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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C})$ = 0.004 Å
R factor = 0.047
wR factor = 0.149
Data-to-parameter ratio = 10.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*N,N',N''*-Tribenzyloxydicarbonimidic diamide

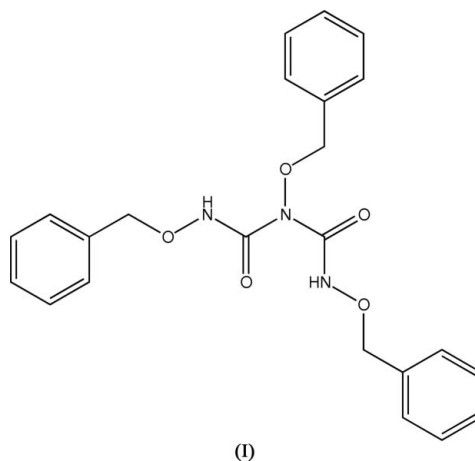
The asymmetric unit of the title compound (systematic name: *N,N',N''*-tribenzyloxyiminodicarbonic diamide), $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_5$, consists of two molecules. In the crystalline state, the molecules are assembled into centrosymmetric dimers by strong $\text{N}-\text{H}\cdots\text{O}=\text{C}$ intermolecular hydrogen bonds. The results of IR and NMR spectroscopic analysis are in good agreement with the crystallographic study.

Received 20 December 2005

Accepted 6 February 2006

Comment

Hydroxamic acids are weak organic acids with various applications in pharmaceuticals, food additives, and extractive metallurgy (Kaczka *et al.*, 1962; Matzanke *et al.*, 1989; Hersko *et al.*, 1992; Rogers, 1987; Ghio *et al.*, 1992; Crumbliss, 1991). Their importance and applications originate primarily from their ability to form stable metal-ion binding sites (Crumbliss, 1991). Desferrioxamine B, a tris-hydroxamic acid, and hydroxyurea (Navarra & Preziosi, 1998) and its derivatives (Gale, 1968; Chung & Kim, 2001) are the most important compounds containing the hydroxamate group, due to their use in medicine (thalasaemia major, melanoma, resistant chronic myelocytic leukaemia, and recurrent, metastatic, or inoperable carcinoma of the ovary, and recently in the treatment of HIV).



N,N,N''-Tris(benzyloxy)dicarbonimidic diamide, (I), was synthesized in the course of developing new derivatives of hydroxamic acids and hydroxyureas to evaluate their chemical and metal-binding properties. This compound was designed to combine the main characteristics of both of the above-mentioned compounds, because of the three hydroxamate functional groups incorporated into the molecule. In addition, we have recently published the structure of the chloride salt of

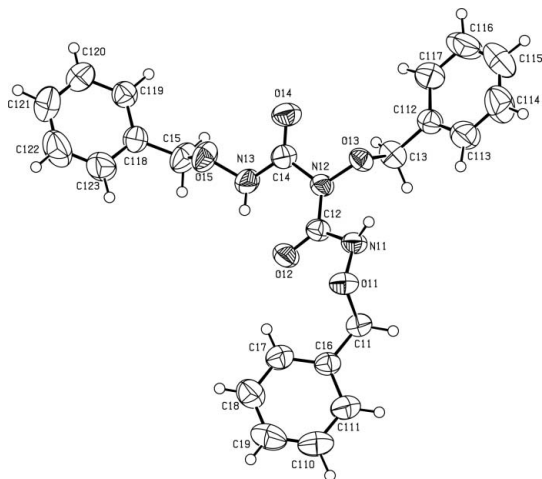


Figure 1

A view of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary small radii. Only one molecule is shown. The other molecule is essentially identical in appearance and has the same atom-numbering scheme but starting with 2 (e.g. atom C123 in molecule 1 is labeled C223 in molecule 2).

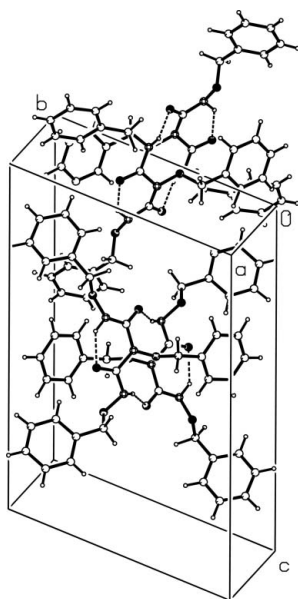


Figure 2

The crystal packing of the title compound. Hydrogen bonds are indicated by dashed lines.

betainohydroxamic acid (Matković-Čalogović *et al.*, 2003) in order to investigate the correlation between the electronic properties of the hydroxamate substituents and the hydroxamate C–N bond length.

The asymmetric unit of (I) (Fig. 1) consists of two crystallographically independent molecules. We observed no significant difference in the conformation of these two molecules. Selected bond lengths are reported in Table 1. Other geometric parameters (bond lengths and angles) are comparable with those in similar structures (Larsen, 1976) and with those in the Cambridge Structural Database (Version 1.7; Allen, 2002). Six-membered rings are formed by strong N–H···O=C intramolecular hydrogen bonds (Table 2).

The crystal packing is characterized by hydrogen-bonding interactions between the molecules. Fig. 2 illustrates the centrosymmetric dimers in the crystal structure which are connected by strong N–H···O=C hydrogen bonds. The crystal structure also contains weaker C–H···O=C contacts [the shortest one is H220···O12 of 2.64 (3) Å] and relatively close H···H contacts [shortest: H216···H222ⁱ = 2.25 (5) Å; symmetry code: (i) $x - 1, y - 1, z$], and there is also clear evidence of C–H··· π contacts [shortest: H113···C228ⁱⁱ = 2.89 (3) Å; symmetry code: (ii) $1 - x, 1 - y, -z$].

Experimental

N,N,N'-tris(benzyloxy)dicarbonimidic diamide was synthesized by the following procedure: a mixture of 3.19 g (0.02 mol) of *O*-benzyloxyamine hydrochloride and triphosgene in 50 ml of toluene was heated for 2 h at 393 K. An excess of solvent was removed under reduced pressure and the resulting benzyloxycarbonyl chloride was used in the next reaction step without further purification. A solution of benzyloxycarbonyl chloride in dioxane was added dropwise to a suspension of *O*-benzyloxyamine hydrochloride (1.59 g, 0.01 mol) and triethylamine (3.03 g, 0.03 mol) in 50 ml dioxane at 273–278 K over a period of 15 minutes. After mixing for 3 h at room temperature, the white precipitate (triethylamine hydrochloride) was removed by filtration, and the filtrate was evaporated under reduced pressure to afford an oil, *N,N,N'*-tris(benzyloxy)dicarbonimidic diamide (I), which was then crystallized from water. Following crystallization from a diethyl ether–cyclohexane mixture, a white precipitate of (I) (3.79 g, 91%) was isolated (m.p. 351–353 K). The purity was checked by thin-layer chromatography (acetone–hexane, 1:2, $R_f = 0.71$) and by NMR spectroscopy. NMR spectra were recorded on a Bruker Avance 600 MHz in DMSO-*d*₆ solution. Chemical shifts δ are given in p.p.m., with TMS as internal standard. The FT–IR spectrum of (I) was recorded from KBr pellets on a Perkin–Elmer Paragon 500 FT–IR spectrometer.

IR (KBr, ν_{\max} , cm^{-1}): 3287 (*s*), 3036 (*w*), 3032 (*w*), 2943 (*w*), 2888 (*w*), 1716 (*vs*), 1556 (*vs*), 1364 (*m*), 1298 (*m*), 1215 (*m*), 1198 (*m*), 1028 (*m*), 965 (*m*), 904 (*m*), 839 (*w*), 783 (*w*), 750 (*s*), 700 (*s*), 610 (*w*), 543 (*m*), 501 (*m*).

¹H NMR (DMSO-*d*₆, δ , p.p.m.): 10.92 (*s*, 2H, NH), 7.45–7.33 (*m*, 15H, ar. H), 4.8 (*s*, 2H, –CH₂–), 4.76 (*s*, 4H, 2 –CH₂–)

¹³C NMR (DMSO-*d*₆, δ , p.p.m.): 153.02, 135.56, 134.01, 130.12, 128.97, 128.88, 128.42, 128.38, 128.20, 77.80 and 77.49.

Single crystals were grown from a saturated solution of (I) in diethyl ether, by slow evaporation at room temperature. The beaker containing the solution was covered with aluminium foil to slow down evaporation. Crystals of good quality were obtained after three weeks, and these were stable for months when exposed to the atmosphere.

Crystal data

C₂₃H₂₃N₃O₅
 $M_r = 421.44$
 Triclinic, $P\bar{1}$
 $a = 8.9947$ (17) Å
 $b = 13.820$ (3) Å
 $c = 18.714$ (3) Å
 $\alpha = 100.763$ (14)°
 $\beta = 90.447$ (14)°
 $\gamma = 107.227$ (16)°
 $V = 2177.9$ (8) Å³

$Z = 4$
 $D_x = 1.285$ Mg m^{−3}
 Mo $K\alpha$ radiation
 Cell parameters from 1132 reflections
 $\theta = 4.6$ – 27.5°
 $\mu = 0.09$ mm^{−1}
 $T = 295$ K
 Prism, colourless
 $0.60 \times 0.36 \times 0.21$ mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	5022 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.021$
Absorption correction: none	$\theta_{\text{max}} = 25.0^\circ$
16124 measured reflections	$h = -9 \rightarrow 10$
7635 independent reflections	$k = -16 \rightarrow 14$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0919P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.149$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{Å}^{-3}$
7635 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{Å}^{-3}$
744 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.0052 (13)

Table 1
Selected bond lengths (Å).

C12—O12	1.219 (2)	C24—N22	1.426 (2)
C12—N11	1.360 (3)	C22—O22	1.216 (2)
C12—N12	1.397 (2)	C22—N21	1.358 (3)
C14—O14	1.207 (2)	C22—N22	1.407 (2)
C14—N13	1.354 (3)	N12—O13	1.4040 (19)
C14—N12	1.418 (2)	N13—O15	1.409 (2)
C24—O24	1.209 (2)	N22—O23	1.4022 (19)
C24—N23	1.355 (3)	N21—O21	1.411 (2)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N13—H13N \cdots O12	0.88 (3)	1.92 (3)	2.627 (2)	136 (2)
N23—H23N \cdots O22	0.90 (3)	1.90 (3)	2.650 (2)	140 (2)
N11—H11N \cdots O13 ⁱ	0.89 (2)	2.75 (3)	3.286 (1)	119 (1)
N11—H11N \cdots O14 ⁱ	0.89 (2)	2.05 (3)	2.896 (2)	158 (2)
N21—H21N \cdots O24 ⁱⁱ	0.90 (2)	2.06 (3)	2.926 (2)	160 (2)
N21—H21N \cdots O23 ⁱⁱ	0.90 (2)	2.66 (3)	3.275 (2)	126 (2)

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

The positions of the H atoms were obtained from a difference Fourier map and they were included in the refinement process with isotropic displacement parameters.

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, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

The authors thank the Ministry of Science, Education and Sports of the Republic of Croatia for financial support (grant Nos. 0119632 and 0006441).

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