Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3,5-Bis(2,4-dinitrophenyl)-4-nitro-1*H*-pyrazole acetone monosolvate

Logesh Mathivathanan

Deparment of Chemistry, University of Puerto Rico – Rio Piedras, San Juan, PR 00936, USA
Correspondence e-mail: mathivathanan.logesh@gmail.com

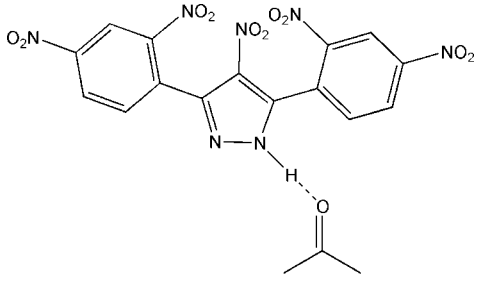
Received 17 October 2011; accepted 10 January 2012

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.064; wR factor = 0.202; data-to-parameter ratio = 15.2.

The title structure, $C_{15}H_7N_7O_{10}\cdot C_3H_6O$, was prepared by pentanitration of 3,5-diphenyl-1*H*-pyrazole. The proton attached to a pyrazole N atom forms a hydrogen bond with the O atom of the acetone solvent molecule, owing to the NO_2 enhanced acidity of the proton. The NO_2 group on the phenyl C atom is twisted by 33.9 (2)° from coplanarity with the ring in order to avoid a short intramolecular O···O contact with an O atom of an adjacent pyrazole-bonded NO_2 group.

Related literature

For the nitration of 1*H*-pyrazole, see: Maresca *et al.* (1997). For the crystal structure of 3,5-diphenyl-1*H*-pyrazole, which shows a hydrogen-bonded tetrameric structure, see: Raptis *et al.* (1993). For a crystallographic and *ab initio* study of 1*H*-pyrazoles, see: Foces-Foces *et al.* (2000).



Experimental

Crystal data

$C_{15}H_7N_7O_{10}\cdot C_3H_6O$
M_r = 503.35
Monoclinic, $P2_1/c$
a = 14.886 (10) Å
b = 7.678 (5) Å
c = 19.801 (13) Å
β = 104.944 (9)°
V = 2187 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 298 K
0.31 × 0.19 × 0.18 mm

Data collection

Bruker SMART 1K CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.836, T_{max} = 0.977
15182 measured reflections
5041 independent reflections
2703 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.202
S = 1.03
5041 reflections
332 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O11^{i}	0.92 (3)	1.87 (4)	2.786 (4)	177 (3)

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

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); 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*.

The author thanks IFN-EPSCoR at the University of Puerto Rico for a graduate fellowship and Dr Raphael G. Raptis for his comments and for the use of X-ray facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QK2027).

References

Bruker (2005). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Foces-Foces, C., Alkorta, I. & Elguero, J. (2000). *Acta Cryst.* B**56**, 1018–1028.
Maresca, K. P., Rose, D. J. & Zubieta, J. (1997). *Inorg. Chim. Acta*, **260**, 83–88.
Raptis, R. G., Staples, R. J., King, C. & Fackler, J. P. (1993). *Acta Cryst.* C**49**, 1716–1719.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2012). E**68**, o411 [**doi:10.1107/S1600536812001146**]

3,5-Bis(2,4-dinitrophenyl)-4-nitro-1*H*-pyrazole acetone monosolvate

L. Mathivathanan

Comment

Aromatic electrophilic nitration (Maresca *et al.*, 1997) of 3,5-diphenyl-1*H*-pyrazole using nitration mixture (H_2SO_4/HNO_3) produces the title compound, 3,5-bis-(2,4-dinitrophenyl)-4-nitro-1*H*-pyrazole. The crystal structure of the parent 3,5-diphenyl-1*H*-pyrazole is a H-bonded tetrameric structure (Raptis *et al.*, 1993), while the title compound (I) is not. Poly-nitration, in addition to a H-bonding to the solvent acetone molecule prevents tetramer formation in (I) (Fig. 1). H-bonding induced supramolecular network formation in 1*H*-pyrazoles has been summarized by Foces-Foces *et al.* (2000).

An intermolecular dipole-dipole interaction makes N4 and O2(1-*x*, *y*-1/2, 1/2-*z*) lie at 2.89 Å. In (I), all the NO_2-groups are coplanar or nearly coplanar to their carrier rings, except the one attached to C5, which is twisted by 33.9 (2) relative to the phenyl ring in order to avoid a short intramolecular contact with O2.

Experimental

For a general procedure for nitration of pyrazole, see Maresca *et al.* (1997). A flask containing 5 ml of conc. H_2SO_4 and 5 ml HNO_3 kept in an ice bath was charged with 3,5-diphenyl-1*H*-pyrazole (97%, Aldrich; 2.0 g, 9.07 mmol) followed by the addition of 10 ml of H_2SO_4. The mixture was heated at 110° C for 2 days. After conventional neutralization and extractions, several colourless crystals of the title compound (I) were obtained from acetone.

Refinement

All non-hydrogen atoms were refined anisotropically. Most H-atoms were positioned geometrically (C—H = 0.93 and 0.96 Å) and treated as riding (U_{iso}(H) = 1.2U_{eq}(C)). The pyrazole nitrogen H2A was located in a difference Fourier map and was then fully refined.

Figures

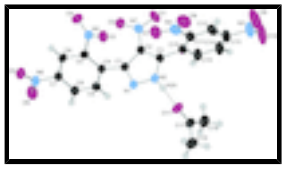


Fig. 1. Molecular structure of the title compound (I) showing 30% thermal ellipsoids and atom labeling scheme. The symmetry transformation for the shown acetone molecule is *x*, 1/2-*y*, *z*-1/2.

3,5-Bis(2,4-dinitrophenyl)-4-nitro-1*H*-pyrazole acetone monosolvate

Crystal data

$C_{15}H_7N_7O_{10}·C_3H_6O$ $F(000) = 1032$

M_r = 503.35	D_x = 1.529 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 5811 reflections
a = 14.886 (10) Å	θ = 2.1–27.1°
b = 7.678 (5) Å	μ = 0.13 mm^{-1}
c = 19.801 (13) Å	T = 298 K
β = 104.944 (9)°	Polygon, colourless
V = 2187 (2) Å^3	0.31 × 0.19 × 0.18 mm
Z = 4	

Data collection

Bruker SMART 1K CCD diffractometer	5041 independent reflections
Radiation source: fine-focus sealed tube	2703 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.068
φ and ω scans	θ_{max} = 28.0°, θ_{min} = 2.1°
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	h = −19→18
T_{min} = 0.836, T_{max} = 0.977	k = −10→8
15182 measured reflections	l = −25→25

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.064	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.202	$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 1.6838P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(\Delta/\sigma)_{max}$ = 0.005
5041 reflections	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
332 parameters	$\Delta\rho_{min}$ = −0.27 e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0141 (17)

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}
O1	0.47956 (18)	−0.0956 (4)	0.26917 (13)	0.0968 (10)
O2	0.59247 (15)	−0.0052 (4)	0.22802 (11)	0.0746 (7)
O3	0.55406 (17)	−0.1803 (3)	0.08688 (13)	0.0730 (7)
O4	0.70324 (18)	−0.1641 (3)	0.12926 (15)	0.0868 (8)
O5	0.82468 (17)	0.3068 (4)	0.00361 (16)	0.0910 (9)
O6	0.7904 (2)	0.5619 (4)	0.03522 (18)	0.1034 (10)
O7	0.3592 (2)	−0.3312 (4)	0.12047 (15)	0.0919 (8)
O8	0.2556 (2)	−0.5123 (4)	0.13596 (16)	0.1052 (10)
O9	0.0670 (4)	−0.3824 (9)	0.2888 (3)	0.205 (3)
O10	0.0655 (3)	−0.1292 (9)	0.3325 (2)	0.187 (3)
O11	0.13846 (15)	0.4236 (3)	0.49406 (14)	0.0766 (7)
N1	0.38256 (16)	0.1537 (3)	0.05753 (13)	0.0565 (6)
N2	0.31564 (17)	0.0836 (4)	0.08520 (13)	0.0575 (7)
N3	0.0923 (3)	−0.2335 (10)	0.2962 (2)	0.1284 (19)
N4	0.2938 (2)	−0.3698 (4)	0.14388 (16)	0.0764 (8)
N5	0.6270 (2)	−0.1003 (3)	0.10191 (14)	0.0612 (7)
N6	0.77797 (18)	0.4055 (4)	0.02940 (16)	0.0678 (7)
N7	0.50947 (19)	−0.0255 (4)	0.22360 (13)	0.0632 (7)
C1	0.46197 (19)	0.1219 (4)	0.10473 (14)	0.0471 (6)
C2	0.44426 (18)	0.0326 (4)	0.16222 (14)	0.0490 (7)
C3	0.34937 (19)	0.0095 (4)	0.14748 (14)	0.0509 (7)
C4	0.54864 (18)	0.1890 (4)	0.09021 (13)	0.0471 (6)
C5	0.62536 (19)	0.0882 (4)	0.08719 (14)	0.0480 (6)
C6	0.70118 (19)	0.1549 (4)	0.06789 (15)	0.0531 (7)
H6	0.7512	0.0847	0.0656	0.064*
C7	0.69967 (19)	0.3305 (4)	0.05218 (15)	0.0521 (7)
C8	0.6277 (2)	0.4380 (4)	0.05695 (16)	0.0563 (7)
H8	0.6295	0.5564	0.0474	0.068*
C9	0.5529 (2)	0.3668 (4)	0.07611 (15)	0.0535 (7)
H9	0.5041	0.4388	0.0798	0.064*
C10	0.2870 (2)	−0.0633 (5)	0.18751 (15)	0.0578 (8)
C11	0.2586 (2)	−0.2379 (5)	0.18530 (16)	0.0624 (8)
C12	0.1955 (2)	−0.2936 (6)	0.22124 (18)	0.0798 (11)
H12	0.1764	−0.4093	0.2193	0.096*
C13	0.1618 (2)	−0.1736 (7)	0.25983 (19)	0.0853 (13)
C14	0.1888 (3)	−0.0032 (7)	0.2649 (2)	0.0913 (13)
H14	0.1658	0.0744	0.2924	0.110*
C15	0.2510 (3)	0.0513 (6)	0.2283 (2)	0.0812 (11)
H15	0.2694	0.1674	0.2310	0.097*
C16	0.0075 (3)	0.2910 (6)	0.4196 (2)	0.0893 (12)
H16A	0.0173	0.3761	0.3867	0.134*
H16B	−0.0549	0.3008	0.4244	0.134*

H16C	0.0168	0.1764	0.4032	0.134*
C17	0.0743 (2)	0.3214 (4)	0.48844 (18)	0.0609 (8)
C18	0.0603 (3)	0.2265 (6)	0.5498 (2)	0.0834 (11)
H18A	0.0700	0.1042	0.5444	0.125*
H18B	−0.0019	0.2454	0.5536	0.125*
H18C	0.1038	0.2681	0.5913	0.125*
H2A	0.256 (2)	0.082 (5)	0.0567 (18)	0.075 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0783 (17)	0.142 (3)	0.0701 (16)	−0.0068 (17)	0.0195 (13)	0.0425 (16)
O2	0.0506 (13)	0.108 (2)	0.0623 (13)	0.0001 (12)	0.0096 (10)	0.0091 (12)
O3	0.0783 (16)	0.0507 (13)	0.1029 (18)	−0.0055 (12)	0.0467 (14)	−0.0059 (12)
O4	0.0821 (17)	0.0677 (16)	0.114 (2)	0.0257 (14)	0.0310 (15)	0.0248 (14)
O5	0.0710 (16)	0.0891 (19)	0.131 (2)	0.0153 (14)	0.0578 (16)	0.0194 (17)
O6	0.100 (2)	0.0686 (18)	0.162 (3)	−0.0261 (16)	0.069 (2)	−0.0075 (18)
O7	0.108 (2)	0.0742 (18)	0.106 (2)	−0.0130 (16)	0.0497 (18)	−0.0134 (15)
O8	0.124 (2)	0.0762 (19)	0.103 (2)	−0.0379 (18)	0.0081 (18)	−0.0121 (15)
O9	0.189 (5)	0.263 (7)	0.197 (5)	−0.123 (5)	0.111 (4)	0.003 (4)
O10	0.159 (4)	0.299 (7)	0.145 (4)	−0.057 (4)	0.116 (3)	−0.024 (4)
O11	0.0555 (13)	0.0701 (15)	0.0989 (18)	−0.0122 (12)	0.0104 (12)	0.0034 (13)
N1	0.0487 (13)	0.0669 (16)	0.0573 (14)	0.0051 (12)	0.0197 (11)	0.0084 (12)
N2	0.0440 (13)	0.0720 (18)	0.0573 (14)	0.0031 (12)	0.0145 (12)	0.0073 (12)
N3	0.082 (3)	0.223 (6)	0.088 (3)	−0.044 (3)	0.036 (2)	0.024 (3)
N4	0.085 (2)	0.069 (2)	0.0689 (18)	−0.0151 (17)	0.0088 (16)	0.0013 (15)
N5	0.0655 (17)	0.0499 (15)	0.0749 (17)	0.0105 (14)	0.0305 (14)	0.0040 (12)
N6	0.0544 (15)	0.069 (2)	0.0849 (19)	−0.0030 (14)	0.0275 (14)	0.0056 (15)
N7	0.0565 (15)	0.0789 (19)	0.0539 (14)	−0.0019 (13)	0.0134 (12)	0.0097 (13)
C1	0.0482 (15)	0.0452 (15)	0.0502 (14)	0.0015 (12)	0.0168 (12)	−0.0008 (11)
C2	0.0481 (15)	0.0528 (17)	0.0472 (14)	0.0007 (12)	0.0143 (12)	0.0030 (12)
C3	0.0504 (16)	0.0543 (17)	0.0508 (15)	0.0001 (13)	0.0182 (12)	0.0013 (12)
C4	0.0461 (14)	0.0479 (15)	0.0485 (14)	0.0028 (12)	0.0140 (12)	−0.0001 (11)
C5	0.0493 (15)	0.0420 (15)	0.0543 (15)	0.0060 (12)	0.0163 (12)	0.0016 (12)
C6	0.0470 (15)	0.0532 (17)	0.0608 (17)	0.0090 (13)	0.0167 (13)	0.0000 (13)
C7	0.0443 (15)	0.0521 (17)	0.0617 (17)	−0.0024 (13)	0.0171 (13)	−0.0002 (13)
C8	0.0584 (17)	0.0437 (15)	0.0699 (18)	0.0006 (14)	0.0224 (15)	−0.0004 (13)
C9	0.0545 (16)	0.0461 (16)	0.0637 (17)	0.0062 (13)	0.0221 (14)	0.0014 (13)
C10	0.0495 (16)	0.070 (2)	0.0552 (16)	−0.0024 (15)	0.0162 (13)	0.0050 (14)
C11	0.0522 (17)	0.075 (2)	0.0559 (17)	−0.0110 (16)	0.0071 (14)	0.0053 (15)
C12	0.064 (2)	0.103 (3)	0.067 (2)	−0.030 (2)	0.0062 (17)	0.015 (2)
C13	0.058 (2)	0.140 (4)	0.062 (2)	−0.020 (2)	0.0228 (17)	0.011 (2)
C14	0.078 (3)	0.129 (4)	0.080 (3)	−0.006 (3)	0.044 (2)	−0.004 (2)
C15	0.079 (2)	0.093 (3)	0.085 (2)	−0.003 (2)	0.047 (2)	−0.007 (2)
C16	0.071 (2)	0.094 (3)	0.094 (3)	−0.009 (2)	0.006 (2)	−0.009 (2)
C17	0.0443 (16)	0.0538 (18)	0.084 (2)	0.0033 (14)	0.0152 (15)	−0.0014 (15)
C18	0.070 (2)	0.090 (3)	0.094 (3)	−0.002 (2)	0.028 (2)	0.006 (2)

Geometric parameters (Å, °)

O1—N7	1.228 (3)	C4—C9	1.398 (4)
O2—N7	1.226 (3)	C5—C6	1.380 (4)
O3—N5	1.216 (3)	C6—C7	1.382 (4)
O4—N5	1.226 (3)	C6—H6	0.9300
O5—N6	1.225 (4)	C7—C8	1.375 (4)
O6—N6	1.216 (4)	C8—C9	1.378 (4)
O7—N4	1.218 (4)	C8—H8	0.9300
O8—N4	1.224 (4)	C9—H9	0.9300
O9—N3	1.200 (8)	C10—C15	1.391 (5)
O10—N3	1.209 (7)	C10—C11	1.402 (5)
O11—C17	1.219 (4)	C11—C12	1.385 (5)
N1—C1	1.327 (4)	C12—C13	1.372 (6)
N1—N2	1.365 (3)	C12—H12	0.9300
N2—C3	1.333 (4)	C13—C14	1.365 (6)
N2—H2A	0.92 (3)	C14—C15	1.380 (5)
N3—C13	1.480 (5)	C14—H14	0.9300
N4—C11	1.481 (5)	C15—H15	0.9300
N5—C5	1.476 (4)	C16—C17	1.484 (5)
N6—C7	1.471 (4)	C16—H16A	0.9600
N7—C2	1.418 (4)	C16—H16B	0.9600
C1—C2	1.411 (4)	C16—H16C	0.9600
C1—C4	1.485 (4)	C17—C18	1.477 (5)
C2—C3	1.378 (4)	C18—H18A	0.9600
C3—C10	1.478 (4)	C18—H18B	0.9600
C4—C5	1.394 (4)	C18—H18C	0.9600
C1—N1—N2	104.7 (2)	C7—C8—C9	118.7 (3)
C3—N2—N1	113.6 (2)	C7—C8—H8	120.7
C3—N2—H2A	130 (2)	C9—C8—H8	120.7
N1—N2—H2A	116 (2)	C8—C9—C4	121.6 (3)
O9—N3—O10	124.3 (5)	C8—C9—H9	119.2
O9—N3—C13	118.2 (6)	C4—C9—H9	119.2
O10—N3—C13	117.5 (6)	C15—C10—C11	117.7 (3)
O7—N4—O8	124.0 (4)	C15—C10—C3	117.4 (3)
O7—N4—C11	118.4 (3)	C11—C10—C3	124.8 (3)
O8—N4—C11	117.6 (3)	C12—C11—C10	121.2 (4)
O3—N5—O4	125.0 (3)	C12—C11—N4	117.2 (3)
O3—N5—C5	118.6 (3)	C10—C11—N4	121.6 (3)
O4—N5—C5	116.4 (3)	C13—C12—C11	118.2 (4)
O6—N6—O5	124.1 (3)	C13—C12—H12	120.9
O6—N6—C7	118.1 (3)	C11—C12—H12	120.9
O5—N6—C7	117.7 (3)	C14—C13—C12	122.9 (3)
O2—N7—O1	123.6 (3)	C14—C13—N3	119.5 (5)
O2—N7—C2	118.4 (2)	C12—C13—N3	117.7 (5)
O1—N7—C2	118.0 (3)	C13—C14—C15	118.4 (4)
N1—C1—C2	109.9 (2)	C13—C14—H14	120.8
N1—C1—C4	117.4 (2)	C15—C14—H14	120.8

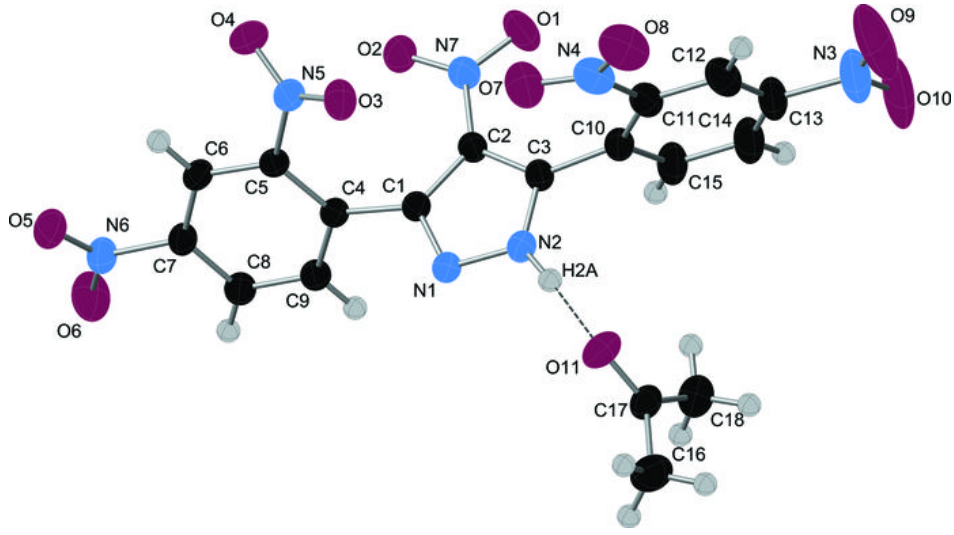
C2—C1—C4	132.7 (2)	C14—C15—C10	121.6 (4)
C3—C2—C1	106.6 (2)	C14—C15—H15	119.2
C3—C2—N7	125.4 (3)	C10—C15—H15	119.2
C1—C2—N7	128.0 (3)	C17—C16—H16A	109.5
N2—C3—C2	105.2 (2)	C17—C16—H16B	109.5
N2—C3—C10	121.2 (3)	H16A—C16—H16B	109.5
C2—C3—C10	133.4 (3)	C17—C16—H16C	109.5
C5—C4—C9	117.0 (3)	H16A—C16—H16C	109.5
C5—C4—C1	125.3 (3)	H16B—C16—H16C	109.5
C9—C4—C1	117.7 (2)	O11—C17—C18	121.1 (3)
C6—C5—C4	122.9 (3)	O11—C17—C16	120.6 (3)
C6—C5—N5	116.5 (2)	C18—C17—C16	118.4 (3)
C4—C5—N5	120.6 (2)	C17—C18—H18A	109.5
C5—C6—C7	117.2 (3)	C17—C18—H18B	109.5
C5—C6—H6	121.4	H18A—C18—H18B	109.5
C7—C6—H6	121.4	C17—C18—H18C	109.5
C8—C7—C6	122.5 (3)	H18A—C18—H18C	109.5
C8—C7—N6	118.6 (3)	H18B—C18—H18C	109.5
C6—C7—N6	118.9 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O11^{i}	0.92 (3)	1.87 (4)	2.786 (4)	177 (3)

Symmetry codes: (i) *x*, −*y*+1/2, *z*−1/2.

Fig. 1


O4
O2
N7
O1
O8
N4
C12
N3
O9
N5
O3
O7
O10
C11
C14
C13
C10
C2
C3
C6
C5
C4
C1
C15
O5
N6
N2
C7
C8
H2A
C9
N1
O6
O11
C17
C18
C16