

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2-[(6-Nitro-1,3-benzodioxol-5-yl)methylidene]malononitrile

S. Karthikeyan,^a K. Sethusankar,^{a*} Anthonisamy Devaraj^b and Manickam Bakthadoss^b^aDepartment of Physics, RKM Vivekananda College (Autonomous), Chennai 600 004, India, and ^bDepartment of Organic Chemistry, University of Madras, Maraimalai Campus, Chennai 600 025, India
Correspondence e-mail: ksethusankar@yahoo.co.in

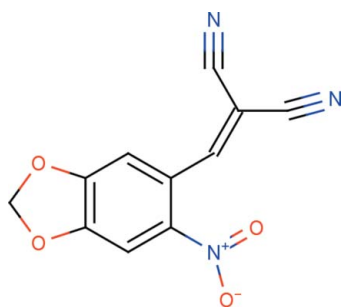
Received 2 November 2011; accepted 21 November 2011

Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.048; wR factor = 0.142; data-to-parameter ratio = 21.4.

In the title compound, $\text{C}_{11}\text{H}_5\text{N}_3\text{O}_4$, the nitro group is rotated by $29.91(16)^\circ$ out of the plane of the adjacent aryl ring. The 1,3-benzodioxole ring is nearly planar, with a maximum deviation of $0.0562(10)$ Å. The dioxolene ring adopts an envelope conformation on the $\text{O}-\text{C}-\text{O}$ C atom. In the crystal, molecules are linked *via* $\text{C}-\text{H}\cdots\text{O}$ interactions, resulting in $R_2^2(6)$ and $R_2^2(12)$ graph-set motifs.

Related literature

For applications of malononitrile derivatives, see: Brimblecombe *et al.* (1972). For related structure, see: Loghmani-Khouzani *et al.* (2009). For comparison of molecular dimensions, see: Allen *et al.* (1987). For puckering parameters, see: Cremer & Pople (1975). For graph-set motif notations, see: Bernstein *et al.* (1995).



Experimental

Crystal data

 $\text{C}_{11}\text{H}_5\text{N}_3\text{O}_4$
 $M_r = 243.18$
Triclinic, $P\bar{1}$ $a = 7.0953(2)$ Å
 $b = 8.8847(3)$ Å
 $c = 9.2212(3)$ Å $\alpha = 84.470(2)^\circ$
 $\beta = 67.634(2)^\circ$
 $\gamma = 78.874(2)^\circ$
 $V = 527.30(3)$ Å³
 $Z = 2$ Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 295$ K
 $0.30 \times 0.28 \times 0.25$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer
13806 measured reflections3494 independent reflections
2700 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.142$
 $S = 1.03$
3494 reflections163 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C1}-\text{H1B}\cdots\text{O1}^{\text{i}}$	0.97	2.53	3.2692 (16)	133
$\text{C8}-\text{H8}\cdots\text{O4}^{\text{ii}}$	0.93	2.52	3.3640 (17)	152

Symmetry codes: (i) $-x, -y + 1, -z + 2$; (ii) $-x - 1, -y + 2, -z + 1$.

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and Mercury (Macrae *et al.* 2008); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

SK and KS thank Dr Babu Varghese, Senior Scientific Officer, SAIF, IIT, Chennai, India, for the X-ray intensity data collection and Dr V. Murugan, Head of the Department of Physics, RKM Vivekananda College, for providing facilities in the department for carrying out this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2314).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Brimblecombe, R. W., Green, D. M. & Muir, A. W. (1972). *Br. J. Pharmacol.* **44**, 561–576.
- Bruker (2008). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Loghmani-Khouzani, H., Abdul Rahman, N., Robinson, W. T., Yaeghoobi, M. & Kia, R. (2009). *Acta Cryst. E* **65**, o2545.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.

supplementary materials

Acta Cryst. (2011). E67, o3469 [doi:10.1107/S1600536811049816]

2-[(6-Nitro-1,3-benzodioxol-5-yl)methylidene]malononitrile

S. Karthikeyan, K. Sethusankar, A. Devaraj and M. Bakthadoss

Comment

The malononitrile derivative is used to investigate a variety of possible pharmacological effects when administered by various routes to whole animals and when applied to isolated organs and tissues (Brimblecombe *et al.*, 1972). Also, it is a component of "tear gas" commonly referred as CS gas, which is used as a riot control agent.

In the title compound $C_{11}H_5N_3O_4$, the benzodioxole ring is nearly planar with a maximum deviation 0.0562 Å for the atom O2. The O=N=O angle is much larger than the ideal tetrahedral or trigonal values, respectively, doubtless as a consequence of the substantial negative charge on the paired O atoms. The bond lengths C9—C10 = 1.4388 (16) Å and C9—C11 = 1.4342 (16) Å is significantly shorter than the expected value for a C—C single bond because of conjugation effects.

In the dioxole ring C1/O2/C2/C7/O1, the deviation of atom C1 is -0.0724 (16) Å. The dioxole ring adopts a *envelope* conformation on C1 with puckering parameters (Cremer & Pople, 1975): $Q_2 = 0.1145$ (13) Å and $\phi_2 = 36.7$ (6)°. The malononitrile group (C9—C10≡N2) and (C9—C11≡N3) is almost linear, with the angle around central carbon atoms C10 and C11 being 179.14 (15)° and 179.09 (15)° respectively.

The values of the torsion angles C5—C4—C8—C9 = -154.85 (11)° and C4—C5—N1—O4 = -151.10 (12)° indicates that the conformation of molecule is (-)*anti*-periplanar. The nitro group is not co-planar to the benzodioxole ring to which it is attached, making a dihedral angle of 29.76 (4)°. The benzodioxole unit is oriented at a dihedral angle of 36.90 (4)° with respect to the malononitrile group. The triple bond distances C10≡N2 and C11≡N3 are in agreement with the literature values (1.138 (7) Å; Allen *et al.*, 1987). The title compound exhibits structural similarities with the already reported related structures (Loghmani-Khouzani *et al.*, 2009).

The crystal packing is stabilized by non-classical intermolecular C—H...O interactions. The molecules are linked into centrosymmetric dimers. Atom C1 acts as a donor to dioxole O1ⁱ, so forming an $R^2_2(6)$ graph-set motif and atom C8 acts as a donor to nitro group O4ⁱⁱ at forming an $R^2_2(12)$ graph-set motif (Bernstein, *et al.*, 1995). Symmetry codes: (i) -x, 1-y, 2-z; (ii) -1-x, 2-y, 1-z).

Experimental

To a solution of malononitrile (0.082 g, 1.24 mmol) in dichloromethane (5 ml), pyrrolidine (0.073 g, 1.03 mmol) was added and stirred well for 10 minutes. To this solution 6-nitrobenzo[d][1,3]dioxole-5-carbaldehyde (0.2 g, 1.03 mmol) was added and stirring was continued for 12 h. After the completion of the reaction as evidenced by *TLC*, the reaction mixture was poured into 2 N HCl solution (10 ml) and extracted using 25 ml of dichloromethane. The organic layer thus obtained was concentrated under reduced pressure. Column purification (silica gel, mesh size: 60–120) of the crude mixture using 15% ethyl acetate in hexanes successfully provided the desired 2-((6-nitrobenzo[d][1,3]dioxol-5-yl)methylene)malononitrile in 90% yield (0.23 g).

Refinement

The hydrogen atoms were placed in calculated positions with C—H = 0.93 Å to 0.97 Å and refined in the riding model with fixed isotropic displacement parameters: $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic and methylene groups.

Figures

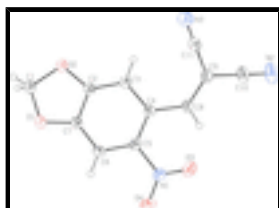


Fig. 1. The molecular structure of the title compound with the atom numbering scheme, displacement ellipsoids are drawn at 30% probability level. H atoms are present as small spheres of arbitrary radius.

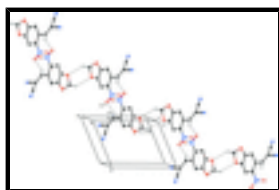


Fig. 2. The packing arrangement of the title compound viewed down *a* axis. The dashed lines indicate C—H...O intermolecular interactions, which forms $R^2_2(6)$ and $R^2_2(12)$ centrosymmetric dimers. The symmetry codes: (i) $-x, 1-y, 2-z$; (ii) $-1-x, 2-y, 1-z$.

2-[(6-Nitro-1,3-benzodioxol-5-yl)methylidene]malononitrile

Crystal data

$\text{C}_{11}\text{H}_5\text{N}_3\text{O}_4$

$M_r = 243.18$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.0953\ (2)\ \text{\AA}$

$b = 8.8847\ (3)\ \text{\AA}$

$c = 9.2212\ (3)\ \text{\AA}$

$\alpha = 84.470\ (2)^\circ$

$\beta = 67.634\ (2)^\circ$

$\gamma = 78.874\ (2)^\circ$

$V = 527.30\ (3)\ \text{\AA}^3$

$Z = 2$

$F(000) = 248$

$D_x = 1.532\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3494 reflections

$\theta = 1.0\text{--}31.6^\circ$

$\mu = 0.12\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Block, yellow

$0.30 \times 0.28 \times 0.25\ \text{mm}$

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

graphite

ω scans

13806 measured reflections

3494 independent reflections

2700 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 31.6^\circ$, $\theta_{\text{min}} = 2.3^\circ$

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.048$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.142$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2 + 0.0833P]$
3494 reflections	where $P = (F_o^2 + 2F_c^2)/3$
163 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1956 (2)	0.45131 (18)	0.79855 (15)	0.0499 (3)
H1A	0.2553	0.3433	0.7969	0.060*
H1B	0.2182	0.4995	0.8792	0.060*
C2	0.13009 (16)	0.60560 (13)	0.61230 (12)	0.0335 (2)
C3	0.13982 (17)	0.70725 (13)	0.48999 (12)	0.0345 (2)
H3	0.2663	0.7286	0.4190	0.041*
C4	-0.04642 (16)	0.77900 (12)	0.47404 (12)	0.0309 (2)
C5	-0.23081 (16)	0.74097 (12)	0.58573 (13)	0.0331 (2)
C6	-0.24088 (17)	0.63890 (13)	0.71134 (13)	0.0373 (2)
H6	-0.3660	0.6171	0.7842	0.045*
C7	-0.05588 (18)	0.57270 (13)	0.72113 (12)	0.0351 (2)
C8	-0.04545 (17)	0.90159 (12)	0.35650 (13)	0.0347 (2)
H8	-0.1612	0.9786	0.3818	0.042*
C9	0.10476 (19)	0.91503 (13)	0.21576 (14)	0.0386 (2)
C10	0.0900 (2)	1.05218 (15)	0.12130 (16)	0.0478 (3)
C11	0.2814 (2)	0.79907 (17)	0.14691 (15)	0.0491 (3)
N1	-0.42888 (15)	0.80802 (11)	0.57275 (13)	0.0417 (2)
N2	0.0804 (3)	1.16093 (16)	0.04706 (18)	0.0707 (4)

supplementary materials

N3	0.4220 (2)	0.7081 (2)	0.09043 (17)	0.0760 (5)
O1	-0.02108 (14)	0.46924 (11)	0.82958 (10)	0.0483 (2)
O2	0.28869 (13)	0.52328 (11)	0.64860 (10)	0.0457 (2)
O3	-0.43369 (15)	0.84163 (11)	0.44228 (12)	0.0507 (3)
O4	-0.58153 (15)	0.82535 (14)	0.69255 (14)	0.0674 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0424 (7)	0.0658 (8)	0.0332 (6)	0.0027 (6)	-0.0132 (5)	0.0108 (5)
C2	0.0307 (5)	0.0392 (5)	0.0288 (5)	-0.0007 (4)	-0.0115 (4)	-0.0001 (4)
C3	0.0298 (5)	0.0412 (5)	0.0304 (5)	-0.0058 (4)	-0.0101 (4)	0.0036 (4)
C4	0.0308 (5)	0.0307 (5)	0.0304 (5)	-0.0039 (4)	-0.0114 (4)	0.0004 (4)
C5	0.0279 (5)	0.0323 (5)	0.0367 (5)	-0.0011 (4)	-0.0111 (4)	-0.0009 (4)
C6	0.0306 (5)	0.0396 (6)	0.0343 (5)	-0.0040 (4)	-0.0056 (4)	0.0033 (4)
C7	0.0364 (5)	0.0372 (5)	0.0272 (5)	-0.0026 (4)	-0.0094 (4)	0.0024 (4)
C8	0.0349 (5)	0.0324 (5)	0.0388 (5)	-0.0057 (4)	-0.0167 (4)	0.0030 (4)
C9	0.0410 (6)	0.0401 (6)	0.0386 (6)	-0.0114 (5)	-0.0190 (5)	0.0086 (4)
C10	0.0602 (8)	0.0460 (7)	0.0449 (7)	-0.0211 (6)	-0.0253 (6)	0.0122 (5)
C11	0.0415 (7)	0.0632 (8)	0.0361 (6)	-0.0077 (6)	-0.0108 (5)	0.0109 (5)
N1	0.0309 (5)	0.0360 (5)	0.0550 (6)	-0.0031 (4)	-0.0153 (4)	0.0051 (4)
N2	0.1052 (13)	0.0544 (7)	0.0656 (9)	-0.0313 (8)	-0.0436 (9)	0.0243 (6)
N3	0.0539 (8)	0.0989 (12)	0.0516 (8)	0.0105 (8)	-0.0062 (6)	0.0049 (8)
O1	0.0414 (5)	0.0590 (6)	0.0362 (4)	-0.0034 (4)	-0.0116 (4)	0.0164 (4)
O2	0.0336 (4)	0.0603 (6)	0.0375 (4)	0.0003 (4)	-0.0141 (3)	0.0121 (4)
O3	0.0472 (5)	0.0499 (5)	0.0639 (6)	-0.0064 (4)	-0.0329 (5)	0.0056 (4)
O4	0.0323 (5)	0.0746 (7)	0.0705 (7)	0.0072 (5)	-0.0034 (5)	0.0157 (6)

Geometric parameters (\AA , $^\circ$)

C1—O1	1.4319 (17)	C5—N1	1.4614 (14)
C1—O2	1.4334 (15)	C6—C7	1.3635 (15)
C1—H1A	0.9700	C6—H6	0.9300
C1—H1B	0.9700	C7—O1	1.3525 (13)
C2—O2	1.3547 (13)	C8—C9	1.3420 (16)
C2—C3	1.3641 (15)	C8—H8	0.9300
C2—C7	1.3850 (16)	C9—C11	1.4342 (19)
C3—C4	1.4068 (14)	C9—C10	1.4388 (16)
C3—H3	0.9300	C10—N2	1.1355 (18)
C4—C5	1.4016 (15)	C11—N3	1.138 (2)
C4—C8	1.4597 (14)	N1—O4	1.2145 (15)
C5—C6	1.3887 (15)	N1—O3	1.2230 (14)
O1—C1—O2	107.04 (9)	C7—C6—H6	122.1
O1—C1—H1A	110.3	C5—C6—H6	122.1
O2—C1—H1A	110.3	O1—C7—C6	128.09 (10)
O1—C1—H1B	110.3	O1—C7—C2	110.03 (10)
O2—C1—H1B	110.3	C6—C7—C2	121.87 (10)
H1A—C1—H1B	108.6	C9—C8—C4	126.91 (10)

O2—C2—C3	128.07 (10)	C9—C8—H8	116.5
O2—C2—C7	109.65 (9)	C4—C8—H8	116.5
C3—C2—C7	122.28 (10)	C8—C9—C11	124.80 (11)
C2—C3—C4	118.30 (10)	C8—C9—C10	119.43 (12)
C2—C3—H3	120.9	C11—C9—C10	115.74 (11)
C4—C3—H3	120.9	N2—C10—C9	179.14 (15)
C5—C4—C3	117.50 (9)	N3—C11—C9	179.09 (15)
C5—C4—C8	121.96 (9)	O4—N1—O3	123.24 (11)
C3—C4—C8	120.12 (9)	O4—N1—C5	118.09 (11)
C6—C5—C4	124.20 (10)	O3—N1—C5	118.67 (10)
C6—C5—N1	115.70 (10)	C7—O1—C1	105.81 (9)
C4—C5—N1	120.10 (10)	C2—O2—C1	105.89 (9)
C7—C6—C5	115.83 (10)		
O2—C2—C3—C4	179.32 (11)	C3—C2—C7—C6	0.79 (18)
C7—C2—C3—C4	-0.78 (17)	C5—C4—C8—C9	-154.85 (11)
C2—C3—C4—C5	0.01 (16)	C3—C4—C8—C9	32.75 (16)
C2—C3—C4—C8	172.74 (10)	C4—C8—C9—C11	8.72 (19)
C3—C4—C5—C6	0.80 (17)	C4—C8—C9—C10	-173.31 (10)
C8—C4—C5—C6	-171.78 (10)	C6—C5—N1—O4	29.91 (16)
C3—C4—C5—N1	-178.10 (9)	C4—C5—N1—O4	-151.10 (12)
C8—C4—C5—N1	9.32 (16)	C6—C5—N1—O3	-148.95 (11)
C4—C5—C6—C7	-0.81 (17)	C4—C5—N1—O3	30.04 (15)
N1—C5—C6—C7	178.14 (10)	C6—C7—O1—C1	-173.03 (12)
C5—C6—C7—O1	-179.34 (11)	C2—C7—O1—C1	7.55 (14)
C5—C6—C7—C2	0.01 (17)	O2—C1—O1—C7	-12.15 (14)
O2—C2—C7—O1	0.17 (14)	C3—C2—O2—C1	172.11 (12)
C3—C2—C7—O1	-179.75 (10)	C7—C2—O2—C1	-7.80 (14)
O2—C2—C7—C6	-179.29 (10)	O1—C1—O2—C2	12.26 (14)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C1—H1B...O1 ⁱ	0.97	2.53	3.2692 (16)	133
C8—H8...O4 ⁱⁱ	0.93	2.52	3.3640 (17)	152

Symmetry codes: (i) $-x, -y+1, -z+2$; (ii) $-x-1, -y+2, -z+1$.

Fig. 1

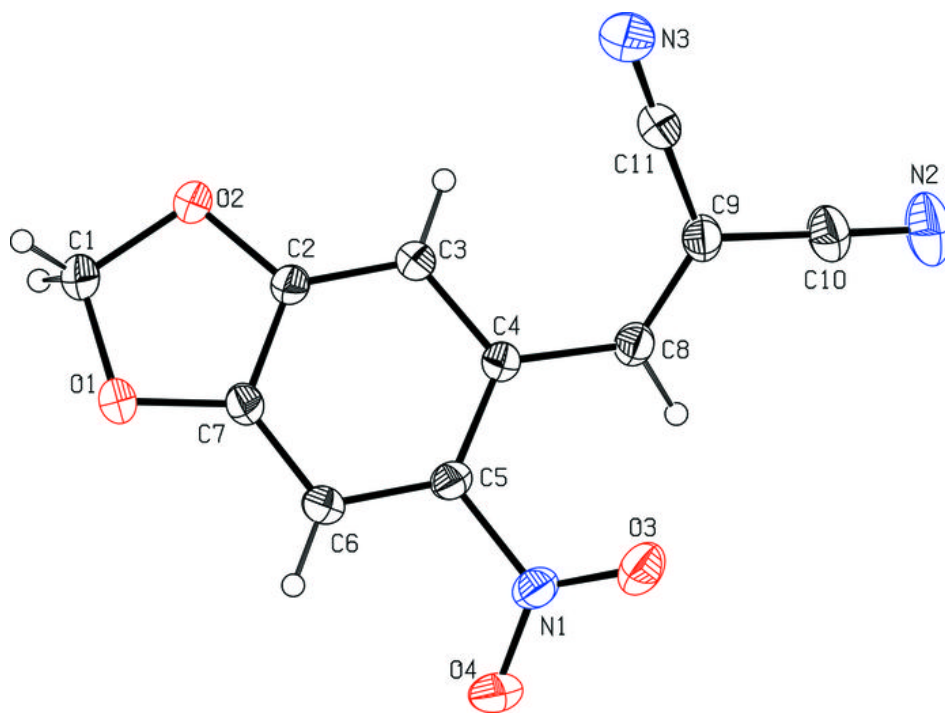


Fig. 2

