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Spectral study of proton transfer along the hydrogen bond NH···N in complexes of polyfluorinated aromatic NH donors with amines[1]

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Abstract

The influence of solvent on the equilibrium between the neutral and ionized forms of polyfluorinated aromatic secondary amines in various solvents containing aliphatic amines or tetramethylguanidine has been studied by electronic absorption spectroscopy in the near UV region. The influence of the solvent dielectric permittivity and the proton accepting ability of its molecules are discussed. Possible mechanisms of stabilization of the anion in low- and medium-polarity solvents are suggested.

1. Introduction

As has been shown by the measurements of IR spectra and thermodynamic characteristics of complexes with the hydrogen bond NH···B formed by secondary amines R_2NH (R = polyfluorinated aryl radical) with proton acceptors B [1], these compounds possess high proton donating power. The equilibrium NH acidity of these compounds is also sufficiently high [2], so that the appearance of ionic forms may be expected with a proton transferred at the interaction of the NH donors with strong organic bases in solvents of low and medium polarity. The poor tendency for self-association makes them more feasible NH acids for studying proton transfer along the NH···N bond than, for example, nitroamines [3].

2. Results and discussion

In this work the compounds $(C_6F_5)_2NH$ (**I**), $(4\text{–}CF_3C_6F_4)_2NH$ (**II**), $(\gamma\text{–}NC_5F_4)_2NH$ (**III**) and $(4\text{–}NCC_6F_4)_2NH$ (**IV**), which were synthesized using the method in ref. 4, and their complexes with tributylamine (TBA), dibutylamine (DBA) and tetramethylguanidine (TMG) have been studied. According to the data from ref. 1 the proton donating power of fluoroamines increases in the series **I** < **II** < **III**: compound **IV** was not studied earlier by spectral methods. The electronic absorption spectra in the near UV region have been used for the study of equilibria between molecular

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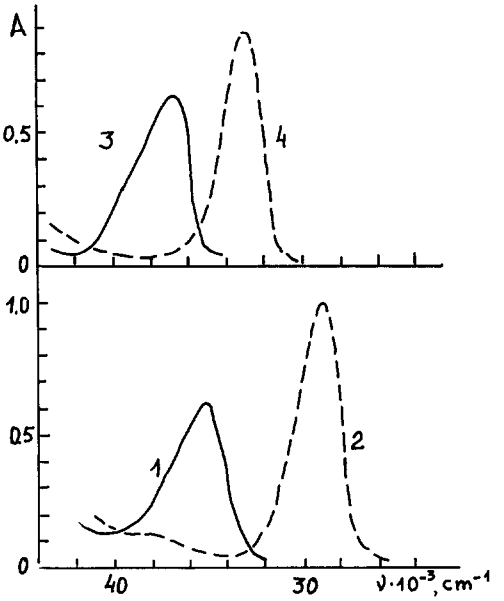

Fig. 1. Spectra of $(p\text{-}CF_3C_6F_4)_2NH$, 1.1×10^{-4} M (1,2) and $(\gamma\text{-}NC_5F_4)_2NH$, 1.1×10^{-4} M (3,4) in isopropyl alcohol solution (1,3) and in the presence of KOH (2,4).

and ionized forms of fluoroamines; the efficacy of this technique has been demonstrated in a number of papers devoted to the analysis of the structure of complexes formed by aromatic OH donors [5–11]. The measurements of spectra of fluoroamines **I–IV** in alcoholic solutions showed that the first absorption band in each case, located at 38 700, 34 800, 36 600 and 32 000 cm^{-1}, (258, 287, 273 and 312 nm) correspondingly, vanishes after the addition of KOH to the solution, and the anionic band appears, which is displaced to lower frequencies by 5800–6300 cm^{-1} (Fig. 1). The frequencies and amplitude intensities of the neutral form bands are in agreement with the data presented in ref. 4. It can be seen from Fig. 1 that for these compounds the bands of neutral and acidic forms hardly overlap at all, have comparable intensities and lie in the region of transparency of the various solvents; these features offer considerable scope for the study of equilibria with proton transfer. So these compounds seem to be rather suitable for the investigation of proton transfer equilibria.

In hexane solution the absorption bands of these fluoroamines (except **I**) retain the remnants of vibrational structure, which is blurred and vanishes when passing to more active solvents (chloroform, dichloroethane, alcohols). When a hydrogen bond with a proton acceptor is formed, as in the case of phenols, this band is shifted to

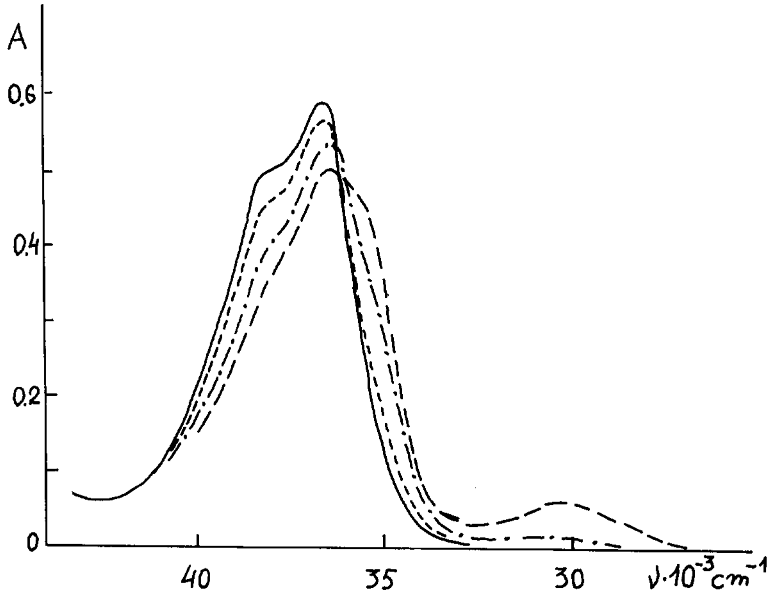

Fig. 2. Spectra of $(\gamma\text{-}NC_5F_4)_2NH$, 1.1×10^{-4} M in hexane (——) and in the presence of $(C_4H_9)_3N$, 6.4×10^{-3} M (---), 20×10^{-3} M (–•–•–), 32×10^{-3} M (– – –).

lower frequencies by 1000–1500 cm^{-1}; a typical example is shown in Fig. 2. It is seen that with increasing concentration of TBA in solution the intensity of the free **III** band at 37 600 cm^{-1} decreases, and the band at 36 500 cm^{-1} of molecular complexes with the hydrogen bond NH$\cdots$N gradually increases. At a 200–300-fold excess of TBA virtually all fluoroamine molecules are bound into complexes. The band of the complex in hexane solution also bears evidence of vibrational structure. The band of the fluoroamine **III** in complex with hexametapol, $(Me_2N)_3PO$ has a similar shape and its low-frequency shift has the same magnitude. At a large excess of TBA the band of the anion arises in the spectrum at 32 000 cm^{-1}, which is 1100–1200 cm^{-1} higher than in alcoholic solutions containing bases. Hence in hexane solution there is an equilibrium between the molecular complexes of fluoroamine with TBA and the ionic complexes, the latter having the structure of a tight anion–cationic pair. This equilibrium is essentially shifted to the left.

The studied fluoroamines are more thoroughly deprotonated by TMG, a strong organic base; its proton accepting power in formation of molecular complexes with hydrogen bonds as well as of ionic pairs in solvents of low polarity is comparable and even exceeds the proton accepting power of aliphatic amines [12]. It is seen in Fig. 3 that in the presence of TMG in the spectrum of **II** there appear simultaneously the band of a molecular complex with hydrogen bonds and the band of the fluoroamine anion, which is produced as a result of proton transfer along the hydrogen bond NH$\cdots$N to the imine nitrogen of TMG.

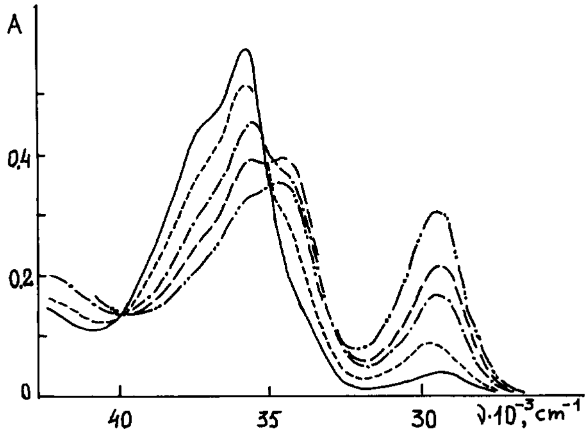

Fig. 3. Spectra of $(p\text{-}CF_3C_6F_4)_2NH$, 1.0×10^{-4} M in hexane in the presence of $(Me_2N)H_2CNH$, 1.9×10^{-4} M (—), 3.2×10^{-4} M (---), 6.4×10^{-4} M (-·-·-), 12×10^{-4} M (– – –), 19×10^{-4} M (— · · —).

Such experiments have been carried out in several solvents to ascertain qualitatively the principal mechanisms of initiating proton transfer by intermolecular interaction with the surroundings. The solvents with dielectric permittivities in the range 2–40 have been used. Their molecules are essentially different in terms of the mechanisms of dominating intermolecular interaction. The molecules of alcohols possess pronounced proton donating and proton accepting functions; chloroform is a weak proton donor, and acetonitrile has a large dipole moment and also is a weak proton acceptor. The molecule of dichloroethane is apparently the least able to form hydrogen bonds with dissolved molecules and with their complexes. Hexane is obviously the most inert apolar solvent.

Unfortunately, in all solvents studied, with the exception of hexane, the bands of free fluoroamine and its hydrogen bonded complex with nitrogen-containing proton acceptors are badly overlapping, so that it is practically impossible to estimate even semiqualitatively the fraction of fluoroamine molecules forming hydrogen bonds with the acceptor. Therefore it is reasonable to present a tentative summary of data obtained in a diagram showing the dependence of the intensity of the anionic band on the concentration of the base at a constant concentration of fluoroamines in a series of measurements (Fig. 4). It is seen that at the same concentrations of donor and acceptor molecules the equilibrium shifts to the ionized form of the fluoroamine as the dielectric permittivity of the solvent increases. This result seems to be rather prevalent. It was repeatedly emphasized in studies of proton transfer in non-polar solvents; see for example refs. 13–15. However, it is remarkable here that the alcohols do not stand out by their activity against this group of solvents, although usually the substantial additional stabilization of an ionized form occurs in alcoholic media on account of the hydrogen bonding solvation of the

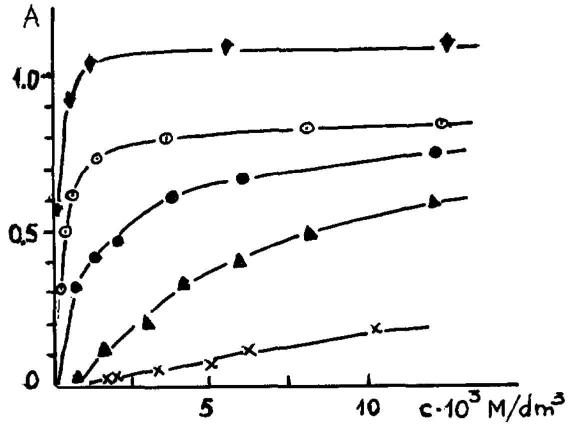

Fig. 4. Absorbance of the $(\gamma\text{–NC}_5\text{F}_4)_2\bar{\text{N}}$ band as a function of the $(\text{C}_4\text{H}_9)_2\text{NH}$ concentration in the solvents: ×, chloroform, ▲, dichloroethane, ●, isoamyl alcohol, ⊙, isopropyl alcohol, ◆, acetonitrile.

anion. In ethylene glycol and acetonitrile, the solvents with nearly the same values of dielectric permittivity but with substantially different mechanisms of local intermolecular interactions, the curves of spectrophotometric titrations are close. Hence, the formation of hydrogen bonds of anions with proton donating solvent molecules is of little importance, and the dominant mechanism responsible for the formation of ionic structures is the influence of the dielectric properties of the solvent medium.

Some additional information about the interaction of the anion with the solvent can be obtained from analysis of the absorption band frequencies of the anion. The available data prove that the anionic band frequency decreases in the solvent series hexane–chloroform–alcohols–acetonitrile, dichloroethane. This dependence is not strong; the total shift is 1000–1500 cm^{-1}. The band position in different alcohols is nearly the same, whereas the band frequency in ethylene glycol is 500–800 cm^{-1} higher than in acetonitrile. Thus there may exist a certain specific interaction of the anion with alcohols. The conclusion of a poor solvation of fluoroamine anions in alcoholic solutions is in accordance with the general notion of the charge distribution of the anion. Due to the high electronegativity of fluorine atoms the excessive negative charge is spread over the whole ion and the charge density in the vicinity of the nitrogen atom is not high. Therefore the proton accepting ability of the fluoroamine anion is low and its solvation in alcoholic solution is slight. Thus the system fluoroamine–aliphatic amine may be considered convenient for the experimental verification of models describing the influence of dielectric properties of a solvent on the processes of formation and dissociation of ionic pairs.

This involves the important problems of the ionic pair structure in a low-polarity solvent, the structure of the cation, and the mechanism of its interaction with the anion. From the spectra in Fig. 2 it is seen that in hexane solution, in the presence of a moderate excess of aliphatic amines, while the anionic band had not yet appeared in the spectrum, the set of curves has an isosbestic point. However, as the concentration of amine increases and the band of the anion becomes clearly observable, the curves do not pass through the isosbestic point. This is clearly seen in Fig. 3 where the equilibrium in the system is shifted to the right. This proves that the proton transfer in a molecular complex with a hydrogen bond is not a monomolecular process. It would appear reasonable to suppose that the cation is stabilized due to the formation of the hydrogen bond with the second molecule of amine, so that the ionic pair has the composition 1 : 2:

$$\text{Ar}_2\text{NH} + \text{NAlk}_3 \rightleftharpoons \text{Ar}_2\text{NH}\cdots\text{NAlk}_3$$
$$\overset{+\text{NAlk}_3}{\rightleftharpoons} \text{Ar}_2\bar{\text{N}}\cdot\text{Alk}_3\overset{+}{\text{N}}\text{HNAlk}_3$$

There is numerous evidence, including spectroscopic data, that cations BHB$^+$ are often formed in systems containing phenols or carboxylic acids and organic bases [15–17].

If the molecules of a solvent have proton accepting centers, such a mechanism can take place with the participation of a solvent, formally with the composition of a 1 : 1 complex:

$$\text{Ar}_2\text{NH}\cdots\text{NAlk}_3 \overset{+\text{S}}{\rightleftharpoons} \text{Ar}_2\bar{\text{N}}\cdot\text{Alk}_3\overset{+}{\text{N}}\text{H}\cdots\text{S}$$

(S = solvent). This seems to be the case in system IV with TMG in isopropyl alcohol solution, where the equilibrium is strongly shifted to the right and the complete ionization of the fluoroamine occurs at a content of fluoroamine close to

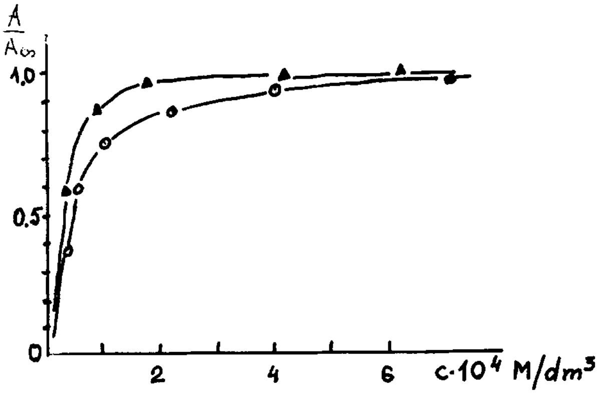

Fig. 5. Fraction of the ionized form of $(p\text{-}NCC_6F_4)_2NH$, 1.0×10^{-4} M, as a function of tetramethylguanidine concentration in the solvents: ▲, isopropyl alcohol, ⊙, acetonitrile, A_∞, absorbance of the anion band at a large excess of the base.

the stoichiometric ratio (Fig. 5). In acetonitrile solution the titration of the fluoroamine is slower, the complete ionization being achieved at a content of TMG several times greater than in isopropanol. Here the low proton accepting ability of the solvent molecules hampers the formation of ionic species of 1 : 1 composition and this tendency proves to be stronger than the influence of the medium.

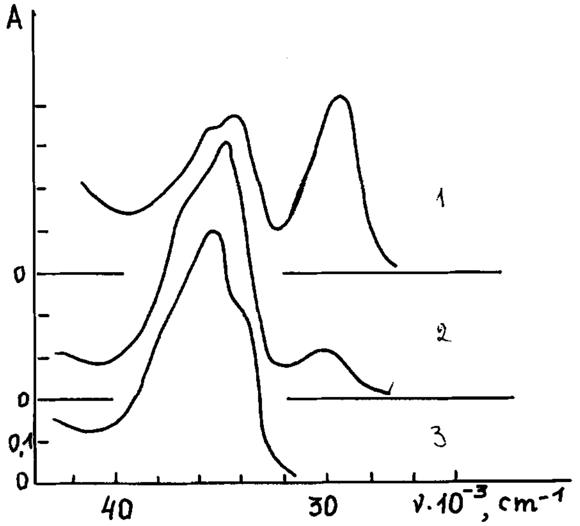

Fig. 6. Spectra of $(p\text{-}CF_3C_6F_4)_2NH$, 1.0×10^{-4} M in hexane in the presence of 1.9×10^{-3} M tetramethylguanidine (1), 37×10^{-3} M dibutylamine (2), 45×10^{-3} M tributylamine (3).

It follows from the spectral data that the sequence of ionization abilities of fluoroamines in all the solvents is the same as their proton donating abilities in hydrogen bonded complexes: **I** < **II** < **III** < **IV**. Somewhat surprisingly, fluoroamine **I** is a much weaker acid than the other compounds; we managed to observe its anionic band only on interaction with the strongest base, TMG, and in the most active solvent, acetonitrile.

Finally, some useful conclusions can be drawn from comparison of the proton accepting ability of various bases, both in hydrogen bonded complexes and by protonation. It is seen from Fig. 6 that in the most inert solvent, hexane, the strongest base is TMG, which is protonated most readily, followed by DBA, the weakest base being TBA. The same order of basicity is observed in all solvents and for all fluorinated amines. This sequence is in agreement with pK_a values measured in aqueous solutions but is in contradiction to the values of basicity and proton affinity for tertiary and secondary amines obtained in the gaseous phase [18]. This means that the hydrogen bonded complex of the fluorinated NH donor with a secondary amine interacts with the solvent more strongly than the complex with a tertiary amine, and this interaction stimulates proton transfer in the molecular complex. Even van der Waals interactions with hexane molecules prove to be sufficient to invert the sequence of the basicities of amines in comparison with the gas phase. This sequence is qualitatively the same in all solvents from hexane to water, in spite of the large differences in the mechanism and the magnitude of interaction of the complex with molecules of surrounding solvent. The same conclusion was made from the spectroscopic measurements of thermodynamic characteristics of hydrogen bonded complexes and ionic pairs formed by polyfluorinated naphthol with secondary and tertiary aliphatic amines in hydrocarbon solvents [19].

3. Acknowledgment

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4. References

[1] E.V. Borisenko, E.V. Maximov, Y.A. Zavjalova, G.S. Denisov and G.G. Furin, Spectrosc. Lett., 26 (1993) 1139.
[2] V.M. Vlasov, M.I. Terechova, E.S. Petrov, A.I. Shatenshtein and G.G. Yakobson, Zh. Org. Khim., 17 (1981) 2025.
[3] Y.V. Ulashkievicz, G.S. Denisov, A.G. Bazanov and I.V. Zelinski, Zh. Prikl. Spektrosk., 36 (1982) 643.
[4] G.G. Furin, A.O. Miller, G.G. Yakobson, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1 (1985) 127.
[5] R. Scott, S. Vinogradov, J. Phys. Chem., 73 (1969) 1890.
[6] R.A. Hudson, R.M. Scott, S. Vinogradov, J. Phys. Chem., 76 (1972) 1989.
[7] Z. Pawelka, L. Sobczyk, Rocz. Chem., 49 (1975) 1383.
[8] A. Koll, L. Sobczyk, M. Rospenk, J. Chem. Soc., Faraday Trans. 1, 77 (1981) 2309.
[9] G.S. Denisov, V.M. Schreiber, Dokl. Akad. Nauk SSSR, 215 (1974) 627.
[10] Th. Zeegers-Huyskens, P. Huyskens, in H. Ratajczak and W.J. Orville-Thomas (Eds.), Molecular Interactions, Vol. 2, Wiley, Chichester, 1981, p. 1.
[11] A.S.N. Murthy, A. Ram Reddy, Spectrochim. Acta, Part A, 37 (1981) 805.
[12] G.V. Gusakova, G.S. Denisov, A.L. Smolyansky, Zh. Obshch. Khim., 59 (1989) 2343.
[13] H. Baba, A. Matsuyama, H. Kokubun, Spectrochim. Acta, Part A, 25 (1969) 1709.
[14] J. Fritsch, G. Zundel, J. Phys. Chem., 85 (1981) 556.
[15] H. Romanowski, L. Sobczyk, J. Phys. Chem., 79 (1975) 2535.
[16] E. Bartoszak, Z. Dega-Szafran, M. Grunwald-Wyspianska, M. Jaskolski and M. Szafran, J. Chem. Soc. Faraday Trans., 89 (1993) 2085.
[17] Z. Malarski, L. Sobczyk, E. Grech, J. Mol. Struct., 177 (1987) 339.
[18] S.G. Lias, J.F. Liobman, R.D. Levin, J. Phys. Chem. Ref. Data, 13 (1984) 695.
[19] Y.A. Bazavluk, A.N. Delnov, G.S. Denisov, Zh. Prikl. Spectrosk., 48 (1988) 799.