Crystal structure of 25,27-dibenzoyloxy-26,28-dihydroxythiacalix[4]arene, C₃₈H₂₄O₆S₄

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Discussion

The calixarenes, a class of molecules with excellent binding affinity to various substrate molecules, have caught the eyes of chemists from all over the world. Substitution of the methylene bridges between the aromatic rings in calixarene by sulfur atoms has been reported [2]. The properties of these thiacalixarenes are different from those of the original calixarenes, which makes thiacalixarenes become a new type of building blocks and molecular scaffolds for molecular receptors. A variety of thiacalixarene derivatives have been synthesized, such as tetranitrothiacalix[4]arene [3], tetraaminothiacalix[4]arene [4], and dinitrothiacalix[4]arene [5]. We have reported the crystal structure of dinitrothiacalix[4]arene [6].

In the crystal the title molecule takes an 1,2-alternate conformation. The two benzoyl-containing phenyl rings adopt *anti* positions for avoiding steric hindrance and are nearly parallel to each other. The dihedral angles between the benzoyl-containing phenyl rings and the attached benzoyl groups are 79.4°. The two benzoyl groups are symmetrically positioned at the two sides of the mean plane of the bridging sulfur atoms and are also nearly parallel to each other. The dihedral angles between the benzoyl groups and the mean plane are 71.9°. The distances from the centroids of the phenyl rings of the benzoyl groups to the mean plane of the bridging sulfur atoms are 4.34 Å. The dihedral angles between the phenyl rings and the mean plane of the bridging sulfur atoms are 56.3° for the two benzoyl-containing phenyl rings, 67.7° for the other two phenyl rings. The distances from the centroids of the phenyl rings to the mean plane of the bridging sulfur atoms are 1.32 Å for the two benzoyl-containing phenyl rings, and 1.43 Å for the other two phenyl rings.

Abstract

C₃₈H₂₄O₆S₄, triclinic, $P\bar{1}$ (no. 2), $a = 10.690(1)$ Å, $b = 12.647(2)$ Å, $c = 13.615(2)$ Å, $\alpha = 97.685(9)^\circ$, $\beta = 108.450(9)^\circ$, $\gamma = 110.478(9)^\circ$, $V = 1572.7$ Å³, $Z = 2$, $R_g(F) = 0.049$, $wR_{\text{ref}}(F^2) = 0.122$, $T = 295$ K.

Source of material

Thiacalix[4]arene [1] (2 g) was dissolved in pyridine (120 ml) and cooled in an ice bath. Benzoyl chloride (1.5 ml) was added, and the mixture was stirred for 2 h and then allowed to warm slowly to room temperature over another hour. The precipitate was collected and washed with pyridine, water, and methanol to obtain a white powder. The white powder was recrystallized from CHCl₃/CH₃OH to obtain colorless crystals (yield 1.12 g, 39.4 %).

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.2 × 0.3 × 0.6 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.53 cm ⁻¹
Diffractionmeter, scan mode:	Bruker P4, ω
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6490, 5519
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3903
$N(\text{param})_{\text{refined}}$:	435
Program:	SHELXTL [7]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1A)	2i	0.5908	0.6824	0.6828	0.076
H(4B)	2i	−0.1448	−0.1722	0.8013	0.070
H(4A)	2i	1.0522	0.7030	0.7033	0.069
H(5A)	2i	1.0955	0.7210	0.5506	0.073
H(6A)	2i	0.9283	0.5962	0.3854	0.064
H(10A)	2i	0.3142	0.3850	0.7609	0.067
H(11A)	2i	0.4570	0.2836	0.8091	0.072
H(12A)	2i	0.6827	0.3491	0.8011	0.067
H(15A)	2i	0.5498	0.0953	0.5799	0.064
H(16A)	2i	0.3351	−0.0325	0.5812	0.077
H(17A)	2i	0.1350	0.0104	0.5346	0.075
H(18A)	2i	0.1515	0.1835	0.4904	0.072

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(19A)	2i	0.3669	0.3132	0.4918	0.064
H(23A)	2i	0.3164	−0.1760	0.8743	0.064
H(24A)	2i	0.3984	−0.2153	1.0372	0.072
H(25A)	2i	0.4029	−0.1090	1.1904	0.065
H(29A)	2i	−0.2136	0.1293	0.7007	0.065
H(30A)	2i	0.0004	0.2330	0.6842	0.073
H(31A)	2i	0.1883	0.1763	0.7365	0.066
H(34A)	2i	0.4060	0.4150	0.9916	0.070
H(35A)	2i	0.2957	0.5364	0.9349	0.088
H(36A)	2i	0.0600	0.4891	0.9165	0.091
H(37A)	2i	−0.0690	0.3186	0.9515	0.082
H(38A)	2i	0.0378	0.1932	1.0013	0.065

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
S(1)	2i	0.65170(6)	0.40708(5)	0.30889(5)	0.0572(2)	0.0575(3)	0.0551(3)	0.0305(2)	0.0260(2)	0.0148(2)
S(2)	2i	0.85931(6)	0.54569(6)	0.75965(5)	0.0498(2)	0.0894(4)	0.0533(3)	0.0328(3)	0.0187(2)	0.0231(3)
S(3)	2i	0.32807(5)	0.07836(5)	1.23989(5)	0.0423(2)	0.0565(3)	0.0535(3)	0.0200(2)	0.0190(2)	0.0093(2)
S(4)	2i	0.23001(6)	−0.01111(6)	0.80232(5)	0.0497(2)	0.0770(3)	0.0571(3)	0.0313(2)	0.0304(2)	0.0224(2)
O(1)	2i	0.6498(2)	0.6535(1)	0.6973(1)	0.0556(7)	0.0634(8)	0.0872(9)	0.0292(6)	0.0349(7)	0.0400(7)
O(2)	2i	0.6249(1)	0.4016(1)	0.5229(1)	0.0422(6)	0.0516(7)	0.0561(7)	0.0209(5)	0.0227(5)	0.0200(6)
O(3)	2i	0.7279(2)	0.2767(1)	0.5578(2)	0.0579(7)	0.0697(8)	0.137(1)	0.0385(6)	0.0520(8)	0.0474(9)
O(4)	2i	−0.0596(2)	−0.1335(1)	0.8126(1)	0.0471(6)	0.0597(7)	0.0833(9)	0.0261(6)	0.0320(6)	0.0360(7)
O(5)	2i	0.2113(1)	0.1026(1)	1.0127(1)	0.0430(6)	0.0458(6)	0.0596(8)	0.0243(5)	0.0224(5)	0.0177(6)
O(6)	2i	0.4353(2)	0.2427(1)	1.0577(2)	0.0438(7)	0.0546(8)	0.105(1)	0.0214(6)	0.0301(7)	0.0186(8)
C(1)	2i	0.7801(2)	0.5011(2)	0.4385(2)	0.0463(8)	0.0448(9)	0.057(1)	0.0261(7)	0.0244(8)	0.0197(8)
C(2)	2i	0.7574(2)	0.4869(2)	0.5322(2)	0.0378(8)	0.0451(9)	0.060(1)	0.0199(7)	0.0235(8)	0.0199(8)
C(3)	2i	0.8596(2)	0.5613(2)	0.6323(2)	0.0427(8)	0.052(1)	0.056(1)	0.0266(7)	0.0212(8)	0.0161(9)
C(4)	2i	0.9848(2)	0.6506(2)	0.6371(2)	0.0437(9)	0.055(1)	0.071(1)	0.0188(9)	0.0200(9)	0.0141(1)
C(5)	2i	1.0099(2)	0.6624(2)	0.5457(2)	0.051(1)	0.054(1)	0.088(1)	0.0223(9)	0.036(1)	0.027(1)
C(6)	2i	0.9097(2)	0.5883(2)	0.4469(2)	0.0522(9)	0.054(1)	0.070(1)	0.0279(8)	0.0330(8)	0.0302(9)
C(7)	2i	0.6793(2)	0.4911(2)	0.7511(2)	0.0500(9)	0.056(1)	0.042(1)	0.0218(8)	0.0195(8)	0.0150(8)
C(8)	2i	0.5928(2)	0.5531(2)	0.7241(2)	0.0523(9)	0.048(1)	0.045(1)	0.0192(8)	0.0229(8)	0.0156(8)
C(9)	2i	0.4557(2)	0.5129(2)	0.7263(2)	0.0524(9)	0.051(1)	0.042(1)	0.0245(8)	0.0202(8)	0.0155(8)
C(10)	2i	0.4058(2)	0.4119(2)	0.7585(2)	0.053(1)	0.063(1)	0.054(1)	0.0180(9)	0.0285(8)	0.020(1)
C(11)	2i	0.4908(2)	0.3508(2)	0.7871(2)	0.065(1)	0.059(1)	0.057(1)	0.024(1)	0.024(1)	0.025(1)
C(12)	2i	0.6261(2)	0.3905(2)	0.7826(2)	0.063(1)	0.061(1)	0.051(1)	0.0322(9)	0.0216(9)	0.0212(9)
C(13)	2i	0.6241(2)	0.2968(2)	0.5405(2)	0.0485(9)	0.052(1)	0.060(1)	0.0237(8)	0.0268(8)	0.0200(9)
C(14)	2i	0.4804(2)	0.2175(2)	0.5358(2)	0.0477(9)	0.050(1)	0.046(1)	0.0182(8)	0.0231(8)	0.0124(8)
C(15)	2i	0.4698(2)	0.1134(2)	0.5622(2)	0.053(1)	0.052(1)	0.058(1)	0.0244(9)	0.0217(9)	0.0186(9)
C(16)	2i	0.3412(3)	0.0367(2)	0.5625(2)	0.068(1)	0.053(1)	0.070(1)	0.016(1)	0.034(1)	0.021(1)
C(17)	2i	0.2221(2)	0.0625(2)	0.5352(2)	0.054(1)	0.061(1)	0.067(1)	0.012(1)	0.032(1)	0.010(1)
C(18)	2i	0.2321(2)	0.1660(2)	0.5087(2)	0.049(1)	0.068(1)	0.065(1)	0.0247(9)	0.0274(9)	0.016(1)
C(19)	2i	0.3607(2)	0.2434(2)	0.5093(2)	0.052(1)	0.055(1)	0.057(1)	0.0228(9)	0.0255(9)	0.0157(9)
C(20)	2i	0.3155(2)	−0.0058(2)	1.1186(2)	0.0391(8)	0.046(1)	0.053(1)	0.0194(7)	0.0203(8)	0.0142(8)
C(21)	2i	0.2674(2)	0.0179(2)	1.0207(2)	0.0371(8)	0.0442(9)	0.059(1)	0.0199(7)	0.0228(7)	0.0169(8)
C(22)	2i	0.2666(2)	−0.0443(2)	0.9275(2)	0.0388(8)	0.050(1)	0.053(1)	0.0215(7)	0.0215(7)	0.0178(8)
C(23)	2i	0.3165(2)	−0.1328(2)	0.9352(2)	0.0517(9)	0.053(1)	0.063(1)	0.0273(8)	0.0274(9)	0.0119(9)
C(24)	2i	0.3658(2)	−0.1562(2)	1.0331(2)	0.0571(9)	0.063(1)	0.078(1)	0.0381(8)	0.031(1)	0.024(1)
C(25)	2i	0.3675(2)	−0.0934(2)	1.1248(2)	0.0499(9)	0.063(1)	0.064(1)	0.0317(8)	0.0260(9)	0.0252(9)
C(26)	2i	0.0847(2)	0.0322(2)	0.7766(2)	0.0461(9)	0.054(1)	0.043(1)	0.0199(8)	0.0205(8)	0.0118(8)
C(27)	2i	−0.0466(2)	−0.0342(2)	0.7816(2)	0.0446(8)	0.052(1)	0.0425(9)	0.0210(8)	0.0197(7)	0.0169(8)
C(28)	2i	−0.1584(2)	0.0035(2)	0.7547(2)	0.0418(9)	0.051(1)	0.0397(9)	0.0190(8)	0.0142(7)	0.0133(8)
C(29)	2i	−0.1391(2)	0.1045(2)	0.7189(2)	0.061(1)	0.058(1)	0.050(1)	0.0321(9)	0.0192(9)	0.0166(9)
C(30)	2i	−0.0109(2)	0.1674(2)	0.7102(2)	0.066(1)	0.058(1)	0.062(1)	0.024(1)	0.026(1)	0.030(1)
C(31)	2i	0.1006(2)	0.1323(2)	0.7403(2)	0.053(1)	0.054(1)	0.055(1)	0.0121(9)	0.0251(9)	0.0203(9)
C(32)	2i	0.3071(2)	0.2141(2)	1.0273(2)	0.0447(9)	0.048(1)	0.051(1)	0.0197(8)	0.0219(8)	0.0130(8)
C(33)	2i	0.2314(2)	0.2911(2)	0.9990(2)	0.0552(9)	0.0452(9)	0.044(1)	0.0252(8)	0.0221(8)	0.0133(8)
C(34)	2i	0.3095(3)	0.3947(2)	0.9815(2)	0.069(1)	0.050(1)	0.061(1)	0.0257(9)	0.0324(9)	0.0166(9)
C(35)	2i	0.2443(3)	0.4680(2)	0.9491(2)	0.103(2)	0.061(1)	0.070(1)	0.043(1)	0.038(1)	0.027(1)
C(36)	2i	0.1039(3)	0.4396(2)	0.9378(2)	0.109(1)	0.074(1)	0.064(1)	0.066(1)	0.023(1)	0.025(1)
C(37)	2i	0.0260(3)	0.3368(2)	0.9582(2)	0.067(1)	0.076(1)	0.069(2)	0.046(1)	0.018(1)	0.013(1)
C(38)	2i	0.0896(2)	0.2622(2)	0.9883(2)	0.057(1)	0.055(1)	0.057(1)	0.0299(9)	0.0230(9)	0.0165(9)

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