

Acta Cryst. (1997). **C53**, 1451–1452**Tris(3-chlorophenyl)phosphine Oxide**OMAR BIN SHAWKATALY,^a KUPPUKANNU RAMALINGAM,^{a†} SUPPRAMANIAN SELVAKUMAR,^a HOONG-KUN FUN^b AND ABDUL RAZAK IBRAHIM^b^a*Chemical Sciences Programme, Centre for Distance Education, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and* ^b*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: omarsa@usm.my*

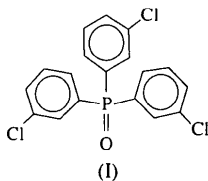
(Received 24 March 1997; accepted 21 April 1997)

Abstract

In the title compound, C₁₈H₁₂Cl₃OP, the P—O bond distance is 1.483 (3) Å and the mean C—Cl distance is 1.741 (4) Å. Two sets of significantly different P—C—C bond angles are observed: 115.8 (3) and 124.3 (3)°. However, the mean O—P—C bond angle [112.0 (1)°] indicates near-ideal tetrahedral coordination at the P atom. The presence of bulky chloro substituents is manifested by the different orientations of the phenyl rings.

Comment

Triphenylphosphine oxide has been shown to co-crystallize with a number of proton donors (Al-Farhan, 1993; Lynch, Smith, Byriel & Kennard, 1992; Fenske, Teichert & Becher, 1976). Formation of crystalline complexes with UO₂²⁺ has also been reported (Panotoni, Graziani, Croatto, Zarli & Bombieri, 1968). There has been considerable ambiguity about the stereochemistry of triphenylphosphine oxide; four crystal structure reports have been published (Bandoli, Bortolozzo, Clemente, Croatto & Panotoni, 1970; Ruban & Zabel, 1976; Spek, 1987; Baures & Silverton, 1990), each involving a different space group. This report describes the crystal structure of a related compound, tris(3-chlorophenyl)phosphine oxide, (I).



The P—O distance in (I), 1.483 (3) Å, is similar to the value reported recently for triphenylphosphine oxide,

† On leave from: Department of Chemistry, Annamalai University, Annamalaiagar 608 002, Tamilnadu, India.

1.487 (2) Å (Baures & Silverton, 1990). The mean P—C bond distance is 1.813 (3) Å, which is slightly longer than the distances observed in triphenylphosphine oxide and its compounds; P—C 1.799 (3) Å in OPPh₃ (Baures & Silverton, 1990) and P—C 1.76 (1) Å in its adduct with tricarboxylic acid (Lynch, Smith, Byriel & Kennard, 1992). This slight lengthening is probably due to the presence of electronegative chloro substituents in the phenyl rings. The mean Cl—C distance is 1.742 (4) Å. The C—C bond lengths in the phenyl rings are normal.

The mean O—P—C bond angle is 112.0 (1)°, indicating tetrahedral coordination at the P atom. The C—P—C bond angles show considerable variation: 105.2 (1), 106.7 (2) and 108.7 (1)° for C1—P—C7, C1—P—C13 and C7—P—C13, respectively. All the phenyl rings are planar. The dihedral angles between the planes of the phenyl rings and the planes containing O, P and the corresponding *ipso*-C atom are 26.5 (1), 22.4 (1) and 16.9 (1)°. In contrast, in the unsubstituted analogue, these angles are 77.2 (1), 36.3 (1) and 11.9 (1)°.

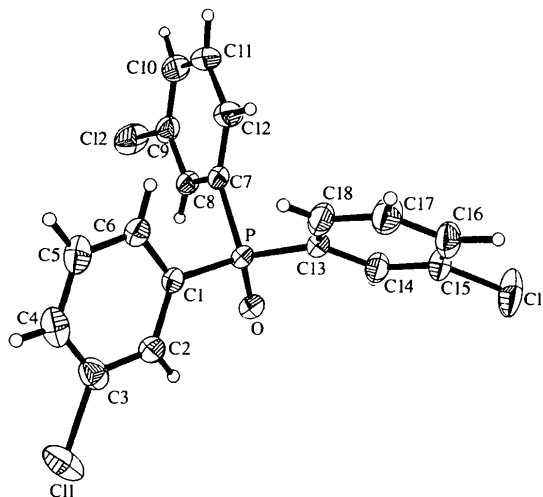


Fig. 1. A view of the title compound with displacement ellipsoids drawn at the 30% probability level; H atoms are shown as spheres of arbitrary size.

Experimental

Fine light-yellow crystals of the title compound were separated as a by-product. A reaction mixture containing Cr(CO)₆ and tris(3-chlorophenyl)phosphine (1:1 ratio) was heated under reflux for 6 h and then reduced to half its volume. A light-yellow solid separated, which was repeatedly recrystallized from a solvent mixture of toluene–dichloromethane–*n*-hexane (1:2:1). Crystals of the title compound separated on the sides of the container as a result of aerial oxidation of the phosphine, leaving the pale Cr(CO)₅[P(C₆H₄Cl)₃] compound at the bottom.

*Crystal data*C₁₈H₁₂Cl₃OP $M_r = 381.60$

Triclinic

 $P\bar{1}$ $a = 6.1930 (10) \text{ \AA}$ $b = 9.0770 (10) \text{ \AA}$ $c = 15.8820 (2) \text{ \AA}$ $\alpha = 90.690 (10)^\circ$ $\beta = 96.390 (10)^\circ$ $\gamma = 101.750 (10)^\circ$ $V = 868.1 (2) \text{ \AA}^3$ $Z = 2$ $D_x = 1.460 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 39

reflections

 $\theta = 4.82\text{--}12.46^\circ$ $\mu = 0.620 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Thin rod

 $0.46 \times 0.22 \times 0.22 \text{ mm}$

Light yellow

Data collection

Siemens P4 diffractometer

 $\theta/2\theta$ scans

Absorption correction:

empirical ψ scans

(Siemens, 1994)

 $T_{\min} = 0.637$, $T_{\max} = 0.872$

5055 measured reflections

3963 independent reflections

2387 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.019$ $\theta_{\max} = 27.49^\circ$ $h = -1 \rightarrow 8$ $k = -11 \rightarrow 11$ $l = -20 \rightarrow 20$

3 standard reflections

every 97 reflections

intensity decay: $<3\%$ *Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.061$ $wR(F^2) = 0.175$ $S = 0.908$

3963 reflections

256 parameters

All H atoms refined

 $w = 1/[\sigma^2(F_o^2) + (0.1125P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.67 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.38 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Universiti Sains Malaysia for a Visiting Postdoctoral Research Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1324). Services for accessing these data are described at the back of the journal.

References

- Al-Farhan, K. A. (1993). *Z. Kristallogr.* **208**, 181–186.
- Baures, P. W. & Silverton, J. V. (1990). *Acta Cryst.* **C46**, 715–717.
- Bandoli, G., Bortolozzo, G., Clemente, D. A., Croatto, U. & Panotoni, C. (1970). *J. Chem. Soc. A*, pp. 2278–2280.
- Fenske, D., Teichert, H. & Becher, H. J. (1976). *Chem. Ber.* **109**, 363–369.
- Lynch, D. E., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1992). *Aust. J. Chem.* **45**, 835–844.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Panotoni, C., Graziani, R., Croatto, U., Zarli, B. & Bombieri, G. (1968). *Inorg. Chim. Acta*, **2**, 43–48.
- Ruban, G. & Zabel, V. (1976). *Cryst. Struct. Commun.* **5**, 671–677.
- Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1987). *Acta Cryst.* **C43**, 1233–1235.

Acta Cryst. (1997). **C53**, 1452–1454***p*-Nitrobenzaldehyde Isonicotinoyl-hydrazone**

HOONG-KUN FUN,^a ZHONG-LIN LU,^b CHUN-YING DUAN,^b
YU-PENG TIAN,^b XIAO-ZENG YOU,^b YU-MEI GUO^c AND
XIAO-YANG GONG^c

^a*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia,*
^b*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Center for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, People's Republic of China, and*
^c*The Hospital of County Gangu, Gansu Province 741200, People's Republic of China. E-mail: hkfun@usm.my*

(Received 25 March 1997; accepted 30 May 1997)

Abstract

Molecules of the hydrazone C₁₃H₁₀N₄O₃ are planar and exist in the keto tautomeric form. The configuration at the azomethine C=N double bond is *E*. The structure is stabilized by a network of hydrogen bonds.

Table 1. *Selected geometric parameters* (\AA , $^\circ$)

P—O	1.483 (3)	C11—C3	1.740 (4)
P—C7	1.810 (3)	C12—C9	1.741 (4)
P—C13	1.812 (3)	C13—C15	1.744 (4)
P—C1	1.816 (3)		
O—P—C7	111.7 (2)	C6—C1—P	123.9 (3)
O—P—C13	111.88 (14)	C2—C1—P	116.4 (3)
C7—P—C13	108.69 (14)	C12—C7—P	124.7 (3)
O—P—C1	112.35 (14)	C8—C7—P	115.3 (2)
C7—P—C1	105.16 (14)	C18—C13—P	124.3 (3)
C13—P—C1	106.7 (2)	C14—C13—P	115.8 (3)

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: direct methods *SHELXTL/PC* (Sheldrick, 1990) and *PARST* (Nardelli, 1983). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grants 09-02-05-6034 and 09-02-05-6024. KR thanks