Crystal Structure of 4'-Chlorobenzoylmethylenetriphenylphosphorane ylide, C₂₆H₂₀ClOP

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The crystal structure of a colorless phosphorus ylide, Ph₃PCHCOC₆H₄Cl, was determined by the X-ray diffraction method. All atoms occupy general positions in the monoclinic space group, *C2/c*, and have the following unit-cell dimensions: *a* = 16.6184(9) Å, *b* = 10.9196(6) Å, *c* = 23.5465(12) Å, β = 100.366(4)°, *Z* = 8 and *V* = 4203.2(4) Å³.

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Phosphorus ylides are important reagents in organic chemistry, especially in the synthesis of naturally occurring products with biological and pharmacological activities.¹ The chemistry of organic phosphorus compounds has shown remarkable growth throughout the past 5 decades. Meanwhile, it has attracted much interest, especially concerning extensive utilization of the organophosphorus derivatives as plasticizers for synthetics, extraction agents, oxidation inhibitors for lubricants, flotation agents, complexing agents for transition metals, and insecticides.^{2,3}

Preparation: This compound was prepared according to a published method.⁴ Colorless crystals of Ph₃PCHCOC₆H₄Cl (in Fig. 1) were obtained from a methanol solution by slow evaporation of the solvent.

Single crystal X-ray diffraction analysis was performed on a STOE IPDS-II two-circle diffractometer using graphite-monochromated Mo *K*_α X-ray radiation (λ = 0.71073 Å). Data collection was performed at 120(2)K using the ω -scan technique and the STOE X-Area software package.⁵ The crystal structure was solved by direct methods and refined by using the X-STEP32 crystallographic software package.^{6,7} All of the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located at ideal positions. Table 1 provides the crystallographic results and refinement information.

All hydrogen atoms were refined with the riding model to

final *R* indices of *R*₁ (0.0377) and *WR*₂ (0.0989). Selected bond lengths and angles are given in Table 2.

Table 1 Crystal and experimental data

Compound	C ₁₆ H ₆ ClCOPPh ₃
Empirical formula	C ₂₆ H ₂₀ ClOP
<i>F</i> _w	414.84
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> (Å)	16.6184(9)
<i>b</i> (Å)	10.9196(6)
<i>c</i> (Å)	23.5465(12)
α (°)	90
β (°)	100.366(4)
γ (°)	90
Volume (Å ³)	4203.2(4)
<i>Z</i>	8
$\Delta\rho$	0.011
<i>D</i> _{calc} (Mg/m ³)	1.311
Absorption coefficient (mm ⁻¹)	0.273
<i>F</i> (0 0 0)	1728
Crystal size (mm)	0.50 × 0.16 × 0.12
θ range for data collection (°)	2.24 to 29.19
Limiting indices	−22 ≤ <i>h</i> ≤ 22, −14 ≤ <i>k</i> ≤ 14, −23 ≤ <i>l</i> ≤ 32
Reflections collected/unique (<i>R</i> _{int})	15184/5571 (0.0388)
Completeness to θ	97.9%
Absorption correction	Numerical
Maximum and minimum transmission	0.970 and 0.020
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5571/0/262
Goodness-of-fit on <i>F</i> ²	1.088
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0377, <i>wR</i> ₂ = 0.0989
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0400, <i>wR</i> ₂ = 0.1005
Largest difference in peak and hole (eÅ ⁻³)	0.405 and −0.412
Crystal data have been deposited at the Cambridge Crystallographic Data Center under the number CCDC 648308.

Fig. 1 Chemical structure.

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Fig. 2 ORTEP drawing, showing the atom-numbering scheme.

An ORTEP plot (Fig. 2) shows that in the molecule of the title compound, 4'-chlorobenzoylmethylenetriphenylphosphorane ylide, $C_{26}H_{20}ClOP$, the geometry around the P atom is nearly tetrahedral, and the O atom is oriented *cis* to the P atom. The chlorophenyl ring of the benzoyl group is twisted with respect to the plane of the carbonyl group through an angle of $-3.99(18)^\circ$. The P-C(8) (1.7198(13)) and C(8)-C(7, sp^2) (1.4031(16)) bond lengths are shorter than the (P⁺-C (sp^3) (1.800) and (1.511) normal values, respectively. This is due to the ylidic resonance and intermediate between common values for single and double bonds (for example P-C = 1.80 and P = C = 1.66 Å). The CO bond also is longer (1.2580) (15) than the normal value (1.210). This bond distance suggests resonance delocalization in these molecules (scheme 1).

Scheme (1)

Table 2 Selected key bond lengths (Å), bond angles ($^\circ$) and torsion angles ($^\circ$)

C(7)-O(1)	1.2580(15)
C(7)-C(8)	1.4031(16)
C(6)-C(7)	1.5110(16)
C(8)-P(1)	1.7198(13)
C(8)-H(8)	0.9300
C(9)-P(1)	1.8037(12)
C(15)-P(1)	1.8177(12)
C(21)-P(1)	1.8097(13)
<i>Bond angles</i>	
O(1)-C(7)-C(8)	123.04(11)
O(1)-C(7)-C(6)	118.03(11)
C(8)-C(7)-C(6)	118.91(11)
C(7)-C(8)-P(1)	120.51(9)
C(7)-C(8)-H(8)	119.7
P(1)-C(8)-H(8)	119.7
C(8)-P(1)-C(9)	105.03(6)
C(8)-P(1)-C(21)	114.26(6)
C(9)-P(1)-C(21)	107.84(5)
C(8)-P(1)-C(15)	116.07(6)
C(9)-P(1)-C(15)	108.13(6)
C(21)-P(1)-C(15)	105.18(6)
<i>Torsion angles</i>	
O(1)-C(7)-C(8)-P(1)	-3.98(18)
C(1)-C(6)-C(7)-C(8)	-4.42(18)
C(1)-C(6)-C(7)-O(1)	173.84(12)
C(5)-C(6)-C(7)-O(1)	-3.69(17)

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