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## Four Simple Pyridazin-3(2H)-ones

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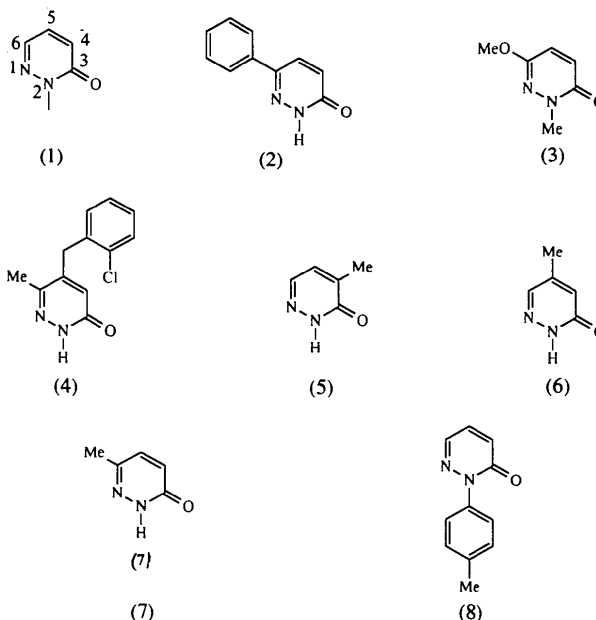
### Abstract

The structures of four simple pyridazin-3(2H)-ones, the isomeric 4-methylpyridazin-3(2H)-one [C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O, (5)], 5-methylpyridazin-3(2H)-one monohydrate and 6-methylpyridazin-3(2H)-one monohydrate [C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O·H<sub>2</sub>O, (6)·H<sub>2</sub>O and (7)·H<sub>2</sub>O] and 2-(*p*-tolyl)pyridazin-3(2H)-one [C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O, (8)], have been determined. Compounds (6) and (7), which crystallize as monohydrates, show extensive hydrogen bonding while molecules of (5) form hydrogen-bonded dimers. In (8), there are no strong hydrogen bonds as in compounds (5)–(7), the closest intermolecular contacts being pairwise C—H···O interactions.

### Comment

The pyridazin-3(2H)-one heterocyclic system (1) has important pharmaceutical (Baraldi *et al.*, 1994; Prout *et al.*, 1994) and agrochemical (Cremlyn, 1991) applications, but relatively little is known about the structural characteristics of simple derivatives of this ring system. Examples in the literature include an extensive range of 6-aryl derivatives [*e.g.* (2)] which was studied to ascertain the relationship between their structures and their cardiovascular properties (Prout *et al.*, 1994), the 6-methoxy compound (3) (Ottersen, 1974) and the 5,6-dialkyl derivative (4) (Moreau, Metin, Coudert & Couquelet, 1995). Some years ago, one of the present authors developed a convenient route to 2-, 5- and 6-substituted pyridazinones (McNab & Stobie, 1982) and

published details of their NMR spectra (McNab, 1983). With the availability of samples from this earlier work, we now report the results of our structural studies on 4-, 5- and 6-methylpyridazin-3(2H)-one, (5)–(7), and the simple 2-aryl derivative, (8).



Compounds (6) and (7) crystallized as monohydrates and while this clearly affects the crystal packing (see below), it appears to have little effect on the intramolecular geometric parameters. The majority of the bond lengths in compounds (5)–(8) lie within the ranges published previously (Prout *et al.*, 1994); for the C-methyl derivatives (5)–(7), corresponding bond lengths generally lie within two e.s.d.'s of each other. The most substantial differences are in the N1/C6/C5 region of the 4-methyl compound (5) where both N1—C6 and C6—C5 are the shortest in the series. In the *N*-aryl example (8), the C6—C5 bond length is again short but the N2—N3 bond is unusually long. This last feature may be due to competitive delocalization of the N2 lone pair into the aryl ring rather than into the adjacent carbonyl group; this effect is also reflected in the short C=O bond length.

The bond angles at the carbonyl group are essentially the same in all four compounds (5)–(8) and are independent of the presence of substituents on either N2 or C4. The endocyclic angle is always about 115.5° with the exocyclic angles having values around either 119 or 125°. In all cases, the presence of a substituent reduces the endocyclic angle at that position; for example, the mean angle at C6 for compounds (5), (6) and (8) is 124.5 (4) but this is reduced to 121.3 (2)° in the 6-substituted compound (7). The exocyclic bond angles at the substituents are unsymmetrical and differ by 3.5–

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6.7°. There is no obvious pattern to this effect; for example, the 4-methyl substituent is bent towards the adjacent carbonyl group in (5) [ $C4m-C4-C3$  117.9(4) cf.  $C4m-C4-C5$  124.6(5)°] whereas the opposite is true for the 1-aryl group in (8) [ $C1p-N2-C3$  120.6(3) cf.  $C1p-N2-N1$  114.2(3)°]. Similarly, the disposition of the formal double bonds is inconsistent with respect to these angles in the C-methyl series.

In the molecules of (7), all non-H atoms lie on crystallographic mirror planes so that the heavy-atom skeleton is ideally planar. In (6), although none of the ring atoms (N1–C6) deviates from its least-squares plane by more than 0.013(1) Å, the exocyclic atoms C5 $m$  and O3 lie on opposite sides of the ring plane by 0.055(3) and 0.023(3) Å, respectively. A similar situation exists in (5) where no ring atom deviates significantly from the plane but, despite the adjacent substituents, both deviations of the exocyclic atoms are smaller and that for O3 [0.034(7) Å] now appears greater than that for the methyl C atom C4 $m$  [0.019(9) Å]. In the *N*-aryl compound (8), the planarity of the pyridazinone ring is reduced with deviations ranging from 0.009(3) to 0.029(3) Å; the bridgehead atom C1 $p$  of the tolyl ring lies in the plane of the pyridazinone ring but O3 is displaced by 0.118(6) Å. The two six-membered rings are twisted by 59.32(14)°, thereby avoiding an approach between O3 and the H atom on C2 $p$  closer than 2.83(5) Å.

Molecules of (5), (6) and (7) are linked by intermolecular hydrogen bonding (Table 6). In (7).H<sub>2</sub>O, mol-

ecules are hydrogen bonded *via* one N—H···O(water) and two C=O···H—O(water) contacts to generate a flat (ideally so for the non-H atoms) double layer running along the *a* axis, with alternate molecules related by the *a* glide plane (Fig. 3). There are no such contacts between the layers. In (6).H<sub>2</sub>O, the situation is similar but alternate molecules are related by the 2<sub>1</sub> screw axis parallel to *b* (Fig. 2). The non-H atoms of one layer are close to planar, their mean deviation being only 0.123 Å. The interactions in (6) and (7) are very similar to those observed in 4,5-dihydro-6-methylpyridazin-3(2*H*)-one (Prout *et al.*, 1994). In (5), molecules form centrosymmetric dimers (Fig. 1) *via* two equivalent hydrogen bonds and there are no other contacts of such importance; were compounds (5) and (6) to be recrystallized under anhydrous conditions they might be expected to form such dimers.

In (8), there are no strong hydrogen bonds as in compounds (5)–(7); substitution at position 2 has removed the potential for N—H···O hydrogen bonds and the presence of the relatively hydrophobic *p*-tolyl group renders C=O···H(water) contacts unlikely. The closest intermolecular contacts are pairwise interactions of the type C—H···O between centrosymmetrically related molecules. Overall, molecules pack in a herring-bone motif as shown in Fig. 4.

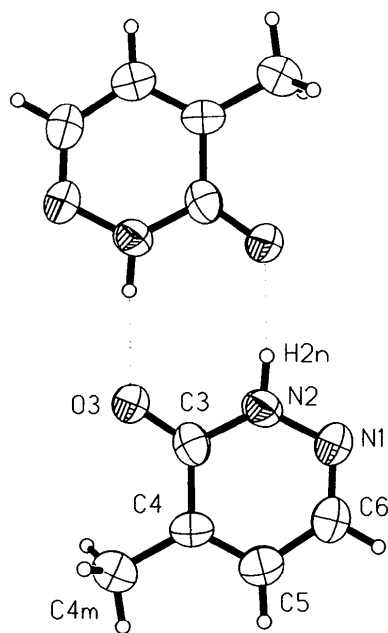


Fig. 1. A view of one hydrogen-bonded dimer of (5). Displacement ellipsoids are shown at the 50% probability level.

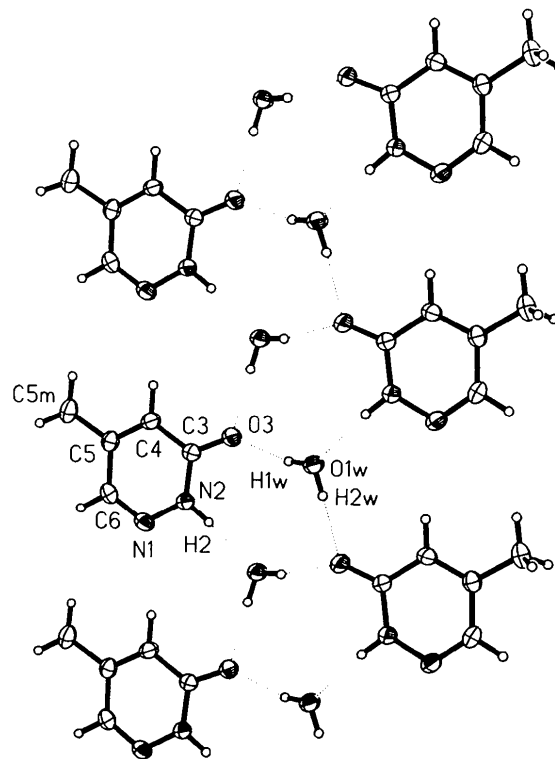


Fig. 2. A view of the hydrogen-bonded network in (6).H<sub>2</sub>O. Displacement ellipsoids are shown at the 50% probability level.

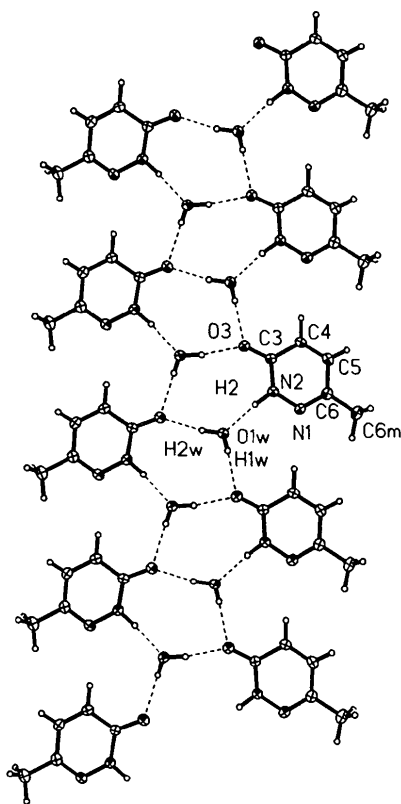


Fig. 3. A view of the hydrogen-bonded network in (7).H<sub>2</sub>O. Displacement ellipsoids are shown at the 50% probability level.

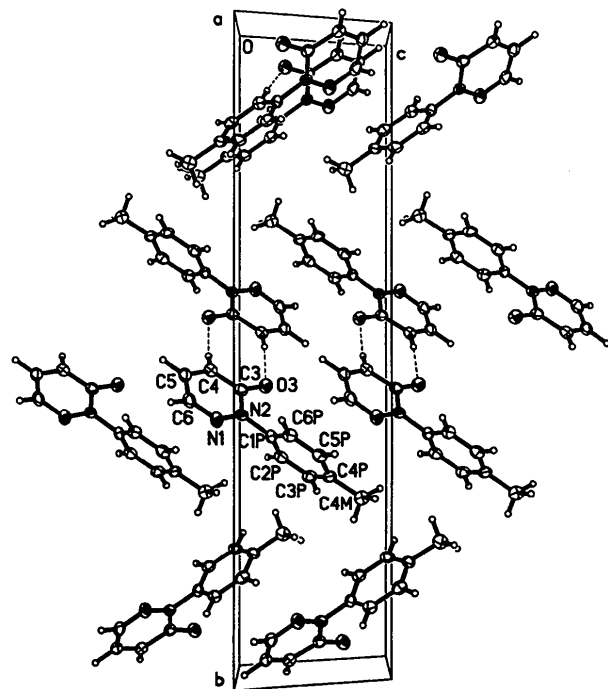


Fig. 4. A packing diagram showing the herring-bone arrangement of molecules of (8). Displacement ellipsoids are shown at the 50% probability level.

## Experimental

Compound (5) was prepared by thermolysis of the corresponding 6-carboxylic acid and crystals were grown from acetone by slow evaporation (McNab, 1983). Compound (6) was prepared by flash vacuum pyrolysis (FVP) of the 'BuNH—N=CH—C(Me)= 5-derivative of Meldrum's acid and crystals were obtained by slow evaporation from an acetone solution (McNab & Stobie, 1982). Compound (7) was synthesized by FVP of the 'BuNH—N=C(Me)—CH= 5-derivative of Meldrum's acid and crystals were grown by slow evaporation from a methanol solution (McNab & Stobie, 1982). Finally, compound (8) was prepared by FVP of the *p*-Me—C<sub>6</sub>H<sub>4</sub>—NH—N=CH—CH=5-derivative of Meldrum's acid (McNab & Stobie, 1982) and crystals were grown from MeOH.

## Compound (5)

### Crystal data

C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O  
*M<sub>r</sub>* = 110.12  
 Orthorhombic  
*Pbca*  
*a* = 11.8328 (16) Å  
*b* = 7.5583 (14) Å  
*c* = 12.387 (3) Å  
*V* = 1107.8 (4) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.320 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 62 reflections (at  $\pm\omega$ )  
 $\theta$  = 12–18°  
 $\mu$  = 0.096 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Plate  
 0.54 × 0.47 × 0.02 mm  
 Colourless

### Data collection

Stoe Stadi-4 four-circle diffractometer  
 $\omega$ -2 $\theta$  scans with  $\omega$  width (1.8+0.35tan $\theta$ )°  
 Absorption correction: none  
 1510 measured reflections  
 943 independent reflections  
 340 observed reflections  
 [*I* > 2 $\sigma$ (*I*)]

*R*<sub>int</sub> = 0.0563  
 $\theta_{\max}$  = 25.05°  
*h* = -1 → 14  
*k* = -1 → 9  
*l* = -14 → 1  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 15%

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.0566  
 $wR$ (*F*<sup>2</sup>) = 0.1085  
*S* = 1.075  
 936 reflections  
 74 parameters  
 H atoms attached to N2, C5 and C6 were initially placed in calculated positions with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C,N). Methyl group H atoms were located in a difference Fourier map and thereafter treated as part of a rigid methyl group allowed to rotate about the C4—C4m vector with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C4m).

$w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.009$   
 $\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient: 0.002 (2)  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (5)
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	x	y	z	$U_{\text{eq}}$
N1	0.9376 (4)	0.1594 (7)	0.7239 (3)	0.064 (2)
N2	0.9349 (3)	0.0897 (6)	0.6224 (3)	0.0527 (13)
C3	0.8421 (4)	0.0609 (6)	0.5613 (3)	0.0461 (15)
O3	0.8535 (3)	-0.0006 (5)	0.4680 (2)	0.0552 (10)
C4	0.7352 (4)	0.1051 (7)	0.6094 (4)	0.047 (2)
C4 $m$	0.6312 (4)	0.0711 (7)	0.5454 (4)	0.064 (2)
C5	0.7364 (5)	0.1730 (8)	0.7095 (4)	0.059 (2)
C6	0.8404 (5)	0.1990 (8)	0.7629 (4)	0.067 (2)

**Compound (6)***Crystal data*C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O.H<sub>2</sub>O $M_r = 128.13$ 

Monoclinic

 $P2_1/c$  $a = 6.903 (2) \text{\AA}$  $b = 6.302 (2) \text{\AA}$  $c = 14.406 (3) \text{\AA}$  $\beta = 92.12 (3)^\circ$  $V = 626.3 (3) \text{\AA}^3$  $Z = 4$  $D_x = 1.359 \text{ Mg m}^{-3}$  $D_m$  not measured*Data collection*

Stoe Stadi-4 four-circle diffractometer equipped with Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)  $\omega$ - $2\theta$  scans with on-line profile fitting (Clegg, 1981)

Absorption correction: none  
1649 measured reflections

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0412$   
 $wR(F^2) = 0.1054$   
 $S = 1.099$   
1099 reflections  
115 parameters  
All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.228P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.010$

Mo  $K\alpha$  radiation $\lambda = 0.71073 \text{\AA}$ Cell parameters from 42 reflections (at  $\pm\omega$ ) $\theta = 14\text{--}18^\circ$  $\mu = 0.106 \text{ mm}^{-1}$  $T = 150.0 (2) \text{ K}$ 

Tablet

 $0.47 \times 0.43 \times 0.27 \text{ mm}$ 

Colourless

1102 independent reflections

881 observed reflections

 $[I > 2\sigma(I)]$  $R_{\text{int}} = 0.0138$  $\theta_{\text{max}} = 25.02^\circ$  $h = -8 \rightarrow 8$  $k = 0 \rightarrow 7$  $l = 0 \rightarrow 17$ 

3 standard reflections  
frequency: 60 min  
intensity decay: <2%

 $\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$ 

Extinction correction:  
*SHELXL93* (Sheldrick, 1993)

Extinction coefficient:  
0.022 (5)

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

O3	0.8803 (2)	0.1834 (2)	0.14900 (9)	0.0360 (4)
C4	0.7547 (3)	0.1309 (3)	-0.00545 (13)	0.0269 (5)
C5	0.6893 (2)	0.2246 (3)	-0.08465 (12)	0.0266 (5)
C5 $m$	0.6177 (3)	0.1028 (4)	-0.1680 (2)	0.0372 (5)
C6	0.6880 (3)	0.4514 (3)	-0.08675 (13)	0.0294 (5)
O1 $w$	1.1247 (2)	0.2657 (2)	0.30062 (10)	0.0335 (4)

**Compound (7)***Crystal data*C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O.H<sub>2</sub>O $M_r = 128.13$ 

Orthorhombic

 $Pnma$  $a = 6.325 (2) \text{\AA}$  $b = 6.322 (3) \text{\AA}$  $c = 15.597 (4) \text{\AA}$  $V = 623.7 (4) \text{\AA}^3$  $Z = 4$  $D_x = 1.365 \text{ Mg m}^{-3}$  $D_m$  not measured*Data collection*

Stoe Stadi-4 four-circle diffractometer equipped with Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)  $\omega$ - $2\theta$  scans

Absorption correction: none  
1317 measured reflections  
785 independent reflections

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0481$   
 $wR(F^2) = 0.1229$   
 $S = 1.074$   
777 reflections  
78 parameters  
All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.071P)^2 + 0.280P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.07$

Mo  $K\alpha$  radiation $\lambda = 0.71073 \text{\AA}$ Cell parameters from 33 reflections (at  $\pm\omega$ ) $\theta = 12\text{--}16.5^\circ$  $\mu = 0.107 \text{ mm}^{-1}$  $T = 150.0 (2) \text{ K}$ 

Block

 $0.46 \times 0.31 \times 0.15 \text{ mm}$ 

Colourless

538 observed reflections [ $I > 2\sigma(I)$ ] $R_{\text{int}} = 0.0573$  $\theta_{\text{max}} = 27.56^\circ$  $h = -8 \rightarrow 1$  $k = -8 \rightarrow 1$  $l = -1 \rightarrow 20$ 

3 standard reflections  
frequency: 60 min  
intensity decay: <1%

 $\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$ 

Extinction correction:  
*SHELXL93* (Sheldrick, 1993)

Extinction coefficient:  
0.007 (4)

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (6)
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	x	y	z	$U_{\text{eq}}$
N1	0.7407 (2)	0.5709 (3)	-0.01673 (11)	0.0296 (4)
N2	0.8020 (2)	0.4691 (2)	0.06166 (11)	0.0257 (4)
C3	0.8172 (2)	0.2557 (3)	0.07282 (12)	0.0250 (4)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (7)
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	x	y	z	$U_{\text{eq}}$
N1	0.5427 (3)	1/4	0.48297 (14)	0.0255 (6)
N2	0.4348 (3)	1/4	0.55796 (14)	0.0249 (6)
C3	0.2206 (4)	1/4	0.5679 (2)	0.0267 (7)
O3	0.1431 (3)	1/4	0.64140 (13)	0.0434 (7)
C4	0.1019 (4)	1/4	0.4894 (2)	0.0263 (6)
C5	0.2059 (4)	1/4	0.4144 (2)	0.0287 (7)
C6	0.4325 (4)	1/4	0.4126 (2)	0.0268 (7)
C6 $m$	0.5506 (5)	1/4	0.3296 (2)	0.0379 (8)
O1 $w$	0.7277 (4)	1/4	0.68677 (15)	0.0552 (9)

## Compound (8)

## Crystal data

$C_{11}H_{10}N_2O$   
 $M_r = 186.21$   
 Monoclinic  
 $P2_1/c$   
 $a = 5.700$  (4) Å  
 $b = 26.428$  (18) Å  
 $c = 6.712$  (5) Å  
 $\beta = 110.94$  (7)°  
 $V = 944.3$  (12) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.310$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 33 reflections (at  $\pm\omega$ )  
 $\theta = 11.5$ – $13.0$ °  
 $\mu = 0.087$  mm<sup>-1</sup>  
 $T = 150.0$  (2) K  
 Lath  
 $0.66 \times 0.33 \times 0.10$  mm  
 Colourless

## Data collection

Stoe Stadi-4 four-circle diffractometer equipped with Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)  
 $\omega$ - $2\theta$  scans with  $\omega$  width  $(1.8 + 0.34\tan\theta)$ °  
 Absorption correction: none  
 1248 measured reflections  
 1230 independent reflections

870 observed reflections [ $I > 2\sigma(I)$ ]  
 $R_{int} = 0.0113$   
 $\theta_{max} = 22.60$ °  
 $h = -6 \rightarrow 5$   
 $k = 0 \rightarrow 28$   
 $l = 0 \rightarrow 7$   
 3 standard reflections frequency: 60 min intensity decay: <1%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0538$   
 $wR(F^2) = 0.1336$   
 $S = 1.081$   
 1206 reflections  
 168 parameters  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 1.88P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.017$

$\Delta\rho_{max} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.18$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient: 0.026 (7)  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 5. Comparison of molecular geometry parameters (Å, °) for compounds (5)–(8)

Compound	(5)	(6)	(7)	(8)
N1—C6	1.282 (6)	1.300 (2)	1.300 (3)	1.293 (6)
N1—N2	1.363 (5)	1.353 (2)	1.354 (3)	1.366 (5)
N2—C3	1.351 (6)	1.358 (2)	1.364 (3)	1.389 (5)
C3—O3	1.253 (5)	1.252 (2)	1.247 (3)	1.237 (5)
C3—C4	1.438 (6)	1.428 (3)	1.437 (4)	1.429 (6)
C4—C5	1.342 (6)	1.348 (3)	1.342 (4)	1.345 (6)
C5—C6	1.411 (7)	1.430 (3)	1.434 (4)	1.413 (7)
C6—N1—N2	114.6 (5)	116.3 (2)	117.4 (2)	116.6 (4)
N1—N2—C3	126.7 (5)	126.1 (2)	126.8 (2)	124.9 (3)
O3—C3—N2	119.2 (4)	119.2 (2)	119.7 (2)	119.6 (4)
O3—C3—C4	124.3 (4)	125.2 (2)	125.3 (2)	125.3 (4)
N2—C3—C4	116.4 (4)	115.6 (2)	115.0 (2)	115.1 (4)
C5—C4—C3	117.5 (5)	120.6 (2)	119.1 (2)	120.3 (4)
C4—C5—C6	119.7 (5)	117.2 (2)	120.5 (3)	118.6 (4)
N1—C6—C5	125.0 (5)	124.2 (2)	121.3 (2)	124.2 (4)

Table 6. Hydrogen-bonding parameters (Å, °)

Compound	D—H...A	H...A	D—H...A
(5)	N2—H2...O3 <sup>iv</sup>	1.93 (2)	170 (5)
(6)	O1w—H1w...O3	1.96 (3)	168 (2)
(6)	O1w—H2w...O3 <sup>iii</sup>	1.87 (4)	177 (2)
(6)	N2—H2...O1w <sup>iii</sup>	1.89 (3)	171 (2)
(7)	N2—H2...O1w	1.80 (4)	174 (4)
(7)	O1w—H1w...O3 <sup>i</sup>	1.95 (4)	178 (3)
(7)	O1w—H2w...O3 <sup>ii</sup>	1.84 (5)	170 (4)
(8)	C4—H4...O3 <sup>i</sup>	2.41 (5)	174 (4)

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

Crystals of (7) show tetragonal metric symmetry. However, preliminary examination of the intensities of reflections equivalent under  $4/m$  symmetry showed poor agreement while those related by  $mmm$  symmetry did not differ significantly. After data collection, attempts to merge the data assuming tetragonal symmetry gave  $R_{int} = 0.52$  compared with 0.06 for orthorhombic symmetry. Examination of the intensity-weighted reciprocal lattice (*XPREP*; Sheldrick, 1995) showed no indication of fourfold symmetry along  $c$ . The possibility of tetragonal diffraction symmetry was therefore discounted.

For all compounds, data collection: *DIF4* (Stoe & Cie, 1990); cell refinement: *DIF4*; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL93*.

We thank EPSRC for provision of a four-circle diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1367). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (8)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{eq}$
N1	-0.0989 (7)	0.40064 (15)	1.1007 (6)	0.0294 (10)
N2	0.0124 (6)	0.40630 (12)	0.9525 (5)	0.0220 (9)
C3	0.1940 (8)	0.4423 (2)	0.9624 (6)	0.0239 (11)
O3	0.2642 (5)	0.44748 (11)	0.8093 (5)	0.0302 (9)
C4	0.2818 (9)	0.4712 (2)	1.1547 (7)	0.0258 (11)
C5	0.1789 (8)	0.4649 (2)	1.3049 (7)	0.0277 (11)
C6	-0.0148 (9)	0.4288 (2)	1.2688 (7)	0.0295 (12)
C1p	-0.0931 (8)	0.3749 (2)	0.7666 (6)	0.0222 (10)
C2p	0.0591 (9)	0.3422 (2)	0.7074 (7)	0.0259 (11)
C3p	-0.0439 (9)	0.3135 (2)	0.5273 (7)	0.0269 (11)
C4p	-0.2958 (8)	0.3162 (2)	0.4020 (7)	0.0254 (11)
C4m	-0.4043 (12)	0.2849 (2)	0.2034 (9)	0.0408 (14)
C5p	-0.4448 (9)	0.3492 (2)	0.4660 (7)	0.0275 (11)
C6p	-0.3453 (8)	0.3784 (2)	0.6468 (7)	0.0248 (11)

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

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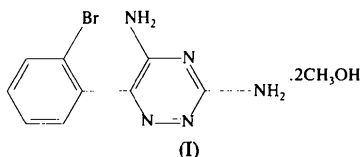
(Received 25 January 1994; accepted 18 September 1995)

#### Abstract

The structure of the title compound,  $C_9H_8BrN_5 \cdot 2CH_3OH$ , 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  $\pi$  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*).



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  $99.0(1)^\circ$ . There are significant differences in the bond lengths within the phenyl ring, the longest being C1—C6 at  $1.401(2) \text{ \AA}$  and the shortest being C3—C4 at  $1.360(7) \text{ \AA}$ . There is a marked distortion about the common axis of the phenyl and triazine rings, denoted by atoms C3t, C6t, C1 and C4 (Fig. 2). This may be caused by steric hindrance between the Br atom on the phenyl ring and the  $\pi$  electrons associated with the triazine ring. Atom C4 is displaced  $0.106(1) \text{ \AA}$  from the triazine ring plane, while the non-bonding angle given by  $C3t \cdots C6t \cdots C4$  is  $174.0(1)^\circ$ . The external angles about the C6t atom display marked asymmetry, with a difference of  $6.4^\circ$ , as do those about the C5t atom (Table 2).

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

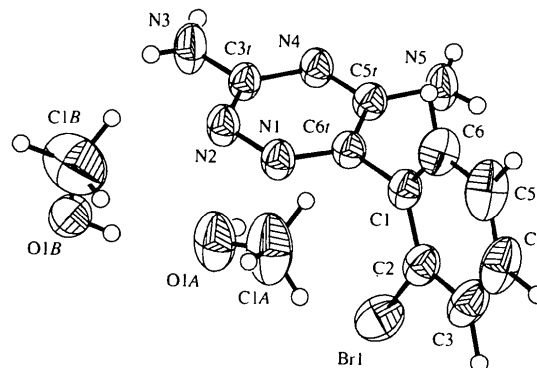


Fig. 1. Displacement-ellipsoid plot of the title molecule with ellipsoids plotted at the 50% probability level.

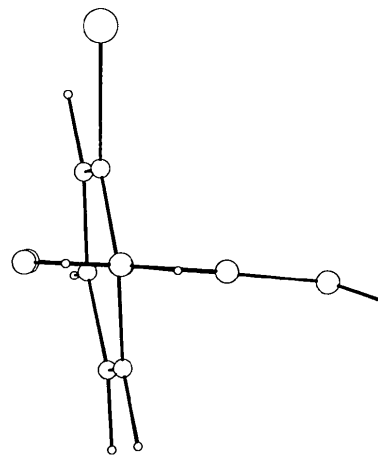


Fig. 2. View along the  $C3t \cdots C6t$  direction illustrating the dihedral angle and distortion of the molecule about the common ring axis (SNOOPI; Davies, 1983).