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Cocrystals of 2-(2,4,5,7-tetranitrofluoren-9-ylidene)propanedinitrile and 2,4,5,7-tetranitrofluoren-9-one with chlorobenzene

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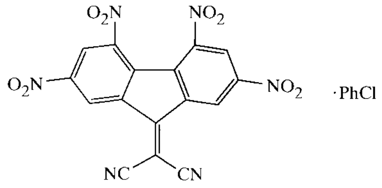
Crystallization of 2,4,5,7-tetranitro-9-(dicyanomethylene)-fluorene [DTeF; systematic name: 2-(2,4,5,7-tetranitro-fluorene-9-ylidene)propanedinitrile] and 2,4,5,7-tetranitro-fluoren-9-one (TeNF) from chlorobenzene in the presence of π-donor compounds yielded the chlorobenzene solvate, $C_{16}H_4N_6O_8 \cdot C_6H_5Cl$, and the bis(chlorobenzene) solvate, $C_{13}H_4N_4O_9 \cdot 2C_6H_5Cl$, respectively. Both structures comprise mixed stacks of twisted fluorene moieties interspersed with nearly parallel chlorobenzene molecules. Solvent-free crystals of DTeF and TeNF were obtained from pure chlorobenzene.

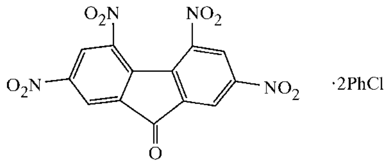
Comment

2,4,5,7-Tetranitro-9-(dicyanomethylene)fluorene (DTeF) and 2,4,5,7-tetranitrofluoren-9-one (TeNF) are strong electron acceptors with potentially useful photoelectronic properties (Pravednikov *et al.*, 1978). They readily form charge-transfer (CT) complexes with donor molecules (Brown *et al.*, 1974; Grigg *et al.*, 1978; Baldwin & Baughman, 1993; Shah & Baughman, 1994), particularly with tetrathiafulvalene (TTF) and its derivatives (Soriano-García *et al.*, 1989; Perepichka *et al.*, 1998, 2000; Bryce, Moore *et al.*, 1999; Batsanov *et al.*, 2001). CT complexes of DTeF and TeNF with bis(ethylenedioxy)-tetrathiafulvalene (BEDO-TTF) have interesting electric properties, *i.e.* (TeNF)(BEDO-TTF) is a semiconductor, while $(DTeF)(BEDO\text{-}TTF)_2$ shows metallic conductivity (Horiuchi *et al.*, 1996).

In a search for new CT complexes, we attempted to cocrystallize DTeF with the π-donor compounds 4-iodo-4′,5,5′-trimethyltetrathiafulvalene, (III) (John *et al.*, 1998), or 8,9-bis(methylsulfanyl)acenaphtho[1,2-*b*][1,4]dithiine, (IV) (Bryce, Lay *et al.*, 1999), and TeNF with *N*,*N*-dimethylaminoferrocene, (V), from chlorobenzene solutions. Unexpectedly, we obtained instead the chlorobenzene solvates, DTeF·PhCl, (I), and TeNF·2PhCl, (II), respectively. Even more surprisingly, crystallization of the same acceptor compounds from pure chlorobenzene gave only the previously known solvent-free phases of DTeF (Silverman *et al.*, 1974) or TeNF (Chetkina *et al.*, 1987; Baughman, 1987). Thus, the presence of compounds (III)–(V) in solution affects the composition of the growing crystal without these compounds themselves being incorporated into the structure. Although, at present, we have no evidence of how general this effect is or of its possible mechanism, it certainly deserves attention. A plausible explanation (which, of course, requires much more experimental data to be proven) is that complexes between the electron donor (DTeF or TeNF) and acceptor [(III)–(V)] molecules exist in solution and, due to CT, these are solvated more strongly than the isolated acceptor molecules. However, the CT complexes themselves are highly soluble and are not precipitated under these conditions. On cooling or on slow evaporation, the acceptor component of the CT complex starts to crystallize first, but due to the strong association between this component and the chlorobenzene solvent, desolvation does not occur and the mixed stack of acceptor molecules and solvent is formed. Obviously, this effect cannot be observed if the CT complex has low solubility and crystallizes first.



(I)



(II)

Complexes (I) and (II) do not exhibit CT bands in their UV–visible spectra and can be described as host–guest complexes of neutral molecules, in agreement with the structural data (see below). The DTeF molecule in (I) (Fig. 1) has essentially the same geometry as in the solvent-free phase studied at room temperature, apart from the usual systematic errors caused by thermal libration in the latter (*i.e.* a shortening of most bonds by 0.01–0.02 Å).

In (I), the longest bonds in the benzene rings are the fused ones, C10—C11 and C12—C13, while the opposing C2—C3 and C6—C7 bonds are the shortest [average 1.418 (2) *versus* 1.382 (2) Å], as shown in Table 1. A similar relationship was observed in pure TeNF [1.41 (1) *versus* 1.36 (1) Å], although the effect was somewhat exaggerated by thermal motion. Aromatic π delocalization is largely confined to the benzene rings. The C11—C12 bond linking the rings remains essentially single at 1.482 (2) Å, compared with the standard single $C_{arene}—C_{arene}$ bond of 1.490 Å (Allen *et al.*, 1987). The

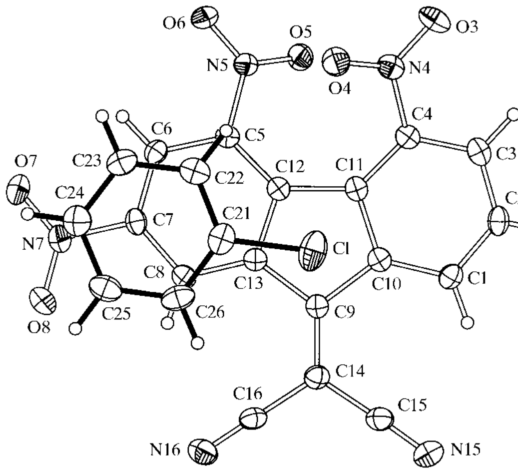


Figure 1
The asymmetric unit of (I), viewed as a parallel projection on the fluorene mean plane. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

exocyclic C9═C14 bond of 1.357 (2) Å is longer than the standard double bond of 1.331 Å (Allen *et al.*, 1987) due to π conjugation with the cyano groups, while the C9—C10 and C9—C13 bond distances [average 1.481 (2) Å] reveal the absence of conjugation between C9═C14 and the benzene rings. Note that the accumulation of negative charge on DTeF should result in the five-membered ring acquiring aromatic character.

The fluorene system of (I) has a twisted conformation, caused by steric crowding between the nitro groups in the 4- and 5-positions. These groups tilt out of the fluorene plane in opposite directions, dragging with them the adjacent parts of the fluorene moiety, especially atoms C4 and C5. Thus, atoms C1, C2, C7, C8, C9, C10, C12, C13, C14, C16 and N16 lie in one plane (plane *A*) to within ±0.03 Å. The deviations of other atoms from this plane are: C3 0.22, C4 0.32, C5 −0.26, C6 −0.20, C11 0.10, C15 −0.11 and N15 −0.21 Å. The torsion angles around the C4—N4 and C5—N5 bonds [22.6 (1) and 28.3 (1)°, respectively] are larger than those around the C2—N2 and C7—N7 bonds [15.1 (1) and 7.4 (1)°, respectively], and the C4—N4 and C5—N5 bonds are tilted out of the sp^2 planes of C4 and C5 by 4.4 (1) and 8.1 (1)°, respectively, which also reveals the steric strain.

The DTeF and chlorobenzene molecules in (I) form an infinite mixed stack (Fig. 2), wherein the planes of the benzene rings and the fluorene plane *A* are parallel to within 1°, with uniform interplanar separations of *ca* 3.36 Å. The Cl atom is situated over the centre of the five-membered fluorene ring and the resulting Cl···C distances range from 3.464 (3) to 3.623 (3) Å. The stacks pack in a herring-bone motif, stabilized by interstack non-valent interactions; Cl···O7($x, \frac{1}{2}-y, \frac{1}{2}+z$) 3.077 (2) Å and O2···N5($x, -\frac{1}{2}-y, \frac{1}{2}+z$) 2.912 (2) Å, *cf.* the standard van der Waals contacts Cl···O of 3.33 and O···N of 3.28 Å (Rowland & Taylor, 1996).

In structure (II) (Fig. 3), the bond geometry of the TeNF molecule is in good agreement with the results of the two independent room-temperature studies of pure TeNF (Chetkina *et al.*, 1987; Baughman, 1987). The five-membered ring of TeNF displays even less π conjugation than in DTeF, with essentially single bonds at C11—C12 [1.502 (9) Å], and C9—C10 and C9—C13 [average 1.51 (1) Å]. The twist of the fluorene moiety is similar to that in DTeF; in (II), the average deviation of the 13 fluorene C atoms from their mean plane is 0.110 Å, and the maximum deviations are 0.17 (C4) and −0.22 Å (C5), compared with values of 0.115, 0.23 and −0.20 Å, respectively, in (I). Unlike DTeF, TeNF contains no extensive planar fragment. The torsion angles around the C2—N2, C4—N4, C5—N5 and C7—N7 bonds of 9.2 (2), 29.8 (2), 35.6 (2) and 3.1 (2)°, respectively, reflect steric crowding between the 4- and 5-nitro groups and the absence of strain elsewhere.

The structure of (II) also comprises infinite mixed stacks, parallel to the *a* axis, wherein TeNF molecules are interspersed with pairs of chlorobenzene molecules (Fig. 4). The latter are inclined by 17.2 (2) and 8.5 (1)° to the mean fluorene plane

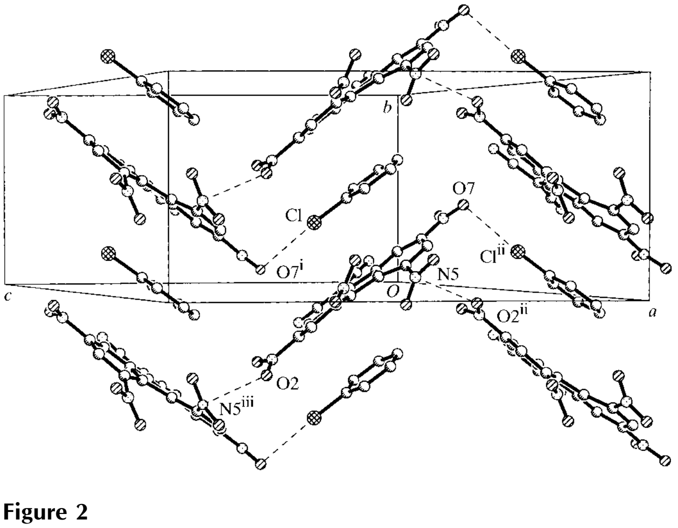


Figure 2
The crystal packing of (I), showing the short intermolecular contacts [symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$].

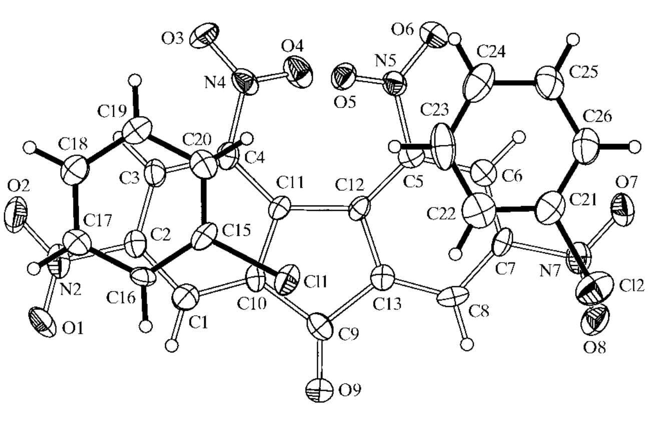


Figure 3
The asymmetric unit of (II), viewed as a parallel projection on the fluorene mean plane. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

and by 17.6 (2)° to each other. Hence, the interplanar separations are wider than in (I) by *ca* 0.1 Å. Unlike (I), the molecular planes of adjacent stacks in (II) are nearly parallel.

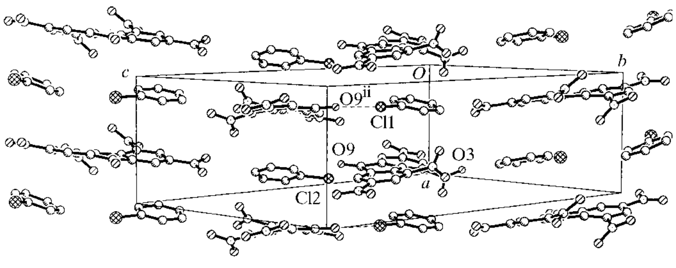


Figure 4
The crystal packing of (II), showing the short intermolecular contacts [symmetry code: (ii) $x - 1, -\frac{1}{2} - y, \frac{1}{2} + z$].

The interstack contacts Cl1···O9($x - 1, -\frac{1}{2} - y, \frac{1}{2} + z$) [3.198 (7) Å] and Cl2···O3($1 - x, 1 - y, -z$) [3.118 (8) Å] are shorter than the normal van der Waals contact of 3.33 Å (Rowland & Taylor, 1996).

Experimental

For the preparation of (I), DTeF (5.6 mg, 0.014 mmol) was dissolved in hot chlorobenzene (3.0 ml), compound (III) (10.4 mg, 0.028 mmol) added and the solution left to cool slowly to room temperature, affording fine yellow crystals of solvate (I). Repeating the procedure, scaled up fivefold, gave identical crystals. Analysis calculated for $C_{22}H_9ClN_6O_8$: C 50.74, H 1.74, Cl 6.81, N 16.14%; found: C 50.42, H 1.85, Cl 6.95, N 16.07%. By a different route, using an alternative π-donor compound, DTeF (7.0 mg, 0.017 mmol) was dissolved in hot chlorobenzene (7.0 ml), compound (IV) (5.9 mg, 0.018 mmol) added and the solution allowed to cool to room temperature before being left to evaporate slowly for several days, again yielding crystals of (I). For the preparation of (II), TeNF (10.0 mg, 0.028 mmol) was dissolved in hot chlorobenzene (8.0 ml), compound (V) (20.0 mg, 0.082 mmol) added and the solution left at room temperature to evaporate slowly for two weeks, whereupon crystals of solvate (II) were formed, but only in small amounts and insufficient for elemental analysis. Control experiments were carried out as follows: DTeF (6.0 mg) was dissolved in hot chlorobenzene (2.5, 3.5 and 5.0 ml were used in three runs) and crystallized by slow evaporation. X-ray determination of the unit cell identified the crystals as solvent-free DTeF (Silverman *et al.*, 1974). The same procedure was repeated with TeNF.

Compound (I)

Crystal data

$C_{16}H_4N_6O_8 \cdot C_6H_5Cl$
$M_r = 520.80$
Monoclinic, $P2_1/c$
$a = 16.823$ (2) Å
$b = 8.360$ (6) Å
$c = 17.461$ (3) Å
$\beta = 118.33$ (1)°
$V = 2161.6$ (16) Å^3
$Z = 4$
$D_x = 1.600$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 512 reflections
$\theta = 12$–20°
$\mu = 0.24$ mm^{-1}
$T = 150$ (2) K
Prism, yellow
0.28 × 0.22 × 0.18 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
ω scans
22 991 measured reflections
4962 independent reflections
4169 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\rm max} = 27.5°$
$h = -21 \rightarrow 20$
$k = -10 \rightarrow 10$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.092$
$S = 1.10$
4962 reflections
370 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 1.4795P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C1—C2	1.391 (2)	C8—C13	1.393 (2)
C1—C10	1.393 (2)	C9—C10	1.480 (2)
C2—C3	1.378 (2)	C9—C13	1.481 (2)
C2—N2	1.477 (2)	C9—C14	1.357 (2)
C3—C4	1.389 (2)	C10—C11	1.419 (2)
C4—N4	1.478 (2)	C11—C12	1.482 (2)
C4—C11	1.395 (2)	C12—C13	1.417 (2)
C5—C6	1.387 (2)	C14—C15	1.444 (2)
C5—C12	1.398 (2)	C14—C16	1.446 (2)
C5—N5	1.4730 (19)	C15—N15	1.147 (2)
C6—C7	1.386 (2)	C16—N16	1.147 (2)
C7—N7	1.481 (2)	Cl—C21	1.7508 (18)
C7—C8	1.386 (2)		
C3—C4—N4	115.93 (14)	C12—C5—N5	122.00 (13)
C11—C4—N4	122.00 (14)	C6—C5—C12	121.71 (14)
C3—C4—C11	121.43 (15)	C22—C21—C26	122.09 (16)
C6—C5—N5	115.98 (13)		

Compound (II)

Crystal data

$C_{13}H_4N_4O_9 \cdot 2C_6H_5Cl$
$M_r = 585.30$
Orthorhombic, $P2_12_12_1$
$a = 6.984$ (1) Å
$b = 15.088$ (2) Å
$c = 23.217$ (2) Å
$V = 2446.5$ (5) Å^3
$Z = 4$
$D_x = 1.589$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 266 reflections
$\theta = 10$–18°
$\mu = 0.33$ mm^{-1}
$T = 150$ (2) K
Needle, pale yellow
0.52 × 0.03 × 0.02 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
ω scans
14 660 measured reflections
2485 independent reflections (plus 1827 Friedel-related reflections)
2896 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.138$
$\theta_{\rm max} = 25°$
$h = -8 \rightarrow 8$
$k = -17 \rightarrow 14$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.150$
$S = 1.26$
4312 reflections
361 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 6.6293P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.39$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.04 (14)

All H atoms in (I) were refined independently in an isotropic approximation [C—H = 0.94 (2)–0.97 (2) Å]. In (II), the H atoms were treated as riding, with C—H = 0.95 Å and $U_{\rm iso}$(H) fixed at 1.2$U_{\rm eq}$ of the parent C atom. The reflections from (II) were generally weak [average $I/\sigma(I)$ ratio of 6.0] and surrounded with very anisotropic peaks of diffuse scattering, hence the high $R_{\rm int}$, final R and S values. Although the crystal faces were indexed, an absorption correction by numerical integration ($T_{\rm max}$ = 0.993 and $T_{\rm min}$ = 0.847) resulted in no overall improvement.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1995); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1068). Services for accessing these data are described at the back of the journal.

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