

Andrei S. Batsanov^{a*} and
 Igor F. Perepichka^b
^aDepartment of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, and ^bL. M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk 83114, Ukraine

 Correspondence e-mail:
 a.s.batsanov@durham.ac.uk

Key indicators

 Single-crystal X-ray study
 T = 110 K
 Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
 R factor = 0.067
 wR factor = 0.172
 Data-to-parameter ratio = 10.5

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

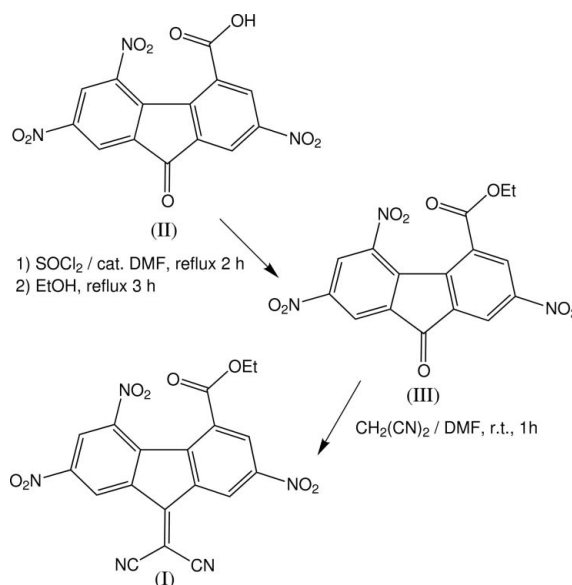
Ethyl 9-dicyanomethylene-2,5,7-trinitrofluorene-4-carboxylate

 The title compound, $\text{C}_{19}\text{H}_9\text{N}_5\text{O}_8$, has a warped fluorene ring system due to steric repulsion between the 4-ethoxycarbonyl and 5-nitro groups.

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Comment

 The title compound, (I), has been obtained in the course of our studies of electron acceptors of the fluorene series and their charge-transfer complexes and radical ion salts with π -electron donors, e.g. tetrathiafulvalene family donors (Perepichka *et al.*, 1998, 2000, 2002; Batsanov *et al.*, 2001, 2002; Kuz'mina *et al.*, 2002).

 The molecular structure of (I) is strongly influenced by steric repulsion between the nitro and ethoxycarbonyl groups in positions 4 and 5, respectively. This overcrowding, indicated, for example, by the short (intramolecular) non-bonding distances $\text{N}4 \cdots \text{O}5$ [2.730 (5) \AA] and $\text{C}17 \cdots \text{O}4$ [2.711 (6) \AA], causes the above-mentioned substituents to tilt out of the fluorene plane in opposite directions. Furthermore, the fluorene aromatic system itself loses planarity and adopts a warped (twisted) conformation, the deviations (\AA) of its C atoms from the mean plane being: C1 -0.186 (4), C2 -0.149 (4), C3 0.135 (4), C4 0.245 (4), C5 -0.226 (4), C6 -0.145 (4), C7 0.070 (4), C8 0.138 (4), C9 0.033 (4), C10 -0.039 (4), C11 0.060 (5), C12 -0.013 (5) and C13 0.078 (4). Similar distortions are typical for other fluorene derivatives with bulky substituents in positions 4 and 5, e.g. 9-dicyanomethylene-2,4,5,7-tetranitrofluorene (Silverman *et al.*, 1974;

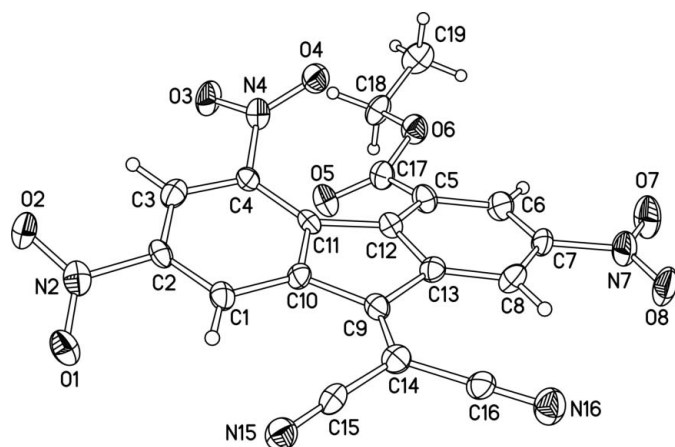


Figure 1
The molecular structure of (I). Atomic displacement ellipsoids are drawn at the 50% probability level.

Batsanov *et al.*, 2001), 9-dicyanomethylene-4,5-dinitrofluorene-2,7-disulfonamide (Batsanov & Perepichka, 2004) or 9-dicyanomethylene-4-bromo-2,5,7-trinitrofluorene (Perepichka *et al.*, 2002).

Experimental

To a suspension of 2,5,7-trinitro-9-oxofluorene-4-carboxylic acid (10.0 g, 27.8 mmol), (II), in thionyl chloride (50 ml) a catalytic amount of *N,N*-dimethylformamide (2 drops) was added. The mixture was refluxed for 2 h (full dissolution occurring in 15–20 min) and then evaporated under reduced pressure until dry. Ethanol (50 ml) was added to the residue, the mixture was refluxed for 3 h and left to cool for crystallization. The precipitate was filtered off, washed with cold ethanol (2 × 20 ml) and dried to yield crude compound (III) (9.1 g, 84%; m.p. 426–430 K). This was dissolved in boiling dioxane (25 ml), filtered hot and the filtrate was diluted with hot ethanol (100 ml). On cooling, the solid was filtered off, washed with ethanol and dried. This procedure was repeated to give pure compound (III) (7.2 g, 67%) as yellow crystals (m.p. 434–435 K). ¹H NMR (200 MHz, acetone-*d*₆): δ 8.99 (1H, *d*, *J* = 2.0 Hz, H-3), 8.83 (1H, *d*, *J* = 2.0 Hz, H-6), 8.78 (1H, *d*, *J* = 2.2 Hz, H-8), 8.69 (1H, *d*, *J* = 2.2 Hz, H-1), 4.42 (2H, *q*, *J* = 7.2 Hz, CH₂), 1.43 (3H, *t*, *J* = 7.2 Hz, CH₃). ¹³C NMR (50 MHz, acetone-*d*₆): δ 186.21 (C=O), 165.44 (–CO₂–), 150.71, 150.56, 147.36, 144.19, 140.30, 140.08, 139.18, 132.90, 131.05, 126.38, 122.95, 122.00, 63.84 (CH₂), 14.32 (CH₃). MS (EI): *m/z* 387 (*M*⁺, 100%). HRMS (EI): *m/z* 387.03447; calculated exact mass: 387.03388. Analysis found: C 49.52, H 2.40, N 10.89%; C₁₆H₉N₃O₉ requires: C 49.62, H 2.34, N 10.85%.

Compound (III) (5.0 g, 12.9 mmol) was dissolved in *N,N*-dimethylformamide (25 ml), malonitrile (2.2 g, 33.3 mmol) was added to this solution and the mixture was stirred at room temperature for 1 h (the product began to precipitate in 30 min). 2-Propanol (100 ml) was added to the mixture and it was allowed to stand at 273 K for 1–2 h. The solid was filtered off, washed with 2-propanol and dried to yield crude compound (I) (5.2 g, 93%; m.p. 539–543 K). It was dissolved in boiling dioxane (75 ml), hot 2-propanol was added to the solution and the product left to crystallize. The solid was filtered off, washed with 2-propanol and dried. The purification procedure was repeated once more, to afford pure compound (I) (4.8 g, 85%) as bright-yellow crystals (m.p. 543–545 K). ¹H NMR (200 MHz, acetone-*d*₆ + half a drop CF₃CO₂D): δ 9.69 (1H, *d*, *J* = 2.0 Hz, H-8),

9.60 (1H, *d*, *J* = 2.0 Hz, H-1), 9.04 (1H, *d*, *J* = 2.0 Hz, H-6), 8.88 (1H, *d*, *J* = 2.0 Hz, H-3), 4.43 (2H, *q*, *J* = 7.2 Hz, CH₂), 1.44 (3H, *t*, *J* = 7.2 Hz, CH₃). ¹³C NMR (100 MHz, acetone-*d*₆ + 0.5 drop CF₃CO₂D): δ 165.30 (–CO₂–), 154.81, 141.14, 140.14, 139.25, 137.49, 133.05, 130.49, 125.76, 124.75, 123.70, 121.52, 117.74, 113.96, 113.37, 113.32, 110.17, 63.96 (CH₂), 14.36 (CH₃). MS (EI): *m/z* 435 (*M*⁺, 100%). Analysis found: C 52.52, H 2.03, N 16.15%; C₁₉H₉N₅O₈ requires: C 52.42, H 2.08, N 16.09%. Compound (I) was dissolved in hot acetonitrile and left to cool slowly to yield single crystals of X-ray quality.

Crystal data

C ₁₉ H ₉ N ₅ O ₈	<i>D</i> _x = 1.615 Mg m ^{−3}
<i>M</i> _r = 435.31	Mo Kα radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 1107 reflections
<i>a</i> = 19.481 (2) Å	<i>θ</i> = 3.1–22.6°
<i>b</i> = 8.620 (1) Å	<i>μ</i> = 0.13 mm ^{−1}
<i>c</i> = 10.814 (1) Å	<i>T</i> = 110 (2) K
<i>β</i> = 99.40 (1)°	Prism, yellow
<i>V</i> = 1791.6 (3) Å ³	0.18 × 0.07 × 0.07 mm
<i>Z</i> = 4	

Data collection

Bruker SMART 1 K CCD area-detector diffractometer	1518 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>ω</i> scans	<i>R</i> _{int} = 0.126
Absorption correction: none	<i>θ</i> _{max} = 25.0°
7993 measured reflections	<i>h</i> = −13 → 22
3079 independent reflections	<i>k</i> = −9 → 10
	<i>l</i> = −12 → 12

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.5406P]$
$R[F^2 > 2\sigma(F^2)] = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.172$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.03	$\Delta\rho_{\text{max}} = 0.41 \text{ e } \text{Å}^{-3}$
3079 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e } \text{Å}^{-3}$
292 parameters	Extinction correction: <i>SHELXTL</i>
H-atom parameters constrained	Extinction coefficient: 0.018 (2)

Table 1

Selected geometric parameters (Å, °).

N15–C15	1.152 (6)	C10–C11	1.412 (6)
N16–C16	1.147 (6)	C11–C12	1.502 (7)
C9–C14	1.352 (7)	C12–C13	1.397 (7)
C9–C10	1.465 (7)	C14–C16	1.444 (7)
C9–C13	1.495 (6)	C14–C15	1.446 (7)
C2–C1–C10	116.9 (4)	C6–C5–C12	117.7 (5)
C3–C2–C1	123.3 (4)	C7–C6–C5	119.2 (5)
C2–C3–C4	118.0 (5)	C6–C7–C8	124.3 (5)
C3–C4–C11	121.4 (4)	C7–C8–C13	116.0 (5)

The diffraction was rather weak, with a mean *I*/σ(*I*) ratio of 5.2. The methyl group was refined as a rigid body (C–H = 0.98 Å) rotating around the C–C bond, with a common (refined) *U*_{iso} value for all three H atoms. Other H atoms were treated as riding in idealized positions, with *Csp*³–H = 0.99 Å and *Csp*²–H = 0.95 Å, and *U*_{iso}(H) = 1.3*U*_{eq}(C) and 1.2*U*_{eq}(C), respectively.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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