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DYNAMIC ^{19}F NMR STUDIES
THE TORSIONAL BARRIER IN PENTAFLUOROBENZALDEHYDE , ITS CONJUGATE ACID AND PROTONATED PENTAFLUOROACETOPHENONE

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SUMMARY

An upper limit of the barrier to internal rotation around the phenyl-carbonyl bond in pentafluorobenzaldehyde dissolved in a freon mixture has been estimated from low temperature ^{19}F NMR study .Protonation of this compound increases drastically the free energy of activation $\Delta G^{\neq}$ .Complete lineshape analysis leads to $\Delta G^{\neq}(273\ K) = 60.4$ kJ/mol ,comparable to the value obtained for protonated benzaldehyde .This result,as well as those obtained by CNDO/2 calculations support the conclusions that protonated pentafluorobenzaldehyde is planar in the ground state.This is not the case for protonated pentafluoroacetophenone in which the lower barrier height when compared to protonated acetophenone has been related to the steric strain and dipole repulsion.

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INTRODUCTION

The barrier to internal rotation in aromatic carbonyl compounds has been studied extensively since the work of Anet [1] in the early sixties.Proton dynamic NMR (DNMR) was first used but the barrier could only be determined for benzaldehydes and acetophenones bearing a strong electron donating group like p-methoxy or p-dimethylamino[1] . Protonation [2] or complexation [3] have been shown to increase drastically the rotational barrier which could be easily measured in complexed [3] and protonated benzaldehydes [2] [4] by ^{1}H NMR .Since the early 70s , ^{13}C DNMR with broad band decoupling is currently used. This technique has two advantages : very simple spectra of non-spin coupled AB type and large chemical shift differences between the exchanging carbon signals ,which allow the measurement of low barriers (20 to 35 kJ/mole) in an accessible temperature range.Thus it was possible to estimate the free energy of activation, $\Delta G^{\neq}$, for the rotation around the phenyl-carbonyl bond in p-substituted acetophenones [5] and their conjugate acids [6] .

These various studies have shown that the barrier to interna rotation,which originates from the double bond character of the phenyl-carbonyl bond,can be related to the electronic effect of the ring substituents. Thus,for example, the substitution by a fluorine atom in the para position increases the barrier height, an opposite effect is observed with ortho or meta substitution [2] [4] .

It has previously been pointed out by Fewster [7] ,based on far infrared spectroscopy data ,that the barrier (V_2) in pentafluorobenzaldehyde is much lower than that obtained by the same technique for benzaldehyde in the gas phase (7.5 and 19.2 kJ/mole respectively [7]) . As it is well known that the values estimated in the gas phase are always lower than those obtained by DNMR in a solvent ,we have applied ^{19}F DNMR to the study of the torsional barrier in pentafluorobenzaldehyde dissolved in a freon mixture .As will be discussed later ,it was not possible to obtain an accurate value of this very low barrier but it was possible to measure $\Delta G^{\neq}$ for the protonated pentafluorobenzaldehyde and the protonated pentafluoroacetophenone .

Fluorine DNMR has been used some time for conformational studies [8] .However it does not present the same advantages that ^{13}C NMR : large chemical shift differences are commonly observed but the strong couplings (10 to 20 Hz) between the different fluorine atoms lead to more complicated systems, as will be the case in this study of five strongly coupled nuclei.The complexity of such spectra necessitates longer computer times for the theoretical line shape calculations but is an advantage for the precision of the obtained activation parameters as expressed by Binsch [9] .

RESULTS AND DISCUSSION

Pentafluorobenzaldehyde

^{19}F NMR spectra of pentafluorobenzaldehyde dissolved in a freon mixture ($CHCl_2F$ / $CHClF_2$, 1:1) have been recorded at various temperatures ranging from -150 to - 60°C (Figure 1).

At -150°C the spectrum shows a broadening of the two ortho signals,the meta fluorines being still far from coalescence . Solubility problems and technical difficulties to reach lower

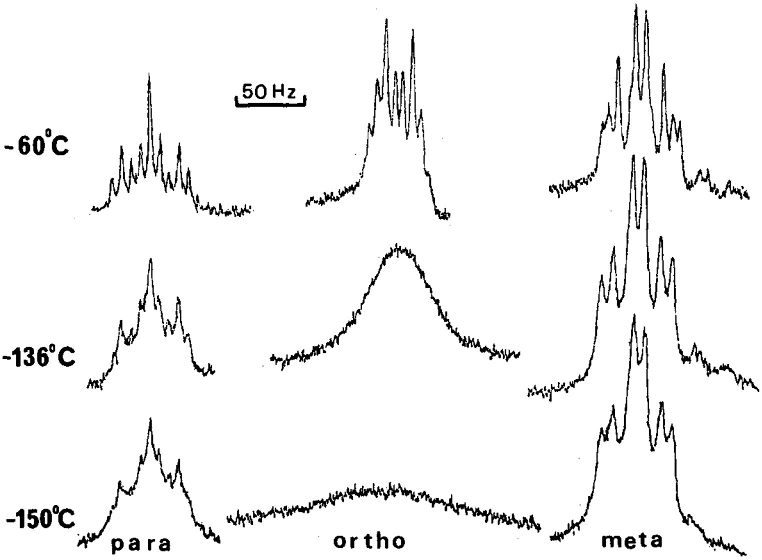


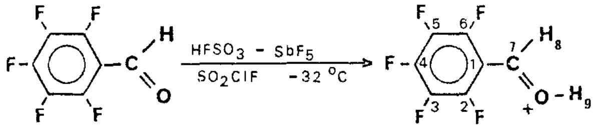
Fig.1. Temperature dependence of the ^{19}F NMR spectra of pentafluorobenzaldehyde dissolved in freon mixture .

temperatures do not allow the observation of the splitting of the ortho signals . However an upper limit of the barrier height can be obtained , assuming a chemical shift difference of 500 Hz [10] between the exchanging nuclei . This yields a value of 22 kJ/mol which is lower than $\Delta G^{\neq}$ in benzaldehyde (31.7 kJ/mol) obtained by ^{13}C DNMR [11] . This is in agreement with the decrease of the V_2 potential observed in the gas phase [7] .The barrier decrease can be related to an increased steric effect and dipole repulsion in the ground state.The molecule might be non-planar in the ground state as indicated by dipole moment measurements [12] .

Protonated pentafluorobenzaldehyde

(a) Low temperature ^1H NMR spectra

When a carbonyl compound is dissolved at low temperature in the superacid $HSO_3F-SbF_5-SO_2ClF$,the proton on the carbonyl oxygen appears in the 12-14 ppm range [13] .



In the case of pentafluorobenzaldehyde this proton appears as a doublet ($^3J(H-H) = 9$ Hz) at 12.5 ppm and the coupled aldehydic proton at 10.1 ppm .The magnitude of this coupling constant is in agreement with a cis configuration about the C=O double bond [13] .When the temperature is raised,the $C=OH^+$ signal shows no broadening even at + 30°C ,indicating that the exchange process with the acidic medium remains slow and does not affect the intramolecular process .

(b) Low temperature ^{19}F NMR spectra

At -32°C the ^{19}F NMR spectrum of protonated pentafluorobenzaldehyde indicates slow rotation around the phenyl carbonyl bon (Figure 2). The two ortho fluorines show a chemical shift difference of more than 900 Hz whereas the meta fluorines are separated by only 20 Hz . In analogy with the ^1H spectra of protonated benzaldehydes we assume that the fluorines on C-2 and C-3 (cis to the carbonyl oxygen) appear at lower field than the fluorines on C-6 and C-5 respectively . The chemical shifts are collected in Table 1 and are in agreement with previous values given by Olah and Mo [14] .

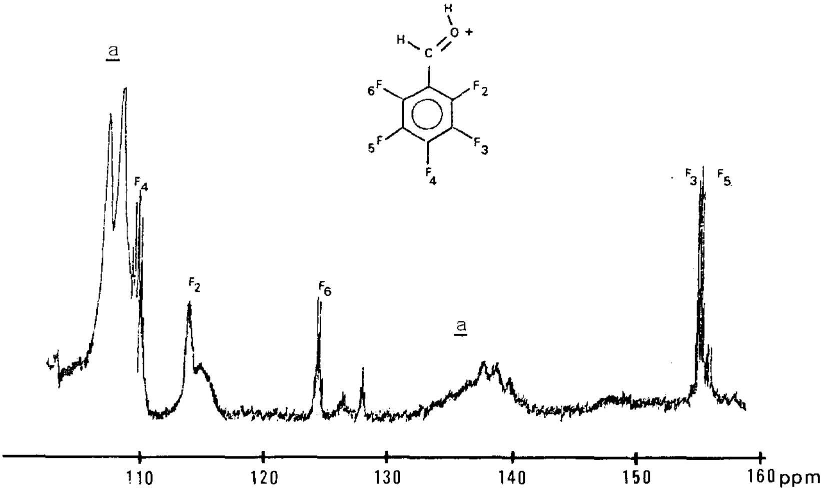


Fig. 2. The low temperature (-32°C) ^{19}F NMR spectrum of pentafluorobenzaldehyde protonated in HSO_3F-SbF_5-SO_2ClF .
a) acid solvent peaks .

TABLE I

^{19}F chemical shifts for protonated pentafluorophenyl compounds (in ppm from external CCl_3F)

Subst.	T (°C)	F-2	F-3	F-4	F-5	F-6
CHO	-60	113.4	153.8	109.4	154.0	123.6
MeCO	-116	117.0	155.8	122.3	156.1	120.6

TABLE II

Coupling constants in protonated pentafluorobenzaldehyde and pentafluoroacetophenone obtained from iterative LAOCOON-3 calculations (in Hz)

parameter	$CHOH^+$	$MeCOH^+$
J_{23}	-20.7	-22.2
J_{24}	21.8	21.1
J_{25}	6.9	7.2
J_{26}	-14.6	-14.7
J_{34}	-20.4	-20.3
J_{35}	-1.6	-1.0
J_{36}	8.0	7.0
J_{45}	-20.3	-20.2
J_{46}	25.4	21.3
J_{56}	-20.2	-21.6

The spectrum analysis at low temperature was performed with the computer program LAOCOON 3 [15].The spectral parameters have been obtained as follows : the spectrum is near first order and some coupling constants could be measured directly.The couplings between the different fluorine atoms and the aldehydic proton,which should be of the magnitude of 1 Hz [16] could not be observed ,the resolution of the spectra being not better than 2 Hz due to the viscosity of the acidic medium.The same is true for the J(F-H) couplings with the acidic proton which should be even less .Thus these couplings were included in the estimation of the transverse relaxation time T_2 . The $4J_{35}$ meta coupling is not apparent in the lines of the meta fluorines and is apparently lower than 2 Hz.It can be assumed that the protonation of the formyl group does not affect very much this coupling and it was taken equal to -1.6 Hz ,considering that in the free base this coupling was estimated to -1.2 Hz [17]. We checked also that the line shape is not affected in the coalescence region when we take $^4J_{35} = 0$. The signs of the coupling constants could not be estimated and those reported by Dean <u>et al</u>. [17] for unprotonated benzaldehyde were used.

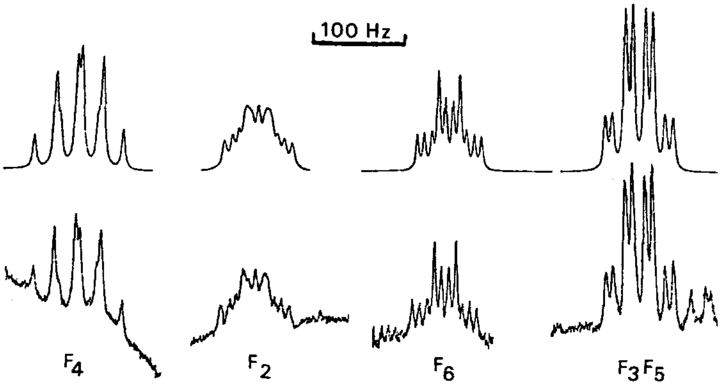


Fig. 3. experimental (below) and LAOCOON-3 simulated spectrum of protonated pentafluorobenzaldehyde .

The calculated spectra were compared to the experimental one and the values of all coupling constants reported in Table II were obtained with use of the iterative procedure of LAOCOON-3. (Figure 3).The comparison of the values of the coupling constants in the free base and in the conjugate acid shows that the protonation has little effect on the ortho and para couplings. The $^4J_{24}$ and $^4J_{46}$ coupling constants are the most sensitive to C-1 substitution , as observed by other authors [18].

When the temperature is raised , one can first observe the coalescence of the meta signals (Figure 4).As a consequence of the large chemical shift difference of the two ortho fluorines the coalescence of the two ortho signals is effective only at a temperature higher than + 30°C , where the exchange with the acidic medium becomes important and affects the line shape [19]. The para signal is not affected by the exchange process .

The complete line shape analysis was thus performed on the meta fluorines in the range -30 , + 30°C , using an extended version of the DNMR2 program of Binsch [20] ,allowing calculations on exchanging systems like ABCDE $\rightleftarrows$ AA'CBB'
The meta fluorines show no apparent shift variation with the temperature .The T_2 was estimated from the high field line of

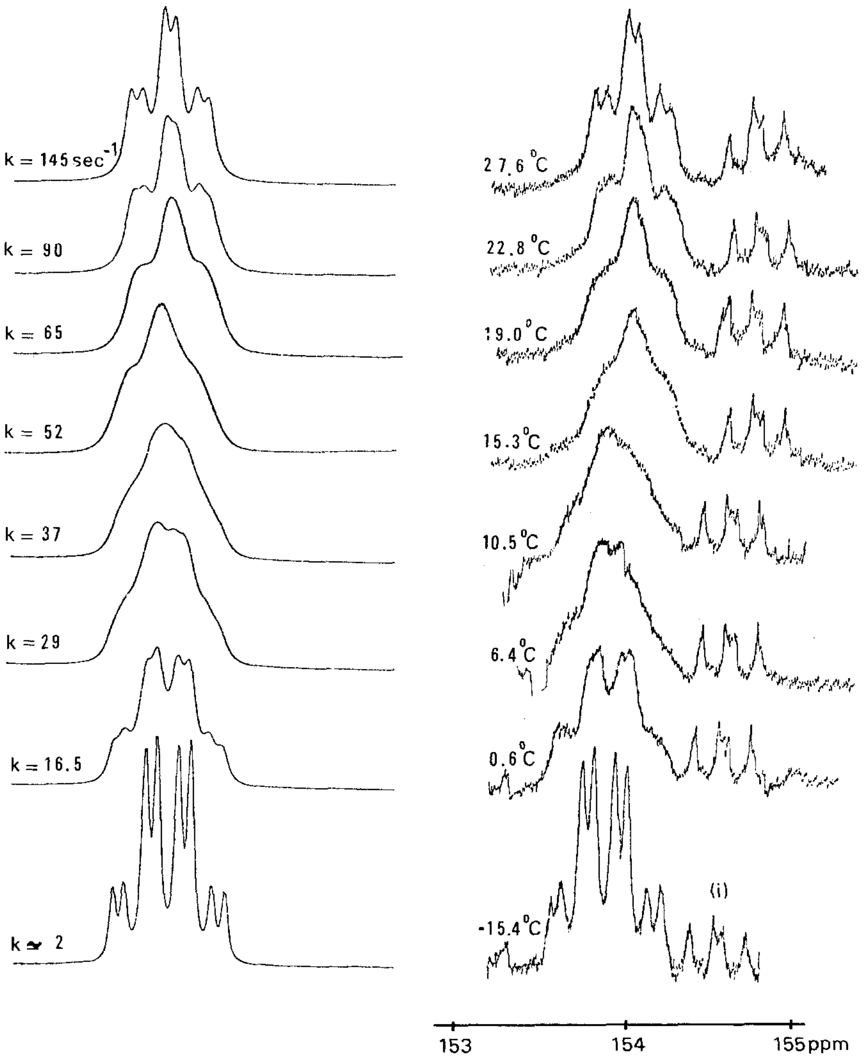


Figure 4 . The total lineshape analysis performed on the meta fluorines of protonated pentafluorobenzaldehyde . (i = impurity) .

the para fluorine signals which are not involded in the exchange process . $\Delta G^{\neq}$ was calculated at each temperature by the Eyring formula , the transmission factor being considered equal to unity. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained by a least square treatment of $\Delta G^{\neq} = \Delta H^{\neq} - T . \Delta S^{\neq}$. The experimental and calculated spectra are shown in Figure 4 .

TABLE III

Rate constants and $\Delta G^{\neq}$ values for protonated pentafluorobenzaldehydes.

T(°C)	k(sec-1)	$\Delta G^{\neq}$(kJ/mol) ± 0.46 [a]
27.6	145	61.15
22.8	90	61.31
19.0	65	61.28
15.3	52	61.00
10.5	37	60.75
6.4	29	60.40
0.6	16.5	60.39
-5.3	9.8	60.19
-15.4	≃2	b)

From these values one can calculated $\Delta S^{\neq}$ = - 37 ± 14 J/mol.K [a] and $\Delta H^{\neq}$ = 50.1 ± 4 kJ/mol [a].

a) the errors on $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were estimated as proposed by Sandström et al. [30]. b) this value was not used for the estimation of the entropy and enthalpy of activation .

As can be seen from Table 3 , $\Delta G^{\neq}$ is not very temperature dependent (0.8 kJ/mol over a range of 40°) .This is reflected by the low $\Delta S^{\neq}$ value (- 37.7 J/mol.K) which is comparable to the values of the entropy of activation in protonated benzaldehydes [2] . Negative entropy values have been reported for other exchange processes [21] and can be accounted for by an increased solvent interaction in the non planar transition state.

The free energy of the torsional barrier ,interpolated to 273 K (60.4 kJ/mol) is very close to the value obtained at the same temperature in protonated benzaldehyde (61 kJ/mol).

The para substitution of an hydrogen atom by a fluorine atom increases the torsional barrier by ca. 3 kJ/mol [2] .The substitution in the ortho or meta position decreases $\Delta G^{\neq}$ [4] . The participation of the electronic and steric effects on the non-variation of the barrier height in protonated pentafluorobenzaldehyde compared to protonated benzaldehyde will now be discussed.

c) Comparison of energy results of various protonated fluorobenzaldehydes

Let us consider the six protonated compounds : benzaldehyde (I) ,ortho-fluorobenzaldehyde O-cis (IIa) and O-trans (IIb), metafluorobenzaldehyde (III) , para-fluorobenzaldehyde (IV) and pentafluorobenzaldehyde (V) which barriers at -40°C are respectively 60.6 ,54.9 ,58.6,57.8,63.6 and 58.9 kJ/mol . (The $\Delta G^{\neq}$ values for compounds I ,IV and V have been obtained from their $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values [2] ,for compounds IIa ,IIb and III from reference [4]).

The electronic effect of a fluorine atom in the para position can be represented by the difference $\Delta G^{\neq}(IV) - \Delta G^{\neq}(I) = 3.0$ kJ/mol and the electronic effect of an ortho fluorine can be assumed to be approximately the same . The decrease of the barrie: height in IIa and IIb compared to IV can thus be attributed to the steric strain and dipole repulsion which more than compensate for the electronic effect.Thus the resulting effect of the ortho substitution is an increase of 8.7 kJ/mol of the ground state energy ($\Delta G^{\neq}(IV) - \Delta G^{\neq}(IIa)$). As the electronic effect of a meta fluorine can be obtained from $\Delta G^{\neq}(I) - \Delta G^{\neq}(III) = 2.8$ kJ/mol , it is now possible to estimate the barrier in protonated pentafluorobenzaldehyde : $\Delta G^{\neq}(V) = 60.6 - 2\times2.8 - 8.7 + 3\times3.0 = 55.3$ kJ/mol ,in fair agreement with the value obtained by complete line shape analysis .

Protonated pentafluoroacetophenone

Pentafluoroacetophenone ,dissolved in HSO_3F-SbF_5-SO_2ClF ,is easily protonated on oxygen , as can be seen from the low temperature proton NMR spectrum which displays a signal at 14.26 ppm corresponding to the protonated carbonyl . The methyl appears at 3.61 ppm .

^{19}F NMR study

The low temperature ^{19}F NMR spectrum of protonated pentafluoroacetophenone , recorded at -116°C , shows the non equivalence of both the two ortho and the two meta fluorines .

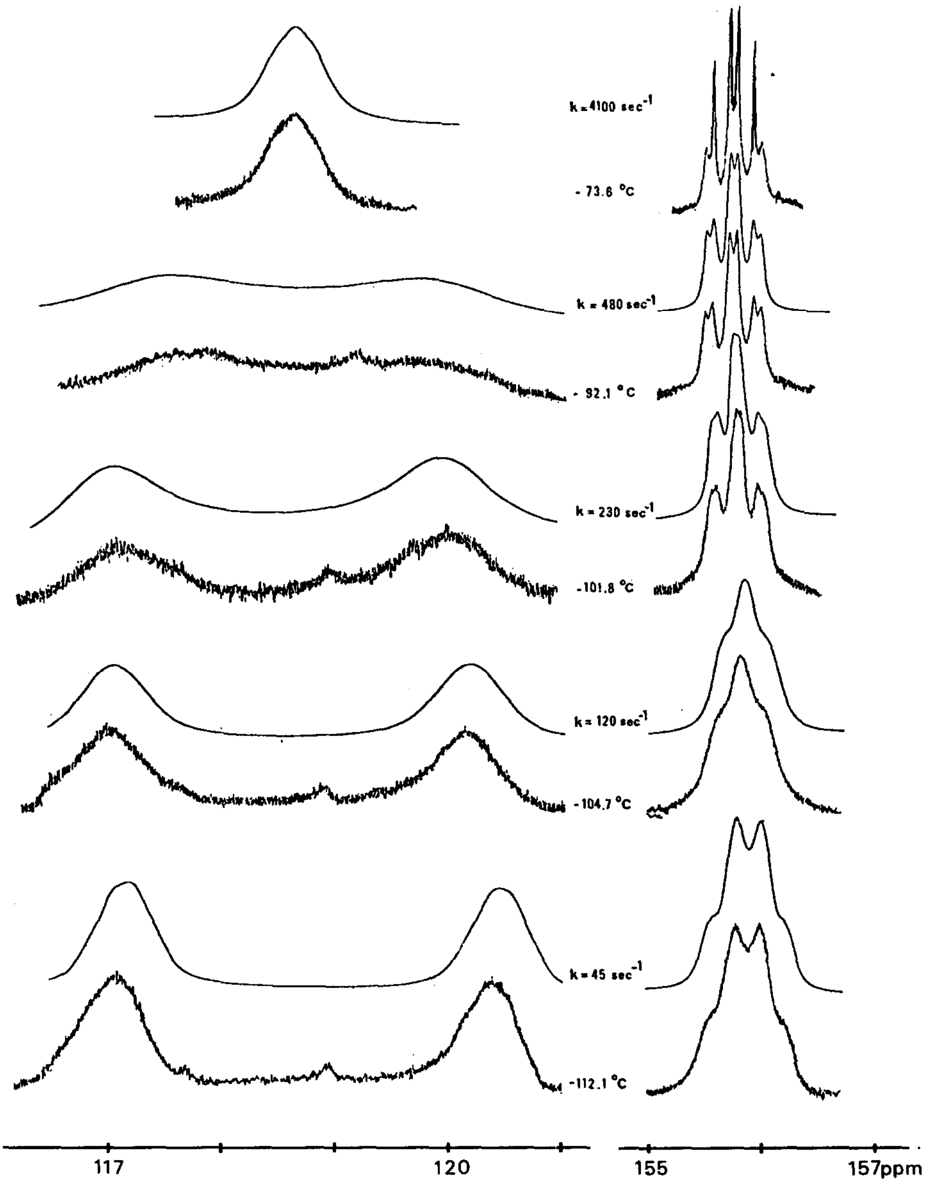


Fig. 5. Experimental and calculated line shapes for the ortho (left) and meta (right) signals in protonated pentafluoroacetophenone .

Complete resolution of the peaks was however not obtained at that temperature .The fine structure of the different signals is not apparent ,due to the fact that the rotation even at this low temperature is too fast .Lower temperature spectra could unfortunately not be obtained (loss of solubility in SO_2ClF and solvent freezing) .Attempts to record spectra at lower temperatures using SO_2F_2 as solvent were also unsuccessfull.

The chemical shifts at low temperature were measured directly on the spectrum ,taking the center of the signals and are collected in Table I . The mean values of the coupling constants could be obtained from the high temperature spectrum (-74°C) .The values of the coupling constants were adjusted by simulation of the low temperature spectrum with the LAOCOON and DNMR 5 programs . The precision is not as good as for the preceeding case (0.5 - 1 Hz) . The spectral parameters are collected in Table II .

Complete line shape analysis has been performed by simulation of the experimental spectra recorded between -116°C and -74°C. It was possible to follow the coalescence of both ortho and meta fluorines (Figure 5) .The chemical shifts of the ortho fluorines were temperature dependent and in the region of coalescence , the chemical shift difference has been extrapolated from values measured at low temperature where the exchange rate is low . The chemical shift difference between the two meta fluorines is less affected by the temperature variation . $\Delta G^{\neq}$ was calculated for each temperature (Table IV) . $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained in the usual way .Here also $\Delta G^{\neq}$ is not very temperature dependent and $\Delta S^{\neq}$ is small (-24 kJ/mol).

Compared to the barrier height in protonated acetophenone (48.1 kJ/mol) [6] , the value found here is much lower.This can be explained by the fact that even the protonated form of pentafluoroacetophenone is not planar in the ground state . Dipole moment measurements [12] have indicated that in the free base the acetyl group is twisted out of the ring plane by an angle of 58° .The protonation on oxygen,which increases the double bond character of the phenyl-carbonyl bond,reduces

TABLE IV

Rate data for protonated pentafluoroacetophenone

T(°C)	k(sec^{-1})	$\Delta G^{\neq}$ (kJ/mol) ± 0.35
-115.8	25	33.42
-112.1	45	33.45
-108.4	75	33.55
-104.7	120	33.68
-101.8	230	33.36
-95.8	330	34.05
-92.1	480	34.25
-88.4	950	33.90
-84.7	1200	34.26
-81.0	3100	34.03
-73.6	4100	34.34

$\Delta H^{\neq}$ = 36.1 ± 1.7 kJ/mol ; $\Delta S^{\neq}$ = - 24 ± 8 J/mol.K.

certainly the twist angle as confirmed by the value of 34° obtained from the formula :

$$\cos^2\theta = \frac{\Delta G^{\neq} \text{ pentafluoroacétophenone } H^+}{\Delta G^{\neq} \text{ pentafluorobenzaldehyde } H^+ - EE(Me)}$$

where EE(Me) represents the electronic contribution of the methyl group to the barrier decrease when replacing the protonated formyl group by a protonated acetyl group(7.2 kJ/mol from ref. 22).

Another argument for a nonplanar ground state in protonated pentafluoroacetophenone is that the chemical shift difference of the two meta fluorines in that compound is greater than in the protonated formyl compound.This can be related to a deviation of planarity as we have observed earlier the same effect in alpha-chlorotolylketones protonated in superacid media [22] . Thus α,α,α, trichlorotolylketone which is certainly not planar presents a chemical shift difference of the meta carbons much largerthan the dichloro and the monochloro compounds .

The CNDO/2 calculated barrier of torsion in protonated pentafluorobenzaldehyde

This last decade ,good results could be obtained by use of semi-empirical methods in the study of the conformation of small molecules .Some authors have claimed recently that the CNDO/2 method is not able for the estimation of rotational barriers in conjugated systems [23] . However it appears in the litterature that good values of the V_2 potential can be obtained for such systems and that the substituent effects can be fairly well reproduced when complete geometry optimization is performed on both the ground and the transition states [24] .

Starting from the optimized geometry of protonated benzaldehyde [2] , the C-F bond lenghts have been optimized simultaneously and a value of 1.345 Å was obtained which is reasonable for a C-F bond lenght [25] . A complete optimization of the benzene ring would be very time consuming .Thus a standard geometry was used (C-C = 1.397 Å , all angles equal to 120°)[26] The C_{ϕ} - C_{CHOH^+} bond was optimized at 1.398 Å in the ground state ,which is less than the lenght of this bond in protonated benzaldehyde as estimated by Dewar [27] (1.414 Å).The C=O bond lenght (1.314 Å) is in agreement with other results obtained from CNDO/2 calculations (1.300 in protonated benzaldehyde [2] , 1.320 Å in protonated formaldehyde [28]). The optimized O-H bond lenght (1.036 Å) is also in agreement with earlier results on protonated benzaldehyde [2]).

In the transition state (formyl plane perpendicular to the ring plane) the loss of conjugation between the phenyl ring and the protonated formyl group is well represented by the increase of the C_{ϕ} - C_{CHOH^+} bond length (+0.015 Å) and the decrease of the C=O bond length (-0.011 Å).

The optimized geometries are reported in Table V.

The potential of the barrier to rotation around the phenyl-carbonyl bond was obtained by difference between the total energies of the ground and the transition states.The value of 54.2 kJ/mol is plausible and should correspond to the torsional barrier in the gas phase .

TABLE V

CNDO/2 optimized geometries of the ground and transition states of protonated pentafluorobenzaldehyde.

	ground state	transition state
C - F	1.345	1.345
C_1-C_7	1.398_0	1.413_4
C_7=O	1.314_6	1.303_6
C_7-H_8	1.118_7	1.120_6
O -H_9	1.036_5	1.038_6
$C_1C_7H_8$	123.0	123.2
C_1C_7O	121.0	120.7
C_7OH_9	112.7	114.4

standard geometry was used for the ring (all C-C ≃ 1.397 Å, all angles = 120°) .

In order to verify the planarity of the protonated pentafluorobenzaldehyde in the ground state , the total energy was calculated as a function of the twist angle θ .The C_{ϕ} - C_{CO} and C=O bonds were optimized for each value of θ.The results

TABLE VI

The variation of total energy with the twist angle as obtained by CNDO/2 calculations .

θ	C_1 - C_7	C=O	Et(a.u.)	ΔEt(Kj/mol)[a]
0°	1.398_0	1.314_6	-207.955554	0.0
10°	1.398_5	1.314_6	-207.955007	1.4
20°	1.399_7	1.313_7	-207.953205	6.2
30°	1.404_3	1.312_3	-207.950468	13.3
40°	1.404_3	1.308_0	-207.947106	22.2
50°	1.406_7	1.306_0	-207.943530	31.6
70°	1.410_6	1.305_2	-207.937415	47.7
90°	1.413_4	1.303_6	-207.934917	54.2

a) energy difference between the twisted form and the planar form .

are reported in Table VI and it can be seen that the lowest energy corresponds to an angle equal to 0° .However one can observe that a deviation of planarity of 10° increases the energy by only 1.4 kJ/mol .Thus a slight torsion of the formyl group is possible (ca 5°).

EXPERIMENTAL

Pentafluorobenzaldehyde and pentafluoroacetophenone were commercial products and were used after distillation.Protonation was performed by dissolving at low temperature the carbonyl compound in a mixture of $HFSO_3$: SbF_5 (1:1) .The concentration was 0.2 mole of base per mole of magic acid .An equal volume of SO_2ClF was then added .

The ^{19}F NMR spectra were run on a Varian XL 100 spectrometer in the CW mode.The temperature was monitored by means of a thermocouple placed inside the probe.This thermocouple was calibrated before and after recording of the spectra with another thermocouple placed inside a spinning sample tube filled with the solvent .

The original $DNMR_2$ program of Binsch [20] was modified because its extent to treat five spin exchanging systems would necessitate more than 120,000 core storage words (decimal) .Such storage possibility is seldom available on computer systems and the program structure was modified in order to reduce its size . Thus the modified version ,$DNMR_5$, including the plotting subroutine allowing partial plots needs only 78694 words (decimal) .Execution time for one calculation on a five spin system as studied here is about 4 minutes on the Univac 1110 computer .More details ,the listing of the modified version with input and output data can be obtained on request .

The CNDO/2 calculations have been performed with a version of the CNINDO program of Pople and Dobosh [29] . All calculations have been made on the Univac 1110 computer system of the Centre de Calcul de Strasbourg-Cronenbourg.

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