Tetrathiafulvalene *S*-Oxide: a Potential 'Donor impurity' in the Organic Metal TTF-TCNQ

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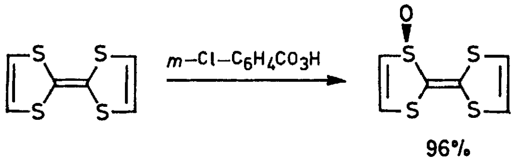
Tetrathiafulvalene *S*-oxide, which because of its size similarity with tetrathiafulvalene is a potential ' donor impurity ' in the organic metal TTF-TCNQ, was prepared and characterized spectroscopically. Experiments in which tetrathiafulvalene *S*-oxide was purposely doped into TTF-TCNQ indicate, however, that the *S*-oxide is not of major importance for the electrical conductivity of the TTF-TCNQ crystals. The surface of TTF-TCNQ crystals, which had been exposed to air, was analysed by means of ESCA spectroscopy. The results strongly indicate the presence of a totally oxidized surface

DURING the last few years a group of quasi one-dimensional organic conductors has been intensively investigated because of their unique electrical properties.[1,2] A large body of these so-called organic metals are based on the parent TTF-TCNQ system [$\Delta^{2,2'}$-bis-1,3-dithiole (tetrathiafulvalene)-7,7,8,8-tetracyano-*p*-quinodimethane]. In order to investigate the intrinsic physical properties of these conductors, much work has been done on preparing single crystals of high purity and crystalline perfection.

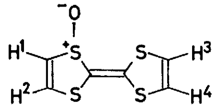
Since these materials (TTF-TCNQ) have a characteristic solid-state structure of separate uniform stacks of TTF and TCNQ molecules, and since the electrical properties are quasi one-dimensional, impurities (and/or defects) disrupting the uniform stacking may seriously influence the physical properties of the solids.[3] It is thus important to identify and remove impurities in these materials, preferentially those that as a result of size similarities with the composite molecules of the conducting organic solids may enter the lattice.

Here we report the preparation and properties of a potential ' donor impurity ' in TTF-TCNQ, tetrathiafulvalene *S*-oxide (TTF-ox), which is always present in TTF that has been exposed to oxygen.

TTF-ox was prepared in analytical, pure form by oxidation of TTF with *m*-chloroperbenzoic acid in a stoicheiometric amount in ethereal solution from which the *S*-oxide precipitates as a yellow crystalline solid in almost quantitative yield. The fact that the oxide simply precipitates from the ethereal reaction mixture probably accounts for the very high yield obtained. If the reaction was carried out in methylene chloride, where TTF-ox is soluble, the oxide could only be obtained in a poor yield after chromatographic separation of the reaction products. Similarly, tetramethyltetrathiafulvalene (TMTTF), which is almost insoluble in ether, was oxidized in methylene chloride, to afford the corresponding *S*-oxide in 37% yield. The low yields of the *S*-oxides obtained when using methylene chloride as solvent are believed to result from reoxidation of the primarily formed monoxide. However, we were not able to isolate, and characterize, compounds that could be assigned to peroxidized structures by treating TTF-ox with stoicheiometric amounts of peracid in methylene chloride.



The structure of TTF-ox was verified by ^1H n.m.r. spectroscopy, where two separate AB systems, corresponding to four different hydrogen atoms, are observed (Figure 1). The protons attached to the ring containing the $\overset{+}{S}-\overset{-}{O}$ moiety exhibit the greater difference in chemical shift ($\Delta\delta_{H^1H^2} = 0.857$ p.p.m.) as a consequence of a strong shielding effect from the oxygen atom. This effect is only weakly reflected in the difference in chemical shift for the protons in the unoxidized ring ($\Delta\delta_{H^3H^4} = 0.073$ p.p.m.).



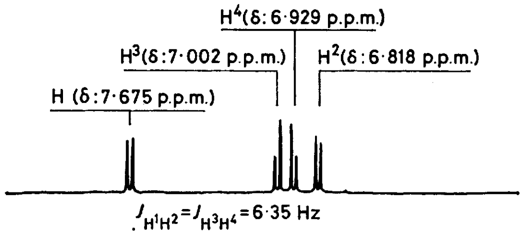


FIGURE 1 270 MHz ^1H n.m.r. spectrum of tetrathiafulvalene *S*-oxide (CD_3OD)

TTF-ox was first detected by mass spectrometry in samples of TTF that had been exposed to oxygen.[4] Apart from the molecular ion ($m/e = 220$), the fragmentation of TTF-ox induced by electron impact (Figure 2) is very similar to that recently reported for pure TTF.[4] It is, furthermore, seen that the relative intensity of the peak $m/e = 220$ is 0.14, which means that a relatively

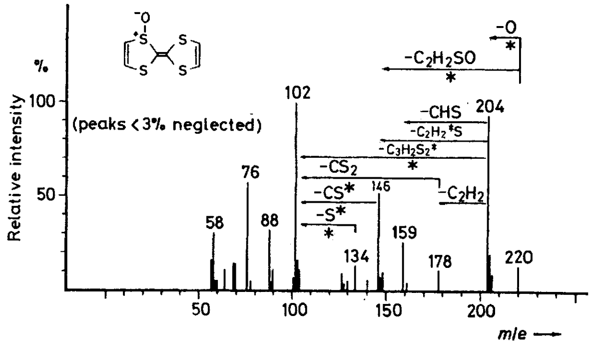


FIGURE 2 Electron-impact-induced fragmentation of tetrathiafulvalene *S*-oxide

high concentration of the oxide (*ca.* 1%) is needed in samples of impure TTF if TTF-ox is to be detected by routine mass spectrometric investigations. However, the *S*-oxide was detected by mass spectrometry as well as by t.l.c. in solid-state samples of pure TTF that had been exposed to air (in the dark) for 30 min. Likewise, the oxide was found present in a solution of TTF in acetonitrile through which had been passed a slow stream of oxygen (in the dark) for only 5 min. The diffusion coefficients for TTF and TTF-ox were determined to 2.47 ± 0.02 ($10^5 \cdot D_{\mathrm{TTF}}$) and 2.45 ± 0.04 ($10^5 \cdot D_{\mathrm{TTF\text{-}ox}}$) cm^2/s, respectively (acetonitrile, 38.5 °C),[5] indicating that the oxide may mimic TTF also in the dynamic situation on the surface of the growing crystals.

In order to determine the influence of small amounts of *S*-oxide on the electrical properties of TTF–TCNQ, we performed preliminary studies of the electrical *b*-axis conductivity of doped samples (prepared as described in the Experimental section). In all cases we chose samples without visual defects.

In Figure 3 is shown log $\sigma_{\parallel}$ *vs.* $1/T$ for typical samples in a series with varying *S*-oxide concentration (0.004—0.1%), the vertical positions of the individual curves being arbitrary.

Defects in TTF–TCNQ at the 20—1 000 p.p.m. level have previously been reported to have distinct effects on the temperature dependence of the conductivity as well as on the absolute value at room temperature.[3] The conductivity anomalies at 53 and 38 K shift downward in temperature with increasing defect level and are considerably broadened; $\sigma_{\mathrm{max.}}/\sigma$ (300 K) and σ (300 K) both decrease with increasing defect level.

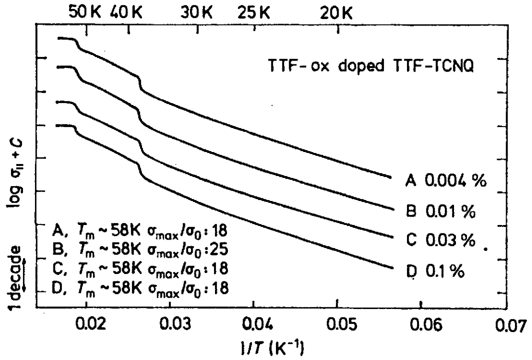


FIGURE 3 Logarithm of *b*-axis conductivity *vs.* inverse temperature for four *S*-oxide-doped samples of TTF–TCNQ. The constant *C* is arbitrary for each sample

The results plotted in Figure 3 cover nominal impurity levels from 40 to 1 000 p.p.m. However, there is almost no effect on $\sigma(T)$. Room-temperature conductivities and normalized maximum conductivities are similar to those of pure specimens. The 38 K anomaly is sharp in all samples, but it tends to shift down slightly for high oxide concentrations. For the 53 K anomaly we find no shift but a tendency to increased smearing with increasing concentration of TTF-ox. This is also illustrated in Figure 4, where $\mathrm{d}(\log_{10}R)/\mathrm{d}(1/T)$ is plotted *versus* $1/T$. The anomaly shows up as a peak. Here it should be noted that the shoulder to the right becomes more marked at higher concentrations.

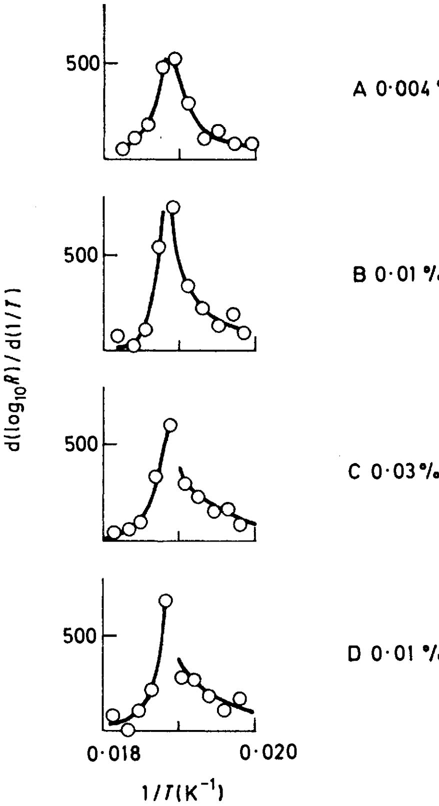


FIGURE 4 Derivative of $\log_{10}R$ with respect to inverse temperature in the vicinity of the 53 K anomaly for the four samples from Figure 3

From these studies we can conclude that the *S*-oxide is not of major importance for electrical conductivity. First because the *S*-oxide does not enter the crystals to any appreciable extent. [Using the data of ref. 6 as a rough guide, the observed shift of the 38 K transition would correspond to a defect level of the order of 10^{-5} (nominal impurity level 10^{-3}).] Secondly, because the *S*-oxide in the lattice mimics TTF introducing only an extremely weak disorder potential into the crystals, which seems rather unlikely in view of the permanent dipole moment of the TTF-ox molecule.

TTF–TCNQ crystals of poor quality, in general unsuitable for conductivity measurements, are obtained by increasing the concentration of the oxide to 1—2%. This quality is probably not a specific effect of the *S*-oxide, but rather reflects a tendency for crystals to be of poor quality when grown in impure media.

In connection with the above-mentioned reaction between TTF and molecular oxygen affording TTF-ox, we investigated a possibly analogous reaction between the TTF–TCNQ complex and molecular oxygen. The surface of TTF–TCNQ crystals, which had been prepared from pure TTF and TCNQ followed by exposure to air, was studied by means of ESCA spectroscopy. The signals corresponding to the sulphur 2*s* and oxygen 1*s* electrons are shown in Figure 5. It is seen that the S_{2s} signal contains contributions from signals at 230.8 and 228.8 eV, respectively, the area ratio being almost exactly 1 : 3. Furthermore, the area of the smaller S_{2s} contribution is found to be equal to the O_{1s} signal, corrected for a small signal due to the presence of water. No other S_{2s} signals are observed. Finally, it should be mentioned that the part of the ESCA spectrum of TTF–TCNQ mentioned above is identical to that of pure TTF-ox. On this basis we conclude that the surface of TTF–TCNQ that has been exposed to air is totally oxidized and probably consists of a mixture of TTF-ox and TCNQ molecules, since no evidence is found of the existence of a charge-transfer complex between the two types of molecule. Furthermore, the existence of a possible charge-transfer complex would be expected to change the position of the ESCA signals in the complex relative to the pure TTF-ox, which is not the case.

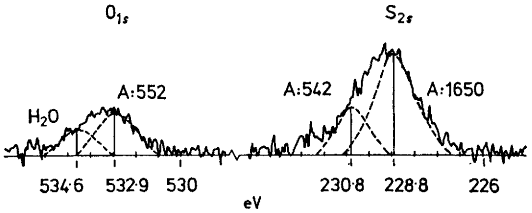


FIGURE 5 ESCA spectrum of the surface of TTF–TCNQ crystals, which have been exposed to air, in the S_{2s} and O_{1s} regions

Based on the conductivity data, which apparently exclude the presence of TTF-ox in the TTF–TCNQ lattice, we suggest that only the very outer parts (10—20 Å) of the crystals are oxidized, a fact that can be regarded as an advantage because this layer may act as a coating of the crystal surface, thus protecting the inner parts of the crystals.

EXPERIMENTAL

Purification of Tetrathiafulvalene.—TTF (500 mg) in dry methylene chloride (3 ml) was applied to a 15-cm column (diameter = 2 cm) prepared from Al_2O_3 (50 g) (Woelm, neutral super I) in dry ether. The column was eluted with dry, deoxygenated ether (*ca.* 100 ml). The eluate was kept under Ar to prevent air oxidation. Evaporation yielded pure TTF (460 mg) [t.l.c., CH_2Cl_2–EtOH (9 : 1), R_F = 0.82], which was stored under Ar.

Preparation of Tetrathiafulvalene S-*Oxide (TTF-ox).*—*m*-Chloroperbenzoic acid (190 mg, 1.1 mmol) dissolved in ether (10 ml) was added to a solution of TTF (204 mg, 1.0 mmol) in ether (15 ml). The yellow solid immediately precipitated was filtered off, washed with ether (4 × 5 ml), and dried *in vacuo*; yield 211 mg (96%), m.p. 159—160 °C [Found: C, 32.6; H, 2.0; S, 58.0. Calc. for TTF-ox ($C_6H_4S_4O$): C, 32.74; H, 1.89; S, 58.18], $\nu_{max.}$ 3 080m, 3 058m, 3 040m, 1 539s, 1 520m, 1 502vs, 1 480sh, 1 259s, 1 100m, 1 093sh, 1 005vs, 991vs, 854s, 812m, 804s, 709s, 680m, 665s, 620m, 598m, 538s, 495m, and 466s; $\lambda_{max.}$ 395 nm (ε 9 400 l mol^{-1} cm^{-1}).

Preparation of Tetramethyltetrathiafulvalene S-*Oxide (TMTTF-ox).*—*m*-Chloroperbenzoic acid (66 mg, 0.38 mmol) dissolved in methylene chloride (5 ml) was added to TMTTF (90 mg, 0.35 mmol) in methylene chloride (10 ml). The reaction mixture immediately changed from orange to dark green in colour. No precipitation was observed. Evaporation to dryness afforded a dark green crystalline product, which was washed with ether (4 × 5 ml) and dried *in vacuo*; yield 70 mg. The product was applied to p.l.c. (methylene chloride–ethanol, 9 : 1). The yellow TMTTF-ox (R_F = 0.50) was extracted with cold methylene chloride; evaporation of the solvent and recrystallization from methylene chloride–hexane gave a yield of 35 mg (37%), m.p. 235—240 °C (decomp.) [Found: C, 43.3; H, 4.8; S, 46.1. Calc. for TMTTF-ox ($C_{10}H_{12}S_4O$): C, 43.48; H, 4.35; S, 46.38]. TMTTF was isolated in 11% yield together with minor amounts of several other products (in all 25 mg) which were not analysed further. The product had the following physical characteristics: $\nu_{max.}$ 2 921w, 1 669w, 1 615w, 1 500vs, 1 440s, 1 179m, 1 080m, 1 027s, 992s, 849s, 750m, 566s, 522w, 478s, 465m, and 449w; $\lambda_{max.}$ 369 nm (ε 5 200 l mol^{-1} cm^{-1}); δ (60 MHz) 2.03 (s) and 2.13 (s).

Reaction between Tetrathiafulvalene and Molecular Oxygen.—Oxygen was slowly passed through a solution of TTF (25 mg) in dry acetonitrile (5 ml) in the dark for 5 min. By t.l.c. (methylene chloride–ethanol, 9 : 1), TTF-ox (R_F = 0.55) was detected in small amounts. A sample of pure TTF in the solid state was placed in the air (dark) for 30 min. After dissolution of the solid in methylene chloride, the *S*-oxide could be detected by t.l.c. In both cases the oxide was also observed by mass spectrometry.

Preparation of TTF-ox Doped TTF–TCNQ Crystals.—The crystals were grown by diffusive crystallization in H-tubes, where a solution of the acceptor (TCNQ) was placed in one leg and the donor (TTF with varying concentrations of TTF-ox) in the other. The tube was carefully filled with solvent (acetonitrile) and the components allowed to diffuse together (temperature: 35.0 °C).

Conductivity Measurements.—The measurements were carried out using the standard method [6] with the samples mounted on four gold wires (13 μm diam.) and with silver paste contacts (DuPont 7941). Measuring currents were in the range 0.05—50 μA, chosen so that ohmic sample heating was negligible. All the measurements reported were made during heating cycles.

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