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N-Methyl-*N*-(2-nitrophenyl)nitramine and *N*-methyl-*N*-(3-nitrophenyl)-nitramine

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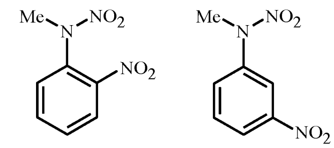
The structures of the two title isomeric compounds (systematic names: *N*-methyl-*N*,2-dinitroaniline and *N*-methyl-*N*,3-dinitroaniline, both $C_7H_7N_3O_4$) are slightly different because they exhibit different steric hindrances and hydrogen-bonding environments. The aromatic rings are planar. The –N(Me)NO_2 and –NO_2 groups are not coplanar with the rings. Comparison of the geometric parameters of the *ortho*, *meta* and *para* isomers together with those of *N*-methyl-*N*-phenylnitramine suggests that the position of the nitro group has a strong influence on the aromatic ring distortion. The crystal packing is stabilized by weak C—H···O hydrogen bonds to the nitramine group.

Comment

Nitramines and related *N*-nitro compounds have attracted significant attention from researchers in view of their applications in rocket fuel and as explosives (Williams, 1982). The compounds of this series are particularly interesting since the nitro group in *N*-methyl-*N*-nitroaniline and its derivatives can undergo a rearrangement at elevated temperatures, under acid conditions or on photolysis (Growenlock *et al.*, 1997). Owing to the presence of an N—N bond, these compounds are also very active in photochemical reactions (Mialocq & Stephenson, 1986), and their structures have been investigated in recent years (Daszkiewicz *et al.*, 2000; Prezhdo *et al.*, 2001; Zhukhlistova *et al.*, 2002). In the molecular structures of typical secondary aromatic nitramines, there are two planar π-electron fragments, *viz.* the aromatic ring and the nitramine (NNO_2) group, which are not coplanar. The π electrons of the nitramine group are not conjugated within the aromatic ring. The twisted conformation of *N*-methyl-*N*-phenylnitramines is probably a result of intermolecular interactions.

Our earlier investigations have been devoted to aromatic nitramines with selected substituents (Daszkiewicz *et al.*, 1995, 2002). To obtain further information about the differences in structures of the compounds substituted by a nitramine group, since the structure of *N*-methyl-*N*-(4-nitrophenyl)nitramine has already been published (Anulewicz *et al.*, 1993), we have prepared the *ortho* and *meta* derivatives.



(I) (II)

The molecular structures of *N*-methyl-*N*-(2-nitrophenyl)-nitramine, (I), and *N*-methyl-*N*-(3-nitrophenyl)nitramine, (II), are shown in Figs. 1 and 2, respectively and selected geometric parameters are shown in Tables 1 and 3. In both molecules, the aromatic rings are slightly deformed by electronic and steric interactions. In (I), the average C—C bond length is 1.389 (2) Å, whereas in (II), it is 1.395 (2) Å. The largest difference between the shortest and longest C—C bonds is 0.031 (3) Å in (I), whereas in (II), the difference is 0.011 (3) Å. The bond-length difference is undoubtedly caused by the presence of the –N(Me)NO_2 and –NO_2 groups connected to atoms C1 and C2. Such a distortion of the aromatic ring was not observed in the structure of unsubstituted *N*-methyl-*N*-phenylnitramine (Prezhdo *et al.*, 2001), in which the C—C bonds are in the range 1.364 (4)–1.376 (4) Å.

Comparison of the geometric parameters of the *ortho*, *meta* and *para* isomers, together with those of *N*-methyl-*N*-phenylnitramine, suggests that the position of the nitro group has a strong influence on the aromatic ring distortion. The presence of the nitro group in the *meta* position in (II) significantly increases the C2—C3—C4 angle [to 123.4 (1)°]. It should be noted that the two neighbouring C—C—C angles are decreased [C1—C2—C3 = 117.5 (1)° and C3—C4—C5 = 117.8 (1)°] and the two subsequent angles are slightly increased [C6—C1—C2 = 120.8 (1)° and C4—C5—C6 = 120.6 (1)°]. Similar effects have also been found in *N*-methyl-*N*-(4-nitrophenyl)nitramine; the C3—C4—C5 angle is similarly increased [to 122.9 (2)°], whereas the two neighbouring angles are decreased to 118.3 (2)° (Anulewicz *et al.*, 1993).

At the position in which the nitramine group is connected in (II), the C6—C1—C2 angle is increased from 120 to 120.8 (1)°;

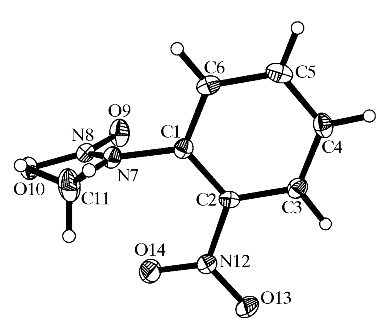


Figure 1
The molecular structure of (I), showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

in the *para*-substituted compound, the increase is larger [1.7 (2)°]. In (I), however, this angle is decreased by 1.4 (1)°. It should be mentioned that the C—C—C angle to which the $–NO_2$ group is connected and that to which the –N(Me)NO_2 group is connected are quite similar [2.2 (1)° for the *ortho* and *para*, but 2.6 (1)° for the *meta* compound]. Taking into account only the geometric structures of (I) and (II), it seems that the deformation of the aromatic ring is caused more by steric hindrance than by the π-electron interactions.

In both structures, the nitro groups are not coplanar with the aromatic rings; the group is twisted by 11.9 (2)° for (I) and by 22.1 (2)° for (II) with respect to the ring plane. A much smaller twist [2.5 (2)°] is observed in the *para* isomer (Anulewicz *et al.*, 1993). In the overcrowded structure of (I), the position of the nitro group causes an increase of the C1—C2—N12 angle to 121.8 (1)° and a decrease of the C3—C2—N12 angle to 117.5 (1)°. In (II), both related angles are smaller than 120° [by 2.6 (1) and 0.8 (1)°].

In both studied molecules, the N—NO_2 group is not coplanar with the aromatic ring, which suggests a lack of interaction between these two groups. In (I) and 4-nitro-*N*-methyl-*N*-phenylnitramine, the *N*-methylnitramine group is twisted along the C_{ar}—N bond by −80.4 (1) and −72.3 (2)°, respectively. This is a characteristic feature of *N*-methyl-*N*-(4-nitrophenyl)nitramine derivatives. It should be noted, however, that *N*-methyl-*N*-phenylnitramine has a smaller twist angle [−66.3 (2)°], whereas in (II), the group is twisted by an even smaller angle [−49.6 (1)°].

The bond lengths and angles of the nitramine group agree with the corresponding values found in *N*-methyl-*N*-(4-nitrophenyl)nitramine. Atom N7 lies slightly out of the plane of the benzene ring [the deviation is 0.026 (1) Å in (I) and 0.109 (1) Å in (II)]. In (II), the sum of the valence angles around atom N7 [360.0 (1)°] indicates trigonal hybridization of the amine N atom. In (I), however, this sum is 358.9 (1)° and atom N7 lies 0.086 (1) Å from the C1/N8/C11 plane.

The N7—N8 bond lengths [1.349 (2) Å for (I) and 1.355 (1) Å for (II)] have values intermediate between those of typical single (1.45 Å) and double (1.25 Å) bonds, as expected (Allen *et al.*, 1995; Daszkiewicz *et al.*, 2002). Similar effects have also been observed in all derivatives of *N*-methyl-*N*-phenylnitramine (Cady, 1967; Prezhdo *et al.*, 2001; Zhukhlistova *et al.*, 2002).

In both title structures, the crystal packing is stabilized by weak intermolecular C—H···O hydrogen bonds (Tables 2 and 4), forming an extended three-dimensional network in each case. The polarity of the nitramine group and the distribution of the partial charges influence the formation of hydrogen bonds. In both studied structures, the hydrogen bonds involve only the O atoms of the nitro group connected to atom N7. The NO_2 group bound to the phenyl ring does not participate in the hydrogen-bonding scheme in either compound.

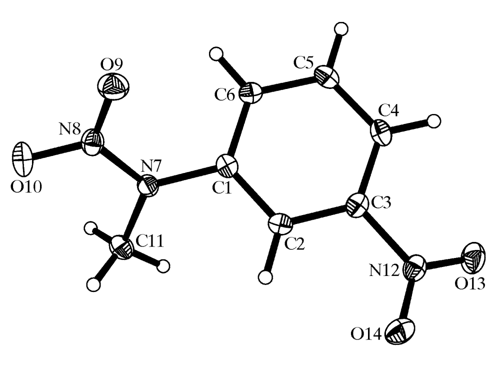


Figure 2
The molecular structure of (II), showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

For the preparation of (I), solid *N*-methyl-2-nitroaniline (3 g, 20 mmol) was added in portions to cold acetic anhydride (30 ml) containing nitric acid (1.7 ml, 41 mmol, HNO_3, d = 1.5). The solution was kept for 30 min at room temperature and evaporated *in vacuo* (323 K). The residue was crystallized from methanol and recrystallized from ethanol, producing *N*-methyl-*N*-(2-nitrophenyl)-nitramine, (I), as colourless crystals (2.5 g, 63%, m.p. 340–341 K). MS (*m*/*z*) (intensity): 197 (M^+, 4), 151 (97), 134 (100), 121 (11), 105 (38), 93 (60), 77 (69); IR (KBr, cm^{-1}): 1530, 1523 (ν_{as} N—O), 1345, 1295 (ν_s N—O); ^{1}H NMR ($CDCl_3$): δ 8.24–7.43 (*m*, 4H, aromatic H atoms), 3.74 (*s*, 3H, *N*-methyl group). *N*-Methyl-*N*-(3-nitrophenyl)nitramine, (II), was prepared according to the above procedure. The nitramine was obtained in 72% yield as colourless crystals (m.p. 347–348 K). MS (*m*/*z*) (intensity): 197 (M^+, 2), 151 (100), 122 (10), 105 (80), 93 (4), 77 (16); IR (KBr, cm^{-1}): 1528 (ν_{as} N—O), 1351, 1291 (ν_s N—O); ^{1}H NMR ($CDCl_3$): δ 8.33–8.22 (*m*, 2H), 7.74–7.67 (*m*, 2H, aromatic H atoms), 3.78 (*s*, 3H, *N*-methyl group).

Compound (I)

Crystal data

$C_7H_7N_3O_4$
M_r = 197.16
Monoclinic, $P2_1/n$
a = 7.0470 (8) Å
b = 14.4473 (12) Å
c = 8.1165 (8) Å
β = 90.814 (8)°
V = 826.26 (14) Å^3
Z = 4
D_x = 1.585 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5344 reflections
θ = 3.2–26.0°
μ = 0.13 mm^{-1}
T = 100.0 (1) K
Irregular, colourless
0.2 × 0.2 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scan
5344 measured reflections
1591 independent reflections
1294 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 26.0°
h = −8 → 8
k = −17 → 11
l = −10 → 10

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.089
S = 1.05
1591 reflections
156 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.024 (4)

Table 1
Selected geometric parameters (Å, °) for (I).

N7—N8	1.349 (2)		
C6—C1—C2	118.6 (1)	C3—C4—C5	120.2 (1)
C6—C1—N7	117.4 (1)	C6—C5—C4	120.0 (1)
C2—C1—N7	123.9 (1)	C1—C6—C5	120.8 (1)
C3—C2—C1	120.8 (1)	N8—N7—C1	117.51 (10)
C3—C2—N12	117.5 (1)	N8—N7—C11	119.01 (11)
C1—C2—N12	121.8 (1)	C1—N7—C11	122.36 (11)
C2—C3—C4	119.6 (1)		
C6—C1—N7—N8	101.4 (1)	C1—C2—N12—O13	−168.0 (1)
C2—C1—N7—N8	−82.2 (2)	C3—C2—N12—O14	−168.2 (1)
C3—C2—N12—O13	11.8 (2)	C1—C2—N12—O14	12.0 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O10^{i}	0.95 (2)	2.46 (2)	3.336 (2)	155 (1)
C6—H6···O9^{ii}	0.96 (2)	2.59 (2)	3.341 (2)	135 (1)
C4—H4···O9^{iii}	0.92 (2)	2.60 (2)	3.195 (2)	123 (1)

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

Compound (II)

Crystal data

$C_7H_7N_3O_4$
M_r = 197.16
Monoclinic, $P2_1/c$
a = 8.7322 (11) Å
b = 13.6510 (16) Å
c = 7.5547 (12) Å
β = 111.195 (13)°
V = 839.6 (2) Å^3
Z = 4
D_x = 1.560 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5281 reflections
θ = 3.3–26.0°
μ = 0.13 mm^{-1}
T = 100.0 (1) K
Irregular, colourless
0.4 × 0.4 × 0.3 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scan
5281 measured reflections
1637 independent reflections
1417 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 26.0°
$h = -10 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -9 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.078
S = 1.08
1637 reflections
155 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.2056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

N7—N8	1.355 (1)		
C2—C1—C6	120.8 (1)	C6—C5—C4	120.6 (1)
C3—C2—C1	117.5 (1)	C5—C6—C1	119.9 (1)
C4—C3—C2	123.4 (1)	N8—N7—C1	119.64 (9)
C4—C3—N12	119.2 (1)	N8—N7—C11	117.22 (10)
C2—C3—N12	117.4 (1)	C1—N7—C11	123.15 (10)
C3—C4—C5	117.8 (1)		
C2—C1—N7—N8	132.12 (11)	C2—C3—N12—O13	157.2 (1)
C6—C1—N7—N8	−51.32 (15)	C4—C3—N12—O14	158.7 (1)
C4—C3—N12—O13	−22.4 (2)	C2—C3—N12—O14	−21.7 (2)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O10^{iv}	0.97 (1)	2.57 (1)	3.132 (2)	117 (1)
C6—H6···O9^{v}	0.96 (1)	2.41 (1)	3.198 (2)	139 (1)

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

In (I), the C—H bond distances are in the range 0.917 (17)–0.985 (19) Å and the U_{iso}(H) values are in the range 0.020 (4)–0.052 (6) Å^2. For compound (II), the ranges are 0.942 (16)–0.983 (17) Å and 0.013 (3)–0.031 (4) Å^2, respectively.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *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: FR1523). Services for accessing these data are described at the back of the journal.

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