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Bis(2,6-dimethylphenyl) Chlorothiophosphate

Muhittin Aygün,[a] Şamil Işık,[a] Mustafa Odabaşoğlu,[b] M. Nawaz Tahir,[c] Ahmet Erdönmez[a] and Orhan Büyükgüngör[a]

[a]*Department of Physics, Faculty of Buca Education, Dokuz Eylul University, 35510 Buca/Izmir, Turkey,* [b]*Department of Chemistry, Ondokuz Mayís University, TR-55139 Samsun, Turkey, and* [c]*Department of Physics Engineering, Hacettepe University, Beytepe 06532, Ankara, Turkey. E-mail: aygunm@samsun.omu.edu.tr*

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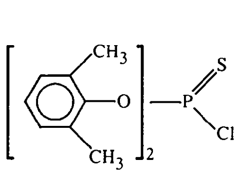
Abstract

The title compound, $C_{16}H_{18}ClO_2PS$, displays distorted tetrahedral geometry around the P atom and has twofold axial symmetry, with the S and Cl atoms disordered about the twofold axis. The distance between these partially populated sites is 0.40 (2) Å. The dihedral angle between the two dimethylphenyl rings is 74.54 (8)° and the P—O bond distance is 1.566 (2) Å.

Comment

The use of phosphorus compounds in food manufacture, water treatment, insecticides, detergents, oil additives and resins, and biochemical studies on phosphate metabolism, has attracted many scientists to the study of their spectroscopic and various other properties (Corbridge, 1956; Bellamy & Beecher, 1952; Pastor *et al.*, 1988). The molecular structure of the title compound, (I), has been determined and the results are presented here.



(I)

A perspective view of the molecule with the atomic numbering scheme is shown in Fig. 1. The disordered S and Cl atoms are positioned nearly symmetrically on either side of the molecule with respect to the twofold axis. The partially populated S and Cl atoms are within 0.40 (2) Å of each other; their positions are not as certain as the formal standard uncertainty would suggest. The asymmetric unit corresponds to one half of the molecule, with the P atom sitting on the twofold axis along **b**. The rest of the molecule is generated by the symmetry operation $(1 - x, y, \frac{3}{2} - z)$. This disorder is similar to that seen in *N*-[1-(2-benzo[*b*]thienyl)ethyl]-*N'*-carbamoylurea (Henry *et al.*, 1996).

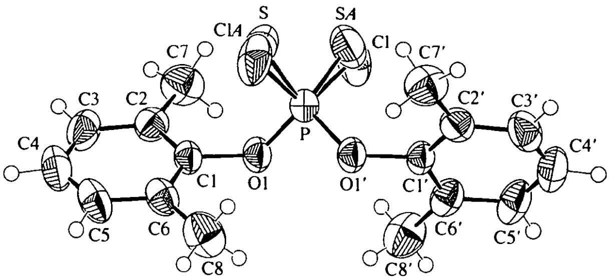


Fig. 1. View of the title molecule drawn using *ORTEP*II (Johnson, 1976) with 50% probability ellipsoids.

The S, Cl and two O atoms have severely distorted tetrahedral geometry about the P atom [angles 101.3 (1)–113.7 (3)°]. The P═S bond length of 1.914 (9) Å agrees well with the reported value of 1.908 (1) Å for tris(*O*-4-*tert*-butylphenyl)thiophosphate (Büyükgüngör *et al.*, 1995). The P—Cl bond length of 1.976 (7) Å agrees well with the value of 1.981 (1) Å reported for 2-(2,6-di-*tert*-butyl-4-methylphenoxy)-2,4,4,6,6,8,8-heptachlorocyclo-$2\lambda^5,4\lambda^5,6\lambda^5,8\lambda^5$-tetraphosphazatetraene (Hökelek *et al.*, 1996). The mean bond lengths averaged over each type of bond agree well with the values observed in similar compounds (Odabaşoğlu *et al.*, 1992; Krishnaiah *et al.*, 1996).

The angles C1—C2—C3 [116.0 (2)°], C5—C6—C1 [116.4 (2)°] and C2—C1—C6 [124.6 (2)°] within the dimethylphenyl rings appear to be unusual; the diversity of these angles is probably due to the steric effects of the methyl groups. Each dimethylphenyl ring is nearly planar, with a maximum deviation from the plane defined by the six ring atoms of 0.011 (1) Å, while the substituent atoms C7, C8 and O1 deviate by 0.057 (4), 0.047 (5) and 0.045 (3) Å, respectively, from this plane.

Experimental

The synthesis of the title compound and the ^{1}H NMR, IR and UV spectroscopic characterizations have been described by Odabaşoğlu & Gümrükçüoğlu (1993). IR (KBr) data for the title compound are as follows: 1195–940 (C—O—P), 705 (P═S), 515 cm^{-1} (P—Cl). Colourless semi-transparent crystals suitable for X-ray diffraction were obtained by slowly cooling a saturated solution in hot *n*-hexane to room temperature.

Crystal data

$C_{16}H_{18}ClO_2PS$	Mo $K\alpha$ radiation
$M_r = 340.78$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25 reflections
$C2/c$	$\theta = 9.67–18.35°$
$a = 18.049 (1)$ Å	$\mu = 0.442$ mm^{-1}
$b = 8.637 (1)$ Å	$T = 293 (2)$ K
$c = 13.908 (1)$ Å	Prismatic
$\beta = 128.25 (5)°$	$0.34 \times 0.30 \times 0.23$ mm
$V = 1702.7 (3)$ Å^3	Colourless, semi-transparent
$Z = 4$	
$D_x = 1.329$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	1162 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$\theta_{max} = 23.53°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 20$
$T_{min} = 0.882$, $T_{max} = 0.903$	$k = 0 \rightarrow 9$
1269 measured reflections	$l = -15 \rightarrow 12$
1269 independent reflections	3 standard reflections frequency: 120 min intensity decay: 1.52%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.003$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
$wR(F^2) = 0.087$	$\Delta\rho_{min} = -0.19$ e Å^{-3}
$S = 1.141$	Extinction correction: none
1269 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
141 parameters	
All H atoms refined	
$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 1.0525P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	1/2	0.03435 (9)	3/4	0.0496 (2)
S†	0.4656 (7)	0.1728 (11)	0.8239 (9)	0.081 (2)
ClA†	0.4634 (6)	0.1391 (10)	0.8413 (8)	0.085 (2)
O1	0.58104 (9)	−0.0806 (2)	0.84275 (12)	0.0479 (4)
C1	0.67350 (12)	−0.0869 (2)	0.8779 (2)	0.0434 (4)
C2	0.74426 (14)	−0.0095 (2)	0.9825 (2)	0.0511 (5)
C3	0.8347 (2)	−0.0236 (3)	1.0159 (2)	0.0670 (7)
C4	0.8508 (2)	−0.1120 (3)	0.9486 (3)	0.0712 (7)
C5	0.7785 (2)	−0.1889 (3)	0.8472 (2)	0.0655 (6)
C6	0.68706 (14)	−0.1794 (2)	0.8085 (2)	0.0525 (5)
C7	0.7258 (2)	0.0823 (4)	1.0567 (3)	0.0728 (7)
C8	0.6084 (2)	−0.2666 (4)	0.6993 (3)	0.0772 (8)

† Site occupancy = 0.50.

Table 2. *Selected geometric parameters (Å, °)*

P—O1	1.566 (2)	O1—C1	1.420 (2)
P—S	1.914 (9)	C2—C7	1.494 (3)
P—ClA	1.976 (7)	C6—C8	1.490 (4)
O1^i—P—O1	101.33 (12)	C1—O1—P	127.42 (12)
O1^i—P—S	113.0 (3)	C2—C1—C6	124.6 (2)
O1—P—S	113.7 (3)	C2—C1—O1	118.0 (2)
S—P—S^i	102.7 (6)	C1—C2—C3	116.0 (2)
O1^i—P—ClA	107.8 (3)	C1—C2—C7	122.0 (2)
O1—P—ClA	105.9 (3)	C5—C6—C1	116.4 (2)
ClA—P—ClA^i	125.5 (5)	C1—C6—C8	122.2 (2)
O1^i—P—O1—C1	124.3 (2)	P—O1—C1—C2	94.9 (2)
S—P—O1—C1	−114.2 (3)	P—O1—C1—C6	−89.2 (2)
S^i—P—O1—C1	2.3 (3)	O1—C1—C2—C3	177.8 (2)
ClA—P—O1—C1	−123.2 (3)	O1—C1—C2—C7	−1.4 (3)
ClA^i—P—O1—C1	13.3 (3)	O1—C1—C6—C5	−177.5 (2)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

The intensities were corrected for Lorentz–polarization and absorption effects. The structure was solved by direct methods and refined using full-matrix least-squares techniques with all non-H atoms anisotropic. The H atoms were located from difference Fourier maps and refined isotropically. The C—H bond lengths range from 0.92 (3) to 0.99 (3) Å, while U_{iso} values range from 0.075 (7) to 0.13 (1) Å^2. The disorder appears to be restricted to one pair of symmetry-related atoms with equal proportions in the molecule. Modelling of this as a disordered overlap of S and Cl atoms was successful, with no constraints or restraints necessary on the geometrical parameters.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1051). Services for accessing these data are described at the back of the journal.

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Ethylenediammonium Bis(monohydrogen oxalate) Monohydrate and Two Modifications of Trimethylenediammonium Bis(monohydrogen oxalate) Monohydrate

John C. Barnes,[a] Rayne W. Longhurst[a] and Timothy J. R. Weakley[b]

[a]*Department of Chemistry, University of Dundee, Perth Road, Dundee DD1 4HN, Scotland, and* [b]*Department of Chemistry, University of Oregon, Eugene, OR 97403-1253, USA. E-mail: j.c.barnes@dundee.ac.uk*

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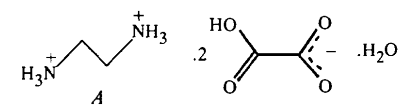
Abstract

Essential features of the crystal structures of $[NH_3\text{-}(CH_2)_nNH_3]^{2+}.2(HOOCCOO)^-.H_2O$ ($0 < n < 6$) are preserved through changes of conformation and space group. In each of the title structures, ethylenediammonium bis(monohydrogen oxalate) monohydrate, $C_2H_{10}N_2^{2+}.2C_2HO_4^-.H_2O$, and two modifications of trimethylenediammonium bis(monohydrogen oxalate) monohydrate, $C_3H_{12}N_2^{2+}.2C_2HO_4^-.H_2O$, the cation and the water molecule occupy special positions. Linear hydrogen-bonded (Hoxalate)$_n$ chains are parallel to and connected to hydrogen-bonded spirals in which the water molecules link anions and cations. Unique to each structure are additional hydrogen bonds, perpendicular to these chains, which connect cations and anions into three-dimensional arrays.

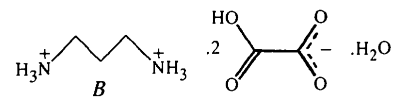
Comment

The hydrogen oxalate ion is an important species in solution. The close proximity of the COOH groups in oxalic acid leads to a wide separation of the pK_a values (1.37 and 3.81; McAuley & Nancollas, 1960) compared with, for example, succinic acid, (HOOC—CH_2—)$_2$, for which the pK_a values are 4.0 and 5.21 (Yasada *et al.*, 1960). There are many reports of the hydrogen oxalate ion in crystals. The ion is usually near-planar and connected into chains by short (2.49–2.57 Å) hydrogen bonds, with O—H typically 0.88 (3) and H···O 1.68 (3) Å (*e.g.* Küppers, 1973).

In the present work, the title salts, ethylenediammonium bis(monohydrogen oxalate) monohydrate, (1), and two modifications of trimethylenediammonium bis(monohydrogen oxalate) monohydrate, (2) and (3), were the only crystalline products obtained from aqueous mixtures of oxalic acid and ethylenediamine, or trimethylenediamine, regardless of the ratio of the components. Trimethylenediamine samples contained (2) and



(1)



(2), (3)

(3) as morphologically different forms in a ratio of approximately 1:4. The same stoichiometry [cation^{2+}.-2(Hoxalate).H_2O] is known for the tetramethylenediammonium (Babu, Weakley & Murthy, 1998) and hexamethylenediammonium (Vijayalakshmi & Srinivasan, 1983) salts. Although some of these crystals are monoclinic and others orthorhombic, the three-dimensional hydrogen-bonded networks are very similar. The water molecule and the cation lie on special positions, making the N atoms equivalent. The atomic numbering schemes for the ethylenediammonium cation, the trimethylenediammonium cation and the anion are shown in Fig. 1, while details of the symmetries and conformations are given in Table 2.

Packing diagrams are shown in Figs. 2, 3 and 4 for (1), (2) and (3), respectively. In each case, the hydrogen oxalate anions are connected into chains (perpendicular to the page in each figure) by O15—H151···O12′ hydrogen bonds. Tetrahedral hydrogen bonding of the water molecule (O21) connects these anions and the cations into two symmetry-related spirals linked at the water molecules. Fig. 5 shows these spirals with the repeat unit [N1—H11···O21—H211···O11···H12′—N1′], in which N1···O21, O21···O11 and O11···N1′ distances average 2.77 (1), 2.72 (1) and 2.83 (1) Å, respectively. The angles at the H atoms are in the range 157–175°. (Symmetry codes for the individual structures are given in the tables.)

Unique to each structure are the symmetry relationships between the anions in the chain and the interaction of the H13 atom (bonded to N1 but not used in the interactions described above) with O atoms of the anion to give two possible but less satisfactory hydrogen bonds, with N1···O distances in the range 2.8–3.2 Å and angles at hydrogen in the range 129–151°.