Synthesis and Conformational Analysis of Dicationic *N*,*N*′-Bridged Bis(benzimidazolium) and Bis(imidazolium) Macrocycles

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Two-step alkylations of benzimidazole, 2-methylbenzimidazole, and imidazole at their nitrogen atoms with various bifunctional alkylating agents have afforded a series of 16-membered quaternary azacyclophanes. Of these macrocycles, those bearing methyl or methoxy groups on the azole or at the aromatic bridges have been found to exist as mixtures of conformers. In some cases, the structures of the conformers have been determined by NMR methods and X-ray crystallography, and have been correlated with the results of a computer-aided conformational search.

Introduction

Recently, azaaromatic onium macrocycles (cyclophanes) have attracted much attention due to their supramolecular structures coupled with their positively charged character. In biochemical host−guest processes such as enzyme−substrate interactions, onium compounds play an important role in the electrostatic binding of the substrate to the enzyme.[1] The fast rates and high specificities of enzymatic reactions partly originate from the electrostatic stabilization of charged transition states by onium moieties.[2] Therefore, onium cyclophanes possessing a relatively hydrophobic cavity (binding site) and onium residues at defined positions on the macrocycle (catalytic site) can be used as artificial enzymes or as receptors to study inclusion electrostatic catalysis.[1]

Although a great number of macrocyclic and linear azaaromatic compounds, in which quaternary ammonium units constitute essential parts of the structure, have been known for a long time,[1] imidazolium cyclophanes (**I**) (Figure 1) have only been reported in the last few years,[3−8] despite the fact that imidazole compounds are frequently encountered in biological systems (quite recently, benztriazolium cyclophanes have also been described[9]).

Another aspect that has aroused interest in bridged bis(imidazolium) and dibenzimidazolium salts (**Ia** and **IIb**) has been the recent preparation of *N*,*N*′-dialkylimidazol-2-ylidenes[10] as isolable nucleophilic carbenes derived from imidazolium salts by simple deprotonation. By analogy, both **I** and **II** were expected to be potential precursors of macrocyclic carbenes or their tetraazafulvalene-type dimers.[11,12]

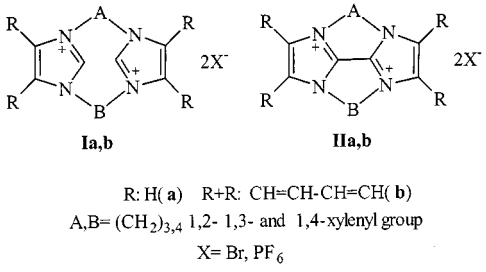
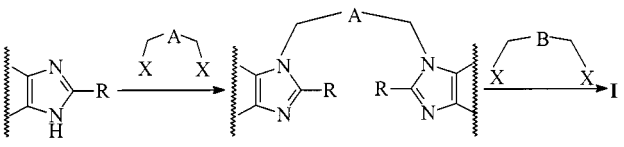


Figure 1. General formula of *N*,*N*′-bridged imidazolium and bridged 2,2′-biimidazolium salts

Generally, bis(azolium) salts (**I**) have been synthesized by two-step procedures.[3−5,7,8,11] A bifunctional alkylating agent (α,ω-dihaloalkanes, xylenyl bromides) is first condensed on the N(1) atom of imidazole or benzimidazole in the presence of base (NaH, NaOH, KOH/PTC). In the next step, the linear precursor thus formed is cyclized at the N(2) atoms with the same or a different alkylating reagent to afford quaternary salts **I** (Scheme 1). A similar approach can be used for the preparation of dibenzimidazolium salts **II**, although one-pot cycloalkylations of 2,2′-bibenzimidazole have also been described.[11]



Scheme 1. Synthetic approach to bis(imidazolium) salts **I**

Some interesting reactions of the bridged dications **I** and **II** have been reported.[11,12] Treatment of the bis(imidazolium) dication **Ia** [A,B = $(CH_2)_3$] with either KH in DMSO or with $NaNH_2$ in NH_3 afforded tetraazafulvalene **IIIa** (*n* =

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3) rather than bis(carbene) **IIIa′** (n = 3). A similar result was achieved when bis(imidazolium) dication **IIa** [A,B = $(CH_2)_3$] was reduced with Na in liquid NH_3, whereas compound **Ia** [A,B = $(CH_2)_4$] under the same conditions gave the stable bis(carbene) **IIIa′** (n = 4).[12] The corresponding doubly bridged benzimidazolium salts **Ib** and **IIb** showed somewhat different behaviour. Electrolysis of **IIb** [A,B = $(CH_2)_{3,4}$] in MeCN at −1.1 V or treatment of **Ib** [A,B = $(CH_2)_{3,4}$] with base (NaH/MeCN, anaerobic conditions) both led to the air-sensitive **IIIb** (n = 3,4) and no bis(carbene) intermediates could be detected. Upon exposure to air, compounds **IIIb** were rapidly oxidized to ureaphanes **IV** (n = 3, 4).[11] A further transformation of **Ib** (A,B = CH_2CH_2O) to dibenzotetra(aza)crown-6 (**V**) has also been described[13] (Figure 2).

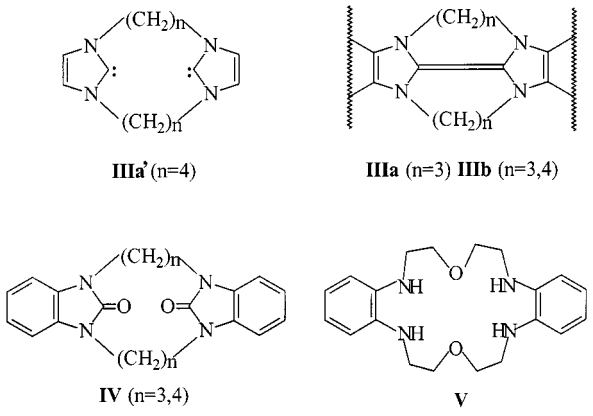
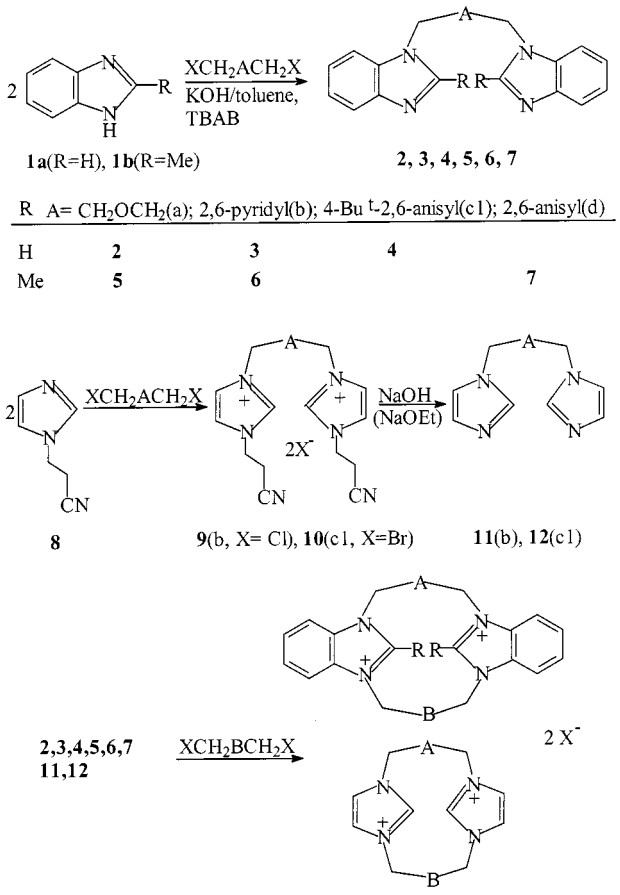


Figure 2. Chemical transformations of azolium salts **I** and **II**

It should be emphasized that, with the sole exception of **13**,[13] 16-membered onium cyclophanes in which the azaaromatic moieties are linked through crown ether and/or calixarene subunits have not hitherto been reported. In this paper, we report our results concerning the preparation and conformational analysis of quaternary macrocycles of this type with a view to the future exploitation of their synthetic potential for the construction of novel ureaphane and azacrown supramolecules.

Results and Discussion

Our synthetic approach was based on the two-step method described by others[3−5,7,8,11] (Scheme 1). The linear intermediates used, **2**−**7** and **11**, **12**, are shown in Scheme 2. The bis(benzimidazole)s **2**−**7** were prepared by condensation of benzimidazole and 2-methylbenzimidazole with bis(2-chloroethyl) ether, bis(2,6-chloromethyl)pyridine, and bis(2,6-bromomethyl)anisoles, respectively, in toluene/DMSO solvent mixtures in the presence of aqueous KOH and tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst. This method was first employed by Ecke et al.[13] for the preparation of compound **2**. In contrast, bis(imidazole)s **11**, **12** were obtained using a protection−deprotection method developed for the selective monoalkylation of imidazole.[14] Thus, 1-(cyanoethyl)imidazole was quaternized using the appropriate alkylating agent and then the cyanoethyl group was removed (Hoffman-type β-elimination) by treatment with aqueous NaOH or ethanolic NaOEt.



Scheme 2. Synthesis of the bis(benzimidazole) and bis(imidazole) precursors

The cyclizations of compounds **2**−**7** and **11**, **12** were carried out using various alkylating reagents in boiling acetone, MeCN, or $MeNO_2$, depending on the reactivity of the reactants used. In the case of the more reactive imidazole derivatives **11**, **12**, the alkylating agent was added dropwise to a solution in acetone or MeCN at 60 °C. Although the bis(benzimidazole)s are weaker nucleophiles, they were also cyclized in MeCN with the reactive bis(2,6-chloromethyl)-4-*tert*-butylphenol and bis(2,6-bromomethyl)anisole derivatives. Bis(2,6-chloromethyl)pyridine and diethylene glycol ditosylate, which reacted more sluggishly, required the use of $MeNO_2$ as the solvent for the ring closure. At the end of the reaction (monitored by TLC, eluting with methanol/water/aq. NH_4Cl, 16:3:1), the products were precipitated from the solution in moderate yields accompanied by some minor impurities. The quaternary salts (Figure 3) were found to be soluble in H_2O and/or MeOH, EtOH, hence the contamination could be removed by recrystallization.

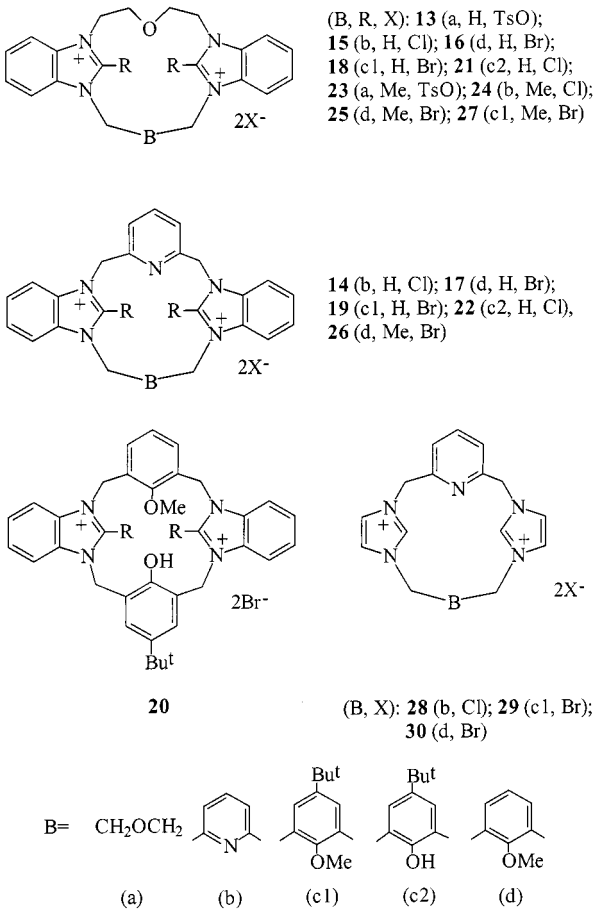


Figure 3. The synthesized quaternary azolium salts

Structure Determination of the Macrocyclic Salts

The structures of the macrocycles were determined by ^{1}H NMR measurements (NOESY and ROESY) and, in the case of compound **30**, by X-ray crystallography. In some instances, conformational analyses were carried out by computational methods. The conformational spaces of **18** and of *anti*- and *syn*-**23** were explored by the particularly efficient Low-Mode (LMOD) conformational search protocol[15] as implemented in BatchMin 7.0 (MacroModel V7.0).[16] These LMOD calculations were carried out using the MM2 force field[17] and a distance-dependent dielectric constant ($\varepsilon = 1.0$). 5000 LMOD search steps were applied for each molecule and unique conformations within 50 kJ/mol of the global minimum after energy minimization were retained for the MINTA calculation.[18] The MINTA integrals providing the basis for the binding free-energy calculation were evaluated as block averages using 52000 independent, single-point energy calculations per conformation.

Depending on the steric demand of the constituents, the azolium macrocycles exist in various conformations, as can be concluded from analysis of the ^{1}H NMR measurements obtained in [D$_6$]DMSO (Table 1).

The benzimidazolium salts **13**−**15** and imidazolium salt **28**, comprising flexible (diethylene)oxy and/or 2,6-(dimethylene)pyridyl groups, exhibit averaged chemical shifts for the methylene protons (Table 1). The introduction of one phenolic moiety into the bridge (**21**, **22**) led to a reduction in the flexibility of the macrocyclic ring, as manifested in the ArCH$_2$N proton signals of compounds **21** and **22** appearing at $\delta = 5.84/5.85$ as broad singlets at room temperature that sharpened as the temperature was raised. The methylene signals of the NCH$_2$CH$_2$O groups are also averaged on the NMR time scale.

The ^{1}H NMR spectra of those compounds (**16**−**19**) in which the two benzimidazole moieties are linked through (diethylene)oxy or 2,6-(dimethylene)pyridyl groups and one 2,6-(dimethylene)anisole bridge show a similar signal pattern. The steric proximity of the benzimidazole N=CH and anisole MeO protons indicated by the NOESY cross-peaks for **18** suggests that this molecule exists exclusively in the *cone*-like conformation. The rigid conic structure is also evidenced by the characteristic AB coupling pattern of the ArCH$_2$N proton signals, as well as by the diastereotopic appearance of the geminal methylene protons in the NCH$_2$CH$_2$O group (Figure 4, **A**). The computed structure of **18** resembles that shown in Figure 4, **B**. It is of interest to note that the conic structure is also preferred by compound **20**, which comprises two anisyl bridges.

To compare the flexibilities of the macrocyclic rings, we studied the effects of a 2-Me substituent on the benzimidazole unit (**23**, **24**). Here, in contrast to **21** and **22**, the rotation of the benzimidazole moieties is hindered by the 2-Me groups, resulting in the co-existence of *anti* and *syn* conformers in a 3:1 ratio. The characteristic differences in the Me as well as the condensed aromatic proton signals are of diagnostic value for the determination of conformations (Figure 5, **A**). In the *anti* conformer, the Me group is located above the plane of the opposite benzimidazole phenyl ring (see Figure 5, **A**) and due to its anisotropic shielding effect the Me signal is subjected to a significant upfield shift and appears at $\delta = 1.99$. In the minor *syn* conformer, the Me groups ($\delta = 2.92$) are unaffected, but the steric proximity of the two benzimidazole rings is reflected in a diamagnetic shielding of the aromatic proton signals. Once again, computer-aided analysis supported the structures suggested by the NMR-spectroscopic data (Figure 5, **B**).

The total energies of the *anti* and *syn* conformations of **23** were calculated to be 54.42 and 52.97 kJ/mol, respectively; conformational free energies were estimated as 954.28 and 955.60 kJ/mol, respectively, by MINTA. Although the calculated difference in the total energies suggests a *syn* preference, the difference in free energies ($\Delta G°$)[19] is 1.32 kJ/mol in the present case, which, according to the linear relationship with product distribution, corresponds to a calculated *anti*/*syn* product ratio of 63:37. The experimental distribution of the two conformers was found to be 3:1, which indicates that a reasonable theoretical approximation was achieved. An analogous situation was found for **24**, where the *anti*/*syn* conformer ratio was also found to be 3:1.

Table 1. Selected ^{1}H NMR spectroscopic data (δ) for the macrocyclic azolium salts

	CH_2O	CH_2N	$CH_3(O)$	$ArCH_2N$	$PyCH_2N$
13	4.70 t	3.94 t			
14					5.88 s
15	4.13 m	4.84 m			5.85 m
28					5.60 s
21	4.73 t	3.90 t		5.84 br	
22				5.85 br	5.80 s
16	4.68 s	3.90 s	4.05 s	5.58 d, 5.93 d (J = 14.7)	
17			4.03 s	5.58 d, 6.04 d (J = 14.8)	5.72 d, 5.84 d (J = 15.8)
18	4.72 m	3.90 m	4.07 s	5.61 d, 5.91 d (J = 14.7)	
19		4.00 s	5.57 d, 6.02 d (J = 14.8)	(J = 15.8)	5.75 d, 5.83 d
20		4.31 s, 4.34 s	5.58 d, 5.82 d	(J = 14.6)	
			5.59 d, 5.83 d	(J = 14.8)	
23	3.80, 3.86 m	4.53, 4.72 m	1.99 s (*anti*)		
		4.70 br	2.92 s (*syn*)		
24	3.84, 4.00 d	4.65, 4.77 d	2.14 s (*anti*)		5.68 d, 5.91 d
			2.98 s (*syn*)		5.83 m
29		3.91 s	5.18 d, 5.70 d (J = 14.5)		5.40 d, 5.52 d (J = 15.2)
30			3.95 s (major)[a]	5.25 d, 5.66 d (J = 14.5)	5.42 d, 5.51 d (J = 15.0)
			3.87 s (minor)[b]		

[a] 8.85 s (NCHN). − [b] 9.62 s (NCHN).

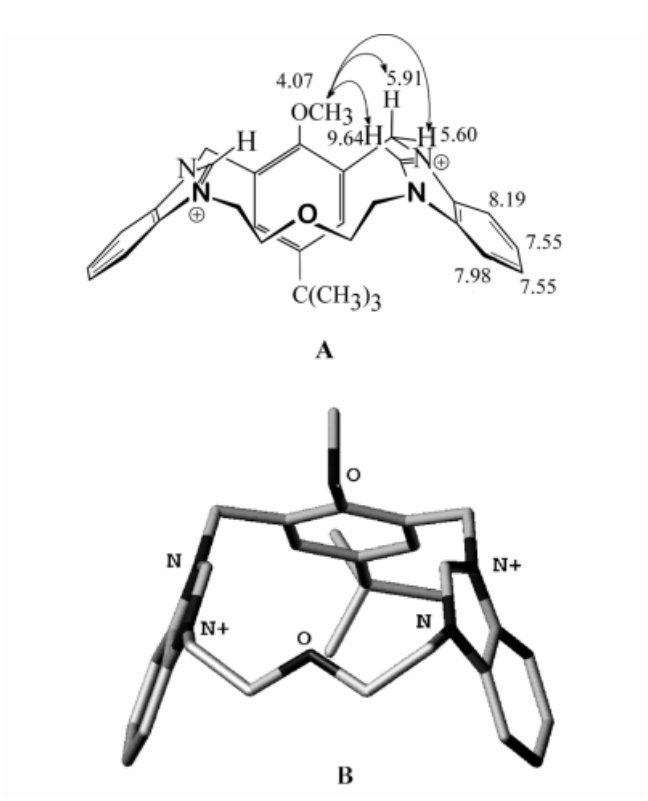


Figure 4. Conformation of **18** established by the steric proximity of protons (indicated by double arrows) (**A**) and by computer-aided conformational analysis (**B**)

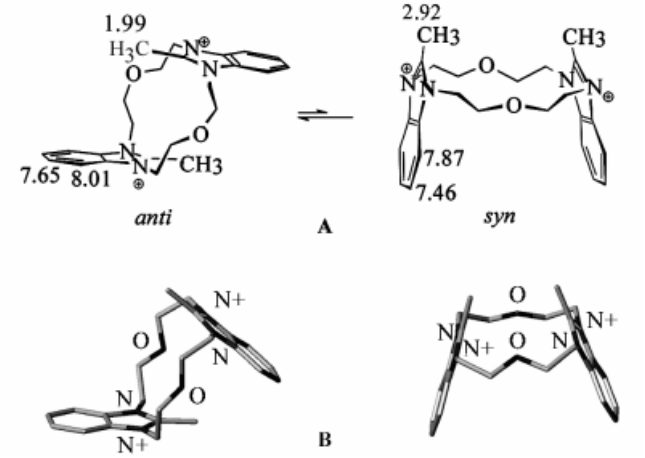


Figure 5. *anti*/*syn* conformation of **23** based on ^{1}H NMR (**A**) and computer-aided analysis (**B**)

We next tried to introduce an anisyl moiety into the macrocyclic ring of **23** and **24** in order to obtain sterically crowded macrocycles **25**−**27**. The ^{1}H NMR spectra of the products were complicated (some impurities could not be removed despite repeated recrystallization) and we were unable to elucidate the conformations of the individual components in the mixtures. By comparison of the spectra of **25**−**27** with those of **23** and **24**, it seems most likely that in the major conformers the 2-methylbenzimidazole units are in a *syn* arrangement on the basis of the chemical shifts of the Me and the aromatic proton signals: *syn*-**23** (δ = 2.92,

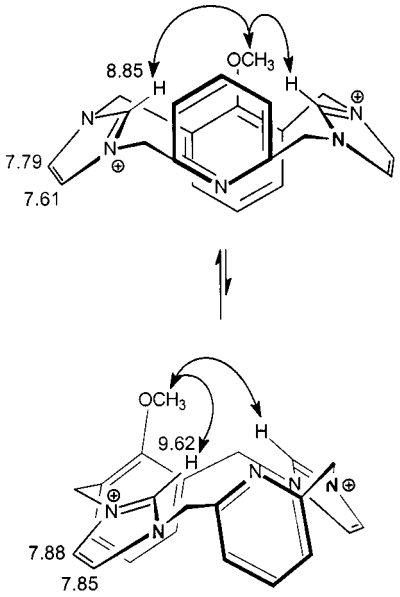


Figure 6. Conformational equilibrium of **30** determined by ROESY measurements

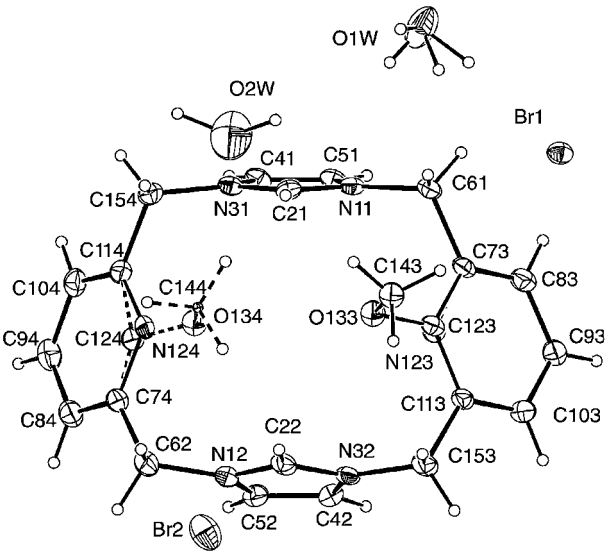


Figure 7. Perspective view of the final model of the asymmetric unit of crystal structure **30**·2H_2O showing atomic and residue numbering for non-H atoms; broken lines indicate chemical bonds between minor disordered atomic sites, four H sites to O1W are also due to disorder

7.46, 7.87), **25** (δ = 3.00, 6.78, 6.94, 7.15, 7.50), **27** (δ = 3.00, 6.81, 6.91, 7.13, 7.48), *syn*-**24** (δ = 2.98, 7.29, 7.38), **26** (δ = 2.84, 6.96, 7.08, 7.25). It is noteworthy that the replacement of one pyridine unit in the imidazolium salt **28** by anisyl so as to afford **29** and **30** diminished the conformational motion of the ring and a 3:1 mixture of two conformers was obtained. ROESY measurements on **30** were indicative of steric proximity of the MeO group and the imidazole methine protons in both conformers, from which it was concluded that these three constituents were in a similar arrangement, but that the direction of the pyridine ring was different (Figure 6).

In the minor component, the significant downfield shift of the signal due to the methine protons (δ = 9.62) proves that these protons reside in the plane of the pyridine ring, resulting in an enhancement of the chemical shift. The same signal in the major component is upfield shifted to δ = 8.85, which can be rationalized in terms of the methine protons residing above the plane, in the diamagnetic shielding region of the pyridine ring. We succeeded in preparing crystals of **30** suitable for X-ray crystallographic analysis. Surprisingly, the structure in the solid state was found to be that of the minor rather than the major conformer. This observation underlines the importance of phase-dependent interactions, which can be decisive in the determination of the actual structure.

Compound **30** crystallizes as a dihydrate from aqueous solution and has an almost circular shape (Figure 7). As indicated in the molecular diagram, the final structure model comprises a disordered methoxy moiety, together with its bridgehead carbon atom, with respect to the pyridine nitrogen atom, and vice versa. The disorder stems from approximately 75%:25% populated and 180° rotated molecular positions in the crystal (i.e., on average, every fourth molecule is rotated by 180° and resides in essentially the same position in the crystal such that the pyridine ring overlaps with the methoxyphenyl moieties). Apart from this, there are probable disorders in the hydrogen positions of one of the water molecules as well. As expected, both water molecules and both anions are extensively involved in the hydrogen-bond network of the crystal (Table 2).

Table 2. Geometric parameters of the hydrogen bonds (Å, °) for **30**·2H_2O with only meaningful e.s.d. values retained; translation of symmetry codes to equivalent positions: *i*: *x*, 3/2 − *y*, 1/2 + *z*; *ii*: 1 − *x*, 1 − *y*, 1 − *z*; *iii*: *x*, 1/2 − *y*, 1/2 + *z*; *iv*: *x*, 1/2 − *y*, −1/2 + *z*

D−H···A	D−H	H···A	D···A	D−H···A
O1W-H11W···Br2$_i$	0.94	2.49	3.413(6)	168
O1W-H31W···Br1	1.06	2.68	3.303(5)	117
O1W-H41W···Br1	1.06	2.28	3.303(5)	162
O2W-H12W···Br2$_i$	1.06	2.47	3.408(7)	147
O2W-H22W···Br2$_{ii}$	1.03	2.33	3.352(8)	175
C154-H10E···Br2$_{iii}$	0.97	2.83	3.771(5)	164
C21-H21···O2W	0.93	2.47	3.255(9)	143
C52-H52B···O1W$_{iv}$	0.93	2.44	3.373(7)	177
C61-H61A···Br1	0.97	2.91	3.557(6)	125

Preliminary chemical transformations of compounds **13** and **14** have been carried out. Treatment with NaH in DMF without protection from air according to ref.[11] afforded ureaphanes (type **IV**), whereas hydrolysis with strong aqueous base furnished dibenzo(aza)crowns (type **V**). These results will be reported in more detail in a forthcoming paper.

Conclusion

A series of 16-membered quaternary azacyclophanes has been synthesized by the alkylation of bis(benzimidazole) and bis(imidazole) precursors with various dialkylating

agents. The flexibility of the macrocyclic ring has been systematically varied by applying bridging units and azoles with different steric requirements. Thus, single conformers or mixtures of conformers were obtained, the structures of which have been determined. According to the results of preliminary experiments, the benzimidazolium salts may provide a facile new access to ureaphane and azacrown supramolecules.

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded with samples in [D_6]DMSO solution (unless stated otherwise) at 500 and 125 MHz, respectively, with a Bruker Avance DRX-500 spectrometer. Chemical shifts are given in δ units. Complete ^{1}H and ^{13}C signal assignments were achieved by utilizing DEPT-135, TOCSY, HMQC, HMBC [optimized for 7 Hz long-range *J*(C,H) couplings], phase-sensitive NOESY, and ROESY (τ_{mixing} = 0.5 s) methods. − Precoated silica gel plates (Merck 60 F_{254}) were used for analytical TLC, with benzene/MeOH (8:2 and 7:3) for the linear precursors and MeOH/water/aq. NH_4Cl (16:3:1) for the quaternary salts as eluent mixtures. Solvents (acetone, MeCN, and $MeNO_2$) were dried prior to use. − Imidazole, benzimidazole, 2-methylbenzimidazole, bis(2-chloroethyl) ether, and diethylene glycol ditosylate were purchased from Fluka. Bis(2,6-chloromethyl)pyridine,[20] bis(2,6-bromomethyl)anisole,[21] bis(2,6-bromomethyl)-4-*tert*-butylanisole,[22] bis(2,6-chloromethyl)-4-*tert*-butylphenol,[23] and 1-(2-cyanoethyl)-imidazole[24] were prepared as described in the literature.

General Procedure for Synthesis of the Linear Precursors 2−7: A mixture of benzimidazole (**1a**) or 2-methylbenzimidazole (**1b**) (0.02 mol), toluene (20 mL), DMSO (2 mL), the alkylating agent (0.011 mol), 50% aqueous KOH solution (8 mL), and TBAB catalyst (0.25 g) was agitated at 80 °C for 8−12 h. In each case, a portion of the product precipitated from the solution, was collected by filtration and combined with the remainder recovered from the toluene phase, washed with water, dried, and purified by recrystallization to furnish a white solid.

1,5-Bis(1-benzimidazolyl)-3-oxapentane (2): Reactants: **1a** and bis(2-chloroethyl) ether; yield: 1.8 g (60%); m.p. 104−106 °C (EtOH/water) (ref.[13] m.p. 73 °C); R_f = 0.55 (benzene/MeOH, 7:3). − ^{1}H NMR ($CDCl_3$): δ = 3.65 (t, 4 H, CH_2N), 4.18 (t, 4 H, CH_2O), 7.23 (m, 6 H, ArH), 7.75 (m, 4 H, ArH).

2,6-Bis[(1-benzimidazolyl)methyl]pyridine (3): Reactants: **1a** and bis(2,6-chloromethyl)pyridine (10 h); yield: 3.26 g (93%); m.p. 115−117 °C (MeOH/water), R_f = 0.58 (benzene/MeOH, 7:3). − ^{1}H NMR ($CDCl_3$): δ = 5.30 (s, 4 H, CH_2), 6.76 (d, *J* = 7.8, 2 H, ArH), 7.15 (m, 6 H, ArH), 7.38 (t, 1 H, ArH), 7.73 (d, *J* = 7.8, 2 H, ArH), 7.92 (s, 2 H, NCHN).

2,6-Bis[(1-benzimidazolyl)methyl]-4-*tert*-butylanisole (4): Reactants: **1a** and bis(2,6-bromomethyl)-4-*tert*-butylanisole (8 h); yield: 2.2 g (52%); m.p. 178−180 °C (EtOH); R_f = 0.60 (benzene/MeOH, 8:2). − ^{1}H NMR ($CDCl_3$): δ = 1.08 (s, 9 H, *t*Bu), 3.61 (s, 3 H, MeO), 5.38 (s, 4 H, CH_2), 7.05 (s, 2 H, ArH), 7.28 (m, 4 H, ArH), 7.36 (m, 2 H, ArH), 7.82 (m, 2 H, ArH), 7.96 (s, 2 H, NCHN).

1,5-Bis[1-(2-methylbenzimidazolyl)]-3-oxapentane (5): Reactants: **1b** and bis(2-chloroethyl) ether (12 h); yield: 1.4 g (42%); m.p. 118−120 °C (dissolved in dilute HCl, clarified with charcoal, and precipitated with NH_4OH); R_f = 0.45 (benzene/MeOH, 7:3). − ^{1}H NMR ($CDCl_3$): δ = 2.47 (s, 6 H, Me), 3.61 (t, 4 H, CH_2N), 4.12 (t, 4 H, CH_2O), 7.2 (m, 6 H, ArH), 7.67 (d, *J* = 7.1, 2 H, ArH).

2,6-Bis[1-(2-methylbenzimidazolyl)methyl]pyridine (6): Reactants: **1b** and bis(2,6-chloromethyl)pyridine (10 h); yield: 1.7 g (45%); m.p. 214−216 °C (toluene); R_f = 0.58 (benzene/MeOH, 8:2). − ^{1}H NMR ($CDCl_3$): δ = 2.57 (s, 6 H, Me), 5.34 (s, 4 H, CH_2), 6.74 (d, *J* = 7.8 Hz, 2 H, ArH), 7.22 (m, 6 H, ArH), 7.47 (t, 1 H, ArH), 7.73 (d, *J* = 7.9 Hz, 2 H, ArH).

2,6-Bis[1-(2-methylbenzimidazolyl)methyl]anisole (7): Reactants: **1b** and bis(2,6-bromomethyl)anisole (10 h); yield: 2.0 g (52%); m.p. 250 °C (toluene); R_f = 0.44 (benzene/MeOH, 8:2). − ^{1}H NMR ($CDCl_3$): δ = 2.65 (s, 6 H, Me), 3.84 (s, 3 H, MeO), 5.45 (s, 4 H, CH_2), 6.66 (d, *J* = 7.7, 2 H, ArH), 6.90 (t, 1 H, ArH), 7.26 (m, 6 H, ArH), 7.90 (d, *J* = 7.8 Hz, 2 H, ArH).

2,6-Bis[(1-imidazolyl)methyl]pyridine (11): 1-(2-Cyanoethyl)-imidazole (5.45 g, 0.045 mol) and bis(2,6-chloromethyl)pyridine (3.52 g, 0.02 mol) were refluxed in MeCN (50 mL) for 8 h. The solvent was then removed in vacuo to leave **9** as a sticky solid, which was redissolved in hot water (30 mL), clarified with charcoal, and treated with 25% aqueous NaOH (10 mL) at ambient temperature. The deprotection took place in 1 h to afford **11** as white solid upon cooling of the solution. Yield: 3.0 g (65%); m.p. 118−120 °C; R_f = 0.73 (benzene/MeOH, 8:2). − ^{1}H NMR: δ = 5.64 (s, 4 H, CH_2), 7.55 (d, *J* = 7.7 Hz, 2 H, ArH), 7.89 (s, 2 H, ArH), 7.96 (t, 1 H, ArH), 8.02 (s, 2 H, ArH), 8.81 (s, 2 H, NCHN).

4-*tert*-Butyl-2,6-bis[(1-imidazolyl)methyl]anisole (12): 1-(2-Cyanoethyl)imidazole (2.66 g, 0.022 mol) and bis(2,6-bromomethyl)-4-*tert*-butylanisole (3.50 g, 0.01 mol) were allowed to react in boiling acetone (50 mL) for 6 h, which resulted in the formation of **10** as a sticky solid. After decantation of the solvent, the residue was treated with 1 M NaOEt solution (25 mL) at ambient temperature, extracted with EtOAc, and washed with water to give **12** as a white solid. Yield: 2.8 g (85%); m.p. 170−172 °C; R_f = 0.48 (benzene/MeOH, 7:3). − ^{1}H NMR ($CDCl_3$): δ = 1.18 (s, 9 H, *t*Bu), 3.53 (s, 3 H, MeO), 5.12 (s, 4 H, CH_2), 6.90 (s, 2 H, ArH), 7.00 (s, 2 H, ArH), 7.05 (s, 2 H, ArH), 7.53 (s, 2 H, NCHN).

General Procedure for the Synthesis of Quaternary Macrocycles: To a solution of the linear precursor (5 mmol) in a dry solvent (acetone or MeCN: 40 mL; $MeNO_2$: 15 mL), the appropriate alkylating reagent (5 mmol) was either added in a single portion and the resulting mixture was refluxed for 8 h (benzimidazolium macrocycles **13−27**) or a solution of the alkylating reagent (5 mmol in 15 mL of solvent) was slowly added dropwise at 50−60 °C and the mixture was heated to reflux for the same period (imidazolium macrocycles **28−30**). After completion of the reaction, the white solid produced was collected by filtration, thoroughly washed with the same solvent, purified by recrystallization, and dried at 80 °C in vacuo (0.1 Torr).

Compound 13: X = TsO; yield: 2.0 g (55%) ($MeNO_2$); m.p. 270−272 °C (*n*PrOH) (ref.[13] m.p. 279.5−280.5 °C); R_f = 0.58. − $C_{36}H_{40}N_4O_8S_2$ (720.87): calcd. C 59.98, H 5.59, N 7.77; found C 59.11, H 5.65, N 7.63. − ^{1}H NMR: δ = 2.28 (s, 6 H, Me of Ts), 3.94 (t, 8 H, CH_2N), 4.70 (t, 8 H, CH_2O), 7.10 (d, *J* = 7.9, 4 H, TsH), 7.51 (d, *J* = 7.9 Hz, 4 H, TsH), 7.63 (q, 4 H, ArH), 8.05 (q, 4 H, ArH), 9.76 (s, 2 H, NCHN).

Compound 14: X = Cl; yield: 1.3 g (50%) ($MeNO_2$); m.p. > 300 °C (MeOH); R_f = 0.42. − $C_{28}H_{24}N_6Cl_2$ (515.44): calcd. C 65.25, H 4.69, N 16.30, Cl 13.76; found C 64.89, H 4.65, N 16.08, Cl 13.58.

– ^{1}H NMR: δ = 5.88 (s, 8 H, CH_2), 7.34 (m, 8 H, ArH), 7.81 (d, *J* = 7.7 Hz, 4 H, ArH), 8.13 (t, 2 H, ArH), 9.80 (s, 2 H, NCHN).

Compound 15: X = Cl; yield: 1.42 g (59%) ($MeNO_2$); m.p. 285 °C (dec.) (EtOH); R_f = 0.32. – $C_{25}H_{25}N_5OCl_2$ (482.41): calcd. C 62.24, H 5.22, N 14.52, Cl 14.70; found C 61.89, H 5.25, N 14.40, Cl 14.48. – ^{1}H NMR: δ = 4.13 (m, 4 H, CH_2), 4.84 (m, 4 H, CH_2), 5.85 (s, 4 H, CH_2), 7.49 (t, 2 H, ArH), 7.56 (t, 2 H, ArH), 7.80 (d, *J* = 8.0 Hz, 2 H, ArH), 7.88 (d, *J* = 8.0 Hz, 2 H, ArH), 8.07 (m, 2 H, ArH), 10.09 (s, 2 H, NCHN).

Compound 16: X = Br; yield: 1.45 g (48%) (MeCN); m.p. 260 °C (dec.) (water); R_f = 0.52. – $C_{27}H_{28}N_4O_2Br_2$ (600.35): calcd. C 54.02, H 4.70, N 9.33, Br 26.62; found C 53.65, H 4.64, N 9.25, Br 26.34. – ^{1}H NMR: δ = 3.90 (m, 4 H, CH_2), 4.05 (s, 3 H, MeO), 4.68 (s, 4 H, CH_2), 5.58 (d, *J* = 14.7, 2 H, CH_2), 5.93 (d, *J* = 14.7, 2 H, CH_2), 7.35 (t, 1 H, ArH), 7.56 (m, 4 H, ArH), 7.96 (m, 2 H, ArH), 8.11 (m, 2 H, ArH), 9.53 (s, 2 H, NCHN).

Compound 17: X = Br; yield: 1.75 g (56%) (MeCN); m.p. 300 °C (water); R_f = 0.56. – $C_{30}H_{27}N_5OBr_2$ (633.38): calcd. C 56.89, H 4.30, N 11.06, Br 25.23; found C 56.45, H 4.34, N 10.98, Br 25.04. – ^{1}H NMR: δ = 4.03 (s, 3 H, MeO), 5.58 (d, *J* = 14.8 Hz, 2 H, CH_2), 5.72 (d, *J* = 15.8 Hz, 2 H, CH_2), 5.84 (d, *J* = 15.8 Hz, 2 H, CH_2), 6.04 (d, *J* = 14.8 Hz, 2 H, CH_2), 7.41 (t, 1 H, ArH), 7.46 (t, 2 H, ArH), 7.53 (t, 2 H, ArH), 7.62 (d, *J* = 8.2 Hz, 2 H, ArH), 7.88 (d, *J* = 7.8 Hz, 2 H, ArH), 7.99 (d, *J* = 7.7 Hz, 2 H, ArH), 8.03 (d, *J* = 8.3 Hz, 2 H, ArH), 8.08 (t, 2 H, ArH), 9.52 (s, 2 H, NCHN).

Compound 18: X = Br; yield: 1.4 g (42%) (MeCN); m.p. 238 °C (dec.) (water); R_f = 0.40. – $C_{31}H_{36}N_4O_2Br_2$ (656.46): calcd. C 56.72, H 5.53, N 8.53, Br 24.34; found C 56.25, H 5.54, N 8.46, Br 24.01. – ^{1}H NMR: δ = 1.32 (s, 9 H, *t*Bu), 3.90 (m, 4 H, CH_2), 4.07 (s, 3 H, MeO), 4.72 (m, 4 H, CH_2), 5.61 (d, *J* = 14.7 Hz, 2 H, CH_2), 5.91 (d, *J* = 14.7 Hz, 2 H, CH_2), 7.56 (m, 4 H, ArH), 7.98 (m, 2 H, ArH), 8.01 (m, 2 H, ArH), 8.19 (d, *J* = 7.3 Hz, 2 H, ArH), 9.64 (s, 2 H, NCHN).

Compound 19: X = Br; yield: 1.6 g (46%) (MeCN); m.p. 240 °C (dec.) (MeOH); R_f = 0.78. – $C_{34}H_{35}N_5OBr_2$ (689.49): calcd. C 59.23, H 5.12, N 10.16, Br 23.18; found C 58.65, H 5.15, N 9.98, Br 22.91. – ^{1}H NMR: δ = 1.39 (s, 9 H, *t*Bu), 4.00 (s, 3 H, MeO), 5.58 (d, *J* = 14.8 Hz, 2 H, CH_2), 5.75 (d, *J* = 15.8, 2 H, CH_2), 5.83 (d, *J* = 15.8 Hz, 2 H, CH_2), 6.02 (d, *J* = 14.7 Hz, 2 H, CH_2), 7.46 (t, 2 H, ArH), 7.54 (t, 2 H, ArH), 7.65 (d, *J* = 8.0 Hz, 2 H, ArH), 7.88 (d, *J* = 7.4 Hz, 2 H, ArH), 8.08 (m, 5 H, ArH), 9.51 (s, 2 H, NCHN).

Compound 20: X = Br; yield: 2.0 g (56%) (MeCN); m.p. > 300 °C (MeOH/water); R_f = 0.55. – $C_{36}H_{38}N_4O_2Br_2$ (718.53): calcd. C 60.18, H 5.33, N 7.80, Br 22.24; found C 56.65, H 5.37, N 7.68, Br 22.31. – ^{1}H NMR: δ = 1.26 (s, 9 H, *t*Bu), 4.31 (s, 3 H, MeO), 4.34 (s, 3 H, MeO), 5.58 and 5.82 (d, *J* = 14.6, 2 × 2 H, CH_2), 5.59 and 5.83 (d, *J* = 14.8, 2 × 2 H, CH_2), 7.19 (t, 1 H, ArH), 7.47 (m, 4 H, ArH), 7.95 (d, *J* = 7.7, 2 H, ArH), 8.00 (s, 2 H, ArH), 8.06 (d, *J* = 7.6, 2 H, ArH), 8.12 (d, *J* = 7.6, 2 H, ArH), 9.95 (s, 2 H, NCHN).

Compound 21: X = Cl; yield: 2.45 g (86%) (MeCN); m.p. 260–262 °C (MeOH); R_f = 0.65. – $C_{31}H_{36}N_4OCl_2$ (567.56): calcd. C 65.60, H 6.39, N 9.87, Cl 12.49; found C 65.05, H 6.37, N 9.68, Cl 12.30. – ^{1}H NMR: δ = 1.31 (s, 9 H, *t*Bu), 3.90 (t, 4 H, CH_2), 4.73 (t, 4 H, CH_2), 5.84 (br. signal, 4 H, CH_2), 7.57 (t, 2 H, ArH), 7.59 (t, 2 H, ArH), 7.81 (s, 2 H, ArH), 7.98 (d, *J* = 8.0 Hz, 2 H, ArH), 8.16 (d, *J* = 7.5 Hz, 2 H, ArH), 9.62 (s, 2 H, NCHN).

Compound 22: X = Cl; yield: 2.7 g (92%) (MeCN); m.p. 274–277 °C (MeOH); R_f = 0.60. – $C_{33}H_{33}N_5OCl_2$ (586.56): calcd. C 67.57, H 5.67, N 11.94, Cl 12.09; found C 66.87, H 5.70, N 11.75, Cl 11.96. – ^{1}H NMR: δ = 1.36 (s, 9 H, *t*Bu), 5.80 (s, 4 H, CH_2), 5.85 (br. signal, 4 H, CH_2), 7.48 (t, 2 H, ArH), 7.54 (t, 2 H, ArH), 7.73 (d, 2 H, ArH), 7.86 (d, 2 H, ArH), 7.87 (s, 2 H, ArH), 8.05 (d, 2 H, ArH), 8.06 (t, 1 H, ArH), 9.40 (s, 2 H, NCHN), 10.19 (s, 1 H, OH).

Compound 23: X = TsO; yield: 1.6 g (42%) ($MeNO_2$); m.p. 267–269 °C (EtOH); R_f = 0.45. – $C_{38}H_{44}N_4O_8S_2$ (744.84): calcd. C 61.27, H 5.41, N 7.52; found C 60.77, H 5.45, N 7.45. – ^{1}H NMR: δ = 1.99 (s, 6 H, Me), 3.80 and 3.86 (m, 2 × 4 H, CH_2), 4.53 and 4.72 (m, 2 × 4 H, CH_2), 7.64 (br. signal, 4 H, ArH), 8.01 (br. signal, 4 H, ArH). Minor conformer: δ = 2.92 (s, 6 H, Me), 4.70 (br. signal, 16 H, CH_2), 7.46 (br. signal, 4 H, ArH), 7.87 (br. signal, 4 H, ArH).

Compound 24: X = Cl; yield: 1.2 g (48%) ($MeNO_2$); m.p. > 300 °C (EtOH); R_f = 0.42. – $C_{27}H_{29}N_5OCl_2$ (510.47): calcd. C 62.53, H 5.73, N 13.72, Cl 13.89; found C 62.07, H 5.68, N 13.61, Cl 13.46. – ^{1}H NMR: δ = 2.14 (s, 6 H, Me), 3.84 and 4.00 (d, 2 × 2 H, CH_2), 4.65 and 4.77 (d, 2 × 2 H, CH_2), 5.68 and 5.91 (d, *J* = 16.8 Hz, 2 × 2 H, CH_2), 7.64 (t, 4 H, ArH), 7.81 (d, 2 H, ArH), 7.96 (d, 2 H, ArH), 8.05 (t, 1 H, ArH), 8.06 (d, 2 H, ArH). Minor conformer: δ = 2.98 (s, 6 H, Me), 5.83 (m, 4 H, CH_2), 7.29 (t, 2 H, ArH), 7.38 (t, 2 H, ArH), 7.58 (d, 2 H, ArH), 7.79 (d, 2 H, ArH), 7.90 (d, 2 H, ArH), 8.08 (t, 2 H, ArH).

Compound 25: X = Br; yield: 2.3 g (73%) (MeCN); m.p. > 300 °C (EtOH/water); R_f = 0.47. – $C_{29}H_{32}N_4O_2Br_2$ (628.41): calcd. C 55.43, H 5.13, N 8.92, Br 25.43; found C 54.07, H 5.18, N 8.69, Br 26.16. – ^{1}H NMR (selected data for the major component): δ = 3.00 (s, Me), 6.78, 6.94, 7.15, 7.50 (br. s, ArH).

Compound 26: X = Br; yield: 1.7 g (51%) (MeCN); m.p. 266–270 °C (EtOH/water); R_f = 0.41. – $C_{32}H_{31}N_5OBr_2$ (661.44): calcd. C 58.11, H 4.72, N 10.59, Br 24.16; found C 57.57, H 4.68, N 10.39, Br 24.97. – ^{1}H NMR (selected data for the major component): δ = 2.84 (s, Me), 6.96, 7.08, 7.25 (br. s, ArH).

Compound 27: X = Br; yield: 2.2 g (66%) (MeCN); m.p. 266–268 °C (dec.) (EtOH); R_f = 0.44. – $C_{32}H_{38}N_4O_2Br_2$ (670.49): calcd. C 57.32, H 5.71, N 8.36, Br 22.83; found C 56.09, H 5.67, N 8.29, Br 23.54. – ^{1}H NMR (selected data for the major component): δ = 3.00 (s, Me), 6.81, 6.91, 7.13, 7.48 (br. s, ArH).

Compound 28: X = Cl; yield: 0.95 g (46%) (acetone); m.p. > 300 °C (water); R_f = 0.32. – $C_{20}H_{20}N_6Cl_2$ (415.32): calcd. C 57.84, H 4.85, N 20.23, Cl 17.07; found C 57.32, H 4.90, N 20.11, Cl 16.94. – ^{1}H NMR: δ = 5.60 (s, 8 H, CH_2), 7.59 (d, 4 H, ArH), 7.64 (s, 4 H, ArH), 8.00 (t, 2 H, ArH), 9.17 (s, 2 H, NCHN).

Compound 29: X = Br; yield: 1.65 g (56%) (MeCN); m.p. > 300 °C (water); R_f = 0.55. – $C_{26}H_{31}N_5OBr_2$ (589.37): calcd. C 52.99, H 5.30, N 11.88, Br 27.11; found C 52.42, H 5.25, N 11.67, Br 26.90. – ^{1}H NMR: δ = 1.28 (s, 9 H, *t*Bu), 3.91 (s, 3 H, MeO), 5.18 (d, *J* = 14.5 Hz, 2 H, CH_2), 5.40 (d, *J* = 15.2 Hz, 2 H, CH_2), 5.52 (d, *J* = 15.1 Hz, 2 H, CH_2), 5.70 (d, *J* = 14.5 Hz, 2 H, CH_2), 7.44 (d, *J* = 12.1 Hz, 4 H, ArH), 7.67 (d, *J* = 7.7 Hz, 2 H, ArH), 7.75 (s, 2 H, ArH), 8.01 (t, 1 H, ArH), 8.72 (s, 2 H, NCHN).

Compound 30: X = Br; yield: 1.1 g (41%) (acetone); m.p. 250 °C (dec.) (water); R_f = 0.43. – $C_{22}H_{23}N_5OBr_2$ (533.26): calcd. C 49.55, H 4.35, N 13.13, Br 29.97; found C 48.99, H 4.37, N 12.98, Br 29.42. – ^{1}H NMR: δ = 3.95 (s, 3 H, MeO), 5.25 and 5.66 (d, *J* = 14.5 Hz, 2 × 2 H, CH_2), 5.42 and 5.51 (d, *J* = 15.0 Hz, 2 × 2

H, CH_2), 7.34 (t, 1 H, ArH), 7.61 (s, 2 H, ArH), 7.62 (d, 2 H, ArH), 7.74 (d, 2 H, ArH), 7.79 (s, 2 H, ArH), 7.98 (t, 2 H, ArH), 8.85 (s, 2 H, NCHN). Minor conformer: δ = 3.87 (s, 3 H, MeO), 7.28 (t, 1 H, ArH), 7.41 (d, 2 H, ArH), 7.49 (d, 2 H, ArH), 7.85 (s, 2 H, ArH), 7.88 (s, 2 H, ArH), 7.98 (t, 2 H, ArH), 9.62 (s, 2 H, NCHN).

X-ray Crystallographic Study: Shiny needle-like crystals of **30**·$2H_2O$ were grown by diffusion of acetone vapour into an aqueous solution of **30** equilibrated at ambient temperature. Crystals suitable for X-ray diffraction measurements were formed within 48−72 h. A selected crystal was sealed in a capillary; it would have decomposed in about a minute if exposed to air. Diffraction data were collected at ambient temperature with an automated four-circle instrument[25] [$C_{22}H_{23}N_5OBr_2$·$2H_2O$, monoclinic space group $P2_1/c$ (No. 14), a = 17.439(4), b = 9.191(1), c = 17.781(3) Å, β = 117.15(1)°, V = 2535.9(8) Å^3, Z = 4, $D_{calcd.}$ = 1.491 g/cm^3]. Of 5793 collected reflections, 5478 were considered as independent (R_{int} = 0.014) and were subsequently corrected for absorption effects using a semiempirical approach.[26] An initial structure model was obtained by a direct method procedure (SHELXS-97)[27] as **30**·$3H_2O$. This model was easily refined[28] by applying anisotropic displacement parameters for the non-hydrogen atoms [R_1 = 0.0530 for 2492 $F_o > 4\sigma(F_o)$ and 0.1486 for all 5490 data]. However, unusually high ADPs at the methoxy group and at the bridgehead C atom, the pyridine N atom, and at a putative water site enclosed in the cavity, together with a significant residual density linking the pyridine N atom to this "water" at a distance of 1.5 Å, all pointed to the existence of a disorder in the structure. Indeed, a highly symmetrical molecular shape was confirmed by analysis of the non-crystallographic symmetry [C_{2v} Continuous Symmetry Measure (CSM): 2.43; average R.M.S. deviation 0.4 Å, program PLATON,[29] and references therein]. A subsequent disorder model was then refined to convergence and adopted as the final structure model [final residuals: R_1 = 0.0545 for 2480 $F_o > 4\sigma(F_o)$ and 0.1502 for all 5478 data and 301 parameters]. Some atoms of the disordered parts of the model were treated with isotropic displacement parameters in order to avoid matrix singularities in the refinement. The symmetry measures of this model as implemented in PLATON suggest a fairly symmetrical self-complementary molecular shape (CSM data for the $C_{s[x,y,-z]}$ symmetry element in the final model were: CSM = 0.274, max. diff.: 0.097, RMS = 0.052, tolerance: 0.20).[30] − Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155924. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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