

Methyl 2-methyl-3,5-dinitrobenzoate

Abdul Rauf Raza,^a Aisha Saddiqa,^a M. Nawaz Tahir,^{b*}
 Muhammad Danish^a and Mohammad Saeed Iqbal^c

^aDepartment of Chemistry, University of Sargodha, Sargodha, Pakistan, ^bDepartment of Physics, University of Sargodha, Sargodha, Pakistan, and ^cDepartment of Chemistry, Government College University, Lahore, Pakistan
 Correspondence e-mail: dmntahir_uos@yahoo.com

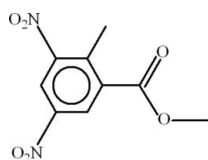
Received 26 December 2009; accepted 27 December 2009

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.041; wR factor = 0.097; data-to-parameter ratio = 9.7.

In the title compound, $\text{C}_9\text{H}_8\text{N}_2\text{O}_6$, the methyl ester group is almost planar (r.m.s. deviation = 0.002 Å) and is oriented at a dihedral angle of 24.27 (16)° with respect to the benzene ring. The nitro groups make dihedral angles of 4.2 (5)° and 60.21 (11)° with the benzene ring. In the crystal, molecules are linked by $\text{C}-\text{H}\cdots\text{O}$ interactions, resulting in zigzag chains.

Related literature

For a related structure, see: Tahir *et al.* (2009).



Experimental

Crystal data

$\text{C}_9\text{H}_8\text{N}_2\text{O}_6$	$V = 1043.30$ (16) Å ³
$M_r = 240.17$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 6.7948$ (5) Å	$\mu = 0.13$ mm ⁻¹
$b = 8.8478$ (8) Å	$T = 296$ K
$c = 17.3539$ (17) Å	$0.30 \times 0.10 \times 0.09$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer	6284 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2005)	1510 independent reflections
$T_{\min} = 0.985$, $T_{\max} = 0.987$	1001 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	156 parameters
$wR(F^2) = 0.097$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{\max} = 0.16$ e Å ⁻³
1510 reflections	$\Delta\rho_{\min} = -0.17$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C9}-\text{H9C}\cdots\text{O2}^i$	0.96	2.56	3.353 (4)	140

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); 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 PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON.

The authors acknowledge the Higher Education Commission, Islamabad, Pakistan, and Bana International, Karachi, Pakistan, for funding the purchase of the diffractometer at GCU, Lahore and for technical support, respectively.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5296).

References

- Bruker (2005). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Tahir, M. N., Raza, A. R., Saddiqa, A., Danish, M. & Saleem, I. (2009). *Acta Cryst.* **E65**, o2819.

supplementary materials

Acta Cryst. (2010). E66, o288 [doi:10.1107/S1600536809055494]

Methyl 2-methyl-3,5-dinitrobenzoate

A. R. Raza, A. Saddiqa, M. N. Tahir, M. Danish and M. S. Iqbal

Comment

Our work is aimed at the synthesis of various isocoumarins and the title compound (I, Fig. 1) is an intermediate for their preparation.

We have reported crystal structures of 2-Methyl-3,5-dinitrobenzoic acid (Tahir *et al.*, 2009) and the title compound is its methyl ester.

In the title compound benzene ring A (C1–C6) is of course planar. The methyl ester B (O2/C7/O1/C8) is also planar with a maximum r. m. s. deviation of 0.0014 Å from the mean square plane. The dihedral angle between A/B is 24.27 (16)°. Two nitro groups C (O3/N1/O4) and D (O5/N2/O6) are oriented at dihedral angles of 60.21 (11)° and 4.22 (51)° respectively, with the benzene ring. The dihedral angle between C/D is 63.24 (25)°. The molecules are stabilized due to intra as well inter-molecular and C–H···O interactions (Table 1, Fig. 2) in the form of zigzag polymeric chains.

Experimental

H₂SO₄ (5 ml) was added as a catalyst to a stirred solution of 2-methyl-3,5-dinitrobenzoic acid (1 g, 4.4 mmol) (Tahir *et al.*, 2009) in MeOH (20 ml) and refluxed for 5 h. The progress of reaction was monitored by TLC. The crystals were immediately obtained upon gradual cooling followed by pouring reaction mixture to beaker. The crude product was filtered and consecutive washing with MeOH and H₂O afforded impure crystals of (I). The recrystallization from CHCl₃ afforded (69.3%) colourless needles of the title compound (I).

Refinement

In the absence of significant anomalous scattering effects, Friedel pairs were merged. The H-atoms were positioned geometrically (C–H = 0.93–0.96 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.2$ for aryl and 1.5 for methyl H atoms.

Figures

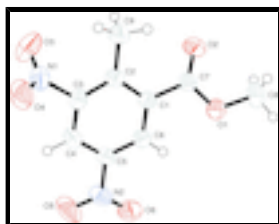


Fig. 1. View of (I) with displacement ellipsoids drawn at the 50% probability level.

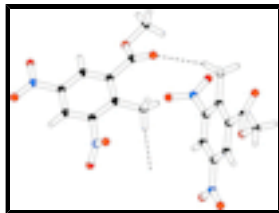


Fig. 2. Partial packing diagram of (I).

Methyl 2-methyl-3,5-dinitrobenzoate

Crystal data

$C_9H_8N_2O_6$

$M_r = 240.17$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 6.7948$ (5) Å

$b = 8.8478$ (8) Å

$c = 17.3539$ (17) Å

$V = 1043.30$ (16) Å³

$Z = 4$

$F(000) = 496$

$D_x = 1.529$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1510 reflections

$\theta = 2.4$ – 28.3°

$\mu = 0.13$ mm⁻¹

$T = 296$ K

Needle, colourless

$0.30 \times 0.10 \times 0.09$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: 7.40 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)

$T_{\min} = 0.985$, $T_{\max} = 0.987$

6284 measured reflections

1510 independent reflections

1001 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -5 \rightarrow 9$

$k = -11 \rightarrow 9$

$l = -23 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.097$

$S = 1.02$

1510 reflections

156 parameters

0 restraints

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 0.0609P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.16$ e Å⁻³

$\Delta\rho_{\min} = -0.17$ e Å⁻³

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.7519 (3)	0.6592 (2)	0.08307 (14)	0.0613 (8)
O2	0.9455 (3)	0.4581 (2)	0.07824 (14)	0.0640 (8)
O3	0.4935 (4)	-0.0440 (3)	0.14759 (15)	0.0822 (10)
O4	0.2279 (3)	0.0187 (2)	0.08784 (14)	0.0704 (9)
O5	0.0268 (4)	0.4613 (3)	0.26197 (17)	0.0929 (10)
O6	0.1892 (3)	0.6626 (3)	0.23914 (14)	0.0731 (9)
N1	0.3765 (4)	0.0489 (3)	0.12346 (13)	0.0495 (8)
N2	0.1635 (3)	0.5275 (3)	0.23353 (14)	0.0552 (10)
C1	0.6122 (3)	0.4298 (3)	0.11981 (14)	0.0356 (8)
C2	0.5898 (3)	0.2738 (3)	0.10750 (14)	0.0348 (8)
C3	0.4175 (4)	0.2112 (3)	0.13733 (14)	0.0388 (8)
C4	0.2759 (4)	0.2888 (3)	0.17786 (15)	0.0417 (9)
C5	0.3090 (4)	0.4397 (3)	0.18916 (15)	0.0393 (8)
C6	0.4714 (4)	0.5114 (3)	0.16018 (15)	0.0414 (9)
C7	0.7890 (4)	0.5130 (3)	0.09141 (16)	0.0403 (9)
C8	0.9151 (5)	0.7524 (3)	0.0570 (3)	0.0850 (16)
C9	0.7325 (4)	0.1820 (3)	0.06173 (17)	0.0491 (10)
H4	0.16360	0.24127	0.19659	0.0500*
H6	0.48749	0.61477	0.16753	0.0497*
H8A	1.02426	0.74060	0.09162	0.1274*
H8B	0.87514	0.85644	0.05607	0.1274*
H8C	0.95366	0.72162	0.00616	0.1274*
H9A	0.83335	0.14382	0.09519	0.0737*
H9B	0.79104	0.24423	0.02263	0.0737*
H9C	0.66471	0.09904	0.03793	0.0737*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0486 (11)	0.0371 (11)	0.0983 (17)	-0.0068 (9)	0.0159 (12)	0.0010 (11)
O2	0.0356 (10)	0.0614 (13)	0.0950 (17)	0.0043 (10)	0.0103 (11)	0.0042 (13)
O3	0.104 (2)	0.0439 (13)	0.0988 (19)	0.0038 (14)	-0.0224 (16)	0.0074 (12)
O4	0.0598 (13)	0.0670 (14)	0.0843 (17)	-0.0270 (11)	-0.0044 (13)	-0.0147 (13)

supplementary materials

O5	0.0706 (16)	0.0951 (18)	0.113 (2)	-0.0172 (15)	0.0572 (16)	-0.0307 (16)
O6	0.0693 (15)	0.0584 (15)	0.0916 (19)	0.0121 (12)	0.0221 (14)	-0.0147 (13)
N1	0.0574 (15)	0.0460 (15)	0.0450 (14)	-0.0120 (13)	0.0060 (12)	-0.0029 (11)
N2	0.0467 (14)	0.0669 (19)	0.0520 (16)	0.0031 (13)	0.0099 (12)	-0.0151 (14)
C1	0.0305 (12)	0.0395 (16)	0.0367 (14)	-0.0004 (11)	-0.0031 (11)	-0.0010 (11)
C2	0.0325 (13)	0.0404 (15)	0.0315 (13)	0.0011 (12)	-0.0033 (11)	0.0000 (11)
C3	0.0438 (15)	0.0372 (15)	0.0355 (14)	-0.0059 (13)	-0.0059 (12)	0.0005 (11)
C4	0.0354 (14)	0.0507 (17)	0.0389 (16)	-0.0069 (13)	0.0014 (12)	0.0003 (13)
C5	0.0311 (13)	0.0474 (16)	0.0395 (15)	0.0006 (12)	0.0022 (10)	-0.0071 (12)
C6	0.0380 (14)	0.0405 (15)	0.0457 (16)	-0.0013 (12)	-0.0032 (12)	-0.0018 (12)
C7	0.0357 (14)	0.0414 (16)	0.0437 (16)	-0.0032 (12)	-0.0005 (12)	-0.0011 (12)
C8	0.066 (2)	0.049 (2)	0.140 (4)	-0.0214 (17)	0.028 (2)	0.010 (2)
C9	0.0468 (15)	0.0458 (16)	0.0547 (19)	0.0022 (13)	0.0062 (15)	-0.0038 (13)

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

O1—C7	1.326 (3)	C2—C9	1.494 (4)
O1—C8	1.454 (4)	C3—C4	1.375 (4)
O2—C7	1.191 (3)	C4—C5	1.368 (4)
O3—N1	1.218 (4)	C5—C6	1.369 (4)
O4—N1	1.214 (3)	C4—H4	0.9300
O5—N2	1.204 (4)	C6—H6	0.9300
O6—N2	1.212 (4)	C8—H8A	0.9600
N1—C3	1.482 (4)	C8—H8B	0.9600
N2—C5	1.474 (4)	C8—H8C	0.9600
C1—C2	1.405 (4)	C9—H9A	0.9600
C1—C6	1.388 (4)	C9—H9B	0.9600
C1—C7	1.493 (4)	C9—H9C	0.9600
C2—C3	1.395 (3)		
C7—O1—C8	116.3 (2)	C1—C6—C5	120.0 (2)
O3—N1—O4	124.7 (3)	O1—C7—O2	123.1 (3)
O3—N1—C3	118.4 (3)	O1—C7—C1	111.4 (2)
O4—N1—C3	116.9 (2)	O2—C7—C1	125.5 (2)
O5—N2—O6	123.9 (3)	C3—C4—H4	122.00
O5—N2—C5	118.4 (3)	C5—C4—H4	122.00
O6—N2—C5	117.7 (2)	C1—C6—H6	120.00
C2—C1—C6	120.9 (2)	C5—C6—H6	120.00
C2—C1—C7	121.4 (2)	O1—C8—H8A	109.00
C6—C1—C7	117.7 (2)	O1—C8—H8B	109.00
C1—C2—C3	115.1 (2)	O1—C8—H8C	109.00
C1—C2—C9	123.0 (2)	H8A—C8—H8B	109.00
C3—C2—C9	121.8 (2)	H8A—C8—H8C	109.00
N1—C3—C2	118.8 (2)	H8B—C8—H8C	110.00
N1—C3—C4	115.8 (2)	C2—C9—H9A	109.00
C2—C3—C4	125.4 (2)	C2—C9—H9B	109.00
C3—C4—C5	116.5 (2)	C2—C9—H9C	109.00
N2—C5—C4	118.6 (2)	H9A—C9—H9B	109.00
N2—C5—C6	119.2 (2)	H9A—C9—H9C	110.00
C4—C5—C6	122.2 (3)	H9B—C9—H9C	109.00

C8—O1—C7—O2	-0.4 (5)	C7—C1—C6—C5	-178.3 (2)
C8—O1—C7—C1	178.9 (3)	C2—C1—C7—O1	157.0 (2)
O3—N1—C3—C2	60.3 (3)	C2—C1—C7—O2	-23.7 (4)
O3—N1—C3—C4	-121.3 (3)	C6—C1—C7—O1	-24.1 (3)
O4—N1—C3—C2	-119.0 (3)	C6—C1—C7—O2	155.2 (3)
O4—N1—C3—C4	59.4 (3)	C1—C2—C3—N1	176.8 (2)
O5—N2—C5—C4	4.3 (4)	C1—C2—C3—C4	-1.4 (4)
O5—N2—C5—C6	-176.2 (3)	C9—C2—C3—N1	0.4 (4)
O6—N2—C5—C4	-175.8 (3)	C9—C2—C3—C4	-177.8 (3)
O6—N2—C5—C6	3.7 (4)	N1—C3—C4—C5	-178.2 (2)
C6—C1—C2—C3	1.1 (3)	C2—C3—C4—C5	0.1 (4)
C6—C1—C2—C9	177.4 (2)	C3—C4—C5—N2	-178.9 (2)
C7—C1—C2—C3	179.9 (2)	C3—C4—C5—C6	1.7 (4)
C7—C1—C2—C9	-3.8 (4)	N2—C5—C6—C1	178.5 (2)
C2—C1—C6—C5	0.6 (4)	C4—C5—C6—C1	-2.0 (4)

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C9—H9C \cdots O2 ⁱ	0.96	2.56	3.353 (4)	140

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

Fig. 1

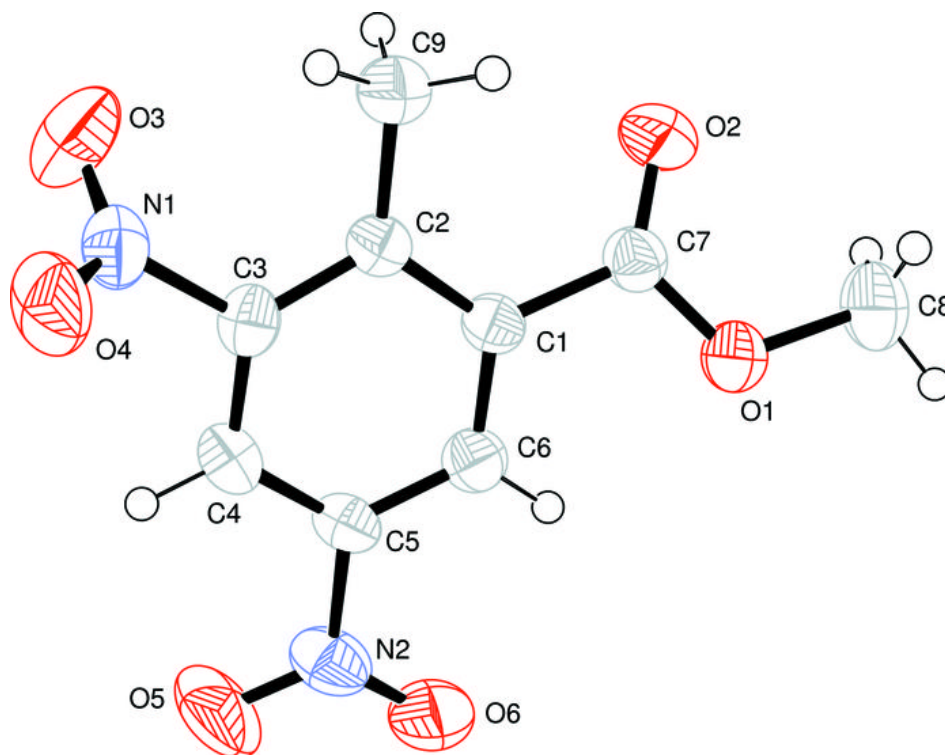


Fig. 2

