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Monique Perrin[a]; Claude Bavoux[a]; Sylvain Lecocq[a]
[a] Université Claude Bernard—Lyon I. Laboratoire de Cristallographie, Villeurbanne cedex, France

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Change of Conformation Induced by Complexation in *p-tert*-butyldihomooxacalix[4]arene

MONIQUE PERRIN*, CLAUDE BAVOUX and SYLVAIN LECOCQ

Université Claude Bernard—Lyon I, Laboratoire de Cristallographie, 43, boulevard du 11 Novembre 1918, 69622 Villeurbanne cedex, France

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The crystal structure of *p-tert*-butyldihomooxacalix[4]arene is reported: Space group $P2_1/c$ a = 16.855(2), b = 18.526(4), c = 13.175(3) Å, β = 105.85(2)°. The conformation of the macrocycle is compared with the ones found for various complexes of the same calixarene. Striking changes are observed; they concern the dimethyleneoxa bridge which exhibits a very asymmetric and nonplanar geometry in the uncomplexed molecule compared with the shape it presents in complexes. The calixarenic moiety of the molecule itself exhibits some changes in the depth of the bowl and in its symmetry.

INTRODUCTION

Many studies have been made about possibilities of changes of conformation of calixarenes and about their ability to complex molecules. One example studied in our group concerns *p*-isopropylcalix[4]arene[1] in the solid state: when it is complexed with *para*-xylene, chloroform or toluene, the macrocycle exhibits fourfold symmetry; with other solvents the symmetry is C_{2v} and when the cavity is empty, it loses its fourfold axis, as well as the C_{2v} symmetry. Here we present a work on *p-tert*-dihomooxacalix[4]arene (CALO). In this compound, one of the four methylene bridging groups is replaced by CH_2-O-CH_2. This group induces some new specificities for the calix[4]arene: it has good flexibility which may allow more easily changes of conformation; it modifies the circular hydrogen bonding scheme on the OH groups observed in other calix[4]arenes and it increases the size of the cavity which may facilitate the trapping of guests.

We have shown the ability of CALO to complex small neutral molecules: after evaporation of the solvent in a CALO-solvent mixture and analysis of the resulting powder, the formation of various compounds in the solid state has been proved, mostly when the solvent is a ketone, an amine, an heterocycle or an aromatic[2]. Crystal structures of some complexes have been determined by Perrin[3] (1:1 complex with metaxylene (CALMX)), Armah[4] (same compound), Harrowfield[5] (1:1 complex with dimethylformamide (CALDMF) and the hydrated triethylammonium salt of the uranyl-ion complex (CALUO2)), Bavoux[2,6] (1:2 complexes with triethylamine

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*Corresponding author.

(CALTEA) and with tetrahydrofuran (CALTHF)) and Asfari[7] (triple inclusion complex of europium, dimethylsulfoxide and acetone (CALEUR)).

When diisopropylbenzene is used as solvent, crystallization occurs without participation of the small neutral molecule. The determination of the structure of the uncomplexed CALO is then possible and is presented here. Its conformation is compared with the one observed when the macrocycles form inclusion compounds with guests. The complexes for which the structure is available may be divided in two categories, depending of the nature of the guest: small neutral molecules (meta-xylene, DMF, THF, triethylamine) or ions (uranyl or europium).

RESULTS AND DISCUSSION

Crystal Structure of the p-tert Butyldihomooxacalix[4]arene

Figure 1 gives the numbering scheme and shows the conformation of the molecule; the striking feature is its very asymmetrical shape on each side of the plane through O(1) and C(14) and perpendicular to the figure. Table I gives some torsional angles: values of C(2)-O(1)-C(2')-C(3) and C(2')-O(1)-C(2)-C(1) are, respectively, −163.6(7)° and 69(1)°; carbon atoms of the dimethyleneoxa bridge are very asymmetrically situated on each side of the oxygen. The five atoms C(1), C(2), O(1), C(2') and C(3) are not coplanar and the largest distances of these atoms from their mean plane are 0.287(6) Å on one side and 0.50(1) Å on the other side of this plane.

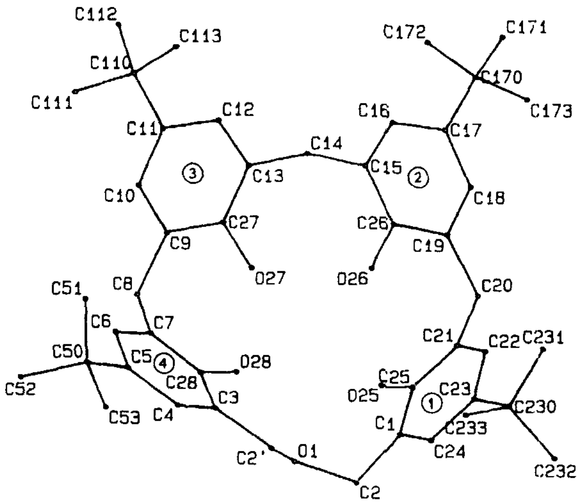

FIGURE 1 Numbering scheme

The calixarene has a conical shape; we define, as usual in calixarenes, the reference plane R generated by the carbons of the three methylenes and we attribue the numbers 1, 2, 3 and 4, respectively, to the phenolic ring bearing C(25), C(26), C(27) and C(28). The inclinations of 1, 2, 3 and 4 with respect to R are, respectively, 129.3(3), 129.4(3), 132.8(3) and 128.4(2)°. A circular hydrogen bonding network characterizes calixarenes. The O...O distances have the following values: O(1)...O(25) = 2.996(8), O(25)...O(26) = 2.704(9), O(26)...O(27) = 2.652(7), O(27)...O(28) = 2.660(9) and O(28)...O(1) = 2.566(9) Å. The last distance corresponds to a very strong interaction and, except for O(1)...O(25), all values prove the existence of hydrogen bonds between O(25), O(26), O(27), O(28) and O(1).

Figure 2 is a stereoview of the arrangement in CALO. It consists of dimers in which a *tert*-butyl group of each molecule fits the cavity of an other one. Dimers are stacked, keeping the same orientation in the $\vec{a}$ direction and making zigzags along $\vec{c}$. Dimers belonging to a layer in the ($\vec{a}$ $\vec{c}$) plane are rotated by 98.6(2)° with respect with the ones of the next layer in the $\vec{b}$ direction.

Conformation of the Uncomplexed and Complexed Macrocycle

The data available for CALMX, CALDMF, CALTHF, CALTHEA, CALUO2 and CALEUR induce us to compare the conformation of the macrocycle in these complexes with the conformation

TABLE I Torsional angles

Atom 1	Atom 2	Atom 3	Atom 4	Angle	Atom 1	Atom 2	Atom 3	Atom 4	Angle
C2	O1	C2′	C3	−163.6(0.7)	C2′	O1	C2	C1	68.8(1.0)
O1	C2′	C3	C28	21.6(1.2)	O1	C2	C1	C25	70.3(1.1)
C2′	C3	C28	C7	174.4(0.8)	C2	C1	C25	C21	173.3(0.8)
C3	C28	C7	C8	−177.2(0.8)	C1	C25	C21	C20	−174.5(0.8)
C28	C7	C8	C9	88.9(1.0)	C25	C21	C20	C19	−91.5(1.1)
C7	C8	C9	C27	−91.4(1.0)	C21	C20	C19	C26	86.1(1.0)
C8	C9	C27	C13	−179.8(0.7)	C20	C19	C26	C15	177.3(0.7)
C9	C27	C13	C14	177.1(0.7)	C19	C26	C15	C14	−177.5(0.7)
C27	C13	C14	C15	86.5(1.0)	C26	C15	C14	C13	−89.0(1.0)

previously found in CALO. Figure 3 represents two views of the calixarene in CALO and in CALMX. The following observations can be done:

1. In all compounds the macrocycle keeps a conical shape with a more or less symmetrical geometry. If we define, as previously in CALO, planes 1, 2, 3, 4 and R and if we consider the plane M through O(1) and C(14) and perpendicular to R, the values of angles R/1, R/2, R/3 and R/4 precisely define the geometry of the calix (Table II). For CALMX and CALDMF, M is a crystallographic mirror plane; for CALO, CALTHF and CALUO2, differences less than 5° exist between values of these angles on each side of M which can be considered as a pseudo symmetry plane for the calixarenic moiety. In CALTEA values of 138.2 and 139.4° on one side of M and 124.6 and 127.9° on the other side reveal a very asymmetric orientation of the phenolic rings on each side of M. CALEUR may be considered as an intermediate case in this point of view with differences of about 10°. In CALMX, CALDMF, CALTHF and CALUO2, the calix has a steeper shape on each side of C(14) (R/2 and R/3 angles between 121.9 and 127.1°) than on each side of the CH_2-O-CH_2 chain (R/1 and R/4 angles between 130.0 and 141.4°).

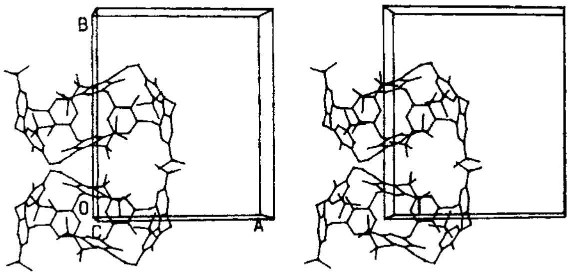

FIGURE 2 Stereoview of the crystal structure

2. Contrary to the conformation found previously in CALO, the dimethyleneoxa chain presents a symmetry (for CALMX and CALDMF) or a pseudo symmetry on each side of the ether oxygen in all complexes. In these compounds, differences between values of torsional angles C(2′)-O(1)-C(2)-C(1) and C(2)-O(1)-C(2′)-C(3) are always smaller than 6°. The mean plane B of the five atoms of this chain has been calculated; with no atom situated at more than 0.07 Å from B, the chain can be considered planar in CALMX, CALDMF, CALTHF and CALUO2; values of the previous torsion angles situated between 175.0 and 177.6° confirm this fact. In CALTEA and CALEUR, the chain cannot be considered as planar; O(1) is situated at 0.217 Å from B, on one side of B in CALTEA; the same atom is 0.236 Å from B, but on the other side of B in CALEUR. In CALO, the five atoms exhibit a zigzag arrangement on each side of B, C(1), O(1) and C(3) situated, respectively, at 0.133, 0.287 and 0.222 Å from it, on one side, C(2) and C(2′) at 0.143 and 0.499 Å from it, are oriented on the other side.

3. In complexes, the orientation of B with respect to R is always more or less the same with angles B/R between 15.4 and 28.5° (Table III). All atoms of the chain are on the same side of R,

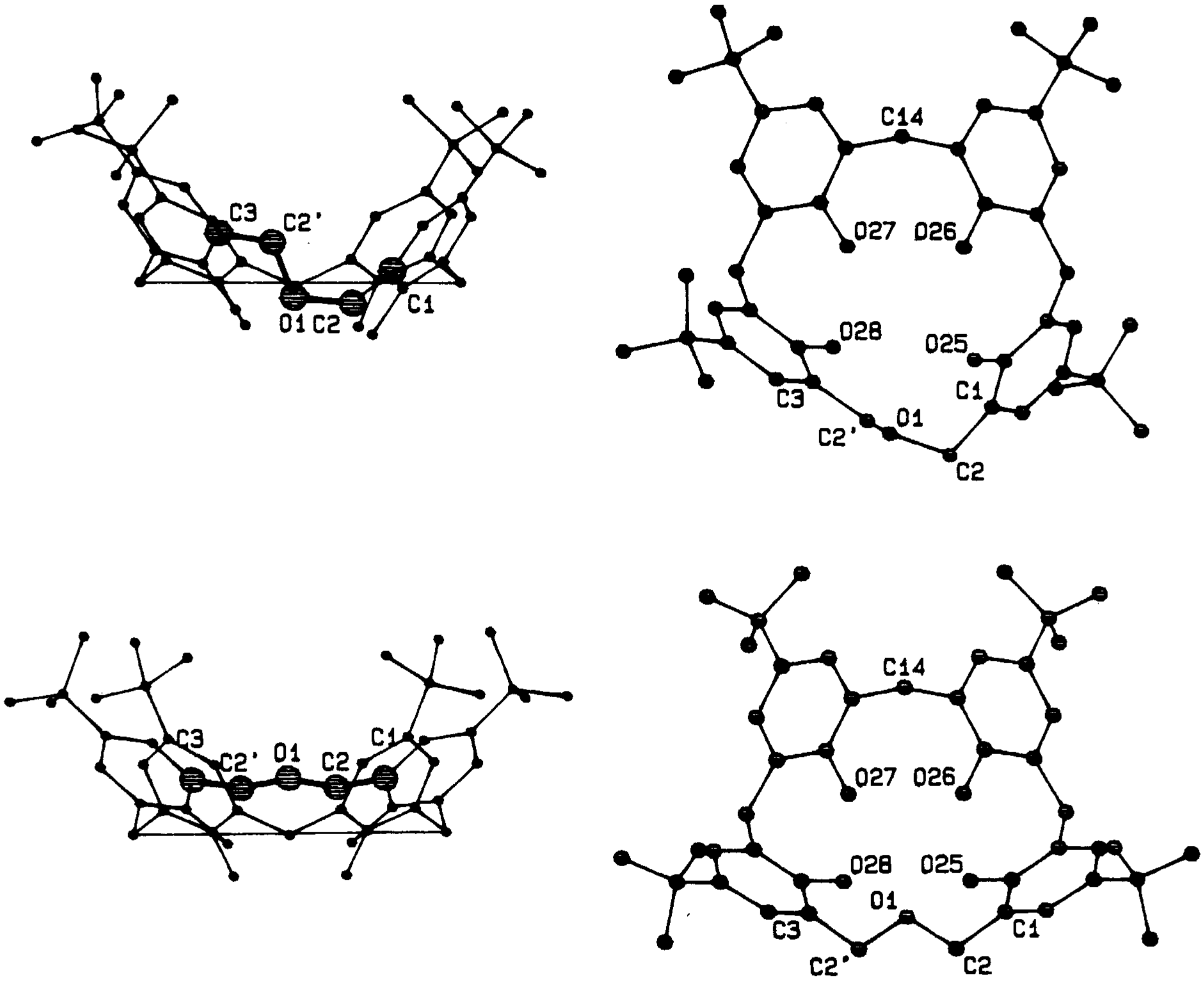

FIGURE 3 Conformation of the macrocycle in CALO (above) and in CALMX (below)

oriented toward the upper rim. In CALMX, CALDMF, CALTHF, CALTEA and CALUO2. C(1), O(1) and C(3) are farther from R than C(2) and C(2') (Figure 3). This geometry corresponds to the most symmetric shape of the chain on each side of plane M. In CALEUR, C(3) is the farthest, then C(1), C(2'), O(1) and C(2). The situation is very different in CALO; the value of

TABLE II Angles between the reference plane R and the mean planes of the phenolic rings

Compound	R/1	R/2	R/3	R/4
CALO	129.3	129.4	132.8	128.4
CALMX	136.5	124.2	124.2	136.5
CALDMF	141.4	121.9	121.9	141.4
CALTHF	133.2	122.2	127.1	138.4
CALTEA	138.2	139.4	124.6	127.9
CALUO2	130.9	124.5	121.9	130.0
CALEUR	126.3	121.0	129.7	115.6

TABLE III Angles between the reference plane R and the mean plane of the dimethyleneoxa bridge B and distances between atoms of B and R

Compound	B/R	O(1)/R	C(1)/R	C(3)/R	C(2)/R	C(2')/R
CALO	61.5	−0.456	0.169	1.082	−0.620	0.844
CALMX	15.4	1.345	1.320	1.320	1.095	1.095
CALDMF	23.1	0.971	0.924	0.924	0.588	0.588
CALTHF	17.4	1.312	1.269	1.264	1.014	1.014
CALTEA	28.5	1.269	1.048	1.131	0.634	0.753
CALUO2	24.8	1.013	0.981	1.019	0.609	0.654
CALEUR	26.5	0.483	0.711	1.023	0.281	0.496

B/R angle is 61.5°. C(3), C(2') and C(1) are situated on the same side of R and oriented toward the upper rim as previously noted. C(2) and O(1) are situated on the other side of R, and oriented toward the lower rim (Figure 3). Here the chain has a completely asymmetric arrangement with respect with the calixarenic moiety of the molecule.

4. The specificity of calixarenes is due to the possibility of a circular hydrogen bonding network on the phenolic groups. In complexes with small neutral molecules, CALMX, CALDMF and CALTHF, where the guest is located in the cavity, with only CH_3-π interactions with the host, O...O distances vary from 2.747 to 2.867 Å. A regular circular network of hydrogen bonds includes the five oxygens. In CALTEA two sorts of interactions connect host and guest: CH_3-π contacts between the macrocycle and a triethylamine molecule encapsulated in it, and a hydrogen bond between the same macrocycle and another triethylamine molecule. This bond is characterized by an O...N distance of 2.65 Å. O(26) is the donor for this hydrogen bond and a double acceptor from O(25) and O(27); the calixarene is partly deprotonated on O(26). Values of 2.560 Å for O(26)...O(27) and 2.606 Å for O(25)...O(26) correspond to the very strong hydrogen bonds connected to the deprotonation of O(26). The distance O(27)...O(28) = 2.855 Å corresponds to a classical hydrogen bond but distances O(1)...O(25), 3.082 Å, and O(28)...O(1), 3.145 Å, correspond to very weak interactions on each side of O(1).

In metal ion complexes (CALUO2 and CALEUR), the different situation is due to the deprotonation of the calixarene and strong coordinative interactions between oxygens and metal. In CALEUR the macrocycle is triply deprotonated and the five donor oxygens have strong interactions with the europium ion (O...M distances from 2.23 to 2.67 Å). In CALUO2 the macrocycle is fully deprotonated and only four phenolic oxygens have strong in-

TABLE IV Crystal data

Formula unit	$C_{45}O_5H_{58}$	Formula wt	678.96
Crystal system	monoclinic	Space group	$P2_1/c$
Cell dimensions			
a, Å	16.855(2)	b, Å	18.526(4)
c, Å	13.175(3)	β, deg	105.82(2)
V, Å^3	4022(2)	Dc, g. cm^{-3}	1.121
Z	4	F(000)	1472
μ, cm^{-1}	5.26 (Cukα)		
No of coll. reflect.	8313	No of obs. reflect.	2158
		Limit for obs. reflect.	$I > 2\sigma(I)$
R [= Σ|Δ F|/Σ|Fo|]	0.061	S [goodness of fit]	2.18
No of param. refined	632	Max/min. peak height in the final Fourier map, e Å^{-3}	0.11/−0.07

TABLE V Fractional atomic coordinates and B(eq)

Atom	X	Y	Z	B(eq)
O1	*0.8178(3)*	0.2273(3)	−0.1042(4)	5.2(2)
C1	0.7122(5)	0.1697(5)	−0.2455(7)	4.8(3)
C2	0.7558(6)	0.2377(6)	−0.2040(8)	5.8(3)
C2′	0.8854(6)	0.1869(6)	−0.1153(8)	5.4(3)
C3	0.9350(5)	0.1597(4)	−0.0077(7)	4.4(3)
C4	1.0151(6)	0.1368(5)	−0.0001(8)	4.8(3)
C5	1.0641(5)	0.1057(5)	0.0911(8)	4.9(3)
C50	1.1518(6)	0.0789(6)	0.1005(9)	6.2(3)
C51	1.1567(8)	0.0021(7)	0.118(2)	19(1)
C52	1.2113(7)	0.1156(9)	0.193(2)	13.8(7)
C53	1.1774(9)	0.094(1)	0.007(1)	22(1)
C6	1.0299(6)	0.0989(5)	0.1761(8)	4.7(3)
C7	0.9506(5)	0.1220(4)	0.1720(7)	3.7(2)
C8	0.9173(6)	0.1112(5)	0.2640(7)	4.0(3)
C9	0.8727(4)	0.0416(4)	0.2665(6)	3.4(2)
C10	0.9160(5)	−0.0186(5)	0.3099(6)	4.1(2)
C11	0.8787(5)	−0.0830(5)	0.3136(6)	4.6(3)
C110	0.9254(6)	−0.1496(5)	0.3634(9)	5.7(3)
C111	1.0174(6)	−0.1356(7)	0.402(1)	10.5(5)
C112	0.8946(8)	−0.1722(7)	0.458(1)	8.7(5)
C113	0.9122(8)	−0.2091(6)	0.280(1)	9.1(5)
C12	0.7937(6)	−0.0857(5)	0.2704(7)	4.7(3)
C13	0.7467(4)	−0.0281(4)	0.2250(6)	3.5(2)
C14	0.6540(4)	−0.0349(5)	0.1822(6)	3.7(2)
C15	0.6223(4)	−0.0510(5)	0.0643(7)	3.9(2)
C16	0.6087(5)	−0.1197(5)	0.0293(8)	4.6(3)
C17	0.5775(5)	−0.1389(5)	−0.0764(8)	4.5(3)
C170	0.5607(7)	−0.2157(6)	−0.110(1)	7.1(4)
C171	0.486(1)	−0.2393(9)	−0.085(2)	20(1)
C172	0.626(1)	−0.2626(7)	−0.055(2)	18(1)
C173	0.549(2)	−0.2277(8)	−0.222(1)	18(1)
C18	0.5594(5)	−0.0826(6)	−0.1459(8)	4.3(3)
C19	0.5706(4)	−0.0116(5)	−0.1176(7)	3.9(2)
C20	0.5462(5)	0.0478(6)	−0.1965(8)	4.6(3)
C21	0.6118(5)	0.0805(5)	−0.2408(6)	4.0(2)
C22	0.6249(5)	0.0513(5)	−0.3325(7)	4.7(3)
C23	0.6792(6)	0.0811(5)	−0.3832(7)	5.1(3)
C230	0.6893(7)	0.0511(7)	−0.4881(8)	6.5(3)
C231	0.652(1)	−0.0222(8)	−0.511(1)	11.9(6)
C232	0.648(2)	0.100(1)	−0.5738(9)	17(1)
C233	0.7770(9)	0.043(1)	−0.483(1)	17.3(8)
C24	0.7225(6)	0.1403(5)	−0.3384(8)	5.3(3)
C25	0.6578(5)	0.1386(4)	−0.1958(7)	4.2(3)
O25	0.6503(4)	0.1721(3)	−0.1077(5)	5.2(2)
C26	0.6026(4)	0.0024(5)	−0.0099(7)	3.9(3)
O26	0.6089(4)	0.0736(3)	0.0182(5)	4.5(2)
C27	0.7870(5)	0.0361(4)	0.2219(6)	3.5(2)
O27	0.7407(4)	0.0943(3)	0.1796(5)	4.4(2)
C28	0.9040(5)	0.1528(4)	0.0792(7)	4.3(3)
O28	0.8242(4)	0.1734(3)	0.0767(5)	5.1(2)

teractions with the uranyl ion (O...M distances from 2.24 to 2.27 Å for phenolic oxygens and O(1)...M = 3.534 Å). For the two examples studied, O...O distances vary from 2.826 to 3.069 Å; these large values are associated with the coordination of the metal ion.

Surprisingly, in CALO, where no guest interferes, the network of hydrogen bonds is very irregular. Only the asymmetry of the molecule, associated with steric hindrance explains the very strong hydrogen bonds between O(1) and O(28), O(28) and O(27), O(27) and O(26), compared to the usual interaction O(25)...O(26), or the very weak interaction between O(1) and O(25). These constraints make the four phenolic oxygens noncoplanar (χ^2 about 1580): O(26) and O(27) are situated, respectively, at 0.133 and 0.135 Å on each side of their mean plane P. On the contrary, in the complexes, the four oxygens are more or less coplanar with no distance of one of them to their mean plane larger than 0.023 Å.

5. In all compounds, the stabilization of the structure is obtained when the cavity is fitted by atoms or molecules; molecules of guests are available in complexes and in the empty form, a *tert*-butyl group of a neighbouring molecule plays this role.

EXPERIMENTAL SECTION

Data Collection

A single crystal of CALO was put in a glass capillary for X-ray analysis. Intensity data were obtained with an ENRAF-NONIUS CAD-4 diffractometer at room temperature using graphite-monochromatized CuKα radiation (λ = 1.54178 Å). Accurate unit cell dimensions were determined by least-squares fit of 25 reflections in the range $9 < \theta < 40°$. Diffraction data were collected using $\omega - 2\theta$ scan mode with a θ maximum at 73°. Three standard reflections were measured every hour to control intensity variations. The total loss in intensity during the exposure time was about 1%. Lorentz and polarization corrections were applied and absorption effects were corrected. The corresponding calculations were done by programs of SDP[8] series. Crystals data are given in Table IV.

Structure Analysis and Refinement

The structure was solved by direct methods using the program MULTAN[9] and refined by full matrix least-squares methods with SHELX-76[10]. Hydrogens were obtained from difference Fourier maps or located at their theoretical positions and refined isotropically. Anisotropic parameters were given to other atoms. Table V gives fractional atomic coordinates and thermal parameters of non hydrogen atoms. Tables of fractional atomic coordinates and thermal parameters for hydrogens, anisotropic thermal parameters, all bond distances and angles, Fo and Fc are available as supplementary material.

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