Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-(2,4-Dinitrophenyl)-3,3-dinitroazetidine

Biao Yan,[a,b] Hai-Xia Ma,[b]* Yin Hu,[b] Yu-Lei Guan[b] and Ji-Rong Song[b]

[a]School of Chemistry and Chemical Engineering, Yulin University, Yulin 719000 Shaanxi, People's Republic of China, and [b]School of Chemical Engineering, Northwest University, Xi'an 710069 Shaanxi, People's Republic of China
Correspondence e-mail: donghuhai@qq.com

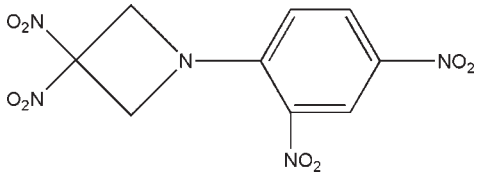
Received 18 November 2009; accepted 20 November 2009

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.118; data-to-parameter ratio = 10.8.

In the title compound, $C_9H_7N_5O_8$, the dihedral angle between the mean plane of the azetidine ring and that of the benzene ring is 26.1 (1)°; the planes of the two nitro groups of the azetidine ring are aligned at 88.7 (1)°.

Related literature

Highly nitrated small-ring heterocycles are good candidates for energetic materials because of the increased performance from the additional energy release upon opening of the strained ring system during decomposition, see: Frumkin *et al.* (1999). Azetidine-based explosives, such as 1,3,3-trinitroazetidine (TNAZ) demonstrate excellent performance, see: Archibald *et al.*, (1990); Hiskey & Coburn (1994*a*,*b*). The title compound is a derivative of 3,3-dinitroazetidine (DNAZ) (Hiskey *et al.*, 1992, 1993), which is a derivative of TNAZ. For the use of DNAZ in the preparation of a variety of solid energetic compounds, see: Ma *et al.* (2009*a*,*b*,*c*); Gao *et al.* (2009).



Experimental

Crystal data

$C_9H_7N_5O_8$
M_r = 313.20
Monoclinic, $P2_1/n$
a = 8.113 (2) Å
b = 10.676 (3) Å
c = 14.398 (4) Å
β = 104.681 (4)°
V = 1206.3 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 293 K
0.31 × 0.26 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: none
5860 measured reflections
2140 independent reflections
1670 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.118
S = 1.20
2140 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We thank the National Natural Science Foundation of China (No. 20603026) and the Natural Science Foundation of Shaanxi Province, China (No. 2009JQ2002) for generously supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2691).

References

Archibald, T. G., Gilardi, R., Baum, K. & George, C. (1990). *J. Org. Chem.* **55**, 2920–2924.
Bruker (2003). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Frumkin, A. E., Churakov, A. M., Strelenko, Y. A., Kachala, V. V. & Tartakkovsky, V. A. (1999). *Org. Lett.* **1**, 721–724.
Gao, R., Ma, H. X., Yan, B., Song, J. R. & Wang, Y. H. (2009). *Chem. J. Chin. Univ.* **30**, 577–582.
Hiskey, M. A. & Coburn, M. D. (1994*a*). US Patent No. 5 336 784.
Hiskey, M. A. & Coburn, M. D. (1994*b*). *Chem. Abstr.* **121**, 300750s.
Hiskey, M. A., Coburn, M. D., Mitchell, M. A. & Benicewicz, B. C. (1992). *J. Heterocycl. Chem.* **29**, 1855–1856.
Hiskey, M. A., Stincipher, M. M. & Brown, J. E. (1993). *J. Energ. Mater.* **11**, 157–165.
Ma, H. X., Yan, B., Li, Z. N., Guan, Y. L., Song, J. R., Xu, K. Z. & Hu, R. Z. (2009*a*). *J. Hazard. Mater.* **169**, 1068–1073.
Ma, H. X., Yan, B., Li, Z. N., Song, J. R. & Hu, R. Z. (2009*b*). *J. Therm. Anal. Calorim.* **95**, 437–444.
Ma, H. X., Yan, B., Song, J. R., Lü, X. Q. & Wang, L. J. (2009*c*). *Chem. J. Chin. Univ.* **30**, 371–381.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2009). E**65**, o3215 [**doi:10.1107/S1600536809049861**]

1-(2,4-Dinitrophenyl)-3,3-dinitroazetidine

B. Yan, H.-X. Ma, Y. Hu, Y.-L. Guan and J.-R. Song

Comment

Highly nitrated small-ring heterocycles are good candidates for energetic materials because of the increased performance from the additional energy release upon opening of the strained ring system during decomposition (Frumkin *et al.*, 1999). Azetidine-based explosives, such as 1,3,3-trinitroazetidine (TNAZ) (Archibald *et al.*, 1990; Hiskey *et al.*, 1994*a*,*b*) demonstrate excellent performance partly because of the high strain associated with the four-membered ring. As one of the important derivates of TNAZ, 3,3-dinitroazetidine (DNAZ) (Hiskey *et al.*, 1992; Hiskey *et al.*, 1993) can prepare a variety of solid energetic compounds (Ma *et al.*, 2009*a*,*b*,*c*; Gao *et al.*, 2009). The title compound (I) is a DNAZ derivates. The dihedral angle between the azetidine ring and benzene ring is 26.1° and the planes of two nitryl of azetidine ring is 88.7°. There are no important intermolecular contacts in the crystal structure.

Experimental

A solution of DNAZ (0.2353 g, 1.6 mmol), 2,4-dinitrochlorobenzene (0.33 ml, 1.6 mmol), and $NaHCO_3$ (0.28 g, 3.2 mmol) in dichloromethane (30.0 ml) was stirred under reflux for 20 h. The reaction mixture was concentrated in vacuo, water (30 ml) was added, and the unstable mixture was extracted rapidly with dichloromethane (3 * 15 ml). The combined extracts were dried ($MgSO_4$,), the solvent was concentrated *in vacuo*, and ethanol (20 ml) was added, and the residue was filtrated to give the yellow compound in 30% yield. Crystals were obtained from dichloromethane, by slow evaporation at room temperature. Elemental analysis calculated for $C_9H_7N_5O_8$: C 34.61, N 22.36, H 2.253%; found: C 34.61, N 22.22, H 2.249%. IR (KBr, cm^{-1}): 3100.29, 1585.18, 1526.85, 1335.18, 1304.76, 869.25, 820.72.

Refinement

H atoms were placed at calculated idealized positions and refined using a riding model, with C—H distances in the range 0.93–0.97 Å.

Figures

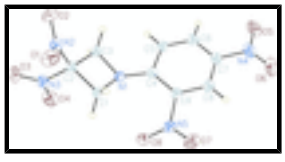


Fig. 1. The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as spheres of arbitrary radius.

1-(2,4-Dinitrophenyl)-3,3-dinitroazetidine

Crystal data

$C_9H_7N_5O_8$	$F(000) = 640$
$M_r = 313.20$	$D_x = 1.724$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 1904 reflections
$a = 8.113$ (2) Å	$\theta = 2.4$–$26.0°$
$b = 10.676$ (3) Å	$\mu = 0.15$ mm^{-1}
$c = 14.398$ (4) Å	$T = 293$ K
$\beta = 104.681$ (4)°	Block, yellow
$V = 1206.3$ (6) Å^3	0.31 × 0.26 × 0.20 mm
$Z = 4$	

Data collection

Bruker APEXII diffractometer	1670 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.019$
graphite	$\theta_{max} = 25.1°$, $\theta_{min} = 2.4°$
φ and ω scans	$h = -9\rightarrow9$
5860 measured reflections	$k = -11\rightarrow12$
2140 independent reflections	$l = -17\rightarrow17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.118$	H-atom parameters constrained
$S = 1.20$	$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 0.0921P]$ where $P = (F_o^2 + 2F_c^2)/3$
2140 reflections	$(\Delta/\sigma)_{max} = 0.028$
199 parameters	$\Delta\rho_{max} = 0.21$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	0.56725 (18)	0.14099 (15)	0.95776 (10)	0.0576 (4)
N1	0.06769 (18)	0.16834 (14)	0.89752 (10)	0.0360 (4)
C4	−0.0303 (2)	0.25527 (16)	0.92696 (11)	0.0324 (4)
O8	−0.18514 (19)	0.22095 (15)	0.72839 (10)	0.0566 (4)
N2	0.4618 (2)	0.14859 (15)	0.88135 (11)	0.0419 (4)
C9	−0.1501 (2)	0.33688 (17)	0.86745 (11)	0.0334 (4)
N3	0.3038 (2)	−0.04265 (16)	0.84420 (11)	0.0435 (4)
N5	−0.20374 (19)	0.32296 (17)	0.76316 (11)	0.0429 (4)
C1	0.1375 (2)	0.16202 (18)	0.81278 (12)	0.0376 (4)
H1A	0.1660	0.2430	0.7906	0.045*
H1B	0.0689	0.1131	0.7602	0.045*
C3	0.2168 (2)	0.10713 (18)	0.96128 (12)	0.0384 (4)
H3B	0.1908	0.0288	0.9886	0.046*
H3A	0.2834	0.1618	1.0105	0.046*
N4	−0.2936 (2)	0.53426 (18)	1.04331 (15)	0.0556 (5)
C7	−0.2070 (2)	0.43720 (19)	1.00353 (13)	0.0411 (5)
O3	0.4390 (2)	−0.07976 (16)	0.83333 (12)	0.0679 (5)
C6	−0.0999 (2)	0.35558 (19)	1.06406 (13)	0.0441 (5)
H6	−0.0866	0.3606	1.1300	0.053*
C2	0.2905 (2)	0.09108 (16)	0.87430 (12)	0.0340 (4)
C8	−0.2340 (2)	0.42800 (18)	0.90514 (13)	0.0388 (4)
H8	−0.3082	0.4828	0.8648	0.047*
O1	0.4830 (2)	0.19814 (17)	0.80972 (11)	0.0655 (5)
O7	−0.2721 (2)	0.41195 (17)	0.71504 (11)	0.0671 (5)
O6	−0.3804 (2)	0.61021 (15)	0.98923 (15)	0.0718 (5)
O4	0.1762 (2)	−0.10369 (15)	0.83337 (12)	0.0678 (5)
C5	−0.0131 (2)	0.26685 (19)	1.02664 (12)	0.0407 (5)
H5	0.0596	0.2125	1.0683	0.049*
O5	−0.2740 (3)	0.5369 (2)	1.13090 (13)	0.0877 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0396 (8)	0.0687 (11)	0.0560 (9)	−0.0018 (7)	−0.0034 (7)	0.0035 (7)
N1	0.0336 (8)	0.0430 (9)	0.0315 (7)	0.0082 (7)	0.0083 (6)	0.0019 (6)
C4	0.0289 (9)	0.0349 (10)	0.0344 (9)	−0.0039 (7)	0.0098 (7)	−0.0011 (7)
O8	0.0486 (9)	0.0709 (11)	0.0446 (8)	0.0096 (8)	0.0012 (6)	−0.0167 (7)
N2	0.0366 (9)	0.0427 (9)	0.0457 (9)	0.0007 (7)	0.0092 (7)	0.0018 (7)
C9	0.0295 (9)	0.0389 (10)	0.0311 (8)	−0.0015 (8)	0.0062 (7)	−0.0005 (7)

N3	0.0490 (10)	0.0384 (9)	0.0433 (9)	0.0025 (8)	0.0123 (7)	−0.0007 (7)
N5	0.0306 (8)	0.0574 (11)	0.0387 (9)	0.0037 (8)	0.0050 (7)	0.0027 (8)
C1	0.0342 (10)	0.0451 (11)	0.0338 (9)	0.0067 (8)	0.0089 (7)	0.0017 (8)
C3	0.0375 (10)	0.0404 (11)	0.0364 (9)	0.0059 (8)	0.0075 (7)	0.0039 (8)
N4	0.0443 (10)	0.0497 (12)	0.0779 (13)	−0.0058 (9)	0.0253 (9)	−0.0222 (10)
C7	0.0352 (10)	0.0414 (11)	0.0497 (11)	−0.0052 (8)	0.0164 (8)	−0.0131 (9)
O3	0.0609 (10)	0.0625 (11)	0.0811 (11)	0.0189 (8)	0.0196 (8)	−0.0179 (8)
C6	0.0430 (11)	0.0556 (13)	0.0356 (9)	−0.0058 (9)	0.0135 (8)	−0.0069 (9)
C2	0.0320 (9)	0.0330 (10)	0.0359 (9)	0.0019 (7)	0.0068 (7)	0.0003 (7)
C8	0.0309 (9)	0.0364 (10)	0.0483 (10)	−0.0013 (8)	0.0086 (8)	0.0015 (8)
O1	0.0474 (9)	0.0908 (13)	0.0596 (9)	−0.0145 (8)	0.0159 (7)	0.0171 (8)
O7	0.0700 (11)	0.0777 (12)	0.0478 (8)	0.0224 (9)	0.0043 (7)	0.0165 (8)
O6	0.0689 (11)	0.0460 (10)	0.1116 (14)	0.0094 (9)	0.0432 (10)	−0.0049 (10)
O4	0.0725 (11)	0.0498 (10)	0.0845 (11)	−0.0217 (8)	0.0263 (9)	−0.0118 (8)
C5	0.0397 (10)	0.0480 (12)	0.0339 (10)	0.0030 (9)	0.0083 (8)	0.0032 (8)
O5	0.0877 (13)	0.1094 (16)	0.0693 (11)	0.0103 (11)	0.0260 (10)	−0.0450 (11)

Geometric parameters (Å, °)

O2—N2	1.2133 (19)	C1—C2	1.530 (2)
N1—C4	1.358 (2)	C1—H1A	0.9700
N1—C1	1.471 (2)	C1—H1B	0.9700
N1—C3	1.473 (2)	C3—C2	1.528 (3)
C4—C5	1.412 (2)	C3—H3B	0.9700
C4—C9	1.420 (2)	C3—H3A	0.9700
O8—N5	1.224 (2)	N4—O6	1.217 (2)
N2—O1	1.209 (2)	N4—O5	1.231 (2)
N2—C2	1.499 (2)	N4—C7	1.449 (3)
C9—C8	1.375 (3)	C7—C6	1.375 (3)
C9—N5	1.461 (2)	C7—C8	1.381 (3)
N3—O4	1.199 (2)	C6—C5	1.370 (3)
N3—O3	1.213 (2)	C6—H6	0.9300
N3—C2	1.504 (2)	C8—H8	0.9300
N5—O7	1.223 (2)	C5—H5	0.9300
C4—N1—C1	132.01 (15)	C2—C3—H3B	113.9
C4—N1—C3	124.20 (14)	N1—C3—H3A	113.9
C1—N1—C3	93.91 (13)	C2—C3—H3A	113.9
N1—C4—C5	117.53 (15)	H3B—C3—H3A	111.1
N1—C4—C9	126.61 (15)	O6—N4—O5	122.96 (19)
C5—C4—C9	115.86 (16)	O6—N4—C7	118.91 (19)
O1—N2—O2	125.62 (17)	O5—N4—C7	118.1 (2)
O1—N2—C2	116.82 (15)	C6—C7—C8	121.05 (18)
O2—N2—C2	117.57 (16)	C6—C7—N4	119.64 (18)
C8—C9—C4	121.83 (16)	C8—C7—N4	119.31 (18)
C8—C9—N5	115.41 (15)	C5—C6—C7	119.63 (17)
C4—C9—N5	122.54 (16)	C5—C6—H6	120.2
O4—N3—O3	125.76 (19)	C7—C6—H6	120.2
O4—N3—C2	115.52 (16)	N2—C2—N3	105.99 (14)
O3—N3—C2	118.72 (17)	N2—C2—C3	116.55 (14)

O7—N5—O8	123.01 (16)	N3—C2—C3	114.47 (15)
O7—N5—C9	118.51 (17)	N2—C2—C1	116.00 (15)
O8—N5—C9	118.39 (15)	N3—C2—C1	114.20 (14)
N1—C1—C2	88.22 (12)	C3—C2—C1	89.46 (13)
N1—C1—H1A	113.9	C9—C8—C7	119.30 (17)
C2—C1—H1A	113.9	C9—C8—H8	120.3
N1—C1—H1B	113.9	C7—C8—H8	120.4
C2—C1—H1B	113.9	C6—C5—C4	122.15 (17)
H1A—C1—H1B	111.1	C6—C5—H5	118.9
N1—C3—C2	88.23 (12)	C4—C5—H5	118.9
N1—C3—H3B	113.9		
C1—N1—C4—C5	−151.31 (18)	O1—N2—C2—C3	−140.71 (18)
C3—N1—C4—C5	−15.0 (3)	O2—N2—C2—C3	39.7 (2)
C1—N1—C4—C9	28.7 (3)	O1—N2—C2—C1	−37.3 (2)
C3—N1—C4—C9	165.05 (17)	O2—N2—C2—C1	143.13 (16)
N1—C4—C9—C8	−175.18 (17)	O4—N3—C2—N2	−178.93 (15)
C5—C4—C9—C8	4.9 (3)	O3—N3—C2—N2	1.3 (2)
N1—C4—C9—N5	10.4 (3)	O4—N3—C2—C3	51.2 (2)
C5—C4—C9—N5	−169.55 (16)	O3—N3—C2—C3	−128.56 (18)
C8—C9—N5—O7	23.2 (2)	O4—N3—C2—C1	−50.0 (2)
C4—C9—N5—O7	−162.06 (18)	O3—N3—C2—C1	130.29 (18)
C8—C9—N5—O8	−153.55 (17)	N1—C3—C2—N2	122.10 (16)
C4—C9—N5—O8	21.2 (2)	N1—C3—C2—N3	−113.44 (15)
C4—N1—C1—C2	148.25 (19)	N1—C3—C2—C1	3.06 (14)
C3—N1—C1—C2	3.19 (14)	N1—C1—C2—N2	−122.59 (15)
C4—N1—C3—C2	−152.23 (17)	N1—C1—C2—N3	113.68 (16)
C1—N1—C3—C2	−3.19 (14)	N1—C1—C2—C3	−3.07 (14)
O6—N4—C7—C6	175.89 (19)	C4—C9—C8—C7	−2.9 (3)
O5—N4—C7—C6	−3.2 (3)	N5—C9—C8—C7	171.93 (16)
O6—N4—C7—C8	−4.3 (3)	C6—C7—C8—C9	−1.1 (3)
O5—N4—C7—C8	176.56 (19)	N4—C7—C8—C9	179.16 (17)
C8—C7—C6—C5	2.7 (3)	C7—C6—C5—C4	−0.4 (3)
N4—C7—C6—C5	−177.53 (18)	N1—C4—C5—C6	176.83 (18)
O1—N2—C2—N3	90.61 (19)	C9—C4—C5—C6	−3.2 (3)
O2—N2—C2—N3	−88.97 (19)		

Fig. 1