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3,5-Diamino-6-(2-fluorophenyl)-1,2,4-triazine–dimethylformamide (1/1)

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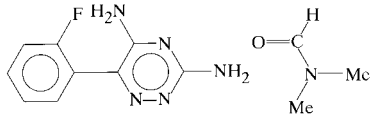
The title compound, $C_9H_8FN_5\cdot C_3H_7NO$, contains two independent complexes in the asymmetric unit, each consisting of one 3,5-diamino-6-(2-fluorophenyl)-1,2,4-triazine molecule and one dimethylformamide solvent molecule. One triazine molecule is disordered over two conformations within the crystal, the occupancies being 62 (1) and 38 (1)%. The phenyl ring of this molecule resolves into two conformations rotated by almost 180° about the bridging bond between the two rings, while the triazine rings approximately superimpose on each other. The triazine molecules of the asymmetric unit differ in the dihedral angles between their respective phenyl and triazine ring planes, these being 57.6 (2)° for the fully occupied, and 76.9 (6) and 106.8 (8)° for the partially occupied molecules. An extensive network of hydrogen bonds maintains the crystal structure.

Comment

The work presented on the title compound, (I), forms part of an ongoing investigation into structure–activity studies on analogues of the anticonvulsant lamotrigine. The structure of lamotrigine (Janes *et al.*, 1989), and a number of these analogues (Janes & Palmer, 1995*a*,*b*, 1996; Janes, 1999) have been reported, and investigations of these structures have been undertaken (Janes & Palmer, 1995*c*). The asymmetric unit comprises two analogue molecules and two dimethylformamide solvent molecules. Fig. 1 presents a displacement ellipsoid plot with the asymmetric unit labelled, and shows a hydrogen-bonded layer of molecules within the unit cell. One of the analogue molecules exhibits disorder having two positions for its phenyl ring orientated almost 180° apart in rotation about the bridging bond between the rings, the attached fluorine being located on opposite sides of the ring, and the triazine ring placed such that the atoms almost superimpose on one another. The analogue structures reported here will be referred to as the 'fully occupied' and as the 'percentage occupied' structures for ease of distinction. In Fig. 2, the top view is that of the fully occupied molecule, while the middle and lower views are those of the partial occupancy molecules. The structure with the fluorine labelled F2′ in Fig. 1 is 62 (1)% occupied, while that for F2″ (omitted for clarity) is 38 (1)%. The principal moieties of the disordered structures, being almost superimposable upon one another, were resolved using similarity restraints in *SHELXL*97 (Sheldrick, 1997).



(I)

The phenyl and triazine rings of the fully occupied analogue molecule are both planar, the overall root mean square deviations (r.m.s.d.) for these atoms being 0.006 Å for the phenyl ring and 0.018 Å for the triazine ring. The fluorine attached to the phenyl ring deviates by only 0.023 (8) Å from its ring plane. The N atoms of the amino groups also deviate from their triazine ring plane by −0.071 (8) for N3 and 0.074 (8) Å for N5. For the 62% occupied molecule the r.m.s.d. for the ring atoms are 0.010 and 0.019 Å for the phenyl and triazine rings, respectively. The fluorine F2′ does not deviate significantly from its phenyl-ring plane. The N atoms of the amino groups of the triazine ring barely deviate from their ring plane [by −0.05 (3) for N3′ and 0.14 (3) Å for N5′]. The 38% occupied molecule has r.m.s.d. values of 0.022 and 0.018 Å for its phenyl and triazine rings, respectively. The fluorine F2″ is 0.04 (2) Å from its phenyl ring, while atoms N3″ and N5″ are 0.04 (4) and −0.17 (4) Å, respectively, from their ring plane.

The dihedral angles between the phenyl and triazine rings of the analogue molecules within the asymmetric unit show

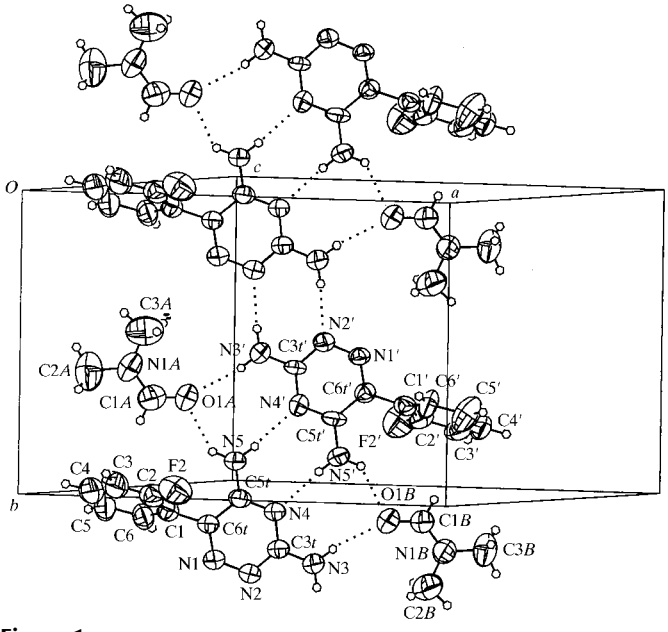


Figure 1
View of the molecular structure of (I), showing the atom-numbering scheme (displacement ellipsoids at 50% probability) for the asymmetric unit and the chains of hydrogen bonds formed between molecules within, and between, the unit cells. F2′ is 62% occupied and F2″ (not shown) is 38% occupied.

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significant differences. That for the fully occupied is 57.6 (2)°, while for the partially occupied molecule the dihedral angles are 76.9 (6)° for the 62% occupied, and 106.8 (8)° for the 38% occupied structures. The 2-fluorophenyl analogue has been solved as a methanolate (Janes & Palmer, 1995*a*), and this structure also comprises two analogue and two solvent molecules as the asymmetric unit, although in this case, no disorder is present. Here, the dihedral angles are 50.8 (1) and 125.0 (1)° between the phenyl and triazine ring planes. The diversity of dihedral angles observed for this analogue reveals that there must exist a high degree of flexibility for rotation about the bridging bond between the rings, at least between the extreme values of the dihedral angles, without any significant penalty to the internal energetics of the molecule.

The two rings of the analogue molecules for the fully and partially occupied structures exhibit some degree of distortion away from being coaxial, as seen in Fig. 2. This distortion can be further illustrated by focusing on the distances of the specific coaxial atoms, namely C4, C1, C6*t* and C3*t*, from their opposing ring planes. For the fully occupied structure, carbon C1 of the phenyl ring is nominally coplanar with the opposing triazine ring atoms lying only −0.019 (7) Å from its least-squares mean plane, but C4 is −0.13 (2) Å from the same plane. Likewise, C6*t* of the triazine ring is 0.062 (8) Å from the phenyl ring plane, while C3*t* deviates by 0.26 (1) Å from the same ring. Similarly, for the 62% occupied structure, carbon C1′ is only 0.02 (2) Å from the corresponding triazine ring plane, while C4′ is 0.15 (4) Å from this same plane. Also, C6*t*′ is 0.08 (2) Å while C3*t*′ is 0.30 (4) Å from their related phenyl ring. For the 38% occupied structure, C1″ and C4″ are −0.05 (2) and −0.29 (5) Å from their triazine ring plane, respectively. Additionally, C6*t*″ and C3*t*″ are −0.11 (3) and −0.27 (6) Å, respectively, from their phenyl ring plane.

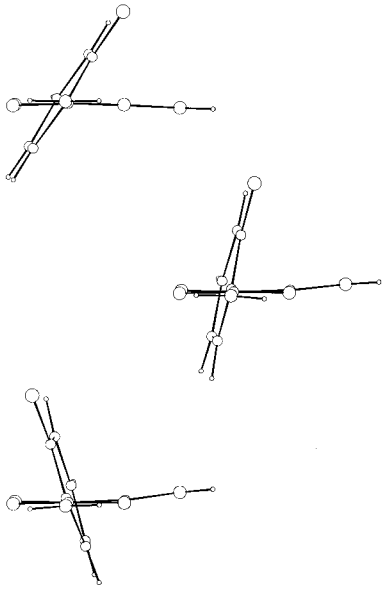

Figure 2
Views of the analogue molecules along the C3*t*—C6*t* direction showing the differences in dihedral angles between the two rings of the molecule, viewed with the triazine ring horizontal. The fully occupied structure is at the top, the 62% occupied is in the middle and the 38% occupied is at the bottom.

There is extensive hydrogen bonding within the structure that maintains the framework of the molecules within the unit cell (Fig. 1 and Table 1). The molecules of the asymmetric unit are arranged as a nearly centrosymmetric dimer *via* hydrogen bonding. These dimeric pairs are further bonded to the solvent molecules and to neighbouring analogue molecules to produce a chain of hydrogen bonds throughout the crystal. Whilst the phenyl ring moieties of the partially occupied analogue molecules exhibit a near 180° rotation about the bridging bond between them and their respective triazine rings, the latter rings maintain a near comparable juxtaposition to the adjacent fully occupied analogue molecule. This results in maintaining the triazine rings of the partially occupied moieties in a suitable orientation for hydrogen bonding. A similar pattern of hydrogen bonding is found in the 2-fluorophenyl methanolate structure (Janes & Palmer, 1995*a*) which also has two analogue and two solvent molecules comprising the asymmetric unit. However, a difference between these two structures, in respect of their hydrogen bonding, is that of the seven possible hydrogen-bonding atoms of the triazine rings, atoms N1 and N1′ (and N1″) are not utilized in this structure while they are in the comparable methanolate, bonding to the solvent-molecule H atoms of the hydroxyl group.

Experimental

The material for this study was provided by Wellcome Pharmaceuticals (UK), now GlaxoWellcome. The crystals were grown by slow evaporation from a dimethylformamide solution at room temperature. Mounting was in a capillary due to the discovery that the crystals were sensitive to the bonding agent used initially to make attachment to a fibre.

Crystal data

$C_9H_8FN_5\cdot C_3H_7NO$
M_r = 278.30
Orthorhombic, $Pna2_1$
a = 17.0016 (10) Å
b = 10.6540 (10) Å
c = 15.9038 (10) Å
V = 2880.7 (4) Å^3
Z = 8
D_x = 1.283 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 7.5–26.0°
μ = 0.813 mm^{-1}
T = 296 (2) K
Block, colourless
0.4 × 0.3 × 0.3 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
5092 measured reflections
2750 independent reflections
1815 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 70.06°
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 19$
3 standard reflections
every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.167
S = 1.129
2750 reflections
498 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.102P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.026
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0070 (9)

Table 1
Selected geometric parameters (Å, °).

C1—C6*t*	1.490 (5)	N2—C3*t*	1.346 (4)
F2—C2	1.346 (6)	C3*t*—N3	1.338 (5)
C6*t*—N1	1.303 (4)	C3*t*—N4	1.338 (4)
C6*t*—C5*t*	1.429 (5)	N4—C5*t*	1.326 (5)
N1—N2	1.353 (4)	C5*t*—N5	1.347 (4)
N1—C6*t*—C5*t*	120.4 (3)	N3—C3*t*—N2	116.3 (3)
N1—C6*t*—C1	117.0 (3)	N4—C3*t*—N2	125.8 (3)
C5*t*—C6*t*—C1	122.5 (3)	C5*t*—N4—C3*t*	116.3 (3)
C6*t*—N1—N2	120.6 (3)	N4—C5*t*—N5	117.9 (3)
N1—N2—C3*t*	117.0 (3)	N4—C5*t*—C6*t*	119.8 (3)
N3—C3*t*—N4	117.9 (3)	N5—C5*t*—C6*t*	122.3 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H31···O1*B*	0.86	2.22	3.073 (5)	170
N5—H52···O1*A*	0.86	2.18	2.854 (5)	135
N3—H32···N2′^{i}	0.86	2.05	2.900 (7)	171
N5—H51···N4′	0.86	2.18	2.996 (8)	159
N3′—H31′···O1*A*	0.86	2.18	3.019 (11)	165
N3′—H32′···N2^{ii}	0.86	2.07	2.923 (11)	175
N5′—H52′···O1*B*	0.86	2.22	2.903 (8)	137
N5′—H51′···N4	0.86	2.11	2.964 (10)	169
N3—H32···N2′′^{i}	0.86	2.22	3.074 (11)	176
N5—H51···N4′′	0.86	2.25	3.061 (10)	157
N3′′—H32′′···O1*A*	0.86	2.22	3.055 (14)	164
N3′′—H31′′···N2^{ii}	0.86	2.24	3.053 (17)	157
N5′′—H52′′···O1*B*	0.86	2.07	2.742 (11)	134
N5′′—H51′′···N4	0.86	2.26	3.076 (13)	159

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

The absolute structure of (I) was assigned arbitrarily.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CADRAL* (unpublished; FCF Korber, University of Leeds, England) and *CADSHEL* (unpublished; JB Cooper, Birkbeck College, University of London, England); program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SNOOPI* (Davies, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1376). Services for accessing these data are described at the back of the journal.

References

Davies, E. K. (1983). *SNOOPI*. University of Oxford, England.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Janes, R. W. (1999). *J. Chem. Crystallogr.* **29**, 163–167.
Janes, R. W., Lisgarten, J. N. & Palmer, R. A. (1989). *Acta Cryst.* C**45**, 129–132.
Janes, R. W. & Palmer, R. A. (1995*a*). *Acta Cryst.* C**51**, 440–442.
Janes, R. W. & Palmer, R. A. (1995*b*). *Acta Cryst.* C**51**, 685–688.
Janes, R. W. & Palmer, R. A. (1995*c*). *Theochem. J. Mol. Struct.* **339**, 95–101.
Janes, R. W. & Palmer, R. A. (1996). *Acta Cryst.* C**52**, 2627–2629.
Sheldrick, G. M. (1976). *SHELX*76. University of Cambridge, England.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.