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NMR and X-Ray Study of Cyclotetraveratrilene Derivatives

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Abstracts: A conformational study of cycloveratrilenes **3** and **4** by high resolution NMR at low temperature for **3** and room temperature for **4** along with X-ray crystallography is reported. From these experiments we found a dynamic process, where magnetic and topologic environment are exchanged by conformational variations through rotations.
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Introduction

Several derivatives of cycloveratrilene with n=2-6 (Figure 1) have been prepared and identified in connection with differents studies and applications,[1,2] including a study of mesomorphic properties of some cyclotriveratrilenes (CTV) (n=3).[3] The molecules with n=2 and 4 were shown by ^1H NMR to be highly flexible, and undergoing fast ring inversions and pseudo rotations.[4-6] In contrast the CTV, has a rigid structure with C_{3v} symmetry, which undergoes extremely slow ring inversion even at 200°C.[7,8]

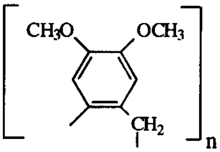

Figure 1

For cyclotetraveratrylene (CTTV) n=4 two conformations have been considered: the "sofa" (2a) Figure 2 with C_{2h} symmetry and the "boat" (2b) with C_{2v} symmetry.[4] The more symmetric "crown" (2c) conformer with C_{4v} symmetry is unstable, apparently due to steric interactions between the aromatic rings.[4,5] In a dynamic NMR investigation of CTTV in chloroform solution, White and Gesner[4,5] observed only one species which they showed was consistent with the "sofa" form, however, they suggested, that the fast pseudorotation of this conformation probably proceeds *via* the "crown" form, although no signals due to the latter were observed by ^1H NMR experiments, even at low temperatures, where the process is very slow.

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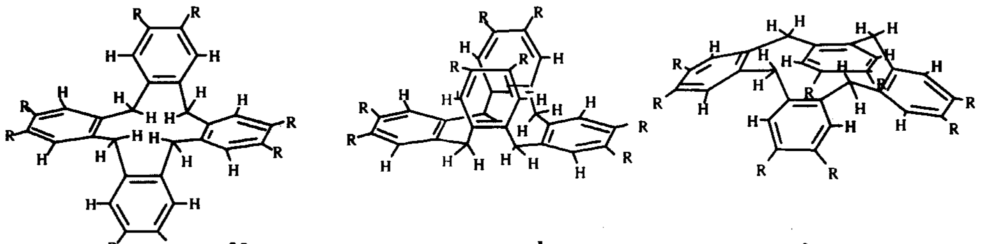

R= OCH_3,

Figure 2

In order to form adduct compounds between cyclotetraveratrylene derivatives with fullerenes, we have synthetized the octahydroxyorthocyclophane (**3**) and the octamethoxydiketoneorthocyclophane (**4**) (Figure 3). This was done in an effort to try to stabilize the "crown" conformer, since it would be this conformer that would be more susceptible of reacting with fullerenes, as has been found, for example, for calixarene and other macrocycles.[9,11] The derivatives **3** and **4** were synthetized as described in the experimental section and shown in figure **3**.

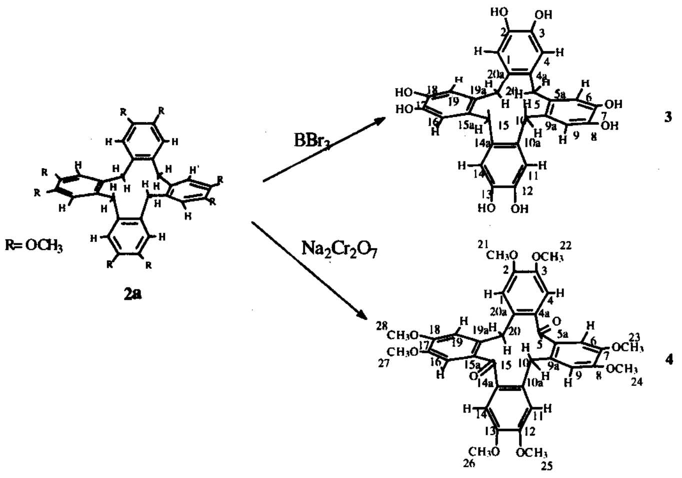

Figure 3

Results and Discussion

Room temperature ^1H NMR spectra of the octahydroxyorthocyclophane (**3**) in deuterated acetone showed two broad signals, the first at 6.59 ppm for the aromatic and hydroxylic protons, and the second at 3.95 ppm, assigned to the protons of the methylene group. Similar broad signals were observed for the cyclotetraveratrylene **2a** at room temperature.[4]

At low temperatures, the broadened signals of **3** were resolved showing a broad signal at 7.15 ppm assigned to the hydroxylic hydrogens (δ_H), two singlets at 6.73 and 6.20 ppm due to non equivalent benzenoid protons, and an AB system, δ_A=3.64 ppm, (J= 15.5 Hz) and δ_B=2.89 ppm, (J= 15.5 Hz) assigned to the diasterotopic methylene protons (δ_H) (see Figure **4**).

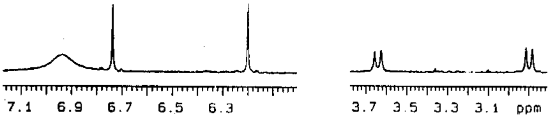

Figure 4. ^{1}H NMR 500 MHz spectra of **3** in acetone-d_6 - D_2O at -50 °C.

The phase-sensitive NOESY spectrum[12,14] at low temperature of **3** showed cross peak betwen the two non-equivalent aromatic protons and both of the two non-equivalent methylene hydrogens (see Figure 5a). These observed interactions suggest a dynamic process of four equivalent conformers where the magnetic and topologic enviroments of the two aromatic and the methylene protons are exchanged by conformational changes, through rotations of the sp^3-sp^2-sp^2-sp^3 bonds[12] (see Figure 6). This exchange may be explained with the itinerary shown in Figure 6, where the pseudoaxial hydrogen at C-20 (for numbering see Figure 3) in conformers A and B (solid ball) changes to pseudoequatorial hydrogen at C-20 in conformers C and D. Complementary, the pseudoecuatorial hydrogen at C-20 in conformers A and B (empty ball) becomes pseudoaxial in conformers C and D. The hydrogens at C-1 in conformers A and D are equivalents, but

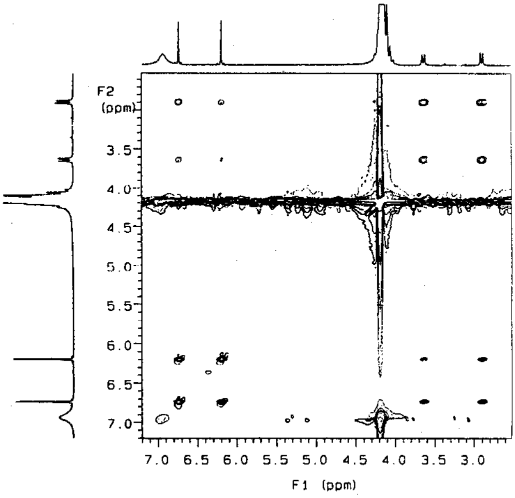

Figure 5a. NOESY spectrum of 3

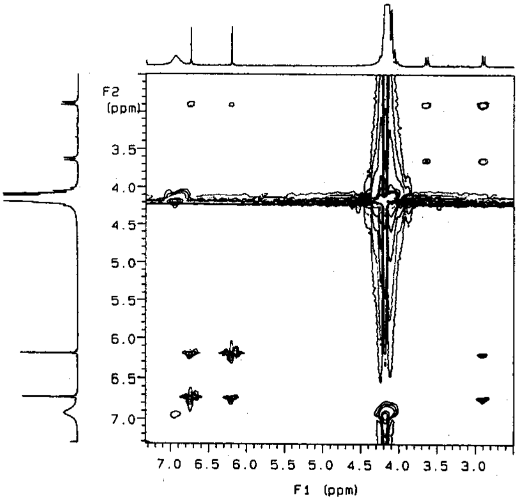

Figure 5c. ROESY spectrum of 3

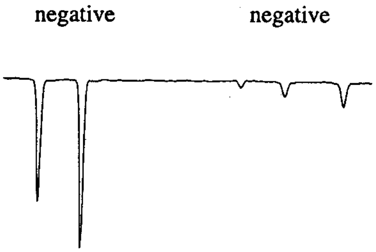

Figure 5b. 1D Cross section at δ 6.397 from NOESY spectrum of **3**

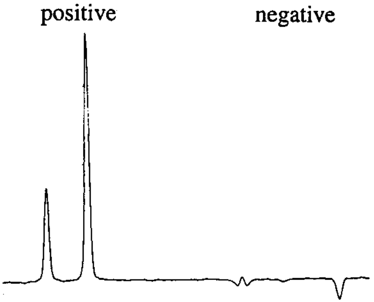

Figure 5d. 1D Cross section at δ 6.379 from ROESY spectrum of **3**

magnetically different to the hydrogen at C-19 in the same conformers. Moreover, the topological environment between these hydrogens is interchanged in conformers B and C. This dynamic process coincides with a "sofa" conformer and it is confirmed by the observed negative crosspeaks in the NOESY spectrum, acoording to the chemical exchange for the aromatic and methylene hydrogens. Figure 5b shows a cross section of the signal at δ 6.739 (aromatic hydrogen) clearly indicating the negative phase of the diagonal and cross peaks.[13,14]

Roesy spectrum of **3** (figure5c), confirmed the chemical exchange in this dynamic process, since the phases are inverted. Considering the same cross section (signal at δ 6.739, figure 5d), the diagonal peak and cross peaks due to aromatics hydrogens are positive. The observed negative phase for the correlation at high field is due to spatial interaction between the aromatic and methylenic protons[14,15].

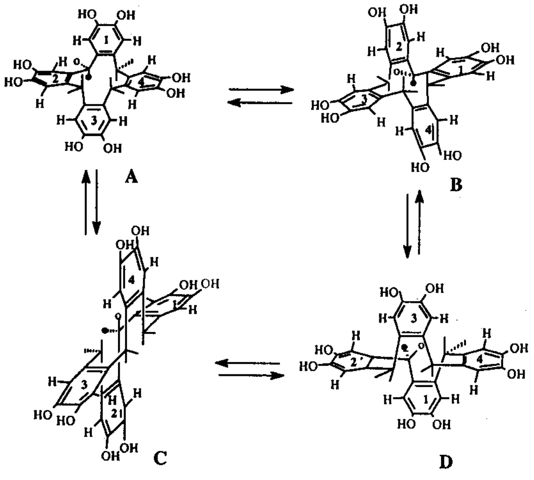

Figure 6. Interconvertion of equivalent conformers of **3** by a dynamic process.

In order to confirm if the stable conformer corresponds with that of a "sofa" shape, the X-ray crystallographic determination of compound **3** was achieved. The ORTEP view and unit cell are shown in Figures 7a,b. Crystal data collection are summarized in the table 1. The final atomic parameters are given in the table 2, and the bond distances and angles in the table 3. One half molecule was determinated and completed by symmetry (symmetry code: X,Y, Z, X,1-Y, Z). Two phenyl groups form dihedral angle of 94.4^0 with respect to the other phenyl groups.

For compound **4** internal rotations are slower compared with that of **3**, since at room temperature all

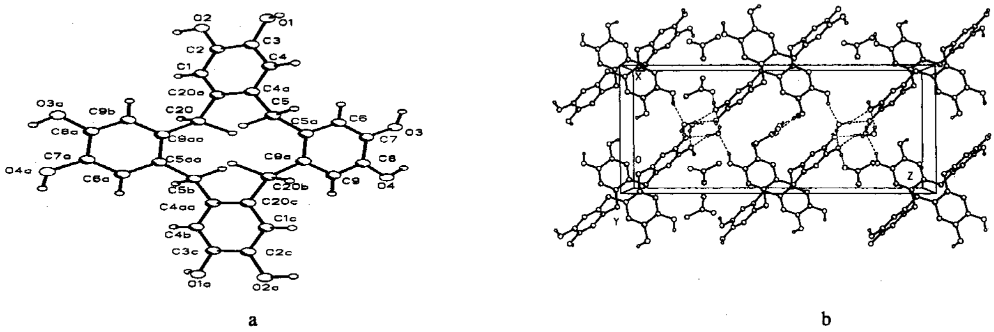

Figure 7. a) ORTEP view with atomic labeling and b) Crystal packing of **3**.

Table 1. Crystalographic Data for **3** and **4** :

Empirical formula	$C_{14}H_{12}O_4$ with H_2O $1.5CH_3COCH_3$ **3**	$C_{19}H_{19}Cl_3O_5$ **4**
Formula weight	349.4	433.7
Crystal system	monoclinic	monoclinicc
Space group	$P2_1/c$	$P2_1/n$
Z	4	4
a(Å)	10.261(2)	9.752(2)
b(Å)	7.042(1)	13.7480(10)
c(Å)	25.153(2)	15.344(3)
β^o	90.44(1)	96.240(0)
Volumen ($Å^3$)	1817.3(1)	2045.0(4)
Diffractometer used	SIEMENS P4	SIEMENS P4
Radiation	Cu Kα (λ = 1.54178 Å)	CuKα (λ = 1.54178, Å)
$\mu(mm^{-1})$	0.804	4.295
ρcalc.(Mg cm^{-3})	1.277	1.409
2θ range (^{O})	3 - 110	3 - 110
Scan type	$\theta/2\theta$	$\theta/2\theta$
Scan speed (^{O} min^{-1})	4 - 60	1 - 60
hkl range	$0 \leq h \leq 10$ $0 \leq k \leq 7$ $-26 \leq l \leq 26$	$0 \leq h \leq 10$ $0 \leq k \leq 14$ $-16 \leq l \leq 16$
F(000)	744	896
R(%)	6.49	8.98
wR(%)	6.30	11.69
Goodness-of-fit	1.35	1.57
Independent reflections	2228 (R int. = 7.13%)	2571 (R int. = 2.87%)
Observed reflections ($F>4\sigma F$)	1756	2050
$\Delta\rho$max ($eÅ^{-3}$) / $\Delta\rho$min ($eÅ^{-3}$)	0.7768 / 0.8986	

the signals in the ^{1}H NMR spectrum are clearly defined. In the NOESY spectrum for compound **4**, again, as in the case of compound **3**, the magnetic and topologic environment of the nuclei are interchanged by conformational process. For instance, the conformational process A $\leftrightarrows$ B interchanges the chemical shifts of the following nuclei: C1→C19, C4→C6, C3→C7, C2→C8, C21→C24, C22→C23. Selected **NOESY** interactions are shown in Figure 8. NOE effects and chemical exchanges are operating according the positive and negative phases observed in NOESY spectrum of **4**, indicated in table 4. The observed cross peaks in the NOESY spectrum stablish conformational changes analogous to those observed for compound **3** (see Figure 6), which are only in agreement with a "sofa" conformer. The non-equivalent aromatic hydrogens displayed clear spatial interactions with the methylenic protons similar to that showed in Figure 5a The presence of positive diagonal peaks and inverted cross peaks in the ROESY spectrum with respect to those observed in the NOESY confirmed the conformational change (table 4). The assignments for ^{1}H and ^{13}C were unambiguosly determined by HMBC and HMQC experiments, and are shown in tables 5 and 6 respectively. As expected, this structure possesses a C_2 symmetry axis and all the nmr assignments are in agreement with the predicted chemicals shifts.

Figure 8. Selected interactions observed in the NOESY spectrum for compound **4**

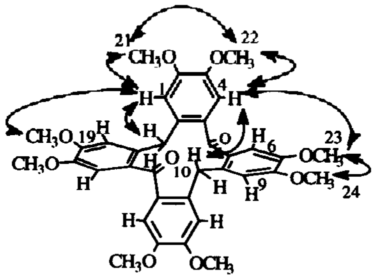

Table 4. Observed interactions in the NOESY and ROESY spectrum for compound **4**, cross peak +, -.

	Phase of the cross peak			Phase of the cross peak	
Interaction	NOESY	ROESY	Interaction	NOESY	ROESY
H(4)-H(6)	-	+	CH3-O-(21)	+	-
H(4)-H(10)	+	-	CH3-O-(21)	+	-
H(4)-H(22)	+	-	CH3-O-(21)	+	-
H(4)-H(23)	+	-	CH3-O-(21)	-	+
H(1)-H(19)	-	+	CH3-O-(22)	+	-
H(1)-H(20)	+	-	CH3-O-(22)	+	-
H(1)-H(21)	+	-	CH3-O-(22)	+	-
H(1)-H(28)	+	-	CH3-O-(22)	-	+
H(6)-H(4)	-	+	CH3-O-(23)	+	-
H(6)-H(10)	+	-	CH3-O-(23)	+	-
H(6)-H(22)	+	-	CH3-O-(23)	-	+
H(6)-H(23)	+	-	CH3-O-(23)	+	-
H(19)-H(1)	-	+	CH3-O-(28)	+	-
H(19)-H(20)	+	-	CH3-O-(28)	+	-
H(19)-H(21)	+	-	CH3-O-(28)	-	+
H(19)-H(28)	+	-	CH3-O-(28)	+	-

X-ray diffraction was also recorded for compound **4**. This compound, crystallize with a chloroform molecule, in space group P $2_1/c$, and the asymmetric unit corresponds with half of the molecule [the C(1) - C(7a)**i** and C(1)**i** - C(7a) distances are equal to 1.528 (7), symmetry code: (**i**) 1-x, 2-y ,-z].

A plot of the molecule **4** is shown in figure 9a. This molecule presents a "sofa" conformation, and it is approximately planar in C(5)-C(5a)-C(9a)-C(20a). The carbonyl group and the aromatic ring (C(1) to C(20a)) with respect to the plane are *exo* and *endo* respectively, (the angles between the carbonyl group and aromatic ring with the plane are 46.1° and 80.4°). Moreover, the carbonyl group is not coplanar with the aromatic ring (C(1) to C(20a)) has been the O atoms *cis* with respect to the C(1). [torsion angle O(5)-C(5)-C(4a)-C(20a) 34.1(8)°].

Table 5 ^{1}H NMR spectral data for compound **4**.

^{1}H	δ ppm
1	6.949
4	7.046
6	6.501
9	6.143
10	4.135(d, J=17.0) 3.625(d, J=17.0)
21(CH_3-O)	4.051
22(CH_3-O)	3.954
23(CH_3-O)	3.598
24(CH_3-O)	3.584

Table 6. ^{13}C NMR Chemical shifts for compound **4**.

^{13}C	δ ppm
1	114.184
2	149.954
3	147.401
4	112.585
4a	134.452
5	198.825
5a	130.977
6	112.308
7	146.509
8	152.076
9	113.538
9a	136.944
10(20b)	36.125
10a(20c)	133.991
21	56.240
22	56.024
23	56.024
24	55.685

The view of the crystalline packing is shown in Figure 9b. The crystal data collection, atomic coordinates, coefficients and geometric parameters are summarized in the tables 1,2 and 3.

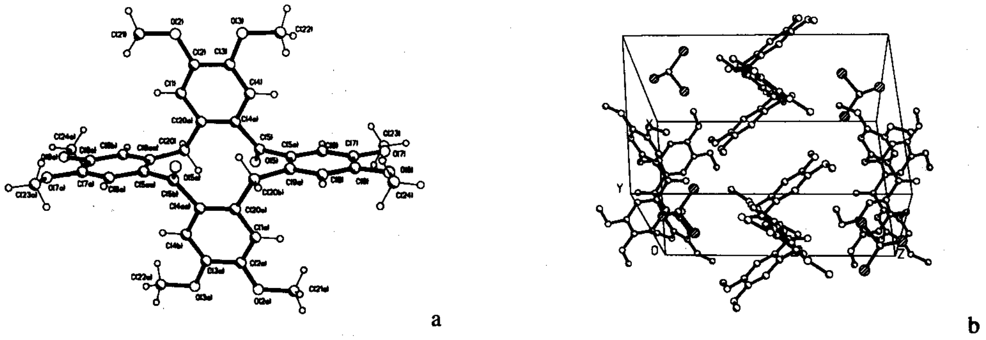

Figure 9. a) ORTEP view and b) Crystalline packing of **4**.

Table 2. Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients (Å^2 x 10^3) for **3** and **4**

Compound 3					Compound **4**				
	x	y	z	U(eq)		x	y	z	U(eq)
O(1)	3434(3)	1598(4)	2024(1)	52(1)	C(1)	8145(6)	10204(4)	555(4)	49(2)
O(2)	4324(3)	5098(4)	1951(1)	57(1)	C(2)	8588(6)	9674(4)	1297(4)	55(2)
O(3)	3754(3)	918(5)	-805(1)	61(1)	C(3)	7898(6)	8810(4)	1472(4)	47(2)
O(4)	2138(3)	1953(4)	-1622(1)	55(1)	C(4)	6788(6)	8515(4)	911(3)	43(2)
C(1)	2889(3)	5762(5)	1197(1)	37(1)	C(4A)	6355(5)	9050(3)	138(3)	37(2)
C(2)	3385(4)	4561(5)	1588(1)	40(1)	C(5)	5186(5)	8606(3)	-469(3)	36(2)
C(3)	2912(4)	2733(5)	1626(1)	39(1)	C(6)	4013(6)	7023(4)	-310(3)	41(2)
C(4)	1956(4)	2108(5)	1274(1)	37(1)	C(7)	3131(6)	6420(4)	63(3)	46(2)
C(4A)	1446(3)	3296(5)	882(1)	35(1)	C(8)	2367(6)	6777(4)	716(4)	47(2)
C(5)	386(4)	2542(5)	512(1)	36(1)	C(9)	2500(6)	7750(4)	956(3)	46(2)
C(5A)	803(3)	2345(5)	-65(1)	35(1)	C(20)	6575(6)	10556(3)	-816(3)	43(2)
C(6)	2041(4)	1682(5)	-171(2)	42(1)	C(9A)	3390(6)	8366(3)	573(3)	40(2)
C(7)	2510(4)	1506(5)	-686(2)	42(1)	C(20a)	7016(5)	9906(3)	-30(3)	39(2)
C(8)	1705(4)	2026(5)	-1111(1)	39(1)	C(5A)	4164(5)	8001(3)	-54(3)	36(1)
C(9)	469(4)	2627(5)	-1012(1)	38(1)	C(21)	10348(8)	10809(5)	1769(6)	82(3)
C(9A)	-25(4)	2812(5)	-498(1)	35(1)	C(22)	7714(8)	7442(5)	2410(4)	63(2)
C(20)	1415(4)	6520(5)	420(1)	37(1)	C(23)	3500(9)	5091(4)	-886(5)	71(3)
C(20A)	1927(3)	5153(5)	842(1)	34(1)	C(24)	835(10)	6441(5)	1793(6)	84(3)
O(5)	5368(3)	-1375(4)	2000(1)	49(1)	O(2)	9683(5)	9914(3)	1887(3)	76(2)
O(6)	1899(4)	-1422(5)	2185(2)	72(1)	O(3)	8417(5)	8317(3)	2211(3)	62(1)
C(1A)	696(7)	-3872(9)	2562(3)	99(3)	O(5)	5167(5)	8686(3)	-1248(3)	68(2)
C(2A)	1654(5)	-2313(7)	2583(2)	60(2)	O(7)	2930(5)	5450(3)	-142(3)	60(1)
C(3A)	2283(9)	-1877(10)	3088(3)	104(3)	O(8)	1536(6)	6127(3)	1077(3)	73(2)
O(7)	4696(6)	-1794(9)	-62(2)	60(2)	C(1')	3456(7)	-1132(4)	3930(5)	60(2)
C(1B)	3871(12)	-3924(17)	-705(4)	76(4)	Cl(1)	4861(3)	-1247(2)	3329(2)	114(1)
C(2B)	4575(9)	-3449(16)	-202(4)	58(3)	Cl(2)	3379(3)	-2076(2)	4683(2)	112(1)
C(3B)	5000	-5000	0	114(5)	Cl(3)	1919(2)	-1097(2)	3221(1)	90(1)

Table 3. Geometric parameters (Å,^{o}) for **3** and **4**

Compound 3				Compound **4**			
O(1)-C(3)	1.386 (5)	O(2)-C(2))	1.375(5)	C(1)-C(2)	1.380(7)	C(1)-C(20A)	1.404(7)
O(4)-C(8)	1.365(4)	O(3)- C(7)	1.377(5)	C(2)-C(3)	1.406(8)	C(2)-O(2)	1.364(8)
C(1)-C(2)	1.390 (5)	C(1)-C(20A)	1.393 (5)	C(3)-C(4)	1.369(8)	C(3)-O(3)	1.370(7)
C(2)-C(3)	1.379 (5)	C(3)-C(4)	1.387(5)	C(4)-C(4A)	1.421(7)	C(4A)-C(5)	1.519(7)
C(4)-C(4A)	1.393 (5)	C(4A)-C(5)	1.521 (5)	C(4A)-C(20A)	1.380(7)	C(5)-C(5A)	1.493(7)
C(4A)-C(20A)	1.401(5)	C(5)-C(5A)	1.524(5)	C(5)-O(5)	1.199(6)	C(6)-C(7)	1.365(8)
C(5A)-C(6)	1.382 (5)	C(5A)-C(9A)	1.414 (5)	C(6)-C(5A)	1.404(7)	C(7)-C(8)	1.401(8)
C(6)-C(7)	1.389 (5)	C(7)-C(8)	1.394(5)	C(7)-O(7)	1.380(6)	C(8)-C(9)	1.389(7)
C(8)-C(9))	1.362 (5)	C(9)-C(9A)	1.399 (5)	C(8)-O(8)	1.363(8)	C(9)-C(9A)	1.389(8)
C(9A)-C(20B)	1.516 (5)	C(20)-C(20A)	1.525 (5)	C(20)-C(20A)	1.525(7)	C(20)-C(9AA)	1.528(7)
C(20)-C(9AA)	1.516 (5)	O(6)-C(2A)	1.210(6)	C(9A)-C(5A)	1.380(7)	C(9)-C(20B)	1.528(7)
C(1A)-C(2A)	1.474 (8)	C(2A)-C(3A)	1.452(8)	C(21)-O(2)	1.411(9)	C(22)-O(3)	1.433(8)
O(7)-C(2B)	1.224 (13)	C(1B)-C(2B)	1.489 (14)	C(23)-O(7)	1.412(9)	C(24)-O(8)	1.422(11)
C(2B)-C(3B)	1.280 (11)	C(3B)-C(2BA)	1.280(11)	C(1')-Cl(1)	1.741(8)	C(1')-Cl(2)	1.745(7)
C(2)-C(1)-C(20A)	121.3(3)	O(2)-C(2)-C(1)	123.6(3)	C(2)-C(1)-C(20)	121.8(5)	C(1)-C(2)-C(3)	119.4(5)
O(2)-C(2)-C(3)	117.1(3)	C(1)-C(2)-C(3)	119.3(3)	C(1)-C(2)-O(2)	124.9(5)	C(3)-C(2)-O(2)	115.7(5)
O(1)-C(3)-C(2)	117.0(3)	O(1)-C(3)-C(4)	123.1(3)	C(2)-C(3)-C(4)	119.5(5)	C(2)-C(3)-O(3)	115.8(5)
C(2)-C(3)-C(4)	120.0(3)	C(3)-C(4)-C(4A)	121.4(3)	C(4)-C(3)-O(3)	124.7(5)	C(3)-C(4)-C(4A)	121.0(5)
C(4)-C(4A)-C(5)	119.1(3)	C(4)-C(4A)-C(20A)	118.7(3)	C(4)-C(4A)-C(5)	116.0(4)	C(4)-C(4A)-C(20A)	119.7(4)
C(5)-C(4A)-C(20A)	122.2(3)	C(4A)-C(5)-C(5A)	114.2(3)	C(5)-C(4A)-C(20A)	124.3(4)	C(4A)-C(5)-C(5A)	117.0(4)
C(5)-C(5A)-C(6)	118.7(3)	C(5)-C(5A)-C(9A)	122.8(3)	C(4A)-C(5)-O(5)	120.3(5)	C(5A)-C(5)-O(5)	122.5(5)
C(6)-C(5A)-C(9A)	118.5(3)	C(5A)-C(6)-C(7)	122.4(3)	C(7)-C(6)-C(5A)	121.0(5)	C(6)-C(7)-C(8)	119.8(5)
O(3)-C(7)-C(6)	123.9(3)	O(3)-C(7)-C(8)	117.1(3)	C(6)-C(7)-O(7)	124.8(5)	C(8)-C(7)-O(7)	115.4(5)
C(6)-C(7)-C(8)	118.9(4)	O(4)-C(8)-C(7)	121.2(3)	C(7)-C(8)-C(9)	119.0(5)	C(7)-C(8)-O(8)	116.5(5)
O(4)-C(8)-C(9)	119.5(4)	C(7)-C(8)-C(9)	119.3(3)	C(9)-C(8)-O(8)	124.5(5)	C(8)-C(9)-C(9A)	121.3(5)
C(8)-C(9)-C(9A)	122.8(3)	C(5A)-C(9A)-C(9)	118.1(3)	C(20A)-C(20)-(9AA)	112.2(4)	C(9)-C(9A)-C(5A)	119.2(5)
C(5A)-C(9A)-C(20B)	122.2(3)	C(9)-C(9A)-C(20B)	119.8(3)	C(9)-C(9A)-C(20B)	119.1(5)	C(5A)-C(9A)-(20B)	121.6(5)
C(20A)-C(20)-C(9AA)	115.2(3)	C(1)-C(20A)-C(4A)	119.3(3)	C(1)-C(20A)-C(4A)	118.6(5)	C(1)-C(20A)-C(20)	118.0(5)
C(1)-C(20A)-C(20)	119.4(3)	C(4A)-C(20A)-C(20)	121.3(3)	C(4A)-C(20A)-C(20)	123.4(4)	C(5)-C(5A)-C(6)	118.0(4)
O(6)-C(2A)-C(1A)	119.9(5)	O(6)-C(2A)-C(3A)	121.3(5)	C(5)-C(5A)-C(9A)	122.4(4)	C(6)-C(5A)-C(9A)	119.7(5)
C(1A)-C(2A)-C(3A)	118.7(5)	O(7)-C(2B)-C(1B)	120.4(9)	C(2)-O(2)-C(21)	117.6(6)	C(3)-O(3)-C(22)	116.7(5)
O(7)-C(2B)-C(3B)	131.6(8)	C(1B)-C(2B)-C(3B)	107.9(9)	C(7)-O(7)-C(23)	117.6(5)	C(8)-O(8)-C(24)	118.1(5)
C(2B)-C(3B)-C(2BA)	180.0(1)			Cl(1)-C(1')-Cl(2)	112.1(4)	Cl(1)-C(1')-Cl(3)	110.0(4)

CONCLUSIONS

In summary, we have shown on the bases of chemical shift data from high resolution NMR at low temperature for cyclotetraveratrilene **3** and at room temperature for **4,** that both compounds exist in solution in "different sofa conformations". From NOESY and ROESYexperiments we infered that a dynamic process where the magnetic and topologic environment are exchanged by conformational changes through rotations is present. X-ray diffractions analysis of compounds **3** and **4** showed that in solid state also both compounds prefer a "sofa" conformation.

Experimental Section

General Remarks.

Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet FT-IR Magna 700 Spectrometer NMR spectra were measured on a Varian Unity 500 spectrometer using 500 MHz for protons and 125 MHz for ^{13}C. The chemical shifts are expressed in ppm downfield from tetramethylsilane (δ=0.0 ppm) as an internal standard. HRMS were taken with a JEOL JMS AX505 HA mass spectrometer. X-ray crystalographic data were collected at room temperature on a Siemens P/4 diffractometer.

Cyclotetraveratrilene (2a) was synthesized following a procedure used previously.[16]

Octahydroxyorthocyclophane (3) was obtained by treatment of **2a** with BBr_3 in chloroform for 10 min[4,5] at room temperature, as fine needle crystals mp 344-345 °C lit[4] >350 °C . IR (KBr): 3485, 3441, 2964, 2920,1611, 1511, 1444, 1339, 1295, 1256, 1226,1193, 1139, 1082, 935, 891, 871, 785, 611 cm^{-1}. ^1H NMR (acetone-d_6) δ: 6.59 (Ar-H, OH), 3.78 (CH_2). HRMS Found 488.1474, Calcd. for $C_{28}H_{24}O_8$ 488.1471.

Octamethoxydiketoneorthocyclophane (4) was obtained from the **2a**, by treatement with $Na_2Cr_2O_7$ in water (1ml), glacial acetic acid (30 ml) and the mixture was continously stirred at 100 °C during 1 h, resulting in a yellow floculent precipitated. After 100 ml of water were added, the yellow precipitated was separated by filtration. After dried, the product was column chromatographed in using silica gel as solid support and a 1:1 mixture of hexane: acetate as eluent, affording 1.24 g of fine crystals mp 311-312°C. IR (KBr) 3435, 2941, 2849,1659, 1600, 1513, 1459, 1205, 1124, 1083, 1035, 799 cm^{-1}. HRMS Found 629.2375. Calcd. for $C_{36}H_{37}O_{10}$ 629.2387.

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