Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996*a*)
$T_{\min} = 0.861$, $T_{\max} = 1.000$
31 151 measured reflections
5043 independent reflections
4935 reflections with $I > 0$

$R_{\text{int}} = 0.028$
$\theta_{\max} = 30.13°$
$h = -17 \rightarrow 16$
$k = -10 \rightarrow 10$
$l = -27 \rightarrow 26$
365 standard reflections
frequency: 540 min
intensity decay: none

Refinement

Refinement on F
$R = 0.063$
$wR = 0.053$
$S = 1.283$
4935 reflections
328 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$
$(\Delta/\sigma)_{\max} = 0.010$

$\Delta\rho_{\max} = 0.355$ e Å^{-3}
$\Delta\rho_{\min} = -0.192$ e Å^{-3}
Extinction correction: isotropic (*MolEN*; Fair, 1990)
Extinction coefficient: $2.5\,(4) \times 10^{-6}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H01···O1^{i}	0.89 (1)	2.06 (1)	2.938 (1)	170 (1)
N3—H03···O2^{ii}	0.89 (1)	2.08 (1)	2.970 (1)	170 (1)

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

The measured reflections were corrected for absorption and for systematic variations in the uniformity of the X-ray beam using *SADABS* (Sheldrick, 1996*a*). H atoms were taken from a difference synthesis and were refined with isotropic displacement parameters.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS* in *SHELXTL* (Sheldrick, 1996*b*). Program(s) used to refine structure: *LSFM* in *MolEN* (Fair, 1990). Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *CIF* in *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1301). Services for accessing these data are described at the back of the journal.

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1-Methyl-4-(*N*-methylnitramino)pyridinium bromide

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Abstract

The structure of the title compound, $C_7H_{10}N_3O_2^+\cdot Br^-$, is composed of 1-methyl-4-(*N*-methylnitramino)pyridinium cations and bromide anions, with normal electrostatic interactions. The cations are present in the nitramino form. The N—NO$_2$ nitramino group is twisted 51.5 (4)° out of the plane of the aromatic ring.

Comment

N-Methyl-*N*-(4-pyridyl)nitramine, (1), is a typical secondary aromatic nitramine which can be rearranged to 4-methylamino-3-nitropyridine when heated in an inert solvent. *N*-(4-Pyridyl)nitramine, (2), behaves analogously, but the rearrangement requires more severe conditions and results in much lower yield (Daszkiewicz *et al.*, 1997). X-ray studies have revealed that primary pyridylnitramines such as (2) exist in the nitrimino tautomeric form (Krygowski *et al.*, 1996). The difference in susceptibility of (1) and (2) to the rearrangement may be due to differences in their molecular structures. In a typical secondary aromatic nitramine, the plane of the N—NO$_2$ group is twisted *ca* 70° out of the ring plane along the Ar—N bond (Ejsmont *et al.*, 1998; Anulewicz *et al.*, 1993). In (3), the N—NO$_2$ group is nearly coplanar with the pyridine ring. Despite this difference, the geometries of both the ring and the N—NO$_2$ substituent are not disturbed to the degree implied by the nitrimine formulation (Bujak *et al.*, 1998). The pyridine N atom in (1) retains its nucleophilic character, hence the preparation of (4) is straightforward. We have examined its molecular structure to compare it with the structure of

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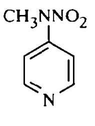
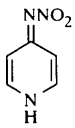
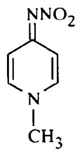
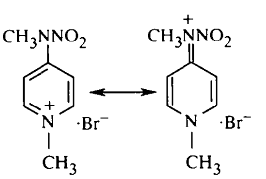
(3), hoping that it will provide some information on the structure–reactivity relationship within the pyridylnitramine series.


(1)


(2)


(3)


(4a) (4b)

The only chemical structural difference between (3) and the cation of (4) is the extra methyl group bonded to the amide-N atom, N7. Its presence lengthens the N—N bond by *ca* 0.03 Å [1.329 (2) in (3) and 1.358 (4) Å in (4)], shortens the N—O bonds by *ca* 0.02 Å [1.239 (2) in (3) and 1.222 (4) Å in (4)], and increases the O—N—O angle from 120.0 (1) to 125.2 (3)°. The length of the C4—N7 bond is increased from 1.368 (2) in (3) to 1.403 (4) Å in (4). These small differences in the geometry of molecules (3) and (4) reflect some significant variations in the charge distribution within the N_2O_2 group. The electronic structure of the 1-methyl-4-(*N*-methylnitramino)pyridinium cation may be considered as the resonance hybrid of two canonical structures (4*a*) and (4*b*). The most spectacular difference between the molecular structures of (3) and (4) is in the torsion angle about the C4—N7 bond: in the cation, the N—NO_2 plane is twisted 51.5 (4)° out of the plane of the pyridine ring whereas in (3) it is almost coplanar to the ring [twist angle 7.4 (2)°]. This twist, although much larger than in (3), is still significantly smaller than is typical for secondary aromatic nitramines. The C4—N7 bond is unusually long, suggesting that the *N*-methylnitramino substituent may rotate relatively freely. Consequently, resonance within the cation should be excluded and the interaction between the positively charged ring and the polarizable nitramino group is of an inductive nature. The bond lengths and angles within the pyridine ring indicate that its aromaticity is not disturbed by the substituents at the N1 and C4 positions. Thus, form (4*a*) seems to be a much better representation of the electronic structure of the cation than the alternative form (4*b*).

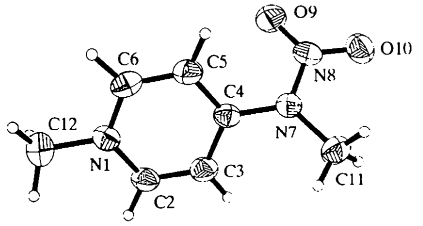


Fig. 1. Molecular structure of compound (4) showing 50% probability displacement ellipsoids.

Experimental

N-Methyl-*N*-(4-pyridyl)nitramine (0.60 g, 3.9 mmol) was dissolved in a mixture of acetone and diethyl ether (1:1, 20 ml). An excess of liquid methyl bromide (5 ml, 91 mmol) was added and the mixture was left for 24 h at room temperature. The crude product was collected by filtration and crystallized (0.85 g, yield 88%) from 2-propanol (20 ml); m.p. 425 K, according to differential scanning calorimetry.

Crystal data

$C_7H_{10}N_3O_2^+ \cdot Br^-$
$M_r = 248.09$
Orthorhombic
Pbca
$a = 10.480\,(2)$ Å
$b = 11.949\,(2)$ Å
$c = 15.005\,(3)$ Å
$V = 1879.0\,(6)$ Å^3
$Z = 8$
$D_x = 1.754$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 8$–15°
$\mu = 4.347$ mm^{-1}
$T = 295\,(2)$ K
Plate
0.4 × 0.3 × 0.1 mm
Colourless

Data collection

Kuma KM-4 diffractometer
ω–θ scans
Absorption correction: semi-empirical from ψ scans (*SHELXTL*; Sheldrick, 1990)
$T_{\min} = 0.143$, $T_{\max} = 0.647$
3059 measured reflections
1639 independent reflections

1104 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\max} = 25.07°$
$h = -12 \rightarrow 0$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 0$
2 standard reflections every 50 reflections intensity decay: 0.72%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.082$
$S = 1.000$
1639 reflections
158 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.1823P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.524$ 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, °)*

O9—N8	1.222 (3)	N7—C4	1.403 (4)
O10—N8	1.221 (4)	N7—C11	1.453 (4)
N8—N7	1.358 (4)	N1—C12	1.474 (5)
O10—N8—O9	125.2 (3)	N8—N7—C4	119.8 (3)
O10—N8—N7	116.8 (3)	N8—N7—C11	116.7 (3)
O9—N8—N7	117.9 (3)	C4—N7—C11	123.5 (3)
N8—N7—C4—C3	129.3 (3)	N8—N7—C4—C5	−52.2 (4)

Data collection: *Kuma Diffraction Software* (Kuma, 1997). Cell refinement: *Kuma Diffraction Software*. Data reduction: *Kuma Diffraction Software*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1290). Services for accessing these data are described at the back of the journal.

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4-(4-Biphenyl)-2,3,5,6-tetrafluoropyridine, a new material for application in light-emitting diodes

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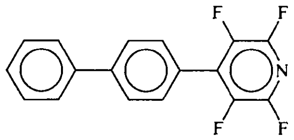
Abstract

Thin films of the title compound, $C_{17}H_9F_4N$, are used as electron-transport layers in organic light-emitting diodes. The molecules crystallize in a layered structure, with the aromatic planes of neighbouring molecules approximately parallel to each other. The conformation of the molecule is expressed by tilting of the pyridyl and phenyl planes by 46.8 (1) and 40.3 (1)°, respectively, relative to the central benzene ring.

Comment

The title compound, (I), was synthesized for application in organic-based light-emitting diodes (LEDs). This partly fluorinated compound is a suitable material for electron-transport layers in heterostructured devices (Winkler *et al.*, 1998). LEDs are sandwich devices built from thin films of electrodes, hole- and electron-transport layers, and the electroluminescent layer (Adachi *et al.*, 1990). The electrical and optical properties of the electroluminescent layer depend strongly on the orientation and conformation of the molecules in the other layers. Therefore, knowledge of the crystal structure of the title compound is necessary for the determination of the preferred growth and orientation of the molecules within these thin films.



(I)

Single crystals of (I), synthesized and purified according to Winkler (1997), were grown from a toluene solution. Within the crystal, the molecules are packed in a layered structure. These layers are parallel to (001) and the individual molecules are arranged perpendicular to the layer. Therefore, the thickness of one layer corresponds to the length of the molecule. However, two neighbouring molecules in one layer are centrosymmetric relative to each other, which results in a reverse arrangement of the pyridyl rings, as depicted in Fig. 1. A centre of symmetry of space group $P\bar{1}$ is located in the middle of the two central benzene rings, which are therefore parallel to each other. The outer phenyl and pyridyl rings of these two neighbouring molecules are tilted 6.6 (6)° relative to each other. Between these aromatic planes, the closest intermolecular distance is that between the two atoms C9 and $C11^{i}$, at 3.486 (2) Å [symmetry code: (i) $1-x$, $1-y$, $-z$]. It is probable that parallel packing of neighbouring molecules is the main interaction in the title compound, as is often observed in systems with fluorinated aromatic rings (Dahl, 1994). This parallel packing is also observed in other fluorinated aromatics, such as 2,3,5,6-tetrafluorobiphenyl (Goodhand & Hamor, 1978) and 2,3,4,5,6-pentafluorobiphenyl (Brock *et al.*, 1978), and in the biphenyl perfluorobiphenyl complex (Naae, 1979).

The inter-ring C5—C6 and C9—C12 bond lengths are 1.489 (2) Å and 1.498 (2) Å, respectively; these two

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