Calixarene/azolium cyclophane hybrids: synthesis, structure and conformations

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Abstract

The synthesis, structure, and conformational behaviour of three imidazolium cyclophanes that incorporate one or two 4-tert-butylphenol or 4-tert-butylanisole groups as *meta*-disubstituted linkers in the macrocycle is described. The cyclophanes containing anisole moieties adopt a cone conformation in the solid state, which, in solution, is not labile on the NMR timescale. The cyclophanes containing one or two phenol moieties adopt conformations other than the cone in the solid state and are labile in solution on the NMR timescale. The phenol cyclophanes are readily deprotonated, and structural and conformational studies for a variety of the associated cyclophanes are also reported.

Keywords cyclophane · NMR · X-ray crystal structure · conformation · imidazolium · calixarene

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Introduction

Azolium-linked cyclophanes have interested chemists for several decades [1], particularly in respect of their synthesis [2-9], interesting structural properties and conformational behaviours [3, 8, 10-14], anion-binding properties [15-17], interesting mass spectrometry [18], and their ability to act as precursors of *N*-heterocyclic carbenes (NHCs) and NHC-metal complexes [19-25]. Much of the conformational behaviour of azolium-linked cyclophanes is reminiscent of the behaviour of calixarenes [26]. In this paper we describe a study of cyclophane salts **3**.2Br, **4**.2Br, and **5**.2Br, compounds that are hybrids of the azolium-linked cyclophane **1**.2Br and tert-butylcalix[4]arene **2** (Scheme 1). In this set, the imidazolium moieties are retained but one or both of the arene moieties have been replaced by 4-tert-butylphenol or 4-tert-butylanisole moieties serving as *meta*-disubstituted linking groups in the cyclophane macrocycle.

We reported previously that the cation of the bis(phenol) cyclophane salt **3**.2Br adopts a cone conformation in the solid state (i.e., a conformation in which the OH groups and the imidazolium C2-H protons lie on the same face of the macrocycle) [11]. ^{1}H NMR studies have shown that in solutions containing **3**.2Br, while the cyclophane cation predominantly existed in the cone conformation, the 1,3-alternate conformation (in which the OH groups lie on the opposite face of the macrocycle compared to the imidazolium C2-H protons) is also present; at room temperature these two conformations interconverted rapidly on the NMR timescale, but were "frozen out" at -73 °C [11]. The bis(anisole) cyclophane salt **4**.2PF_6 is also known, and has been reported to exist in the cone conformation in solution [27]. A study of the effect of counterion (F^-, Cl^-, NO_3^-, SCN^-) on the solid state structures exhibited by cyclophanes closely related to $\mathbf{3}^{2+}$ (but having Cl or Me in place of one or both of the tert-butyl groups) found that the cyclophane cation could adopt cone or 1,2-alternate conformations in the solid state, with some anions being involved in H-bonding interactions with the phenolic OH groups or the imidazolium C2-H proton, or both [13, 14].

Against this background, we have undertaken a detailed comparison of the structural and conformational aspects of **3**.2Br, **4**.2Br, and **5**.2Br in the solid state and in solution, including

examination of the effect of removal of the phenolic protons from the phenol cyclophanes $\mathbf{3}^{2+}$ and $\mathbf{5}^{2+}$.

Results and discussion

Syntheses

The syntheses of the present calixarene/azolium cyclophane hybrids are summarised in Scheme 2. Bis(bromomethyl)arenes were prepared by treatment of the appropriate arene with paraformaldehyde and hydrobromic acid in glacial acetic acid, using methods based on those reported in the literature [28, 29]. Treatment of the resulting bis(bromomethyl)arenes with imidazole in the presence of K_2CO_3 afforded the bis(imidazolylmethyl)arenes, which were in turn converted into cyclophanes by treatment with additional bis(bromomethyl)arene. Three calixarene/azolium cyclophane hybrids were synthesized: the bis(anisole) cyclophane **4**.2Br, the bis(phenol) cyclophane **3**.2Br, and the mono(phenol) cyclophane **5**.2Br. While the syntheses were relatively straightforward, a few salient points deserve comment.

Bis(bromomethylation) of 4-tert-butylanisole was best performed at temperatures below 60 °C — at higher temperatures, the reaction mixture darkened and the yield of the bis(bromomethyl)phenol **6** was diminished. If a large excess of HBr in acetic acid was used in this reaction, the methyl ether was apparently cleaved, with a bromomethyl ether resulting. Conversion of the bis(bromomethyl)phenol **8** into the bis(imidazolymethyl)phenol **9** was achieved directly, but the yield was poor and the product difficult to purify. Instead, we found it easier to obtain the bis(imidazolymethyl)phenol **9** from the ester **10**, which was de-acylated under the conditions of the bromomethylation experiment. The ester **10** was conveniently obtained in a one-pot reaction from 4-tert-butylphenol, by addition of acetic anhydride to the bromomethylation reaction mixture containing **8**.

The bis(anisole) cyclophane $\mathbf{4}^{2+}$ was obtained as its bromide salt **4**.2Br, by addition of a solution of the bis(bromomethyl)anisole **6** in acetone to a solution of the

bis(imidazolylmethyl)anisole **7** in acetone at room temperature, and crystallised from the reaction mixture in essentially pure form, as indicated by NMR spectroscopy. An analytically pure sample was obtained by recrystallisation from methanol/ethanol. The synthesis of the bis(phenol) cyclophane salt **3**.2Br was a little trickier than for **4**.2Br, the solvent used in the synthesis of **3**.2Br being important. The synthesis of **3**.2Br was achieved by simultaneous addition of separate chloroform solutions of the bis(bromomethyl)phenol **8** and the bis(imidazolylmethyl)phenol **9** to refluxing chloroform. Initial experiments [11] that used a mixture of acetonitrile and acetone resulted in the formation of significant amounts of an insoluble, presumably polymeric, byproduct and **3**.2Br was isolated in only 37% yield after recrystallisation from methanol. When the solvent was chloroform, the precipitate of crude **3**.2Br was pure (as indicated by ^{1}H NMR spectroscopy) and the yield was increased to 84%. The rate of addition of the solutions of **8** and **9** was also important — if the solutions were added too quickly, polymers formed, the crude product requiring purification by recrystallisation, and the yield was diminished.

The mono(phenol) cyclophane $\mathbf{5}^{2+}$ was prepared by the reaction of 1,2-bis(imidazolylmethyl)benzene and the bis(bromomethyl)phenol **9**, but was isolated as its bromide salt **5**.2Br in only 23% yield after recrystallisation from ethanol/methanol. Examination of the mother liquor by NMR spectroscopy showed numerous very broad signals, suggesting that the synthesis of $\mathbf{5}^{2+}$ was complicated by the formation of polymeric byproducts. Interestingly, when a pure sample of **5**.2Br was recrystallised by diffusion of vapours of diethyl ether into a solution of the cyclophane in methanol, the crystals obtained were of the formulation [(**5**)(**5**-H)].3Br.3(MeOH), in which the cyclophane units, one as the phenoxide, formed hydrogen-bonded dimers (Scheme 3). The apparent propensity of $\mathbf{5}^{2+}$ to undergo deprotonation may be a factor contributing to the poor yield in which this cyclophane was obtained.

The zwitterionic cyclophane (**3**-2H) (Scheme 4) was a desirable target because of its potential to serve as a halide-free precursor of *N*-heterocyclic carbenes. In the light of the behaviour of the mono(phenol) cyclophane $\mathbf{5}^{2+}$, we explored the preparation of (**3**-2H) by treatment of the

bis(phenol) cyclophane salt **3**.2Br with a base, presuming this transformation to proceed stepwise, via the phenol-phenoxide cyclophane (**3**-H) (Scheme 4). Treatment of **3**.2Br with two equivalents of sodium methoxide in methanol solution, or two equivalents of sodium hydride in DMF, yielded a product for which no phenolic protons could be detected by ^{1}H NMR spectroscopy. This product is tentatively assigned as the zwitterionic bis(phenoxide) cyclophane (**3**-2H) (see discussion of NMR below), but we cannot conclusively exclude the possibility that the product is instead the phenol-phenoxide cyclophane salt (**3**-H).Br. Indeed, an X-ray diffraction study of crystals that formed in the NMR samples showed that they contained the hydrogen-bonded dimer [(**3**-H)$_2$].2Br (Scheme 4, and see below).

The cyclophane salts **3**.2Br, **4**.2Br, and **5**.2Br were insoluble in non-polar solvents including THF, diethyl ether, acetone, chloroform and hexane, but dissolved readily in methanol, DMF, DMSO and water, and had some solubility in hot acetonitrile. The bis(anisole) cyclophane salt **4**.2Br was somewhat more soluble in organic solvents than its phenol counterpart **3**.2Br (for example, **4**.2Br could be dissolved in ethanol) but had lower solubility in water, DMSO and DMF, presumably reflecting the decreased hydrogen-bonding potential of **4**$^{2+}$ compared to **3**$^{2+}$.

Structural Studies

Of the compounds presently described, **3**.2Br, [(**3**-H)$_2$].2Br, **4**.2Br, and [(**5**)(**5**-H)].3Br have been the subject of 'low'-temperature single crystal X-ray structure determinations, comprising an interesting sequence wherein, in the first three, the phenolic (OH)$_2$ hydrogen atoms become successively removed or replace by methyl groups, while, in the fourth, one of the aromatic arrays is replaced by an unsubstituted *o*-phenylene group. Interest is enhanced by the existence of a previous study of a different solvate of **3**.2Br [11], which is found to exist as a different isomer. We deal with each one in detail; structural parameters are presented in Table 1 (below) and Table S1 (Online Resource 1; bond distances and angles).

3.2Br. The previous study [11] of this nicely ordered compound **3**.2Br was of its tris(methanol) solvate, triclinic $P\bar{1}$, $Z = 2$, wherein a single formula unit (plus solvent), devoid of crystallographic symmetry, comprises the asymmetric unit of the structure; the molecule is in the cone conformation with quasi-2m/C_{2v} symmetry. The phenolic hydrogen atoms approach a methanolic oxygen atom and a bromide counterion respectively (H,O(12)…O(02) 1.92(4), 2.667(3); H,O(32)…Br(2) 2.37(4), 3.150(2) Å); the methanolic hydroxyl groups all have close approaches to the other bromide counterion: (H,O(01)…Br(1) 2.29(7), 3.217(3); H,O(02)…Br(1) 2.55(5), 3.312(3); H,O(03)…Br(1) 2.37(5), 3.271(3) Å (Fig. 1a). The cone of the cation is empty. The diverse hydrogen-bonding is contained within the totality of the asymmetric unit (Fig. 1b).

The results of the present study of **3**.2Br (the monoclinic 'polymorph') are consistent with its description as a bis(methanol)bis(chloroform) solvate. Again the structure is nicely ordered, and, despite the greater complexity of the solvation, crystallographically simpler, the array being centro-symmetric with only one half of the formula unit comprising the asymmetric unit of the structure. Such symmetry requirements are incompatible with a 'cone' description of the cation, so that the gross conformation is of a 'Z' — the 1,2-alternate isomer — with the counterpart pairs of equivalent rings lying inversely parallel to each other requiring, notably, that the carbon and hydroxylic hydrogen atoms in each pair of such, be opposed in their directions, pre-empting any possibility of any intramolecular hydrogen-bonding of the type found in the other isomer. The 'protonic' hydrogen atoms of all components (phenolic, methanol, chloroform) are associated with interactions with the bromide ion (Fig. 1b(i)) (Br…H,O(12) 2.48(2), 3.2740(13); Br…H,O (MeOH) 2.53(2), 3.323(2); Br…H,C(Cl_3) 2.67(est.), 3.667(2) Å), again contained discretely within the asymmetric/formulaic unit (Fig. 1b(ii)).

[(**3**-H)$_2$].2Br.2(MeCN). Apart from one of the tert-butyl groups, modelled as rotationally disordered about its pendant bond over two equally populated sets of sites, the structure of this compound, wherein one formula unit comprises the asymmetric unit of the structure in the triclinic space group $P\bar{1}$, is well-defined, with one of the phenolic hydroxyl groups being deprotonated, so

that the cation in its cone conformation is singly charged, with a single bromide counterion, and a pair of solvating acetonitrile molecules. Cations approach each other pairwise about crystallographic inversion centres (Fig. 2a) in consequence of interaction between protonated and deprotonated phenolic groups (O(32)…H,O(12)' 1.66(2), 2.445(2) Å). Closest approaches to the bromide ion less than 3 Å arise from diverse CH hydrogen atoms drawn from all ring systems.

4.2Br. In the structure of this compound, with phenolic hydrogen atoms replaced by methyl groups, resulting in a doubly charged cation with a pair of bromide counterions, a single formula unit accompanied by a pair of solvating methanol molecules plus a single diethyl ether molecule, comprises the asymmetric unit of the structure in chiral space group $P4_32_12$. The cation again is in the 'cone' conformation which, in this case, includes the diethyl ether molecule, with contacts between the oxygen atom and hydrogen atoms of well-ordered tert-butyl groups to either side of 2.74, 2.7_9 Å (est.) (Fig. 3a); the quasi-axis of the cone is closely but not exactly aligned with *c*. The methyl group of one of the methanol solvating molecules is modelled as disordered over a pair of sites, occupancies set at 0.5 after trial refinement; one of the anions is also modelled thus (Br(3,4)), disordered about one of the 2-axes. The fully occupied bromide ion sites (Br(1,2)) are associated with hydrogen bonds from methanol molecules 1,2: Br(1)…H,O(10) 2.90(2), 3.299(7); Br(2)…H,O 2.38(est.), 3.202(6) Å. A projection of the unit cell contents down *c* (Fig. 3b) shows the alignment of the cations about the *c* axis, and the formation of channels between them which contain the disordered components of the structure (bromides Br(3,4), and one of the methanol methyl groups).

[(**5**)(**5**-H)].3Br. In this compound, one of the (*m*-)phenolic groups is replaced by an *o*-phenylene component, devoid of any substituent or phenol/phenoxide. The other phenoxy component is found to be a protonated/deprotonated composite of a pair of macrocyclic constituents associated by a hydrogen-bond linking the pair of components, the phenolic hydrogen being observed nearer O(112) in late difference maps and included at that position, albeit not susceptible of stable refinement O(212)…H,O(112) 1.76, 2.582(4) Å; note that C-O(112,212) are 1.364(6), 1.317(5) Å respectively (Fig. 4). One of these composites, together with the appropriate $(Br^-+(Br^-)_2)$

anion array and three methanol solvent molecules, the OH approaches of which constitute the dominant interactions of the former, comprises the asymmetric unit of the nicely ordered monoclinic $P2_1/c$ structure: Br(1)…H,O(2) 2.3_4 (est.), 3.182(4); Br(1)…H,O(3) 2.5_0 (est.), 3.323(4); Br(3)…H,O(1) 2.4_3, 3.228(4) Å. The 'asymmetry' of these interactions is noted, Br(2) having no hydroxylic-OH associations but, rather, interactions with tert-butyl and aromatic hydrogen components to a greater degree than the other anions. The shortest of these is Br(2)…H(13A)(C(13)) 2.7_9 (est.), most of the others lying beyond 3 Å. One solvated formula unit, [(**5**)(**5**-H)].3Br.3(MeOH) with a composite cation comprises the asymmetric unit (again discrete) of the structure. Both cations may be described as "partial cones" but there are gross differences between them, as evidenced by the interplanar dihedral angles (Table 1).

NMR Studies

Like calixarenes, azolium linked cyclophanes can adopt various conformations in solution, and NMR spectra are often broadened by the effects of exchange between conformations [11, 12]. For the bis(anisole) cyclophane $\mathbf{4}^{2+}$, interpretation of the NMR spectra is straightforward. ^{1}H NMR spectra of fresh solutions of **4**.2Br in CD_3OD (Fig. 5) showed signals consistent with the presence of only the "cone" conformation of the cyclophane, i.e., the conformation in which the methoxy groups of the anisole moieties and the C2-H bonds of the imidazolyl moieties lie on the same face of the of the macrocyclic ring (Scheme 5). This result is not unexpected, given that the cone conformation was seen in the solid state study (see above). It is noteworthy that the ^{1}H NMR signals due to the benzylic protons of $\mathbf{4}^{2+}$ appear as sharp doublets. This result shows that the cone conformation of $\mathbf{4}^{2+}$ is not labile, i.e., interconversion between the two equivalent cones (Scheme 5) is slow on the NMR timescale, so that the *endo* and *exo* environments of the benzylic protons remain distinct.

As the solution aged, new signals emerged in the ^{1}H NMR spectra, and these signals are attributed to the "1,3-alternate" conformation, i.e., the conformation in which the methoxy groups

of the anisole moieties lie on the opposite face of the macrocyclic ring compared to the C2-H bonds of the imidazolyl moieties (Scheme 6). Equilibrium between the cone and 1,3-alternate conformations was reached in about four hours in CD_3OD solution at room temperature, the cone:1,3-alternate ratio at equilibrium being 3:1. A previous study [27] of **4**.2PF_6 found that, for solutions of that salt in DMSO-d_6 solution, $\mathbf{4}^{2+}$ existed in the cone conformation, but did not note whether the 1,3-alternate conformation was also observed.

The ^{1}H NMR chemical shifts of the various protons in each conformation are generally similar, except for those of the C2-H protons. The C2-H protons of the cone conformation are highly deshielded, their ^{1}H NMR signal appearing at δ 9.2 ppm. In the 1,3-alternate conformation, however, the C2-H protons are oriented towards the cavity between the aromatic rings of the anisole moieties, and shielding by the ring current of these moieties results significant upfield shift of the signal due to these protons, to δ 8.2 ppm.

The interconversion of the cone and 1,3-alternate conformations of $\mathbf{4}^{2+}$ can be envisaged to occur via rotation of the imidazolium moieties about their N-N axes, with the C2-H group passing through the centre of the macrocycle. The time required for equilibrium to be reached between the cone and 1,3-alternate conformations, and the fact that all ^{1}H NMR signals for both conformations of $\mathbf{4}^{2+}$ were sharp, indicate that conformational changes for $\mathbf{4}^{2+}$ occur only very slowly on the NMR timescale. This result contrasts with the situation for $\mathbf{3}^{2+}$. In solutions of **3**.2Br in CD_3OD, interconversion between cone and 1,3-alternate conformations of $\mathbf{3}^{2+}$ is rapid at room temperature, but can be slowed at low temperature, and at -73 °C, the cone:1,3-alternate ratio is 2:1 [11]. The slower rate of exchange seen in the bis(anisole) cyclophane $\mathbf{4}^{2+}$ may reflect increased steric crowding near the centre of the macrocyclic ring due to the presence of the methyl groups — increased steric crowding would inhibit rotation of the imidazolium moieties about their N-N axes, thereby inhibiting interconversion of cone and 1,3-alternate conformations. In principle, the interconversion of cone and 1,3-alternate conformations could also be achieved by rotation of the anisole moieties about the axes defined by the benzylic carbons in the macrocycle. Such a process

would require the methoxy groups of the anisole moieties to swing through the centre of the macrocycle, which would appear unlikely on steric grounds.

NMR studies of **5**.2Br were undertaken using solutions in CD_3OD (at low temperatures) and DMSO-d_6 (at high temperatures). This salt was not sufficiently soluble in aprotic, low-melting solvents for low temperature studies, and thus H/D exchange reactions were unavoidable complications to the low temperature NMR studies. As a consequence of H/D exchange, signals due to the phenolic proton in $\mathbf{5}^{2+}$ could not be detected in CD_3OD, and signals due to the imidazolium C2-H protons slowly diminished during the course of NMR experiments. Nevertheless, NMR studies revealed interesting results about the conformations of $\mathbf{5}^{2+}$ in solution.

Signals due to two conformations of the mono(phenol) cyclophane $\mathbf{5}^{2+}$ are evident in ^{1}H NMR spectra of solutions of **5**.2Br in CD_3OD at -70 °C (Fig. 6 and Fig. 7). The number of signals and splitting patterns seen for each conformation are consistent with the conformations having a plane of symmetry, i.e., having their imidazolium units oriented in the same direction (Scheme 7). The ^{1}H NMR signal for the imidazolium C2-H proton of the minor conformation of $\mathbf{5}^{2+}$ appears at δ 9.34 ppm, in the region expected for an imidazolium C2-H proton that is not exposed to shielding by ring currents from aromatic rings in the cyclophane structure. We thus assign the minor conformation as the cone conformation (Scheme 7). The C2-H proton of the major isomer gives rise to a ^{1}H NMR signal at δ 8.86 ppm, in the region expected when the proton is shielded by the ring current from only one aromatic ring in the cyclophane structure. We thus assign the major conformation as one of the possible partial cone structures (Scheme 7). In the solid state structure of [(**5**)(**5**-H)].3Br.3(MeOH) (see above), $\mathbf{5}^{2+}$ adopts the partial cone conformation in which the phenolic proton and the C2-H protons are on the same face of the macrocycle, but we do not believe that the available NMR data allows for a convincing assignment of a particular partial cone to the major conformation in solution.

Fig. 8 shows the ^{1}H NMR spectra for **3**.2Br and for the product obtained by treatment of **3**.2Br with base (two equivalents of either sodium methoxide or sodium hydride in methanol or

DMF respectively). The spectrum for the sample treated with base (Fig. 8b) shows only one signal in the extreme downfield region (δ 10.43 ppm), and a heteronuclear multiple bond correlation (HMBC) experiment confirmed that this signal was due to imidazolium C2-H protons and not phenolic protons. No signal was detected that could reasonably be assigned to a phenolic proton. The possibility that phenolic protons were present but not detectable due to exchange-broadening of their NMR signals seems unlikely because other signals in the spectrum were relatively sharp, and a signal due to adventitious moisture (which would be expected to be broadened by any rapid OH exchange processes occurring in the sample), was sharp and at usual chemical shift for water in CD_3CN (~ 2.18 ppm). With these considerations in mind, we tentatively assign the product of the reaction of **3**.2Br with two equivalents of base as the zwitterionic bis(phenoxide) cyclophane (**3**-2H).

The number of signals in the ^1H NMR spectrum of (**3**-2H), and the downfield shift of the signal due to the C2-H protons, are consistent with the cyclophane adopting a cone conformation. The appearance of signals due to the benzylic CH_2 protons as doublets indicates that the cone conformation is not labile, i.e., interconversion between the two possible equivalent cones is slow on the NMR timescale. This result is in contrast with the situation for the bis(phenol) cyclophane $\mathbf{3}^{2+}$ (Fig. 8a), where rapid interconversion of conformations, including the two cone conformations, results in the CH_2 protons being rendered equivalent on the NMR timescale [11]. This decreased conformational lability of (**3**-2H) compared to $\mathbf{3}^{2+}$ may be rationalised in a various ways, for example: the bis(phenoxide) cyclophane (**3**-2H) may be 'locked' into a cone conformation by hydrogen-bonding between the phenoxide oxygens and the imidazolium C2-H proton; solvation of the phenoxide oxygens may make the effective size of the phenoxide groups too large to allow them to pass through the centre of the cyclophane cavity; or, electrostatic repulsion between the phenoxide groups may prevent 'flipping' of the phenoxide rings by preventing the oxygen end from swinging through the cyclophane cavity.

Conclusion

A number of cyclophane compounds that are hybrids of calixarenes and azolium-linked cyclophanes have been synthesized, and their conformational behaviour has been explored by NMR and X-ray diffraction methods. The conformations of the cyclophane macrocycles can be interpreted in terms of cone, partial cone, 1,2-alternate, and 1,3-alternate structures that have been used to describe conformations of calix[4]arenes. When the arene component of the cyclophane is derived from anisole, bis(anisole) cyclophane adopts a cone conformation in both the solid state and in solution, and the conformation in solution is not labile on the NMR timescale. When one or two phenol moieties are present in the cyclophane, the phenol cyclophanes are labile on the NMR timescale in solution, rapidly interconverting between different conformations, and in the solid state show partial cone or 1,2-alternate conformations. The phenol groups are readily deprotonated, leading to formation of interesting H-bonded cyclophane dimers.

Experimental section

Nuclear magnetic resonance spectra were recorded using Bruker ARX-300, AV-500, or AV 600 spectrometers at ambient temperature unless otherwise stated. Mass spectra were obtained by Dr Tony Reeder using a VG Autospec Mass Spectrometer via either fast atom bombardment (FAB) with a cesium ion source and a *m*-nitrobenzyl alcohol matrix, electrospray (ES) or electron impact (EI) ionisation. Microanalyses were performed by the Microanalytical Laboratory at the Research School of Chemistry, Australian National University, Canberra, Australia.

All solvents were distilled prior to use. Deoxygenation of solvents was performed by bubbling nitrogen through the solvent for at least 30 min, or by at least three freeze-pump-thaw cycles. Methanol was distilled from magnesium methoxide and stored over 3 Å molecular sieves. Acetonitrile was pre-dried over 3 Å molecular sieves then distilled from phosphorus pentoxide and stored over 3 Å molecular sieves. Dichloromethane was pre-dried over calcium chloride then distilled from phosphorus pentoxide and stored over 4 Å molecular sieves. AR grade DMF and

DMSO were stored over 4 Å molecular sieves for at least three months before use and diethyl ether and THF were distilled from sodium/benzophenone and used immediately.

1,2-Bis(imidazolylmethyl)benzene [30] and 4-tert-butylanisole [31] were synthesized as described previously.

*2,6-Bis(bromomethyl)-4-*tert*-butylanisole (**6**)*

This compound was prepared using a modification of the procedure described by Ashram et al. [32]. A mixture of 4-tert-butylanisole (900 mg, 5.5 mmol), paraformaldehyde (635 mg, 21.9 mmol) and a solution of HBr in acetic acid (46% w/v, 4 mL, 22.7 mmol) was stirred at 60 ºC for 17 h. The solution was poured into ice (ca. 20 g), and the mixture was allowed to warm to room temperature and was then extracted with hexanes (5 x 30 mL) and dichloromethane (1 x 30 mL). The combined organics were washed with aqueous sodium hydrogencarbonate solution (saturated, 1 x 40 mL) and water (1 x 40 mL), dried ($MgSO_4$) and concentrated on a rotary evaporator. The oily residue was recrystallised from hexanes to yield the product as a white powder (559 mg, 36%). The spectroscopic data were consistent with the literature [32]. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 1.31 (s, 9H, 3 x CH_3), 4.01 (s, 3H, OCH_3), 4.56 (s, 4H, 2 x CH_2), 7.36 (s, 2H, 2 x ArH). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 28.30 (2 x CH_2), 31.42 (3 x CH_3), 34.60, 62.28 (OCH_3), 129.46 (Ar CH), 131.19 (Ar CCH_2), 148.09 (Ar C-^{t}Bu), 154.46 (Ar C-OCH_3).

*2,6-Bis(bromomethyl)-4-*tert*-butylphenol (**8**)*

This compound was prepared using a modification of the method described by Bright and Cammarata [33]. 4-tert-Butylphenol (2.194 g, 7.96 mmol) was added portionwise to an ice-cold, stirred solution of paraformaldehyde (1.29 g, 44.5 mmol) in HBr / glacial acetic acid (33 % w/v, 25 mL, 102 mmol) and the resulting mixture was stirred at 0 ºC for 1 h. The solution was allowed to warm to room temperature and was stirred for a further 3 h. The solution was poured into ice (ca. 100 g) and allowed to warm to room temperature. The mixture was extracted with ether (3 x 50 mL)

and the combined ether extracts were washed with water until the water washings were no longer acidic (5 x 80 mL) and the organics were dried ($MgSO_4$) and concentrated in vacuo leaving a yellow oil that solidified on cooling. The waxy solid was recrystallised from hot hexanes to give the product as colourless needles (2.50 g, 51%). ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 1.30 (s, 9H, CH_3), 4.57 (s, 4H, 2 x CH_2), 7.26 (s, 2H, 2 x ArH). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 30.18 ($C(CH_3)_3$), 31.49 (CH_2), 34.32 ($C(CH_3)_3$), 124.66 ($ArCCH_2$), 128.52 (ArCH), 144.29 (ArC-^{t}Bu), 151.21 (ArC-OH).

*1-Acetoxy-2,6-bis(bromomethyl)-4-*tert*-butylbenzene (**10**)*

4-tert-Butylphenol (4.003 g, 26.6 mmol) was added portionwise to an ice-cold solution of paraformaldehyde (2.01 g, 69.3 mmol) in HBr / acetic acid (33% w/v, 33 mL, 187 mmol) over 30 min. The resulting solution was stirred at 0 ºC for 60 min, warmed to room temperature and stirred for a further 90 min. Acetic anhydride (15 mL, 159 mmol) was added and the mixture was stirred at room temperature for 36 h. The solution was poured into ice (ca. 50 g) and neutralised with aqueous potassium carbonate solution (saturated). The mixture was extracted with ether (3 x 75 mL) and the ether extracts were washed with aqueous sodium hydrogencarbonate solution (saturated, 1 x 100 mL) and water (1 x 100 mL), dried ($CaCl_2$) and the solvent was removed in vacuo to yield an orange solid that was recrystallised from hexanes (charcoal) to afford the product as colourless needles (4.57 g, 45%). The spectroscopic data were consistent with the literature [34]. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 1.32 (s, 9H, 3 x CH_3), 2.44 (s, 3H, CH_3), 4.38 (s, 4H, 2 x CH_2), 7.39 (s, 2H, 2 x ArH). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 20.92 (CH_3), 28.28 (CH_2), 31.36 (CH_3), 34.74 ($C(CH_3)_3$), 128.84 (Ar CH), 130.35 (Ar CCH_2), 145.44 (Ar C-^{t}Bu), 150.01 (Ar C-OAc), 168.90 (C=O). HRMS (FAB) m/z: 376.9760 ($C_{14}H_{19}O_2{}^{79}Br_2$ [M+1] requires 376.9752).

*2,6-Bis(imidazol-1-ylmethyl)-4-*tert*-butylphenol (**9**)*

A solution of 1-acetoxy-2,6-bis(bromomethyl)-4-tert-butylbenzene (**10**) (2.185 g, 5.78 mmol) in DMF (15 mL) was added dropwise over 45 min to a stirred mixture of imidazole (3.914 g, 57.9 mmol) and potassium carbonate (4.01 g, 29 mmol) in DMF (30 mL) at 80 ºC. The resulting mixture was stirred at 80 ºC for 3.5 h. The mixture was cooled and the solution was decanted from the solid and the solid was extracted with chloroform (2 x 60 mL). The combined organic phases were concentrated under reduced pressure, ether (250 mL) was added and the mixture was boiled for 10 mins then allowed to stand, uncovered for 18 h and a precipitate formed. The ether was decanted from the solid and the solid was triturated with boiling ether (2 x 50 mL). The resulting solid was collected and dried under vacuum to give the product as a pale yellow solid (1.29 g, 72%). Spectroscopic data were comparable with the literature [11]. ^{1}H NMR (500.13 MHz, d_6-DMSO): δ 1.15 (s, 9H, 3 x CH_3), 5.17 (s, 4H, 2 x CH_2), 6.87 (s, 2H, 2 x H4), 7.02 (s, 2H, 2 x ArH), 7.13 (s, 2H, 2 x H5), 7.68 (s, 2H, 2 x H2), 9.12 (br s, $W_{h/2}$ = 13 Hz, 1H, OH). ^{13}C NMR (125.77 MHz, d_6-DMSO): δ 31.13 (CH_3), 33.66 ($C(CH_3)_3$), 45.31 (CH_2), 119.55 (C5), 125.05 (Ar CCH_2), 126.00 (Ar CH), 128.27 (C4), 137.37 (C2), 142.38 (Ar C-^{t}Bu), 149.83 (COH).

*2,6-Bis(imidazol-1-ylmethyl)-4-*tert*-butylanisole (**7**)*

A solution of 2,6-bis(bromomethyl)-4-tert-butylanisole (**6**) (203 mg, 0.58 mmol) in DMF (ca. 5 mL) was added portionwise to a stirred mixture of imidazole (394 mg, 5.78 mmol) and potassium carbonate (400 mg, 2.89 mmol) in DMF (ca. 20 mL) at 60 ºC and, once the addition was complete, the mixture was stirred for a further 17 h. The solvent was removed under vacuum, water (30 mL) was added to the residue and the mixture was extracted with chloroform (3 x 20 mL). The chloroform extracts were dried ($MgSO_4$) and concentrated under vacuum. The residue was recrystallised from acetone/water to give the product as a pale yellow powder (122 mg, 65%). The NMR data were comparable to the literature [8]. ^{1}H NMR (300.13 MHz, d_6-DMSO): δ 1.14 (s, 9H, 3 x CH_3), 3.68 (s, 3H, OCH_3), 5.21 (s, 2H, CH_2), 6.90 (s, 2H, H4 or H5), 7.03 (s, 2H, ArH), 7.15 (s,

2H, H4 or H5), 7.72 (s, 2H, 2 x H2). ^{13}C NMR (75.47 MHz, d_6-DMSO): δ 31.00 (3 x CH_3), 34.04 ($C(CH_3)_3$), 44.90 (CH_2), 61.45 (OCH_3), 119.78 Ar CH), 125.88, 128.53 (C4 and C5), 130.39 (Ar CCH_2), 137.66 (C2), 146.98 (Ar C-^{t}Bu), 153.16 (Ar C-OMe).

*Bis(anisole) cyclophane salt **4**.2Br*

A solution of 2,6-bis(bromomethyl)-4-tert-butylanisole (**6**) (75 mg, 0.22 mmol) in acetone (20 mL) was added dropwise over 30 min to a stirred solution of 2,6-bis(imidazolylmethyl)-4-tert-butylanisole (**7**) (70 mg, 0.22 mmol) in acetone (20 mL) at room temperature and the mixture was stirred at room temperature for 17 h. The resulting precipitate was collected and dried under vacuum for 6 h to afford a white powder (99 mg, 72%). Samples for elemental analysis were recrystallised from hot ethanol/methanol. The salt **4**.2Br crystallised having the cyclophane $\mathbf{4}^{2+}$ in the cone conformation, but when the crystals were re-dissolved in methanol, an equilibrium mixture was obtained, containing $\mathbf{4}^{2+}$ in cone and 1,3-alternate conformations in the ratio 3:1 respectively. ^{1}H NMR (500.13 MHz, d_4-methanol): cone conformer, δ 1.31 (s, 18H, 6 x CH_3), 4.19 (s, 6H, 2 x OCH_3), 5.16 (d, $^2J_{HH}$ = 14 Hz, 4 x CHH), 5.71 (d, $^2J_{HH}$ = 14 Hz, 4 x CHH), 7.50 (apparent d, splitting = 2 Hz 4H, 2 x H4 and 2 x H5), 7.71 (s, 4H, 4 x ArH), 9.21 (s, 2H, 2 x H2); 1,3-alternate conformer, δ 1.42 (s, 18H, 6 x CH_3), 3.75 (s, 6H, 2 x OCH_3), 5.21 (d, $^2J_{HH}$ = 14.5 Hz, 4 x CHH), 5.57 (d, $^2J_{HH}$ = 14.5 Hz, 4 x CHH), 7.68 (apparent d, splitting = 2 Hz 4H, 2 x H4 and 2 x H5), 7.80 (s, 4H, 4 x ArH), 8.23 (s, 2H, 2 x H2). ^{13}C NMR (125.77 MHz, d_4-methanol): cone conformer, δ 31.61 (CH_3), 35.63 ($C(CH_3)_3$), 50.33 (CH_2), 63.41 (OCH_3), 123.18 (C4 and C5), 130.07 (Ar CCH_2), 131.50 (Ar CH), 138.14/138.18 (C2), 150.94 (ArC-^{t}Bu), 156.49 (ArC-OCH_3); 1,3-alternate conformer, δ 31.71 (CH_3), 35.73 ($C(CH_3)_3$), 50.84 (CH_2), 62.52 (OCH_3), 123.77 (C4 and C5), 129.54 (Ar CCH_2), 131.98 (Ar CH), 136.76 (C2), 150.88 (Ar C-^{t}Bu), 165.53 (Ar C-OCH_3). HRMS (FAB) m/z: 593.2459 ($C_{32}H_{42}N_4O_2{}^{79}Br$ [M-Br] requires 593.2491), 595.2447 ($C_{32}H_{42}N_4O_2{}^{81}Br$

[M-Br] requires 595.2471). Anal. calcd. for $C_{32}H_{42}N_4O_2Br_2 \cdot 0.5CH_3OH$: C 56.53, H 6.42, N 8.11. Found: C 56.46, H 6.38, N 8.00.

*Bis(phenol) cyclophane salt **3**.2Br*

This compound was prepared using a modification of our previous method [11]. Two separate solutions, 2,6-bis(imidazole-1-ylmethyl)-4-tert-butylphenol (**9**) (1.52 g, 4.53 mmol) in chloroform (100 mL) and 2,6-dibromomethyl-4-tert-butylphenol (**8**) (1.40 g, 4.52 mmol) in chloroform (100 mL) were added dropwise to refluxing chloroform (150 mL) over 5 h. Once the addition was complete the mixture was refluxed for 17 h. The resulting solid was collected and dried under vacuum for 8 h to afford a white powder (2.446 g, 84%). Samples for analysis were prepared by recrystallisation from methanol. Crystals suitable for the X-ray work were grown by diffusion of vapours between chloroform and a solution of the cyclophane salt in methanol. ^{1}H NMR (500.13 MHz, d_6-DMSO, room temperature): δ 1.25 (s, 18H, 6 x CH_3), 5.40 (br s, $W_{H/2}$ 26 Hz, 8H, 4 x CH_2), 7.60 (s, 4H, 4 x ArH), 7.70 (d, $^2J_{H\text{-}H}$ = 1.4 Hz, 4H, 2 x H4 2 x and 5), 8.73 (br s, $W_{h/2}$ = 25 Hz, 2H, 2 x H2), 9.64 (s, 2H, 2 x OH). ^{13}C NMR (125.77 MHz, d_6-DMSO): δ 31.2 (CH_3), 34.0 ($C(CH_3)_3$), 48.9 (CH_2), 122.4 (C4 and C5), 123.7 (CCH_2), 129.6 (Ar CH), 135.3 (Ar CCH_2), 143.4 (Ar C-^{t}Bu), 151.4 (COH).

*Mono(phenol) cyclophane salt **5**.2Br and the "dimer" [(**5**)(**5**-H)].3Br.*

A solution of 2,6-dibromomethyl-4-tert-butylphenol (**9**) (1.006 g, 2.99 mmol) in chloroform (ca. 70 mL) and a solution of 1,2-bis(imidazolylmethyl)benzene (707 mg, 2.99 mmol) in chloroform/acetonitrile (60 mL/10 mL) were added simultaneously to refluxing chloroform (150 mL) over 2.5 h. Once the addition was complete, the reaction mixture was refluxed for a further 17 h. The solvent was removed under vacuum and the residue was recrystallised from ethanol/methanol to give a white powder (689 mg, 23%). ^{1}H NMR (500.133 MHz, d_6-DMSO): δ

1.3 (s, 9H, 3 x CH_3), 5.18 (d, $^2J_{H,H}$ = 14 Hz, 2H, 2 x Hb), 5.38 (br d, 2H, 2 x Ha), 5.75 (d, $^2J_{H,H}$ = 14 Hz, 2H, Hb), 5.80 (br d, 2H, 2 x Ha), 7.59 (m, 2H, 2 x 2 x H3a), 7.63 (s, 2 H, 2 x H5), 7.83 (s, 2H, 2 x H4), 7.84 (br s, 2H, 2 x H3b), 7.94 (m, 2H, 2 x H2a), 8.6 (s, 2H, 2 x H2), 9.2 (s, 1H, OH). ^{13}C NMR (125.771 MHz, d_6-DMSO): δ 31.26 (CH_3), 34.07 ($C(CH_3)_3$), 48.48 (Cb), 50.47 (Ca), 121.15 (C3b), 123.18 (C2b), 129.57 (C5), 130.28 (C3a), 133.08 (C2a), 133.28 (C1a), 134.31 (C2), 143.47 (Ar C-^{t}Bu), 151.03 (Ar C-OH). HRMS (FAB) m/z: 493.1609 ($C_{26}H_{30}N_4O^{79}Br$ [M-Br] requires 493.1603). Anal. calcd. for $C_{26}H_{30}N_4OBr_2 \cdot H_2O$: C 52.72, H 5.44, N 9.46. Found: C 52.68, H 5.63, N 9.25. Attempts to obtain crystals suitable for X-ray diffraction studies, by the diffusion of vapours of diethyl ether into a solution of **5**.2Br in methanol at 4 ºC, yielded [(**5**)(**5**-H)].3Br as a methanol solvate.

*Phenol/phenoxide cyclophane salt (**3**-H).Br and the bis(phenoxide) (**3**-2H)*

Method 1: A solution of the bis(phenol) cyclophane salt **3**.2Br (530 mg, 0.82 mmol) in dry methanol (8 mL) was added to a stirred solution of sodium methoxide (89 mg, 1.65 mmol) in methanol (2 mL) and the resulting solution was stirred at room temperature for 24 h. The solvent was removed under vacuum and the residue was extracted with dry acetonitrile (10 mL). The extract was filtered through a short plug of Celite and the filtrate was concentrated under vacuum to leave a yellow solid. Acetonitrile (5 mL) was added to the solid and the mixture was stirred for 10 min then allowed to stand for 30 min before the mixture was filtered through Celite and the solvent was removed under vacuum to give the product as a yellow solid (110 mg, 24 %). The product was tentatively identified as the bis(phenoxide) (**7**-2H) on the basis of its ^{1}H and ^{13}C NMR spectra (see below).

Method 2: The bis(phenol) cyclophane salt **3**.2Br (290 mg, 0.45 mmol) was dissolved in DMF (ca. 6 mL) and the solution was concentrated by approximately one third under vacuum at room temperature. Sodium hydride (60% dispersion in mineral oil, 40 mg, 1.0 mmol) was added and the mixture was stirred at room temperature for 15 h. The solvent was removed under vacuum and the

residue was extracted with anhydrous acetonitrile. The mixture was filtered through Celite and the filtrate was concentrated under vacuum. The residue was washed with anhydrous ether until it became a solid, which was collected and dried under vacuum. The solid was suspended in acetonitrile (ca. 3 mL) and the mixture was stirred for 5 min then allowed to stand at room temperature for 15 min. The mixture was filtered and ether (ca. 15 mL) was added to the filtrate. The resulting precipitate was collected and dried under vacuum for 2 h to afford a white powder (65 mg, 25%). The product was tentatively identified as the bis(phenoxide) (**3**-2H) on the basis of its ^{1}H and ^{13}C NMR spectra. ^{1}H NMR (500.13 MHz, CD_3CN): δ 1.22 (s, 9H, 3 x CH_3), 4.56 (br d, $^{2}J_{HH}$ = 13 Hz, 4H, CHH), 5.77 (br d, $^{2}J_{H,H}$ = 13 Hz, 4H, CHH), 7.03 (apparent d, splitting = 1.4 Hz, 4H, 2 x H4 and 2 x H5), 7.26 (s, 4H,4 x H3'), 10.43 (s, 2H, 2 x H2). ^{13}C NMR (125.77 MHz, CD_3CN): δ 32.12 (CH_3), 34.11 ($C(CH_3)_3$), 52.19 (CH_2), 122.02 (C4 and C5), 124.00 (Ar CCH_2), 128.43 (C2), 129.22 (Ar CH), 131.60 (Ar C-^{t}Bu), 167.10 (Ar C-OH). HRMS m/z: 485.2921 ($C_{30}H_{37}N_4O_2$ [**7**-H] requires 485.2917), 484.2847 ($C_{30}H_{36}N_4O_2$ [**7**-2H] requires 484.2838). Attempts to obtain crystals of the zwitterionic bis(phenoxide) cyclophane (**3**-2H) suitable for X-ray diffraction studies, by slow evaporation of a d_3-acetonitrile solution of the material prepared by method 1, instead yielded the phenol-phenoxide salt (**3**-H).Br, as its CD_3CN solvate.

Structure determinations

Full spheres of CCD area-detector diffractometer data were measured (ω-scans, monochromatic Mo Kα radiation, λ = 0.7107$_3$ Å, T ca 100 K) yielding $N_{t(otal)}$ reflections, these merging to N_{unique} (R_{int} cited) after 'empirical'/multiscan absorption correction, and used in the full-matrix least squares refinements on F^2, refining anisotropic displacement parameters for the non-hydrogen atoms, hydrogen atom treatment following a riding model (reflection weights: $(\sigma^2(F_o^2) + (aP)^2 (+ bP))^{-1}$ ($P = (F_o^2 + 2F_c^2)/3)$); N_o reflections had $I > 2\sigma(I)$. Neutral atom complex scattering factors were

employed within the SHELXL97 program [35]. Pertinent results are given in Tables 1, 2 and S1 (Online Resource 1), the text and Figures, the latter showing non-hydrogen atom displacement envelopes at the 50% probability amplitude level. Full *.cif* depositions reside with the Cambridge Structural Database, CCDC 1038207-1038210.

Variata

3.2Br.2($CHCl_3$).2(MeOH). Hydroxylic hydrogen atom parameters were refined in (x,y,z,U_{iso}), also the case in [(**3**-H)$_2$].2Br.4(MeCN); in [(**5**)(**5**-H)].3Br.3(MeOH), the data would not support meaningful refinement of such and they were constrained. In [(**3**-H)$_2$].2Br.4(MeCN), one of the tert-butyl groups was modelled as rotationally disordered over two sets of sites of equal occupancy about its pendant, after trial refinement. In **4**.2Br.2(MeOH).(Et_2O), one bromine atom, lying close to a 2-axis, was modelled as disordered about it; one of the methoxy carbon atoms was also modelled as disordered over a pair of sites. The absolute structure parameter refined to –0.006(11).

Supplementary material

A table of selected bond distances and angles is supplied as electronic supplementary material. CCDC 1038207-1038210 contain the relevant cif files, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

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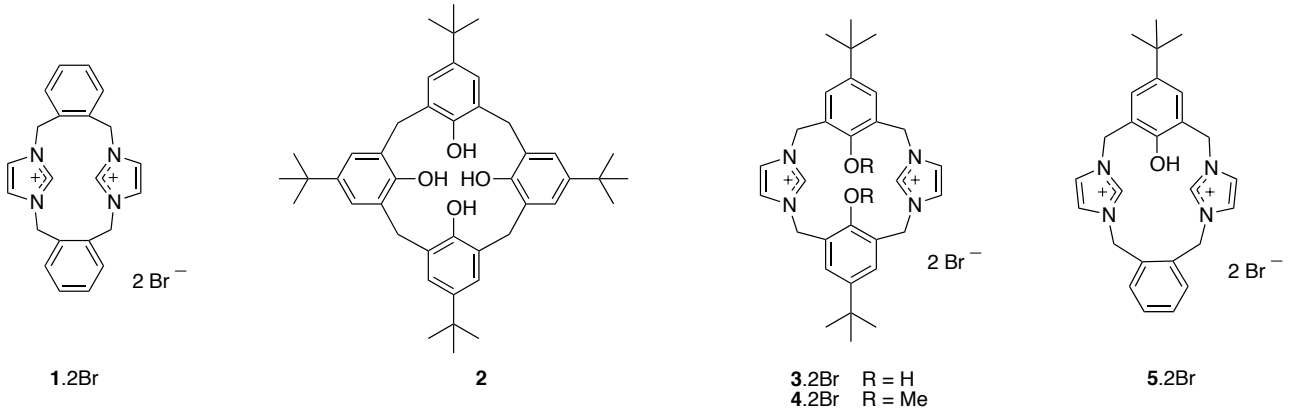
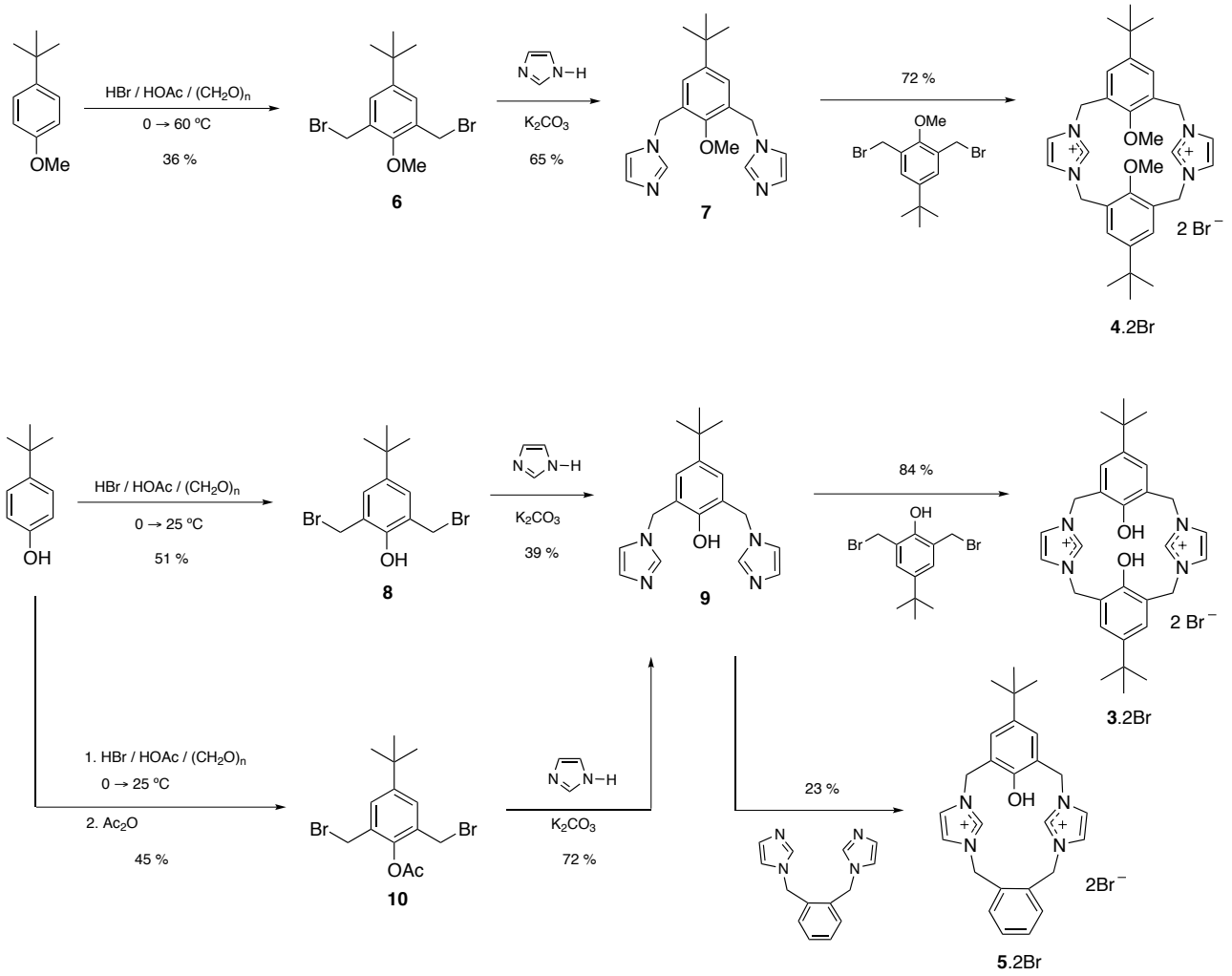
Scheme captions

Scheme 1 Cyclophanes **1** - **5**

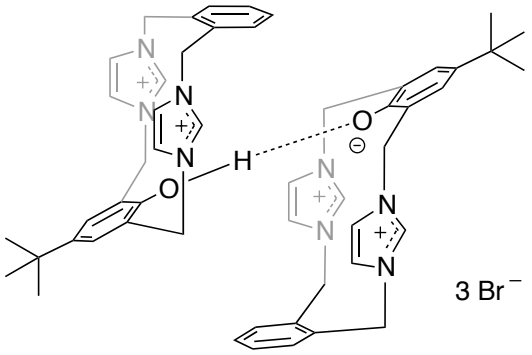


1.2Br **2** **3**.2Br R = H **4**.2Br R = Me **5**.2Br

Scheme 2 Synthesis of calixarene /azolium cyclophane hybrids.

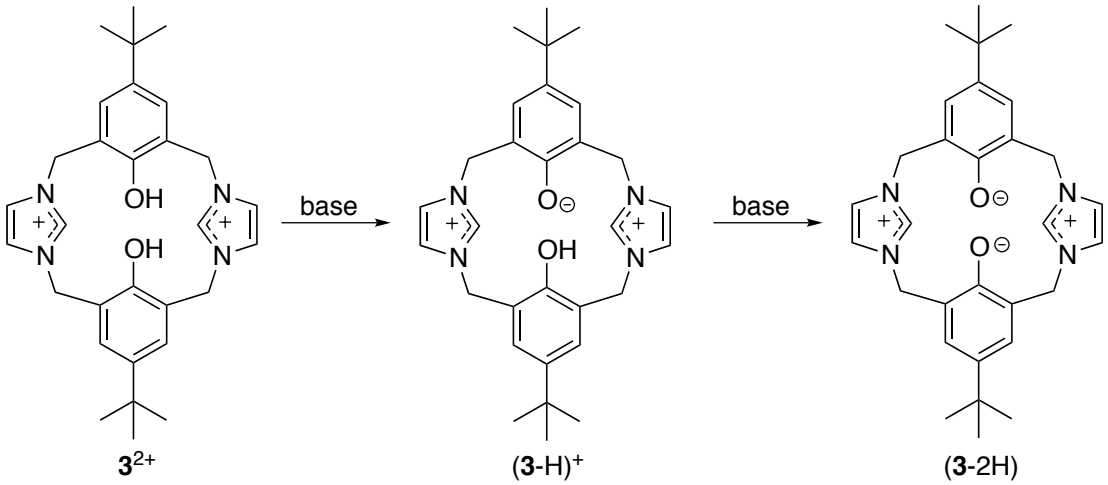


Scheme 3 The salt [(**5**)(**5**-H)].3Br, obtained during attempts to grow crystals of **5**.2Br for an X-ray study

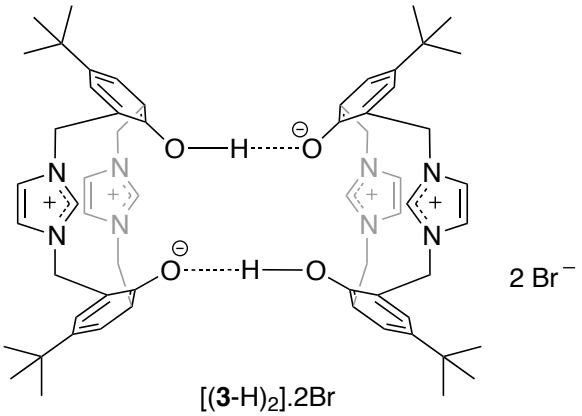


[(**5**)(**5**-H)].3Br

Scheme 4 Successive deprotonation of the bis(phenol) cyclophane $\mathbf{3}^{2+}$

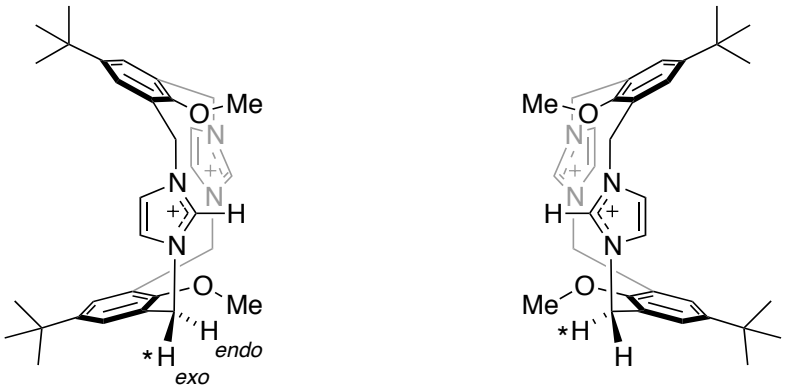


$\mathbf{3}^{2+}$ (**3**-H)$^{+}$ (**3**-2H)

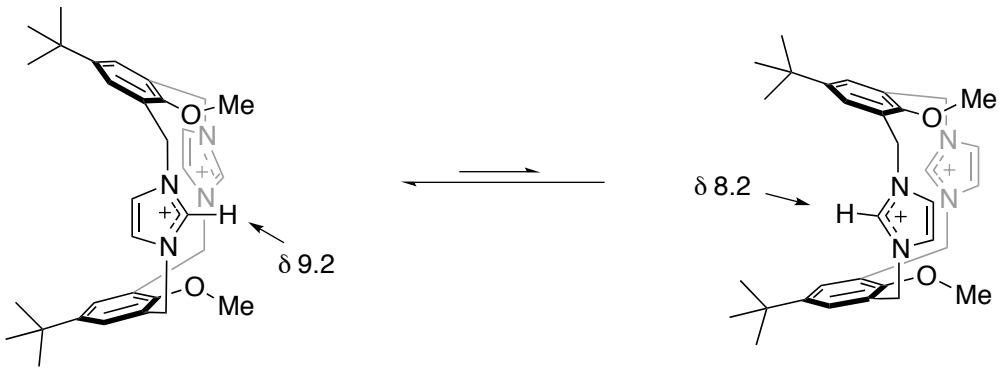


[(**3**-H)$_2$].2Br

Scheme 5 The two equivalent cone conformations of the cyclophane $\mathbf{4}^{2+}$, with one benzylic proton marked with an asterisk to highlight the different (*exo* vs *endo*) environments that that proton experiences in the two forms.

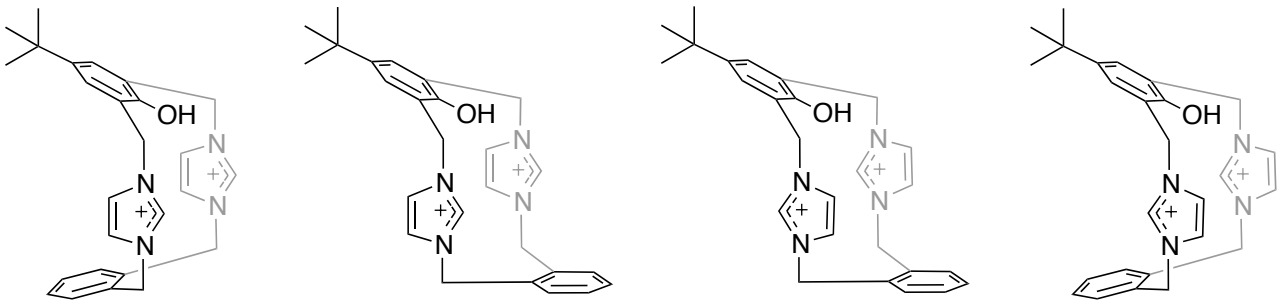


Scheme 6 Conformations of $\mathbf{4}^{2+}$ in equilibrium in solutions of **4**.2Br.



cone conformation 1,3-alternate conformation

Scheme 7 Conformations of the mono(phenol) cyclophane $\mathbf{5}^{2+}$ that have a plane of symmetry.



cone partial cone partial cone 1,3-alternate

Figure Captions

Fig. 1 a (i) Projection of the asymmetric unit components of the crystal structure of triclinic **3**.2Br.3(MeOH) (the cation being in its cone isomeric form; from the data of ref. [11]), showing the close hydrogen-bonding interactions therein;

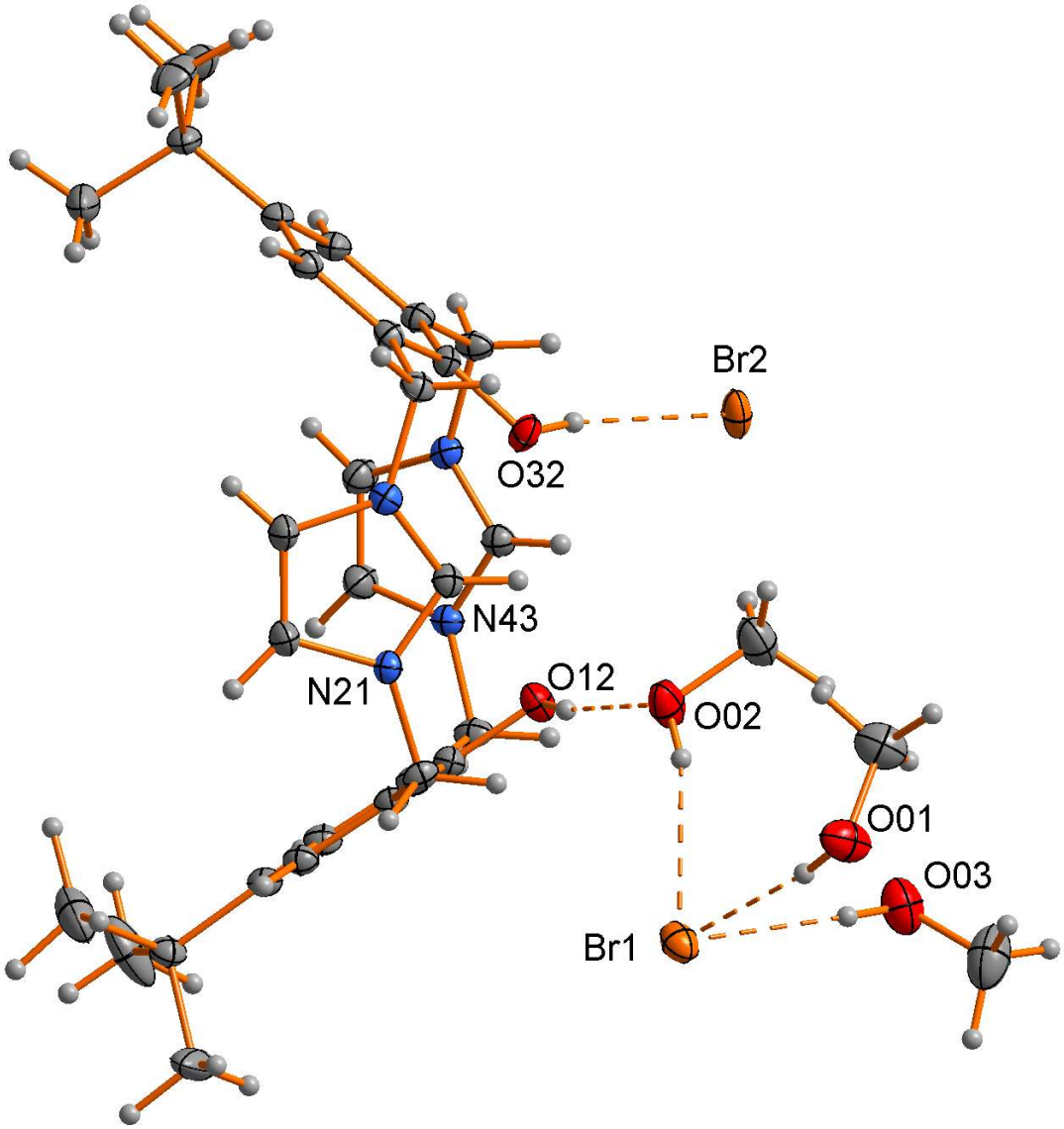


Fig. 1 a (ii) Unit cell contents of the crystal structure of triclinic **3**.2Br.3(MeOH), projected down *a*; note the discrete nature of the formulaic asymmetric unit, and the inclusive approach of a tert-butyl group of a neighbouring cation to the cation cone.

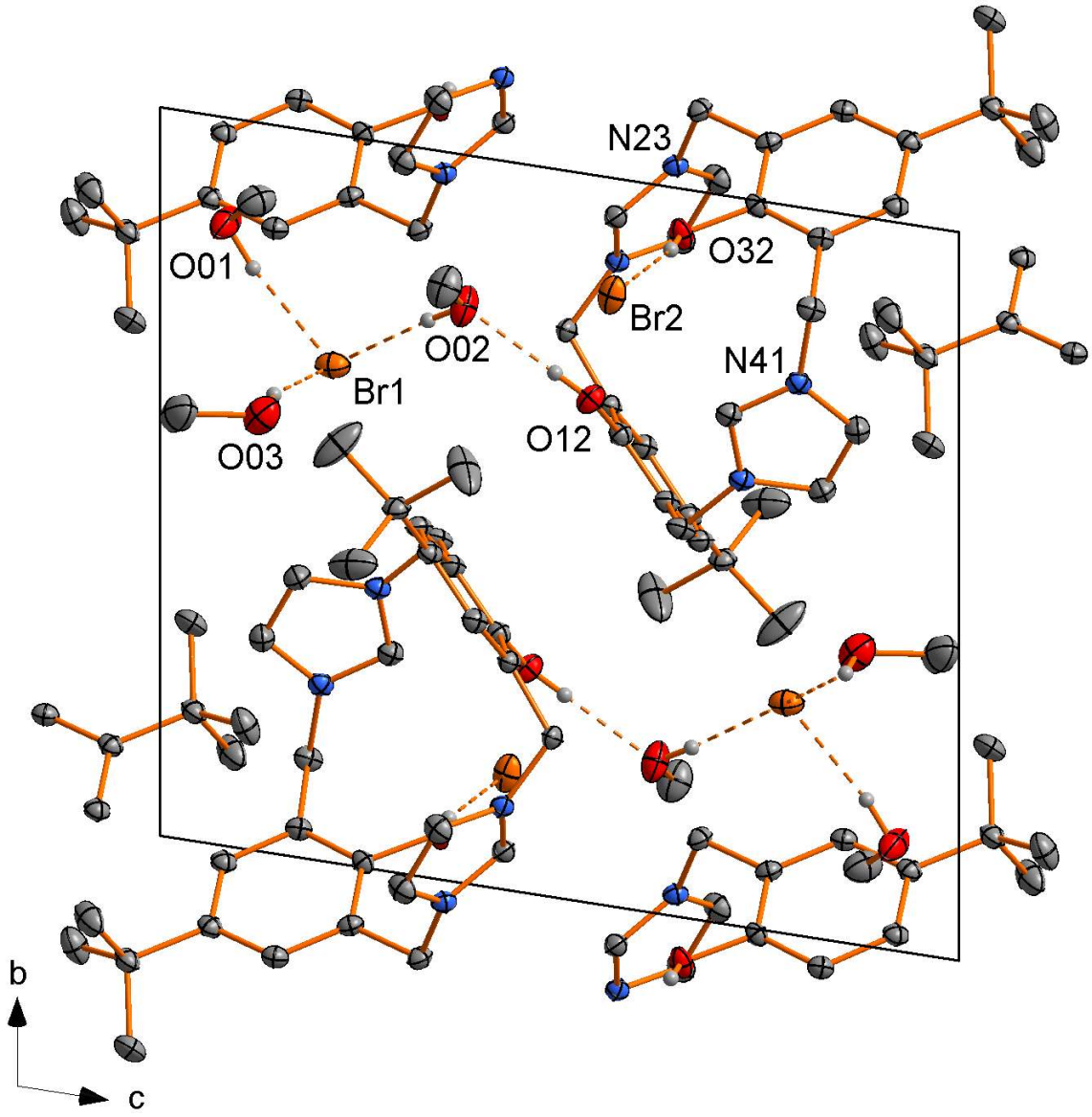


Fig. 1 b (i) Projection of the components of the crystal structure of monoclinic **3**.2Br.2(MeOH).2($CHCl_3$) (the 1,2-alternate isomer of the cation), showing the hydrogen-bonding interactions;

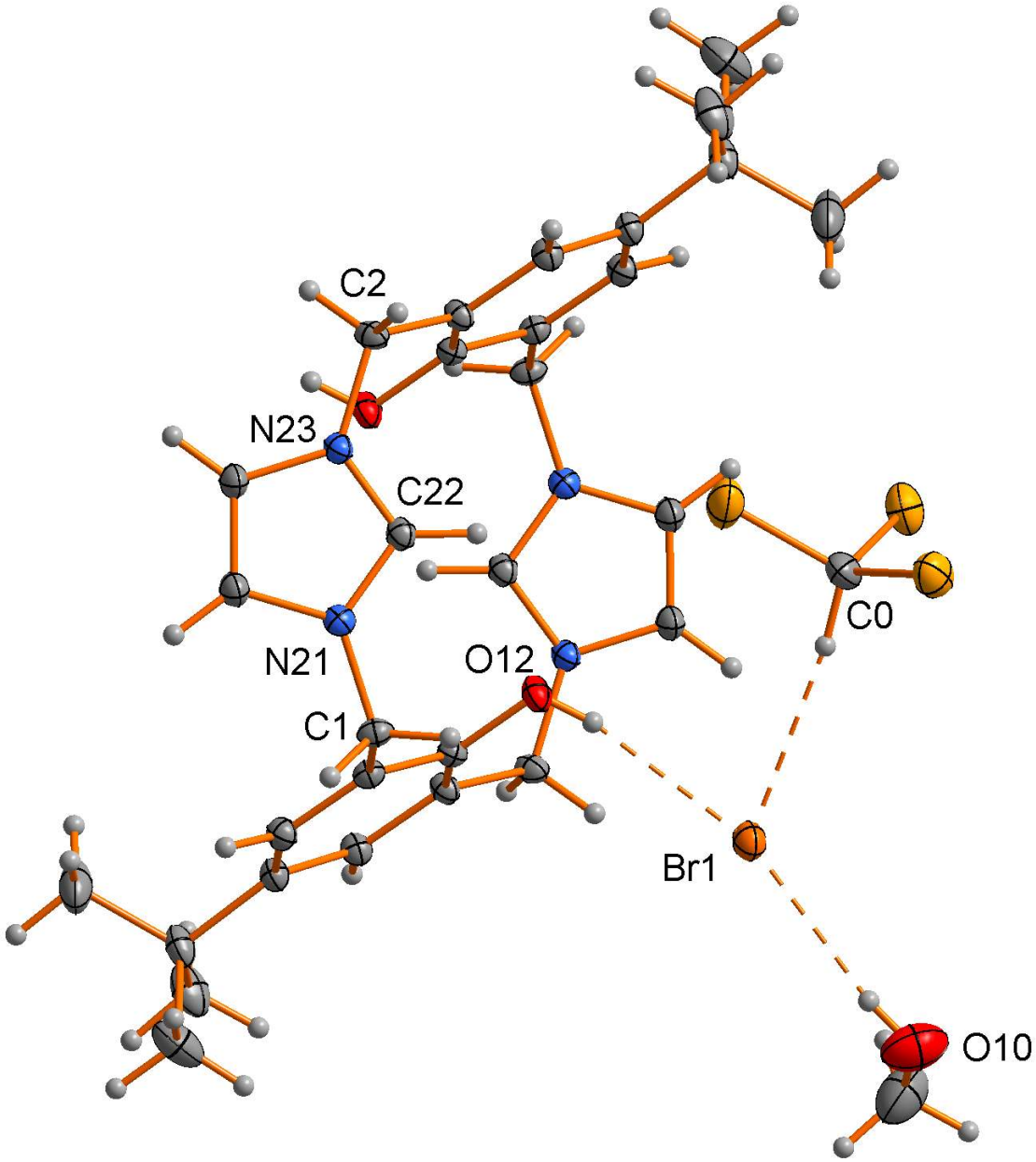


Fig. 1 b (ii) Unit cell contents of monoclinic **3**.2Br.2(MeOH).2($CHCl_3$), projected down *a*.

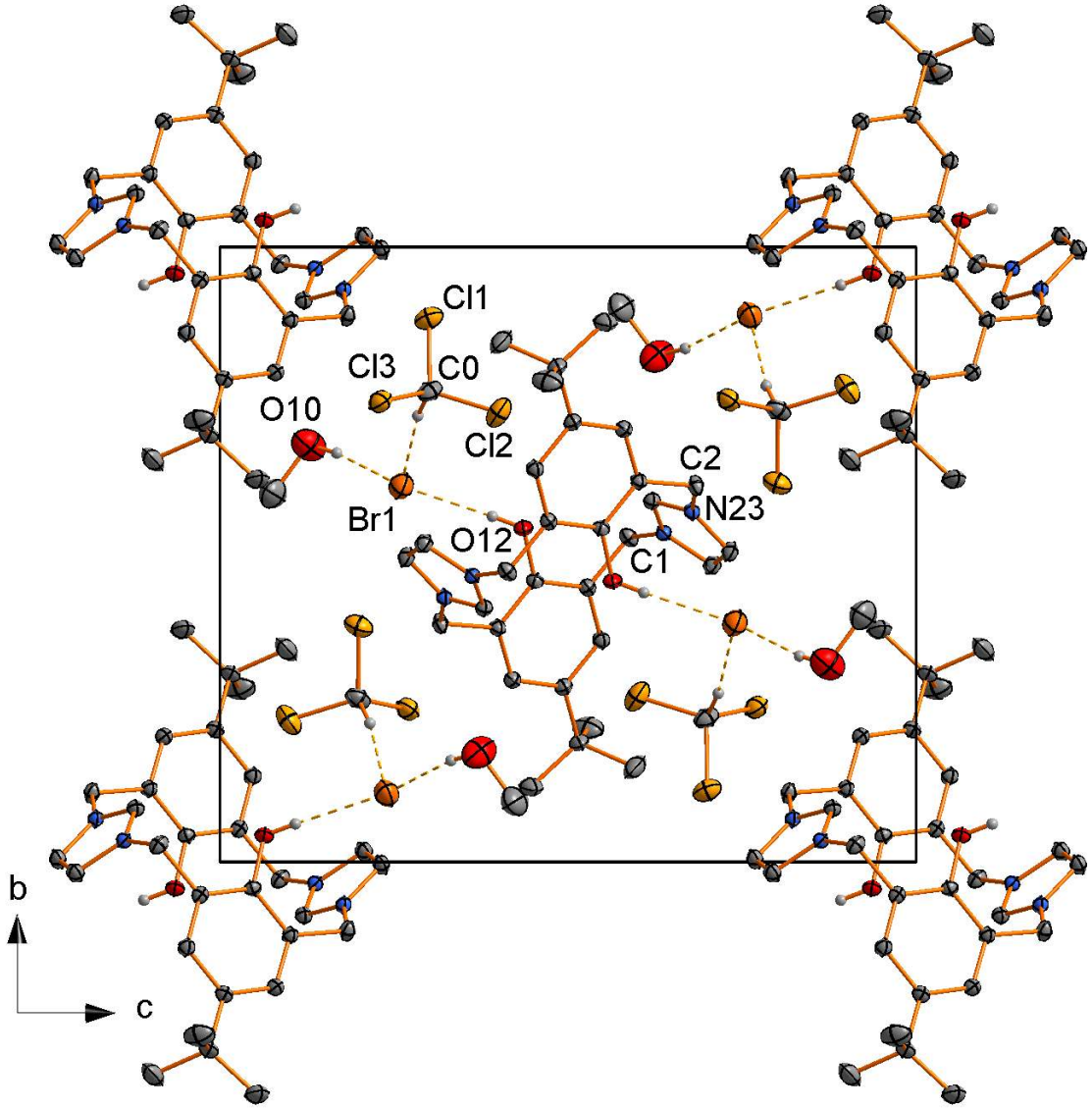
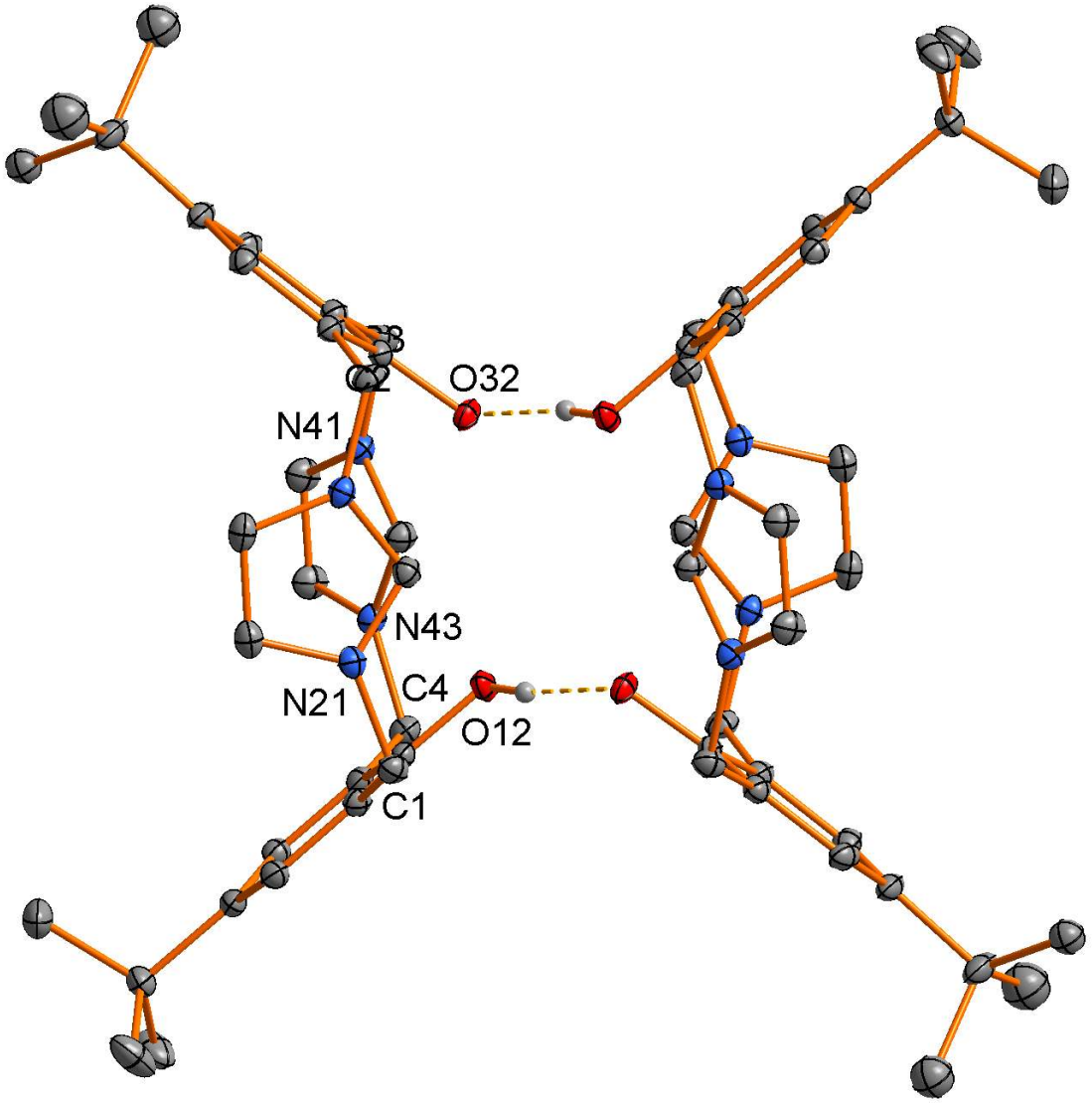


Fig. 2a (i,ii) Projections of a centrosymmetrically related cation pair of [(**3**-H)$_2$].2Br.4(MeCN), showing the hydrogen-bonds between the pair. Of particular interest is the approach (shown in (ii)) of the carbenoid-H(42) to one of the oxygen atoms H(42)…O(12), and to the inversion-related H(22) (H…H 2.29(est.)).



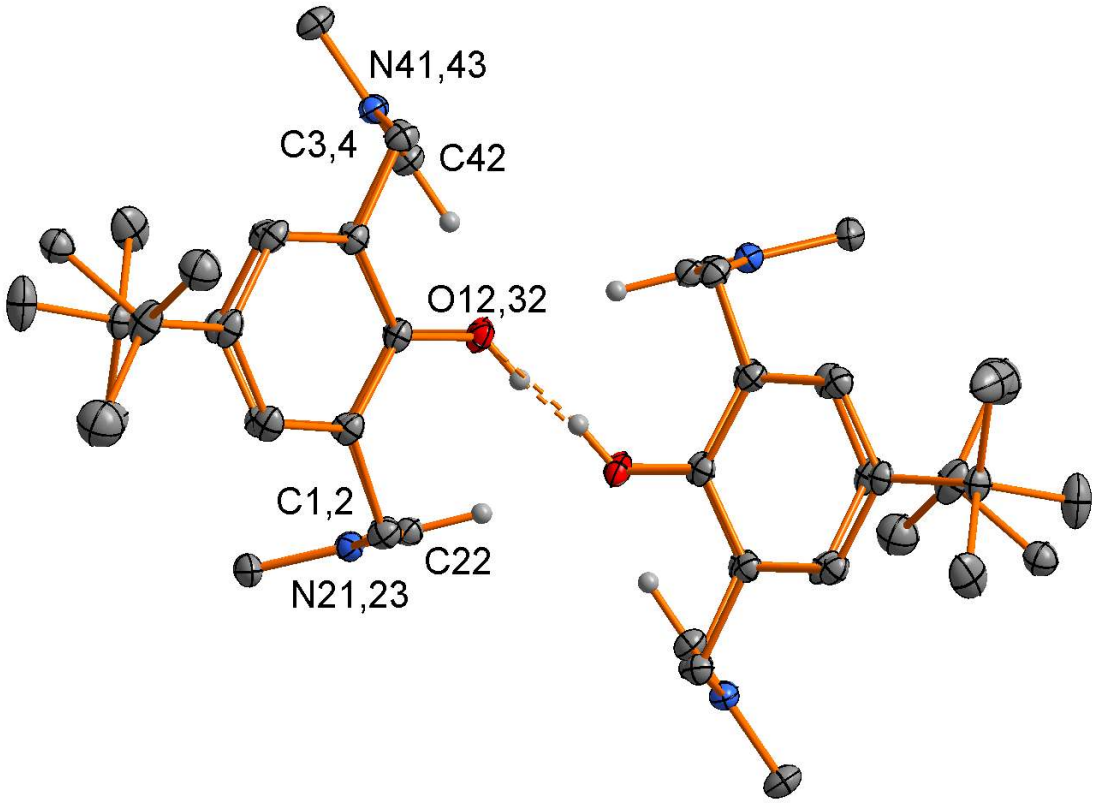

N41,43
C3,4
C42
O12,32
C1,2
C22
N21,23

Fig. 2b Unit cell contents of [(**3**-H)$_2$].2Br.4(MeCN), projected down *a*. The approach of the tert-butyl group from an inversion-related neighbouring cation to the cation cone is clearly visible.

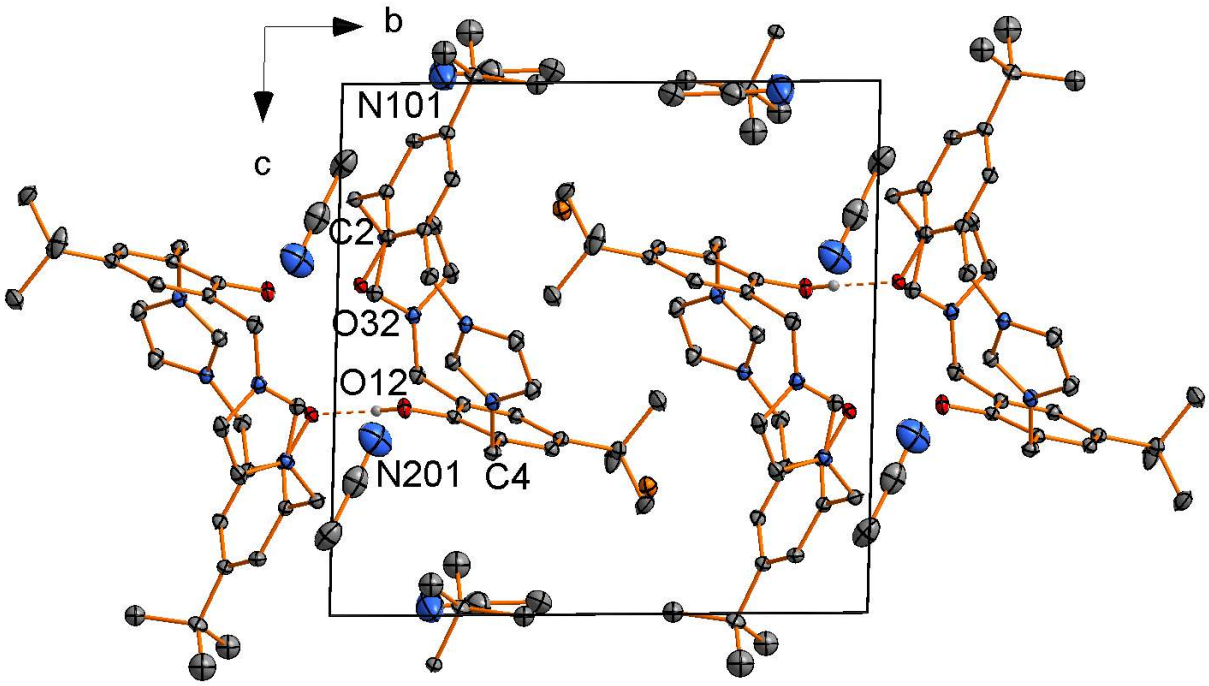


Fig. 3a Projection of the cation of **4**.2Br.2(MeOH).(Et_2O), showing inclusion of the diethyl ether molecule within its cone conformation. One component only of disordered methyl group 12 is shown.

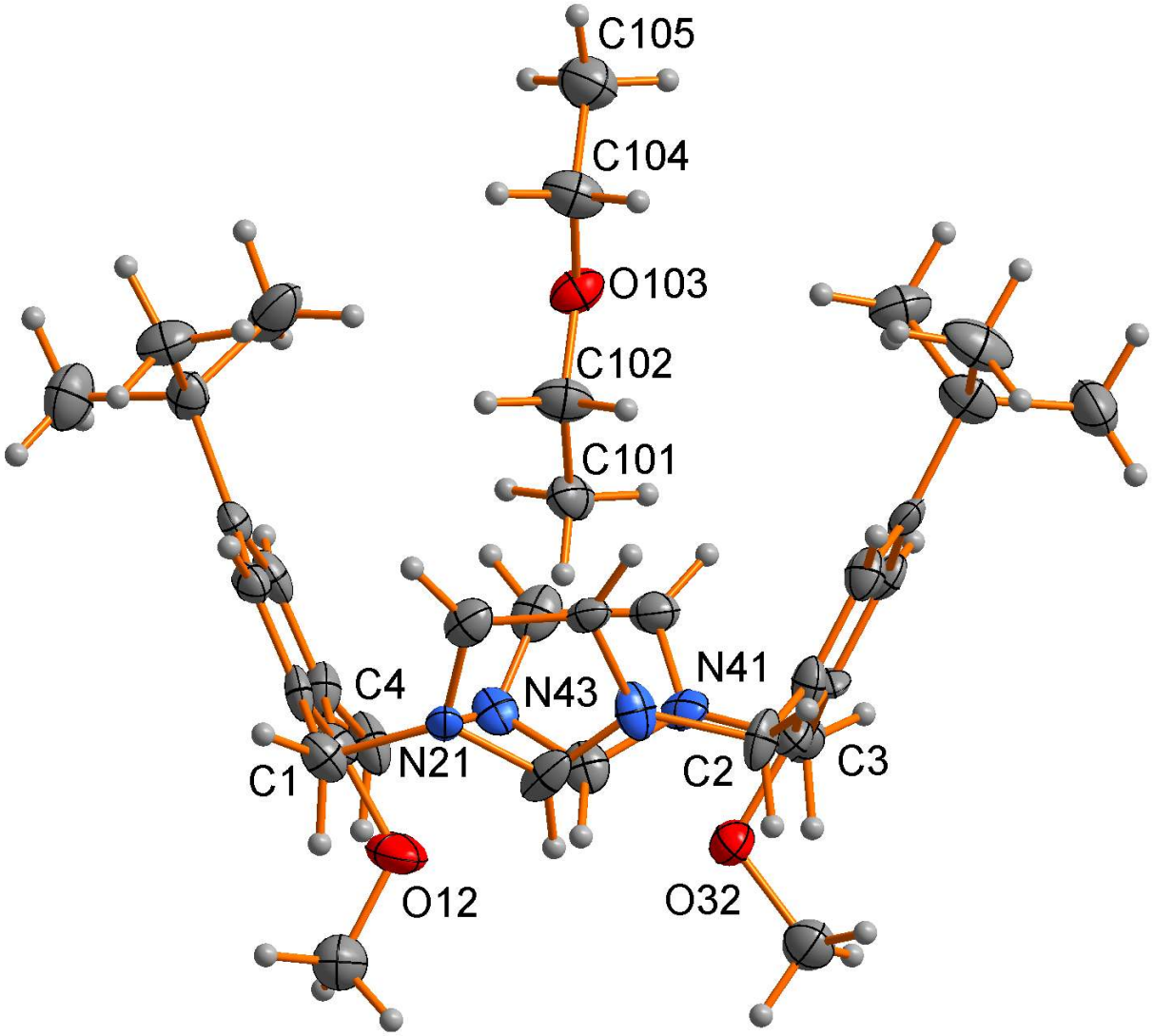


Fig. 3b Unit cell contents of **4**.2Br.2(MeOH).(Et_2O) projected down *c*, showing the channels parallel to that axis.

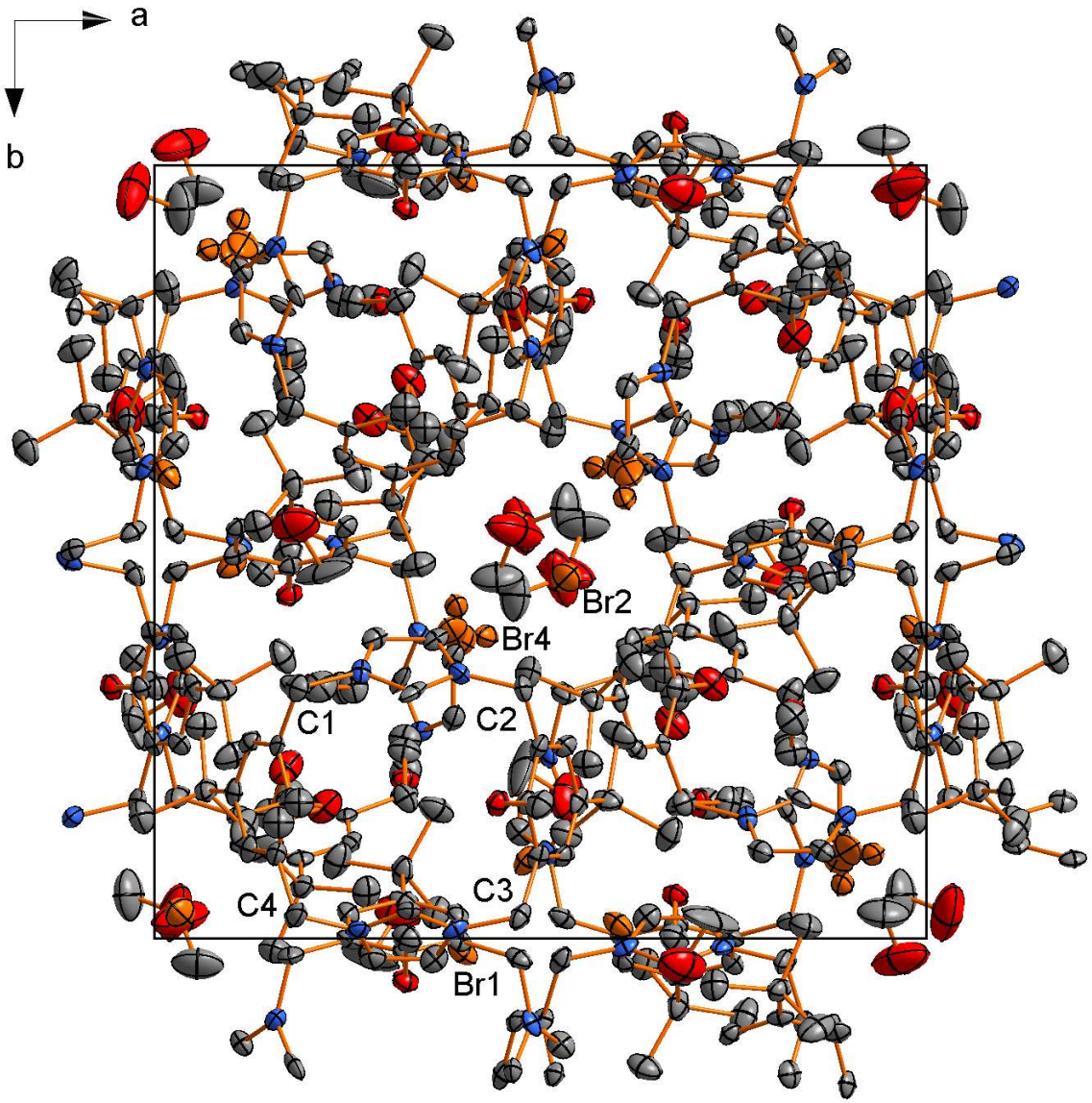


Fig. 4a Projection of the two components of the cation composite of [(**5**)(**5**-H)].3Br.3(MeOH), showing their association via hydrogen-bonding through the one phenolic hydrogen atom.

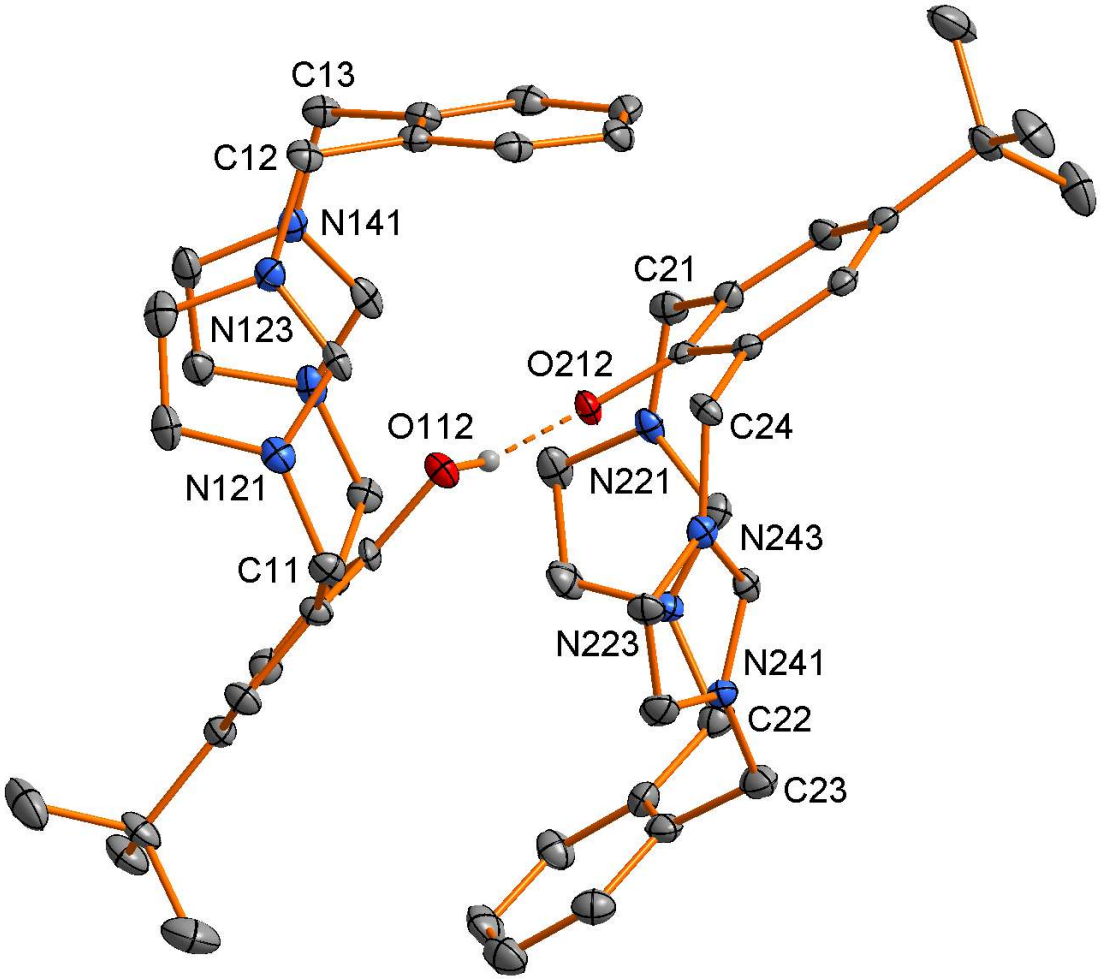


Fig. 4b Unit cell contents of [(**5**)(**5**-H)].3Br.3(MeOH), projected down *a*.

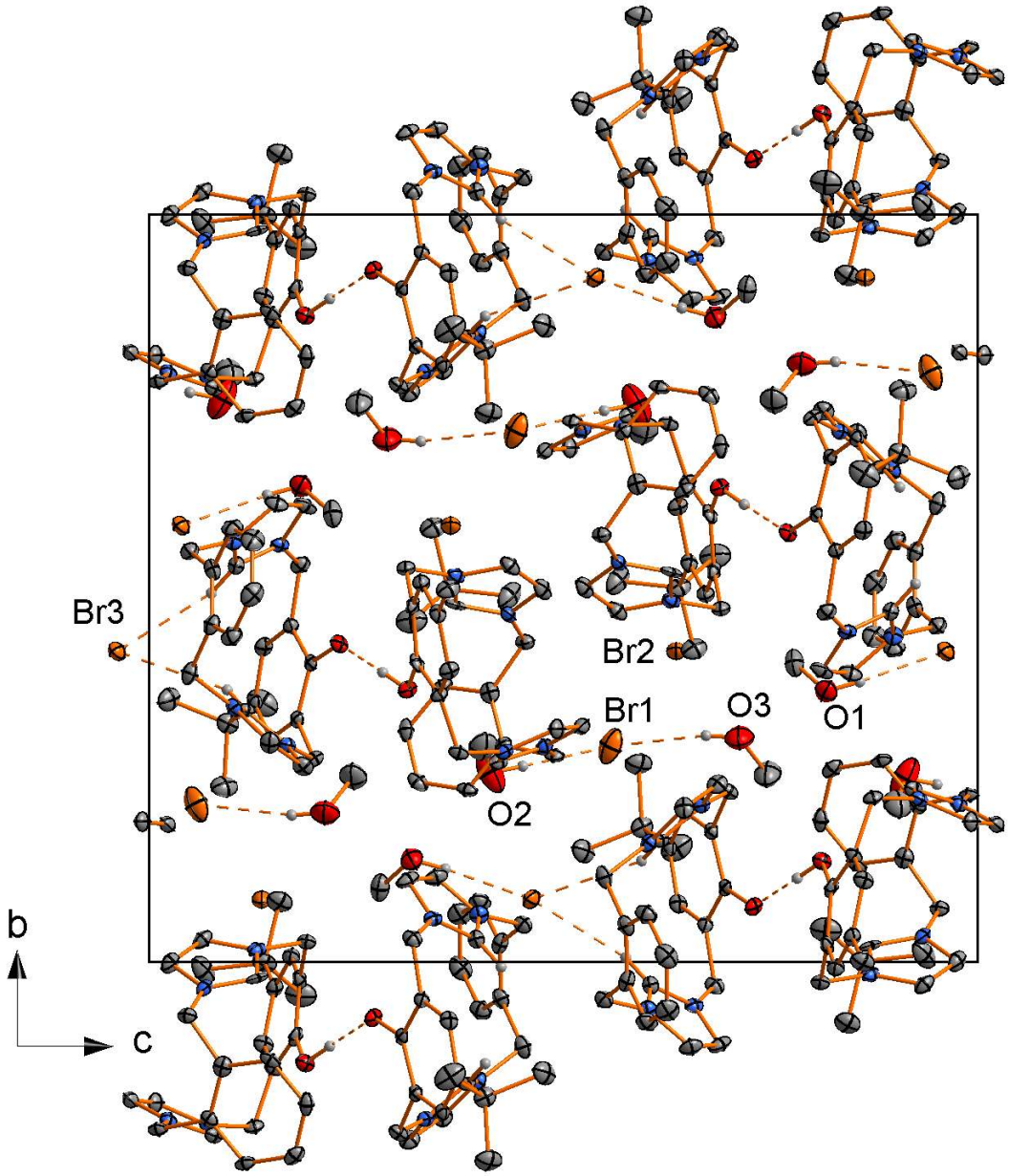


Fig. 5 ^{1}H NMR spectra (500 MHz, room temperature) of: **a**, a freshly prepared solution of **4**.2Br in CD_3OD; and **b**, the same solution after 8 hours at room temperature. In **a**, signals due to the cone conformation are labelled, while in **b** only signals due to the 1,3-alternate conformation are labelled. Solvent signals are marked with asterisks (*).

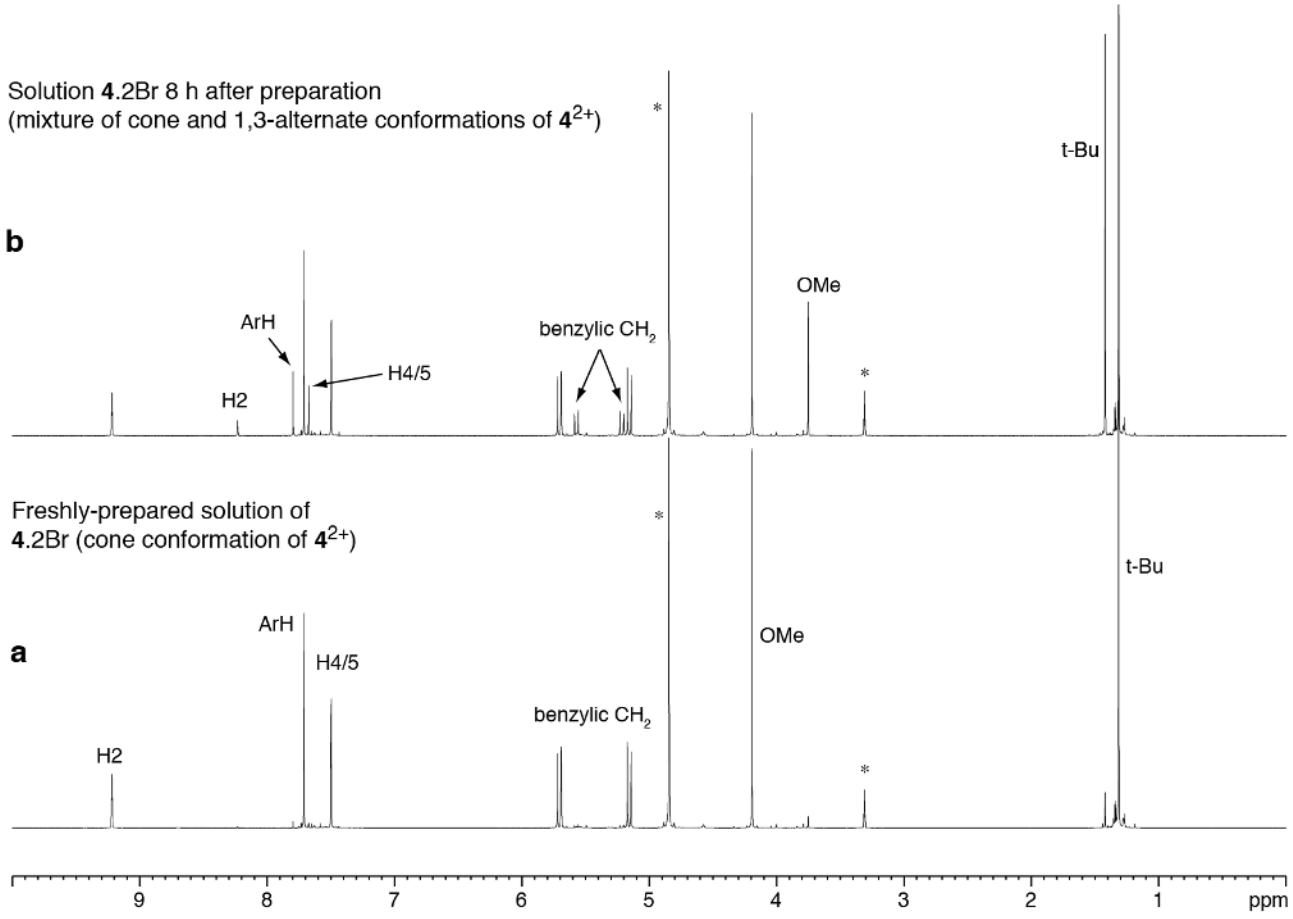


Fig. 6 ^{1}H NMR spectra (500 MHz, CD_3OD) for a solution of the mono(phenol) cyclophane salt **5**.2Br, recorded at the temperatures specified. Resonances marked with an asterisk (*) are due to residual solvent protons, and resonances marked with a tilde (~) have been cropped for clarity.

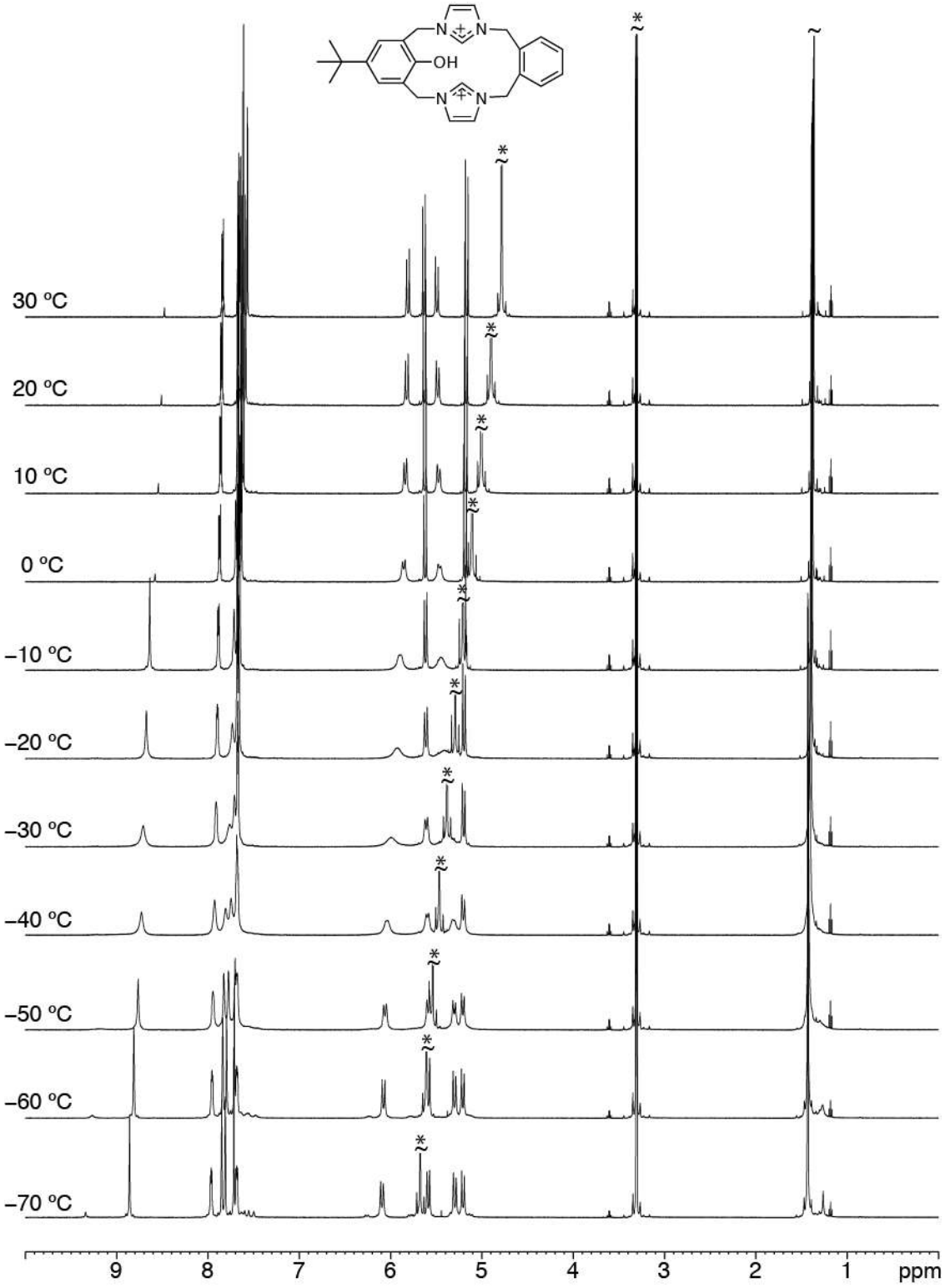


Fig. 7 Downfield region of the ^{1}H NMR spectrum (500 MHz) of a solution of **5**.2Br in at CD_3OD at -70 °C, showing signals due to aromatic and benzylic protons. The signal marked with a tilde (~) is due to the residual solvent OH signal. Signals marked with arrows are due to the minor (cone) conformation of $\mathbf{5}^{2+}$.

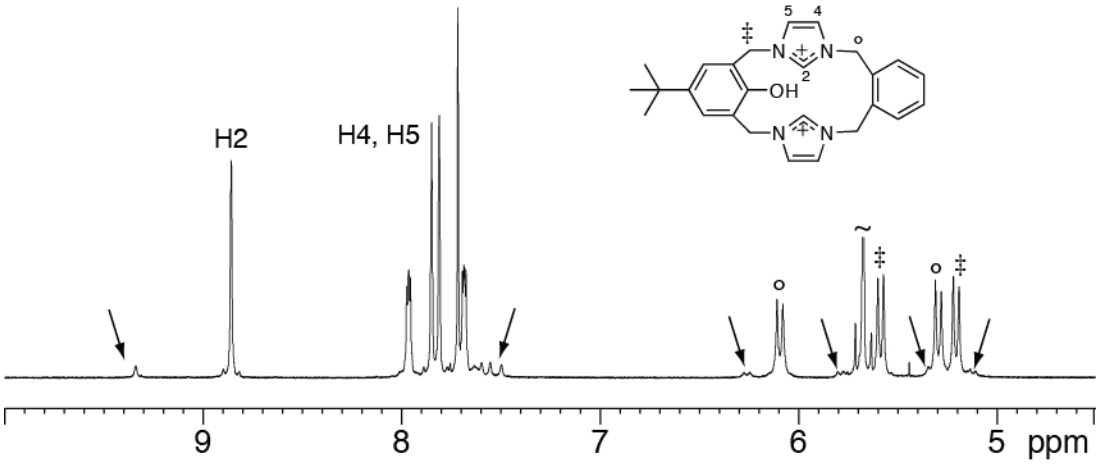


Fig. 8 ^{1}H NMR spectra (500 MHz, ambient temperature) for: **a**, a solution of **3**.2Br in DMSO-d_6, and **b**, a solution of (**3**-2H) in CD_3CN. Resonances marked with asterisks (*) are due to traces of solvent impurities (MeOH in **a**, ether in **b**). Resonances marked with a cross (×) are due to the residual protons in the NMR solvent and resonances marked with tilde (~) have been cropped for clarity.

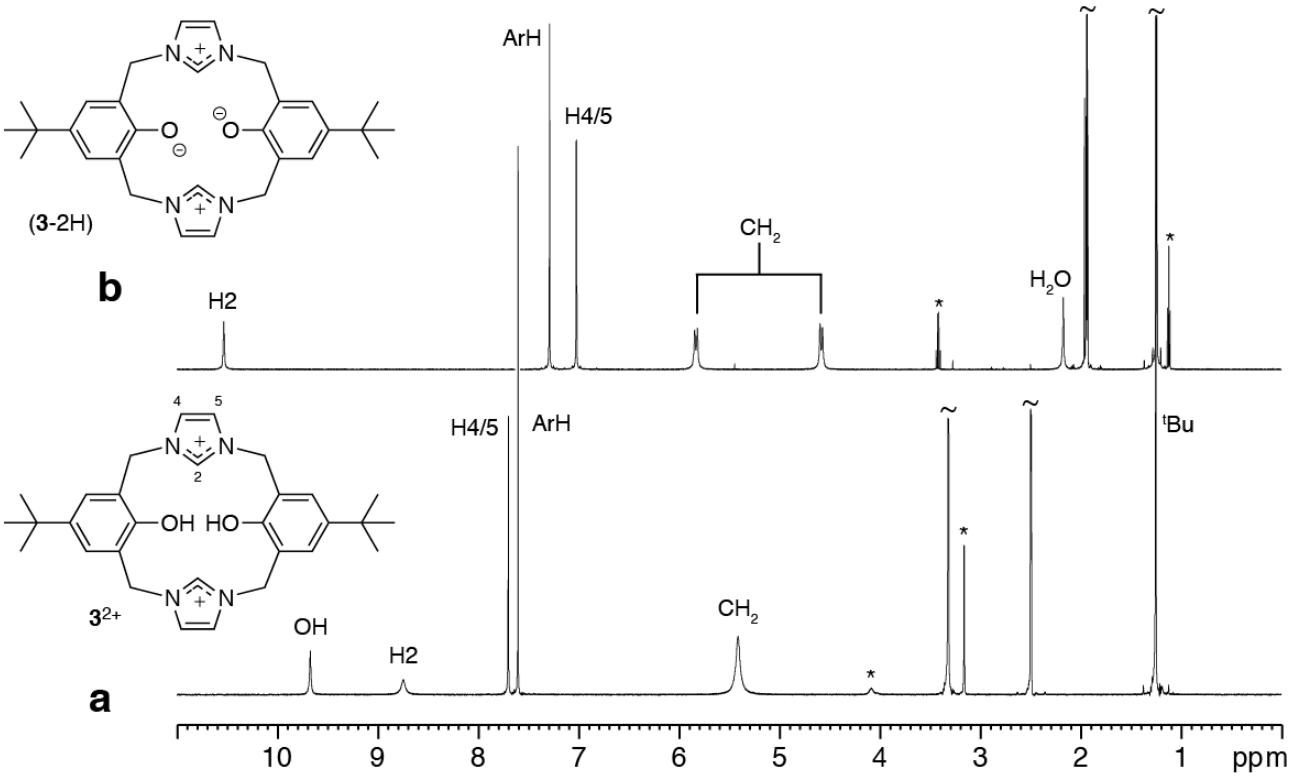


Table 1 Interplanar dihedral angles (degrees)

Compound	Ar$^{o,\prime}$/Ar$^{\prime\prime\prime\prime}$	im$^{o,\prime}$/im$^{\prime\prime,\prime\prime\prime}$	Ar$^{o,\prime}$/im$^{\prime\prime,\prime\prime\prime}$	Ar$^{\prime\prime,\prime\prime\prime}$/im$^{o,\prime}$,im$^{\prime\prime,\prime\prime\prime}$
[(**3**-H)$_2$].2Br.4(MeCN)	78.84(6)	69.21(8)	81.45(6), 60.06(6)	81.72(6), 56.52(7)
4.2Br.2(MeOH).(Et$_2$O)	51.5(2)	64.3(3)	80.3(2), 77.4(3)	73.7(3), 75.2(3)
3.2Br.3(MeOH)[a]	73.45(8)	40.07(12)	81.64(10), 77.26(10)	81.45(10), 72.64(10)
3.2Br.2(CHCl$_3$).2(MeOH)			73.83(6)	
[(**5**)(**5**-H)].3Br.3(MeOH)	49.1(2)	31.7(2)	81.3(2), 73.2(2)	73.9(2), 75.9(2)
	5.5(2)	83.6(2)	65.5(2), 63.7(2)	61.0(2), 62.6(2)

[a] from the deposition of ref. [11] (CCDEC: RAJXEG) (*T* ca 153 K); refinement on |*F*|

Table 2 Crystal/refinement data

Compound·S	[(**3**-H)$_2$].2Br.4(MeCN) [L(OH)O]$^{3+}$Br$^-$·2MeCN	**3**.2Br.3(MeOH)[a] [L(OH)$_2$]$^{2+}$(Br$^-$)$_2$·3MeOH	**3**.2Br.2($CHCl_3$).2(MeOH) [L(OH)$_2$]$^{2+}$(Br$^-$)$_2$·$CHCl_3$·2MeOH	**4**.2Br.2(MeOH).(Et_2O) [L(OMe)$_2$]$^{2+}$ (Br$^-$)$_2$·2MeOH·Et_2O	[(**5**)(**5**-H)].3Br.3(MeOH) [L'(OH)]$^{3+}$(Br$^-$)$_3$·3MeOH
Formula	$C_{34}H_{43}BrN_6O_2$	$C_{33}H_{50}Br_2N_4O_5$	$C_{34}H_{48}Br_2Cl_6N_6O_4$	$C_{38}H_{60}Br_2N_4O_5$	$C_{55}H_{71}Br_3N_8O_5$
M_r	647.7 Da	742.6 Da	949.3 Da	812.7 Da	1163.9 Da
Crystal system	Triclinic	Triclinic	Monoclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)	$P2_1/n$ (C_{2h}^5, No.14)	$P4_32_12$ (D_4^8, No. 96)	$P2_1/c$ (C_{2h}^5, No.14)
Unit cell	a = 10.3398(5) Å	a = 10.5409(7) Å	a = 8.8405(8) Å	a = 16.9990(5) Å	a = 15.0785(3) Å
	b = 12.9830(6) Å	b = 13.3867(9) Å	b = 14.2630(10) Å	(b = 16.9990(5) Å)	b = 17.9733(3) Å
	c = 13.2703(6) Å	c = 14.1980(10) Å	c = 16.252(2) Å	c = 29.049(2) Å	c = 19.9507(4) Å
	α = 88.032(4)°	α = 92.181(2)°	α = 90°	α = 90°	α = 90°
	β = 71.508(4)°	β = 105.020(2)°	β = 95.838(2)°	β = 90°	β = 92.892(2)°
	γ = 78.519(4)°	γ = 112.622(2)°	γ = 90°	γ = 90°	γ = 90°
V	1654.85(13) Å^3	1764.7(2) Å^3	2038.6(3) Å^3	8394.2(7) Å^3	5400.0(2) Å^3
Density (Z)	1.30_8 Mg.m^{-3} (2 f.u.)	1.39_8 Mg.m^{-3} (2 f.u.)	1.54_6 Mg.m^{-3} (2 f.u.)	1.28_6 Mg.m^{-3} (8 f.u.)	1.43_2 Mg.m^{-3} (4 f.u.)
μ_{Mo}/mm^{-1}	1.28 mm^{-1}	2.34 mm^{-1}	2.42 mm^{-1}	1.97 mm^{-1}	2.30 mm^{-1}
$'T'_{min/max}$	0.85	0.91	0.79	0.87	0.79
Specimen/mm^3	0.30x0.27x0.08 mm^3	0.24x0.20x0.18 mm^3	0.38x0.26x0.24 mm^3	0.24x0.15x0.08 mm^3	0.27x0.11x0.05 mm^3
$2\theta_{max}$ (N_t)	63° (52038)	75° (36085)	70° (36155)	50° (39737)	55° (57966)
N (R_{int})	10262 (0.024)	17998 (0.036)	9021 (0.036)	7369 (0.123)	12134 (0.069)
N_o ($I > 2\sigma(I)$)	8633	9093	6678	3999	6942
$R1$ (*S*)	0.038 (1.13)	0.039 (1.10)	0.036 (0.98)	0.058 (0.97)	0.058 (1.00)
wR2 (*a*(,*b*))	0.113 (0.067, 0.42)	0.050 (n/a)	0.101 (0.049, 1.38)	0.089 (0.021, -)	0.168 (0.078, -)
$\|\Delta\rho\|_{max}$	1.20 eÅ^{-3}	1.74 eÅ^{-3}	0.71 eÅ^{-3}	0.79 eÅ^{-3}	2.93 eÅ^{-3}

[a] from the deposition of ref. [11] (CCDEC: RAJXEG) (*T* ca 153 K); refinement on |*F*|)

Supporting information — Online Resource 1

Calixarene/azolium cyclophane hybrids: synthesis, structure and conformations

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Contents:

Table S1 Selected ligand geometries

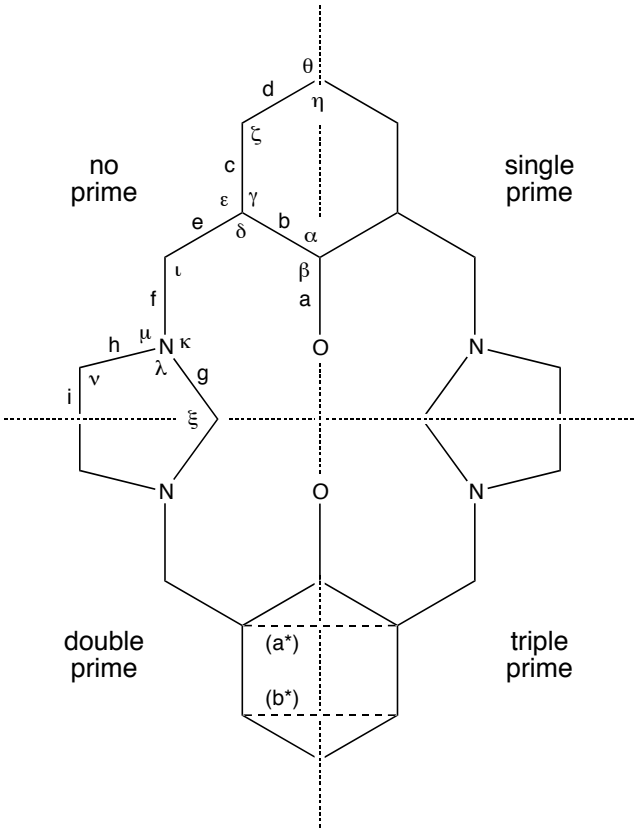
Cation	($\mathbf{3}$-H)$^{+}$LH^{+}		$\mathbf{4}^{2+}$LMe$_2^{2+}$		$\mathbf{3}^{2+}$LH$_2^{2+}$ ^{a}		$\mathbf{3}^{2+}$LH$_2^{2+}$
Section	° '	" '"	° '	" '"	° '	" '"	° '
Distances (Å)							
a	1.345(2)	1.338(2)	1.405(7)	1.377(7)	1.363(4),	1.363(3)	1.372(2)
b	1.409(2), 1.407(2)	1.412(2), 1.413(2)	1.386(8), 1.342(8)	1.380(8), 1.392(7)	1.401(3), 1.399(3)	1.400(3), 1.398(4)	1.396(2), 1.398(2)
c	1.397(2), 1.393(2)	1.399(2), 1.394(2)	1.358(7), 1.390(8)	1.388(8), 1.360(7)	1.398(4), 1.393(4)	1.393(3), 1.400(3)	1.388(2), 1.397(2)
d	1.396(2), 1.400(2)	1.394(2), 1.399(2)	1.361(8), 1.409(8)	1.436(8), 1.384(7)	1.396(3), 1.397(4)	1.399(4), 1.396(3)	1.394(2), 1.394(2)
e	1.507(2), 1.509(2)	1.508(2), 1.508(2)	1.536(8), 1.513(8)	1.503(8), 1.518(8)	1.507(3), 1.506(4)	1.508(4), 1.510(3)	1.507(2), 1.507(2)
f	1.479(2), 1.488(2)	1.478(2), 1.489(2)	1.501(7), 1.477(7)	1.473(7), 1.478(7)	1.481(3), 1.479(4)	1.477(4), 1.480(4)	1.476(2), 1.478(2)
g	1.332(2), 1.335(2)	1.337(2), 1.332(2)	1.325(6), 1.330(7)	1.348(7), 1.327(7)	1.338(3), 1.334(4)	1.332(3), 1.333(3)	1.331(2), 1.331(2)
h	1.383(2), 1.378(2)	1.380(2), 1.382(2)	1.375(7), 1.346(7)	1.374(7), 1.362(7)	1.384(3), 1.379(3)	1.377(3), 1.376(4)	1.374(2), 1.373(2)
i	1.356(2), 1.360(2)		1.360(7), 1.338(7)		1.351(4)	1.353(4)	1.356(2)
O…H(C)	0.79(2)		1.39(2)/1.54(2) ^{b}	1.448(6)	0.77(4)	0.80(4)	0.80(2)
Angles (degrees)							
α	117.75(13)	117.25(14)	121.9(7)	121.0(6)	119.4(2)	119.4(2)	119.66(13)
β	123.17(13), 119.04(13)	122.88(13), 119.84(14)	119.7(6), 118.4(6)	118.8(6), 120.0(6)	124.3(2), 116.3(2)	116.4(2), 124.0(2)	117.65(13), 122.64(13)
γ	120.16(14), 120.60(14)	120.40(14), 120.68(14)	119.5(6), 117.6(6)	118.8(6), 119.9(6)	119.0(2), 120.0(2)	120.2(2), 118.9(2)	119.86(13), 118.96(13)
δ	119.80(13), 119.96(13)	119.90(13), 120.08(14)	119.4(6), 121.2(7)	120.8(7), 119.8(5)	121.8(2), 118.5(2)	118.8(2), 121.6(2)	119.62(13), 122.26(13)
ε	119.95(14), 119.43(13)	119.66(14), 119.17(14)	120.8(6), 120.9(6)	120.4(6), 120.3(6)	119.1(2), 121.4(2)	121.0(2), 119.5(2)	120.52(13), 118.69(13)
ζ	122.61(14), 122.34(14)	122.55(16), 122.35(14)	121.9(6), 122.1(6)	120.9(6), 122.2(6)	122.9(2), 122.1(2)	121.7(2), 122.8(2)	121.88(13), 122.30(13)
η	116.43(14)	116.54(14)	116.9(6)	117.2(6)	116.6(2)	116.9(2)	117.22(13)
θ	122.51(14), 121.00(14)	122.50(15), 120.93(15)	124.1(6), 118.8(6)	120.3(6), 122.5(6)	120.5(2), 122.8(2)	121.5(2), 121.5(2)	119.87(13), 122.90(14)
ι	110.00(12), 113.34(12)	110.48(12), 114.42(13)	109.4(5), 110.5(5)	110.0(5), 109.8(4)	110.6(2), 110.8(2)	110.2(2), 112.3(2)	110.84(12), 113.28(13)
κ	125.91(13), 125.83(13)	126.03(13), 125.33(13)	126.6(6), 124.7(6)	124.6(6), 125.9(5)	127.5(2), 125.8(2)	126.4(2), 125.8(2)	126.51(13), 127.00(13)
λ	108.81(13), 108.64(13)	108.73(13), 108.72(13)	108.6(5), 108.5(5)	108.2(5), 108.0(5)	108.4(2), 109.1(2)	108.8(2), 108.9(2)	109.05(13), 108.81(13)
μ	125.17(13), 125.45(13)	125.11(35), 125.73(13)	124.4(5), 126.2(6)	127.1(5), 125.9(5)	123.7(2), 124.9(2)	124.5(2), 125.3(2)	124.31(13), 124.19(13)
ν	106.97(14), 107.14(14)	107.07(14), 106.83(14)	107.4(6), 107.7(6)	107.0(6), 107.4(6)	107.0(3), 106.7(3)	107.3(2), 107.3(2)	106.70(13), 107.19(13)
ξ	108.41(14)	108.66(14)	108.8(6)	108.3(6)	108.4(2)	108.0(2)	108.24(13)

^{a} from the deposition of ref. [11] (CCDEC: RAJXEG) (*T* ca 153 K); refinement on |*F*|

^{b} O–C(Me) distances (disordered)

(cont.)

Cation	$\mathbf{5}^{2+}LH^{2+}$ (cation 1)		$(\mathbf{5}\text{-H})^{+}\ LH^{+}$ (cation 2)	
Section	° ' " "'		° ' " "'	
Distances (Å)				
a	1.364(5)	1.405(6)*	1.318(5)	1.401(7)*
b	1.405(6), 1.392(6)	1.380(7)*	1.426(6), 1.409(6)	1.378(7)*
c	1.397(6), 1.392(6)	1.393(6), 1.388(6)	1.376(6), 1.391(6)	1.389(6), 1.399(6)
d	1.409(6), 1.373(6)	1.397(6), 1.385(6)	1.401(6), 1.393(6)	1.379(7), 1.389(7)
e	1.492(6), 1.508(6)	1.504(6), 1.513(6)	1.496(6), 1.494(6)	1.524(6), 1.509(7)
f	1.478(6), 1.493(6)	1.476(5), 1.480(5)	1.470(6), 1.479(5)	1.475(6), 1.481(6)
g	1.327(5), 1.323(5)	1.319(6), 1.337(6)	1.331(6), 1.321(6)	1.330(5), 1.333(5)
h	1.383(6), 1.372(6)	1.386(6), 1.383(6)	1.374(6), 1.393(5)	1.368(6), 1.376(6)
i	1.359(7), 1.337(2)		1.346(7), 1.346(6)	
O…H	0.84			
Angles (degrees)				
α	118.6(4)		116.5(4)	
β	116.9(4), 1.240(4)		120.9(4), 122.6(4)	
γ	119.7(4), 119.5(4)	118.8(4), 119.4(4)	120.1(4), 121.3(4)	119.1(4), 118.4(4)
δ	119.8(4), 120.0(4)	122.3(4), 122.5(4)	118.5(4), 118.4(4)	123.9(4), 124.4(4)
ε	120.1(4), 120.1(4)	118.9(4), 118.1(4)	121.4(4), 120.0(4)	116.9(4), 117.2(4)
ζ	121.5(4), 122.9(4)	120.9(4), 121.4(4)	123.6(4), 122.3(4)	121.9(5), 121.4(5)
η	116.8(4)	119.9(4), 119.5(4)	115.8(4)	119.4(5), 119.7(5)
θ	119.3(4), 123.7(4)	- -	120.3(4), 123.9(4)	- -
ι	109.5(4), 107.4(4)	112.1(4), 111.0(4)	111.8(4), 111.0(3)	113.2(4), 113.2(4)
κ	124.2(4), 124.1(4)	125.2(4), 124.7(4)	125.8(4), 127.0(4)	124.6(4), 125.6(4)
λ	108.0(4), 108.6(4)	108.0(4), 107.6(4)	108.1(4), 108.0(4)	108.3(4). 108.4(4)
μ	126.4(4), 125.9(4)	126.5(4), 127.4(4)	125.7(4), 125.0(4)	127.0(4), 126.0(4)
ν	106.9(4), 107.5(4)	107.0(4), 107.5(4)	107.2(4), 107.2(4)	107.5(4), 107.2(4)
ξ	110.0(4)	108.7(4)	108.8(4)	109.3(4)



The dashed lines pertain to the phenylene ring in $\mathbf{5}^{2+}$.