

References

- Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Klug, H. P. & Alexander, L. (1944). *J. Am. Chem. Soc.* **66**, 1056–1064.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Ohba, S., Shiokawa, K. & Saito, Y. (1987). *Acta Cryst.* **C43**, 189–191.

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Structure of Bis(triethylammonium) Phenylphosphonosulfate

MITSUNORI IZUMI AND KAZUHIKO ICHIKAWA*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

MAMORU SUZUKI AND ISAO TANAKA

Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060, Japan

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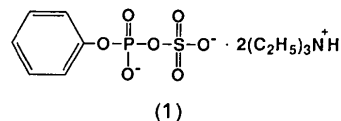
Abstract

Each N—H bond of the two triethylammonium cations faces each of the non-bridging O atoms of the monoanionic phosphate moiety in the phenylphosphonosulfate dianion. The N...O distances of 2.676 (9) and 2.736 (9) Å show the existence of intermolecular N—H...O hydrogen bonds. No direct interactions exist between the two cations and the monoanionic sulfate group.

Comment

Many structural studies have been reported for compounds of biologically important mono-, di- or triphosphate esters (e.g. Calvo, 1967; Aoki, 1979; Kennard *et al.*, 1971). The phosphatosulfate ester bond is very important in biological sulfate-transfer reactions (Peck, 1974), but its structural study has

not been reported. In this paper we report the structure of the title compound (1) and discuss the nature of the phosphatosulfate chain.



The phenyl phosphatosulfate (PPS) was synthesized as described in the literature (Benkovic & Hevey, 1970; Tagaki, Eiki & Tanaka, 1971) and then converted to the title salt. Colourless crystals for data collection were prepared by the dissolution of the salt in acetone followed by the addition of ethyl acetate. Elemental analysis found: C, 47.53; H, 8.21; N, 6.18; S, 6.95%. Calculated for $C_{18}H_{37}N_2O_7PS$: C, 47.36; H, 8.17; N, 6.14; S, 7.02%.

The two triethylammonium cations neutralize the two negative charges of the dianion of (1). As seen from Fig. 1, each of the atoms N(1) and N(2) has a tetrahedral configuration (including the N—H⁺ bond). Each of the N(2)—H(37) and N(1)—H(36) bonds faces the two non-bridging O atoms of the monoanionic phosphate moiety, O(3) and O(2), respectively; the intermolecular bond angles N(2)—H(37)...O(3) and N(1)—H(36)...O(2) are 172.9 (10) and 153.0 (9)°, respectively. The intermolecular distances O(2)...H(36) and O(3)...H(37) are 1.720 (11) and 1.592 (11) Å, N(2)...O(3) and N(1)...O(2) are 2.676 (9) and 2.736 (9) Å, respectively. These values correspond to the hydrogen-bond lengths between each triethylammonium cation and the nearest non-bridging O atom of PPS^{2-} . The literature values are as follows: (i) the N—H...O hydrogen-bond lengths

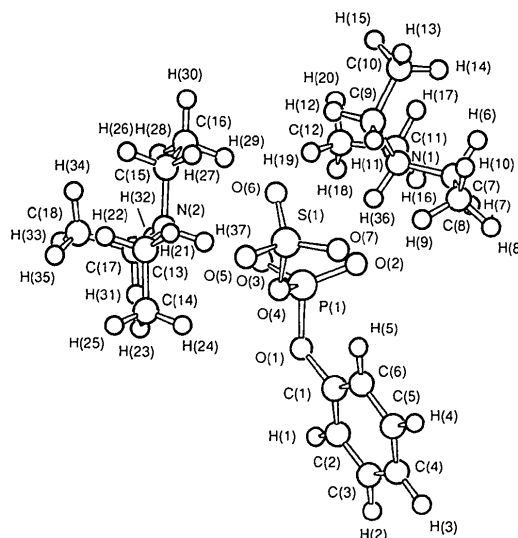


Fig. 1. Molecular structure of the title compound with atomic numbering scheme.

are 1.58–1.89 Å in nucleosides and nucleotides (Jeffrey & Saenger, 1991); (ii) the intermolecular N...O distances are 2.79 (10) (O—H...N) and 2.89 (14) Å (N—H...O) in organic homomolecular crystals (Kuleshova & Zorkii, 1981). While the monovalent anion of the phosphate moiety in (1) interacts with two cations, the sulfate moiety does not interact with any. Thus the non-bridging phosphate O atoms have a much higher affinity for protons than the non-bridging sulfate O atoms.

Experimental

Crystal data



$M_r = 456.53$

Triclinic

$P\bar{1}$

$a = 14.251$ (7) Å

$b = 10.062$ (9) Å

$c = 8.691$ (9) Å

$\alpha = 103.91$ (6)°

$\beta = 90.65$ (7)°

$\gamma = 99.98$ (5)°

$V = 1190.1$ Å³

$Z = 2$

$D_x = 1.274$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from 47

reflections

$\mu = 0.244$ mm⁻¹

$T = 293$ K

Parallelepiped

$0.3 \times 0.2 \times 0.1$ mm

Colourless

Data collection

MAC science DIP100

diffractometer

Oscillation scans

Absorption correction:

none

9378 measured reflections

4347 independent reflections

4075 observed reflections

$[I > 0]$

$\theta_{\max} = 25.3^\circ$

$h = 0 \rightarrow 17$

$k = -12 \rightarrow 11$

$l = -10 \rightarrow 10$

Standard reflections not mea-

sured (data collection by

area detector; see below)

Refinement

Refinement on F

$R = 0.0831$

$wR = 0.0831$

$S = 2.0188$

4075 reflections

263 parameters

H-atom parameters not re-

fined

$w = 1$

$(\Delta/\sigma)_{\max} = 0.022$

$\Delta\rho_{\max} = 0.4$ e Å⁻³

$\Delta\rho_{\min} = -0.76$ e Å⁻³

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	x	y	z	B_{eq}
S(1)	0.2365 (1)	0.1832 (2)	0.0886 (3)	3.60 (6)
P(1)	0.2177 (1)	0.4489 (2)	0.2926 (2)	2.87 (6)
O(1)	0.2222 (3)	0.5906 (5)	0.2355 (6)	3.35 (18)
O(2)	0.3065 (4)	0.4520 (5)	0.3846 (6)	3.61 (19)
O(3)	0.1241 (4)	0.4298 (5)	0.3650 (6)	3.93 (19)
O(4)	0.2113 (3)	0.3401 (5)	0.1200 (6)	3.15 (17)

O(5)	0.1903 (5)	0.1184 (6)	-0.0642 (7)	5.36 (26)
O(6)	0.1937 (6)	0.1272 (7)	0.2126 (8)	6.40 (32)
O(7)	0.3380 (4)	0.2039 (7)	0.0904 (11)	7.21 (33)
N(1)	0.3599 (5)	0.2792 (7)	0.5555 (8)	3.79 (24)
N(2)	-0.0389 (4)	0.2563 (6)	0.2484 (8)	3.51 (22)
C(1)	0.2992 (5)	0.6586 (7)	0.1693 (8)	2.89 (23)
C(2)	0.2990 (6)	0.7968 (8)	0.1769 (10)	3.90 (29)
C(3)	0.3718 (7)	0.8704 (8)	0.1104 (11)	4.66 (35)
C(4)	0.4434 (6)	0.8075 (8)	0.0364 (10)	4.20 (32)
C(5)	0.4416 (6)	0.6688 (8)	0.0289 (10)	3.95 (30)
C(6)	0.3703 (5)	0.5921 (7)	0.0943 (9)	3.44 (27)
C(7)	0.4669 (6)	0.3202 (9)	0.5606 (11)	4.85 (35)
C(8)	0.5100 (7)	0.2733 (11)	0.4006 (14)	6.09 (45)
C(9)	0.3266 (7)	0.1243 (9)	0.5045 (11)	4.89 (36)
C(10)	0.3600 (9)	0.0457 (11)	0.6145 (15)	6.94 (53)
C(11)	0.3222 (8)	0.3459 (10)	0.7108 (11)	5.57 (42)
C(12)	0.2149 (9)	0.3285 (14)	0.7079 (14)	7.15 (56)
C(13)	-0.0388 (6)	0.1949 (10)	0.0723 (11)	4.82 (34)
C(14)	-0.0225 (8)	0.3015 (13)	-0.0257 (13)	6.43 (48)
C(15)	-0.0483 (7)	0.1422 (10)	0.3359 (12)	5.16 (38)
C(16)	-0.0467 (10)	0.1951 (14)	0.5124 (14)	7.70 (58)
C(17)	-0.1098 (6)	0.3507 (9)	0.2908 (12)	5.03 (36)
C(18)	-0.2122 (7)	0.2801 (13)	0.2581 (16)	7.09 (52)

Table 2. Selected geometry (Å, °)

P(1)—O(1)	1.610 (6)	N(1)—C(11)	1.506 (13)
P(1)—O(2)	1.480 (6)	N(1)···O(2)	2.736 (9)
P(1)—O(3)	1.484 (6)	N(1)—H(36)	1.090 (12)
P(1)—O(4)	1.622 (5)	N(2)—C(13)	1.507 (12)
S(1)—O(4)	1.640 (5)	N(2)—C(15)	1.512 (12)
S(1)—O(5)	1.428 (7)	N(2)—C(17)	1.494 (12)
S(1)—O(6)	1.427 (9)	N(2)···O(3)	2.676 (9)
S(1)—O(7)	1.424 (10)	N(2)—H(37)	1.089 (12)
N(1)—C(7)	1.507 (12)	O(2)···H(36)	1.720 (11)
N(1)—C(9)	1.503 (12)	O(3)···H(37)	1.592 (11)
O(1)—P(1)—O(2)	110.9 (3)	H(36)—N(1)—C(7)	108.0 (8)
O(1)—P(1)—O(3)	104.2 (3)	H(36)—N(1)—C(9)	104.8 (8)
O(1)—P(1)—O(4)	98.9 (3)	H(36)—N(1)—C(11)	107.3 (8)
O(2)—P(1)—O(3)	120.3 (3)	C(7)—N(1)—C(9)	112.7 (7)
O(2)—P(1)—O(4)	111.1 (3)	C(7)—N(1)—C(11)	110.3 (7)
O(3)—P(1)—O(4)	109.2 (3)	C(9)—N(1)—C(11)	113.4 (7)
O(4)—S(1)—O(5)	101.6 (4)	H(37)—N(2)—C(13)	108.4 (8)
O(4)—S(1)—O(6)	105.1 (4)	H(37)—N(2)—C(15)	107.2 (8)
O(4)—S(1)—O(7)	104.7 (4)	H(37)—N(2)—C(17)	103.9 (8)
O(5)—S(1)—O(6)	113.4 (5)	C(13)—N(2)—C(15)	110.0 (7)
O(5)—S(1)—O(7)	114.1 (5)	C(13)—N(2)—C(17)	112.9 (7)
O(6)—S(1)—O(7)	115.9 (5)	C(15)—N(2)—C(17)	114.0 (7)
P(1)—O(2)···H(36)	125.0 (4)	N(1)—H(36)···O(2)	153.0 (9)
P(1)—O(3)···H(37)	126.9 (5)	N(2)—H(37)···O(3)	172.9 (10)
P(1)—O(4)—S(1)	124.7 (3)		

Crystals became disordered rapidly when allowed to dry in air. Thus, a single crystal was sealed inside an X-ray capillary tube for use with the X-ray experiment. A rapid data-collection system, MAC science DIP100 using Fuji Imaging Plate as an X-ray detector (Tanaka *et al.*, 1990), was used to measure the intensity data to minimize radiation damage. The overall R_{merge} value was 0.0297 [$R_{\text{merge}} = \sum \sum |I(h)_j - \langle I(h) \rangle| / \sum \sum I(h)_j$, where $I(h)$ is the measured diffraction intensity and the summation includes all observations]. The structure was solved by the Monte Carlo MULTAN method (Furusaki, 1979). H atoms were located in a difference electron density map except for the methyl H atoms, the locations of which were calculated by assuming the staggered form.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71320 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1022]

References

- Aoki, K. (1979). *J. Chem. Soc. Chem. Commun.* pp. 589–591.
 Benkovic, S. J. & Hevey, R. C. (1970). *J. Am. Chem. Soc.* **92**, 4971–4977.
 Calvo, C. (1967). *Acta Cryst.* **23**, 289–295.
 Furusaki, A. (1979). *Acta Cryst.* **A35**, 220–224.
 Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*, p. 130. Berlin: Springer-Verlag.
 Kennard, O., Isaacs, N. W., Motherwell, W. D. S., Coppola, J. C., Wampler, D. L., Larson, A. C. & Watson, D. G. (1971). *Proc. R. Soc. London Ser. A*, **325**, 401–436.
 Kuleshova, L. N. & Zorkii, P. M. (1981). *Acta Cryst.* **B37**, 1363–1366.
 Peck, H. D. Jr (1974). *Enzymes*, **10**, 651–669.
 Tagaki, W., Eiki, T. & Tanaka, I. (1971). *Bull. Chem. Soc. Jpn*, **44**, 1139–1141.
 Tanaka, I., Yao, M., Suzuki, M., Hikichi, K., Matsumoto, T., Kozasa, M. & Katayama, C. (1990). *J. Appl. Cryst.* **23**, 334–339.

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Structure of Diethyl 5,11,17,23-Tetra-*tert*-butyl-26,28-bis(2-methoxyethoxy)-calix[4]arene-25,27-bis(oxyacetate)

ABDELHALIM GUELZIM,* SAAD KHRIFI AND FRANCOIS BAERT

Laboratoire de Dynamique et de Structure des Matériaux Moléculaires, URA CNRS 801, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

ZOUHAIR ASFARI AND JACQUES VICENS

Laboratoire de Chimie Analytique et Minérale, URA CNRS 405, Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, 1 Rue Blaise Pascal, 67008 Strasbourg, France

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Abstract

We present here the synthesis and X-ray crystal structure of a new 2 + 2' modified *p-tert*-butylcalix[4]arene, diethyl {5,11,17,23-tetra-*tert*-butyl-26,28-bis(2-methoxyethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosal(25),3,5,7(28),9,11,13(27),15,17,19(26),-21,23-dodecaene-25,27-diyldioxy}diacetate, bearing glycol methyl ether and ethyl ester functional groups. ¹H NMR spectra of this compound indicated that it has a cone conformation; this is confirmed by the crystallographic study.

Comment

Calix[4]arenes are a new class of macrocyclic compounds, which are easily transformed into various derivatives at the 'lower rim' by complete alkylation of the phenolic functional groups (Gutsche, 1989; Vicens & Böhmer, 1991). As a result of selective 1,3-dialkylation of *p-tert*-butylcalix[4]arene (Gutsche, 1989; Vicens & Böhmer, 1991), conformationally stable modified-tetrameric structures with the 2 + 2' functional group disposition having distal 1,3-regiochemistry have been developed. They are synthesized by treatment of *p-tert*-butylcalix[4]arene with various electrophiles such as ethyl bromoacetate, chloroacetone, bromopinacolone and chloroacetonitrile in basic conditions (Collins, McKervey & Harris, 1989; Collins *et al.*, 1991).

Final atomic coordinates of non-H atoms and equivalent isotropic thermal parameters are listed in Table 1; bond lengths and angles are shown in Table 2. As depicted in Fig. 1, the molecule clearly shows a cone structure, although slightly distorted in two regions. Molecular geometry can be related to the mean molecular plane of the methylene groups where the CH₂ bridges show out-of-plane distances of –0.188, 0.189, –0.188 and 0.187 Å. With respect to this ideal plane, we can distinguish a hydrophilic region above it, created by the oxygens of the ether and ester groups, and a hydrophobic cavity below it, created by the aromatic and *tert*-butyl groups. The conformation of the macrocycle may be defined by the dihedral angles between the aromatic rings and this mean molecular plane, which are 44.3, 85.7, 132.9 and 93.7°. The relative dihedral angles between two adjacent rings are 79.1, 84.9, 86.4 and 80.9°, and between two opposite rings are 88.7 and 80.5°.

The conformation of the ester chains may be conveniently described by the C(1)—O(1)—C(7)—C(8) and C(35)—O(6)—C(36)—C(37) torsion angles which are 95.2 and 86.4°, respectively, whereas the corresponding values for the ether oxide chains, C(21)—O(4)—C(22)—C(23) and C(50)—O(9)—C(51)—C(52), are 173.7 and 165°, respectively. Therefore the ether oxide chains attached to the aromatic rings are almost parallel to each other and perpendicular to the mean molecular plane. Thus the methylene groups of the ether oxide chains point outwards, whereas the methylene groups of the ester chains point inwards and the COOEt moieties are inside the hydrophilic cavity (Fig. 2). Bond angles involving the bridging methylenes are 112.0 (11), 110.4 (11), 112.3 (10) and 106.1 (10)°, which deviate slightly from the theoretical value of 109.5°. This shows that the macrocycle conformation, in the absence of any intramolecular hydrogen bonding, is mainly determined by steric interaction between the different chains. This is also confirmed by the torsion angles involving the bridging methylene C atoms