Constructor graph description of hydrogen bonding in a supramolecular assembly of N,N′-bis(2-hydroxy-1-methylethyl)phthalamide

Ilia A. Guzei,[a]* Lara C. Spencer,[a] Robert W. McGaff,[b] Heidi M. Kieler[b] and Jerome R. Robinson[b]

[a]Department of Chemistry, University of Wisconsin–Madison, 1101 University Avenue, Madison, WI 53706, USA, and [b]Department of Chemistry, University of Wisconsin–La Crosse, 1725 State Street, La Crosse, WI 54601, USA
Correspondence e-mail: iguzei@chem.wisc.edu

Hydrogen bonds of four types (N—H···O=C, N—H···OH, O—H···O=C and O—H···OH) connect molecules of the title compound, $C_{14}H_{20}N_2O_4$, in the crystal into sheets folded into a zigzag pattern. The intermolecular interactions are discussed in terms of the first- through fourth-level graph sets, and a constructor graph helps visualize the supramolecular assembly.

Comment

For several years, we have been interested in reactions of nitriles with various metal centers from both the transition series and the main group. Recently, we have focused on reactions of 1,2-dicyanobenzene (phthalodinitrile) with various metal-containing reagents. In previous papers, we described the syntheses and solid-state structures of (methanol)phthalocyaninatomagnesium(II) (Guzei et al., 2005), a pair of chiral modified phthalocyaninate complexes of Ni of general formula [14,28-$(RO)_2$Pc]Ni[II], where R is either methyl or ethyl, and Pc is the phthalocyaninate ligand (Molek et al., 2001), and chiral 'helmet' phthalocyaninate complexes of Fe[II] and Co[II] of general formula (L)(diiPc)M[II], where M represents the metal, L is methanol, a methanol/water mixture or 4-hydroxypyridine, and diiPc is a bicyclic pentadentate 14,28-(1,3-diiminoisoindolinato)phthalocyaninate ligand (Kieler et al., 2006).

The present paper describes an unexpected product, N,N′-bis(2-hydroxy-1-methylethyl)phthalamide, (I), formed in the reaction of excess neat (R)-2-amino-1-propanol with 1,2-dicyanobenzene in the presence of iron(II) acetate after one week at 403 K. This reaction was carried out in an attempt to prepare diastereomers of (L*)(diiPc)Fe, where L* represents the chiral propanol derivative, but (metal-free) (I) was produced instead (Fig. 1).

The absolute configuration of (I) was inferred from the configuration around the asymmetric C atom in the starting material. The dihedral angle between the amide planes and the plane of the benzene ring is 56.23 (12)° for the N1/C4/O2 plane and 42.73 (10)° for the N2/C11/O3 plane; these values are significantly larger than the corresponding angles in the related compounds N-(2-hydroxy-1,1-dimethylethyl)benzamide [25.77 (12)°; Gerkin, 2000] and 4-aminohippuric acid [20.9 (1)°; Dobson & Gerkin, 1999], but closer in value to that in tetraethyl 4,8-dibromo-1,2,3,5,6,7-hexahydro-s-indacene-2,2,6,6-tetracarboxylate [47.7 (2)°; Kawai et al., 2004].

(I)
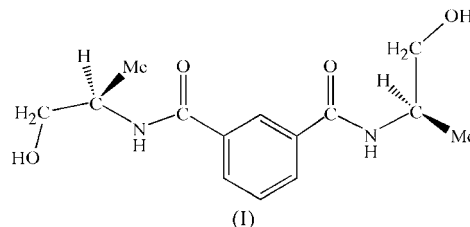
The most interesting structural feature of (I) is its crystal packing and intermolecular interactions. We will primarily be concerned with strong hydrogen-bonding interactions of types N—H···O and O—H···O; nevertheless, we also list the possible secondary (weaker) intermolecular contacts of types C—H···O and C—H···π in Table 1 for completeness. Each molecule participates in eight strong hydrogen-bonding interactions with six other molecules, in four of which it acts as a donor while in the other four it acts as an acceptor (Fig. 2). The four hydrogen bonds denoted **a–d** (Table 1) link molecules into two-dimensional sheets perpendicular to the c axis (Fig. 3).

Hydrogen bonds **a–d** are considered strong because of their relatively short D···A distances and D—H···A angles falling within the range 150–180°. A search of the Cambridge Structural Database (Version 5.28, January 2007 release; Allen, 2002) for relevant hydrogen-bonding interactions in compounds containing a modified skeleton of N-(2-hydroxy-1-methylethyl)benzamide revealed the following. Hydrogen bond **a** [2.7990 (14) Å] is noticeably shorter than the lengths
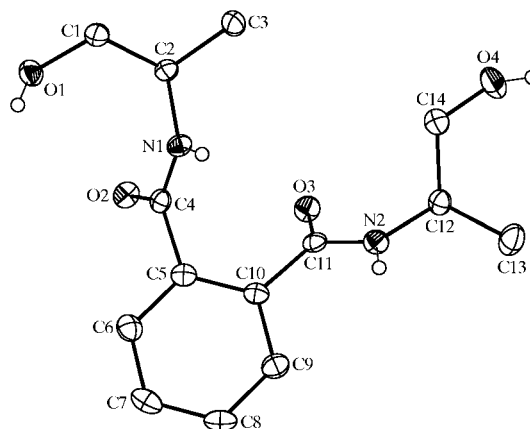

Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. All H atoms attached to C atoms have been omitted.

of 30 N—H···O=C hydrogen bonds averaged for 22 compounds [2.94 (7) Å]. The longest hydrogen bond, **b** [2.8961 (15) Å], is comparable to the average length of 2.97 (6) Å found for seven N—H···OH bonds in seven compounds. The strong bond **c** [2.7227 (14) Å] is in good agreement with the average value of 2.79 (11) Å computed for ten O—H···OH bonds in ten compounds. The shortest bond, **d** [2.6773 (14) Å], is not statistically different from the average of five O—H···O=C bonds in three compounds [2.79 (15) Å].

The use of a constructor graph representation of the hydrogen-bond interactions in the lattice of (I) facilitates the interpretation of the intermolecular association (Fig. 4 and Table 1). We note in passing that there are only three papers found in the IUCr journals for the keywords 'constructor graph' (Grell *et al.*, 1999; Motherwell *et al.*, 1999, 2000). The constructor graph reveals different level graph-set patterns according to the definitions put forward by Grell *et al.* (1999) and Bernstein *et al.* (1995). Each type of hydrogen bond connects the molecules of (I) into chains with the following first-level graph-set motifs: $C(4)$ for **a**, $C(10)$ for **b**, $C(13)$ for **c** and $C(7)$ for **d**. The combination of these is also a first-level graph-set, $N_1 = C(4)C(10)C(13)C(7)$. Owing to the absence of

inversion symmetry in the system, chains **a**, **b** and **d** propagate only in the [100] direction, while the direction of bond **c** alternates from [010] to [01̄0] as a result of the twofold screw axis in the plane of the hydrogen-bonded sheet. Thus, to traverse the constructor graph in the direction of the hydrogen bonds **a**, **b** and **d**, one must move from top to bottom and right to left. The periodicity of the hydrogen-bonding patterns is a full length of the *b* axis in the *b* direction and *a*/2 in the *a* direction. This is illustrated by the alternating orientation of the molecules (filled and open circles) and of hydrogen bonds **c** and **d**, as well as by the alternating pairwise positions of bonds **a** and **b** when one travels in the *a* direction (Fig. 4).

Once the constructor graph representation was determined we observed that searching for higher-level graph sets using this method was considerably easier than examining packing diagrams with actual molecules. For example, from Fig. 4 it is apparent that bonds **a** and **b** form a ring system R, and little effort is needed to complete the assignment as $R_2^2(14)$, which is a binary graph set $N_2(\overleftrightarrow{a\ b})$. [Symbols $\overrightarrow{a}$ and $\overleftarrow{b}$ denote the fact that in order to complete the ring, the **a** bond is traveled from donor to acceptor (in the direction of the arrow in Fig. 4) and the **b** bond is traveled from acceptor to donor.] Minimal ternary ring systems (N_3) involve three hydrogen bonds, *viz.* $\overrightarrow{a}\ \overrightarrow{c}\ \overleftarrow{d}\ R_3^3(14)$ and $\overrightarrow{b}\ \overrightarrow{c}\ \overleftarrow{d}\ R_3^3(14)$. Viewed along the *c* axis, the hydrogen-bonding sheets accordion into a zigzag pattern and stack in an antiparallel fashion (Fig. 5*a*); this is schematically shown in Fig. 5(*b*), in which the 'vertical' parts contain **a** bonds only, while the 'diagonal' elements contain the other three
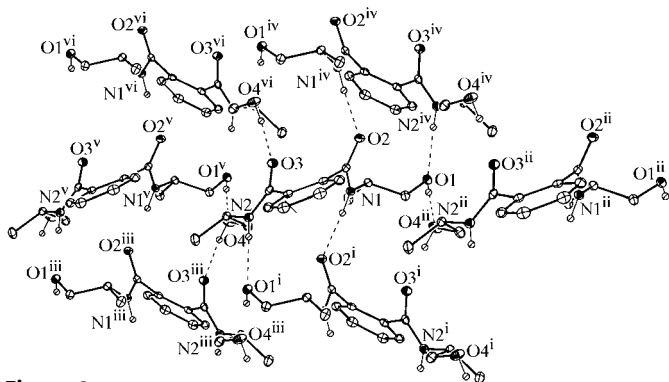

Figure 2
Each molecule forms eight strong hydrogen bonds with six other molecules. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (ii) $x, y + 1, z$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, -z$; (v) $x, y - 1, z$; (vi) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$.]
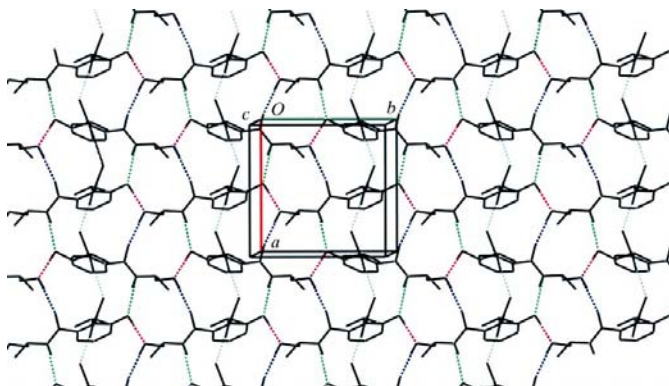

Figure 3
The two-dimensional network of hydrogen bonds in (I), viewed along the *c* axis. Hydrogen bonds are shown as dashed lines.
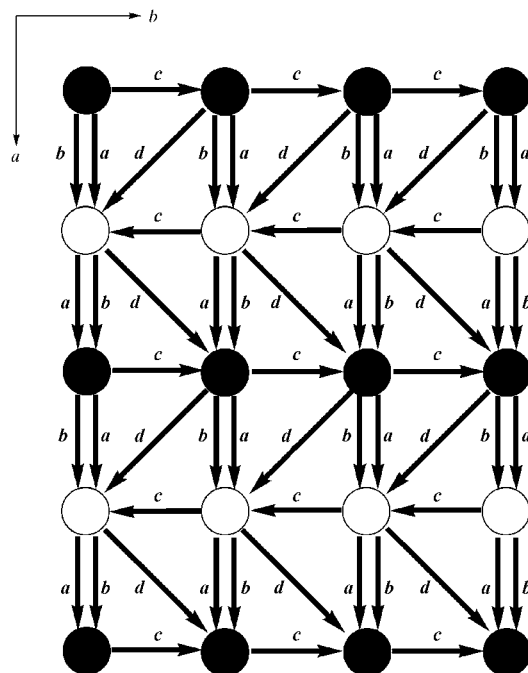

Figure 4
The constructor graph representation of the hydrogen-bonding interactions in (I), viewed along the *c* axis. Each molecule of (I) is a vertex shown as either a filled or an open circle, representing the 'front' or 'back' of the molecule. The arrows denote four types of hydrogen bonds labeled with letters according to Table 1. Arrows originate at the hydrogen donor molecules and point to hydrogen-bond acceptor molecules.
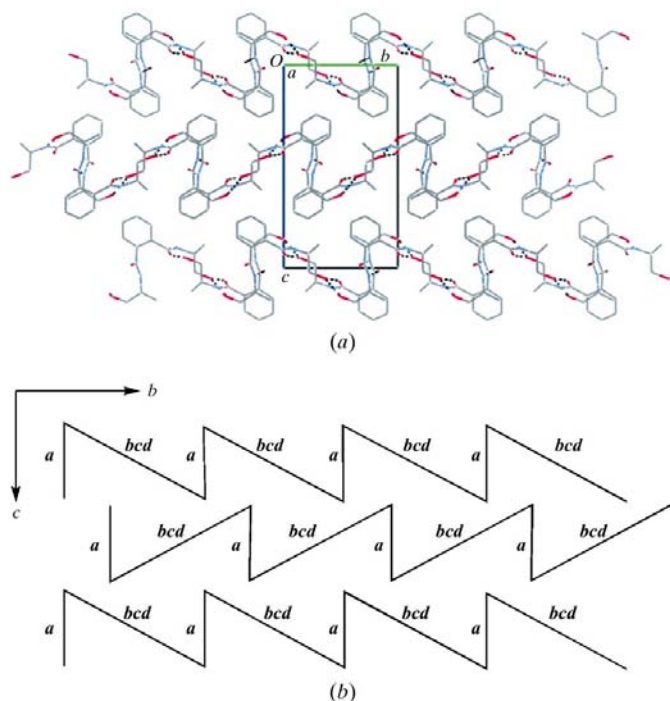
Figure 5
(a) The molecular packing of (I), showing hydrogen-bond interactions and viewed along the a axis. (b) A schematic representation of the zigzag molecular arrangement in the crystal of (I). The letters correspond to the hydrogen bonds listed in Table 1. The 'vertical' parts contain hydrogen bonds **a** only, while the 'diagonal' links contain the other three bond types, *viz.* **b**, **c** and **d**.

bond types, *yiz.* **b**, **c** and **d**, which form the easily identifiable rings $\vec{a}\,\vec{c}\,\overleftarrow{d}\,R_3^3(14)$ and $\vec{b}\,\vec{c}\,\overleftarrow{d}\,R_3^3(14)$. Additionally, the latter three bonds form $\vec{b}\,\vec{c}\,\vec{d}\,C_3^3(8)$ chains (also a ternary or third-level graph set) that run along the a axis; as a result of the crystallographic symmetry, the periodicity of the sequence $\vec{b}\,\vec{c}\,\vec{d}\,\vec{b}\,\vec{c}\,\vec{d}$ is equal to that of sequence $\vec{a}\,\vec{a}\,\vec{a}\,\vec{a}$ (start with the upper right molecule in Fig. 4 and follow these two sequences to the lower right molecule). With the help of Fig. 4, one can recognize other chains in either direction or larger ring systems in which each type of bond is encountered more than once. A minimal quaternary system such as a $C_4^4(18)\,\vec{a}\,\vec{b}\,\vec{c}\,\vec{d}$ chain can be constructed as an exercise to obtain the highest-level quaternary graph set N_4, but it does not represent a pattern that can be considered an important building unit for the hydrogen-bonding network.

Experimental

An unexpected product, (I), was formed in the reaction of neat excess (R)-2-amino-1-propanol with 1,2-dicyanobenzene (194.5 mg, 1.518 mmol) in the presence of iron(II) acetate (43.9 mg, 0.252 mmol) for one week at 403 K. Diffraction-quality crystals were obtained following flash column chromatography on silica gel by slow evaporation of the eluting solvent, *viz.* a 90:10 mixture of dichloromethane and methanol. A solution fluorescence spectrum of (I) as eluted from the column exhibited a peak at 490 nm with an excitation wavelength of 466 nm. The fluorescence of (I) and possible role of iron species in its formation will be the subject of a forthcoming paper.

Crystal data

$C_{14}H_{20}N_2O_4$	$V = 1438.78\,(14)$ Å^3
$M_r = 280.32$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 9.1548\,(5)$ Å	$\mu = 0.10$ mm^{-1}
$b = 9.3937\,(5)$ Å	$T = 100\,(2)$ K
$c = 16.7305\,(10)$ Å	$0.50 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD 1000 area-detector diffractometer	23813 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	2063 independent reflections
	1817 reflections with $I > 2\sigma(I)$
$T_{min} = 0.954$, $T_{max} = 0.981$	$R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	185 parameters
$wR(F^2) = 0.083$	H-atom parameters constrained
$S = 1.13$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
2063 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C5–C10 ring.

	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
a	N1—H1A···O2^i	0.88	1.93	2.7990 (14)	171
b	N2—H2···O1^i	0.88	2.04	2.8961 (15)	163
c	O1—H1···O4^{ii}	0.84	1.89	2.7227 (14)	170
d	O4—H4···O3^{iii}	0.84	1.84	2.6773 (14)	174
	C2—H2A···Cg^{iv}	1.00	2.921	3.880 (2)	161
	C8—H8···O4^{vii}	0.95	2.60	3.5235 (18)	163
	C3—H3B···O^{viii}	0.98	2.62	3.5542 (17)	159

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

All H atoms were placed in idealized locations and refined as riding, with U_{iso}(H) values of 1.2 or 1.5 (methyl and hydroxy H atoms) times U_{eq} of the parent atom. The Friedel pairs were merged for the final refinement. The absolute configuration was assigned by reference to an unchanging chiral center in the synthetic procedure.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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