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Study of calixarenes-dyes. Structure of *p*-tetrakis(phenylazo)calix[4]arene

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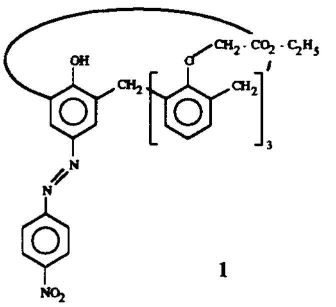
The first crystal structure of a calixarene-dye, that of *p*-tetrakis-(phenylazo)calix[4]arene, is presented in this work. Recrystallization of this purified substance in N,N-dimethylformamide afforded crystals suitable for X-ray diffraction. The compound crystallizes in the triclinic space groupe $P\bar{1}$ with $a = 14.477(3)$, $b = 15.699(3)$, $c = 11.251(5)$ Å, $\alpha = 95.29(3)$, $\beta = 89.94(3)$, $\gamma = 112.35(2)°$, and $D_c = 1.290$ g/cm^3 for $Z = 2$. Refinement based on 6932 observed reflections afforded a final R value of 0.089. These calixarene-N,N-dimethylformamide 1:1 crystals have a high density for a compound constituted only of hydrogen, oxygen and nitrogen atoms. This is due to the penetration of a benzylazo group of a calixarene molecule in the cavity of a neighbouring calixarene molecule. A hydrogen bond is established between the oxygen atom of the N,N-dimethylformamide and an oxygen atom of the calixarene; $CH_3...\pi$ interactions also exist between an aromatic nucleus of the phenylazo group and N,N-dimethylformamide. The crystal can be described as a series of layers of calixarene molecules and N,N-dimethylformamide molecules in parallel planes. In theory, the two phenyl groups linked by the azo group in the same moiety, which correspond to a conjugated molecule, should be coplanar. This is in fact the case for two moieties. However, interactions within the calixarene cavity disturb the plane of the third phenyl/azophenyl group and create an angle of 25.6° between the two phenyl groups. For the fourth fragment, interactions between the phenylazo group and N,N-dimethylformamide modify the angle between the phenyl group even more significantly (56.5°).

INTRODUCTION

To date, only five publications concern the diazo coupling with calixarenes.[1,2,3,4,5] -the first,[1] published in 1989, deals with the synthesis of *p*-tetrakis-(4-nitrophenylazo)calix[4]arene and shows the much higher formation rate of the di-, tri- and tetrasubstituted derivatives in comparison to the monosubstituted derivative. This result can be attributed to the specific hydrogen bonding effect among the calix[4]arene OH-groups. The second publication[2] extends the previous synthesis to six other azocalixarenes: *p*-tetrakis - (3-nitrophenylazo), *p*-tetrakis - (4-chlorophenylazo), *p*-tetrakis-(phenylazo), *p*-tetrakis-(4-methylphenylazo), *p*-tetrakis-(4-sulfonicphenylazo) and *p*-tetrakis - (4-trimethylammoniumphenylazochlorure) calix[4]arenes. It is shown that for the last compound, the first two pKa values are very low (0.5 and 2) demonstrating a very strong association with the OH-groups and which again can be explained by the specific hydrogen bonding effect. The third publication[3] describes the synthesis of *p*-hexakis-(4-phenylazo) calix[6]arene and its selective properties for the solvent extraction of silver and mercury ions. The fourth publication[4] redescribes the synthesis of the five above-mentioned azocalixarenes and studies the phenomenon of autoaccelerative diazo coupling which leads primarily to the formation of the tetrasubstituted calixarene. The compounds synthesized are considered as chromogenic calixarenes which show high Li^+ selectivity. The fifth publication[5] deals with selective extraction of Li^+ by the azocalix[4]arene derivative **1**. The interest of azocalixarenes is to constitute a new class of host molecules which have a selectivity for certain metal ions. The presence of metal ions gives rise to spectral changes.



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The aim here is to acquire a better understanding of the conformation of azocalixarenes in the solid state and their interactions with other organic substances. These azocalixarenes can be considered as pigments i.e. as dyes used in the solid state. The crystal structure of a calixarene-dye has been determined for the first time; it is that of the *p*-tetrakis(phenylazo)calix[4]arene **2**.

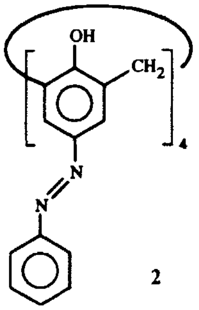

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Table 1 Crystal data

Molecular formula: $C_{52}H_{40}N_8O_4$, C_3H_7NO
Molecular weight: 840.941, 73.095
Crystal system: triclinic
Space group: $P\bar{1}$
$a = 14.477(3)$ Å $b = 15.699(3)$ Å $c = 11.251(5)$ Å
$\alpha = 95.29(3)°$ $\beta = 89.94(3)°$ $\gamma = 112.35(2)°$
Volume $= 2353(1)$ Å^3
$Z = 2$
$D = 1.290$ g/cm^3
$F(000) = 960$
CuKα radiation: $\lambda = 1.54056$ Å, $\mu = 6.47$ cm^{-1}
Residual peak: 0.23 e.Å^{-3}

EXPERIMENTAL

Synthesis

The *p*-tetrakis(phenylazo)calix[4]arene **2** was prepared by diazo coupling reaction of calix[4]arene and benzene diazonium salt.

An aqueous solution of 0.2 mL of aniline (2.195 mmol) was converted into the diazonium ion at a temperature of about 0 °C by the action of sodium nitrite (2.195 mmol) in the presence of hydrochloric acid (5.5 mmol). A solution of 0.2329 g of calix[4]arene (2.195/4 mmol), 120 mL of acetone and 0.18 mL pyridine (2.195 mmol) was added to the solution of phenyldiazonium salt at 0 °C. Pyridine was used to obtain the basic form of calix[4]arene because it is this form which participates in the diazo coupling.

The orange precipitate was collected by filtration and washed with methanol. The product decomposes at 308 °C (Shinkai: 280 °C).[4]

Crystallization of the last product was obtained by partial evaporation of a N,N-dimethylformamide solution of *p*-tetrakis(phenylazo)calix[4]arene. A total evaporation of solvent involves collapse of the crystal.

X-ray data

A crystal was sealed with mother liquor in a glass Lindeman capillary for X-ray analysis. Accurate unit-cell dimensions were obtained by a least-squares fit of 25 reflections in the range ($4° < \theta < 40°$) measured on an ENRAF-Nonius CAD-4 diffractometer. A summary of crystal data and collection parameters is given in Table 1.

Intensity data were collected up to $\theta = 73°$ by using the ($\omega - 2\theta$) scan mode with monochromated CuKα radiation. Three standard reflections were measured every hour to control intensity variation. Lorentz and Polarization corrections were applied and absorption was corrected with the programs PSI and EAC of SDP.[6] 9881 reflections were measured, 9379 considered as unique, 6932 used in the refinement ($F > 3\sigma(F)$ or $I > 1.5\sigma(I)$).

Structure analysis and refinement

The structure was solved and refined by SHELX 76.[7] From direct methods, the analysis of the first E-map showed three of the four phenolic units of the calix[4]arene linked by the methylene groups and two -N=N-groups at *para* position to the hydroxy groups. The next Fourier maps computed revealed the positions of all non-hydrogen atoms of the azocalix[4]-arene. The parameters of non H-atoms were adjusted by several cycles of full-matrix least-squares calculations, first with isotropic and then with anisotropic temperature factors. H positions were calculated at theoretical positions and refined isotropically. The initial u values were 0.05. The H atoms of the hydroxyl groups could not be located, as is often the case with calixarenes.

Considering the guest molecule, the first atoms revealed were O and N with an occupation factor of 1. Around the N-atom, six C-atoms were revealed. Therefore, we introduced two positions for the guest molecule, with the sum of their occupation factors equal to one.

During the refinement, the temperature factors of O and N were considered anisotropic and a same temperature factor for the C-atoms was kept isotropic.

At the end of the refinement the R value, calculated with 6932 F_{hkl}, is $R = 0.089$ with a goodness of fit of 1,87. Residual electron density map showed a highest residual peak of ca. 0.23 e.Å^{-3}.

DISCUSSION

Figure 1 shows the numbering scheme of the atoms of azocalix[4]arene and DMF and the numbering of the rings.

Final atomic parameters are given in Table 2. Usual calculations for the description of the conformation and the packing were computed with PARST (Nardelli, 1983). Bond distances and angles are deposited as supplementary data.

The azocalix[4]arene has a cone conformation; the

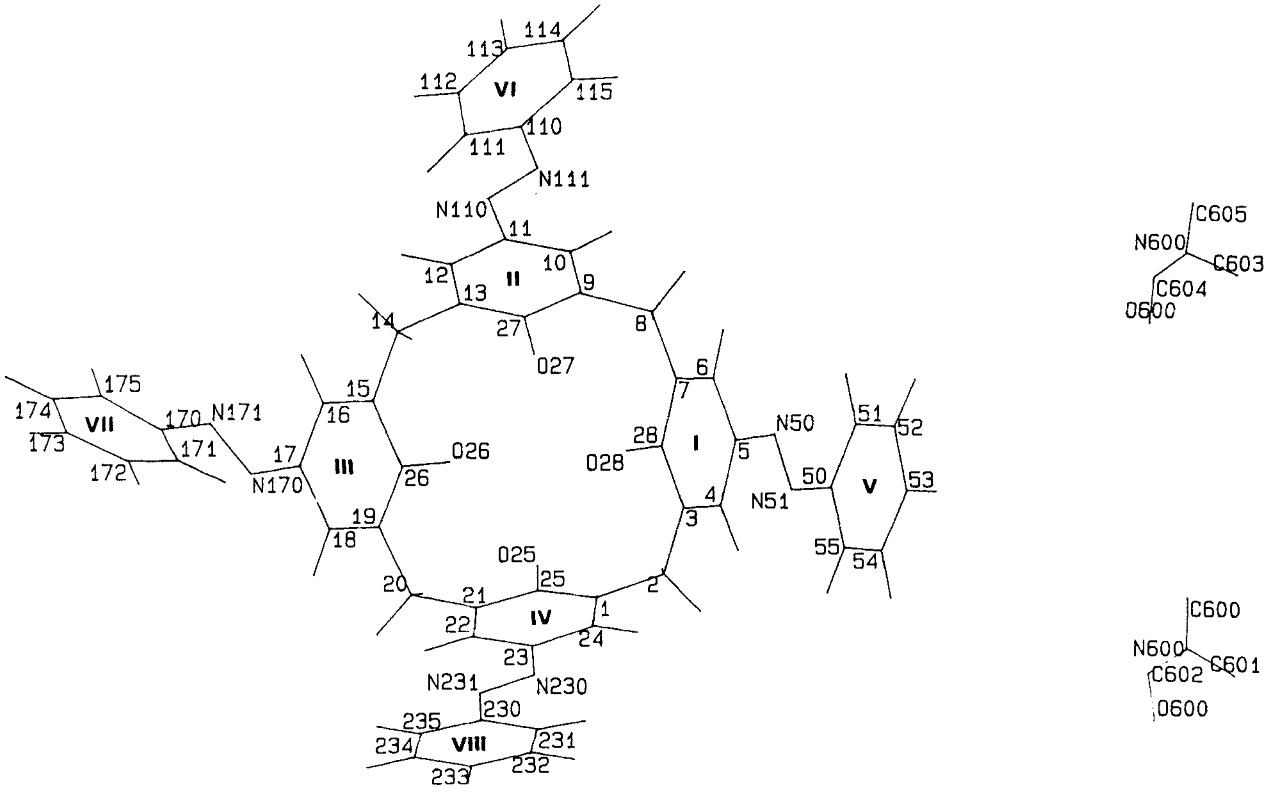

Figure 1 Numbering scheme.

phenolic units (I→IV) make angles of 128.5(2), 123.0(2), 131.0(2) and 115.4(2)° respectively with the least squares plane defined by the four bridging methylene groups which are alternatively above and below the mean plane by about 0.03(1) Å. Looking at the azo groups, the N = N bonds are in good agreement with the values usually found.[8,9,10] However the N—C distances are larger and the N=N—C angles smaller for two azo groups (between rings II–VI and III–VII); some characteristic values are listed in Table 3. The dihedral angles between planes of the phenolic ring and phenyl ring were calculated:

planes I–V : 9.0(3)°
planes II–VI : 25.6(3)°
planes III–VII : 56.5(3)°
planes IV–VIII : 4.9(3)°

It is seen that only two of the four phenolic residues are approximately coplanar. The two others are disturbed and are the same as above concerning distorsion at the azo groups.

The intramolecular O—O distances are:

O(25)...O(28) : 2.885(7) Å
O(25)...O(26) : 2.693(7) Å
O(26)...O(27) : 2.647(7) Å
O(27)...O(28) : 2.622(7) Å

These values are in good agreement with intramolecular H-bonds between the hydroxy groups usually found in calix[4]arenes except the value 2.885 Å which is greater and is discussed below.

Concerning the guest molecule, two positions were found around O(600)—N(600) bond: a rotation of 23.08(7)° is calculated between these two positions. It is noted that the values of bond distances and bond angles are not very good as is often found for the case of disordered guest molecules in calixarenes as hosts.[11,12]

Figure 2 shows the conformation of the macrocycle as well as the intra and intermolecular H-bonds. Indeed the oxygen atom of the guest molecule is at distance of 2.70(1) Å from O(25): this situation corresponds to an intermolecular H-bond between the host and the guest. The different values quoted around oxygen atoms are O(25)...O(28): 2.885(7) Å, O(25)...O(600): 2.70(1) Å and O(28)...O(600): 3.17(1) Å. These various interactions explain the increasing value of the intramolecular O(25)...O(28) H-bond.

To explain the other interactions of the guest molecule with the host, Fig 3 was drawn. It shows three calixarenes with symmetries: x, y, z (A), $-x+1$, $-y+2$, $-z+2$ (−A2) and $-x+1$, $-y+2$, $-z+1$ (−A1). The guest molecule ($x-1$, y, z) is surrounded by these three calixarenes; it lies inside the cavity of A with interactions with ring V (A) particularly

Table 2. Positional and thermal parameters with esd's in parentheses

Atom	*x*	*y*	*z*	*B*(Å^2)	*Atom*	*x*	*y*	*z*	*B*(Å^2)
C(1)	0.6960(5)	0.6499(5)	0.5548(6)	3.8(2)	C(50)	0.2538(6)	0.4455(6)	0.8528(8)	5.1(3)
C(2)	0.6928(5)	0.5830(5)	0.6434(6)	4.6(2)	C(51)	0.2132(7)	0.4553(7)	0.964(1)	7.5(4)
C(3)	0.6503(5)	0.6035(5)	0.7604(6)	4.0(2)	C(52)	0.1120(9)	0.4085(9)	0.976(1)	11.0(5)
C(4)	0.5514(5)	0.5623(5)	0.7798(7)	4.4(2)	C(53)	0.0533(9)	0.3539(9)	0.878(2)	11.7(6)
C(5)	0.5117(5)	0.5861(5)	0.8879(7)	4.3(2)	C(54)	0.0932(8)	0.3445(7)	0.768(1)	8.9(4)
C(6)	0.5766(6)	0.6518(5)	0.9729(7)	4.2(2)	C(55)	0.1932(6)	0.3900(6)	0.7591(9)	6.3(3)
C(7)	0.6763(5)	0.6942(5)	0.9568(7)	4.3(2)	C(110)	0.5272(7)	1.0522(7)	1.215(1)	6.7(3)
C(8)	0.7471(6)	0.7653(5)	1.0518(7)	4.9(2)	C(111)	0.5097(8)	1.1154(8)	1.158(1)	7.8(4)
C(9)	0.7645(5)	0.8649(5)	1.0296(7)	4.5(2)	C(112)	0.4386(9)	1.1523(9)	1.208(1)	9.1(5)
C(10)	0.7001(6)	0.9069(6)	1.0789(7)	5.0(2)	C(113)	0.3934(9)	1.122(1)	1.307(1)	9.6(5)
C(11)	0.7129(6)	0.9949(6)	1.0518(7)	5.1(2)	C(114)	0.4128(9)	1.058(1)	1.366(1)	11.0(6)
C(12)	0.7847(6)	1.0427(5)	0.9784(7)	5.0(2)	C(115)	0.4816(8)	1.0195(9)	1.319(1)	10.2(5)
C(13)	0.8532(5)	1.0049(5)	0.9310(7)	4.6(2)	C(170)	0.7812(9)	1.2932(7)	0.4999(9)	7.1(4)
C(14)	0.9357(5)	1.0607(5)	0.8520(7)	4.7(2)	C(171)	0.6853(8)	1.2568(8)	0.452(1)	7.8(4)
C(15)	0.9027(5)	1.0490(5)	0.7226(7)	4.3(2)	C(172)	0.6457(9)	1.3169(8)	0.407(1)	8.6(4)
C(16)	0.8688(5)	1.1090(5)	0.6756(7)	4.5(2)	C(173)	0.704(1)	1.411(1)	0.414(1)	9.2(5)
C(17)	0.8379(6)	1.0985(5)	0.5580(8)	4.6(2)	C(174)	0.801(1)	1.4468(8)	0.467(1)	8.2(4)
C(18)	0.8377(5)	1.0203(5)	0.4799(7)	4.8(2)	C(175)	0.8424(9)	1.3881(7)	0.514(1)	7.7(4)
C(19)	0.8733(5)	0.9605(5)	0.5254(7)	3.9(2)	C(230)	0.4144(6)	0.7183(6)	0.2365(7)	4.9(2)
C(20)	0.8717(5)	0.8759(5)	0.4410(7)	4.4(2)	C(231)	0.3290(6)	0.6460(7)	0.2522(8)	6.3(3)
C(21)	0.7792(5)	0.7903(5)	0.4571(6)	3.9(2)	C(232)	0.2411(7)	0.6398(9)	0.199(1)	8.0(4)
C(22)	0.6917(5)	0.7766(5)	0.3985(6)	3.9(2)	C(233)	0.2377(8)	0.704(1)	0.131(1)	9.0(5)
C(23)	0.6056(5)	0.6997(5)	0.4164(7)	4.1(2)	C(234)	0.3236(9)	0.777(1)	0.115(1)	11.9(6)
C(24)	0.6093(5)	0.6388(5)	0.4949(6)	4.0(2)	C(235)	0.4100(7)	0.7830(8)	0.168(1)	8.9(4)
C(25)	0.7827(5)	0.7253(5)	0.5333(6)	3.9(2)					
C(26)	0.9055(5)	0.9704(5)	0.6429(7)	4.1(2)					
C(27)	0.8403(5)	0.9163(5)	0.9588(7)	4.5(2)					
C(28)	0.7143(5)	0.6690(5)	0.8476(7)	4.2(2)					
O(25)	0.8742(3)	0.7398(3)	0.5847(5)	5.0(2)					
O(26)	0.9429(4)	0.9142(3)	0.6917(5)	4.7(2)					
O(27)	0.9087(4)	0.8786(3)	0.9166(5)	5.1(2)					
O(28)	0.8132(4)	0.7070(4)	0.8260(5)	5.5(2)					
N(50)	0.4103(5)	0.5446(4)	0.9132(6)	4.9(2)					
N(51)	0.3561(5)	0.4890(4)	0.8314(6)	4.9(2)					
N(110)	0.6487(5)	1.0437(5)	1.0948(7)	6.3(2)					
N(111)	0.5962(6)	1.0052(5)	1.1747(7)	6.9(3)					
N(170)	0.7970(5)	1.1553(5)	0.5010(7)	6.3(2)					
N(171)	0.8297(6)	1.2369(6)	0.5513(7)	7.1(3)					
N(230)	0.5111(5)	0.6796(5)	0.3607(6)	4.9(2)					
N(231)	0.5105(5)	0.7356(5)	0.2902(6)	5.1(2)					
O(600)	0.9445(6)	0.6193(6)	0.668(1)	12.6(4)					
N(600)	1.0890(8)	0.676(1)	0.778(8)	10.2(5)					
C(602)	1.014(2)	0.600(2)	0.724(2)	9.0(7)					
C(604)	1.032(3)	0.680(2)	0.706(3)	10.4(9)					
C(600)	1.181(2)	0.673(2)	0.831(2)	10.6(5)					
C(605)	1.198(3)	0.740(2)	0.806(3)	10.6(5)					
C(601)	1.080(2)	0.775(2)	0.773(2)	10.6(5)					
C(603)	1.081(2)	0.575(2)	0.813(3)	10.6(5)					

between C(603) and C(51)→C(54) with bond values 3.49→3.68 Å. The interactions with calixarene −A2 are very weak and concern the N atoms (N(110), N(111)). On the contrary it is seen that the mean plane of the DMF molecule is almost parallel to the ring VII (−A1): dihedral angles have values 14.5(3)° and 9.4(3)° depending on the two positions of the disordered guest molecule. The distances between the atomsC(170)→C(175) and N(600), O(600) and C(600)→C(605) vary from 3.36 to 3.68 Å while the distances of atoms of the guest to the mean plane of ring VII (−A1) have values between 3.23 and 3.90 Å. Probably these reciprocal interactions between ring VII and guest explain the dihedral angle (56.5°) quoted in the description of the conformation of the calix[4]arene studied here.

Figure 3 shows too the interpenetration of several calixarenes: the rings VII (−A1) and VI (−A2) lie

Table 3 Selected bond distances (Å) and bond angles (deg)

Atom 1	*Atom 2*	*Distance*	*Atom 1*	*Atom 2*	*Distance*	*Atom 1*	*Atom 2*	*Distance*
C(5)	N(50)	1.402(9)	N(50)	N(51)	1.247(8)	N(51)	C(50)	1.41(1)
C(11)	N(110)	1.47(1)	N(110)	N(111)	1.23(1)	N(111)	C(110)	1.50(2)
C(17)	N(170)	1.44(1)	N(170)	N(171)	1.27(1)	N(171)	C(170)	1.48(2)
C(23)	N(230)	1.42(1)	N(230)	N(231)	1.24(1)	N(231)	C(230)	1.44(1)

Atom 1	*Atom 2*	*Atom 3*	*Angle*	*Atom 1*	*Atom 2*	*Atom 3*	*Angle*
C(5)	N(50)	N(51)	115.3(7)	N(50)	N(51)	C(50)	117.3(7)
C(11)	N(110)	N(111)	111.0(8)	N(110)	N(111)	C(110)	111.3(8)
C(17)	N(170)	N(171)	110.6(7)	N(170)	N(171)	C(170)	110.3(7)
C(23)	N(230)	N(231)	114.2(6)	N(230)	N(231)	C(230)	114.9(6)

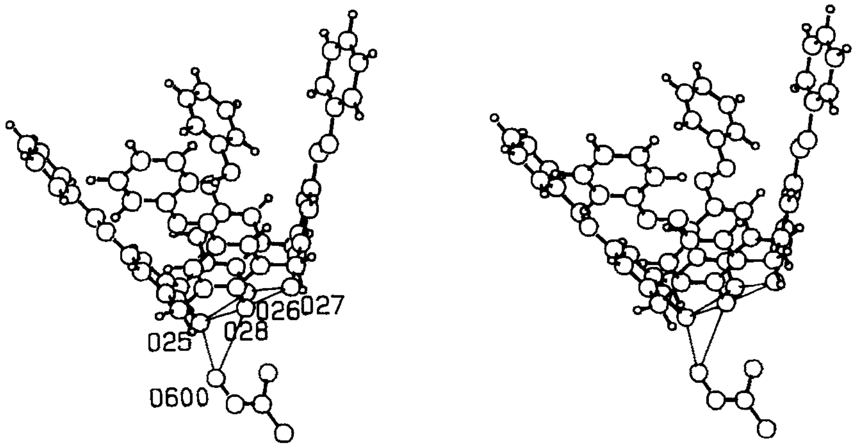

Figure 2 Conformation of the azocalix[4]arene and intra and intermolecular H-bonds.

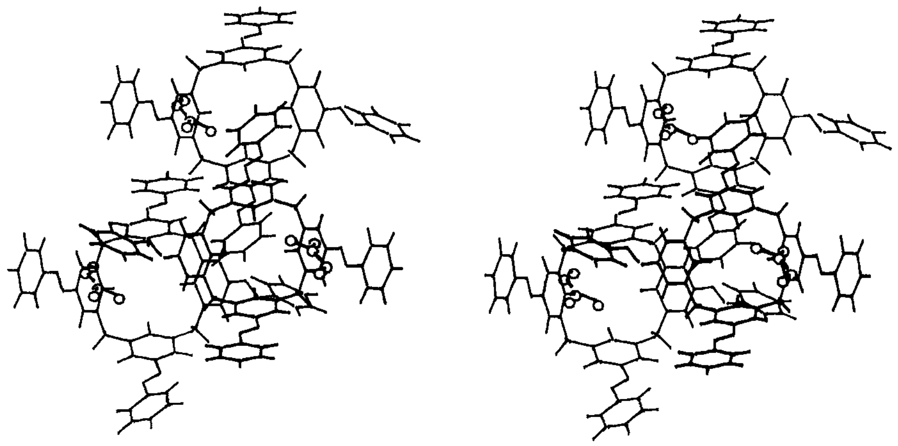

Figure 3 Interactions between the guest and three calixarene macrocycles.

inside the cavity of calixarene A. Therefore the density of this 1:1 complex is high 1.290 g.cm^{-3}.

An illustration of the packing is given in Fig 4. The view shows the calixarenes, held together with weak interactions, giving a slice parallel to the plane oyz. These interactions, as explained above, take place when a phenyl group of one calixarene lies inside the cavity of the neighbouring macrocycle. Between the slices a plane with DMF molecules ensures the cohesion in the "a" direction with both hydrogen

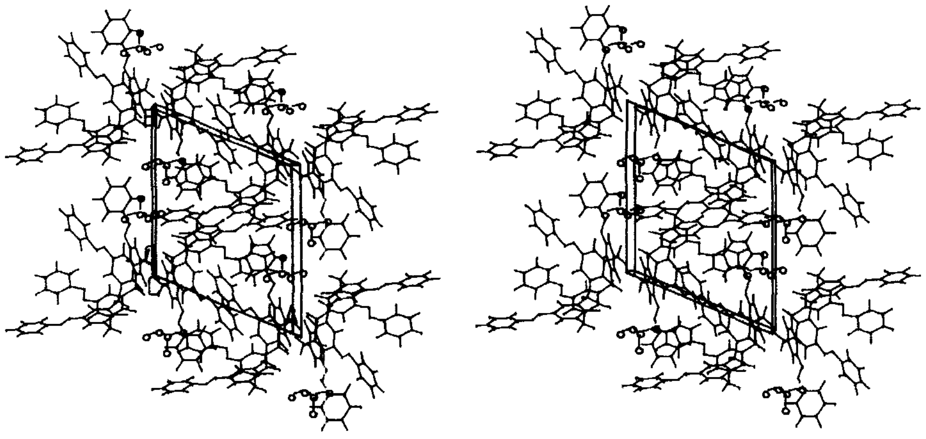

Figure 4 Packing of the azocalix[4]arene along [001].

bonds O(600)...O(25) and interactions $CH_3...\pi$ between DMF and the phenyl plane numbered VII.

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