nity to use the *SHELXTL-Plus* program system in his laboratory.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1371). Services for accessing these data are described at the back of the journal.

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Phenyl 2-Pyridyl Ketone at 150 K

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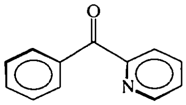
Abstract

Crystals of phenyl 2-pyridyl ketone, $C_{12}H_9NO$, suitable for X-ray diffraction were obtained by sublimation. Their structure, which was determined at 150 K, yields geometric parameters comparable with those found for the iso(valence)electronic analogues of benzophenone and 2,2′-dipyridyl ketone [Bock *et al.* (1998). *Struct. Chem.* In the press]. Both the phenyl and pyridine rings are twisted considerably out of the central C—C(O)—C plane.

Comment

The structure of phenyl 2-pyridyl ketone, (I), has not been determined previously although it is of interest as a parent model compound for oxygen and nitrogen lone-pair interactions in 2-pyridyl-substituted molecules and, especially, as a connecting link between the crystal structures of benzophenone (Brandon *et al.*, 1965; Fleischer *et al.*, 1968) and di2-pyridyl ketone (Bock *et al.*, 1998).



(I)

Commercially available phenyl 2-pyridyl ketone can be sublimed at 303 K yielding colourless blocks. Examination of the lattice packing (Fig. 1) shows two characteristic motifs resulting from weak intermolecular interactions. Among several rather long C—H···O contacts of up to 3.40 Å, the one between O1 and C15$(-x, y-\frac{1}{2}, \frac{3}{2}-z)$ has a distance of only 3.260 (3) Å (Fig. 1*a*), with a C—H···O angle of 135.0 (5)°. As every molecule is involved in two of these hydrogen-bridge contacts, undulating layers form in the *yz* plane; these are connected to each other *via* weak π–π interactions (Fig. 1*a*). The interplanar distance between the phenyl and pyridine rings of adjacent molecules is 3.44 (2) Å, *i.e.* it exceeds by only 0.04 Å twice the van der Waals radius of a π-system of 1.70 Å (Pauling, 1962). The interplanar angle of about 9° is rather small, but the ring centroids are shifted about 1.40 (2) Å parallel to each other, which results in a distance of 3.71 (1) Å. The interaction proceeds along the *x* axis and leads to polymeric chains which are connected to each other *via* hydrogen bridges.

The structure of the molecule deviates significantly from planarity because the phenyl and pyridine rings are rotated around the OC—C-*ipso* axes (Fig. 1*b*): the phenyl ring is twisted relative to the planar group C11—C(O)—C21 to give a C12—C11—C1—O1 torsion angle of 155.6 (2)°; the pyridine ring is also twisted with O1—C1—C21—N1 = 131.0 (2)°. The larger torsion of the pyridine ring is due to the repulsion of the nitrogen electron pair at N1. A weak C12—H···N1 interaction is also observed.

Bond lengths and angles, as well as the torsion angles of the phenyl and pyridine rings (Table 1), are comparable with those found in the structures of benzophenone (Brandon *et al.*, 1965; Fleischer *et al.*, 1968) and di2-pyridyl ketone (Bock *et al.*, 1998). For instance, in the crystal structure of benzophenone, which crystallizes in the same orthorhombic space group $P2_12_12_1$, both phenyl rings are twisted by about 30° compared with a value of 24.4 (2)° for the phenyl ring in phenyl 2-pyridyl ketone. Furthermore, the pyridine ring in the title compound exhibits a torsion angle of 131.0 (2)°, which differs significantly from that of 17.0 (1)° for one of the pyridine rings in di2-pyridyl ketone. A value of only 41.2 (2)° for the other pyridine

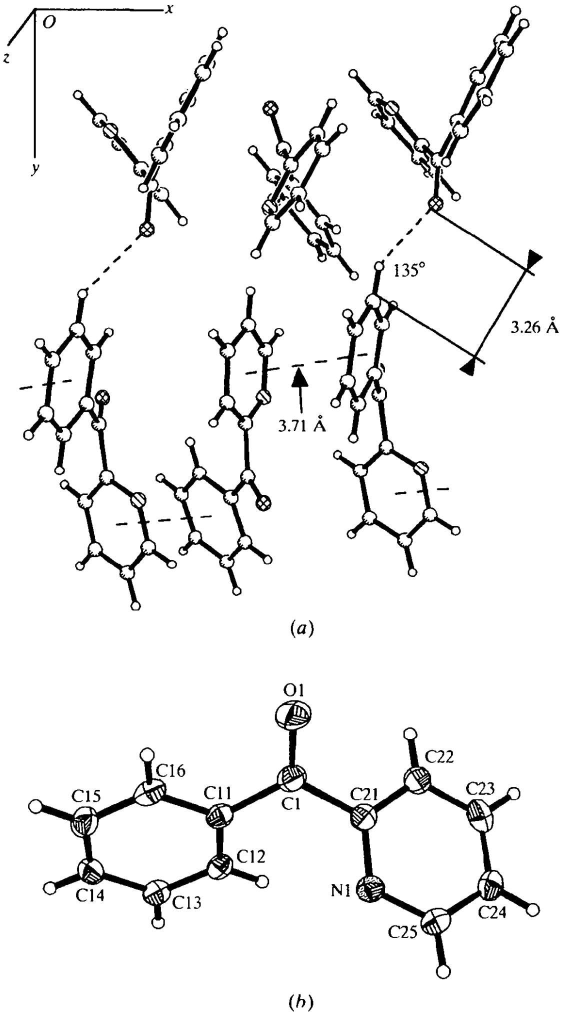


Fig. 1. Crystal structure of phenyl 2-pyridyl ketone showing (*a*) the π–π interactions and the weak intermolecular hydrogen bridges, and (*b*) the atom-numbering scheme (displacement ellipsoids are drawn at the 50% probability level).

ring in this latter compound resembles the phenyl-ring torsion angle of the title compound. The *ipso*-angle [C11—C1—C21 = 118.91 (13)°] is of standard size. The geometry of the phenyl ring is strictly hexagonal, while that of the pyridine ring corresponds with that in 2,2′-dipyridyl ketone (Bock *et al.*, 1998).

Experimental

Phenyl 2-pyridyl ketone is commercially available. Crystals of the title compound were grown by sublimation.

Crystal data

$C_{12}H_9NO$
$M_r = 183.20$
Orthorhombic
$P2_12_12_1$
$a = 7.855\ (2)$ Å
$b = 9.982\ (2)$ Å
$c = 11.589\ (2)$ Å
$V = 908.7\ (3)$ Å^3
$Z = 4$
$D_x = 1.339$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 96 reflections
$\theta = 7.5$–$15.0°$
$\mu = 0.086$ mm^{-1}
$T = 150\ (2)$ K
Block
0.60 × 0.40 × 0.25 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2024 measured reflections
1854 independent reflections
1672 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

$\theta_{\rm max} = 30°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 14$
$l = -1 \rightarrow 16$
4 standard reflections every 100 reflections intensity decay: 95%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.106$
$S = 1.036$
1853 reflections
128 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.3001P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.309$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.167$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.017 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.213 (2)	C21—N1	1.339 (2)
C1—C11	1.488 (2)	C25—N1	1.332 (2)
C1—C21	1.497 (2)		
O1—C1—C11	121.61 (15)	N1—C21—C22	123.5 (2)
C11—C1—C21	118.91 (13)	N1—C21—C1	116.22 (14)
C12—C11—C16	119.5 (2)	C22—C21—C1	120.2 (2)
C12—C11—C1	120.97 (14)	C25—N1—C21	116.76 (15)
C16—C11—C1	119.29 (14)		

All of the H-atom positions were located in the difference electron-density map, positioned with ideal geometry and refined with free isotropic displacement parameters using a riding model [$U_{\rm iso} = 1.2U_{\rm eq}$]. The absolute structure parameter was found to be −1 (2). The absolute structure was therefore assigned arbitrarily.

Data collection: *XSCANS* (Siemens, 1994*a*). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*94 (Sheldrick, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *XP*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1015). Services for accessing these data are described at the back of the journal.

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Key Intermediates in the Synthesis of 2,2′-Biphosphole

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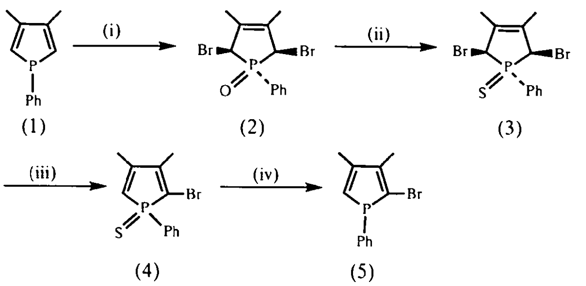
Abstract

The crystal structures of three key intermediates in the synthesis of 2,2′-biphosphole are reported. Molecules of 2,5-dibromo-3,4-dimethyl-1-phenyl-2,5-dihydrophosphole 1-oxide, $C_{12}H_{13}Br_2OP$, and 2,5-dibromo-3,4-dimethyl-1-phenyl-2,5-dihydrophosphole 1-sulfide, $C_{12}H_{13}Br_2PS$, each contain a phospholene ring with a chair conformation. In the molecules, the α-H atoms are *trans* to the P=O or P=S groups, thus demonstrating that the sulfurization takes place with the retention of the stereochemistry at phosphorus. In 2-bromo-3,4-dimethyl-1-phenylphosphole 1-sulfide, $C_{12}H_{12}BrPS$, the phosphole ring is perfectly planar.

Comment

Within the framework of a project concerning the design and synthesis of new C_2-symmetry chiral bidentate ligands, we were interested in 2,2′-biphosphole and the possibility of formation of transition metal complexes with this chiral ligand (Gouygou *et al.*, 1997). Two approaches to the synthesis of 2,2′-biphosphole have been reported (Mercier *et al.*, 1986; Deschamps & Mathey, 1992). We have used the most attractive route, which involves the preparation of 2-bromophosphole. The synthesis of 2-bromo-3,4-dimethyl-1-phenylphosphole, (5), proceeds in four steps starting from 3,4-dimethyl-1-phenylphosphole, (1). Although the formation and spectroscopic characterizations of the intermediates (2) (2,5-dibromo-3,4-dimethyl-1-phenyl-2,5-dihydrophosphole 1-oxide), (3) (2,5-dibromo-3,4-dimethyl-1-phenyl-2,5-dihydrophosphole 1-sulfide) and (4) (2-bromo-3,4-dimethyl-1-phenylphosphole 1-sulfide) have already been mentioned, they have not been fully characterized by X-ray analysis. We have isolated (2), (3) and (4) as crystals suitable for X-ray investigations and their structures are reported here.



(i) (*a*) *m*-Cl-C_6H_4-CO_3H, CH_2Cl_2, 273 K
(*b*) $pyH^+Br_3^-$, CH_2Cl_2, 298 K
(ii) 0.5eq. P_4S_{10}, toluene, reflux
(iii) KOH, MeOH/CH_2Cl_2, 298 K
(iv) PMe_3, toluene, reflux

The structure of compound (2) is shown in Fig. 1. As observed in the related compound 3,4-dimethyl-1-supermesityl-3-phospholene (Li *et al.*, 1992), the phospholene ring has a chair conformation with a dihedral angle of 22.7 (3)° between the C1—C2—C3—C4 and C1—P1—C4 planes. The α-H atoms are *trans* to the P=O group, which confirms the stereochemistry

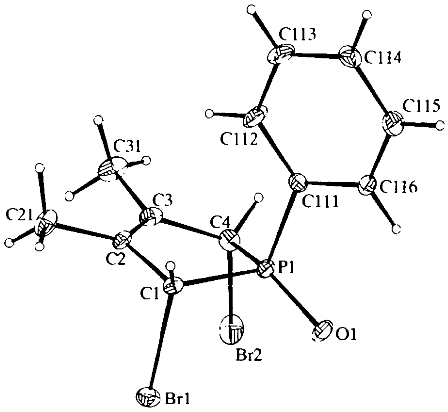


Fig. 1. Molecular view of molecule (2) showing 50% probability displacement ellipsoids.

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