

Tris(2-pyridyl)phosphine oxide: how C—H···O and C—H···N interactions can affect crystal packing efficiency

Richard J. Bowen, Manuel A. Fernandes,* Patricia W. Gitari and Marcus Layh*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, PO Wits 2050, South Africa
Correspondence e-mail: marcus@aurum.chem.wits.ac.za

Received 22 January 2004

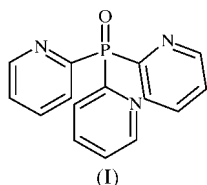
Accepted 19 February 2004

Online 11 March 2004

Tris(2-pyridyl)phosphine oxide, (I), $C_{15}H_{12}N_3OP$, is isomorphous with tris(2-pyridyl)phosphine. Because of a combination of C—H···O and C—H···N interactions, the crystal packing is denser in the title compound than in the related compounds triphenylphosphine oxide and tris(2-pyridyl)phosphine.

Comment

Tris(2-pyridyl)phosphine oxide, (I), has been used as a ligand in the coordination chemistry of transition metals and a number of complexes have been characterized by X-ray crystallography [Cambridge Structural Database (CSD; Allen, 2002) reftcodes XAMNUU (Anderson *et al.*, 2000), QATYUF and QATZAM (Casares *et al.*, 2001), VOPREX (Keene *et al.*, 1991), and MAWYOY (Espinet *et al.*, 2000)]. The solid-state structure of free (I) is, however, still outstanding. Crystallographic data for (I) are presented in this paper.



Compound (I) is isomorphous with the parent compound tris(2-pyridyl)phosphine (TP; CSD reftcode GEKTIZ; Keene *et al.*, 1988), with the O atom replacing the lone pair in the phosphine [$a = 9.162$ (1) Å, $b = 9.163$ (1) Å, $c = 16.071$ (2) Å and $\beta = 100.92$ (1)°; space group $P2_1/c$]. With the exception of the O atom, the coordinates of the two structures are related by $(1 - x, y, \frac{1}{2} - x)$. The molecular geometry of (I) (Fig. 1) is pyramidal, with a propeller-type arrangement of the three pyridyl rings, and shows considerable deviation from C_{3v} symmetry. One of the N atoms is pointing to the same side as

the O atom, while the remaining two N atoms point in the opposite direction. The P—C bond distances (Table 1) are comparable to those in TP [mean 1.828 (3) Å], but slightly longer than those in triphenylphosphine oxide (TPO; mean 1.800 Å; Brock *et al.*, 1985). An opposite trend is observed for the P=O bond, which is slightly shorter in (I) [1.479 (1) Å] than in TPO [1.491 (2) and 1.494 (2) Å; Brock *et al.*, 1985].

No classical (strong) hydrogen bonding occurs in the structure of (I). Molecules are bound together by weak C—H···O and C—H···N interactions (Table 2 and Fig. 2). The same C—H···N interaction exists in TP, the intermolecular C···N distances being 3.341 and 3.353 (2) Å in TP and (I), respectively.

Three forms of TPO, *viz.* one orthorhombic (form I) and two monoclinic (forms II and III), have been described in the literature (Brock *et al.*, 1985; Spek, 1987; Thomas & Hamor, 1993; see Table 3). Unique to form II is a pair of molecules connected by C—H···O interactions, forming a ring described by the graph-set motif $R_2^2(12)$ (Etter, 1990; Bernstein *et al.*, 1995). Extending the C—H···O network produces a chain of rings (Bernstein *et al.*, 1995) running along the a axis (in $P2_1/c$, *e.g.* reftcode TPEPHO06; Brock *et al.*, 1995). A similar chain of $R_2^2(12)$ C—H···O rings runs along the b axis in (I). In the structure of (I), the additional C—H···N interaction seems to reinforce the $R_2^2(12)$ C—H···O ring, leading to C—H···O contacts that are significantly shorter than those found in form II of TPO. Intermolecular C···O distances in TPO are in the range 3.488–3.586 Å (reftcodes TPEHO10 and TPEPHO11; Falvello *et al.*, 2002), while they are considerably shorter in (I) [3.202 (2) and 3.313 (2) Å].

The three polymorphs of TPO have calculated densities in the range 1.215–1.285 Mg m⁻³, considerably lower than that of (I) (1.422 Mg m⁻³). Molecular volumes range from 380.3 Å³ (at 295 K) in form III (Spek, 1987) to 365.9 Å³ (at 153 K; Brock *et al.*, 1985) in form I and 365.3 Å³ (at 153 K; Brock *et al.*, 1985) in form II. The molecular volume of (I) [328.35 (5) Å³] is considerably smaller, possibly as a conse-

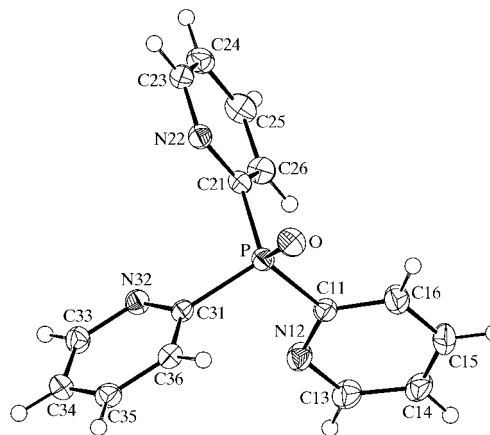


Figure 1

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

quence of the reduced number of H atoms (three per molecule) and/or the packing in (I), which is more efficient because of additional C—H...N contacts (Fig. 2) that are not found in the carbon analogue.

The cell volume and calculated crystal density in TP are 1325 (2) Å³ and 1.330 Mg m⁻³ (at 283–303 K), respectively. The fact that TPO and TP have almost identical molecular volumes indicates that there is little cost in inserting the extra O atom into the TP structure. Thus, it seems logical that the extra C—H...O interactions in (I) promote more efficient packing. Since (I) and TP are isomorphous and the crystal packing of (I) is directed by weak interactions, it is likely that the structure of TP is also dominated by weak interactions. It is therefore possible that, in place of the C—H...O interactions, the TP structure has interactions between the equivalent CH groups and the phosphine lone pair. The two closest C...P

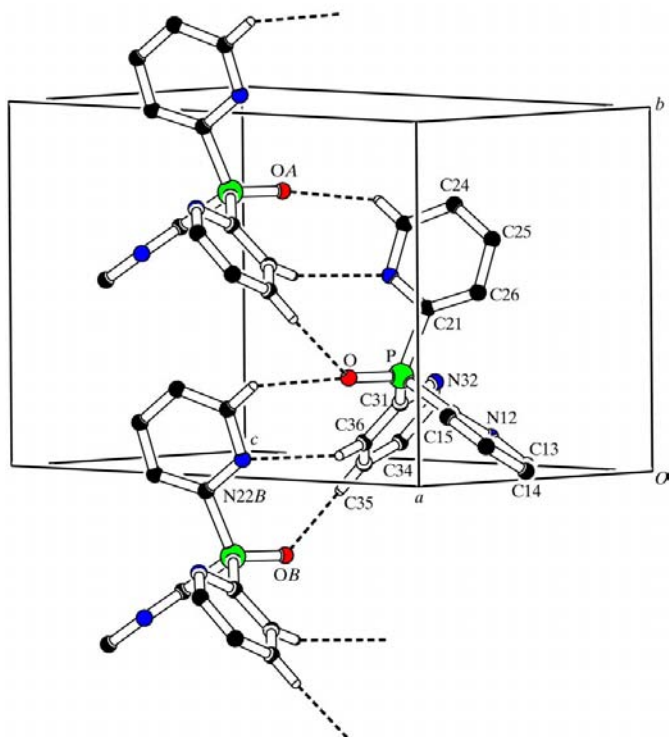


Figure 2

Intermolecular close contacts in (I). Atoms labelled with the suffixes *A* and *B* are in the symmetry positions $(2 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and $(2 - x, y - \frac{1}{2}, \frac{1}{2} - z)$, respectively.

(*D*...*A*) distances in the two structures are 4.319 and 4.249 Å for TP, and 4.443 and 4.374 Å for (I). Although rarely mentioned in the literature, such interactions have been described previously (Desiraju & Steiner, 1999). However, since these C...P distances in TP are somewhat longer than examples cited in the above reference (3.19–3.83 Å), the interaction must be considered very weak, certainly when compared with the C—H...O interaction in (I). Note that this C—H...P interaction is not unreasonable given that a C...O distance of 4.0 Å is regarded as a reasonable upper limit for a C—H...O interaction (Desiraju, 1991, 1996; Taylor & Kennard, 1982).

Experimental

Tris(2-pyridyl)phosphine oxide was obtained as a by-product during the attempted synthesis of phenyltris(2-pyridyl)phosphonium bromide from tris(2-pyridyl)phosphine and bromobenzene under reflux conditions. Crystals suitable for X-ray analysis were obtained by dissolving the crude product in methanol and cooling the solution to 213 K.

Crystal data

C ₁₅ H ₁₂ N ₃ OP	<i>D_x</i> = 1.422 Mg m ⁻³
<i>M_r</i> = 281.25	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 1007 reflections
<i>a</i> = 9.0807 (9) Å	<i>θ</i> = 2.3–28.2°
<i>b</i> = 9.1550 (9) Å	<i>μ</i> = 0.21 mm ⁻¹
<i>c</i> = 16.0629 (16) Å	<i>T</i> = 173 (2) K
<i>β</i> = 100.409 (2)°	Prism, light brown
<i>V</i> = 1313.4 (2) Å ³	0.24 × 0.20 × 0.17 mm
<i>Z</i> = 4	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	<i>R</i> _{int} = 0.026
<i>φ</i> and <i>ω</i> scans	<i>θ</i> _{max} = 28.3°
8966 measured reflections	<i>h</i> = -11 → 12
3251 independent reflections	<i>k</i> = -9 → 12
2589 reflections with <i>I</i> > 2σ(<i>I</i>)	<i>l</i> = -21 → 21

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0454 <i>P</i>) ² + 0.563 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.036	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.096	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.02	Δρ _{max} = 0.41 e Å ⁻³
3251 reflections	Δρ _{min} = -0.36 e Å ⁻³
181 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

P—O	1.4792 (11)	P—C11	1.8200 (15)
P—C31	1.8173 (15)	P—C21	1.8211 (15)
O—P—C31	113.99 (7)	O—P—C21	113.60 (7)
O—P—C11	111.88 (7)	C31—P—C21	104.06 (7)
C31—P—C11	105.95 (7)	C11—P—C21	106.65 (7)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C23—H23...O ⁱ	0.95	2.50	3.313 (2)	144
C35—H35...O ⁱⁱ	0.95	2.46	3.202 (2)	134
C36—H36...N22 ⁱⁱ	0.95	2.53	3.353 (2)	145

Symmetry codes: (i) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Table 3

Cell parameters (Å, °), volume (Å³) and determination temperature (K) for the various forms of triphenylphosphine oxide.

Form	Space group	<i>a</i>	<i>b</i>	<i>c</i>	<i>β</i>	<i>V</i>	<i>T</i>
I†	<i>Pbc</i>	28.898 (3)	9.094 (2)	11.138 (2)	—	2929.0	153
II†	<i>P2</i> ₁ / <i>c</i>	10.952 (2)	8.687 (2)	16.221 (6)	108.78 (2)	1461.1	153
III‡	<i>P2</i> ₁ / <i>c</i>	15.066 (1)	9.037 (2)	11.296 (3)	98.47 (1)	1521.2	295

† Brock *et al.* (1985). ‡ Spek (1987).

H atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H bond lengths of 0.95 Å and $U_{\text{iso}}(\text{H})$ values equal to $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

The authors thank CANSA and the University of the Witwatersrand for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1045). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Anderson, P. A., Astley, T., Hitchman, M. A., Keene, F. R., Moubaraki, B., Murray, K. S., Skelton, B. W., Tiekink, E. R. T., Toftlund, H. & White, A. H. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3505–3512.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Brock, C. P., Schweizer, W. B. & Dunitz, J. D. (1985). *J. Am. Chem. Soc.* **107**, 6964–6970.
- Bruker (1998). *SMART-NT*. Version 5.050. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINT-Plus* (Version 6.02; includes *XPREP* and *SADABS*) and *SHELXTL* (Version 5.1; includes *XS*, *XL*, *XP* and *XSHELL*). Bruker AXS Inc., Madison, Wisconsin, USA.
- Casares, J. A., Espinet, P., Martín-Alvarez, J. M., Espino, G., Pérez-Manrique, M. & Vattier, F. (2001). *Eur. J. Inorg. Chem.* pp. 289–296.
- Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.
- Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, pp. 238–239. New York: Oxford University Press Inc.
- Espinet, P., Hernanado, R., Iturbe, G., Villafañe, F., Orpen, A. G. & Pascual, I. (2000). *Eur. J. Inorg. Chem.* pp. 1031–1038.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Falvello, F. R., Tomas, M. & Soler, T. (2002). Private communication.
- Keene, R. F., Snow, M. R. & Tiekink, E. R. T. (1988). *Acta Cryst.* **C44**, 757–758.
- Keene, R. F., Stephenson, P. J. & Tiekink, E. R. T. (1991). *Inorg. Chim. Acta*, **187**, 217–220.
- Spek, A. L. (1987). *Acta Cryst.* **C43**, 1233–1235.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Taylor, R. & Kennard, O. J. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
- Thomas, J. A. & Hamor, T. A. (1993). *Acta Cryst.* **C49**, 355–357.