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Synthesis and Crystal Structure of a Novel Calix[8]arene Ester Derivative

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Abstract: The synthesis and crystal structure of a novel calix[8]arene ester are reported herein. The calix[8]arene ester derivative has been characterized by IR, NMR and X-ray crystal analysis. The X-ray structure analysis revealed that the 8 phenolic hydroxy groups of the calix[8]arene have been substituted by 4 diethyl dibromomalonate molecules with each two adjacent hydroxy oxygen atoms attached to a bridge diethyl malonate.

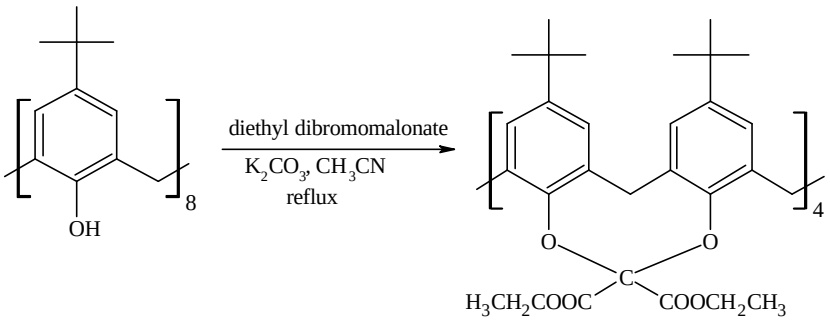
Keywords: Synthesis, crystal structure, calix[8]arene ester derivative.

Calixarenes are certainly among the most fascinating macrocyclic receptors in supramolecular chemistry[1], and play a key role as building blocks in constructing large and sophisticated supramolecular systems. In the previous studies on calixarene chemistry, central concerns have been focused on the stereochemistry and molecular recognition properties of calixarene molecules[2]. Carboxylic ester groups attached to calixarene have a profound effect on the complexation affinity for the alkali cations[3]. In this paper, we report the synthesis and structural characterization of a novel *p*-tert-butylcalix[8]arene O, O′-bridged diethyl malonate substituted derivative.

Experimental

Under a nitrogen atmosphere, *p*-tert-butylcalix[8]arene was first treated with 8 equiv. of potassium carbonate in acetonitrile at room temperature for 3 h for preliminary deprotonation. Then, 8 equiv. of diethyl dibromomalonate was added and the reacting mixture was refluxed for additional 24 h. After removing of the solvent, the residue dissolved in CH_2Cl_2, washed with hydrochloric acid (1 mol/L), and the CH_2Cl_2 was removed by evaporation. After that CH_3OH was added to the residue, a white solid product was obtained. The colorless single crystals were obtained by recrystallization from 1:1 CH_2Cl_2/CH_3CH_2OH. The procedure follows the **Scheme** below:

Scheme



^{1}H NMR and ^{13}C NMR spectra were recorded on an Avance 500 Brüker spectrometer, $CDCl_3$ as solvent. IR spectra were measured on Nicolet-FT-IR-170X spectrophotometer. Elemental analysis was carried out with a Perkin-Elmer 240C analyser. Anal. calcd. for $C_{116}H_{144}O_{24}$: C 72.47, H 7.55; found: C 71.90, H 7.45; mp > 300°C. Selected FT-IR (KBr, cm^{-1}): 2964, 2870 (–CH_3, –CH_2); 1767 (EtOOC-C–COOEt); 1480 (-Ph); 1364 (–$C(CH_3)_3$, δ); 1298, 1240 (EtOOC–C–COOEt); 1192, 1137, 1107, 1055 (Ar–O–R). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 1.08, 1.21-1.28 (overlap, 24H, Ar–(CC**H**$_3$)$_3$, CO_2CH_2C**H**$_3$), 3.45 (d, 4H, J = 15.0, Ar–C**H**$_2$–Ar), 4.10 - 4.24 (overlap, 4H, CO_2C**H**$_2CH_3$), 4.73 (d, 4H, J=15.0, Ar–C**H**$_2$–Ar), 6.85 (s, 1H, **H**–Ar), 6.99 (s, 1H, **H**–Ar), 7.05 (s, 1H, **H**–Ar), 7.29 (s, 1H, **H**–Ar). ^{13}C NMR (125 MHz) δ 31.70 (s, CO_2CH_2**C**H_3) 31.81 (s, Ar–(C**C**H$_3$)$_3$), 34.66 (s, Ar–(**C**CH$_3$)$_3$), 37.37 (s, Ar–**C**H$_2$–Ar), 62.79 (s, CO_2**C**H_2CH_3), 63.01 (s, CO_2**C**H_2CH_3), 125.24, 125.51, 126.91 (s, **Ar**), 147.40 (s, **C**$O_2CH_2CH_3$), 147.92 (s, **C**$O_2CH_2CH_3$), 165.46 (s, **C**($CO_2C_2H_5$)).

X-ray crystallography

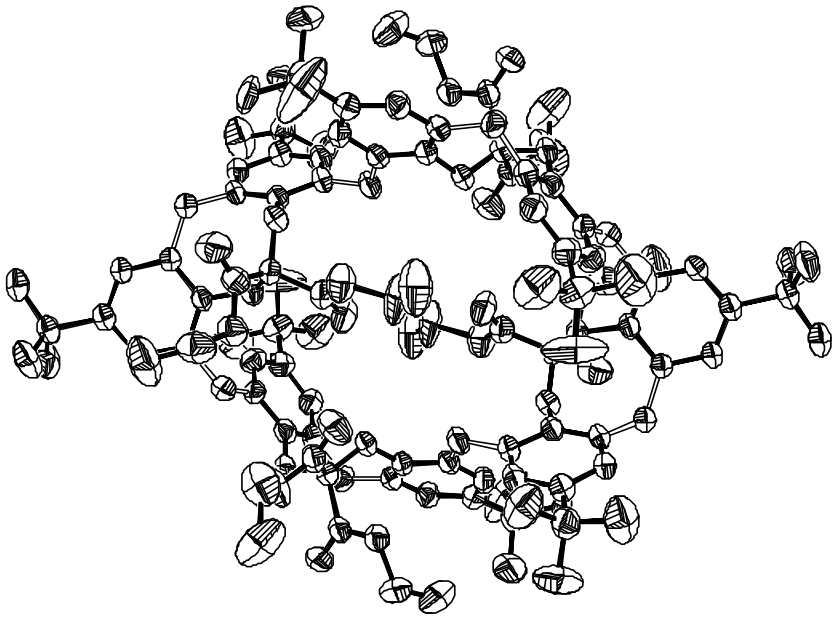
A colorless grain crystal with a dimension of 0.4×0.5×0.5 mm was mounted on a glass fiber. All measurements were made on a Brüker P4 dffractometer equipped with graphite monochromatized Mo K_α radiation (= 0.71073 Å) at 294 ±1 K. The data were collected to maximum 2θ value of 42° for 6210 reflections. The crystal structure belongs to monoclinic crystal system, space group $P2_1/n$, cell dimensions, a = 18.625 (4), b = 14.318 (3), c = 20.991 (4) Å, = 95.40 (3)°, V = 5573 (2) Å^3, D_c = 1.146 g/cm^3, Z = 2, F (000) = 2064, $R1$ = 0.0647, $wR2$ = 0.1476. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matrix least-square refinement on F^2 converged with $R1$ = 0.0647 and $wR2$ = 0.1476 for 3264 observed reflections [$I \geq 2\sigma$ (I)]. The final difference electron density map shows no features. Data collection was controlled by XSCANS program. Computations were performed using the SHELXTL

NT ver. 5.10 program package[4] on an IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated[5].

The crystal structure and the molecular packing in the unite cell are shown in **Figure 1** and **Figure 2**. The molecular structure of the title compound shows that all *tert*-butyl groups locate on the same upper rim indicating a cone conformation (point to the viewer from paper plane) of the calixarene. The ester groups locate rather randomly because of the stereo hindrance existing between them. It can also be seen that each two adjacent benzene rings are near coplaner. This may atributed to the bridge linkage of diethyl malonate.

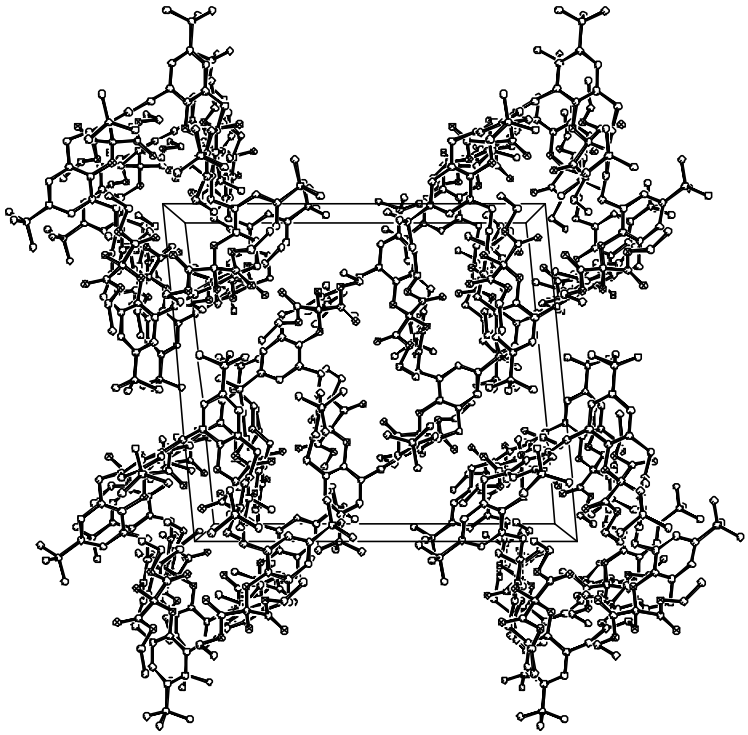
Further studies on the complexation properties of the calixar[8]ene derivative are currently under investigation.

Figure 1 The structure of the title compound



ORTEP drawing for the structure of $C_{116}H_{144}O_{24}$ with 35% probability ellipsoids

Figure 2 Packing of the title compound



Ackonwledgment

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