Preparation, Solid-state Characterisation and *X*-Ray Crystal Structure of a 1 : 1 Complex of Tetrathiafulvalene and *m*-Dinitrobenzene (TTF–*m*DNB)

Martin R. Bryce* and Stephen R. Davies
Department of Chemistry, University of Durham, Durham DH1 3LE
Michael B. Hursthouse and Majid Motevalli
Department of Chemistry, Queen Mary College, London E1 4NS

A crystalline 1 : 1 complex of tetrathiafulvalene (TTF) and *m*-dinitrobenzene (*m*DNB) has been prepared in high yield and characterised by i.r. and u.v. spectroscopy, bulk magnetic susceptibility data, four-probe d.c. conductivity, and single-crystal *X*-ray analysis. There is essentially no intermolecular charge transfer in the complex which has low conductivity σ_{rt} 2.7 × 10^{-9} S cm^{-1}. The structure consists of molecules arranged in an alternating donor-acceptor fashion along the *a* axis. Projection onto the plane of TTF shows that there is no eclipsing overlap between the TTF moiety and the neighbouring *m*DNB molecules.

Complexes of the electron donor tetrathiafulvalene (TTF) have attracted considerable attention since the discovery fifteen years ago of remarkably high electrical conductivity exhibited by TTF–TCNQ (7,7,8,8-tetracyanoquinodimethane).[1] The literature now abounds with electrical, structural, and magnetic studies of a wide range of donor–acceptor complexes based on this archetypal organic metal.[2] The vast majority of work has focussed on the most highly conducting materials, but the study of insulating complexes of TTF, *e.g.* TTF–tetrafluoro-TCNQ[3] and TTF–halogenobenzoquinones,[4] and the insulating complex dibenzo-TTF–TCNQ[5] has also added greatly to our understanding of the physics and chemistry of intermolecular interactions in the organic solid state. Cowan and Wiygul have recently emphasised that in order to refine the principles that should be applied to the design of new molecules, it is important to fully characterise complexes with the entire range of electrical properties.[2f] We have a continuing interest in new charge transfer complexes related to organic metals, and in this context we now report the preparation, properties, and a single-crystal *X*-ray diffraction study of a complex of TTF with the electron acceptor *m*-dinitrobenzene (*m*DNB). This acceptor has an aromatic ground state, rather than the quinonoid ground state of TCNQ and the halogenobenzoquinones. However, while our work was in progress, a report from an Italian group demonstrated that acceptors with an aromatic ground state, *viz.* 1,4-dicyanotetrazine, 1,3,5-tricyanotriazine, and 2,4-dicyano-6-hydroxytriazine, form moderately conducting complexes with TTF ($\sigma_{max.}$ 0.5 S cm^{-1}).[6] Thus attainment of aromaticity at the radical anion stage is not a prerequisite for conductivity in a donor–acceptor pair.

A black, highly crystalline 1 : 1 complex was obtained in good yield by slow cooling of a toluene solution of TTF and *m*DNB. All the data obtained agree and show that TTF–*m*DNB is a neutral, insulating complex.[†] The i.r. spectrum of TTF–*m*DNB consists of sharp peaks typical of an insulating complex, and it does not display a charge-transfer absorption band or the broad bands in the i.r. region that are typical of conducting complexes. These i.r. data are supported by optical measurements; the u.v. spectrum of a powdered sample of TTF–*m*DNB does not show any absorption characteristic of the TTF radical cation (2.2—2.8 eV).[7] Furthermore, the solid-state e.s.r. signal obtained from TTF–*m*DNB is vanishingly weak and the bulk magnetic susceptibility of the complex is constant over the temperature range 20—300 K, $\chi = 162.1 \times 10^{-6}$ emu mol^{-1}; in agreement with the calculated value from Pascal's constant for TTF and *m*DNB, $\chi = 159.5 \times 10^{-6}$ emu mol^{-1}. These data clearly point to a diamagnetic complex that has no unpaired electrons. Consistent with these data, the single-crystal conductivity (four-probe d.c. measurement) is that of an insulator, $\sigma_{rt} = 2.7 \times 10^{-9}$ S cm^{-1}.

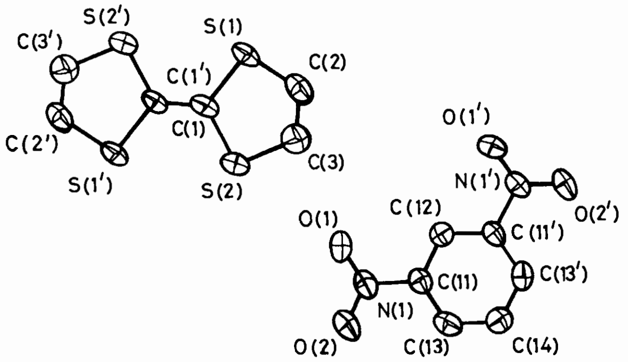

Figure 1. Atom-numbering scheme for TTF and *m*DNB molecules

The single-crystal *X*-ray structure of TTF–*m*DNB consists of mixed stacks of TTF and *m*DNB molecules arranged in alternating donor–acceptor fashion along the *a* axis (Figure 2). The TTF molecules lie on centres of symmetry, the *m*DNB molecules on two-fold axes. A projection onto the molecular plane of a TTF molecule shows that there is no face-to-face overlap between the TTF molecule and the neighbouring *m*DNB molecules. This is in marked contrast to the eclipsed donor–acceptor packing of other neutral TTF complexes in which the acceptor is of similar size to *m*-dinitrobenzene *viz.* TTF–chloranil,[8] TTF–bromanil,[8] TTF–*p*-dinitrobenzene,[9] and TTF–1,3,5-trinitrobenzene.[10] The tilt angle between the planes of the TTF and *m*DNB molecules is 8.2°. A projection along the *c* axis is shown in Figure 3. The relative molecular orientation of the component molecules in this complex accounts for the neutral, insulating properties observed in the solid-state measurements described above. All intermolecular distances in the TTF–*m*DNB complex are greater than the sum of the van der Waal's radii for the appropriate atoms. There are no close inter-stack sulphur–sulphur contacts in TTF–*m*DNB [the

---

[†] Neutral complex refers to a complex in which there is no intermolecular charge transfer, and the component molecules are present in their neutral states.

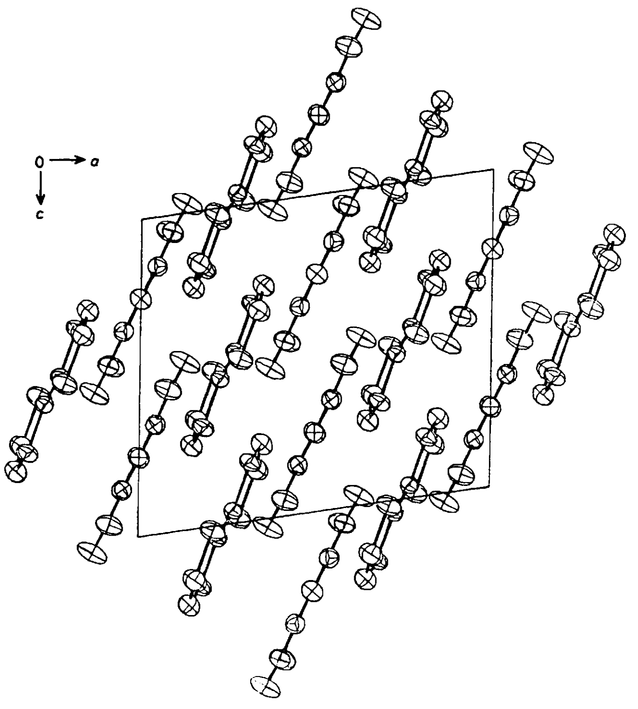

Figure 2. *X*-Ray crystal structure of TTF–*m*DNB viewed along *b* axis

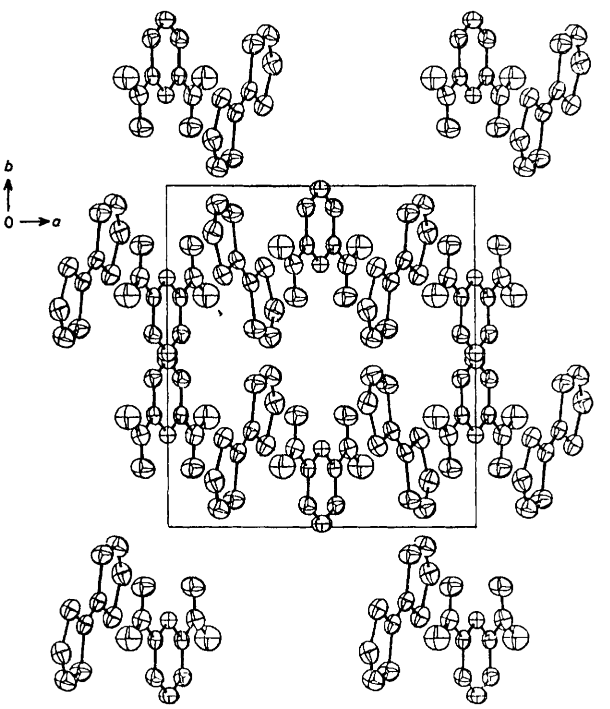

Figure 3. *X*-Ray crystal structure of TTF–*m*DNB viewed along *c* axis

minimum intermolecular non-bonded S–S distance is 3.250(5) Å]. This is noteworthy in the light of the growing number of organic conductors based on TTF derivatives that do show inter-stack sulphur–sulphur interactions.[2c–e]

Table 1. Variation in tetrathiafulvalene bond lengths with degree of charge transfer ρ

Compound	ρ	Ring C=C (Å)	Central C=C (Å)
TTF–*m*DNB	0	1.314(5)	1.342(5)
TTF	0	1.314(3)	1.349(3)
TTF–*p*DNB	0	1.317(4)	1.349(3)
TTF–chloranil	0	1.314(5)	1.354(5)
TTF–X[a]	0	1.315(4)	1.342(3)
TTF–TCNQ	0.59	1.323(3)	1.369(3)
TTF–$Cl_{0.67}$	0.67	1.32(1)	1.38(1)
TTF–$HgCl_3$	1.0	1.31(1)	1.41(1)

[a] X = Benzo[1,2-*c*:4,5-*c*′]bis[1,2,5-thiadiazole]-4,8-dione.

Table 2. Crystal data, intensity data, collection parameters, and details of refinement for TTF–*m*DNB

Chemical formula	$C_{12}H_{12}N_2O_4S_4$
M_r	376.478
Crystal system	Monoclinic
a (Å)	11.629 0(1)
b (Å)	12.674(2)
c (Å)	10.389(2)
α (°)	90
β (°)	99.27(1)
γ (°)	90
V (Å^3)	1 511.21(4)
Space group	*C*2/*c*
D_c (g cm^{-3})	1.65
Z	4
F(000)	776
Radiation	Mo-K_α, λ = 0.710 69 Å
μ (cm^{-1})	6.205
θ min./max.	1.5, 25
T	291 K
Total data measured	1 524
Total data unique	1 323
Total data observed	1 055
Significant test	$F_0 > 3\sigma(F_0)$
No. of parameters	118
Absorption correction	ψ-scan
Weighting scheme	$1/[\sigma^2(F_0) + 0.000\,049\,6F_0^2]$
Final $R = \Sigma\|\Delta F\|/\Sigma\|F_0\|$	0.0323
Final $Rg = [\Sigma w(\Delta F)^2/\Sigma w\|F_0^2\|]^{\frac{1}{2}}$	0.0343

Analysis of the bond lengths of the tetrathiafulvalene moiety in TTF complexes has been used to provide evidence for the degree of charge transfer, ρ, as neutral TTF has significantly different bond lengths from that of cationic TTF species.[11] This analysis also holds well for dibenzo-TTF complexes.[5b] However, too much emphasis should not be placed on these data as the bond lengths reported in the literature for many TTF salts have large standard deviations often resulting from partially disordered structures (*e.g.* TTF–tetrafluoro-TCNQ, ρ = 1.0).[3a] The bond lengths that appear to be sensitive to ρ are the central and, to a lesser extent, the ring C=C double bonds [*viz.* C(1)–C(1′) and C(2)–C(3), respectively, in the present structure]. Table 1 compares these lengths for TTF–*m*DNB with those of neutral TTF,[12] three neutral complexes *viz.* TTF–chloranil,[8] TTF–*p*-dinitrobenzene,[9] and TTF–benzo-[1,2-*c*:4,5-*c*′]bis[1,2,5-thiadiazole]-4,8-dione,[13] two partially ionic complexes *viz.* TTF–TCNQ (ρ = 0.59)[14] and TTF–$Cl_{0.67}$ (ρ = 0.67),[15] and one fully ionic complex *viz.* TTF–$HgCl_3$ (ρ = 1.0).[16] These data support the other solid-state data for TTF–*m*DNB and strongly suggest that TTF is present as a neutral species in the present structure.

The differences in redox potentials of the constituent molecules is known to be one of the many factors which govern the degree of charge transfer and mode of stacking for a donor–acceptor pair.[2a,8,17] Based on collated values[17,18] for oxidation potentials of a wide variety of donors and reduction potentials of a number of acceptors, the formation of a neutral complex between TTF and *m*DNB is to be expected, in line with Torrance's theories.[17] It should be emphasised that the

Table 3.

Bond lengths (Å)

C(1)–S(1)	1.759(4)	C(2)–S(1)	1.728(5)
C(1)–S(2)	1.753(4)	C(3)–S(2)	1.734(5)
C(1)–C(1a)	1.342(5)	C(3)–C(2)	1.314(5)
C(12)–C(11)	1.375(4)	C(13)–C(11)	1.374(4)
N(1)–C(11)	1.469(4)	C(14)–C(13)	1.379(4)
O(1)–N(1)	1.216(4)	O(2)–N(1)	1.224(3)

Bond angles (°)

C(2)–S(1)–C(1)	94.8(2)	C(3)–S(2)–C(1)	94.6(2)
S(2)–C(1)–S(1)	114.2(2)	C(3)–C(2)–S(1)	118.1(3)
C(2)–C(3)–S(2)	118.3(3)	C(13)–C(11)–C(12)	122.6(3)
N(1)–C(11)–C(12)	118.5(3)	N(1)–C(11)–C(13)	118.8(3)
C(11)–C(12)–C(11)	116.7(4)	C(14)–C(13)–C(11)	119.0(3)
C(13)–C(14)–C(13)	120.0(4)	O(1)–N(1)–C(11)	118.7(3)
O(2)–N(1)–C(11)	117.5(3)	O(2)–N(1)–O(1)	123.8(3)

Key to symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*); 1.5 − *x*, 0.5 − *y*, −*z*.

Table 4. Fractional atomic co-ordinates (× 10^4)

	x	*y*	*z*
S(1)	6 817(1)	2 389(1)	1 845(1)
S(2)	7 138(1)	4 191(1)	144(1)
C(1)	7 282(2)	2 827(2)	407(2)
C(2)	6 512(2)	3 638(2)	2 366(3)
C(3)	6 657(3)	4 442(3)	1 609(3)
C(11)	5 431(2)	8 269(2)	1 556(2)
C(12)	5 000	7 700(3)	2 500
C(13)	5 458(2)	9 353(2)	1 551(2)
C(14)	5 000	9 898(3)	2 500
N(1)	5 873(2)	7 694(2)	510(2)
O(1)	5 807(2)	6 736(2)	489(2)
O(2)	6 277(2)	8 215(2)	−303(2)

aromatic triazine and tetrazine acceptors referred to earlier are considerably more electron deficient than *m*DNB. However, this present study clearly emphasises that the role of crystal-packing forces in influencing the donor–acceptor overlap (or lack of it for TTF–*m*DNB) in mixed stack TTF complexes cannot be predicted. In this respect the present structure is markedly different from the isomeric TTF–*p*-dinitrobenzene complex.[9] TTF–*m*DNB is one of the first complexes formed by TTF (or a TTF derivative) with an acceptor of a similar size that does not exhibit eclipsed stacking in a projection perpendicular to the TTF plane, either with itself (segregated stack) or with the acceptor (mixed stack).

Experimental

I.r. spectra were recorded using a Perkin Elmer 577 spectrophotometer; u.v. spectra were recorded using a Varian 2300 spectrophotometer and e.s.r. spectra were obtained on a Brucker ER 200D SRC spectrometer. Conductivity measurements were obtained on three separate needles; four pressure contacts were made using silver paste and a Keithley 228 voltage/current source was used. Bulk susceptibility data were obtained using a Faraday balance.

Preparation of TTF–*m*DNB *Complex*.—A solution of TTF (80 mg, 0.39 mmol) in hot toluene (3 ml) was added to a solution of *m*DNB (66 mg, 0.39 mmol) in hot toluene (2 ml). The solution instantly turned very dark and was cooled slowly to 0 °C. The resulting black crystals were harvested, washed with cold hexane (3 ml), and dried under reduced pressure to afford 123 mg (84%) of the complex, m.p. 105—108 °C (Found: C, 38.4; H, 2.0; N, 7.3. $C_{12}H_8N_2O_4S_4$ requires C, 38.7; H, 2.2; N, 7.5%); $\nu_{max.}$(KBr) 3 077, 1 597, 1 525, 1 335, 1 252, 900, 797, 725, 707, and 662 cm^{-1}; $\lambda_{max.}$(KBr) 225, 303, 318, and 370sh nm.

Crystal Structure Determination for TTF–*m*DNB.—Data were collected on a CAD 4 diffractometer with Mo-K_α radiation following previously detailed procedures.[19] Crystal data and experimental parameters are summarised in Table 2. Bond lengths and angles are given in Table 3. Fractional atomic co-ordinates for all atoms are given in Table 4. The structure was solved by direct methods (SHELX 86)[20] and developed and refined using standard Fourier and least-squares procedures (SHELX 80).[21] Non-hydrogen atoms were refined anisotropically, hydrogens isotropically.*

Acknowledgements

We thank S.E.R.C. for the award of a studentship to S. R. D. and for support of the crystallographic work.

References

1 J. Ferraris, D. O. Cowan, V. V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948.

2 For reviews and monographs see: (*a*) J. B. Torrance, *Acc. Chem. Res.*, 1979, **12**, 79; (*b*) J. S. Miller (ed.), 'Extended Linear Chain Compounds,' vol. 1—3, Plenum, New York, 1982—1983; (*c*) M. R. Bryce and L. C. Murphy, *Nature*, 1984, **309**, 119; (*d*) F. Wudl, *Acc. Chem. Res.*, 1984, **17**, 227; (*e*) 'Proceedings of the International Conference on Synthetic Metals,' Kyoto, published in *Synth. Met.*, 1987, vol. 19; (*f*) D. O. Cowan and F. M. Wiygul, *Chem. Eng. News*, 1986, July 21, 28.

3 (*a*) F. M. Wiygul, T. J. Emge, and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, 1982, **90**, 163; (*b*) F. M. Wiygul, R. M. Metzger and T. J. Kistenmacher, *ibid.*, 1984, **107**, 115.

4 J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, *Phys. Rev. Lett.*, 1981, **46**, 253; A. Girlando, C. Pecile, A. Brillante, and K. Syassen, *Solid State Commun.*, 1986, **57**, 891; T. Mitani, Y. Tokura, Y. Kaneko, K. Takaoka, T. Koda, and G. Saito, *Synth. Met.*, 1987, **19**, 515.

5 (*a*) T. J. Kistenmacher, T. J. Emge, F. M. Wiygul, W. A. Bryden, J. S. Chappell, J. P. Stokes, L.-Y. Chiang, D. O. Cowan, and A. N. Bloch, *Solid State Commun.*, 1981, **39**, 415; (*b*) T. J. Emge, F. M. Wiygul, J. S. Chappel, A. N. Bloch, J. P. Ferraris, D. O. Cowan, and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, 1982, **87**, 137.

6 A. Berlin, G. A. Pagani, and F. Sannicolo, *J. Chem. Soc., Chem. Commun.*, 1986, 1579; *Synth. Met.*, 1987, **19**, 415.

7 J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, *Phys. Rev. B*, 1979, **19**, 730.

8 J. J. Meyerle, J. B. Torrance, and J. I. Crowley, *Acta Crystallogr. Sect. B*, 1979, **35**, 2988.

9 M. R. Bryce, A. S. Secco, J. Trotter, and L. Weiler, *Can. J. Chem.*, 1982, **60**, 2057.

10 M. R. Bryce, S. R. Davies, J. A. K. Howard, and O. Johnson, unpublished work.

11 T. J. Emge, F. M. Wiygul, J. S. Chappel, A. N. Bloch, J. P. Ferraris, D. O. Cowan, and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, 1982, **87**, 137 and references therein.

12 W. F. Cooper, N. C. Kenny, J. W. Edmonds, A. Nagel, F. Wudl, and P. Coppens, *Cryst. Struct. Commun.*, 1974, **3**, 23.

13 A. Gieren, V. Lamm, T. Huber, M. Rabben, R. Neidlein, and D. Droste, *Chem. Ber.*, 1984, **117**, 1940.

14 T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr. Sect. B*, 1974, **30**, 763.

15 T. J. Kistenmacher, Modulated Structures, A.I.P. Conference Proceedings, 1979, **53**, 193.

---

* Supplementary data (see section 5.6.3. of Instructions for Authors, in the January issue). Hydrogen-atom co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

16 T. J. Kistenmacher, M. Rossi, C. C. Chiang, R. P. Van Duyne, T. Cape, and A. R. Siedle, *J. Am. Chem. Soc.*, 1978, **100**, 1958.
17 J. B. Torrance, *Mol. Cryst. Liq. Cryst.*, 1985, **126**, 55.
18 E. C. M. Chen and W. E. Wentworth, *J. Chem. Phys.*, 1975, **63**, 3183.
19 R. A. Jones, K. M. A. Malik, M. B. Hursthouse, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.
20 SHELX 86. Programme for Crystal Structure Solution, G. M. Sheldrick, University of Gottingen, 1986.
21 SHELX 80. Enlarged version of SHELX 76, Programme for Crystallographic Calculations, G. M. Sheldrick, University of Cambridge, 1976.

Received 13*th November* 1987; *Paper* 7/2016