^{13}C NMR Studies on Some Tris-(dialkylamino)phosphines, Tris-(dialkylamino)phosphine Chalcogenides and Tris(dialkyl-amino)arsines

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Recently, several tris(dialkylamino)phosphines, $(R_2N)_3P$, tris(dialkylamino)phosphine chalcogenides, $(R_2N)_3PX$, and one tris(dialkylamino)arsine, Mor_3As, have been studied by X-ray methods.[1] The asymmetric structure in the solid with one essentially sp^3 hybridized nitrogen atom and with one long and two short $P-N$ or $As-N$ bonds appears to be general for this class of compounds. No information, however, is presently available with regard to their preferred structure in solution. All attempts by NMR or other spectroscopic methods to prove their asymmetric structure in solution, even at very low temperatures, have failed.[2]

In the present communication we report the results from a ^{13}C NMR study on several compounds of the general type $(R_2N)_3P$, $(R_2N)_3PX$ (X = O, S, Se and Te) and $(R_2N)_3As$ made from various cyclic and acyclic secondary amines. Since several of the compounds had previously been studied by X-ray methods, it was of interest to examine in which way and to what extent the ^{13}C-resonances of the amino groups were influenced by changes in hetero atom, variations in bond lengths and especially differences in hybridization of the nitrogen atoms. As expected,[2] in all the compounds the dialkylamino groups were equal on the NMR time scale causing only average shifts to be observed but leaving no ambiguities with regard to assignments. The results are summarized in Tables 1 and 2.

For the majority of the compounds the ^{13}C-resonances are found to be quite insensitive to the central atom being phosphorus or arsenic and to the chalcogen atom in the pentacovalent species. Apart from the phenyl substituted aminophosphines and the corresponding selenides, entries 19 to 22 in Table 1, there appears also to be only a small dependence upon the oxidation state of the phosphorus atom, even though the X-ray studies showed a significant difference in both the $P-N$ bond lengths and the average hybridization of the

nitrogen atoms in the corresponding tervalent and pentacovalent species.[1,3] With the exception of the phosphines and the arsines derived from the fairly bulky amines, diethylamine and dipropylamine, the last entries in Table 2, the chemical shifts for the α-carbon atoms, designated C(2) in the Tables, are within 2 ppm from the parent amines, cf. Table 2. The effect upon the β- and γ-carbon atoms, C(3) and C(4), is for all compounds negligible compared with that for C(2).

Within the pentacovalent phosphorus species there is a slight but distinct downfield trend with increasing size of the chalcogen atom; the major differences appear to be within the oxides and the sulfides and between the selenides and the tellurides. In this respect the data resemble what has previously been observed for ^{31}P shifts[4] and for IR frequencies[5] in $(Me_2N)_3PX$. The downfield shift from the selenides to the tellurides may be due to the increase of the dipolar nature of the $P-X$ bond from the phosphine selenides to the phosphine tellurides.[6] A compensation between sterically induced upfield shifts and varying downfield shifts due to differences in the electron-withdrawing power of the chalcogen atoms may well be the cause of the small effects observed in the present study. The slight but distinct upfield shift upon quarternization of dialkylamines is well documented.[7] A detailed study on ^{13}C-resonances in $(Et_2N)_nPCl_{3-n}$ and $(Et_2N)_nPEt_{3-n}$ (n = 0, 1, 2 and 3) has recently been published.[8]

From the tervalent phosphorus compounds to the corresponding arsines a small but general downfield shift from 1 to 2 ppm for the α-carbon atoms is observed, cf. Table 2. This shift difference appears not to be dependent upon the donor ability of the various amines as measured by their $\sum \alpha^x$ or pK_a values.[9] Apparently the less electronegative arsenic atom[1,10] is deshielding the amino carbon atoms relative to the phosphorus atom. A similar trend has been observed for triaryl compounds in the fifth main group.[11,12]

The upfield shifts in the compounds derived from diethylamine and dipropylamine is presumably of steric origin;[13] $(Et_2N)_3PO$ and $(n-Pr_2N)_3PO$ are most difficult to prepare from $POCl_3$ and these two amines[14,15] while the phosphine oxides from dimethylamine, piperidine, morpholine and pyrrolidine are readily prepared. Likewise, the third dialkylamine molecule is reacting only slowly when $(Et_2N)_3P$ and $(n-Pr_2N)_3P$ and the corresponding arsines are to be made from phosphorus trichloride and arsenous trichloride, respectively, and the parent amines in hydrocarbons or diethyl ether as solvent.

The $^2J_{PNC}$ coupling constants are for all compounds of the expected order of magnitude. For the tervalent species the coupling constants are ~15

Table 1. ^{13}C NMR chemical shifts (ppm from TMS) and ^{31}P $-$ ^{13}C nuclear spin coupling constants (in Hz) for some tris(dialkylamino)phosphines, $(R_2N)_3P$, and some tris(dialkylamino)phosphines chalcogenides, $(R_2N)_3PX$ (X=O, S, Se and Te) in C_6D_6 at ambient temperature.

Mor   Pip   Pyrr

No.	Compound[a]	Chemical shift (ppm)[b]			Coupling constants[c]	
		C(2)	C(3)	C(4)	$\|^2J_{31_{P-N-13_C}}\|$	$\|^3J_{31_{P-N-C-13_C}}\|$
1	Mor$_3$P	47.4	68.1		15.3	5.9
2	Mor$_3$PO	45.4	67.3		<0.6	6.0
3	Mor$_3$PS	46.2	67.0		<0.6	6.8
4	Mor$_3$PSe	46.5	66.8		<0.6	7.3
5	Mor$_3$PTe	47.5	66.5		<0.6	7.7
6	Pip$_3$P	47.3	27.4	26.1	17.1	6.0
7	Pip$_3$PS	46.7	26.6	25.2	1.7	6.0
8	Pip$_3$PSe	46.9	26.4	25.1	<0.6	6.0
9	Pip$_3$PTe	47.8	26.0	25.1	1.7	6.9
10	Pyrr$_3$P	47.7	26.3		16.6	4.9
11	Pyrr$_3$PSe	47.9	26.3		5.2	7.7
12	Pyrr$_3$PTe	48.8	26.3		4.2	7.7
13	(Me$_2$N)$_3$P	37.9			18.9[d]	
14	(Me$_2$N)$_3$PO	36.8			3.4[d]	
15	(Me$_2$N)$_3$PSe	37.7			3.4[d]	
16	(Et$_2$N)$_3$P[e]	39.9	14.1		19.7	3.4
17	(Et$_2$N)$_3$PSe	40.5	13.7		4.2	3.4
18	(n-Pr$_2$N)$_3$P	49.0	22.4	12.0	18.0	2.5
19	Mor$_2$PhP	50.1	68.2		12.8	6.8
20	Mor$_2$PhPSe	45.6	66.4		<0.6	8.6
21	MorPh$_2$P	50.2	67.9		12.0	6.0
22	MorPh$_2$PSe	45.8	66.1		<0.6	10.3

[a] Mor, morpholino; Pip, piperidino; Pyrr, pyrrolidino. [b] ±0.05 ppm. [c] ±0.5 Hz; <0.6 Hz indicates not observable coupling. [d] $^2J_{PC}$-values of 19.15, 3.4 and 3.3 Hz for (Me$_2$N)$_3$P, (Me$_2$N)$_3$PO and (Me$_2$N)$_3$PS, respectively, reported in Ref. 7. [e] Shifts of 40.1 and 14.1 ppm and coupling constants of 20.1 and 3.0 Hz reported in Ref. 8.

$-$ 20 Hz and are presumably positive [16] while for the pentacovalent compounds these couplings are small or nonobservable. This observation conforms with the view that these couplings are due to interactions between the phosphorus lone pair and the nitrogen lone pair, the smaller the dihedral angle, the larger the coupling constants.[17,18] The $^3J_{PNC}$ couplings are apparently independent of the oxidation state of the phosphorus atom.

Experimental. The compounds, prepared and purified as previously described [1,3,6] were examined in *ca.* 15 % v/v C_6D_6 solutions at ambient probe temperature on a BRUKER CXP100 spectrometer operating at 22.64 MHz. The broad band proton decoupled ^{13}C spectra were run at a spectral width

of about 4 kHz and a data memory size of 8 or 16K depending upon the required resolution. The spectra were obtained using 10 mm O.D. sample tubes with internal ^{2}H lock to C_6H_6.

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Table 2. ^{13}C NMR chemical shifts (ppm from TMS) for some secondary amines, R_2NH, and the corresponding tris(dialkylamino)phosphines, $(R_2N)_3P$, and tris(dialkylamino)arsines, $R_2N)_3As$, in C_6D_6.

	C(2)	δ ppm	C(3)	δ ppm	C(4)
Morpholine	47.1		68.3		
Mor$_3$P	47.4	+0.3	68.1	−0.2	
Mor$_3$As	48.3	+1.2	68.6	+0.3	
Piperidine	47.9		27.7		25.8
PiP$_3$P	47.3	−0.6	27.4	−0.3	26.1
Pip$_3$As	48.8	+0.9	28.3	+0.6	26.2
Pyrrolidine	47.5		25.9		
Pyrr$_3$P	47.7	+0.2	26.3	+0.4	
Pyrr$_3$As	48.7	+1.2	26.4	+0.5	
Me$_2$NH	38.5 [a]				
(Me$_2$N)$_3$P	37.9	−0.6			
(Me$_2$N)$_3$As	39.7	+1.2			
Et$_2$NH	44.3		15.7		
(Et$_2$N)$_3$P	39.9	−4.4	14.1	−1.6	
(Et$_2$N)$_3$As	41.0	−3.3	15.2	−0.5	
(n-Pr)$_2$NH	52.3 [b]		23.9		12.0
((n-Pr)$_2$N)$_3$P	49.0	−3.3	22.4	−1.5	12.0

[a] From observed shift in D_2O, 38.2 ppm, Ref. 7, and the average difference in C_6D_6 and D_2O of ∼0.3 ppm as observed for several dialkylamines, *cf.* Ref. 19. [b] From Ref. 13.

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