

PROTON TRANSFER IN COMPLEXES OF 2-HEPTAFLUORONAPHTHOL  
WITH ALIPHATIC AMINES IN AN INERT SOLVENT AND IN THE  
GASEOUS PHASE

A.N. Delnov, G.S. Denisov and G.G. Furin

Physics Institute, A.A. Zhdanov Leningrad State  
University, and Institute of Organic Chemistry, USSR  
Academy of Sciences, Novosibirsk

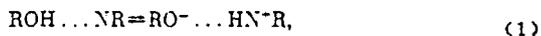
The structure of complexes of 2-heptafluoro-  
naphthol with aliphatic amines was investigated  
according to electron absorption and fluorescence  
spectra in the temperature range 130-180°C in the  
gaseous phase and in a hydrocarbon solvent. In  
the gaseous phase, in contrast to a solution, the  
complex with an intermolecular hydrogen bond OH...N  
in the ground and excited states has a molecular  
structure. Proton phototransfer does not take  
place either in solution or in the gaseous phase.

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A study of complexes with hydrogen bonds formed by  
molecules that behave like strong acids and bases in  
aqueous solutions shows that the structure of such a  
complex depends largely on its interaction with the

surrounding medium [1]. Whereas in inert nonpolar solvents such as alkanes or  $\text{CCl}_4$  and in inert gas matrices the complex formed by hydrogen halides or trifluoroacetic acid and amines has an ion pair structure, in the gaseous phase the absence of proton transfer from donor to acceptor has been demonstrated both experimentally and theoretically in several cases [2-8]. An attempt is made in the present work, on the basis of electron absorption and emission spectra, to establish the structure of complexes formed in the gaseous phase between 2-heptafluoronaphthol (HFN)  $\text{C}_{10}\text{F}_7\text{OH}$  and aliphatic amines, and to investigate to what extent the process of proton transfer in the ground and basic states is hindered in the gaseous phase compared with an inert solvent.

It was previously found [9] that in these systems in hydrocarbon solvents an equilibrium exists between a molecular complex with a hydrogen bond, and an ion pair



the equilibrium being strongly displaced to the right at room temperature. On account of the low vapour pressure of the complexes the absorption spectra of the gaseous phase in our experiments can be successfully observed only at temperatures above  $150^\circ\text{C}$ , and fluorescence spectra only above  $130^\circ\text{C}$ . At these temperatures the concentration of the ion pairs in solution in alkanes is lower than the concentration of molecular complexes in free molecules of HFN [9]. Accordingly the experimental conditions were chosen so that it was possible to compare the absorption and fluorescence spectra of the solutions, when the existence of the ion forms is reliably recorded, with the

spectra of gaseous mixtures of similar composition at the same temperature. Triethylamine and diethylamine, which differ substantially as regards their affinity for protons, were chosen as acceptors [10]. n-dodecane was chosen as solvent.

The absorption and fluorescence spectra were recorded on Specord UV-VIS and Hitachi-850 instruments. The experiments were performed in sealed quartz ampoules 13 mm in diameter, placed in a furnace with quartz windows. The naphthol concentration in the solution and in the vapour under conditions of complete vaporisation was  $(1.5-2.0) \times 10^{-4}$  mole/l, and the amine concentration was  $(0.1-0.3)$  mole/l. The absence of any thermal decomposition of the substance was checked spectroscopically. The accuracy of the temperature measurement is  $\pm 2^\circ\text{C}$ .

At a temperature of  $\sim 150^\circ\text{C}$  the heptafluoronaphthol anion band at  $28,800\text{ cm}^{-1}$  at the edge of the band corresponding to the molecular form is still visible in the absorption spectrum of HFN solutions in dodecane with a large excess of amine. The intensity of the band decreases with increasing temperature, and becomes unnoticeable above  $200^\circ\text{C}$ . In the HFN spectrum in the gaseous phase and under a similar excess of amine, the ion form band is not observed right up to the minimum temperature of  $150^\circ\text{C}$ , at which the spectrum can be successfully recorded. The absorption spectrum of the HFN anion in the ion complex with trioctylamine in solution at  $20^\circ\text{C}$ , as well as of the HFN triethylamine system in solution and in the gaseous phase at  $170^\circ\text{C}$ , when the ion form band in solution is fully visible, are illustrated by way of example in Fig. 1. In the gaseous phase, in the presence of both diethyl ether and triethylamine, the spectrum of the

molecular form of HFN is slightly shifted to lower frequencies, and the vibrational structure is somewhat blurred (Fig. 1). These changes in the spectrum of naphthol vapour indicate the formation of a molecular complex with a hydrogen bond [9]. Such data are obtained for the HFN-diethylamine system, for which a roughly 1.5 times greater concentration of ion pairs in the solution may be expected. This evaluation is performed according to the results given in [9]: for a solution in undecane at 170°C the ratio of concentrations of molecular complex and ion pair in the system  $\text{HFN}+(\text{C}_2\text{H}_5)_2\text{N}$  is about 4.5, and in the system  $\text{HFN}+(\text{C}_2\text{H}_5)_2\text{NH}$  is about 3.5. In this connection, the proportion of naphthol included in the composition of the molecular complexes and ion pairs is roughly 60% and 13% in the first system, and 70% and 20% in the second system. It is clear that if equilibrium (1) exists in the gaseous phase, it will be strongly shifted to the left compared with a solution in alkanes.

The fluorescence spectra enable this conclusion to be confirmed. The structureless fluorescence band of HFN at 170°C in a hydrocarbon solvent has a maximum at a frequency of  $27,100\text{ cm}^{-1}$  (Fig. 2), and in the gaseous phase at  $26,750\text{ cm}^{-1}$  (Fig. 3). Under the formation of a molecular complex with a hydrogen bond this band undergoes a noticeable low-frequency shift, which is larger than in the absorption spectrum: in the presence of diethyl ether at 170°C in solution this shift is  $1200\text{ cm}^{-1}$  (Fig. 2), in the gaseous phase is  $450\text{ cm}^{-1}$  (Fig. 3), and in diethyl ether at 20°C the shift is  $1700\text{ cm}^{-1}$ . At the same time the quantum yield is reduced 6-7-fold. A significantly larger shift is observed during proton transfer and the form-

1637  
 ation of an ion pair. In an inert solvent at 20°C the HFN anion in the ion complex with an aliphatic amine has a wide structureless fluorescence band with a

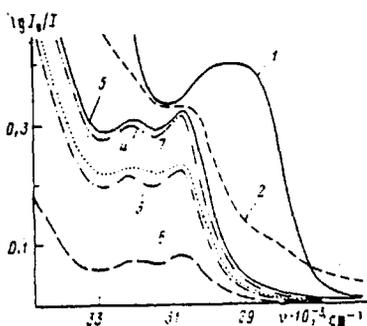


Fig. 1

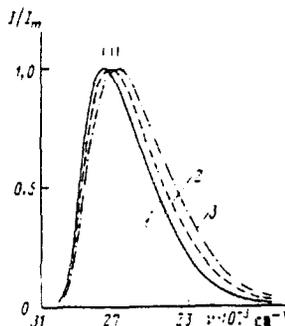


Fig. 3

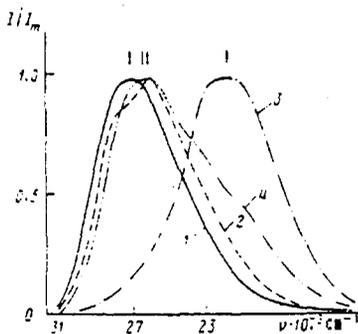


Fig. 2

Fig. 1. Absorption spectra of HFN: in solution in dodecane ( $1.5 \times 10^{-4}$  mole/l) in the presence of 0.15 mole/l of trioctylamine at 20°C (1), triethylamine at 170°C (2); in the gaseous phase at 130 (3), 170°C (4), in the presence (1:10<sup>3</sup>) of diethyl ether at 170°C (5), and of triethylamine at 170 (6) and 200°C (7)

Fig. 2. Fluorescence spectra of solutions of HFN ( $1.5 \times 10^{-4}$  mole/l) in dodecane at 170°C (1); in dodecane in the presence (0.15 mole/l) of diethyl ether at 170°C (2),  $\nu_b = 30,800$  cm<sup>-1</sup>; trioctylamine at 20°C (3); triethylamine at 170°C (4),  $\nu_b = 29,400$  cm<sup>-1</sup>

Fig. 3. Fluorescence spectra at 170°C of HFN vapours (1); in the presence (1:10<sup>3</sup>) of diethyl ether (2), triethylamine (3),  $\nu_b = 30,800$  cm<sup>-1</sup>

maximum  $\nu_m$  at  $21,700\text{ cm}^{-1}$  (Fig. 2), and the quantum efficiency is roughly 4 times less than in the case of free naphthol molecules. At a temperature of about  $150^\circ\text{C}$ , as in the absorption spectrum this band is observed in the form of a shoulder on the edge of the molecular form band, and at a temperature above  $200^\circ\text{C}$  it is practically unnoticeable. Fluorescence spectra of the HFN-triethylamine system in solution and in the gaseous phase at  $170^\circ\text{C}$  are illustrated in Figs. 2 and 3. In contrast to the solution, in the gaseous phase fluorescence of the ion complex is absent and cannot be recorded up to  $130^\circ\text{C}$ . In the presence of triethylamine the HFN fluorescence band lies at  $\nu_m\ 26,000\text{ cm}^{-1}$ , and that of diethylamine at  $\nu_m\ 26,100\text{ cm}^{-1}$  (in solution,  $26,300\text{ cm}^{-1}$  and  $26,200\text{ cm}^{-1}$  respectively). The excitation spectra, as in the case of the complex with diethyl ether, coincide with the absorption spectra. Thus, in the gaseous phase in the temperature range  $130\text{--}180^\circ\text{C}$  complexes of HFN with aliphatic amines have only a molecular structure. The position of the fluorescence bands of these complexes leads to the conclusion that, in the gaseous phase, a secondary aliphatic amine does not differ from a tertiary aliphatic amine as regards proton acceptor ability.

Heptafluoronaphthol and its anion do not fluoresce in aqueous solution, and accordingly an evaluation of the acidity in the excited electron state may be made only from the position of the absorption bands of the neutral and deprotonated forms. In both aqueous and aprotic solvents the long-wave shift due to ionisation of HFN is  $1500\text{--}1700\text{ cm}^{-1}$ . According to the reaction scheme given in [11], this corresponds to an increase in  $pK_s$  in the excited state of  $3\text{--}3.5$  units. The shift of the electron band of HFN in the fluorescence spec-

trum as a result of the formation of a hydrogen bond with diethyl ether is greater than in the absorption spectrum (150 and 1200  $\text{cm}^{-1}$  in a solution in dodecane, and 100 and 450  $\text{cm}^{-1}$  in the gaseous phase) and this may be regarded as evidence of the strengthening of the hydrogen bond under electron excitation. However, under excitation of the tautomeric complex between HFN and amines, a band due to expulsion of the anion is not observed in the molecular form band in the gaseous phase, and in solution no shift of the equilibrium in the direction of the ion pair can be detected: with an increase in temperature the luminescence spectra change in a similar manner to the absorption spectra. Clearly, the equilibrium between the molecular complex and ion pair cannot shift noticeably during the lifetime of the excited state, since no phototransfer of a proton from HFN to amines is observed in solution or in the gaseous phase in the temperature range 130-180°C.

The results obtained show that interaction between the complex and molecules of a nonpolar solvent play an important rôle in the formation of ion pairs, initiating transfer of a proton via the hydrogen bond. It is difficult to say anything definite about the mechanism of this interaction, though various possibilities are considered in [1, 12].

#### REFERENCES

1. G.S. Denisov, A.I. Kulbida and V.M. Schreiber, Molecular Spectroscopy, edited by S.F. Bureiko, Leningrad State University, Leningrad, 1983, 6th edtn.
2. N.S. Golubev and G.S. Denisov, Khim. Fizika, 1982, 1, No. 5, p. 563.
3. A.I. Kulbida and V.M. Schreiber, J. Molec.

Struct., 1978, 47, p. 323.

4. A. Breiz, A. Karpfen, H. Lischka and P. Schuster, Chem. Phys., 1984, 89, No. 3, p. 337.

5. Z. Latajka, S. Sakai, K. Morokuma and H. Ratajczak, Chem. Phys. Lett., 1984, 110, No. 5, p. 464.

6. E.J. Goodwin, N.W. Howard and A.C. Legon, Chem. Phys. Lett., 1986, 131, No. 4/5, p. 319.

7. V.A. Mikheev and V.M. Schreiber, Optika i Spektroskopiya, 1984, 57, No. 1, p. 3.

8. P.G. Jasien and W.J. Stevens, Chem. Phys. Lett., 1986, 130, No. 1-2, p. 127.

9. Yu.A. Bazavluk, A.N. Delnov and G.S. Denisov, Zh. Prikl. Spektroskopii, 1988, 48, No. 5, p. 799.

10. S.G. Lias, J.F. Liebman and R.D. Levin, J. Phys. A. Chem. Ref. Data, 1984, 13, No. 3, p. 695.

11. S. Parker, Photoluminescence in Solutions, Mir, Moscow, 1972.

12. A.I. Kulbida, Khim. Fizika, 1982, 1, No. 6, p. 802.