Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Displaced π–π stacking and hydrogen bonds in 3-bromo-*N*-(2-hydroxy-1,1-dimethylethyl)benzamide

Yao-Wen Wu,[a] Ru-Ji Wang,[b] Yu-Yang Jiang,[a]* Hua Fu[a] and Yu-Fen Zhao[a]

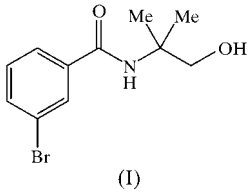
[a]Key Laboratory of Bioorganic Phosphorus Chemistry, Ministry of Education, Department of Chemistry, School of Life Sciences and Engineering, Tsinghua University, Beijing 100084, People's Republic of China, and [b]Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China
Correspondence e-mail: yuyang_jiang@yahoo.com.cn

Received 2 October 2003
Accepted 7 November 2003
Online 10 February 2004

The molecules of the title compound, $C_{11}H_{14}BrNO_2$, are assembled into a two-dimensional network by a combination of hydrogen bonds and stacking interactions. The phenyl rings are stacked along the *c* direction by displaced π–π interactions, forming a lipophilic layer. The aliphatic amide residues are interconnected along [100] by O—H···O, N—H···O and C—H···O hydrogen bonds, forming hydrophilic layers.

Comment

Synthetic *N*-(2-hydroxy-1,1-dimethylethyl)amides are commonly used as intermediates in the synthesis of oxazoline compounds which have various uses in modern organic synthesis (Boyd & Hansen, 1953; Grant & Meyers, 1994). Gerkin (2000) reported the crystal structure of *N*-(2-hydroxy-1,1-dimethylethyl)benzamide, (II), as one of a series of reports on hydrogen bonding and C—H···O interactions in aromatic compounds. In the present paper, we report the structure of 3-bromo-*N*-(2-hydroxy-1,1-dimethylethyl)benzamide, (I), which differs from (II) in that it contains an additional Br substituent.



(I)

In the structure of (I) (Fig. 1), both hard and soft hydrogen bonds and parallel-displaced π–π stacking interactions (Hobza *et al.*, 1994; Müller-Dethlefs & Hobza, 2000) are present. As shown in Fig. 2, the molecules are assembled in (010) sheets by a combination of stacking interactions and intermolecular hydrogen bonds.

Each aliphatic amide residue in (I) is involved in two hydrogen bonds and one weak but significant C—H···O interaction. An O—H···O hydrogen bond links the molecules at (x, y, z) and ($1-x$, $1-y$, $2-z$), while an N—H···O hydrogen bond reinforced by a C—H···O interaction (Steiner & Desiraju, 1998) links the molecules at (x, y, z) and ($2-x$, $1-y$, $2-z$). In combination, these hydrogen bonds generate a chain of centrosymmetric rings along [100] (Fig. 2), and the chains are further linked by π-stacking interactions.

The distance between the phenyl planes of the molecules at (x, y, z) and ($2-x$, $1-y$, $1-z$) is 3.54 Å, and the distance between the ring centroids is 3.79 Å, which may lead to lower quadrupole–quadrupole energy and hence a more stable structure, according to *ab initio* calculations (Hobza *et al.*, 1994). The phenyl rings stack along [001] *via* displaced π–π interactions, forming a lipophilic layer on either side of the central polar layer.

The hydrogen-bonded aliphatic amide residues aligned along the [100] direction form a hydrophilic layer. The two oppositely polar moieties are extensively interconnected through stacking interactions and multiple hydrogen bonds (Table 1) that stabilize the structure (Fig. 2).

Compared with the structure of (II), the introduction of a bromine substituent at the 3-position of the phenyl ring alters the whole crystal structure. In (II), there is one intramolecular O—H···O hydrogen bond, one intermolecular N—H···O hydrogen bond and four significant C—H···O interactions, and a central molecule is linked directly to five neighboring molecules, forming a two-dimensional network, so the two oppositely polar-assembled layers and the stacking interactions observed in (I) are not present in (II).

It is interesting to compare the dihedral angles between the best-fit phenyl plane and the amide plane (C7/O1/N1) of (I) [13.7 (7)°] and (II) [25.77 (12)°] (with the same atom-numbering scheme as in Fig. 1). Presumably, the twist between the phenyl and amide planes serves to minimize steric repulsion between the lone pair on atom O1 and the adjacent phenyl H atom (H6). This assumption is supported by a comparison with the structure of 4,6-dimethyl-3-(4,4-dimethyl-2-oxazolinyl)-*N*-(2-hydroxy-1,1-dimethylethyl)salicylamide (Inamoto *et al.*, 1996), which contains a methyl group at

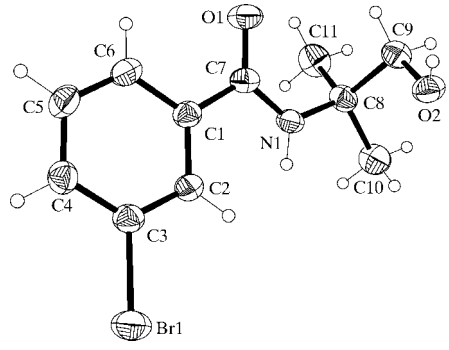


Figure 1
View of the molecule of (I), showing ellipsoids at the 35% probability level and the atomic numbering scheme. H atoms are included as spheres of arbitrary size.

  DOI: 10.1107/S0108270103025824

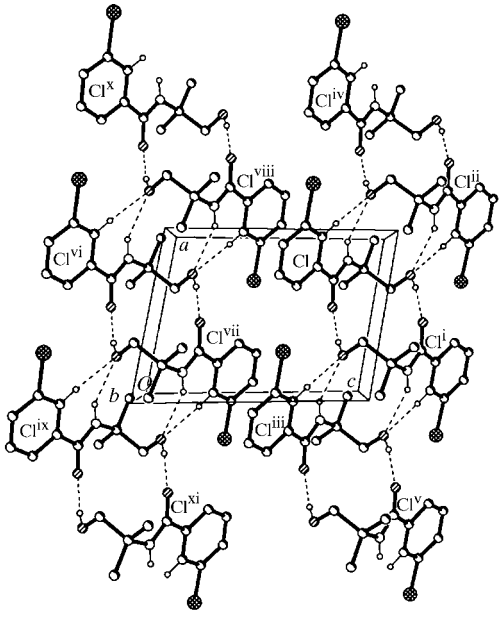


Figure 2
A packing view along the *b* direction. Key: double-hatched circles indicate Br, single-hatched circles O, open circles N and H, and partially shaded circles C atoms. [Symmetry codes: (i) $1-x, 1-y, 2-z$; (ii) $2-x, 1-y, 2-z$; (iii) $-1+x, y, z$; (iv) $1+x, y, z$; (v) $-x, 1-y, 2-z$; (vi) $x, y, -1+z$; (vii) $1-x, 1-y, 1-z$; (viii) $2-x, 1-y, 1-z$; (ix) $-1+x, y, -1+z$; (x) $1+x, y, -1+z$; (xi) $-x, 1-y, 1-z$.]

the 6-position of the phenyl ring that is markedly twisted out of the amide plane, *viz*. by 88.4 (9)°. In (II), atom O1 as the acceptor is involved in three hydrogen bonds [an intramolecular O—H···O bond, with $D\cdots A$ = 2.628 (11) Å, and two short C—H···O interactions], while atom O1 in (I) as acceptor is only involved in one intermolecular O—H···O hydrogen bond [$D\cdots A$ = 2.734 (4) Å] that is obviously weaker than those in (II). This seems to mean that the more electrons atom O1 accepts, the more twist there is between the two planes in order to minimize steric repulsion with the adjacent phenyl-ring H atom. Therefore, the torsion to make the amide plane non-coplanar with the phenyl plane is due to the steric repulsion between the lone pair on atom O1 and the adjacent atom or group at the 6-position of the phenyl ring.

Experimental

Compound (I) was synthesized according to the method of Meyers *et al.* (1974) with crystals grown by slow evaporation of a methylene chloride solution.

Crystal data

$C_{11}H_{14}BrNO_2$
M_r = 272.14
Triclinic, $P\overline{1}$
a = 7.2713 (10) Å
b = 8.5860 (9) Å
c = 9.8424 (14) Å
α = 77.123 (11)°
β = 77.785 (12)°
γ = 79.825 (10)°
V = 580.03 (13) Å^3
Z = 2
D_x = 1.558 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34 reflections
θ = 4.9–16.8°
μ = 3.52 mm^{-1}
T = 293 (2) K
Prism, colorless
0.4 × 0.4 × 0.3 mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.242, T_{max} = 0.350
2551 measured reflections
2034 independent reflections
1748 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 25.0°
$h = -1 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.097
S = 1.03
2034 reflections
136 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 1.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2B···O1^{i}	0.82	1.92	2.734 (4)	169
N1—H1A···O2^{ii}	0.86	2.38	3.173 (4)	153
C2—H2A···O2^{ii}	0.93	2.35	3.277 (5)	176

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

H atoms were treated as riding, with C—H = 0.93–0.97 Å, N—H = 0.86 Å and O—H = 0.82 Å.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We are grateful to the National Natural Science Foundation of China (project No. 20132020) for financial support and thank Dr Ming Sun, Dr Xiaohong Liu and Miss Ying Jin for their advice, support and encouragement.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1280). Services for accessing these data are described at the back of the journal.

References

Boyd, R. N. & Hansen, R. H. (1953). *J. Am. Chem. Soc.* **75**, 5896–5897.
Bruker (1997). *XSCANS* (Version 2.2) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Gerkin, R. E. (2000). *Acta Cryst.* C**56**, 1218–1219.
Grant, T. G. & Meyers, A. I. (1994). *Tetrahedron*, **50**, 2997–2360.
Hobza, P., Selzle, H. L. & Schlag, E. W. (1994). *Chem. Rev.* **94**, 1767–1784.
Inamoto, K., Kiokawa, M., Nakashima, M. & Tokii, T. (1996). *Inorg. Chim. Acta*, **249**, 251–254.
Meyers, A. I., Temple, D. L., Haidukewych, D. & Mihelich, E. D. (1974). *J. Org. Chem.* **39**, 2787–2793.
Müller-Dethlefs, K. & Hobza, P. (2000). *Chem. Rev.* **100**, 143–167.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Steiner, T. & Desiraju, G. R. (1998). *J. Chem. Soc. Chem. Commun.* pp. 891–892.