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Tri-2-furyl-phosphine oxide: an oxidation product of the weak Lewis base tri-2-furylphosphine

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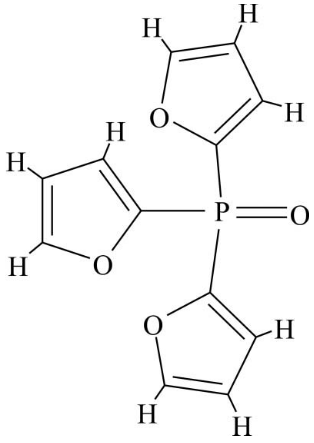
Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.004 Å; R factor = 0.034; wR factor = 0.099; data-to-parameter ratio = 14.1.

The title compound, $C_{12}H_9O_4P$, was prepared by the oxidation of tri-2-furylphosphine. The P=O bond length is 1.478 (2) Å and the C—P bond lengths range from 1.774 (2) to 1.785 (2) Å. The tri-2-furyl-phosphine oxide molecule displays a very distorted confirmation (not propeller-like) due to the large variation in O—P—C—C torsion angles [5.6 (3), 8.5 (3) and 118.0 (3)°]. The crystal structure involves intermolecular C—H···O hydrogen bonds.

Related literature

For methods of oxidizing tertiary phosphines, see: Barton *et al.* (1997); Lim *et al.* (2002); Mandimutsira *et al.* (2002). A unique reaction reported in the case of tri-2-furylphosphine is the partial oxidation of the ligand while attempted coordination to a Hg^{II} center. A mixed ligand/ligand oxide complex of Hg^{II} was characterized crystallographically (Bachechi *et al.*, 2005), although the crystal structure of the uncomplexed, oxidized ligand has not been reported.

For related literature, see: Allen & Ward (1980); Andersen & Keay (2001); Farina *et al.* (1988).



Experimental

Crystal data

$C_{12}H_9O_4P$
M_r = 248.16
Orthorhombic, $P2_12_12_1$
a = 8.0837 (8) Å
b = 10.9362 (17) Å
c = 13.4690 (15) Å
V = 1190.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.23 mm^{-1}
T = 290 (2) K
1.0 × 0.49 × 0.48 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.877, T_{max} = 0.895
2455 measured reflections
2183 independent reflections
2043 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
3 standard reflections every 120 reflections intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.099
S = 1.07
2183 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 905 Friedel pairs
Flack parameter: −0.01 (6)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···O4^{i}	0.93	2.44	3.325 (3)	158
C6—H6A···O4^{ii}	0.93	2.49	3.394 (3)	163
C12—H12A···O4^{iii}	0.93	2.50	3.309 (3)	146
C10—H10A···O3^{iv}	0.93	2.50	3.397 (3)	163

Symmetry codes: (i) $-x+\frac{3}{2}, -y, z+\frac{1}{2}$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1998); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2038).

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supplementary materials

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Tri-2-furyl-phosphine oxide: an oxidation product of the weak Lewis base tri-2-furylphosphine

D. Jenkins, R. E. Sykora and **Z. Assefa**

Comment

Tertiary phosphines with heterocyclic substituents have attracted a great deal of attention in the design and development of tailor-made ligands for transition-metal coordination (Andersen & Keay, 2001) and important organic reactions (Farina *et al.*, 1988). Although the chemical reactivities of R_3P phosphines are by and large determined by steric and electronic factors, these properties are closely inter-related. The increase in steric bulk of the *R* groups is known to reduce the s-character of the phosphorous lone pair, and makes the ligand more Lewis basic (Andersen & Keay, 2001). With a cone angle of 134°, tri-2-furylphosphine (TFP) has comparable size to that of triphenylphosphine (145°). However, their electronic properties are quite different. TFP is a substantially weaker Lewis base and, therefore a poorer σ-donor than PPh_3. It is in fact reported (Allen & Ward, 1980) that the 2-furyl group is the most electron-withdrawing substituent among the tri(hetero)aryl phosphines. As a result, its electronic properties and also its reactivity are expected to be different. It appears that due to its electronic properties, TFP is currently the choice in a wide variety of metal-catalyzed reactions for carbon-carbon and carbon-heteroatom bond formation.

Oxidation of tertiary phosphines to their respective phosphine oxides is well known for PPh_3 and related phosphines, and has been accomplished using several techniques including oxidation with H_2O_2 (Barton *et al.*, 1997) and NO (Lim *et al.*, 2002). An alternative method of synthesis employing oxygen atom transfer routes by metal oxides are also well documented (Mandimutsira *et al.*, 2002). These methods are likely also suitable for tri-2-furylphosphine. A unique reaction reported in the TFP case involved partial oxidation of the ligand while attempted coordination to a Hg(II) center. A mixed ligand/ligand oxide complex of Hg(II) was characterized crystallographically (Bachechi *et al.*, 2005), although the sole oxidized ligand has not been reported. Our initial unexpected synthesis of the title compound (**I**) was carried out while attempting to coordinate TFP to a Au(I) center in THF solvent. A rational synthesis has since been discovered (See Experimental section for details). Fig. 1 illustrates the molecular structure of (**I**) along with the atom numbering scheme. The four closest intermolecular interactions are shown in the hydrogen bonding table. All of these interactions are at ranges that are slightly longer than the sum of the atoms van der Waals radii, and are therefore not relatively strong interactions. Not surprisingly, the majority (three) of these interactions are to the oxide moiety.

Experimental

tri-2-furylphosphine (TFP) is commercially available and was used as received from Aldrich. The initial synthesis of the TFP oxide was obtained unexpectedly while attempting to coordinate TFP to a Au(I) center. However, the compound can easily be oxidized using the following procedure. TFP (20 mg, 0.086 mmol) is dissolved in 4 ml THF. After addition of a few drops of H_2O_2 (30%), the solution is stirred for 3 h. After partial evaporation of the solvent and overnight refrigeration, a solid white product is formed. Recrystallization is attained in a THF/diethyl ether (2:1) solution.

The product was characterized using several spectroscopic techniques in addition to the X-ray analysis. ^{31}P-NMR in $CDCl_3$ of the tri-2-furylphosphine oxide (R_3PO) shows a single band at a significantly down-field position when compared to the unoxidized ligand, ^{31}P-NMR: (CDCl$_3$, δ, p.p.m.): −10.38 (*s*). ^{1}H-NMR (CDCl$_3$): 6.57 (1*H*), 7.18 (1*H*), 7.80 (1*H*). The unoxidized TFP ligand (R_3P) has a ^{31}P-NMR single band at −77.18 p.p.m., and ^{1}H-NMR (CDCl$_3$): 6.42 (1*H*), 6.81 (1*H*), 7.67 (1*H*). Due to the large size of the crystal used for the diffraction experiment, the beam tunnel that was used was large (2 mm i.d.) to ensure that the crystal was completely inside of the X-ray beam during the diffraction experiment.

Refinement

H atoms were placed in calculated positions and allowed to ride during subsequent refinement, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and C—H distances of 0.93 Å for all H atoms.

Figures

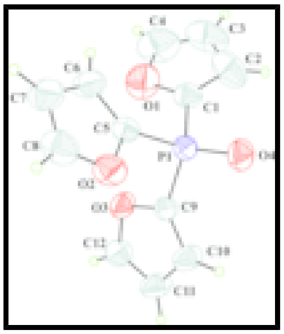

Fig. 1. The molecular structure of **I**, with the atom-numbering scheme included. Displacement ellipsoids for non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary size.

Tri-2-furyl-phosphine oxide

Crystal data

$C_{12}H_9O_4P$
$M_r = 248.16$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 8.0837$ (8) Å
$b = 10.9362$ (17) Å
$c = 13.4690$ (15) Å
$V = 1190.7$ (3) Å^3
$Z = 4$

$F_{000} = 512$
$D_x = 1.384$ Mg m^{-3}
Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8.1–11.8°
μ = 0.23 mm^{-1}
$T = 290$ (2) K
Prism, colorless
1.0 × 0.49 × 0.48 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
$T = 290(2)$ K
θ/2θ scans

$R_{\text{int}} = 0.018$
$\theta_{\text{max}} = 25.4°$
$\theta_{\text{min}} = 2.4°$
$h = 0\rightarrow9$
$k = 0\rightarrow13$

Absorption correction: ψ scan (North *et al.*, 1968)	$l = -16 \rightarrow 16$
$T_{\min} = 0.877$, $T_{\max} = 0.895$	3 standard reflections
2455 measured reflections	every 120 reflections
2183 independent reflections	intensity decay: none
2043 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 0.1689P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{\max} < 0.001$
$wR(F^2) = 0.099$	$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{\min} = -0.23$ e Å^{-3}
2183 reflections	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
155 parameters	Extinction coefficient: 0.029 (3)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 905 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.01 (6)
Hydrogen site location: inferred from neighbouring sites	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
P1	0.77262 (6)	0.09125 (5)	0.24066 (4)	0.03648 (18)
O1	0.8209 (4)	0.31874 (17)	0.15987 (16)	0.0788 (7)
O2	0.7664 (2)	0.09724 (15)	0.43842 (11)	0.0538 (4)
O3	0.47834 (19)	0.20950 (13)	0.23857 (15)	0.0480 (4)
O4	0.8335 (2)	−0.03428 (14)	0.22293 (14)	0.0529 (4)
C1	0.8511 (3)	0.1956 (2)	0.15066 (16)	0.0450 (5)
C2	0.9358 (5)	0.1725 (4)	0.0685 (2)	0.0816 (10)
H2A	0.9696	0.0967	0.0448	0.098*
C3	0.9645 (5)	0.2918 (4)	0.0236 (2)	0.0881 (12)

H3A	1.0227	0.3071	−0.0346	0.106*
C4	0.8941 (6)	0.3723 (4)	0.0795 (3)	0.0953 (13)
H4B	0.8934	0.4559	0.0668	0.114*
C5	0.8257 (3)	0.1579 (2)	0.35641 (15)	0.0380 (5)
C6	0.9141 (4)	0.2562 (3)	0.3848 (2)	0.0573 (7)
H6A	0.9664	0.3129	0.3440	0.069*
C7	0.9106 (4)	0.2547 (4)	0.4909 (2)	0.0714 (9)
H7A	0.9623	0.3104	0.5328	0.086*
C8	0.8210 (4)	0.1604 (3)	0.51835 (19)	0.0647 (7)
H8A	0.7982	0.1398	0.5839	0.078*
C9	0.5522 (2)	0.09714 (18)	0.23460 (16)	0.0371 (5)
C10	0.4375 (3)	0.0104 (2)	0.2246 (2)	0.0559 (7)
H10A	0.4561	−0.0733	0.2201	0.067*
C11	0.2819 (3)	0.0700 (2)	0.2222 (2)	0.0583 (7)
H11A	0.1788	0.0331	0.2159	0.070*
C12	0.3125 (3)	0.1888 (2)	0.2306 (2)	0.0524 (6)
H12A	0.2319	0.2496	0.2311	0.063*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0337 (3)	0.0355 (3)	0.0402 (3)	0.0013 (2)	0.0009 (2)	−0.0019 (2)
O1	0.1116 (19)	0.0550 (12)	0.0698 (12)	−0.0135 (12)	0.0208 (13)	0.0142 (9)
O2	0.0612 (10)	0.0566 (10)	0.0435 (8)	−0.0071 (9)	0.0058 (7)	0.0098 (7)
O3	0.0412 (8)	0.0327 (7)	0.0702 (11)	0.0022 (6)	−0.0025 (8)	−0.0087 (7)
O4	0.0481 (8)	0.0417 (9)	0.0689 (10)	0.0095 (7)	−0.0009 (8)	−0.0094 (8)
C1	0.0406 (12)	0.0552 (14)	0.0391 (11)	−0.0060 (11)	−0.0013 (10)	0.0019 (10)
C2	0.079 (2)	0.117 (3)	0.0483 (15)	0.013 (2)	0.0168 (15)	0.0023 (17)
C3	0.079 (2)	0.136 (4)	0.0498 (17)	−0.018 (2)	0.0137 (16)	0.031 (2)
C4	0.115 (3)	0.098 (3)	0.073 (2)	−0.033 (2)	0.009 (2)	0.037 (2)
C5	0.0350 (10)	0.0426 (11)	0.0363 (10)	−0.0016 (10)	0.0022 (8)	0.0044 (8)
C6	0.0588 (15)	0.0679 (17)	0.0451 (12)	−0.0230 (14)	0.0018 (11)	−0.0017 (12)
C7	0.0658 (17)	0.103 (2)	0.0450 (14)	−0.0295 (18)	−0.0008 (12)	−0.0156 (14)
C8	0.0609 (16)	0.095 (2)	0.0382 (12)	−0.0053 (16)	0.0016 (11)	0.0041 (13)
C9	0.0337 (10)	0.0327 (10)	0.0450 (11)	0.0025 (8)	0.0009 (8)	−0.0004 (10)
C10	0.0428 (12)	0.0328 (11)	0.092 (2)	0.0000 (9)	−0.0011 (13)	0.0022 (12)
C11	0.0365 (11)	0.0480 (13)	0.0902 (19)	−0.0049 (10)	−0.0032 (12)	0.0032 (13)
C12	0.0354 (11)	0.0480 (13)	0.0740 (16)	0.0070 (9)	−0.0017 (11)	−0.0032 (12)

Geometric parameters (Å, °)

P1—O4	1.4777 (16)	C3—H3A	0.9300
P1—C5	1.774 (2)	C4—H4B	0.9300
P1—C1	1.782 (2)	C5—C6	1.346 (3)
P1—C9	1.7846 (19)	C6—C7	1.429 (4)
O1—C4	1.366 (4)	C6—H6A	0.9300
O1—C1	1.374 (3)	C7—C8	1.313 (4)
O2—C8	1.353 (3)	C7—H7A	0.9300
O2—C5	1.375 (3)	C8—H8A	0.9300

O3—C12	1.364 (3)	C9—C10	1.333 (3)
O3—C9	1.367 (2)	C10—C11	1.417 (3)
C1—C2	1.326 (4)	C10—H10A	0.9300
C2—C3	1.457 (5)	C11—C12	1.328 (3)
C2—H2A	0.9300	C11—H11A	0.9300
C3—C4	1.291 (6)	C12—H12A	0.9300

O4—P1—C5	116.31 (11)	O2—C5—P1	115.06 (16)
O4—P1—C1	111.51 (11)	C5—C6—C7	105.3 (2)
C5—P1—C1	104.39 (11)	C5—C6—H6A	127.3
O4—P1—C9	111.01 (10)	C7—C6—H6A	127.3
C5—P1—C9	105.48 (10)	C8—C7—C6	107.6 (3)
C1—P1—C9	107.53 (11)	C8—C7—H7A	126.2
C4—O1—C1	105.8 (3)	C6—C7—H7A	126.2
C8—O2—C5	106.20 (19)	C7—C8—O2	110.9 (2)
C12—O3—C9	106.11 (16)	C7—C8—H8A	124.6
C2—C1—O1	110.8 (3)	O2—C8—H8A	124.6
C2—C1—P1	129.0 (3)	C10—C9—O3	109.83 (18)
O1—C1—P1	120.20 (18)	C10—C9—P1	132.34 (17)
C1—C2—C3	104.9 (3)	O3—C9—P1	117.82 (14)
C1—C2—H2A	127.5	C9—C10—C11	107.1 (2)
C3—C2—H2A	127.5	C9—C10—H10A	126.5
C4—C3—C2	107.4 (3)	C11—C10—H10A	126.5
C4—C3—H3A	126.3	C12—C11—C10	106.4 (2)
C2—C3—H3A	126.3	C12—C11—H11A	126.8
C3—C4—O1	111.2 (4)	C10—C11—H11A	126.8
C3—C4—H4B	124.4	C11—C12—O3	110.6 (2)
O1—C4—H4B	124.4	C11—C12—H12A	124.7
C6—C5—O2	110.0 (2)	O3—C12—H12A	124.7
C6—C5—P1	134.91 (18)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8A···O4^{i}	0.93	2.44	3.325 (3)	158
C6—H6A···O4^{ii}	0.93	2.49	3.394 (3)	163
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Symmetry codes: (i) −*x*+3/2, −*y*, *z*+1/2; (ii) −*x*+2, *y*+1/2, −*z*+1/2; (iii) −*x*+1, *y*+1/2, −*z*+1/2; (iv) −*x*+1, *y*−1/2, −*z*+1/2.

Fig. 1