the fourth number is the number of individual values included in the average.

(20) (a) Radonovich, L. J.; Zuerner, E. C.; Efner, H. F.; Klabunde, K. J. *Inorg. Chem.* **1976**, *15*, 2976. (b) Morosin, B. *Acta Crystallogr., Sect. B* **1974**, *30*, 838. (c) Starovskii, O. V.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1961**, *2*, 162.

(21) (a) Brice, M. D.; Dellaca, R. J.; Penfold, B. R. *Chem. Commun.* **1971**, 72. (b) Dellaca, R. J.; Penfold, B. R. *Inorg. Chem.* **1971**, *11*, 1855. (c) Anderson, B. B.; Behrens, C. L.; Radonovich, L. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1976**, *98*, 5390. (d) For a review of arene–metal chemistry see: Gastinger, R. G.; Klabunde, K. J. *Transition Met. Chem.* **1979**, *4*, 1.

(22) Electron-diffraction studies: (a) Renova, I. A.; Bochvar, D. A.; Christyakov, A. L.; Struchkov, Y. T.; Alekseev, N. V. *J. Organomet. Chem.* **1969**, *18*, 337. (b) Hedberg, L.; Hedberg, K. *J. Chem. Phys.* **1970**, *53*, 1228.

(23) Scroggins, W. T.; Rettig, M. F.; Wing, R. M. *Inorg. Chem.* **1976**, *15*, 1381.

(24) (a) X-ray diffraction study: Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Crystallogr.* **1956**, *9*, 373. (b) Neutron diffraction study: Willis, B. T. M. *Ibid.* **1960**, *13*, A114. (c) Electron-diffraction study: Bohn, R. K.; Haaland, A. *J. Organomet. Chem.* **1966**, *5*, 470.

(25) The plane described by the equation $0.890X + 0.455Y + 0.000Z = 1.770$ where $X$, $Y$, and $Z$ are othogonal coordinates along $\vec{\mathbf{a}}$, $\mathbf{b}$, and $\vec{\mathbf{c}}$, respectively, of the crystal system.

(26) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 260.

(27) Lide, Jr., R. D. *Tetrahedron* **1962**, *17*, 125.

(28) Reference 26, pp 224–228.

(29) (a) Cotton, F. A.; Day, V. W.; Hazen, Jr., E. E.; Larsen, S. *J. Am. Chem. Soc.* **1973**, *95*, 4834. (b) Cotton, F. A.; Day, V. W.; Hazen, Jr., E. E.; Larsen, S.; Wong, S. T. K. *Ibid.* **1974**, *96*, 4471. (c) Baumgarten, H. E.; McMahan, D. G.; Elia, V. J.; Gold, B. I.; Day, V. W.; Day, R. O. *J. Org. Chem.* **1976**, *41*, 3798. (d) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(30) Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *J. Organomet. Chem.* **1976**, *121*, C18.

(31) Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 132.

(32) Least-squares mean plane defined by $0.457X + 0.000Y - 0.890Z = 1.591$ with each atom coplanar to within 0.01 Å.

(33) Least-squares mean plane defined by (a) $-0.528X + 0.000Y + 0.849Z = 1.699$. (b) $0.140X + 0.000Y + 0.990Z = 3.218$. (c) $-0.724X + 0.000Y + 0.690Z = 2.032$.

(34) The angle subtended at rhodium by the centers of gravity for the hexamethylbenzene ring and the four $\eta^4$-bonded hexamethylcyclohexadiene atoms is 171°.

(35) The van der Waals diameter[26] for a methyl group is 4.00 Å.

# Crystal Structure and Properties of Tetrathiafulvalenium Triiodide

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**Abstract:** Slow cooling of a hot acetonitrile solution of tetrathiafulvalene (TTF) and iodine yields a mixture of crystalline products including monoclinic crystals of high iodine content: $TTF{\cdot}I_3$. A single-crystal X-ray structure analysis has been carried out on these crystals of symmetry $P2_1/n$ with four molecules per unit cell. The cell parameters are $a = 9.411$ (2) Å, $b = 18.787$ (3) Å, $c = 7.771$ (1) Å, $\beta = 103.2$ (1)°, and $V = 1374$ (1) Å$^3$. The structure consists of integrated stacks along the $\langle 102 \rangle$ axis with $TTF^+$ dimers interspersed between pairs of triiodide ions. Consistent with the structural results, single-crystal measurements indicate that this material exhibits high electrical resistivity with $\sigma_{RT} < 9 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$.

## Introduction

Considerable attention in recent years has been focused on the chemistry and physics of materials which exhibit highly anisotropic electrical, optical, and magnetic properties.[3] Of particular interest have been organic and metal-organic solids which exhibit metal-like charge transport along one crystalline axis. The discovery of the "organic metal" tetrathiafulvalene–tetracyanoquinodimethane (TTF-TCNQ) prompted a number of studies of TTF as an electron donor and precursor for other highly conductive solids. Halogen oxidation, for example, yields a variety of charge-transfer salts.[4]

One direction of activity in our laboratories and others has involved the iodine-containing TTF salts, $TTF{\cdot}I_x$. The stoichiometries prepared to date range from $x = 0.71$ to 3.0, but detailed single-crystal characterization has been restricted to a limited number of low iodine phases. The most conductive of these is $TTF{\cdot}I_{0.71}$[4a,b] with a room temperature conductivity of ca. 300 $\Omega^{-1}$ cm$^{-1}$ along the needle axis. This material possesses an ordered, modulated crystal structure containing stacks of eclipsed, partially oxidized TTF molecules[4h] and parallel chains of $I^-$ ions.[4h,5] Two additional phases of intermediate stoichiometry with $x \sim 2.0$ have been isolated which vary only in the degree of order-disorder. The first $TTF{\cdot}I_2$ structure (space group *Immm*) contains disordered chains of triiodide ions and disordered TTF stacks ($(TTF^{0.7+})(I_3^-)_{0.7}$).[4c,6,7] Preliminary X-ray crystallographic investigations suggest that the second $TTF{\cdot}I_2$ phase (space group *Fddd*) is a superstructure of the first $TTF{\cdot}I_2$ phase with ordered TTF stacks, but again with disordered triiodide ions.[6,7] Full expositions of the $TTF{\cdot}I_2$ structures, spectroscopy, and transport properties are in preparation. In view of the accumulating knowledge on the above TTF–iodine complexes, it would clearly be of interest to investigate, for comparative purposes, the phase of greatest iodine content. This would provide information on how the crystal structure,[8] degree of partial oxidation, and transport properties adjust to the increased dopant level. Such information might also shed light on how large amounts of iodine are sometimes accommodated in metal glyoximate[9] and phthalocyanine[10] lattices. Here, again, phases with very high iodine content have been isolated.[9,10] We report here the synthesis, X-ray diffraction structure determination, and single-crystal conductivity of the high-iodine TTF phase, $TTF{\cdot}I_3$.

## Experimental Section

**Synthesis of $TTF{\cdot}I_3$.** Tetrathiafulvalenium triiodide was prepared under a nitrogen atmosphere by adding dropwise a solution of 80 mg (0.39 mmol) of TTF (Aldrich Chemical Co.) in 10 mL of acetonitrile (freshly distilled from $P_2O_5$ under nitrogen) to a stirring solution of 120 mg (0.47 mmol) of triply sublimed $I_2$ in 10 mL of freshly distilled acetonitrile. Sufficient acetonitrile was added until the total volume was 50 mL. The solution was heated to 50 °C with constant stirring until all of the solid present dissolved. Upon slow cooling to room temperature, a mixture of crystals of $TTF{\cdot}I_{0.71}$, $TTF{\cdot}I_2$, and, in trace amounts, $TTF{\cdot}I_3$ resulted. The product was then washed with freshly distilled benzene and dried with a stream of nitrogen. The morphology of the $TTF{\cdot}I_3$ crystals is sufficiently different from the other phases

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**Table I.** Fractional Atomic Coordinates and Anisotropic Thermal Parameters

| atom | $x$ | $y$ | $z$ | $\beta_{12}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| I(1) | 0.34364(5) | −0.12731(2) | 0.62281(6) | 0.01029(6) | 0.00230(1) | 0.01948(10) | 0.00085(2) | 0.00253(6) | −0.00117(3) |
| I(2) | 0.36909(4) | 0.02401(2) | 0.70257(5) | 0.00699(5) | 0.00205(1) | 0.01434(8) | 0.00016(2) | 0.00241(5) | 0.00072(2) |
| I(3) | 0.37473(5) | 0.17644(2) | 0.79679(7) | 0.01207(2) | 0.00180(1) | 0.02430(11) | −0.00078(2) | 0.00441(7) | 0.00130(3) |
| S(1) | 0.2568(2) | 0.0726(8) | 0.1492(2) | 0.0077(2) | 0.00171(4) | 0.0188(3) | −0.00062(7) | 0.0035(2) | −0.00033(9) |
| S(2) | 0.0096(2) | 0.0641(8) | 0.3138(2) | 0.0095(2) | 0.00188(4) | 0.0130(3) | 0.00075(7) | 0.0036(2) | −0.00029(8) |
| S(3) | −0.0098(2) | −0.1074(8) | 0.2256(2) | 0.0088(2) | 0.00178(4) | 0.0148(3) | −0.00053(7) | 0.0032(2) | 0.00036(8) |
| S(4) | 0.2390(2) | −0.0942(8) | 0.0646(2) | 0.0082(2) | 0.00175(4) | 0.0161(3) | 0.00062(7) | 0.0034(2) | −0.00070(8) |
| C(1) | 0.1204(6) | −0.0530(3) | 0.1738(7) | 0.0060(6) | 0.00162(14) | 0.0090(8) | 0.0005(2) | 0.0013(6) | 0.0000(3) |
| C(2) | 0.1306(6) | 0.0188(3) | 0.2127(7) | 0.0056(6) | 0.00166(14) | 0.0102(9) | 0.0001(2) | 0.0007(6) | −0.0001(3) |
| C(3) | 0.2024(8) | 0.1492(3) | 0.2370(9) | 0.0123(10) | 0.00149(15) | 0.0190(13) | −0.0008(3) | 0.0020(14) | −0.0009(4) |
| C(4) | 0.0905(8) | 0.1434(3) | 0.3132(9) | 0.0157(11) | 0.00157(16) | 0.0161(12) | 0.0007(4) | 0.0024(10) | −0.0010(4) |
| C(5) | 0.0529(8) | −0.1848(3) | 0.1436(9) | 0.0108(9) | 0.00154(15) | 0.0198(14) | −0.005(3) | 0.0005(10) | −0.0001(4) |
| C(6) | 0.1653(8) | −0.1783(3) | 0.0701(9) | 0.0123(9) | 0.00186(17) | 0.0177(13) | 0.0007(3) | 0.0014(10) | −0.0006(4) |
| H(3) | 0.255(10) | 0.193(4) | 0.209(11) | | | | | | |
| H(4) | 0.039(10) | 0.186(4) | 0.356(11) | | | | | | |
| H(5) | −0.006(10) | −0.230(4) | 0.162(11) | | | | | | |
| H(6) | 0.218(10) | −0.218(4) | 0.013(11) | | | | | | |

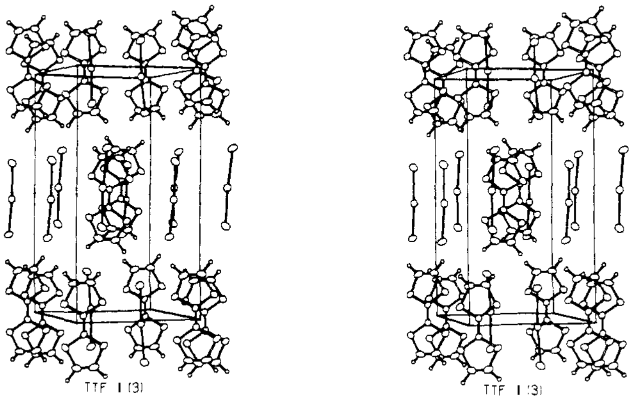


Figure 1. Stereoscopic view of the molecular packing of TTF·$I_3$. The monoclinic $b$ axis is vertical.

to be easily separated by inspection. Insufficient quantities of material were obtained for elemental analysis.

**X-ray Diffraction Study.** TTF·$I_3$ has four molecules per unit cell with space-group symmetry $P2_1/n$. Least-squares refinement of cell parameters using ten high-order reflections gave the unit cell dimension $a = 9.411$ (2), $b = 18.787$ (3), and $c = 7.771$ (1) Å, with $\beta = 103.2$ (1)° and $V = 1374$ (1) Å$^3$.

Single-crystal intensities from a polyhedral crystal were collected on the Oak Ridge computer-controlled diffractometer using filtered molybdenum radiation. Of the 3915 unique reflections measured, 3284 had intensities greater than $1\sigma$. A twin or perhaps an unidentified second phase was present and caused at least 75 reflections, mainly in the ($hk0$) zone, to have excessive observed intensity. The ($0k0$) reflections were all affected. An absorption correction applied to the data gave transmittancy factors of 0.13–0.17.

**Structure Solution and Refinement.** The three iodine atom positions were found using the direct-methods program MULTAN of Germain, Main, and Woolfson.[11] These matched the heavy-atom vectors of the Patterson map. The sulfur and carbon atoms were then found using a Fourier map computed with phases based on iodine atom positions. The four hydrogen atoms were placed in idealized positions and their positional parameters included in the refinement.

Refinement of all nonhydrogen atoms with anisotropic thermal motion and hydrogen atom positions led to an $R$ index of 0.078 on $F^2$ for all 3915 reflections. The refinement was based on 3090 reflections with 75 reflections deleted because of the twinning problem and reflections $<1.5\sigma$ omitted. The $R(F^2)$ index for the reflections used in the refinement was 0.054. Tables of the final $|F_o|$ and $|F_c|$ values for the 3915 reflections are available upon request.[12]

Atomic scattering factors for S, C, H, and the central I were taken directly from the International Tables for X-ray Crystallography.[13] Scattering factors for the two outer iodines in the triiodide were taken as the average of the scattering factors for $I^0$ and $I^-$, since it has been shown that the negative charge in the triiodide ion is distributed among the outer iodines, while the central iodine is approximately neutral.[9a,14] The real and imaginary anomalous-dispersion scattering-factor correlation of Cromer and Liberman[15] was included.

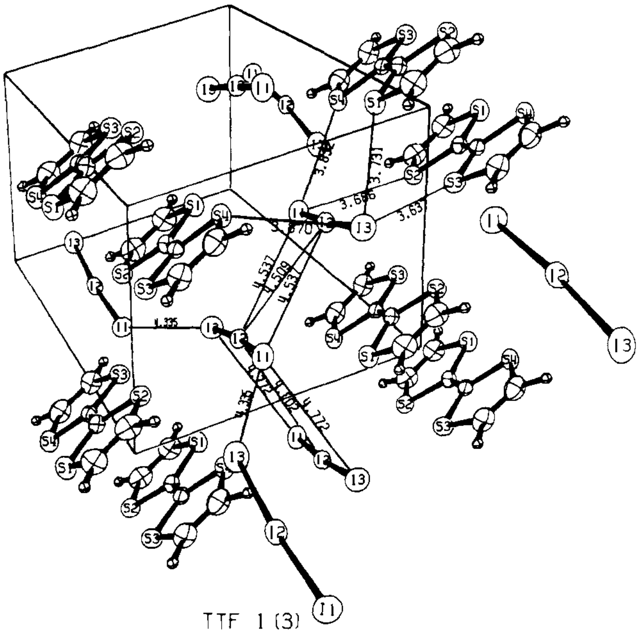


Figure 2. View of stacking within a sheet of $(TTF)_2^{2+}$ dimers and triiodide ions in the $ac$ plane. The zigzagging triiodide chains along $b$ also are shown.

**Electrical Conductivity Measurements.** The samples examined for dc conductivity studies (using the apparatus described previously[9]) were nearly hexagonal prisms, with all dimensions on the order of a few tenths of a millimeter. The small crystal size permitted only two probe conductivity measurements, though orientations both parallel and perpendicular to the hexagonal plane could be examined. Samples were mounted by pressure contact between two spring-loaded brass pins.

## Results and Discussion

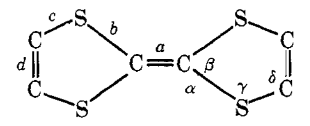
The reaction of TTF with iodine in acetronitrile, followed by slow cooling, yields TTF·$I_x$ phases of various stoichiometries (see Experimental Section for methodology). The small quantities of TTF·$I_3$ crystals formed were mechanically separated from the other phases.

***Description of the Structure.*** The final atomic coordinates and anisotropic temperature factors are given in Table I. A stereoscopic view of the unit cell contents is shown in Figure 1 and the $I_3^-$ ion close contacts are illustrated in Figure 2. The

**Table II.** Selected Distances and Angles in TTF·$I_3$

| | | | |
|---|---|---|---|
| | Bond Distances (Å) | | |
| I(1)-I(2) | 2.907(1) | S(3)-C(5) | 1.743(7) |
| I(2)-I(3) | 2.953(1) | S(4)-C(1) | 1.731(6) |
| S(1)-C(2) | 1.715(6) | S(4)-C(6) | 1.730(7) |
| S(1)-C(3) | 1.718(7) | C(1)-C(2) | 1.382(7) |
| S(2)-C(2) | 1.718(6) | C(3)-C(4) | 1.326(11) |
| S(2)-C(4) | 1.724(7) | C(5)-C(6) | 1.317(11) |
| S(3)-C(1) | 1.713(6) | | |
| | Nonbonded Contacts (Å) | | |
| I(1)-S(2)′ | 3.686(2) | I(3)-S(4) | 3.870(2) |
| -S(4)‴ | 3.832(2) | I(1)-C(1) | 3.898(5) |
| -S(1)″ | 3.911(2) | I(2)-C(2) | 3.955(5) |
| I(2)-S(3)′ | 3.881(2) | I(3)-C(4) | 3.933(7) |
| -S(2)′ | 3.882(2) | I(3)-C(6) | 3.902(7) |
| -S(1)″ | 3.895(2) | S(1)-S(3)⁗ | 3.351(2) |
| -S(4)″ | 3.946(2) | S(2)-S(4)⁗ | 3.372(2) |
| -S(1)‴ | 3.959(2) | C(1)-C(2)⁗ | 3.434(7) |
| -S(4)‴ | 3.989(2) | C(3)-C(5)⁗ | 3.424(9) |
| I(3)-S(3)′ | 3.637(2) | C(4)-C(6)⁗ | 3.439(10) |
| -S(1)‴ | 3.732(2) | | |
| | Bond Angles (deg) | | |
| I-I-I | 175.40(2) | S(3)-C(1)-S(4) | 115.1(2) |
| S(1)-C(2)-C(1) | 122.1(4) | S(1)-C(2)-S(2) | 115.7(3) |
| S(2)-C(2)-C(1) | 122.1(4) | C(4)-C(3)-S(1) | 116.6(5) |
| S(3)-C(1)-C(2) | 123.3(4) | C(3)-C(4)-S(2) | 118.1(5) |
| S(4)-C(1)-C(2) | 121.5(4) | C(6)-C(5)-S(3) | 117.0(5) |
| C(2)-S(1)-C(3) | 95.2(3) | C(5)-C(6)-S(4) | 117.4(5) |
| C(2)-S(2)-C(4) | 94.2(3) | | |
| C(1)-S(3)-C(5) | 95.2(3) | | |
| C(6)-S(4)-C(1) | 95.1(3) | | |

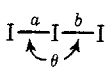
**Table III.** Dimensions of TTF Molecule Averaged over Assumed *mmm* Molecular Symmetry



| | TTF[a] 295 K | TTF-TCNQ[b] 298 K | TTF·$I_{0.71}$[c] 295 K | TTF·$I_3$[d] 295 K | TTF·Br[e] |
|---|---|---|---|---|---|
| *a*, Å | 1.349(3) | 1.369(4) | 1.350 | 1.382(7) | 1.393 |
| *b*, Å | 1.757(2) | 1.743(4) | 1.732 | 1.719(8) | 1.720 |
| *c*, Å | 1.726(4) | 1.736(5) | 1.721 | 1.728(11) | 1.724 |
| *d*, Å | 1.314(3) | 1.323(4) | 1.336 | 1.322(11) | 1.332 |
| α, deg | 122.8(2) | 122.6(3) | 122.9 | 122.5(8) | 122.3 |
| β, deg | 114.5(2) | 114.7(3) | 114.3 | 115.4(4) | 115.5 |
| γ, deg | 94.4(2) | 94.9(3) | 95.7 | 94.9(5) | 95.1 |
| δ, deg | 118.3(4) | 117.6(4) | 117.2 | 117.3(6) | 117.2 |

[a] Phillips, T. E.; Kistenmacher, T. J.; Ferraris, J. P.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1973**, 471-472. [b] Kistenmacher, T. J.; Phillips, T. E.; Cowan, D. O. *Acta Crystallogr., Sect. B* **1974**, *30*, 763-768. [c] Obtained by Fourier refinement; comparable standard errors are unavailable. Reference 6c. [d] This work. [e] Reference 16.

**Table IV.** Bond Angles and Distances in Triiodide Ions


$$\mathrm{I}\overset{a}{—}\mathrm{I}\overset{b}{—}\mathrm{I}$$

| | θ, deg | *a*, Å | *b*, Å |
|---|---|---|---|
| TTF·$I_3$[a] | 175.40(2) | 2.9533(8) | 2.9078(7) |
| $((C_6H_5)CONH_2)_2H^+I_3^-$ [b] | 177.2(5) | 2.959(8) | 2.900(8) |
| | 176.5(4) | 2.943(8) | 2.921(8) |
| $(C_6H_5)_4AsI_3$[c] | 175.61(5) | 2.920(2) | 2.920(2) |
| $CsI_3$[e] | 177.9(1) | 3.042(4) | 2.840(4) |
| $NH_4I_3$[d] | 180.0(1) | 3.113(4) | 2.791(4) |
| $Cu(S_2CNBu_2)_2I_3$ [e] | 176.5(3) | 2.919(7) | 2.899(7) |
| $(phenacetin)_2 \cdot H^+I_3^- \cdot I_2$[f] | 180 | 2.907(1) | 2.907(1) |

[a] This work. [b] This structure contains parallel chains of triiodide ions, with two types of $I_3^-$ moieties: Reddy, J. M.; Knox, K.; Robin, M. B. *J. Chem. Phys.* **1964**, *40*, 1082-1089. [c] Runsink, J.; Swen-Walstra, S.; Migchelsen, T. *Acta Crystallogr., Sect. B* **1972**, *28*, 1331-1335. [d] Cheesman, G. H.; Finney, A. J. T. *Acta Crystallogr., Sect. B* **1970**, *26*, 904-906. [e] Wijnhoven, J. G.; Van den Hark, T. E. M.; Beurkeus, P. T. *J. Cryst. Mol. Struct.* **1972**, *2*, 189-196. [f] Herbstein, F. H.; Kapon, M. *Nature (London)* **1972**, *239*, 153-154.

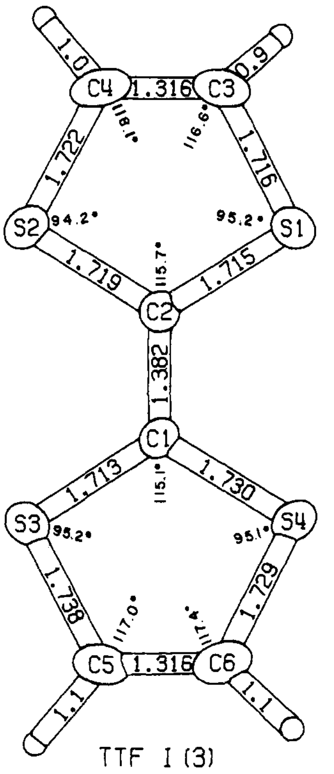


Figure 3. Bond distances and angles in the TTF$^+$ ion. Probability ellipsoids (50%) and the numbering scheme are also shown.

crystal structure consists of integrated stacks of cofacial $(TTF)_2^{2+}$ dimers in alternation with pairs of triiodide ions. The TTF$^+$ cation is distorted somewhat from planarity, with all sulfur atoms 0.01-0.03 Å below (i.e., toward the other molecule of the dimer) and all carbon atoms 0.0-0.03 Å above the least-squares best plane. The spacing between least-squares best planes for the TTF$^+$ ions within the dimer is 3.40 (1) Å, but the S-S distances of 3.351 (2) and 3.373 (2) Å are somewhat shorter. The molecular packing in TTF·$I_3$ is reminiscent of that communicated for TTF·Br (and isomorphous TTF·Cl), also integral oxidation state salts.[4i,j,16] In these materials, integrated stacks of $(TTF)_2^{2+}$ dimers and halide ions also occur. The interplanar spacing between members of the dimer appears to be somewhat larger in the present case (3.40 (1) Å) than in TTF·Br (3.34 Å).[4i,j,16] These interplanar spacings are considerably shorter than the TTF spacings of 3.55 (1) Å found in the segregated stack structures of TTF·$I_{0.71}$ and TTF·$I_2$. The spacings in the present case are also shorter than in the eclipsed $(TTF)_2^{2+}$ dimers of $(TTF)_2Ni(S_4C_4H_4)$ (here the S-S distance is given as 3.48 Å).[17] The direct axis fractional components of the TTF$^+$ plane normal in TTF·$I_3$ are (0.0679, −0.0099, 0.1166), which is approximately along the ⟨102⟩ direction. The TTF$^+$ ions are almost exactly superimposed with a slight lateral offset of about 0.25 Å perpendicular to the long axis of the molecule.

The molecular structural parameters for TTF·$I_3$ are summarized in Table II. In Figure 3, the bond distances and angles within the tetrathiafulvalenium ion are illustrated. These indicate that the cation is rather symmetrical, even though this is not required by the crystallographic symmetry. A comparison of the $\mathrm{TTF^+}$ structural data with that of other TTF cations as well as with neutral TTF is set out in Table III. It can be seen that oxidation is accompanied by lengthening of the exocyclic double bond (a) and shortening of the contacts between the two carbon atoms involved in the exocyclic double bond and the sulfur atoms (b). The metrical parameters for $\mathrm{TTF^+}$ in the present study are experimentally indistinguishable from those in $\mathrm{TTF\cdot Br}$.[16]

The $\mathrm{TTF\cdot I_3}$ crystal structure also contains parallel, zigzagging chains of triiodide ions. The arrangement of the triiodide ions is illustrated in Figure 2. The triiodide ion deviates slightly from linearity with an I-I-I angle of 175.40 (2).° This slight bending is frequently observed in structures of triiodides (Table IV) and reflects the rather flat potential energy surface for molecular distortion.[18] The fact that the terminal iodine atoms of the $\mathrm{I_3^-}$ ion are slightly displaced toward the positively charged $\mathrm{(TTF)_2^{2+}}$ dimer can be explained on an electrostatic basis. The negative charge in $\mathrm{I_3^-}$ is localized principally on these two atoms.[9a,14] The slight asymmetry in the I-I distances, 2.908 (1) and 2.953 (1) Å, presumably also reflects the environment and ready deformability of the $\mathrm{I_3^-}$ ion. The I-S contacts are illustrated in Figure 2, and the closest distances are in the range 3.636 (2) to 3.989 (2) Å. These values are typical of the I-S contacts found in $\mathrm{TTF\cdot I_x}$ systems. In the more closely packed $\mathrm{TTF\cdot I_{0.7}}$ structure, the I-S contacts are as small as 3.53 Å.[4h] As shown in Figure 2, the closest contact between proximate $\mathrm{I_3^-}$ ions is 4.335 (1) Å.

**Electrical Conductivity.** The room temperature dc conductivities of two single-crystal samples of $\mathrm{TTF\cdot I_3}$ were measured parallel to the hexagonal plane and found to have values of $6 \times 10^{-9}$ and $9 \times 10^{-10}\ \Omega^{-1}\ \mathrm{cm^{-1}}$. The dc conductivity of the latter sample was also measured perpendicular to the hexagonal plane. Here the geometry put the precise value of the conductivity beyond the limitations of the instrumentation, although an upper limit of $9 \times 10^{-9}\ \Omega^{-1}\ \mathrm{cm^{-1}}$ was determined. Finally, a small polycrystalline sample was examined and found to have $\sigma = 8 \times 10^{-10}\ \Omega^{-1}\ \mathrm{cm^{-1}}$.

## Conclusions

This work shows the high iodine phase of the $\mathrm{TTF\cdot I_x}$ system, $x = 3$, to be an integrated stack material with integral formal oxidation states, i.e., $\mathrm{TTF^+I_3^-}$. Not surprisingly, such a structure gives rise to high electrical resistivity. As in the case of the other known integral oxidation state tetrathiafulvalenium salts,[4h,i] the structural motif in $\mathrm{TTF\cdot I_3}$ consists of integrated stacks of alternating $\mathrm{(TTF)_2^{2+}}$ dimers and pairs of counteranions. Those factors which govern the stability of various possible crystal structures in TTF salts have been discussed at length.[4h,i,19,20] It appears that the present structural result can be best rationalized in terms of electrostatic destabilization with respect to the partially oxidized situation of an integral oxidation state (+1) segregated stack structure.[4h,i,19] In addition, the close interplanar separation in $\mathrm{(TTF)_2^{2+}}$ suggests enhanced covalent bonding[20,21] between the cationic moieties in the integral oxidation state case.

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**Supplementary Material Available:** A listing of structure amplitude tables for $\mathrm{TTF\cdot I_3}$ (20 pages). Ordering information is given on any current masthead page.

## References and Notes

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(2) Camille and Henry Dreyfus Teacher-Scholar.

(3) (a) Devreese, J. T.; Evrard, V. E.; Van Doren, V. E. "Highly Conducting One-Dimensional Solids"; Plenum Press: New York, 1979. (b) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79–86. (c) Miller, J. S.; Epstein, A. J. *Ann. N.Y. Acad. Sci.* **1978**, 313. (d) Keller, H. J., Ed. "Chemistry and Physics of One-Dimensional Metals"; Plenum Press: New York, 1977. (e) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1–151. (f) Keller, H. J., Ed. "Low Dimensional Cooperative Phenomena"; Plenum Press: New York, 1975. (g) Soos, Z. G.; Klein, D. J. In "Molecular Associations", Foster, R., Ed.; Academic Press: New York, 1975; Chapter 1.

(4) (a) Warmack, R. J.; Callcott, T. A.; Watson, C. R. *Phys. Rev. B.* **1975**, *12*, 3336–3338. (b) Somoano, R. B.; Gupta, A.; Hadek, V.; Datta, T.; Jones, R.; Herman, A. M. *J. Chem. Phys.* **1975**, *63*, 4970–4976. (c) Johnson, C. K.; Watson, Jr., C. R.; Warmack, R. J. *Abstr. Am. Crystallogr. Assoc.* **1975**, *3*, 19. (d) Daly, J. J.; Sanz, F. *Acta Crystallogr., Sect. B* **1975**, *31*, 620–621. (e) LaPlaca, S. J.; Corfield; P. W. R.; Thomas, R.; Scott, B. A. *Solid State Commun.* **1975**, *17*, 635–638. (f) LaPlaca, S. J. *Bull. Am. Phys. Soc.* **1975**, *20*, 496. (g) Johnson, C. K.; Watson, C. R., Jr.; Warmack, R. J. *Chem. Div. Annu. Prog. Rep., Oak Ridge Natl. Lab.* **1976**, 102–103. (h) Johnson, C. K.; Watson, C. R., Jr. *J. Chem. Phys.* **1976**, *64*, 2271–2286. (i) Scott, B. A.; LaPlaca, S. J.; Torrance, J. B.; Silverman, B. D.; Welber, B. *J. Am. Chem. Soc.* **1977**, *99*, 6631–6639. (j) Scott, B. A.; LaPlaca, S. J.; Torrance, J. B.; Silverman, B. D.; Welber, B. In ref 3c, pp 369–376.

(5) For $^{129}$I Mössbauer studies see: (a) Marks, T. J. In ref 3c, pp 594–616. (b) Teitelbaum, R. C.; Marks, T. J., manuscript in preparation.

(6) Marks, T. J.; Teitelbaum, R. C.; McClure, M. S.; Kannewurf, C. R.; Johnson, C. K.; Ruby, S. L.; *Bull. Am. Phys. Soc.* **1979**, *24*, 233.

(7) (a) Resonance Raman studies indicate that the major polyiodide constituent is a slightly distorted triiodide.[6,7b] (b) Teitelbaum, R. C.; Marks, T. J., unpublished results. (c) Johnson, C. K., manuscript in preparation.

(8) For discussions of the structural chemistry of low-dimensional materials see: (a) Kistenmacher, T. J. In ref 3c, pp 333–342. (b) Megtert, S.; Pouget, J. P.; Comes, R. In ref 3c, pp 234–243. (c) Stucky, G. D.; Schultz, A. J.; Williams, J. M. *Annu. Rev. Mater. Sci.* **1977**, *7*, 301–339. (d) Bespalov, B. P.; Titov, V. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1975**, *44*, 1091–1108. (e) Dahm, D. J.; Horn, P.; Johnson, G. R.; Miles, M. G.; Wilson, J. D. *J. Cryst. Mol. Struct.* **1975**, *5*, 27–34. (f) Herbstein, F. H. *Perspect. Struct. Chem.* **1971**, *IV*, 166–395.

(9) (a) Cowie, M. A.; Gleizes, A.; Grynkewich, G. W.; Kalina, D. W.; McClure, M. S.; Scaringe, R. P.; Teitelbaum, R. C.; Ruby, S. L.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2921–2936. (b) Brown, L. D.; Kalina, D. W.; McClure, M. S.; Ruby, S. L.; Schultz, S.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *Ibid.* **1979**, *101*, 2937–2947.

(10) (a) Schramm, C. J.; Stojakovic, D. R.; Hoffman; B. M.; Marks, T. J. *Science* **1978**, *200*, 47–48. (b) Petersen, J. L.; Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 286–288. (c) Scaringe, R. P.; Schramm, C. J.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J., submitted for publication. (d) Stojakovic, D. R. Ph.D. Thesis, Northwestern University, Aug 1977.

(11) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368–376.

(12) See paragraph at end of paper regarding supplementary material.

(13) Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-ray Crystallography", Vol. IV; Kynoch Press: Birmingham, England, 1974.

(14) (a) Potasek, M. J.; Debrunner, P. G.; Morrison, W. H., Jr.; Hendrickson, D. N. *J. Chem. Phys.* **1974**, *70*, 2203–2206. (b) Datta, S. N.; Ewig, C. S.; Van Wazer, J. R. *J. Mol. Struct.* **1978**, *48*, 407–416.

(15) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

(16) LaPlaca, S. J., private communication.

(17) Kasper, J. S.; Interrante, L. V.; Secaur, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 890–891.

(18) (a) Brown, R. D.; Nunn, E. K. *Aust. J. Chem.* **1966**, *19*, 1567–1576. (b) Migchelsen, T.; Vos, A. *Acta Crystallogr.* **1967**, *22*, 812–815. (c) Rundle, R. E. *Acta Crystallogr.* **1961**, *14*, 585–589.

(19) (a) Torrance, J. B.; Silverman, B. D. *Phys. Rev. B* **1977**, *15*, 788–801. (b) Silverman, B. D. *Ibid.* **1978**, *17*, 2482–2485. (c) Epstein, A. J.; Lipari, N. O.; Sandman, D. J.; Nielsen, P. *Ibid.* **1976**, *13*, 1569–1579. (d) Metzger, R. M. In ref 3c, pp 145–164, and references cited therein.

(20) (a) Silverman, B. D. *J. Chem. Phys.* **1979**, *70*, 1614–1620. (b) Salahub, D. R.; Messmer, R. P.; Herman, F. *Phys. Rev. B* **1976**, *13*, 4252–4257.

(21) Interrante, L. V.; Browall, K. W.; Hart, H. R., Jr.; Jacobs, I. S.; Watkins, G. D.; Wee, S. H. *J. Am. Chem. Soc.* **1975**, *97*, 889–890.