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Humidity Control of Isostructural Dehydration and Pressure-Induced Polymorphism in 1,4-Diazabicyclo[2.2.2]octane Dihydrobromide Monohydrate

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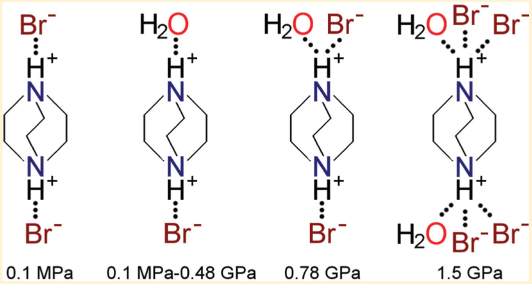
S Supporting Information

ABSTRACT: 1,4-Diazabicyclo[2.2.2]octane dihydrobromide (dabco2HBr, $[C_6H_{14}N_2]^{2+}\cdot 2Br^-$) is extremely sensitive to humidity levels, by absorbing or releasing water from its structure. The gradual changes of water contents, in turn, modifies the crystal symmetries, albeit all polar at ambient pressure. The full water contents control has been achieved for the sample sealed in a high-pressure chamber. Isobaric crystallization of dabco2HBr from ethanol solution at dry conditions yields anhydrate dabco2HBr, and in open air two polymorphic hemihydrates dabco2HBr$\cdot{}^1/_2H_2O$ and an isostructural monohydrate α-dabco2HBr$\cdot H_2O$; three more monohydrate dabco2HBr$\cdot H_2O$ polymorphs have been obtained by isothermal and isochoric crystallizations in a diamond-anvil cell. All the structures have been determined in situ by single-crystal X-ray diffraction. The anhydrate dabco2HBr, its hemihydrates α and β, and monohydrates α, β, and γ all crystallize in polar space groups: *Cmc*2$_1$ (dabco2HBr, β-dabco2HBr$\cdot{}^1/_2H_2O$, β-dabco2HBr$\cdot H_2O$), *Pbc*2$_1$ (α-dabco2HBr$\cdot{}^1/_2H_2O$ and α-dabco2HBr$\cdot H_2O$) and *P*2$_1$ (γ-dabco2HBr$\cdot H_2O$). However, all these crystals exhibit clear isostructural relations. Only the highest-pressure δ-dabco2HBr$\cdot H_2O$ monohydrate is centrosymmetric, space group *Pmmn*. Systematic structural transformations accompanying the hydration and pressure increase have been monitored: pressure gradually increases number of H-bonds involving each of the ammonium groups, from one to three, and the H-acceptor capacity of Br$^-$ anions from zero to three.



1. INTRODUCTION

NH$^+\cdots$N bonded complexes of 1,4-diazabicyclo[2.2.2]-octane (dabco) with monohydrogen mineral acids exhibit intriguing dielectric properties. These complexes of dabco with acids $HClO_4$ and HBF_4, dabcoHClO$_4$ and dabcoHBF$_4$ respectively, were the first NH$^+\cdots$N bonded substances for which ferroelectric properties were reported.[1] The spontaneous polarization in the dabco complex with $HReO_4$, dabcoHReO$_4$,[2] is the only known structure where the NH$^+\cdots$N bonds are parallel to the spontaneous polarization ($\mathbf{p_s}$) in the ferroelectric phase, whereas in most ferroelectrics of KDP-type (KDP is an abbreviation for potassium dihydrogen phosphate KH_2PO_4) the OH$\cdots$O bonds are nearly perpendicular or considerably inclined to $\mathbf{p_s}$.[3] More recently, anisotropic relaxor properties were found in the dabco 1:1 complexes with HI and HBr acids, dabcoHI[4] and dabcoHBr,[5] the first organic and anisotropic relaxors of stoichiometric composition. It was established that these relaxor crystals are composed of nanodomains, with disproportionate dabco2H$^+$ dications and neutral dabco molecules formed at the domain boundaries. Furthermore, dabcoHI exhibits a rich phase diagram of 10 documented polymorphs, labeled I−X, of which relaxor properties were evidenced in two polymorphs, V and X.[6] It was found that high-pressure crystallizations of dabcoHI from methanol and aqueous solution proceed differently than at ambient pressure. All dabco monosalts mentioned above, including dabcoHI, yield exclusively anhydrous crystals when crystallized from aqueous or methanol solution at normal conditions. Above 0.5 GPa, dabcoHI crystallized from aqueous solution favorably forms a monohydrate, α-dabcoHI$\cdot H_2O$, and above 1.4 GPa another monohydrate, β-dabcoHI$\cdot H_2O$ is formed.[7] Methanol solution yields unsolvated dabcoHI crystals below 1.8 GPa, and at this pressure only the dabco disalt (denoted dabco2HI) precipitated from the monosalt solution in the form of dabco2HI$\cdot 3CH_3OH$ solvate. Above 2.4 GPa the reaction of N-methylation of dabco takes place. Hydrobromide of dabco, dabcoHBr, is isostructural with dabcoHI polymorph V when crystallized from aqueous solution at normal conditions[8] and has analogous relaxor properties.[5] However, its phase diagram is very different:[5,9] there are only three dabcoHBr phases in the range of temperature and pressure analogous to that of 10 dabcoHI polymorphs. No methanol solvate of dabcoHBr, analogous to dabco2HI$\cdot 3CH_3OH$, has been obtained at high pressure. In order to better understand the hydration of dabco monosalts, we have extended our study to dabco dihydrobromide, dabco2HBr, crystallized at varied thermodynamic conditions. It was aimed at investigating the ambient-pressure crystallization of diprotonated

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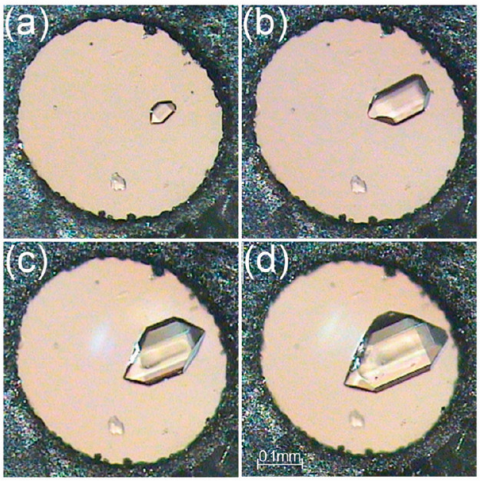


Figure 1. Isothermal growth of dabco2HBr·H_2O monohydrate in phase β from aqueous solution at 296 K: (a) one seed at 0.12 GPa, (b, c) a single-crystal growth, and (d) the sample at 0.48 GPa. The ruby chip for pressure calibration lies between the sample and the bottom edge of the gasket.

dabco salt, the pressure effect on its hydrates types, and the range of pressure and temperature destabilizing their structure.

2. EXPERIMENTAL METHODS

2.1. Synthesis. Five grams of crystalline 1,4-diazabicyclo[2.2.2]-octane (dabco, Aldrich, analytical grade 99%) was dissolved in 12 mL of ethanol. Then 5.03 mL (7.3 g) equimolar quantity with dabco of bromic acid (HBr) was poured into this solution. Two kinds of crystals precipitated: 0.79 g at once and of the remaining solution 6.02 g after the solvent evaporated. Single-crystal and powder X-ray diffraction measurements showed that dabcoHBr precipitated first, and dabco2HBr later. dabcoHBr formed nice hexagonal single crystals, whereas practically all the dabco2HBr crystals had defects of different sorts.

2.2. Crystals Growth at Ambient Pressure. dabco2HBr crystals obtained in the reaction were of low quality and recrystallizations were undertaken. The best single crystals were obtained from ethanol solution, yielding small rectangular plates. However, even samples that appeared good gave diffraction patterns with split and diffused reflections, and many samples had to be tested before satisfactory single-crystals were selected. The crystals were very sensitive to changing conditions, stress, and contact with other solvents. Two types of crystals occurred of very similar habit. The first type of crystal had the symmetry of orthorhombic space group $Pbc2_1$, and it included two hydrates labeled as type α: hemihydrate α-dabco2HBr·$^1/_2H_2O$ and monohydrate α-dabco2HBr·H_2O. The second β-type crystal of orthorhombic space-group symmetry $Cmc2_1$ was initially found only for hemihydrate β-dabco2HBr·$^1/_2H_2O$, but later the samples of the same crystal-symmetry of space group $Cmc2_1$ were obtained of ethanol solution in a drybox in a form of anhydrate β-dabco2HBr samples. The crystals of both symmetry types α and β have similar structures in this sense, that the unit cell of type α is the doubled unit cell of type β along [100], and the positions of dabco2H$^+$ centroids and of the Br$^-$ anions are approximately the same. The main differences between these structures are in the orientation of the dabco2H$^+$ dications and in the presence and position of water molecules. The low quality of many of the single crystals was caused by their aggregation and high sensitivity to humidity, leading to transformations during the sample handling and measurements. It should be stressed that the water contents determined at ambient pressure is only approximate. Because of the high sensitivity of dabco2HBr to humidity level, the water content was difficult to control during the experiments. It appears that the water contents between 0 and $^1/_2$ favored the β-type structure, and those between $^1/_2$ and 1 favored the α type. However, in the discussion below the approximate hydration levels of 0, $^1/_2$, and 1 will be used for the structures determined for the bare samples (at 0.1 MPa). Most importantly, the "breathing" of the samples with water considerably affected the quality of structural data obtained from the diffraction experiments. All disadvantages of changing humidity were circumvented in the high-pressure experiments in confined experimental environments.

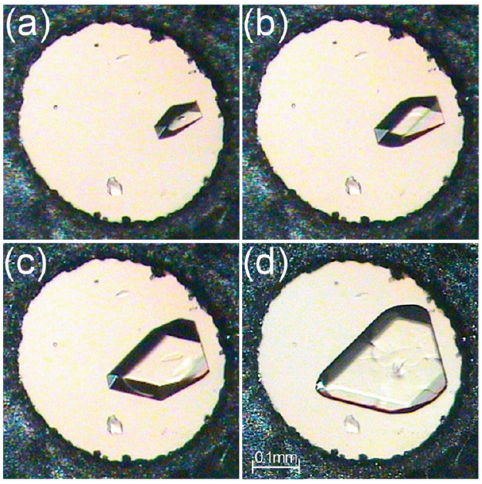


Figure 2. Isochoric growth of a single-crystal γ-dabco2HBr·H_2O hydrate from aqueous solution: (a) one small grain after dissolving polycrystalline mass at 376 K; (b) the same crystal at 360 K; (c) 343 K; (d) the single-crystal at 0.78 GPa/296 K (cf. Figure 1).

2.3. High-Pressure Crystallization. High-pressure crystallizations of dabco2HBr performed in situ in a diamond-anvil cell (DAC)[10] provided a much more precise control of experimental conditions and hence resulted in much better quality of samples and more precise results. The gasket was made of steel foil, 0.1 mm thick, with a spark-eroded hole, 0.4 mm in diameter. Pressure in the DAC was calibrated by the ruby-fluorescence method[11] using a Betsa PRL spectrometer, with an accuracy of 0.05 GPa. In the first of high-pressure crystallizations, the chamber of the DAC, equipped with steel disks supporting the diamond anvils, was loaded with saturated aqueous solution of dabco2HBr. Distilled water was used. A single crystal was grown in isothermal conditions at 296 K (Figure 1). The collected X-ray diffraction data revealed a monohydrate stoichiometry and that the crystal is isostructural with the β-type anhydrate and hemihydrate; hence, this monohydrate has been denoted as β-dabco2HBr·H_2O.

Subsequently, pressure was increased to 0.78 GPa; however the single crystal was crushed and a new crystal was grown in isochoric conditions. First, the DAC was heated until all crushed fragments but one dissolved at 376 K, and then temperature was slowly lowered to 296 K (Figure 2). The X-ray measurement revealed another monohydrate, denoted as γ-dabco2HBr·H_2O.

After the diffraction data was collected, the pressure was further increased to 1.5 GPa. The single crystal was grown in isochoric conditions of the nucleous obtained at 433 K and then cooled slowly for 5 h. Several times defects appeared on the crystal faces and the crystallization process had to be repeated until the single-crystal sample was obtained (Figure 3). The X-ray diffraction measurement revealed yet another monohydrate, labeled as phase δ.

2.4. X-ray Diffraction Analyses. Small rectangular crystals were chosen for ambient-pressure measurements. Their quality was checked by diffraction. The single-crystal data have been measured with a KUMA KM4-CCD diffractometer; for crystals enclosed in the DAC a procedure for high-pressure experiments was applied.[12] The CrysAlis software[13] was used for the data collections and the preliminary reduction of the data. In the high-pressure data after correcting intensities for the effects of DAC and sample absorption and sample shadowing by the gasket, the sample reflections overlapping with diamond reflections were eliminated.[14] All structures were solved straightforwardly by direct methods and refined by full-matrix least-squares.[15] Anisotropic temperature factors were refined for all non-H atoms in the structure of phase γ and only for bromide ions in the others phases. The ethylene H-atoms, water hydrogens, and amine protons in the structures were located from molecular geometry (d_{O-H} = 0.95 Å, d_{C-H} = 0.97 Å, and d_{N-H} = 0.86 Å) and their U_{iso} parameters were constrained to 1.2 times U_{eq}/U_{iso} values of the carrier atoms. Although several β-dabco2HBr·$^1/_2H_2O$ crystals were studied, the obtained structural parameters were inaccurate due to the low quality of the samples. Their quality was affected by their susceptibility to humidity changes, and subsequent transformations to α-dabco2HBr·$^1/_2H_2O$, clearly observed as the a-parameter doubling. The selected crystal data and the structure-refinements details are listed in Table 1 and in Table S1 of Supporting Information. Structural drawings were prepared using the X-Seed interface of POV-Ray and Mercury.[16,17]

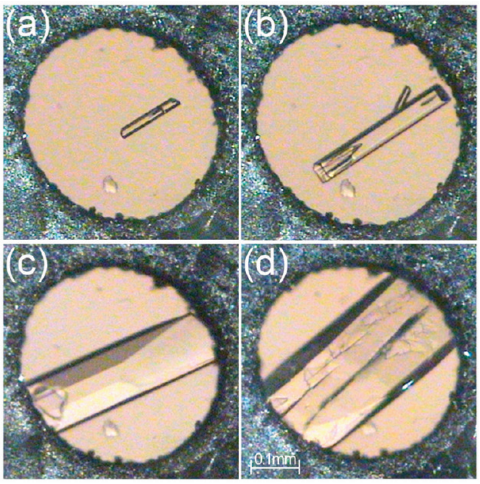


Figure 3. Stages of isochoric growth of δ-dabco2HBr·H_2O monohydrate from aqueous solution: (a) a nucleus at 430 K; (b) the single-crystal at 375 K with another small crystal growing on its side — it was dissolved by heating the sample to 415 K, after which the slow cooling was resumed; (c) the single crystal at 345 K; and (d) at 1.50 GPa/296 K (cf. Figures 1 and 2).

3. RESULTS AND DISCUSSION

3.1. Ambient-Pressure Hydration. Ambient-pressure isobaric crystallization of dabco2HBr of ethanol solution, performed in the open air, yields a mixture of hemihydrate and monohydrate crystals, which are very similar in morphology. When exposed to air, their faces deteriorate because dabco2HBr crystals are hygroscopic, even in moderately humid air. All monohydrate crystals obtained at ambient pressure from various solutions were in the form of polymorph α-dabco2HBr·H_2O. Aqueous solution was not used for crystallizations because dabco2HBr dissolves very well in water. The best quality crystals were obtained from ethanol solution with an excess of HBr. The attempts to crystallize dabco2HBr by sublimation was unsuccessful. After 48 h, crystals left in open vessels were overgrown by other small crystals. Hemihydrated α-dabco2HBr·$^1/_2H_2O$ and monohydrated α-dabco2HBr·H_2O were obtained concomitantly in this way. Our attempts to crystallize the pure monohydrate form from various solutions led to the conclusion that in the initial stages of crystallization the monohydrate is formed, and on decreased H_2O concentration the hemihydrate precipitates. These hemihydrates and monohydrates can also interconvert after removing the crystals from solution, depending on humidity conditions. Subsequent crystallizations in a drybox from dry ethanol solution yielded anhydrate dabco2HBr, of the β-type structure, which in open air slowly acquired water within the β-type structure and eventually, on sufficiently high water contents, converted into the α-type hemihydrate and monohydrate

Table 1. Selected Crystal Data of dabco2HBr Anhydrate, dabco2HBr·$^1/_2H_2O$ Hemihydrates, and Monohydrate dabco2HBr·H_2O Polymorphs α, β, γ, and δ

	dabco2HBr	dabco2HBr·$^1/_2H_2O$		dabco2HBr·H_2O			
structure type	β	α	β	α	β	γ	δ
formula	$C_6H_{14}N_2Br_2$	$C_6H_{15}N_2Br_2O_{1/2}$	$C_6H_{15}N_2Br_2O_{1/2}$	$C_6H_{16}N_2Br_2O$	$C_6H_{16}N_2Br_2O$	$C_6H_{16}N_2Br_2O$	$C_6H_{16}N_2Br_2O$
p (GPa)	0.0001	0.0001	0.0001	0.0001	0.48(5)	0.78(5)	1.50(5)
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	$Cmc2_1$	$Pbc2_1$	$Cmc2_1$	$Pbc2_1$	$Cmc2_1$	$P2_1$	$Pmmn$
unit cell (Å,°)							
a	7.0917(13)	14.3848(18)	7.272(2)	15.015(3)	7.185(3)	6.516(4)	7.2844(19)
b	12.280(3)	12.4619(12)	12.467(3)	12.486(2)	12.382(6)	12.037(3)	10.918(4)
c	11.4693(18)	11.3029(11)	11.265(4)	11.2364(16)	11.119(3)	6.792(3)	5.663(4)
β	90	90	90	90	90	113.06(5)	90
V (Å^3)	998.8(3)	2026.2(4)	1021.3(5)	2106.5(6)	989.2(7)	490.2(4)	450.4(4)
Z/Z'	4/0.5	8/2	4/0.5	8/2	4/0.5	2/1	2/0.25
ρ (g/cm^3)	1.822	1.856	1.841	1.842	1.961	1.979	2.153
completeness (%)	96.2	99.9	96.7	95.3	36.4	19.2	41.3
R_1/wR_2 ($I > 2\sigma_1$)	0.1259/0.3407	0.0355/0.0572	−/−	0.1059/0.3029	0.0640/0.1349	0.0322/0.0577	0.0532/0.1308
R_1/wR_2 (all data)	0.1860/0.3557	0.0645/0.0595	−/−	0.1705/0.3203	0.0845/0.1446	0.0490/0.0617	0.0608/0.1396

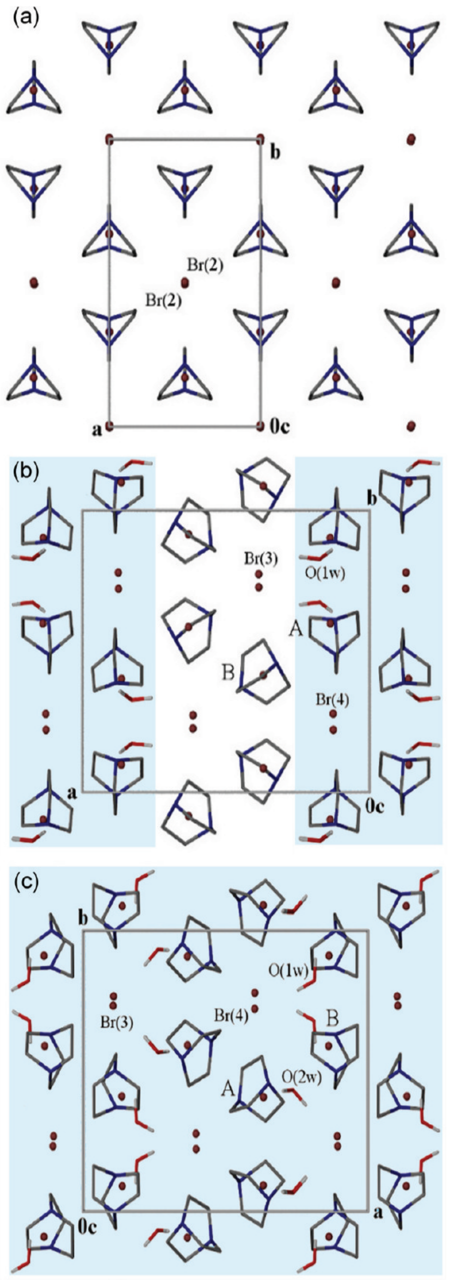


Figure 4. Ambient-conditions (0.1 MPa, 296 K) crystal structures of (a) β-dabco2HBr; (b) α-dabco2HBr$\cdot{}^{1}/_{2}H_2O$; and (c) α-dabco2HBr$\cdot H_2O$, all projected down crystal direction [001]. In drawing (a), the dications are superimposed with anions Br(1); in drawings (b) and (c) dications A (with atoms labeled 1−6) are superimposed with anions Br(2) and dications B (atomic labels 11−16) are superimposed with anions Br(1). All hydrogen atoms of dications have been omitted for clarity and only those in the water molecules have been shown.

α-dabco2HBr$\cdot H_2O$, as evidenced by X-ray powder diffraction and thermal gravimetry. In dry air a reverse dehydration into the anhydrate β-type structure dabco2HBr takes place over a day or two for small crystals, with a considerable deterioration of their diffracting quality. Crystals α-dabco2HBr$\cdot{}^{1}/_{2}H_2O$ and α-dabco2HBr$\cdot H_2O$ are isostructural: their space group symmetry is the same and unit-cell dimensions are similar (Table 1 and Figure 4). Positions of ions are very similar too, although small differences in the orientation of dabco2H$^+$ cations can be easily seen in Figure 4. It can be noted that the structures of α-hemihydrate and α-monohydrate can be considered as built of two types layers perpendicular to [x], one between $-{}^{1}/_{4} < x < {}^{1}/_{4}$ and the second between ${}^{1}/_{4} < x < {}^{3}/_{4}$, and that the latter layer in the dabco2HBr$\cdot{}^{1}/_{2}H_2O$ hemihydrate is devoid of water molecules. Within the first layer, $-{}^{1}/_{4} < x < {}^{1}/_{4}$, in both hemi- and monohydrate structures, the locations of the water molecules are similar, but their orientation is clearly different.

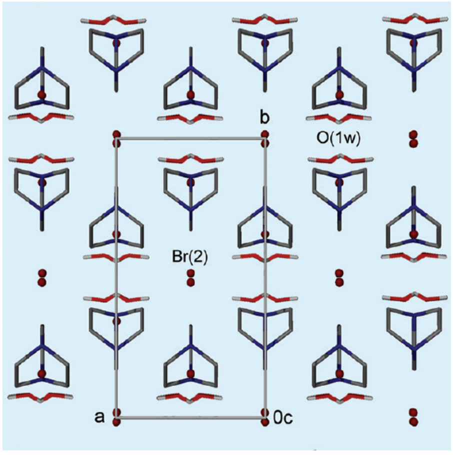
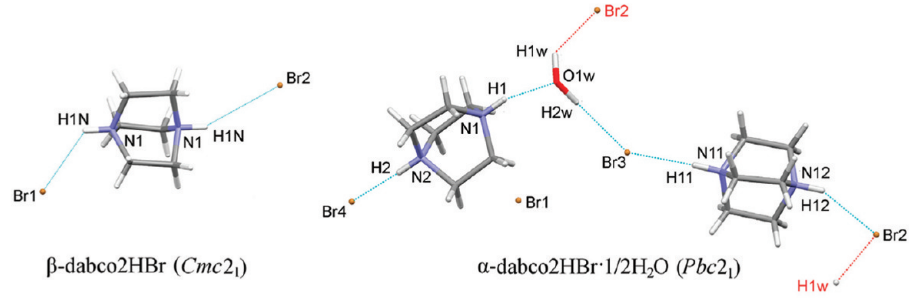


Figure 5. The crystal structure of β-dabco2HBr$\cdot H_2O$ at 0.48 GPa. The dications are superimposed with anions Br(1). The water molecule is disordered and located in two positions but with one common site for one of the hydrogen atoms. Hydrogen atoms of the dications have been omitted for clarity.

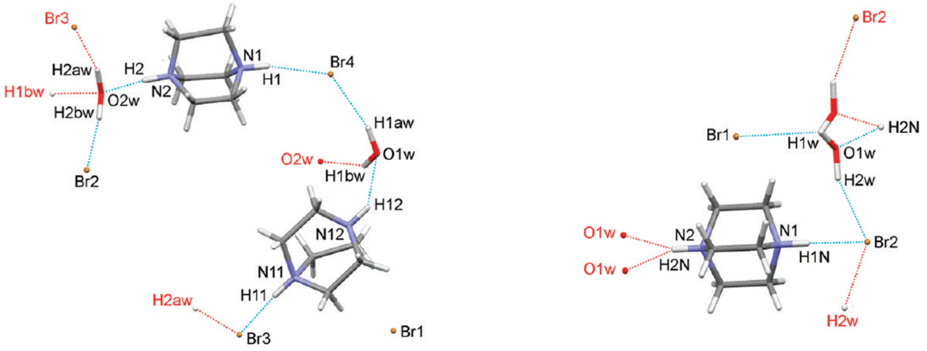
The structure of the anhydrate β-dabco2HBr resembles those of α-dabco2HBr$\cdot H_2O$ and α-dabco2HBr$\cdot{}^{1}/_{2}H_2O$. Apart from the absence of water molecules, halved unit-cell parameter *a*, halved unit-cell volume and halved *Z* number (number of formula units in the unit cell) compared to the α-mono- and α-hemihydrate structures, and despite different space-group symmetry of α-monohydrate and β-anhydrate, the arrangement of ions is similar (Figure 4) and the α and β-type structures exhibit a considerable three-dimensional isostructurality.[18] It may be due to the dominant role of electrostatic interactions between ions and a lesser role of the interactions involving water molecules in these crystals.

3.2. Pressure-Induced Polymorphism of Monohydrates.

The isothermal crystallization at 0.48 GPa leads to the monohydrate polymorph β-dabco2HBr$\cdot H_2O$, isostructural with the ambient-pressure anhydrous β-dabco2HBr and hemihydrate β-dabco2HBr$\cdot{}^{1}/_{2}H_2O$ (Figures 4 and 5 and Table 1). The β-anhydrate, β-hemihydrate, and β-monohydrate crystals are isostructural in this way that they have the same space-group symmetry, similar unit-cell dimensions (Table 1), and similar positions of the ions. The main difference between the β-type anhydrate and monohydrate is the presence of disordered H_2O molecules. The β-type crystals are also isostructural with the α-type analogues, as explained above (Figures 4 and 5). The main differences between the α- and β-type structures are in the orientation of the cations, which in the β-type structures are located on the mirror planes, absent in the α-type structures. Because of the misalignment of the cations in type α phases, there are two symmetry-independent cations and the unit-cell parameter *a* is doubled. It is plausible that a factor favoring the



β-dabco2HBr ($Cmc2_1$) α-dabco2HBr·1/2H_2O ($Pbc2_1$)



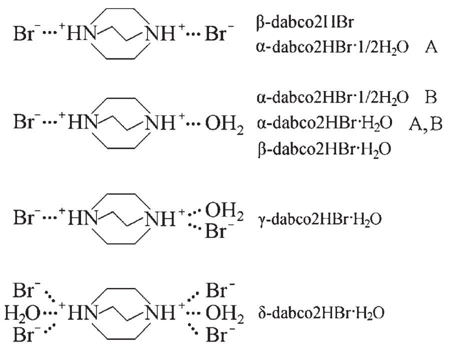
α-dabco2HBr·H_2O ($Pbc2_1$) β-dabco2HBr·H_2O ($Cmc2_1$)

γ-dabco2HBr·H_2O ($P2_1$) δ-dabco2HBr·H_2O ($Pmmn$)

Figure 6. Aggregation of ions and water molecules in β-dabco2HBr, α-dabco2HBr·$^1/_2H_2O$, and dabco2HBr·H_2O α, β, γ, and δ phases. The blue dotted lines mark symmetry-independent hydrogen bonds, and their symmetry-equivalent H-bonds are represented by red dotted lines; black labels mark symmetry-independent atoms, whereas those in their symmetry-equivalent positions have red labels. Two half-occupied sites of the disordered water molecule in β-dabco2HBr·H_2O have been shown. Short contacts involving CH_2 groups have been omitted for clarity.

misorientation of the cations — and thus transformation the β-type structures into type α — is the presence of water molecules at ambient pressure. In α-type hydrates, the water molecules are located on one side of the dication, away from its mirror plane, and in this way they break the symmetry of β-type crystals, except for the β-dabco2HBr hydrate where the water molecule is disordered. In the α-type hemihydrate and hydrate, and β-hemihydrate the water molecules form H-bonds to one of the amine protons of the dications and mediates in the H-bonding to a Br^- anion (Figure 6). In the α-type structures these H-bonds force the cations to change their orientation by pulling the nitrogen atom toward this side where the H-bonded H_2O molecule and Br^- anion are located. Consequently, the mirror-plane symmetry is broken and the unit cell doubles along $[x]$ in the α-type crystals, compared to the β-type ones. In terms of crystals symmetry, it is much higher for β-dabco2HBr·H_2O than for the α-dabco2HBr·H_2O: in the α-structures there are two symmetry-independent formula units ($Z' = 2$) and the structures are ordered, while in the β-monohydrate only half of the formula unit is symmetry independent ($Z' = 1/2$) and the water

Scheme 1. Hydrogen Bonds Formed by the dabco2H$^+$ Cations in the Structures of β-dabco2HBr, Hemihydrate α-dabco2HBr·$^1/_2H_2O$, and Monohydrate dabco2HBr·H_2O Phases α, β, γ, and δ^{a}



[a] The right column lists the structures where the H-bonding patterns are present (cf. Figure 6). Symmetry-independent dications of α-dabco2HBr·$^1/_2H_2O$ and α-dabco2HBr·H_2O are labeled A and B.

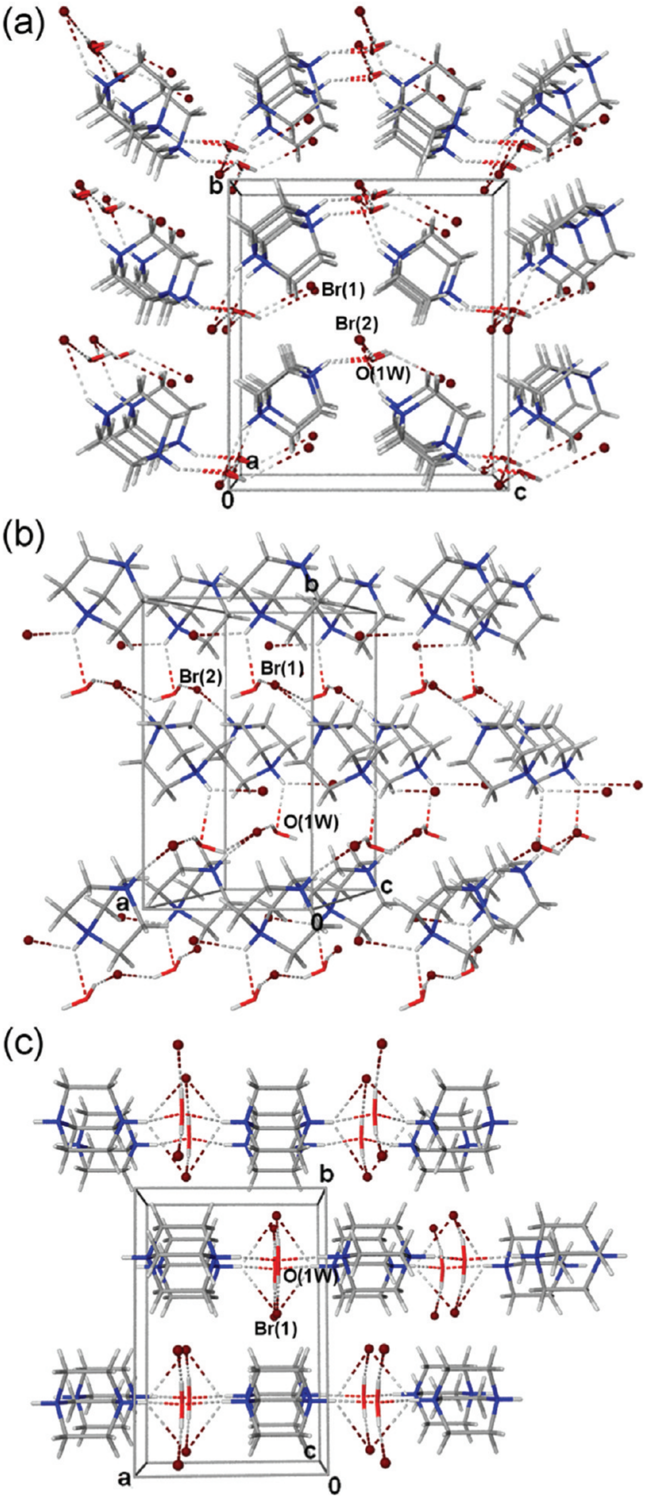


Figure 7. Autostereograms[20] of the structures of dabco2HBr$\cdot$$H_2O$ high-pressure monohydrates: (a) phase β at 0.48 GPa/296 K (two $NH^+\cdots OH_2$ bonds are to one disordered water molecule); (b) phase γ at 0.78 GPa/296 K; and (c) phase δ at 1.50 GPa/296 K. Hydrogen bonds involving N, O, and Br atoms are marked with dashed lines.

Scheme 2. Hydrogen-Bonding Coordination of the Br^- Anions (Left Column) in β-dabco2HBr Anhydrate, Hemihydrate α-dabco2HBr$\cdot{}^1/_2H_2O$ and Monohydrate dabco2HBr$\cdot H_2O$ phases α, β, γ, and δ[a]

Br^-	$Br(1)^s$ $Br(1)^\alpha$
$>NH^+\cdots Br^-$	$Br(1,2)$ $Br(4)^s$ $Br(1)^\gamma$
$Br^-\cdots HOH$	$Br(2)^\alpha$ $Br(1)^\beta$
$>NH^+\cdots Br^-\cdots HOH$	$Br(2,3)^s$ $Br(3,4)^\alpha$
$>NH^+\cdots Br^-$ $\cdots HOH$ $\cdots HOH$	$Br(2)^\beta$ $Br(2)^\gamma$
$>NH^+$ $>NH^+$ $\cdots Br^-\cdots HOH$	$Br(1)^\delta$

[a] The right column lists the Br^- anions H-bonded in the specified manner: superscripts s, α, β, γ, δ indicate the α-hemihydrate and monohydrates α, β, γ, and δ, respectively; Br(1,2) anions with no superscript refer to the anhydrate structure.

molecules are disordered. In the α- and β-type structures, on hydratation of the anhydrate and hemihydrates, the water molecules gradually replace the $NH^+\cdots Br^-$ bonds on one side of the dications, as illustrated in Figure 6 and Scheme 1. Thus, in the anhydrate β-dabco2HBr only $NH^+\cdots Br^-$ bonds are formed by the dications; in hemihydrate α-dabco2HBr$\cdot{}^1/_2H_2O$ every second dication forms one $NH^+\cdots OH_2$ bond, and in α-dabco2HBr$\cdot H_2O$ and β-dabco2HBr$\cdot H_2O$ all dications are $NH^+\cdots OH_2$ bonded on one side and $NH^+\cdots Br^-$ bonded on the other. In all these structures, α-hemihydrate, α-monohydrate, and β-monohydrate, the water molecule mediates the hydrogen bonds between the protonated amine and the Br^- anion: $NH^+\cdots OH_2\cdots Br^-$.

Polymorph γ-dabco2HBr$\cdot H_2O$ (at 0.78 GPa) reveals another systematic change in the H-bonding pattern of dabco2H^{2+} dications: one of the amine protons becomes involved in a (bifurcated) three centered hydrogen bond to Br^- and H_2O (Scheme 1).

3.3. H-Bonding Coordination.

It is apparent from Figures 4 and 6 that even in the isostructural α-dabco2HBr$\cdot{}^1/_2H_2O$ and α-dabco2HBr$\cdot H_2O$, despite similar positions of ions and water molecules, the H-bonding patterns are considerably different. In all monohydrates, the dications are each H-bonded at least to one Br^- anion. There are unique or repeated H-bonding types (Figures 6 and 7; Scheme 1; Table S2 in the Supporting Information). For β-dabco2HBr and dication A of α-hemihydrate both amines are H-bonded to two Br^- anions each (Scheme 1). In all monohydrate polymorphs, both $NH^+\cdots Br^-$ and $NH^+\cdots OH_2$ bonds are formed. In the lower range of pressure (dication B of hemihydrate β-dabco2HBr$\cdot H_2O$, both dications in α-dabco2HBr$\cdot H_2O$ and one in β-dabco2HBr$\cdot H_2O$), one amine is $NH^+\cdots Br^-$ bonded and the other amine is $NH^+\cdots OH_2$ bonded to a water molecule. In γ-dabco2HBr$\cdot H_2O$, one amine remains $NH^+\cdots Br^-$ bonded and the other becomes shared between Br^- and H_2O in a bifurcated (three-centered) hydrogen bond. Both protons form trifurcated H-bonds in the δ phase. Along with the increasing number of H-bonds involving NH^+ group pressure systematically increases also the H-accepting capacity of Br^- anions: in α-hemihydrate and α-monohydrate there are Br^- anions accepting no H-bonds, and H-accepting capacity of Br^- increases to three in β, γ, and δ dabco2HBr$\cdot H_2O$ (Scheme 2). No similar systematic pressure dependence has been noted for the H-bonding capacity of water

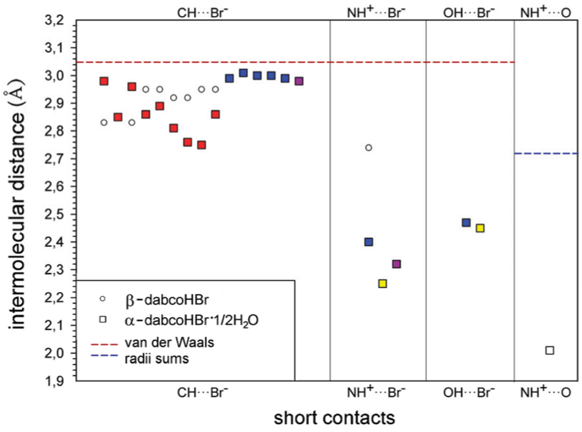


Figure 8. Intermolecular and interionic contacts shorter than the sums of van der Waals radii[19] in β-dabco2HBr and α-dabco2HBr·$^1/_2$$H_2O$ at ambient conditions. The square symbols of symmetry-independent anions in α-dabco2HBr·$^1/_2$$H_2O$ have been discriminated by colors: contacts of Br(1) are shown in red, those of Br(2) in blue, Br(3) in yellow, and Br(4) in purple.

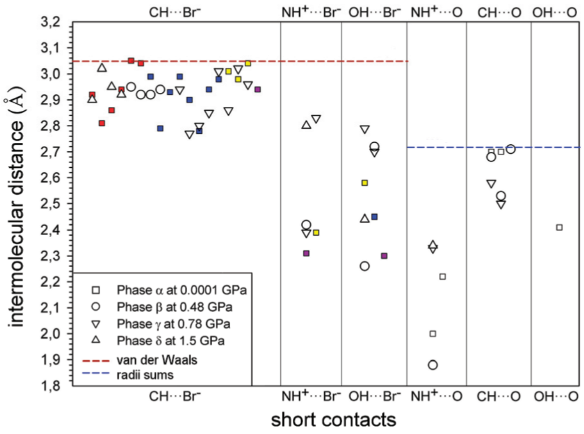


Figure 9. Intermolecular and interionic contacts involving H-atoms in dabco2HBr·H_2O polymorphs α, β, γ, and δ shorter than the sums of van der Waals radii.[19] The square symbols of symmetry-independent anions in phase α have been discriminated by colors: contacts of Br(1) are shown in red, those of Br(2) blue, Br(3) yellow, and Br(4) purple.

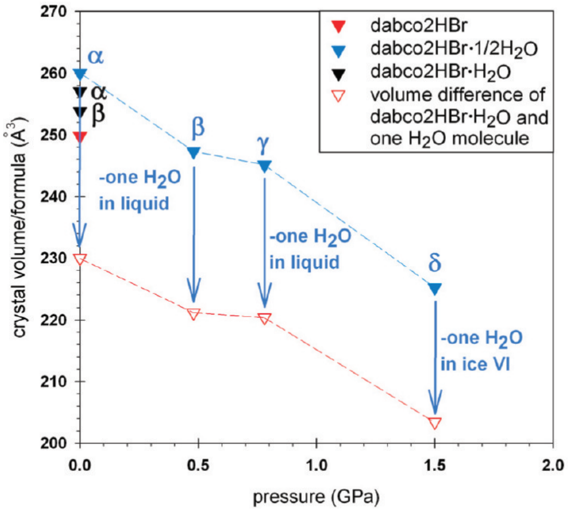


Figure 10. The crystal volume per formula unit in the function of pressure for dabco2HBr anhydrate, hemihydrates, and monohydrates. The blue arrows indicate the volume of one H_2O molecule in liquid[23] and ice VI,[24] depending on the pressure range; empty triangles show difference between the volume of dabco2HBr·H_2O formula units and one H_2O molecule. Much smaller volume differences are observed between monohydrates and anhydrate β.

molecules, each involved in three or four H-bonds in the hemihydrate and monohydrate crystals (Scheme S1 in Supporting Information). The criteria applied for identifying H-bonds have been based on the H···acceptor distances compared with the sums of appropriate van der Waals radii[19] (Figures 8 and 9). It can be observed that all the pressure-induced H-bonds are considerably shorter than the van der Waals radii sums.

3.4. Intermolecular and Interionic Contacts. There is a considerable number of short contacts involving CH_2 groups in the dabco2HBr structures. It can be observed from the plots in Figures 8 and 9 that short $NH^+\cdots O$ contacts are characteristic both of hemihydrates and monohydrates, but $CH\cdots O$ contacts appear in the monohydrates only. It illustrates that the incorporation of water molecules between large ions is advantageous for the close packing in dabco2HBr monohydrates and explains the small volume increase of the hydrated dabco2HBr forms compared to the anhydrate (Figure 10). The formation of short contacts involving methylene H-atoms is consistent with the observed pressure-generated hydrogen bonds $CH\cdots O$ and $CH\cdots N$.[21,22]

4. CONCLUSIONS

At normal conditions dabco2HBr can absorb and its hydrates release water depending on air humidity. The gradual absorption of water leads to the transformations of crystals between anhydrate, hemihydrates, and monohydrates with similar structures of isostructural types α and β. High pressure stabilizes the monohydrate structures, and no higher hydrates have been obtained. The high-pressure β-monohydrate at 0.48 GPa is isostructural with the β-type anhydrate and more remotely similar to the α-type monohydrate, obtained at 0.1 MPa. Apparently, increased pressure favors more the higher-symmetry β-structure ($Z' = 1/2$) with disordered water molecules, than lower-symmetry α structure ($Z' = 2$) with all atoms ordered. Thus, both structures are stabilized due to a higher entropy contribution: in the β-monohydrate it is connected with the water molecule disorder, whereas in α-monohydrate there are four times more configurations in the molecular/ionic arrangement. Higher pressure naturally eliminates the disorder, and still higher pressure leads to systematic transformations of the hydrogen-bonding patterns in the structures of γ and δ monohydrates, with the H-donor capacity of NH^+ groups and H-acceptor capacity of Br^- anions increasing. There are clear isostructural relations between monohydrates α, β, and γ. In the highest-pressure δ-monohydrate, each NH^+ proton is involved in trifurcated (six centered) H-bond to Br^- and water molecule, and the Br^- anion is 3-fold coordinated. It is remarkable that only monohydrate polymorphs of dabco2HBr have been obtained in high pressure and that high humidity at normal conditions lead to another monohydrate, too. Furthermore, in the highest-pressure polymorphs the γ-dabco2HBr·H_2O and δ-dabco2HBr·H_2O the bifurcated and trifurcated H-bonds formed by the NH^+ group are similar to that observed at 1.4 GPa in the β-dabco2HI·H_2O, to one water molecule and one I^- anion, despite considerable differences between all these structures.[25] The formation of bifurcated and trifurcated H-bonds involving the NH^+, Br^-/I^-, and H_2O groups is consistent with their increased H-donor and H-acceptor capacities in high pressure. The polar crystals of α, β, and γ types and their isostructural relations involving changing crystalline water contents from anhydrate, through hemihydrates to monohydrates crystals, is a unique feature, which can be applied in electronical humidity sensors.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed crystallographic information on high-pressure anhydrate, hemihydrates, and hydrates of dabco2HBr (Table S1), the shortest intermolecular interactions (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org. The CIF files can also be obtained from the Cambridge Crystallographic Data Centre (CCDC) as Nos. 818932 β-dabco2HBr, 818933 α-dabco2HBr·$^1/_2H_2O$, 818934 β-dabco2HBr·$^1/_2H_2O$, 818935 α-dabco2HBr·H_2O, 818936 β-dabco2HBr·H_2O, 818938 γ-dabco2HBr·H_2O and 818937 δ-dabco2HBr·H_2O.

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REFERENCES

(1) Katrusiak, A.; Szafrański, M. *Phys. Rev. Lett.* **1999**, *82*, 576–579.
(2) Szafrański, M.; Katrusiak, A.; McIntyre, G. J. *Phys. Rev. Lett.* **2002**, *89*, 5507–5510.
(3) Slater, J. C. *J. Chem. Phys.* **1941**, *9*, 16.
(4) Szafrański, M.; Katrusiak, A. *J. Phys. Chem. B* **2008**, *112*, 6779–6785.
(5) Szafrański, M. *J. Phys. Chem. B* **2009**, *113*, 9479–9488.
(6) Olejniczak, A.; Katrusiak, A.; Szafrański, M. *Cryst. Growth Des.* **2010**, *10*, 3537–3546.
(7) Olejniczak, A.; Katrusiak, A. *CrystEngComm* **2010**, *12*, 2528–2532.
(8) Katrusiak, A.; Ratajczak-Sitarz, M.; Grech, E. *J. Mol. Struct.* **1999**, *474*, 135–141.
(9) Budzianowski, A.; Katrusiak, A. *J. Phys. Chem. B* **2006**, *110*, 9755–9758.
(10) Merrill, L.; Bassett, W. A. *Rev. Sci. Instrum.* **1974**, *45*, 290–294.
(11) Piermarini, G. J.; Block, S.; Barnett, J. D.; Forman, R. A. *J. Appl. Phys.* **1975**, *46*, 2774–2778.
(12) Budzianowski, A.; Katrusiak, A. In *High-Pressure Crystallography*; Katrusiak, A.; McMilan, P., Eds: Kluwer: Dordrecht, 2004; pp 101−112.
(13) *Xcalibur CCD System, CrysAlisPro Software System*, version 1.171.33; Oxford Diffraction Ltd.: Wrocław, Poland, 2009.
(14) Katrusiak, A. *REDSHABS*; Adam Mickiewicz University: Poznań, Poland, 2003.
(15) Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112–122.
(16) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1*, 189–191.
(17) 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. *J. Appl. Crystallogr.* **2008**, *41*, 466–470.
(18) Fabian, L.; Kalman, A. *Acta Crystallogr. B* **2004**, *60*, 547–558.
(19) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.
(20) Katrusiak, A. *Mol. Graph. Model.* **2001**, *19*, 363–367.
(21) Dziubek, K. F.; Jęczmiński, D.; Katrusiak, A. *J. Phys. Chem. Lett.* **2010**, *1*, 844–849.
(22) Olejniczak, A; Katrusiak, A. *J. Phys. Chem. B* **2008**, *112*, 7183–7190.
(23) Bridgman, P. W. *J. Chem. Phys.* **1935**, *3*, 597–605.
(24) Kuhs, W. F.; Finney, J. L.; Vettier, C.; Bliss, D. V. *J. Chem. Phys.* **1984**, *81*, 3612–3623.
(25) Olejniczak, A.; Katrusiak, A. *Cryst. Growth Des.* **2011**, DOI: 10.1021/cg101653x.