# Ethyl 9-dicyanomethylene-2,5,7-trinitro-fluorene-4-carboxylate

Andrei S. Batsanov[a]* and Igor F. Perepichka[b]

[a]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, and [b]L. 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 $\sigma$(C–C) = 0.007 Å
$R$ 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.

The title compound, $C_{19}H_9N_5O_8$, has a warped fluorene ring system due to steric repulsion between the 4-ethoxycarbonyl and 5-nitro groups.

## 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 $\pi$-electron donors, *e.g.* tetrathiafulvalene family donors (Perepichka *et al.*, 1998, 2000, 2002; Batsanov *et al.*, 2001, 2002; Kuz'mina *et al.*, 2002).
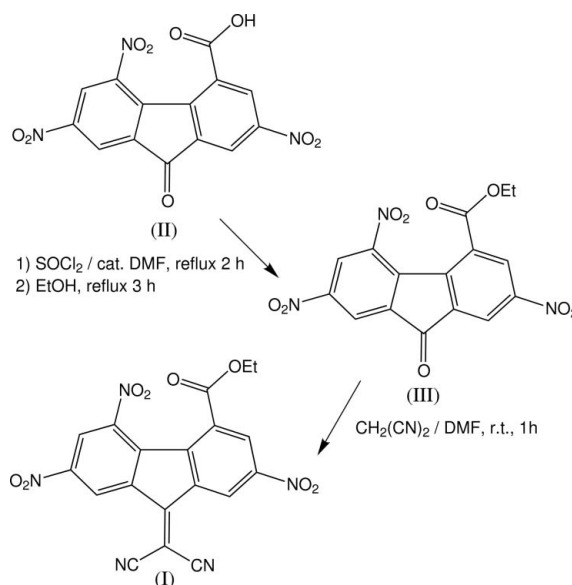


The molecular structure of (I) is strongly influenced by steric repulsion between the nitro and ethoxycarbonyl groups in positions 4 and 5, respectively. This overcrowding, indicated, for example, by the short (intramolecular) non-bonding distances N4···O5 [2.730 (5) Å] and C17···O4 [2.711 (6) Å], causes 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 (Å) 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;
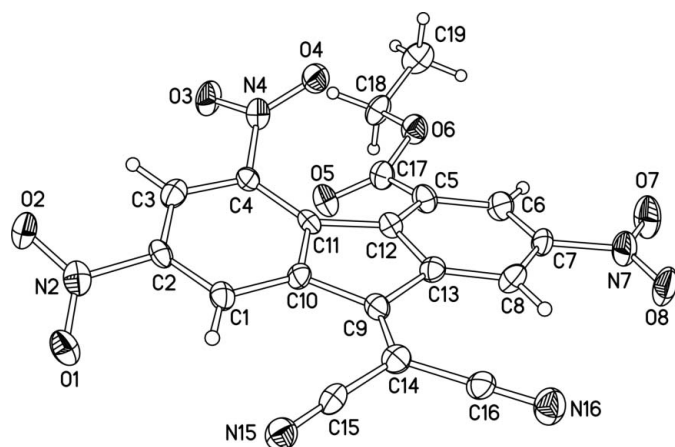
**Figure 1**
The molecular structure of (I). Atomic displacement ellipsoids are drawn at the 50% probability level.

Batsanov *et al.*, 2001), 9-dicyanomethylene-4,5-dinitro-fluorene-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). $^1$H NMR (200 MHz, acetone-$d_6$): $\delta$ 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). $^{13}$C NMR (50 MHz, acetone-$d_6$): $\delta$ 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%; $C_{16}H_9N_3O_9$ 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). $^1$H NMR (200 MHz, acetone-$d_6$ + half a drop CF3CO2D): $\delta$ 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). $^{13}$C NMR (100 MHz, acetone-$d_6$ + 0.5 drop CF3CO2D): $\delta$ 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%; $C_{19}H_9N_5O_8$ 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*

| | |
|---|---|
| $C_{19}H_9N_5O_8$ | $D_x = 1.615$ Mg m$^{-3}$ |
| $M_r = 435.31$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 1107 |
| $a = 19.481 (2)$ Å | reflections |
| $b = 8.620 (1)$ Å | $\theta = 3.1$–$22.6°$ |
| $c = 10.814 (1)$ Å | $\mu = 0.13$ mm$^{-1}$ |
| $\beta = 99.40 (1)°$ | $T = 110 (2)$ K |
| $V = 1791.6 (3)$ Å$^3$ | Prism, yellow |
| $Z = 4$ | $0.18 \times 0.07 \times 0.07$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART 1 K CCD area-detector diffractometer | 1518 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.126$ |
| Absorption correction: none | $\theta_{max} = 25.0°$ |
| 7993 measured reflections | $h = -13 \rightarrow 22$ |
| 3079 independent reflections | $k = -9 \rightarrow 10$ |
| | $l = -12 \rightarrow 12$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0632P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.067$ | $+ 0.5406P]$ |
| $wR(F^2) = 0.172$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.03$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3079 reflections | $\Delta\rho_{max} = 0.41$ e Å$^{-3}$ |
| 292 parameters | $\Delta\rho_{min} = -0.37$ e Å$^{-3}$ |
| H-atom parameters constrained | Extinction correction: *SHELXTL* |
| | 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 $I/\sigma(I)$ 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 C$sp^3$—H = 0.99 Å and C$sp^2$—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: *SAINT* (Bruker, 1999); data reduction: *SAINT*; 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*.

## References

Batsanov, A. S., Bryce, M. R., Lyubchik, S. B. & Perepichka, I. F. (2002). *Acta Cryst.* E**58**, o1106–o1110.

Batsanov, A. S. & Perepichka, I. F. (2004). *Acta Cryst.* E**60**, o1892–o1894.

Batsanov, A. S., Perepichka, I. F., Bryce, M. R. & Howard, J. A. K. (2001). *Acta Cryst.* C**57**, 1299–1302.

Bruker (1997). *SMART* (Version 5.054) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SAINT*. Version 6.01. Bruker AXS Inc., Madison, Wisconsin, USA.

Kuz'mina, L. G., Perepichka, I. F., Perepichka, D. F., Howard, J. A. K. & Bryce, M. R. (2002). *Crystallogr. Rep.* **47**, 251–261.

Perepichka, D. F., Bryce, M. R., Perepichka, I. F., Lyubchik, S. B., Christensen, C. A., Godbert, N., Batsanov, A. S., Levillain, E., McInnes, E. J. L. & Zhao, J. P. (2002). *J. Am. Chem. Soc.* **124**, 14227–14238.

Perepichka, I. F., Kuz'mina, L. G., Perepichka, D. F., Bryce, M. R., Goldenberg, L. M., Popov, A. F. & Howard, J. A. K. (1998). *J. Org. Chem.* **63**, 6484–6493.

Perepichka, I. F., Popov, A. F., Orekhova, T. V., Bryce, M. R., Andrievskii, A. M., Batsanov, A. S., Howard, J. A. K. & Sokolov, N. I. (2000). *J. Org. Chem.* **65**, 3053–3063.

Silverman, J., Yannoni, N. F. & Krukonis, A. P. (1974). *Acta Cryst.* B**30**, 1474–1480.