Triphenylphosphine oxide–3-chloro-benzoic acid (1/1)

Khalid A. Al-Farhan

Department of Chemistry, College of Science, King Saud University, PO Box 2455, Riyadh 11451, Saudi Arabia
Correspondence e-mail: farhank@ksu.edu.sa

In the title compound, $C_{18}H_{15}OP \cdot C_7H_5ClO_2$, the triphenyl-phosphine oxide molecule forms a single directed hydrogen bond with the 3-chlorobenzoic acid molecule, with an $O \cdots O \!=\! P$ distance of 2.607 (2) Å. The C—Cl and C=O bonds adopt a *cisoid* conformation in the 3-chlorobenzoic acid molecule.

Comment

Triphenylphosphine oxide (TPPO) is a very useful molecule for hydrogen-bond model studies. Its bulky shape, its conformational flexibility *via* rotation of the phenyl rings about the P—C bonds and the electron-density concentration at the phosphoryl O atom make it capable of forming strong, medium and weak hydrogen bonds of different types with various H-atom donors (Al-Farhan *et al.*, 1990; Fuquen & Lechat, 1992; Baures, 1991). The hydrogen bond itself is of major interest in chemistry and biology. Because the hydrogen bond is sufficiently strong and directional, it is able to control and direct the structures of molecular assemblies. This control is both reliable and reproducible enough to be used in molecular recognition and crystal engineering (Desiraju & Steiner, 1999; Etter & Baures, 1988; Etter *et al.*, 1986, 1990; Rebek *et al.*, 1987, 1988). As part of our hydrogen-bond studies involving TPPO, the crystal structure determination of the 1:1 adduct with 3-chorobenzoic acid, (I), was undertaken and the results are presented here.
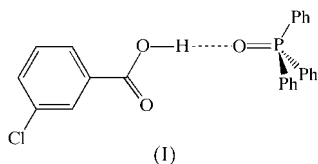
In (I) the TPPO and 3-chlorobenzoic acid molecules are linked by a single directed hydrogen bond (graph-set *D*; Etter, 1990). A view of the adduct with the atom-numbering scheme is given in Fig. 1 and selected geometric parameters are given in Table 1.

The relevant distances and angles within the directed hydrogen-bond interaction in (I) are O2—H1 = 0.85 (3) and O1···O2 = 2.607 (2) Å, and O2—H1···O1 = 171 (3), C19—O2···O1 = 115.98 (15) and P1—O1···O2 = 151.8 (1)°. As a result of the hydrogen bonding, the P1—O1 distance of 1.492 (2) Å is 0.013 Å longer than the P—O distance in free TPPO (Al-Farhan, 1992). The P1—O1 and O1···O2 values in (I) compare with the values of 1.492 (2) and 2.630 (4) Å (Fuquen & Lechat, 1992) and 1.496 (2) and 2.645 (2) Å (Gramstad *et al.*, 1986) for the TPPO adducts with 4-nitro-phenol and pentafluorophenol, respectively.
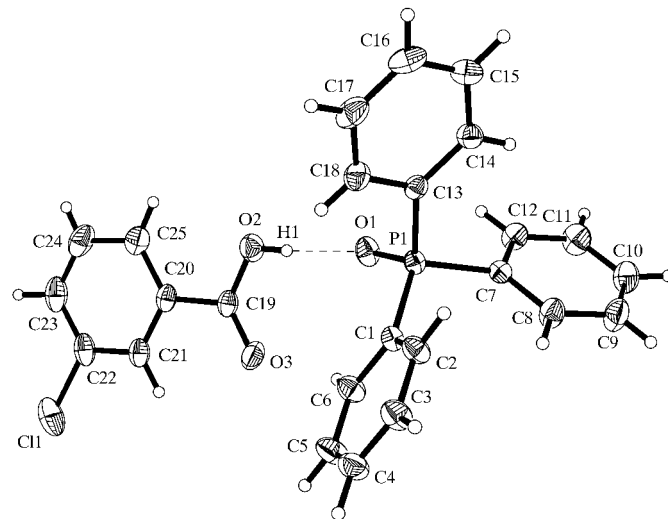

Figure 1
A view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The hydrogen bond is indicated by a dashed line.

The dihedral angles between the TPPO phenyl rings in (I), C1–C6/C7–C12, C1–C6/C13–C18 and C7–C12/C13–C18, are 70.3 (1), 66.2 (1) and 81.5 (1)°, respectively. The O—P—C—C torsion angles of TPPO are 21.2 (2), 33.3 (2) and 74.8 (2)°, and these are distinctly different from the minimum-energy conformation (threefold symmetry and torsion angles of 40°) deduced from analysis of the observed conformations of a wide range of TPPO derivatives (Bye *et al.*, 1982).

The significant structural change in 3-chlorobenzoic acid is that the C—Cl and C=O bonds have adopted a *cisoid* conformation in (I), whereas they are in a *transoid* conformation in the crystal structure of pure 3-chlorobenzoic acid (Gougoutas & Lessinger, 1975). The dihedral angle between the plane of the benzene ring and that of the carboxylic acid group is 3.0 (4)°.

Examination of the structure with *PLATON* (Spek, 2003) showed that there were no solvent-accessible voids in the crystal lattice of (I).

Experimental

The title compound was prepared by mixing equimolar amounts of TPPO and 3-chlorobenzoic acid in CCl$_4$. Slow evaporation of the solvent afforded colourless crystals of (I) suitable for X-ray analysis.

organic compounds

Crystal data

$C_{18}H_{15}OP \cdot C_7H_5ClO_2$
$M_r = 434.83$
Monoclinic, $P2_1/n$
$a = 8.845\ (1)$ Å
$b = 16.101\ (1)$ Å
$c = 16.029\ (2)$ Å
$\beta = 103.97\ (1)°$
$V = 2215.2\ (4)$ Å^3
$Z = 4$
$D_x = 1.304$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 17.4–17.5°$
$\mu = 0.27$ mm^{-1}
$T = 296\ (2)$ K
Plate, colourless
$0.3 \times 0.3 \times 0.1$ mm

Data collection

Siemens $P4$ diffractometer
$\theta/2\theta$ scans
5044 measured reflections
3868 independent reflections
3343 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25°$

$h = -1 \rightarrow 10$
$k = -1 \rightarrow 19$
$l = -19 \rightarrow 18$
3 standard reflections
  every 200 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.118$
$S = 1.02$
3868 reflections
295 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 1.0553P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.041 (2)

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.492 (2)	Cl1—C22	1.745 (3)
P1—C1	1.803 (2)	C19—C20	1.495 (3)
P1—C7	1.802 (2)	O2—C19	1.308 (3)
P1—C13	1.803 (2)	O3—C19	1.209 (3)
O1—P1—C1	112.96 (9)	C12—C7—P1	117.15 (16)
O1—P1—C7	109.93 (9)	C14—C13—P1	122.73 (16)
O1—P1—C13	112.25 (10)	C18—C13—P1	118.14 (17)
C1—P1—C7	108.81 (9)	O3—C19—O2	124.0 (2)
C1—P1—C13	105.88 (9)	O3—C19—C20	122.1 (2)
C7—P1—C13	106.73 (9)	O2—C19—C20	113.9 (2)
C2—C1—P1	122.23 (15)	C21—C20—C19	117.7 (2)
C6—C1—P1	118.48 (16)	C25—C20—C19	122.0 (2)
C8—C7—P1	123.93 (16)		
O1—P1—C1—C6	21.2 (2)	O1—P1—C13—C18	74.8 (2)
O1—P1—C7—C12	33.3 (2)	O3—C19—C20—C25	176.6 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H1$\cdots$O1	0.85 (3)	1.76 (3)	2.607 (2)	171 (3)

H atoms were found in a difference Fourier map and were treated as riding (C—H = 0.96 Å) with refinable isotropic displacement parameters, except for the H atom of the carboxylic acid group, which was allowed to refine freely.

Data collection: XSCANS (Siemens, 1995); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Siemens, 1995); software used to prepare material for publication: SHELXL97.

References

Al-Farhan, K. A. (1992). J. Crystallogr. Spectrosc. Res. 22, 687–689.
Al-Farhan, K. A., Beagley, B., El-Sayrafi, O., Gott, G., McAuliffe, C., MacRory, P. & Pritchard, R. (1990). J. Chem. Soc. Dalton Trans. pp. 1243–1250.
Baures, P. W. (1991). Acta Cryst. C47, 2715–2716.
Bye, E., Schweizer, W. B. & Dunitz, J. D. (1982). J. Am. Chem. Soc. 104, 5893–5898.
Desiraju, G. R. & Steiner, T. (1999). Editors. The Weak Hydrogen Bond in Structural Chemistry and Biology. New York: Oxford University Press Inc.
Etter, M. C. (1990). Acc. Chem. Res. 23, 120–126.
Etter, M. C. & Baures, P. W. (1988). J. Am. Chem. Soc. 110, 639–640.
Etter, M. C., Gillard, R., Gleason, W., Rasmussen, J., Duerst, R. & Johnson, R. (1986). J. Org. Chem. 110, 5405–5408.
Etter, M. C., Urbanczyk-Lipkowska, Z., Zia-Ebrahimi, M. & Panunto, T. (1990). J. Am. Chem. Soc. 112, 8415–8426.
Fuquen, R. M. & Lechat, J. R. (1992). Acta Cryst. C48, 1690–1692.
Gougoutas, Z. & Lessinger, L. (1975). J. Solid State Chem. 12, 51–62.
Gramstad, T., Husebye, S. & Maartmann, K. (1986). Acta Chem. Scand. Ser. B, 40, 26–30.
Rebek, J. Jr, Askew, B., Ballester, P., Buhr, C., Jones, S., Nemeth, D. & Williams, K. (1987). J. Am. Chem. Soc. 109, 5033–5035.
Rebek, J. Jr, Askew, B., Ballester, P. & Costero, A. (1988). J. Am. Chem. Soc. 110, 923–927.
Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
Siemens (1995). SHELXTL (Version 5.03) and XSCANS (Version 2.1). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). J. Appl. Cryst. 36, 7–13.