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Weak hydrogen bonds in σ -1,4-difluorobenzene-ammonia: A rotational study

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ABSTRACT

Structural and energetic features of the complex 1,4-difluorobenzene-ammonia have been investigate by rotational spectroscopy. The complex adopts a σ configuration, with the nitrogen of ammonia in the plane of the aromatic ring. Two weak hydrogen bonds, C–H…N and N–H…F, represent the linkages between ammonia and 1,4-difluorobenzene.

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1. Introduction

Gas-phase studies on molecular complexes are able to elucidate the nature of the intermolecular interactions, isolated from other environmental effects. In particular, the analysis of their rotational spectra gives the possibility of discriminating between different molecular conformers and provides some estimates of the binding energies and internal dynamics.

One of the most important non-covalent interactions – also because of its biological relevance – is hydrogen bonding (H-bond). Many H-bond investigations have involved water, which has been found to form relatively strong H-bonds with organic or biological molecules, either as a proton donor or a proton acceptor [1–6].

In contrast with water, ammonia in its molecular complexes with organic or biomolecules, frequently acts preferably as a proton acceptor forming an intermolecular H-bond through the nitrogen lone pair [7–11]. Indeed, in all the investigated systems where ammonia could play the double proton donor/acceptor role, $F_3CH\cdots NH_3$ [7], $CH_3OH\cdots NH_3$ [8], pyrrole $\cdots NH_3$ [9], *tert*-butanol $\cdots NH_3$ [10] and glycidol $\cdots NH_3$ [11], only the forms where NH₃ has a basic behavior have been observed.

A few rotationally resolved electronic spectroscopy studies on adducts of ammonia with larger molecules confirm this trend, such as in the case of 1-naphtol···NH₃ [12], hydroquinone···NH₃ [13], and aniline···NH₃ [14].

In anisole…NH₃, where ammonia can play only the proton donor role towards the ether oxygen, the NH₃ group lies out of the plane of the aromatic ring and it is bonded to anisole via three weak, N-H…O, C_{Me} -H…N and N-H… π contacts [15,16].

The location of ammonia in anisole is reminiscent of the complex benzene–ammonia, where the NH_3 group points one of its hydrogen atoms towards the benzene ring electronic π -cloud [17]. This structure is also very similar to that of benzene–water [18], where the water molecule is positioned above the benzene plane.

The insertion of electronegative substituents (such as F atoms) in the aromatic ring could alter the geometry of the complex because a more classical (such as N–H···F) H-bond could be favored with respect to the N–H··· π bounding one. This is the case for the water complexes with partially substituted fluorobenzenes, where the water molecule lies on the plane of the benzene ring. Water constitutes with the fluorobenzene molecule a pseudo six-member ring, in which the principal interaction is between the fluorine atom and one of the hydrogen atoms of the water molecule and a secondary interaction is present involving the oxygen lone pair and the hydrogen atom in the phenyl ring [19,20].

The interpretations of the spectroscopical evidences of complexes of NH₃ with fluoroderivatives of benzene, are often based on *ab initio* calculations, and are frequently controversial. In the case of fluorobenzene \cdots NH₃, the results of one-color resonant two-photon ionization (R2PI) and IR-vibrational predissociation spectroscopy in the region of the NH stretches were interpreted in terms of a out of plane (π) complex [21], while a two-color resonance enhanced multiphoton ionization (REMPI) spectroscopy study indicated the complex to have a planar (σ) heavy atoms skeleton [22]. Regarding 1,4-difluorobenzene-ammonia (1,4-DFB-NH₃), the results of both techniques mentioned above were interpreted in terms of a π -complex [21,23].

In this Letter we present the results of a Fourier transform microwave spectroscopic study of 1,4-DFB-NH₃. Analysis of this experimental investigation is found to be consistent with the most stable σ -conformer as shown in Fig. 1. Also included are certain intermolecular parameters.

2. Experimental details

A gaseous mixture of 1% anhydrous ammonia (99.99% pure, Sigma–Aldrich) in Helium was passed over a sample of 1,4-DFB (\geq 99%, supplied by Aldrich and used without further purification)



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Fig. 1. Sketch of the most stable conformer (σ) of 1,4-DFB-NH₃.

at room temperature, and expanded through a solenoid valve (General Valve series 9) into the Fabry–Perot resonator chamber. The backing pressure was kept at 3.5 MPa in order to reach a concentration of about 3% of p-DFB in the gas mixture prior to the expansion.

The microwave spectra of the complex has been recorded in the frequency range 6–18 GHz using a CoBRA version [24] of a Balle–Flygare type [25] molecular beam Fourier transform microwave spectrometer already described elsewhere [26], updated with the FTMW++ set of programs [27].

The estimated accuracy of the measured frequencies is about 2 kHz and the resolving power is about 7 kHz.

3. Theoretical calculations

Previously available *ab initio* calculations for 1,4-DFB-NH₃ [20] found two different stable structures (σ and π shapes) of the complex, but the spectroscopic constants relevant to the rotational spectrum were not reported. For this reason, we optimized the two available structures at the MP2/6-311++G^{**} level of calculation using the GAUSSIAN03 software package [28]. We obtained a slightly different conformation for the π species. Vibrational frequencies in the harmonic approximation indicated that both our σ and π conformations are energy minima. All binding energies were corrected for basis set superposition errors (BSSE) using the counterpoise procedure [29]. The calculated rotational constants, dipole moment components, quadrupole coupling constants and energy differences are shown in Table 1. In addition, the theoretical value of the V_3 barrier to internal rotation of the ammonia moiety is reported for conformer σ . Furthermore, the dissociation energy was evaluated considering the ZPE correction and the counterpoise procedure. All these values are reported in Table 1.

The *ab initio* calculated electronic density shows (see Fig. 2) a somehow 'cooperative' effect of the two $(N-H\cdots F \text{ and } C-H\cdots N)$ intermolecular bonds, but it indicates the $C-H\cdots N$ interaction to be the stronger one.

4. Rotational spectra

According to the calculated values of rotational constants, of the dipole moment components and of the relative intensities of the predicted rotational transitions in our frequency range, the first search has been targeted to the low *J*, μ_a R-type transitions. After a first scan, the $6_{0.6} \leftarrow 5_{0.5}$, $6_{1.6} \leftarrow 5_{1.5}$ and $6_{1.5} \leftarrow 5_{1.4}$ transitions have been assigned. Subsequently more μ_a and some weaker μ_b R-type transitions have been measured. No μ_c type transitions have been detected, according to the co-planarity of the ammonia N atom with the aromatic ring.

$$= \mathbf{J} + \mathbf{I} \tag{1}$$

has been adopted in the fitting procedure, where I is the nuclear spin and F represents the total angular momentum.

No line splitting ascribed to an internal rotation motion has been observed.

All measured lines (deposited in Supplementary material) were fitted with the Watson's semirigid Hamiltonian in the S reduction and Ir representation [30] using the Pickett's suite of programs SPFIT [31]. The derived spectroscopic parameters are reported in Table 2.

5. Conformation and structure

The inertial defect calculated from the experimental rotational constants is $\Delta = -0.930 \text{ u}\text{Å}^2$, quite smaller (in absolute value) than the value expected for two out of plane ammonia hydrogens $(\approx -2.7 \text{ u}\text{Å}^2, [32])$. This small value is probably due to an almost free rotation of the NH₃ group, and it will be discussed in the next section, but it is only compatible with a planar configuration of the heavy atoms of the complex. Also the values of the quadrupole coupling constants correlate much better with the *ab initio* values of the σ -complex. There are, however, considerable discrepancies between the experimental and *ab initio* values of Tables 1 and 2. This kind of difference has been observed in other cases. In some complexes of NH₃ [7,8,10] having an almost linear X-H···N H-bond nearly co-linear with the *a*-axis, it has been interpreted as a reduction that arises from zero point angular oscillations of the NH₃ moiety relative to the *a*-axis of the complex. In 1,4-DFB-NH₃, such an approach is not possible because the C-H···N linkage is not colinear with the *a*-axis. Alternatively, such a reduction has been explained in terms of charge transfer for strongly bound complexes, but this seems not to be our case.

After these preliminary considerations, we can calculate the effective values of the intermolecular structural parameters, reproduce the experimental values of the rotational constants, obtaining a partial effective r_0 structure, while keeping the geometry of the monomers fixed to the calculated values in the complex. The defined intermolecular parameters are shown in Fig. 1. The corresponding fitted values for the $R_{\text{H}...\text{N}}$ distance and the θ angle are reported in Table 3 together with the values from the equilibrium structure. From the derived structure the intermolecular distance C–F···H–N has been calculated to be 2.476 Å.

6. Internal dynamics and dissociation energy

Aspects of internal dynamics of the complex can be obtained from the experimental evidences.

The inertial defect provides the possibility to estimate the internal rotation barrier. As discussed above, to the only out of plane atoms, two ammonia hydrogens, corresponds an inertial defect $\Delta \approx -2.8 \text{ u}\text{Å}^2$. The decrease to the observed value of $-0.930 \text{ u}\text{Å}^2$ is attributable to the corrections of the ground state rotational constants, with respect to the rigid limit, according to:

$$A_{00} = A_{\rm r} + W_{00}^{(2)} F \rho a^2,$$

$$B_{00} = B_{\rm r} + W_{00}^{(2)} F \rho b^2,$$

$$C_{00} = C_{\rm r},$$
(2)

where A_r , B_r and C_r are the 'rigid' rotational constants in the limit of the very high barrier. The $W_{00}^{(2)}$ are the Hersbach's barrier-dependent perturbation sums relative to the *A* sublevels of the ground state

Table 1

Calculated spectroscopic parameters of 1,4-DFB-NH₃.

	σ	π
A (MHz)	2974	1935
B (MHz)	818	1125
C (MHz)	644	933
$\mu_{a}(D)$	1.9	0.2
$\mu_{\rm b}$ (D)	0.4	0.8
μ_{c} (D)	0.0	1.3
χ_{aa} (MHz)	-2.92	1.95
$\chi_{\rm bb}$ (MHz)	0.82	0.86
χ_{cc} (MHz)	2.10	-2.81
ΔE (kJ mol ⁻¹)	0 ^a	4.5
$D_{\rm e} (\rm kJ mol^{-1})^{\rm b}$	17.3	12.8
ΔE_0 (kJ mol ⁻¹	0 ^a	3.5
$D_0 (\text{kJ mol}^{-1})^{\text{b}}$	13.1	9.7
ΔE^{CP} (kJ mol ⁻¹)	0 ^a	6.4
D_0^{CP} (kJ mol ⁻¹) ^b	11.3	4.9
$V_3 (cm^{-1})$	130	

^a The absolute values of the energy, of the zero point corrected energy and of the counterpoise corrected energy of the σ species are -486.160410, -486.041197 and -486.158130 H_a, respectively.

^b D_{e} , D_{0} and D_{0}^{CP} are the equilibrium, zero point corrected, and counterpoise corrected dissociation energies, respectively.

[33] and $\rho_{\rm g} = \lambda_{\rm g} I_{\alpha}/I_{\rm g}$. A value of $V_3 \approx 60~{\rm cm}^{-1}$ would correlate with the observed change in \varDelta with respect to the high barrier case. However, since the ammonia group out of plane vibrations would also give a negative contribution to the effective inertial defect so, probably the V_3 value is actually much lower. This result is in agreement with the fact that we did not observe *E*-species transitions nearby the *A*-species ones. The experimental evidence also indicates that the *ab initio* value of the barrier ($V_3 = 130~{\rm cm}^{-1}$) is overestimated.

The hydrogen bond stretching force constant can be estimated using the pseudo diatomic approximation which considers the two molecular subunits of the complex as two rigid parts. This model can be applied if the intermolecular stretching motion, directed along the hydrogen bond mean direction, is almost parallel to the *a*-axis of the complex.

By assuming a Lennard-Jones type potential, the zero point dissociation energy of the complex can be derived applying the approximate expressions [34]:

$$k_{\rm s} = 16\pi^4 (\mu_{\rm A} R_{\rm CM})^2 [4B_{\rm A}^4 + 4C_{\rm A}^4 - (B_{\rm A} - C_{\rm A})^2 (B_{\rm A} + C_{\rm A})^2]/(hD_{\rm J}), \qquad (3)$$

$$E_{\rm D} = 1/72k_{\rm s} R_{\rm CM}^2, \qquad (4)$$



Fig. 2. The electronic density of $\sigma\text{-}1,4\text{-}DFB\cdots NH_3$ suggests that the C–H $\cdots N$ interaction is stronger than the N–H $\cdots F$ one.



Fig. 3. Recorded $7_{0,7}$ - $6_{0,6}$ transitions of the complex. The ¹⁴N hyperfine structure (the *P*-*P*^{*r*} component lines are indicated) agrees with the quadrupole coupling constants of the σ form.

Table 2						
Spectroscopi	c parameters (S	reduction, I ^r 1	representation) of (σ-1,4-DFE	3-NH3.
A (A A I I -)	2040 220 (2)3	$D_{(1-1)}$	0.1.40 (1)		$(\mathbf{N} \mathbf{A} \mathbf{I} \mathbf{I}_{-})$	2 001

A (MHz)	3048.228 (2) ^a	D _J (kHz)	0.149(1)	χ _{aa} (MHz)	-2.001 (7)
B (MHz)	808.1610 (3)	$D_{\rm JK}$ (kHz)	[0] ^b	χ_{bb} (MHz)	0.437 (7)
C (MHz)	639.5514 (2)	$D_{\rm K}$ (kHz)	20.6 (4)	χ _{cc} (MHz)	1.564 (7)
		d_1 (kHz)	-0.0379 (6)	σ (kHz)	2
⊿ (uŲ)	-0.930	d_2 (kHz)	-0.51 (5)	N ^c	76

^a Error in parentheses in units of the last digit.

^b Fixed to zero because undetermined in the fit.

^c Number of lines in the fit.

Number of fines in the fit.

Table 3

 r_0 and r_e (MP2_{CP}/6-311++G^{**}) values of the intermolecular parameters.

	<i>r</i> ₀	r _e
$R_{\rm N-H}$ (Å)	2.48 (1) ^a	2.427
θ (°)	145.8 (1)	148.0
$R_{\rm H-F}$ (Å)	2.469 ^b	2.514

^a Error in parentheses in units of the last digit.

^b Derived from the other two parameters r_0 structure.

where B_A and C_A are the rotational constants of the adduct; D_J the centrifugal distortion constant; μ_A is the reduced mass of the complex and R_{CM} is the distance between the centers of mass of the two subunits. From the partial r_0 structure a R_{CM} value of 3.792 Å is derived, the corresponding k_s is 5.1 N/m and E_D results in a value of 10.1 kJ mol⁻¹. This value is similar to the values reported for other complexes of ammonia [7–11] and in a quite good agreement with the *ab initio* D_0^{CP} value of Table 1.

7. Conclusions

The molecular complex 1,4-DFB \cdots NH₃ has been characterized by molecular beam microwave spectroscopy. The values of the derived spectroscopic parameters allowed unequivocal discrimination between the two possible hydrogen bonded structures that could represent the ground state conformation of the dimer. Contrary to the conclusions of previous spectroscopic studies [21,23], the preferred conformer consistent with this current high resolution analysis is the σ configuration. This form of the complex is characterized by two weak H-bonds, with the ammonia molecule acting preferably as a proton acceptor of the ring C–H bond, but showing also some propensity as proton donor to the ring fluorine atom.

A partial r_0 structure has been derived, which describes the geometry of the complex in term of intermolecular parameters. The distance between the center of mass of the two molecular subunits derived from this structure has been used to estimate the dissociation energy of the complex. The geometry and energetic description of the 1,4-DFB···NH₃ complex are consistent with the previous ammonia complexes studied. The presence of electronegative substituents in the benzene molecule dramatically affects the characteristics of the hydrogen bond with respect to benzene ammonia. The shape of the complex is rather similar to that of 1,4-DFB···H₂O, with two weak H-bond linkages to the aromatic counterpart.

Since the π -conformer is calculated (see Table 1) to be only 6.4 kJ mol⁻¹ higher in energy than the σ -species, one could expect its spectrum to be observed too. We did not observe additional spectra with our experiments. This could be due to the fact that less stable conformers can relax into the global minimum when the pathways correspond to low interconversion barriers. It has been shown, indeed, that for barriers smaller than 2kT (ca. 420 cm⁻¹ in our case), such a relaxation takes place in cases of a single degree of freedom for conformational relaxation [35].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.12.025.

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