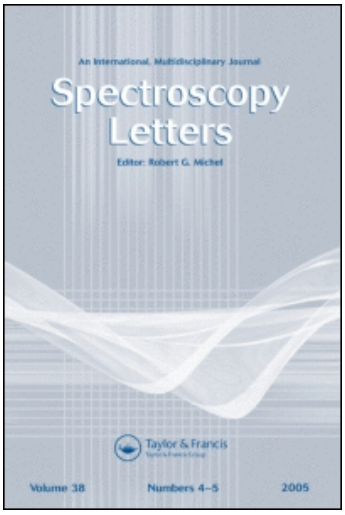

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SPECTRAL AND ENERGY DATA FOR BIS (POLYFLUORO-ARYL) AMINE COMPLEXES WITH HYDROGEN NH...B BOND

Key words: IR spectroscopy, hydrogen bond,
bis (polyfluoro-aryl) amine,
enthalpy of hydrogen bonds

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ABSTRACT

In the IR spectra of complexes of $(C_6F_5)_2NH$, $(4\text{-}CF_3C_6F_4)_2NH$ and $(\gamma\text{-}NC_5F_4)_2NH$ with acetonitrile, tetrahydrofurane, dimethylformamide, dimethylsulfoxide and hexametapole, the $\nu(NH)$ band has a complex structure due to Fermi resonance with low-frequency

vibration combinations. In the range of 15-65°C the equilibrium constants and complex formation enthalpies in CCl_4 solution have been determined.

INTRODUCTION

Secondary amines of R_2NH type, where R is the polyfluorinated aryl radical, are potentially strong NH-acids and are therefore a prospective object for investigating the hydrogen bond NH...B. Increased acidity of amines with pentafluorphenyl rings is demonstrated by the data on the equilibrium NH-acidity in DMSO (9-phenylfluorene as standard, pK + 18.5, counterion K +): $C_6F_5NH_2$ 23.1, $(C_6F_5)_2NH$ 12.6 and $C_6F_5NHC_5F_4N$ 9.4 lg units [1]. The acidifying effect of the polyfluoroaryl fragment has been shown to depend on the substituents, as shown by pK measurements on passing from C_6F_5 to 2,3,5,6-tetrafluoropyridyl group (pK decreases by 3.9 lg units) and by the effect of R substituent in para-position of tetrafluorophenyl group (e.g., pK varies in the series of R substituents: NMe_2-F-CF_3-CN as follows: 13.6- 12.6- 10.6- 9.1) [1].

The data on the proton-donating ability of such compounds in complexes with typical proton acceptors, on the possibility and conditions of proton transfer over the hydrogen bond, on the shape of the band. ν(NH...B) in vibrational spectrum must be useful both for better understanding of the energetics and spectral manifestations of a strong NH...B bond and for characterizing the intermolecular interactions of fluoroaromatic amines which represent a new class of protonodonors.

For that purpose we have studied spectral and thermodynamic data for the complexes of secondary amines $(C_6F_5)_2NH$ (I), $(4\text{-}CF_3C_6F_4)_2NH$ (II) and $(\gamma\text{-}NC_5F_4)_2NH$ (III) with acceptors: acetonitrile, tetrahydrofurane, dimethylformamide, dimethylsulfoxide and hexametapole in CCl_4 solution.

EXPERIMENTAL

The compounds I-III were synthesized according to [2]. The IR spectra in the range of 2400-3600 cm^{-1} were obtained on a Specord IR 75 Carl Zeiss. Jena instrument. The measurements were carried out in the temperature range 15-65°C with an accuracy of ±1°C. The spectral moments of bands were found by numerical integration with an accuracy for free molecule bands being 1-2 cm^{-1}, for bands of complexes 3-5 cm^{-1}. The integral intensities of absorption bands were measured using planimetry in coordinates A, ν_c with an accuracy of about 7-10 %.

RESULTS AND DISCUSSION

The spectra of CCl_4 solutions of compounds I-III show an intense single band in the range of $\nu(NH)$, which corresponds to monomer amine molecules; the parameters of the band are given in Tab.1. In the using range of concentrations C < 0.02 mol/dm^3, no evidence of self-association of amines is found. Increased temperature of solution results in the high-frequency shift of the band $\nu(NH)$, its slight broadening and decreased integrated intensity. In the range of 15-65°C these parameters change approximately linearly. The temperature variations of frequency and width of the band $\nu(NH)$ of amines I-III are of about

TABLE 1

Parameters of absorption band $\nu(NH)$ of fluorinated amines and their complexes with proton acceptors in CCl_4 solutions at 25°C.

Amine, proton acceptor	M_1, cm^{-1}	$2M_2^{1/2}$, cm^{-1}	$B \cdot 10^{-3}$, $dm^3\ M^{-1}\ cm^{-2}$
(I) $(C_6F_5)_2NH$	3416	28*	13
CH_3CN	3271	186	37
$(CD_2)_4O$	3148	267	58
$DCCON(CD_3)_2$	3130	280	75
$(CH_3)_2SO$	3101	263	79
$[(CD_3)_2N]_3PO$	2961	314	98
(II) $(4\text{-}CF_3C_6F_4)_2NH$	3412	29*	16
CH_3CN	3197	258	60
$(CD_2)_4O$	3069	289	99
$DCCON(CD_3)_2$	3037	325	105
$(CH_3)_2SO$	3003	310	116
$[(CD_3)_2N]_3PO$	2834	366	132
(III) $(\gamma\text{-}NC_5F_4)_2NH$	3407	31*	16
CH_3CN	3165	261	62
$(CD_2)_4O$	3030	301	88
$DCCON(CD_3)_2$	2978	348	122
$(CH_3)_2SO$	2947	357	136
$[(CD_3)_2N]_3PO$	2825	364	140

* Band halfwidth $\Delta\nu_{1/2}(NH)$

the same order of magnitude as for alcohols and phenols [3,4], pyrrole and indol [5].

In the presence of a proton acceptor B, the intensity of the band $\nu(NH)$ decreases and a new wide band appears which is shifted towards low frequencies and belongs to hydrogen bond *NH...B* complexes, Fig. 1-3. The band has a clear-cut structure which specifically changes for stronger hydrogen bonds and greater low-frequency shifts. For complexes with a strong bond the band consists of up to 10-15 components. One can observe in Fig. 1-3 sequential increase of intensities of the low-frequency components of the wide band $\nu(NH)$ with increase of the proton-accepting ability of B. Many components retain their position in the frequency scale. Some components are also observed as very weak bands in the spectrum of free amine molecules. As the band's center of gravity shifts to low frequencies, the high-frequency components pass through the intensity maximum to become weaker. Such a behavior is typical of Fermi-resonant structure of bands of hydrogen bond complexes. It serves as a criterion to explain the origin of a structure due to Fermi resonance of vibration $\nu(AH)$ with overtones and combination tones of low-frequency vibrations. A similar behavior of the band $\nu(NH)$ is observed, for example, in the spectra of imidazole complexes with various proton acceptors [6,7]. Comparing the spectra of amine I-III complexes, one can notice a certain similarity in the band form of these complexes. This is naturally explained by the similarity of frequencies of low-frequency vibrations interacting with $\nu(NH)$ in the molecules of similar structure I-III. The frequencies of these vibrations

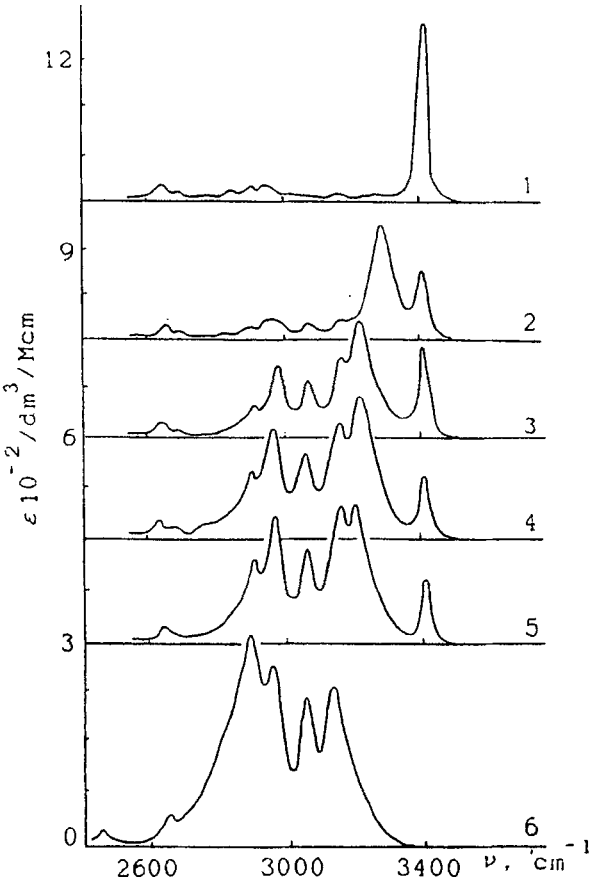

Fig. 1. The absorption bands $\nu(NH)$ of the compound $(C_6F_5)_2NH$ (I) in H-bonded complexes with different proton acceptors in CCl_4. (Concentrations of compounds in solution noted in brackets, M dm^{-3})

1: (1) (0.012); 2: (1) (0.015)+CH_3CN (0.3);
3: (1) (0.014)+$(CD_2)_4O$ (0.26);
4: (1) (0.02)+$DCCON(CD_3)_2$ (0.05);
5: (1) (0.02)+$(CH_3)_2SO$ (0.04);
6: (1) (0.07)+$[(CD_3)_2N]_3PO$ (0.100).

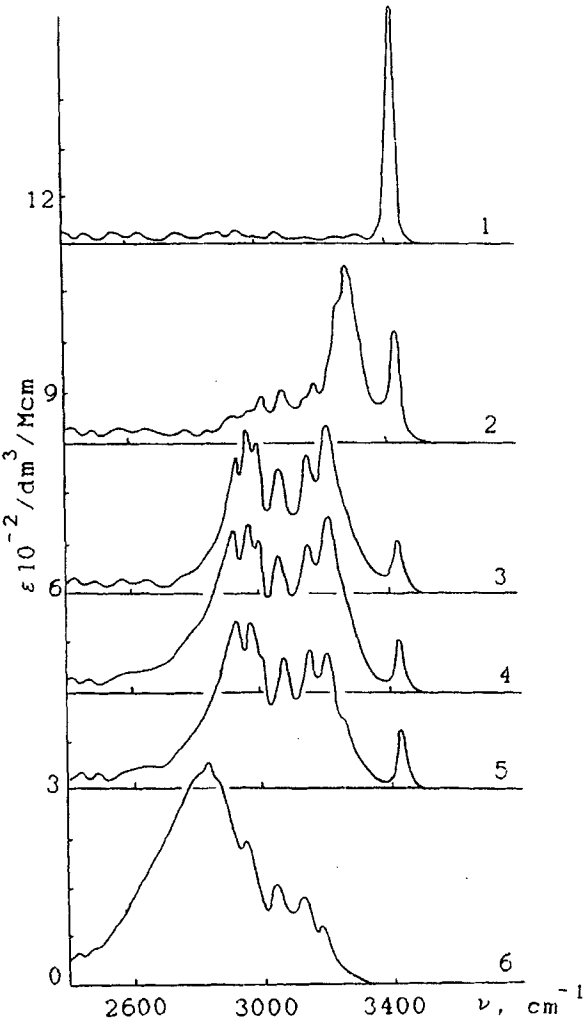

Fig.2. The absorption bands $\nu(NH)$ of the compound $(4\text{-}CF_3C_6F_4)_2NH$ (II) in H-bonded complexes with different proton acceptors in CCl_4.

1: (2) (0.01); 2: (2) (0.02)+CH_3CN (0.35);
3: (2) (0.012)+$(CD_2)_4O$ (0.35);
4: (2) (0.02)+$DCCON(CD_3)_2$ (0.07);
5: (2) (0.02)+$(CH_3)_2SO$ (0.02);
6: (2) (0.066)+$[(CD_3)_2N]_3PO$ (0.100).

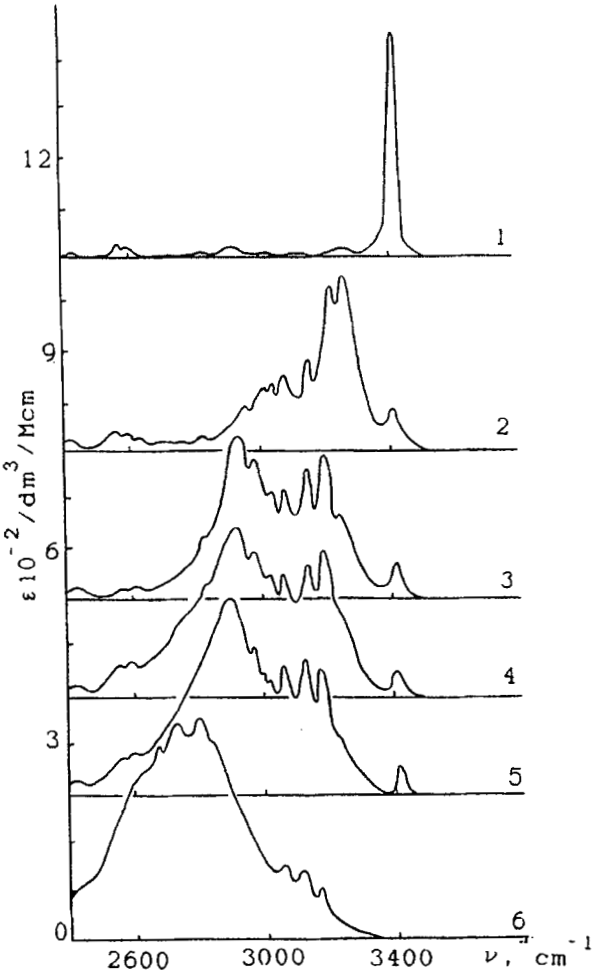

Fig.3. The absorption bands $\nu(NH)$ of the compound $(\gamma\text{-}NC_5F_4)_2NH$ (III) in H-bonded complexes with different proton acceptors in CCl_4.

1: (3) (0.012); 2: (3) (0.02)+CH_3CN (0.4);

3: (3) (0.03)+$(CD_2)_4O$ (0.23);

4: (3) (0.02)+$DCCON(CD_3)_2$ (0.03);

5: (3) (0.02)+$(CH_3)_2SO$ (0.05);

6: (3) (0.069)+$[(CD_3)_2N]_3PO$ (0.100).

remain almost constant in the series of complexes, i.e. they do not depend on the strength of the hydrogen bond *NH*...B.

Table 1 lists the values of band moments of complexes: the zero moment M_0 (integrated intensity), the first moment M_1 (center of gravity of the band) and the second central moment M_2 characterizing the band width. The effective half-width is related to the second moment as follows: $\Delta\nu_{1/2} \simeq 2M_2^{1/2}$. It is seen from these data that in the series of proton acceptors, the low-frequency shift of the band's center of gravity, its integrated intensity and, with some exceptions, effective half-width increase successively with the strength of hydrogen bond for all three amines. The low-frequency shift reaches 400-500 cm^{-1}, the half-width 350-400 cm^{-1}, the integrated intensity increases by almost an order, exceeding 10^5 $dm^3/mol\ cm^2$. All this is typical for the strongest complexes of *NH* donors [8] and the values considerably exceed the corresponding parameters for the non-fluorinated amines [9,10].

The radical C_6F_5 has a high electro-negativity and the positive charge on *NH* hydrogen greatly increases due to electron density shift towards the rings. However, the acidity of this group in compounds I-III is still insufficient for proton transfer to aliphatic amines in C_6H_{14} or CCl_4 solutions. As shown by the UV and IR spectra, no ionic forms of compounds I-III are formed in excess of dibutylamine or tributylamine in these solvents.

At higher temperatures the band's center of gravity is shifted to higher frequencies , the effective half-width increases and the integrated

intensity decreases. These changes are greater by about an order than for the band $\nu(NH)$ of free molecules, the relative change of integrated intensity being several times as great. The character of temperature dependence of M_1 and M_2 is in qualitative agreement with the conclusions of refs. [11,12] which estimated the contribution to M_1 and M_2 of the hot and sum- and difference- transitions with participation of low-frequency vibrations of the complex.

Thermodynamic characteristics of the complexes, equilibrium constants $K=[AB]/[A][B]$ and enthalpies ΔH were measured by the intensity of the band $\nu(NH)$ of free molecules in the presence of an acceptor at four or five temperatures in the range of 288-338 K. After graphical separation of this band from the band of the complexes its integrated intensity was measured and the concentration of free molecules of the proton donor [A] was calculated. The concentrations of complexes [AB] and free molecules of acceptor [B] were calculated using balance equations for the proton donor $[A_0]=[AB]+[A]$ and acceptor $[B_0]=[AB]+[B]$. The calculations were allowed for temperature dependence of solvent density and absorption coefficient of the band $\nu(NH)$. The enthalpy value was calculated from Vanthoff formula. The results are given in Tab.2. For complexes with hexametapole the Table gives only estimates. The calculation of enthalpy using the correlation dependence between enthalpy and integrated intensity increment of the band $\nu(NH)$ on hydrogen bonding [13] gives similar results varying within 10% in both directions.

TABLE 2

Equilibrium constants K and enthalpies -ΔH of complexes of fluorinated amines I-III with acceptors

Proton acceptor	$K_{25}°$, $dm^3 M^{-1}$			-ΔH, kcal M^{-1}		
	I	II	III	I	II	III
CH_3CN	4.5	15	24	2.9	4.1	4.5
$(CD_2)_4O$	9.0	18	32	3.7	5.1	5.2
$DCCON(CD_3)_2$	37	160	520	4.3	5.7	6.8
$(CH_3)_2SO$	76	415	940	4.6	7.0	7.9
$[(CD_3)_2N]_3PO$				~8	~9	~10

It is seen from Tab.2 that the proton-donating ability of polyfluorinated secondary arylamines increases in the series I < II < III; changes in spectral parameters of the band ν(NH) are in agreement with changes in thermodynamic characteristics of the complexes. The proton-donating ability of amines I-III is comparable to that of OH donors such as monochloroacetic acid, or trichlorophenol.

Thus we have shown in this work that polyfluoroaromatic amines I-III are strong proton donors in the hydrogen bond. The ν(NH) band of complexes with strong proton acceptors has a great width and a clear-cut structure resulting mainly from the Fermi-resonant interaction with low-frequency vibration combinations. For quantitative description of this structure it is reasonable to investigate the form of ν(ND) bands in deuterated donor complexes and to fulfill complete identification of vibrational spectrum.

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