and appears to involve orbital interactions.[46] In TTF2 it appears that the inclination to form the stacks (chains, in the present case) is modulated by competition with the neighboring chain, leading to the unusual structure observed.

Concluding Remarks

The newly discovered second polymorph of TTF crystallizes in a very unusual manner, with four independent half molecules in the asymmetric unit, and exhibiting virtually none of the plane-to-plane stacking features characteristic of this family of compounds. The crystal structures of both polymorphs are characterized by intermolecular networks of S⋯S van der Waals interactions. We have shown that considerable care must be exercised in defining which of these interactions should be included in the determination of the nature of the network. The availability of two polymorphic structures also facilitated a comparison of the utility of three parameter sets for calculating lattice energies based on the atom⋯atom method. All three potentials indicate that TTF2 is less stable than TTF1, with differences in calculated lattice energies in the range expected for polymorphic structures. However, the calculated values for the lattice energy are all greater (i.e., more stable) than the experimental sublimation energy of TTF1. A more critical evaluation of these potential parameters, in particular those employed for interactions including sulfur, awaits the determination of the sublimation energy of TTF2 and other polymorphic sulfur-containing systems, as well as the appropriate crystal structure determinations and lattice energy calculations.

(44) A referee has correctly pointed out that the calculation of the minimized lattice energy is a 7-parameter optimization for TTF1 anmd a 29-parameter optimization for TTF2 and that the performance of the optimization routine may differ in the two cases. A difference in the number of parameters to be optimized can be expected for any, indeed perhaps most, polymorphic systems, although it is quite large here. One of the hard tests for the lattice energy programs and parameters is the treatment of such polymorphic systems, and carrying out that test is one of our purposes here. We observed no evidence for any unusual behavior of the optimization procedure.

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