The Equilibrium and the Vibrational Spectra of the *t*-Butylamine-Chloroform System

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The thermodynamic constants, ΔH° and ΔS°, of the *t*-butylamine (TBA)–chloroform-*d* system in carbon tetrachloride are obtained from the analysis of the Raman intensities observed in the C–D stretching region of chloroform-*d*, while the ΔH° on the associated species of TBA·$CDCl_3$ and $(TBA)_2$·$CDCl_3$ are evaluated to be −14.2 and −22.6 kJ/mol respectively. The IR or Raman spectrum of a solid sample, adjusted by the rapid cooling of a gaseous or liquid one respectively, with the TBA: chloroform ratio of ≈ 1 is compared with that of TBA in the gaseous, liquid, or solid state; it is confirmed, on the basis of the assignments of the observed frequencies, that the solid sample consists almost entirely of the associated species of TBA·$CHCl_3$. Only one associated species of $(TBA)_2$·$CHCl_3$ is also obtained by the crystallization of the gaseous sample with the molar ratio of 2.0. The NH_2 group vibrations in TBA·$CHCl_3$ or $(TBA)_2$·$CHCl_3$ are related intimately in their frequencies and band shapes to those in gaseous or solid TBA respectively.

t-Butylamine (TBA) associates itself[1] and forms a weak hydrogen bond with chloroform. On account of those properties of TBA, we are interested in the thermodynamic properties of the present system. Here, we try to evaluate the thermodynamic constants, ΔH° and ΔS°, by means of an analysis of the Raman intensities of the C–D stretching region of the system, using carbon tetrachloride as a solvent; hereafter, we will denote an associated species $(TBA)_m\cdot(CHCl_3)_n$ as a m : n species.

There are many studies of the vibrational spectra of self-associated species in the solid state by using the matrix-isolation technique, but no spectrum of a solid composed of two kinds of molecules capable of the formation of a weak hydrogen bond has yet been reported, as far as we know. We report here, on the basis of assignments of the vibrational spectra, that the solid sample made by the rapid cooling of a liquid or gaseous sample with a TBA : chloroform ratio of ≈ 1 or ≈ 2 consists almost entirely of the 1 : 1 or 2 : 1 species respectively. Although partial information on the structure or the bonding of associated species is obtained from the vibrational spectra of an equilibrium system in the liquid state, it is, of course, apparent that more definite information is obtained from those of a solid consisting of the associated species.

We here assign the IR and Raman spectra of the 1 : 1 species and the IR spectrum of the 2 : 1 species, by referring to those of the related compounds $(CX_3)_3CY$, where X refers to H or D, and Y to OH,[2] CN,[3] or halogen,[4–6] and compare the NH_2 group vibrations of the two species with those of gaseous or solid TBA.

Experimental

TBA or carbon tetrachloride was purified by distillation after drying with anhydrous calcium oxide or calcium chloride respectively. Chloroform was also purified by distillation after removing the ethanol, while commercially obtained chloroform-*d* was used as it was. The liquid Raman samples were adjusted *in vacuo*, so the molarity was determined by assuming that $n=PV/RT$ and by the volumetry of a liquid sample adjusted at 233 K by Hg; the molarities of TBA and chloroform-*d* in the carbon tetrachloride solution were, respectively, for three samples: (i) 3.72 and 1.93, (ii) 2.87 and 2.73, and (iii) 1.99 and 3.83. The Raman spectra were observed in the range from 223 to 244 K by adjusting them within ±0.5 K by the use of ethanol and liquid nitrogen.

The solid IR sample was obtained by the deposit of a gaseous sample with a molar ratio of $R=P_{TBA}/P_{CHCl_3}$ on a KRS-5 plate cooled at 77 K in a cryostat; the spectrum was then observed without any annealing. The solid Raman sample was obtained by the rapid cooling of a liquid sample with an adequate R, and the Raman spectrum was observed at 113±2 K. The IR or Raman spectrum of solid TBA was also observed in the same way.

The IR spectrum was observed by using a JASCO-IRA spectrometer in the range of 4000—330 cm^{-1}, and the Raman one, by using a JASCO-R800 spectrometer and a 514.5 nm line of the Ar$^+$ ion laser with the power of 200 mW. The observed frequencies were calibrated by those of a polystyrene film or indene for the IR or Raman spectrum respectively; they are believed to be accurate within ±2 cm^{-1}.

The Equilibrium of the TBA-Chloroform-*d* System in Carbon Tetrachloride

The polarized Raman spectrum of the C–D stretching region of Sample (i) at 223 K is given in Fig. 1, together with the one analyzed by two Foight functions[7,8] by means of the least-squares method. The higher and lower frequency components in Fig. 1 are assinged to the C–D stretching mode of the $CDCl_3$ monomer (hereafter,

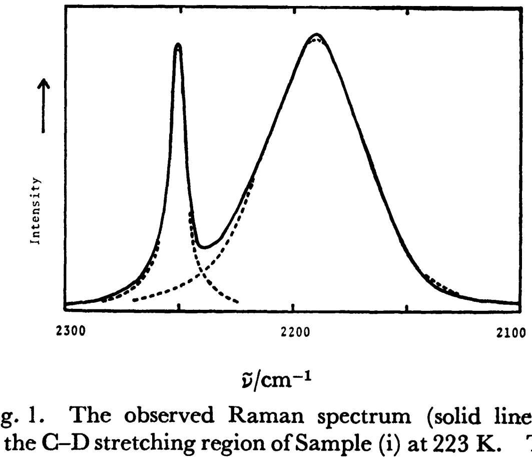


Fig. 1. The observed Raman spectrum (solid line) of the C–D stretching region of Sample (i) at 223 K. Two Foight functions analyzed are given by the broken lines.

$CDCl_3$) and the associated species respectively. The peak shift $\Delta\nu_{C-D}$ obtained from the analyzed band origins is 61.5—57.0 cm^{-1} in the order of the increase in temperature for Sample (ii). The observed relative intensity, $I_{R,O}$, is defined by S_{mn}/S_M, where S_{mn} and S_M are the band areas obtained from the parameters of the Foight functions for the associated species and $CDCl_3$ respectively; it is summarized in Table 1, where $I_{R,O}$ is found to be distributed over the sufficiently wide region of 5.69—0.73.

Under the assumption that some associated species give the lower frequency band, we analyze $I_{R,O}$ as follows: The equilibrium constant is defined by:

$$K_{mn} = \frac{C_{mn}}{C_t^m C_M^n}, \tag{1}$$

where C_t, C_M, and C_{mn} are the molarities of TBA, $CDCl_3$, and the m : n species respectively in the equilibrium state. K_{mn} relates to $\Delta H°$ and $\Delta S°$ as follows:

$$\ln K_{nm} = -\Delta H^\circ_{mn}/RT + \Delta S^\circ_{mn}/R. \tag{2}$$

The molarity of each species in the equilibrium state in the presence of some associated species is determined by using an iterative Newton method.[9] The calculated relative intensity, $I_{R,C}$, is defined by:

$$I_{R,C} = \sum \beta_{mn} C_{mn}/C_M, \tag{3}$$

where β_{mn} is the intensity ratio of each m : n species to $CDCl_3$, and the summation is carried out for all the associated species with chloroform.

The values of $\Delta H°$, $\Delta S°$, and β are adjusted by the least-squares method on the assumption that these parameters are constant in the range of temperature and concentration used here. The results obtained by taking K_{11} and K_{21} into consideration are given in Table 1. If only K_{11} is used, $I_{R,C}$ disagrees as a whole with $I_{R,O}$. The results obtained using K_{11}, K_{21}, and K_{20} are not better than those in Table 1. The NH_2 proton chemical shift of TBA[1] in cyclohexane at 24.5 °C has been analyzed by using only K_{30}, whose value is 2.3. An attempt to take K_{30} into consideration results, however, in less convergence. Since there should be small amounts of the species other than the 1 : 1 and 2 : 1 species under such high molarities of TBA and chloroform as are used here, the disagreement of about 5% found between $I_{R,O}$ and $I_{R,C}$ may, thus, be caused by not taking them into account.

TABLE 1. THE OBSERVED AND CALCULATED RELATIVE INTENSITIES

Sample	T/K	$I_{R,O}$	$I_{R,C}$
(i)	244	3.72	3.56
	238	3.92	4.06
	233	4.47	4.47
	229	4.99	4.91
	223	5.69	5.62
(ii)	244	1.41	1.50
	238	1.52	1.62
	233	1.56	1.70
	229	1.66	1.79
	223	1.80	1.91
(iii)	244	0.73	0.69
	238	0.75	0.72
	233	0.78	0.75
	229	0.82	0.77
	223	0.85	0.80

TABLE 2. THE VALUES OBTAINED FOR $\Delta H°$, $\Delta S°$, AND β

ΔH°_{11}	−14.2
ΔS°_{11}	−58.5
ΔH°_{21}	−22.6
ΔS°_{21}	−90.3
β_{11}	1.78
β_{21}	0.62

ΔH°_{mn}/kJ mol^{-1}, ΔS°_{mn}/J K^{-1} mol^{-1}

The adjusted values for the parameters are given in Table 2, where ΔH°_{11} is −14.2 kJ/mol, larger than the −17.0[10] or −19[11] kJ/mol reported for the 1 : 1 species of triethylamine with chloroform. $\Delta\nu_{C-D}$ observed here is smaller than the 79 cm^{-1} [11] reported for the 1 : 1 species of triethylamine with chloroform. These facts reflect well the basicities of the two amines. ΔH°_{21} suggests that ΔH°_{20} is about −8.4 kJ/mol if the dimer has such an open-chain structure as is found in the 2 : 1 species to be shown later. The values of β indicate that the intensity of the C–D stretching in the 1 : 1 or 2 : 1 species is, respectively, stronger or weaker than that in $CDCl_3$. This means that the intensity depends on the spatial structures of the associated species; the C–D stretching frequencies of these species are nearly the same as those treated here.

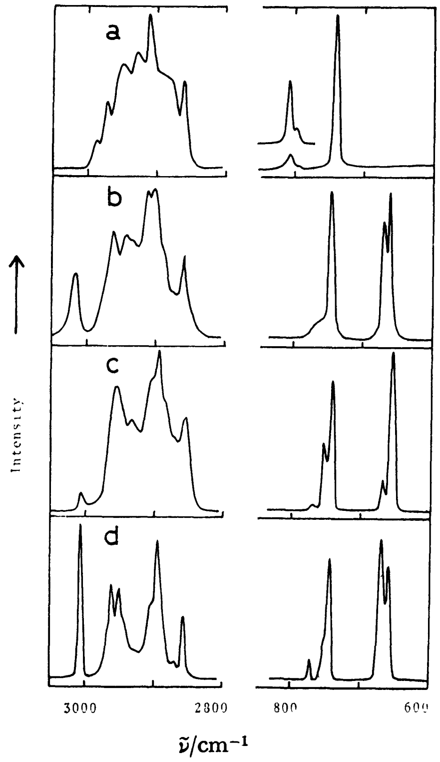


Fig. 2. The Raman spectra of the C–H and CCl_3 stretching regions of TBA and the TBA–chloroform system. (a) Gaseous TBA, (b) the liquid sample with R=0.66 at 212 K, (c) the solid sample with R=0.97 at 113 K, and (d) the solid sample with R=0.50 at 113 K.

The Vibrational Assignment of the 1 : 1 Species

The Confirmation of the 1 : 1 Species in $R \approx 1$. In Fig. 2 the Raman spectra of the C–H and CCl_3 stretching regions of the TBA–chloroform system in the solid and liquid states are compared with those of TBA in the gaseous state. By a comparison of Fig. 2-c (R=0.97) with 2-a (gas) or the spectrum of solid chloroform,[12–14] the weak bands at 3008 and 667 cm^{-1} in Fig. 2-c are assigned to the C–H stretching mode and the CCl_3 symmetric stretching mode of excess chloroform respectively (hereafter, H* denotes the hydrogen atom of chloroform), and the strong bands at 2895 and 657 cm^{-1}, to those of chloroform in the associated species. This assignment for excess chloroform is further confirmed by comparing the spectra in Fig. 2-c with those in Fig. 2-d (R=0.50), where the bands at 3005 and 669 cm^{-1} are relatively intensified. Similarly, by an examination of the Raman bands in the 1200—1280 cm^{-1} region, the two weak bands at 1211 and 1202 cm^{-1} observed for the sample with R=0.50 are assigned to the C–H* bending of excess chloroform, and the band near 1277 cm^{-1} observed for the samples with R=0.97 and 0.50, to that of chloroform in the associated species. The fact that bands due to excess chloroform are weak in the sample with R=0.97 is, thus, explained by the relation of $0.97TBA+CHCl_3 \rightarrow 0.97TBA \cdot CHCl_3 + 0.03CHCl_3$, with reference made also to the fact that there is no appearance of the bands characteristic of the 2 : 1 species, which will be discussed later. Thus, the solid sample with R=0.97 is found to consist mostly of the 1 : 1 species.

Most of the bands observed in the IR spectrum for the solid sample with R=1.03 are nearly consistent in their frequencies with those in the Raman spectrum with R=0.97, as is shown in Table 3, which indicates that the solid IR sample also consists mostly of the 1 : 1 species. Thus, the bands observed in both spectra for the solid samples with $R \approx 1$ are to be assigned on the basis of the 1 : 1 species, except for several weak ones regarded as other species.

The Band Due to Chloroform. From the assignment of the bands due to chloroform described above and given in Table 3, it is found that the C–H* stretching mode shifts to frequencies lower by 113 cm^{-1} than that of the isolated molecule, and the C–H* bending mode to ones higher by about 70 cm^{-1}, while, of the vibrations of the CCl_3 group, only the CCl_3 symmetric stretching mode shifts lower by about 10 cm^{-1}. These shifts can be explained reasonably by the interaction of chloroform with TBA through the hydrogen atom of the former with the nitrogen atom of the latter. Of the degenerate vibrations of chloroform in the 1 : 1 species, only the C–H* bending splits into two bands, whose separation is 13 cm^{-1}. On the other hand, the observed site splittings of excess chloroform in R=0.50 are nearly the same as the respective ones of solid chloroform.[12,13]

The Bands Due to the NH_2 *Group.* If chloroform interacts with TBA in the way described above, one can expect that the spectral features on TBA in the 1 : 1 species will differ from those on solid TBA, especial-

Table 3. The observed frequencies ($\tilde{\nu}/cm^{-1}$) and their assignments of the 1 : 1 species

Raman (R=0.97)	IR (R=1.03)	Assign.
3351 m	3358 w	NH_2 sym. str.
	3326 vw	D
3287 s		NH_2 sym. str.
	3244 w	D
	3168 w	D
3008 w		C–H* str.[a]
2955 vs	2955 s	CH_3 asym. str., 2 E
2936 m	2937 sh	CH_3 asym. str., A_1
2905 sh		CH_3 sym. str., A_1
2895 vs	2898 s	C–H* str.
2880 sh 2865 sh	2866 m	CH_3 sym. str., E
2854 s		$1447 \times 2 = 2894$
2771 m		$1392 + 1371 = 2763$
2704 m		$1392 + 1323 = 2715$
	2510 m	$1271 \times 2 = 2542$
1589 w	1585 s	NH_2 bend.
	1563 m	$1245 + 320 = 1565$
1472 w	1470 s	CH_3 asym. bend., E
1460 m	1460 m	CH_3 asym. bend., E
1451 w		CH_3 asym. bend., A_2
1447 m		CH_3 asym. bend., A_1
	1392 m	CH_3 sym. bend., A_1
	1371 s 1366 s	CH_3 sym. bend., E
1323 m	1318 m	C–N str.
1292 w		$945 + 345 = 1290$
1277 m	1284 m 1271 m	C–H* bend.
1248 m 1222 m	1245 s 1221 s	CC_3 asym. str., E
1203 sh		C–H* bend.[a]
	1127 w	D
1112 w	1110 w-m	NH_2 twis.
1043 w	1040 s	CH_3 asym. rock., E
999 w	1000 w	CH_3 asym. rock., A_2
	964 w	D
945 m	946 s	CH_3 sym. rock., A_1
927 m 915 m	918 w	CH_3 sym. rock., E
902 w		$458 \times 2 = 916$
893 m	894 vs	NH_2 wag.
	873 sh	D
776 vw		CCl_3 asym. str.[a]
755 w	754 vs	CCl_3 asym. str.
744 s		CC_3 sym. str., A_1
667 w		CCl_3 sym. str.[a]
657 vs	662 s	CCl_3 sym. str.
	482 b,w	D
458 m	459 s	CCN bend., E
	410 b,w	D
366 s	369 s	CCl_3 sym. bend.
345 m	346 w	CC_3 asym. bend., E
320 w		NH_2 tors.
261 s		CCl_3 asym. bend.
114 w		
85 sh		
65 s		N···H str.
52 sh		
33 w		

a) Excess chloroform.

ly in the regions characteristic of the NH_2 group. The strong and medium Raman bands at 3287 and 3351 cm^{-1} are assigned to the NH_2 symmetric and asymmetric stretching modes respectively. They are the frequencies characteristic of the non-hydrogen bonded NH_2 group and are in a frequency region lower by 28 cm^{-1} than those of gaseous TBA.

The weak Raman band at 1589 cm^{-1} and the medium one at 893 cm^{-1} have their IR counterparts at 1589 and 894 cm^{-1} respectively; the former is assigned to the NH_2 bending mode, and the latter, to the wagging mode. In Fig. 2-a, the band at 811 cm^{-1}, which is a highly polarized one without any rotational structures,[15] is assigned to the NH_2 wagging mode, and the weak one at 799 cm^{-1}, to a combination band, $345+458=803$ cm^{-1}. The weak Raman band at 1112 cm^{-1} in Table 3, whose IR counterpart is at 1110 cm^{-1}, is probably to be assigned to the NH_2 twisting mode rather than to be regarded as a combination band, because this band is considerably influenced by circumstances; it shifts to higher frequencies in solid TBA or the 2 : 1 species, as is shown in Table 4, though the NH_2 twisting mode of methylamine[16] or hydroxylamine[17] has been estimated from *ab initio* calculations to be about 1250 cm^{-1}. The NH_2 torsion of gaseous TBA has been assigned to the strong IR band at 245 cm^{-1}.[18] For the 1 : 1 species, there is no Raman band in this region, but a weak one at 320 cm^{-1}, which is not attributable to any of the skeletal bending modes. We assign this band to the NH_2 torsion of the 1 : 1 species. The NH_2-group frequencies thus assigned to the 1 : 1 species are summarized in Table 4, along with those for TBA and the 2 : 1 species.

TABLE 4. THE VIBRATIONAL FREQUENCIES ($\tilde{\nu}/cm^{-1}$) OBSERVED FOR THE NH_2 GROUP OF TBA IN SEVERAL STATES

	Gas		1:1 Species		Solid		2 : 1 Species
	IR	Raman	IR	Raman	IR	Raman	IR
Stretching		3379	3358	3351	3333	3333	3328
	3319	3315		3287	3253	3249	3248
					3165	3163	3168
Bending	1624	1629	1585	1589	1612	1608	1609
					1602		1584
Twisting	1111	1106	1110	1112	1127	1131	1130
							1109
Wagging	814	811	894	893	966	964	963
					894	894	877
Torsion	245[a]			320	480	482	498
					404	404	415
					396		
					339		

a) From Ref. 18.

The Bands Due to CH_3 Groups. By referring to the theoretical[19,20] and experimental[2,3] studies of the P-R separation, some typical bands observed with P-R separations of about 23 and 20 cm^{-1} for TBA can be regarded as the parallel and perpendicular ones respectively. These separations indicate that TBA has a slightly asymmetric oblate top, as would be expected for this molecule.

The vibrational modes of the methyl groups of the 1 : 1 species can be approximately interpreted as referring to the normal modes of such molecules with three methyl groups as trimethylacetonitrile[3] or $[(CH_3)_3AlCl]^-$.[21]

The medium band at 2936 cm^{-1} (Fig. 2-c) corresponds to the medium band at 2945 cm^{-1} (Fig. 2-b), which is a polarized band, and the very strong band at 2955 cm^{-1} (Fig. 2-c) splits into two sharp bands, at 2961 and 2951 cm^{-1} (Fig. 2-d). The former is assigned to the CH_3 asymmetric stretching mode (A_1), and the latter, to the CH_3 asymmetric stretching modes (E) accidentally degenerated from two more bands. There is no Raman band in the CH_3 symmetric bending region of the 1 : 1 species, but there are three IR bands whose spectral features correspond well to those of the IR-nitrogen-matrix spectrum of *t*-butyl alcohol.[2] The assignment of the bands due to the CH_3 rocking can be confirmed by examining the spectra for gaseous TBA in Fig. 3, where the IR or Raman band at 941 cm^{-1} has a parallel-type envelope or a sharp Q branch respectively and is assigned to the symmetric rocking mode (A_1). This assignment correlates well with that in *t*-butyl alcohol[2] or trimethylacetonitrile,[3] but not to that in *t*-butyl chloride.[4] The A_1 mode of *t*-butyl chloride has been assigned to the band at 1155 cm^{-1} on the basis of the normal coordinate analysis; it is noticeably higher than those of the three related compounds. This fact may be explained in terms of the vibrational coupling between the CH_3-rocking and the C-X-stretching mode (X=Cl, NH_2, OH, or CN).

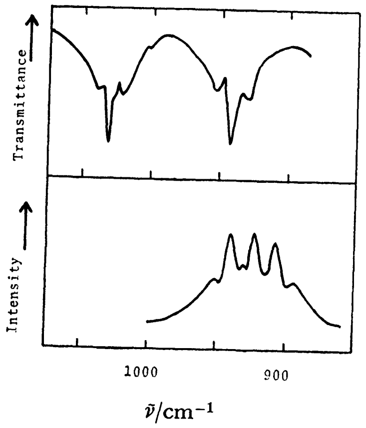


Fig. 3. The IR (upper) and Raman (lower) spectra of the CH_3 rocking region of gaseous TBA.

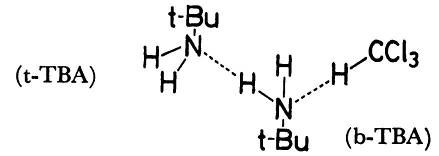
The Band Due to the Skeleton of TBA and the Lattice Modes. The CC_3 symmetric stretching mode is assigned to the strong Raman band at 744 cm^{-1}, and the CC_3 asymmetric ones, to two medium Raman bands at 1222 and 1248 cm^{-1}. The C–N stretching mode is assigned to the Raman band at 1323 cm^{-1}, which is a polarized band in liquid TBA. These stretching frequencies correlate well with those in *t*-butyl alcohol[2] or trimethylacetonitrile,[3] but not with those in *t*-butyl chloride.[4] The CC_3 asymmetric deformation and CCN bending vibrations are assigned to two medium Raman bands, at 345 and 458 cm^{-1} respectively, by comparing them with the IR or Raman bands in gaseous TBA; two bands with strong rotational structures[15] are observed at 351 and 450 cm^{-1} in the Raman spectrum, and also two band with a perpendicular-type envelope at 347 and 447 cm^{-1} in the IR one.

A weak Raman band is observed at 428 or 429 cm^{-1} in liquid or solid TBA respectively; it may be assigned to the CC$_3$ symmetric bending mode. However, we could observe no band in this region of either the IR or Raman spectrum in the 1 : 1 species.

There are five Raman bands in the region of lattice vibrations of the 1 : 1 species. The strong band at 65 cm^{-1} can reasonably be assigned to the hydrogen-bonded N···H stretching mode, because there is no band in that region of solid TBA and chloroform.[12,13] The IR bands denoted by D in Table 3 are attributably to the species with excess TBA.

The 2 : 1 Species

One can expect, by analogy with the previous section, that the solid sample with $R\approx2$ consists mainly of the 2 : 1 species. The IR spectrum of the solid sample with $R=2.0$ is given for the stretching, wagging, and torsion regions of the NH$_2$ group in Fig. 4, in which the stretching region has nearly the same spectral features as those observed for solid TBA in Fig. 5. A sharp band at about 3330 cm^{-1} in Fig. 4 or 5 lies almost in the middle of the two NH$_2$ stretching frequencies of the 1 : 1 species; it is assigned to the non-hydrogen-bonded N–H stretching mode. The other two bands have band shapes characteristic of the hydrogen-bonded stretching modes. We assign them to the two components of the Fermi resonance of the hydrogen-bonded N–H stretching mode, with an overtone of the NH$_2$ bending mode, and propose that solid TBA has a polymeric chain structure consisting of bridged TBA, which has both hydrogen-bonded and non-hydrogen-bonded N–H groups, and that the 2 : 1 species has bridged and terminal TBA, b-TBA, and t-TBA, such as:



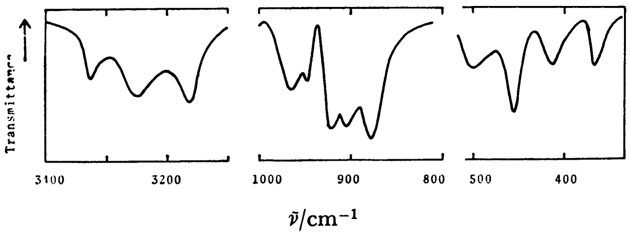


Fig. 4. The IR spectrum of the NH$_2$ stretching, wagging, and torsional regions of the solid sample with $R=2.0$ at 77 K.

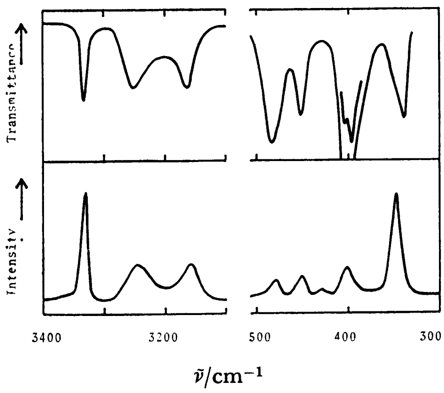


Fig. 5. The IR (upper) and Raman (lower) spectra of the NH$_2$ stretching and torsional regions of solid TBA at 77 and 113 K respectively.

The IR bands due to the NH$_2$ stretching modes of t-TBA are still expected to be as weak as those of TBA in the gaseous state or the 1 : 1 species.

A strong band at 877 cm^{-1} is assigned to the NH$_2$ wagging mode, which is observed at 894 cm^{-1} for the 1 : 1 species. From this fact, it is concluded that this sample consists almost entirely of the 2 : 1 species as expected.

There are some bands characteristic of the 2 : 1 species, including the band mentioned above. Two bands, at 1609(b) and 1584(t), 1130(b) and 1109(t), or 963(b) and 877(t) cm^{-1}, are assigned to the bending, twisting or wagging modes respectively of the NH$_2$ groups, while the bands indicated by b in parentheses can be attributed to b-TBA, and those by t, to t-TBA, with reference to the bands observed for solid TBA or the 1 : 1 species. Of the two bands at 498 and 415 cm^{-1}, the former is assigned to the NH$_2$ torsion of b-TBA, while the latter may be a component of the Fermi resonance of the NH$_2$ torsion of b-TBA with the other mode, because this frequency is too high to be assigned to the NH$_2$ torsion of t-TBA as against 320 cm^{-1} in the 1 : 1 species. The two C–N stretching modes are at 1332 and 1316 cm^{-1}.

From the fact that the frequencies due to chloroform of the 2 : 1 species are nearly in accord with those of the 1 : 1 species, the basicity of an open-chain dimeric TBA is found to be almost equal to that of the monomeric one. The TBA in the present study is classified into non-bridged and bridged types. The wagging mode in non-bridged TBA shifts to the higher-frequency region in the order of gaseous TBA, the 2 : 1 species, and the 1 : 1 species; a similar shift can be expected for the torsion, though it is not observed for the 2 : 1 species. On the other hand, the NH$_2$-group frequencies of bridged-TBA of the 2 : 1 species correlate well with those of solid TBA.

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