

Preparation, properties, and X-ray crystal structure of a 1:1 complex of tetrathiafulvalene and *p*-dinitrobenzene

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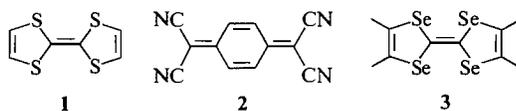
A crystalline complex of tetrathiafulvalene and *p*-dinitrobenzene has been prepared and characterised by esr and ir spectroscopy, bulk magnetic susceptibility, dc conductivity, and an X-ray diffraction analysis. It is a neutral 1:1 complex which is an insulator at room temperature, $\sigma_{RT} = 2.5 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$. The complex crystallizes in the triclinic system, space group $P\bar{1}$ with cell constants $a = 6.915(1)$, $b = 7.615(1)$, $c = 8.149(1) \text{ \AA}$, $\alpha = 79.39(1)$, $\beta = 69.55(1)$, $\gamma = 70.81(1)^\circ$, $Z = 1$. Data were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by direct methods and refined to an R -value of 0.028 for 1222 observed reflections. The structure consists of molecules stacked in an alternating donor-acceptor fashion along the c -axis. Mixed sheets parallel to $(01\bar{2})$ are comprised of tetrathiafulvalene and *p*-dinitrobenzene molecules arranged end-on in the $[021]$ direction.

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On a préparé un complexe cristallin du tétrathiafulvalène et du *p*-dinitrobenzène et on l'a caractérisé par la rpe, la spectroscopie ir, la susceptibilité magnétique de groupe, la conductivité cd, et par l'analyse de diffraction de rayons X. C'est un complexe neutre 1:1 qui est un isolant à la température ambiante, $\sigma_{RT} = 2,5 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$. Le complexe cristallise dans le système triclinique et appartient au groupe d'espace $P\bar{1}$ avec $a = 6,915(1)$, $b = 7,615(1)$, $c = 8,149(1) \text{ \AA}$, $\alpha = 79,39(1)$, $\beta = 69,55(1)$, $\gamma = 70,81(1)^\circ$, $Z = 1$. On a recueilli les données à l'aide d'un diffractomètre Enraf-Nonius CAD-4. On a résolu la structure par des méthodes directes et on l'a affiné jusqu'à une valeur de R de 0,028 pour 1222 réflexions observées. La structure comporte alternativement des molécules de donneur et de receveur qui sont entassées suivant l'axe c . Les couches mixtes parallèles à $(01\bar{2})$ comprennent des molécules de tétrathiafulvalène et de *p*-dinitrobenzène arrangées en positions tête-queue dans la direction $[021]$.

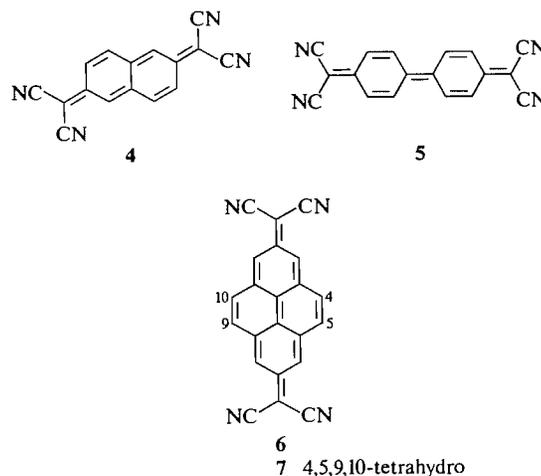
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Since the discovery of metallic conductivity in the complex of tetrathiafulvalene (1) and tetracyanoquinodimethane (2) (TTF-TCNQ), great interest has been focussed on the synthesis and properties of related organic charge transfer complexes (1). Many new donors have been prepared; the majority are sulphur and selenium heterocycles, and their complexes with TCNQ have certainly contributed to our understanding of this field (2). Recently, certain salts of tetramethyltetraseleno-fulvalene (3) have exhibited superconductivity at low temperature (3).



It is noticeable that there has been considerably less work reported on new electron acceptors. Substitution on the basic TCNQ skeleton has been shown generally to lower the conductivity of charge-transfer complexes formed (4). An alternative approach has been to vary the TCNQ skeleton by extending the conjugated π system while retaining the high degree of symmetry and the dicyanomethylene groups of the TCNQ. Accordingly, the acceptors TNAP (4) (5), TCNDQ (5) (6), and the

pyrene analogues 6 (6c, 7) and 7 (8) have been synthesized and their charge-transfer complexes studied, but none has room temperature conductivity substantially above that of TTF-TCNQ.



It has become apparent that the range of electron acceptors should be extended and Torrance *et al.* have recently reported that the tetrahalo-*p*-benzoquinones form both metallic and semi-conducting complexes with TTF and its derivatives (9). These complexes were the first, that do not contain TCNQ or a TCNQ-like molecule, to display the

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two essential prerequisites for high conductivity; namely, segregated stacks of donors and acceptors, and incomplete charge transfer. They also exhibit several striking new phenomena that have increased our knowledge of intermolecular interactions in the solid state (9b).

We now report the preparation, properties, and an X-ray diffraction analysis of a complex of TTF with the electron acceptor *p*-dinitrobenzene (DNB). DNB was chosen as an acceptor because it resembles TCNQ in two important ways. Both molecules are of similar size; it is possible that the failure of some of the larger acceptors to form complexes with TTF may be due to their incompatible molecular dimensions. DNB has the same high symmetry as TCNQ (D_{2h}); the key role of the symmetry of the TCNQ radical anion in dictating stacking arrangements in TTF-TCNQ has been shown (10). Electron spin resonance studies of the radical anions of aromatic compounds show that the electronegativity of the nitro group is similar to that of the dicyanomethylene group (11). Thus the two acceptors, TCNQ and DNB, should have similar spin and charge distributions in their radical ions.

A 1:1 complex was obtained quantitatively by evaporation of a toluene solution of TTF and DNB. All the data obtained suggest that TTF-DNB is a neutral, insulating complex. The solid state esr signal has a *g*-value at 2.0018 consistent with a free electron of a π -radical, but the signal is very weak. The esr signal was about 7 G wide and no proton hyperfine splitting could be detected in this signal. The ir spectrum of TTF-DNB consists of sharp peaks typical of insulating complexes; organic metals are characterised by very broad bands in the infrared region (12). The magnetic susceptibility of the complex between 78 and 295 K is constant, again suggesting a diamagnetic complex with no unpaired electrons. The single crystal conductivity is that of an insulator, $\sigma = 2.5 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 300 K.

The crystal structure of TTF-DNB consists of stacks along the *c*-axis of alternating TTF and DNB molecules (Fig. 1). It is further characterised by mixed sheets of TTF and DNB molecules which are parallel to (01 $\bar{2}$). Peculiar to this structure is the end-on packing arrangement (... TTF ... DNB ... TTF ...) in the [021] direction within the sheets. The intrastack interplanar spacing between TTF and DNB averages 3.64 Å, where the averaging is between the plane of the benzene ring and the two (S(1), C(2), C(3), S(2)) planes in the "chair-like" TTF molecule (*vide infra*); furthermore, the planes of the DNB ring and S(1), C(2), C(3), S(2) moieties are not parallel but subtend angles of 2.6(2)°.

Generally, the above structural features are common in donor-acceptor charge-transfer complexes, although the interplanar spacing of 3.64 Å is larger than in even the weak CT-complexes TTF-X, where X is chloranil, fluoranil (13), or bromanil (14).

In view of the apparent lack of charge-transfer properties in the present structure, it is interesting to compare the overlap of TTF and DNB within the stacks. Figure 2 shows the projection of the TTF molecule onto the plane of the DNB ring. All intermolecular contacts are at least the sum of the van der Waals radii for any two atoms, indicating a minimum energy crystal packing. The angle between the long molecular axes of TTF and DNB is 126°. This is in contrast to the suggestion, based on crystal packing arguments in TTF-bromanil and TTF-chloranil by Mayerle, Torrance, and Crowley (13), that in donor-acceptor complexes, if both donor and acceptor molecules have a long molecular axis, they tend to line up. In light of the present study of the TTF-DNB complex, where crystal packing forces appear to be the controlling factor affecting the relative orientations of molecules, the above suggestion by Mayerle *et al.* should perhaps stress an increased role of orbital overlap in determining relative molecular orientations in D-A complexes.

Both the interplanar separation and relative molecular orientation in the present complex seem to prohibit any experimentally observable charge transfer interactions (i.e. conductivity and spectroscopic measurements). However, it is interesting to note the differences between the internal angles (122.5° at C(5) and averaging 118.8° at C(4) and C(6)) in the DNB ring in TTF-DNB (Fig. 3) and the corresponding angles (123.4° and 118.3°) in the neutral *p*-DNB structure (15). The fact that these angles are slightly closer to 120° in the current structure implies an increased electron density in the benzene ring relative to neutral *p*-DNB. The short C-N bond of 1.467(2) Å in the present complex compared to 1.478(2) Å in neutral *p*-DNB is consistent with this implication. Increased electron density in the DNB ring is not explicable on the basis of the electron-withdrawing NO₂ substituents and therefore, some interaction between DNB and TTF is inferred. However, the extent of this interaction must be small when considering the other physical properties of the complex.

The C-C bond lengths in the present DNB molecule are not significantly different from those in the neutral *p*-DNB structure. The geometry of the NO₂ group is essentially the same in both compounds. Noteworthy is the slightly skewed

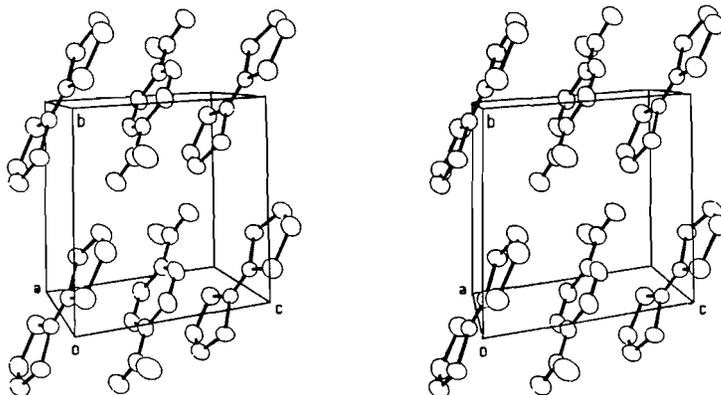


FIG. 1. Stereoview approximately down *a* of the unit cell contents.

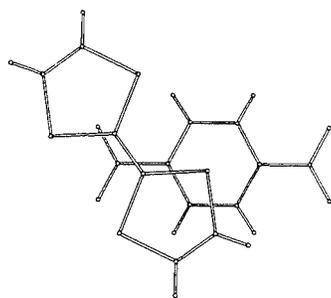


FIG. 2. Projection of the TTF molecule onto the plane of the DNB ring.

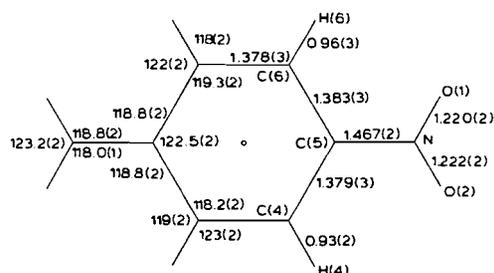
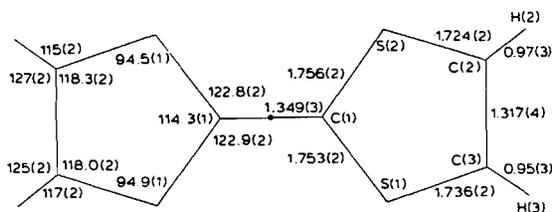


FIG. 3. Bond lengths (Å) and angles (deg) in TTF (top) and *p*-DNB (bottom).

orientation of the NO₂ plane with respect to the benzene ring plane; the two planes are twisted about the C—N bond by 1.1° (Table 1), considerably less than the 10° twist in neutral *p*-DNB.

The TTF molecule can be described by three planes (Table 1) forming a "chair-like" structure. In liquid crystals TTF was also found to adopt a non-planar conformation (16). Bond lengths and angles compare favorably with neutral TTF (17) and are generally not significantly different from those in TTF-chloranil and TTF-bromanil (13).

Experimental

Infrared spectra were run on a Perkin-Elmer model 710 spectrometer; solid spectra were run as KBr discs. Electron spin resonance spectra were obtained on a Varian E-3 spectrometer operating at 9.1 GHz. Bulk magnetic susceptibility data were obtained using a Gouy magnetic balance (18).

Tetrathiafulvalene was purified by gradient sublimation. *p*-Dinitrobenzene was recrystallized from ethanol. Toluene was freshly distilled from sodium under nitrogen.

TTF-DNB complex

A solution of TTF (204 mg, 1.0 mmol) in 5 mL of hot toluene was added to a solution of DNB (168 mg, 1.0 mmol) in 5 mL of hot toluene. The resulting dark solution was allowed to cool to room temperature and evaporated to dryness under a stream of nitrogen to give 372 mg (100%) of the complex as long black needles, mp 134°C. *Anal.* calcd. for C₁₂H₈N₂O₄S₄: C 38.70, H 2.15, N 7.53; found: C 38.89, H 2.15, N 7.62. Ir (KBr) ν_{max}: 1529, 1324, 1260, 1129, 1050, 1001, 836, 795, 782, 720, 658 cm⁻¹; esr (powder) very weak singlet, *g* = 2.0018 (7 G wide).

A crystal with well-defined faces along the *c*-axis and measuring 0.22 × 0.07 × 0.42 mm³ was employed in the crystallographic study. Preliminary Weissenberg and precession photographs indicated a triclinic structure. The crystal data (at 22°C) are:

C₆H₄S₄·C₆H₄N₂O₄ fw = 372.5
 Triclinic, *a* = 6.915(1), *b* = 7.615(1), *c* = 8.149(1) Å, α = 79.39(1), β = 69.55(1), γ = 70.81(1)°, *V* = 378.5(2) Å³, *Z* = 1, ρ_c = 1.634 g cm⁻³, μ(MoKα; λ = 0.71073 Å) = 5.75 cm⁻¹, space group *P*1 from structure analysis.

Intensities were measured on an Enraf-Nonius CAD-4 dif-

TABLE 1
(a) Least-squares planes by Hamilton's method*
(x , y , and z are fractional coordinates referred to the unit cell)

Plane 1 defined by atoms S(1), C(2), C(3), and S(2) Equation: $-0.5498x + 2.7683y - 6.8871z + 0.2302 = 0$ Distances from the plane (Å): S(1), 0.0000; C(2), -0.0007 ; C(3), 0.0006; S(2), 0.0000
Plane 2 defined by atoms S(1), C(1), and S(2) Equation: $0.4801x - 2.5908y + 6.9751z - 0.2485 = 0$
Plane 3 defined by atoms N, O(1), O(2), and C(5) Equation: $-0.4632x + 2.9958y - 6.7448z + 3.6166 = 0$ Distances from the plane (Å): N, 0.0003; O(1), -0.0002 ; O(2), -0.0001 ; C(5), -0.0001
Plane 4 defined by C(4), C(5), and C(6) Equation: $-0.5473x + 3.0622y - 6.7125z + 3.6354 = 0$

*Reference 21.

(b) Dihedral angles between planes

Planes	Angle (deg)
1,2	178.2(2)
1,3	1.8(2)
1,4	2.6(2)
2,3	176.5(2)
2,4	175.8(2)
3,4	1.1(2)

TABLE 2. Final positional (fractional $\times 10^5$, H $\times 10^3$) and isotropic thermal parameters ($U \times 10^3$ Å²) with estimated standard deviations in parentheses

Atom	x	y	z	* U_{eq}/U_{iso}
S(1)	15021(8)	12607(7)	7211(8)	54
S(2)	49943(8)	25209(7)	9488(7)	49
O(1)	77946(24)	26346(24)	59971(24)	67
O(2)	44230(24)	41012(20)	68800(20)	57
N	59136(25)	27938(22)	61962(21)	45
C(1)	42723(27)	7812(23)	3523(23)	38
C(2)	23874(40)	39205(30)	17205(30)	60
C(3)	8249(38)	33616(31)	16186(30)	61
C(4)	71207(29)	-1106(28)	47684(26)	45
C(5)	54338(26)	13377(24)	55831(22)	38
C(6)	33076(28)	14828(28)	58227(25)	44
H(2)	219(4)	507(4)	219(3)	78(8)
H(3)	-67(5)	400(4)	199(3)	78(8)
H(4)	855(4)	-18(3)	458(3)	65(7)
H(6)	220(4)	254(3)	637(3)	66(7)

* U_{eq} is one third the trace of the diagonalized anisotropic temperature factor matrix.

fractometer in the θ range 1.0–27.0° with an ω -2 θ scan and graphite monochromatized MoK α radiation; scan speeds ranged from 1.01 and 10.06 deg min⁻¹. The ω scan angle, (1.00 + 0.35 tan θ)°, was extended 25% on both sides for background measurement. A variable horizontal aperture (2.00 + 0.50 tan θ) mm was employed and the vertical aperture remained constant at 4 mm. Crystal orientation and intensity controls were monitored periodically throughout data collection.

Data processing included the application of Lorentz and polarization corrections in the usual manner. An additional correction was made to account for the slight variation ($\pm 3\%$) in the intensities over the duration of data collection. Of the 1640 accessible data, 1222 (74.5%) had $I \geq 3\sigma(I)$, where $\sigma^2(I) = S +$

$2B + (0.04(S - B))^2$, S = scan count and B = time-averaged background.

On the basis of the E -statistics, the centrosymmetric space group $P\bar{1}$ was chosen and later confirmed to be correct by the subsequent structure refinement. MULTAN (19) yielded the positions of all non-hydrogens in the asymmetric unit which consisted of half a TTF molecule and half a DNB molecule. Following several cycles of full-matrix least-squares refinement, a difference-Fourier synthesis provided the hydrogen positions. The remainder of the refinement included 11 non-hydrogen atoms with anisotropic thermal parameters and 4 hydrogen atoms with isotropic temperature factors yielding a total of 116 variables. Anomalous scattering factors, from ref. 20a, were used for S atoms; all other scattering factors were taken from ref. 20b. On the final cycle of refinement the mean and maximum parameter shifts were 0.017 and 0.141 σ , respectively; the standard error in an observation of unit weight was 1.207. R -values, defined as $R = \sum ||F_o| - k|F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}$, were 0.028 and 0.037, respectively, for the 1222 observed data with $I > 3\sigma(I)$ employed in the refinement, whereas for the complete data set $R = 0.047$ and $R_w = 0.037$. The quantity $\sum w(|F_o| - k|F_c|)^2$ was minimized in the refinement where $w = 1/\sigma^2(F_o)$, $\sigma^2(F_o)$ being derived from the previously defined $\sigma^2(I)$. The suitability of the chosen weights was confirmed by a weighting analysis program. A difference map, calculated after convergence, showed random fluctuations in electron density up to 0.25 e/Å³. Final atomic positional parameters and temperature factors are presented in Table 2.²

Acknowledgements

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²Tables of observed and calculated structure factor amplitudes, anisotropic thermal parameters for non-H atoms, and torsion angles are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

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