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9-Dicyanomethylene-4,5-dinitrofluorene-2,7-disulfonamide

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The title compound, $C_{16}H_8N_6O_8S_2$, has a twisted fluorene moiety due to steric repulsion between the 4- and 5-nitro groups.

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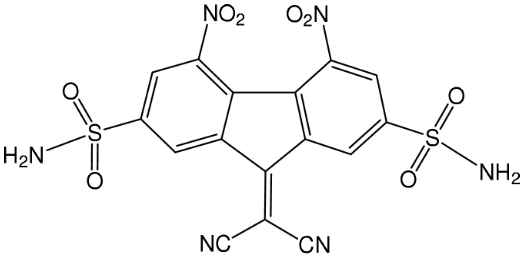
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.007 Å
R factor = 0.041
wR factor = 0.106
Data-to-parameter ratio = 9.8

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

Comment

2,4,5,7-Tetranitro-9-dicyanomethylenefluorene (DTeF) (Silverman *et al.*, 1974) is a strong electron acceptor, used as a component of charge-transfer complexes (CTC) (Perepichka *et al.*, 1998; Batsanov, Bryce *et al.*, 2001; Batsanov, Perepichka *et al.*, 2001). We also prepared and structurally characterized similar complexes with 2,7-bis(n-butylsulfonyl)- and 2,7-bis(phenylsulfonyl)-9-dicyanomethylene-4,5-dinitrofluorene (Perepichka *et al.*, 2000). The title compound, (I), was prepared in the course of the same study.



(I)

The fluorene system of (I), like that of DTeF, adopts a twisted conformation (Fig. 1), due to steric repulsion between the nitro groups in positions 4 and 5 [intramolecular contacts O42···N5 = 2.646 (5) Å and O51···N4 = 2.674 (5) Å]. The strain is relieved by (i) both nitro groups tilting out of the aromatic plane in opposite directions and (ii) the fluorene moiety itself twisting substantially. Thus, the 13 C atoms of the fluorene moiety show an average deviation of 0.13 Å from their mean plane. Both benzene rings adopt 'sofa' conformations, atoms C11 and C12 deviating by 0.12 and 0.06 Å from the planes of the essentially planar moieties C1–C4/C10 and C5–C8/C13, respectively. The latter planes form a dihedral angle of 15.2 (3)°. The twist around the C9═C14 bond, *i.e.* the dihedral angle between the C9/C10/C13/C14 and C9/C14/C15/C16/N15/N16 planes, is 11.5 (3)°. The bond lengths and angles in (I) (Table 1) are consistent with those observed in other distorted fluorene systems.

The NH_2 groups adopt *trans* orientations with respect to the mean fluorene plane. All amine H atoms participate in intermolecular hydrogen bonds (Table 2), although one of these (H71···O41) is very weak.

Experimental

4,5-Dinitro-9-fluorenone-2,7-disulfonyl dichloride [(II); 200 mg, 0.43 mol] (Mysyk *et al.*, 1997) was dissolved in dry dioxane (10 ml) and ammonia (35% solution in water, 0.2 ml) was added dropwise with intense stirring. The mixture was stirred at room temperature for 1 h and poured into water. The solid was filtered off, washed with warm water, dried and recrystallized from acetone, yielding pale yellow crystals of 4,5-dinitro-9-fluorenone-2,7-disulfonamide, (III) (130 mg, yield 71%, m.p. >573 K). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.63 (2H, *d*, J = 1.5 Hz, H-3,6), 8.50 (2H, *d*, J = 1.5 Hz, H-1,8), 7.19 (4H, *s*, SO_2NH_2); ^{13}C NMR (100 MHz, acetone-d_6): δ 186.56 (C═O), 149.28, 147.15, 139.40, 136.61, 128.86, 126.07. Analysis found: C 36.42, H 1.95, N 13.18, S 14.89%; $C_{13}H_8N_4O_9S_2$ requires: C 36.45, H 1.88, N 13.08, S 14.97%. Compound (III) (300 mg, 0.70 mmol) and malononitrile (100 mg, 167 mmol) in dimethylformamide (1.5 ml) were stirred at room temperature for 4 h and diluted with methanol (5 ml), resulting in precipitation. After keeping this solution at 273 K for 6 h, the solid obtained was filtered off and washed with water, yielding crude product (I) as a yellow–green solid. This was dissolved in a minimal amount of hot acetone and diluted with a fourfold volume of hot methanol. On cooling, a bright yellow solid was collected, washed with methanol and dried, giving 210 mg of (I) (yield 63%), m.p. >573 K. ^{1}H NMR (300 MHz, acetone-d_6 + *ca* 0.2 drop CF_3CO_2D): δ 9.36 (2H, *d*, J = 1.4 Hz, H-1.8), 8.71 (2H, *d*, J = 1.4 Hz, H-3,6), 7.32 (4H, *s*, SO_2NH_2). Analysis found: C 40.22, H 1.65, N 17.78, S 13.37; $C_{16}H_8N_6O_8S_2$ requires: C 40.34, H 1.69, N 17.64, S 13.46%. Single crystals of (I) of X-ray quality were obtained by slow evaporation (over several days) at room temperature of a solution of (I) (10 mg) in PhCl (10 ml) and acetonitrile (3 ml).

Crystal data

$C_{16}H_8N_6O_8S_2$
M_r = 476.40
Orthorhombic, $Pna2_1$
a = 9.574 (2) Å
b = 10.778 (6) Å
c = 17.461 (5) Å
V = 1801.8 (12) Å^3
Z = 4
D_x = 1.756 Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 25 reflections
θ = 15.5–25.0°
μ = 3.30 mm^{-1}
T = 150 (2) K
Needle, yellow
0.45 × 0.06 × 0.05 mm

Data collection

Rigaku AFC-6*S* four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (*TEXSAN*; Molecular Structure Corporation, 1989)
$T_{\min}$ = 0.745, $T_{\max}$ = 0.848
2381 measured reflections
1942 independent reflections
1730 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.033
$\theta_{\max}$ = 75.1°
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 13$
$l = -1 \rightarrow 21$
3 standard reflections every 147 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.106
S = 1.03
1942 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.7842P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.37 e Å^{-3}
$\Delta\rho_{\min}$ = −0.43 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.01 (3)

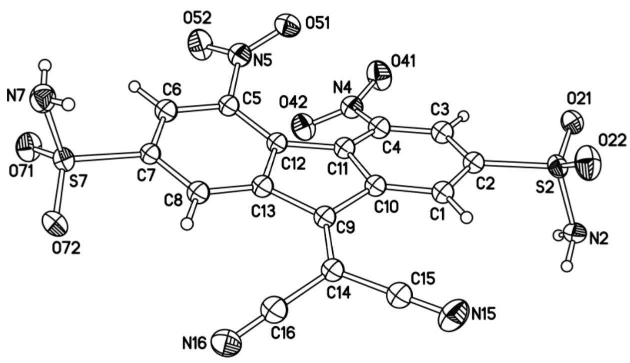


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected geometric parameters (Å, °).

S2—O22	1.424 (4)	C6—C7	1.384 (6)
S2—O21	1.433 (4)	C7—C8	1.394 (6)
S2—N2	1.612 (4)	C8—C13	1.387 (7)
S2—C2	1.785 (5)	C9—C14	1.358 (6)
S7—O72	1.428 (4)	C9—C13	1.469 (6)
S7—O71	1.432 (3)	C9—C10	1.475 (6)
S7—N7	1.606 (4)	C10—C11	1.410 (6)
S7—C7	1.784 (5)	C11—C12	1.473 (6)
C1—C2	1.383 (7)	C12—C13	1.429 (6)
C1—C10	1.396 (6)	C14—C15	1.435 (6)
C2—C3	1.381 (7)	C14—C16	1.446 (7)
C3—C4	1.393 (6)	C15—N15	1.144 (7)
C4—C11	1.387 (7)	C16—N16	1.146 (7)
C4—N4	1.476 (6)	N4—O41	1.218 (5)
C5—C12	1.387 (6)	N4—O42	1.236 (5)
C5—C6	1.391 (6)	N5—O52	1.219 (5)
C5—N5	1.465 (6)	N5—O51	1.239 (5)
C2—C1—C10	117.7 (4)	C14—C9—C10	127.1 (4)
C3—C2—C1	122.6 (4)	C13—C9—C10	106.8 (4)
C3—C2—S2	117.4 (4)	C1—C10—C11	121.5 (4)
C1—C2—S2	120.0 (4)	C1—C10—C9	130.4 (4)
C2—C3—C4	118.2 (5)	C11—C10—C9	108.0 (4)
C11—C4—C3	121.7 (4)	C4—C11—C10	117.4 (4)
C11—C4—N4	122.2 (4)	C4—C11—C12	134.2 (4)
C3—C4—N4	115.8 (4)	C10—C11—C12	108.3 (4)
C12—C5—C6	122.6 (4)	C5—C12—C13	116.8 (4)
C12—C5—N5	122.7 (4)	C5—C12—C11	135.2 (4)
C6—C5—N5	114.5 (4)	C13—C12—C11	107.8 (4)
C7—C6—C5	118.5 (4)	C8—C13—C12	121.7 (4)
C6—C7—C8	121.9 (4)	C8—C13—C9	130.2 (4)
C6—C7—S7	117.8 (3)	C12—C13—C9	107.9 (4)
C8—C7—S7	120.2 (4)	C9—C14—C15	123.4 (4)
C13—C8—C7	118.3 (4)	C9—C14—C16	122.2 (4)
C14—C9—C13	125.9 (4)	C15—C14—C16	114.4 (4)
C1—C2—S2—N2	79.0 (4)	C8—C7—S7—N7	96.3 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···O72$^{\rm i}$	0.89	2.03	2.878 (6)	159
N2—H22···O52$^{\rm ii}$	0.89	2.10	2.925 (5)	153
N7—H71···O41$^{\rm iii}$	0.89	2.51	3.116 (6)	126
N7—H72···N2$^{\rm iv}$	0.89	2.24	3.103 (6)	162

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (ii) $x, y - 1, z$; (iii) $1 - x, 2 - y, z - \frac{1}{2}$; (iv) $1 - x, 1 - y, z - \frac{1}{2}$.

Owing to an insufficient number of observed reflections, only the S, O and N atoms were refined with anisotropic displacement parameters, the C atoms being refined in isotropic approximation. Amine H atoms were refined in isotropic approximation, then constrained with the same bond direction but idealized N—H bond lengths (0.89 Å). Other H atoms were treated as riding in idealized positions, with C—H bond lengths of 0.95 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); 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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