

A neutral complex of an azino-DTDAF compound with TCNQ

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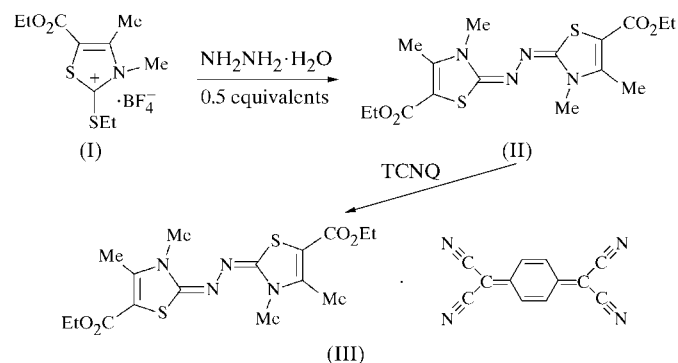
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In the crystal structure of the title 1:1 complex, ethyl 2-[[5-(ethoxycarbonyl)-2,3-dihydro-3,4-dimethyl-1,3-thiazol-2-ylidene]hydrazono]-2,3-dihydro-3,4-dimethyl-1,3-thiazole-5-carboxylate-7,7,8,8-tetracyano-*p*-quinodimethane (1/1), $C_{16}H_{22}N_4O_4S_2 \cdot C_{12}H_4N_4$, the planar donor and tetracyano-*p*-quinodimethane (TCNQ) molecules are each located on inversion centres and are stacked alternately. The bond lengths indicate that, in this complex, the donor and acceptor are neutral, as confirmed by IR investigation.

Comment

Extended dithiadiazafulvalenes (DTDAF) which possess an azino spacer group between the two thiazole rings are inter-

esting candidates for the synthesis of molecular materials (Barlow *et al.*, 1976). Indeed, the insertion of an azino spacer group induces a wider difference between the two oxidation potentials of the donor than for DTDAF alone (Hünig *et al.*, 1974). Therefore, the window of potential stability of the cation radical species is increased. In the course of our study on azino-DTDAF compounds and their ability to form complexes with various organic acceptors, we prepared the title complex, (III).



The azino-DTDAF derivative (II) was prepared using thiazolium salt (I) as the starting material (Bellec *et al.*, 1999). This salt reacts in a basic medium with hydrazine monohydrate to afford (II). The strategy used is outlined in the Scheme above (Hünig *et al.*, 1964). The title complex, (III), was obtained by mixing a solution of donor (II) with a solution of TCNQ.

The crystal structure determination of (III) reveals a stoichiometry of one donor molecule per TCNQ molecule (Fig. 1). Both molecules possess crystallographic C_i symmetry. The

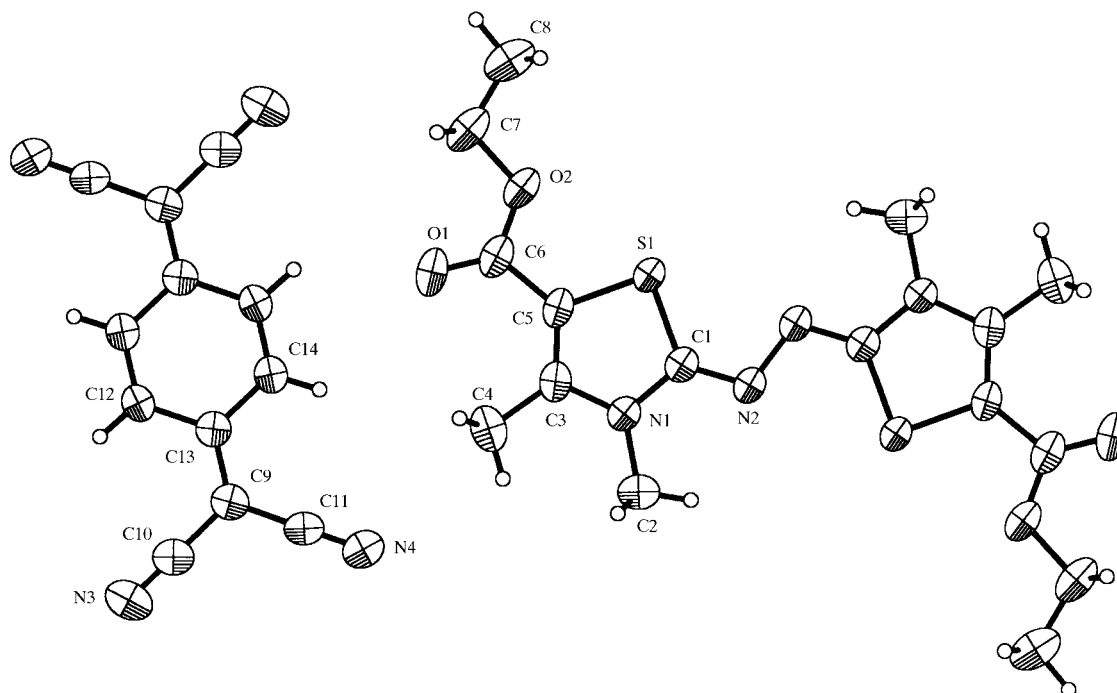


Figure 1

A view of (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as small spheres of arbitrary radii.

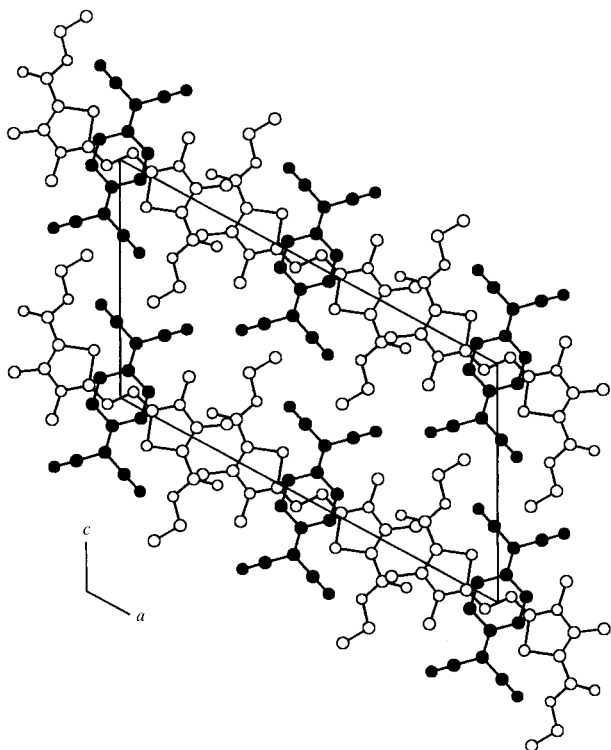


Figure 2
The crystal packing of (III) viewed along the *b* axis. H atoms have been omitted for clarity.

planar donor and TCNQ molecules form infinite alternating stacks along the *b* axis, wherein the planes of the donor and acceptor are parallel, with an interplanar separation of $\frac{b}{2}$ (3.41 Å; Fig. 2). Interestingly, within the stacks, the long axis of the TCNQ molecule is perpendicular to that of the donor.

No short intermolecular contacts are observed either within or between the stacks. The bond distances of TCNQ in (III) are essentially the same as in crystals of pure TCNQ (Long *et al.*, 1965).

Using the empirical formula of Kistenmacher (Kistenmacher *et al.*, 1982), which correlates bond lengths with the formal charge of the TCNQ in various charge-transfer salts, we found no charge transfer on TCNQ in (III). Therefore, complex (III) is neutral. This was confirmed by the nitrile stretching absorption band in the FT-IR spectra ($\nu_{\text{CN}} = 2218 \text{ cm}^{-1}$), which is close to the value for neutral TCNQ ($\nu_{\text{CN}} = 2224 \text{ cm}^{-1}$). This neutral complex finds its origin in the difference between the redox potential of the donor and the acceptor. Indeed, the azino-DTDAF derivative (II) oxidizes at $E_1 = 0.48 \text{ V}$, far above the reduction potential of TCNQ ($E_1 = 0.20 \text{ V}$ versus a saturated calomel electrode).

Experimental

The synthesis of (II) was carried out according to the method of Hünig *et al.* (1964). To a solution of 5-(ethoxycarbonyl)-2-(ethylthio)-3,4-dimethyl-1,3-thiazolium tetrafluoroborate, (I) (1.00 g, 3 mmol), in acetonitrile (5 ml) and ethanol (5 ml), hydrazine hydrate (0.073 ml, 1.5 mmol) and triethylamine (0.84 ml, 6 mmol) were added. The

mixture was stirred under an inert atmosphere at room temperature for 1 h. The yellow precipitate which formed was filtered off, washed with ethanol and recrystallized from acetonitrile to give donor (II) in 70% yield (m.p. 535 K). Spectroscopic analysis, ^1H NMR (200 MHz, CDCl_3 , δ , p.p.m.): 1.33 (*t*, 6H), 2.53 (*s*, 6H), 3.40 (*s*, 6H), 4.25 (*q*, 4H); elemental analysis (%), found (calculated): C 48.30 (48.23), H 5.57 (5.56), N 14.09 (14.06), S 16.21 (16.09). Cyclic voltammetry measurements were carried out in Bu_4NPF_6 as the supporting electrolyte at room temperature in CH_2Cl_2 versus a saturated calomel electrode. The title complex was prepared by mixing a hot acetonitrile solution of TCNQ (0.042 g, 0.2 mmol) with a hot dichloromethane solution of (II) (0.04 g, 0.1 mmol). Dark purple crystals of (III), suitable for X-ray diffraction studies, were obtained by slow evaporation of the solution at room temperature.

Crystal data

$\text{C}_{16}\text{H}_{22}\text{N}_4\text{O}_4\text{S}_2 \cdot \text{C}_{12}\text{H}_4\text{N}_4$
 $M_r = 602.70$
Monoclinic, $C2/m$
 $a = 20.960$ (4) Å
 $b = 6.8198$ (14) Å
 $c = 11.730$ (2) Å
 $\beta = 118.67$ (3)°
 $V = 1471.2$ (5) Å³
 $Z = 2$

$D_x = 1.361 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4723 reflections
 $\theta = 2.1\text{--}25.9^\circ$
 $\mu = 0.23 \text{ mm}^{-1}$
 $T = 293$ (2) K
Parallelepiped, dark purple
 $0.3 \times 0.3 \times 0.3 \text{ mm}$

Data collection

Stoe IPDS area-detector diffractometer
Rotation scans, ϕ increment 2°
7171 measured reflections
1526 independent reflections
1135 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 26.1^\circ$
 $h = -25 \rightarrow 25$
 $k = -7 \rightarrow 7$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.108$
 $S = 0.97$
1526 reflections
128 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.073P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.039 (5)

Table 1

Selected interatomic distances (Å).

S1—C1	1.746 (2)	N3—C10	1.133 (4)
S1—C5	1.760 (3)	N4—C11	1.142 (4)
N1—C3	1.378 (3)	C9—C13	1.367 (4)
N1—C1	1.383 (3)	C9—C11	1.433 (4)
N1—C2	1.457 (4)	C9—C10	1.443 (4)
N2—C1	1.289 (3)	C12—C14	1.332 (4)
N2—N2 ⁱ	1.410 (5)	C12—C13	1.448 (4)
C3—C5	1.349 (4)	C13—C14 ⁱⁱ	1.446 (4)

Symmetry codes: (i) $2 - x, -y, -z$; (ii) $1 - x, -y, -z$.

H atoms were introduced at calculated positions, with C—H = 0.93–0.97 Å, included in the structure-factor calculations and refined using a riding model.

Data collection: *EXPOSE* in *IPDS* (Stoe, 1999); cell refinement: *SELECT* and *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1545). Services for accessing these data are described at the back of the journal.

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