Electronic Absorption Spectra of Ion Pairs Composed of Substituted Amine Picrates in Acetonitrile[1]

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Abstract: The spectra of the undissociated forms of triethylammonium, 2,4-lutidinium, pyridinium, and anilinium picrates in acetonitrile are shifted to shorter wavelengths as compared to the spectrum of the picrate ion. In order to calculate these spectra from the over-all spectra of 0.01 *M* amine picrate (BHA) solutions, the ionic dissociation constants K^{d}_{BHA} and formation constants K^{f}_{BHA} were determined and found equal to 4.4×10^{-3} and 6×10^{9} for triethylammonium, 3.6×10^{-3} and 2×10^{5} for lutidinium, 3.0×10^{-3} and 6×10^{3} for pyridinium, and 1.1×10^{-3} and 4×10^{2} for anilinium picrates, respectively. The wavelength of maximum absorption and the absorbance index at λ_{max} were 373 mμ and $1.9_2 \times 10^{4}$ for picrate ion, respectively, and for the undissociated picrates in the order mentioned 356 and 1.8×10^{4}, 347 and 1.85×10^{4}, 346 and 1.74×10^{4}, and 348 and 1.5×10^{4}. It is concluded that the undissociated forms of the picrates are present mainly as ion pairs, except anilinium picrate, 20% of which may be present in a molecular form. Qualitative confirmation of this conclusion was derived from infrared spectra. Homoconjugation constants, $[B_2H^+]/[BH^+][B]$, were estimated equal to 0 for triethylammonium, 8 for lutidinium, 7 for pyridinium, and 4 for anilinium from spectrophotometric data in picrate solutions containing excess base.

In a study of the spectrophotometric titration in acetonitrile (AN) of 0.01 *M* picric acid (denoted as HA) with an uncharged base B, it was found that a plot of the absorbance *vs.* concentration of B (expressed in per cent of concentration of HA) did not yield a straight line from the origin to the equivalence point (reaction line), even when salt formation was quantitative. On the other hand, the reaction line was found to be straight in the titration with tetraalkylammonium hydroxide, the salt formed being practically completely dissociated into ions at a concentration of 0.01 *M*. At the high concentration (0.01 *M*) of picric acid used, the titrations were carried out at the long wavelengths of the order of 480 mμ, where the molar absorptivity of the picrate ion is some 200 times smaller than at the wavelength of maximum absorption. At 480 mμ the molar absorptivity of the amine salt BHA was found to be not only considerably smaller than that of the tetraalkylammonium salt, but it varied with the base used.

Since the homoconjugation constant $K^{f}_{HA_2^-}$ of picric acid is negligibly small,[2] the obvious interpretation of the above observations is that the absorption spectrum of the undissociated salt BHA is shifted to shorter wavelengths as compared to that of A^- and that it is different for different bases.

In order to calculate the absorption spectrum of the undissociated salt from that of a solution in AN of the salt, it was necessary to know the ionic dissociation constant K^{d}_{BHA} of the salt.

$$K^{d}_{BHA} = [BH^+][A^-]f^2/[BHA] \qquad (1)$$

$$f_{BH^+} = f_{A^-} = f$$

When the base B was so weak that salt formation was incomplete during the neutralization, it was also necessary to know the formation constant K^{f}_{BHA} of the salt

$$K^{f}_{BHA} = [BHA]/[B][HA] \qquad (2)$$

activity coefficients of uncharged species being taken equal to one.

Both constants were calculated from data obtained in the conductometric titration of 0.01 *M* picric acid with B. When salt formation is quantitative at the equivalence point (*e.g.*, triethylamine), the conductance attains a constant value at this point and remains constant with an excess of base, provided there is no homoconjugation of B with BH^+ to form B_2H^+.[3] When salt formation at the equivalence point is not complete, the conductance continues to increase with excess of base and becomes constant when salt formation is quantitative, provided B_2H^+ formation is negligible. With the weak bases aniline, pyridine, and 2,4-dimethylpyridine (2,4-lutidine) used in the present study, the conductance after complete salt formation started to increase as a result of B_2H^+ formation when the excess of base became very large (Figure 1), the salt B_2HA being essentially completely dissociated.

Experimental Section

Chemicals. Acetonitrile was purified and dispensed as described previously.[4] Picric acid was the same product as used previously.[2] Purification of the following bases have been described elsewhere: triethylamine,[5] 2,4-dimethylpyridine (lutidine),[6] pyridine,[6] and aniline.[6] Triethylammonium and anilinium perchlorates were the same products used in another study.[7] The former was found to contain 0.3% free perchloric acid. Tetrabutylammonium picrate was prepared in this laboratory by Gracias.[8]

Instrumentation. Techniques for conductometric[6] and potentiometric measurements[2] have been described elsewhere. $E°$ of the glass electrode used in the present work was determined in picrate buffers and found equal to +0.702 V. *vs.* 0.010 *M* $AgNO_3$ in AN | Ag.

Spectrophotometric Measurements. Spectra of 1.08×10^{-2} *M* picrates were run in a Cary Model 15 recording spectrophotometer from 280 to 430 mμ in a Rik quartz adjustable path-length cell at path length 0.067 mm from 430 to 460 mμ in a 1.00-mm "Herasil" cell (Precision Cells, Inc., New York, N. Y.), and from

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-67.

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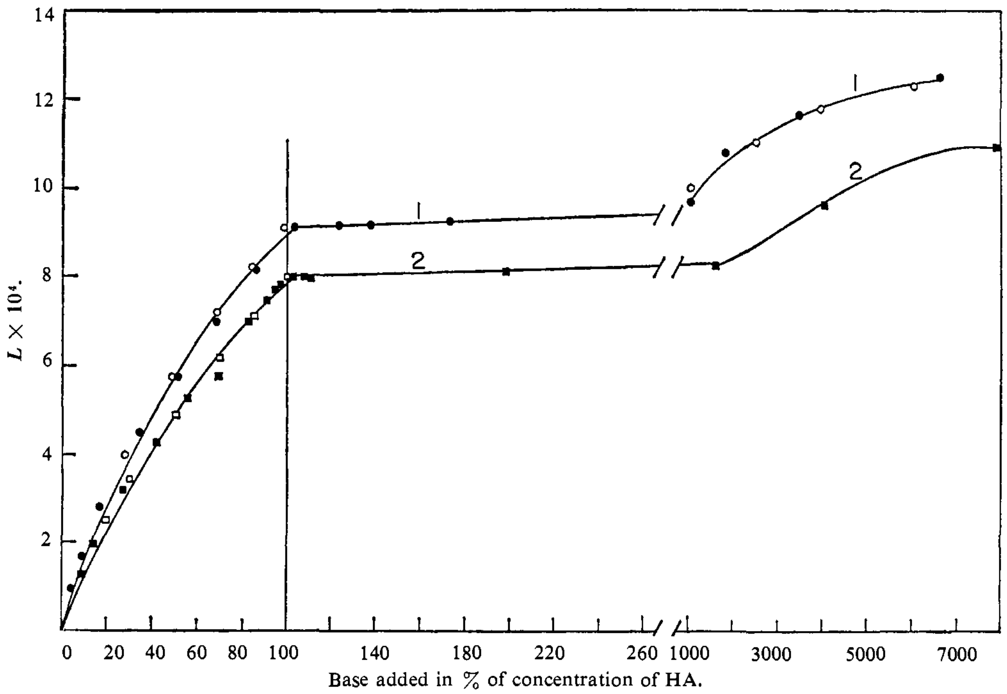

Figure 1. Calculated and experimental conductometric titration curves of picric acid with amines: (1) 1.42×10^{-2} M picric acid with pyridine, (2) 1.08×10^{-2} M picric acid with lutidine (closed symbols, experimental points; open symbols, calculated points).

460 to 490 mμ in a 1-cm Pyrex glass-stoppered cell. The path length of the 0.067-mm cell was determined at 370 mμ in 0.0130 M tetrabutylammonium picrate, the value of ϵ_{Pi^-} having been determined in a more dilute solution in a 1-mm cell. Spectrophotometric titrations were carried out in a Beckman DU spectrophotometer in a 1-cm cell at 480 mμ. At this wavelength the absorption indices of the undissociated picrate species are very small (Table I). Beer's law at 480 mμ was found to hold up to at least 0.01 M for picrate ion and undissociated triethylammonium picrate, but not for a solution of the amine picrate.

Infrared spectra were recorded as described elsewhere.[9] A 112-μ KBr cell was used.

Results

Conductometric Titrations of Picric Acid with Uncharged Amine Bases. Conductometric titration curves of 1.08×10^{-2} and 1.42×10^{-2} M picric acid with 2,4-lutidine and pyridine, respectively, are presented in Figure 1. Experimental and calculated titration curves of 1.87×10^{-2} M picric acid with triethylamine[10] and 1.08×10^{-2} M aniline with picric acid[11] up to a 200% excess of base over acid have been presented elsewhere. In the present investigation the specific conductivity of 1.08×10^{-2} M picric acid solutions containing large excesses of triethylamine or aniline was found to be at the following percentages of base with reference to acid: 100% (for comparison), 8.40×10^{-4}, 4.02×10^{-4}; 1000%, 8.43×10^{-4}, 5.5×10^{-4}; 3000%, 8.46×10^{-4}, 5.82×10^{-4}; and at 6000%, 8.52×10^{-4} and 5.93×10^{-4}, respectively. Salt formation is virtually complete at the equivalence point in the titration of about 1×10^{-2} M picric acid with triethylamine, 2,4-lutidine, and pyridine; values of $K^f{}_{BHA}$ are tabulated in Table I. Hence the titration curves in Figure 1 were calculated taking C_s, the analytical salt concentration, equal to that of base added up to the equivalence point. Simple dissociation of the salt was assumed. Values of $K^d{}_{BHPi}$ were derived from Fuoss and Kraus plots of the conductance data in Figure 1 up to 100% neutralization. The following values of ionic mobilities were previously reported: picrate, 77;[12] 2,4-lutidinium, 87;[6] and pyridinium, 99.[1] Using the above data neutralization curves could be calculated. It is seen in Figure 1 that there is close agreement between experimental and calculated curves.

Table I. Formation and Dissociation Constants and Spectral Characteristics of Undissociated Amine Picrates

Amine base	$K^d{}_{BHA} \times 10^3$	$K^f{}_{BHPi}$[a]	$K^f{}_{B_2H^+}$	λ_{max}, mμ	$\epsilon_{max} \times 10^{-4}$	$\epsilon_{480} \times 10^{-2}$
Bu_4NOH	∞	∞	...	373	1.9_2	1.00
Et_3N	4.4	6.4×10^9	0	356	1.8	0.38
2,4-Lutudine	3.6	2.2×10^5	8 (5[b])	347	1.8_5	0.11
Pyridine	3.0	6.4×10^3	7	346	1.7_4	0
Aniline	1.1	4.2×10^2	4	348	1.5	0.24

[a] Calculated from $pK^d{}_{HPi} = 11.0$[2] and values of $-pK^f{}_{BH^+} = 18.4_6$, 14.0_5, 12.3, and 10.5_6 for triethylamine, 2,4-lutidine, pyridine, and aniline, respectively,[6,11] using the relation $pK^d{}_{HPi} - pK^f{}_{BH^+} = pK^d{}_{BHPi} + pK^f{}_{BHPi}$. [b] Potentiometric value (see text).

When salt formation is incomplete at the equivalence point, as is the case in the titration of 1.0×10^{-2} M aniline with picric acid,[11,13] $K^f{}_{BHA}$ and $K^d{}_{BHA}$, found to be $4.2_5 \times 10^2$ and 1.04×10^{-3}, respectively, are estimated from the conductivity of equimolar mixtures by the method of Elliott and Fuoss.[14] Knowing $K^f{}_{BHA}$ and $K^d{}_{BHA}$ and neglecting B_2H^+ formation, the titration curve of 1.08×10^{-2} M picric acid with aniline has been calculated by Coetzee.[11] The concentrations of each of the species involved in the titration of 1.0×10^{-2} M

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[9] I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **85**, 2195 (1963).

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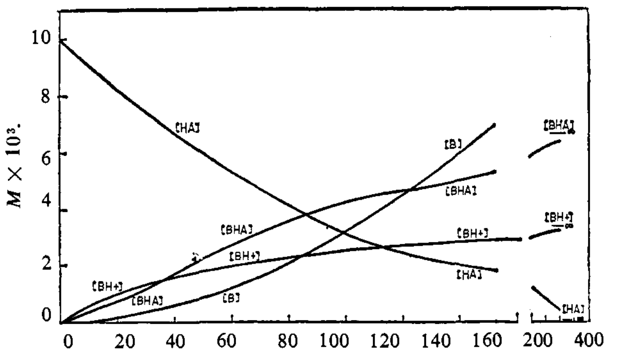

Figure 2. Calculated concentration of various species in titration of 1.00×10^{-2} M picric acid with aniline. K^d_{BHPi} and K^f_{BHPi} taken as 1.1×10^{-3} and 4.2×10^2, respectively.

picric acid are plotted against percentage of base with reference to acid in Figure 2.

In the present work the titration of 1.08×10^{-2} M picric acid with triethylamine has been carried out and, as expected, the calculated and experimental curve were found to be in good agreement. No increase of conductance was observed after the equivalence point, even when the concentration of base was equal to 0.4 M. The conclusion is justified that there is no or only negligible formation of $(Et_3N)_2H^+$. The increase in conductivity beyond the equivalence point in the titration of 1.08×10^{-2} and 1.42×10^{-2} M picric acid with 2,4-lutidine and pyridine, respectively, and to a much lesser extent, with aniline, is apparently due to B_2H^+ formation, the dissociation constant of the salt B_2HPi being much greater than that of the simple picrate salt. Owing to the uncertainties involved in viscosity corrections in solutions containing a large excess of base and in ionic strength corrections and also the unavailability of values of the ionic mobility of B_2H^+, the calculated data in a large excess of base require a reasonable guess of λ_{0,B_2H^+} and can only be very approximate. The only titration curve involving B_2H^+ formation calculated beyond 200% excess of base over acid was that of 1.42×10^{-2} M picric acid with pyridine (Figure 1). Values of λ_{0,B_2H^+} and $K^f_{B_2H^+}$ of 70 and 7, respectively, have been taken, the latter estimated from spectrophotometric titration data as discussed in the next section.

Absorption Spectra of Amine–Picrate Ion Pairs. Absorption spectra of 1.08×10^{-2} M tetrabutylammonium picrate and of 1.08×10^{-2} M picric acid in the presence of 1.30×10^{-2} M triethylamine, 2,4-lutidine, pyridine, and 3.4×10^{-2} M aniline are shown in Figure 3. All absorbances were corrected for that of free base, which never exceeded 2% of the total absorbance at wavelengths longer than 280 mμ. From the conductance data presented in the previous section, it can be concluded that, in the above picric acid solutions containing the specified excess of base, salt formation is complete, yet B_2H^+ formation is negligible. Knowing K^d_{BHPi} (Table I), $[BH^+]$ (equal to $[Pi^-]$) and [BHPi] were calculated. Since Bu_4NPi is essentially completely dissociated in 0.01 M solution, its spectrum is that of the simple picrate ion; the contribution of this ion to the observed absorbance in picric acid–amine solutions at each wavelength has been calculated. Subtracting this value from the total absorbance yields the absorbance due to that of undissociated BHPi. Resulting spectra of undissociated BHPi are plotted in Figure 4. To cover a wide range of absorption indices at wavelengths longer than 460 mμ, a logarithmic ordinate scale was used.

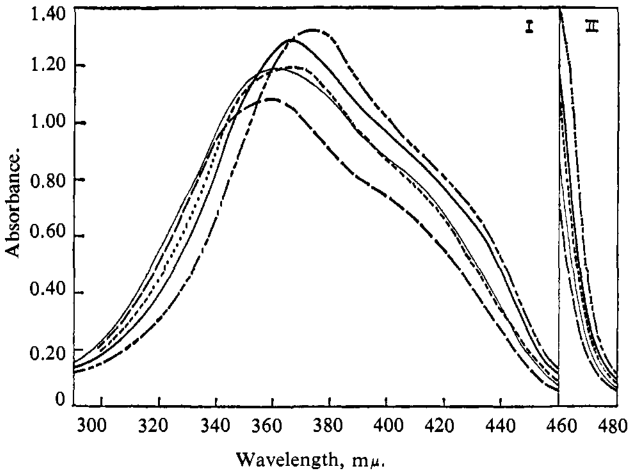

Figure 3. Absorption spectra of mixtures of 1.08×10^{-2} M picric acid with various amines at 20–212% excess of base: ——, triethylamine; - - -, lutidine; ——, pyridine, 20% excess base; — — —, aniline, 212% excess base; — - - —, 1.08×10^{-2} M tetrabutylammonium picrate. Cell path length: (I), 0.067 mm, (II) 1 mm.

We find (Figure 4) that the absorption spectra in AN of undissociated amine picrates are shifted to shorter wavelengths as compared to that of the picrate ion (Table I). The shoulder found at the longer wavelength side of the maximum in the spectrum of the picrate ion becomes more pronounced in the spectra of undissociated amine picrates.

In order to decrease the correction for the absorption of the picrate ions, the absorption spectra of 1.08×10^{-2} M picric acid with the same concentrations of triethylamine, pyridine, and aniline as in Figure 4 were measured in the presence of 0.2 M $BHClO_4$. At this high concentration of BH^+ ion the picrates are virtually completely in the undissociated forms. Up to 430 mμ, the absorption spectrum of the undissociated picrates agreed very closely with those calculated in Figure 4.

Spectrophotometric Titration of Picric Acid with Amines at 480 mμ. Experimental spectrophotometric titration curves at 480 mμ of 1.08×10^{-2} M picric acid with triethylamine and 2,4-lutidine, 1.42×10^{-2} M picric acid with pyridine, and 1.00×10^{-2} M picric acid with aniline are presented in Figure 5. At this wavelength the absorbance index of the simple picrate ion, ϵ_{Pi^-}, is much greater than ϵ_{BHPi} (see Table I), the latter calculated from the absorbance at 480 mμ in picric acid solutions containing 120% of base with reference to acid (300% for aniline) as described above. Picric acid does not absorb at 480 mμ. Use of the values of ϵ_{BHPi}, ϵ_{Pi^-} (equal to 1.0×10^2), and the calculated values of $[Pi^-]$ and [BHPi] at various percentage neutralization were made in the calculation of spectrophotometric titration curves presented in Figure 5. Incomplete salt formation of anilinium picrate was taken into account in the calculated data. Additive adsorbance of Pi^- and BHPi species was assumed. In general, the calculated and experimental titration curves shown in Figure 5 are in close agreement.

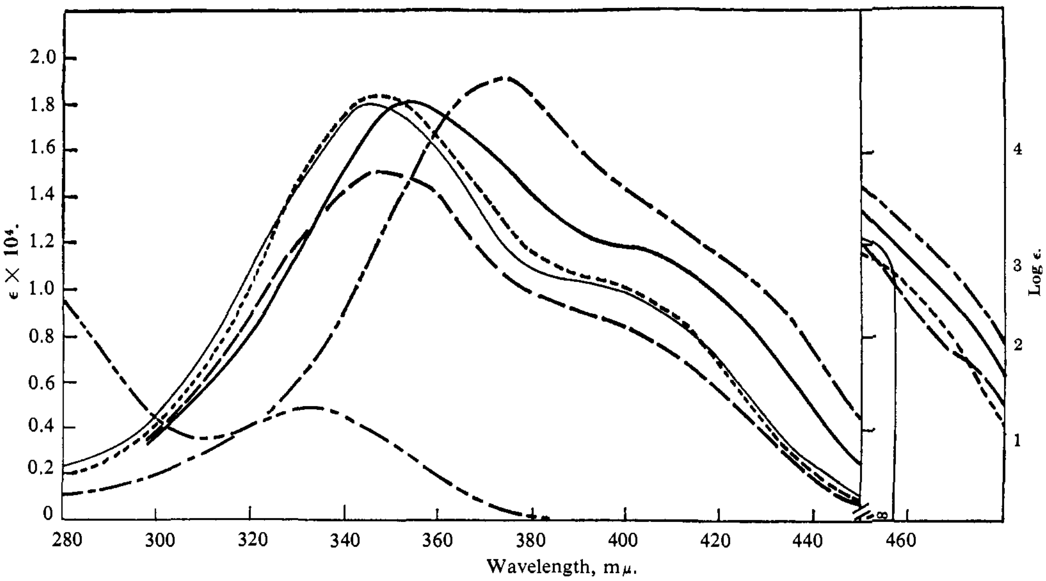

Figure 4. Calculated spectra of undissociated amine picrates from 1.08 × 10^{-2} M picric acid solutions containing 120–212% excess base: ——, triethylamine; - - - -, lutidine; ——, pyridine; — —, aniline; — - —, tetrabutylammonium picrate; — - - —picric acid.

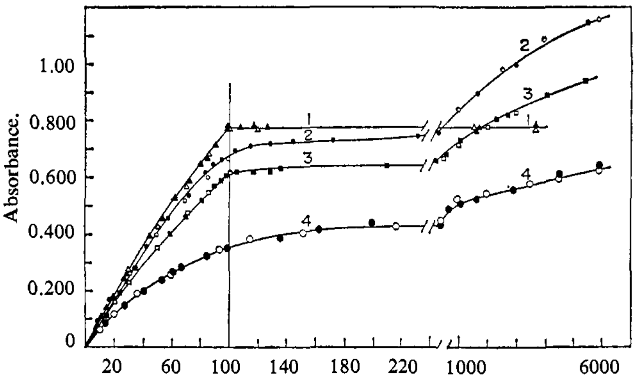

Figure 5. Spectrophotometric titration of picric acid with amines at 480 mμ: (1) triethylamine, (2) pyridine, (3) lutidine, and (4) aniline. 1.42 × 10^{-2} and 1.00 × 10^{-2} M picric acid in (2) and (4), respectively; (1) and (3), 1.08 × 10^{-2} M picric acid. Cell path length 1.00 cm (closed symbols, experimental points; open symbols, calculated).

Upon addition of a large excess of the bases 2,4-lutidine, pyridine, and aniline to the above picric acid solutions, the absorbance at 480 mμ was found to increase as a result of homoconjugation of the base (Figure 5) concurrent with formation of simple picrate ions, *viz.*

$$\mathrm{BHPi} + \mathrm{B} \rightleftharpoons \mathrm{B_2H^+} + \mathrm{Pi^-}$$

the salt B_2HPi being extensively dissociated. In the above solutions the total picrate species, C_s, is equal to

$$C_s = [\mathrm{BH^+}] + [\mathrm{B_2H^+}] + [\mathrm{BHPi}] \qquad (1)$$

and the electroneutrality condition is

$$[\mathrm{BH^+}] + [\mathrm{B_2H^+}] = [\mathrm{Pi^-}] \qquad (2)$$

Combining eq 1 and 2 with $K^f_{\mathrm{B_2H^+}}$ and K^d_{BHPi}

$$K^f_{\mathrm{B_2H^+}} = [\mathrm{B_2H^+}]/[\mathrm{B}][\mathrm{BH^+}]$$

$$K^d_{\mathrm{BHPi}} = [\mathrm{BH^+}][\mathrm{Pi^-}]f^2/[\mathrm{BHPi}]$$

$$f_{\mathrm{Pi^-}} = f_{\mathrm{BH^+}} = f$$

eq 3 results

$$[\mathrm{BH^+}]\{1 + K^f_{\mathrm{B_2H^+}}[\mathrm{B}]\}\{f^2[\mathrm{BH^+}] + K^d_{\mathrm{BHPi}}\} - C_sK^d_{\mathrm{BHPi}} = 0 \qquad (3)$$

where

$$[\mathrm{B}] = C_b - C_s - [\mathrm{B_2H^+}] \qquad (4)$$

C_b being the analytical concentration of base added. In eq 3 it has been assumed that K^d_{BHPi} is unchanged in presence of large excess of base and that B_2HPi is completely dissociated.

To calculate the absorbance in the presence of a large excess of base, a guess is made of $K^f_{\mathrm{B_2H^+}}$ and $[\mathrm{B_2H^+}]$, [B] being calculated from eq 4. $[\mathrm{BH^+}]$ is found from eq 3 knowing $K^f_{\mathrm{B_2H^+}}$ and [B]. From the definition of $K^f_{\mathrm{B_2H^+}}$ and the values of [B] and $[\mathrm{BH^+}]$, $[\mathrm{B_2H^+}]$ is then calculated, and hence $[\mathrm{Pi^-}]$ from eq 2 and also [BHPi] from eq 1. Absorbance indices of $\mathrm{Pi^-}$ and of BHPi at 480 mμ listed in Table I were used in the calculation of the absorbance in the presence of a large excess of base. The calculations were repeated and the value of $K^f_{\mathrm{B_2H^+}}$ yielding the best fit between the calculated and observed titration curves was entered in Table I. For pyridine $K^f_{\mathrm{B_2H^+}} = 7.0$ is in fair agreement with the value of 4.2 obtained by Coetzee[3] from potentiometric measurements.

Potentiometric Estimation of $K^f_{\mathrm{B_2H^+}}$ of Lutidinium. The pa_H values of solutions of 3.3 × 10^{-3} M lutidinium perchlorate containing lutidine were as follows: 8.5 × 10^{-2} M lutidine, 16.05; 0.280 M, 16.35; 0.40 M, 16.6; 0.544 M, 16.8; 0.67 M, 17.0; 0.80 M, 17.1. Values of 14.05 and 5 are found for $pK^d_{\mathrm{BH^+}}$ and $K^f_{\mathrm{B_2H^+}}$, respectively, the latter in fair agreement with a value of 8 derived from spectrophotometric data (Figure 5).

Infrared Spectra. Infrared spectra were run of solutions of triethylammonium, lutidinium, and anilinium picrates in AN. The portion of the spectra which interests us lies in the region of hydrogen-bond absorption from 2300 to 2500 $\mathrm{cm^{-1}}$ and is reproduced in Figure 6. Strong solvent bands at 2283, 2936, and 2990 $\mathrm{cm^{-1}}$ are present[15] but the bands due to hydrogen bonding in the above picrates are quite evident.

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(15) Spectrum of AN is given in a previous paper.[9]

Discussion

Electronic absorption spectra of undissociated amine picrates have been determined in solvents of low dielectric constant,[16] but no data are available on their absorption spectra in solvents with intermediate dielectric constant of the order of 40. Acetonitrile has a dielectric constant of 36, and no indication of ion association, except of formation of undissociated BHA, has been obtained in this solvent.

From absorption spectra in a series of alcohols, acetone, and AN of very dilute solutions of sodium picrate in the presence of 2-3 *M* sodium perchlorate, Izmailov[17] concluded that the spectrum of undissociated sodium picrate (ion pairs) differs from that of the picrate ion. The use of large concentrations of sodium perchlorate and the poor degree of purity of the solvent may have affected his observed spectrum. In our work we have observed abnormalities at longer wavelengths in the spectra of 0.10 *M* amine picrates in the presence of 0.2 *M* amine perchlorate.

From our experimental observations that (1) $\lambda_{\max}$ in AN of undissociated picrates does not differ much from that of the picrate ion and (2) $\epsilon_{\max}$ of the undissociated picrates does not differ much from that of the picrate ion, (3) from the infrared spectra (see below), it may be concluded that undissociated amine picrates in AN are composed mainly of ion pairs. Since $\epsilon_{\max}$ of undissociated anilinium picrate is about 20% less than that of the picrate ion, a small fraction of BHA may be present as molecular form(s).

The dipole moments of tetrabutyl, triethylammonium, and anilinium picrates as measured in benzene and dioxane solutions by Maryott[18] and Geddes and Kraus[19] are 17.8, 11.7, and 6.7 D, respectively, in order of decreasing base strength of the amine.

Typical "salt bands" occurring in the infrared spectra of piperidinium and anilinium picrates in the solid state from 3.4 to 4.5 μ have been attributed to ion pairs in equilibrium with the molecular form(s).[20] Two "ionic"bands at 2840 and 2570 cm^{-1} attributed to the structure $O^- \cdots H^+\text{-}NH_2R$ have been reported in anilinium picrate solutions in carbon tetrachloride.[21] We find in the infrared spectra $\nu_{\max}$ of triethyl-2,4-lutidinium and anilinium picrates in AN (Figure 6) at about 2710, 2650, and 2560 cm^{-1}, respectively. This confirms the conclusion that at least a large fraction of these picrates in the undissociated form are strongly hydrogen bonded and that the strength of the hydrogen bond increases with increasing acid strength of BH^+ as indicated by decreasing $\nu_{\max}$ in the above order.[22]

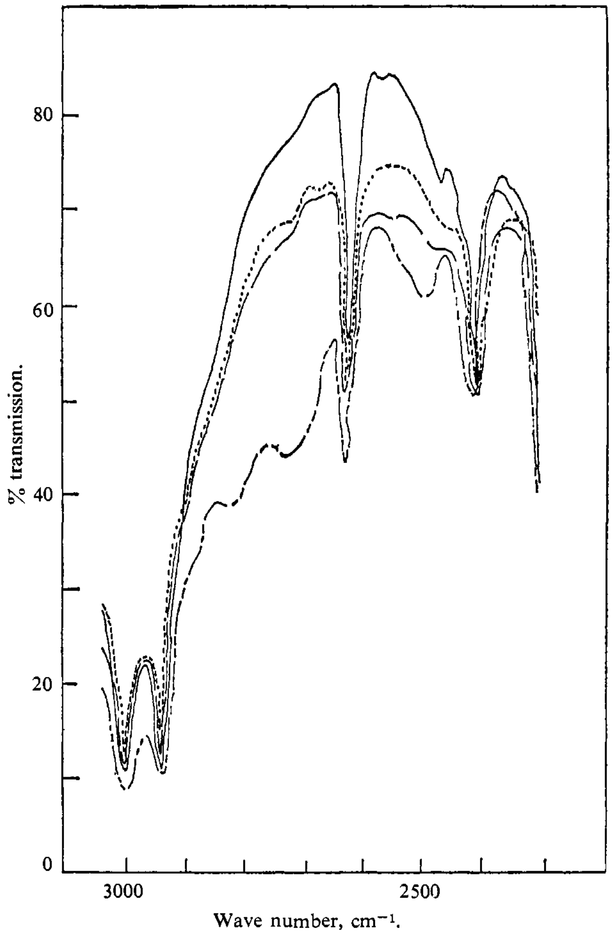

Figure 6. Infrared spectra of mixtures of picric acid and amines in the region 2300–2900 cm^{-1}: — - - - —, 0.20 *M* HPi, 0.25 *M* Et_3N; - - - -, 0.067 *M* HPi, 0.70 *M* lutidine; — —, 0.067 *M* HPi, 0.12 *M* aniline; ——, solvent (112-μ KBr cell).

Briegleb determined the infrared spectrum of the molecular picric acid–indole complex in the solid state, in which the salt bands were absent while the N–H stretching band occurred at 2.9–3.0 μ. In fact, AN solutions containing 0.01 *M* picric acid and 1 *M* indole are deep red as in the solid state.[20]

No attempt has been made in the present investigation to characterize possible n → π* and π → π* transitions in pyridinium and anilinium picrates, respectively, from the effect of solvent polarity upon the absorption maximum.[23-25] Pyridinium and anilinium picrates in the solid state have been found to be n → π* and π → π* compounds, respectively, as inferred by Kross and Fassel[26] from the asymmetric nitro group stretch at 1506, 1548 and 1525, 1491 cm^{-1}, respectively.

In our experiments the asymmetric nitro group stretching bands could not be studied because of overlapping with the asymmetrical CH_3^- doublet (ν_6) of AN at 1440 cm^{-1}.

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