Crystal structure of [mono-*O*-(diethoxy)thiophosphonato]tetra-*tert*-butylcalix[4]arene, C₄₈H₆₆O₆PS

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Fig. 1. View of the molecular structure. For clarity, H atoms have been omitted and only the major component of the ethoxy group is represented.

Abstract

C₄₈H₆₆O₆PS, monoclinic, *P*12₁/*n*1 (No. 14), *a* = 13.563(2) Å, *b* = 20.834(3) Å, *c* = 17.156(3) Å, β = 106.86(2)°, *V* = 4639.5 Å³, *Z* = 4, *R*_g(*F*) = 0.069, *R*_w(*F*²) = 0.161, *T* = 291 K.

Source of material

The title compound was obtained as the minor product in the synthesis of the 1,3-dithiophosphonato compound, in an analogous manner to the 1,3-dioxophosphonato compound [1]. Colorless crystals were grown by slow evaporation of a methanolic solution and sealed in the presence of the mother liquor in thin glass capillaries.

The positions of the H atoms for phenolic C atoms were first determined from successive difference syntheses. Then, H atoms were included in further refinement calculations with idealized geometry and constrained to ride on their parent C atom with isotropic displacement parameters fixed at 1.2 *x*U_{eq} of their respective C atom. For the ethoxy C atoms, C–O and C–C distance restraints (1.42 Å and 1.52 Å, respectively) were applied. Due to the large number of parameters to be refined with respect to the number of observed structure factors, the phenolic C atoms were given isotropic displacement parameters, the remaining non-H atoms were refined anisotropically. During the course of the

Fig. 2. View of the chain of molecules running parallel to the [101] direction.

refinement, a positional disorder was detected for the ethoxy group bonded to O6. Further refinement with fixed site occupancy factors 0.75 and 0.25, estimated from the relative heights of the electron density, gave acceptable results. For the final step, these partially occupied ethoxy group sites were refined isotropically, in separate blocks. The H atoms of the phenylic hydroxyl groups and those associated with the disordered ethoxy group were not located.

Discussion

Phosphorylated calix[4]arenes have attracted interest owing to their potentialities as useful reagents in the synthesis of chiral molecules capable of enantio- or diastereo-selective recognition and as selective complexing agents for solvent extraction of metal ions [2, 3, 4]. The molecule adopts a very slightly distorted cone conformation (Fig. 1). The phosphorus atom and its substituents point outside the macrocycle below the lower rim formed by the phenolic O atoms. One of the ethoxy groups, disordered over two positions, is placed in the intermolecular space while the other is partially intermolecularly included within the macrocycle of a neighbouring molecule, symmetry related (−1/2+*x*, 1/2−*y*, −1/2+*z*). This contributes to form an infinite molecular chain-like pattern running parallel to the [101] direction, as illustrated in Fig. 2. There are no close contacts between the ethoxy group and the macrocycle and no solvent sites were evidenced within the cavity. The intermolecular contacts uniquely correspond to normal Van der Waals separation.

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Table 1. Data collection and handling.

Crystal:	colorless, trigonal prism, size 0.35 x 0.45 x 0.45 mm
Wavelength:	Mo K α radiation (0.71703 Å)
μ :	1.49 cm ⁻¹
Diffractionmeter, scan mode:	Nonius CAD4, $\omega/2\theta$
$2\theta_{\max}$:	36.3°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3326, 3166
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2124
$N(\text{param})_{\text{refined}}$:	383
Programs:	SDP [5], SHELXS-86 [6], SHELXL-93 [7], ORTEP-III [8]

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
C(20)	4e		0.2318(5)	0.1882(4)	0.4287(4)	0.040(2)
H(211)	4e		0.0438(5)	0.2316(3)	0.4065(5)	0.056
H(212)	4e		0.0117(5)	0.1891(3)	0.4706(5)	0.056
C(22)	4e		0.0954(5)	0.2680(4)	0.5220(4)	0.039(2)
C(23)	4e		0.1097(5)	0.2547(4)	0.6036(4)	0.044(2)
H(23)	4e		0.0950(5)	0.2136(4)	0.6181(4)	0.053
C(24)	4e		0.1448(5)	0.2999(4)	0.6650(5)	0.046(2)
C(25)	4e		0.1679(5)	0.3600(4)	0.6408(5)	0.050(2)
H(25)	4e		0.1929(5)	0.3912(4)	0.6804(5)	0.059
C(26)	4e		0.1555(5)	0.3757(4)	0.5603(5)	0.045(2)
C(27)	4e		0.1166(5)	0.3291(4)	0.5019(5)	0.042(2)
H(281)	4e		0.1620(6)	0.4509(3)	0.4839(5)	0.060
H(282)	4e		0.1677(6)	0.4741(3)	0.5721(5)	0.060
H(301)	4e		0.4333(8)	0.5525(5)	0.7593(6)	0.111
H(302)	4e		0.5294(8)	0.5781(5)	0.7356(6)	0.111
H(303)	4e		0.5402(8)	0.5583(5)	0.8258(6)	0.111
H(311)	4e		0.4270(8)	0.4377(5)	0.7994(6)	0.128
H(312)	4e		0.5339(8)	0.4482(5)	0.8646(6)	0.128
H(313)	4e		0.5195(8)	0.3918(5)	0.8019(6)	0.128
H(321)	4e		0.6687(8)	0.5023(6)	0.7306(6)	0.155
H(322)	4e		0.6659(8)	0.4312(6)	0.7598(6)	0.155
H(323)	4e		0.6802(8)	0.4877(6)	0.8224(6)	0.155
H(341)	4e		0.6922(9)	0.1215(6)	0.6157(7)	0.164
H(342)	4e		0.6729(9)	0.1640(6)	0.6852(7)	0.164
H(343)	4e		0.7841(9)	0.1389(6)	0.6921(7)	0.164
H(351)	4e		0.7923(7)	0.1673(6)	0.5268(6)	0.149
H(352)	4e		0.8811(7)	0.1812(6)	0.6067(6)	0.149
H(353)	4e		0.8379(7)	0.2367(6)	0.5445(6)	0.149
H(361)	4e		0.7364(8)	0.2730(5)	0.7059(6)	0.138
H(362)	4e		0.8038(8)	0.3011(5)	0.6537(6)	0.138
H(363)	4e		0.8470(8)	0.2456(5)	0.7159(6)	0.138
H(381)	4e		0.2074(8)	0.0509(4)	0.6592(5)	0.105
H(382)	4e		0.3281(8)	0.0533(4)	0.6858(5)	0.105
H(383)	4e		0.2714(8)	-0.0119(4)	0.6878(5)	0.105
H(391)	4e		0.3662(9)	-0.0303(5)	0.5196(7)	0.167
H(392)	4e		0.3675(9)	-0.0611(5)	0.6033(7)	0.167
H(393)	4e		0.4243(9)	0.0042(5)	0.6012(7)	0.167
H(401)	4e		0.1701(9)	-0.0377(4)	0.4790(6)	0.123
H(402)	4e		0.1119(9)	-0.0058(4)	0.5357(6)	0.123
H(403)	4e		0.1792(9)	-0.0673(4)	0.5648(6)	0.123
H(421)	4e		0.0856(8)	0.3209(5)	0.8371(5)	0.108
H(422)	4e		0.0106(8)	0.3193(5)	0.7483(5)	0.108
H(423)	4e		0.0944(8)	0.3733(5)	0.7738(5)	0.108
H(431)	4e		0.2686(7)	0.2918(5)	0.8630(5)	0.104
H(432)	4e		0.2784(7)	0.3460(5)	0.8022(5)	0.104
H(433)	4e		0.3134(7)	0.2758(5)	0.7906(5)	0.104
H(441)	4e		0.1397(8)	0.2110(4)	0.8264(6)	0.109
H(442)	4e		0.1757(8)	0.1883(4)	0.7519(6)	0.109
H(443)	4e		0.0605(8)	0.2080(4)	0.7393(6)	0.109
C(49)	4e	0.25	0.027(4)	0.4983(8)	0.299(4)	0.19(3)
C(50)	4e	0.25	0.119(3)	0.522(2)	0.277(2)	0.09(1)

Table 2. Atomic coordinates and displacement parameters ($\text{\AA}^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
C(47)	4e	0.75	0.022(1)	0.4933(8)	0.345(1)	0.130(6)
C(48)	4e	0.75	0.110(1)	0.5356(9)	0.332(1)	0.163(7)
H(451)	4e		-0.044(1)	0.3489(6)	0.1756(5)	0.171
H(452)	4e		-0.138(1)	0.3258(6)	0.2044(5)	0.171
H(461)	4e		-0.1073(9)	0.2526(6)	0.1108(7)	0.151
H(462)	4e		-0.0885(9)	0.2189(6)	0.1955(7)	0.151
H(463)	4e		0.0054(9)	0.2420(6)	0.1669(7)	0.151
C(1)	4e		0.4648(6)	0.4240(3)	0.5281(5)	0.042(2)
C(2)	4e		0.5203(6)	0.4412(3)	0.6068(5)	0.046(2)
H(2)	4e		0.5919(6)	0.4390(3)	0.6216(5)	0.055
C(3)	4e		0.4739(6)	0.4614(4)	0.6634(5)	0.047(2)
C(4)	4e		0.3670(6)	0.4627(3)	0.6396(5)	0.046(2)
H(4)	4e		0.3337(6)	0.4760(3)	0.6771(5)	0.055
C(5)	4e		0.3080(6)	0.4450(3)	0.5623(5)	0.042(2)
C(6)	4e		0.3588(6)	0.4261(3)	0.5064(5)	0.040(2)
H(71)	4e		0.5893(6)	0.4210(3)	0.4833(5)	0.059
H(72)	4e		0.4847(6)	0.4104(3)	0.4153(5)	0.059
C(8)	4e		0.5395(6)	0.3272(4)	0.4780(4)	0.043(2)
C(9)	4e		0.6263(6)	0.3039(4)	0.5353(5)	0.050(2)
H(9)	4e		0.6754(6)	0.3330(4)	0.5641(5)	0.060
C(10)	4e		0.6431(6)	0.2388(4)	0.5516(5)	0.045(2)
C(11)	4e		0.5682(5)	0.1977(4)	0.5063(4)	0.045(2)
H(11)	4e		0.5772(5)	0.1539(4)	0.5161(4)	0.054
C(12)	4e		0.4806(5)	0.2179(3)	0.4474(4)	0.036(2)
C(13)	4e		0.4679(6)	0.2837(4)	0.4337(5)	0.040(2)
H(141)	4e		0.4394(5)	0.1313(4)	0.3927(4)	0.054
H(142)	4e		0.3704(5)	0.1875(4)	0.3463(4)	0.054
C(15)	4e		0.3198(5)	0.1516(3)	0.4387(4)	0.038(2)
C(16)	4e		0.3311(6)	0.0966(4)	0.4865(4)	0.050(2)
H(16)	4e		0.3902(6)	0.0720(4)	0.4934(4)	0.060
C(17)	4e		0.2587(6)	0.0767(4)	0.5243(5)	0.047(2)
C(18)	4e		0.1732(6)	0.1158(4)	0.5139(5)	0.050(2)
H(18)	4e		0.1236(6)	0.1047(4)	0.5393(5)	0.060
C(19)	4e		0.1594(5)	0.1704(4)	0.4675(4)	0.038(2)

Table 3. Atomic coordinates and displacement parameters ($\text{\AA}^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	4e	0.0030(2)	0.3694(1)	0.3545(2)	0.067(2)	0.067(2)	0.081(2)	0.009(2)	-0.001(2)	0.019(2)
S(1)	4e	-0.1112(2)	0.3810(2)	0.3943(2)	0.083(2)	0.162(4)	0.169(3)	0.029(2)	0.025(2)	0.014(3)
O(5)	4e	-0.0043(6)	0.3146(3)	0.2867(4)	0.127(6)	0.101(6)	0.061(5)	-0.005(5)	-0.037(4)	0.005(5)
O(6)	4e	0.0414(6)	0.4319(3)	0.3133(4)	0.123(6)	0.101(6)	0.114(6)	0.014(5)	-0.024(5)	0.028(5)
C(45)	4e	-0.067(1)	0.3158(6)	0.2056(5)	0.18(2)	0.12(1)	0.12(1)	0.00(1)	0.05(1)	0.02(1)
C(46)	4e	-0.0641(9)	0.2515(6)	0.1661(7)	0.13(1)	0.18(1)	0.083(9)	-0.01(1)	0.044(8)	-0.003(9)
O(1)	4e	0.3019(4)	0.4103(3)	0.4284(3)	0.060(4)	0.069(4)	0.041(4)	-0.002(3)	0.002(3)	-0.004(3)
O(2)	4e	0.3826(4)	0.3069(2)	0.3743(3)	0.060(4)	0.052(4)	0.038(3)	0.010(3)	0.006(3)	0.005(3)
O(3)	4e	0.2170(4)	0.2411(2)	0.3786(3)	0.067(4)	0.049(4)	0.056(4)	0.009(3)	0.018(3)	0.021(3)
O(4)	4e	0.1053(4)	0.3445(2)	0.4193(3)	0.043(3)	0.056(4)	0.044(4)	0.006(3)	0.004(3)	0.008(3)
C(7)	4e	0.5229(6)	0.3997(3)	0.4709(5)	0.050(5)	0.049(6)	0.051(6)	-0.008(4)	0.017(5)	0.009(5)
C(14)	4e	0.4030(5)	0.1699(4)	0.3999(4)	0.049(5)	0.043(5)	0.042(5)	0.008(4)	0.012(4)	-0.005(4)
C(21)	4e	0.0675(5)	0.2139(3)	0.4610(5)	0.043(5)	0.044(5)	0.046(5)	-0.009(4)	0.004(4)	-0.004(4)
C(28)	4e	0.1918(6)	0.4416(3)	0.5414(5)	0.062(6)	0.035(5)	0.054(6)	0.008(4)	0.017(5)	0.000(4)

Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(29)	4e	0.5333(7)	0.4792(5)	0.7508(5)	0.074(8)	0.067(7)	0.050(7)	-0.005(6)	0.007(6)	-0.001(6)
C(30)	4e	0.5065(8)	0.5486(5)	0.7697(6)	0.126(9)	0.083(9)	0.064(7)	-0.012(7)	0.022(7)	-0.016(6)
C(31)	4e	0.5004(8)	0.4351(5)	0.8096(6)	0.15(1)	0.104(9)	0.058(7)	-0.015(8)	0.007(7)	0.012(7)
C(32)	4e	0.6471(8)	0.4747(6)	0.7674(6)	0.084(9)	0.21(1)	0.077(8)	-0.002(9)	-0.009(7)	-0.038(9)
C(33)	4e	0.7418(7)	0.2141(5)	0.6124(6)	0.057(7)	0.078(8)	0.057(7)	0.017(6)	-0.002(6)	-0.006(6)
C(34)	4e	0.7208(9)	0.1541(6)	0.6553(7)	0.105(9)	0.12(1)	0.14(1)	0.015(8)	-0.026(8)	0.05(1)
C(35)	4e	0.8204(7)	0.1984(6)	0.5686(6)	0.067(7)	0.20(1)	0.097(9)	0.049(8)	0.011(7)	-0.004(9)
C(36)	4e	0.7863(8)	0.2629(5)	0.6779(6)	0.124(9)	0.105(9)	0.080(8)	0.035(8)	-0.027(7)	-0.029(8)
C(37)	4e	0.2681(8)	0.0146(4)	0.5725(5)	0.095(8)	0.044(6)	0.047(7)	0.010(6)	0.027(6)	0.014(5)
C(38)	4e	0.2688(8)	0.0279(4)	0.6592(5)	0.119(9)	0.080(8)	0.063(8)	0.001(7)	0.024(6)	0.016(6)
C(39)	4e	0.3654(9)	-0.0214(5)	0.5743(7)	0.18(1)	0.098(9)	0.18(1)	0.075(9)	0.11(1)	0.097(9)
C(40)	4e	0.1734(9)	-0.0281(4)	0.5344(6)	0.15(1)	0.060(7)	0.091(8)	-0.022(8)	0.027(8)	0.011(6)
C(41)	4e	0.1567(7)	0.2860(4)	0.7537(5)	0.070(7)	0.047(6)	0.057(7)	-0.009(5)	0.031(6)	-0.003(5)
C(42)	4e	0.0795(8)	0.3290(5)	0.7808(5)	0.122(9)	0.105(8)	0.063(7)	0.004(7)	0.058(7)	-0.012(6)

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