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3,5-Diamino-6-(2-bromophenyl)-1,2,4-triazine Dimethanol Solvate: an Analogue of Lamotrigine

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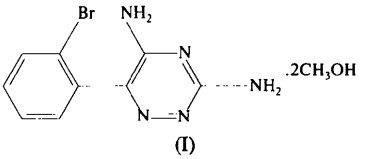
Abstract

The structure of the title compound, $C_9H_8BrN_5.2CH_3OH$, exhibits marked distortion in its conformation about the common axis of the phenyl and triazine rings which may arise from steric hindrance between the Br atom and the π electrons of the triazine ring. An extensive network of hydrogen bonds maintains the crystal structure which has one analogue molecule and two methanol solvent molecules per asymmetric unit.

Comment

The title compound, (I), is an analogue of the anticonvulsant compound lamotrigine [3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazine; Janes, Lisgarten & Palmer, 1989]. The structure was determined as part of an ongoing investigation into structure–activity studies of lamotrigine analogues (Janes & Palmer, 1995*a*,*b*).



(I)

The Br atom is coplanar with the phenyl ring and the N3 and N5 atoms of the amino groups are coplanar with the triazine ring (Fig. 1). The dihedral angle between these rings is 99.0 (1)°. There are significant differences in the bond lengths within the phenyl ring, the longest being C1—C6 at 1.401 (2) Å and the shortest being C3—C4 at 1.360 (7) Å. There is a marked distortion about the common axis of the phenyl and triazine rings, denoted by atoms C3*t*, C6*t*, C1 and C4 (Fig. 2). This may be caused by steric hindrance between the Br atom on the phenyl ring and the π electrons associated with the triazine ring. Atom C4 is displaced 0.106 (1) Å from the triazine ring plane, while the non-bonding angle given by C3*t*···C6*t*···C4 is 174.0 (1)°. The external angles about the C6*t* atom display marked asymmetry, with a difference of 6.4°, as do those about the C5*t* atom (Table 2).

Extensive hydrogen bonding maintains the crystal structure. The molecule has two centrosymmetrically

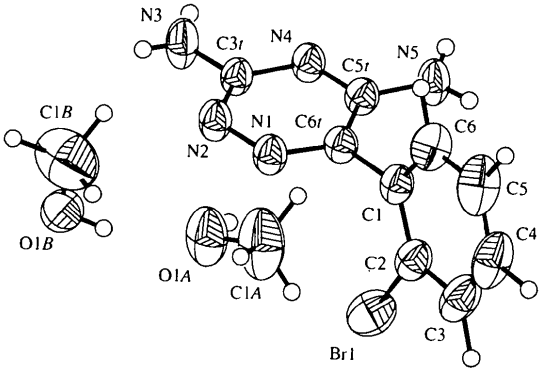


Fig. 1. Displacement-ellipsoid plot of the title molecule with ellipsoids plotted at the 50% probability level.

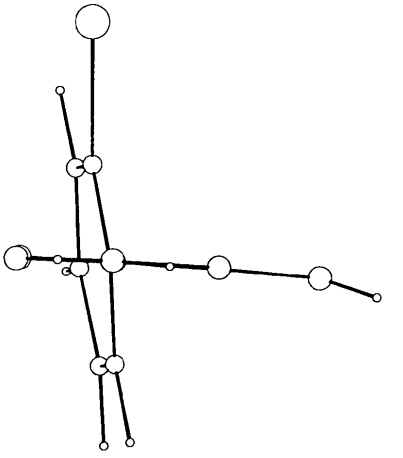


Fig. 2. View along the C3*t*···C6*t* direction illustrating the dihedral angle and distortion of the molecule about the common ring axis (*SNOOPI*; Davies, 1983).

related dimers connected by the hydrogen bonding of the N2 atom to the H32 atom of one molecule, and of the N4 atom to the H52 atom of another molecule. It is of interest to note that a potential hydrogen-bonding lone pair on atom O1*A* remains unbonded. The entire hydrogen-bonding framework is detailed in Table 3.

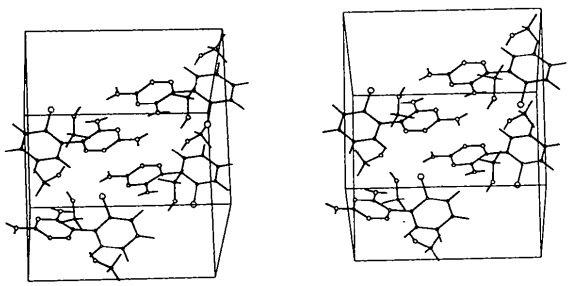


Fig. 3. Stereoview of the molecular packing, with the *b* axis nearly horizontal, showing the nature of the hydrogen-bonding framework (*SNOOPI*; Davies, 1983).

Experimental

The title compound was supplied by Wellcome Pharmaceuticals (UK). The crystal for analysis was prepared by slow evaporation from methanol solution and was mounted in a capillary tube to prevent drying and loss of crystallinity.

Crystal data

$C_9H_8BrN_5.2CH_4O$
M_r = 330.2
Monoclinic
$P2_1/c$
a = 10.516 (3) Å
b = 12.855 (4) Å
c = 11.623 (2) Å
β = 109.10 (2)°
V = 1484.6 Å^3
Z = 4
D_x = 1.48 Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 9.5–31°
μ = 3.594 mm^{-1}
T = 293 K
Prismatic
0.30 × 0.30 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
T_{min} = 0.19, T_{max} = 0.99
4280 measured reflections
2509 independent reflections
2048 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.0483
θ_{max} = 70°
$h = -17 \rightarrow 17$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: <10%

Refinement

Refinement on F
R = 0.0496
wR = 0.0577
2048 reflections
209 parameters
Only H-atom U's refined
$w = 13.4954/[\sigma^2(F) + 0.000170F^2]$
$(\Delta/\sigma)_{max}$ = 0.196
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C1	0.1560 (3)	0.1731 (3)	0.4331 (4)	0.044 (2)
C2	0.1889 (4)	0.0930 (3)	0.5190 (4)	0.050 (2)
C3	0.1540 (5)	−0.0095 (3)	0.4869 (5)	0.064 (3)
C4	0.0829 (5)	−0.0329 (3)	0.3692 (5)	0.070 (3)
C5	0.0457 (5)	0.0443 (4)	0.2829 (5)	0.077 (3)
C6	0.0816 (5)	0.1470 (3)	0.3133 (5)	0.061 (3)
Br2	0.2826 (1)	0.1256	0.6841	0.069 (1)
N1	0.3281 (3)	0.3008 (2)	0.4679 (3)	0.046 (2)
N2	0.3808 (3)	0.3970 (2)	0.4925 (3)	0.047 (2)
C3*t*	0.3011 (3)	0.4715 (3)	0.5140 (3)	0.042 (2)
N4	0.1719 (3)	0.4582 (2)	0.5097 (3)	0.044 (2)
C5*t*	0.1210 (3)	0.3626 (3)	0.4824 (4)	0.042 (2)
C6*t*	0.2040 (3)	0.2814 (3)	0.4628 (3)	0.041 (2)
N3	0.3544 (4)	0.5660 (3)	0.5406 (4)	0.058 (2)
N5	−0.0069 (3)	0.3474 (3)	0.4739 (4)	0.053 (2)
O1*A*	0.5165 (3)	0.1643 (3)	0.4140 (4)	0.081 (2)
C1*A*	0.4453 (6)	0.0840 (5)	0.3414 (8)	0.104 (5)
O1*B*	0.7329 (3)	0.2597 (3)	0.8611 (4)	0.069 (2)
C1*B*	0.6940 (7)	0.2536 (7)	0.7329 (7)	0.112 (6)

Table 2. *Selected geometric parameters (Å, °)*

C1—C2	1.396 (6)	C3*t*—N4	1.353 (4)
C4—C5	1.373 (7)	C3*t*—N3	1.331 (4)
C1—C6*t*	1.484 (5)	C1*A*—O1*A*	1.387 (6)
N2—C3*t*	1.349 (4)	C3—C4	1.360 (7)
C5*t*—C6*t*	1.426 (5)	C6—C1	1.401 (3)
C2—Br2	1.895 (4)	N1—N2	1.346 (4)
C2—C3	1.386 (5)	N4—C5*t*	1.337 (4)
C5—C6	1.386 (6)	C5*t*—N5	1.330 (5)
C6*t*—N1	1.311 (4)	C1*B*—O1*B*	1.412 (9)
C1—C2—C3	121.7 (3)	N1—N2—C3*t*	117.0 (3)
C4—C5—C6	120.9 (5)	N4—C5*t*—C6*t*	119.5 (3)
C2—C1—C6*t*	122.6 (4)	N2—C3*t*—N3	116.8 (3)
C6*t*—N1—N2	121.2 (3)	C6*t*—C5*t*—N5	122.5 (3)
C3*t*—N4—C5*t*	116.4 (3)	C3—C4—C5	120.4 (4)
C5*t*—C6*t*—C1	123.0 (3)	C6—C1—C2	117.6 (4)
N4—C5*t*—N5	118.0 (3)	C1—C6*t*—N1	116.6 (3)
C3—C2—Br2	119.2 (3)	N2—C3*t*—N4	125.4 (3)
C2—C3—C4	119.4 (4)	C5*t*—C6*t*—N1	120.4 (3)
C5—C6—C1	119.9 (5)	N4—C3*t*—N3	117.8 (3)
C6—C1—C6*t*	119.6 (4)	C1—C2—Br2	119.1 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H32···N2^{i}	0.72 (5)	2.26 (5)	2.971 (6)	170 (4)
N5—H52···N4^{ii}	0.81 (5)	2.29 (5)	3.083 (4)	167 (5)
O1*A*—H1*A*···N1	0.79 (8)	2.11 (8)	2.865 (5)	163 (7)
N3—H31···O1*B*^{iii}	0.84 (6)	2.21 (6)	3.006 (5)	158 (6)
N5—H51···O1*B*^{iv}	0.84 (4)	2.33 (4)	2.959 (4)	132 (4)
O1*B*—H1*B*···O1*A*^{v}	0.81 (6)	1.94 (6)	2.725 (5)	163 (5)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $x-1, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Programs used to solve structure: *SHELX*76 (Sheldrick, 1976). Programs used to draw figures: *SNOOPI* (Davies, 1983). Additional molecular geometry calculations: *XANADU* (Roberts & Sheldrick, 1976) and *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*S*)-(+)-Homoterpenyl Methyl Ketone

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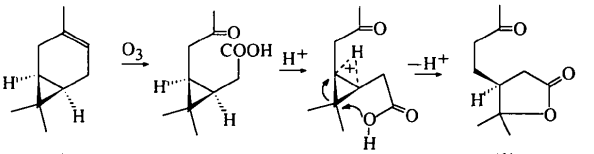
Abstract

In (+)-5,5-dimethyl-4-(3-oxobutyl)tetrahydrofuran-2-one, $C_{10}H_{16}O_3$, the absolute configuration at the chiral C atom is *S*. The five-membered ring adopts a deformed envelope conformation with the asymmetric C atom in the flap position. The oxobutyl group is planar.

Comment

Molecules containing γ-lactone subunits are useful compounds displaying interesting properties with regard to flavour and fragrance or their use in pharmaceutical chemistry. They also constitute an important class of synthetic intermediates for access to a variety of heterocyclic compounds (Giordano *et al.*, 1992; Matsuki *et al.*, 1994). Homoterpenyl methyl ketone (1) has been employed for the stereoselective synthesis of racemic β-vetivone (Bozzato, Bachmann & Pesaro, 1974). Recently, lactone (1) was reported to be an intermediate in the synthesis of methyl-*trans*-chrysanthemate (Zhu-Jin, Ren-Rong & Yu-Gui, 1987). Optically active lactone (1) can be prepared from natural (+)- or (−)-α-pinene (Arcus & Bennett, 1955; Zhu-Jin *et al.*, 1987). Optical rotations of homoterpenyl methyl ketone (1) (in $CHCl_3$) are reported to be $[\alpha]_D$ = +58.6° (*c* = 5.27) (Arcus & Bennett, 1955), −58.6° (*c* = 55) (MacRae, Alberts, Carman & Shaw, 1979) and −57.73° (*c* = 17) (Zhu-Jin *et al.*, 1987). However, no pure enantiomers of α-pinene are commercially available and therefore homoterpenyl methyl ketone (1) obtained by the method described by Arcus & Bennett (1955) and Zhu-Jin *et al.* (1987) is racemized. The laevo-rotary enantiomer can be produced in another way by microbial oxidation of 1,8-cineole (MacRae *et al.*, 1979).



(3) (2) (1)

In the course of our investigation, we observed that when (−)-*cis*-3-acetonyl-2,2-dimethylcyclopropylacetic acid (2), obtained from (+)-car-3-ene (3) (Naves & Grampoloff, 1961), was treated with 85% orthophosphoric acid at 368 K, it resulted in the formation of (+)-lactone (1) in a yield of over 60%. After purification and crystallization, the molecular structure of (+)-lactone (1) was determined (Fig. 1) using data collected at room temperature. The absolute configuration at the chiral atom C3 was established to be *S*. The five-membered ring adopts a deformed envelope conformation with the C3 atom in the flap position. The oxobutyl group (C5, C6, C7, C8, O3) is planar, and the C5—C6 bond is antiperiplanar with respect to C7—C8 [torsion angle C5—C6—C7—C8 = 179.8 (2)°]. Fig. 2 presents a view of the crystal packing in (+)-lactone (1) showing the inter- and intramolecular hydrogen-bond contacts shorter then 2.65 Å (Table 3).

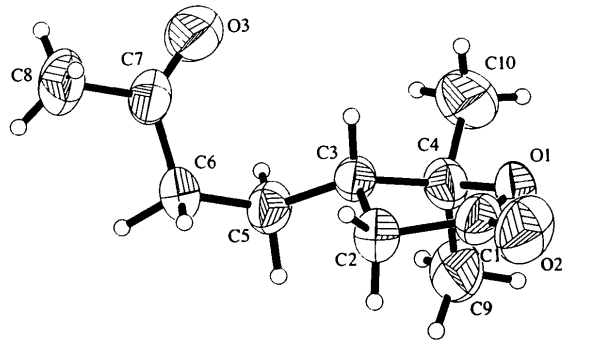


Fig. 1. Molecular structure of (+)-lactone (1) showing 50% probability displacement ellipsoids.