Synthesis, X-ray and conformational studies of novel tetrazole-containing macrocycles: 4,13-dioxa-1,7,8,9,17,18,19,20-octaazatricyclo[14.2.1.1^{7,10}]icosa-8,10(20),16(19),17-tetraene and 4,14-dioxa-1,7,8,9,10,18,19,20-octaazatricyclo[15.2.1.0^{7,10}]icosa-8,10,17(20),18-tetraene †

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Alkylation of 1,5-bis(tetrazol-5-yl)-3-oxapentane by 2,2′-dichlorodiethyl ether under conditions of high dilution led to two isomeric crown-like macrocycles: 4,13-dioxa-1,7,8,9,17,18,19,20-octaazatricyclo[14.2.1.1^{7,10}]icosa-8,10(20),16(19),17-tetraene **2** and 4,14-dioxa-1,7,8,9,10,18,19,20-octaazatricyclo[15.2.1.0^{7,10}]icosa-8,10,17(20),18-tetraene **3**. The crystal structures of both compounds were determined. In the crystalline state, macrocycle **2** exists in *syn*-form with a symmetry near C_s, whereas macrocycle **3** has only C_1 symmetry. The latter was observed to adopt two different conformations in the crystalline state. An AM1 conformational analysis of macrocycle **2** revealed 30 different conformations, one of which is similar to the observed crystal structure.

Introduction

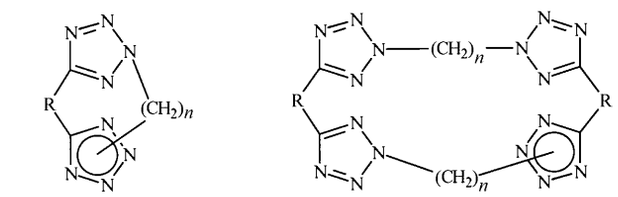
The search for novel macrocyclic ligands that are capable of selectively binding metal ions is a major area of modern coordination chemistry research. A great deal of work has been carried out on crown-like macrocycles containing azole or azine fragments in this context.[1,2] Macrocycles containing pyrazole,[3] imidazole,[4] 1,2,4-triazole,[5] pyridine[6] and 1,3,5-triazine[7] rings are well known. However, information about tetrazole-containing macrocycles, which would be expected to have high complex-forming activity, is very scarce. Among this group of compounds, only the cyclophanes shown in Scheme 1 have been reported.[8–14] Crown-like tetrazole-containing macrocyclic ethers represent an important example of this class of compound that has yet to be studied.

In the present study we report the first tetrazole-containing derivatives of 12-crown-4: 4,13-dioxa-1,7,8,9,17,18,19,20-octaazatricyclo[14.2.1.1^{7,10}]icosa-8,10(20),16(19),17-tetraene **2** and 4,14-dioxa-1,7,8,9,10,18,19,20-octaazatricyclo[15.2.1.0^{7,10}]icosa-8,10,17(20),18-tetraene **3**. The NMR-(^{1}H, ^{13}C) and IR-spectral properties and X-ray crystal structure of these compounds are reported. A conformational analysis of compound **2** has also been performed using the AM1 method.

Results and discussion

Synthesis

A well-established synthetic route to crown ethers involves the alkylation of bifunctional substrates by corresponding electrophiles, including 2,2′-dichloroethyl ether.[15] We have used 1,5-bis(tetrazol-5-yl)-3-oxapentane **1** in this context as the bifunctional substrate.[16] It is well known that the alkylation of monocyclic tetrazoles generally leads to a mixture of N^1- and N^2-isomers.[17] In the case of compound **1**, a more complex picture may be predicted, *i.e.* in addition to the formation of macrocycles **2**–**4** (Scheme 2) a competing processes might be expected to give open-ring and macrocyclic derivatives of higher molecular weight. All of the reactions in the current study were carried out under high dilution conditions in order to suppress these competing processes.



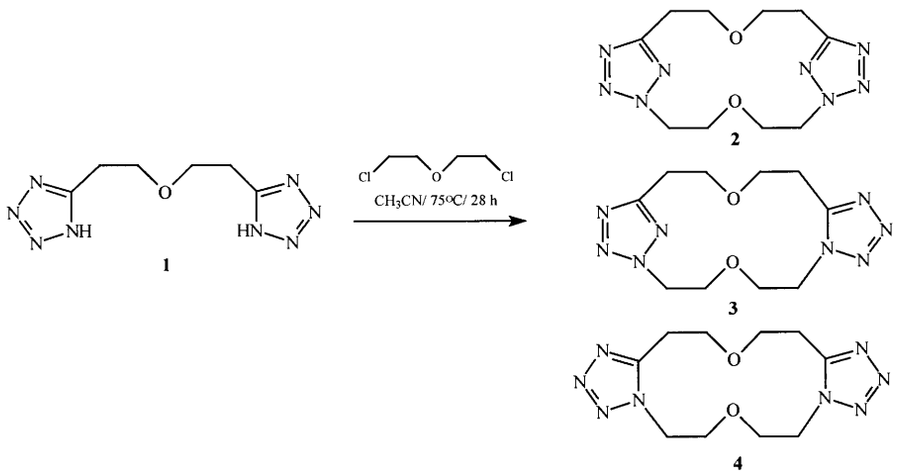
Scheme 1

Two compounds were isolated in low yield, by chromatography, from the crude product mixture obtained from the reaction shown in Scheme 2.[18] These were identified as the isomeric crown-like macrocycles: 4,13-dioxa-1,7,8,9,17,18,19,20-octaazatricyclo[14.2.1.1^{7,10}]icosa-8,10(20),16(19),17-tetraene **2** and 4,14-dioxa-1,7,8,9,10,18,19,20-octaazatricyclo[15.2.1.0^{7,10}]icosa-8,10,17(20),18-tetraene **3**. A further isomer **4** was observed by ^{1}H NMR in the crude product but it was not isolated due to its low yield. According to known literary data, cyclophanes containing only 1,5-disubstituted tetrazole subheterocyclic rings are not described.[8–11]

Spectroscopy

All the expected signals were observed in the ^{1}H and ^{13}C NMR spectra of compounds **2** and **3**. The spectra of these compounds differ principally from one to another by the isomeric nature of the tetrazole rings.

† Crystal data for compounds **2** and **3** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b006217k/



Scheme 2

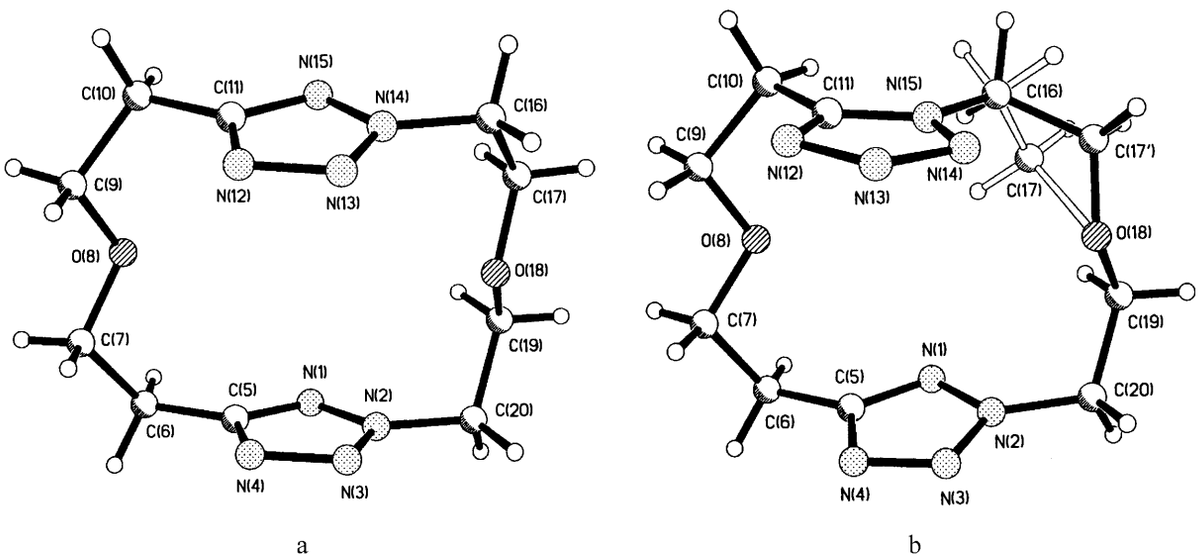


Fig. 1 The structures of macrocycles **2** and **3** by X-ray analysis.

Compound 2. The ^{1}H NMR spectrum of this compound contained 4 triplets corresponding to the 16 protons of the 8 distinct methylene groups. The chemical shift of the proton signal of the α-methylene groups adjacent to nitrogen was observed at 4.69 ppm: a value characteristic for tetrazole cycles substituted at the 2,5-position. Resonances were observed for all the 5 nonequivalent carbons in the ^{13}C NMR spectrum. According to the data of Butler and Flemming,[14] the observed signals for the tetrazole ring carbons at 163.9 ppm and the N–CH_2 group at 52.1 ppm are consistent with a 2,5-disubstituted tetrazole.

Compound 3. The ^{1}H NMR spectrum of **3** was more complex and consisted of 8 triplets each of which correspond to a single methylene group. The signals of the α-methylene group bonded to a nitrogen atom of the tetrazole were observed at 4.72 (N^2–CH_2) and 4.20 ppm (N^1–CH_2) and are characteristic of the 1,5- and 2,5-disubstituted tetrazole sub-units present in the macrocycle. The presence of the latter unit was confirmed by ^{13}C NMR spectroscopy with 10 signals being observed for the nonequivalent carbons. The resonances for the carbons of the tetrazole ring at 164.0 and 153.3 ppm and of the methylene group at 52.3 and 46.4 ppm are consistent with a tetrazole ring substituted in both the 1,5- and the 2,5-positions.[13]

The IR spectra of compounds **2** and **3** gave identical absorption bands at 1510, 1350, 1220, 1050 and 910 cm^{-1}, which correspond to valence vibrations of the tetrazole ring. The bands observed at 1130–1115 cm^{-1} correspond to vibrations of the ether units.

X-Ray crystal structures

The spatial structure of the crown-like macrocycles was studied in order to provide important information on their ability to act as efficient and highly selective ligands for coordination chemistry. These macrocycles might be expected to exist in different conformations depending upon the mutual displacement of the tetrazole rings as well as upon the mobility of the macrocycle skeleton itself. In the present study, the solid state molecular structures of compounds **2** and **3** were determined by X-ray analysis. Perspective drawings of compounds **2** and **3** are shown with atom labeling in Fig. 1.

It is apparent that, in the crystalline state, compound **2** has a symmetry close to that of the C_s point group (Fig. 1a) and the planes defined by each of the tetrazole cycles are practically parallel with the fragments N^3–N^4 and N^{12}–N^{13} on one face of the macrocycle (*syn*-like conformation). In the case of compound **3**, the tetrazole rings are located so that N^3–N^4 and the top of angle N^{12}–N^{13}–N^{14} are on one face of the macrocycle and the planes of the aromatic tetrazole rings are almost parallel. Macrocycle **3** exists in two different macrocyclic skeleton conformations that differ only in the coordinates of the C^{17} atom (Fig. 1b). The transition from one conformation to the other would result from rotation about C^{16}–C^{17}–O^{18} with preservation of the position of all the remaining atoms.

Conformational analysis

Of the two macrocycles investigated in the present study, compound **2** was considered the most appropriate for a

Table 1 Dihedral angles, dipole moments (μ), and relative enthalpies of formation (E) of the 30 most stable conformers of macrocycle **2** in the gas phase as calculated by the AM1 method

Conformer	Torsion angles[a] 1 2 3 4	5 6 7 8	9 10 11 12	13 14 15 16	Type[b]	μ/D	E/kcal mol^{-1}
i	− + − 0	0 + 0 +	+ − − +	+ − + −	*anti*	1.20	0[c]
ii	− + − 0	− − − 0	0 − − 0	0 0 + −	*anti*	2.43	0.32
iii	− + − 0	− − − 0	0 − − 0	0 + + −	*anti*	1.08	0.42
iv	− 0 − +	− 0 + −	+ − − 0	− + + −	*anti*	3.22	0.54
v	0 + + +	0 + 0 +	+ − − 0	− + + 0	*anti*	0.41	0.62
vi	− + − 0	0 + 0 +	+ − 0 −	− 0 + −	*anti*	1.68	0.87
vii	− 0 − +	0 0 + −	+ − − 0	0 + 0 −	*anti*	4.85	0.90
viii	− + − 0	0 + 0 −	+ − + 0	+ + + −	*anti*	2.95	0.95
ix	+ 0 + +	0 + 0 +	− + − 0	0 + + −	*syn*	4.25	1.00
x	− + − 0	0 + 0 +	+ − + +	0 + + −	*anti*	3.14	1.02
xi	+ − + 0	0 − 0 −	0 + + 0	0 − − 0	*syn*	4.37	1.10[d]
xii	0 − − −	0 − − +	− + − 0	0 + + −	*syn*	2.96	1.16
xiii	+ − + 0	+ + 0 +	− + − 0	0 + + −	*syn*	3.01	1.17
xiv	0 − − 0	0 + 0 +	− + − 0	0 + + −	*syn*	4.88	1.18
xv	+ − + 0	+ + 0 +	− + − 0	0 + + −	*syn*	3.05	1.18
xvi	0 + 0 +	− 0 0 +	− + − 0	0 + + −	*syn*	5.45	1.26
xvii	0 − − 0	0 + + −	− + − 0	− − − +	*anti*	3.09	1.27
xviii	0 + + 0	0 − 0 −	+ − + 0	0 − + +	*syn*	3.26	1.35
xix	0 − − 0	0 + 0 +	− + − 0	0 + + −	*syn*	4.49	1.40
xx	0 − − 0	0 + 0 +	− + + 0	+ + + −	*anti*	6.25	1.42
xxi	− 0 − +	0 + − +	0 − − 0	− − 0 −	*anti*	4.70	1.48
xxii	0 − − 0	− − − 0	− + 0 0	− + + −	*syn*	3.23	1.81
xxiii	0 − − 0	0 + 0 +	− + 0 0	− + + 0	*syn*	3.92	1.84
xxiv	0 − − 0	0 + 0 +	− 0 − +	0 0 + −	*syn*	3.82	1.85
xxv	0 + − 0	0 + 0 +	− + 0 0	− + + 0	*syn*	3.96	1.94
xxvi	0 − − 0	0 + 0 +	− + 0 0	− + + −	*syn*	4.88	1.98
xxvii	0 − − 0	0 + − +	− + − 0	− − 0 −	*syn*	5.73	2.16
xxviii	0 + 0 0	− + 0 +	0 − − 0	0 + + 0	*anti*	4.76	2.78
xxix	0 − − +	0 0 0 +	− + 0 0	− + + −	*syn*	3.62	3.29
xxx	0 − − 0	0 + 0 +	− + 0 0	− + + −	*syn*	4.14	3.53

[a] Dihedral angles: 1: $N^4C^5C^6C^7$, 2: $N^1C^5C^6C^7$, 3: $C^5C^6C^7O^8$, 4: $C^6C^7O^8C^9$, 5: $C^7O^8C^9C^{10}$, 6: $O^8C^9C^{10}C^{11}$, 7: $C^9C^{10}C^{11}N^{15}$, 8: $C^9C^{10}C^{11}N^{12}$, 9: $N^3N^2C^{20}C^{19}$, 10: $N^1N^2C^{20}C^{19}$, 11: $N^2C^{20}C^{19}O^{18}$, 12: $C^{20}C^{19}O^{18}C^{17}$, 13: $C^{19}O^{18}C^{17}C^{16}$, 14: $O^{18}C^{17}C^{16}N^{14}$, 15: $C^{17}C^{16}N^{14}N^{15}$, 16: $C^{17}C^{16}N^{14}N^{13}$ (+ for angles from 0 to 2/3π; − for angles between 0 and −2/3π, and 0 for angles between 2/3π and 4/3π). [b] Relative tetrazole rings' orientation. [c] The enthalpy of formation of conformer **i** is $\Delta_f H$ 139.27 kcal mol^{-1}. [d] Corresponds to the conformer determined to occur in the crystalline state by X-ray analysis.

theoretical conformational analysis. To this end, we report the use of AM1 semiempirical methods to perform a conformational analysis that is analogous to that reported for other macrocycles.[19,20] Table 1 lists the 30 most frequently repeated low-energy conformations in order of increasing energy. The maximal difference in the enthalpies of formation of the different conformers is no greater than 3.53 kcal mol^{-1}. In contrast, the maximal difference in dipole moments is quite considerable being more than 6 D. The solid state and solution energy distributions of the conformers will differ from those listed in Table 1 due to intramolecular interactions. It is possibly for this reason that conformer **xi** corresponds most closely to the X-ray crystallographic structure determined for compound **2**. This structure has a dipole moment that is 3 D higher than that of the lowest energy conformer **i**. All conformations (**xi** which is close to C_s) have only C_1 symmetry. The six lowest energy conformations **i**–**vi** are shown in Fig. 2. These conformations differ in the coordinates of the sp^3-carbon and ether oxygen atoms. Moreover, the mutual twisting of the tetrazole rings has an important influence on the diameter of the macrocycle hole-size. It is possible to identify two basic sets of conformers that differ by the relative displacement of the tetrazole cycles: *syn*- and *anti*-conformers. The thermodynamically most stable conformers, shown in Fig. 2, belong to the second group (*anti*-forms).

The six lowest *syn*-conformers are shown in Fig. 3. The conformers of the first group are energetically less stable than those of the second *anti*-group. However, the dipole moments of the *syn*-conformers are typically higher than those of the *anti* ones. The disposition of the tetrazole rings in parallel planes is more characteristic for the *syn*-group.

Of the conformations listed in Table 1, 13 belong to the group with mutually *anti*-oriented tetrazole cycles and 17 to the *syn*-oriented group. The most characteristic differences between the *syn*- and *anti*-conformers is evident in structures **xi** and **xx**, which differ only by the mutual positioning of the tetrazole rings while possessing practically the same macrocyclic skeletons (Table 1). The difference in the stability of these two conformers is quite small, only 0.32 kcal mol^{-1}. Thus, it may be concluded that the thermodynamic stability of the different conformations of the macrocycle **2** is governed predominantly by movement of the CH_2CH_2–O–CH_2CH_2 fragments, whereas rotation of the tetrazole ring may be considered to be a secondary process. However, the diameter of the hole of the macrocycle **2** is defined predominantly by the minimal distance between the nitrogen atoms in different tetrazole cycles. Rotation of the tetrazole cycles changes the diameter and thus the selectivity of metal-ion coordination.

It should be noted that the C_s symmetry *syn*-conformer **xi** may also be more stable in polar solvents as demonstrated by the "simplified" NMR spectra of macrocycle **2** in DMSO-d_6.

Conclusion

Alkylation of 1,5-bis(tetrazol-5-yl)-3-oxapentane by 2,2′-dichlorodiethyl ether provides a route to novel crown-like macrocycles with 1,5- and 2,5-disubstituted tetrazole subfragments. A conformer of macrocycle **2** that was observed by X-ray analysis in its crystal structure was also found to be among the 30 lowest energy calculated conformers within 1.1 kcal mol^{-1} of the global minimum in the gas phase. This disagreement between the experimentally determined conformer

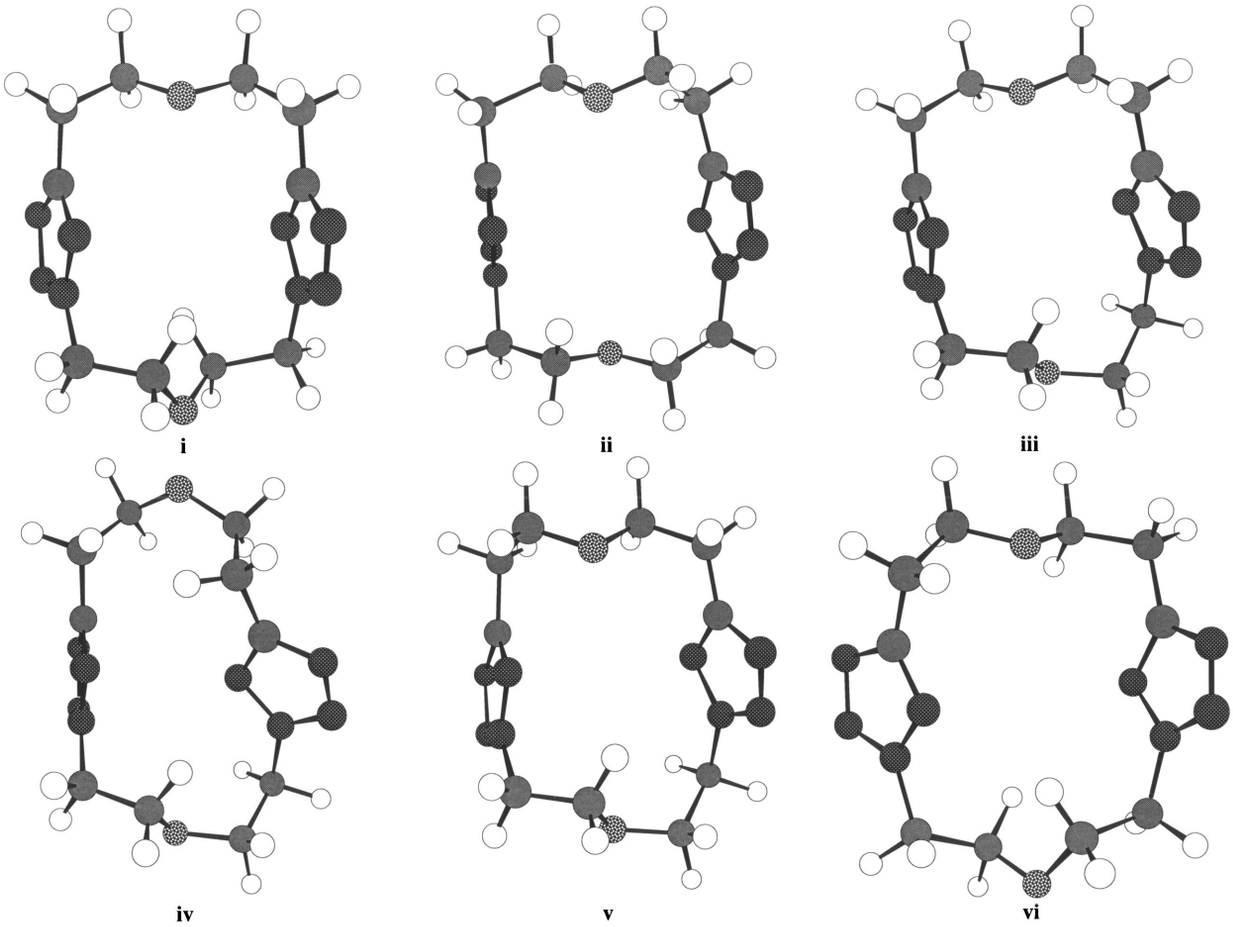


Fig. 2 The six lowest energy *anti*-conformers **i**–**vi**.

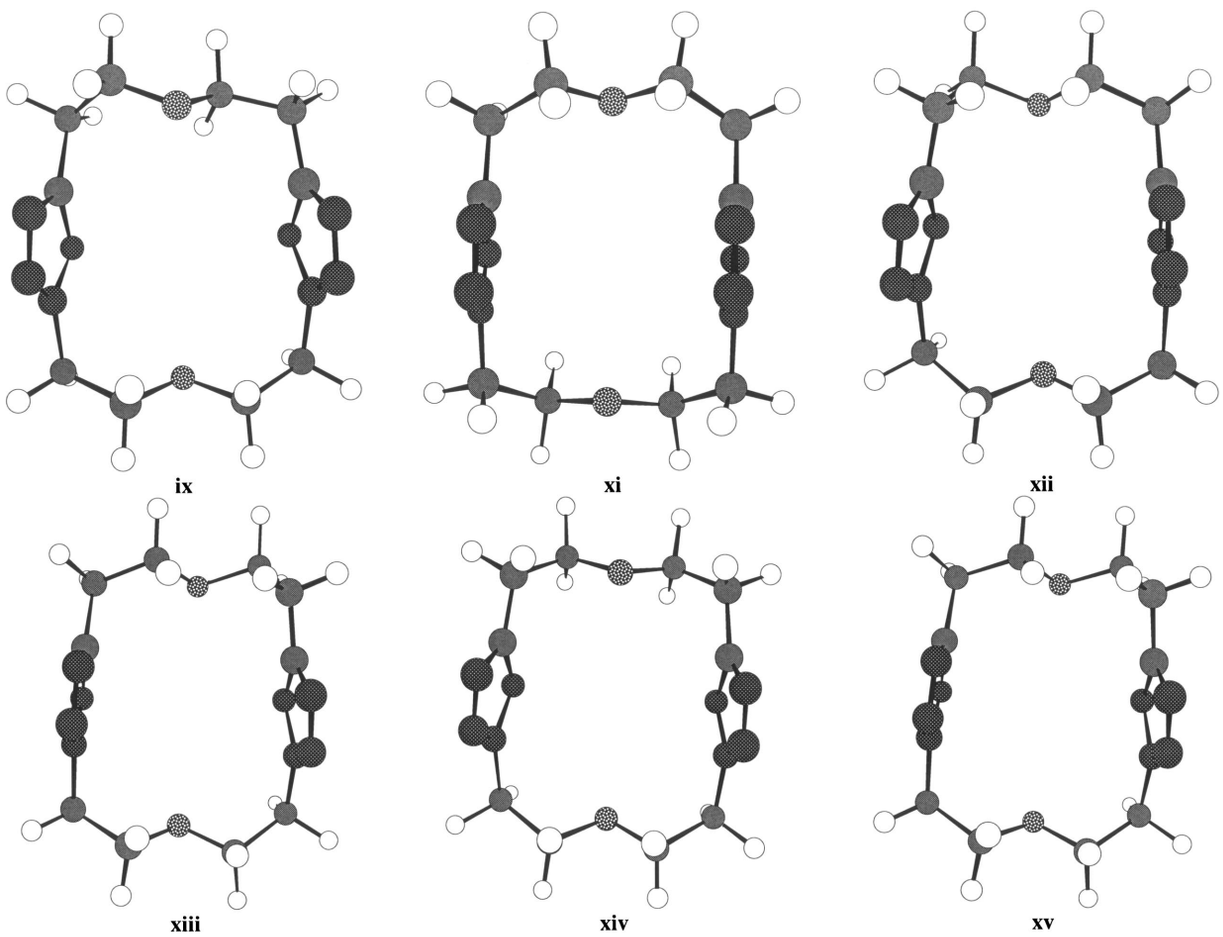


Fig. 3 The six lowest energy *syn*-conformers **ix**, **xi**–**xv**.

Table 2 Crystal data and data-collection parameters for compounds **2** and **3**

	2	**3**
Chemical formula	$C_{10}H_{16}N_8O_2$	$C_{10}H_{16}N_8O_2$
Formula weight	280.31	280.31
Crystal system	Orthorhombic	Monoclinic
Space group	*Pna2*(1)	*Pn*
a/Å	11.416(3)	8.372(7)
b/Å	14.876(4)	9.454(8)
c/Å	7.9735(16)	9.387(8)
α/°	90	90
β/°	90	113.2(17)
γ/°	90	90
wR (all data)	*R*1 = 0.0387	*R*1 = 0.1470
*R*1 ($I > 2\sigma(I)$)	*R*1 = 0.0336	*R*1 = 0.0971
V/Å^3	1354.1(6)	682.8(10)
Z	4	2
μ/mm^{-1}	0.102	0.102
Temperature/K	158(2)	176(2)
No. reflections measured	4429	3751
No. independent reflections	1470	1231
$R_{(int)}$	0.1242	0.3197

in the crystal state and the global minimum in the gas phase is governed by intermolecular interactions. The hole-size in the tetrazole-containing macrocycles is governed by their conformational state.

Experimental

^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-300 apparatus at 300 and 75 MHz, respectively, in DMSO-d_6. The chemical shifts are reported in ppm (δ). IR data were recorded on Perkin-Elmer Spectrum 1000 spectrophotometer in KBr disks. Melting points are uncorrected. A Kratos MS80RFA mass spectrometer was used for determination of high resolution spectra, operating at source potential of 4 kV, a temperature of 250 °C and ionizing energy of 70 eV.

All measurements for X-ray analysis were made with a Siemens CCD area detector using graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. Intensities were corrected for Lorentz and polarisation effects and for absorption. The structures were solved by direct methods using SHELXS and refined on F^2 using all data by full-matrix least squares procedures with SHELXL-96. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$. Where $P = [\max(F_o)^2 + 2F_c^2]/3$. Crystal data and data-collection parameters for compounds **2** and **3** are given in Table 2.

Quantum-chemical AM1 calculations were carried out using the MOPAC program.[21] The starting geometries for the AM1 minimization were generated by a successive step-by-step variation of the coordinates of the sp^3-carbon and oxygen atoms, as well as by rotation of the tetrazole cycles around two of their exocyclic bonds. Following minimization, all the identical conformations were excluded and the 30 most frequently repeated low-energy conformations were selected.

All reagents and solvents were purchased from Fluka. 2,2′-Dichlorodiethyl ether was additionally purified by vacuum distillation. 1,5-Bis(tetrazol-5-yl)-3-oxapentane **1** was synthesized by the known procedure.[16]

Preparation of macrocycles 2 and 3

Solutions of 2.10 g (10 mmol) of ditetrazole **1** in 25 ml of acetonitrile and 1.43 g (10 mmol) of 2,2′-dichlorodiethyl ether in 25 ml of acetonitrile were added simultaneously by means of precision pumps to a suspension of 1.38 g of K_2CO_3 in 500 ml acetonitrile warmed to 75 °C during 5 hours so that the dosing velocity was maintained at 5 ml h^{-1}. The reaction mess was then kept at the same temperature during 28 hours. After cooling the excess amount of potassium carbonate was filtered off and the solvent was evaporated under vacuum. The residual mixture was separated using a preparative chromatography column (350 × 22 mm) on Fluka Kiesel gel 100 (63–200 mesh) with an elution mixture of chloroform–methanol from 100:0 to 97.5:2.5 v/v to give 220 mg (8%) of compound **2** and 100 mg (4%) of compound **3**.

Compound 2. Colourless crystals, mp 194.5–195.5 °C (MeOH). HRMS (EI) calcd. for $C_{10}H_{16}O_2N_8$ $[M - N_2]^+$ 252.1335, found 252.1337. ^{1}H NMR δ 2.93 (4H, t, *J* 5.3 Hz, 2 2,5-tetrazole C^5–CH_2CH$_2$O), 3.74 (8H, t, *J* 5.3 Hz, 2 2,5-tetrazole C^5–CH$_2$CH_2O), 3.90 (4H, t, *J* 4.8 Hz, 2 2,5-tetrazole N^2–CH_2CH$_2$O), 4.68 (4H, t, *J* 4.8 Hz, 2 2,5-tetrazole N^2–CH_2CH$_2$O). ^{13}C NMR δ 25.7 (2,5-tetrazole C^5–*C*H$_2$CH$_2$O), 52.1 (2,5-tetrazole N^2–*C*H$_2$CH$_2$O), 67.5, 67.7 (CH$_2$*C*H$_2$-O*C*H$_2$CH$_2$), 163.9 (2,5-tetrazole *C*^{5}).

Compound 3. Colourless crystals, mp 137.0–137.5 °C (MeOH). HRMS (EI) calcd. for $C_{10}H_{16}O_2N_8$ $[M+H]^+$ 281.1475, found 281.1458. ^{1}H NMR δ 2.87 (2H, t, *J* 5.7 Hz, 1,5-tetrazole C^5–CH_2CH$_2$O), 3.10 (2H, t, *J* 5.7 Hz, 1,5-tetrazole C^5–CH_2CH$_2$O), 3.84 (4H, tt, *J* 5.7, 4.4 Hz, CH$_2$CH_2OCH_2CH$_2$), 3.92 (2H, t, *J* 5.7 Hz, CH$_2$CH_2OCH_2CH$_2$), 4.03 (2H, t, *J* 4.8 Hz, CH$_2$CH_2OCH_2CH$_2$), 4.20 (2H, t, *J* 5.7 Hz, 1,5-tetrazole N^1–CH_2CH$_2$O), 4.72 (2H, t, *J* 4.8 Hz, 2,5-tetrazole N^2–CH_2CH$_2$O). ^{13}C NMR δ 24.0 (2,5-tetrazole C^5–*C*H$_2$CH$_2$O), 26.1 (1,5-tetrazole C^5–*C*H$_2$CH$_2$O), 46.4 (1,5-tetrazole N^1–*C*H$_2$CH$_2$O), 52.3 (2,5-tetrazole N^2–*C*H$_2$CH$_2$O), 67.4, 68.3, 68.4, 68.5 (2 CH$_2$*C*H$_2$O*C*H$_2$CH$_2$), 153.3 (1,5-tetrazole *C*^{5}), 163.9 (2,5-tetrazole *C*^{5}).

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