Conformational effects in molecular tectons containing protonated benzimidazole cations†‡

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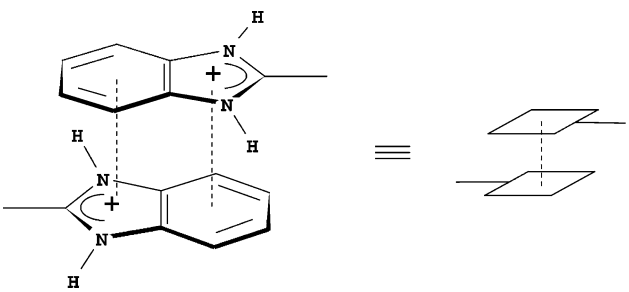
The conformational preferences of protonated 2-benzimidazole cations have been modelled. Non-alkylated benzimidazoles show no strong conformational preferences, but methylation at the N1 position leads to high rotational barriers. The crystal structures are reported for five salts of protonated cations where two or three benzimidazoles are linked by ethylene or cyclohexyl spacers and for one copper(I) complex of a bis-benzimidazole ligand. The conformations observed in the solid state agree with the models. Stacking between benzimidazoles is observed in all cases but one where a high symmetry structure involving six edge-to-face interactions is preferred. Hydrogen bonding to anions or solvent molecules is observed for all salts of protonated benzimidazoles. The packing coefficients of the structures show small but significant variations.

Introduction

The reliable prediction *ab initio* of the crystal structure of any compound is generally agreed to be impossible at present.[1] Progress towards this goal is however being made by theoretical developments,[2,3] and by experimental studies, largely centred around the modification of molecules with known crystal structures with the object of modifying the packing in a more or less predictable way. An important conceptual advance was made by Desiraju[4] who introduced the notion of the supramolecular synthon, a link between two molecules associated with the interaction between two functionalities, one on each molecule. One may thus dissect a crystal structure in terms of the supramolecular synthons which link the molecules into a three-dimensional network. Searches of crystallographic databases have allowed estimation of the frequency with which a given synthon is observed and thus of its robustness. Most recognised synthons are easily understood in terms of the current theory of intermolecular forces. The identification of a synthon allows its incorporation into a new molecule (or rather pair of molecules) with a reasonable hope that the associated link will be observed in the crystal structure. A molecule which contains two or more synthons and for which the association mode may be predicted is often referred to as a molecular tecton[5–7] which can be regarded as an intelligent building block in that it can assemble into an extended crystal structure in a predictable way.

We have previously shown that protonated benzimidazoles show a strong tendency to stack in a head-to-tail arrangement in the solid state as shown in Scheme 1,[8] with the protonated imidazole moiety above the electron-rich phenyl fragment. The benzimidazoles may further show hydrogen bonding through the N–H functions, and in the tetrahalogenometallate salts studied N–H···Cl–M hydrogen bonding[9] was observed.

In systems with two benzimidazole functions the stacking directions will depend on their relative orientations (Scheme 2), and consequently upon the conformation adopted by the benzimidazole ring with respect to the organic spacer. The control of the conformation of the bis-benzimidazole cation can thus control the dimensionality of the crystal, two parallel benzimidazoles leading to a layered structure (Scheme 2b), while non-parallel benzimidazoles show stacking in two distinct orientations, and lead to three-dimensional arrangements (Scheme 2c and 2d). We show here how the conformation of bis-benzimidazole cations may be modified by the nature of the organic spacer and by *N*-methylation of the benzimidazole. We were aware of no studies of the conformation of 2-substituted benzimidazoles and consequently have undertaken



Scheme 1

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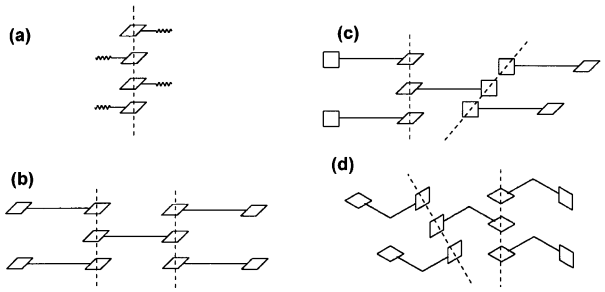
† Electronic supplementary information (ESI) available: Table S1: details of hydrogen bonding in crystal structures. Figures showing atomic numbering. Details of crystal structures as .cif files. See DOI: 10.1039/b602468h

‡ Dedicated to Professor Jacques Weber on the occasion of his retirement.



Scheme 2 The dependence of the stacking upon the relative orientation of benzimidazoles.

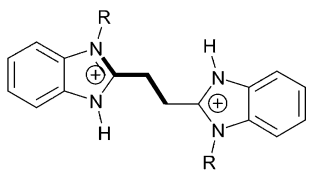
a short theoretical study of the question. Crystal structures of a number of benzimidazole cations were then determined in order to confirm the conclusions of the theoretical study.

Results

Conformational studies

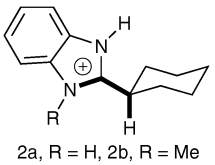
The benzimidazole cations studied here possess conformational freedom, and the conformation which is adopted will influence the structure of the crystalline product. We have studied the case of 1,2-bis(benzimidazol-2-onium)ethane, and that of benzimidazole cations bonded to cyclohexane rings. We have equally studied the effect of *N*-methylation of the benzimidazole. The general method was to optimise the geometry of the molecule studied by molecular mechanics with MM+[10] then carry out a single point semi-empirical calculation using AM1[11] to obtain atomic charges. These charges were injected into MM+ to complete geometry optimisation. The rotation barrier was then calculated using fixed charges. We also carried out calculations at a higher level with a number of methods (SCF and DFT) on the model system 2-isopropylimidazolonium, and the results showed good agreement with those obtained by the simpler method presented above. For the purposes of this study we have examined only the torsion about the bond linking the benzimidazole to the organic spacer (Scheme 3). A bis-benzimidazole cation will thus be characterised by two such torsion angles. We have not considered in this work the conformational effects in the organic spacer.

For the simple cation **1a** we would not expect a large rotational barrier and this is confirmed by the results. Minima are found at torsion angles of 90° and 270°, and the maxima are at 0° and 180°. The calculated barrier is only 2.8 kJ/mol, close to kT at room temperature. *N*-Methylation of the benzimidazoles changes both the barrier and the preferred



1a, R = H, 1b, R = Me

Scheme 3 1,2-Bis(benzimidazol-2-onium)ethane. The bonds used to define the torsion angle are shown in bold.



2a, R = H, 2b, R = Me

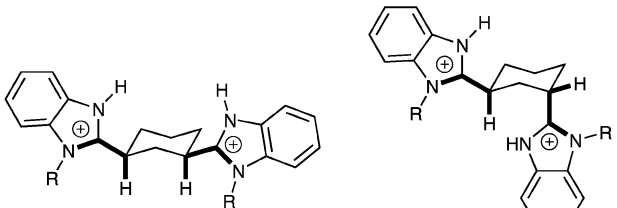
Scheme 4 (Benzimidazol-2-onium)cyclohexane. The bonds used to define the torsion angle are shown in bold. The *syn*-conformation is shown.

conformation. The minimum is now found at a torsion angle of 180°, and the maximum at 0°, with an energy of 16.4 kJ/mol. We conclude that the methylation of a benzimidazole nitrogen may be used to control the conformation.

The cyclohexane compound **2a** (Scheme 4) again shows a low barrier to rotation of roughly 2 kJ/mol, the minimum corresponding to the plane of the benzimidazole lying almost in the plane of symmetry of the molecule, with torsion angles of 0° or 180°. Methylation in **2b** increases the barrier to 20 kJ/mol with a maximum for torsion angles close to 110° and 250°. The minima now correspond to torsions of 30–45° and 315–330° where the methyl group is turned slightly away from the axial hydrogen of the cyclohexane. The *anti*-conformation lies some 7.5 kJ/mol above the minimum.

There are two possibilities for 1,3-disubstituted cyclohexanes **3** and **4** (Scheme 5). The *cis*-diastereomer **3a** shows no major differences from **2a** and may rotate freely at room temperature: the most unfavourable conformation is 12 kJ/mol above the minimum, and the lowest pathway for rotation requires only 2.5 kJ/mol. Methylation (**3b**) again locks the conformation into the *syn–syn* arrangement shown in Scheme 5, and the barrier is now significantly higher (39 kJ/mol for the lowest energy pathway). The *anti*-conformation lies about 12 kJ/mol above the minimum. The *trans*-diastereomer shows significant differences. In **4a** rotation of the equatorial benzimidazole is similar to the previous cases **2a** and **3a**, but rotation of the axial benzimidazole is hindered with a barrier of over 120 kJ/mol. The minimum energy is found for values around 90° and 270°. In the methylated molecule **4b** the conformation of the axial benzimidazole is essentially locked with torsion angles in the range −60° to +60° only accessible. This results in the methyl group of the axial benzimidazole being directed away from the cyclohexane ring. The *syn*-conformation is again favoured for the equatorial benzimidazole with the *anti*-conformation some 20 kJ/mol higher.

We may conclude from these calculations that the non-methylated benzimidazolonium cations show no strong con-



3a, R = H; 3b, R = Me 4a, R = H; 4b, R = Me

Scheme 5 Disubstituted cyclohexanes: the *cis*-diastereomer is shown left and the *trans*- on the right.

Table 1 Details of X-ray crystal structure determinations

	[**1b**H_2][$MnCl_4$]	[**3b**H_2]Cl_2 0.5 CH_3CN	[**3b**H_2][$MnCl_4$] H_2O	[Cu(**4b**)$_2$](PF_6) CH_3CN	[**5a**H_3]$Cl_3 \cdot 2MeOH$	[**5b**H_3]$Br_3 \cdot 4H_2O$
Formula	$(C_{18}H_{20}N_4)MnCl_4$	$(C_{22}H_{26}N_4)Cl_2$ $(C_2H_3N)_{0.5}$	$(C_{22}H_{26}N_4)$ $MnCl_4(H_2O)$	$[Cu(C_{22}H_{24}N_4)_2]$ $(PF_6)(C_2H_3N)$	$(C_{27}H_{27}N_6)Cl_3$ $(CH_4O)_2$	$(C_{30}H_{33}N_6)Br_3$ $(H_2O)_4$
M	489.1	437.7	561.3	938.5	606.0	789.5
Diffractometer	Stoe STADI4	Stoe STADI4	Stoe IPDS	Stoe STADI4	Stoe STADI4	Stoe IPDS
System	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Trigonal
a (Å)	16.640(1)	15.483(3)	9.5492(8)	25.217(2)	8.5221(7)	16.6939(9)
b (Å)	13.269(1)	12.705(1)	9.8088(9)	23.274(2)	11.804(1)	16.6939(9)
c (Å)	18.770(1)	23.177(2)	14.7179(13)	15.056(4)	14.884(1)	20.5208(11)
α (°)	90	90	84.185(10)	90	90	90
β (°)	90	90.971(8)	86.801(10)	90	95.929(7)	90
γ (°)	90	90	65.969(9)	90	90	120
V (Å^3)	4144.3(5)	4559(1)	1252.4(2)	8836(3)	1489.2(2)	4952.7(5)
T (K)	200	200	200	220	200	200
Space group	*Cmca*	$P2_1/c$	$P\bar{1}$	*Pbca*	$P2_1$	$R\bar{3}$
Z	8	8	2	8	2	6
μ (mm^{-1})	10.015 (Cu(Kα))	2.693 (Cu(Kα))	0.98 (Mo(Kα))	1.635 (Cu(Kα))	3.088 (Cu(Kα))	3.71 (Mo(Kα))
Ref. measured	2633	5679	19221	5430	3845	22725
R_{int}	0.048	0.051	0.046	[a]	0.040	0.087
Observed	1148	3676	3418	3240	3258	1505
No. variables	158	533	301	585	386	140
$R(F)$	0.046	0.066	0.029	0.088	0.051	0.028
$wR(F)$	0.044	0.062	0.030	0.074	0.049	0.028
S(all)	1.58(3)	1.25(1)	1.17(1)	1.22(1)	2.47(4)	1.12(2)
Flack param.					0.01(3)	
Solution	Multan87	Multan87	SIR97	Multan87	Multan87	SIR97
Packing coeff.	0.676	0.662	0.663	0.656	0.686	0.689

[a] Only one octant was measured.

formational preference (with the exception of axial substituents on cyclohexane), but that methylation generally favours one particular conformation. In bis-benzimidazolonium cations this allows one to control the relative orientation of the hydrogen bond donors.

Crystal structures

Details of the crystal structure determinations are given in Table 1.

Crystal structure of [1bH$_2$][MnCl$_4$]. The crystal structure of non-methylated [**1a**H_2][$MnCl_4$] was reported in our earlier publication[8] and showed the [**1a**H_2]$^{2+}$ cation to lie on a twofold axis and to adopt a stepped conformation. The torsion angle is 114.4(5)°. The mutual inclination of the planes of 50.5° allowed chelation of the [$MnCl_4$]$^{2-}$ anion by hydrogen bonds, and led to the development of stacking interactions in two directions, leading to a three-dimensional structure. In methylated [**1b**H_2][$MnCl_4$] the two halves of the cation are again related by a twofold symmetry axis. The cation adopts the *trans* conformation predicted by molecular mechanics, with a torsion angle of 179.9(5)°, and is essentially planar with the two benzimidazole planes inclined at 5.9°. As a result of this there is only one stacking direction possible. The cations lie in the *ac* plane with their long axis roughly along *c*, and the stacking along *b*, leading to brickwork type layers (Fig. 1). The pairs of stacked benzimidazoles are almost coplanar (interplane angle 3.89(3)°) with a mean interplane distance of 3.331 Å.

The tetrahedral [$MnCl_4$]$^{2-}$ anions lie between the layers on a plane of symmetry (Fig. 2). The methylation of the cation reduces the number of hydrogen bond donors and each cation can form only two hydrogen bonds instead of four for

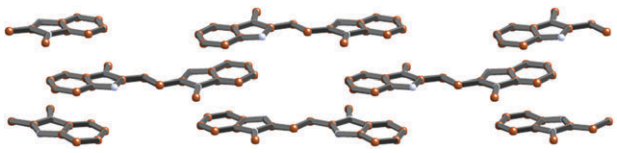


Fig. 1 Stacking of cations in [**1b**H_2][$MnCl_4$].

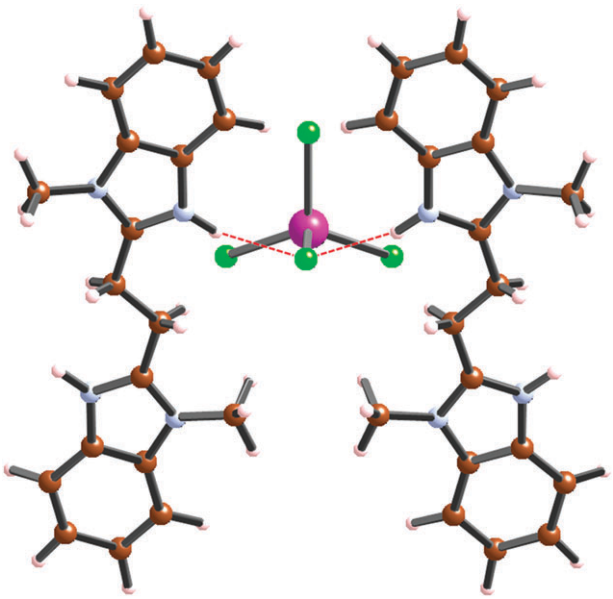


Fig. 2 N–H···Cl···H–N hydrogen bonds link layers of cations in [**1b**H_2][$MnCl_4$]. The drawing is tilted slightly to show the hydrogen bonds.

$[\mathbf{1a}H_2]^{2+}$. Cl1 forms two hydrogen bonds to H1 atoms on different cations (distance 2.34(5) Å) and thus links the layers together. Cl2 shows short intermolecular distances which may be weak hydrogen bonds to a methyl hydrogen (2.57(2) Å) and an aromatic hydrogen (2.61(5) Å). The hydrogen bonding to Cl1 appears to influence the Mn–Cl bond which is significantly longer (2.413(2) Å) than the other two (2.340(1) and 2.358(2) Å). Although there is less hydrogen bonding than in $[\mathbf{1a}H_2][MnCl_4]$, the packing coefficient is significantly greater (0.676 compared to 0.650).

Crystal structures of $[\mathbf{3b}H_2]Cl_2$ 0.5 CH_3CN and $[\mathbf{3b}H_2][MnCl_4]H_2O$. Two salts of the cation $[\mathbf{3b}H_2]^{2+}$ were studied. In $[\mathbf{3b}H_2]Cl_2$ 0.5 CH_3CN there are two crystallographically independent cations. In one the torsion angles defined above are close to 0°, and in the other the benzimidazoles are tilted in such a way as to maintain a plane of symmetry, with torsion angles of roughly ±36°. The results of the modelling above suggest that torsion angles below 45° lie within 1 kJ/mol of the minimum, and so the two forms would not differ greatly in energy. The cations stack together as shown below to give zigzag chains along the *c* axis (Fig. 3). The mean stacking distances are 3.42 and 3.59 Å and the interplanar angles 8.15(3) and 7.33(2)°, respectively. The protonated benzimidazoles are hydrogen bonded to chloride ions. Two molecules of acetonitrile are found in a cavity formed by four cations around a centre of inversion.

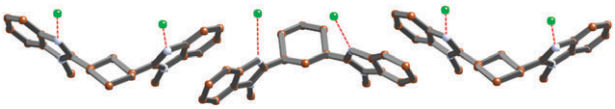


Fig. 3 Packing of two non-equivalent cations to form zig-zag chains in $[\mathbf{3b}H_2]Cl_2$ 0.5 CH_3CN. The *c* axis runs horizontally. Each N–H function is hydrogen bonded to a chloride.

In $[\mathbf{3b}H_2][MnCl_4]H_2O$ the cations adopt a quite different conformation: the benzimidazoles are both tilted by +46°. This leads to stacking in two roughly perpendicular directions. The structure may best be described as formed from dimers linked by a stacking interaction between two cations along the *b* axis (mean distance 3.374(10) Å). The dimers are then assembled into layers by a second stacking along the *a* axis (separation 3.409(8) Å) (Fig. 4). In both cases the planes are related by a centre of inversion and are thus parallel. The offset of the benzimidazoles results in two C–H bonds of the cyclohexyl fragments lying close to the plane of the benzimidazole, and roughly above the centre of a phenyl moiety (distance from plane *ca.* 2.8 Å) suggesting a possible C–H···π interaction. The $[MnCl_4]^{2-}$ anions are held in the structure by hydrogen bonds, but only one chloride is H-bonded to a benzimidazole. Two others form hydrogen bonds to the water molecule which in turn acts as a hydrogen bond acceptor for the second protonated benzimidazole. The Mn–Cl distances for the three chloro-ligands involved in hydrogen bonding (2.3810(9), 2.3724(7), 2.3894(8) Å) are significantly longer than the fourth (2.3499(9) Å).

Crystal structure of $[Cu(\mathbf{4b})_2](PF_6)\cdot CH_3CN$. This compound is slightly different in that it is a complex of copper(I)

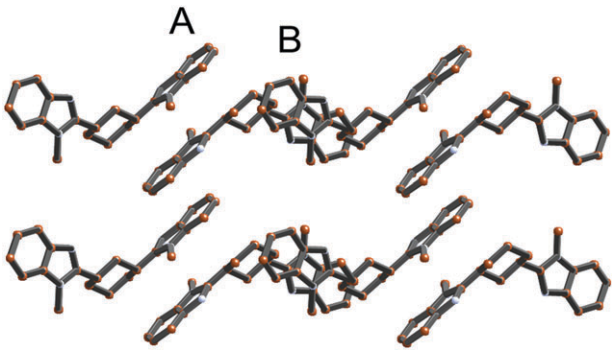


Fig. 4 Packing of cations in $[\mathbf{3b}H_2][MnCl_4]H_2O$. The stacking interaction denoted A runs along the *a* axis (vertical), while that denoted B involves only a pair of benzimidazoles along the *b* axis.

rather than a protonated benzimidazole. The structure of the $[Cu(\mathbf{4b})_2]^+$ cation is shown in Fig. 5. The two ligand molecules are quite similar. The equatorial benzimidazoles adopt a basically *syn* conformation with torsion angles of +34 and +39°, while the two axial benzimidazoles show torsions of −47 and −50°. These values lie within the energetically accessible regions deduced from the modelling studies.

The cations are organised in sheets (Fig. 6) in the *ab* plane and show an interesting stacking arrangement. The coordinated equatorial benzimidazole of one ligand stacks with the uncoordinated axial benzimidazole of a neighbouring complex. The stacking distances lie between 3.6 and 3.9 Å, and the interplane angles between 4.9 and 11.3°. Each complex thus participates in four stacking interactions and may be regarded

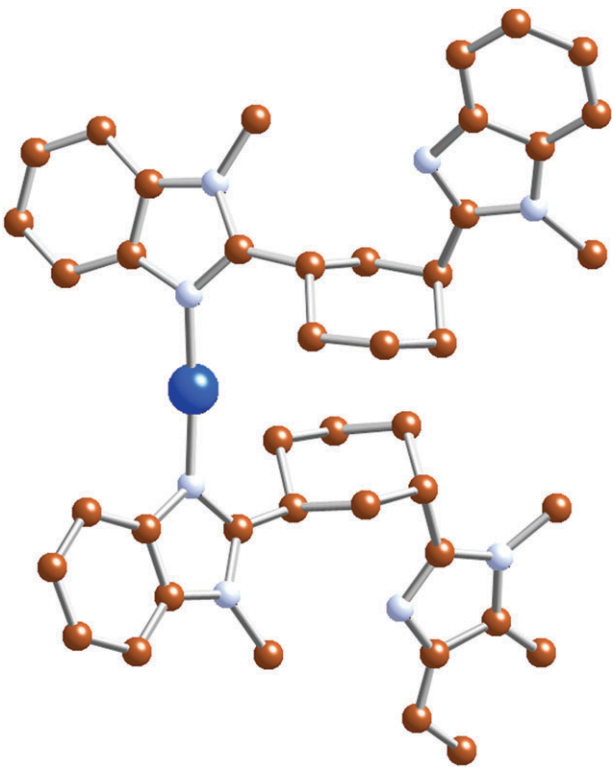


Fig. 5 Structure of the cation $[Cu(\mathbf{4b})_2]^+$ with hydrogens omitted for clarity. The stereoisomer shown has the configuration *S*-[Cu(*RR*-**4b**)$_2$].

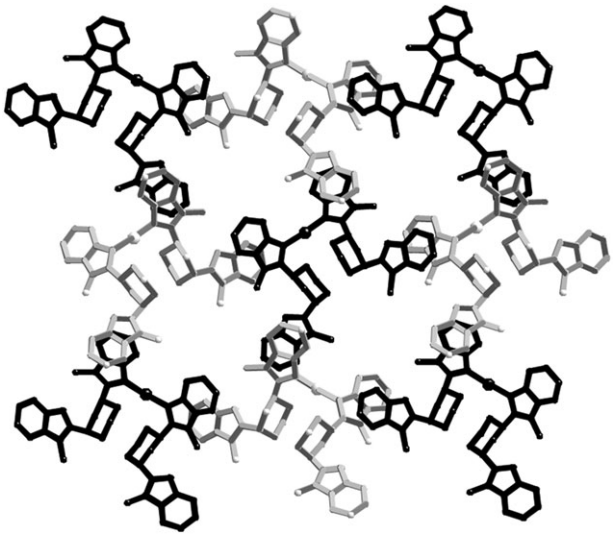


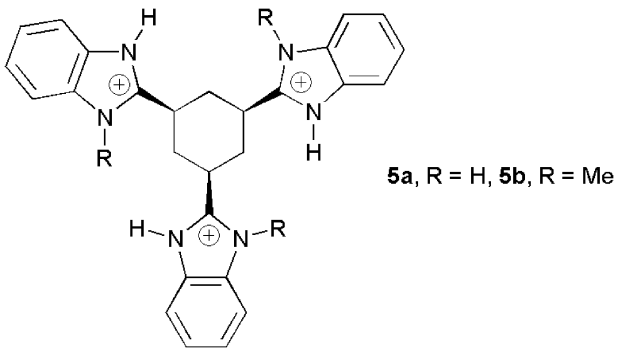
Fig. 6 The weaving of the $[Cu(\mathbf{4b})_2]^+$ cations showing the four stacking interactions of each cation. The view is down the *c* axis.

as a fourfold node. Molecules along the *b* axis are related by a twofold screw axis, and those along the *a* axis by a glide plane. Following along one of these axes the complexes are alternately the upper and lower partners in the stack, leading to a woven topology. As can be seen from the figure, it is a rather open weave. The sheets stack on top of each other so that a channel runs parallel to the *c* axis, and the channels are occupied by PF_6^- anions (which are disordered) and an acetonitrile molecule. There are some edge-to-face interactions between the sheets.

Crystal structure of $[\mathbf{5a}H_3]Cl_3 \cdot 2MeOH$. As an example of a non-methylated benzimidazole bound to a cyclohexane ring we have studied the 1,3,5 trisubstituted derivative **5a** in the form of its tris-hydrochloride salt (Scheme 6).

The cation adopts a conformation with the three benzimidazoles inclined with respect to the least squares plane passing through the six carbon atoms of the cyclohexane ring by 45.0, 21.6, and 22.8° (Fig. 7). The third benzimidazole is tilted in the opposite sense to the other two and this allows the formation of a chelating pair of hydrogen bonds to Cl3.

The cations are linked by stacking between benzimidazoles 2 and 3 into ribbons along the *a* axis. The cations are also linked



Scheme 6

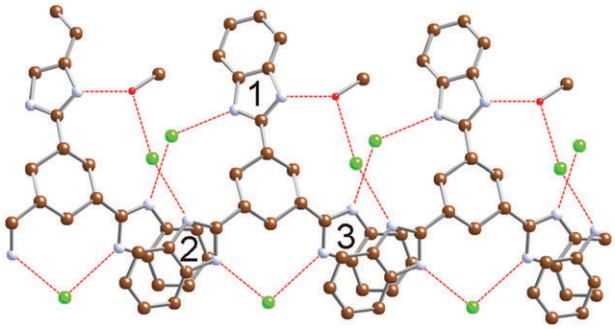


Fig. 7 Structure of $[\mathbf{5a}H_3]Cl_3 \cdot 2MeOH$ looking down *b* and showing the stacked ribbons along the *a* axis (horizontal).

by Cl1 which hydrogen bonds to benzimidazole NH functions on adjacent molecules and a N–H···O–H···Cl2···H–N interaction involving one of the methanols of solvation. The ribbons are related by a twofold screw axis along *b* which results in the development of stacking between benzimidazole 1 on one ribbon and benzimidazoles 2 and 3 on the two neighbouring ribbons. One possible C–H···π interaction between a cyclohexyl hydrogen and a benzimidazole plane is observed. The tilting of the benzimidazoles renders the cation chiral (although the racemization barrier is very low), and we may note that the salt crystallises in the non-centrosymmetric group $P2_1$, and thus undergoes resolution upon crystallization.

Crystal structure of $[\mathbf{5b}H_3]Br_3 \cdot 4H_2O$. The cation $[\mathbf{5b}H_3]^{3+}$ adopts a propeller-like structure and lies on a crystallographic three-fold axis (Fig. 8). The benzimidazoles show the expected *syn*-conformation with a torsion angle of 50°. No stacking

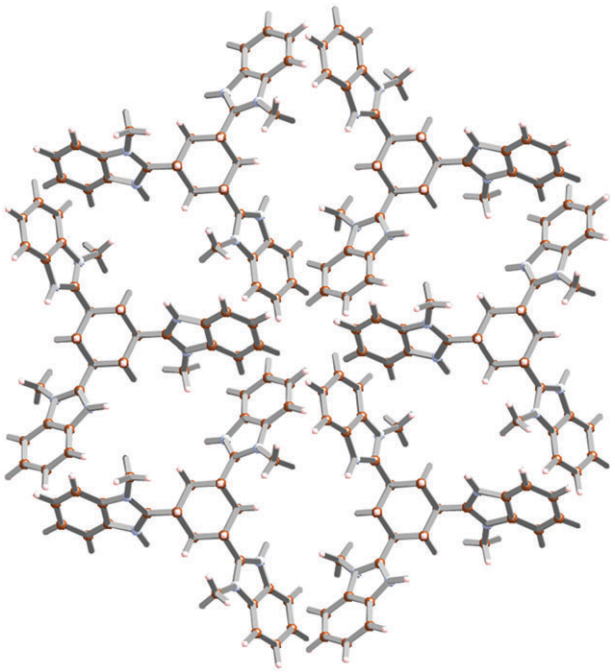


Fig. 8 Structure of the cation $[\mathbf{5b}H_3]^{3+}$ showing the sixfold phenyl embrace at the centre of the drawing.

interaction is observed, but the cations are arranged in sheets about the $\bar{3}$ axis in such a way as to show a 'sextuple phenyl embrace' involving six edge-to-face interactions. This type of interaction was first noticed by Dance and Scudder,[12] most frequently in complexes of PPh_3 and PPh_4^+ salts. To our knowledge this is the first occurrence of such a motif involving six different molecules. One of the aryl C–H bonds (H5) is directed roughly towards the centre of a neighbouring ring and lies 2.53 Å above the plane of the ring. The molecules show alternate *P* and *M* helicity, and the protonated benzimidazole functions are directed alternately above and below the sheets of the cations. Benzimidazoles in neighbouring sheets are parallel, and close (interplane distance close to 3.6 Å), but no significant overlap is observed.

The bromide anions do not interact directly with the cations, but hydrogen bond to water molecules which act as hydrogen bond acceptors from the protonated benzimidazole. A cluster of six symmetry related water molecules lies between the cyclohexane rings of neighbouring layers and is within hydrogen bonding distance of the bromide ions. This water cluster shows only partial occupation (Fig. 9).

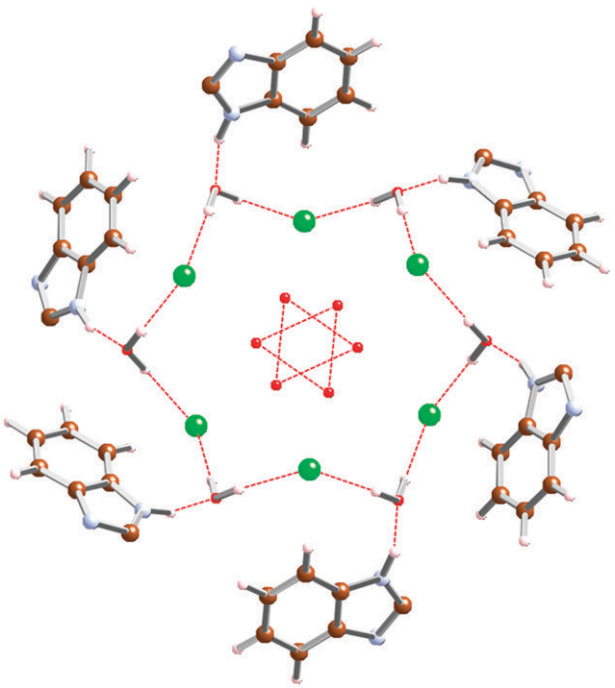


Fig. 9 The hydrogen bonding network of $[\mathbf{5b}H_3]Br_3 \cdot 3H_2O$. Bromides lie alternately above and below the plane of the six oxygen atoms of water molecules which are hydrogen bonded to benzimidazoles. In the centre of the figure there is a partially occupied cluster assumed to be water molecules directly registered with the cyclohexane rings of the cations.

Discussion

The molecular modelling results agree with the expected low rotational barriers for non-methylated benzimidazoles. Methylation, however, does significantly increase the barriers and leads to preferred conformations. In the case of the system with the ethylene spacer, this favours the adoption of a planar conformation by the cation, and in the cyclohexane systems the adoption of a *syn*-conformation. The theoretical results are in agreement with the observed crystal structures for $[\mathbf{1b}H_2][MnCl_4]$, $[\mathbf{3b}H_2]Cl_2$, and $[\mathbf{3b}H_2][MnCl_4]$ although in the last two compounds the flexibility is sufficient to allow stacking either in one direction ($[\mathbf{3b}H_2]Cl_2$) or two ($[\mathbf{3b}H_2][MnCl_4]$). This flexibility limits the predictability of the stacking shown by the $[\mathbf{3b}H_2]^{2+}$ cation. The stacking interaction of Scheme 1 is observed in five of the six structures reported here, including a slight modification where one of the benzimidazoles is complexed to Cu(I) rather than protonated.

Hydrogen bonding is always observed for the protonated benzimidazole, although in many cases it is not directly to the anion, but is relayed through a bridge of the form N^+–H···O–H···X^- where the intermediate hydroxyl function is supplied by water or an alcohol solvent. In $[\mathbf{5a}H_3]Cl_3$ the low barrier to rotation for the non-methylated benzimidazole allows the adoption of a conformation forming a hydrogen bonded chelate between a chloride and two protonated benzimidazoles. If we compare the packing coefficients of $[\mathbf{1a}H_2][MnCl_4]$ and $[\mathbf{1b}H_2][MnCl_4]$ we may note that the reduction in the number of hydrogen bonds from four in $[\mathbf{1a}H_2][MnCl_4]$ to two in $[\mathbf{1b}H_2][MnCl_4]$ is not accompanied by any decrease in packing efficiency, indeed the contrary is true. We suspect that this may arise from the ease with which the planar cations may be packed in $[\mathbf{1b}H_2][MnCl_4]$.

At the beginning of this work we supposed that the tris-benzimidazolonium-cyclohexane systems would act as three-fold nodes, each cation showing three distinct stacks. This is the case in $[\mathbf{5a}H_3]Cl_3$ but the cation adopts a rather low symmetry conformation. In $[\mathbf{5b}H_3]Br_3$ no stacking at all is seen, each cation forming instead six C–H···π interactions which incidentally allow the retaining of a high degree of symmetry for the molecule in the crystal. We surmise that this may arise since the layer structures observed allow a closer packing, and in agreement with this, we note that these two structures show the highest packing coefficients of the compounds studied.

The crystal structure of $[Cu(\mathbf{4b})_2](PF_6) \cdot CH_3CN$ shows an unusual woven topology in which each $[Cu(\mathbf{4b})_2]^+$ cation is involved in four stacking interactions leading to a 'one over, one under' weave.[13] Woven structures are relatively rare in chemistry but have been reported for linear coordination chains[13,14] and for the complex of AuI with a long chain diphosphine where aurophilic interactions are important.[15] The stacking interactions here involve pairing of the coordinated benzimidazole, presumably slightly electron poor as a result of the coordination of copper, with the second benzimidazole where the conformation of the benzimidazole with respect to the cyclohexane ring is such as to preclude the approach of a metal ion, and whose electron density is thus presumably not depleted. Interestingly, this is the only structure without hydrogen bonding.

Finally, we may return to the question why the benzimidazole stacking interaction is not observed at all in $[\mathbf{5b}H_3]Br_3$. The absence of an interaction which is known to be favourable and when in principle it could be observed implies the compensation of the loss by some other interaction. This must be the weak van der Waals interactions between atoms.

Kitaigorodsky has argued that these forces are maximised by close packing[16] of molecules, and notably by the adoption of high coordination numbers by molecules in an organic solid. A major success of this approach is the prediction of which space groups will be most frequent, a prediction which agrees remarkably well with the observed distribution.[16,17] There is at first sight an apparent contradiction between this close packing approach and the synthon approach to crystal packing:[4] the first seeks to minimise the empty space in between molecules in a crystal, while the second concentrates on the links between pairs of molecules. Since most molecules carry only a limited number of functionalities which can participate in supramolecular synthons, the synthons alone will not lead to the high coordination numbers associated with crystal packing. The contradiction is of course only apparent: if the energies of the interactions are considered, strong to medium hydrogen bonds[18] will always dominate the weak van der Waals forces, and lead to synthon determined structures, but weaker interactions (such as the weak hydrogen bond[19]) may have energies comparable with the van der Waals forces.

If we accept the arguments of Kitaigorodsky, the extent of close packing may be measured by the packing coefficient, the sum of the molecular volumes in the unit cell divided by the cell volume. Although the packing coefficient was recently described as a useful crystal structure descriptor[17] it is virtually never quoted in routine crystal structure reports. We therefore calculated the packing coefficients for the structures reported here using Gavezzotti's method.[20] The range of values is quite small, from 0.656 to 0.689. The lowest coefficient is observed for $[Cu(\mathbf{4b})_2](PF_6)\cdot CH_3CN$ where the anion was found to be disordered and the solvent molecule showed rather high thermal motion. The two highest values (0.686 and 0.689) were found for the tris-benzimidazole-cyclohexane cations. These results are consistent with preferring a structure giving a closer packing rather than the expression of a rigidly directed synthon. Although the calculation of these coefficients requires a choice of van der Waals radii, they do offer a means of comparing packing in compounds with different compositions, and we believe that their use should be encouraged.

Conclusions

The conclusions of the modelling studies have been supported by the structural studies, and show the effect of *N*-methylation on conformation. We have recently shown how this may affect the coordination modes of other benzimidazole based ligands.[21] The resulting control of the conformation of the cations leads to modification of the crystal packing.

The stacked benzimidazole synthon of Scheme 1 has been observed in five of the six structures presented here. Together with the four examples given in our previous paper[8] this gives a 90% probability of observation, and further examples will be the object of a subsequent paper. It may therefore be assumed to be robust, but it should be borne in mind that a synthon has a probability and not a certainty of being observed in a crystal.[22,23] Aakeröy has discussed recently how conformational flexibility can facilitate the synthesis of solids but limit the predictability of structure,[24] and the residual conformational freedom observed in the cations here confirms this.

Experimental

General

Solvents and starting materials were purchased from *Fluka AG* (Buchs, Switzerland) and were used without further purification unless otherwise stated. Dimethylformamide (DMF) was distilled from CaH_2. UV-Vis spectra: *Cary IE* or *Perkin-Elmer Lambda-5* UV/VIS/NIR spectrometers; quartz cells of 1 or 0.1 cm path lengths; λ_{max} (ε) in nm. IR spectra: *Perkin-Elmer Spectrum-One* or *883* instruments, KBr discs; ν in cm^{-1}. NMR spectra: *Varian Gemini-300* or *Bruker Advance-400* machines at 300 (or 400) (^1H) and 74.44 MHz (^{13}C) at 22 °C; chemical shifts δ in ppm with respect to $SiMe_4$, J in Hz. MS: electron impact at 70 eV with *VG 7000E* and *Finnigan 4000* instruments, electrospray ionisation (ESI) with *Finnigan MatSSQ7000* instrument of the Mass Spectrometry Laboratory, University of Geneva; in m/z (rel. %). Elemental analyses were performed by Dr H. Eder, University of Geneva.

Synthesis of compounds

1,2-Bis(*N*-methyl-benzimidazol-2-yl)ethane (1b). To 1,2-bis (benzimidazol-2-yl)ethane[8] (3.00 g, 11.5 mmol) in freshly distilled dry dimethylformamide (DMF, 200 cm^3) at −10 °C was added sodium hydride (55–60% dispersion in oil, 0.9 g, 23 mmol) under a nitrogen atmosphere. The suspension was stirred overnight to yield a clear solution and methyl iodide (3.27 g, 23.0 mmol) was carefully added. The suspension was stirred under a nitrogen atmosphere for a further 24 h at room temperature. The dimethylformamide was removed under reduced pressure and water (100 cm^3) was added to the brown residue which was extracted with chloroform (5 × 50 cm^3). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered and reduced *in vacuo* where a white solid precipitated. Diethyl ether (200 cm^3) was added to ensure complete precipitation of the product which was filtered and recrystallised from ethanol to yield a pure white solid. Yield (2.47 g, 74%); ^1H NMR (300 MHz, D_2O) δH 7.52 (m, 4H, Ar), 7.17 (m, 4H, Ar), 3.79 (s, 6H), 3.46 (s, 4H); ^{13}C NMR (75 MHz, D_2O) δC 154.4, 142.1, 135.9, 121.4, 121.1, 118.2, 109.7, 29.4, 24.0.

1,2-Bis(*N*-methyl-benzimidazol-2-yl)ethane dihydrochloride ((1bH$_2$)Cl$_2$). 1,2-Bis(*N*-methyl-benzimidazol-2-yl)ethane (2.034 g, 7.01 mmol) was dissolved in the minimum amount of ethanol at room temperature and conc. hydrochloric acid was added until the first signs of precipitation whilst controlling the temperature at *ca.* 25 °C. The solution was left at −20 °C overnight and the resulting pale green precipitate was filtered, washed with diethyl ether and dried under vacuum at 60 °C. Yield (1.397 g, 55%); Found: C, 52.2; H, 5.8; N, 13.5. $C_{18}H_{18}N_4\cdot 2HCl\cdot 3H_2O$ requires C, 51.8; H, 6.3; N, 13.4%. IR (KBr, ν_{max}/cm^{-1}) 3251br,s, 1630m, 1564m, 1533s, 1488s, 1463s, 1408w, 1328w, 1254w, 1200w, 1166w, 1141w, 1103w, 956w, 907m, 863w, 767s, 661m, 548m, 442m cm^{-1}. ^1H NMR (300 MHz, D_2O) δH 7.85 (m, 2H, Ar), 7.78 (m, 2H, Ar), 7.67 (m, 4H, Ar), 4.08 (s, 6H), 3.91 (s, 4H); ^{13}C NMR (75 MHz, D_2O) δC 149.8, 132.7 (C^9), 130.0, 126.9, 126.5.

Manganese(II) 1,2-bis-(*N*-methyl-benzimidazol-2-yl)ethane tetrachloride, [1bH$_2$][MnCl$_4$]. A solution of manganese(II) dichloride tetrahydrate (0.083 g, 0.42 mmol) in ethanol (10 cm^3) was added to 1,2-bis(*N*-methyl-benzimidazol-2-yl)ethane dihydrochloride (0.151 g, 0.42 mmol) in hot ethanol (20 cm^3). The resulting white precipitate was filtered, washed with diethyl ether and air dried. The product was recrystallised by vapour diffusion of diethyl ether into a saturated methanolic solution of the complex to yield clear cubic like crystals. The crystals were dried under vacuum at 60 °C. Yield (0.149 g, 73%); Found: C, 44.5; H, 4.2; N, 11.5. $C_{18}H_{20}N_4 \cdot MnCl_4$ requires H, 4.1; N, 11.5%. IR (KBr, ν_{max}/cm^{-1}) 3300–2700brs, 1623m, 1555s, 1531s, 1481s, 1466s, 1418m, 1366w, 1322w, 1293w, 1252w, 1157w, 1130w, 1102w, 1007w, 918w, 863w, 772s, 748w, 723w, 669w, 552w, 433w.

1,3-Bis-(benzimidazol-2-yl)cyclohexane (3a and 4a). 5.16 g (0.03 mole) of a mixture of *cis*- and *trans*-1,3-cyclohexanedicarboxylic acid and 8.3 g (0.06 mole) of 1,2-phenylenediamine were mixed with 100 ml of H_3PO_4 85% in a flask under magnetic stirring. The solution was heated 4 hours at 200 °C to give a blue solution. The mixture was allowed to cool to room temperature and 600 ml of water poured into it. The pH was brought to 5–6 with NaOH 5 M. The precipitate was filtered and suspended in 300 ml of a 10% aqueous solution of Na_2CO_3 and left overnight. The blue precipitate was filtered and dissolved in methanol and treated with activated charcoal in methanol. Filtration and evaporation of the methanol gave a beige solid which could be recrystallized from methanol. 6.7 g of compound are collected (0.021 mol, 70%). Found C 75.7; H 6.3; N 17.6. $C_{20}H_{20}N_4$ requires C 75.9; H 6.4; N 17.7. mp > 180 °C. IR (KBr, ν_{max}/cm^{-1}) 3394w, 2928vs,vbr, 1934w, 1892w, 1774w, 1621m, 1590m, 1538m, 1482m, 1456vs, 1349m, 1312m, 1272s, 1155m, 1045s, 1025s, 1001m, 927m, 868m, 766m, 740s. MS(EI): *m*/*z* 316(M$^{\bullet+}$, 88%), 315(15), 262(19), 261(57), 185(46), 173(12), 172(100), 171(32), 169(12). ^{1}H-NMR δ_H (300 MHz, $CDCl_3$) 1.72–1.81 (3H, m), 1.94–2.21 (4H, m), 2.44–2.49 (1H, dd, ^3J = 1.15 Hz), 3.1–3.18 (2H, m), 7.15–7.19 (4H$_{ar}$ m, ^3J = 3.15 Hz), 7.68–7.49 (4H$_{ar}$ d, ^3J = 2.34 Hz).

***cis*- and *trans*-1,3-Bis-(*N*-methylbenzimidazol-2-yl)cyclohexane (3b and 4b).** 5 g (0.015 mol) of 1,3-bis(benzimidazol-2-yl)cyclohexane (**3a** and **4a**) were dissolved in 300 ml of dry DMF. The flask was put in ice and 2.2 equivalents of NaH (55–65% dispersed in oil, 1.5 g, 0.034 mol) were added to the mixture under an atmosphere of N_2. The solution was kept 15 minutes in the ice and then 1 hour at room temperature. The flask was then put back into the ice, under N_2 (until the end of the reaction), and 2.2 equivalents of CH_3I (2.05 ml, 0.033 mol) were added to the solution. The solution was allowed to warm up to room temperature and left for 15 hours under magnetic stirring, after which the solvent was evaporated and the product was extracted with CH_2Cl_2. The final product is a mixture of *cis*- and *trans*-1,3-bis(*N*-methylbenzimidazol-2-yl)-cyclohexane. We observed in certain cases that the *trans*-diastereomer had almost disappeared during the synthesis. The following procedure allows regeneration of a mixture of diastereomers: 3 g (8.72 mmol) of **3a** were dissolved in 400 ml of dry DMF under nitrogen. The solution was cooled in an ice bath and two equivalents of sodium hydride (60% suspension in oil, Fluka, 0.698 g, 17.44 mmol) added. After 30 minutes, the flask was removed from the ice bath, and slowly heated to 100 °C. After 48 hours the solution was filtered, and the DMF evaporated to give a mixture of diastereomers, which were separated by column chromatography on SiO_2. The eluent was, at first, a mixture of CH_2Cl_2/hexane, 95/5, then 100% CH_2Cl_2 and finally CH_2Cl_2/methanol, 95/5. 2.9 g (8.4 mmol) of product are collected, 56%.

3b: MM: 344. mp >180 °C, MS-EI: 344(M$^{\bullet+}$, 64%), 289(42), 198(41), 186(72), 172(60). IR (KBr, ν_{max}/cm^{-1}) 3059m, 2958m, 2917s, 2850s, 1612m, 1498m, 1475s, 1444s, 1413s, 1349m, 1331m, 1252m, 1230m, 1108m, 1004m, 737vs. ^{1}H-NMR: δ_H (300 MHz, $CDCl_3$), 1.61–1.76 (1H, m), 1.94–2.07 (2H, m), 2.16–2.19 (3H, m), 2.34–2.40 (2H, m), 3.09–3.21 (2H, m), 3.78 (6H, s), 7.20–7.31 (6H, m), 7.71–7.74 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δC 26.06, 29.85, 30.50, 35.74, 36.57, 108.88, 119.43, 121.19, 122.19, 135.83, 142.41, 157.44. UV-Vis (λ_{max}(EtOH)/nm) 252 (ε/dm^3 mol^{-1} cm^{-1} 14000), 276 (15000), 283 (16000).

4b: mp 144–145 °C. ^{1}H-NMR: δ_H (300 MHz, $CDCl_3$) 1.8–1.84 (2H, m), 2.04–2.06 (4H, m), 2.36–2.39 (2H, t, ^3J = 6 Hz), 3.84 (6H, s), 3.91–3.98 (2H, q, ^3J = 6 Hz), 7.25–7.35 (6H, m), 7.75–7.78 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δC: 21.62, 29.8, 29.98, 31.19, 33.91, 109.01, 109.24, 121.05, 122.05, 135.78, 142.53, 158.44.

***cis*-1,3-Bis-(*N*-methylbenzimidazol-2-yl)cyclohexane dihydrochloride, [3bH$_2$]Cl$_2$ (CH$_3$CN)$_{0.5}$.** 70 mg (5×10^{-4} mole) of **3b** and 1 ml of a solution of HCl 0.1 M were dissolved in a minimum of acetonitrile and placed in an atmosphere of diisopropyl ether. 110 mg of white crystals were collected (53%). These monocrystals were suitable for X-ray analysis. IR (KBr, ν_{max}/cm^{-1}) 3105–2575vs,br, 1884m, 1721m, 1620s, 1552s, 1522s, 1487s, 1470s, 1381m, 1352w, 1317m, 1285w, 1242m, 1207w, 1172m, 1139m, 1125s, 1102s, 1044w, 1008s, 976s, 928w, 897s, 872s, 839s, 799m, 776s, 759vs, 738m, 697w, 650m, 597s, 533m. ^{1}H NMR δ_H (300 MHz, $CDCl_3$), 1.97 (2H, m), 2.12 (2H, m), 2.16 (2H, m), 2.59 (1H, m), 2.83 (1H, m), 4.21 (6H, s), 4.32 (2H, m), 7.42 (6H, m), 7.81 (2H, m), 9.63 (2H, s). ^{13}C-NMR (101 MHz, $CDCl_3$) δC 25.13, 29.60, 32.38, 33.78, 34.58, 111.37, 115.81, 125.74, 126.05, 132.40, 132.85, 156.04.

***cis*-1,3-Bis-(*N*-methylbenzimidazol-2-onium)cyclohexane tetrachloromanganate, [3bH$_2$][MnCl$_4$]H$_2$O.** *cis*-1,3-Bis-(*N*-methylbenzimidazol-2-yl)cyclohexane dihydrochloride, **[3bH$_2$]Cl$_2$** (40 mg, 0.09 mmol) was dissolved in a mixture of 2.5 ml of acetonitrile and 0.25 ml of water. A solution of manganese(II) chloride tetrahydrate (18 mg, 0.09 mmol) in 2.5 ml acetonitrile and 0.5 ml of water was added and the mixture stirred at room temperature for two hours. Slow evaporation of the solution gave colourless crystals of [3bH$_2$][MnCl$_4$]H$_2$O of quality suitable for X-ray diffraction (37 mg, 72%). Found C 46.8; H 5.0; N 9.9%. $C_{22}H_{26}N_4MnCl_4 \cdot H_2O$ requires C 47.1; H 5.0; N 10.0%. IR (KBr, ν_{max}/cm^{-1}) 3382w, 3522m, 3098–2644br,s, 2325w, 1982w, 1939w, 1852w, 1807w, 1719w, 1624m, 1549m, 1519s, 1481s, 1463s, 1379m, 1364m, 1321m, 1252s, 1239m, 1204m, 1161m, 1136m, 1103m, 1040w, 1008w, 997w, 935w,

887m, 832m, 764s, 662w, 588m, 573w, 531m, 514m, 483w, 421s, 403s, 393s.

Bis-(*trans*-1,3-bis-(*N*-methylbenzimidazol-2-yl)cyclohexane) copper hexafluorophosphate acetonitrile, $[Cu^{I}(4b)_2](PF_6)(CH_3CN)$. 103 mg (0.3 mmol) of **4b** and 56 mg (0.15 mmol) of $[Cu(CH_3CN)_4](PF_6)$ were dissolved in a minimum of acetonitrile and left in an atmosphere of diisopropyl ether. After a few days, colorless crystals were formed. These monocrystals were suitable for X-ray analysis. MM: 938.47. Found C 58.2; H 5.5; N 13.4. $C_{46}H_{51}N_9CuF_6P$ requires C 58.9; H 5.5; N 13.4. IR (KBr, ν_{max}/cm^{-1}): 3080s, 2930vs, 2830s, 2260m, 1955w, 1915w, 1880w, 1610s, 1480vs, 1460vs, 1405vs, 1370s, 1325s, 1310s, 1280s, 1240s, 1220s, 1170m, 1150m, 1120s, 1095s, 1060m, 1040m, 1010s, 980w, 950m, 910m, 880s, 835vs,br, 795s, 655w. ^{1}H NMR δ_H (300 MHz, $CDCl_3$), 1.686–1.72 ($2H_4$, quintuplet, ^3J = 6.0 Hz), 2.02–2.20 ($2H_3$, quintuplet, ^3J = 6.6 Hz), 2.27–2.31 ($2H_1$, t, ^3J = 5.7 Hz), 3.83 (6H, s, 2 × CH_3), 3.99–4.04 ($2H_2$, quintuplet, ^3J = 5.7 Hz), 7.2–7.3 ($4H_{arom}$, m), 7.43–7.46 ($2H_{arom}$, m), 7.64–7.67 ($2H_{arom}$, m). ES-MS: (in CH_3CN): m/z = 751.4 (100%, Cu^+L_2), 448.3 (20%, $Cu^+L(CH_3CN)$), 407.2 (16%, Cu^+L), 345.2 (20%, LH^+).

***cis*-1,3,5-Tris-(benzimidazol-2-yl)cyclohexane trihydrochloride, $[5aH_3]Cl_3(CH_3OH)_2$.** 1,3,5-Cyclohexane tricarboxylic acid (1.081 g, 5 mmol) and 1,2-phenylenediamine (1.782 g, 16.5 mmol) were suspended in 100 ml of phosphoric acid (85%) in a three necked flask with a thermometer, mechanical stirrer, and Claisen condenser. The solution was heated with stirring to 190 °C for 24 hours, with distillation of water to reach and maintain the desired temperature. The mixture was cooled to room temperature and poured into water (700 ml). The pH was adjusted to 11 with NaOH (5 M). The brown precipitate was filtered off (Büchner funnel) and washed with water. It was suspended in 10% Na_2CO_3 solution (700 ml) and heated with stirring for one hour; then filtered and washed with water. The crude product was dried for 12 hours at 70 °C and 10^{-2} Torr to give 2.43 g of dark brown product. This was purified by treatment with activated charcoal in methanol followed by recrystallisation to give pure **5a** (1.02 g, 47%). Found C 69.0; H 6.2; N 17.6%. $C_{27}H_{24}N_6 \cdot 2H_2O$ requires C 69.2; H 6.0; N 17.9%, mp 333 °C. MS-EI: 432 ($M^{\bullet+}$, 28%), 288 (100), 216 (10), 172 (47), 145 (82). IR (KBr, ν_{max}/cm^{-1}) 3390s, 3050br,s, 2920s, 1618m, 1523s, 1450s, 1416s, 1352m, 1266s, 1220m, 1108m, 828m, 670s, 615m, 516m, 432m, 417m. ^{1}H-NMR: δ_H (300 MHz, D_6-DMSO), 2.05 (3H, dd, J = 12.5 Hz), 2.59 (3H, d, J = 12.9 Hz), 3.33 (3H, t, J = 12 Hz), 7.07 (6H, m), 7.38 (3H, m), 7.49 (3H, m), 12.24 (3H, s).

The hydrochloride salt was obtained by dissolving 45.5 mg (0.01 mmol) in a minimum of warm methanol to which 25 µl (0.3 mmol) concentrated hydrochloric acid was added. Standing for one night at room temperature gave small pale yellow crystals of $[5aH_3]Cl_3(CH_3OH)_2$.

***cis*-1,3,5-Tris-(*N*-methylbenzimidazol-2-yl)cyclohexane trihydrobromide, $[5bH_3]Br_3(H_2O)_4$.** *cis*-1,3,5-Tris-(benzimidazol-2-yl)cyclohexane (**5a**) (216.2 mg, 0.5 mmol) was dissolved in 30 ml of dry DMF under nitrogen. The solution was cooled in ice and sodium hydride (60% in oil, 66 mg, 1.65 mmol) added. After 15 minutes in ice, the solution was stirred for 4 hours at room temperature. It was cooled again in ice and methyl iodide (232.6 mg, 1.65 mmol) added. The solution was allowed to warm to room temperature and stirred overnight. The DMF was removed under vacuum, and the solid product partitioned between semi-saturated ammonium chloride (50 ml) and dichloromethane (50 ml). The aqueous phase was extracted twice with 50 ml portions of dichloromethane. The combined organic phases were dried on sodium sulfate, filtered on cellulose and evaporated. The product was recrystallised from dichloromethane/hexane, and dried at 70 °C under vacuum (150.8 mg, 70%). MS-EI: 475 ($M^{\bullet+}$, 38%), 316 (100), 237 (14), 184 (25), 159 (63). mp 323 °C, decomp. IR (KBr, ν_{max}/cm^{-1}) 2927s, 2853m, 1663m, 1613m, 1498m, 1470s, 1445s, 1407s, 1328s, 1272s, 1234m, 1145m, 1096m, 1007m, 849m 767s, 745vs, 723m, 425m. ^{1}H-NMR: δ_H (300 MHz, D_6-DMSO), 2.12 (3H, dd, J = 12.5 Hz), 2.35 (3H, d, J = 12.9 Hz), 3.59 (3H, t, J = 12 Hz), 3.87 (9H, s), 7.17 (6H, m), 7.52 (6H, m).

The hydrobromide salt was obtained by dissolving 45.5 mg (0.01 mmol) in a minimum of warm methanol to which 25 µl (0.3 mmol) concentrated hydrobromic acid was added. Slow cooling of the solution gave pale yellow crystals of $[5bH_3]Br_3 \cdot (H_2O)_4$. ^{1}H-NMR: δ_H (400 MHz, D_6-DMSO), 2.38 (3H, dd, J = 12 Hz), 2.71 (3H, d, J = 12 Hz), 4.17 (9H, s), 4.30 (3H, m, J = 12 Hz), 7.58 (6H, m), 7.83 (3H, d, J = 7.6 Hz), 7.98 (3H, d, J = 7.6 Hz).

X-ray crystal structures

Details of the crystal structure determinations are given in Table 1. Structures were refined using the XTAL 3.2 program[25] and other calculations used the ORTEP-II program.[26] Details of individual structure determinations are given below.§

$[1bH_2][MnCl_4]$. All hydrogens were observed and refined with isotropic atomic displacement factors fixed at 0.05 Å^2. Bond angle and distance restraints were applied to the hydrogens of the methyl groups.

$[3bH_2]Cl_2$ 0.5 CH_3CN. NH hydrogens were observed and refined with isotropic atomic displacement factors fixed at 0.05 Å^2. Bond angle and distance restraints were applied to other hydrogens. All hydrogens were fixed in the last stages of refinement.

$[3bH_2][MnCl_4]$ H_2O. Hydrogens bonded to methyl groups and to oxygen were refined with bond angle and distance restraints, N–H hydrogens were observed and refined. Other hydrogens were calculated.

$[Cu(4b)_2](PF_6)CH_3CN$. Very fragile crystals were obtained from acetonitrile by diffusion of diethyl ether. The crystals showed a phase transition around 200 K accompanied by loss of the diffraction pattern. The collection was therefore carried out at 220 K, but was of poor quality. Hydrogens bonded to methyl groups were refined with bond angle and distance restraints and fixed in the last stages of refinement. Four fluorines of the PF_6^- anion were disordered in a plane and

§ CCDC reference numbers 602150–602154. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602468h

refined with two populations of 70 and 30%. The acetonitrile molecule showed high atomic displacement parameters but was not disordered.

$[5aH_3]Cl_3 \cdot 2MeOH$. NH and OH hydrogens were observed and refined with isotropic atomic displacement factors fixed at 0.05 $Å^2$. Bond angle and distance restraints were applied to other hydrogens which were fixed in the last stages of refinement. Once out of the mother liquor the crystals lose included methanol.

$[5bH_3]Br_3 \cdot 4H_2O$. Hydrogens bound to O1w were refined with restrictions on bond angle and distances. The water molecule (O2w) situated around the $\bar{3}$ axis was assigned a population parameter of 1/3, and the hydrogen bound to it was observed and refined with restraints. The other hydrogens were calculated.

Molecular volumes

Molecular volumes of the different molecules and ions were calculated using the method of Gavezzotti[20] with the van der Waals radii from his work except for sulfur which was taken from Bondi.[27] Radii for transition metals were fixed at 2.0 Å. For solvent molecules and anions which are often disordered or poorly determined values were either taken from the literature[20,28,29] or were calculated from molecules generated using HyperChem[10] and optimised by molecular mechanics.[10] The molecular volumes thus obtained were used to calculate the packing coefficient by dividing by the sum of the volumes by the unit cell volume.

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