Studies of Hydrogen Bonding. Part XXXII.* The Structure of Hydrogen-bonded Complexes between p-Fluorophenol and Various Nitriles

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Experimental and vectorial calculated dipole moments of hydrogen-bonded complexes between nitriles of the type R_nXCN (X=C, Si, P or S) and p-fluorophenol indicate strongly that the O−H proton in p-fluorophenol is located in a plane perpendicular to the triple bond of the $C \equiv N$ group.

Furthermore, the K_{ass} ΔH and Δv_{OH} values are determined for the 1:1 hydrogen-bonded complexes.

There is still controversy[2-8] as to whether the proton in the H-bond between a proton donor and a nitrile, is located in a plane perpendicular to, or along the axis of the $C \equiv N$ group. In order to obtain further information about the hydrogen-bonding site, we have extended our study to nitriles of the type R_nXCN (X=C, Si, P or S) with the main purpose to ascertain whether the association takes place perpendicular to or along the $C \equiv N$ group.

EXPERIMENTAL

Materials. Carbon tetrachloride was purified chromotographically by using basic aluminium oxide and Molecular Sieve Type 4Å. p-Fluorophenol (4FP) was purified by several recrystallizations from petroleum ether and the white needles were dried over phosphorus pentoxide in a desiccator. Nitriles not commercially available were prepared by literature methods.[9-11] Their purity was checked by GLC and mass spectroscopy.

Infrared measurements. All measurements were carried out with a Perkin-Elmer 399B infrared spectrophotometer. Quartz absorption cells (Hellma N. 160 QI) of 10.00 mm path length were used to determine the association constants (K_{ass}). The spectra were run at 25, 35 and 50 °C in the ground state stretching vibration region of the proton donor O−H band immediately after preparing the solutions. The concentration of p-fluorophenol was kept at 0.0025 M and the concentration range of the proton acceptor was 0.01−0.2 M. The solutions were made up by weighing, and the molarity of each solution was calculated at various temperatures from the change in density with temperature of carbon tetrachloride. The K_{ass} and ΔH values tabulated in Table 1 are the mean values of five separate determinations (for details see Ref. 12). The Δv_{OH} (Δv_{OH}=stretching frequency of free O−H minus frequency of hydrogen-bonded O−H) values are estimated to be accurate within $\pm 3-5$ cm^{-1}, ΔH values within ± 2 kJmol^{-1} and K_{ass} values within 10 %.

Experimental dipole moments. The dipole moment measurements were carried out in carbon tetrachloride at 20 ± 0.05 °C. The instruments and the method of evaluation of the

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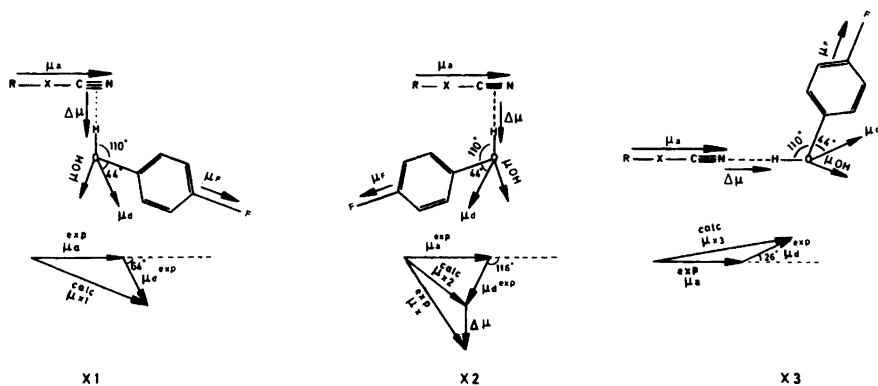
* For Part XXXI see Ref. 1.

Fig. 1. Possible structures of the hydrogen-bonded complex between *p*-fluorophenol and various nitriles.

Table 1. Data on hydrogen bonding between *p*-fluorophenol and various nitriles based on IR measurements. Solvent, carbon tetrachloride.

Proton acceptor	$K_{ass}^{20}/$ M^{-1}	$K_{ass}^{35}/$ M^{-1}	$K_{ass}^{50}/$ M^{-1}	$\Delta V_{OH}/$ cm^{-1}	$-\Delta H/$ $kJmol^{-1}$	$-\Delta S/$ $JK^{-1}mol^{-1}$
CCl_3CN	0.34	0.31	0.26	80	7.0	33.0
C_6F_5CN	1.1	0.9	0.70	108	11.9	39.7
$m\text{-}CF_3C_6H_4CN$	3.8	2.7	1.8	136	19.6	55.8
CH_3SCN	4.1	3.0	1.8	148	21.6	62.0
$p\text{-}FC_6H_4CN$	4.3	3.0	2.0	148	20.1	56.4
C_6H_5CN	6.1	4.5	2.6	156	22.4	61.3
$(C_6H_5)_2PCN$	7.3	5.2	3.2	156	21.6	57.3
CH_3CN	8.4	4.7	3.2	165	25.3	68.7
$CH_2CH_2CH_2CH_2CHCN$	9.0	5.8	3.5	174	24.8	66.3
$(CH_3)_3SiCN$	10.0	7.8	4.0	170	24.1	62.9

Table 2. Experimental, μ^{exp}, and calculated, μ^{calc}, dipole moments and the corresponding polarization data α, β and γ of the nitriles and of *p*-fluorophenol.

Acceptor	α	β	γ	$\mu_a^{exp}/$ D	$\mu_a^{calc}/$ D
CCl_3CN	5.142	0.0755	−0.1050	1.94	1.90
C_6F_5CN	5.660	0.0509	−0.0622	2.35	2.58
$m\text{-}CH_3C_6H_4CN$	13.739	0.1745	0.2650	3.50	3.55
CH_3SCN	35.766	0.3128	0.0020	3.57	
pFC_6H_4CN	11.923	0.2417	0.1550	2.70	2.58
C_6H_5CN	31.886	2.7232	0.2510	4.07	4.05
$(C_6H_5)_2PCN$	16.012	0.2361	0.5755	4.07	4.0^a
CH_3CN	58.603	0.6012	−0.3572	3.48	3.47
$CH_2CH_2CH_2CH_2CHCN$	28.845	0.4458	−0.1150	3.74	3.85
$(CH_3)_3SiCN$	31.616	0.6673	−0.4974	4.06	3.47
$p\text{-}FC_6H_4OH$	7.056	0.2115	0.1923	2.05^b	2.14^b

[a] Ref. 17. [b] Means μ_d^{exp} and μ_d^{calc}.

dipole moments were the same as reported in detail elsewhere.[12,13] The mass fraction range of p-fluorephenol and of the nitriles were $1 \cdot 10^{-3} - 5 \cdot 10^{-3}$. The experimental polarization data α, β and γ, and the corresponding dipole moments, μ^{exp}, of p-fluorophenol and the nitriles are tabulated in Table 2.

To evaluate the experimental dipole moments of the hydrogen-bonded complexes, we need to know the concentration of the free proton donor, free proton acceptor and the hydrogen-bonded complex in the reaction mixture. By using the K_{ass} values obtained by IR measurements (see Table 1), the mass fraction of the different species in the mixture could be calculated (for details see ref. 12). The experimental dipole moments, μ_x^{exp} of the hydrogen-bonded complexes in carbon tetrachloride at 20 °C are listed in Table 3.

Calculation of dipole moments of nitriles and p-fluorophenol. The calculated dipole moments of the various nitriles, μ_a^{calc}, and of p-fluorophenol, μ_d^{calc} presented in Table 2, were obtained by using bond and group moments.[14] The C−O−H angle and the angle between the group moments Ph−F (μ_F=1.47 D) and Ph−OH (μ_{OH}=1.55 D) in p-fluorophenol, were assumed to be 110 and 90°, respectively.[14] Hence, the dipole moment of p-fluorophenol was calculated to be 2.14 D [$\mu_d^{calc}=(1.47^2+1.55^2)^{\frac{1}{2}}$]. The angle, a, between μ_F and μ_d^{exp} was found to be 44° (cos$a$=1.47/2.05), as shown in Fig. 1. As can be seen from Table 2, the calculated dipole moments of the various nitriles (μ_a^{calc}) and of p-fluorophenol (μ_d^{calc}) agree very well with the experimental values. This is a good indication of that the assumed angles 110 and 90° in p-fluorophenol are reasonable. This finding is very important because these angles are involved in the calculations of the dipole moment of the various complexes, as shown in Fig. 1.

Calculation of dipole moments of the various hydrogen-bonded complexes. Previous CNDO/2 calculations on the complex between phenol and acetonitrile showed that the total energies of the various types of out-of-plane models were unfavourable as compared with those in plane.[7] Consequently, we have in this study only considered the structures X1, X2 and X3 as candidates of the 1:1 hydrogen-bonded complex (see Fig. 1). The corresponding dipole moments, μ_{x1}, μ_{x2} and μ_{x3} were calculated vectorially from experimental values of μ_a and μ_d by using the equation $\mu_x^{calc}=(\mu_a^2+\mu_d^2+2\mu_a\mu_d\cos\theta)^{\frac{1}{2}}$ where θ is the angle between the direction in which μ_a^{exp} and μ_d^{exp} are acting in the complex. The angles, θ, in the structures X1, X2 and X3 are 64, 116 and 26°, respectively. The vectorially calculated dipole moments are presented in Table 3 along with the experimental values.

Calculation of $\Delta\mu$. A method to study the structure of hydrogen-bonded complexes is to compare the experimental dipole of a hydrogen-bonded complex with the vector sum of the individual moments of the components. The formation of a hydrogen bond, however, brings about displacement of electrons,[15,7,12] and hence to a difference between the experimental dipole moment and the vectorial sum of the components. This difference can be expressed in terms of a dipole increment, $\Delta\mu$, defined by the vector equation

$$\overrightarrow{\Delta\mu}=\overset{exp}{\overrightarrow{\mu_x}} -(\overset{exp}{\overrightarrow{\mu_d}}+\overset{exp}{\overrightarrow{\mu_a}})$$

where μ_x^{exp}, μ_d^{exp} and μ_a^{exp} are the experimental dipole moments of the hydrogen-bonded complex, p-fluorophenol and the nitrile, respectively. In this consideration we have to assume that the additional dipole moment, $\Delta\mu$, is directed along the hydrogen bond, from the proton acceptor towards the proton donor[15,16] *i.e.*, we do not take into account the electronic redistribution in other parts of the hydrogen-bonded complex. By comparison of the experimental dipole moments with those calculated by using the structures X1, X2 and X3, we can see (Table 3) that the experimental values always are in between those calculated from X1 and X2 and far from those calculated from X3. This can be taken to mean that we are dealing with π-complexes and not with n-complexes. Furthermore, since all the μ_{x2}^{calc} values are lower than the corresponding μ_x^{exp} values, the only structure that can serve as a model for the hydrogen-bonded complex is X2, as shown in Fig. 1. The additional dipole moment, $\Delta\mu$, can then be calculated by using the equation,

$$\overset{exp}{\overrightarrow{\mu_x}} =\overset{calc}{\overrightarrow{\mu_{x2}}} + \overrightarrow{\Delta\mu} \text{ (see Fig. 1)}$$

Table 3. Experimental, μ_x^{exp}, and calculated dipole moments, μ_{x1}^{calc}, μ_{x2}^{calc}, μ_{x3}^{calc} and additional dipole moments, $\Delta\mu$, of various structures (see Fig. 1) of hydrogen-bonded complexes between *p*-fluorophenol and various nitriles. Solvent, carbon tetrachloride.

Proton acceptor	$\mu_x^{exp}/$ D	$\mu_{x1}^{calc}/$ D	$\mu_{x2}^{calc}/$ D	$\mu_{x3}^{calc}/$ D	$\Delta\mu/$ D
CCl_3CN	2.5	3.4	2.1	3.9	1.69
C_6F_5CN	2.9	3.7	2.4	4.3	1.66
m-$CH_3C_6H_4CN$	4.1	4.8	3.2	5.4	1.82
CH_3SCN	3.6	4.8	3.3	5.5	1.42
p-FC_6H_4CN	3.2	4.0	2.6	4.6	1.62
C_6H_5CN	4.4	5.3	3.7	6.0	1.26
$(C_6H_5)_2PCN$	4.7	5.3	3.7	6.0	1.70
CH_3CN	4.0	4.8	3.2	5.4	1.69
$CH_2CH_2CH_2CH_2CHCN$	4.0	5.0	3.4	5.7	1.28
$(CH_3)_3SiCN$	4.8	5.3	3.7	6.0	2.02

The $\Delta\mu$ values are tabulated in Table 3. The extraordinarily large $\Delta\mu$ values are in accordance with those found for the system phenol–nitriles.[7]

RESULTS AND DISCUSSION

As can be seen from Figs. 2 and 3, log K_{ass} and ΔH form linear correlations with $\Delta\nu_{OH}$. The correlation equations are:

log K_{ass}=0.0156 $\Delta\nu_{OH}$−1.66 (at 20 °C)
n=10, r=0.99
and

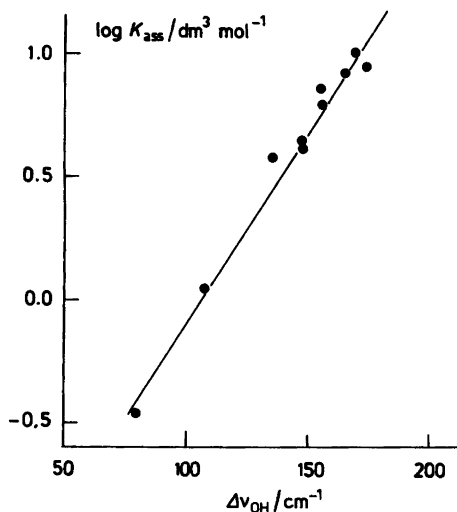*Fig. 2.* Log K_{ass} *vs.* frequency shift, $\Delta\nu_{OH}$, for the association of *p*-fluorophenol with various nitriles.
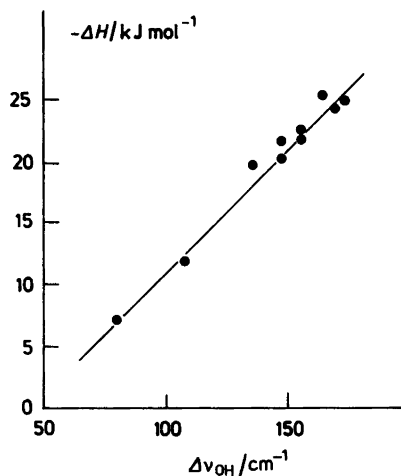
Fig. 3. Frequency shift, $\Delta\nu_{OH}$, *vs.* $-\Delta H$ for hydrogen-bonded complexes between *p*-fluorophenol and various nitriles.

$-\Delta H = 0.1980 \ \Delta\nu_{OH} - 8.70$

$n = 10, \ r = 0.99$

The obtained linear correlations substantiate strongly that we are dealing with the same type of hydrogen-bonded complexes, *i.e.*, the complexation site is the same for all the nitriles studied, independent of X in R_nXCN. The hydrogen-bonding tendency, however, is very much dependent on the group attached to the $C \equiv N$ group, *e.g.* the association constant for the system $p\text{-}FC_6H_4OH/CCl_3CN$ is 25 times less than for $p\text{-}FC_6H_4OH/CH_3CN$. The most obvious reason for this is that the CCl_3 group reduces the π-electron density in the triple bond as compared with a CH_3 group. Furthermore, a comparison of CH_3SCN with $(C_6H_5)_2PCN$ and $(CH_3)_3SiCN$ demonstrates clearly that the tendency of a $C \equiv N$ group to form a H-bond, follows the trend expected from the electronegativities of the S, P and Si atoms.

CNDO/2 calculations[7] of the 1:1 complex between phenol and acetonitrile have shown a considerable charge redistribution in both interacting molecules. Comparison of the gross orbital changes in different atoms before and after complexation, revealed that the atoms in the proton acceptor part of the complex, except methyl C, decrease their total charge, whereas the atoms in the proton donor part, with the exception of C and H in $C-O-H$, increase their charge. The net charge transfer from acetonitrile to phenol was found[7] to be equal to 0.0558 electron. Therefore, it seems the assumption we made that the additional dipole moment, $\Delta\mu$, is directed along the H-bond from the proton acceptor towards the proton donor, is well-founded. The only structure in Fig. 1 which can then be considered as a candidate for the 1:1 hydrogen:bonded complex between p-fluorophenol and various nitriles is structure X2. In the structures X1 and X3 the additional dipole moment, $\Delta\mu$, has to be directed in the opposite direction in order to explain why the experimental dipole moments, μ_x^{exp}, are less than those calculated from the structures X1 and X3 (see Table 3).

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