Conformations and Vibrational Dynamics of Six Monoalkyltrifluoroacetamides. Low-Resolution Microwave and Gas-Phase NMR Spectroscopic Studies

Nancy S. True* and Brian D. Ross

Department of Chemistry, University of California, Davis, California 95616 *(Received: November 16, 1983)*

Low-resolution microwave spectra of six *N*-alkyltrifluoroacetamides ($F_3C(O)NHR$; R = CH_3, C_2H_5, *i*-C_3H_7, *n*-C_3H_7, *i*-C_4H_9, *t*-C_4H_9) display band series consistent with a single species having the R group oriented syn to the carbonyl moiety. $^5J_{H-F}$ coupling constants observed in gas- and liquid-phase NMR spectra of *N*-methyltrifluoroacetamide confirm this assignment. For each molecule the observed rotational constants, anomalously broad microwave bandwidths, and absence of resolvable fine structure are consistent with predicted effects of rapid intramolecular vibrational redistribution (IVR). Sufficient state density for rapid IVR in these molecules occurs at low internal energies.

Introduction

For gaseous molecules, low-resolution microwave (LRMW) and NMR spectroscopy can yield complementary information about conformations and large-amplitude vibrations in suitably selected cases. The present study reports gas-phase conformational data for *N*-alkyltrifluoroacetamides obtained with both techniques. These results demonstrate the dominant conformational species in *N*-alkyltrifluoroacetamides with alkyl substituents ranging in size from *N*-methyl to *N*-*tert*-butyl has the alkyl group syn to the carbonyl group. Qualitative features of LRMW spectra of each molecule are consistent with rapid intramolecular vibrational redistribution involving the low-frequency torsional vibrations.

Rotational isomerism about the C–N peptide bond in a wide variety of amides has been studied by liquid-phase NMR spectroscopy,[1,2] and two conclusions of general applicability can be made. First, rotational barrier magnitudes are in the range 15–20 kcal/mol, demonstrating considerable partial double-bond character, and these values are somewhat solvent dependent.[3] Second, for monoalkyl-substituted amides, the predominant conformation present, on the basis of the magnitude of long-range coupling constants, has the alkyl group syn to the carbonyl carbon.[2] This orientation is also dominant in acyl halides,[4] esters,[5] and thioesters[6] where the nitrogen is replaced with either a CH_2, O, or S, irrespective of the nature of the substituent on the carbonyl carbon.

Gas-phase structural and conformational studies of amides are rare. Electron diffraction studies of *N*-methylformamide[7] and *N*-methylacetamide[8] are consistent with conformers having the alkyl groups oriented syn to the carbonyl group although the presence of small amounts of anti conformers could not be ruled out on the basis of these data. Semiempirical SCF–MO calculations at the MINDO/3 level yielded a relative energy of 1.5 kcal/mol for the anti conformer of *N*-methylacetamide.[9] Recently, we have obtained exchange-broadened gas-phase ^1H NMR spectra of *N*,*N*-dimethylacetamide,[10] *N*,*N*-dimethyltrifluoroacetamide,[11] and *N*,*N*-dimethylcarbamyl chloride[12] which are consistent with exchange rates which are faster by factors of ca. 20 and free energies of activation which are ca. 2 kcal/mol lower than corresponding values obtained for condensed-phase samples.

Very few studies of amides have been directed toward characterizing the internal rotation potential functions of bonds directly adjacent to the central peptide bond. The conformation about the *N*-alkyl bond in amides has been studied by NMR spectroscopy using lanthanide shift reagents as structural probes.[13,14] For *N*-ethylacetamide, a gauche conformer with the methyl group rotated 90° out of the plane of the other ($\tau_2 = 90°$) heavy atoms is most consistent with the experimental data. These studies are not sensitive to the barrier height, however. For *N*-isopropylacetamide, lanthanide shift data are most consistent with an asymmetrical structure with the methine hydrogen approximately 30° out of the plane defined by the peptide bond and atoms immediately adjacent to it.

Recently, we have observed microwave band spectra of species undergoing rapid vibrational redistribution.[15] Molecules with vibrational state densities in excess of a threshold of 5–50 states/cm^{-1} can undergo rapid vibrational redistribution,[16–18] and this collection of molecules produces intense R-branch a-type microwave band spectra devoid of K structure.

Since large molecules such as *N*-alkyltrifluoroacetamides have large vibrational partition functions, the population fraction in the ground state at 300 K is typically less than 1%. In these cases the vibrationally averaged structure is a much more relevant parameter than the ground-state structure, and for many heavy molecules the fraction of rapidly relaxing molecules can have a profound effect on this structure. Below we will show that microwave spectra of *N*-alkyltrifluoroacetamides are compatible with rapid vibrational redistribution, demonstrating effective coupling between the trifluoromethyl top internal rotation and the low-frequency vibrations in the alkyl chains.

Experimental Section

Sample Preparation. *N*-Alkyltrifluoroacetamides were prepared by the action of the appropriate amine on trifluoroacetic anhydride. In a typical reaction, trifluoroacetic anhydride (0.01 mol) was added dropwise from a syringe tube to the well-stirred amine at 0 °C. The mixture was then allowed to warm to room temperature and was stirred for 3 h under anhydrous conditions, and the product was then directly distilled. Yields were in the range 90–95%. All *N*-alkyltrifluoroacetamides exhibited the following characteristic strong absorptions in the infrared region: 3400–3250 cm^{-1} (N–H stretch), 1700–1650 cm^{-1} (amide C═O), and 1250–1150 cm^{-1} (broad, C–F stretch). NMR spectra and

---

[1] Jackman, L. M. In "Dynamic Nuclear Magnetic Resonance"; L. M., Jackman, Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 203–250.

[2] Stewart, W. E.; Siddall, T. H., III *Chem. Rev.* **1970**, *70*, 517–551.

[3] Drakenberg, T.; Dahlqvist, K.-I.; Forsen, S. *J. Phys. Chem.* **1972**, *76*, 2178–2183.

[4] (a) Thomas, L. P.; True, N. S.; Bohn, R. K. *J. Phys. Chem.* **1978**, *82*, 480–483. (b) Thomas, L. P.; True, N. S.; Bohn, R. K. *Ibid.* **1980**, *84*, 1785–1789.

[5] See, for example: True, N. S.; Bohn, R. K. *J. Phys. Chem.* **1978**, *82*, 478–479 and references cited therein.

[6] See, for example: True, N. S.; Silvia, C. J.; Bohn, R. K. *J. Phys. Chem.* **1981**, *85*, 1132–1137 and references cited therein.

[7] Kitano, M.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 631–634.

[8] Kitano, M.; Fukuyama, T.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 384–387.

[9] Hoesterley, B.; Neely, W. C.; Wordley, S. D. *Chem. Phys. Lett.* **1983**, *94*, 311–315.

[10] Ross, B. D.; True, N. S. *J. Phys. Chem.*, in press.

[11] Ross, B. D.; True, N. S.; Decker, D. L. *J. Phys. chem.* **1983**, *87*, 89–94.

[12] Ross, B. D.; True, N. S., submitted for publication in *J. Phys. Chem.*

[13] Schmidt, P.; Doskocilova, D.; Schneider, B. *J. Mol. Struct.* **1973**, *15*, 383.

[14] Doskocilova, D.; Schneider, B. *J. Mol. Struct.* **1976**, *31*, 337.

[15] True, N. S. *Chem. Phys. Lett.* **1983**, *101*, 326–330.

[16] Stewart, G. M.; McDonald, J. D. *J. Chem. Phys.* **1981**, *75*, 5949–5950.

[17] Stewart, G. M.; McDonald, J. D. *J. Chem. Phys.* **1983**, *78*, 3907–3915.

[18] Nesbitt, D. J.; Leone, S. R. *Chem. Phys. Lett.* **1982**, *87*, 123–127.

0022-3654/84/2088-3216$01.50/0

gas chromatographic analysis using a 6-ft SE-30 column of all samples used in subsequent microwave studies showed no detectable impurities. Observed boiling points (±1 °C at 760 torr) of *N*-alkyltrifluoroacetamides, $CF_3(O)C{-}NH(R)$, were as follows: R = CH_3, 160 °C; R = C_2H_5, 130 °C; R = *n*-C_3H_7, 156 °C; R = *i*-C_3H_7, 159 °C; R = *t*-C_4H_9, 171 °C; R = *i*-C_4H_9, 179 °C. The methyl derivative has a melting point of 48 °C.

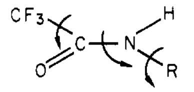
Microwave Measurements. All microwave measurments were obtained with a HP-8460A microwave spectrometer. Spectra of *N*-methyl- and *N*-*tert*-butyltrifluoroacetamides were obtained from 26.5 to 40 GHz. Spectra of *N*-ethyl-, *N*-isopropyl-, *N*-*n*-propyl-, and *N*-isobutyltrifluoroacetamides were obtained from 18 to 26.5 GHz. All spectra were recorded at room temperature and at ca. −30 °C. Acquisition parameters were the following: scan rate, 10 MHz/s; detector time constant, 1 s; Stark field, 3200 V/cm; detector crystal current, 150 mA. Samples were distilled into the cells to pressures of 30–70 mtorr. Reported frequencies are averaged over forward and reversed scans. Frequency accuracy, which is dependent on the shape and width of the bands, is ca. 50 MHz for the broad absorbances produced by *N*-alkyltrifluoroacetamides. Additional spectra of *N*-methyl- and *N*-ethyltrifluoroacetamide were obtained at −30 °C at 400 V/cm Stark field with a scan rate of 0.5 MHz/s in an attempt to observe K structure.

NMR Measurements. ^1H NMR spectra were obtained on a Nicolet 4.8-T wide-bore spectrometer with proton observation at 200.067 MHz. Liquid spectra were obtained for 1% samples in $CDCl_3$ in 5-mm tubes. Gas-phase spectra of samples containing the vapor pressure of the molecule at room temperature, generally ca. 0.2 torr, and approximately 2600 torr of SF_6[11] were obtained by using a 20-mm probe with a 17-cm^3 active volume. For gas-phase spectra typically 1000 transients were collected with a 2-s acquisition time and stored in 16 K of memory prior to Fourier transformation to produce spectra with signal/noise (S/N) ratios of at least 25/1. Temperature-dependent studies were performed with a 12-mm probe as described previously.[11]

Calculations. Experimental evidence, obtained by NMR studies in liquid-crystal solvents, indicates that the three bonds involving the nitrogen atom in acetamides are nonplanar.[19] However, since the N–H dihedral angle has almost no effect on calculated $B + C$ values, we assumed that the $O{=}C(C){-}NHR$ fragment is planar in the *N*-alkyltrifluoroacetamides studied. Rotational constants were calculated as a function of the torsional angles in the alkyl chains for both the syn and anti planar orientations about the peptide bond in all the trifluoroacetamides studied. Geometrical parameters used in these studies combined structural data reported in a high-resolution microwave spectroscopy study of methyl trifluoroacetate[20a] for the $CF_3{-}C{=}O$ fragment, data reported in an electron diffraction study of *N*-methylacetamide,[8] and geometry used for specific R groups[20b] in previous structural calculations of esters These parameters are listed in supplementary Table I, along with bond dipole moments[21] which were used to estimate *a*-axis moments in the series of trifluoroacetamides studied.

In order to ascertain if these molecules have sufficient vibrational-state density for rapid IVR, the internal energy dependence of this quantity was calculated by using a Rabinovitch–Setzer direct-count procedure.[22,23] Vibrational analyses for even the simplest trifluoroacetamides have not been reported. Therefore, relevant reported frequencies of methyl trifluoroacetate[19] and *N*-methylacetamide[23] were used in these calculations. Since torsional frequencies which are not known make the largest contribution to the state density, torsional frequencies were varied to ascertain uncertainties in state densities.

TABLE I: Summary of Low-Resolution Microwave Spectral Data of Trifluoroacetamides



R	$B + C$, MHz	fwhm, MHz	S/N
CH_3	2767.8 (2)	200	10
tert-butyl	1244.7 (7)	250	50
ethyl	1839.2 (1.5)	300	20
isopropyl	1436.1 (1.5)	300	25
n-propyl	1174.7 (1.2)	250	5
isobutyl	1016.0 (8)	250	15

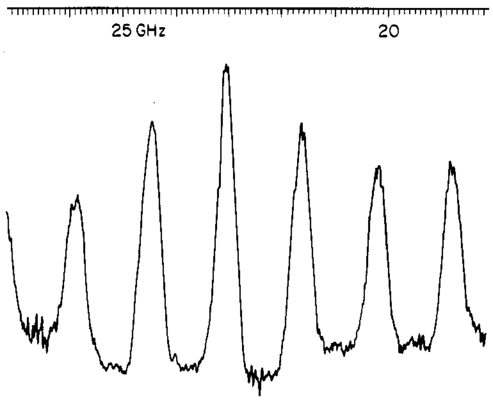


Figure 1. Low-resolution microwave spectrum of *N*-isopropyltrifluoroacetamide. Spectral data are summarized in supplementary Table II. Band frequencies appear in supplementary Table III.

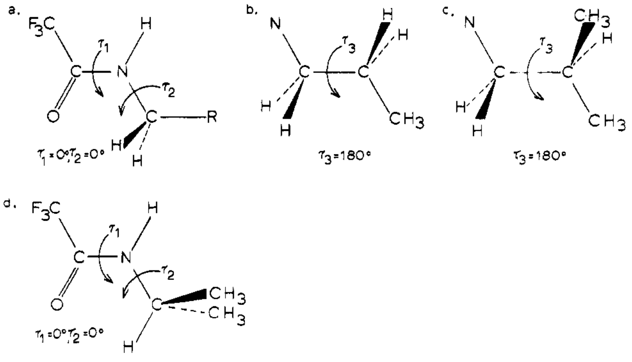


Figure 2. Torsional angle definitions of *N*-alkyltrifluoroacetamides: (a) τ_1 and τ_2 for *N*-ethyl- (R = CH_3), *N*-*n*-propyl- (R = CH_2CH_3), and *N*-isobutyltrifluoroacetamides (R = $CHC(CH_3)_2$); (b) τ_3 for *N*-*n*-propyltrifluoroacetamide; (c) τ_3 for *N*-isobutyltrifluoroacetamide; (d) τ_1 and τ_2 for *N*-isopropyltrifluoroacetamide.

Results

Low-Resolution Microwave Studies. Table I contains a summary of LRMW spectral data of six *N*-alkyltrifluoroacetamides. First we will describe features common to all spectra obtained and then discuss the structural implications of observed rotational constants for individual molecules.

At room temperature each molecule produces one R-branch a–type band series compatible with a single spectroscopic species. In each case bands are smooth and structureless. Figure 1 shows a representative spectrum of *N*-isopropyltrifluoroacetamide at 300 K which displays a single series of broad (ca. 300 MHz) structureless bands. For ethyl- and isopropyltrifluoroacetamide additional spectral traces were recorded at ~−30° C with scan rates of 0.5 MHz/s at Stark fields ranging from 800 to 3200 V/cm. Even at low Stark fields we failed to resolve any individual lines for either molecule. For each molecule listed in Table I there is a trend of increasing bandwidth with *J* value. Uncertainties in the base line and the spectral signal/noise ratio makes a quantitative measure of this trend impossible. In order to obtain

---

[19] Khetrapal, C. L.; Kunwar, A. C.; Ramaprasad S. *Mol. Cryst. Liq. Cryst.* **1976**, *34*, 123–126.

[20] (a) Jones, G. I. L.; Summers, T. D.; Owen, N. L. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 100–112. (b) Fitzwater, S.; Bartell, L. S. *J. Mol. Struct.* **1977**, *37*, 113–119.

[21] Smyth, C. P. *J. Phys. Chem.* **1937**, *41*, 209.

[22] (a) Rabinovitch, B. S.; Setzer, D. W. *Adv. Photochem.* **1964**, *3*, 1–82. (b) Robinson, P. A.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972; pp 110–112.

[23] Itoh, K.; Shimanouchi, T. *Biopolymers* **1970**, *9*, 383.

information about the conformations of these molecules, $B + C$ was calculated as a function of the relevant torsional angles shown in Figure 2. Below we discuss assignments of species with one, two, or three asymmetric internal rotors, respectively.

(*a*) *One Asymmetric Internal Rotor* (*about C–N Bond* (τ_1)). Since the rotational constant sum, $B + C$, is invariant to torsional orientations of groups with threefold symmetry, the only torsional angle which can be characterized by LRMW spectroscopy for *N*-methyl- and *N*-*tert*-butyltrifluoroacetamide is about the C–N peptide bond (τ_1).

Using the structural parameters listed in supplementary Table I, we calculated the torsional dependence of the rotational constant sum, $B + C$ (τ_1), for *N*-methyltrifluoroacetamide, which can be described by the sinusoidal function

$$B + C\,(\tau_1) = 2729\ (80)\ \text{MHz} + 465\ (28)\ (1 - \cos \tau_1)\ \text{MHz} \tag{1}$$

Uncertainties arise from uncertainties in the structural parameters. The large uncertainty in the second term arises from uncertainties in the CNC angle. The observed value of $B + C$ is 2767.8 (2) MHz, consistent with a $\tau_1 + 0°$ syn structure. It is useful to place an upper limit on the concentration of the anti species which might be present in the gas phase. No bands of any other species were observed, and the S/N of the observed band series was 10/1. Ray's asymmetry parameter ($\kappa = 2B - A - C/A - C$) ranges from −0.85 to 0 as τ_1 varies from 0° (syn) to 180° (anti). We estimate that structures with torsional angles greater than 90° would not produce band spectra. However, the anti conformer is predicted to have a large μ_a dipole moment, 1.4 D, and therefore should produce an intense line spectrum. Portions of the microwave spectra of *N*-methyltrifluoroacetamide were scanned under high-resolution conditions, and no strong lines were observed.

Similarly, for *tert*-butyltrifluoroacetamide the torsional dependence of $B + C$ can be described by a sinusoidal function

$$B + C\,(\tau_1) = 1264\ (38)\ \text{MHz} + 260\ (16)\ (1 - \cos \tau_1)\ \text{MHz} \tag{2}$$

and the observed value, 1244.7 (7) MHz, is compatible with a syn conformer having the *tert*-butyl group oriented syn to the carbonyl group. *syn*- and *anti-tert*-butyltrifluoroacetamides have κ values of −0.95 and −0.74, respectively, and both conformers would be observable. On the basis of reasonable structural parameters (supplementary Table I), the anti conformer of *N*-*tert*-butyltrifluoroacetamide is predicted to have a $B + C$ value of ca. 3200 MHz. Appropriate portions of its LRMW spectrum were scanned under high-resolution conditions at ca. −30 °C. No lines were observed. Calculated a-axis dipole moments are ca. 0.8 and 1.8 for the syn and anti conformers. On the basis of these results and the observed spectral S/N ratio of 50/1 for the syn absorbances, we estimate that any anti species which may be present must comprise less than 5% of the total sample.

(*b*) *Two Asymmetric Internal Rotors* (*about C–N* (τ_1) *and N–C* (τ_2) *Bonds*). Characterization of conformational species of *N*-ethyl- and *N*-isopropyltrifluoroacetamides is operationally similar since each molecule has two $B + C$ sensitive torsional angles. For both molecules $B + C$ was calculated as a function of the N–C (τ_2) torsional angle holding τ_1 fixed in syn (0°) and anti (180°) configurations.

For *N*-ethyltrifluoroacetamide it is convienient to define τ_2 as 0° when the alkyl group is anti planar to the peptide bond (this is the most extended form of the molecule) and 180° when it is syn. With this definition

$$B + C\,(\tau_2) = 1753\ (52)\ \text{MHz} + 125\ (8)\ (1 - \cos \tau_2)\ \text{MHz} \tag{3}$$

for $\tau_1 = 0°$ (syn) and

$$B + C\,(\tau_2) = 2208\ (66)\ \text{MHz} + 587\ (35)\ (1 - \cos \tau_2)\ \text{MHz} \tag{4}$$

for $\tau_1 = 180°$. The observed value of $B + C$ for *N*-ethyltrifluoroacetamide, 1839.2 (1.5) MHz, is clearly incompatible with any conformation having $\tau_1 = 180°$. It fits a structure with $\tau_1 = 0°$ and $\tau_2 \sim 70°$. The observed bandwidth, ~300 MHz, is larger than expected on the basis of the calculated κ value of −0.96 for this conformer. The calculated *a*-axis dipole moment for *syn*-*N*-ethyltrifluoroacetamide ranges from ca. 0.7 to ca. 1.0 D as a function of orientation about the *N*-ethyl bond.

LRMW a-type band intersites are a function of κ as well as the *a*-axis dipole moment. Although anti conformers are more asymmetric than syn conformers, they have larger calculated dipole moments. For *N*-ethyltrifluoroacetamide, LRMW spectra of anti conformers about τ_1 would be marginally observable, on the basis of model calculations. The anti–anti ($\tau_1 = 180°$, $\tau_2 = 0°$) conformer has a calculated κ of −0.72 and an *a*-axis dipole moment of ca. 1.50. The observed spectra are not consistent with significant (i.e., >30%) concentrations of anti conformers.

Both syn ($\tau_1 = 0°$) and anti ($\tau_1 = 180°$) structures of *N*-isopropyltrifluoroacetamide have minimum calculated values of $B + C$ when the methine hydrogen is syn planar to the peptide bond. Defining τ_2 with respect to the orientation of the methine hydrogen and with $\tau_2 = 0°$ for the syn-planar orientation, we may describe the calculated variation in $B + C$ (τ_2) of *N*-isopropyltrifluoroacetamide by the following functions.

For syn ($\tau_1 = 0°$)

$$B + C\,(\tau_2) = 1419\ (42)\ \text{MHz} + 72\ (4)\ (1 - \cos \tau_2)\ \text{MHz} \tag{5}$$

and for anti ($\tau_1 = 180°$)

$$B + C\,(\tau_2) = 1899\ (57)\ \text{MHz} + 322\ (19)\ (1 - \cos \tau_2)\ \text{MHz} \tag{6}$$

The observed value of $B + C$, 1436.1 (1.5) MHz, is only consistent with a syn ($\tau_1 = 0°$) structure. The effective torsional angle about τ_2 is ca. 40°. The calculated value of κ for such a conformer is ~−0.96, but the observed bandwidths (300 MHz) are not consistent with a rigid, nearly prolate configuration.

For isopropyltrifluoroacetamide, calculations indicate that κ ranges from −0.94 to −0.36 as a function of τ_2 for anti τ_1 values with a calculated *a*-axis dipole moment of ~2 D, roughly twice that of the observed syn conformer. An anti-anti structure ($\kappa \sim -0.94$, $\mu_a \sim 2$ D) would produce an a–type band spectrum roughly 4 times more intense than that of the observed syn form ($\kappa \sim -0.96$, $\mu_a \sim 1$ D) if both species were present in equal concentrations. Since only the syn species was observed with a spectral S/N of 25/1, significant amounts of an anti-anti conformer of *N*-isopropyltrifluoroacetamide can be ruled out.

(*c*) *Three Asymmetric Internal Rotors* (*about C–N* (τ_1), *N–C* (τ_1), *N–C* (τ_2), *and C–C* (τ_3) *Bonds*). For *N*-*n*-propyl- and *N*-isobutyltrifluoroacetamides, $B + C$ is sensitive to the orientation about three torsional angles. It is reasonable to again consider only syn ($\tau_1 = 0°$) and anti ($\tau_1 = 180°$) planar orientations of these alkyl groups with respect to the peptide bands, and it is reasonable to consider gauche and anti staggered orientations about τ_3 (OCCC) within the alkyl chains.

Only one conformational species of *N*-*n*-propyltrifluoroacetamide with a $B + C$ value of 1174.7 (1.2) MHz was observed in LRMW spectra. The most extended syn ($\tau_1 = 0°$) form of this molecule has a calculated $B + C$ value of 1120 MHz corresponding to a $\tau_1 = 0°$, $\tau_2 = 0°$, $\tau_3 = 180°$ structure. The $\tau_1 = 180°$, $\tau_2 = 0°$, $\tau_3 = 180°$ structure which is the most extended anti form has a calculated $B + C$ value of 1460 MHz. The observed form is clearly not consistent with an anti configuration about the peptide bond. The calculated torsional dependence of $B + C$ (τ_2) for $\tau_1 = 0°$, $\tau_3 = 180°$ has the form

$$B + C\,(\tau_2) = 1119\ (33)\ \text{MHz} + 94\ (6)\ (1 - \cos \tau_2)\ \text{MHz} \tag{7}$$

For structures with $\tau_3 = 60°$ and $-60°$ calculated $B + C$ values are ca. 200 MHz or 20% larger. The observed value is consistent with a torsional angle, τ_2, of ca. 65°, close to that observed for *N*-ethyltrifluoroacetamide. The observed bandwidths are broad, ca. 250 MHz, while the calculated κ value is −0.99.

Anti conformers of *N*-*n*-propyltrifluoroacetamide which also have anti configuration in the alkyl chain are predicted to produce observable LRMW spectra. Since the S/N, 5/1 obtained for this spectrum is so low, we cannot rule out the presence of appreciable quantities of anti species.

Similar calculations for *N*-isobutyltrifluoroacetamide demonstrate that the single conformational species observed, which has a $B + C$ value of 1016.0 (8) MHz, is consistent with a syn ($\tau_1 = 0°$) structure with an effective τ_2 value, defined with respect to the methine hydrogen of $\sim 60°$, similar to that observed for *N*-*n*-propyltrifluoroacetamide where the τ_3 torsional angle is also staggered.

NMR Spectra. Gas-phase ^{1}H NMR spectra were obtained for *N*-methyl- and *N*-ethyltrifluoroacetamide. The very low volatilities of the larger trifluoroacetamides preclude gas-phase NMR studies. Two types of experiments were performed. High-pressure studies were performed to observe coupling constants, and temperature-dependent studies were performed to search for line-broadening effects indicative of chemical exchange.

$^5J_{\text{H-F}}$ coupling occurs predominately by the through-space mechanism.[24] Therefore, larger couplings are expected for protons of a methyl group located anti to the carbonyl carbon. In *N*,*N*-dimethyltrifluoroacetamide, the two methyl resonances have very similar chemical shifts, 3.098 and 3.215 ppm in the gas phase referenced to gaseous Me_4Si. In the liquid phase, the upfield resonance is a quartet with $^5J_{\text{H-F}}$ of 0.7 Hz (syn) and the downfield resonance has a $^5J_{\text{H-F}}$ of 1.5 Hz (anti). Earlier studies reversed these assignments.[25,26] Under slow exchange conditions, at high bath gas pressures (long T_2), it is possible to obtain gas-phase ^{1}H NMR spectra with natural line widths less than 1.0 Hz. For *N*,*N*-dimethyltrifluoroacetamide, activation parameters are high; coalescence in the gas phase is observed at 46 °C on our 4.8-T spectrometer. Slow-exchange spectra are obtained at room temperature with partially resolved coupling. Since long-range $^5J_{\text{H-F}}$ coupling constants differ by a factor of 2 for the two methyl resonances, it is possible to use this parameter to conformationally assign spectra of monosubstituted amides.

Gas-phase NMR spectra of *N*-methyltrifluoroacetamide with a S/N of 50/1 display a well-resolved doublet centered 2.846 ppm downfield from gaseous Me_4Si. The observed line shape and 1.43-Hz line width are consistent with a $^5J_{\text{H-F}}$ coupling constant of ca. 0.6 Hz and agree with expectations for a syn conformer. The $^3J_{\text{H-H}}$ coupling constant is 4.91 Hz. Gas-phase NMR spectra of *N*-ethyltrifluoroacetamide with a S/N of 25/1 are also consistent with a single species. In this case, the proton resonance for the methylene group was broad and coupling constants could not be estimated. Liquid-phase NMR spectra (S/N > 500/1) of all six *N*-alkyltrifluoroacetamides at 300 K are consistent with a single species. The $^5J_{\text{H-F}}$ coupling constant is 0.589 for methyltrifluoroacetamide, and the $^5J_{\text{H-F}}$ coupling is not resolvable for ethyltrifluoroacetamide or any of the larger species.

Temperature-dependent line-width and frequency measurements were obtained for gaseous *N*-methyltrifluoroacetamide over the range of 10–100 °C. ν_{CH_3} ranged from 2.852 ppm at 10 °C to 2.838 ppm at 100 °C. N-H decoupled line widths were temperature invariant over this range, demonstrating that if exchange is occurring, then the population in the higher energy site is much smaller.[27]

Discussion

A principal result of this study is that *N*-alkyltrifluoroacetamides preferentially adopt the syn conformation about the peptide bond. Of the six trifluoroacetamides studied, *N*-*tert*-butyltrifluoroacetamide has the bulkiest R group, and on the basis of model calculations and a careful search of the rotational spectrum, an upper limit of 5% can be placed on the relative population of the anti conformer. Although calculated asymmetry parameters far from the prolate limit and lower S/N ratios for other *N*-alkyltrifluoroacetamides yield less definitive results for upper limit anti population estimates, LRMW spectra are not consistent with appreciable amounts of anti conformers for any of the molecules studied. Gas-phase NMR spectra of *N*-methyl- and *N*-ethyltrifluoroacetamide with a S/N of 50/1 and 25/1, respectively, are consistent with a single conformational species, and in the case of *N*-methyltrifluoroacetamide, the observed coupling constants confirm that the observed species has the methyl group oriented syn to the carbonyl group.

These results are consistent with previous liquid studies of monoalkylformamides and -acetamides. For monoalkylformamides, the dominant conformational form has the alkyl group syn to the carbonyl group. The percentage of the syn conformer is 92% for *N*-methylformamide and 70–80% for *N*-*tert*-butylformamide.[2] LRMW spectra of *N*-*tert*-butylformamide are consistent with ca. 70% syn conformer.[28] Resonances from anti conformers were not detected in liquid NMR spectra of *N*-methylacetamide and *N*-*tert*-butylacetamide. Other amides with larger substituents on the carbonyl carbon exist exclusively in the syn conformation as evidenced by NMR spectroscopy.[2]

Characterization of the alkyl chain torsional angles, τ_2 and, where pertinent, τ_3, is less straightforward since two contrasting models will predict the observed $B + C$ values. The observed $B + C$ values are consistent with rigid conformers having gauche ($\tau_2 \approx 70°$) torsional angles in all cases. Recently, however, we have demonstrated that large populations of rapidly relaxing, vibrationally excited species are present for large, nonrigid molecules at room temperature.[28] Depending on the shape of the low-frequency vibrational potential functions, these species can have effective torsional angles quite different from those of conformers in their ground vibrational states. Below we discuss spectral predictions based on rigid conformational models and predictions allowing for rapid vibrational redistribution and demonstrate that the second model can explain several unusual spectral features observed in LRMW spectra of *N*-alkyltrifluoroacetamides.

The most unusual feature is the simplicity of the LRMW spectra observed. For each molecule studied only one spectroscopic species was observed, in contrast to LRMW studies of many other molecules of similar structural complexity which demonstrate complex conformational mixtures. For example, three spectroscopic species have been observed in LRMW spectra of ethyl esters[29] and as many as five species in LRMW spectra of *N*-propyl esters.[30] Occasionally, additional band series have been observed[31,32] in LRMW spectra of esters at low temperatures, but the low sample volatility of the amides studied precluded measurements at temperatures much below ambient. Other unusual features include the large observed bandwidths, generally 200–300 MHz, which do not correlated with calculated asymmetry parameters. In every case, the bands display a total absence of resolvable fine structure when scanned under typical high-resolution conditions. No sharp lines were observed in any of the spectra recorded. Consider as an illustrative example *N*-ethyltrifluoroacetamide. The torsional angle $\tau_2 \sim 70°$, compatible with the observed $B + C$ value, is reasonable on the basis of comparisons with compounds of similar structure such as ethyl esters and ethyl thioesters. A similar structure was also compatible with results obtained from NMR studies using lanthanide shift reagents for *N*-ethylacetamide in the liquid phase.[13,14] A gauche conformer, however, has a calculated κ value of ca. −0.96 (2), and most gauche molecules of similar asymmetry produce very narrow bands under LRMW conditions, frequently with sharp, well-resolved vibrational satellite structure.[6] In contrast, the observed bands are smooth, structureless, and ca. 300 MHz wide. An alternate interpretation considers the effects of rapid vibrational redistribution. Infrared fluorescence measurements of 23 representative molecules demonstrate that collisionless vibrational

---

[24] Harris, R. K. "Nuclear Magnetic Resonance Spectroscopy"; Pitman Publishing Co.: London, 1983.

[25] Abramson, K. H.; Inglefield, P. T.; Krakower, E.; Reeves, L. W. *Can. J. Chem.* **1966**, *44*, 1685–1698.

[26] Reeves, L. W.; Shaddick, R. C.; Shaw, K. N. *Can. J. Chem.* **1971**, *49*, 3683–3691.

[27] Anet, F. A. L.; Basus, V. J. *J. Magn. Reson.* **1978**, *32*, 339–343.

[28] True, N. S. *J. Mol. Struct.* **1984**, *112*, 333–336.

[29] True, N. S.; Bohn, R. K. *J. Am. Chem. Soc.* **1976**, *98*, 1188–1194.

[30] True, N. S.; Bohn, R. K. *J. Phys. Chem.* **1978**, *82*, 466–473.

[31] True, N. S.; Bohn, R. K. *J. Phys. Chem.* **1977**, *81*, 1667–1671.

[32] True, N. S.; Bohn, R. K. *J. Phys. Chem.* **1978**, *82*, 474–477.

redistribution can occur in molecules with internal energy contents where the state density is ca. 5-50 states/cm^{-1}.[17] Since *N*-ethyltrifluoroacetamide has several low-frequency torsional vibrations and low-frequency vibrations involving the amine group, we expect it will achieve high state densities at low internal energies. Using available spectral data employing a direct-count procedure, and including all vibrational and rotational states, we calculated the energy dependence of the state density. A state density of 50 states/cm^{-1} is achieved at ca. 0.1 kcal/mol for this molecule, and a state density of 100 states/cm^{-1} is achieved at an internal energy of 0.2 kcal/mol. The very low critical energy is primarily the result of the low torsional frequency, 25 cm^{-1}, used for the trifluoromethyl top and the small rotational constants ($B + C \sim 1.8$ GHz) of this molecule. These calculations assume a twofold potential with a 5 kcal/mol barrier for τ_2.

The same set of assumed vibrational frequencies was used to calculate the total vibrational partition function of *N*-ethyltrifluoroacetamide at 300 K which is ca. 6000. Of special interest is the population of molecules with energy in excess of the threshold for rapid IVR. We estimate this population as between 80% and 96% of the total. These rapidly vibrationally redistributing molecules will have an average rotational constant which depends on the form of the internal rotation potential function and the rotational constant dependence on torsional angles. Since torsional potential functions about τ_2 for *N*-ethyltrifluoroacetamide are completely unknown, an effective $B + C$ for rapidly vibrationally redistributing molecules cannot be estimated. Bands of these molecules are expected to be lifetime broadened and widths limited by the Stark field used in these experiments.

N-Ethyltrifluoroacetamide is a structural analogue of ethyl trifluoroacetate. We would expect it to have a slightly lower internal energy threshold for rapid IVR since low-frequency deformation of the N-H group would contribute to its state density. It is informative to compared the present results with those obtained previously for ethyl trifluoroacetate. Ethyl trifluoroacetate displays a very intense series of broad, structureless bands and in addition two weak-band series. The weak series increase in intensity at low temperature, demonstrating that the corresponding species are more stable than those producing the intense series. Ethyl trifluoroacetate has a vibrational state density of 100 states/cm^{-1} at an internal energy of 0.2 kcal/mol, and the origin of the intense-band series has recently been attributed to molecules whose internal energies ($\sim$1 kcal/mol) are above the threshold for rapid vibrational redistribution.[15]

In the rapid IVR formalism, since ground-state band spectra were not observed, the ground-state conformation cannot be established except in symmetric cases such as *N*-methyl- and *N*-*tert*-butyltrifluoroacetamide. For the more asymmetric trifluoroacetamides, the ground state may have a different effective torsional angle with a population too small to detect at room temperature and/or its geometry may be close to the effective torsional angle of the rapidly redistributing molecules and produce unresolvable spectra. Experimental results cannot differentiate between these two possibilities.

Despite this ambiguity, it is possible to distinguish the conformation about bonds with high rotational barriers, and an unambiguous result of this study is the preferential syn conformation about the peptide bond of *N*-alkyltrifluoroacetamides.

Acknowledgment. This research was supported by the National Institutes of Health through Grant No. PHS-GM-29985-01. We thank Gerald Lindley for help with preliminary calculations.

Supplementary Material Available: Tables containing structural parameters used in rotational constant calculations and assigned microwave bands of *N*-alkyltrifluoroacetamides (4 pages). Ordering information is given on any current masthead page.

Thermodynamic, Kinetic, Structural, and Surface Studies of $Y_6Fe_{23-x}Mn_x$ Alloys and Their Hydrides

George Bayer and W. E. Wallace*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received: November 21, 1983)

Pressure-composition isotherms at 0 and 22 °C were obtained for the systems Y_6Fe_{23}-H_2, Y_6Mn_{23}-H_2, and $Y_6Fe_{23-x}Mn_x$-H_2 with $x = 1, 3, 5, 14$, and 18. These isotherms were used to derive enthalpies and entropies of desorption. The ternary systems for the regime $11.50 \leq x \leq 17.25$ exhibit very anomalous magnetic properties and their hydrides display anomalous thermodynamics, e.g., negative entropies of desorption of hydrogen. Hydride stability was greatest for the end-member systems. Crystallographic work shows that all ternaries and all hydrides occur in the Th_6Mn_{23} structure, fcc and space group *Fm*3*m*. Hydrogen absorption is rapid in all cases; little activation is required. In the case of Y_6Fe_{23} a short induction period was involved for initial H_2 absorption whereas there was none for Y_6Mn_{23}. By Auger spectroscopy it has been found that Mn segregates to the surface in Y_6Mn_{23}, whereas in Y_6Fe_{23} the surface is Fe deficient. The surface composition of Y_6Mn_{23} resembles that observed earlier for rare earth-Mn intermetallic compounds.

Introduction

In recent years the rare earth-Mn and rare earth-Fe compounds of 6:23 stoichiometry and their hydrides have been intensively studied[1-8] in this laboratory and elsewhere. The R_6Mn_{23} systems and their hydrides have been particularly well studied. The heavy rare earths form 6:23 compounds with both Mn and Fe,[9] but the Fe compounds are much more difficult to prepare, and they have been the subject of much less study than their Mn analogues. Both the Mn and Fe compounds absorb significant amounts of hydrogen under ambient conditions, the Mn absorbing approximately 23

---

(1) V. K. Hardman, Ph.D. Dissertation, University of Missouri—Rolla, Rolla, MO, 1979.

(2) F. Pourarian, E. B. Boltich, W. E. Wallace, R. S. Craig, and S. K. Malik, *J. Magn. Magn. Mater.*, **21**, 128 (1980).

(3) F. Pourarian, E. B. Boltich, W. E. Wallace, and S. K. Malik, *J. Less-Common Met.*, **74**, 153 (1980).

(4) A. T. Pedziwiatr, E. B. Boltich, W. E. Wallace, and R. S. Craig in "Electronic Structure and Properties of Hydrogen in Metals", P. Jena and C. B. Satterthwaite, Eds., Plenum Press, New York, 1983, p 367.

(5) K. Hardman, J. J. Rhyne, and W. J. James, *J. Appl. Phys.*, **52**, 2049 (1981).

(6) J. J. Rhyne, K. Hardman-Rhyne, H. K. Smith, and W. E. Wallace, *J. Less-Common Met.*, **94**, 95 (1983).

(7) Kay Hardman-Rhyne, H. Kevin Smith, and W. E. Wallace, *J. Less-Common Met.*, **96**, 201 (1984).

(8) H. Kevin Smith, W. E. Wallace, and R. S. Craig, *J. Less-Common Met.*, **94**, 89 (1983).

(9) W. E. Wallace, "Rare Earth Intermetallics", Academic Press, New York, 1980, p 180.

0022-3654/84/2088-3220$01.50/0