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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]

[a]Department of Chemistry, University of Sargodha, Sargodha, Pakistan, [b]Department of Physics, University of Sargodha, Sargodha, Pakistan, and [c]Department of Chemistry, Government College University, Lahore, Pakistan
Correspondence e-mail: dmntahir_uos@yahoo.com

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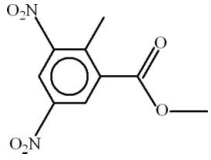
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.097; data-to-parameter ratio = 9.7.

In the title compound, $C_9H_8N_2O_6$, 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 C—H···O interactions, resulting in zigzag chains.

Related literature

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



Experimental

Crystal data

$C_9H_8N_2O_6$
M_r = 240.17
Orthorhombic, $P2_12_12_1$
a = 6.7948 (5) Å
b = 8.8478 (8) Å
c = 17.3539 (17) Å
V = 1043.30 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 296 K
0.30 × 0.10 × 0.09 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
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_{int} = 0.034

Refinement

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

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9C···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*.

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

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Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
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supporting information

Acta Cryst. (2010). E**66**, o288 [https://doi.org/10.1107/S1600536809055494]

Methyl 2-methyl-3,5-dinitrobenzoate

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S1. 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.

S2. Experimental

H_2SO_4 (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 H_2O afforded impure crystals of (I). The recrystalization from $CHCl_3$ afforded (69.3%) colourless needles of the title compound (I).

S3. Refinement

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

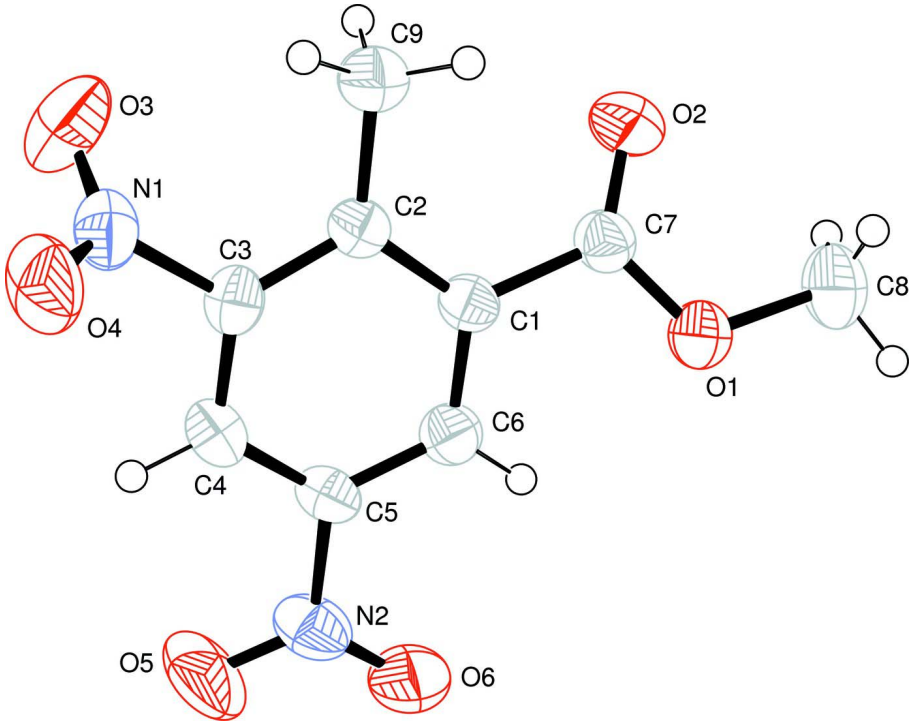

Figure 1

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

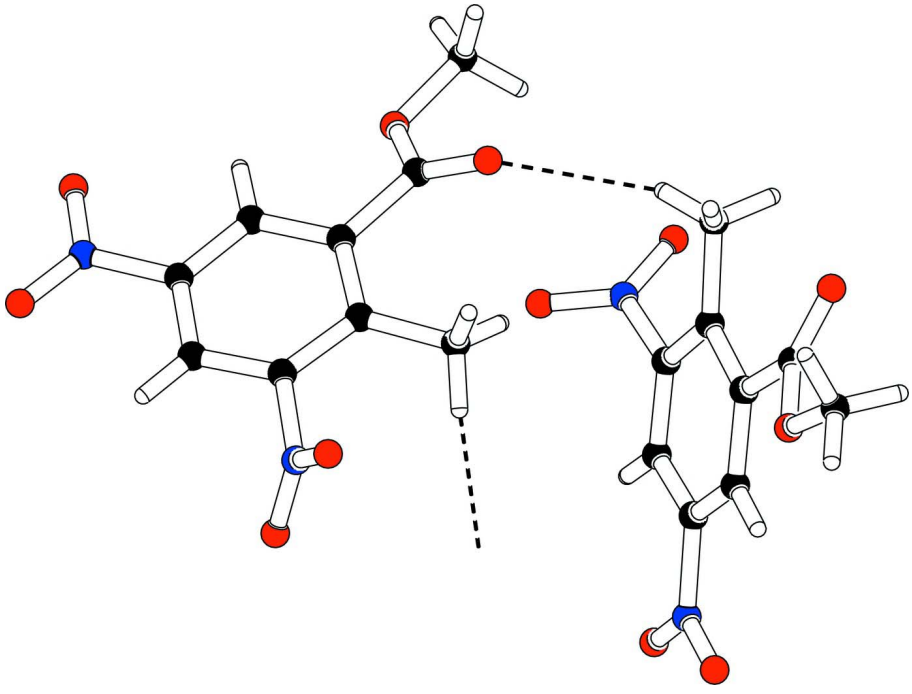

Figure 2

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) Å^3
$Z = 4$
$F(000) = 496$
$D_x = 1.529$ 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 × 0.10 × 0.09 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
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 $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.4°$
$h = -5 \rightarrow 9$
$k = -11 \rightarrow 9$
$l = -23 \rightarrow 21$

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

	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)
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 (Å, º)

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 (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*C*···O2^{i}	0.96	2.56	3.353 (4)	140

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