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HYDROGEN BONDED BIMOLECULAR COMPLEXES OF CARBOXYLIC ACIDS IN THE VAPOR PHASE

OBSERVATION AND CHARACTERIZATION BY LOW RESOLUTION MICROWAVE SPECTROSCOPY

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Abstract—Various carboxylic acids and amides are shown to form H-bonded bimolecules with trifluoroacetic acid in the vapor phase. These bimolecules have been observed directly by low resolution microwave spectroscopy which gives rotational constants in agreement with those calculated with the assumption of a planar, 8-membered ring geometry for the H-bonded portion of the structure. A number of combinations did not provide observable spectra, and reasons are proposed why the bimolecules probably did not form in certain of these cases. Approximate dipole moments are obtained for the H-bonded bimolecular complexes.

Costain and Srivastava[1] first reported microwave spectra from H-bonded bimolecules of the type shown in Fig. 1, in particular, trifluoroacetic acid with formic, acetic and fluoroacetic acids. We have observed similar results for a wide range of carboxylic acids and amides combined with trifluoroacetic acid.

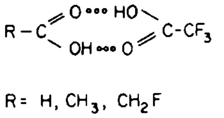


Fig. 1. The structure of hydrogen-bonded bimolecules.

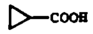
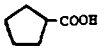
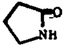
Table 1 lists the compounds, together with the observed rotational constants B + C obtained from the mean spacing of the low resolution a-type R-branch transitions. Also shown are the calculated values of B + C obtained by assuming that the monomers are unperturbed but doubly H-bonded in an 8-membered planar ring configuration with an O–O distance of 2·67 Å and a N–O distance of 2·71 Å in the acid-acid and acid-amide combinations respectively. Figure 2 shows two typical spectra from this series. The bands shown have widths of 30–45 MHz which are considerably narrower than those of comparable spectra for molecules of this size.

These spectra are examples of low resolution microwave spectroscopy[1,2] which furnishes useful approximate structural information for large, nearly prolate molecules. Each absorption band is comprised of clusters of lines arising from rotational states with various values of K and various vibrational satellites thereof but corresponding to the same ΔJ = + 1 rotational transition.[2] The spacing of these bands is close to the rotational constant B + C, where A, B and C, the rotational constants, are proportional to the inverse of the moments of inertia about the principal molecular axes a, b and c.[3] Thus the rotational constant B + C is sensitive to the structural parameters of the molecule giving rise to the microwave spectrum.

Band spectra were not observed for the molecule pairs listed in Table 2. Most of these are expected to exist in some conformations which are close enough to the prolate limit and which have a sufficiently strong a-component of the dipole moment to give observable low resolution band spectra. We therefore believe that the lack of observable spectra must be due to the presence of a number of conformations, none of which are highly populated, or due to a low association constant in the vapor phase, although the factors affecting the latter are ill-understood.

The more acidic carboxylic acids in solution do show a lesser tendency to dimerize in the vapor.[4] Trifluoroacetic acid is a desirable partner because of its dipole moment,

Table 1. Observed hydrogen-bonded bimolecules

H-B Bimolecule (with CF_3COOH)	Observed B+C	Calculated B+C
$HCOOH^a$	1154.4 MHz[b]	1154.1 MHz[b]
CH_3COOH^a	833.8 ± 2	832.4
CH_2FCOOH^a	611.4[b]	611.3[b]
CH_3CH_2COOH	636.9 ± 3	636.6
$(CH_3)_2CHCOOH$	533.2 ± 2	532.2
$(CH_3)_3CCOOH$	466.0 ± 2	464.1
$CH_2CHCOOH$	656.0 ± 4	652.9
$(CH_3)_2C{=}CHCOOH$	420.5 ± 3	434.7
	539.6 ± 2	530.7
	439. ± 10	430.
	382. ± 13	387.
CH_3CONH_2	817.9 ± 2	816.5
$CH_3CH_2CONH_2$	624.4 ± 2	623.7
	579.1 ± 2	586.5

a. First reported Ref. (1).
b. Values from Ref. (1).

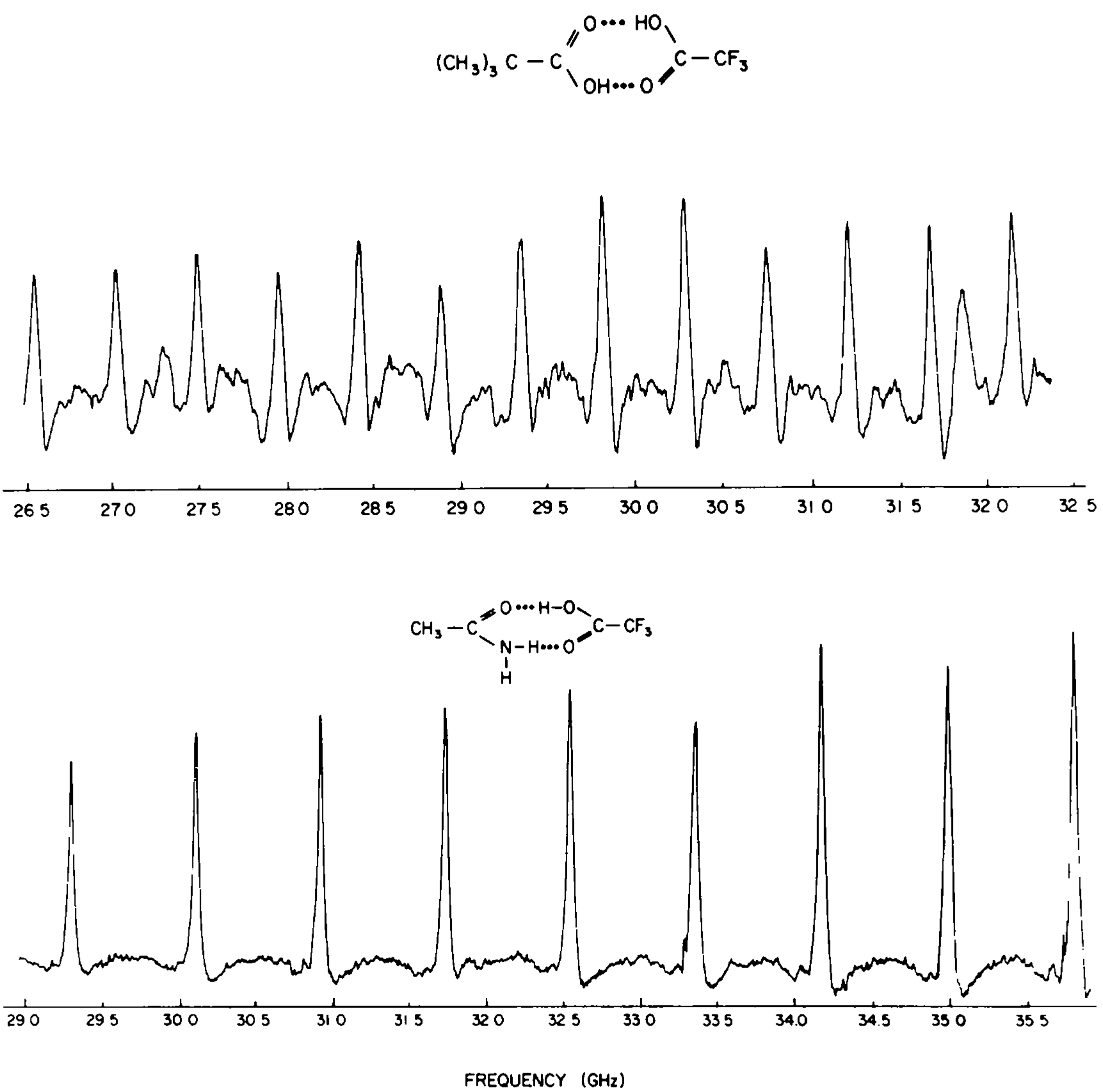
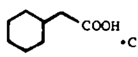
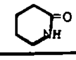


Fig. 2. Typical low resolution microwave spectra of hydrogen-bonded bimolecules. (Peaks at 27·3 and 31·9 GHz in the top spectrum are due to excess trifluoroacetic acid).

Table 2. Hydrogen-bonded bimolecules not observed

A.	$BrCH_2COOH\cdot CF_3COOH$
	$ClCH_2COOH\cdot CF_3COOH$
	$N{\equiv}CCH_2COOH\cdot CF_3COOH$
B.	$CH_3CH_2CH_2COOH\cdot CF_3COOH$
	 COOH $\cdot CF_3COOH$
C.	$HCONHCH_3\cdot CF_3COOH$
	$CH_3CONHCH_3\cdot CF_3COOH$
D.	 $\cdot CF_3COOH$

but it is quite acidic; therefore, its partner must be relatively non-acidic. This may explain why the bimolecules of group A are not observed. Computer simulations using bond moments and an assumed dipole moment of 2·35 Debye for the trifluoromethyl group show that of the group A bimolecules, only the one containing cyanoacetic acid will have insufficient a-dipole moment component to be observed.

The group B bimolecules, if they are formed, are probably not observed due to the several conformations among which the molecules are partitioned. They are expected to have the other physical characteristics necessary for observation.

Acetamide H-bonded to trifluoroacetic acid provides the strongest bimolecule low resolution microwave spectrum that we have observed. Thus, it is interesting that the bimolecules of groups C and D were not observed. Computations reveal that they would be nearly prolate and would have a large a-dipole moment were they to exist. Stereoelectronic factors must force the N-methyl amides to adopt a conformation unfavorable to the formation of two H-bonds with trifluoroacetic acid. This is supported by the observation of Elzaro and Schwendeman[5] that N-methylformamide in the gas phase adopts the conformation with N-Me *cis* to the CO oxygen exclusively.

It is not clear why the bimolecule of group D is not observed, in view of the observation of a γ-butyrolactam-containing bimolecule.

Table 3. Experimentally determined dipole moments of hydrogen-bonded bimolecules

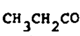
Bimolecule	a-Component of Dipole Moment (Debye)
$CH_3COOH \cdot CF_3COOH$	2.99±0.5
$(CH_3)_3CCOOH \cdot CF_3COOH$	2.28±0.5
 $COOH \cdot CF_3COOH$	2.53±0.5
$CH_3CONH_2 \cdot CF_3COOH$	3.09±0.5
$CH_3CH_2CONH_2 \cdot CF_3COOH$	2.73±0.5
 $\cdot CF_3COOH$	1.75±0.5
$CH_2{=}CHCOOH \cdot CF_3COOH$	1.30±0.5
$(CH_3)_2C{=}CHCOOH \cdot CF_3COOH$	0.81±0.5

Table 4. Dipole moments of trifluoromethyl compounds

Compound	Dipole Moment[a] (Debye)
HCF_3	1.645
CH_3CF_3	2.35
CF_3COOH	2.28
ϕ-CF_3	2.86
$CH_2{=}CH-CF_3$	2.45

a. A. L. McClellan, Tables of Experimental Dipole Moments, San Francisco, W. H. Freeman & Co., 1963.

When a static electric field is applied to molecules in the gas phase, their individual microwave absorption lines are split by the molecular Stark effect.[6] We have found that the application of a static electric field will broaden low resolution microwave absorption bands, because it splits the individual lines which comprise the bands. Furthermore, the rate of increase of the broadening with increasing electric field may be roughly correlated with the a-component of the molecular dipole moment, in the case of R-branch low resolution microwave bands.

This low resolution molecular Stark effect may be used to determine the approximate a-dipole moment components of the H-bonded bimolecules as shown in Table 3. These dipole values are quite reasonable when compared to those in the literature for trifluoromethyl compounds generally (see Table 4).

EXPERIMENTAL

Conditions

The chemicals used for these experiments are reagent grade, checked for identity by IR spectroscopy and used as received. Samples of the appropriate carboxylic acids and amides were expanded from the same glass sample holder, in proportion to their vapor pressures, into the waveguide-cell of the microwave spectrometer. When a mixture of compounds failed to give evidence of bimolecule formation, the component compounds were introduced to the waveguide-cell separately, in various proportions to assure that no spectrum could be observed.

Low resolution microwave absorption spectra were recorded in the R and K bands on a Hewlett-Packard-8460A microwave spectrometer at room temp (21–24°C). The spectra were recorded at a scan rate of 10 MHz per sec with a 1 sec recorder time constant. 1600 V base-to-peak Stark field was found to modulate the transitions sufficiently for a strong spectrum to be recorded at −50 d.B. gain with total gas pressures of 50–100 μ Hg in the cell.

Rotational constants were calculated for trial structures using H. Pickett's computer program, CART.†

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†This program that computes rotational constants from bond angles and distances is available on request.