

SYNTHESIS OF SUBSTITUTED HETEROCYCLIC CYCLOPHANES[†]

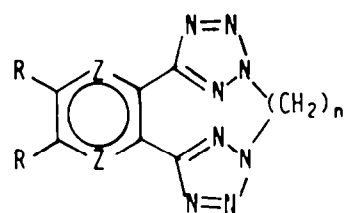
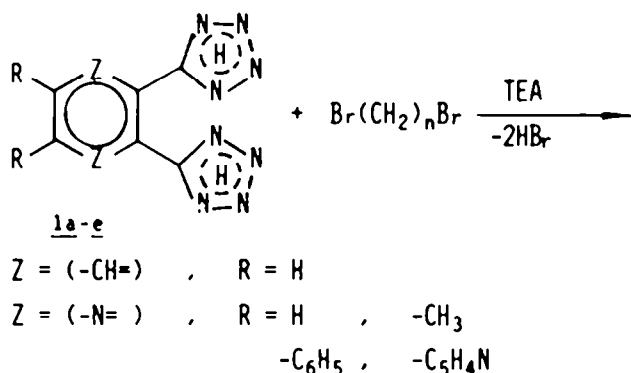
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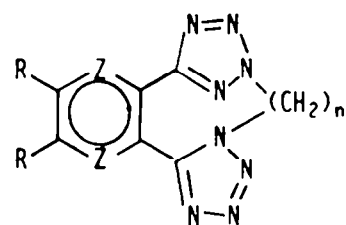
Abstract- The reaction of 1,2-bis-(5-tetrazolyl)benzene or 1,2-bis-(5-tetrazolyl)pyrazines with dibromoalkane in the presence of triethylamine gave the corresponding symmetric and asymmetric cyclophanes. The structure of which was partially characterized by spectral (infrared, ¹H-nmr) methods and fully elucidated by single crystal X-ray analysis.

A series of antihypertensive alkyltetrazoles, prepared by the alkylation of 5-alkyl- or 5-aryltetrazoles, was previously reported.² The alkylation of 5-substituted tetrazoles furnishes a mixture of 1- and 2-substituted isomers, the ratio of which is dependent on the nature of the 5-substituent.³ Although the 2-substituted isomer is the predominant one obtained with 5-aryltetrazoles.⁴ Steric factors can also play a role in the ratio of isomers formed.⁵

The preparation of 5-substituted tetrazoles is reported in the literature.^{6,7} We



(isomer A) 3, 5, 7, 9 and 11



(isomer B) 4, 6, 8 and 10

prepared o-bis-tetrazoles 1a-e from the reaction of aromatic o-dinitriles with ammonium azide in dimethylformamide.

We bridged the nitrogens in 1a-e with alkane chains -(CH₂)_n- to symmetric cyclophanes (isomer A) 3a-e , 5a-c , 7a-c , 9a-e and 11a-e and asymmetric cyclophanes (isomer B) 4a-e , 6a-b , 8a-b and 10a-b by stirring the 1a-e with Br(CH₂)_nBr in dichloromethane at 40°C for one day, the recovered product separated by column chromatography, and the isomers characterized. The results are summarized in Tab. 2-10. The reactions with Br(CH₂)_nBr (n=3,4) lead to polymer. We will report about the results of the cyclization with dibromomethane and dibromoethane other where.

[†] Dedicated to Prof. Dr. Edward C. Taylor on the occasion of the 65. birthday.

We analysed the compounds 3c and 4c by X-ray analyses and found that molecule 3c is built symmetrically. On the other side the structure of 4c is asymmetrically (Fig.1-3). The $^1\text{H-nmr}$ -spectrum of the symmetrical compound 3c shows only one signal for the $-\text{CH}_2-$ protons positioned alpha to the nitrogen, contributed by four protons. The aromatic protons appear as two (2H) absorptions. In contrast, 4c shows in the proton-nmr-spectrum two resonance signals for the alpha-methylene group, each of them is caused by two protons, the aromatic protons appear also in more signals.

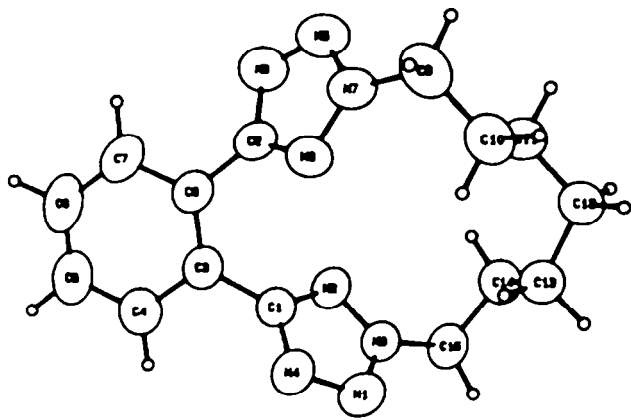


Figure 1. Symmetric cyclophane 3c: The benzene ring is planar. So are the tetrazole rings make angles of $58.5(2)^\circ$ and $38.3(2)^\circ$ with the plane of the benzene ring. The molecular packing shows no intermolecular distances shorter than the sums of the van der Waals radii of the atoms.

Figure 2. In the crystal two molecules of asymmetric cyclophane 4c and two water molecules, which are located between, are held together by intermolecular hydrogen bondings. The structure contains centrosymmetric dimers by hydrogen bond formation.

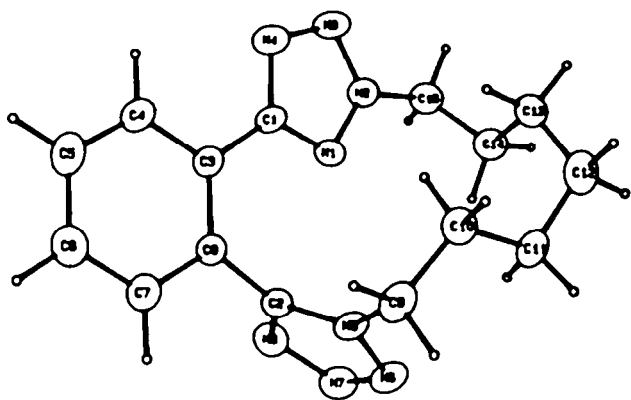
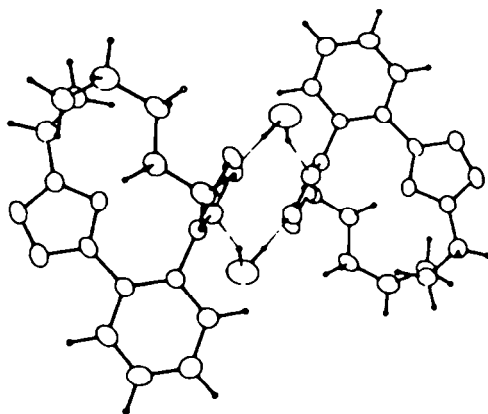


Figure 3. Asymmetric cyclophane 4c: The molecule contains three planar parts: the benzene ring and the two tetrazole rings. The tetrazole rings make angles of 7.7° and 85.6° with the plane of the benzene ring.

Comparison of the $^1\text{H-nmr}$ -spectra allows structure assignment of the other isolated compounds. On account of this spectroscopical resemblance we postulate the structures given in the formula scheme.

Crystal Data of compound 3c: formula $\text{C}_{15}\text{H}_{18}\text{N}_8$, mol weight: 310.36, crystal color: colorless transparent, crystal dimensions: $0.33 \times 0.35 \times 0.73 \text{ mm}^3$, crystal system orthorhombic, space group: $\text{Pc}2_1\text{n}$, space group number: 33, a: $8.4312(7) \text{ \AA}$, b: $12.1496(7)$, c: $15.4006(9)$, v: $1577.6(3) \text{ \AA}^3$, z: 4, Dcalc: 1.307 g/cm^3 , linear absorption coeff.: 6.6 cm^{-1} , radiation: Cu-K α , scan mode: ω , scan range: quadrant, $(2\theta)_{\text{max}}$: 120° , number of independent reflections: 1230, reflections used with $I > \sigma(I)$: 1229, number of variables: 208, R(F): 0.043, wR(F): 0.046.

Crystal Data of compound 4c: formula $\text{C}_{15}\text{H}_{18}\text{N}_8\text{H}_2\text{O}$, mol weight: 328.38, crystal color: colorless transparent, crystal dimensions: $0.05 \times 0.20 \times 0.65 \text{ mm}^3$, crystal system orthorhombic, space group: $\text{Pbc}a$, space group number: 61, a: $6.9845(6) \text{ \AA}$, b: $20.487(2)$, c: $22.586(1)$, v: $3231.8(8) \text{ \AA}^3$, z: 8, Dcalc: 1.349 g/cm^3 , linear absorption coeff.

7.17 cm⁻¹, radiation: Cu-K α , scan mode: ω , scan range: (2 θ)_{max}: 110^o, number of independent reflections: 2022, reflection used with I > σ (I): 1829, number of variables: 271, R(F): 0.081, wR(F): 0.082.

Table of Positional Parameters and Their Estimated Standard Deviations of 3c :

Atom	x	y	z	Atom	x	y	z
N1	0.2001(5)	0.5144	0.5458(3)	C14	-0.0766(6)	0.7266(4)	0.5525(3)
N2	-0.0090(5)	0.4990(4)	0.6325(2)	C15	-0.0358(6)	0.6199(4)	0.5052(3)
N3	0.0531(5)	0.5450(3)	0.5627(2)	H4	0.1480	0.2251	0.6535
N4	0.2360(5)	0.4442(4)	0.6087(3)	H5	0.1016	0.0853	0.7573
N5	-0.0509(6)	0.5414(4)	0.9151(3)	H6	0.0165	0.1354	0.8993
N6	0.1311(5)	0.5817(4)	0.8213(2)	H7	-0.0179	0.3294	0.9381
N7	0.0725(5)	0.6665(4)	0.8669(2)	H91	0.2537	0.7741	0.8973
N8	-0.0805(5)	0.5361(4)	0.9008(3)	H92	0.0825	0.8304	0.9033
C1	0.1094(5)	0.4353(4)	0.6602(3)	H101	0.2208	0.7656	0.7397
C2	0.0316(6)	0.5020(5)	0.8437(3)	H102	0.2313	0.8894	0.7747
C3	0.0927(5)	0.3577(4)	0.7324(3)	H111	-0.0462	0.9045	0.7658
C4	0.1141(6)	0.2445(4)	0.7122(3)	H112	-0.0560	0.7810	0.7300
C5	0.0844(7)	0.1649(5)	0.7741(3)	H121	0.1125	0.9452	0.6382
C6	0.0359(6)	0.1940(5)	0.8549(4)	H122	-0.0725	0.9256	0.6213
C7	0.0183(6)	0.3055(5)	0.8779(3)	H131	0.1531	0.7531	0.5946
C8	0.0477(5)	0.3860(4)	0.8149(3)	H132	0.1028	0.8339	0.5173
C9	0.1453(7)	0.7779(5)	0.8677(4)	H141	-0.1495	0.7691	0.5165
C10	0.1639(6)	0.8214(4)	0.7757(4)	H142	-0.1258	0.7079	0.6076
C11	0.0099(6)	0.8476(5)	0.7317(3)	H151	-0.1351	0.5824	0.4861
C12	0.0291(7)	0.8885(4)	0.6394(4)	H152	0.0276	0.6348	0.4523

Table of Positional Parameters and Their Estimated Standard Deviations of 4c :

Atom	x	y	z	Atom	x	y	z
N1	0.8589(7)	0.1466(2)	0.1689(2)	C15	0.7740(1)	0.2629(4)	0.1666(3)
N2	0.8360(7)	0.2037(3)	0.1960(2)	O1	0.5072(9)	0.4310(4)	0.4154(3)
N3	0.8770(8)	0.2024(3)	0.2529(2)	H4	0.9880(8)	0.0290(3)	0.2980(2)
N4	0.9268(7)	0.1417(3)	0.2648(2)	H5	1.0540(9)	-0.0890(3)	0.3020(2)
N5	1.0522(7)	0.0667(3)	0.0615(2)	H6	1.0740(9)	-0.1490(3)	0.2060(3)
N6	0.9629(8)	0.0843(3)	0.0110(2)	H7	1.0260(9)	-0.0860(3)	0.1220(2)
N7	0.7883(9)	0.0643(3)	0.0177(2)	H91	1.3130(9)	0.0840(3)	0.0220(3)
N8	0.7638(8)	0.0344(3)	0.0707(2)	H92	1.3090(9)	0.0480(3)	0.1000(3)
C1	0.9172(7)	0.1088(3)	0.2132(2)	H101	1.4170(9)	0.1570(3)	0.1060(3)
C2	0.9324(8)	0.0365(3)	0.0982(3)	H102	1.2310(9)	0.1610(3)	0.1340(3)
C3	0.9662(7)	0.0400(3)	0.2087(2)	H111	1.1100(1)	0.1910(3)	0.0280(3)
C4	1.0016(8)	0.0053(3)	0.2611(3)	H112	1.3200(1)	0.1970(3)	0.0110(3)
C5	1.0435(8)	-0.0601(3)	0.2602(3)	H121	1.2100(1)	0.3110(3)	0.0350(3)
C6	1.0523(9)	-0.0933(3)	0.2071(3)	H122	1.3600(1)	0.2880(3)	0.0860(3)
C7	1.0199(9)	-0.0591(3)	0.1551(3)	H131	1.1000(1)	0.3390(3)	0.1440(3)
C8	0.9755(7)	0.0066(3)	0.1553(2)	H132	1.1700(1)	0.2530(3)	0.1610(3)
C9	1.2613(9)	0.0827(4)	0.0686(3)	H141	0.8570(9)	0.2290(3)	0.0810(3)
C10	1.2926(9)	0.1502(4)	0.0906(3)	H142	0.8400(1)	0.3210(3)	0.0900(3)
C11	1.2360(9)	0.2044(4)	0.0479(3)	H151	0.8170(9)	0.3040(3)	0.2020(3)
C12	1.2380(1)	0.2722(4)	0.0736(4)	H152	0.6500(9)	0.2590(3)	0.1530(3)
C13	1.1100(1)	0.2841(4)	0.1260(3)	H01	0.4160	0.4648	0.4296
C14	0.8890(1)	0.2749(4)	0.1121(3)	H02	0.6250	0.4316	0.4570

Experimental Section

Infrared spectra were recorded on Perkin-Elmer 398 spectrophotometers, ^1H -nmr-spectra on a Bruker WH 270. All melting points are uncorrected. The procedures reported below are representative for the preparation of the products shown in tables 1-10.

Preparation of o-Bis-tetrazoles 1a-e:

A mixture of the dinitriles (0.1 mol), sodium azide (0.22 mol), lithium chloride (0.22 mol) and ammonium chloride (0.22 mol) in 75 ml of anhydrous DMF was stirred and maintained at 125°C for 24h. Solvent was removed under reduced pressure. The residue was dissolved in 200 ml water and acidified with concentrated hydrochloric acid. Caution: HN_3 was evolved. The precipitate was collected and washed with water. Recrystallization from ethanol.

Table (1) 5-substituted o-Bis-tetrazoles
N4HC-R-CHN4

No.	-R-	Product	M.p. ^o C	Molecular formula	Calcd.		Analyses	
			Yield%		Found.	C	H	N
1a	A	1,2-bis-(5-tetrazolyl)-benzene	237 dec. 75	$\text{C}_8\text{H}_6\text{N}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$	43.05 43.29	3.16 3.14	50.20 50.47	
1b	B	1,2-bis-(5-tetrazolyl)-pyrazine	265 dec. 58	$\text{C}_6\text{H}_4\text{N}_{10}$	33.34 33.59	1.87 1.90	64.80 64.52	
1c	C	1,2-bis-(5-tetrazolyl)-5,6-dimethylpyrazine	231 dec. 51	$\text{C}_8\text{H}_8\text{N}_{10} \cdot \frac{1}{2}\text{H}_2\text{O}$	37.95 37.89	3.58 3.70	55.31 55.10	
1d	D	1,2-bis-(5-tetrazolyl)-5,6-diphenylpyrazine	271 dec. 65	$\text{C}_{18}\text{H}_{12}\text{N}_{10} \cdot \text{H}_2\text{O}$	55.95 55.87	3.65 3.70	36.25 35.97	
1e	E	1,2-bis-(5-tetrazolyl)-5,6-di-(2-pyridyl)pyrazine	282 dec. 70	$\text{C}_{16}\text{H}_{10}\text{N}_{12} \cdot \text{H}_2\text{O}$	49.48 49.41	3.11 3.20	43.28 42.98	

A = phenyl-, B = pyrazinyl-, C = 5,6-dimethylpyrazinyl-, D = 5,6-diphenylpyrazinyl- and E = 5,6-di-(2-pyridyl)pyrazinyl-.
1a) M.p. = 236-37°C dec. (Lit. 7).

General procedure for preparing of cyclophanes:

To a suspension of 5 mmol of 1,2-bis-tetrazoles 1a-e and 10 mmol of dibromoalkane in 50 ml of anhydrous dichloromethane was added a solution of 10 mmol of triethylamine in 5 ml dichloromethane at r.t., the solution was stirred and maintained at 40°C for 24h, the solvent was evaporated and the residue chromatographed on a column of silica gel, elution with a mixture of n-hexan and ethylacetate.

Table (2) Symmetric 2-(1,2)benzeno-1,3-bis-(5,2)tetrazolo-cyclophanes 3a-e

No.	Product	M.p. ^o C	Molecular formula	Calcd.		Analyses	
		Yield		Found.	C	H	N
3a	5 2-(1,2)benzeno-1,3-bis-(5,2)-tetrazolo-cyclooctaphane	192-93 14	$\text{C}_{13}\text{H}_{14}\text{N}_8$	55.31 55.54	5.00 5.24	39.69 39.40	
3b	6 2-(1,2)benzeno-1,3-bis-(5,2)-tetrazolo-cyclononaphane	166-68 21	$\text{C}_{14}\text{H}_{16}\text{N}_8$	56.74 56.50	5.44 5.40	37.81 37.53	
3c	7 2-(1,2)benzeno-1,3-bis-(5,2)-tetrazolo-cyclodecaphane	119-20 19	$\text{C}_{15}\text{H}_{18}\text{N}_8$	58.05 58.01	5.84 6.04	36.10 35.81	
3d	8 2-(1,2)benzeno-1,3-bis-(5,2)-tetrazolo-cycloundecaphane	110-12 15	$\text{C}_{16}\text{H}_{20}\text{N}_8$	59.24 58.91	6.21 6.14	34.54 34.38	
3e	10 2-(1,2)benzeno-1,3-bis-(5,2)-tetrazolo-cyclotridecaphane	160-62 13	$\text{C}_{18}\text{H}_{24}\text{N}_8$	61.34 61.08	6.86 6.88	31.79 31.74	

Table (3) Asymmetric 2-(1,2)benzeno-1(5,1),3(5,2)-bis-tetrazolo-cyclophanes
4a-e

No.	n	Product	M.p. ^o C Yield%	Molecular formula	Calcd. Found.	Analyses C H N
4a	5	2-(1,2)benzeno-1(5,1),3(5,2)-bis-tetrazolo-cyclooctaphane	184-86 9	C ₁₃ H ₁₄ N ₈	55.31 5.00 55.05 5.27	39.69 39.41
4b	6	2-(1,2)benzeno-1(5,1),3(5,2)-bis-tetrazolo-cyclononaphane	159-60 12	C ₁₄ H ₁₆ N ₈	56.74 5.44 56.46 5.40	37.81 37.53
4c	7	2-(1,2)benzeno-1(5,1),3(5,2)-bis-tetrazolo-cyclodecaphane	128-30 13	C ₁₅ H ₁₈ N ₈ ·H ₂ O	54.86 6.14 54.80 6.16	34.12 33.97
4d	8	2-(1,2)benzeno-1(5,1),3(5,2)-bis-tetrazolo-cycloundecaphane	118-20 8	C ₁₆ H ₂₀ N ₈ · $\frac{1}{2}$ H ₂ O	57.64 6.34 57.49 6.13	33.60 33.35
4e	10	2-(1,2)benzeno-1(5,1),3(5,2)-bis-tetrazolo-cyclotridecaphane	127-29 5	C ₁₈ H ₂₄ N ₈	61.34 6.86 61.04 6.68	31.79 31.90

Table (4) Symmetric 2-(2,3)pyrazino-1,3-bis-(5,2)-tetrazolo-cyclophanes

5a-c

No.	n	Product	M.p. ^o C Yield%	Molecular formula	Calcd. Found.	Analyses C H N
5a	5	2-(2,3)pyrazino-1,3-bis-(5,2)-tetrazolo-cyclooctaphane	241-42 13	C ₁₁ H ₁₂ N ₁₀	46.47 4.25 46.34 4.38	49.26 49.31
5b	7	2-(2,3)pyrazino-1,3-bis-(5,2)-tetrazolo-cyclodecaphane	200-01 15	C ₁₃ H ₁₆ N ₁₀	49.99 5.16 50.05 5.02	44.84 44.58
5c	8	2-(2,3)pyrazino-1,3-bis-(5,2)-tetrazolo-cycloundecaphane	139-41 11	C ₁₄ H ₁₈ N ₁₀	51.52 5.55 51.34 5.59	42.91 42.98

Table (5) Asymmetric 2-(2,3)pyrazino-1(5,1),3(5,2)-bis-tetrazolo-cyclophanes

6a-b

No.	n	Product	M.p. ^o C Yield%	Molecular formula	Calcd. Found.	Analyses C H N
6a	7	2-(2,3)pyrazino-1(5,1),3(5,2)-bis-tetrazolo-cyclodecaphane	183-85 7	C ₁₃ H ₁₆ N ₁₀	49.99 5.16 49.84 5.18	44.84 44.73
6b	8	2-(2,3)pyrazino-1(5,1),3(5,2)-bis-tetrazolo-cycloundecaphane	162-64 5	C ₁₄ H ₁₈ N ₁₀	51.52 5.55 51.54 5.70	42.91 42.65

Table (6) Symmetric 2-(2,3)5,6-dimethylpyrazino-1,3-bis-(5,2)tetrazolo-cyclophanes

7a-c

No.	n	Product	M.p. ^o C Yield%	Molecular formula	Calcd. Found.	Analyses C H N
7a	5	2-(2,3)5,6-dimethylpyrazino-1,3-bis-(5,2)tetrazolo-cyclooctaphane	273-74 12	C ₁₃ H ₁₆ N ₁₀ ·H ₂ O	47.26 5.49 47.18 5.20	42.39 42.16
7b	7	2-(2,3)5,6-dimethylpyrazino-1,3-bis-(5,2)tetrazolo-cyclodecaphane	233-35 13	C ₁₅ H ₂₀ N ₁₀	52.93 5.92 52.78 6.13	41.15 41.42
7c	8	2-(2,3)5,6-dimethylpyrazino-1,3-bis-(5,2)tetrazolo-cycloundecaphane	176-77 12	C ₁₆ H ₂₂ N ₁₀	54.22 6.25 54.37 5.98	39.52 39.27

Table (7) Asymmetric 2-(2,3)-5,6-dimethylpyrazino-1(5,1),3(5,2)-bis-tetrazolo-cyclophanes

8a-b

No.	n	Product	M.p. ^o C Yield%	Molecular formula	Calcd. Found.	Analyses C H N
8a	7	2-(2,3)5,6-dimethylpyrazino-1(5,1),3(5,2)-bis-tetrazolo-cyclodecaphane	202-05 6	C ₁₅ H ₂₀ N ₁₀	52.93 5.92 52.65 6.21	41.15 41.45
8b	8	2-(2,3)5,6-dimethylpyrazino-1(5,1),3(5,2)-bis-tetrazolo-cycloundecaphane	182-84 5	C ₁₆ H ₂₂ N ₁₀	54.22 6.25 54.10 6.19	39.52 39.61

Table (8) Symmetric 2-(2,3)5,6-diphenylpyrazino-1,3-bis-(5,2)tetrazolo-cyclophanes

No.	Product	M.p. ^o C Yield%	Molecular formula	Calcd. Found.	Analyses		
					C	H	N
9a	5 2-(2,3)5,6-diphenylpyrazino-1,3-bis-(5,2)tetrazolo-cyclooctaphane	244-46 8	C ₂₃ H ₂₀ N ₁₀ ·H ₂ O	60.78 60.57	4.87 4.58	30.81 30.54	
9b	6 2-(2,3)5,6-diphenylpyrazino-1,3-bis-(5,2)tetrazolo-cyclononaphane	254 14	C ₂₄ H ₂₂ N ₁₀	63.98 63.73	4.92 4.92	31.09 31.02	
9c	7 2-(2,3)5,6-diphenylpyrazino-1,3-bis-(5,2)tetrazolo-cyclodecaphane	227-28 13	C ₂₅ H ₂₄ N ₁₀ ·H ₂ O	62.22 62.45	5.43 5.18	29.03 28.91	
9d	8 2-(2,3)5,6-diphenylpyrazino-1,3-bis-(5,2)tetrazolo-cycloundecaphane	212-14 11	C ₂₆ H ₂₆ N ₁₀	64.05 64.21	5.58 5.65	28.72 28.51	

Table (9) Asymmetric 2^{5,6}-di(2-pyridyl)-2-(2,3)pyrazino-1(5,1),3(5,2)-bis-tetrazolo-cyclophanes

No.	Product	M.p. ^o C Yield%	Molecular formula	Calcd. Found.	Analyses		
					C	H	N
10a	7 2 ^{5,6} -di(2-pyridyl)-2-(2,3)-pyrazino-1(5,1),3(5,2)-bis-tetrazolo-cyclodecaphane	229-30 11	C ₂₃ H ₂₂ N ₁₂	58.96 58.93	5.16 4.87	35.87 35.70	
10b	8 2 ^{5,6} -di(2-pyridyl)-2-(2,3)-pyrazino-1(5,1),3(5,2)-bis-tetrazolo-cycloundecaphane	231-33 9	C ₂₄ H ₂₄ N ₁₂ · $\frac{1}{2}$ H ₂ O	58.88 58.82	5.14 5.03	34.33 34.04	

Table (10) Symmetric 2^{5,6}-di(2-pyridyl)-2-(2,3)pyrazino-1,3-bis-(5,2)tetrazolo-cyclophanes

No.	Product	M.p. ^o C Yield%	Molecular formula	Calcd. Found.	Analyses		
					C	H	N
11a	5 2 ^{5,6} -di(2-pyridyl)-2-(2,3)pyrazino-1,3-bis-(5,2)tetrazolo-cyclooctaphane	257-58 14	C ₂₁ H ₁₈ N ₁₂ · $\frac{1}{2}$ H ₂ O	56.37 56.39	4.27 4.20	37.56 37.27	
11b	6 2 ^{5,6} -di(2-pyridyl)-2-(2,3)pyrazino-1,3-bis-(5,2)tetrazolo-cyclononaphane	237 18	C ₂₂ H ₂₀ N ₁₂	58.39 58.39	4.45 4.54	37.14 37.08	
11c	7 2 ^{5,6} -di(2-pyridyl)-2-(2,3)pyrazino-1,3-bis-(5,2)tetrazolo-cyclodecaphane	240 16	C ₂₃ H ₂₂ N ₁₂ · $\frac{1}{2}$ H ₂ O	57.84 57.89	5.27 4.99	35.19 34.98	
11d	8 2 ^{5,6} -di(2-pyridyl)-2-(2,3)pyrazino-1,3-bis-(5,2)tetrazolo-cycloundecaphane	244 14	C ₂₄ H ₂₄ N ₁₂	59.98 59.85	5.03 4.75	34.98 34.73	
11e	10 2 ^{5,6} -di(2-pyridyl)-2-(2,3)pyrazino-1,3-bis-(5,2)tetrazolo-cyclotridecaphane	202-04 10	C ₂₆ H ₂₈ N ₁₂	61.40 61.17	5.55 5.66	33.04 33.06	

¹H-NMR-Data of some compounds:

3b: 8.00, 7.65 2(m;2H), 4.60 (t;4H), 2.05 (m;4H), 1.25 (m;4H). 4b: 7.90, 7.60 2(m;2H), 4.59, 3.40 2(t;2H), 1.98, 1.82, 1.51, 1.35 4(m;2H). 3c: 7.87, 7.61 2(m;2H), 4.56 (t;4H), 1.87 (m;4H), 1.33 (m;6H). 4c: 8.39, 7.85, 7.75, 7.65 4(m;1H), 4.71-4.21 (m;2H), 4.25 (t;1H), 3.90 (d;1H), 1.67 (s;2H) 1.35-1.05 (m;6H), 0.83 (s;2H). 3e: 7.85, 7.60 2(m;2H), 4.55 (t;4H), 1.90 (m;4H), 1.25 (m;12H). 4e: 8.40 (m;1H), 7.80-7.25 (m;3H), 4.60, 4.00 2(m;2H), 1.90 (m;4H), 1.15 (m;12H). 5c: 9.10 (s;2H) 7.80 (t;4H), 2.00 (m;4H), 1.35 (s;8H). 6b: 9.20, 9.05 2(m;1H), 4.90-4.20 (m;4H), 1.90 (m;4H), 1.18 (s;8H). 7b: 4.64 (t;4H), 2.67 (s;6H), 1.76-1.65 (m;4H), 1.23-1.07 (m;6H). 8a: 4.70-4.63 (m;2H), 4.38, 4.17 2(d;1H), 1.68 (m;2H), 1.21-1.10 (m;6H), 0.95-0.84 (m;2H). 9d: 7.70-7.25 (m;10H), 4.65 (t;4H), 2.25-1.60 (m;4H), 1.35 (s;8H). 10a: 8.35 (d;2H), 7.99 (m;4H), 7.41 (m;2H), 4.71 (t;4H), 1.76 (s;4H), 1.76 (s;4H), 1.16 (d;6H). 11c: 4.78-4.32 (m;4H), 1.80-1.66 (m;4H), 1.60-0.92 (m;6H). (3b, 4b, 3c, 4c, 3e and 4e: 270 MHz-CDCl₃), (5c, 6b and 9d: 60 MHz-DMSO), (7b, 8a, 10a and 11c: 270 MHz-DMSO).

Summary - We have described in this paper the first synthesis of cyclophanes containing the tetrazol ring system by bridging the corresponding o-bis-tetrazoles with alkyl-chains.

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