ELSEVIER

Journal of Molecular Structure 560 (2001) 151–159

Journal of
MOLECULAR
STRUCTURE

www.elsevier.nl/locate/molstruc

Structure of 1:1 and 1:2 complexes formed by aromatic NH and OH proton donors with aliphatic amines. Possibility of homoconjugated NHN$^+$ cation formation

J.P. Castaneda, G.S. Denisov, V.M. Schreiber*

Institute of Physics, St. Petersburg University, Peterhof, 198904 St. Petersburg, Russian Federation

Received 10 April 2000; revised 8 September 2000; accepted 8 September 2000

Abstract

Structure of the complexes with NH···N hydrogen bond formed by bis(2,3,5,6-tetrafluoro-4-trifluoromethyl-phenyl)-amine ((4-$CF_3C_6F_4)_2NH$, FA) as proton donor with aliphatic amines (dibutyl-, tributyl- and trimethylamines) as proton acceptors in aprotic solvents (isooctane and methylene chloride) in a wide range of concentrations and temperatures have been studied by IR and UV spectra. Quantitative treatment of the spectra by a computer program based on factor analysis reveals the equilibrium between free molecules and FA–aliphatic amine complexes of 1:1 and 1:2 composition, the latter having an ionic structure with proton transferred from FA to the aliphatic amine. Thermodynamic characteristics of the 1:1 and 1:2 complexes for FA + dibutylamine system have been measured. Appearance of IR bands indicating formation of NHN$^+$ homoconjugated cation has been detected in FA + trimethylamine solution in methylene chloride at temperatures 190–150 K. Spectral manifestations of the complexes containing the (trimethylamine-H-trimethylamine)$^+$ cation, formed by FA and OH proton donor (pentachlorophenol) are compared. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen bond; Proton transfer; Homoconjugated cation; Bis(2; 3; 5; 6-tetrafluoro-4-trifluoromethyl-phenyl)-amine; UV spectra; IR spectra

1. Introduction

Majority of work, where proton transfer equilibria in aprotic media have been detected and structure of the ionic complexes formed has been investigated by spectroscopy methods, concerns the systems with strong hydrogen bonds of OH···N and HalH···N types [1–5]. A few similar studies were performed for systems with NH···N bonds. At the same time studies of the proton transfer in the NH···N bonded complexes seem to be of essential interest, keeping in mind their biological importance.

In most cases the acidity of NH proton donors is not very high; their interaction with typical organic bases, such as aliphatic amines, in aprotic solvents results in formation of molecular hydrogen bonded complexes without proton transfer. However, during the last years several systems have been found where the proton transfer occurs in the complexes formed by strongest NH-acids and N-bases [6–9]. In particular, a number of works were devoted to studies of the extremely strong N-bases, so-called proton sponges. Protonation of these compounds results in formation of a cation containing very strong intramolecular

---

* Corresponding author. Fax: +7-812-428-7240.
E-mail address: v.schreiber@pobox.spbu.ru (V.M. Schreiber).

PII: S0022-2860(00)00739-0

H-bond $[NHN]^+$ [10–14]. Such hydrogen bridges are nonlinear because of structural limitations, as well as majority of other intramolecular H-bonds. No such limitations exist in case of the complexes of bases with conjugated acids, i.e. homoconjugated cations with intermolecular hydrogen bond $[NHN]^+$, but the experimental studies of these complexes in solutions are complicated often by the existence of several competing equilibria. Recently, an attempt to analyze structural and spectral data referred to formally symmetrical bonds [OHO], [NHN], [FHF] has been undertaken in Refs. [15–17].

The perspective objects for studies of spectral and thermodynamic characteristics of proton transfer equilibria in systems with NH···N bonds are fluorinated secondary aromatic amines. It has been found that some of these molecules are strong acids [18,19] and can protonate aliphatic amines even in aprotic solvents [6]. In the present communication we report the results of spectroscopic study of several systems containing hydrogen bonds NH···N with participation of perfluorinated secondary aromatic amine bis-(4-CF_3-2,3,5,6-tetrafluoro-phenyl)amine ($(4\text{-}CF_3C_6F_4)_2NH$, FA) as the NH proton donor. Aliphatic amines dibutylamine (DBA), tributylamine (TBA) and trimethylamine (TMA) have been chosen as proton acceptors.

The aims of the work are:

1. To study the structure of the complexes formed by FA with these acceptors, to determine their composition, spectral and thermodynamic characteristics by means of electronic and vibrational spectra.
2. To elucidate conditions promoting proton transfer and formation of ionic structures, such as $NH^+\cdots N^-$ or $(N\cdots H\cdots N)^+X^-$, to find out spectral manifestations of proton transfer in UV and IR region.
3. To develop the effective technique of spectral analysis of systems with chemical equilibria, free of subjective factors and using maximum spectral information.

FA has convenient absorption bands in the UV region, sensitive to hydrogen bond formation and ionization. This makes it possible to carry out a parallel study by electronic and vibrational spectra and, on the other hand, to compare FA with aromatic OH proton donor pentachlorophenol C_6Cl_5OH (PCP).

Aprotic solvents have been used; in particular, nonpolar isooctane was compared with slightly polar methylene chloride.

2. Experimental

IR spectra were recorded with an FT-IR Bruker IFS-28 instrument, UV spectra with Specord M-40 C.Zeiss spectrophotometer equipped with a computer. Home-made cryostats for UV and IR regions were used for measurements in the temperature interval 300–85 K.

FA has been synthesized as described in Ref. [20]. The amines and the solvents used were purified by repeated vacuum distillation over KOH and P_2O_5.

To increase the reliability of qualitative interpretation of spectra, determination of the number and composition of the complexes and quantitative estimation of thermodynamic parameters approaches have been developed, which enables one to use all the information contained in spectra.

The approach is based on factor analysis of a set of spectra obtained at constant temperature within a range of concentrations, corresponding to maximum equilibrium shift from the left to the right. A similar approach has been used earlier in Refs. [21–23]. To realize this approach, a computer program in Pascal 7.0 has been compiled (see Ref. [23] for details). It processes a set of 10–50 spectra consisting of 100–1000 points in 3–60 min with an Intel Pentium 133 computer, with 8 Mb RAM. In the first stage the program allows the determination of the number of components, the additive sum of which can reproduce all the spectra of the set. The determined number of the components is used to formulate the hypothesis of the scheme of equilibria taking place in the system. On the second stage this hypothesis is introduced into the program, and the set of spectra is processed to find the equilibrium constants and spectra of all the individual components. No hypothesis about the band shapes or other spectral parameters is used. This procedure reduces to a minimum the subjective factor, connected with the choice of analytical wavelengths and with overlapping bands separation. Having repeated the measurements at several temperatures one can obtain the enthalpy and the entropy of studied processes by the vant-Hoff law.

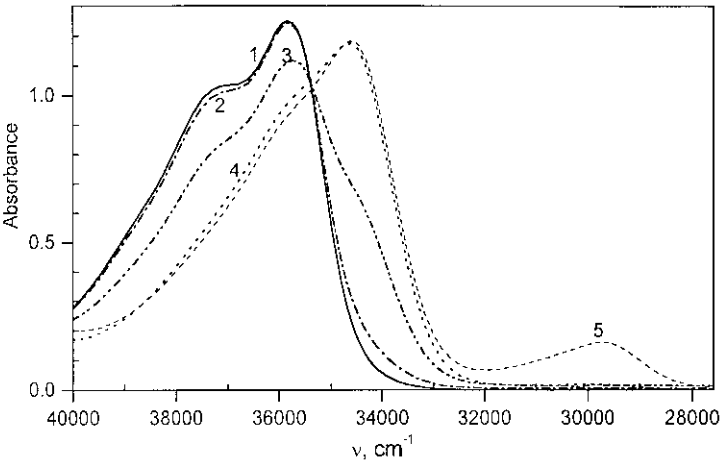

Fig. 1. UV spectra of FA + DBA solutions in isooctane. Concentration dependence. FA: 2 × 10^{-4} mol/l; DBA: (1) 0; (2) 5 × 10^{-4}; (3) 5 × 10^{-3}; (4) 0.1; and (5) 0.5 mol/l. $T = 291$ K $d = 2$ mm.

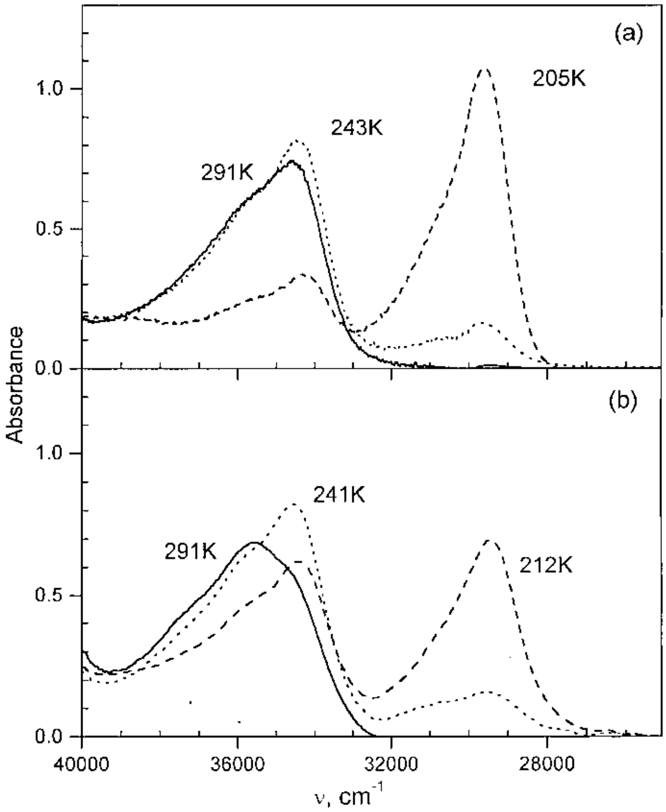

Fig. 2. Temperature effect on UV spectra of isooctane solutions: (a) FA, 3.3 × 10^{-4} mol/l, +DBA, 0.1 mol/l; and (b) FA, 3.3 × 10^{-4} mol/l, +TBA, 0.1 mol/l. $d \approx 0.9$ mm.

Table 1
Thermodynamic parameters of the FA + DBA system in isooctane solution [23]

T (K)	K_1 (l/mol)	K_2 (l/mol)
291	163 ± 2	0.221 ± 0.003
262	910 ± 8	0.89 ± 0.01
253	3900 ± 100	1.05 ± 0.01
243	9400 ± 400	1.09 ± 0.02
ΔH (kcal/mol)	−(12 ± 2)	−(5 ± 1)
ΔS (cal/mol K)	−(30 ± 6)	−(20 ± 5)

3. Results and discussion

The UV spectra of FA + DBA solutions in isooctane in the region of the longwave $\pi \rightarrow \pi^*$ band are shown in Fig. 1. Spectrum of the FA solution reveals the band near 35 840 cm^{-1} with distinguishable traces of vibronic structure. The addition of some amount of DBA leads to the appearance of the band shifted to lower frequencies by about 1250 cm^{-1}. Its intensity increases with increase of DBA concentration. The profile of this band is similar to that of free FA. With further increase of DBA concentration a new band at 29 680 cm^{-1} appears and grows in the region typical for absorption of an FA anion. Temperature decrease causes similar changes. At first the increase of the intensity of the bands near 34 600 and 29 680 cm^{-1} and decrease of the band near 35 840 cm^{-1} are observed. Further cooling results in the increase of the band at 29 680 cm^{-1} in relation to the band at 34 600 cm^{-1} (Fig. 2a). All these changes are reversible.

The number of independent components found from treatment of these spectra by the abovementioned program is equal to 3. The analysis of similar sets of spectra obtained at different temperatures (262, 253, 243 K) gave the same result. It is natural to suppose that these three components correspond to free FA molecules, 1:1 hydrogen bonded molecular complex and 1:2 complex containing the FA anion, FA$^-$. Thus the existence of two equilibria was postulated:

$$(CF_3C_6F_4)_2NH + NHBu_2 \overset{K_1}{\leftrightarrow} (CF_3C_6F_4)_2NH\cdots NHBu_2 \quad (1)$$

$$(CF_3C_6F_4)_2NH\cdots NHBu_2 + NHBu_2 \overset{K_2}{\leftrightarrow} [(CF_3C_6F_4)_2N]^- \times [Bu_2HNHNHBu_2]^+ \quad (2)$$

The equilibrium constants K_1 and K_2 were calculated at each temperature (the accuracy ~10%) (Table 1), as well as the individual spectra of the components. Fig. 3 shows these spectra obtained at 262 K. The values of the enthalpy and the entropy changes corresponding to equilibria (1) and (2) are also presented in the table.

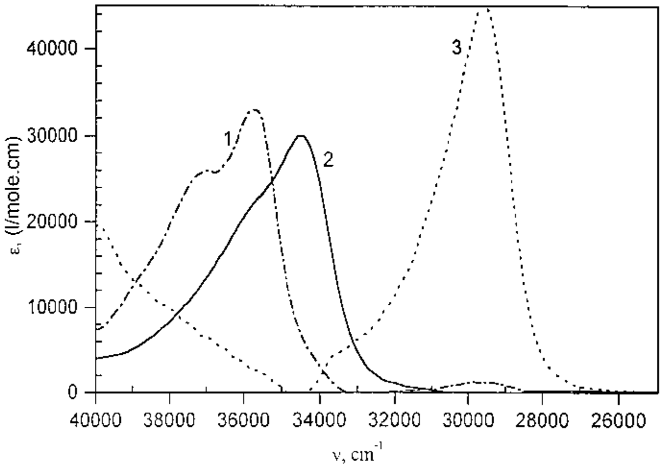

Fig. 3. Calculated spectra of (1) free FA; (2) 1:1; and (3) 1:2 complexes in FA + DBA solutions in isooctane.

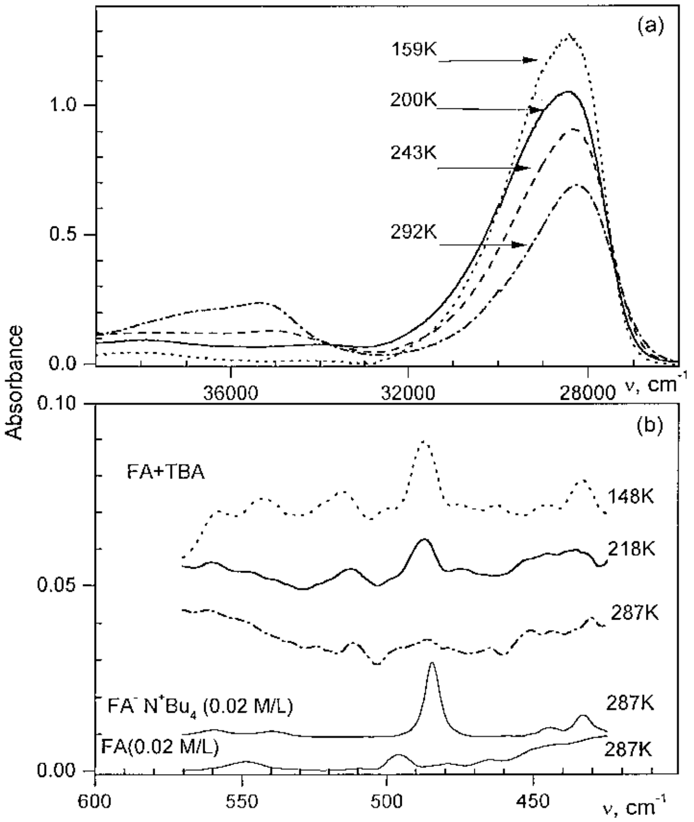

Fig. 4. Temperature changes of FA + TBA spectra in CH_2Cl_2 solution: (a) UV spectrum (FA, 3×10^{-4} mol/l; TBA, 0.1 mol/l; $d \approx 0.9$ mm); and (b) IR spectrum (FA, 0.02 mol/l; TBA, 0.04 mol/l; $d \approx 0.1$ mm).

It should be noted that the spectrum of FA + DBA system depends strongly on solvent polarity. In particular, in ethanol solution only the anion band is observed, the maximum of this band being shifted to lower frequencies by about 1000 cm^{-1}. Hence, the position of this band is sensitive to the strength and the type of anion–cation interaction and to solvation properties of the surrounding molecules. This is confirmed by spectrum of tetrabutylammonium salt $[(CF_3C_6F_4)_2N]^-[NBu_4]^+$ in CH_2Cl_2 solution where the anion band is observed at 27 800 cm^{-1}. In this case there is no hydrogen bond between the anion and the cation, perturbation of the anion is minimum and the spectrum obtained under such conditions can be used as a model of the free anion spectrum. One can conclude that the large blue shift of the FA anion band in ionic complexes with amines in neutral nonpolar solvents, such as isooctane, is caused by hydrogen bonding with the cation. Correspondingly, an increase or decrease of this shift can be considered as an indication of strengthening or weakening of perturbation of the anion by hydrogen bonding with a counterion or surroundings. Particularly, the intermediate position of the band in the spectrum of the ethanol solution is determined by two factors: some increase of the charge separation and weakening of anion–cation interaction in more polar medium, which shifts the band towards lower frequencies, and some strengthening of anion–solvent interaction due to proton donating ability of the alcohol molecules, which leads to a blue shift.

Similar experiments have been carried out for the FA + TBA and FA + TMA systems. In the case of TBA the equilibrium (1) in isooctane at the room temperature (Fig. 2b) is shifted towards free molecules compared with DBA (Fig. 2a). At lower

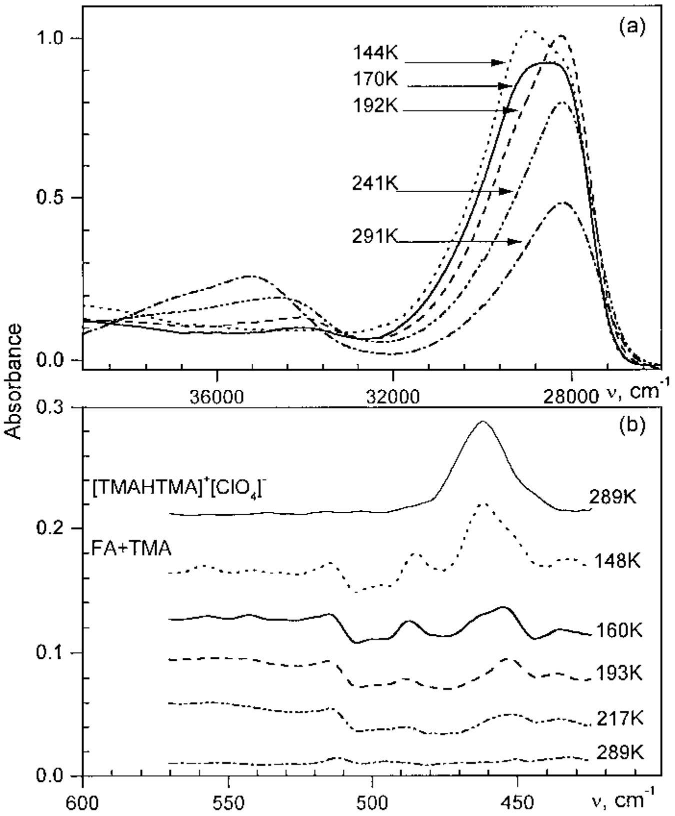

Fig. 5. Temperature changes of FA + TMA spectra in CH_2Cl_2 solution: (a) UV spectra (FA, 3×10^{-4} mol/l; TMA, 0.2 mol/l; $d \approx 0.9$ mm). and (b) IR spectra (FA, 0.02 mol/l; TMA, 0.2 mol/l; $d \approx 0.1$ mm).

temperatures the spectra of FA solutions containing TBA and DBA are rather similar.

In the more polar solvent, methylene chloride, the equilibrium between the molecular and ionic complexes shifts to the right (Fig. 4a). One can note that the anion band position is shifted to the red compared with isooctane. It becomes closer to the band observed for tetrabutylammonium salt. It means probably that the anion–cation interaction becomes weaker due to higher polarity of the solvent. Formation of the anion FA^- in CH_2Cl_2 is confirmed by the IR spectrum where a band at 485 cm^{-1} appears. This band is also observed in the spectrum of $[(CF_3C_6F_4)_2N]^-[NBu_4]^+$ and can be used as a characteristic feature of the anion (Fig. 4b).

The UV spectra of the FA + TMA solutions within the temperature range 290–190 K reveal a picture similar to that observed with TBA as the proton acceptor. However, at lower temperatures (190–145 K) in the overcooled solution[1] new remarkable effects have been detected. In particular, the band of anion becomes a doublet. A new, high-frequency component of the doublet with maximum near 29 040 cm^{-1} grows gradually with temperature decrease in relation to the low-frequency band at 28 200 cm^{-1} (Fig. 5a).

From the first view such changes of the anion band on cooling in this temperature interval seem surprising. Usually, different kinds of aggregation processes, which can be provoked by temperature decrease, are accompanied by increase of the charge separation. Therefore one would expect a rather opposite direction of the band shift. On the other hand, the position of the new component is rather close to that

---

[1] Solutions of studied substances in CH_2Cl_2 remain liquid and transparent below the melting temperature of the solvent down to ~145 K.

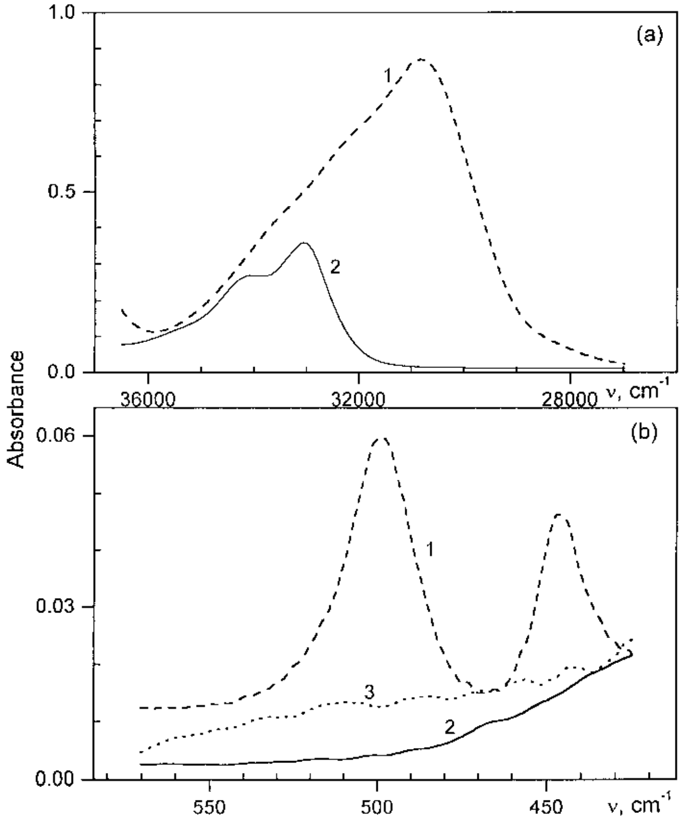

Fig. 6. (a) UV and (b) IR spectra of PCP + TMA solutions in dichloromethane: (1) TMA + PCP; (2) PCP; and (3) TMA. Concentrations: UV — PCP, 0.015, TMA, 0.11 mol/l, $d = 0.1$ mm; IR — PCP, 0.02, TMA, 0.4 mol/l, $d = 0.13$ mm.

of the band of the FA + DBA complex in ethanol solution. Taking into account the above-mentioned facts one can suggest that some rearrangement of the complex takes place under these conditions, which is accompanied by strengthening of perturbation of the anion by interaction with the counterion or with the solvent.

Simultaneously, new features appear on cooling in the IR spectrum. Besides the band at 485 cm^{-1} belonging to the anion, a new band appears at 460 cm^{-1} (Fig. 5b). At the lowest temperature its intensity reaches ~100 km/mol. The most probable assignment of this band is δ(CNC) vibration of homoconjugated cation TMAHTMA$^+$. The reasons for such suggestion are the following.

For the first time the presence of stable TMAHTMA$^+$ cation has been detected by IR spectroscopy in acetonitrile solutions containing both trimethylammonium salt of a strong acid such as HBF_4 or $HClO_4$ and an excess of free base [24]. It was noted also that similar BHB$^+$ cations are not formed by higher tertiary aliphatic amines because of steric hindrances. Later, the formation of TMAHTMA$^+$ cation in complexes with strong acids was confirmed by low-temperature NMR measurements [25]. Recently it has been found [26] that IR spectra of TMA complexes with PCP of 2:1 composition in chloroform solution reveal the features typical for the TMHTMA$^+$ cation. No indications of formation of similar cation in the case of TBA were obtained. It has been shown also in Ref. [26], both experimentally and by ab initio calculations, that characteristics of the bands belonging to bending vibrations of TMA can be used as a criterion of hydrogen bond strength and proton location in the complexes of TMA.

Free TMA molecule reveals the band corresponding to symmetrical (A_1) bending vibration of NC_3 group at frequency 370 cm^{-1} with intensity about 10 km/mol. As it was found in Ref. [26], this band undergoes significant blue shift and increase of intensity when TMA is involved in hydrogen bonding. Both effects become stronger with H-bond strengthening and reach a maximum in the case of symmetrical hydrogen bond. Proton transfer to TMA leads to reverse decrease of intensity. The corresponding band of monocation $TMAH^+$ has similar or even less intensity than in free TMA depending on hydrogen bond strength between the cation and the anion.

For the homoconjugated cation $TMAHTMA^+$ the calculations performed in Ref. [26] give the optimized structure with two unequal NH distances and predict a doublet of bands in the δNC_3 (A_1) region. The relative intensities of two components of this doublet turned out to be very sensitive to the basis set used for calculations [27]. Thus, according to calculations at 3-21G** level the intensities of the components are comparable: ~27 and 80 km/mol at 454 and 506 cm^{-1}, correspondingly. Calculations at 6-31G** level, which give slightly different geometrical parameters of the $TMAHTMA^+$ cation, give the band at 430 cm^{-1} with negligibly small intensity (about 0.1 km/mol) and at 470 cm^{-1} with intensity 83 km/mol. These results obtained for free isolated cation can be considered as indication that parameters of this doublet in real systems should be very sensitive to interaction with a counterion and surroundings. Indeed, the spectrum of solution containing the salt $[TMAHTMA]^+[ClO_4]^-$ (Fig. 5b), where perturbation of the cation is less, reveals a single intensive band at 460 cm^{-1}, while in the case of PCP + TMA 1:2 complex two bands with comparable intensities are observed (Fig. 6). In both cases the intensities of the bands are close to the calculated ones.

Fig. 5 shows that spectrum of the FA + TMA 1:2 system in the discussed region is similar to that observed in the case of the $[TMAHTMA]^+[ClO_4]^-$ solution, but not in the case of the PCP–TMA complex. This means that perturbation of the cation by the FA^- anion is lesser than by the pentachlorophenolate anion, the interaction between FA^- and $TMAHTMA^+$ seems to be weaker.

Thus, one can conclude that at low temperatures in the overcooled solution, the reorganization of the 1:2 FA + TMA complex takes place, which includes the formation of the $TMAHTMA^+$ cation. It is also accompanied by stronger perturbation of the anion, manifested in additional blue shift of the UV band of the anion. Since the vibrational spectrum of the cation gives no evidence of the strong anion–cation interaction, it seems more reasonable to connect this blue shift (and may be the reorganization itself) with solvent effects.

It is known that dielectric permittivity, ϵ, of methylene chloride increases significantly with cooling: from $\epsilon \approx 9$ at the room temperature till to $\epsilon \approx 16$ at temperatures close to freezing point [28]. According to results of studies of dielectric relaxation times in overcooled liquids [29], the character of the temperature dependence of orientational mobility in the vicinity of solute molecules does not change with transition to the overcooled state. Therefore, it is natural to expect further significant increase of the local dielectric permittivity in the vicinity of the complex in the temperature range between crystallization and glass transition temperatures. The extrapolation of $\epsilon(T)$ dependence [28] to the temperature region 180–140 K gives ϵ values in the range of 20–25, which is close to ϵ of the ethanol solution. One can suggest that such an increase of the local polarity causes stronger anion and cation separation, which promotes formation of the structure of homoconjugated cation on the one hand, and strengthening of the anion solvatation by CH_2Cl_2 molecules, similar to observed in ethanol solution, on the other.

It is interesting to compare these results with the results of studies of the complexes formed by PCP with the same tertiary amines. As it was mentioned, in chloroform solution at room temperature, PCP also forms, with TMA, 1:2 complexes with transferred proton, which reveal a typical anion band in UV spectrum and the bands of the homoconjugated $TMAHTMA^+$ cation in the IR spectrum (Fig. 6) [26]. Formation of the similar cation with participation of TBA was not detected in the case of PCP and in the case of FA. The difference between PCP and FA is that in the latter case the structure typical for homoconjugated cation is formed only at low temperatures in the overcooled solution. At higher temperatures 1:2 complexes formed by FA with TMA and TBA are rather similar. However, the structure of the cation in such complexes is not quite clear. Though the cation includes two amine molecules, its structure is not equal to that of the homoconjugated cation. This structure can be more “loose” or positions of the two amine molecules are not equal. In any case some rearrangement of the complex occurs under cooling, which includes the formation of “normal” homoconjugated TMAHTMA$^+$ cation and the strengthening of perturbation of the anion.

In addition, it should be mentioned that the IR spectra of homoconjugated ions with symmetrical hydrogen bonds often reveal the extremely broad (continuous) absorption caused by vibrations of the bridging proton. According to Ref. [30], studies of parameters and intensity distribution of this absorption in the case of $(N\cdots H\cdots N)^+$ bonds can give information about the lengths of the $N\cdots N$ distance and the shape of proton potential. The spectra of the FA + TMA solutions, obtained in the present work, also show a broad absorption, which is spread over the region of bending and skeletal bands of donor and acceptor molecules. One can notice that the intensity of its low-frequency part increases with cooling. However, the overlapping with numerous strong bands of the solvent, FA and TMA makes the separation and detailed investigation of the proton part of absorption in the whole region difficult.

Acknowledgements

The work is supported by Russian Foundation of Basic Research (grant 99-03-33163). The authors thank Prof. G.G. Furin who synthesized the sample of FA.

References

[1] L. Sobczyk, J. Mol. Struct. 177 (1988) 111.
[2] J.E. Del Bene, W.B. Person, K. Szczepaniak, Mol. Phys. 89 (1996) 47.
[3] A.J. Barnes, A.C. Legon, J. Mol. Struct. 448 (1998) 101.
[4] M. Habeeb, Appl. Spectrosc. Rev. 32 (1997) 103.
[5] J.E. Del Bene, M.J.T. Jordan, Int. Rev. Phys. Chem. 18 (1999) 119.
[6] V.E. Borisenko, G.S. Denisov, Y.A. Zavjalova, G.G. Furin, J. Mol. Struct. 151 (1994) 322.
[7] G. Schroeder, B. Brzezinski, B. Leska, A. Jarczewski, E. Grech, J. Nowicka-Scheibe, J. Mol. Struct. 354 (1995) 131.
[8] G. Schroeder, B. Brzezinski, D. Podebski, E. Grech, J. Mol. Struct. 416 (1997) 11.
[9] B. Brzezinski, G. Wojciechowski, G. Zundel, L. Sobczyk, E. Grech, J. Mol. Struct. 508 (1999) 175.
[10] Z. Malarski, L. Sobczyk, E. Grech, J. Mol. Struct. 177 (1988) 339.
[11] T. Glowiak, Z. Malarski, L. Sobczyk, E. Grech, J. Mol. Struct. 270 (1992) 441.
[12] A.L. Llamas-Saiz, C. Foces-Foces, J. Elguero, J. Mol. Struct. 328 (1994) 297.
[13] K. Wozniak, H. He, J. Klinowski, T.L. Barr, S.E. Hardcatle, J. Phys. Chem. 100 (1996) 11 408.
[14] E. Bartoszak-Adamska, E. Grech, M. Jaskolski, Polish J. Chem. 72 (1998) 347.
[15] H. Benedict, H.-H. Limbach, M. Wehlan, W.P. Fehlhammer, N.S. Golubev, R. Janoschek, J. Am. Chem. Soc. 120 (1998) 2939.
[16] H. Benedict, I.G. Shenderovich, O.L. Malkina, V.G. Malkin, G.S. Denisov, N.S. Golubev, H.-H. Limbach, J. Am. Chem. Soc. 122 (2000) 1979.
[17] J.E. Van Verth, W.H. Saunders, T.W. Kermis, Can. J. Chem. 76 (1998) 821.
[18] V.M. Vlasov, G.G. Yakobson, M.I. Terekhova, E.S. Petrov, A.I. Shatenstein, J. Fluoresc. Chem. 16 (1980) 561.
[19] V.E. Borisenko, E.V. Maximov, G.S. Denisov, G.G. Furin, Y.A. Zavjalova, Spectrosc. Lett. 26 (1993) 1139.
[20] G.G. Furin, A.O. Miller, G.G. Yakobson, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. khim. 1 (1985) 127 (in Russian).
[21] G.S. Denisov, B.S. Terushkin, Molecular Spectroscopy, Issue 5, Leningrad State University, 1981, p. 232 (in Russian).
[22] G.S. Denisov, V.A. Mikheev, A.B. Sokornov, T.V. Sokornova, B.S. Terushkin, V.M. Schreiber, Zh. Prikl. Spektr. 42 (1985) 66 (in Russian).
[23] J.P. Castaneda, G.S. Denisov, V.M. Schreiber, Zh. Obshch. Khim. 70 (2000) (in press).
[24] F.N. Masri, J.L. Wood, J. Mol. Struct. 14 (1972) 217.
[25] G.S. Denisov, N.S. Golubev, J. Mol. Struct. 75 (1981) 311.
[26] V.M. Schreiber, M. Rospenk, L. Sobczyk, Chem. Phys. Lett. 304 (1999) 73.
[27] J. Janski, V.M. Schreiber, L. Sobczyk, unpublished data.
[28] S.O. Morgan, H.H. Lowry, J. Phys. Chem. 34 (1930) 2385.
[29] G.P. Johari, J. Mol. Liquids 36 (1987) 255.
[30] G. Zundel, in: I. Prigogine, S.A. Rice (Eds.), Advances in Chemical Physics, Vol. 3, Wiley, New York, 2000.