TABLE I

COUMARIN-3-CARBOXYLIC ACIDS

Compd.[a]	Aldehyde or ketone used	Method used	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
I	Salicylaldehyde	A, B	190–191	100	$C_{10}H_6O_4$	63.16	63.34	3.18	3.38		
II	5-Chlorosalicylaldehyde	A, B	214–215	100	$C_{10}H_5ClO_4$	53.47	53.69	2.24	2.24	15.78	15.94
III	2′-Hydroxyacetophenone	A	194.5–196	44	$C_{11}H_8O_4$	64.70	64.50	3.94	4.14		
IV	2,4-Dihydroxybenzaldehyde	A, B	264–265	85	$C_{10}H_6O_5$	58.26	57.99	2.93	3.14		

[a] I, 3-carboxycoumarin, lit.[2] m.p. 187–188°; II, 3-carboxy-6-chlorocoumarin; III, 3-carboxy-4-methylcoumarin; IV, 3-carboxy-7-hydroxycoumarin, P. C. Mitter and S. K. Saha [*J. Indian Chem. Soc.*, **11**, 257 (1934); *Chem. Abstr.*, **28**, 5069 (1934)] reported m.p. 262°.

TABLE II

SPECTRAL CHARACTERISTICS AND *p*-BROMOPHENACYL DERIVATIVES OF I–IV SERIES

Compd.	Q.r.u.[a]	Ultraviolet absorption, mμ[b] (log ε)	*p*-Bromophenacyl ester formula	M.p., °C.	Bromine, % Calcd.	Bromine, % Found
I	0.432	267.4 (3.90), 300.5 (4.02)	$C_{18}H_{11}BrO_5$	122–123	20.68	20.97
II	1.16	295 (4.00), 340 (3.85)	...	...	...	...
III	2.30	266.4 (3.84), 302.3 (4.03)	$C_{19}H_{13}BrO_5$	151–152	19.91	19.49
IV	196.6	263.7 (3.56), 346 (4.14)	$C_{18}H_{11}BrO_6$	122–123.5	19.81	19.67

[a] See L. L. Woods and J. Sapp, *J. Chem. Eng. Data*, **8**, 235 (1963), for the method of calculating quinine reference units. [b] Spectra were run on a Bausch and Lomb 505 spectrophotometer in Spectrograde methanol.

and calcium carbonate were refluxed together for 90 min. in 50 ml. of absolute ethanol. The mixture was then filtered while boiling hot. The filtrate was diluted with an equal volume of water, chilled for 2–3 hr. in the freezer, and the precipitate was collected and recrystallized twice from absolute ethanol.

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N-H Stretching Frequency in Alkylaminotriphenylphosphonium Salts

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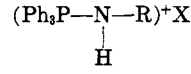
Participation of N–H in hydrogen bonding to anions had been studied quite extensively in the recent years. Most work in this field has been done with ammonium salts.[2] Fujita, *et al.*,[3] and Larsson[4] obtained evidence of hydrogen bonding of the type N–H. . .anion from the lowering of the N–H stretching frequency in hexammine cobalt(III) complexes. Most recently, similar studies on hexammine and pentammine complexes of chromium(III) have been reported.[5]

No hydrogen bond studies in alkylaminotriphenylphosphonium salts (I) have been reported. As recently, some alkylaminotriphenylphosphonium salts, such as chlorides,[6] bromides,[7] iodides,[7] and tetrafluoroborates,[8] became available to us, it was decided to investigate systematically the possible presence of N–H. . .anion-type hydrogen bond in them. This report deals with the results of the investigation and their interpretation.



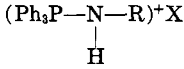
$(Ph_3P\text{—}\underset{\displaystyle H}{\underset{|}{N}}\text{—}R)^+X^-$

I

The results obtained in the present investigation (Table I, Figure 1) can be conveniently discussed under the following two headings.

TABLE I

INFRARED DATA OF ALKYLAMINOTRIPHENYLPHOSPHONIUM SALTS



$(Ph_3P\text{—}\underset{\displaystyle H}{\underset{|}{N}}\text{—}R)^+X^-$

	N-H stretching frequency, cm.$^{-1}$			
	X$^-$			
R	Cl$^-$	Br$^-$	I$^-$	BF$_4^-$
CH_3	2945	2950	2954	3294
C_2H_5	2942	2948	2952	3278
$CH(CH_3)_2$	2938	2946	2952	3257
$C(CH_3)_3$	2934	2941	2948	3241

Effect of the Anion.—Alkylaminotriphenylphosphonium salts possess a secondary N–H group. It is well known that the free N–H moiety of the secondary amines absorbs in the 3500–3200-cm.$^{-1}$ region,[9] whereas, if N–H participates in hydrogen bonding, its absorption is shifted to a lower frequency and the absorption band becomes broader.[9,10] This is actually what was observed especially in the case of alkylaminotriphenylphosphonium chlorides, bromides, and iodides (Figure

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[2] G. Gray and T. C. Waddington, *Trans. Faraday Soc.*, **53**, 901 (1957); A. Tramer, *Compt. rend.*, **249**, 2755 (1959); P. Sauvageau and C. Sandorfy, *Can. J. Chem.*, **38**, 1901 (1960); G. Tsoucaris, *Acta Cryst.*, **14**, 917 (1961).

[3] J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Am. Chem. Soc.*, **78**, 3295 (1956).

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[5] N. Tanaka, M. Kamada, J. Fujita, and E. Kyuno, *Bull. Chem. Soc. Japan*, **37**, 222 (1964).

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[7] H. Zimmer and G. Singh, *J. Org. Chem.*, **28**, 483 (1963).

[8] H. Zimmer and G. Singh, *ibid.*, **29**, 3412 (1964).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 215.

[10] G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," Reinhold Publishing Corp., New York, N. Y., 1960, p. 75.

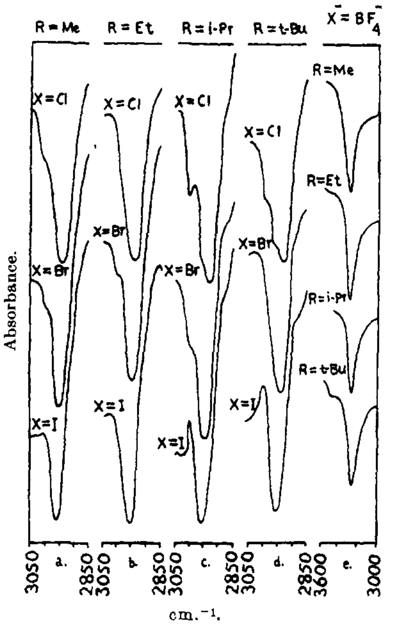

Figure 1.—N-H Stretching frequency in alkylaminotriphenylphosphonium salts, $(Ph_3PNHR)^+X^-$. Concentration in chloroform: a-d, 0.1 mole; e, 0.05 mole.

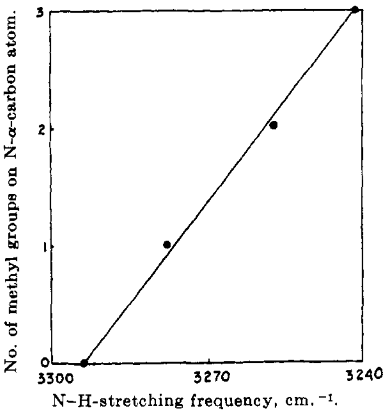

Figure 2.—N-H Stretching frequency in alkylaminotriphenylphosphonium tetrafluoroborates as a function of the number of methyl groups on N-α-carbon atom.

1). From the data recorded in Table I two points are quite clear. Firstly, except in the case of tetrafluoroborates, there is a significant lowering of N-H stretching frequency as compared to that of a free secondary N-H group. Secondly, in any row of Table I the shift in the stretching frequency of N-H is in the order of $BF_4^- \ll I^- < Br^- < Cl^-$. These data are explained by hydrogen bonding of N-H. . .anion type and an increase in the strength of hydrogen bond formed in the order $BF_4^- \ll I^- < Br^- < Cl^-$. This order of hydrogen bonding for halides is the same as reported in the case of hexammine cobalt(III)[3] and chromium(III)[4] complexes, tetraamidophosphonium salts,[11] and tetraalkylammonium halides.[12]

The N-H stretching absorptions in alkylaminotriphenylphosphonium tetrafluoroborates lie within the lower limits of the absorption range of free secondary N-H and are much higher than the corresponding halides. These facts indicate that, if at all hydrogen bond formation occurs between the N-H group and the tetrafluoroborate anion, it is a comparatively very weak interaction. This can be explained quite logically by invoking the large size of the tetrafluoroborate anion. Owing to the large size of the tetrafluoroborate anion there is less charge density on its surface and consequently weaker or hardly any hydrogen bond formation with the N-H group.

Effect of Branching at the N-α-Carbon Atom.—Besides the nature of the anions, it is quite evident from Table I that the branching at the N-α-carbon atom also affects the N-H stretching absorption. A drop in this frequency is noticed as the N-alkyl group becomes more branched. It is not possible to explain the direction of the shift by invoking the inductive effect of the N-alkyl groups, since in that case an opposite shift in the N-H stretching absorption should be observed. An explanation for this observation has been given by Nyquist[13] in the case of N-alkylphosphoramidates. Bulky alkyl groups, because of their steric requirements, elongate the neighboring N-H bond and thus reduce its stretching force constant; as a result of which the N-H stretching frequency is lowered.

Recently, Brandmiller and Seevogel[14] have obtained similar results in alcohols. The introduction of alkyl groups (branching) on the α-carbon reduces the frequency of O-H in alcohols.

It has already been pointed out that, if at all the tetrafluoroborate anion does form a hydrogen bond with the N-H of alkylaminotriphenylphosphonium salts, it is very weak. So the N-H stretching frequency in alkylaminotriphenylphosphonium tetrafluoroborates is affected mainly by the size of the N-alkyl groups. From the preceding discussion it is expected that the branching at the N-α-carbon should have the greatest effect on the stretching frequency of N-H in the observed direction. A linear correlation has been found to exist between the N-H stretch and the number of methyl groups on the N-α-carbon atom (Figure 2).

Experimental

The alkylaminotriphenylphosphonium salts employed in this investigation were prepared and purified as reported previously.[6-8] Spectral grade chloroform, without further purification, was used as a solvent. All measurements were carried out at an average room temperature of 23.5 ± 0.5°. The exact position of the N-H absorption band was found by using the spectrum of polystyrene as a reference.

The infrared spectra of alkylaminotriphenylphosphonium chlorides, bromides, and iodides were obtained on a Perkin-Elmer Model 337 grating spectrophotometer. Solutions of 0.1 *M* concentration in chloroform were used. Matched sodium chloride cells of 0.1-mm. thickness were employed.

Spectroscopic measurements in the case of alkylaminotriphenylphosphonium tetrafluoroborates were carried out in 0.05 *M* chloroform solutions on a Baird-Atomic Model KM-1 spectrophotometer equipped with sodium chloride prism. Sodium chloride cells, 1 mm. thick, were employed.

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