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2,4,6-Trimethyl-*N*-nitroaniline

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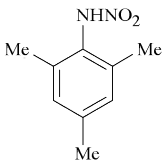
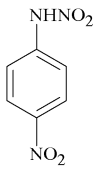
In 2,4,6-trimethyl-*N*-nitroaniline (alternatively called mesitylnitramine), $C_9H_{12}N_2O_2$, the primary nitramino group is planar with a short N—N bond and is nearly perpendicular to the aromatic ring. The methyl group located in the *para* position is disordered, each H atom having half-occupancy. The molecules are linked together along the [100] axis by intermolecular N—H···O hydrogen bonds.

Comment

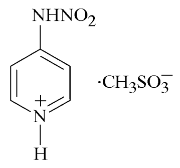
A common feature of primary and secondary *N*-arylnitramines is their ability to rearrange to the corresponding *ortho* and *para* amino–nitro compounds under the influence of an acid (Banthorpe & Thomas, 1965). The molecular structures of *N*-methyl-*N*-phenylnitramine and its ring-substituted derivatives are well elucidated. The geometric parameters of the nitramino group, in particular a long Ar—N bond, a short N—N bond and a large torsion angle on the Ar—N bond, are not influenced by the ring substituents (Daszkiewicz *et al.*, 2000, 2002). The results were unexpected since migration of the *N*-nitro group to the ring requires a nearly coplanar conformation of the nitramine molecule. The geometry of the primary nitramino group has not been so frequently studied, and in most examples the $NHNO_2$ group is connected to an electron-deficient ring, as in mesitylnitramines (III) and (IV).



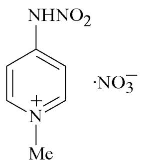
(I)



(II)



(III)



(IV)

The nitramino group in (I) (Fig. 1) is nearly planar, and the sum of the valence angles [358.0 (12)°] around atom N7 indicates trigonal hybridization of the amide N atom. However, atom N7 deviates from the C1/H7/N8 plane by 0.100 (2) Å. The torsion angle along the N—N bond is small at 4.4 (11)° (averaged) and may result from non-valence interactions. The N7—N8 bond length (Table 1) also indicates high bond order. The differences with respect to nitramines (II)–(IV) are small [0.025 (1) Å maximum] but they correspond to the differences in the lengths of the Ar—N bonds. In pyridine derivatives (III) and (IV), these bonds are more than 0.05 Å shorter (Zaleski *et al.*, 2001) than in (I). This may be interpreted as the result of a change in the π-electron distribution within the nitramino group, under the influence of the electron-deficient ring.

The conformations of the molecules confirm this conclusion. In (I), the torsion angle along the C1—N7 bond (*ca* 83.7°) may be caused by the steric hindrance, but in (II), the nitramine group is twisted by approximately 22 and 44° for the two independent molecules (Zaleski *et al.*, 2002). In contrast, in (III) and (IV), the nitramine groups are nearly coplanar with the pyridine ring, indicating conjugation between both π-electron systems. The geometry of the aromatic ring in (I) is not disturbed by the relatively large number of substituents. The difference between a particular C—C bond length and the average value (1.388 Å) does not exceed 0.007 Å. At room temperature, the methyl group in the *para* position rotates along the C—C axis, this being observed as a splitting of the H-atom positions. A decrease of the temperature causes destruction of the crystal as a result of a phase transition.

In the IR spectrum of (I), a strong and broad band, with the maximum at 3226 cm^{-1}, indicates the presence of a hydrogen bond. Despite the acidic properties of primary nitramines, the interaction is weak, as indicated by the long donor–acceptor distance (Table 2). The molecules are joined together along the *a* axis *via* the hydrogen bond, but π–π stacking interactions seem to be a decisive factor in the molecular packing (Fig. 2). The molecules are arranged parallel in columns. Each molecule is 3.524 (2) Å from its neighbours and twisted by 180°. The angle between the molecules belonging to neighbouring stacks is 41.4 (11)°. In the crystal network of (II), the hydrogen bond is addressed to the *p*-nitro group (Zaleski *et al.*, 2002). Comparison of (I) and (II) indicates that the O atom of the nitramine group is a very poor H-atom acceptor. Analogously, the crystal structure of *N*,*N*-dinitroethylenediamine is determined by the local dipole–dipole interactions in spite of the weak (3.007 Å) N—H···O hydrogen bond (Turley, 1968).

The geometries of primary and secondary *N*-arylnitramines are similar in the most characteristic aspects. In (I), the

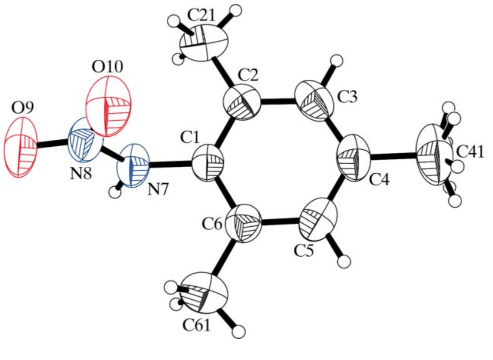


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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environment of amide atom N7 indicates its trigonal hybridization and high N—N bond order. The planar nitramino group is bonded to the benzene ring with a relatively long C—N bond and twisted with respect to the nearly perpendicular position. Such a conformation is an effect of a steric interaction between N–methyl or Ar–methyl groups and the neighbouring substituent.

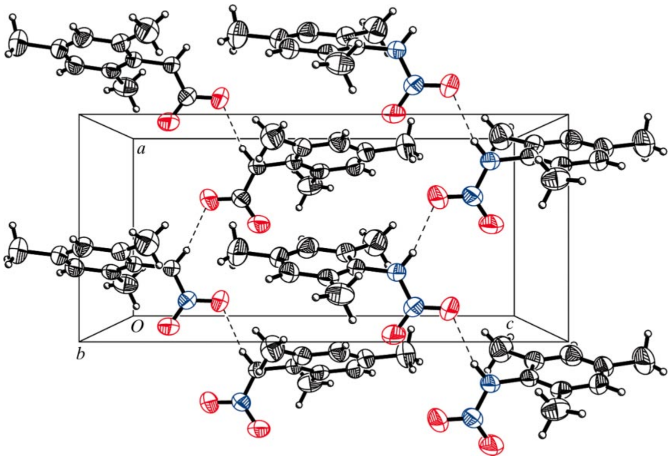

Figure 2
The packing of mesitylnitramine, viewed down *c*, showing the hydrogen-bonding scheme (dashed lines). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Ethyl bromide (2.3 ml, 30 mmol), diluted with absolute diethyl ether (15 ml), was added dropwise to a stirred suspension of magnesium turnings (1.20 g, 50 mmol) in ether (50 ml). A solution of ethyl magnesium bromide was filtered into 2,4,6-trimethylaniline (2.70 g, 20 mmol) dissolved in dry toluene (100 ml). The mixture was stirred and refluxed for 1 h. It was cooled to room temperature, *n*-butyl nitrate (3.60 g, 30 mmol) was added and stirring was continued for 1 h. Water (30 ml) and acetic acid (2 ml) were added to the mixture, and the aqueous layer was separated and discarded. The nitramine was extracted (3 × 30 ml) from the ethereal solution with 1 *M* aqueous potassium hydroxide and precipitated by careful acidification (273 K) with 3 *M* hydrochloric acid. The crude product was collected by filtration, dried in a vacuum and crystallized from *n*-hexane. *N*-(2,4,6-Trimethylphenyl)nitramine (1.60 g, 44%) was obtained as colourless crystals, melting at 386–388 K. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a 1:1 *n*-hexane–diethyl ether solution at room temperature. IR (KBr, ν, cm^{-1}): 3226 (NH proton, stretching vibrations); 1593, 1326 (N—NO$_2$, asymmetric and symmetric stretch). ^{1}H NMR (CDCl$_3$): δ 9.58 (*s*, 1H, nitramine H atom), 6.95 (*s*, 2H, aromatic H atoms), 2.30 (*s*, 3H, *para*-methyl group), 2.24 (*s*, 6H, *ortho*-methyl groups). ^{13}C NMR (CDCl$_3$): δ 140.7 (C-1), 137.1 (C-2 and C-6), 129.6 (C-3 and C-5), 129.4 (C-4), 21.3 (*para*-CH$_3$), 17.9 (*ortho*-CH$_3$).

Differential scanning calorimetry studies showed that mesitylnitramine undergoes a strong first-order phase transition at 230 K on cooling and at 270 K on heating, with ΔH = 0.4 kJ mol^{-1} and ΔS = 1.6 J K mol^{-1}. The single crystal is destroyed and appears as a powder at the phase transition.

Crystal data

$C_9H_{12}N_2O_2$
M_r = 180.21
Orthorhombic, *Pbca*
a = 7.6217 (6) Å
b = 15.8538 (13) Å
c = 16.3696 (12) Å
V = 1978.0 (3) Å^3
Z = 8
D_x = 1.210 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 295 (2) K
Plate, colourless
0.30 × 0.25 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
14835 measured reflections
2650 independent reflections
1329 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.038
$\theta_{\rm max}$ = 29.6°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.142
S = 0.98
2650 reflections
136 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.018
$\Delta\rho_{\rm max}$ = 0.14 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.393 (2)	C5—C6	1.387 (2)
C1—C6	1.394 (2)	N7—N8	1.3405 (17)
C1—N7	1.4310 (19)	N7—H7	0.874 (18)
C2—C3	1.387 (2)	N8—O10	1.2173 (16)
C3—C4	1.385 (3)	N8—O9	1.2290 (17)
C4—C5	1.381 (3)		
C2—C1—C6	122.75 (14)	N8—N7—C1	120.47 (13)
C3—C2—C1	117.15 (16)	N8—N7—H7	114.7 (12)
C4—C3—C2	122.05 (17)	C1—N7—H7	122.8 (12)
C5—C4—C3	118.77 (16)	O10—N8—O9	124.40 (14)
C4—C5—C6	121.91 (18)	O10—N8—N7	118.92 (14)
C5—C6—C1	117.36 (15)	O9—N8—N7	116.64 (14)
C2—C1—N7—N8	−84.18 (19)	C1—N7—N8—O10	5.5 (2)
C6—C1—N7—N8	96.85 (18)	C1—N7—N8—O9	−176.74 (15)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···O9^{i}	0.874 (18)	2.080 (19)	2.9320 (18)	164.6 (17)

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

The H atoms of the benzene ring and the H atom bonded to N7 were refined freely; the C—H bond lengths are 0.937 (17) and 0.941 (18) Å, and the N—H bond length is 0.874 (18) Å. The H atoms of the CH$_3$ groups were placed in calculated positions (C—H = 0.98 Å). The methyl group in the *para* position is disordered, with a site-occupation factor of 0.5.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3024). Services for accessing these data are described at the back of the journal.

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