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The ^{31}P and ^{1}H NMR spectra of mono- and dimethylamino-phosphoryl halides

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Abstract—The proton and phosphorus NMR spectra of some methylamino-phosphoryl chlorides and fluorides are reported. The magnitudes of their chemical shifts and spin–spin coupling constants are consistent with significant fluorine to phosphorus double bonding.

The compounds $Me_2NP(O)Cl_2$, $Me_2NP(O)FCl$, $Me_2NP(O)F_2$, $(Me_2N)_2P(O)F$, $MeNHP(O)Cl_2$ and $MeNHP(O)F_2$ have been prepared and their ^{31}P and ^{1}H nuclear magnetic resonance spectra measured. The proton and fluorine spectra of the dimethylamino phosphoryl fluorides and the proton and phosphorus spectra of dimethylamino phosphoryl dichloride have been reported previously [1–3]. All other spectra are reported here for the first time, as is the preparation of $Me_2NP(O)FCl$.

Our data is given in Table 1 together with those reported by other workers. The proton spectra of the dimethylamino compounds are straightforward and require no further discussion. The spectra of neat $MeNHP(O)Cl_2$, or of solutions in acetonitrile or deuterochloroform, show a four line methyl resonance in the proton region with the expected doublet of doublets due to coupling with both phosphorus and the amino proton. The amino proton resonance is broadened due to the nitrogen quadrupole and shifts significantly on dilution, as might be expected for a proton involved in hydrogen bonding [4]. In the presence of a small amount of ethanol (the amount normally present in reagent grade chloroform) the four line methyl resonance collapses to a doublet with a coupling constant (19·5 Hz) consistent with coupling to phosphorus. Rapid exchange of the proton in the presence of ethanol is clearly indicated. The proton spectrum of $MeNHP(O)F_2$ is similar to that of $MeNHP(O)Cl_2$ except that each of the four components of the methyl resonance is further split into a 1:2:1 triplet by the two fluorines. In this case, however, there is no evidence of proton exchange in the presence of ethanol consistent with the greater basicity of this compound compared to that of the dichloride.

All ^{31}P spectra of fluorine containing compounds show the anticipated splittings due to coupling with fluorine but none of them showed all of the fine structure possible from coupling with the protons present. In contrast, however, the spectra obtained for the chlorides did show all of the expected complexity, i.e. $MeNHP(O)Cl_2$ gave a pair of overlapping quartets and $Me_2NP(O)Cl_2$ a 1:6:15:20:15:6:1 septet. The protons in $MeNHP(O)F_2$ would be expected to split each component of the triplet due to coupling with the fluorines into a pair of quartets, as in the spectrum

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Table 1. Nuclear magnetic resonance data for methylamino phosphoryl halides

Compound	$\delta(CH_3)$ (ppm)	$\delta(H)$ (ppm)	$\delta(P)$ (ppm)	$J(P—CH_3)$ (Hz)	$J(P—F)$ (Hz)	$J(H—CH_3)$ (Hz)	$J(F—CH_3)$ (Hz)	$J(P—H)$ (Hz)	^1H splitting
$MeNHP(O)Cl_2$	2.76	5.9	−18.45	19.9		5.6		15.8	see text
$MeNHP(O)F_2$	2.69	5.1	+0.20	13.8	977.5	5.9	1.2	15	see text
$Me_2NP(O)Cl_2$	2.87		−17.37	16.1					1:1
	2.84*		−16.1*	16.4‡					
$Me_2NP(O)ClF$	2.79		−10.56	13.8	1046.8		1.25		1:1:1:1
$Me_2NP(O)F_2$	2.74		+3.61	11.0	992.2		1.75		1:2:1:1:2:1
	2.78‡			11.0†	997.5†		1.70†		
$(Me_2N)_2P(O)F$	2.59		−16.7	10.2	929		1.5		1:1:1:1
	2.55†			10.4†	948†		1.45†		

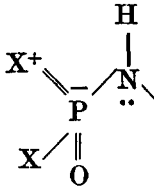
* MOEDRITZER *et al.* [3].

† CAVELL [2], J(P—F) values from ^{19}F spectrum.

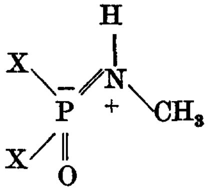
‡ NIXON and SCHMUTZLER [1].

of $MeNHP(O)Cl_2$. The observed spectrum appeared to consist of rather broad 1:4:6:4:1 quintets which must arise from the overlap of the two quartets. For $Me_2NP(O)ClF$ only five of the seven lines expected were observed in each component, and in $Me_2NP(O)F_2$ the broad resonances showed no fine structure due to proton coupling. Thirteen lines are expected in each component of the $(Me_2N)_2P(O)F$ spectrum and we observed nine. Since the two weakest pairs of lines are expected to have intensities respectively 0·0011 and 0·013 times that of the central line it is perhaps not surprising that they escaped detection.

It is interesting to note that the substitution of fluorine for chlorine in the methylamino- and dimethylamino- compounds causes the proton resonances to shift to higher field and the proton–phosphorus coupling constants to decrease. These effects are consistent with the suggestion that increased multiple bonding from fluorine to phosphorus, as compared to that from chlorine to phosphorus, leads to a relative decrease in the multiple bonding between nitrogen and phosphorus, i.e. structure I is relatively more important than structure II in the fluoride whereas the reverse is true of the chloride.



(I)



(II)

Qualitative arguments of this kind cannot in general be extended to ^{31}P chemical shifts since these are very strongly affected (particularly for P^{III} compounds) by asymmetry in the electron density around phosphorus [5]. In the series $Me_2NP(O)Cl_2$ ($\delta = -17{\cdot}37$), $Me_2NP(O)FCl$ ($\delta = -10{\cdot}56$) and $Me_2NP(O)F_2$ ($\delta = +3{\cdot}61$), however, if the change in asymmetry is rather small, it would be reasonable to argue that these data support changes in fluorine to phosphorus double bonding.

EXPERIMENTAL

All the chlorides were prepared by standard methods [6, 7] and the fluorides by fluorination of the corresponding chloride with sodium fluoride in refluxing acetonitrile. In this way were obtained $Me_2NP(O)FCl$ (b.p. 64–66°/28 mm, yield 11%), $Me_2NP(O)F_2$ (b.p. 47–48°/46 mm, yield 24%), $(Me_2N)_2P(O)F$ (b.p. 88–91°/12 mm, yield 23%) and $MeNHP(O)F_2$ (b.p. 63–64°/11 mm, yield 76%). No attempt was made to improve the yields in these reactions.

^{1}H spectra were measured using a Varian A60 spectrometer employing tetramethyl silane as internal standard. ^{31}P spectra were measured with a Varian HA100 spectrometer operating in the HA mode. A sealed capillary containing 85% phosphoric acid was placed in each sample to provide a reference signal. No difference in diamagnetic susceptibility of sample and reference was corrected for in the reported results.

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