The C-F···H-C "Anti-Hydrogen Bond" in the Gas Phase: Microwave Structure of the Difluoromethane Dimer**

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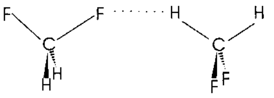
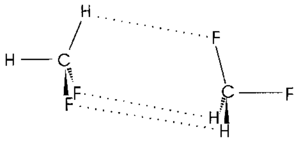
Rotationally resolved spectroscopy combined with supersonic expansions[1] has been very useful in obtaining detailed information on the structure, dynamics, and energetics of intermolecular hydrogen bonding.[2] This kind of data is available for O-H···O, O-H···N, O-H···S, O-H···π, N-H···N, N-H···O, X-H···N, and X-H···O linkages (X = F, Cl, CN).[3]

A few years ago we introduced free jet millimeter wave absorption spectroscopy for the study of molecular complexes,[4] and obtained the first data from high-resolution spectroscopy on the solvation of ethers,[5] cyclic amines,[6] and diazines[7] through the study of the 1/1 complexes with water.

Recently, while investigating the complex of difluoromethane (DFM) with water,[8] we noticed, besides the spectrum of DFM – H_2O, a set of evenly spaced μ_a-R-branch lines. These lines were observed when either argon or neon was used as carrier gas, and persisted when water was removed from the system. Furthermore, they appeared only at backing pressures higher than 300 mbar (see Experimental Section), a feature typical for hydrogen-bonded complexes. This evidence induced us to assign the observed spectrum to the dimer of DFM, $(DFM)_2$, with aliphatic hydrogen atoms possibly acting as proton donors. This is unusual, but becomes plausible when electronegative substituents, such as halogen atoms, are attached to the carbon atom and the aliphatic hydrogen atoms acquire acidic character. With two hydrogen and two fluorine atoms attached to the same carbon atom, DFM can act as a double proton donor and as a double proton acceptor; in a way similar to that, for example, of water,[9] it can form a hydrogen-bonded dimer. At the same time it is small enough to allow high level ab initio calculations. Model calculations based on the geometry of isolated DFM[10] showed that for $(DFM)_2$ conformations **I** and **II** could have rotational constants in agreement with the observed band spacings.



I



II

The 37 measured rotational line frequencies (available in the Supporting Information) have been fitted within the I^r representation of Watson's "S" reduced Hamiltonian,[11] producing the spectroscopic constants given in Table 1. The planar moments of inertia, which give the mass extension along the principal axes, are also reported. The P_{bb} value nearly coincides with the sum of P_{aa} and P_{cc} of isolated DFM. This means that the extension of the dimer along the *b* axes corresponds to the contributions of a CH_2 plus a CF_2 group and that, in agreement with either conformer **I** or **II**, the dimer has a plane of symmetry.

Table 1. Spectroscopic constants of $(DFM)_2$ (I^r representation, "S" reduction).[a]

A [MHz]	6447.7(22)[b]
B [MHz]	1290.238(8)
C [MHz]	1234.614(10)
D_J [kHz][c]	1.796(6)
D_{JK} [kHz]	42.6(2)
H_{JK} [Hz]	−0.86(18)
N	37
σ [MHz]	0.11
P_{aa} [u Å^2]	361.327
P_{bb} [u Å^2]	48.014[d]
P_{cc} [u Å^2]	30.367

[a] A, B, C: rotational constants; D_J, D_{JK}, H_{JK}: centrifugal distortion constants; N: number of transitions in the fit; σ: standard deviation of the fit; P_{aa}, P_{bb}, P_{cc} = planar moments of inertia. [b] Standard errors are given in parentheses in units of the last digit. [c] The remaining quartic and sextic centrifugal distortion parameters have been set to zero because they could not be determined from the fit. [d] Corresponds to the sum of P_{aa} (46.037 u Å^2) and P_{cc} (1.651 u Å^2) of isolated DFM.

Assuming the geometry of DFM to remain unaltered in the dimer, we tried to obtain a plausible ground-state r_0 structure from the experimental rotational constants. This was not possible for form **I** because an unrealistically short length for the C–H···F–C hydrogen bond (less than 1.5 Å) would have been required. In contrast, reasonable values have been obtained for the α, β, and r parameters of species **II** (Figure 1). They are reported in Table 2 together with the hydrogen-bond lengths.

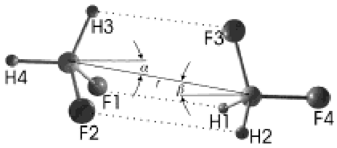


Figure 1. Schematic represention of the triply hydrogen bonded conformer **II**, the most stable, of $(DFM)_2$. α and β are the angles between the C–C direction and the prolongations of the H4–C and F4–C bonds, respectively.

These results have been confirmed by ab initio calculations performed at the MP2/6-31 + G(d,p) level.[12] Only one energy minimum was

Table 2. Hydrogen-bond parameters in $(DFM)_2$ (see Figure 1).

	r_0[a]	ab initio[b]
r [Å]	3.55(1)	3.524
α [°]	8.3(5)	10.6
β [°]	10.5(7)	12.4
H1–F1 [Å]	2.759	2.734[c]
H3–F3 [Å]	2.628	2.588

[a] C_s symmetry. [b] Slightly distorted with respect to the C_s symmetry (C_aF3-C_bH3 = 2.1°). [c] Average of the slightly different H1–F1 and H2–F2 values.

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Table 3. Ab initio evidence for anti-hydrogen bonding in $(DFM)_2$.

	shortening of C–H bond lengths[a]				blue shift of C–H stretches[a]		
	DFM	$(DFM)_2$	Δl		DFM	$(DFM)_2$	$\Delta \nu$
$C{-}H_1$ [Å][b]	1.0859	1.0847	-0.0012	$\nu_{symm.}$ [cm^{-1}]	3185	3198	+13
					3201	+16	
$C{-}H_3$ [Å][b]		1.0842	-0.0017	$\nu_{antisymm.}$ [cm^{-1}]	3282	3302	+20
					3303	+21	

[a] In going from DFM to $(DFM)_2$. [b] See Figure 1.

found, corresponding to conformer **II**. The computed structural hydrogen-bond parameters are also shown, for comparison, in Table 2.

Recently Hobza et al.[13] observed that, while in "normal" hydrogen bonds the A–H bond length (A–H is the proton donor) increases and the ν_{A-H} band undergoes a red shift upon formation of a generic A-H ⋯ B hydrogen bond, the contrary happens in some cases, giving rise to the "anti-hydrogen bond".[13] In the case of $(DMF)_2$ ab initio calculations indicate that upon formation of the C-H ⋯ F-C bond the C–H bond lengths decrease and the C–H stretching frequencies (ν_{C-H}) are blue shifted. These features, which are reported in Table 3, allow us to classify the C-H ⋯ F-C bond in $(DFM)_2$ as anti-hydrogen bonding.

Looking at the geometry and symmetry of the complex, it is likely that the stretching motion leading to the dissociation of the complex should almost be parallel to the *a* axis. This allows us to estimate the stretching force constant k_s by using the approximated Equation (1),[14] where μ_D, R_{CM}, and D_J are the

$$k_s = 16\pi^4(\mu_D R_{CM})^2[4B_D^4 + 4C_D^4 - (B_D - C_D)^2(B_D + C_D)^2]/(hD_J) \quad (1)$$

reduced mass, the distance between the centers of mass, and the first-order centrifugal distortion constant, respectively. The value $k_s = 6.25\,N\,m^{-1}$, corresponding to a harmonic stretching frequency of $64\,cm^{-1}$, has been obtained. The dissociation energy E_D has been evaluated to be $6.6\,kJ\,mol^{-1}$ by assuming a Lennard–Jones potential function using the approximated Equation (2).[15]

$$E_D = 1/72\,k_s R_{CM}^2 \quad (2)$$

Such a dissociation energy corresponds to a binding energy of $2.2\,kJ\,mol^{-1}$ for each C-H ⋯ F-C linkage. This value is much smaller than the bond energy ($8.7\,kJ\,mol^{-1}$) for the O-H ⋯ F-C bond in DFM–H_2O,[8] but the "cooperative effect" of the three weak C-H ⋯ F-C linkages makes the complex sufficiently stable for its detection with our technique.

This is, to our knowledge, the first report on such a small triply hydrogen bonded dimer and on the C-H ⋯ F-C hydrogen (or anti-hydrogen?) bond. Detailed information on the conformation, geometry, and dissociation energy have been obtained from the jet cooled rotational spectrum. Ab initio calculations showed the hydrogen bond to have anti-hydrogen bond features.

Experimental Section

The Stark and pulse modulated free jet absorption millimeter-wave spectrometer (60–78 GHz) has been described elsewhere.[4, 16] The dimer was formed by expanding a mixture of about 5 mol% DFM in argon (or neon) at room temperature and at a pressure of approximately 0.8 bar to about 5×10^{-3} mbar through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.35 mm. An estimated "rotational" temperature of about 10 K was reached. All samples are commercially available and were used without further purification. The accuracy of the frequency measurements was estimated to be 0.05 MHz.

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