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Remote halogen switch of amine hydrophilicity[†]

Michał Andrzejewski, Anna Olejniczak and Andrzej Katrusiak*

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Bromide and iodide anions switch hydrogen-bonding patterns in otherwise isostructural dimethanol solvates *N*-methyl-1,4diazabicyclo[2.2.2]octanium bromide (dabcoCH₃Br·2CH₃OH) and analogous iodide (dabcoCH₃I·2CH₃OH), both synthesized in the high-pressure version of the Menshutkin reaction at 1.2 and 2.4 GPa, respectively. The magnitudes of the high pressure triggering these reactions correspond to identical molecular volumes of both solvates.

The chemical properties of bromide and iodide anions are either similar and characteristic of halogens, or drastically different. In polar solvents anion I⁻ is a strong nucleophile and weak base, while Br⁻ has comparative nucleophilic and basic properties. In radical reactions Br⁻ and I⁻ act differently too, as described by the Kharasch effect.¹ Furthermore, crystalline HBr is ferroelectric, and HI is not.² It was shown recently that in 1,4-diazabicyclo[2.2.2]octane (dabco) hydrobromide (dabcoHBr) hydrogen bonds NH⁺...N and NH⁺...Br⁻ can be interconverted by applying temperature and pressure,³ while in all ten polymorphs of dabco hydroiodide (dabcoHI) only NH⁺...N bonds are present.⁴ Phase III of dabcoHBr and phase V of dabcoHI are isostructural and they both exhibit giant dielectric response, coveted for electronic applications.^{5,6} However, there are no structural similarities whatsoever between dabcoHBr phases I and II and dabcoHI phases I, II, III, IV, VI, VII, VIII and IX.7 Properties of specific functional groups, and in particular their intermolecular and interionic aggregation, are fundamental for molecular biology and chemistry in general. Predictable behaviour of compounds and their functional groups are essential for understanding all dynamic processes, like those in living tissue, membrane transport or transformable molecules and aggregates. Here we report an indirect effect of Br and I anion switching of the hydrophilic and hydrophobic behaviour of a tertiary amine group. This phenomenon has been monitored in isostructural solvates of N-methyl-1,4-diazabicyclo[2.2.2]octanium iodide dimethanol (denoted dabcoCH₃I·2CH₃OH)⁸ and N-methyl-1,4-diazabicyclo[2.2.2]octanium bromide dimethanol (dabcoCH₃Br·2CH₃OH) with notably different H-bonding patterns, where the tertiary

amine group of $dabcoCH_3^+$ is either involved or excluded as the H-acceptor, respectively (Scheme 1).

Both the solvates were obtained in pressure-promoted reactions:

dabcoHX+3CH₃OH $\xrightarrow{p_{\rm T}}$ dabcoCH₃X·CH₃OH+H₂O (1)

where $p_{\rm T}$ is the reaction triggering pressure, 1.2 GPa for X = Br and 2.4 GPa for X = I.

At ambient conditions, unsolvated dabcoCH₃I was obtained in the reaction of dabco with CH₃I, and is applied as a structuredirecting agent in zeolite syntheses.⁹ Other quaternary-amine salts of dabco such as 1-butyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride, are ionic catalysts for Baylis–Hillman reactions.¹⁰ Both these reactions are examples of the quaternization of tertiary amines from alkyl halides known as the Menshutkin reaction,¹¹ which proceeds according to an S_N2 mechanism. To our knowledge, no dabcoCH₃Br syntheses and applications have been reported.

The crystals of dabcoCH₃Br·2CH₃OH and dabcoCH₃I· 2CH₃OH are less isostructural¹² than would appear from their formulae, identical except for exchanged homovalent halogen anions, with the same space-group symmetry, similar unit-cell dimensions and similarly located dabcoCH₃⁺ and Br⁻/I⁻ ions (Fig. 1).[‡] However, despite having the same solvent-accessible volume (Fig. 2), the hydrogen-bonding patterns and positions of methanol molecules are distinctly different. The most striking difference is that in dabcoCH₃I·2CH₃OH one methanol is OH···N hydrogen bonded to the tertiary amine N(4) of dabcoCH₃⁺, while



Scheme 1 Hydrogen-bonding patterns in dabcoCH₃I and dabcoCH₃Br methanol solvates.

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780, Poznań, Poland. E-mail: katran@amu.edu.pl; Fax: +48(61)8291505; Tel: +48(61)8291443

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Fig. 1 Structures of (a) $dabcoCH_3Br\cdot 2CH_3OH$ and (b) $dabcoCH_3I\cdot 2CH_3OH$, both at 1.2 GPa and projected down [010]. Hydrogen bonds are indicated by dotted lines. Two sites of disordered O(1M)H(1M) methanol atoms in $dabcoCH_3Br\cdot 2CH_3OH$ are superimposed in this projection.

in dabcoCH₃Br·2CH₃OH this amine does not form any hydrogen bonds (Fig. 1, Scheme 1). The apparent structural difference between these solvates, connected to the formation of OH····N bonds, is the reverse orientation of methanol molecules. In dabcoCH₃Br·2CH₃OH one methanol molecule is disordered and alternatively OH···Br⁻ bonded to two Br⁻ anions; this methanol also acts as the H-acceptor in an OH···O bond to the other methanol molecule (Fig. 1). In dabcoCH₃I·2CH₃OH one methanol molecule C(1M)H₃O(1M)H is O(1M)H(1M)···N(4) bonded to the cation only, and the other methanol molecule C(2M)H₃O(2M)H forms only one O(2H)H···I⁻ bond. Thus in dabcoCH₃I·2CH₃OH there are two separate differently H-bonded aggregates: CH₃OH···dabcoCH₃⁺, and CH₃OH···I⁻.

It is remarkable that in both dabcoCH₃X·2CH₃OH solvates the interionic N1…N1, N4…N4, and X⁻…N1/N4 distances are nearly identical, while the X⁻…X⁻ distances differ by over 1.5 Å. The contacts of larger I⁻ anions and methyl C(7)H₃ are about 0.7 Å shorter than the sum of the van der Waals radii (1.2 Å for H, 1.85 Å for Br⁻ and 1.98 Å for I⁻ according to Bondi¹³), while analogous distances of the smaller Br⁻ anion in dabcoCH₃Br·2CH₃OH are about 0.1 Å longer than the sum of the van der Waals radii (Table S2 in the ESI†).

We attempted to destabilize the H-bonding patterns in the solvates by changing the pressure of dabcoCH₃I·2CH₃OH between 1.0 and 2.4 GPa, and of dabcoCH₃Br·2CH₃OH between 1.2 and 1.7 GPa. However, in both these pressure ranges the structures compressed monotonically and their H-bonding patterns remained unaffected. It was found that the two pressure magnitudes triggering the N-methylation reaction compress the solvates to approximately equal formula-unit volumes of 288 Å³ calculated as the unit-cell volume divided by the number of formula units, as shown in Fig. 3. At the same pressure of 1.2 GPa, the formula unit of dabcoCH₃Br·2CH₃OH is smaller by *ca*. 17 Å³ than that of dabcoCH₃I·2CH₃OH. This volume difference is smaller than the molecular-volume difference between dabcoHI⁴ and dabcoHBr³ at 0.1 MPa/296 K, equal to 27 Å³, but nearly identical to that at 0.4 GPa.



Fig. 2 Solvent-accessible volumes in the structures of (a) dabcoCH₃Br·2CH₃OH and (b) dabcoCH₃I·2CH₃OH at 1.2 GPa calculated by the Mercury¹⁴ program without the methanol molecules in the structure. The probing radius of 0.5 Å yielded similar void volumes of 107.9 and 107.3 Å³ per unit cell (19.0 and 17.6%), respectively.



Fig. 3 The formula-unit volume V/Z (Table S1[†]) as a function of pressure for dabcoCH₃I·2CH₃OH and dabcoCH₃Br·2CH₃OH. The lines joining the points have been drawn to guide the eye. p_T is the methylation triggering pressure (eqn (1)).

It appears that the hydrophilic behaviour of the tertiary amine in dabcoCH₃I·2CH₃OH and hydrophobic behaviour in dabcoCH₃Br·2CH₃OH is due to a weaker affinity of the I⁻ anions to the hydroxyl H-atoms of methanol than that of Br⁻. Hence, I⁻ binds to one methanol molecule and the other methanol is OH…N bonded to the dabcoCH₃⁺ cation. In dabcoCH₃Br·2CH₃OH the Br⁻ anion attracts both the methanol molecules in this way so that one methanol molecule is directly OH…Br⁻ bonded, and the other methanol is OH…O bonded to the first mediating methanol. The CH₃OH… (CH₃)OH…Br⁻ aggregates engage all the hydroxyl H-donors and consequently no H-bond can be formed to the tertiary amine of dabcoCH₃⁺. Thus this final effect can be associated with the competition between the H-acceptors of the methanol hydroxyl (this H-bonded to Br⁻) and amine N(4).

Our survey of the Cambridge Structural Database (version 1.14)¹⁵ revealed five crystal structures (refcodes: UNICIC, DAJVIV, VIBQUT, YASLOU, HUWLAN) containing the Br⁻ anion and two methanol molecules hydrogen-bonded exactly as in dabcoCH₃Br·2CH₃OH (Scheme 1), whereas only one structure of an analogous aggregate involving the iodide anion has been found (refcode WEPLEI). In this only aggregate of the I⁻ anion, one methanol molecule forms bifurcated bonds to I⁻ and the second methanol molecule. We have also found 4 solvate crystals where methanol is OH…N bonded to an amine nitrogen in the presence of a Br⁻ anion, and 4 structures with I⁻ anions. There are no isostructural relations between any of those structures, analogous to those between dabcoCH₃Br·2CH₃OH.

The effect of hydrophobic and hydrophilic behaviour of the tertiary amine in dabcoCH3Br·2CH3OH and dabcoCH3I·2CH3OH solvates can be attributed to the balance between affinities of anions and the tertiary amine of dabcoCH₃⁺ to hydroxyl H-atoms of methanol molecules, the only H-donors in these solvates. The hydrogen bonding pattern can also be due to the difference in anionic radii (1.96 Å for Br^- and 2.20 Å for I^- , according to Goldschmidt). The resemblance of structures dabcoCH₃Br·2CH₃OH and dabcoCH₃I·2CH₃OH arises from the fact that the methanol molecule in reversed orientations occupies similar volume and requires no symmetry changes. Hence, despite different H-bonding patterns, similar anions, the same cations and methanol molecules are similarly packed in the compressed crystal space. Therefore the different H-bonding patterns can be associated with the anions only, and not with the influence of the crystal environment. On the other hand, the modified H-bonding pattern considerably affects the crystal packing and unit-cell dimensions. To our knowledge this is the first report on a remote Br- and I- anion exchange effect switching the H-bonding pattern involving a tertiary amine. It shows that the hydrophilicity effect of ions can be considerably longer in range than is currently believed, and that the ions do not have to be directly involved in the hydrogen bonds that they modify.

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Notes and references

‡ Crystal data for: **dabcoCH₃Br·2CH₃OH at 296 K/1.2 GPa** (CCDC 869507), monoclinic space group $P2_1/m$, a = 9.270(2) Å, b = 6.7304(13) Å, c = 9.710(4) Å, $\beta = 107.60(4)^\circ$, V = 577.5(3) Å³, Z = 2, D = 1.560 g cm⁻³, GOF on F^2 1.167, R_1 (all data) = 0.0984; **dabcoCH₃Br·2CH₃OH at 296 K/1.7 GPa** (869508), monoclinic space group $P2_1/m$, a = 9.194(4) Å, b = 6.653(3) Å, c = 9.643(9) Å, $\beta = 107.72(7)^\circ$, V = 561.9(6) Å³, Z = 2, D = 1.603 g cm⁻³, GOF on F^2 1.137, R_1 (all data) = 0.1801; **dabcoCH₃I·2CH₃OH at 296 K/1.0 GPa** (869509), monoclinic space group $P2_1/m$, a = 9.059(3) Å, b = 6.7868(17) Å, c = 10.543(4) Å, $\beta = 108.28(3)^\circ$, V = 615.5(3) Å³, Z = 2, D = 1.717 g cm⁻³, GOF on F^2 1.178, R_1 (all data) = 0.0277; **dabcoCH₃I·2CH₃OH at 296 K/1.2 GPa** (869510), monoclinic space group $P2_1/m$, a = 9.040(3) Å, b = 6.7500(9) Å, c = 10.516(3) Å, $\beta = 108.45(3)^\circ$, V = 609.5(3) Å³, Z = 2, D = 1.734 g cm⁻³, GOF on F^2 1.676, R_1 (all data) = 0.0486; **dabcoCH₃I·2CH₃OH at 296 K/2.4 GPa** (869510), monoclinic space group $P2_1/m$, a = 9.040(3) Å, b = 6.7500(9) Å, c = 10.516(3) Å, $\beta = 108.45(3)^\circ$, V = 609.5(3) Å³, Z = 2, D = 1.734 g cm⁻³, GOF on F^2 1.676, R_1 (all data) = 0.0486; **dabcoCH₃I·2CH₃OH at 296 K/2.4 GPa** (869510), monoclinic space group $P2_1/m$, a = 8.879(3) Å, b = 6.6161(9) Å, c = 10.328(3) Å, $\beta = 108.81(3)^\circ$, V = 574.3(2) Å³, Z = 2, D = 1.840 g cm⁻³, GOF on F^2 1.394, R_1 (all data) = 0.0590.

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