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# CH···O and CH···F Links Form the Cage Structure of Dioxane−Trifluoromethane

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The molecular beam Fourier transform microwave spectrum of 1,4-dioxane−trifluoromethane has been assigned and measured. The two subunits form a cage stabilized by one C−H···O and two C−H···F weak hydrogen bonds. The C−H···O link involves the axial lone pair of one of the two equivalent ring oxygens, while the two C−H···F bridges connect trifluoromethane to the two axial hydrogens in positions 3 and 5. The dissociation energy has been estimated from the $D_J$ centrifugal distortion parameter to be ~6.8 kJ/mol.

## Introduction

A considerable effort has recently been dedicated to the investigation of weak hydrogen bonds (WHB) such as CH···O and CH···F. This kind of linkage is ubiquitous, and it has been recognized to play an important role in biological, atmospheric, and supramolecular chemistry.[1] Studies on WHB have been mainly performed by X-ray diffraction[2] and IR spectroscopy in rare gas solutions.[3] However, it is gas-phase investigations, free from the effects of other intermolecular interactions that take place in condensed phases, that give more details on specific or local interactions. Rotational spectroscopy combined with supersonic expansions has been recently used to study the structural and energetic features of these weak interactions. CH···F and CH···O linkages are revealed to be the main factors in the formation of isolated cages such as difluoromethane and dimethyl ether dimers.[4,5] The relative strength of these two interactions has been investigated through the study of the rotational spectrum of the oxirane−trifluoromethane and oxirane−difluoromethane adducts.[6,7] Molecular complexes of dimethyl ether with 1,1-difluoroethene and with trifluoroethene are stabilized by one CH···O interaction and a bifurcated bridge of one fluorine atom with two hydrogens, one for each methyl group, of dimethyl ether.[8]

In the case of the WHB bridged adduct 1,4-dioxane−trifluoromethane (DXN···$CHF_3$), the CH···O interaction can take place with the axial or the equatorial lone pair of the ring oxygen, giving rise to the two plausible configurations, axial or equatorial, both with three CH···O or CH···F WHB linkages, as shown in Figure 1. This unusual kind of axial/equatorial isomerism was already investigated with rotational spectroscopy for the adducts of HF and HCl with tetrahydropyran,[9,10] the axial form being more stable in both cases. For the molecular complexes tetrahydropyran···$H_2O$[11] and 1,4-dioxane···$H_2O$,[12] the rotational spectra have been observed only for the axial conformer.

It is also interesting to see if in the case of DXN···$CHF_3$ the axial configuration within the oxygen lone pairs is the favored one. For this reason we performed the study of the rotational spectrum of DXN···$CHF_3$.

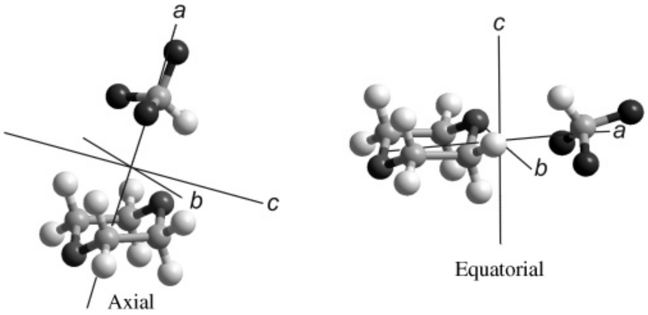

**Figure 1.** Axial and equatorial conformations of DXN−$CHF_3$.

## Experimental Section

Commercial samples of 1,4-dioxane and $CHF_3$ (Aldrich) have been used without further purification.

The molecular beam Fourier transform microwave (MB-FTMW) spectrum in the 6−18.5 GHz frequency region was measured using an MB-FTMW spectrometer described elsewhere.[13] A gas mixture of 2% of $CHF_3$ in He at a total pressure of 2.5 bar was flowed over liquid 1,4-dioxane at room temperature and expanded through the solenoid valve (General Valve, series 9, nozzle diameter 0.5 mm) into the Fabry−Pérot cavity. The frequencies were determined after Fourier transformation of the 8K data points time domain signal, recorded at 100 ns sample intervals. Each rotational transition is split by Doppler effect, enhanced by the coaxial arrangement of the supersonic jet and resonator axes. The rest frequency is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 2 kHz. Lines separated by more than 7 kHz are resolvable.

## Results

**Ab Initio Calculations and Rotational Spectrum.** As a starting point for our study we performed some ab initio calculations at the MP2/6-311++G** level[14] in order to estimate the relative stabilities and the geometries of the two

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**TABLE 1: Experimental Transition Frequencies $\nu$ of DXN···CHF$_3$ Complex**

| $J'_{K'_a,K'_c} \leftarrow J''_{K''_a,K''_c}$ | $\nu$, MHz | $J'_{K'_a,K'_c} \leftarrow J''_{K''_a,K''_c}$ | $\nu$, MHz |
|---|---|---|---|
| a-Type Transitions | | | |
| $6_{0,6} \leftarrow 5_{0,5}$ | 7406.213 | $9_{1,9} \leftarrow 8_{1,8}$ | 10978.335 |
| $6_{1,6} \leftarrow 5_{1,5}$ | 7323.818 | $9_{1,8} \leftarrow 8_{1,7}$ | 11259.324 |
| $6_{1,5} \leftarrow 5_{1,4}$ | 7512.172 | $9_{2,8} \leftarrow 8_{2,7}$ | 11123.041 |
| $6_{2,5} \leftarrow 5_{2,4}$ | 7419.092 | $9_{2,7} \leftarrow 8_{2,6}$ | 11174.806 |
| $6_{2,4} \leftarrow 5_{2,3}$ | 7434.577 | $9_{3,7} \leftarrow 8_{3,6}$ | 11136.382 |
| $6_{3,4} \leftarrow 5_{3,3}$ | 7422.641 | $9_{3,6} \leftarrow 8_{3,5}$ | 11138.187 |
| $6_{3,3} \leftarrow 5_{3,2}$ | 7422.856 | $9_{4,6} \leftarrow 8_{4,5}$ | 11132.426 |
| $6_4 \leftarrow 5_4$[a] | 7420.700 | $9_{4,5} \leftarrow 8_{4,4}$ | 11132.446 |
| $7_{0,7} \leftarrow 6_{0,6}$ | 8633.851 | $10_{0,10} \leftarrow 9_{0,9}$ | 12298.311 |
| $7_{1,7} \leftarrow 6_{1,6}$ | 8542.751 | $10_{1,10} \leftarrow 9_{1,9}$ | 12194.866 |
| $7_{1,6} \leftarrow 6_{1,5}$ | 8762.242 | $10_{1,9} \leftarrow 9_{1,8}$ | 12505.960 |
| $7_{2,6} \leftarrow 6_{2,5}$ | 8654.353 | $10_{2,9} \leftarrow 9_{2,8}$ | 12356.312 |
| $7_{2,5} \leftarrow 6_{2,4}$ | 8678.992 | $10_{2,8} \leftarrow 9_{2,7}$ | 12426.380 |
| $7_{3,5} \leftarrow 6_{3,4}$ | 8660.336 | $10_{3,8} \leftarrow 9_{3,7}$ | 12374.708 |
| $7_{3,4} \leftarrow 6_{3,3}$ | 8660.831 | $10_{3,7} \leftarrow 9_{3,6}$ | 12377.798 |
| $7_4 \leftarrow 6_4$[a] | 8657.796 | $10_{4,7} \leftarrow 9_{4,6}$ | 12370.001 |
| $8_{0,8} \leftarrow 7_{0,7}$ | 9858.553 | $10_{4,6} \leftarrow 9_{4,5}$ | 12370.051 |
| $8_{1,7} \leftarrow 7_{1,6}$ | 10011.350 | $11_{0,11} \leftarrow 10_{0,10}$ | 13513.254 |
| $8_{2,7} \leftarrow 7_{2,6}$ | 9889.028 | $11_{1,11} \leftarrow 10_{1,10}$ | 13410.490 |
| $8_{2,6} \leftarrow 7_{2,5}$ | 9925.688 | $11_{1,10} \leftarrow 10_{1,9}$ | 13751.053 |
| $8_{3,6} \leftarrow 7_{3,5}$ | 9898.252 | $11_{2,10} \leftarrow 10_{2,9}$ | 13588.758 |
| $8_{3,5} \leftarrow 7_{3,4}$ | 9899.239 | $11_{2,9} \leftarrow 10_{2,8}$ | 13680.292 |
| $8_{4,5} \leftarrow 7_{4,4}$ | 9895.026 | $11_{3,9} \leftarrow 10_{3,8}$ | 13613.198 |
| $8_{4,4} \leftarrow 7_{4,3}$ | 9895.040 | $11_{3,8} \leftarrow 10_{3,7}$ | 13618.202 |
| $9_{0,9} \leftarrow 8_{0,8}$ | 11080.081 | | |
| c-Type Transitions | | | |
| $2_{2,0} \leftarrow 1_{1,0}$ | 7444.257 | $5_{4,2} \leftarrow 4_{3,2}$ | 17815.968 |
| $5_{1,4} \leftarrow 4_{0,4}$ | 8085.600 | $5_{4,1} \leftarrow 4_{3,1}$ | 17815.946 |
| $6_{1,5} \leftarrow 5_{0,5}$ | 9421.809 | $9_{1,8} \leftarrow 8_{0,8}$ | 13556.106 |
| $7_{1,6} \leftarrow 6_{0,6}$ | 10777.839 | $10_{1,9} \leftarrow 9_{0,9}$ | 14981.983 |
| $4_{3,2} \leftarrow 3_{2,2}$ | 13257.410 | $11_{1,10} \leftarrow 10_{0,10}$ | 16434.727 |
| $4_{3,1} \leftarrow 3_{2,1}$ | 13255.221 | $11_{4,8} \leftarrow 10_{4,7}$ | 13607.771 |
| $5_{3,2} \leftarrow 4_{2,2}$ | 14488.846 | $11_{4,7} \leftarrow 10_{4,6}$ | 13607.869 |
| $5_{3,3} \leftarrow 4_{2,3}$ | 14495.405 | | |

[a] Transitions doubly overlapped because of the near-prolate degeneracy of the involved levels. Only $K_a$ is given.

conformers. As for the complexes mentioned in the Introduction,[9−12] the axial conformer was more stable. The theoretically obtained rotational constants were similar to those obtained from the geometries based on the structures of 1,4-dioxane[15] and trifluoromethane[16] monomers and on the parameters of the hydrogen bond in the complex oxirane−CHF$_3$.[6]

We calculated the rotational spectrum with the ab initio rotational constants, and we found six $\mu_a$-type R bands, typical of a near-prolate top, with $J_{\text{upper}}$ in the range from 6 to 11 and with $K_a$ ranging from 0 to 4. We also measured some much weaker $\mu_c$-type lines. The rotational frequencies were fitted with Watson's Hamiltonian ($I^r$ representation, $S$ reduction),[17] determining all quartic and two sextic centrifugal distortion constants. There was no detectable inversion splitting.

All measured transitions are listed in Table 1, while the fitted spectroscopic parameters are shown in Table 2. In Table 3 the ab initio rotational constants for the two conformers are presented and compared with the observed ones; a good agreement is obtained between the values calculated for the axial conformer and the experimentally determined values.

Only a few lines that did not belong to the axial species were left unassigned in the spectrum. We made an attempt to assign them to the equatorial conformer but without success.

**Structure of the Observed Species.** A partial $r_0$ structure was calculated from the three available experimental rotational constants. The three parameters, $r_{\text{O}\cdots\text{H}}$, α, and $\beta$ of Figure 2, were fitted while keeping the geometry of CHF$_3$ fixed to its $r_0$ experimental values[16] and making a little adjustment[18] to the electron diffraction geometry available for DXN.[11] The parameter values were constrained in a 5% confidence interval of the ab initio values (MP2 6-311++G**). The obtained results are shown in Table 4.

**TABLE 2: Spectroscopic Parameters for DXN−CHF$_3$[a]**

| | |
|---|---|
| $A$, MHz | 2280.39395(35) |
| $B$, MHz | 634.221382(68) |
| $C$, MHz | 602.787448(74) |
| $D_J$, kHz | 0.38283(30) |
| $D_{JK}$, kHz | 13.1630(98) |
| $D_K$, kHz | −9.591(18) |
| $d_1$, kHz | −0.01922(20) |
| $d_2$, kHz | −0.01618(14) |
| $H_{JK}$, Hz | −0.133(36) |
| $H_{KJ}$, Hz | −3.07(48) |
| $N$[b] | 65 |
| $J_{\text{max}}$ | 11 |
| $\sigma$,[c] kHz | 1.5 |

[a] Errors expressed in units of the last digits. [b] Number of transitions in the fit. [c] Standard deviation of the fit.

**TABLE 3: Comparison between Experimental and Theoretical Results for DXN···CHF$_3$**

| | observed | 6-311++G** | |
|---|---|---|---|
| | axial | axial | equatorial |
| $A$, MHz | 2280.4 | 2315.5 | 3047.6 |
| $B$, MHz | 634.2 | 662.2 | 538.9 |
| $C$, MHz | 602.8 | 624.7 | 488.0 |
| $\Delta E$, cm$^{-1}$ | | 0 | 218 |

**TABLE 4: Relevant Structural Parameters of Axial DXN···CHF$_3$ (See Figure 2)**

| | $r_0$[a] | $r_e$[b] |
|---|---|---|
| $r_{\text{O}\cdots\text{H}}$, Å | 2.315(85) | 2.330 |
| α, deg | 124.2 (32) | 116.6 |
| $\beta$, deg | 157.8(11) | 157.0 |
| $r_{\text{F}\cdots\text{H}}$, Å | 2.92(1)[c] | 2.81 |
| ∠(CH···F), deg | 132.6(30)[c] | 129.84 |

[a] Standard error in parentheses in units of the last digits. [b] MP2/6-311++G** values. [c] Derived from the obtained partial $r_0$ geometry.

The F···H distance and the C−H···F angles are also significant parameters. They have been derived from the partial $r_0$ structure and are reported in Table 4. The O···H and F···H distances are in line with those observed for the complexes oxirane−CHF$_3$[6] and oxirane−difluoromethane.[7] The deviation from linearity of the C−H···O and C−H···F angles is considerable (124.2° and 132.6°, instead of 180°, respectively), as observed in previously investigated complexes with this type of WHB.[4−8]

**Dissociation Energy.** From the geometry and symmetry of the complex, it is likely that the stretching motion leading to

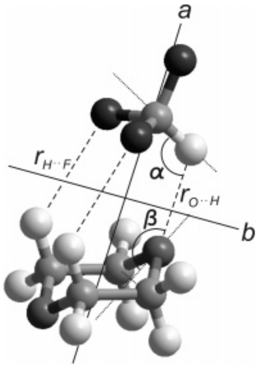

**Figure 2.** Principal axes system and definition of structural parameters of DXN−CHF$_3$ used through the text.

the dissociation of the complex should be almost parallel to the *a*-axis. This allows us to estimate the stretching force constant ($k_S$) by using the approximation[19]

$$k_S = \frac{16\pi^4(\mu R_{CM})^2[4B^4 + 4C^4 - (B - C)^2(B + C)^2]}{hD_J} \quad (1)$$

where $\mu$, $R_{CM}$, and $D_J$ are the reduced mass, the distance between the centers of mass, and the first-order centrifugal distortion constant of the complex, respectively. The value $k_S = 5.0$ N/m, corresponding to a harmonic stretching frequency of 46.5 cm$^{-1}$, has been obtained. The dissociation energy ($E_D$) has been evaluated to be 6.8 kJ/mol by assuming a Lennard-Jones potential function, using the equation[19] $E_D = (^1/_{72})k_S(R_{CM})^2$. Such a dissociation energy corresponds to a binding energy of ~2.3 kJ/mol for each C−H···F or C−H···O linkage. This value is very similar to that of other WHB dimers (or adducts) such as the difluoromethane dimer, dimethyl ether dimer, oxirane−$CHF_3$, and difluoroethene−dimethyl ether (refs 4−6 and 8, $E_D = 4.7-6.7$ kJ/mol).

## Conclusions

The conformation of DXN−$CHF_3$, deduced from the analysis of its rotational spectrum, is cage like and stabilized by three WHBs: two C−H···F and one C−H···O bridges. This last one takes place between the hydrogen of $CHF_3$ and the axial lone pair at the ring oxygen. As for the previously investigated complexes involving tetrahydropyran or 1,4-dioxane,[9−12] the H-bond linkage with the oxygen axial lone pair generates the most stable species. The results are in agreement with the ab initio calculations, and the geometry and energy related features of the WHBs are quite similar to those observed in the difluoromethane dimer[4] and in oxirane−$CHF_3$.[6]

The intermolecular interaction energies in complexes such as DXN···$CHF_3$ are on the order of magnitude of those of van der Waals complexes so that one could ascribe them to dispersion forces. However, the directionality of the C−H···X linkages is always observed, suggesting their classification as WHBs.

The results here reported show the importance of rotational resolved spectroscopies in obtaining detailed chemical information, hardly achievable with other techniques.

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