4-(*N*-Methylthioamido)tetrathiafulvalene: A New *Kappa*-Phase Structure

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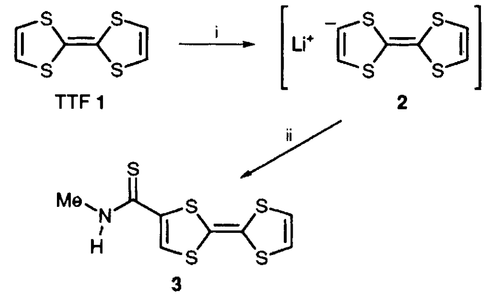
Tetrathiafulvalenyllithium reacts with *N*-methylisothiocyanate to afford the title compound **3**, which is the first example of a neutral tetrathiafulvalene derivative to form a *kappa*-phase structure.

In the development of new conducting and superconducting organic cation radical salts, derivatives of the π-electron donor tetrathiafulvalene (TTF) are of paramount importance, with particular attention focusing on *kappa*-phase crystal structures.[1] The key feature of the *kappa* phase is that the π-donor forms orthogonal dimers which are coupled through weak intermolecular forces, such as van der Waals interactions and close non-bonded chalcogen···chalcogen interactions. There are currently no guidelines to suggest which characteristics of the donor molecule may induce the formation of a κ-structure. This structural motif is very rare: it is restricted to a few salts of the centrosymmetric donors bis(ethylenedithio)-TTF[2] and bis(methylenedithio)-TTF,[3] and the non-centrosymmetric donors methylenedithio-TTF,[4] (*S*,*S*)-dimethyl-bis(ethylenedithio)-TTF[5] and 4-(hydroxymethyl)-4′,5′-ethylenedithio-TTF,[6] and it is formed only with specific counteranions in each case. It is noteworthy that all the fulvalene-based superconductors with T_c values > 10 K possess κ-phase structures, *e.g.* κ-(BEDT–TTF)$_2$Cu[N(CN)$_2$]Cl.[2]

In this communication we report the synthesis and X-ray crystal structure of 4-(*N*-methylthioamido)tetrathiafulvalene **3**; this is the first example of a κ-phase structure in a neutral TTF derivative.

Tetrathiafulvalenyllithium **2** was generated from TTF **1**, using lithium diisopropylamide in dry diethyl ether at −78 °C, as reported previously.[7] Anion **2** was trapped with *N*-methylisothiocyanate to afford compound **3**, m.p. 188–190 °C, in 50% yield (Scheme 1). Dark-purple plates of **3** were obtained by recrystallisation from dichloromethane–hexane.

Cyclic voltammetric data establish that both the first and second solution ionisation potentials of donor **3** are higher than those of TTF **1** measured under identical conditions:† donor **3** $E_1^{1/2} = 0.43$, $E_2^{1/2} = 0.98$ V (*cf.* TTF **1** 0.34, 0.71 V). This result is consistent with the presence of the electron-withdrawing thioamide substituent.



Scheme 1 *Reagents and conditions*: i, lithium diisopropylamide, dry diethyl ether, −78 °C; ii, MeN=C=S, dry diethyl ether, −78 → 20 °C, then aqueous workup

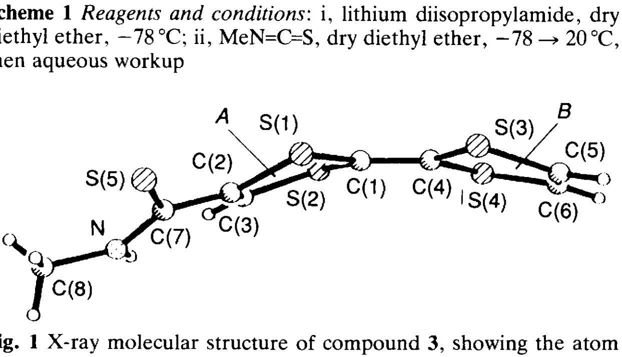


Fig. 1 X-ray molecular structure of compound **3**, showing the atom numbering scheme

The X-ray crystal structure of compound **3** is shown in Fig. 1.‡ Inversionally-related molecules form dimers with ring-over-bonds overlap of the TTF moieties (Fig. 2). The interplanar separation between the central C_2S_4 moieties is 3.40 Å, while the rest of the molecule bends outwards with rings A and B folding along S···S lines by 22.8 and 13.9°, respectively. The thioamide group is conjugated with ring A of the TTF system [the twist around the C(2)–C(7) bond is 12°]. Dimers of **3** are packed in *kappa* fashion with the mean planes of contacting molecules being almost perpendicular and their principle axis essentially parallel (Fig. 3). The shortest S···S distances are approximately equal to double the isotropic van der Waal's radius of sulfur (1.80 Å):[8] S···S contacts form a two-dimensional network linking the dimers into a layer parallel to the (011) plane while it is the N–H(1)···S(5) hydrogen bonds (N···S distance 3.56 Å; H···S distance 2.92 Å) which link molecules into an infinite array parallel to the *z* axis.

Hydrogen-bonding involving (O-H)$_{\mathrm{water}}$···X$_{\mathrm{anion}}$ has been observed in a few conducting and superconducting salts of TTF derivatives, *e.g.* (BEDT–TTF)$_3$Cl$_2$·2H$_2$O,[9] and (BEDO–TTF)$_2$ReO$_4$·H$_2$O,[10] and (O–H)$_{\mathrm{donor}}$···X$_{\mathrm{anion}}$ interactions are present in κ-(EDT–TTFCH$_2$OH)$_2$X salts (X = ClO$_4$ and ReO$_4$).[6] It is also considered that (C–H)$_{\mathrm{donor}}$···anion interactions play an important part in determining the structure of BEDT–TTF cation radical salts.[11] However, the potential role of donor···donor hydrogen bonds in regulating the solid state structures of TTF systems is entirely unexplored.[12] The title compound **3** provides the first example of donor···donor H-bonding in a TTF system to be revealed by X-ray analysis,

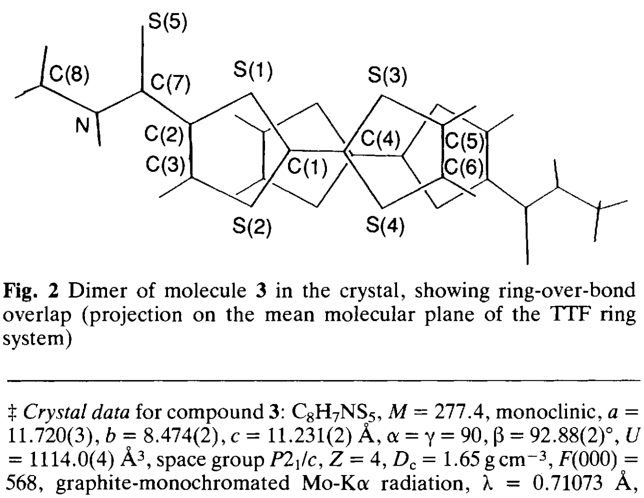


Fig. 2 Dimer of molecule **3** in the crystal, showing ring-over-bond overlap (projection on the mean molecular plane of the TTF ring system)

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† Donor 1 × 10^{-5} mol dm^{-3} solution in dry dichloromethane, electrolyte Bu$_4$N$^+$ ClO$_4^-$ (0.01 mol dm^{-3}), under nitrogen, 20 °C, *vs.* Ag/AgCl, Pt electrode, scan rate 100 mVs^{-1}.

‡ *Crystal data* for compound **3**: $C_8H_7NS_5$, $M = 277.4$, monoclinic, $a = 11.720(3)$, $b = 8.474(2)$, $c = 11.231(2)$ Å, $\alpha = \gamma = 90$, $\beta = 92.88(2)°$, $U = 1114.0(4)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.65$ g cm^{-3}, $F(000) = 568$, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 0.997$ mm^{-1}.

The intensities of 2084 independent reflections with 2θ range 3.0–53.0° were measured on a Siemens R3m/V diffractometer at 20 °C by Wyckoff (limited ω) scan technique of which 1264 reflections were used in calculations, performed with SHELXTPLUS programmes.[13] The structure was solved by direct methods. The refinement of 131 parameters converged at $R = 0.0330$, $R_w = 0.0339$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. (See Notice to Authors, Issue No. 1).

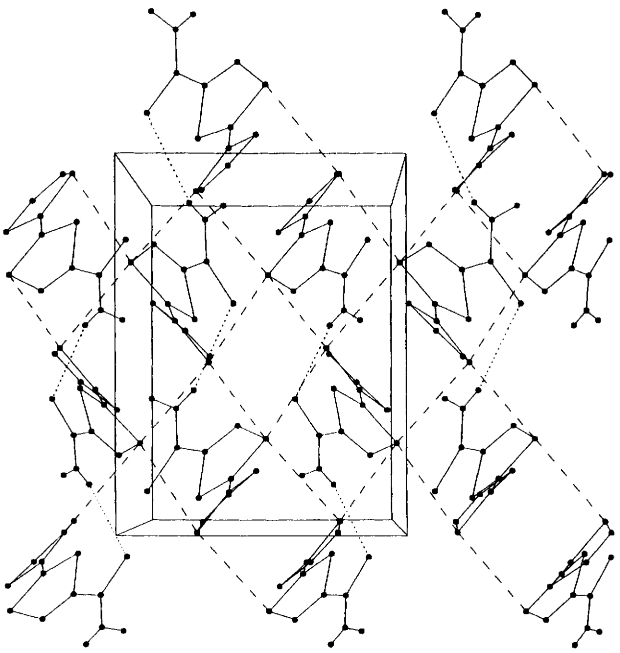

Fig. 3 Crystal packing of compound **3**: projection along plane (100). Intermolecular sulfur...sulfur contacts < 3.60 Å are shown by dashed lines; intermolecular hydrogen bonds are shown by dotted lines

and this may prove to be an important structural feature in the design of new *kappa* phase systems.

Compound **3** forms a 1:1 complex with TCNQ (as judged by C,H,N combustion analysis) isolated as a black powder (50% yield) by cooling an acetonitrile solution containing donor **3** and TCNQ mixed in either a 1:1 or 1:2 ratio. The conductivity of the complex, **3**–TCNQ, is 1.2 S cm^{-1} (two-probe, compressed pellet measurement).[14] Evidence for partial charge-transfer within the complex is provided by the IR spectrum (ν_{max}/cm^{-1} C≡N 2200).[15]

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References

1 Reviews: (*a*) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M-H. Whangbo, *Organic Superconductors (Including Fullerenes)*, Prentice Hall, New Jersey, 1992; (*b*) M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355; (*c*) G. Saito, *Phosphorus, Sulfur & Silicon*, 1992, **67**, 345; (*d*) T. Ishiguro and K. Yamaji, *Organic Superconductors*, Springer-Verlag, Berlin, 1989.

2 J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Strieby Crough, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung and M.-H. Wangbo, *Inorg. Chem.*, 1990, **29**, 3262.

3 P. J. Nigrey, B. Morosin, J. F. Kwak, E. L. Venturini and R. J. Baughman, *Synth. Metals*, 1986, **16**, 1.

4 G. C. Papavassiliou, G. A. Mousdis, J. S. Zambounis, A. Terzis, S. Hountas, B. Hilti, C. W. Mayer and J. Pfeiffer, *Synth. Metals.*, 1988, **27**, B379.

5 J. S. Zambounis, C. W. Mayer, K. Hauenstein, B. Hilti, W. Hofherr, J. Pfeiffer, M. Bürkle and G. Rihs, *Adv. Mater.*, 1992, **4**, 33.

6 P. Blanchard, K. Boubekeur, M. Sallé, G. Duguay, M. Jubault, A. Gorgues, J. D. Martin, E. Canadell, P. Auban-Senzier, D. Jérome and P. Batail, *Adv. Mater.*, 1992, **4**, 579.

7 D. C. Green, *J. Org. Chem.*, 1979, **44**, 1476.

8 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441. In the ellipsoidal model the values are 1.60 and 2.03 Å, along the bond direction and perpendicular to the bond axis, respectively: S. Nyburg and C. Faerman, *Acta. Crystallogr., Sect. B*, 1985, **41**, 274.

9 M. J. Rosseinsky, M. Kurmoo, D. R. Talham, P. Day, D. Chasseau and D. Watkin, *J. Chem. Soc., Chem. Commun.*, 1988, 88.

10 S. Kahlich, D. Schweitzer, I. Heinen, S. E. Lan, B. Nuber, H. J. Keller, K. Winzer and H. W. Helberg, *Solid State Commun.*, 1991, **80**, 195.

11 (*a*) M.-H. Whangbo, D. Jung, J. Ren, M. Evain, J. J. Novoa, F. Mota, S. Alvarez, J. M. Williams, M. A. Beno, A. M. Kini, H. H. Wang and J. R. Ferraro, in *The Physics and Chemistry of Organic Superconductors*, ed. G. Saito and S. Kagoshima, Springer-Verlag, Berlin, 1990, 262; (*b*) A. Pénicaud, K. Boubekeur, P. Batail, E. Canadell, P. Auban-Senzier and D. Jérome, *J. Am. Chem. Soc.*, 1993, **115**, 4101.

12 For a recent account of structural control in a range of organic solids by hydrogen-bonding, see M. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.

13 SHELXTLPLUS, G. M. Sheldrick, Göttingen and Siemens PLC, 1990.

14 F. Wudl and M. R. Bryce, *J. Chem. Educ.*, 1990, **67**, 717.

15 J. S. Chappel, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Amer. Chem. Soc.*, 1981, **103**, 2442.