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N,N-Dimethyl-N'-(o-fluorobenzoyl)hydrazide

Kenneth W. Muir* and David G. Morris

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

Correspondence e-mail: ken@chem.gla.ac.uk

The title dimethylhydrazide o-FC$_6$H$_4$C(O)NHNMe$_2$, or C$_9$H$_{11}$FN$_2$O, is compared structurally both with other aroyl hydrazides, ArC(O)NHNH$_2$, and with related trimethyl-ammonio ylides, Me$_3$N(+)—N(−)C(O)Ar.
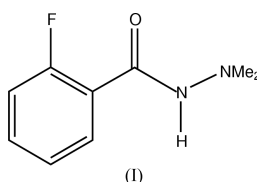
Comment

The title compound, (I), was prepared as a precursor to the corresponding trimethylammonio-stabilized nitrogen ylide Me$_3$N(+)—N(−)—C(O)C$_6$H$_4$—F-o. Its structure was determined in the course of an investigation into the ability of nitrogen ylides to act as ligands with transition metals (Morris *et al.*, 2003).

(I)

The presence of the *ortho*-fluoro substituent causes (I) to adopt a conformation (Fig. 1) which precludes conjugation across the C6—C7 bond [C1—C6—C7—N1 = 122.5 (2)°]. Possibly as a result, the C6—C7 bond [1.509 (2) Å] is 0.02 Å longer than the database average value obtained by Orpen *et al.* (1992) for such bonds, whereas all other bond lengths in (I) agree within 0.008 Å with appropriate average values from the Cambridge Structural Database (Allen, 2002). Phenyl-hydrazides, in general, adopt much flatter conformations than that found in (I). For example, in PhC(O)NHNH$_2$, (II), the C(Ph)—C(Ph)—C(O)—N torsion angle is 30° (Kallel *et al.*, 1992), while in o-HOC$_6$H$_4$C(O)NHNH$_2$, (III), the corresponding angle is only 3° (Mikenda *et al.*, 1993). In (I), the C6—C7—N1—N2 torsion angle is 175.9 (1)°. Corresponding values in other hydrazides are almost invariably close to 180°;
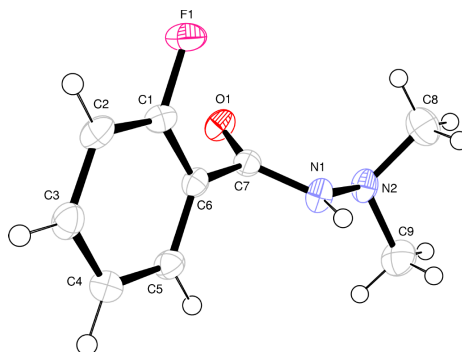

Figure 1
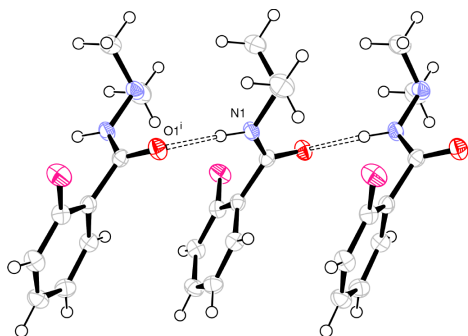View of (I), shown with 50% probability displacement ellipsoids.

Figure 2
Part of a stack of hydrogen-bonded molecules related by the *b*-glide plane normal to the *a* axis. The direction of view is down the *a* axis and *b* runs from left to right in the plane of the drawing.
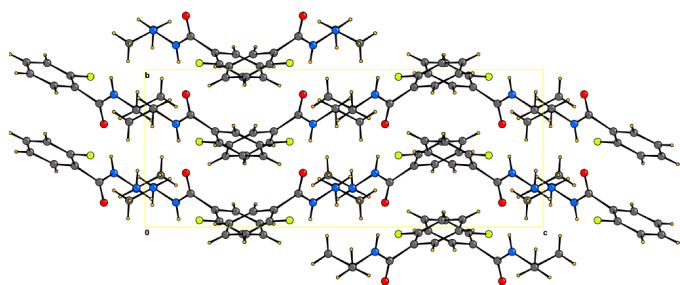

Figure 3
The unit-cell contents, viewed in projection down the *a* axis.

the only exception we are aware of is provided by Ph(CO)NMeNMe$_2$, where this torsion angle is only 8.5° (Knapp *et al.*, 1981), presumably for steric reasons. In (I), the N—N distance [1.420 (2) Å] and C—N—N angle [119.8 (1)°] are typical of hydrazides, such as (II) and (III), whereas in the closely related Me$_3$N(+)—N(–)C(O)Ar ylides, the N—N distances are longer and the C—N—N angles more acute, *e.g.* 1.470 (3) Å and 114.2 (3)° when Ar = Ph (Cameron *et al.*, 1972), and 1.474 (1) Å and 114.8 (1)° when Ar = *p*-Cl—C$_6$H$_4$ (Morris *et al.*, 2003). *QUEST* and *CONQUEST* search programs were used with Version 5.24 of the Cambridge Structural Database (Allen, 2002) to obtain some torsion angles not given by the original authors.

Glide-plane-related molecules connected by N—H···O hydrogen bonds (Fig. 2) form stacks which run parallel to the *b* axis. These stacks pack so that alternate layers parallel to (001) contain, respectively, aromatic rings and terminal NMe$_2$ groups, as can be seen by viewing the contents of the unit cell in projection down the *a* axis (Fig. 3). As expected (Glusker *et al.*, 1994), the F atoms do not participate in the hydrogen bonding.

The atomic U^{ij} values are moderately well reproduced by a **TLS** analysis (Schomaker & Trueblood, 1968): $R_2 = (\Delta U^2/U^2)^{1/2} = 0.10$; they also pass the Hirshfeld (1976) rigid-bond test, the worst discrepancy being $\Delta U = 0.0018$ (12) Å^2 for C4—C5.

Experimental

The title compound was prepared by the method of Smith *et al.* (1968).

Crystal data

C$_9$H$_{11}$FN$_2$O	Mo *K*α radiation
$M_r = 182.2$	Cell parameters from 1794
Orthorhombic, *Pbca*	reflections
$a = 11.8503$ (5) Å	$\theta = 2.9–26.0°$
$b = 7.8530$ (3) Å	$\mu = 0.10$ mm^{-1}
$c = 19.9630$ (9) Å	$T = 100$ (2) K
$V = 1857.77$ (13) Å^3	Needle, colourless
$Z = 8$	$0.40 \times 0.05 \times 0.05$ mm
$D_x = 1.303$ Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.057$
Thick-slice ω and φ scans	$\theta_{max} = 25.9°$
6796 measured reflections	$h = -14 \rightarrow 14$
1797 independent reflections	$k = -9 \rightarrow 9$
1491 reflections with $I > 2\sigma(I)$	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.048P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 0.85P]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0$
1797 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
124 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^i	0.91 (2)	1.98 (2)	2.8801 (19)	168.8 (19)

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

All H atoms were initially located from difference syntheses. The H atom bonded to N1 was freely refined. Other H atoms were positioned geometrically and refined with riding constraints, assuming C—H bond lengths of 0.93 and 0.96 Å, respectively, for sp^2 and sp^3 C atoms. In the case of each of the two methyl groups, a single orientation parameter was also refined.

Data collection: *COLLECT* in *KappaCCD Control Software* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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