Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2-Dicyanomethylene-4,5,5-trimethyl-2,5-dihydrofuran-3-carbonitrile

Su-Yue Li,[a,b] Yin-Yin Song,[a] Zhong-Lu You,[c] Yan-Wei Wen[a] and Jin-Gui Qin[a]*

[a]Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China, [b]Department of Chemistry, Wuhan University of Science and Engineering, Wuhan 430073, People's Republic of China, and [c]Department of Chemistry and Chemial Engineering, Liaoning Normal University, Dalian 116029, People's Republic of China

Correspondence e-mail: jgqin@whu.edu.cn

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.065
wR factor = 0.213
Data-to-parameter ratio = 13.4

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

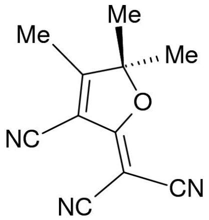
Received 9 May 2005
Accepted 7 June 2005
Online 17 June 2005

In the title compound, $C_{11}H_9N_3O$, the three cyano groups, the C atom of one of the three methyl groups and the dihydrofuran ring atoms lie on a crystallographic mirror plane. A weak C—H···N interaction results in one-dimensional chains.

Comment

In recent years, chromophore-functionalized electro-optic (EO) polymeric materials have been investigated intensively for their potential applications in high-speed photonic devices (Dalton, 2003). This interest has led to extensive explorations of 'push-pull' type chromophores with high molecular second-order nonlinearity (β). Among the three molecular building blocks commonly used for NLO chromophores (electron donor, conjugating bridge and electron acceptor), the development of electron donors and conjugating bridges is already quite mature, such that they can meet most of the synthetic and physical requirements. Therefore, one of the major tasks for optimizing the $\mu\beta$ value (μ is a dipole moment) of a chromophore is the development of novel electron acceptors.

The title compound, (I), is a strong electron acceptor for nonlinear optics (Zhang *et al.*, 1999). Owing to its excellent electron-withdrawing power, chromophores with (I) as acceptors have been reported to possess exceptionally large $\mu\beta$ values (Zhang *et al.*, 2001; Wang *et al.*, 2001; You *et al.*, 2004; Liao *et al.*, 2005). As a part of a project to develop second-order nonlinear optical materials for EO application, we synthesized (I), following the procedure of He *et al.* (2002), and determined its single-crystal structure.



(I)

In the structure of (I) (Fig. 1), the dihydrofuran ring, the three cyano groups and methyl atom C9 lie on a crystallographic mirror plane. The high degree of planarity suggests that the excellent electron-withdrawing power of (I) arises from the cumulative effects of the three cyano groups on the dihydrofuran ring. Atom C10 is displaced from the mirror plane by 1.263 (3) Å. The average C—N bond length [1.136 (4) Å] of the three cyano groups in (I) (Table 1) is slightly shorter than that in acetonitrile, which may possibly be attributed to the much more extensive conjugative effect in

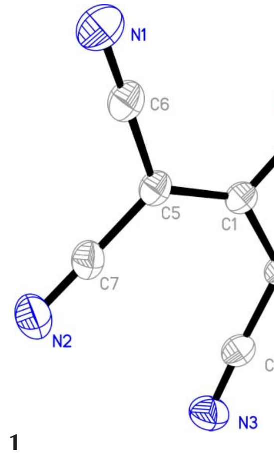


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms). The unlabelled C atom is generated by the symmetry operation ($x, \frac{1}{2} - y, z$).

(I). All the other bond lengths and angles in (I) are within their normal ranges.

In the crystal structure of (I), weak C9—H9*A*···N1 interactions occur (Table 2), linking the molecules into chains propagating along [101] (Fig. 2).

Experimental

3-Hydroxy-3-methyl-2-butanone was prepared according to the literature method (Newman & Lee, 1975). Tetrahydrofuran was dried and distilled over sodium before use. Malononitrile was distilled under reduced pressure before use. Other chemicals were used as received without further purification. Under anhydrous conditions, 3-hydroxy-3-methyl-2-butanone (0.01 mol, 1.0 g) and malononitrile (0.02 mol, 1.32 g) were dissolved in tetrahydrofuran (50 ml) in a 100 ml round-bottomed flask equipped with a reflux condenser and Soxhlet extractor (containing a 4 Å molecular sieve). Anhydrous K_2CO_3 (0.01 mol, 1.38 g) and 18-crown-6 (catalytic amount) were added to the above mixture and refluxed for 20 h. Upon cooling to room temperature, the reaction mixture was concentrated under vacuum to remove the solvent. The residue was dissolved in water and acidified with 6 *M* aqueous HCl to pH 4–5. The crude precipitate was filtered and recrystallized from ethanol to give the title compound (yield 65%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a chloroform solution. After about half of the solvent had evaporated, colourless crystals of (I) were deposited and were collected by filtration (m.p. 474–475 K). IR (KBr, ν, cm^{-1}): 3100, 2230, 1590, 1150; ^{1}H NMR ($CDCl_3$, p.p.m.): δ 2.37 (*s*, 3H), 1.64 (*s*, 6H); ^{13}C NMR ($CDCl_3$, p.p.m.): δ 183.2, 175.1, 110.7, 110.2, 109.5, 104.6, 100.1, 58.5, 25.2, 14.2. Analysis calculated for $C_{11}H_9N_3O$: C 66.31, H 4.56, N 21.10; found: C 66.50, H 4.68, N 20.84%.

Crystal data

$C_{11}H_9N_3O$
M_r = 199.21
Monoclinic, $P2_1/m$
a = 9.485 (2) Å
b = 6.8022 (16) Å
c = 9.681 (2) Å
β = 118.263 (3)°
V = 550.1 (2) Å^3
Z = 2
D_x = 1.203 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 738 reflections
θ = 2.5–22.4°
μ = 0.08 mm^{-1}
T = 298 (2) K
Block, colourless
0.40 × 0.36 × 0.26 mm

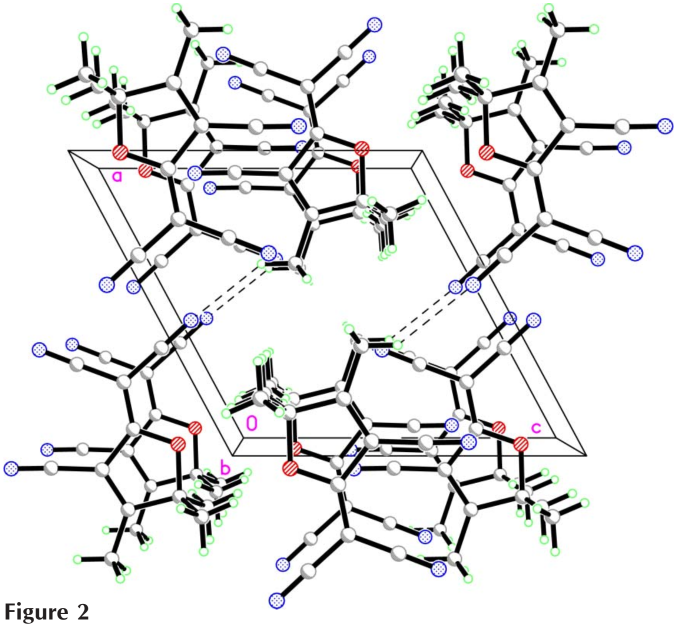


Figure 2
Crystal packing of (I), viewed along the *b* axis. The weak C—H···N interactions are shown as dashed lines.

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.968, T_{max} = 0.979
3143 measured reflections
1182 independent reflections
804 reflections with $I > 2\sigma(I)$
R_{int} = 0.148
θ_{max} = 26.0°
$h = -11 \rightarrow 7$
$k = -7 \rightarrow 8$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.213
S = 0.97
1182 reflections
88 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.128P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected interatomic distances (Å).

C6—N1	1.142 (5)	C8—N3	1.130 (4)
C7—N2	1.136 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···N1^{i}	0.96	2.55	3.365	143

Symmetry code: (i) $x + 1, y, z + 1$.

All H atoms were placed in geometrically idealized positions (C—H = 0.96 Å) and refined as riding with the constraint U_{iso}(H) = 1.5U_{eq}(C) applied.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART or SAINT?*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

o2094 Li *et al.* • $C_{11}H_9N_3O$ *Acta Cryst.* (2005). E**61**, o2093–o2095

The authors thank the National Key Fundamental Research Programme of China and the National Science Foundation of China for financial support.

References

Dalton, L. R. (2003). *J. Phys. Condens. Matter*, **15**, R897–R934.

He, M.-Q., Leslie, T. M. & Sinicropi, J. A. (2002). *Chem. Mater.* **14**, 2393–2400.

Liao, Y., Eichinger, B. E., Firestone, K. A., Haller, M., Luo, J.-D., Kaminsky, W., Benedict, J. B., Reid, P. J., Jen, A. K.-Y., Dalton, L. R. & Robinson, B. H. (2005). *J. Am. Chem. Soc.* **127**, 2758–2766.

Newman, M. S. & Lee, V. (1975). *J. Org. Chem.* **40**, 381–382.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*a*). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Wang, C. H., Woodford, J. N., Zhang, C. & Dalton, L. R. (2001). *J. Appl. Phys.* **89**, 4209–4217.

You, W., Hou, Z.-J. & Yu, L. P. (2004). *Adv. Mater.* **16**, 356–360.

Zhang, C., Dalton, L. R., Oh, M.-C., Zhang, H. & Steier, W. H. (2001). *Chem. Mater.* **13**, 3043–3050.

Zhang, C., Ren, A. S., Wang, F., Zhu, J.-S., Dalton, L. R., Woodford, J. N. & Wang, C. H. (1999). *Chem. Mater.* **11**, 1966–1968.

Acta Cryst. (2005). E**61**, o2093–o2095 Li *et al.* • $C_{11}H_9N_3O$ **o2095**