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Crystal and Molecular Structure of Calix[4]arene Originating from Pyrogallol

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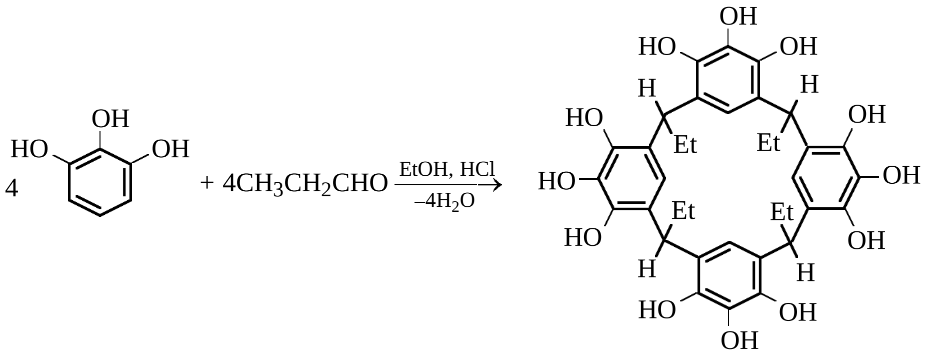
Abstract—First example of X-ray diffraction analysis of the crystal structure of calix[4]pyrogallolarene is reported. The compound was prepared by acid-catalyzed condensation of pyrogallol with propionaldehyde in a water–alcohol medium, and it gave rise to a system of "host–guest" type. Calixarene molecules in a cone conformation are packed in molecular layers; therewith each "host" molecule contains an ethanol molecule in the cavity. Hydroxy groups, ethanol and water molecules form a hydrophilic layer between two layers; as a result arises an endless bilayer structure.

Great interest of researchers is shown lately to the chemistry of calixarenes and their derivatives [1–4]. The calixarene molecules as a rule possess a bowl shape and are therefore capable to include and keep within a wide range of organic molecules and ions. Due to the presence of free hydroxy groups calixarenes are readily subjected to modification that provides a possibility of selective binding of "guests" by favorable location of functional groups on the circumference of the molecule. For instance, we carried out phosphorylation of calix[4]resorcinarenes with hexaalkyltriamidophosphites and obtained cavitands including four dioxaphosphocane fragments [5], and also were prepared first representatives of the boron-containing cavitands [6].

Undeniably interesting as initial space-ordered matrix are calix[4]arenes prepared from pyrogallol and aliphatic or aromatic aldehydes. Up till now the number of publications concerning the synthesis of calixarenes of this type is small [7–10]. We synthesized a new calix[4]pyrogallolarene (**I**) by acid-catalyzed condensation of pyrogallol with propionaldehyde in a water–alcohol solution.



I

Since the calix[4]arenes in general were characterized by high degree of self-organization that notably affected their chemical properties we decided to investigate the crystal and molecular structure of compound **I** for such published data on calix[4]pyrogallolarenes were lacking. At least in Cambridge Structural Database System [11] are described no more than 10 structures of calix[4]resorcinarenes with

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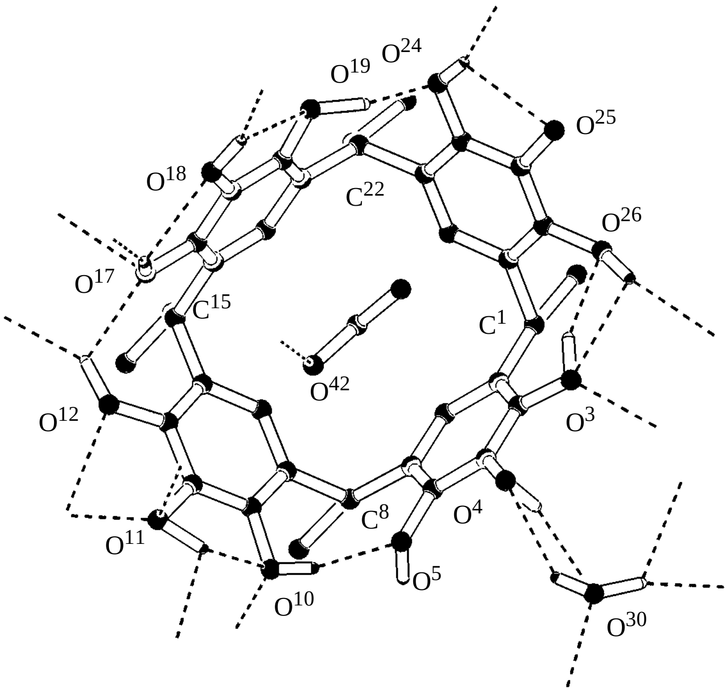

Fig. 1. Geometry of compound **I** molecule in a crystal. Hydrogen bonds are drawn as dash lines. For clear demonstration the remaining solvent molecules and part of hydrogen atoms are not shown. The view along the 0*z* axis.

the free hydroxy groups but no derivatives of pyrogallol are mentioned.

Calixarene **I** molecule in the crystal is in general position in conformation intermediate between cone and 1,3-diplanar, and possesses its proper symmetry C_2 (Fig. 1). If we select as a tentative median plane of the molecule that going through the bridging methylene atoms C^1, C^8, C^{15}, C^{22}, then the planes of benzene rings are at the following angles to this plane: 65.4(1), 41.9(1), 65.0(1), and 44.2(1)°. Dihedral angles between the opposite benzene rings are equal to 49.6(2) and 86.1(1)°. The angles between the neighboring benzene rings in the macrocycle vary a little between 71 and 73°. Symmetrically independent part of the crystal cell consists of a calixarene molecule, three solvate ethanol molecules, and three water molecules. Therewith one of the water molecules is disordered.

The presence of free hydroxy groups in the molecule of compound **I** results in a system of strong intramolecular hydrogen bonds on the upper circumference of the calixarene molecule (Table 1). In some cases the parameters of the hydrogen bonds are comparable with those of covalent O–H bonds. For instance, in the hydrogen bond between the corresponding proton and oxygen of the hydroxy groups $O^{11}–H^{11}\cdots O^{10}$ the distance $H^{11}\cdots O^{10}$ is 1.78 Å (Table 1). However as in the most calixarene crystal structures the presence of solvent molecules and their participation in hydrogen bonds results in the rupture of a closed system of hydrogen bonds on the circumference and in the instability of the crystals. Nonetheless the conformation of the macroring alters from cone one not because the closed system of hydrogen bonds on the circumference is destroyed but due to the presence of asymmetrical solvate molecule (ethanol) in the cavity of the macroring. In similar cases when in the cavity is located a symmetrical molecule (benzene) even the presence of bulky substituents in the para-positions of the phenyl rings does not affect the symmetrical conformation of the molecule [12]. Yet the hydrogen bonds of the C–H···O type between the methylene protons and hydroxy groups that are present in the structure of compound **I** to a certain degree stabilize the macroring conformation.

The presence in the crystal of a number of solvate molecules results in formation of an extended system of imtermolecular hydrogen bonds (Table 1), involving also contacts of C–H···O type. The protons of some hydroxy groups (H^{12}, H^{18}, H^{24}, H^{26}) take part in bifurcate hydrogen bonds (both intra- and intermolecular ones). Therewith the hydrogen bonds formed between the protons H^{12}, H^{24}, H^{26} of hydroxy groups and the oxygen atoms (O^3, O^{10}, O^{17} respectively) of the hydroxy groups of symmetrically bonded calixarene molecules (Table 2) lead to formation of an

Table 1. Characteristics of intra- and intermolecular hydrogen bonds in the crystal of compound **I**

Triad D–H···A	D–H, Å	H···A, Å	D···A, Å	∠DHA, deg
Intramolecular				
$O^{3}-H^{3}\cdots O^{26}$	0.9403	1.9050	2.754(5)	148.95
$O^{10}-H^{10}\cdots O^{5}$	0.8523	1.9037	2.730(5)	162.88
$O^{11}-H^{11}\cdots O^{10}$	1.0664	1.7837	2.691(5)	140.15
$O^{12}-H^{12}\cdots O^{17}$	1.0566	2.3645	2.843(4)	105.96
$O^{17}-H^{17}\cdots O^{18}$	0.8299	2.3261	2.736(5)	111.07
$O^{18}-H^{18}\cdots O^{19}$	0.9008	2.1651	2.661(5)	113.91
$O^{19}-H^{19}\cdots O^{24}$	1.1056	1.6336	2.722(5)	167.08
$O^{24}-H^{24}\cdots O^{25}$	0.7312	2.3609	2.687(5)	108.79
$O^{26}-H^{26}\cdot\cdot O^{3}$	0.9825	2.3753	2.754(5)	102.07
$C^{1}-H^{1}\cdots O^{26}$	1.0355	2.3846	2.877(6)	107.90
$C^{15}-H^{15}\cdots O^{12}$	1.0426	2.5364	2.961(5)	103.61
$C^{22}-H^{22}\cdots O^{24}$	1.1213	2.1474	2.834(6)	116.71
Intermolecular				
$O^{4}-H^{4}\cdots O^{30}$	1.0722	2.4192	2.942(6)	108.60
$O^{11}-H^{11}\cdots O^{30\ a}$	1.0664	2.2036	2.712(6)	106.86
$O^{12}-H^{12}\cdots O^{3\ b}$	1.0566	2.0689	2.982(5)	143.11
$O^{17}-H^{17}\cdots O^{42\ c}$	0.8299	1.9761	2.774(4)	160.99
$O^{18}-H^{18}\cdots O^{11\ c}$	0.9008	2.0978	2.867(5)	142.68
$O^{24}-H^{24}\cdots O^{10\ d}$	0.7312	2.0432	2.721(4)	154.42
$O^{26}-H^{26}\cdots O^{17\ e}$	0.9825	2.4169	3.369(5)	163.02
$O^{30}-H^{31}\cdots O^{4}$	0.8250	2.2757	2.942(6)	138.15
$O^{30}-H^{31}\cdots O^{55\ a}$	0.8250	2.5506	2.948(13)	110.98
$O^{30}-H^{32}\cdots O^{11\ e}$	1.0604	1.8736	2.842(6)	149.99
$O^{30}-H^{32}\cdots O^{12\ e}$	1.0604	2.5037	3.263(7)	127.76
$O^{25}-H^{52}\cdots O^{70\ f}$	1.0734	1.7774	2.705(7)	142.01
$O^{62}-H^{62}\cdots O^{55\ a}$	0.9047	1.8871	2.46(2)	119.72
$O^{70}-H^{71}\cdots O^{5}$	0.5902	2.5620	2.949(8)	126.15
$O^{70}-H^{72}\cdots O^{4}$	1.2160	2.1778	3.273(7)	147.96
$O^{70}-H^{72}\cdots O^{5}$	1.2160	2.3799	2.949(8)	105.57
$O^{55}-H^{551}\cdots O^{62\ a}$	1.0849	1.4049	2.46(2)	163.41
$C^{52}-H^{521}\cdots O^{26\ f}$	1.1634	2.3081	2.83(2)	104.24
$C^{54}-H^{541}\cdots O^{55}$	1.0422	2.3220	3.08(3)	128.62
$C^{54}-H^{541}\cdots O^{62\ a}$	1.0422	2.0185	2.47(3)	103.22
$C^{54}-H^{542}\cdots O^{25\ f}$	1.0520	2.2023	2.82(2)	115.36
$C^{54}-H^{542}\cdots O^{26\ f}$	1.0520	2.3692	3.34(2)	153.21

The molecules are in symmetry connection as follows: [a] 1 – *x*, –*y*, 1 – *z*; [b] –1 + *x*, *y*, *z*; [c] –*x*, 1 – *y*, 1 – *z*; [d] *x*, 1 + *y*, *z*; [e] 1 + *x*, *y*, *z*; [f] 1 – *x*, 1 – *y*, 1 – *z*.

Table 2. Characteristics of π-H interactions in the crystal of compound **I**

X–H(I)···Cg(J)[a]	*d*(H···Cg), Å	∠(X–H···Cg), deg
$O^{42}-H^{42}\cdots Cg^{2}$	2.44	170
$C^{40}-H^{401}\cdots Cg^{4}$	2.76	156
$C^{41}-H^{411}\cdots Cg^{1}$	2.61	163
$C^{41}-H^{412}\cdots Cg^{3}$	2.54	166
$C^{52}-H^{521}\cdots Cg^{3b}$	3.35	82
$C^{52}-H^{522}\cdots Cg^{3b}$	2.82	106
$C^{61}-H^{611}\cdots Cg^{1}$	3.18	129

[a] Cg(J) is centroid of aromatic ring (1 – $C^{2}\cdots C^{7}$, 2 – $C^{9}\cdots C^{14}$, 3 – $C^{16}\cdots C^{21}$, 4 – $C^{23}\cdots C^{28}$). [b] The molecules are in symmetry connection as follows: –*x*, 1 – *y*, 1 – *z*.

endless two-dimensional system (layer) of molecules linked by hydrogen bonds (Fig. 2) in the (00*l*) plane. The next layer is turned by 180° with respect to that preceding and somewhat shifted in the direction of the crystallographic axis 0*Y*, and thus the molecules in the two neighboring layers are placed by "head-to-head" type. The hydrogen contact between the H^{18} proton and O^{11} atom in the hydroxy group of another symmetrically bonded molecule provides a combination of two adjacent layers in a bilayer (Fig. 3). Thus the type of spatial arrangement of molecules in the crystal consists in parallel placement of bilayers in the direction of the crystallographic axis *c* (Fig. 3). The general pattern of hydrogen bonds is complicated also by numerous hydrogen bonds between calixarene and solvent molecules (Table 1).

Thus in general the molecules packing in the crystal **I** consists in formation of endless bilayer structure with localization within of lipophilic and hydrophilic regions. Our preliminary study with diffractometric method on the kinetics of degradation of the single crystals of pyrogallolarene I [13] evidenced that at removing solvents the single crystal transformed into polycrystalline state characterized by the presence of disordered bilayers with an internal lipophilic layer. Whereas the presence of solvent molecules in the crystals results in the closest packing in the crystal cell, and according to calculations no more free volume exists in crystals available for solvent.

The molecular packing in the crystal apart the hydrogen bonds is due to a significant extent to π–π interactions between the electronic systems of the benzene rings. Since the distance between the centers of the neighboring benzene rings in the calixarene molecule is virtually uniform and equal to 4.8 Å then according to common views the interactions between these aromatic rings should be about equal. From the π-H interactions should be mentioned the contacts of the protons of hydroxy, methyl, and methylene bonds of the ethanol molecule with the π-system of the aromatic rings: These interactions apparently fix the ethanol molecule in the cavity. The characteristics of these contacts are given in Table 2.

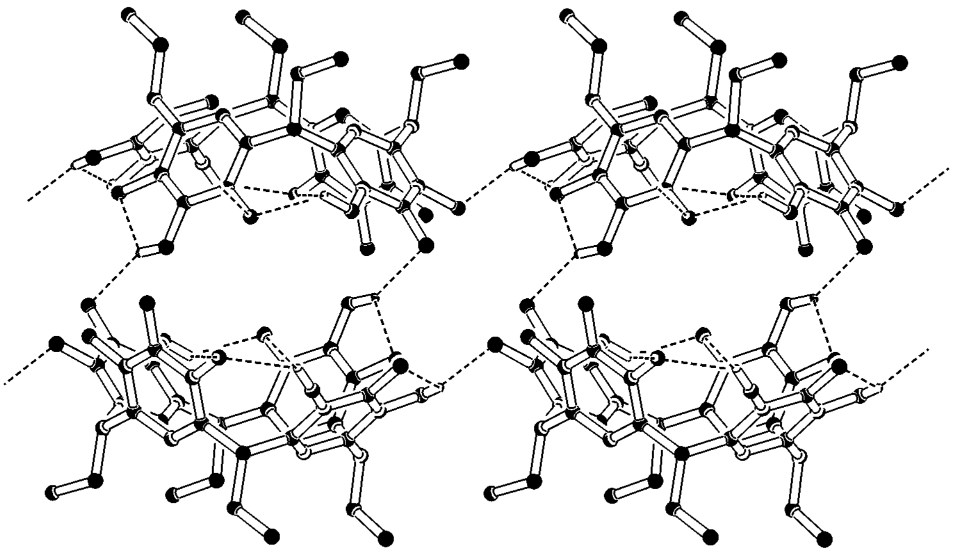

Fig. 2. Packing of molecules in the crystal cell, and hydrophilic layer formation. Hydrogen bonds are shown by dash lines.

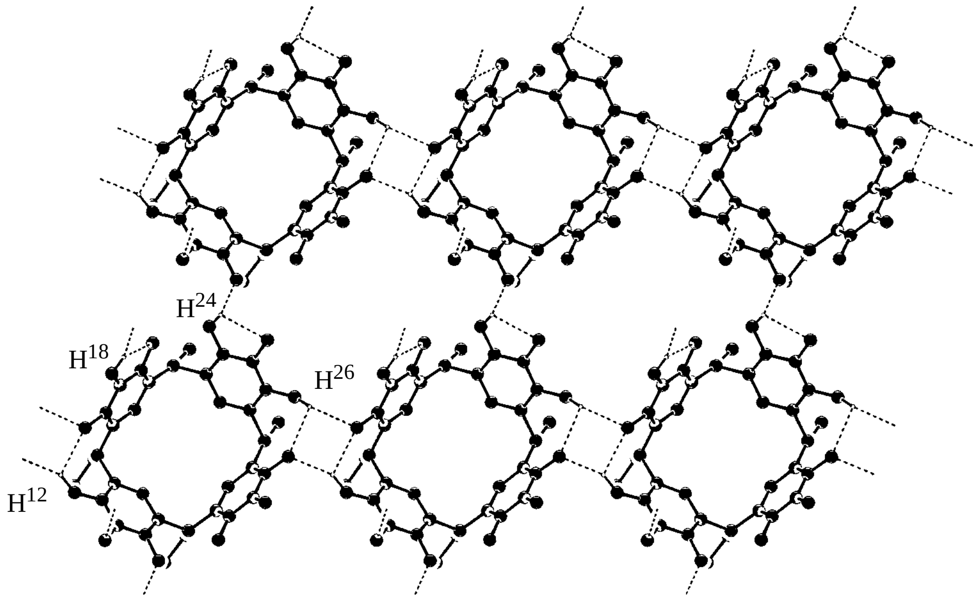

Fig. 3. Formation of bilayer structure with an intermediate hydrophilic layer in the crystals of compound **I**. View along 0*y* axis.

EXPERIMENTAL

X-ray diffraction study on the crystal was carried out on an automatic four-circle diffractometer Enraf-Nonius CAD-4. Since the crystals were unstable due to evaporation of solvent the experiment was performed on a single crystal placed in a glass capillary filled with the mother liquor. The crystals of compound **I**, $C_{36}H_{40}O_{12} \cdot 3C_2H_5OH \cdot 3H_2O$, triclinic. At 20°C a 11.718(7), b 12.582(3), c 15.504(9) Å; α 84.68(3), β 80.46(6), γ 74.63(3)°; V 2171(2) Å^3, Z 2, d_{calc} 1.31 g/cm^3, space group P-1.

The unit cell parameters and intensity of 10109 reflections with 6741 among them of $I \geq 3\sigma$ were measured at 20°C (λCuK_α-irradiation, graphite monochromator, $\omega/2\theta$-scanning, $\theta \leq 74.3°$). In the course of the recording was no intensity decrease observed for three control reflections. The absorption was taken in account empirically (μCu 8.6 cm^{-1}). The structure was solved by the direct method along SIR software [14] and was refined first in isotropic and then in anisotropic approximation save the solvent molecules that were subjected to refinement in isotropic approximation. All the hydrogen atoms were revealed from

Table 3 Coordinates of nonhydrogen atoms of structure **I** and their equivalent isotropic thermal parameters $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å^2)

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
O^{3}	0.3255(2)	0.5776(2)	0.6476(2)	4.45(6)	C^{13}	0.9211(3)	0.6671(3)	0.7295(2)	2.78(7)
O^{4}	0.3831(3)	0.7473(3)	0.5505(2)	5.88(8)	C^{14}	0.7997(3)	0.7020(3)	0.7640(2)	2.93(7)
O^{5}	0.5055(3)	0.8763(3)	0.6103(2)	5.43(7)	C^{15}	1.0039(3)	0.5653(3)	0.7692(2)	2.96(7)
O^{10}	0.7014(2)	0.9498(2)	0.6240(2)	3.66(6)	C^{16}	0.9828(3)	0.4595(3)	0.7416(2)	2.71(7)
O^{11}	0.9335(2)	0.8819(2)	0.5553(2)	3.85(6)	C^{17}	1.0380(3)	0.4206(3)	0.6593(2)	2.79(7)
O^{12}	1.0809(2)	0.7071(2)	0.6188(2)	4.33(7)	C^{18}	1.0195(3)	0.3243(3)	0.6328(2)	3.01(8)
O^{17}	1.1100(2)	0.4772(2)	0.6074(2)	3.90(6)	C^{19}	0.9465(3)	0.2681(3)	0.6853(2)	2.91(7)
O^{18}	1.0778(3)	0.2882(2)	0.5520(2)	4.53(6)	C^{20}	0.8890(3)	0.3045(3)	0.7678(2)	2.61(7)
O^{19}	0.9389(2)	0.1732(2)	0.6508(2)	4.14(6)	C^{21}	0.9093(3)	0.4008(3)	0.7928(2)	2.54(7)
O^{24}	0.7343(2)	0.1113(2)	0.7153(2)	3.60(6)	C^{22}	0.8053(3)	0.2431(3)	0.8244(3)	3.23(8)
O^{25}	0.5178(2)	0.1621(2)	0.6625(2)	4.67(6)	C^{23}	0.6818(3)	0.2749(3)	0.7945(2)	2.77(7)
O^{26}	0.3511(2)	0.3608(2)	0.7066(2)	4.09(6)	C^{24}	0.6506(3)	0.2071(3)	0.7428(2)	2.77(7)
O^{30}	0.1678(3)	0.9152(4)	0.5118(4)	9.5(1)	C^{25}	0.5405(3)	0.2346(3)	0.7150(3)	3.35(8)
O^{42}	0.7784(3)	0.5943(3)	0.5571(2)	5.21(7)	C^{26}	0.4585(3)	0.3328(3)	0.7382(2)	3.06(8)
O^{53}	0.211(2)	0.189(2)	0.867(1)	30.1(7)^{a}	C^{27}	0.4854(3)	0.4023(3)	0.7924(2)	2.76(7)
O^{55}	0.3205(9)	0.0364(9)	0.5691(7)	18.0(3)^{a}	C^{28}	0.5977(3)	0.3725(3)	0.8179(2)	2.82(7)
O^{62}	0.176(1)	1.012(1)	0.7024(9)	21.6(4)^{a}	C^{29}	0.3771(4)	0.5223(4)	0.9187(3)	4.1(1)
O^{70}	0.3564(4)	0.2287(7)	0.5498(3)	12.3(2)	C^{30}	0.3315(4)	0.4343(5)	0.9716(3)	5.3(1)
C^{1}	0.3941(3)	0.5107(3)	0.8203(2)	3.14(8)	C^{31}	0.5778(5)	0.8438(4)	0.8698(4)	5.7(1)
C^{2}	0.4232(3)	0.6089(3)	0.7662(3)	3.11(8)	C^{32}	0.6233(6)	0.9396(5)	0.8918(4)	8.2(1)
C^{3}	0.3887(3)	0.6351(3)	0.6841(3)	3.55(8)	C^{33}	0.9952(4)	0.5683(4)	0.8687(3)	4.16(9)
C^{4}	0.4159(4)	0.7241(4)	0.6336(3)	3.98(9)	C^{34}	1.0341(5)	0.6643(4)	0.8962(3)	6.3(1)
C^{5}	0.4790(3)	0.7883(3)	0.6636(3)	3.85(9)	C^{35}	0.8009(4)	0.2509(4)	0.9209(3)	4.2(1)
C^{6}	0.5161(3)	0.7636(3)	0.7452(3)	3.35(8)	C^{36}	0.7319(6)	0.1741(5)	0.9753(4)	7.1(1)
C^{7}	0.4871(3)	0.6748(3)	0.7939(2)	3.08(8)	C^{40}	0.6819(5)	0.4505(5)	0.5699(4)	6.9(1)
C^{8}	0.5917(4)	0.8331(3)	0.7749(3)	4.29(9)	C^{41}	0.7226(4)	0.5244(4)	0.6171(3)	3.93(9)
C^{9}	0.7230(3)	0.7950(3)	0.7331(2)	2.97(7)	C^{52}	0.227(1)	0.206(1)	0.773(1)	16.9(4)^{a}
C^{10}	0.7687(3)	0.8547(3)	0.6628(3)	3.16(8)	C^{54}	0.316(2)	0.109(2)	0.759(1)	19.4(5)^{a}
C^{11}	0.8880(3)	0.8239(3)	0.6259(3)	3.17(8)	C^{61}	0.140(1)	0.913(1)	0.754(1)	17.0(4)^{a}
C^{12}	0.9641(3)	0.7301(3)	0.6595(3)	3.10(8)	C^{63}	0.026(2)	0.952(2)	0.822(2)	26.6(9)^{a}

[a] Atomic coordinates refined in isotropic approximation.

Table 4. Some bond lengths (*d*, Å), bond (ω, deg) and torsional (φ, deg) angles in the compound **I**

Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
$O^{3}–C^{3}$	1.374(6)	$O^{26}–C^{26}$	1.374(5)	$O^{12}–C^{12}$	1.375(4)	$C^{20}–C^{22}$	1.523(5)
$O^{4}–C^{4}$	1.388(5)	$C^{1}–C^{2}$	1.511(5)	$O^{17}–C^{17}$	1.363(4)	$C^{22}–C^{23}$	1.533(5)
$O^{5}–C^{5}$	1.390(5)	$C^{1}–C^{27}$	1.541(5)	$O^{18}–C^{18}$	1.377(4)	$C^{22}–C^{35}$	1.500(6)
$O^{5}–H^{5}$	1.239(3)	$C^{1}–C^{29}$	1.521(6)	$O^{19}–C^{19}$	1.382(5)	$C^{15}–C^{33}$	1.532(5)
$O^{10}–C^{10}$	1.392(4)	$C^{2}–C^{3}$	1.383(6)	$O^{24}–C^{24}$	1.388(4)	$O^{25}–C^{25}$	1.380(5)
$O^{11}–C^{11}$	1.371(4)	$C^{2}–C^{7}$	1.391(6)	$C^{8}–C^{31}$	1.469(7)	$C^{6}–C^{8}$	1.543(6)
				$C^{13}–C^{15}$	1.534(4)	$C^{8}–C^{9}$	1.534(5)

Table 4. (Contd.)

Angle	ω	Angle	ω	Angle	ω	Angle	ω
$C^2C^1C^{27}$	111.3(3)	$C^1C^2C^3$	120.1(4)	$C^{12}C^{13}C^{15}$	121.4(3)	$C^5C^6C^8$	118.8(4)
$C^2C^1C^{29}$	114.2(4)	$C^1C^2C^7$	122.9(3)	$C^{13}C^{15}C^{16}$	110.6(3)	$C^7C^6C^8$	123.5(4)
$C^8C^9C^{10}$	120.5(3)	$O^3C^3C^2$	123.7(4)	$C^{20}C^{22}C^{23}$	110.7(3)	$C^6C^8C^9$	110.8(3)
$C^8C^9C^{14}$	122.0(3)	$O^3C^3C^4$	115.7(4)	$C^{15}C^{16}C^{21}$	123.5(3)	$O^{24}C^{24}C^{23}$	119.0(3)
$O^{10}C^{10}C^9$	123.8(3)	$O^4C^4C^3$	119.7(4)	$O^{17}C^{17}C^{16}$	118.9(3)	$O^{25}C^{25}C^{26}$	122.6(3)
$O^{11}C^{11}C^{10}$	121.8(3)	$O^4C^4C^5$	119.4(4)	$O^{17}C^{17}C^{18}$	121.5(3)	$C^8C^{31}C^{32}$	111.8(4)
$O^{11}C^{11}C^{12}$	118.5(3)	$C^3C^4C^5$	120.9(4)	$O^{18}C^{18}C^{17}$	117.3(3)	$O^{26}C^{26}C^{27}$	120.7(3)
$O^{12}C^{12}C^{11}$	115.2(3)	$O^5C^5C^4$	118.9(4)	$O^{18}C^{18}C^{19}$	121.7(4)	$C^1C^{27}C^{26}$	120.8(3)
$O^{12}C^{12}C^{13}$	124.3(3)	$O^5C^5C^6$	121.0(4)	$O^{19}C^{19}C^{20}$	124.4(3)	$C^{22}C^{23}C^{28}$	121.8(4)
Angle	φ	Angle	φ	Angle	φ	Angle	φ
$H^3O^3C^3C^2$	–26.2(5)	$H^4O^4C^4C^3$	87.2(4)	$C^4C^5C^6C^8$	176.9(4)	$C^8C^6C^7C^2$	–177.3(4)
$H^5O^5C^5C^4$	130.3(4)	$H^{10}O^{10}C^{10}C^9$	–38.3(5)	$C^5C^6C^8C^9$	–79.8(4)	$C^5C^6C^8C^{31}$	150.5(4)
$H^{11}O^{11}C^{11}C^{10}$	–11.1(4)	$H^{12}O^{12}C^{12}C^{11}$	173.2(3)	$C^7C^6C^8C^9$	97.4(4)	$C^{31}C^8C^9C^{10}$	–126.3(4)
$H^{17}O^{17}C^{17}C^{16}$	–169.7(3)	$H^{18}O^{18}C^{18}C^{17}$	–174.6(3)	$C^6C^8C^9C^{10}$	102.6(4)	$C^{13}C^{15}C^{16}C^{17}$	81.7(4)
$H^{19}O^{19}C^{19}C^{18}$	–147.3(3)	$H^{24}O^{24}C^{24}C^{23}$	160.5(3)	$O^{10}C^{10}C^{11}O^{11}$	–1.6(5)	$C^{22}C^{23}C^{24}O^{24}$	–2.4(5)
$H^{25}O^{25}C^{25}C^{24}$	176.8(3)	$H^{26}O^{26}C^{26}C^{25}$	–97.3(8)	$O^{11}C^{11}C^{12}O^{12}$	1.9(5)	$C^{13}C^{15}C^{33}C^{34}$	–62.8(5)
$C^{27}C^1C^2C^3$	81.7(4)	$C^{29}C^1C^2C^3$	–150.4(4)	$C^{12}C^{13}C^{14}C^9$	–0.9(5)	$O^{17}C^{17}C^{18}O^{18}$	0.5(5)
$C^1C^2C^3O^3$	1.5(6)	$O^3C^3C^4O^4$	–2.3(6)	$C^{33}C^{15}C^{16}C^{17}$	–151.4(3)	$C^{19}C^{20}C^{22}C^{23}$	–80.1(4)
$C^3C^2C^7C^6$	0.7(6)	$O^4C^4C^5O^5$	1.5(6)				

electron density difference series. The hydrogen atoms contribution into the structural amplitudes was taken into account with fixed positional and isotropic thermal parameters. The final values of divergence factors are R 0.074, R_W 0.097 from 4328 independent reflections with $F^2 \geq \sigma$. All calculations were carried out with the use of program package MolEN [15] on the computer Alpha Station 200. The nonhydrogen atoms coordinates and their thermal factors, and also some geometrical characteristics are listed in Tables 3 and 4 respectively. The drawings of the molecule, of the molecules packing in the crystal, and the calculations of intra- and intermolecular interactions were performed with PLATON software [16].

2,8,14,20-Tetraethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecanol (I). In a mixture of 50 ml of ethanol, 50 ml of water, and 25 ml of HCl was dissolved 10 g of pyrogallol, and 4.6 g of propionaldehyde was added. The mixture was maintained for 1 h at 60°C and 3 days at 20°C. The white crystalline product formed was kept in a vacuum (0.01 mm) at 60°C till constant weight. We obtained 6.59 g (50%) of compound **I**, mp 48°C. ^{1}H NMR spectrum [$CD_3C(O)CD_3$], δ, ppm: 0.90 t (12H, CH_3–CH_2, $^3J_{HH}$ 7.1 Hz), 2.29 d.q (8H, CH_2–CH_3, $^3J_{HH}$ 7.8 Hz), 7.12 s (4H arom). Found, %: C 65.02; H 6.01. $C_{36}H_{40}O_{12}$. Calculated, %: C 65.06; H 6.02.

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