Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.095$
$S = 1.017$
2682 reflections
215 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.9201P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.162$ e Å^{-3}
$\Delta\rho_{\min} = -0.136$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0038 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—N2	1.314 (2)	N1—C2	1.425 (2)
C1—N1	1.333 (2)	N3—C8	1.416 (2)
C1—N3	1.341 (2)		
N2—C1—N1	119.38 (15)	C1—N1—C2	126.88 (14)
N2—C1—N3	118.72 (14)	C1—N3—C8	125.69 (13)
N1—C1—N3	121.90 (14)		
N2—C1—N1—C2	151.2 (2)	C1—N1—C2—C3	−29.0 (2)
N2—C1—N3—C8	149.9 (2)	C1—N3—C8—C9	−38.1 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.876 (19)	1.894 (19)	2.753 (2)	166.2 (16)
N2—H2A···O2	0.90 (2)	2.03 (2)	2.906 (2)	166.3 (17)
N2—H2B···O1$^{\text{i}}$	0.889 (19)	2.03 (2)	2.885 (2)	162.2 (17)
N3—H3···O2$^{\text{ii}}$	0.884 (19)	1.937 (19)	2.776 (2)	158.0 (17)

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

All H atoms were clearly seen in a difference Fourier map at an intermediate stage of the refinement. The coordinates of the H atoms were freely refined with an isotropic displacement parameter $U(\text{H}) = 1.2U_{\text{eq}}$ of the parent atom. The data collection was complete up to 25°, but only a partial shell up to 27.5° was measured because the crystal fell off the mounting pin before the end of the data collection. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

The authors are indebted to Dr J. C. Prata Pina for his invaluable assistance in the maintenance of the CAD-4 diffractometer. This work was supported by Fundação para a Ciência e a Tecnologia (FCT).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1285). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1292–1295

4-(*N*-Methylnitramino)pyridine 1-oxide

JACEK ZALESKI, ZDZISŁAW DASZKIEWICZ AND JANUSZ B. KYZIOŁ

Institute of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland. E-mail: zaleski@uni.opole.pl

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Abstract

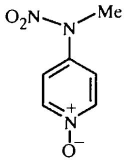
In the title compound, $C_6H_7N_3O_3$, the NNO_2 group is twisted *ca* 59° from the planar pyridine ring. The nitramino group is almost planar, with the N7 atom diverging 0.15 Å from the C4–N8–C11 plane. The lone pair on N7 is included into the *N*-nitro group π-electron system resulting in two independent sets of multicenter

π-orbitals. Significant anisotropy of the temperature dependence of thermal expansion is observed in the range 90–300 K.

Comment

In a typical aliphatic nitrimine, the N—N bond is long and the *N*-nitro substituent may be considered as a free rotating group (Cameron *et al.*, 1979). The 1,4-dihydro-1-methyl-4-nitriminopyridine molecule is nearly planar, indicating strong mesomeric interaction between the aromatic sextet and the NNO_2 π-electron system (Bujak *et al.*, 1998).

It can be anticipated that in 4-(*N*-methylnitramino)-pyridinium 1-oxide, (1), the unshared electron pair of the amide nitrogen may be included into the aromatic system. In such a case, the molecule should have a relatively short C4—N7 bond and long N7—N8 bond as in 4,*N*-dinitrocamphorimine (Cameron *et al.*, 1979).



(1)

The NNO_2 group in (1) is nearly planar: the N7 atom diverges from the C4–N8–C11 plane by 0.15 Å only. The C4—C7 bond is even longer than in the 1-methyl-4-(*N*-methylnitramino)pyridinium cation (Zaleski *et al.*, 1999) [1.430 (4) *versus* 1.403 (4) Å] while the N7—N8 bond is within two standard deviations of the same length. The nitramino group is twisted by *ca* 59° with respect to the pyridine ring, hence there is no conjugation between them. The planarity of the nitramino group indicates trigonal hybridization of the N7 atom. The N7—N8 distance is significantly shorter than that of a typical single N—N bond [1.350 (4) *versus* 1.425 Å]. We must conclude that the lone pair belongs in fact to the π-electron system which is spread on the NNO_2 group. The N—O bond length in the nitramino group of (1) is nearly the same as observed in the $ArNO_2$ group of 4-nitropyridine 1-oxide (Wang *et al.*, 1976; Coppens & Lehman, 1976). The latter contains a three-center π-electron system with two electron pairs occupying one bonding and one non-bonding π-orbital. Within the nitramino group the electron distribution should be analogous, considering the similar N—O bond order. A simple count of electrons confirms this suggestion: there must be three occupied π-orbitals with HOMO of antibonding character.

The N—O bond lengths in the nitro groups of (1) and 4-nitropyridine 1-oxide are the same (1.297 Å) within experimental error. In 4-(*N*,*N*-dimethylamino)pyridine *N*-oxide, (2), this bond is longer by *ca* 0.05 Å (Nakai *et al.*, 1988). An analogous reasoning leads to the conclusion that in (2), the mesomeric interaction shifts the unshared electron pair on the exocyclic-N atom to the antibonding, multicenter π-orbital. There is an alternative possibility for (1): the lone pair is included into the *N*-nitro group π-electron system. It results in the two independent sets of multicenter π-orbitals which are responsible for the geometry of (1) and for the reactivity (explosive!) of this compound.

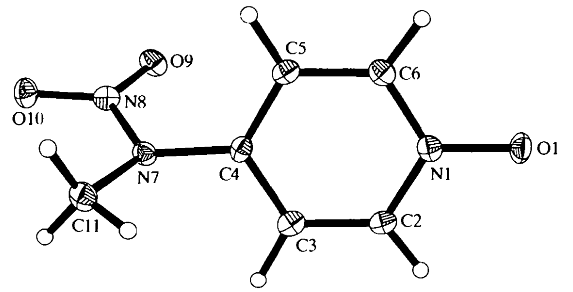


Fig. 1. Molecular structure of (1) at 300 K showing 50% probability displacement ellipsoids.

The molecules of (1) are arranged in chains along the *a* axis connected by C5—H5· · ·O1 hydrogen bonds (Fig. 2). The temperature dependence of lattice parameters between 300 and 90 K shows large anisotropy (Fig. 3). There is almost no expansion along the *a* axis and the largest changes are in the *bc* plane along a direction at *ca* 30° to the *c* axis. To determine the reason of this unusual anisotropy of thermal expansion we have determined the structure of (1) at 90 K also. The molecular structure of (1) does not change with temperature. The lengths of all bonds are the same, within three standard deviations, of those at 300 K. The anomaly in thermal expansion may be explained by weak electro-

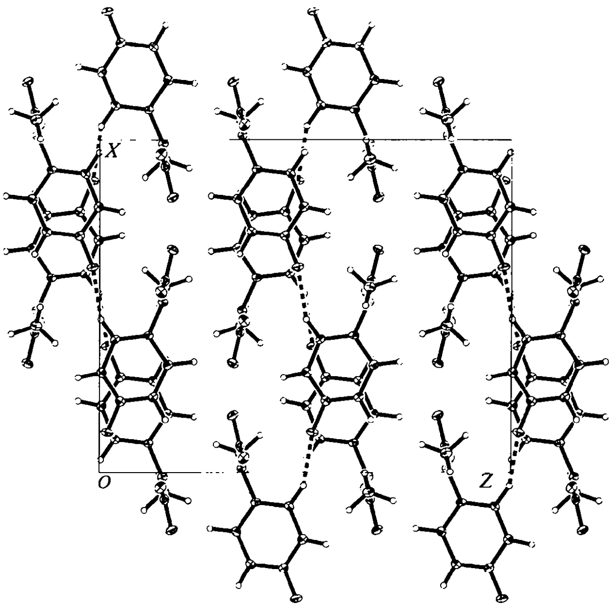


Fig. 2. Projection of the crystal structure of (1) on the *ac* plane at 90 K.

static interactions/hydrogen bonds between O10 and O9 and H3. These interactions bring closer chains of (1) molecules.

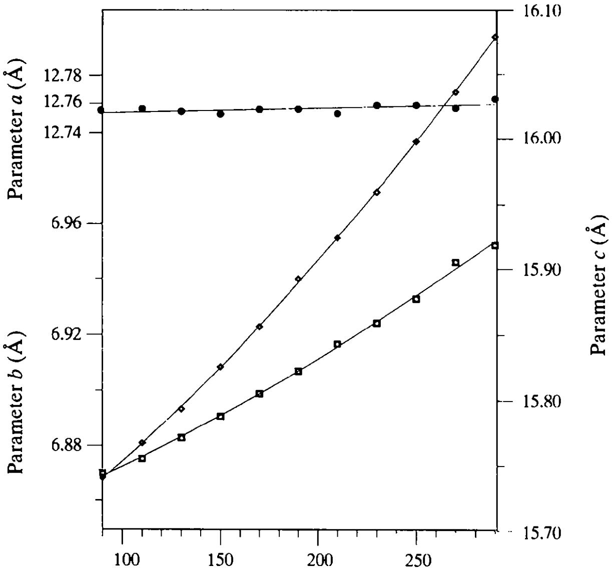


Fig. 3. Temperature dependence of lattice parameters of (1). Scales for all axes on this plot have been chosen to give the same $\Delta l/l$.

Experimental

The title compound was obtained from *N*-methyl-*N*-(4-pyridyl)-nitramine prepared as described previously (Daszkiewicz *et al.*, 1994): *N*-methyl-*N*-(4-pyridyl)nitramine (1.53 g, 10 mmol) was added in portions to a solution of hydrogen peroxide (5 ml of 30% H_2O_2, 50 mmol) in acetic acid (50 ml), the mixture was maintained at 323 K for 24 h and evaporated under vacuum. A non-volatile residue was crystallized several times from methanol yielding 4-(*N*-methylnitramino)pyridinium 1-oxide (0.53 g, 31%) as light yellow crystals (m.p. 401–406 K with decomposition) suitable for X-ray diffraction studies. ^{1}H NMR (DMSO-d_6, p.p.m.): 8.33 (*d*, 2H), 7.58 (*d*, ^3J = 7.5 Hz, 2H, aromatic protons), 3.67 (*s*, 3H, *N*-methyl group); ^{13}C NMR (DMSO-d_6, p.p.m.): 139.5 (C2, C6), 124.0 (C3, C5), 135.9 (C4), the signal of the methyl group is overlapped with the solvent multiplet; IR (KBr, cm^{-1}): 1271 and 1515 (*N*-nitro group), 1296 (nitro-group stretching vibrations).

In the thermal expansion study, lattice parameters were refined at each temperature (20 K intervals) from the setting angles of 28 reflections in the range $18 < 2\theta < 23°$; the temperature was controlled and measured using an Oxford Cryosystems attachment; the accuracy of temperature measurements is ±0.1°.

Compound (1) at 300 K

Crystal data

$C_6H_7N_3O_3$
$M_r = 169.15$
Orthorhombic
Pbca
$a = 12.758$ (3) Å
$b = 6.964$ (1) Å
$c = 16.053$ (3) Å
$V = 1426.3$ (5) Å^3
$Z = 8$
$D_x = 1.575$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 18–23°$
$\mu = 0.133$ mm^{-1}
$T = 293$ (2) K
Plate
0.48 × 0.40 × 0.36 mm
Light yellow

Data collection

Kuma KM-4 diffractometer
ω–θ scans
Absorption correction: none
3354 measured reflections
1716 independent reflections
962 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$

$\theta_{\max} = 28.06°$
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 0$
$l = -21 \rightarrow 0$
2 standard reflections every 50 reflections intensity decay: 0.86%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.180$
$S = 1.092$
1716 reflections
137 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 1.722P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.018$
$\Delta\rho_{\max} = 0.275$ e Å^{-3}
$\Delta\rho_{\min} = -0.298$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1) at 300 K*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
O1	0.37636 (16)	0.2114 (3)	0.52021 (16)	0.0491 (7)
N1	0.28343 (18)	0.2325 (4)	0.55178 (16)	0.0354 (6)
C2	0.2713 (2)	0.2986 (4)	0.6302 (2)	0.0374 (7)
C3	0.1741 (2)	0.3189 (4)	0.6645 (2)	0.0356 (7)
C4	0.0862 (2)	0.2722 (4)	0.61802 (18)	0.0319 (6)
C5	0.0992 (2)	0.2053 (4)	0.53795 (18)	0.0353 (7)
C6	0.1977 (2)	0.1852 (4)	0.50611 (19)	0.0372 (7)
N7	−0.01555 (19)	0.3056 (4)	0.65257 (16)	0.0374 (6)
N8	−0.0813 (2)	0.1543 (4)	0.65851 (16)	0.0404 (6)
O9	−0.0443 (2)	−0.0078 (3)	0.64907 (16)	0.0522 (7)
O10	−0.17248 (18)	0.1887 (4)	0.67699 (17)	0.0580 (7)
C11	−0.0604 (3)	0.4987 (6)	0.6543 (3)	0.0489 (9)

Table 2. *Selected geometric parameters (Å, °) for (1) at 300 K*

O1—N1	1.298 (3)	C4—N7	1.430 (4)
N1—C2	1.350 (4)	C5—C6	1.363 (4)
N1—C6	1.357 (4)	N7—N8	1.350 (4)
C2—C3	1.365 (4)	N7—C11	1.462 (4)
C3—C4	1.386 (4)	N8—O10	1.224 (3)
C4—C5	1.377 (4)	N8—O9	1.233 (3)
N8—N7—C4	117.7 (2)	O10—N8—O9	124.9 (3)
N8—N7—C11	118.2 (3)	O10—N8—N7	117.1 (3)
C4—N7—C11	120.8 (3)	O9—N8—N7	117.9 (3)
C5—C4—N7—N8	60.8 (4)	C4—N7—N8—O10	−170.0 (3)
C3—C4—N7—N8	−123.0 (3)	C11—N7—N8—O10	−10.3 (4)
C5—C4—N7—C11	−98.4 (4)	C4—N7—N8—O9	13.5 (4)
C3—C4—N7—C11	77.8 (4)	C11—N7—N8—O9	173.2 (3)

Table 3. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*		*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1[i]	(300 K)	1.00 (3)	2.25 (3)	3.048 (4)	136 (2)
	(90 K)	0.97 (3)	2.21 (3)	3.009 (4)	139 (3)

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

Compound (1) at 90 K

Crystal data

$C_6H_7N_3O_3$
$M_r = 169.15$
Orthorhombic
Pbca
$a = 12.756$ (3) Å
$b = 6.870$ (1) Å
$c = 15.740$ (3) Å
$V = 1379.4$ (5) Å^3
$Z = 8$
$D_x = 1.629$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 18$–$23°$
$\mu = 0.133$ mm^{-1}
$T = 90.0$ (1) K
Plate
0.48 × 0.40 × 0.36 mm
Light yellow

Data collection

Kuma KM-4 diffractometer
ω–θ scans
Absorption correction: none
1757 measured reflections
1757 independent reflections
1183 reflections with $I > 2\sigma(I)$

$\theta_{max} = 30.87°$
$h = 0 \rightarrow 17$
$k = -9 \rightarrow 0$
$l = -20 \rightarrow 0$
2 standard reflections every 50 reflections intensity decay: 0.32%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.146$
$S = 1.153$
1757 reflections
137 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0066P)^2 + 6.7646P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.423$ e Å^{-3}
$\Delta\rho_{min} = -0.386$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1) at 90 K*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.37956 (17)	0.2110 (3)	0.51814 (15)	0.0171 (5)
N1	0.2860 (2)	0.2321 (4)	0.55015 (16)	0.0130 (5)
C2	0.2743 (2)	0.3028 (4)	0.6305 (2)	0.0129 (6)
C3	0.1766 (2)	0.3244 (4)	0.6659 (2)	0.0134 (6)
C4	0.0887 (2)	0.2740 (4)	0.6184 (2)	0.0117 (6)
C5	0.1008 (2)	0.2037 (4)	0.5367 (2)	0.0127 (6)
C6	0.2001 (2)	0.1838 (4)	0.5036 (2)	0.0134 (6)
N7	−0.0131 (2)	0.3087 (4)	0.65405 (17)	0.0128 (5)
N8	−0.0798 (2)	0.1559 (4)	0.65894 (17)	0.0136 (5)
O9	−0.04386 (18)	−0.0094 (3)	0.64919 (15)	0.0169 (5)
O10	−0.17175 (17)	0.1924 (4)	0.67684 (15)	0.0184 (5)
C11	−0.0585 (3)	0.5049 (5)	0.6559 (2)	0.0160 (6)

For both compounds, cell refinement: *Kuma Diffraction Software* (Kuma, 1997); data reduction: *Kuma Diffraction Software*; program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997*b*); 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: GD1027). Services for accessing these data are described at the back of the journal.

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Zaleski, J., Daszkiewicz, Z. & Kyzioł, J. (1999). *Acta Cryst.* C**55**, 691–693.

Acta Cryst. (1999). C**55**, 1295–1297

(1*R*,2*R*,3*R*,3′*R*,4*R*)-3-[(2-Furyl)hydroxymethyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, a new camphor-based chiral auxiliary

Marcelo Cardoso Branco,[a] Maria Teresa do P. Gambardella,[a] Mario L. A. A. Vasconcellos[b] and Uendel G. Barreiros[b]

[a]*Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560-970 São Carlos SP, Brazil, and* [b]*Núcleo de Pesquisas de Produtos Naturais, Universidade Federal do Rio de Janeiro, Bloco H, CCS, Ilha do Fundão, 21941-590 Rio de Janeiro RJ, Brazil. E-mail: branco@iqsc.sc.usp.br*

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Abstract

Camphor chiral derivatives have proven to be very powerful chiral adjuvants in organic synthesis. The absolute molecular configuration of the title compound, $C_{15}H_{22}O_3$, has been determined due to the chiral