

N,N-Dimethylanilinium 2,4,6-trinitrophenolate

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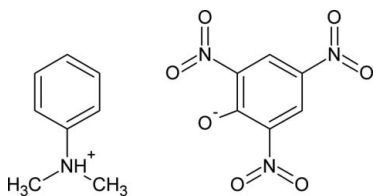
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Key indicators: single-crystal X-ray study; $T = 90$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.023; wR factor = 0.060; data-to-parameter ratio = 10.0.

In the title compound, $\text{C}_8\text{H}_{12}\text{N}^+\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$, there are $\text{N}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions which generate $R_2^1(5)$, $R_2^1(6)$ and $R_1^2(6)$ ring motifs. The supramolecular aggregation is completed by the presence of edge-to-face and offset face-to-face $\pi-\pi$ interactions with centroid-centroid distances of 3.673 and 3.697 Å, respectively.

Related literature

For a detailed account of the design of organic polar crystals, see: Pecaut & Bagieu-Beucher (1993). For hydrogen bonding in nitrophenol complexes, see: In *et al.* (1997); Zadrenko *et al.* (1997); Mizutani *et al.* (1998). For the supramolecular architecture of molecular complexes of trinitrophenols, see: Botoshansky *et al.* (1994); Vembu *et al.* (2003). For details of the monoclinic polymorph of the title compound, see: Takayanagi *et al.* (1996). For hydrogen-bonding criteria, see: Desiraju & Steiner (1999); Desiraju (1989); Jeffrey (1997). For graph-set notation, see: Bernstein *et al.* (1995); Etter (1990).



Experimental

Crystal data

$\text{C}_8\text{H}_{12}\text{N}^+\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$
 $M_r = 350.29$
 Orthorhombic, $Pna2_1$
 $a = 15.9960$ (10) Å
 $b = 9.1491$ (6) Å
 $c = 10.3899$ (9) Å

$V = 1520.55$ (19) Å³
 $Z = 4$
 Cu $K\alpha$ radiation
 $\mu = 1.08$ mm⁻¹
 $T = 90.0$ (5) K
 $0.26 \times 0.24 \times 0.08$ mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.767$, $T_{\max} = 0.919$

16980 measured reflections
 2823 independent reflections
 2755 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.060$
 $S = 1.03$
 2823 reflections
 283 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.14$ e Å⁻³
 $\Delta\rho_{\min} = -0.16$ e Å⁻³
 Absolute structure: Flack (1983), 1309 Friedel pairs
 Flack parameter: 0.07 (12)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N7}-\text{H7}\cdots\text{O16}$	0.892 (17)	1.825 (18)	2.7128 (14)	172.8 (16)
$\text{N7}-\text{H7}\cdots\text{O19}$	0.892 (17)	2.578 (16)	3.0517 (15)	114.0 (12)
$\text{C2}-\text{H2}\cdots\text{O16}$	0.931 (18)	2.341 (17)	3.0464 (16)	132.4 (13)
$\text{C2}-\text{H2}\cdots\text{O24}$	0.931 (18)	2.498 (17)	3.3444 (17)	151.4 (14)
$\text{C8}-\text{H8A}\cdots\text{O19}$	1.001 (18)	2.411 (18)	3.1171 (18)	126.9 (13)
$\text{C9}-\text{H9C}\cdots\text{O19}$	0.997 (18)	2.592 (17)	3.2311 (17)	121.9 (12)
$\text{C9}-\text{H9B}\cdots\text{O21}^i$	0.974 (19)	2.571 (19)	3.5074 (17)	161.3 (14)
$\text{C9}-\text{H9B}\cdots\text{O25}^{ii}$	0.974 (19)	2.476 (18)	3.0794 (18)	119.9 (13)
$\text{C4}-\text{H4}\cdots\text{O21}^{iii}$	0.924 (19)	2.466 (18)	3.1776 (16)	134.0 (14)
$\text{C14}-\text{H14}\cdots\text{O19}^{iv}$	0.941 (18)	2.564 (18)	3.4988 (16)	172.3 (14)
$\text{C9}-\text{H9C}\cdots\text{O22}^v$	0.997 (18)	2.502 (18)	3.3283 (16)	140.0 (13)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{3}{2}, z$; (v) $x+\frac{1}{2}, -y+\frac{3}{2}, z$.

Data collection: APEX2 (Bruker, 2006); cell refinement: APEX2 and SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2565).

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supplementary materials

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N,N-Dimethylanilinium 2,4,6-trinitrophenolate

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Comment

The design of organic polar crystals for quadratic non-linear optical applications is supported by the observation that the organic molecules containing π -electron systems asymmetricized by electron donor and acceptor groups are highly polarizable entities in which problems of transparency and crystal growth may arise from their molecular crystal packing (Pecaut & Bagieu-Beucher, 1993). It is known that nitrophenols act not only as π -acceptors to form various π -stacking complexes with other aromatic molecules, but also as acidic ligands to form salts through specific electrostatic or H-bonding interactions (In *et al.*, 1997). The bonding of electron-donor acceptor complexes strongly depends on the nature of the partners. The linkage could involve not only electrostatic interactions, but also the formation of molecular complexes (Zadrenko *et al.*, 1997). It has been reported that proton transferred thermochromic complexes were formed between phenols and amines in apolar solvents at low temperature if an appropriate H-bonding network between the phenols and amines was present to stabilize it (Mizutani *et al.*, 1998). Pyridinium picrate has been reported in two crystalline phases and it appears in both phases as an internally linked H-bonded ion pair. These two phases are referred to as molecular crystals rather than salts based on their structural arrangements (Botoshansky *et al.*, 1994). A similar structural arrangement has also been reported for 4-dimethylaminopyridinium picrate (Vembu *et al.*, 2003). The monoclinic polymorph of the title compound (CSD Reference Code: REYDEE) has been reported previously (Takayanagi *et al.*, 1996). We have structurally elucidated the orthorhombic polymorph of the title compound as a forerunner to assessing its optical properties and report its structure here.

The asymmetric unit of (I) contains one *N,N*-Dimethylanilinium cation, and one 2,4,6-trinitrophenolate anion. (Fig.1). The crystal structure of (I) is stabilized by N—H \cdots O and C—H \cdots O interactions. The range of H \cdots O distances (Table 1) found in (I) agrees with those found for N—H \cdots O (Jeffrey, 1997) and C—H \cdots O hydrogen bonds (Desiraju & Steiner, 1999). The N7—H7 \cdots O16 and N7—H7 \cdots O19 interactions form a pair of bifurcated donor bonds that link the *N,N*-dimethylanilinium cation and 2,4,6-trinitrophenolate anion and also form a motif of graph set $R^2_1(6)$ (Bernstein *et al.*, 1995; Etter, 1990). Another pair of bifurcated donor bonds consists of the C2—H2 \cdots O16 and C2—H2 \cdots O24 interactions that also link the cation and the anion and form a $R^2_1(6)$ motif. The C8—H8A \cdots O19 and C9—H9C \cdots O19 interactions constitute a pair of bifurcated bonds forming a $R^1_2(6)$ motif that link the cation and the anion. The N7—H7 \cdots O19 and C8—H8A \cdots O19 interactions constitute a pair of bifurcated acceptor bonds that form a $R^1_2(5)$ motif. The above two motifs, $R^1_2(6)$ and $R^1_2(5)$, together form a $R^1_2(5)$ motif by the interplay of the trifurcated acceptor bonds formed by N7—H7 \cdots O19, C9—H8A \cdots O19 and C9—H9C \cdots O19 interactions. There are five intermolecular C—H \cdots O interactions (Table 1) that contribute to the supra-molecular aggregation of the title compound. The intramolecular N—H \cdots O interactions mentioned above also contribute to the formation of cooperative H-bonded network (Fig. 2). There is an offset $\pi\cdots\pi$ stacking interaction, Cg1 \cdots Cg2 ($x, -1+y, z$) at 3.697Å with $\alpha = 3.19$, $\beta = 24.88$ and $\gamma = 24.00$ and the two perpendicular distances being 3.377 and 3.354Å. There is also an edge to face $\pi\cdots\pi$ stacking interaction, Cg1 \cdots Cg2 ($1.5-x, -0.5+y, 0.5+z$) at 3.673Å with $\alpha = 13.75$, $\beta = 25.68$ and $\gamma = 12.78$ and the two perpendicular distances being 3.582 and 3.310Å. Cg1 and Cg2 are the centroids of the C1 \cdots C6 and C10 \cdots C15 rings.

supplementary materials

The interplay of strong N—H \cdots O and weak C—H \cdots O, $\pi\cdots\pi$ interactions with different strengths, directional preferences and distance presents a complex mosaic of interactions. The three dimensional arrangement of the 2,4,6-trinitrophenolate and *N,N*-dimethylanilinium moieties in the unit cell, shows that the title compound is an internally linked hydrogen bonded ion pair and hence can be regarded as a molecular crystal rather than a salt.

Experimental

2,4,6-Trinitrophenol (5.2 mmol) dissolved in aqueous ethanol (25 ml) was added dropwise to *N,N*-dimethylaniline (5.7 mmol) in aqueous ethanol (25 ml). The above solution was constantly stirred at room temperature for 2 hrs. The precipitated product was filtered and recrystallized from aqueous ethanol. Yield 75% (3.9 mmol).

Refinement

All H-atoms were located in difference maps and their positions and isotropic displacement parameters freely refined. The 1309 Friedel pairs (96.2% coverage) were not merged, and the absolute structure was determined by refinement of the Flack (1983) parameter.

Figures

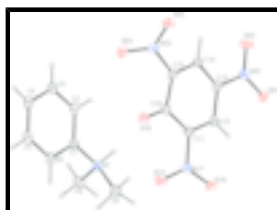


Fig. 1. The asymmetric unit of (I) with the atoms labelled and displacement ellipsoids depicted at the 50% probability level for all non-H atoms. H-atoms are drawn as spheres of arbitrary radius.

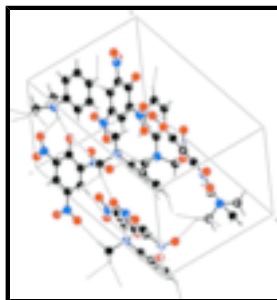


Fig. 2. The molecular packing viewed down the *b*-axis. Dashed lines represent the N—H \cdots O and C—H \cdots O interactions within the lattice.

N,N-Dimethylanilinium 2,4,6-trinitrophenolate

Crystal data

C₈H₁₂N⁺·C₆H₂N₃O₇⁻

M_r = 350.29

Orthorhombic, *Pna*2₁

Hall symbol: P 2c -2n

a = 15.9960 (10) Å

b = 9.1491 (6) Å

D_x = 1.530 Mg m⁻³

Melting point: 401 K

Cu *K*α radiation

λ = 1.54178 Å

Cell parameters from 9564 reflections

θ = 5.5–70.2°

μ = 1.08 mm⁻¹

$c = 10.3899 (9) \text{ \AA}$
 $V = 1520.55 (19) \text{ \AA}^3$
 $Z = 4$
 $F_{000} = 728$

$T = 90.0 (5) \text{ K}$
 Plate, yellow
 $0.26 \times 0.24 \times 0.08 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
 Radiation source: fine-focus sealed tube
 Monochromator: graphite
 $T = 90.0(5) \text{ K}$
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.767, T_{\max} = 0.919$
 16980 measured reflections

2823 independent reflections
 2755 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\max} = 70.2^\circ$
 $\theta_{\min} = 5.6^\circ$
 $h = -19 \rightarrow 19$
 $k = -10 \rightarrow 10$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.060$
 $S = 1.03$
 2823 reflections
 283 parameters
 1 restraint
 Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.2146P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$
 Extinction correction: none
 Absolute structure: Flack (1983), 1309 Friedel pairs
 Flack parameter: 0.07 (12)

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.

supplementary materials

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.37023 (8)	1.31731 (14)	0.30638 (13)	0.0151 (3)
C2	0.28455 (9)	1.29778 (15)	0.30264 (13)	0.0165 (3)
C3	0.23581 (8)	1.40616 (15)	0.24585 (13)	0.0178 (3)
C4	0.27257 (10)	1.53064 (15)	0.19438 (13)	0.0195 (3)
C5	0.35871 (9)	1.54844 (15)	0.20120 (14)	0.0200 (3)
C6	0.40878 (9)	1.44179 (15)	0.25752 (13)	0.0180 (3)
N7	0.42143 (7)	1.20264 (12)	0.37028 (12)	0.0150 (2)
C8	0.49639 (9)	1.15827 (16)	0.29319 (15)	0.0212 (3)
C9	0.44558 (8)	1.25020 (15)	0.50295 (14)	0.0200 (3)
C10	0.28722 (8)	0.85997 (14)	0.41862 (13)	0.0141 (3)
C11	0.34012 (7)	0.75029 (14)	0.47878 (12)	0.0142 (2)
C12	0.31105 (8)	0.62014 (14)	0.52863 (12)	0.0141 (3)
C13	0.22695 (8)	0.58924 (13)	0.52313 (13)	0.0149 (3)
C14	0.17059 (8)	0.68496 (14)	0.46412 (12)	0.0146 (3)
C15	0.20036 (8)	0.81337 (13)	0.41512 (13)	0.0145 (3)
O16	0.31146 (5)	0.97691 (10)	0.36915 (10)	0.0183 (2)
N17	0.42940 (7)	0.77360 (12)	0.48867 (11)	0.0160 (2)
O18	0.47489 (6)	0.66722 (10)	0.50973 (10)	0.0207 (2)
O19	0.45735 (6)	0.89878 (10)	0.47807 (11)	0.0247 (2)
N20	0.19719 (7)	0.45202 (12)	0.57365 (11)	0.0167 (2)
O21	0.24919 (6)	0.36384 (10)	0.61486 (10)	0.0194 (2)
O22	0.12141 (6)	0.42767 (12)	0.57227 (11)	0.0267 (2)
N23	0.13932 (7)	0.90790 (12)	0.35088 (11)	0.0162 (2)
O24	0.14260 (6)	1.04028 (10)	0.36928 (12)	0.0240 (2)
O25	0.08701 (6)	0.84815 (11)	0.28202 (9)	0.0207 (2)
H2	0.2611 (10)	1.2148 (19)	0.3398 (17)	0.017 (4)*
H3	0.1778 (12)	1.3963 (19)	0.2403 (18)	0.023 (4)*
H4	0.2380 (11)	1.600 (2)	0.1572 (16)	0.016 (4)*
H5	0.3856 (11)	1.633 (2)	0.1698 (17)	0.023 (4)*
H6	0.4678 (11)	1.4531 (17)	0.2608 (17)	0.017 (4)*
H7	0.3883 (10)	1.1243 (18)	0.3740 (17)	0.018 (4)*
H8A	0.5236 (11)	1.0734 (18)	0.3373 (18)	0.025 (4)*
H8B	0.5363 (12)	1.2445 (19)	0.2860 (19)	0.028 (5)*
H8C	0.4773 (12)	1.125 (2)	0.208 (2)	0.036 (5)*
H9A	0.4780 (10)	1.3372 (18)	0.4959 (17)	0.017 (4)*
H9B	0.3966 (11)	1.2756 (18)	0.5538 (18)	0.022 (4)*
H9C	0.4760 (11)	1.1692 (19)	0.5467 (17)	0.020 (4)*
H12	0.3479 (11)	0.5528 (18)	0.5656 (17)	0.017 (4)*
H14	0.1134 (11)	0.6615 (17)	0.4590 (17)	0.017 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0177 (6)	0.0136 (6)	0.0140 (6)	0.0022 (5)	-0.0007 (5)	-0.0020 (5)

C2	0.0197 (6)	0.0135 (6)	0.0161 (6)	-0.0011 (5)	0.0012 (5)	-0.0010 (5)
C3	0.0172 (6)	0.0170 (6)	0.0193 (7)	0.0013 (5)	-0.0022 (5)	-0.0039 (5)
C4	0.0281 (7)	0.0146 (6)	0.0158 (6)	0.0041 (6)	-0.0028 (5)	-0.0002 (5)
C5	0.0286 (7)	0.0137 (7)	0.0175 (7)	-0.0029 (5)	0.0024 (6)	-0.0003 (5)
C6	0.0198 (7)	0.0166 (7)	0.0175 (7)	-0.0021 (5)	0.0024 (5)	-0.0017 (5)
N7	0.0142 (5)	0.0132 (5)	0.0174 (5)	-0.0006 (4)	0.0011 (4)	-0.0003 (5)
C8	0.0193 (6)	0.0192 (7)	0.0251 (7)	0.0028 (5)	0.0058 (6)	0.0008 (6)
C9	0.0214 (6)	0.0200 (7)	0.0187 (7)	0.0008 (6)	-0.0046 (6)	-0.0016 (6)
C10	0.0146 (6)	0.0140 (6)	0.0137 (6)	-0.0002 (5)	-0.0013 (5)	-0.0026 (5)
C11	0.0132 (6)	0.0156 (6)	0.0138 (6)	0.0004 (5)	0.0006 (5)	-0.0023 (5)
C12	0.0161 (6)	0.0136 (6)	0.0127 (6)	0.0030 (5)	-0.0003 (5)	-0.0009 (5)
C13	0.0170 (6)	0.0120 (6)	0.0155 (6)	0.0002 (5)	0.0001 (5)	0.0005 (5)
C14	0.0123 (6)	0.0162 (6)	0.0152 (6)	0.0002 (5)	0.0008 (5)	-0.0023 (5)
C15	0.0149 (6)	0.0140 (6)	0.0145 (6)	0.0031 (5)	-0.0007 (5)	0.0000 (5)
O16	0.0177 (4)	0.0152 (5)	0.0219 (5)	-0.0020 (3)	-0.0016 (4)	0.0040 (4)
N17	0.0142 (5)	0.0177 (5)	0.0162 (5)	-0.0005 (4)	-0.0008 (4)	0.0008 (5)
O18	0.0143 (4)	0.0205 (5)	0.0274 (5)	0.0040 (4)	-0.0012 (4)	0.0025 (4)
O19	0.0181 (5)	0.0180 (5)	0.0378 (6)	-0.0050 (4)	-0.0061 (4)	0.0062 (5)
N20	0.0166 (5)	0.0149 (6)	0.0186 (6)	-0.0005 (4)	-0.0009 (5)	0.0007 (4)
O21	0.0201 (4)	0.0144 (5)	0.0235 (5)	0.0035 (4)	-0.0005 (4)	0.0049 (4)
O22	0.0146 (5)	0.0267 (5)	0.0389 (6)	-0.0060 (4)	-0.0035 (4)	0.0098 (5)
N23	0.0135 (5)	0.0193 (6)	0.0156 (5)	0.0017 (4)	0.0009 (4)	0.0034 (5)
O24	0.0221 (5)	0.0140 (5)	0.0360 (6)	0.0036 (4)	-0.0007 (5)	0.0041 (4)
O25	0.0162 (4)	0.0271 (5)	0.0188 (5)	0.0020 (4)	-0.0047 (4)	0.0004 (4)

Geometric parameters (Å, °)

C1—C2	1.3826 (19)	C9—H9C	0.997 (18)
C1—C6	1.3910 (19)	C10—O16	1.2488 (17)
C1—N7	1.4874 (16)	C10—C15	1.4537 (18)
C2—C3	1.3926 (19)	C10—C11	1.4538 (18)
C2—H2	0.931 (18)	C11—C12	1.3794 (19)
C3—C4	1.389 (2)	C11—N17	1.4475 (16)
C3—H3	0.934 (18)	C12—C13	1.3758 (18)
C4—C5	1.389 (2)	C12—H12	0.935 (18)
C4—H4	0.924 (19)	C13—C14	1.3985 (18)
C5—C6	1.391 (2)	C13—N20	1.4417 (17)
C5—H5	0.942 (19)	C14—C15	1.3661 (18)
C6—H6	0.951 (18)	C14—H14	0.941 (18)
N7—C9	1.4962 (18)	C15—N23	1.4652 (16)
N7—C8	1.4980 (18)	N17—O19	1.2344 (14)
N7—H7	0.892 (17)	N17—O18	1.2348 (14)
C8—H8A	1.001 (18)	N20—O22	1.2326 (15)
C8—H8B	1.017 (18)	N20—O21	1.2353 (15)
C8—H8C	0.99 (2)	N23—O24	1.2273 (15)
C9—H9A	0.953 (17)	N23—O25	1.2291 (15)
C9—H9B	0.974 (19)		
C2—C1—C6	122.34 (12)	H9A—C9—H9B	106.3 (14)
C2—C1—N7	117.85 (11)	N7—C9—H9C	109.3 (10)

supplementary materials

C6—C1—N7	119.76 (11)	H9A—C9—H9C	113.0 (14)
C1—C2—C3	118.35 (12)	H9B—C9—H9C	108.9 (14)
C1—C2—H2	119.5 (10)	O16—C10—C15	122.53 (12)
C3—C2—H2	122.1 (10)	O16—C10—C11	125.98 (11)
C4—C3—C2	120.66 (13)	C15—C10—C11	111.39 (11)
C4—C3—H3	118.4 (11)	C12—C11—N17	115.67 (11)
C2—C3—H3	120.9 (11)	C12—C11—C10	124.13 (11)
C3—C4—C5	119.77 (13)	N17—C11—C10	120.21 (11)
C3—C4—H4	117.9 (11)	C13—C12—C11	119.44 (12)
C5—C4—H4	122.3 (11)	C13—C12—H12	119.8 (10)
C4—C5—C6	120.67 (13)	C11—C12—H12	120.7 (10)
C4—C5—H5	122.1 (11)	C12—C13—C14	121.33 (12)
C6—C5—H5	117.2 (11)	C12—C13—N20	119.13 (11)
C1—C6—C5	118.20 (13)	C14—C13—N20	119.47 (11)
C1—C6—H6	121.1 (10)	C15—C14—C13	118.50 (11)
C5—C6—H6	120.7 (10)	C15—C14—H14	121.0 (10)
C1—N7—C9	110.38 (10)	C13—C14—H14	120.5 (10)
C1—N7—C8	113.16 (11)	C14—C15—C10	125.18 (12)
C9—N7—C8	111.39 (11)	C14—C15—N23	116.42 (11)
C1—N7—H7	105.0 (10)	C10—C15—N23	118.37 (11)
C9—N7—H7	110.3 (12)	O19—N17—O18	122.24 (10)
C8—N7—H7	106.3 (11)	O19—N17—C11	119.19 (10)
N7—C8—H8A	108.2 (10)	O18—N17—C11	118.55 (10)
N7—C8—H8B	109.3 (11)	O22—N20—O21	123.25 (11)
H8A—C8—H8B	111.3 (14)	O22—N20—C13	118.55 (11)
N7—C8—H8C	108.4 (12)	O21—N20—C13	118.20 (10)
H8A—C8—H8C	108.1 (15)	O24—N23—O25	123.96 (11)
H8B—C8—H8C	111.3 (16)	O24—N23—C15	118.88 (11)
N7—C9—H9A	108.2 (11)	O25—N23—C15	117.15 (11)
N7—C9—H9B	111.2 (11)		
C6—C1—C2—C3	1.1 (2)	C12—C13—C14—C15	-2.10 (19)
N7—C1—C2—C3	178.45 (12)	N20—C13—C14—C15	-178.99 (12)
C1—C2—C3—C4	0.0 (2)	C13—C14—C15—C10	0.2 (2)
C2—C3—C4—C5	-0.9 (2)	C13—C14—C15—N23	178.23 (11)
C3—C4—C5—C6	0.9 (2)	O16—C10—C15—C14	177.99 (13)
C2—C1—C6—C5	-1.1 (2)	C11—C10—C15—C14	1.40 (19)
N7—C1—C6—C5	-178.45 (12)	O16—C10—C15—N23	0.00 (19)
C4—C5—C6—C1	0.1 (2)	C11—C10—C15—N23	-176.58 (11)
C2—C1—N7—C9	-100.90 (13)	C12—C11—N17—O19	-161.31 (13)
C6—C1—N7—C9	76.55 (15)	C10—C11—N17—O19	19.03 (18)
C2—C1—N7—C8	133.51 (13)	C12—C11—N17—O18	17.45 (17)
C6—C1—N7—C8	-49.04 (16)	C10—C11—N17—O18	-162.20 (12)
O16—C10—C11—C12	-177.78 (13)	C12—C13—N20—O22	177.52 (12)
C15—C10—C11—C12	-1.34 (18)	C14—C13—N20—O22	-5.53 (19)
O16—C10—C11—N17	1.8 (2)	C12—C13—N20—O21	-3.32 (18)
C15—C10—C11—N17	178.28 (11)	C14—C13—N20—O21	173.63 (12)
N17—C11—C12—C13	-179.98 (11)	C14—C15—N23—O24	138.87 (13)
C10—C11—C12—C13	-0.3 (2)	C10—C15—N23—O24	-42.97 (17)
C11—C12—C13—C14	2.17 (19)	C14—C15—N23—O25	-40.50 (17)

C11—C12—C13—N20

179.06 (12)

C10—C15—N23—O25

137.66 (12)

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>
N7—H7 \cdots O16	0.892 (17)	1.825 (18)	2.7128 (14)	172.8 (16)
N7—H7 \cdots O19	0.892 (17)	2.578 (16)	3.0517 (15)	114.0 (12)
C2—H2 \cdots O16	0.931 (18)	2.341 (17)	3.0464 (16)	132.4 (13)
C2—H2 \cdots O24	0.931 (18)	2.498 (17)	3.3444 (17)	151.4 (14)
C8—H8A \cdots O19	1.001 (18)	2.411 (18)	3.1171 (18)	126.9 (13)
C9—H9C \cdots O19	0.997 (18)	2.592 (17)	3.2311 (17)	121.9 (12)
C9—H9B \cdots O21 ⁱ	0.974 (19)	2.571 (19)	3.5074 (17)	161.3 (14)
C9—H9B \cdots O25 ⁱⁱ	0.974 (19)	2.476 (18)	3.0794 (18)	119.9 (13)
C4—H4 \cdots O21 ⁱⁱⁱ	0.924 (19)	2.466 (18)	3.1776 (16)	134.0 (14)
C14—H14 \cdots O19 ^{iv}	0.941 (18)	2.564 (18)	3.4988 (16)	172.3 (14)
C9—H9C \cdots O22 ^v	0.997 (18)	2.502 (18)	3.3283 (16)	140.0 (13)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1/2, y+1/2, z+1/2$; (iii) $-x+1/2, y+3/2, z-1/2$; (iv) $x-1/2, -y+3/2, z$; (v) $x+1/2, -y+3/2, z$.

Fig. 1

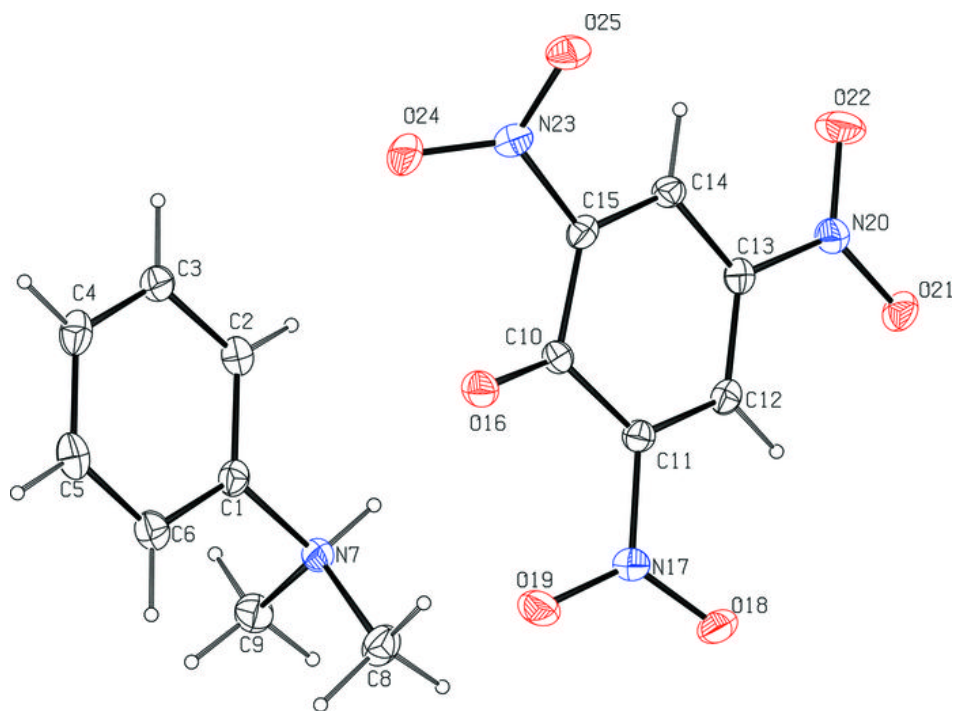


Fig. 2

