

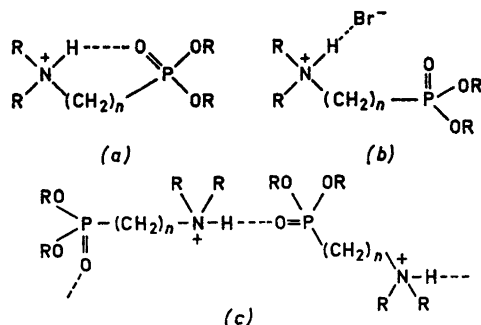
Hydrogen Bonding and Ionization of Trialkylamine Hydrobromides Containing a Phosphoryl Substituent in One of the Alkyl Groups

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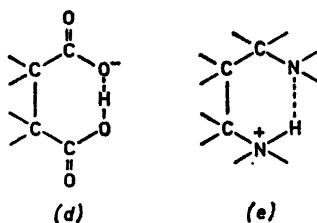
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Contrary to hydroxyalkyl diphenylphosphine oxides, $\text{HO}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$, hydrobromides of trialkylamino-substituted phosphoryl compounds, $[\text{HR}_3\text{N}^+(\text{CH}_2)_n\text{P}(\text{O})\text{R}_2]\text{Br}^-$, show no signs of intramolecular association. This conclusion is based upon the almost equal frequencies, in the solid state and in acetonitrile solution, of the $\text{P}=\text{O}$ vibration bands of the hydrobromides and the methyl bromides of the amines. The observed and predicted $\text{p}K_a$ -values of the amines point to an open chain structure also in water solution.

In a previous work¹ it was shown that hydroxyalkyl diphenylphosphine oxides, $\text{HO}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$, with $n = 1, 2,$ and 3 , in the solid state form strong intramolecular hydrogen bonds between the hydroxyl group and the phosphoryl group. Various dialkylamino-substituted phosphoryl compounds have now been synthesized, and the infrared spectra of their hydrobromides studied in order to find out whether the compounds are intra or intermolecularly associated (a, b, c):



Additional information concerning their association was sought from measurements of their ionization in aqueous solution, since acid-base equilibria, particularly of dibasic acids, are known to be influenced by intramolecular hydrogen bonding.²⁻⁴ Usually, the first ionization constant of the dibasic acids is abnormally large and the second abnormally small, the latter effect being more pronounced. An intramolecular hydrogen bond in the mono-anion is assumed to be the main reason for the observed effect (d):



Gero⁵ has likewise explained the irregular basicity values of diamines as being caused, in part, by internal hydrogen bonding (e). Also in ethylenediamine tetraacetic acid⁶ and ethylenediamine tetra(methylenephosphonic) acid,⁷ internal hydrogen bonds have been postulated to influence the ionization process.

EXPERIMENTAL

In Table 1 are recorded the dialkylamino-substituted phosphoryl compounds studied, together with physical data and bromine analysis of their hydrobromides and methyl bromides. The references quoted in column 2 refer to the applied synthetic methods.

The infrared spectra of the compounds in mull and in acetonitrile solutions were recorded on a Unicam S.P.100 MK 2 infrared instrument.

The pK_a -values of the amines were determined by potentiometric titration of a 2.5×10^{-3} M aqueous solution of the amine with 0.1 M hydrochloric acid.

INFRARED DATA ON TRIALKYLAMINOPHOSPHORYL COMPOUNDS

Hydrogen bonding involving phosphoryl oxygen is known to displace the absorption band of the P=O group 20–30 cm^{-1} towards lower wave numbers.¹⁴ Contrary to the methyl bromides, the hydrobromides of the amino-phosphoryl compounds (Table 1) have an N–H bond available for hydrogen bonding. The presence of an intramolecular (or intermolecular) hydrogen bond between the N–H and the P=O group in the hydrobromides should therefore be revealed through a considerable lower vibration frequency of the P=O group as compared with the corresponding methyl bromides. The almost identical absorption frequencies of the P=O group of the hydrobromides and the methyl bromides (Table 1) accordingly indicate the open chain structure (b), where the ammonium hydrogen is hydrogen bonded to the bromide ion. The strong infrared absorption in the region 2200–2800 cm^{-1} also argues against hydrogen bonding involving the P=O group. Trialkyl amine hydrohalides, but not tetraalkylammonium halides, absorb strongly in this region,

Table 1. Physical data of dialkylamino-substituted phosphoryl compounds, R-P(O)(OC₂H₅)₂.

R	B.p. °C 0.25 mm	n _D ²⁰	HBr-salt % Br		CH ₃ Br-salt % Br		pK _a -values 25°C		ν _{P=O} cm ⁻¹ in mull **		
			calc.	found	calc.	found	found	pre- dicted	free amine	HBr salt	CH ₃ Br salt
(CH ₃) ₂ NCH ₂ ⁸	56-57	1.4304	28.94	28.5	27.54	27.2	5.85	5.4	1270 1243	1256	1255
(C ₂ H ₅) ₂ NCH ₂ ⁹	66-67	1.4341	26.27	26.0	25.12	24.6	6.40	5.8	1263 1237	1253	1251
(C ₂ H ₅) ₂ N(CH ₂) ₂ ¹⁰	75-76	1.4396	25.11	24.9	24.05	24.1	8.20	8.2	1254	1250	1253
(C ₂ H ₅) ₂ N(CH ₂) ₃ ¹¹	85	1.4412	24.06	24.0	23.08	23.2	9.35	9.4	1249	1245	1249
(CH ₃) ₂ N(CH ₂) ₂ O ¹²	70-71	1.4249	26.10	26.2	24.96	24.5	8.00*	7.8	1276	1263	1263
(C ₂ H ₅) ₂ N(CH ₂) ₂ O ¹²	82-83	1.4291	23.91	24.1	22.95	22.7	8.40	8.2	1278	1271	1268
(C ₂ H ₅) ₂ N(CH ₂) ₃ O ¹³	91-92	1.4326	22.95	22.8	22.06	21.9	9.40	9.4	1279	1271	1268

* Tammelin¹² reports 8.03. **The frequencies were almost identical in acetonitrile solution.

and hydrogen bond between the N⁺-H group and the halide ion is known to be the reason for this absorption.¹⁵ It may seem somewhat unexpected that the bromide ion which belongs to the second period is able to outmatch entirely the phosphoryl group in the hydrogen bond formation with the N⁺-H group. Two reasons seem, however, evident:

1. The electrostatic interaction of the positive nitrogen atom with the bromide ion is much stronger than with the phosphoryl group. With a distance of 3.30 Å between nitrogen and bromine in N⁺-H...Br⁻, the electrostatic energy for an assumed dielectric constant of 10 amounts to approximately 10 kcal. In the association N⁺-H...O=P, with 50 % ionic character of the P=O bond, and with the N-O and P-O distances of 2.8 and 1.5 Å, respectively, the electrostatic energy is estimated as 1.7 kcal/mole. In spite of a considerably stronger hydrogen bond in N⁺-H...O=P than in N⁺-H...Br⁻, it seems plausible to assume that the total interaction energy, electrostatic and hydrogen bonding, is greatest for the N⁺-H...Br⁻ interaction.

2. Due to the loss of freedom of rotation, the intramolecular association (a) in solution would be associated with a much greater decrease in entropy than the intermolecular association (b).

These two effects may be sufficient to shift the equilibrium position of the hydrogen bond formation in hydrobromides of aminophosphoryl compounds almost entirely in favour of an intermolecular association (b).

IONIZATION OF TRIALKYLAMINOPHOSPHORYL COMPOUNDS

Intramolecular hydrogen bonding, (a), in the ammonium phosphoryl compounds would hinder the ionization of the involved hydrogen atom. Opening of the rigid ring structure would, however, make a positive contribution to the entropy of ionization. These two effects should thus work in opposite directions. Differences in solvation of intra- and intermolecularly associated compounds might also complicate the total picture. If, however, no internal hydrogen bond exists, an overall acid strengthening effect on the ammonium hydrogen upon introduction of a phosphoryl substituent would be expected. The effect would diminish regularly with increasing number of methylene groups between the ammonium group and the phosphoryl group. The change of pK_a of substituted amine bases, ΔpK_a , has been reported by McGowan¹⁶ to decrease approximately linearly with the number of methylene groups separating the nitrogen atom and the substituent. The magnitude of the transmission coefficient for each methylene group ranged from 0.33—0.53.

In predicting the pK_a -values of the aminophosphoryl compounds in Table 1 a value of 0.5 was chosen for the transmission coefficient, and triethylamine ($pK_a = 10.6$) together with triethylamine substituted in the 2-position with a diethoxyphosphoryl group (compound No. 3, Table 1) were selected as references. When the phosphorus atom is linked through an oxygen atom to the hydrocarbon chain (compounds Nos. V, VI, and VII), the diameter of the oxygen was set equal to that of the methylene group, and an additional ΔpK_a -value of the alkoxy group given by Clark and Perrin¹⁷ was added. The exchange of a methyl group directly attached to the nitrogen atom for ethyl generally results in a decrease of the pK_a -values of tertiary amines of approximately 0.2 pH-units for each group.¹⁷

The pK_a -values thus predicted for the aminophosphoryl compounds (Table 1) correspond fairly well with the observed values. The greatest deviation is found for the α -substituted compounds; however, due to a proximity effect these are often anomalous.¹⁷ If an intramolecular hydrogen bond had been present, the predicted pK_a -values based on additivity of the inductive substituent effects, would have been expected to show little or no correlation with the observed values. This is the case for ionization of dibasic acids where an internal hydrogen bond is formed.

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Received February 12, 1965.