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THE BARRIER TO CARBON-PHOSPHORUS BOND ROTATION IN TRIAROYLPHOSPHINES

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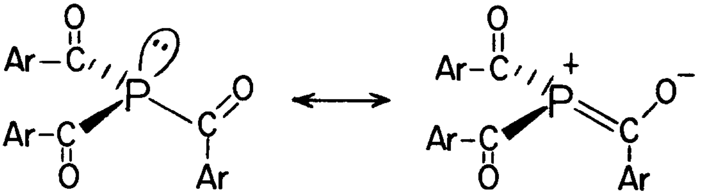
The topic of $\overset{\overset{O}{\|}}{C}$-heteroatom bond-rotation has received considerable attention, particularly that of hindered rotation in amides.[1,2] We now report, via ^{13}C NMR analysis, the first observation of hindered rotation in triaroylphosphines (Ia ↔ Ib) and the determination of the barrier (ΔG*) to C-P bond rotation in tribenzoylphosphine. Also we herein record the carbonyl and selected ^{13}C chemical shifts and ^{31}P chemical shifts for five triaroylphospines (see Tables I and II).

Ia



Ib

Table I. Carbonyl ^{13}C Chemical Shifts[a] (^{31}P-^{13}C Coupling Constants)[b] and ^{31}P Chemical Shifts[c] for R_3P

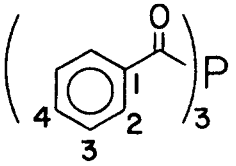
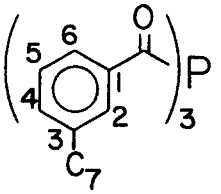
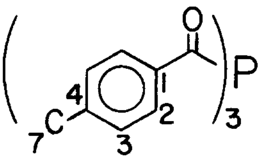
R	δ $^{13}C(^1J_{PC})$	^{31}P
$C_6H_5C(O)$	205.54(33.4)	53.97
$3\text{-}CH_3C_6H_4C(O)$	205.80(33.2)	53.73
$4\text{-}CH_3C_6H_4C(O)$	204.99(33.1)	53.22
$1\text{-}C_{10}H_7C(O)$[d]	208.01(34.3)	67.88
$2\text{-}C_{10}H_7C(O)$[d]	205.54(33.2)	53.47

[a] In ppm (±0.01) downfield from internal TMS. Samples were 200 mg in 2 ml $DCCl_3$. [b] In hertz

(±0.4). [c] In ppm (±0.01) downfield from external 85% H_3PO_4. [d] 100 mg in 2 ml of 1,1,2,2-tetrachloroethane.

The synthesis, chemical properties, infrared and ultraviolet spectral data of the triaroylphosphines examined here have been reported previously.[3] The magnitude of $^{1}J_{PC}$ (33 Hz) for these compounds lies, for example, between that of 14 Hz for trimethylphosphine[4] and 56 Hz for tetramethylphosphonium iodide.[4] This suggests that the hybridization on phosphorus in the triaroylphosphines is between that of pure p and sp^3. The ^{13}C chemical shifts for the aromatic carbons in benzoylphosphines are listed in Table II. The assignments were made based on the observed ^{31}P-^{13}C coupling constants and ^{13}C chemical shifts for related compounds. Due to the extreme complexity of the ^{13}C spectra for the naphthoylphosphines, only the carbonyl carbon (Table I) and the alpha carbon attached thereto were readily apparent and have been reported here [alpha ^{13}C resonances: 1-naphthoyl 137.17 ppm (32.2 Hz) and 2-naphthoyl 137.22 ppm (35.1 Hz)]. The magnitude of the $^{2}J_{PC}$ value (35 Hz) for the phenyl carbon attached to the C=O group was quite interesting. In all but one case [(tri-1-naphthoylphosphine)] was the magnitude of $^{2}J_{PC}$ (35 Hz) larger than that of average $^{1}J_{PC}$ (33 Hz). This observation may be considered consistent with the P lone-pair delocalization into the carbonyl group resulting in π orbital overlap between the phenyl group and phosphorus.[5]

Table II. Aromatic ^{13}C Chemical Shifts[a] (and ^{31}P-^{13}C Coupling Constants)[a] for Substituted Benzoylphosphines.

Carbon Atom			
1	139.97(35.0)	140.09(34.6)	137.84(34.8)
2	128.57(10.0)	128.62(8.2)[b]	128.67(8.1)
3	128.57(10.0)	138.62(s)	129.32(s)
4	133.90(s)	138.67(s)	144.95(s)
5	-	128.46(s)	-
6	-	125.982(8.9)[b]	-
7	-	21.24(s)	21.76(s)

[a] See Table I. [b] May be interchanged.

Similarly, the ^{31}P chemical shift (<u>ca</u>. +53 ppm, downfield from 85% H_4PO_4) for the triaroylphosphines is probably indicative of delocalization of the electron pair on phosphorus into the C=O group (this is supported by $\nu_{C=O}$ appearing at longer wavelengths in the Ir spectra compared to that in aldehydes and ketones).[3] Many phosphines exhibit a <u>negative</u> ^{31}P shift from 85% H_3PO_4. Also, the inability of these phosphines to undergo quaternization contributes to the supposition of phosphorus lone-pair delocalization.[3] The unusually large ^{31}P shift of 67.88 ppm for tri-1-naphthoylphosphine reflects extreme crowding around phosphorus with deformation of the pyramidal configuration compared to that in phosphines with non-bulky groups.[6] In support of this was the observation of a ^{31}P chemical shift of +61.9 ppm for tri-tert-butylphosphine compared to that of +19.4 ppm for tri-2-propylphosphine.[6]

Cooling solutions (D_2CCl_2) of the substituted benzoylphosphines resulted in the appearance of a second doublet for a carbonyl carbon in the ^{13}C spectrum (see Table III). From these data, a value of 15 kcal/mole[7] was obtained for the barrier (ΔG*) to C-P bond rotation. This value for ΔG* is somewhat lower than ΔG* for a variety of amides[1,2] and is likely, in part, due to the increased C-P bond length compared to C-N[8] and the larger size of P vs N.[8]

Table III. Carbonyl ^{13}C Chemical Shifts[a] (^{31}P-^{13}C Coupling Constants)[b] for R_3P.

R	T(°C)	δ $^{13}C(^1J_{PC})$	
$C_6H_5C(O)$	-80	206.97(32.5)	199.85(57.4)
$3\text{-}CH_3C_6H_4C(O)$	-70	207.25(32.1)	200.12(57.3)
$4\text{-}CH_3C_6H_4C(O)$	-70	206.28(31.8)	100.24(57.7)

[a] In ppm (±0.01) downfield from internal TMS. Samples were 200 mg in 2 ml of D_2CCl_2. [b] See Table I.

We suggest, that when C-P bond rotation is slow, only one carbonyl carbon can interact with the phosphorus atom to produce a second shielded carbonyl ^{13}C signal (interaction via overlap of parallel π orbitals on C=O with the lone-pair of electrons on P). This assumption is borne out by the observation that, at low temperature, the relative ratio of the downfield ^{13}C carbonyl signal to the upfield signal is about 2:1.

That the process under investigation here is C-P bond rotation and not pyramidal inversion at phosphorus is reasonably defended since inversion cannot account for two ^{13}C signals in these symmetrical molecules. This argument does not rule out the possibility of inversion at phosphorus proceeding at a faster rate than C-P rotation but this seems unlikely.[9] However no suitable "marker signal" is present in these systems to determine whether inversion is occurring.

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7. ΔG^* obtained from $k_C = \pi\Delta\nu_\infty / 2$ ($T_C = 49.5 \pm 2.5°$; $\Delta\nu_\infty = 179.4$ Hz) and the Eyring equation.
8. C-P bond length = 1.83 Å from D. E. C. Corbridge, "The Structural Chemistry of Phosphorus," Elsevier, New York, NY, 1974; p. 394. C-N bond length = 1.47 Å, van der Waals' radii P = 1.9 Å, N = 1.5 Å from L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, NY, 1060; pp 229, 260.
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