IR-ABSORPTION-SPECTRA INVESTIGATION OF α- and β-HEPTAFLUORONAPHTHOLS AS PROTON DONORS AT THE HYDROGEN BOND

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In studying the hydrogen bond formed by different proton donors – carboxylic acids, phenols, alcohols, the data obtained for perfluoro-substituted compounds, which usually have the highest proton-donor capacity in each respective series, are very valuable. The results of measuring the spectral and thermodynamic characteristics of complexes involving trifluoroacetic [1-3] and pentafluorobenzoic [4] acids, pentafluorophenol [5, 6], and nonafluoro-tert-butanol [7] permit qualifying these compounds (together with hydrogen fluoride, the strongest proton donor among neutral molecules) as having a maximum proton-donor function. Their low proton-acceptor capacity (which explains the low degree of association, especially in the case of alcohols and phenols), the absence of side intermolecular interactions due to other mechanisms, i.e., the practical monofunctionality, and their high chemical stability make them valuable objects in the study of complexing with proton acceptors caused by a strong hydrogen bond.

The proton-donor capacity in the formation of a hydrogen bond in α- (I) and β- (II) heptafluoronaphthols, $C_{10}F_7OH$, was studied by IR spectroscopy in the present article. The spectral [shift of the ν(OH) band and its integral intensity] and thermodynamic (change in the enthalpy and entropy) characteristics of $C_{10}F_7OH...B$ complexes of naphthols (I) and (II) with B proton acceptors of different strength: acetonitrile, methyl ethyl ketone, dioxane, tetrahydrofuran (THF), N-methylvaleramide, tetramethylurea, pyridine, dimethyl sulfoxide (DMSO), hexamethylphosphortriamide (HMPTA) (reaction 1), and of complexes of the ionic type $C_{10}F_7O^-...HN^+R$ of naphthols (I) and (II) with tributyl- and dibutylamine, indicated in the UV spectra by passage of the proton from donor to acceptor (reaction 2), were measured in solution in CCl_4:

$$C_{10}F_7OH + B \rightleftarrows C_{10}F_7OH \cdots B, \tag{1}$$

$$C_{10}F_7OH + B \rightleftarrows C_{10}F_7O^- \cdots HB^+. \tag{2}$$

Two bands of different intensity at 3572 and 3619 cm^{-1} were recorded in the spectrum of naphthol (I) in the region of ν(OH), in agreement with the data in [8], while the ν(OH) band of naphthol (II) was isolated and located at 3569 cm^{-1} (Fig. 1). In comparing the ν(OH) frequency of polyfluorinated hydroxynaphthalenes and phenol derivatives, the doublet nature of the ν(OH) band of naphthol (I) was attributed to the existence of two conformations which differ by the cis- and trans-orientation of the hydroxy group with respect to the fluorine atom in the peri position in [8]. The relative intensity of the two ν(OH) bands in the spectrum did not change in a wide range of temperatures (up to 200°C) [8] so that the proposed isomeric forms should be energetically equivalent. This is a sufficient basis for using any of the components of the ν(OH) band in measurement of the equilibrium constant of the reaction of formation of complexes of naphthol (I) with proton acceptors regardless of the definitive interpretation of its doublet structure, which apparently requires further studies.

The concentration c^a of free molecules of naphthol (I) (based on the intensity at the maximum of the 3619 cm^{-1} band) and naphthol (II) (3569 cm^{-1}) in solutions containing naphthol and different amounts of proton acceptor was measured to determine the equilibrium constants of reactions (1, 2); the absorption factors of the ν(OH) bands of naphthol (I) at 3572 and 3619 cm^{-1}, equal to 281 and 273 liter·mole^{-1}·cm^{-1}, and the ν(OH) bands of naphthol (II) at 3569 cm^{-1}, 479 liter·mole^{-1}·cm^{-1}, were used. In all cases, the condition $c_0^b > c_0^a$ was

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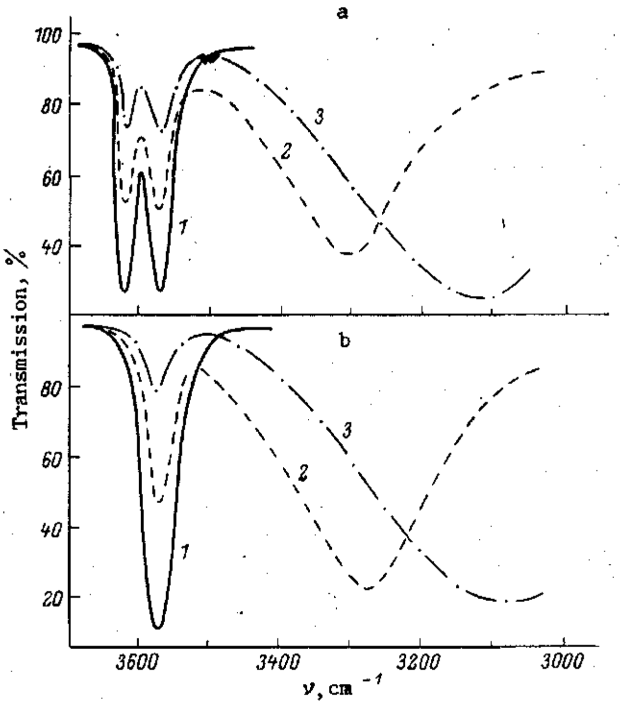

Fig. 1. IR spectra of solutions of α-heptafluoronaphthol (I) (a) and β-heptafluoronaphthol (II) (b) with proton acceptors in CCl_4 at 22°C: 1) without an acceptor, 2) with acetonitrile, 3) with tetrahydrofuran (THF). Concentration (mole/liter): (I) and (II): 0.009, acetonitrile and THF: 0.1; d 0.5 cm.

satisfied, where $c_0{}^a$ and $c_0{}^b$ are the starting concentrations of naphthol and the proton acceptor. The concentrations of the complexes c^{ab} and the free acceptor molecules c^b were found from equations of balance (3, 4), and the equilibrium constants of reactions (1) and (2) were calculated with Eq. (5):

$$c_0^a = c^a + c^{ab}, \tag{3}$$

$$c_0^b = c^b + c^{ab}, \tag{4}$$

$$K = \frac{c^{ab}}{c^a \cdot c^b} = \frac{c_0^a - c^a}{c^a \cdot [c_0^b - (c_0^a - c^a)]}. \tag{5}$$

A correction for the change in the density of the solvent with the temperature according to handbook data [9] was introduced in the calculations, and the temperature dependence of the absorption factor at the maximum of the ν(OH) band of the naphthols was taken into consideration; it is linear in the working range with a factor of −0.42 and −0.28 liter$\cdot$mole$^{-1}\cdot$cm$^{-1}\cdot$K^{-1} for naphthols (I) and (II). The values of the equilibrium constant at each temperature were averaged for 2-5 experiments, and the change in the enthalpy −ΔH and then the entropy −ΔS of processes (1) and (2) were found with the temperature dependence of ln K on 1/T, which is always satisfactorily approximated by a line (Fig. 2). The results obtained are reported in Table 1. The precision of determination of K was estimated at 10-20%, and the error in ΔH was estimated at approximately 10%.

For both naphthols, the increase in K and ΔH is in agreement with an increase in the proton-acceptor capacity of the partners. Naphthols (I) and (II) are very similar in proton-donor capacity: The values of ΔH of their complexes with the acceptors differ insignificantly. On the average, the values of ΔH for naphthol (I) are slightly higher than for naphthol (II), although the difference between them is within the limits of the random experimental error. Pentafluorophenol (III), for which the data on the proton-donor capacity taken from [5] are also reported in Table 1, is the same with respect to the proton-donor strength as naphthols (I) and (II). With the similarity of the values of ΔH for naphthols (I) and (II), the values of the equilibrium constants of processes (1) and (2) with the participation of naphthol (I) are significantly lower (and consequently the values of −ΔS

TABLE 1. Thermodynamic Characteristics of Complexes of Heptafluoronaphthols (I) and (II) and Pentafluorophenol (III) with Proton Acceptors

No.	Proton acceptor	K (22 °C), mole/liter			−ΔH,ᵃ kJ/mole			−ΔS, J/(mole·°K)		
		I	II	III	I	II	III	I	II	III
1	Acetonitrile	9	21	24	23 (20)	22 (23)	22	60	50	49
2	Methyl ethyl ketone	21	53	55	26 (28)	26 (30)	26	61	53	53
3	Dioxane	21	55	—	26 (31)	26 (31)	—	61	55	—
4	THF	41	120	130	30 (34)	30 (34)	29	70	61	56
5	N-Methylvaleramide	270	830	—	34	31	—	70	50	—
6	Tetramethylurea	550	1410	—	34	33	—	64	50	—
7	Pyridine	460	1840	1600	37	38	39	74	66	70
8	DMSO	690	1860	2100	35 (36)	32 (36)	35	65	46	55
9	HMPTA	11200	27700	—	35	33	—	41	26	—
10	Tributylamine	2140	23600	—	52	58	—	111	111	—
11	Dibutylamine	11300	408000	48100	66	65	84	145	111	176

Note. a) The values of ΔH calculated with the method in [11] are reported in parentheses.

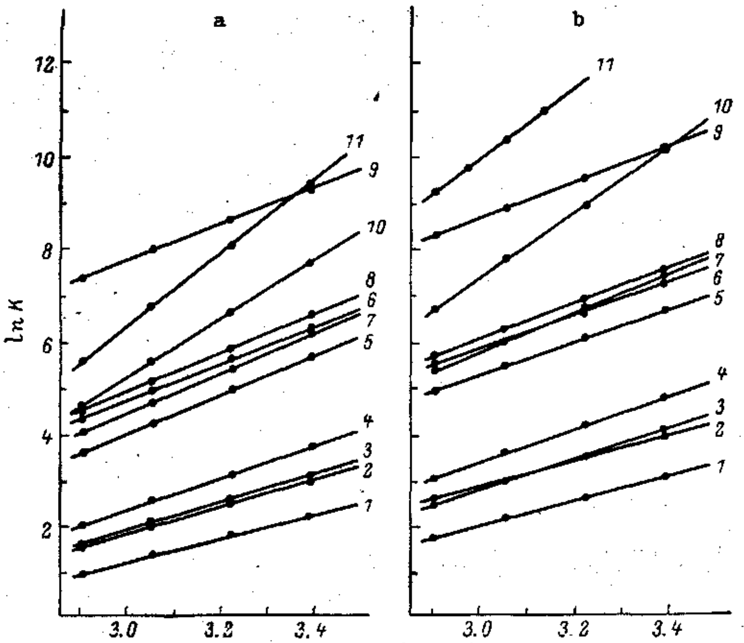

Fig. 2. Dependence of ln K on 1/T for complexes of α-heptafluoronaphththol (I) (a) and β-heptafluoronaphthol (II) (b) with acetonitrile (1), methyl ethyl ketone (2), dioxane (3), THF (4), N-methylvaleramide (5), tetramethylurea (6), pyridine (7), DMSO (8), HMPTA (9), tributyl- (10), and dibutylamine (11).

are higher) than for (II). This result can apparently be attributed to the impossibility of formation of a complex with naphthol (I) in the cis form due to steric hindrances similar to those observed in [10] for some phenol derivatives.

The parameters of the ν(OH) IR band of complexes of naphthols (I) and (II): the frequency of the ν(OH) band of the complex and its integral absorption factor A, were measured for several proton acceptors. These data are reported in Table 2. The values of A were used for estimating the enthalpies of the complexes with a correlation ratio [11], and the total intensity of the doublet band at 3572 and 3619 cm^{-1} was used as the integral intensity of the ν(OH) band of the free molecules in the case of naphthol (I). The values of ΔH obtained (Table 1) are in satisfactory agreement with the values determined with the van't Hoff equation.

TABLE 2. Spectral Characteristics of Complexes of Heptafluoronaphthols (I, II) and Pentafluorophenol (III) with Proton Acceptors

Proton acceptor	$\nu(OH)$, cm^{-1}			$A \cdot 10^{-4}$, liter·mole^{-1}·cm^{-2}	
	I	II	III	I	II
—	3572, 3619	3569	3573	1.8	2.2
Acetonitrile	3310	3270	3280	9	11
Methyl ethyl ketone	3280	3230	3245	13	16
Dioxane	3190	3150	—	15	16
THF	3120	3080	3090	17	18
DMSO	3030	2980	2980	18	20

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer using nonseparable thermostated liquid cells 0.0157, 0.0606, 0.215, 0.5, and 2 cm thick with a scanning rate of 25-64 cm^{-1}/min and slit program 4. The measurements were made at four temperatures in the 22-72°C range, and the temperaure was measured with a precision of 1°K with a copper—constantan thermocouple. A solution of the proton acceptor in CCl_4 at the same temperature as the working solution was placed in the reference channel. The concentration of naphthols and acceptors was varied within the limits of 0.002-0.1 mole/liter; self-association of the naphthols was not observed in this range of concentrations. The integral intensity of the IR absorption was measured by planimetry. The degree of purity and quality of drying of the compounds used in the study was controlled with the IR spectra.

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CONCLUSIONS

The thermodynamic characteristics of complexes of α- and β-heptafluoronaphthols with different proton acceptors in solution in CCl_4 were determined with the IR absorption spectra. In the formation of the molecular OH···B and ionic $O^-\cdots HB^+$ complexes with a hydrogen bond, the changes in the enthalpy for both structural isomers of the heptafluoronaphthols are similar, but the equilibrium constant for the α-isomer is significantly smaller than for the β-isomer.

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