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A 1:1 cocrystal of 2,7-dicyano-9-dicyanomethylene-4,5-dinitrofluorene and benzonitrile

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The title complex contains infinite stacks of alternating $C_{18}H_4N_6O_4$ and C_7H_5N molecules; the former is warped to a much larger extent than in its charge-transfer complex with tetrathiafulvalene.

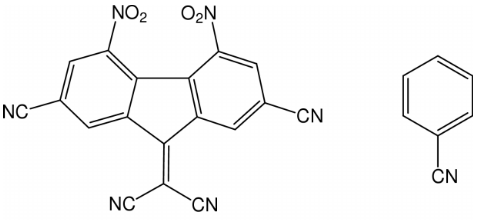
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.105
Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

During our studies of charge-transfer complexes (CTC), we have observed an interesting case of donor-induced cocrystallization (Batsanov *et al.*, 2001). Normally, 2,4,5,7-tetranitro-9-fluorenone (TeNF) and 2,4,5,7-tetranitro-9-dicyanomethylenefluorene (DTeNF) crystallize from chlorobenzene as solvent-free species. However, when tetrathiafulvalene (TTF) was added to the solutions (in an unsuccessful attempt to prepare CTC), both acceptors crystallized from it as solvates, *viz*. TeNF·2PhCl and DTeNF·PhCl.



(I) · PhCN

Herein we report another example of this effect. While attempting to crystallize, from a benzonitrile solution, a CTC of the acceptor 2,7-dicyano-4,5-dinitro-9-dicyanomethylenefluorene, (I), and the donor 2,6-dibutoxy-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene, (II), we obtained instead cocrystals of (I) with the solvent in a 1:1 ratio, *i.e.* (I)·PhCN. A CTC of (I) with TTF, (I)·TTF·PhCl, or (III), has been characterized previously by X-ray crystallography (Perepichka *et al.*, 1998; Kuz'mina *et al.*, 2002), but the crystal structure of pure (I) or of any molecular complex thereof without charge transfer, has not been reported thus far.

The crystal structure of (I)·PhCN comprises infinite mixed stacks, parallel to the *a* axis, of alternating molecules of (I) and benzonitrile (Fig. 1 and Table 1). The fluorene moiety of (I) is warped, as in other fluorene derivatives with nitro substituents in positions 4 and 5 (Silverman *et al.*, 1974; Batsanov *et al.*, 2001). The twist is obviously caused by steric repulsion between the two nitro groups. However, it is noteworthy that the distortion is much stronger in (I)·PhCl than in (III). Thus, the deviation of the 13 fluorene C atoms from their mean plane averages 0.11 Å in (I)·PhCl *versus* 0.06 Å in (III). In (I)·PhCN, both six-membered rings of the fluorene moiety

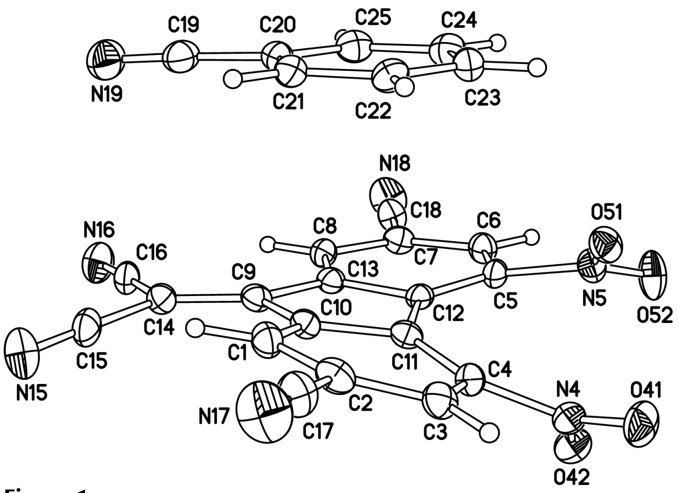


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

adopt envelope conformations: the C1–C4/C10 and C5–C8/C13 moieties are planar, with atoms C11 and C12 tilted out of their respective planes. A similar conformation was observed in (III). However, the dihedral angle between the C1–C4/C10 and C5–C8/C13 moieties in (I)·PhCN equals 15.8 (1)°, against 7.9° in (III). The twist around the C9═C14 bond, *i.e.* the dihedral angle between the C9/C10/C13/C14 and C9/C14–C16/N15/N16 planes, is small in both structures, 4.0 (1)° in (I)·PhCN against 3.7° in (III). The C9═C14 bond itself is marginally longer in (III) than in (I)·PhCN, *viz*. 1.379 (6) and 1.362 (3) Å, respectively, while the adjacent C9—C10 and C9—C13 bonds of the five-membered ring average 1.463 (6) Å in (III) *versus* 1.476 (3) Å in (I)·PhCN. Although each of these differences lies within 3 e.s.d., all of them are consistent with the acceptor molecule (I) in (III) acquiring an overall negative charge, which enhances its aromaticity, while no appreciable charge transfer takes place in (I)·PhCN.

Experimental

Acceptor (I) was prepared as described by Perepichka *et al.* (1998), donor (II) as described by Bryce *et al.* (2000). 5.5 mg (0.015 mmol) of (I) was dissolved in freshly distilled benzonitrile (0.5 ml) in a small (2 ml volume) vial, on heating at 343 K for 10–15 min. 7.8 mg (0.015 mol) of (II) was dissolved in benzonitrile (0.5 ml) at 333 K and the solution was added to that of (I). The brown–green solution was permitted to cool to room temperature and left overnight, whereupon small orange crystals of X-ray quality were formed.

Crystal data

$C_{18}H_4N_6O_4 \cdot C_7H_5N$
$M_r = 471.39$
Triclinic, $P\overline{1}$
$a = 7.211$ (1) Å
$b = 9.480$ (2) Å
$c = 16.451$ (3) Å
$\alpha = 96.16$ (1)°
$\beta = 102.41$ (1)°
$\gamma = 105.30$ (1)°
$V = 1043.2$ (3) Å^3
$Z = 2$
$D_x = 1.501$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 465 reflections
$\theta = 10.4$–24.7°
$\mu = 0.11$ mm^{-1}
$T = 120$ (2) K
Plate, orange
0.25 × 0.15 × 0.05 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: none
6896 measured reflections
4232 independent reflections
2544 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\rm max} = 26.4$°
$h = -8 \rightarrow 9$
$k = -11 \rightarrow 9$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.106$
$S = 0.95$
4232 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O41—N4	1.225 (2)	C7—C8	1.394 (3)
O42—N4	1.234 (2)	C7—C18	1.446 (3)
O51—N5	1.229 (2)	C8—C13	1.383 (3)
O52—N5	1.225 (2)	C9—C14	1.362 (3)
N4—C4	1.471 (3)	C9—C10	1.473 (3)
N5—C5	1.477 (3)	C9—C13	1.478 (3)
N15—C15	1.145 (3)	C10—C11	1.414 (3)
N16—C16	1.145 (3)	C11—C12	1.478 (3)
N17—C17	1.142 (3)	C12—C13	1.419 (3)
N18—C18	1.147 (3)	C14—C16	1.437 (3)
C1—C10	1.383 (3)	C14—C15	1.439 (3)
C1—C2	1.394 (3)	N19—C19	1.149 (3)
C2—C3	1.388 (3)	C19—C20	1.450 (3)
C2—C17	1.446 (3)	C20—C25	1.394 (3)
C3—C4	1.379 (3)	C20—C21	1.395 (3)
C4—C11	1.394 (3)	C21—C22	1.386 (3)
C5—C6	1.378 (3)	C22—C23	1.379 (3)
C5—C12	1.392 (3)	C23—C24	1.391 (3)
C6—C7	1.394 (3)	C24—C25	1.387 (3)
C10—C1—C2	118.9 (2)	C14—C9—C10	126.4 (2)
C3—C2—C1	120.7 (2)	C14—C9—C13	126.9 (2)
C3—C2—C17	118.8 (2)	C10—C9—C13	106.48 (17)
C1—C2—C17	120.4 (2)	C1—C10—C11	121.12 (19)
C4—C3—C2	119.2 (2)	C1—C10—C9	130.80 (19)
C3—C4—C11	121.7 (2)	C11—C10—C9	108.07 (18)
C3—C4—N4	116.63 (19)	C4—C11—C10	117.12 (19)
C11—C4—N4	121.41 (19)	C4—C11—C12	134.7 (2)
C6—C5—C12	121.58 (18)	C10—C11—C12	108.20 (17)
C6—C5—N5	115.92 (19)	C5—C12—C13	117.42 (19)
C12—C5—N5	122.10 (19)	C5—C12—C11	134.72 (18)
C5—C6—C7	119.5 (2)	C13—C12—C11	107.77 (18)
C6—C7—C8	120.9 (2)	C8—C13—C12	121.6 (2)
C6—C7—C18	118.4 (2)	C8—C13—C9	130.11 (19)
C8—C7—C18	120.65 (19)	C12—C13—C9	108.31 (18)
C13—C8—C7	118.65 (19)		

All H atoms were treated using the riding-model approximation, with C—H bond lengths of 0.95 Å and $U_{\rm iso}$ fixed at $1.2U_{\rm eq}$ of the corresponding C atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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