

***N*-Benzyloxy-1*H*-benzotriazole-1-carboxamide: a hydrogen-bonded tetramer based upon a rare $R_4^2(20)$ structural motif**Ivica Đilović,^{a*} Dubravka Matković-Čalogović,^a Ivan Kos^b and Mladen Birus^b^aDepartment of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia, and ^bFaculty of Pharmacy and Biochemistry, University of Zagreb, Ante Kovačića 1, HR-10000 Zagreb, Croatia
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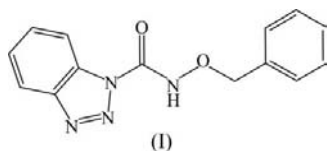
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The title compound, $C_{14}H_{12}N_4O_2$, is the first example of a heterocyclic substituted hydroxamic derivative. The asymmetric unit consists of two molecules. The molecules are linked into centrosymmetric $R_4^2(20)$ tetramers by four strong hydrogen bonds of the $N-H\cdots O$ and $N-H\cdots N$ types. These tetramers are connected through $C-H\cdots O$ interactions into a three-dimensional network.

Comment

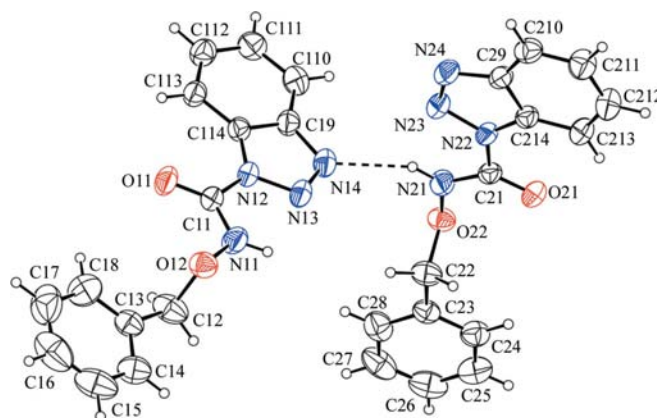
Recently, much attention has been focused on studies of the physicochemical, structural and catalytic properties of 1,3,5-trihydroxy-1,3,5-triazinane-2,4,6-trione (Jadrijević-Mladar Takač *et al.*, 2006; Hirai *et al.*, 2003, 2004; Caira *et al.*, 2006). Active organooxycyanate derivatives have been employed as precursors in the synthesis of 1,3,5-trihydroxy-1,3,5-triazinane-2,4,6-trione. Intensive investigation of the properties of organooxycyanates revealed that, because of their low stability, only some of these compounds could serve as donors of the organooxycyanate group (Staab & Benz, 1961; Major & Hedrick, 1965; Berndt, 1970). Butula & Jadrijević-Mladar Takač (2000) reported that *N*-benzyloxy-1*H*-benzotriazole-1-carboxamide, (I), can be used as a reliable benzyloxyisocyanate donor.



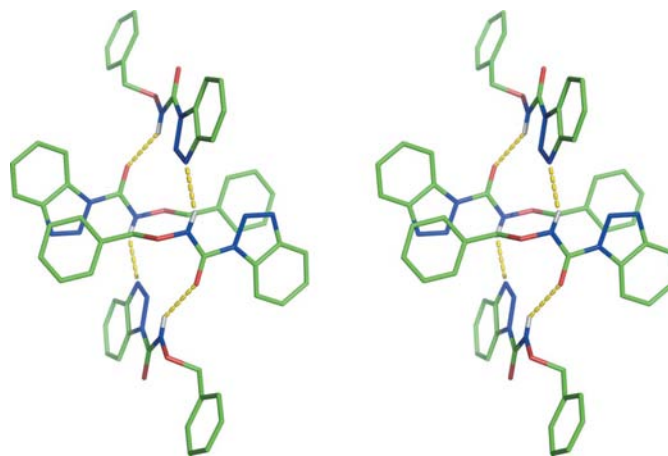
Annealing of (I) to a sufficiently high temperature induces decomposition to benzotriazole [one of the most effective inhibitors of copper corrosion under neutral and alkaline conditions (Cotton & Scholes, 1967)] and benzyloxyisocyan-

ate, a precursor for building 1,3,5-tribenzyloxy-1,3,5-triazinane-2,4,6-trione. The latter can be easily converted to 1,3,5-trihydroxy-1,3,5-triazinane-2,4,6-trione by reduction with hydrogen. The benzyloxyaminocarbonyl group can be reduced easily to the hydroxylamine group, thus providing an alternative path for the synthesis of hydroxamic acids and hydroxyureas. With this goal in mind and in an attempt to understand further the structure of hydroxamic acid and its derivatives (Matković-Čalogović *et al.*, 2003; Đilović *et al.*, 2006, 2007), the structure of (I) was determined using the single-crystal X-ray diffraction method.

The title compound is an example of a valuable precursor in hydroxamic acid chemistry. The asymmetric unit of (I) consists of two crystallographically independent molecules. A *trans* configuration of the carbonyl O atoms with respect to the amide H atom is observed, and the central N atom of the 1,2,3-triazole unit is in a *cis* configuration with respect to the amide N atom (Fig. 1). Compound (I) contains two terminal aromatic (and also planar) substituents (the benzotriazole and phenyl

**Figure 1**

A view of the asymmetric unit of (I), with the atom-labeling scheme. Displacement ellipsoids are shown at the 30% probability level. H atoms have been omitted for clarity.

**Figure 2**

Stereodrawing showing the tetramer of (I). Hydrogen bonds connecting tetramers are indicated with dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

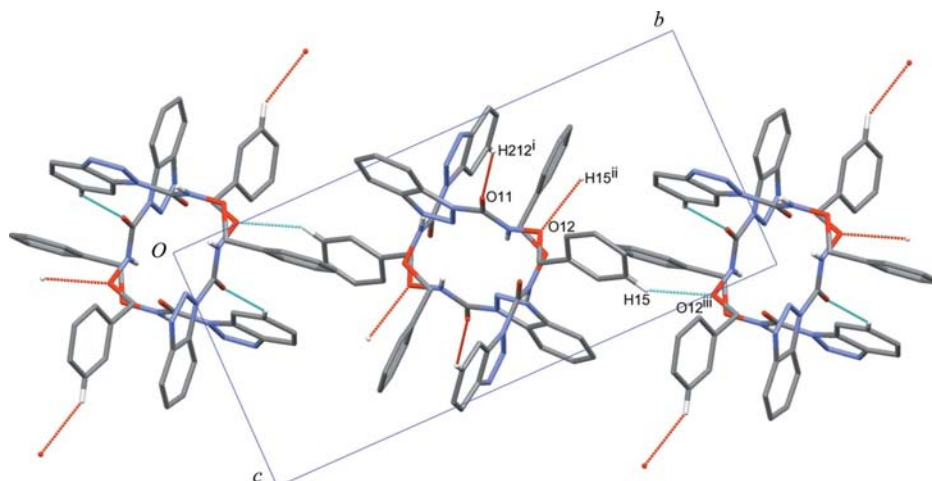


Figure 3
The crystal packing of (I) viewed down the *a* axis. Molecules are connected through C–H···O interactions, which are indicated with dashed lines. [Symmetry codes: (i) $1 + x, y, z$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $x, \frac{3}{2} - y, -\frac{1}{2} + z$.]

rings), which are connected to the *N*-methoxyformamide segment. If we exclude the benzyl group, the rest of molecule is almost planar. The planes of the two symmetrically independent molecules are almost orthogonal [$82.53(1)^\circ$]. The molecules are linked into centrosymmetric tetramers to give a very rare structural motif [$R_4^4(20)$; Etter *et al.*, 1990]. This four-membered ring is formed by molecules found at symmetry sites (x, y, z) and $(-x + 1, -y + 1, -z + 1)$, which are linked together by four hydrogen bonds of the N–H···O and N–H···N types (Table 1 and Fig. 2). In addition, the tetramers in the crystal structure are connected through C–H···O van der Waals interactions to form a three-dimensional network (Table 1 and Fig. 3).

Experimental

Compound (I) was synthesized according to a previously published procedure (Butula *et al.*, 2000). The structure and purity were confirmed by means of thin-layer chromatography, FT-IR and NMR analyses. The compound was crystallized by slow evaporation from a saturated diethyl ether solution at room temperature (the beaker containing the solution was covered with aluminium foil to slow evaporation). Colorless crystals of good quality were obtained after three weeks, and these were stable for several months when exposed to the atmosphere.

Crystal data

$C_{14}H_{12}N_4O_2$	$V = 2685.5(3) \text{ \AA}^3$
$M_r = 268.28$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.4267(9) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 20.6647(7) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 11.0684(5) \text{ \AA}$	$0.80 \times 0.50 \times 0.40 \text{ mm}$
$\beta = 119.020(4)^\circ$	

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	17530 measured reflections
Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2003)	5236 independent reflections
$T_{\min} = 0.929, T_{\max} = 0.964$	3136 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	361 parameters
$wR(F^2) = 0.138$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$
5236 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N11–H11···O21 ⁱ	0.86	2.05	2.785 (2)	143
N21–H21···N14	0.86	2.13	2.900 (3)	149
C15–H15···O12 ⁱⁱ	0.93	2.56	3.380 (5)	148
C212–H212···O11 ⁱⁱⁱ	0.93	2.51	3.252 (6)	137

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

H atoms were constrained to ideal geometry using an appropriate riding model, with C–H = 0.93–0.97 \AA and N–H = 0.86 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3081). Services for accessing these data are described at the back of the journal.

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