Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.089$
$S = 1.011$
3798 reflections
299 parameters
H atoms refined with $U = 0.05$ Å^2
$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.267$ e Å^{-3}
$\Delta\rho_{\min} = -0.261$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C6	1.3600 (8)	C2—C20	1.5412 (9)
O1—C2	1.4767 (7)	C3—N4	1.2744 (9)
C2—N15	1.4311 (8)	N4—C5	1.4070 (9)
C2—C3	1.5209 (9)		
C6—O1—C2	118.07 (5)	C3—C2—C20	108.93 (5)
N15—C2—O1	112.65 (5)	N4—C3—C2	126.58 (6)
N15—C2—C3	107.82 (5)	C3—N4—C5	116.64 (6)
O1—C2—C3	108.09 (5)	C6—C5—N4	120.91 (6)
N15—C2—C20	114.76 (5)	O1—C6—C5	121.56 (6)
O1—C2—C20	104.38 (5)		
C6—O1—C2—N15	87.45 (7)	C3—N4—C5—C6	−12.60 (9)
C6—O1—C2—C3	−31.57 (7)	C3—N4—C5—C10	167.62 (6)
C6—O1—C2—C20	−147.42 (5)	C2—O1—C6—C5	20.64 (8)
N15—C2—C3—N4	−97.57 (8)	C2—O1—C6—C7	−160.37 (6)
O1—C2—C3—N4	24.48 (9)	N4—C5—C6—O1	3.69 (9)
C20—C2—C3—N4	137.32 (7)	C10—C5—C6—O1	−176.54 (5)
C2—C3—N4—C5	−3.24 (10)	N4—C5—C6—C7	−175.26 (6)

The data set consists of the unique half of a parallelepiped rather than a sphere of reciprocal space; the extreme $\theta_{\max}$ is 34.5° and data are complete to $\theta = 23°$.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *DATARED* (Pèpe, 1979). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1201). Services for accessing these data are described at the back of the journal.

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4-Chloro-*N*-methyl-*N*-nitroaniline

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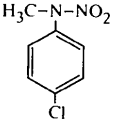
Abstract

The molecular structure of (p-ClC_6H_4)(CH_3)NNO_2 (or $C_7H_7ClN_2O_2$) contains a planar NNO_2 nitroamino group which is twisted about the N—$C_{\rm phenyl}$ bond by *ca* 68° from the plane of the aromatic ring. The structural data are in agreement with the spectral results and indicate that there is no conjugation between the aromatic sextet and the nitroamino group. There are no specific intermolecular interactions.

Comment

Nitramines and related *N*-nitro compounds have attracted much attention during the last few decades. The crystal structures of *N*,*N*-dimethylnitramine and of some cyclic and open-chain aliphatic nitramines have been reported. Within the aromatic series, only tetryl (Cady, 1967) and its analogue (Holden & Dickinson, 1969) have been studied. An interesting feature of *N*-methyl-*N*-phenylnitramine and its derivatives is their ability to rearrange under the influence of acids or at increased temperature. The migration is entirely intramolecular, *i.e.* the *N*-nitro group shifts to an aromatic ring, three or five atoms from its original position, while remaining covalently bound to the aromatic residue (Shine, 1967). The molecular structures of secondary arylnitramines may provide a clue to the nature of the nitramine rearrangement. The title compound, (I), is the first member of the series to have been examined.



(I)

The nitroamino group in (I) is planar. Bond lengths and angles agree with corresponding values in *N,N*-dimethylnitramine (Filhol *et al.*, 1980); the differences do not exceed 0.02 Å and 2°, respectively. The N—N bond in nitramines is significantly longer (1.34 *versus* 1.25 Å) than in hyponitrites and azo compounds (Ogle *et al.*, 1982), but shorter than single bonds (Cameron *et al.*, 1972). It indicates that one π-electron pair from the sextet occupying the set of four-centre π-orbitals occupies an anti-bonding level.

In arylnitramines containing two nitro groups situated *ortho* to the nitramino group, the NNO_2 unit is nearly perpendicular to the aromatic ring. Although there is no steric hindrance in the title molecule, the N2—N1—C1—C2 torsion angle of −65.6 (4)° indicates that there is no conjugation between two sets of multicentre π-orbitals. This accounts for the observation that the ring substituents have no influence on the spectral and electro-optical properties of *N*-methyl-*N*-phenylnitramine derivatives (Daszkiewicz *et al.*, 1995), but not for the migration ability of the *N*-nitro group. The nitroamino group is polar; molecular orbital calculations reveal a strong positive charge on the N2 atom and negative charges on all its neighbours. The interaction of the N—O dipoles plays a role in the crystal structure, but the shortest intermolecular N···O distances (3.08 Å) are longer than would be predicted from the van der Waals radii.

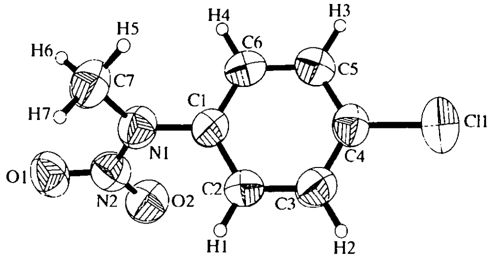


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

Experimental

The title compound was obtained by the action of *n*-butylnitrate on the Grignard compound generated *in situ* from 4-chloro-*N*-methylaniline and ethylmagnesium bromide as described by Daszkiewicz *et al.* (1994). The crude product was crystallized from *n*-hexane. Crystals suitable for X-ray studies were obtained by slow cooling of a methylene chloride solution to 253 K.

Crystal data

$C_7H_7ClN_2O_2$
$M_r = 186.60$
Monoclinic
$P2_1/c$
$a = 6.081\ (1)$ Å
$b = 6.957\ (1)$ Å
$c = 19.707\ (4)$ Å
$\beta = 95.46\ (3)°$
$V = 829.9\ (3)$ Å^3
$Z = 4$
$D_x = 1.493$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 5$–25°
$\mu = 0.418$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped
0.35 × 0.30 × 0.25 mm
Colourless

Data collection

Kuma KM-4 diffractometer
ω–2θ scans
Absorption correction: none
3990 measured reflections
1942 independent reflections
1380 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$

$\theta_{\rm max} = 29.94°$
$h = 0 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 25$
2 standard reflections every 50 reflections intensity decay: 0.90%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.232$
$S = 1.106$
1942 reflections
138 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.1355P)^2 + 0.1940P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.37$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.073 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cl1—C4	1.722 (3)	C1—C6	1.385 (4)
O1—N2	1.229 (3)	C1—C2	1.389 (4)
O2—N2	1.222 (3)	C2—C3	1.370 (5)
N1—N2	1.346 (3)	C3—C4	1.392 (4)
N1—C1	1.423 (4)	C4—C5	1.384 (4)
N1—C7	1.446 (4)	C5—C6	1.380 (4)
N2—N1—C1	118.4 (2)	C2—C1—N1	120.2 (2)
N2—N1—C7	118.8 (3)	C3—C2—C1	119.5 (3)
C1—N1—C7	122.4 (2)	C2—C3—C4	119.8 (3)
O2—N2—O1	125.0 (3)	C5—C4—C3	121.1 (3)
O2—N2—N1	118.3 (3)	C5—C4—Cl1	119.7 (2)
O1—N2—N1	116.6 (3)	C3—C4—Cl1	119.1 (2)
C6—C1—C2	120.5 (3)	C6—C5—C4	118.7 (3)
C6—C1—N1	119.2 (2)	C5—C6—C1	120.4 (3)

Data collection: *Kuma KM-4 Users Guide* (Kuma, 1997). Cell refinement: *Kuma KM-4 Users Guide*. Data reduction: *Kuma KM-4 Users Guide*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

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nity to use the *SHELXTL-Plus* program system in his laboratory.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1371). Services for accessing these data are described at the back of the journal.

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Phenyl 2-Pyridyl Ketone at 150 K

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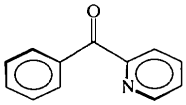
Abstract

Crystals of phenyl 2-pyridyl ketone, $C_{12}H_9NO$, suitable for X-ray diffraction were obtained by sublimation. Their structure, which was determined at 150 K, yields geometric parameters comparable with those found for the iso(valence)electronic analogues of benzophenone and 2,2′-dipyridyl ketone [Bock *et al.* (1998). *Struct. Chem.* In the press]. Both the phenyl and pyridine rings are twisted considerably out of the central C—C(O)—C plane.

Comment

The structure of phenyl 2-pyridyl ketone, (I), has not been determined previously although it is of interest as a parent model compound for oxygen and nitrogen lone-pair interactions in 2-pyridyl-substituted molecules and, especially, as a connecting link between the crystal structures of benzophenone (Brandon *et al.*, 1965; Fleischer *et al.*, 1968) and di2-pyridyl ketone (Bock *et al.*, 1998).



(I)

Commercially available phenyl 2-pyridyl ketone can be sublimed at 303 K yielding colourless blocks. Examination of the lattice packing (Fig. 1) shows two characteristic motifs resulting from weak intermolecular interactions. Among several rather long C—H···O contacts of up to 3.40 Å, the one between O1 and C15$(-x, y-\frac{1}{2}, \frac{3}{2}-z)$ has a distance of only 3.260 (3) Å (Fig. 1*a*), with a C—H···O angle of 135.0 (5)°. As every molecule is involved in two of these hydrogen-bridge contacts, undulating layers form in the *yz* plane; these are connected to each other *via* weak π–π interactions (Fig. 1*a*). The interplanar distance between the phenyl and pyridine rings of adjacent molecules is 3.44 (2) Å, *i.e.* it exceeds by only 0.04 Å twice the van der Waals radius of a π-system of 1.70 Å (Pauling, 1962). The interplanar angle of about 9° is rather small, but the ring centroids are shifted about 1.40 (2) Å parallel to each other, which results in a distance of 3.71 (1) Å. The interaction proceeds along the *x* axis and leads to polymeric chains which are connected to each other *via* hydrogen bridges.

The structure of the molecule deviates significantly from planarity because the phenyl and pyridine rings are rotated around the OC—C-*ipso* axes (Fig. 1*b*): the phenyl ring is twisted relative to the planar group C11—C(O)—C21 to give a C12—C11—C1—O1 torsion angle of 155.6 (2)°; the pyridine ring is also twisted with O1—C1—C21—N1 = 131.0 (2)°. The larger torsion of the pyridine ring is due to the repulsion of the nitrogen electron pair at N1. A weak C12—H···N1 interaction is also observed.

Bond lengths and angles, as well as the torsion angles of the phenyl and pyridine rings (Table 1), are comparable with those found in the structures of benzophenone (Brandon *et al.*, 1965; Fleischer *et al.*, 1968) and di2-pyridyl ketone (Bock *et al.*, 1998). For instance, in the crystal structure of benzophenone, which crystallizes in the same orthorhombic space group $P2_12_12_1$, both phenyl rings are twisted by about 30° compared with a value of 24.4 (2)° for the phenyl ring in phenyl 2-pyridyl ketone. Furthermore, the pyridine ring in the title compound exhibits a torsion angle of 131.0 (2)°, which differs significantly from that of 17.0 (1)° for one of the pyridine rings in di2-pyridyl ketone. A value of only 41.2 (2)° for the other pyridine