

Polymorphs of DABCO monohydrate
as structural analogues of NaCl

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Received 24 March 2010

Accepted 26 April 2010

Online 8 May 2010

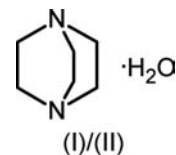
A new crystalline form of 1,4-diazabicyclo[2.2.2]octane (DABCO) monohydrate, $C_6H_{12}N_2 \cdot H_2O$, crystallizing in the space group $P3_1$, has been identified during screening for cocrystals. There are three DABCO and three water molecules in the asymmetric unit, with two DABCO molecules exhibiting disorder over two positions related by rotation around the $N \cdots N$ axis. As in the monoclinic $C2/c$ ($Z' = 2$) polymorph, the molecular components are connected *via* $O-H \cdots N$ hydrogen bonds into a polymeric structure that consists of linear $O-H \cdots N(CH_2CH_2)_3N \cdots H-O$ segments, which are approximately mutually perpendicular. The two polymorphic forms of DABCO monohydrate can be considered as structural analogues of NaCl, with the nearly globular DABCO molecules showing distorted cubic closest packing and all octahedral interstices occupied by water molecules.

Comment

1,4-Diazabicyclo[2.2.2]octane (DABCO) is a common chemical reagent with a wide range of applications. This highly symmetrical diaza compound is a very popular supramolecular substrate for the synthesis of numerous inorganic and organic salts, adducts, coordination compounds and cocrystals, some of which have interesting and promising physical and chemical properties. The DABCO molecule has a globular shape and this is reflected in its two known crystal phases under ambient pressure. Phase II (Nimmo & Lucas, 1976*a*; Sauvajol, 1980), in the space group $P6_3/m$ ($Z = 2$) with unit-cell parameters $a = 6.14$ (2) Å and $c = 9.46$ (2) Å at 298 K, has an approximate hexagonal close-packed (hcp) structure with a c/a parameter ratio of 1.54, compared with a value of 1.63 for an ideal hcp structure. Phase II (Nimmo & Lucas, 1976*b,c*) transforms at 351 K to the cubic phase I, with $a = 8.860$ (5) Å and $Z = 4$ in the space group $Fm\bar{3}m$, *i.e.* to a plastic phase with a cubic close-packed (ccp) structure.

The phase diagram for the DABCO–water system revealed the occurrence of two hydrates for DABCO, *viz.* the monohydrate and the hexahydrate (Farkas *et al.*, 1959), and the crystal structures of both have been reported recently (Laus *et*

al., 2008). DABCO monohydrate, (I), is monoclinic (space group $C2/c$) and has two symmetry-independent DABCO molecules, one ordered and located on a twofold axis, and one located around an inversion centre and therefore disordered over two positions. In this structure, the DABCO molecules are bridged by the water molecules and a one-dimensional polymeric structure is formed *via* $O-H \cdots N$ hydrogen bonds. The triclinic structure of the hexahydrate is more complicated, with four DABCO and 24 water molecules in the asymmetric unit and a complex system of $O-H \cdots N$ and $O-H \cdots O$ hydrogen bonds (Laus *et al.*, 2008).



DABCO is frequently used as a cocrystal former, and in the course of our studies of cocrystals and salts of glycyrrhetic acid a small-scale cocrystallization was set up from ethanol, with DABCO and the acid mixed in a 1:1 molar ratio. To our surprise, the colourless crystalline product was a new polymorph of DABCO monohydrate, (II). When crystallization was repeated from tetrahydrofuran (THF) at 278 K, *i.e.* from a solvent used to obtain polymorph (I) (Laus *et al.*, 2008), but no care was taken to have stoichiometric amounts of THF and water (the THF was not dried), form (II) of DABCO monohydrate precipitated. Polymorph (II) of DABCO monohydrate has a higher symmetry than polymorph (I), as it crystallizes in the trigonal space group $P3_1$ (or $P3_2$) and has three symmetry-independent DABCO molecules and three water molecules in the asymmetric unit ($Z' = 3$). The crystal densities of the two high- Z' polymorphs are very similar, *viz.* 1.203 Mg m^{-3} (173 K) for form (I) and 1.208 Mg m^{-3} (130 K) for form (II).

In this report, we demonstrate that, in spite of the striking difference in the crystal symmetry and the number of molecules in the asymmetric unit, the two polymorphs of DABCO monohydrate can both be considered as structural analogues of NaCl, with the globular DABCO molecules forming an approximate ccp structure and the water molecules occupying all octahedral interstices.

The asymmetric unit of polymorph (II), consisting of three DABCO molecules (labelled *A*, *B* and *C*) and three water molecules, is shown in Fig. 1. Two of the DABCO molecules exhibit disorder. For molecule *C*, two disordered positions, designated *C* and *CC*, were found, which are related by a 22.0° rotation around the $N1C \cdots N2C$ axis and have an occupancy ratio of about 2:1. For molecule *B*, the rotation angle around the $N1B \cdots N2B$ axis is 49.2° and the occupancy of the two positions, *B* and *BB*, is approximately equal. All three DABCO molecules show deviations from ideal D_{3h} symmetry, with the highest absolute value of the $N-C-C-N$ torsion angle among the major positions of 4.5 (8) $^\circ$. The intramolecular $N \cdots N$ distances [2.573 (2)– 2.577 (2) Å] are equal within statistical error for the three molecules and compare well with the $N \cdots N$ distance (2.580 Å) in polymorph (I).

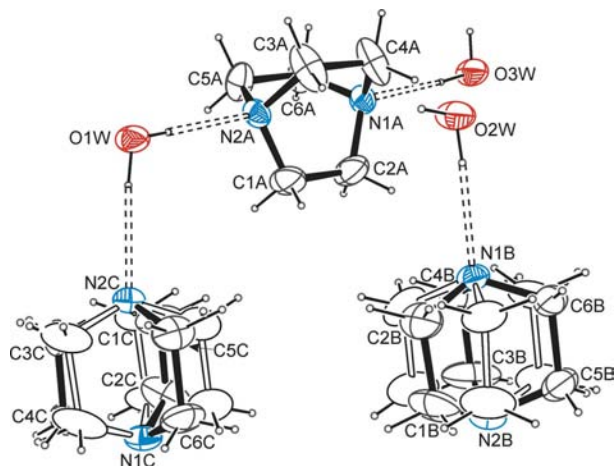


Figure 1

The asymmetric unit of polymorph (II) of DABCO monohydrate, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. For the disordered DABCO molecules, only C and N atoms *B* and *C* are labelled. C atoms *BB* and *CC* are represented by open ellipsoids. Hydrogen bonds are drawn as dashed lines.

Hydrogen bonds between the DABCO and water molecules (Table 1) join all components into a spacious helix parallel to the 3_1 axis (Fig. 2*a*). The O—H...N hydrogen bonds are nearly linear, with the O...N contacts [2.928 (2)–2.952 (2) Å] similar to those found in form (I) (2.949–2.973 Å). In both polymorphs, one-dimensional polymeric structures formed *via*

hydrogen bonds are constructed from linear O—H...N(CH₂CH₂)₃N...H—O segments, with O...O distances of 8.4–8.6 Å, which are directed in three approximately perpendicular directions (Fig. 2). These O...O distances have values similar to the unit-cell parameter of the cubic DABCO form [8.860 (5) Å; Nimmo & Lucas, 1976*b,c*]. The N...O...N angles at the bridging water molecules are 102.12–102.86° in polymorph (I) and 102.00 (7)–102.94 (7)° in polymorph (II). The main difference in the polymeric hydrogen-bonded structures of the two polymorphs can be best seen when the O...O...O...O torsion angles (φ) of subsequent O_{water}—O_{water} segments along the chain are calculated. In polymorph (I), the repeated sequence of torsion angles φ_i along the chain is $\varphi_1 = 95.01^\circ$, $\varphi_2 = 180^\circ$, $\varphi_3 = -95.01^\circ$ and $\varphi_4 = 180^\circ$, and the chain is achiral. In the chiral chain of (II), the sequence of the torsion angles is $\varphi_1 = -88.93 (4)^\circ$, $\varphi_2 = 177.94 (3)^\circ$ and $\varphi_3 = -3.01 (3)^\circ$.

As was pointed out earlier, the two known DABCO phases, hexagonal and cubic, can be related to the hcp and ccp type structures. The question arises as to whether the DABCO monohydrates can be considered analogously, as close-packed structures of DABCO with the interstices occupied by water molecules. From the volume of the unit cell of the hexagonal form, the volume of the DABCO molecule can be estimated to be 150 Å³, and from comparison of the volumes of the unit cells of DABCO and the DABCO monohydrates, the volume of the hydrogen-bonded water molecule can be estimated as 29 Å³. These volumes correspond to spheres of radii 3.3

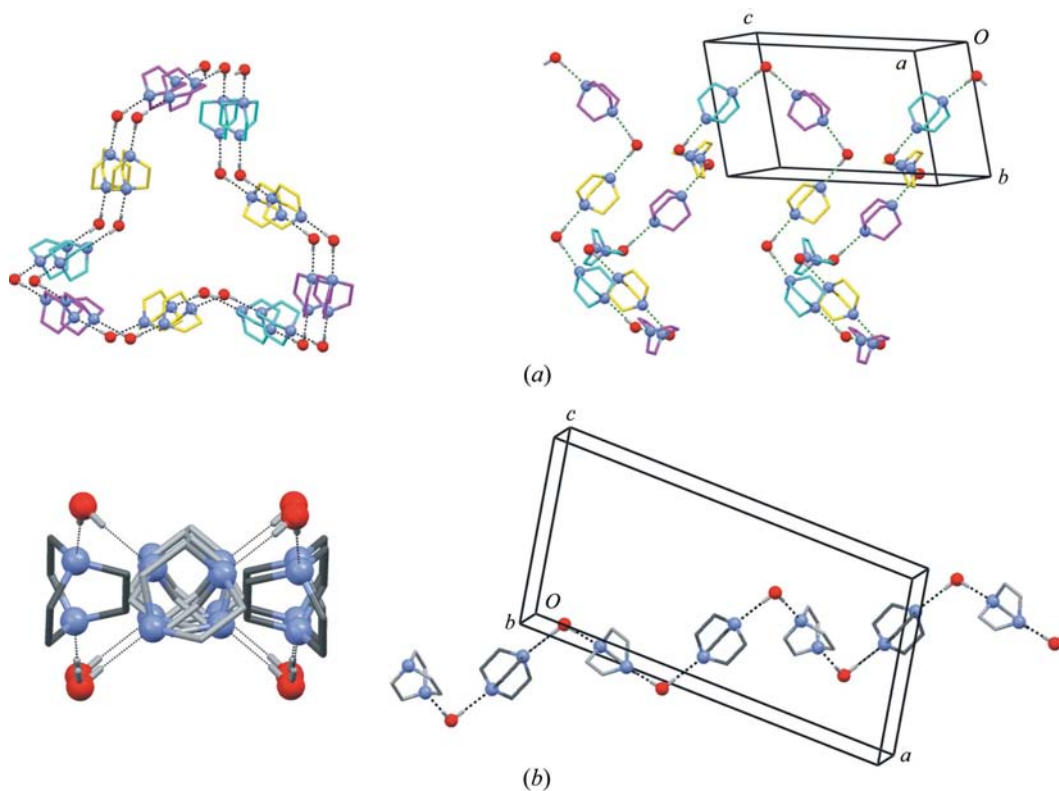


Figure 2

The polymeric structures formed *via* O—H...N hydrogen bonds in the two polymorphs of DABCO monohydrate. (a) Top and side views of the 3_1 helix in polymorph (II). (b) Top and side views of the chain in (I). N and O atoms are represented as spheres. H atoms, except those of the water molecules, have been omitted for clarity. Only one orientation for each disordered DABCO molecule is shown. Hydrogen bonds are shown as dotted lines.

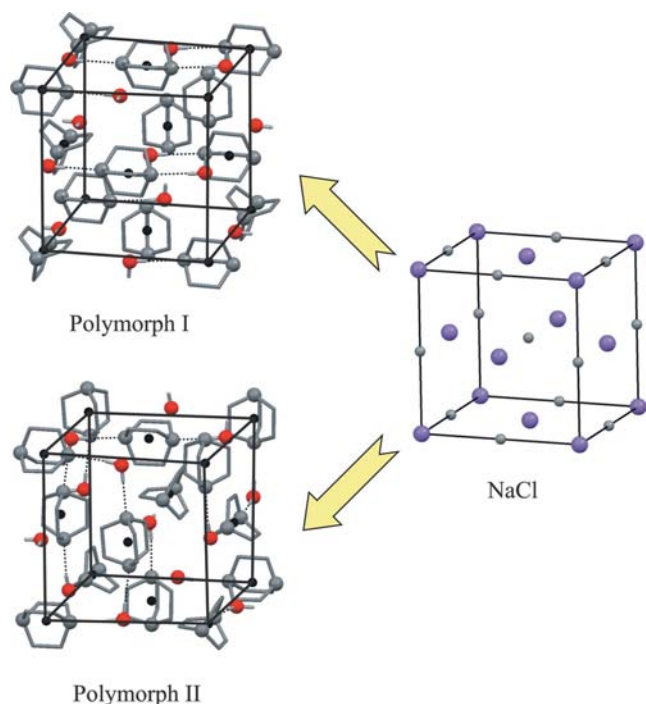


Figure 3

Analogy between the polymorphic structures of DABCO monohydrate and the NaCl structure. Pseudocubic cells are shown for both polymorphs. N and O atoms are represented as spheres. H atoms, except those of the water molecules, have been omitted for clarity. Only one orientation of the disordered DABCO molecules is shown. Hydrogen bonds are shown as dotted lines.

(DABCO) and 1.9 Å (water), and this in turn gives a water/DABCO radii ratio of 0.58. Making an analogy with simple inorganic structures, one may expect that, in the structure of closely-packed DABCO, the water molecules should occupy all octahedral interstices and in such a case two possibilities should be considered, *viz.* the NaCl-type structure, with DABCO in a ccp arrangement, and the NiAs-type structure, with DABCO in an hcp arrangement.

A closer look at the DABCO packing in (II) shows that, if DABCO is treated as a spherical molecule, its arrangement can be approximated to the ccp structure, with one of the pseudocubic $\langle 111 \rangle$ directions parallel to the c axis and the pseudocubic $\langle 100 \rangle$ directions either parallel or perpendicular to the DABCO N...N axes. This agrees well with the angles formed by the N...N vectors of the DABCO molecules with the c axis (55.7° for molecule *A*, 52.6° for molecule *B* and 55.0° for molecule *C*), which are close to the ideal value of 54.7° for the angle between the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions in a cubic lattice. The close-packed layers of DABCO are parallel to (001), $(\bar{1}21)$, $(2\bar{1}1)$ and $(1\bar{1}\bar{1})$, and water molecules occupy all octahedral voids between DABCO molecules that have their centroids arranged in a pseudocubic F lattice (Fig. 3). Therefore, the structure of polymorph (II) can be considered as an analogue of the ionic NaCl structure, with DABCO substituting for the chloride anions and water for the sodium cations. The pseudocubic F cells that can be constructed in form (II) have two shorter edges, corresponding to the OH...N(CH₂CH₂)₃N...HO distances of 8.431 (2) and

8.395 (2) Å, and a set of longer edges, corresponding to O...DABCO...O segments with the DABCO N—N axis perpendicular to the O...O line [9.112 (2)–9.352 (3) Å] (Fig. 3).

Similar packing features can be identified in the structure of monoclinic polymorph (I). Here, as in (II), the DABCO molecules show a ccp arrangement, with one of the close-packed layers easily identified as a (100) layer, with the reciprocal lattice vector \mathbf{a}^* indicating the stacking direction. The remaining layers are parallel to (111), $(10\bar{1})$ and $(1\bar{1}\bar{1})$. Only in the stacking direction of \mathbf{a}^* , corresponding to one of the pseudocubic directions $\langle 111 \rangle$, does separation of the ordered and disordered molecules of DABCO into distinct layers take place. The N...N vectors of DABCO are either virtually parallel or perpendicular to the pseudocubic cell edges. The water molecules are enclosed in octahedral voids and again this polymorph can be treated as a structural analogue of NaCl (Fig. 3).

The question arises as to whether an NiAs analogue, with an hcp DABCO arrangement and water molecules located in octahedral interstices, can be designed. Our analysis of a model of the pseudohexagonal structure showed that linear OH...N(CH₂CH₂)₃N...HO segments could not be constructed in the case of a pseudohexagonal close-packed arrangement of DABCO.

In summary, we would like to emphasise that the identification of a structural analogy between NaCl and the DABCO monohydrates (I) and (II) was very helpful in revealing the striking similarities between the two polymorphic forms, which would otherwise have been limited to the topology of the hydrogen-bond networks.

Experimental

Initially, polymorph (II) of DABCO monohydrate was isolated from a cocrystallization trial in which glycyrrhetic acid (2.5 mg) and DABCO (0.59 mg) were dissolved in ethanol (5 ml) and the solution placed in a closed plastic vial. After a few days, when the ethanol had evaporated, colourless tablet crystals of (II), of a quality suitable for X-ray analysis, were obtained. To check whether polymorph (II) can be obtained from tetrahydrofuran (THF) solution, *i.e.* from the solvent used for crystallization of polymorph (I) (Laus *et al.*, 2008), crystallization of DABCO (540 mg) from undried THF (5 ml) was carried out. The solution was placed in a refrigerator at 278 K for 26 h and only crystals of form (II) were isolated from this crystallization.

Crystal data

$\text{C}_6\text{H}_{12}\text{N}_2 \cdot \text{H}_2\text{O}$	$Z = 9$
$M_r = 130.19$	Cu $K\alpha$ radiation
Trigonal, $P3_1$	$\mu = 0.67 \text{ mm}^{-1}$
$a = 11.03798 (15) \text{ \AA}$	$T = 130 \text{ K}$
$c = 15.2660 (2) \text{ \AA}$	$0.4 \times 0.3 \times 0.1 \text{ mm}$
$V = 1610.78 (4) \text{ \AA}^3$	

Data collection

Oxford SuperNova diffractometer	7274 measured reflections
Absorption correction: multi-scan	2212 independent reflections
(<i>CrysAlis Pro</i> ; Oxford	2183 reflections with $I > 2\sigma(I)$
Diffractometry, 2009)	$R_{\text{int}} = 0.014$
$T_{\text{min}} = 0.677$, $T_{\text{max}} = 0.940$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	1 restraint
$wR(F^2) = 0.116$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$
2212 reflections	$\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$
351 parameters	

Table 1Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W–H11W \cdots N2C	0.85	2.10	2.948 (2)	174
O1W–H21W \cdots N2A	0.85	2.08	2.928 (2)	175
O2W–H12W \cdots N1B	0.85	2.09	2.935 (2)	177
O2W–H22W \cdots N1C ⁱ	0.85	2.09	2.929 (2)	172
O3W–H13W \cdots N2B ⁱⁱ	0.85	2.10	2.952 (2)	177
O3W–H23W \cdots N1A	0.85	2.09	2.934 (2)	176

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

In the absence of significant anomalous scattering effects, Friedel pairs were averaged and the space group $P3_1$ was arbitrarily chosen. All H atoms from water molecules were identified in electron-density difference maps; all O–H distances were standardized to 0.85 \AA and H atoms were refined in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. All C-bound H atoms were placed in calculated positions, with C–H = 0.97 \AA , and were refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The *B* and *C* molecules of DABCO are disordered over two positions. The sum of the occupancy factors for each molecule was constrained to 1.00 and the

occupancy factors refined to 0.681 (5) and 0.528 (16) for the major positions of molecules *B* and *C*, respectively. No restraints were imposed on the geometry of the disordered molecules.

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3127). Services for accessing these data are described at the back of the journal.

References

- Farkas, A., Mills, G. A., Erner, W. E. & Maerker, J. B. (1959). *J. Chem. Eng. Data*, **4**, 334–335.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Laus, G., Kahlenberg, V., Wurst, K., Lörting, T. & Schottenberger, H. (2008). *CrystEngComm*, **10**, 1638–1644.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Nimmo, J. K. & Lucas, B. W. (1976a). *Acta Cryst.* **B32**, 348–353.
- Nimmo, J. K. & Lucas, B. W. (1976b). *Acta Cryst.* **B32**, 597–600.
- Nimmo, J. K. & Lucas, B. W. (1976c). *Acta Cryst.* **B32**, 2729–2730.
- Oxford Diffraction (2009). *CrysAlis Pro*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Sauvajol, J. L. (1980). *J. Phys. Solid State Phys.* **13**, L927–L935.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.