Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Structures of benzoxazine-fused triazoles as potential diuretic agents

Krishnan Ravikumar,[a]* Balasubramanian Sridhar,[a] Jagadeesh Babu Nanubolu,[a] Venkatasubramanian Hariharakrishnan[b] and Awadesh Narain Singh[b]

[a]Laboratory of X-ray Crystallography, CSIR Indian Institute of Chemical Technology, Hyderabad 500 007, India, and [b]S. M. S. Pharma Research Centre, Hyderabad 500 038, India
Correspondence e-mail: sshiya@yahoo.com

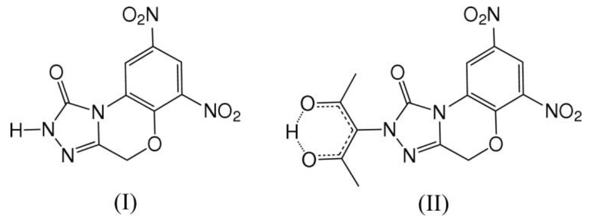
Received 31 May 2012
Accepted 29 June 2012
Online 13 July 2012

6,8-Dinitro-2,4-dihydro-1*H*-benzo[*b*][1,2,4]triazolo[4,3-*d*]-[1,4]oxazin-1-one, $C_9H_5N_5O_6$, (I), a potential diuretic, and its acetylacetone derivative (*E*)-2-(2-hydroxy-4-oxopent-2-en-3-yl)-6,8-dinitro-2,4-dihydro-1*H*-benzo[*b*][1,2,4]triazolo[4,3-*d*]-[1,4]oxazin-1-one, $C_{14}H_{11}N_5O_8$, (II), both crystallize from methanol but in centrosymmetric and noncentrosymmetric space groups, respectively. To the best of our knowledge, this is the first report of crystal structures of benzoxazine–triazole fused systems. The acetylacetone group in (II) exists as the keto–enol tautomer and is oriented perpendicular to the triazol-3-one ring. Of the two nitro groups present, one is rotated significantly less than the other in both structures. The oxazine ring adopts a screw-boat conformation in (II), whereas it is almost planar in (I). N—H$\cdots$N and N—H$\cdots$O hydrogen bonds form centrosymmetric dimers in (I), while C—H$\cdots$O interactions associate the molecules into helical columns in (II).

Comment

Triazole and its derivatives have been attracting interest over the past decade due to their wide range of pharmacological applications (Chen *et al.*, 2000; Duran *et al.*, 2002; Gujjar *et al.*, 2009). Compounds containing triazole have also received considerable attention due to their intriguing physical properties and potential for applications in propellants and explosives (Nimesh & Rajendran, 2010; Katritzky *et al.*, 2006). Furthermore, triazole moieties are attractive connecting units, as they are stable to metabolic degradation and capable of hydrogen bonding (Horne *et al.*, 2004). In recent years, fused triazoles have become increasingly common in pharmaceutical targets and biologically active substances (Lauria *et al.*, 2008).

1,4-Benzoxazines are an important class of molecules and a common heterocyclic scaffold in biologically active and medicinally significant compounds. The therapeutic activities of benzoxazine compounds have been further extended through the development of scaffolds *via* fusion with different nitrogen heterocycles (*e.g.* imidazole, triazole, oxazole, pyrimidine *etc.*). A number of benzoxazines fused with triazoles were synthesized by Shridhar *et al.* (1984) and evaluated for their diuretic activity. 6,8-Dinitro-2,4-dihydro-1*H*-benzo[*b*]-[1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one, (I), was reported to be the most potent of the compounds synthesized, even though it contains none of the usual pharmacophoric features needed for diuretic activity, *e.g.* a strong acidic group like –COOH, –SO_3H or a sulfonamide group, or a strongly basic group such as an amidine group. The present work forms part of a continuing study of the structures of pharmaceutical compounds (Ravikumar & Sridhar, 2009, 2010; Ravikumar *et al.*, 2011) and we report here the crystal structures of (I) and its acetylacetone derivative (*E*)-2-(2-hydroxy-4-oxopent-2-en-3-yl)-6,8-dinitro-2,4-dihydro-1*H*-benzo[*b*][1,2,4]triazolo[4,3-*d*]-[1,4]oxazin-1-one, (II).



(I) (II)

Scheme 1

Compounds (I) and (II) contain heterocyclic ring structures, significant hydrogen-bond acceptor sites and flexible functionalities. Interestingly, both compounds crystallize as solvent-free structures. Compound (I) crystallizes in the centrosymmetric space group $P2_1/n$ and (II) in the noncentrosymmetric space group $Pna2_1$.

The molecular structures of (I) and (II), including the atom-labelling schemes, are shown in Figs. 1 and 2, respectively. The defining feature of the molecular conformations of (I) and (II) is the orientation of the nitro groups. The C7-nitro group is nearly coplanar with the plane of the attached benzene ring [6.8 (1)° in (I) and 3.6 (1)° in (II)], whereas the C1-nitro group is significantly rotated [20.3 (1)° in (I) and 41.5 (1)° in (II)]. This orientational difference may be attributed to repulsion between atom O1 of the C1-nitro group and atom O5 of the neighbouring oxazine ring. It may also be due to the participation of the C1-nitro group only in intermolecular C—H$\cdots$O interactions (Tables 2 and 3). The greater rotation of the C1-nitro group observed in (II) is perhaps due to its interaction with the acetylacetone group.

Computational calculations were performed using the crystallographic structure parameters of (I) and (II) as a starting point. The density functional theory (DFT) method was applied at the B3LYP hybrid exchange correlation function level (Becke, 1993; Lee *et al.*, 1988) using the 6-31G(d,p) basis set (Bauschlicher & Partridge, 1995) as implemented in *GAUSSIAN03* (Frisch *et al.*, 2004). The optimized geometry for the C7-nitro group in both structures is coplanar with the plane of the parent benzene ring [−0.53° for (I) and 1.56° for (II)], while for the C1-nitro group it is twisted [31.4° for (I) and 27.8° for (II)] to avoid repulsion between the juxtaposed O

doi:10.1107/S0108270112029800

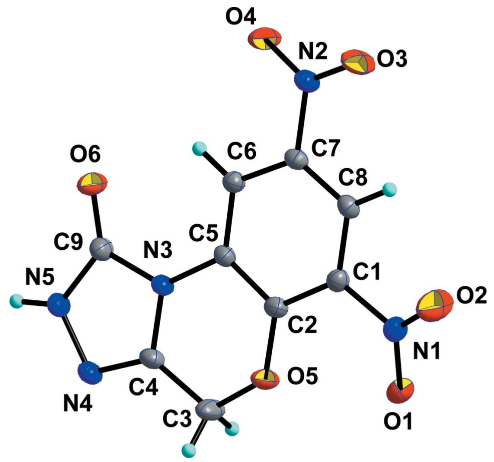


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

atoms, as mentioned above. It can be seen that the computed rotation angles for the nitro groups are slightly different from those observed in the crystal structures, as the calculations were performed on isolated molecules, thus precluding any hydrogen-bonding effects.

Compound (I) contains a strong hydrogen-bond donor (N5—H) and also strong acceptors (N4 and O6) on the triazole ring, which can result in the formation of centrosymmetric motifs such as N—H⋯N dimers (type *A*; Scheme 2) or amide N—H⋯O dimers (type *B*). Of the two possible centrosymmetric motifs, type *B* is stronger than type *A* because of the higher electronegativity and greater acceptor strength of oxygen over nitrogen (Jeffrey, 1997). Interestingly, the structure of (I) does not contain the stronger type *B* motif. Instead, it is assembled only by the weaker type *A* motif (N5—H5N⋯N4).

In order to understand the inherent competition between these two hydrogen-bonded motifs, and thereby to establish their preference of occurrence in similar organic crystal structures, a search of the Cambridge Structural Database (CSD, Version 5.32 with May 2012 updates; Allen, 2002) was undertaken for all molecules containing the 1,2,4-triazol-3-one fragment. The search resulted in 75 hits, of which seven repeated structures were discarded. Of the remaining 68 structures, 25 contain the amide-dimer type *B* motif, two show the N—H⋯N catemer (type *C* in Scheme 2), 20 show the amide-catemer motif (type *D*), one shows the N—H⋯N single-point interaction (type *E*), two show the N—H⋯O single-point interaction (type *F*), one is a hetero dimer (type *G*) and 17 have NH bonded to water, solvent or other strong acceptor groups available in the structure (type *H*). This trend clearly indicates a preference for motif types *B* and *D*. It is surprising to note that none of these 1,2,4-triazol-3-one fragment structures contains the N—H⋯N dimer type *A* motif, and therefore the very presence of the type *A* motif in (I) makes the crystal structure interesting. The absence of the type *B* motif in (I) is likely to arise from the involvement of a carbonyl O atom in the intramolecular C6—H6⋯O6 contact. In (II), all the hydrogen-bonded motifs mentioned above are absent, since the H atom bound to atom N5 is replaced by an acetylacetone group.

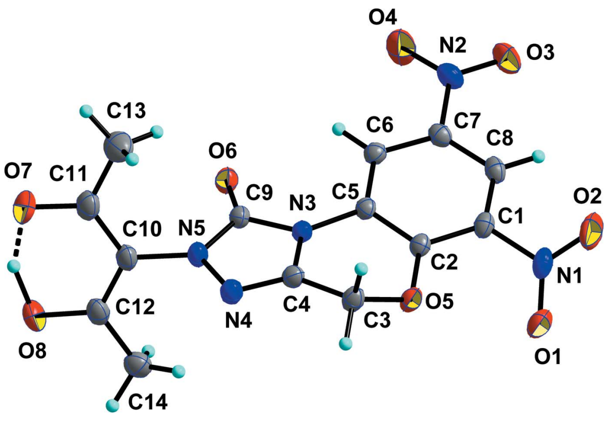
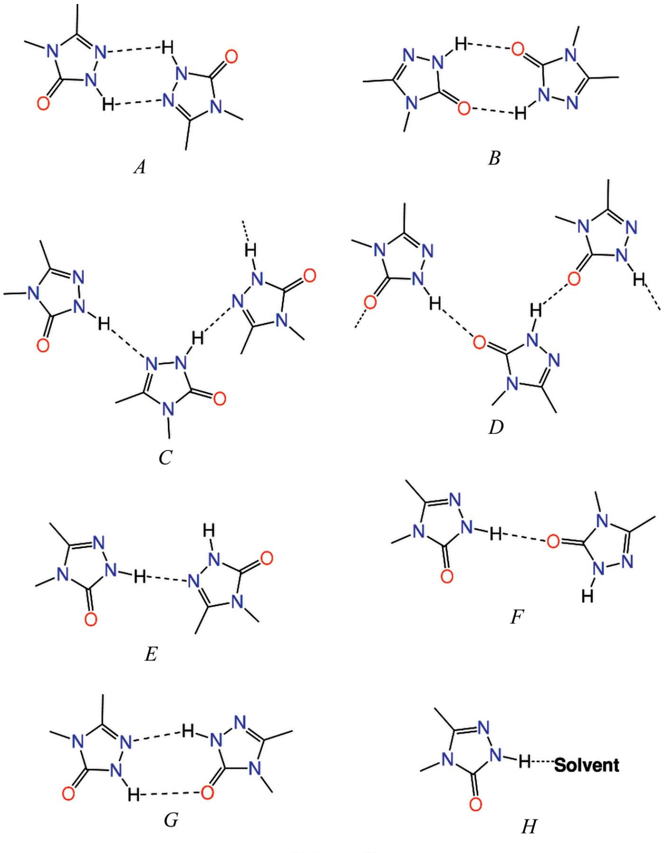


Figure 2
A view of the molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed line indicates the intramolecular hydrogen bond.



Scheme 2

In (II), the effect of the acetylacetone substitution is surprisingly seen in the oxazine ring, even though these two groups are a long way apart. It manifests itself in a lengthening of the C3—O5 bond and a narrowing of the bond angles involving atom C3 of the oxazine ring in (II) compared with unsubstituted (I) (Table 1). It could also be surmised that the participation of atom C3 of the oxazine ring in an inter-

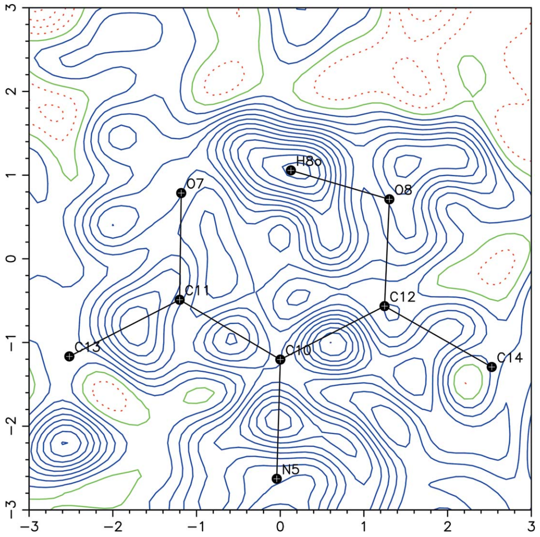
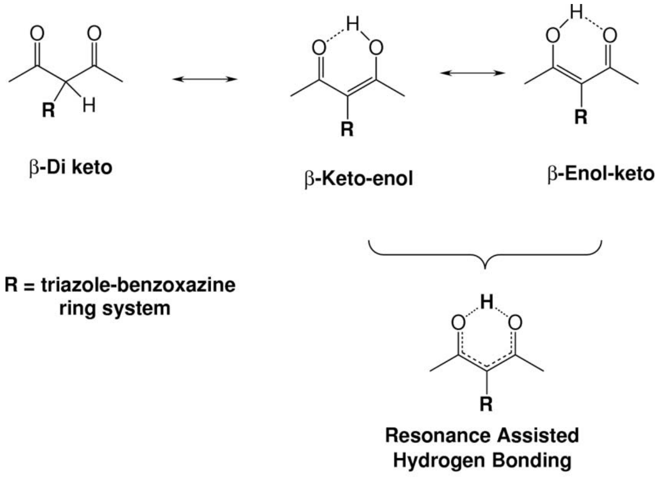


Figure 3
A contoured Fourier difference map slice in the plane of the acetylacetone group of (II), with the site occupancy of atom H8O set at 0.001. The refined positions of the atoms are shown by '+' marks. The contour intervals are 0.1 e Å^{-3}.

molecular C—H$\cdots$O interaction with atom O8 of the acetylacetone group (Table 3) might have influenced the ring distortion. The conformation of the oxazine ring is nearly planar in (I), whereas it is screw-boat in (II).

There are two tautomeric possibilities for the acetylacetone group in (II), *viz.* keto–keto or keto–enol, as shown in Scheme 3. The latter tautomeric structure is generally preferred, due to the intramolecular O—H$\cdots$O hydrogen bond which helps to stabilize it (Bertolasi *et al.*, 2008; Caminati & Grabow, 2006). According to Gilli & Gilli (2000), the keto–enol tautomer has a natural tendency to exhibit resonance-assisted hydrogen bonding (Scheme 3), resulting in a strong hydrogen bond between two carbonyl O atoms. In such circumstances, the carbonyl and enol C—O bond lengths are indistinguishable, and the H atom is at the mid-point between the two carbonyl O atoms (Emsley *et al.*, 1988, 1989). This short hydrogen bond in (II) [O8$\cdots$O7 = 2.487 (4) Å] is apparently symmetric, with its H atom located centrally [O8—H8O = 1.23 (10) Å and H8O$\cdots$O7 = 1.34 (9) Å]. The refined isotropic atomic displacement parameter of atom H8O is somewhat larger than normal; its position and atomic displacement parameter were also refined. A contoured Fourier difference map produced by *PLATON* (Spek, 2009), with the site-occupancy factor of atom H8O set to 0.001, clearly shows that the maximum electron density is at atom H8O, located midway between the two O atoms (Fig. 3). The refined position of the H atom does not necessarily truly represent the majority of the electron-density distribution, and hence an asymmetric nature for this hydrogen bond cannot be precluded. Both carbonyl distances (Table 1) are equivalent and longer than the expected Csp^2═O distance of 1.222 Å and shorter than the expected Csp^2—OH distance of 1.333 Å in the keto–enol fragment (Allen *et al.*, 1987). Furthermore, the equidistant bonds for C12—C10 [1.400 (4) Å] and C10—C11 [1.399 (5) Å] reflect neither a Csp^2—Csp^2 (1.455 Å) nor a Csp^2═Csp^2 bond (1.362 Å) (Allen *et al.*, 1987), but indicate a significant mixed character of both bond types, thus confirming the resonance phenomenon or a partial π-electron delocalization in the keto–enol fragment (Bertolasi *et al.*, 1996).



Scheme 3

A salient feature of this keto–enol tautomeric form in (II) is its influence on the molecular conformation: it is oriented perpendicular to the triazol-3-one ring [C9—N5—C10—C12 = 99.4 (3)°]. Geometry optimization performed on this molecule using density functional theory (DFT) methods also indicated a twisted conformation, with C9—N5—C10—C12 = 71.6°. An overlay of these two conformations is shown in Fig. 4. Differences in torsion angles between experimentally observed and computationally predicted conformers are normally expected, as the former are affected by the crystal environment. This twisting may be necessary to relieve the van der Waals strain that would be present if the molecule were to exist in a planar conformation (*i.e.* without twist), since both the methyl groups (C13 and C14) of the acetylacetone and atoms O6 and N4 of the triazol-3-one ring system are prone to maximum repulsion. The energy calculated for the above-mentioned planar conformation is 13.21 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) higher than that for the twisted conformation.

In the crystal packing of (I), as mentioned above, the molecules form a centrosymmetric dimer connected by inter-

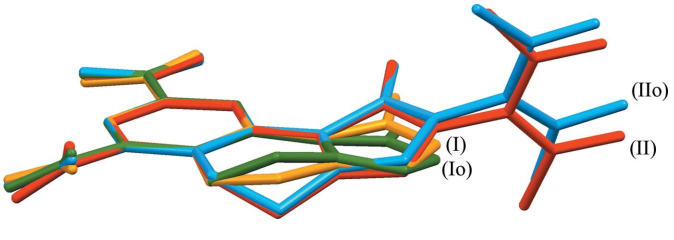


Figure 4
A superposition of the molecular conformations of (I) and (II), along with the respective optimized structures, (Io) and (IIo). The overlay was made by making a least-squares fit through the benzene ring of (I). The r.m.s. deviations (Å) with respect to the conformation of (I) (orange in the electronic version of the journal) are: (II) 0.008 (red), (Io) 0.012 (green) and (IIo) 0.011 (cyan).

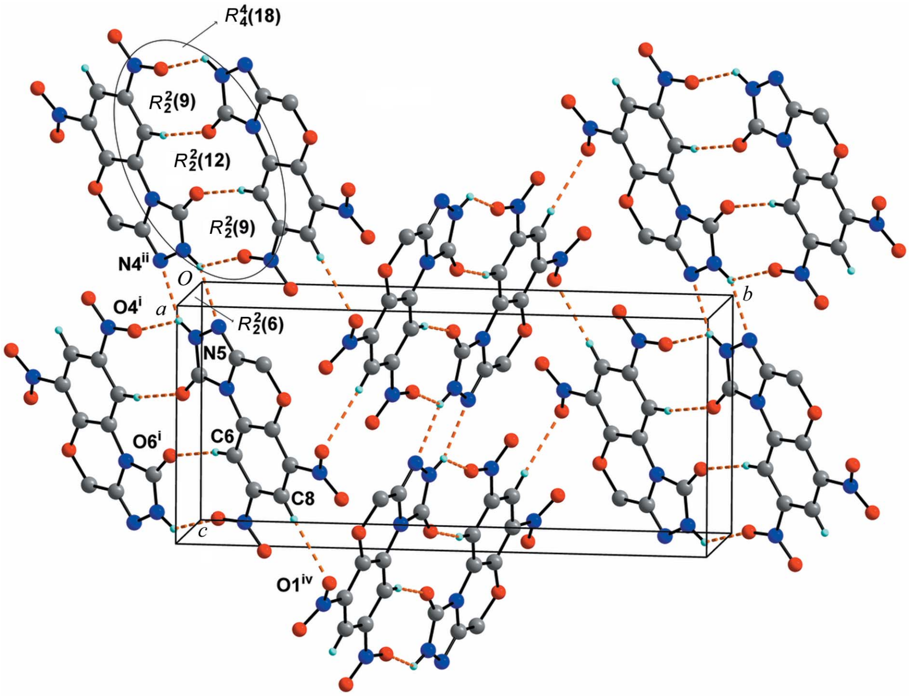


Figure 5

A partial packing diagram for (I), viewed along the *a* axis, showing the formation of $R_2^2(6)$, $R_2^2(9)$ and $R_4^4(18)$ ring motifs. N—H···N, N—H···O and C—H···O interactions are shown as dashed lines. Intermolecular C3—H3*B*···O6^{iii} contacts and H atoms not involved in interactions have been omitted for clarity. Selected atoms of the molecules present in the asymmetric unit are labelled, primarily to provide a key for the coding of the atoms. [Symmetry codes: (i) $-x + 2, -y, -z + 1$; (ii) $-x + 1, -y, -z$; (iii) $x - 1, y, z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.]

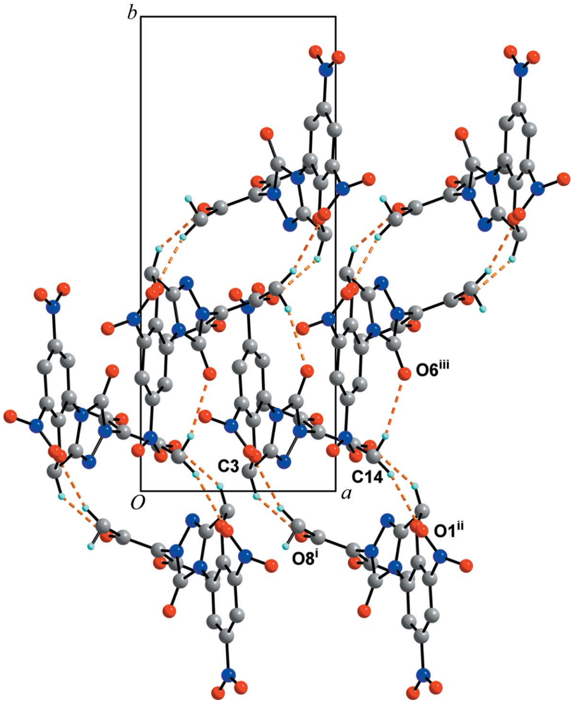


Figure 6

A partial packing diagram for (II), viewed along the *c* axis, showing the formation of helical columns. C—H···O interactions are shown as dashed lines. H atoms not involved in interactions have been omitted for clarity. Selected atoms of the molecules present in the asymmetric unit are labelled, primarily to provide a key for the coding of the atoms. [Symmetry codes: (i) $-x + 2, -y, z + \frac{1}{2}$; (ii) $-x + 2, -y, z - \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z$.]

molecular N5—H5N···N4^{ii} hydrogen bonds (Fig. 5) [$R_2^2(6)$ graph-set motif (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995)] [symmetry code: (ii) $-x + 1, -y, -z$]. Each dimer is further connected to an inversion-related dimer by a quadruple hydrogen-bonding motif *via* N—H···O and a C—H···O interactions (Table 2). This quadruple [$R_4^4(18)$] motif can also be defined in the form of three fused $R_2^2(9)$, $R_2^2(12)$ and $R_2^2(9)$ ring motifs. The alternating arrangement of these motifs facilitates the formation of an infinite tape in the [101] direction. A C8—H8···O1^{iv} interaction connects adjacent tapes in a zigzag fashion [symmetry code: (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$].

In the crystal packing of (II), the molecules are essentially associated by C—H···O interactions (Table 3) and van der Waals forces. It is interesting to note that the molecules are aligned in helical columns which run in the [001] direction (Fig. 6) and are interlinked.

Stacking interactions are seen in both structures. In (I), these are between the triazol-3-one and benzene rings [centroid separation = 3.659 (1) Å], whereas in (II) they are between benzene rings [centroid separation = 3.708 (2) Å]. In (I), short intermolecular O6···O6 and O6···O6^{i} contacts (Table 2) are also observed, which are normal due to the three-centred intra- and intermolecular C6—H6···O6 contacts.

In summary, this is the first report to present the crystal structures of benzoxazine-fused triazoles. The crystallographic study shows the formation of the N—H···N centrosymmetric dimer motif, rather than the commonly observed N—H···O centrosymmetric dimer, between triazol-3-one rings. The resonance-assisted keto–enol tautomer of the acetylacetone group, with enhanced acceptor strength, participates in a C—H···O interaction with an oxazine ring. This influences the molecular conformation of the central oxazine ring in the tricyclic fused-ring system. C—H···O-driven intermolecular interactions play a significant role in the formation of the supramolecular networks.

Experimental

Crystals of (I) and (II) (SMS Pharma Research Centre, Hyderabad) suitable for X-ray diffraction were obtained from methanol solutions by slow evaporation.

Compound (I)

Crystal data

$C_9H_5N_5O_6$
M_r = 279.18
Monoclinic, $P2_1/n$
a = 6.6313 (4) Å
b = 18.5174 (11) Å
c = 8.3354 (5) Å
β = 91.352 (1)°
V = 1023.26 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.16 mm^{-1}
T = 294 K
0.21 × 0.18 × 0.08 mm

Data collection

Bruker SMART APEX CCD area detector diffractometer
10419 measured reflections
2005 independent reflections
1882 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.130
S = 1.03
2005 reflections
186 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.54 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.42 e Å^{-3}

Compound (II)

Crystal data

$C_{14}H_{11}N_5O_8$
M_r = 377.28
Orthorhombic, $Pna2_1$
a = 7.2636 (8) Å
b = 17.673 (2) Å
c = 12.0447 (13) Å
V = 1546.2 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 294 K
0.18 × 0.16 × 0.05 mm

Data collection

Bruker SMART APEX CCD area detector diffractometer
14914 measured reflections
1592 independent reflections
1537 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.098
S = 1.07
1592 reflections
250 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.14 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I) and (II).

	(I)	(II)
C3—O5	1.397 (2)	1.445 (3)
C9—O6	1.209 (2)	1.216 (3)
C9—N5	1.352 (2)	1.360 (3)
N5—N4	1.384 (2)	1.402 (3)
N4—C4	1.287 (2)	1.277 (4)
C11—O7		1.276 (4)
C12—O8		1.278 (4)
C2—O5—C3	122.83 (15)	116.7 (2)
C5—C2—O5	122.54 (15)	121.4 (2)
O5—C3—C4	114.14 (16)	110.0 (2)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5N···O4$^{\rm i}$	0.88 (3)	2.56 (2)	3.172 (2)	127 (2)
N5—H5N···N4$^{\rm ii}$	0.88 (3)	2.23 (2)	2.930 (2)	135 (2)
C3—H3B···O6$^{\rm iii}$	0.97	2.48	3.441 (4)	173
C6—H6···O6$^{\rm i}$	0.93	2.56	3.481 (2)	169
C6—H6···O6	0.93	2.35	2.957 (2)	123
C8—H8···O1$^{\rm iv}$	0.93	2.53	3.458 (2)	176

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

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8O···O7	1.23 (10)	1.34 (9)	2.487 (4)	151 (9)
C3—H3B···O8$^{\rm i}$	0.97	2.43	3.238 (4)	141
C6—H6···O6	0.93	2.46	3.026 (3)	119
C14—H14A···O1$^{\rm ii}$	0.96	2.59	3.385 (4)	140
C14—H14B···N5	0.96	2.56	2.898 (4)	101
C14—H14C···O6$^{\rm iii}$	0.96	2.44	3.361 (4)	160

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

The N-bound H atom of (I) and the O-bound H atom of (II) were located in a difference Fourier map and their positions and isotropic displacement parameters were refined. All other H atoms were located in difference density maps, but were positioned geometrically and included as riding atoms, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene) and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for the methyl groups and 1.2$U_{\rm eq}$(C) otherwise. The methyl groups were allowed to rotate but not to tip. In the absence of significant anomalous scatterers, Friedel pairs were merged in (II).

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

The authors thank Dr J. S. Yadav, Director, IICT, Hyderabad, for his kind encouragement, and Dr K. Bhanuprakash, I&PC division, IICT, for his support with the computations.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CU3013). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Bauschlicher, C. W. & Partridge, H. (1995). *Chem. Phys. Lett.* **240**, 533–540.

Becke, A. D. (1993). *Chem. Phys.* **98**, 5648–5652.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bertolasi, V., Ferretti, V., Gilli, P., Yao, X. & Li, C. J. (2008). *New J. Chem.* **32**, 694–704.

Bertolasi, V., Gilli, P., Ferretti, V. & Gilli, G. (1996). *Chem. Eur. J.* **2**, 925–934.

Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Caminati, W. & Grabow, J.-U. (2006). *J. Am. Chem. Soc.* **128**, 854–857.

Chen, M. D., Lu, S. J., Yuag, G. P., Yang, S. Y. & Du, X. L. (2000). *Heterocycl. Commun.* **6**, 421–426.

Duran, A., Dogan, H. N. & Rollas, H. (2002). *Il Farmaco*, **57**, 559–564.

Emsley, J., Freeman, N. J., Bates, P. A. & Hursthouse, M. B. (1988). *J. Chem. Soc. Perkin Trans. 1*, pp. 297–299.

Emsley, J., Ma, L., Bates, V. V., Motevalli, P. A. & Hursthouse, M. B. (1989). *J. Chem. Soc. Perkin Trans. 2*, pp. 527–533.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Frisch, M. J. *et al.* (2004). *GAUSSIAN03*. Gaussian Inc., Wallingford, Connecticut, USA.

Gilli, G. & Gilli, P. (2000). *J. Mol. Struct.* **552**, 1–15.

Gujjar, R., Marwaha, A., White, J., White, L., Creason, S., Shackleford, D. M., Baldwin, J., Charman, W. N., Buckner, F. S., Charman, S., Rathod, P. K. & Phillips, M. A. (2009). *J. Med. Chem.* **52**, 1864–1872.

Horne, W. S., Yadav, M. K., Stout, C. D. & Ghadiri, M. R. (2004). *J. Am. Chem. Soc.* **126**, 15366–15367.

Jeffrey, G. A. (1997). *An Introduction to Hydrogen Bonding*. New York: Oxford University Press Inc.

Katritzky, A. R., Singh, S. K., Meher, N. K., Doskocz, J., Suzuki, K., Jiang, R., Sommen, G. L., Ciaramitaro, D. A. & Steel, P. J. (2006). *Arkivoc*, **v**, 43–62.

Lauria, A., Patella, C., Dattolo, G. & Almerico, A. M. (2008). *J. Med. Chem.* **51**, 2037–2046.

Lee, C., Yang, W. & Parr, R. G. (1988). *Phys. Rev. B*, **37**, 785–789.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Nimesh, A. & Rajendran, A. G. (2010). *Propell. Explos. Pyrot.* **35**, 1–8.

Ravikumar, K. & Sridhar, B. (2009). *Acta Cryst.* C**65**, o502–o505.

Ravikumar, K. & Sridhar, B. (2010). *Acta Cryst.* C**66**, o317–o320.

Ravikumar, K., Sridhar, B., Bhujanga Rao, A. K. S. & Pulla Reddy, M. (2011). *Acta Cryst.* C**67**, o29–o32.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Shridhar, D. R., Jogibhukta, M., Krishnan, V. S. H., Joshi, P. P., Naidu, M. U. R., Thapar, G. S., Murthy, A. K. & Thomas, G. P. (1984). *Indian J. Chem. Sect. B*, **23**, 1279–1283.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2012). C**68**, o302–o307 [doi:10.1107/S0108270112029800]

Structures of benzoxazine-fused triazoles as potential diuretic agents

Krishnan Ravikumar, Balasubramanian Sridhar, Jagadeesh Babu Nanubolu, Venkatasubramanian Hariharakrishnan and Awadesh Narain Singh

(I) 6,8-dinitro-2,4-dihydro-1*H*- benzo[*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one

Crystal data

$C_9H_5N_5O_6$
M_r = 279.18
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 6.6313 (4) Å
b = 18.5174 (11) Å
c = 8.3354 (5) Å
β = 91.352 (1)°
V = 1023.26 (11) Å^3
Z = 4
$F(000)$ = 568
D_x = 1.812 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7478 reflections
θ = 2.2–28.0°
μ = 0.16 mm^{-1}
T = 294 K
Block, colourless
0.21 × 0.18 × 0.08 mm

Data collection

Bruker SMART APEX CCD area detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
10419 measured reflections
2005 independent reflections
1882 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016
$\theta_{\rm max}$ = 26.0°, $\theta_{\rm min}$ = 2.2°
$h = -8 \rightarrow 8$
$k = -22 \rightarrow 22$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.130
S = 1.03
2005 reflections
186 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2 + 0.6637P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.54 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.42 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.011 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
C1	0.3902 (3)	0.18632 (9)	0.7207 (2)	0.0323 (4)
C2	0.3920 (3)	0.15219 (9)	0.5712 (2)	0.0305 (4)
C3	0.2250 (3)	0.12739 (15)	0.3183 (3)	0.0565 (6)
H3A	0.1924	0.1605	0.2312	0.068*
H3B	0.1116	0.0948	0.3291	0.068*
C4	0.4036 (3)	0.08506 (10)	0.2754 (2)	0.0332 (4)
C5	0.5563 (2)	0.10644 (9)	0.54075 (19)	0.0283 (4)
C6	0.7115 (3)	0.09605 (9)	0.6514 (2)	0.0307 (4)
H6	0.8194	0.0658	0.6295	0.037*
C7	0.7010 (3)	0.13239 (9)	0.7968 (2)	0.0315 (4)
C8	0.5446 (3)	0.17732 (9)	0.8338 (2)	0.0327 (4)
H8	0.5422	0.2011	0.9320	0.039*
C9	0.6972 (3)	0.02825 (11)	0.3202 (2)	0.0380 (4)
N1	0.2243 (3)	0.23402 (9)	0.7655 (2)	0.0421 (4)
N2	0.8655 (2)	0.12332 (9)	0.91554 (18)	0.0395 (4)
N3	0.5540 (2)	0.07363 (8)	0.38799 (17)	0.0305 (4)
N4	0.4373 (2)	0.05221 (9)	0.14260 (18)	0.0390 (4)
N5	0.6202 (2)	0.01789 (10)	0.17026 (19)	0.0401 (4)
O1	0.0629 (2)	0.23051 (9)	0.69463 (19)	0.0523 (4)
O2	0.2598 (3)	0.27718 (13)	0.8715 (3)	0.0926 (8)
O3	0.8652 (3)	0.16065 (10)	1.0354 (2)	0.0658 (5)
O4	0.9952 (3)	0.07943 (11)	0.8897 (2)	0.0739 (6)
O5	0.2489 (2)	0.16699 (8)	0.46012 (17)	0.0501 (4)
H5N	0.669 (4)	−0.0117 (13)	0.097 (3)	0.049 (6)*
O6	0.8478 (2)	0.00415 (11)	0.38480 (19)	0.0656 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0329 (9)	0.0312 (8)	0.0327 (9)	0.0030 (7)	0.0001 (7)	−0.0018 (7)
C2	0.0312 (8)	0.0314 (8)	0.0286 (8)	0.0006 (7)	−0.0039 (7)	0.0012 (7)
C3	0.0465 (12)	0.0800 (16)	0.0419 (11)	0.0227 (11)	−0.0189 (9)	−0.0213 (11)
C4	0.0352 (9)	0.0365 (9)	0.0275 (8)	−0.0003 (7)	−0.0077 (7)	−0.0011 (7)
C5	0.0318 (8)	0.0279 (8)	0.0251 (8)	−0.0023 (6)	−0.0019 (6)	−0.0019 (6)
C6	0.0312 (9)	0.0320 (8)	0.0289 (8)	0.0023 (7)	−0.0026 (7)	−0.0016 (7)
C7	0.0323 (9)	0.0339 (9)	0.0279 (8)	−0.0021 (7)	−0.0051 (7)	−0.0007 (7)
C8	0.0382 (9)	0.0345 (9)	0.0252 (8)	−0.0014 (7)	−0.0013 (7)	−0.0042 (7)

C9	0.0369 (10)	0.0448 (10)	0.0319 (9)	0.0041 (8)	−0.0043 (7)	−0.0100 (8)
N1	0.0421 (9)	0.0463 (9)	0.0379 (9)	0.0111 (7)	0.0000 (7)	−0.0066 (7)
N2	0.0406 (9)	0.0469 (9)	0.0304 (8)	0.0037 (7)	−0.0082 (7)	−0.0039 (7)
N3	0.0320 (8)	0.0333 (7)	0.0257 (7)	0.0017 (6)	−0.0054 (6)	−0.0043 (6)
N4	0.0418 (9)	0.0467 (9)	0.0281 (8)	0.0033 (7)	−0.0066 (6)	−0.0045 (7)
N5	0.0406 (9)	0.0497 (10)	0.0297 (8)	0.0074 (7)	−0.0035 (7)	−0.0114 (7)
O1	0.0364 (8)	0.0703 (10)	0.0501 (9)	0.0126 (7)	0.0010 (6)	−0.0003 (7)
O2	0.0818 (14)	0.1106 (17)	0.0840 (15)	0.0481 (13)	−0.0250 (11)	−0.0634 (13)
O3	0.0725 (11)	0.0766 (12)	0.0470 (9)	0.0220 (9)	−0.0294 (8)	−0.0280 (8)
O4	0.0646 (11)	0.1016 (14)	0.0542 (10)	0.0467 (11)	−0.0252 (8)	−0.0266 (10)
O5	0.0493 (8)	0.0621 (9)	0.0379 (8)	0.0248 (7)	−0.0170 (6)	−0.0143 (7)
O6	0.0528 (10)	0.0937 (13)	0.0494 (9)	0.0371 (9)	−0.0199 (7)	−0.0321 (9)

Geometric parameters (Å, º)

C1—C8	1.385 (2)	C6—H6	0.9300
C1—C2	1.398 (2)	C7—C8	1.370 (3)
C1—N1	1.466 (2)	C7—N2	1.465 (2)
C2—O5	1.338 (2)	C8—H8	0.9300
C2—C5	1.408 (2)	C9—O6	1.209 (2)
C3—O5	1.397 (2)	C9—N5	1.352 (2)
C3—C4	1.472 (3)	C9—N3	1.397 (2)
C3—H3A	0.9700	N1—O2	1.211 (2)
C3—H3B	0.9700	N1—O1	1.212 (2)
C4—N4	1.287 (2)	N2—O4	1.206 (2)
C4—N3	1.369 (2)	N2—O3	1.215 (2)
C5—C6	1.379 (2)	N4—N5	1.384 (2)
C5—N3	1.411 (2)	N5—H5N	0.88 (3)
C6—C7	1.389 (2)		
C8—C1—C2	122.02 (16)	C8—C7—N2	118.21 (15)
C8—C1—N1	116.51 (15)	C6—C7—N2	118.81 (16)
C2—C1—N1	121.47 (16)	C7—C8—C1	118.11 (16)
O5—C2—C1	120.20 (15)	C7—C8—H8	120.9
O5—C2—C5	122.54 (15)	C1—C8—H8	120.9
C1—C2—C5	117.12 (15)	O6—C9—N5	130.48 (18)
O5—C3—C4	114.14 (16)	O6—C9—N3	127.16 (17)
O5—C3—H3A	108.7	N5—C9—N3	102.35 (15)
C4—C3—H3A	108.7	O2—N1—O1	123.05 (17)
O5—C3—H3B	108.7	O2—N1—C1	116.73 (17)
C4—C3—H3B	108.7	O1—N1—C1	120.19 (16)
H3A—C3—H3B	107.6	O4—N2—O3	123.02 (17)
N4—C4—N3	112.20 (16)	O4—N2—C7	118.63 (15)
N4—C4—C3	128.12 (16)	O3—N2—C7	118.36 (16)
N3—C4—C3	119.58 (16)	C4—N3—C9	107.86 (14)
C6—C5—C2	122.14 (15)	C4—N3—C5	122.95 (15)
C6—C5—N3	122.37 (15)	C9—N3—C5	129.15 (14)
C2—C5—N3	115.47 (14)	C4—N4—N5	104.05 (14)
C5—C6—C7	117.62 (16)	C9—N5—N4	113.52 (16)
C5—C6—H6	121.2	C9—N5—H5N	126.1 (15)

C7—C6—H6	121.2	N4—N5—H5N	120.0 (15)
C8—C7—C6	122.97 (16)	C2—O5—C3	122.83 (15)

C8—C1—C2—O5	−174.33 (17)	C6—C7—N2—O4	−6.9 (3)
N1—C1—C2—O5	5.3 (3)	C8—C7—N2—O3	−6.3 (3)
C8—C1—C2—C5	1.5 (3)	C6—C7—N2—O3	172.82 (18)
N1—C1—C2—C5	−178.91 (16)	N4—C4—N3—C9	−0.6 (2)
O5—C3—C4—N4	−169.0 (2)	C3—C4—N3—C9	176.00 (19)
O5—C3—C4—N3	14.9 (3)	N4—C4—N3—C5	177.09 (15)
O5—C2—C5—C6	174.67 (17)	C3—C4—N3—C5	−6.3 (3)
C1—C2—C5—C6	−1.0 (3)	O6—C9—N3—C4	−177.2 (2)
O5—C2—C5—N3	−3.6 (3)	N5—C9—N3—C4	1.3 (2)
C1—C2—C5—N3	−179.30 (14)	O6—C9—N3—C5	5.3 (3)
C2—C5—C6—C7	0.3 (3)	N5—C9—N3—C5	−176.25 (17)
N3—C5—C6—C7	178.44 (15)	C6—C5—N3—C4	−178.15 (16)
C5—C6—C7—C8	0.1 (3)	C2—C5—N3—C4	0.1 (2)
C5—C6—C7—N2	−179.00 (15)	C6—C5—N3—C9	−1.0 (3)
C6—C7—C8—C1	0.3 (3)	C2—C5—N3—C9	177.33 (17)
N2—C7—C8—C1	179.43 (16)	N3—C4—N4—N5	−0.3 (2)
C2—C1—C8—C7	−1.1 (3)	C3—C4—N4—N5	−176.6 (2)
N1—C1—C8—C7	179.21 (16)	O6—C9—N5—N4	176.9 (2)
C8—C1—N1—O2	21.1 (3)	N3—C9—N5—N4	−1.6 (2)
C2—C1—N1—O2	−158.6 (2)	C4—N4—N5—C9	1.2 (2)
C8—C1—N1—O1	−160.87 (18)	C1—C2—O5—C3	−170.4 (2)
C2—C1—N1—O1	19.5 (3)	C5—C2—O5—C3	14.1 (3)
C8—C7—N2—O4	173.97 (19)	C4—C3—O5—C2	−19.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*N*···O4^{i}	0.88 (3)	2.56 (2)	3.172 (2)	127 (2)
N5—H5*N*···N4^{ii}	0.88 (3)	2.23 (2)	2.930 (2)	135 (2)
C3—H3*B*···O6^{iii}	0.97	2.48	3.441 (4)	173
C6—H6···O6^{i}	0.93	2.56	3.481 (2)	169
C6—H6···O6	0.93	2.35	2.957 (2)	123
C8—H8···O1^{iv}	0.93	2.53	3.458 (2)	176

Symmetry codes: (i) −*x*+2, −*y*, −*z*+1; (ii) −*x*+1, −*y*, −*z*; (iii) *x*−1, *y*, *z*; (iv) *x*+1/2, −*y*+1/2, *z*+1/2.

(II) (*E*)-2-(2-hydroxy-4-oxopent-2-en-3-yl)-6,8-dinitro-2,4-dihydro- 1*H*-benzo[*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one

Crystal data

$C_{14}H_{11}N_5O_8$
M_r = 377.28
Orthorhombic, *Pna*2$_1$
Hall symbol: P 2c -2n
a = 7.2636 (8) Å
b = 17.673 (2) Å
c = 12.0447 (13) Å
V = 1546.2 (3) Å^3
Z = 4
F(000) = 776
D_x = 1.621 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 7822 reflections
θ = 2.3–26.7°

$\mu = 0.14$ mm^{-1}
$T = 294$ K

Plate, colourless
0.18 × 0.16 × 0.05 mm

Data collection

Bruker SMART APEX CCD area detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
14914 measured reflections
1592 independent reflections

1537 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.026$
$\theta_{\text{max}} = 26.0°$, $\theta_{\text{min}} = 2.1°$
$h = -8 \rightarrow 8$
$k = -21 \rightarrow 21$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.098$
$S = 1.07$
1592 reflections
250 parameters
1 restraint
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 0.2855P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.21$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.14$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.5177 (4)	0.18433 (15)	0.7492 (2)	0.0384 (5)
C2	0.5769 (3)	0.15006 (13)	0.6516 (2)	0.0346 (5)
C3	0.5564 (4)	0.04210 (15)	0.5339 (2)	0.0413 (6)
H3A	0.4266	0.0445	0.5152	0.050*
H3B	0.5935	−0.0106	0.5336	0.050*
C4	0.6653 (4)	0.08475 (14)	0.4502 (2)	0.0373 (6)
C5	0.6313 (3)	0.19717 (14)	0.5639 (2)	0.0330 (5)
C6	0.6242 (3)	0.27493 (14)	0.5734 (2)	0.0358 (5)
H6	0.6611	0.3061	0.5152	0.043*
C7	0.5603 (4)	0.30506 (14)	0.6720 (2)	0.0381 (5)
C8	0.5064 (3)	0.26158 (15)	0.7605 (2)	0.0399 (6)
H8	0.4638	0.2836	0.8258	0.048*
C9	0.7965 (3)	0.18887 (14)	0.3798 (2)	0.0349 (5)
C10	0.9101 (4)	0.12455 (15)	0.2101 (3)	0.0427 (6)

C11	0.8202 (5)	0.15186 (18)	0.1155 (3)	0.0527 (7)
C12	1.0909 (4)	0.09724 (16)	0.2064 (3)	0.0468 (7)
C13	0.6316 (6)	0.1836 (3)	0.1201 (3)	0.0733 (11)
H13A	0.6081	0.2123	0.0539	0.110*
H13B	0.6205	0.2160	0.1837	0.110*
H13C	0.5440	0.1431	0.1256	0.110*
C14	1.1939 (5)	0.07342 (17)	0.3060 (3)	0.0535 (8)
H14A	1.2827	0.0357	0.2858	0.080*
H14B	1.1099	0.0528	0.3596	0.080*
H14C	1.2559	0.1163	0.3375	0.080*
N1	0.4637 (4)	0.13748 (16)	0.8445 (2)	0.0482 (6)
N2	0.5499 (4)	0.38790 (14)	0.6815 (2)	0.0496 (6)
N3	0.6950 (3)	0.16061 (11)	0.46853 (18)	0.0343 (5)
N4	0.7344 (3)	0.06186 (12)	0.3587 (2)	0.0430 (5)
N5	0.8169 (3)	0.12685 (12)	0.3141 (2)	0.0404 (5)
O1	0.5588 (4)	0.08353 (15)	0.8669 (2)	0.0694 (7)
O2	0.3301 (4)	0.15744 (19)	0.8964 (2)	0.0793 (9)
O3	0.4860 (5)	0.41413 (14)	0.7649 (3)	0.0787 (8)
O4	0.6033 (6)	0.42549 (14)	0.6039 (3)	0.0918 (11)
O5	0.5855 (3)	0.07392 (10)	0.64304 (16)	0.0443 (5)
O6	0.8536 (3)	0.25285 (10)	0.36617 (16)	0.0448 (5)
O7	0.9021 (4)	0.15081 (16)	0.0218 (2)	0.0701 (7)
O8	1.1757 (4)	0.09387 (15)	0.1136 (2)	0.0658 (7)
H8O	1.062 (13)	0.117 (4)	0.046 (9)	0.18 (3)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0374 (12)	0.0493 (14)	0.0285 (12)	−0.0041 (11)	−0.0017 (10)	0.0016 (12)
C2	0.0359 (12)	0.0381 (12)	0.0298 (12)	−0.0021 (10)	−0.0019 (10)	0.0005 (10)
C3	0.0543 (15)	0.0359 (12)	0.0339 (13)	−0.0046 (11)	−0.0002 (11)	−0.0009 (11)
C4	0.0447 (13)	0.0336 (12)	0.0335 (13)	0.0015 (10)	−0.0034 (11)	−0.0015 (10)
C5	0.0343 (11)	0.0370 (12)	0.0277 (11)	0.0008 (9)	−0.0025 (9)	−0.0020 (10)
C6	0.0372 (12)	0.0367 (12)	0.0334 (12)	0.0007 (10)	−0.0027 (10)	0.0011 (10)
C7	0.0360 (12)	0.0388 (12)	0.0395 (14)	0.0017 (9)	−0.0026 (11)	−0.0068 (11)
C8	0.0352 (13)	0.0532 (14)	0.0314 (12)	0.0005 (11)	−0.0008 (10)	−0.0108 (12)
C9	0.0379 (12)	0.0368 (13)	0.0299 (12)	0.0028 (10)	0.0001 (10)	−0.0005 (10)
C10	0.0533 (15)	0.0406 (13)	0.0343 (13)	0.0001 (11)	0.0074 (12)	−0.0055 (11)
C11	0.0679 (19)	0.0528 (17)	0.0375 (16)	−0.0013 (14)	0.0025 (14)	−0.0087 (13)
C12	0.0570 (17)	0.0396 (13)	0.0438 (15)	−0.0007 (12)	0.0091 (13)	−0.0071 (12)
C13	0.076 (2)	0.092 (3)	0.052 (2)	0.018 (2)	−0.0143 (19)	−0.011 (2)
C14	0.0607 (19)	0.0431 (15)	0.0566 (19)	0.0038 (12)	−0.0002 (16)	−0.0045 (14)
N1	0.0534 (14)	0.0641 (15)	0.0271 (11)	−0.0093 (12)	0.0017 (10)	0.0000 (11)
N2	0.0541 (14)	0.0424 (12)	0.0523 (16)	0.0049 (11)	0.0025 (12)	−0.0141 (12)
N3	0.0443 (12)	0.0307 (10)	0.0281 (11)	0.0018 (8)	0.0020 (9)	−0.0008 (8)
N4	0.0563 (13)	0.0364 (11)	0.0365 (12)	−0.0010 (9)	0.0047 (11)	−0.0023 (10)
N5	0.0513 (13)	0.0384 (11)	0.0317 (11)	0.0001 (9)	0.0084 (10)	−0.0023 (9)
O1	0.1046 (19)	0.0631 (14)	0.0405 (12)	0.0089 (13)	0.0057 (13)	0.0144 (11)
O2	0.0641 (15)	0.126 (2)	0.0479 (15)	0.0003 (14)	0.0178 (14)	0.0205 (15)
O3	0.116 (2)	0.0540 (13)	0.0659 (17)	0.0190 (14)	0.0206 (17)	−0.0202 (13)

O4	0.150 (3)	0.0415 (12)	0.084 (2)	−0.0035 (15)	0.046 (2)	−0.0058 (14)
O5	0.0676 (12)	0.0354 (9)	0.0300 (10)	−0.0027 (8)	−0.0003 (9)	0.0032 (8)
O6	0.0596 (12)	0.0374 (9)	0.0374 (10)	−0.0043 (8)	0.0070 (9)	−0.0014 (8)
O7	0.0931 (19)	0.0844 (17)	0.0329 (12)	0.0098 (14)	0.0062 (12)	0.0018 (11)
O8	0.0677 (15)	0.0764 (15)	0.0532 (14)	0.0146 (12)	0.0226 (12)	−0.0030 (12)

Geometric parameters (Å, º)

C1—C8	1.374 (4)	C10—C11	1.399 (5)
C1—C2	1.391 (4)	C10—C12	1.400 (4)
C1—N1	1.468 (3)	C10—N5	1.425 (4)
C2—O5	1.351 (3)	C11—O7	1.276 (4)
C2—C5	1.401 (4)	C11—C13	1.481 (5)
C3—O5	1.445 (3)	C12—O8	1.278 (4)
C3—C4	1.487 (4)	C12—C14	1.475 (5)
C3—H3A	0.9700	C13—H13A	0.9600
C3—H3B	0.9700	C13—H13B	0.9600
C4—N4	1.277 (4)	C13—H13C	0.9600
C4—N3	1.376 (3)	C14—H14A	0.9600
C5—C6	1.380 (4)	C14—H14B	0.9600
C5—N3	1.397 (3)	C14—H14C	0.9600
C6—C7	1.382 (4)	N1—O2	1.207 (4)
C6—H6	0.9300	N1—O1	1.208 (4)
C7—C8	1.371 (4)	N2—O3	1.200 (4)
C7—N2	1.470 (4)	N2—O4	1.210 (4)
C8—H8	0.9300	N4—N5	1.402 (3)
C9—O6	1.216 (3)	O7—H8O	1.34 (9)
C9—N5	1.360 (3)	O8—H8O	1.23 (10)
C9—N3	1.391 (3)		

C8—C1—C2	122.3 (2)	O7—C11—C13	118.0 (3)
C8—C1—N1	117.8 (2)	C10—C11—C13	122.1 (3)
C2—C1—N1	119.9 (2)	O8—C12—C10	119.7 (3)
O5—C2—C1	120.8 (2)	O8—C12—C14	117.0 (3)
O5—C2—C5	121.4 (2)	C10—C12—C14	123.3 (3)
C1—C2—C5	117.8 (2)	C11—C13—H13A	109.5
O5—C3—C4	110.0 (2)	C11—C13—H13B	109.5
O5—C3—H3A	109.7	H13A—C13—H13B	109.5
C4—C3—H3A	109.7	C11—C13—H13C	109.5
O5—C3—H3B	109.7	H13A—C13—H13C	109.5
C4—C3—H3B	109.7	H13B—C13—H13C	109.5
H3A—C3—H3B	108.2	C12—C14—H14A	109.5
N4—C4—N3	112.7 (2)	C12—C14—H14B	109.5
N4—C4—C3	129.3 (2)	H14A—C14—H14B	109.5
N3—C4—C3	117.9 (2)	C12—C14—H14C	109.5
C6—C5—N3	122.8 (2)	H14A—C14—H14C	109.5
C6—C5—C2	121.3 (2)	H14B—C14—H14C	109.5
N3—C5—C2	116.0 (2)	O2—N1—O1	125.1 (3)
C5—C6—C7	117.9 (2)	O2—N1—C1	117.0 (3)
C5—C6—H6	121.1	O1—N1—C1	117.8 (2)

C7—C6—H6	121.1	O3—N2—O4	123.9 (3)
C8—C7—C6	123.2 (2)	O3—N2—C7	118.0 (3)
C8—C7—N2	118.9 (2)	O4—N2—C7	118.0 (2)
C6—C7—N2	117.9 (2)	C4—N3—C9	108.0 (2)
C7—C8—C1	117.6 (2)	C4—N3—C5	122.1 (2)
C7—C8—H8	121.2	C9—N3—C5	129.9 (2)
C1—C8—H8	121.2	C4—N4—N5	103.8 (2)
O6—C9—N5	129.4 (2)	C9—N5—N4	113.0 (2)
O6—C9—N3	128.2 (2)	C9—N5—C10	125.9 (2)
N5—C9—N3	102.4 (2)	N4—N5—C10	121.1 (2)
C11—C10—C12	122.1 (3)	C2—O5—C3	116.7 (2)
C11—C10—N5	119.0 (3)	C11—O7—H8O	102 (5)
C12—C10—N5	118.9 (3)	C12—O8—H8O	104 (5)
O7—C11—C10	119.9 (3)		

C8—C1—C2—O5	−179.6 (2)	C6—C7—N2—O3	176.4 (3)
N1—C1—C2—O5	0.0 (4)	C8—C7—N2—O4	177.8 (3)
C8—C1—C2—C5	1.9 (4)	C6—C7—N2—O4	−2.3 (4)
N1—C1—C2—C5	−178.4 (2)	N4—C4—N3—C9	−1.0 (3)
O5—C3—C4—N4	150.8 (3)	C3—C4—N3—C9	−179.1 (2)
O5—C3—C4—N3	−31.5 (3)	N4—C4—N3—C5	−179.8 (2)
O5—C2—C5—C6	−179.3 (2)	C3—C4—N3—C5	2.1 (4)
C1—C2—C5—C6	−0.9 (4)	O6—C9—N3—C4	−178.3 (3)
O5—C2—C5—N3	−0.3 (4)	N5—C9—N3—C4	0.9 (3)
C1—C2—C5—N3	178.2 (2)	O6—C9—N3—C5	0.3 (4)
N3—C5—C6—C7	−179.4 (2)	N5—C9—N3—C5	179.6 (2)
C2—C5—C6—C7	−0.4 (4)	C6—C5—N3—C4	−165.7 (2)
C5—C6—C7—C8	0.8 (4)	C2—C5—N3—C4	15.2 (4)
C5—C6—C7—N2	−179.1 (2)	C6—C5—N3—C9	15.8 (4)
C6—C7—C8—C1	0.1 (4)	C2—C5—N3—C9	−163.3 (2)
N2—C7—C8—C1	−180.0 (2)	N3—C4—N4—N5	0.7 (3)
C2—C1—C8—C7	−1.5 (4)	C3—C4—N4—N5	178.5 (3)
N1—C1—C8—C7	178.8 (2)	O6—C9—N5—N4	178.7 (3)
C12—C10—C11—O7	1.5 (5)	N3—C9—N5—N4	−0.5 (3)
N5—C10—C11—O7	179.4 (3)	O6—C9—N5—C10	−1.6 (5)
C12—C10—C11—C13	−177.5 (3)	N3—C9—N5—C10	179.2 (2)
N5—C10—C11—C13	0.4 (5)	C4—N4—N5—C9	−0.1 (3)
C11—C10—C12—O8	−3.0 (4)	C4—N4—N5—C10	−179.8 (2)
N5—C10—C12—O8	179.1 (3)	C11—C10—N5—C9	−78.6 (4)
C11—C10—C12—C14	175.3 (3)	C12—C10—N5—C9	99.4 (3)
N5—C10—C12—C14	−2.6 (4)	C11—C10—N5—N4	101.1 (3)
C8—C1—N1—O2	40.2 (4)	C12—C10—N5—N4	−80.9 (3)
C2—C1—N1—O2	−139.5 (3)	C1—C2—O5—C3	149.8 (2)
C8—C1—N1—O1	−137.7 (3)	C5—C2—O5—C3	−31.8 (4)
C2—C1—N1—O1	42.7 (4)	C4—C3—O5—C2	46.0 (3)
C8—C7—N2—O3	−3.5 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8*O*···O7	1.23 (10)	1.34 (9)	2.487 (4)	151 (9)
C3—H3*B*···O8^{i}	0.97	2.43	3.238 (4)	141
C6—H6···O6	0.93	2.46	3.026 (3)	119
C14—H14*A*···O1^{ii}	0.96	2.59	3.385 (4)	140
C14—H14*B*···N5	0.96	2.56	2.898 (4)	101
C14—H14*C*···O6^{iii}	0.96	2.44	3.361 (4)	160

Symmetry codes: (i) −*x*+2, −*y*, *z*+1/2; (ii) −*x*+2, −*y*, *z*−1/2; (iii) *x*+1/2, −*y*+1/2, *z*.

Selected geometric parameters (Å ,°) for (I) and (II)

	(I)	(II)
C3-O5	1.397 (2)	1.445 (3)
C9-O6	1.209 (2)	1.216 (3)
C9-N5	1.352 (2)	1.360 (3)
N5-N4	1.384 (2)	1.402 (3)
N4-C4	1.287 (2)	1.277 (4)
C11-O7		1.276 (4)
C12-O8		1.278 (4)
C2-O5-C3	122.83 (15)	116.7 (2)
C5-C2-O5	122.54 (15)	121.4 (2)
O5-C3-C4	114.14 (16)	110.0 (2)