

Influence of the temperature-dependent dielectric constant on the H/D isotope effects on the NMR chemical shifts and the hydrogen bond geometry of the collidine–HF complex in CDF₃/CDClF₂ solution

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The influence of solvent polarity on the properties of hydrogen-bonded 1:1 complexes of 2,4,6-trimethylpyridine-¹⁵N with HF and DF, labeled below as FHN and FDN, has been studied by multinuclear magnetic resonance spectroscopy in the slow hydrogen bond exchange regime reached below 190 K. Mixtures of CDF₃/CDClF₂ were employed as solvent, which is liquid down to 90 K. In order to evaluate their polarity, the static dielectric constants ϵ_0 of the CHF₃, CHClF₂ and of the binary 1:1 mixture were measured from 160 K down to 90 K. A strong increase of ϵ_0 from 14 at 190 K to 38 at 103 K is observed for the mixtures used in the NMR measurements. Upon cooling, i.e. increase of the dielectric constant, the NMR spectra indicate a gradual transformation of an asymmetric molecular complex F–H···N to a quasi-symmetric complex F^{δ-}···H···N^{δ+} and eventually to a more or less zwitterionic species F⁻···H–N⁺. These changes are not only manifested in the scalar couplings $J(^1\text{H}, ^{19}\text{F})$ and $J(^1\text{H}, ^{15}\text{N})$ but also lead to characteristic primary and secondary H/D isotope effects on the chemical shifts of the hydrogen bonded nuclei. Whereas the primary isotope chemical shift effect ${}^p\Delta(\text{D}/\text{H}) \equiv \delta(\text{F}^2\text{HN}) - \delta(\text{F}^1\text{HN}) = -0.2$ ppm is negative at 190 K and in agreement with an asymmetric hydrogen bond in the molecular complex, it changes its sign when the temperature is lowered, goes through a maximum of +0.27 ppm at $\epsilon_0 \approx 22$ and finally decreases again. The positive value of ${}^p\Delta(\text{D}/\text{H})$ is in agreement with D more confined to the hydrogen bond center compared with H, which constitutes a fingerprint of a quasi-symmetric hydrogen bond involving a single well potential for the proton motion. The quasi-symmetric complex is further characterized by the following NMR parameters, $J(^1\text{H}, ^{19}\text{F}) = 30$ Hz, $J(^1\text{H}, ^{15}\text{N}) = -50$ Hz, $J(^{19}\text{F}, ^{15}\text{N}) = -96$ Hz, $\delta(\text{F}^1\text{HN}) = 20.0$ ppm, $\delta(^{19}\text{FHN}) = -114.2$ ppm, $\delta(\text{FH}^{15}\text{N}) = -63.5$ ppm, and the one-bond H/D-isotope effects $\delta(\text{F}^2\text{HN}) - \delta(\text{F}^1\text{HN}) = +0.27$ ppm, $\delta(^{19}\text{FDN}) - \delta(^{19}\text{FHN}) = 1.4$ ppm and $\delta(\text{FD}^{15}\text{N}) - \delta(\text{FH}^{15}\text{N}) = -3.4$ ppm. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ¹H, ²H, ¹⁹F NMR; hydrogen bond; isotope effect; low-temperature NMR; solvent polarity; static dielectric constant; collidine-hydrofluoride

INTRODUCTION

The potential role of very short and strong hydrogen bonds, so called low-barrier hydrogen bonds, in acid–base catalysis of organic and enzymic reactions has evoked a great interest in recent years.¹ Probably the strongest criticism of this concept based on theoretical grounds

argues that a low-barrier hydrogen bond becomes unstable in a polar environment.² In this case it is proposed that specific solvation leads to charge localization and an equilibrium between two asymmetric tautomers, i.e. A–H···B \rightleftharpoons A⁻···H–B⁺, exhibiting a weaker hydrogen bond, compared with a quasi-symmetric complex of the A^{δ-}···H···B^{δ+} type where the forces on the proton from A and B are equal.³ Recently, using NMR spectroscopy at low temperatures in specially selected solvents, some of us have observed such quasi-symmetric complexes between pyridine derivatives and various acids even though the solvents employed exhibited a very high polarity.^{4–6} Moreover, a monotonous transformation of the type A–H···B →

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$A^{\delta-} \cdots H \cdots B^{\delta+} \rightarrow A^- \cdots H-B^+$ was observed when the temperature was lowered, a fact that was associated with the increase of the electric field or the dielectric constant upon cooling. These conclusions were obtained from a discussion of temperature-dependent chemical shifts and coupling constants across hydrogen bonds. The scope of this study was to obtain more information about these complexes by measuring H/D isotope effects on the NMR parameters of acid–base complexes and by characterizing the influence of the polarity of the solvents used in a more quantitative way.

The reason to select the solvents used carefully is the short lifetime of hydrogen-bonded complexes of low molecular weight. Thus, generally, only single sets of NMR lines are observed, which represent averages over different hydrogen-bonded fast interconverting complexes. In addition, internal rotations, isomerization processes and proton exchange also lead to NMR signal averaging. Usually, the only way to solve these problems is to decrease the sample temperatures below 150 K. Unfortunately, there is not a wide range of solvents available that are suitable for liquid-state NMR below 150 K. Moreover, the solvents also need to contain either deuterium or fluorine as nuclei for magnetic field locks. Examples of solvents that can be applied for such studies in the 85 to 150 K range are 1-monodeuteropropane,⁷ bromotrifluoromethane and vinylchloride,⁸ dimethyl ether,⁹ and methylethyl ether.¹⁰ In addition, *n*-propyl nitrite, C_3H_7ONO , is a promising solvent for low-temperature studies in the future, since it remains liquid between 300 and 94 K.¹¹ Especially useful are solvent mixtures exhibiting lower melting points than their pure components, *via* the formation of eutectic mixtures. For example, mixtures of the freons $CHClF_2$ and $CHCl_2F$ are liquid down to 83 K¹² and have been used in a number of studies.¹³ For a long time, some of us have employed mixtures of CDF_3 and $CDCIF_2$, which remain liquid and fluid down to 95 K.¹⁴ These mixtures are not commercial and are made by fluorination of $CDCl_3$ under pressure. Unfortunately, the composition of the mixtures obtained is variable, as found by integration of the residual 1H signals of the components. As the static dielectric constants ϵ_0 of the components are very different and strongly increase upon cooling,^{15,16} we wanted to establish a quantitative relation between ϵ_0 , temperature and the composition in order to associate to each sample temperature a value of ϵ_0 .

As it turned out that low-temperature dielectric constant measurements are quite demanding, we decided to measure ϵ_0 of the pure compounds CHF_3 and $CHClF_2$ and of their 1:1 mixture, which we expected to exhibit the potentially strongest deviation from an ideal mixing behavior. Thus, we were able to obtain a satisfactory equation for ϵ_0 as a function of temperature and the sample composition. Considering that H/D isotope effects on dielectric constants, permanent molecular dipole moments and molar volumes of liquids are very small,¹⁷ we did not attempt to measure the values of the deuterated analogs.

Our second scope was to apply the $CDF_3/CDCIF_2$ solvent system to the study of the 1:1 complexes between ^{15}N -enriched 2,4,6-trimethylpyridine (collidine) and HF or DF. The protonated form of this complex, labeled as FHN in this paper and representing the ^{19}F , 1H and the ^{15}N nuclei, has

been described previously.⁵ The analysis of the temperature dependence of the one-bond scalar couplings $J(^1H, ^{19}F)$ and $J(^1H, ^{15}N)$ across the hydrogen bond showed that this complex exhibits a quasi-symmetric, low-barrier hydrogen bond of the $F^{\delta-} \cdots H \cdots N^{\delta+}$ type in a highly polar solution at low temperatures. Besides these couplings, this complex also exhibits a two-bond fluorine–nitrogen coupling constant of 96 Hz whose value is temperature insensitive within the margin of error.⁵

In this study, we report a temperature dependence of the chemical shift difference between H and D in the hydrogen bond, i.e. the primary isotope effect $^P\Delta(D/H) \equiv \delta(F^2HN) - \delta(F^1HN)$ on the associated NMR chemical shifts. The sign of $^P\Delta(D/H)$ is known to constitute a sensitive probe to explore the symmetry of the hydron potential.¹⁸ Here, we will show that, using the solvent system mentioned above, lowering the temperature induces a sign change of $^P\Delta(D/H)$, corresponding to the proposed transformation of the asymmetric molecular complex at higher temperatures into the quasi-symmetric complex $F^{\delta-} \cdots H \cdots N^{\delta+}$ exhibiting a single well for the proton and deuteron motion.

This paper is organized as follows. After a short experimental section the NMR and dielectric constants measurements are described, and the implication of the results for the nature of the hydrogen bond between collidine and HF or DF is discussed.

EXPERIMENTAL

Materials

^{15}N -enriched 2,4,6-trimethylpyridine (collidine) was synthesized from 95% ^{15}N -enriched NH_4Cl (Deutero) and 2,4,6-trimethylpyrylium tetrafluoroborate as described previously.¹⁹ In order to prepare the NMR samples, a small amount of 40% HF (Aldrich) in water was added to an excess of the base dissolved in acetone, using a teflon flask. Water and acetone were removed by repeated azeotropic distillation in the presence of increasing amounts of dichloromethane. The latter was then removed *in vacuo* to leave an oily product. Deuteration of the substance was performed by additional repeated distillation from methanol- d_1 (Deutero) solution. The product was placed in an NMR sample tube equipped with a teflon needle valve (Wilmad, Buena, NY) and cooled to 77 K in order to prevent reaction with the glass. The tube was connected to a high-vacuum line and the solvent was added by vacuum transfer.

The solvent mixture $CDF_3/CDCIF_2$ for the low-temperature NMR experiments, whose composition varied between 1:2 and 1:3, was prepared by a modified recipe proposed by Siegel and Anet.²⁰ According to this method, the chlorine atoms of chloroform can be exchanged against fluorine at atmospheric pressure using antimony(III) fluoride as fluorinating agent and antimony(V) chloride as a catalyst. By carrying out the reaction at higher pressures the degree of fluorination can be increased, as proposed previously.¹⁴

In a typical experiment, 20 g $CDCl_3$, 30 g SbF_3 and 1 ml water-free $SbCl_5$ were heated in an autoclave (Berghof-Maasen) at 100 °C until the pressure reached 40 bar. The inner surface of the autoclave should be covered with teflon

to prevent an interaction with the reagents. After cooling to room temperature the autoclave was connected to a high-vacuum line and the freon was condensed into a lecture bottle. Residual acidic by-products, such as HCl, and HF and H₂O, were removed by repeated gas-transfer through a column with KOH pills. The removal of the acidic impurities was controlled by the addition of 5'-O-(4,4'-dimethoxytrityl)-2'-deoxyadenosine, which forms a red-colored trityl cation in the presence of acid traces.

Chemically pure freons CHF₃ and CHClF₂ (99.5%; RNC 'Applied Chemistry', Russia) were used for the dielectric constant measurements.

NMR spectra

The NMR spectra were recorded on a Bruker AMX-500 spectrometer supplied with a probehead allowing a temperature adjustment down to 96 K. The ¹H, ²H and ¹⁹F chemical shifts were measured using the CDF₃ or CHF₃ peaks as internal references and then converted into the usual scales corresponding to TMS and CFC₃. The ¹⁵N chemical shifts were referenced to the peak of free collidine.

Dielectric constant measurements

The static dielectric constant ϵ_0 for CHF₃, CHClF₂ and their 1:1 ($\pm 1\%$) mixture were measured using a home-made LCR meter at 50 kHz. The typical errors were about 2.5% at 30–100 pF and 1% at 150–600 pF. The central electrode of the coaxial cell (11 pF inherent capacitance) was made from electrolytic copper to reduce the temperature gradient. The capacitor was placed in a glass flask, burst pressure 4 bar, with a hermetically sealed connection. The flask was inserted into a thermoinsulated thick-walled copper tumbler, cooled by liquid nitrogen. Temperature was controlled inside the central electrode by a copper–constantan thermocouple with an accuracy of about 0.3 K. The standard calibration thermocouple curve $U(T)$ was used for temperature determination. Melting points of krypton and xenon of a high purity were used to check the quality of the thermometer. The parameters of the system were determined by comparison of the empty ($\epsilon_0 = 1$) and fluoroform-filled cell at 125.2 K ($\epsilon_0 = 40.7$).²¹ Measurements of ϵ_0 were performed under two different conditions, i.e. the slow heating and the slow cooling conditions. Firstly, the gaseous compounds were condensed into the cell at 150 K. In the slow heating experiments, the cell temperature was decreased to 80 K; liquid nitrogen was removed from the insulating envelope, leading to a slow increase of the sample temperature *via* the natural heat flow. By contrast, in the slow cooling experiments, liquid nitrogen was poured into the insulating envelope at 150 K and the sample was slowly cooled to 80 K. The rate of the temperature changes was about 0.05 K s⁻¹. No differences were observed in a control experiment with a slower rate (0.02 K s⁻¹).

RESULTS

Isotope effects on NMR chemical shifts in 1:1 collidine–HF/DF complex

Some typical multinuclear magnetic resonance signals of the 1:1 complexes FHN/FDN between ¹⁵N-enriched collidine

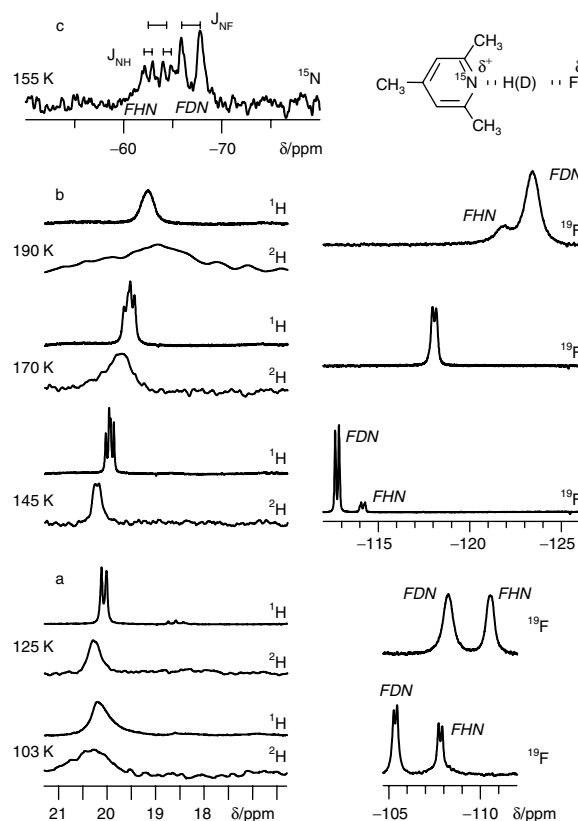


Figure 1. ¹H, ²H, ¹⁵N and ¹⁹F NMR spectra of 1:1 complexes FHN and FDN between ¹⁵N-collidine and HF/DF in CDF₃/CDCIF₂. The deuterium fraction: 55% (a) and (c) and 85% (b).

and HF/DF in CDF₃/CDCIF₂ (composition approximately 1:2) are depicted in Fig. 1. A considerable five- to ten-fold excess of collidine was needed in order to stabilize the 1:1 complexes, otherwise other complexes with more than one HF or DF molecule are formed. The spectra in Fig. 1 stem from different samples with varying deuterium fractions and excess of the base. Well-resolved ¹H signals were obtained only below 200 K and above 100 K, where the line widths are increased at high temperatures by proton and hydrogen bond exchange and at low temperatures by short transverse relaxation times, arising from the increase of the solvent viscosity. For a better signal-to-noise ratio in the ²H spectra, the total concentration of the complex needed to be increased compared with our previous ¹H measurements,⁵ leading to additional line broadening.

The chemical shift of the bonding hydron (proton or deuteron) depends strongly on the temperature and exhibits a maximum at the lowest reachable temperature, i.e. 103 K (Fig. 1a and b). Primary isotope effects on the chemical shifts ${}^P\Delta(D/H) = \delta(F^2HN) - \delta(F^1HN)$ are observed; these are positive except at the highest temperature of 190 K, where resolved signals could be obtained. A similar chemical shift dependence is observed for ¹⁹F (Fig. 1a and b). However, it is interesting to note that the secondary isotope effect on the ¹⁹F chemical shift, ${}^1\Delta^{19}F(D) \equiv \delta({}^{19}FDN) - \delta({}^{19}FHN)$ is positive at low temperatures, becomes immeasurably small at 170 K and changes its sign at higher temperature.

Table 1. Results of the NMR measurements of FHN and FDN as a function of temperature and of the dielectric constant of the solvent mixture CDF₃/CDClF₂^a

T/K	N	ϵ_0	$\delta(\text{F}^1\text{HN})/\text{ppm}$	$\rho\Delta(\text{D}/\text{H})/\text{ppm}$	$\delta(^{19}\text{FHN})/\text{ppm}$	$\delta(^{19}\text{F(D)})/\text{ppm}$	$\delta(\text{FH}^{15}\text{N})/\text{ppm}$	$^1\Delta^{15}\text{N(D)}/\text{ppm}$	$^1\Delta^{15}\text{N(D)}/\text{ppm}$	$J(^1\text{H}, ^{19}\text{F})/\text{Hz}$	$J(^1\text{H}, ^{15}\text{N})/\text{Hz}$	$J(^{19}\text{F}, ^{15}\text{N})/\text{Hz}$
200 ^b	-	-	-	-	-	-	-	-	105 ± 10	-	-	-
190	0.08	13.5	19.18	-0.20 ± 0.05	-124.86	-1.55 ± 0.05	-	-	-	-	-	-
180 ^b	-	-	-	-	-	-	-	-	88 ± 3	-39 ± 3	-	-
170 ^b	-	-	-	-	-	-	-	-	75 ± 3	-42 ± 3	-96 ± 5	-
170	0.08	16.1	19.60	0.16 ± 0.02	-118.05	<0.4	-	-	66 ± 3	-43 ± 3	-96 ± 5	-
155	0.29	20.7	19.95	-	-	-	-63.47 ± 0.05	-3.36 ± 0.05	37 ± 3	-45 ± 3	-96 ± 5	-
150 ^b	-	-	-	-	-	-	-	-	45 ± 3	-45 ± 3	-96 ± 5	-
145	0.08	20.4	19.97	0.27 ± 0.02	-114.18	1.42 ± 0.02	-	-	34 ± 3	-48 ± 3	-96 ± 5	-
145	0.42	24.5	20.02	0.26 ± 0.02	-	-	-	-	25 ± 3	-50 ± 3	-	-
135	0.33	26.1	19.98	0.23 ± 0.02	-	-	-	-	22 ± 3	-50 ± 3	-	-
130	0.42	28.9	20.10	0.20 ± 0.02	-	-	-	-	-	-52 ± 3	-	-
130 ^b	-	-	-	-	-	-	-	-	15 ± 3	-51 ± 3	-96 ± 5	-
125	0.09	25.4	20.02	0.21 ± 0.02	-	-	-	-	14 ± 3	-48 ± 3	-	-
125	0.38	30.0	20.08	0.19 ± 0.02	-	-	-	-	-	-50 ± 3	-	-
125	0.29	28.6	20.09	0.20 ± 0.02	-110.34	2.26 ± 0.02	-	-	-	-51 ± 3	-	-
112 ^b	-	-	-	-	-	-	-	-	-	-54 ± 3	-	-
110	0.09	30.3	20.12	0.18 ± 0.02	-	-	-	-	-	-55 ± 3	-	-
103	0.29	37.7	20.22	0.10 ± 0.05	-107.8	2.46 ± 0.02	-	-	-	-	-96 ± 5	-

^a Primary isotope effect $\rho\Delta(\text{D}/\text{H}) \equiv \delta(\text{F}^2\text{HN}) - \delta(\text{F}^1\text{HN})$, secondary isotope effect $^1\Delta^{19}\text{F(D)} \equiv \delta(^{19}\text{F(DN)}) - \delta(^{19}\text{FHN})$. N: mole fraction of CDF₃ determined by ¹H NMR according to Fig. 4. ϵ_0 : dielectric constant calculated according to Eqn (4).

^b Data taken from Ref. 5.

^{15}N NMR spectra of FHN/FDN mixtures were obtained only around 155 K (Fig. 1c). The secondary isotope effect for the nitrogen nucleus, $^1\Delta^{15}\text{N}(\text{D}) \equiv \delta(\text{FD}^{15}\text{N}) - \delta(\text{FH}^{15}\text{N})$, is negative in this case.

As reported previously,⁵ the NHF complex not only exhibits large scalar couplings $J(^1\text{H}, ^{19}\text{F})$ and $J(^1\text{H}, ^{15}\text{N})$, also has a large value of $J(^{19}\text{F}, ^{15}\text{N})$ of around |96| Hz. This coupling constant is probably negative, because of the negative gyromagnetic ratio of ^{15}N . Within the margin of error, no H/D-isotope effect on $J(^{19}\text{F}, ^{15}\text{N})$ could be observed. Unfortunately, the one-bond couplings $J(^2\text{H}, ^{19}\text{F})$ and $J(^2\text{H}, ^{15}\text{N})$ were not resolved. All important NMR data of NHF and NDF obtained here and in Ref. 5 are collected in Table 1. For each sample temperature the dielectric constant is also given, which was determined as described in the next section.

Dielectric constant measurements

In Fig. 2 we have plotted the static dielectric constant ϵ_0 as a function of temperature for CHF_3 , CHClF_2 and their 1 : 1 mixture. The melting points of CHF_3 (117.7 ± 0.4 K) and CHClF_2 (115.5 ± 0.4 K) determined from the slow heating experiments are in a good agreement with the literature data,²² 117.97 K and 115.73 K respectively. The melting point of the 1 : 1 mixture is considerably lower, i.e. 104.8 ± 0.3 K. Though the values of the dielectric constants for the frozen substances are the same, i.e. 2.8 and temperature insensitive, they depend strongly on temperature in the liquid state. Moreover, in the experiments carried out under slow cooling conditions, a well-pronounced supercooling effect is observed in all cases. Thus the substances are still liquid about 10–15 K below their melting points. Values of the dielectric constants for the freons studied and their 1 : 1 mixture in the temperature region most interesting for the NMR experiments are collected in Table 2.

Usually, the temperature dependence of the dielectric constant can be approximated by the following equation, where A , B and C are parameters and T is the temperature¹¹

$$\epsilon_0 = A + \frac{B}{T - C} \quad (1)$$

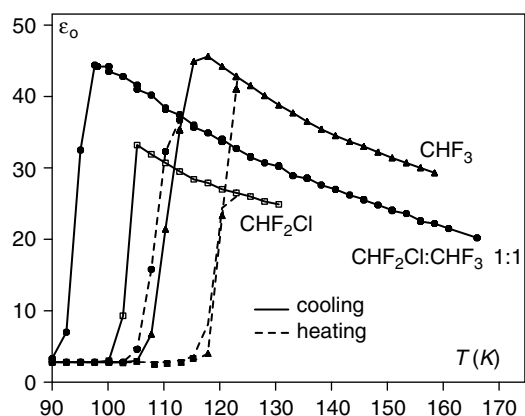


Figure 2. Temperature dependence of the static dielectric constants of CHF_3 , CHClF_2 and their 1 : 1 mixture. The solid lines correspond to the slow cooling and the dotted lines to the slow heating experiments. See text for details.

Table 2. Static dielectric constants of CHF_3 , CHClF_2 and their 1 : 1 mixture. The data were obtained using slow cooling conditions^a

T/K	$N = 1$	$N = 0$	$N = 0.5$
100.0	2.8	3.0	44.2
102.5	2.8	9.3	42.8
105.0	3.0	33.2	41.6
107.5	6.7	31.9	40.2
110.0	21.4	30.7	38.4
112.5	35.3	29.5	37.4
115.0	44.9	28.4	36.0
117.5	45.6	27.9	34.9
120.0	44.2	27.0	33.7
122.5	42.8	26.5	32.7
125.0	41.5	26.0	31.6
127.5	40.1	25.3	30.7
130.0	38.8	24.9	30.2
132.5	37.7		28.9
135.0	36.5		28.5
137.5	35.4		27.6
140.0	34.5		27.0
142.5	33.7		26.2
145.0	33.0		25.6

^a N : mole fraction of CHF_3 ; $1 - N$: mole fraction of CHClF_2 .

For the dielectric constants of the freons studied we find that Eqn (1) is valid in a wide temperature region, including the supercooled liquid-state regime, as indicated in Fig. 3. By non-linear least squares fitting of the data of the pure compounds to Eqn (1) we obtained the parameters $A = -17$, $B = 6500$ K and $C = 14$ K for pure CHF_3 and $A = -6.3$, $B = 3500$ K and $C = 15$ K for pure CHClF_2 . The calculated constants are represented by the solid lines in Fig. 3. The CHF_3 data obtained here are in good agreement with those reported in the literature.²³ Also, by extrapolation of our low-temperature data for CHClF_2 to higher temperatures we obtain a good agreement with the known high-temperature values.¹⁶

The data for the mixture were analyzed as follows. Ideally, the dielectric constant of a binary mixture of two liquids exhibiting a negligible volume increment upon mixing is given by the average value

$$\epsilon_0(m) = \epsilon_0(1)N + \epsilon_0(2)(1 - N) \quad (2)$$

where $\epsilon_0(1)$, $\epsilon_0(2)$ and $\epsilon_0(m)$ are, respectively, the dielectric constants of the pure components 1 and 2 and of the mixture; N is the mole fraction of the first component.²⁴ The dielectric behavior of real mixtures depends on the mutual interaction of the components. Noticeable deviations from additivity have been obtained for polar liquids or substances that are able to form charge transfer complexes.²⁵ In the case of $\text{CHF}_3/\text{CHClF}_2$ mixtures, values of the dielectric constant are about 5–10% less than the values obtained from the Eqn (2). Thus, Eqn (2) has to be modified in order to estimate the dielectric constant for a mixture of any known composition. We assume that the correction term is proportional to

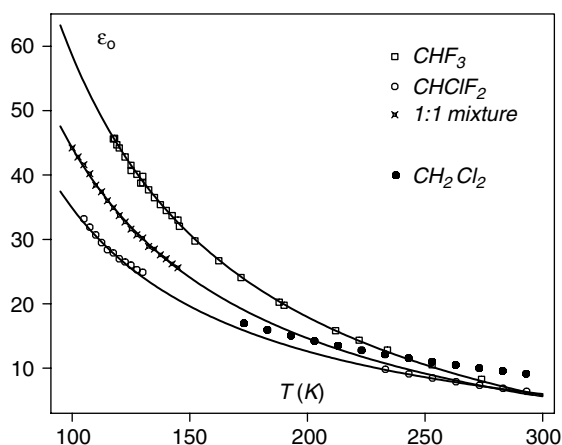


Figure 3. Simulation of the static dielectric constants of CHF_3 ($N = 1$), CHClF_2 ($N = 0$) and their 1:1 ($N = 0.5$) mixture as a function of temperature using Eqn (4), where N is the mole fraction of CHF_3 . The values of the dielectric constants of liquid CHF_3 and CHClF_2 obtained here and reported in Refs 16 and 23 are depicted. The corresponding data of CH_2Cl_2 , published in Ref. 26, are depicted for comparison.

$N(1 - N)$, where N is the mole fraction of CHF_3 , and to T^{-2} , i.e. we write

$$\varepsilon_0(m) = \varepsilon_0(\text{CHF}_3)N + \varepsilon_0(\text{CHF}_2\text{Cl})(1 - N) - G \frac{N(1 - N)}{T^2} \quad (3)$$

The parameter $G = 10^{-5}$ was determined by non-linear least squares fitting of the data of the 1:1 mixture to Eqn (3). As depicted in Fig. 3, the solid line representing the best fit reproduces the data in a very satisfactory way. We have also included the dielectric constants of dichloromethane²⁶ in Fig. 3 for comparison; we note that, above 170 K, the dielectric constants of this solvent and of the freon mixtures studied are of the same order.

For future applications, we can finally express the dielectric constants of CHF_3 and CHClF_2 and of their mixtures as a function of temperature and the mole fraction of CHF_3 as

$$\varepsilon_0(m) = \left(-17 + \frac{6500}{T - 14}\right)N + \left(-6.3 + \frac{3500}{T - 15}\right)(1 - N) - 10^{-5} \frac{N(1 - N)}{T^2} \quad (4)$$

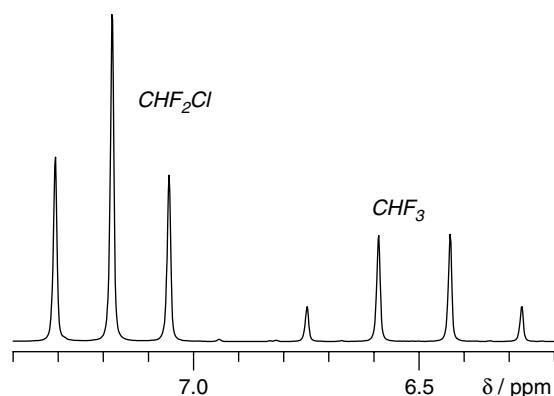


Figure 4. ^1H NMR spectrum of a $\text{CHF}_3/\text{CHClF}_2$ mixture at 200 K. The CHF_3 mole fraction was determined by signal integration and corresponds to $N = 0.3$.

From the standpoint of NMR, the composition of the solvent mixture is conveniently checked by ^1H NMR by integration of the residual solvent protons. An example is shown in Fig. 4, where we obtain a value of $N = 0.3$. Thus, using Eqn (4), we can now calculate the dielectric constant of a given $\text{CHF}_3/\text{CHClF}_2$ solvent mixture as a function of temperature.

DISCUSSION

We have studied the NMR properties of the FH- and FD-collidine hydrogen-bonded complexes FHN and FDN embedded in a polar solvent mixture $\text{CDF}_3/\text{CDClF}_2$ in the slow hydrogen bond exchange regime. These solvent mixtures remain liquid down to temperatures below 100 K, where they are easily supercooled and remain liquid for several hours. They exhibit strong increases of their dielectric constants when the temperature is lowered, which were determined as a function of temperature and solvent composition. Variation of temperature is then useful in order to change the solvent polarity in a convenient way. Thus, we were able to study various NMR parameters, i.e. chemical shifts, H/D isotope effects on chemical shifts and coupling constants of the collidine-HF complex as a function of the solvent polarity.

Electric field and H/D isotope effects on acid-base hydrogen bonds

Before we discuss the results in detail, we will first review a scenario described previously,⁶ illustrated in Fig. 5, of how a strong solvent electric field can transform an acid-base hydrogen-bonded system $\text{A-H} \cdots \text{B}$ into a zwitterionic system of the $\text{A}^- \cdots \text{H}^+ \cdots \text{B}$ type.

The electric dipoles of the individual solvent molecules create a temperature-dependent effective electric field at the solute site. This field is large at low temperatures, where the dipoles are ordered, and small at high temperatures, where they are disordered (Fig. 5a). As a consequence, the temperature-dependent electric field induces in the solute a dipole moment μ that is small at high temperatures but which increases as the temperature is lowered. The dipole moment induced depends on the polarizability of the complex, which consists of two contributions. The electronic contribution is associated with a reorganization of the electrons under the action of the electric field. The nuclear part, which is also called 'nuclear' or 'vibrational' polarizability, is associated with changes of the nuclear geometry.²⁷ In a molecular complex $\text{A-H} \cdots \text{B}$ exhibiting a relatively small permanent electric dipole moment the dipole moment can only be enhanced by charge transfer from B to AH. The energy for the charge separation is provided by the electric field; this energy is minimized by a contraction of the hydrogen bond, as illustrated in Fig. 5b and c. In other words, a molecular complex $\text{A-H} \cdots \text{B}$ contracts in the presence of an electric field. This hydrogen-bond contraction is accompanied by a displacement of the proton to the hydrogen bond center. Once the proton has crossed the center, an increase of the dipole moment is achieved by a further displacement of the proton towards B, accompanied by an increase of the $\text{A} \cdots \text{B}$ distance. These changes have recently been

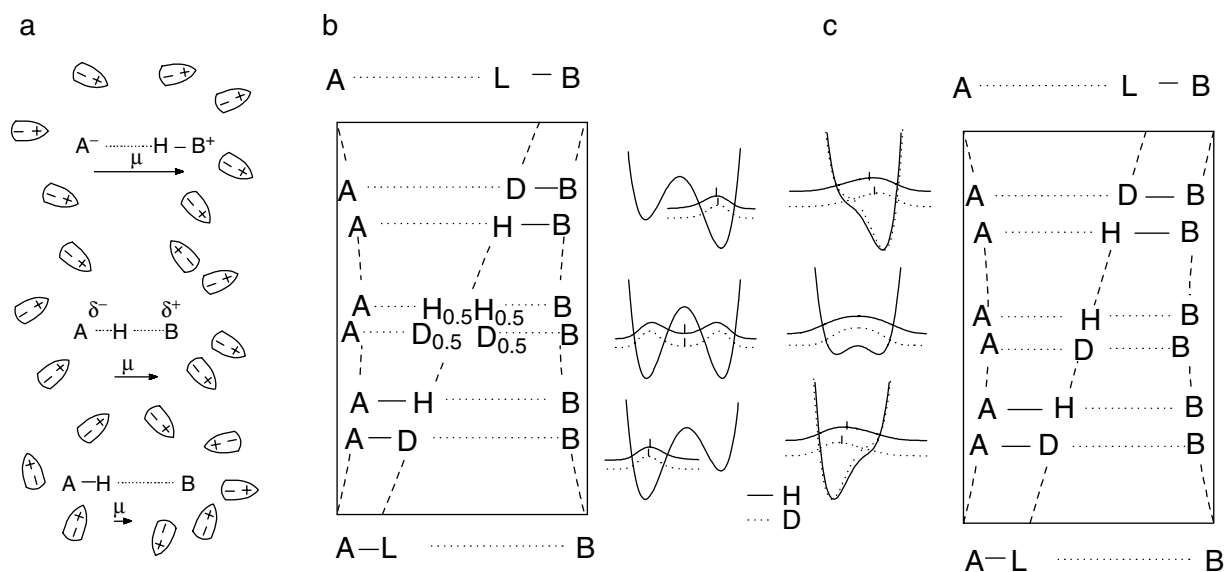


Figure 5. Influence (schematic) of the electric field increase arising from ordering of a polar solvent at low temperatures (a) on the geometries of the acid–base complex AHB. Associated potentials (schematically), of a double well (b) or a single well (c) type, of the hydron motion in a one-dimensional approximation, including the squares of the ground state vibrational wave functions for H and D representing the probabilities of finding H and D. The dashes indicate the average H and D positions.

reproduced by *ab initio* calculation for a number of acid–base complexes.²⁸

Depending on the system being studied, during the transformation, a hydrogen-bonded complex is created exhibiting either a symmetric double well (Fig. 5b) or a single well (Fig. 5c) potential for the proton motion. Both situations exhibit different H/D-isotope effects on the nuclear geometry,^{29,30} as illustrated qualitatively in the one-dimensional approximation in Fig. 5. In this figure, the squares of the strongly anharmonic ground-state proton and deuteron vibrational wave functions are included, where the base lines indicate the zero-point energies, and the small vertical bars the average hydron positions. In the case of a double well (Fig. 5b) the deuteron is always, on average, further away from the hydrogen bond center, leading to an increase of the A...B distance. The same is true in the asymmetric configurations of Fig. 5c. However, in the quasi-symmetric complex of Fig. 5c the deuteron is confined more to the hydrogen bond center than the proton. Deuteration has only a small effect on the geometry, but it may lead to a small contraction of the A...B distance. In this situation, the deuteron absorbs at lower field than the proton, i.e. the primary H/D isotope effects ${}^P\Delta(D/H) = \delta(A^2HB) - \delta(A^1HB)$ are positive, whereas they are negative when the deuteron is located further away from the hydrogen bond center.^{18,27,29} On the other hand, for the ¹⁵N and ¹⁹F nuclei, the secondary isotope effects on the chemical shifts, ${}^1\Delta A(D) = \delta(ADB) - \delta(AHB)$ and ${}^1\Delta B(D) = \delta(ADB) - \delta(AHB)$, are negative when the hydron is close to the corresponding nucleus and positive in the other case.

The collidine–HF complex in CDF₃/CDCIF₂

In Fig. 6 we have plotted the NMR parameters of the FHN and FDN complex (see Table 1) dissolved in CDF₃/CDCIF₂ mixtures as a function of the dielectric constants ϵ_0 , calculated

according to Eqn (4). The various data points stem from different samples with slightly different solvent compositions, i.e. different dielectric constants, determined using Eqn (4) from the intensity ratio of the residual protons of the solvent components according to Fig. 4. The solid lines in Fig. 6 do not represent a theoretical curve; they only serve as guides for the eye, as theoretical expressions for the relations observed are not available at present. Firstly, we note from Table 1 that there are certain entries with the same sample temperatures, but which exhibit different values of ϵ_0 , because of a varying solvent composition, that lead to slightly different NMR parameters. Thus, we are confident that the plots of Fig. 6 represent the results in a better way than if we had plotted the NMR parameters merely as a function of temperature.

When ϵ_0 is increased, $J(^1H, ^{19}F)$ decreases from large values of around 100 Hz to almost to zero, whereas $J(^1H, ^{15}N)$ increases slightly in the 40–55 Hz range. As discussed previously,⁵ these results cannot be explained in terms of a proton tautomerism, but indicate a gradual shift of H away from F towards N, as depicted qualitatively in Fig. 5c. At the same time, the very large heavy atom coupling constant $J(^{19}F, ^{15}N)$ remains constant at around –96 Hz, and indicates the formation of a quasi-symmetric complex of the type $F^{\delta-} \cdots H \cdots N^{\delta+}$ with two approximately half-covalent FH and HN bonds. We assume that the disappearance of $J(^1H, ^{19}F)$ at low temperatures and higher ϵ_0 values is associated with a sign change of this coupling, shortly after the proton has crossed the hydrogen bond center and the complex widens again, as has been found recently for FHF systems.^{4,31} At first sight, this seems to be in contrast to the finding that the chemical shift of H has not yet reached its maximum value (Fig. 6c), which is normally associated with the shortest symmetric hydrogen bond. The shift to lower field, despite the increased F...N distance, is then a result of the chemical asymmetry of the $F^{\delta-} \cdots H \cdots N^{\delta+}$ bridge. The problem is similar to the OH–collidine system, which is described in

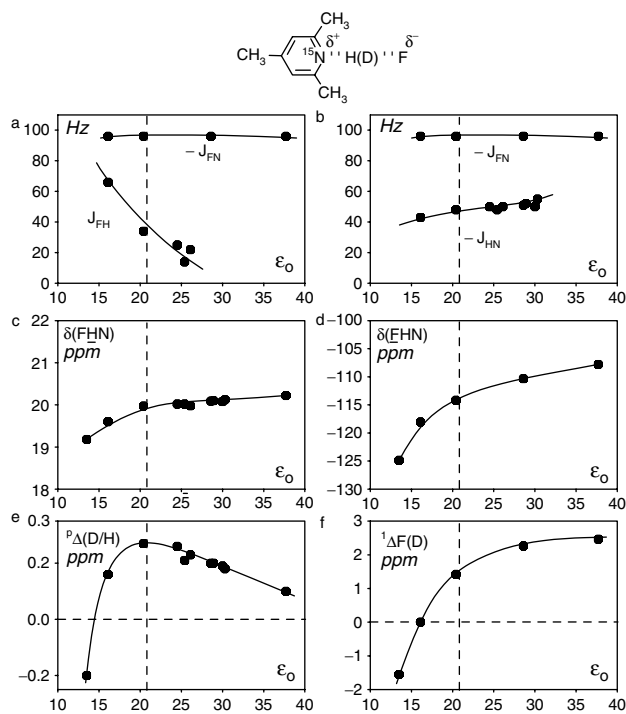


Figure 6. NMR parameters of the FHN and FDN complex dissolved in $\text{CDF}_3/\text{CDCIF}_2$ mixtures as a function of the dielectric constants ϵ_0 . (a) $J(^{19}\text{F}, ^{15}\text{N})$, $J(^1\text{H}, ^{19}\text{F})$ and (b) $J(^1\text{H}, ^{15}\text{N})$ scalar coupling constants; (c) ^1H and (d) ^{19}F NMR chemical shifts; (e) primary, $^p\Delta(\text{D}/\text{H}) \equiv \delta(\text{F}^2\text{HN}) - \delta(\text{F}^1\text{HN})$, and (f) secondary, $^1\Delta^{19}\text{F}(\text{D}) \equiv \delta(^{19}\text{FDN}) - \delta(^{19}\text{FHN})$, H/D isotope effects on the NMR chemical shifts.

more detail in another article of this issue.³² We will try to support this interpretation further in a subsequent paper to be published elsewhere. In contrast, the fluorine chemical shift is displaced continuously to low field when ϵ_0 is increased, which is compatible with a lengthening of the $\text{F} \cdots \text{H}$ distances.

Finally, the measurements of the primary isotope effect on the hydron chemical shift give a more detailed answer concerning the fate of the hydrogen bond FHN at high dielectric constants, depicted in Fig. 6e and f. The secondary H/D isotope effect on the fluorine chemical shift, $^1\Delta^{19}\text{F}(\text{D}) = \delta(^{19}\text{FDN}) - \delta(^{19}\text{FHN})$ is negative at high temperatures, indicating that D is closer to F than H. However, at higher dielectric constants the effect reverses, i.e. D is now further away from F than H. We expect that if we could increase the solvent polarity to a very high value than $^1\Delta^{19}\text{F}(\text{D})$ would again become smaller. As far as the corresponding nitrogen value is concerned, we obtained only a single value, of $^1\Delta^{15}\text{N}(\text{D}) = \delta(\text{FD}^{15}\text{N}) - \delta(\text{FH}^{15}\text{N}) = -3.36$ ppm at 155 K, indicating that D is closer to N than H.

The primary isotope effect, $^p\Delta(\text{D}/\text{H}) = \delta(\text{F}^2\text{HN}) - \delta(\text{F}^1\text{HN})$ is found to be negative at high temperatures, i.e. low dielectric constants, indicating a situation where the deuteron is further away from the hydrogen bond center than the proton, in agreement with the behavior of $^1\Delta^{19}\text{F}(\text{D})$, as expected for a situation prior to the formation of the quasi-symmetric complex. When the dielectric constants are increased by lowering the temperature, $^p\Delta(\text{D}/\text{H})$ crosses zero at $\epsilon_0 \approx 15$, goes

through a maximum value of 0.27 ppm at ϵ_0 around 22 and then decreases again. This value is comparable to the value of 0.32 ppm found for FHF^- .³³ We estimate that this maximum is the best characterization of a chemically asymmetric hydrogen-bonded complex, where the single well potential for the proton, averaged over all various solvent environments, is the most symmetric one, although hydrogen does not need to be located directly in the hydrogen-bond center. The properties of this complex, indicated in Fig. 6 by dashed vertical lines, are then characterized by the coupling constants $J(^1\text{H}, ^{19}\text{F}) = 30$ Hz, $J(^1\text{H}, ^{15}\text{N}) = -50$ Hz, $J(^{19}\text{F}, ^{15}\text{N}) = -96$ Hz, $\delta(\text{F}^1\text{HN}) = 20.0$ ppm, $\delta(^{19}\text{FHN}) = -114.2$ ppm, $\delta(\text{FH}^{15}\text{N}) = -63.5$ ppm, $^p\Delta(\text{D}/\text{H}) = 0.27$ ppm, $^1\Delta^{19}\text{F}(\text{D}) = 1.4$ ppm, $^1\Delta^{15}\text{N}(\text{D}) = -3.4$ ppm. The coupling constants can be compared to $J(^1\text{H}, ^{19}\text{F}) = 124$ Hz for an unperturbed symmetric FHF^- ,⁴ $J(^1\text{H}, ^{15}\text{N}) = |40|$ Hz for the collidine–collidinium homoconjugated complex characterized by a fast proton exchange of the $\text{N} \cdots \text{H} - \text{N}^+ \rightleftharpoons \text{N}^+ - \text{H} \cdots \text{N}$ type³³ and $J(^1\text{H}, ^{15}\text{N})$ of about -57 Hz for symmetric NHN bridges.³⁴ A considerable decrease of $J(^1\text{H}, ^{19}\text{F})$ and a relatively high value of $J(^1\text{H}, ^{15}\text{N})$ in the case of the quasi-symmetric FHN complex is, probably, indicative that H is located somewhat closer to N than to F.

Theoretical calculations predict that a heavy atom coupling constant depends on the bonding proton position³⁵ and correlates to the heavy atom distance.^{28a,36} In contrast, for the system studied, the very large heavy atom coupling constant $J(^{19}\text{F}, ^{15}\text{N})$ remains constant within the margin of error. We associate this finding with the fact that the heavy atom coupling constant reaches its maximal value for the quasi-symmetric geometry, i.e. it remains constant within a small range of hydrogen-bond geometry variations, whereas the corresponding one-bond coupling constants change monotonously.³⁶ Roughly speaking, the amplitude of the changes in the former case is half that of the latter case. Thus, we believe that $J(^{19}\text{F}, ^{15}\text{N})$ depends on the $\text{F} \cdots \text{N}$ distance, but perturbation of the complex symmetry should be much higher in order to detect this effect in an experiment.

CONCLUSIONS

The main result of this study is the observation of a quasi-symmetric hydrogen-bonded complex FHN between HF and collidine induced by a polar medium at a dielectric constant of about 22 and a temperature of about 145 K. This complex exhibits a symmetric single well potential for the proton motion, as characterized by an H/D primary isotope effect of 0.27 ppm on the hydron chemical shift. Thus, this complex represents the uncharged analog to the well-known FHF^- . In contrast to the latter, the hydrogen bond proton is not located in the hydrogen bond center. At smaller dielectric constants and higher temperatures H is closer to F, and at lower temperatures, i.e. higher dielectric constants, it is closer to N. The driving force for the gradual proton shift along the hydrogen bridge is the electric field created by the electric dipoles of the individual solvent molecules at the solute site.

In the future, we will try to extend the above studies to other complexes of FH with various bases; a great challenge

will be the development of equations predicting the behavior of the quantities in Fig. 6. Such equations may perhaps be based on the valence bond order method used by some of us successfully in this field.

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