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Low-Resolution Microwave Spectroscopy. III. Three Conformers in Ethyl Trifluoroacetate, Ethyl Chloroformate, and Ethyl Cyanoformate[1]

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Abstract: Low-resolution microwave spectra of ethyl trifluoroacetate display three a-type band series characterized by $B + C$ values of 1842 ± 2, 1947 ± 2, and 1904 ± 5 MHz associated with three rotameric forms designated extended, compact, and intermediate, respectively. Ethyl chloroformate and ethyl cyanoformate also display band spectra of three conformations with $B + C$ values of 2819 ± 3 MHz (2762 ± 3 MHz, ^{37}Cl), 3061 ± 3 MHz (2989 ± 3 MHz, ^{37}Cl), and 2954 ± 5 MHz (2885 ± 17 MHz, ^{37}Cl) for the chloroformate and 2752 ± 2, 2952 ± 5, and 2870 ± 2 MHz for the cyanoformate. For each compound the rotational constants of the extended species are consistent with a cis-trans [$\tau(\mathrm{O{=}COC}) = 0°$, $\tau(\mathrm{COCC}) = 180°$] heavy-atom planar structure, the compact species with a cis-gauche [$\tau(\mathrm{O{=}COC}) = 0°$, $\tau(\mathrm{COCC}) \sim 90°$] structure, and the intermediate species with a gauche-gauche [$\tau(\mathrm{O{=}COC}) \sim 45°$, $\tau(\mathrm{COCC}) \sim 240°$] structure. The cis-trans and cis-gauche structures have been previously identified in ethyl formate. For all three ethyl esters, the temperature dependence of the band intensities indicates that the extended and compact forms have nearly equal energy and the intermediate species have 1-2 kcal/mol higher energy. Characteristics of the band shape of the intermediate forms suggest that they have unusually flexible configurations.

Studies of the structures of methyl esters have consistently demonstrated the presence of a single conformer while studies of ethyl esters have frequently indicated the presence of more than one conformer.[2] The cis-heavy-atom-planar configuration of Figure 1a is the observed conformation for all methyl esters which have been unambiguously characterized. The cis-planar conformation of methyl chloroformate was determined by electron diffraction.[3] That work and a dipole moment study,[4] which showed a strong temperature dependence of the dipole moment, indicate a large amplitude of torsional motion about the carbonyl carbon to the ether oxygen bond. Methyl formate[5-11] and acetate[9-11] were demonstrated to have the cis-planar configuration. No conclusive evidence for other rotational isomers has been reported for either of these molecules in the gas phase. Similar results were obtained by infrared and microwave spectroscopic studies of methyl chloroformate,[12-15] methyl cyanoformate,[11,16] methyl fluoroformate[11,16] (here the similarity of the atomic masses of fluorine and oxygen prevented an unambiguous deduction of molecular structure), methyl propiolate,[11,16] and methyl trifluoroacetate.[17]

Spectroscopically distinct rotational isomers about both the C-O and O-ethyl bonds are possible for ethyl formates and acetates. Two rotational isomers of ethyl formate have been assigned by microwave spectroscopy[18] to the cis-trans and cis-gauche configurations of Figures 1b and 1c. They differ in energy by 186 ± 60 cal/mol, the planar form being more stable. The trans-trans structure (Figure 1d) was not observed. Small populations of other rotational isomers were not ruled out and models such as Figure 1e involving nonplanar configurations about the C-O bond were not considered. Rotational isomerism in ethyl chloroformate,[19] ethyl cyanoformate,[19] and ethyl fluoroformate[20] have been demonstrated in recent infrared studies. The number and nature of the isomers present could not be unambiguously determined and the evidence for rotational isomerism in ethyl chloroformate was not conclusive. Dipole moment measurements on ethyl chloroformate were interpreted in terms of a trans-trans structure[4] (Figure 1d).

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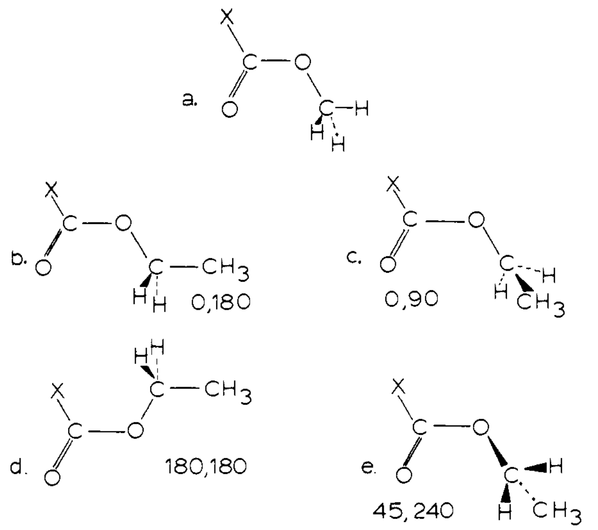

Figure 1. Conformations of methyl formates, (a) planar cis, and ethyl formates: (b) planar cis-trans, (c) cis-gauche, (d) planar trans-trans, and (e) gauche-gauche.

Low-resolution microwave spectroscopy (LRMW) is a powerful technique for determining conformation of selected gaseous compounds.[21,22] From the temperature dependence of LRMW intensities relative energies of the conformers can be determined.[21] This study was undertaken to provide more information on the nature of rotational isomerism in ethyl formates and is the first application of temperature-dependent LRMW to determining energy differences among rotational isomers. This study determines the conformational species present in gaseous ethyl cyanoformate, ethyl chloroformate, and ethyl trifluoroacetate and the energy differences among them. An ab initio molecular orbital calculation on ethyl formate was carried out to help interpret the results.

Experimental Section

All microwave measurements were made on a Hewlett-Packard Model 8460A microwave spectrometer. Spectra of ethyl trifluoroacetate, ethyl chloroformate, and ethyl cyanoformate were obtained from 18 to 40 GHz. For each sample, spectra were recorded at two temperatures: room temperature and a low temperature with the sample cell packed in dry ice. In all cases the Stark voltage was 3200 V/cm and scan rates were 5 or 10 MHz/s with detector time constants of 0.3 or 1 s.

Samples were distilled into the waveguide to pressures of 30–70 mTorr. In order to minimize experimental error in intensity measurements, the sample pressure and crystal current were kept constant while each spectrum was being recorded. The temperature dependence of the intensities was determined from ratios of band areas of the room temperature and low-temperature spectra for each $J + 1 \leftarrow J$ transition observed. Frequency measurements are frequencies of the band maxima averaged over forward and reverse scans. Frequency accuracy is dependent on the shape and width of the bands and ranges from about 30 to 5 MHz for the samples studied.

Samples of ethyl chloroformate and ethyl cyanoformate were obtained from Aldrich Chemical Co. Ethyl chloroformate was fractionally distilled prior to use. Ethyl trifluoroacetate was synthesized from Aldrich Gold Label trifluoroacetic anhydride and reagent grade ethanol. The reaction was carried out at 0 °C with the anhydride present in slight excess. The product was washed several times with a saturated solution of sodium bicarbonate and fractionally distilled. A fraction boiling at 78 °C was used in this study. All samples were characterized by their proton NMR spectra and the purity of each was established to be in excess of 98% by gas–liquid chromatography on an SE-30 column.

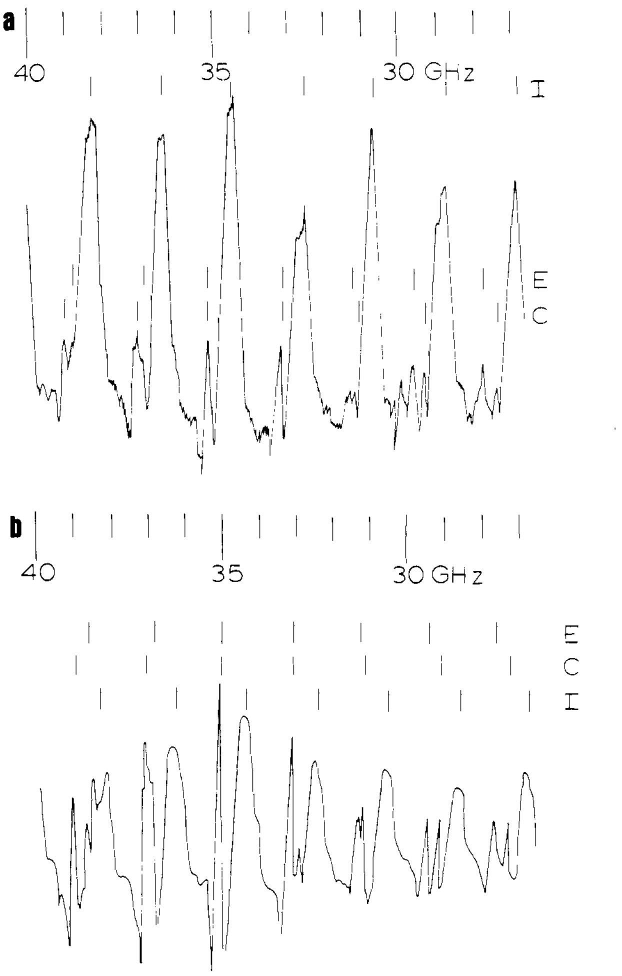

Figure 2. LRMW spectra of ethyl trifluoroacetate. (a) R-band spectrum at 20 °C scanned at 10 MHz/s with a 1-s time constant. The band markers are calculated from $(J + 1)(B + C)$ with $B + C = 1842$, 1947, and 1904 MHz for the extended (E), compact (C), and intermediate (I) species, respectively. (b) Same as (a) except the temperature is ca. −63 °C.

Results

Ethyl Trifluoroacetate. Low-resolution R-band spectra of ethyl trifluoroacetate at 20 °C and low temperature are shown in Figure 2. Three major results can be derived from the spectra.

There are three band series corresponding to rotational spectra of three conformational species. The series are all a-type bands and obey the relationship

$$\nu_a = (B + C)(J + 1) \qquad (1)$$

The spectral data are summarized in Table I. Values of $B + C$ for the three series are 1842 ± 2, 1947 ± 2, and 1904 ± 5 MHz. The corresponding conformers are designated extended, compact, and intermediate, respectively. A low-resolution $B + C$ value may be corrected to an effective ground state rotational constant $B_0 + C_0$ using the empirical relation[22]

$$(B + C)/(B_0 + C_0) = (0.025 \pm 0.005)(\kappa + 1) \qquad (2)$$

where κ is Ray's asymmetry parameter. This equation yields $B_0 + C_0$ values for the three series of 1839 ± 4, 1944 ± 4, and 1900 ± 8 MHz.

The relative intensities of the three band series vary dramatically from room temperature, ~1:1.2:20, to low temperature, ~1:1:5 for the extended, compact, and intermediate species, respectively. Relative energies of the conformers were determined as follows. The entire R-band spec-

Table I. LRMW Spectral Data of Ethyl Trifluoroacetate

$J+1$	ν(20 °C), MHz	ν(−63 °C), MHz	$B+C$ (20 °C), MHz	$B+C$ (−63 °C), MHz
		Extended Conformer		
11	20 270		1842.7	
12	22 125		1842.9	
13	23 950		1842.3	
14	25 815		1843.9	
15	27 625	27 660	1841.6	1844.0
16	29 515	29 490	1844.7	1843.1
17	31 365	31 310	1845.0	1841.8
18	33 115	33 110	1839.7	1839.4
19	35 035	35 045	1843.9	1844.5
20	36 830	36 855	1841.8	1842.8
21	38 660	38 635	1841.0	1839.8
	Av $B+C$		1842 ± 2	
	κ^a		−0.92 ± 0.01	
	Estimated $B_0+C_0{}^b$		1839 ± 4	
		Compact Conformer		
10	19 465		1946.5	
11	21 420		1947.3	
12	23 360		1946.7	
13	25 320		1946.1	
14	27 260	27 260	1947.1	1947.1
15	29 230	29 210	1948.6	1947.3
16	31 160	31 150	1947.0	1946.9
17	33 115	33 110	1947.9	1947.6
18	35 035	35 045	1946.4	1946.9
19	36 980	36 990	1946.3	1946.8
20	38 940	38 950	1947.0	1947.5
	Av $B+C$		1947 ± 2	
	κ^a		−0.95 ± 0.01	
	Estimated $B_0+C_0{}^b$		1944 ± 4	
		Intermediate Conformer		
10	19 200		1920.0	
11	21 085		1916.7	
12	22 975		1914.6	
13	24 930		1917.7	
14	26 787	26 680	1913.4	1905.7
15	28 685	28 560	1912.4	1904.0
16	30 590	30 455	1911.9	1903.4
17	32 480	32 400	1910.6	1905.9
18	34 372	34 305	1909.6	1905.8
19	36 267	36 175	1908.8	1903.4
20	38 175	38 065	1908.8	1903.2
	Av $B+C$		1904 ± 2	
	κ^a		−0.92 ± 0.02	
	Estimated $B_0+C_0{}^b$		1900 ± 8	

[a] Calculated from assumed models, $\kappa = (2A - B - C)/(A - C)$.
[b] Calculated from $(B + C)/(B_0 + C_0) = 0.025\ (\pm 0.005)\ (1 + \kappa)$.[22]

Table II. Band Intensities and Relative Energies of the Three Species of Ethyl Trifluoroacetate, Chloroformate, and Cyanoformate

	Extended	Compact	Intermediate
	Ethyl Trifluoroacetate		
Rel int (20 °C)	1	0.8	20
Rel int (ca. −63 °C)	1	1	5
Rel energy, kcal/mol	0	−0.3 ± 0.5	1.9 ± 0.6
	Ethyl Chloroformate		
Rel int (25 °C)	1	0.4	0.8
Rel int (ca. 63 °C)	1	0.7	0.3
Rel energy, kcal/mol	0	−0.6 ± 0.7	1.7 ± 0.5
	Ethyl Cyanoformate		
Rel int (25 °C)	1	0.6	3
Rel int (ca. 63 °C)	1	0.6	1
Rel energy, kcal/mol	0	−0.2 ± 0.3	1.7 ± 0.4

trum was scanned at 20 °C with the sample pressure, the settings of the detection system, and the crystal current maintained constant. The spectrum was similarly scanned with the sample cell packed in dry ice. The intensity of a given band is a function of many parameters including frequency, J value, dipole moment, Stark voltage, asymmetry parameter, microwave power, detector sensitivity, and the concentration of the absorbing species. The ratio of the intensities of a given band at two temperatures is proportional to the concentration ratio of the species. The energy of the extended conformer was chosen as zero and the ratio of the band areas of that species at the two temperatures defined the constant of proportionality. The energies of the intermediate and compact conformers relative to the extended species were determined by dividing the ratio of the intensities of the bands of one conformer at −63 and 20 °C by the corresponding ratio of the intensities of the extended conformer and setting the ratio equal to $\exp(-\Delta E/210R)/\exp(-\Delta E/293R)$, where ΔE is the energy difference between one conformer and the extended species. The relative energies are 0, −0.3 ± 0.5, and 1.9 ± 0.5 kcal/mol for the extended, compact, and intermediate species, respectively. These results as well as the approximate relative intensities of the band series of the conformers compared to each other are tabulated in Table II.

Uncertainties assigned to conformational energy differences arise from two major sources, the uncertainty in the temperature of the sample and the uncertainty in determining the band areas due to low signal/noise ratios and variation of the crystal current. The temperature of the gas is not well defined when the sample cell is packed in dry ice because it is open to an inlet manifold at room temperature. Also, the ends of the two sample sections of the X-band waveguide were only at about −5 °C to minimize condensation. The exterior surface of one part of the waveguide varied from −72 to −65 °C during runs and the authors estimate the average gas temperature to be −63 ± 15 °C. The band area uncertainty caused by fluctuations in the crystal current (150 ± 15 μA in these experiments) and the signal/noise ratio was estimated by the statistical variation of the ratios of the band areas at the two temperatures. Compared to these two large sources of error other sources of error[23] were judged of negligible importance. For the relatively small energy differences between the extended and compact species, the band area uncertainty is the major source of error. For the larger energy differences between the extended and intermediate forms the uncertainties due to band area and temperature are comparable. The uncertainties reported are the square roots of the sums of the squares of the error estimates of temperature and band area.

There are striking qualitative differences between the bands of the intermediate species and those of the other species. The intermediate bands are very broad, ranging from 280 MHz bandwidth at half-height at J = 10 to 450 MHz at J = 21 at room temperature. The bandwidths in the other series are all about 200 MHz and show no systematic change with J. There is a systematic decrease of $\nu/(J + 1)$ as J increases for the room-temperature spectrum of the intermediate species (Table I). This shift disappears at low temperature and is not evident in the bands of the other species.

Ethyl Chloroformate. Low-resolution K-band spectra of ethyl chloroformate at 25 and ca. −63 °C are shown in Figure 3. These spectra are characterized by six a-type band series which we assign to three rotational isomers displaying resolved chlorine isotopic species. $B + C$ values for these series are 2819 ± 3 MHz (2762 ± 3 MHz), 3061 ± 3 MHz (2989 ± 3 MHz), and 2954 ± 5 MHz (2885 ± 17 MHz) for the extended, compact, and intermediate series, respectively. The parenthetical numbers refer to the ^{37}Cl isotopic

Table III. LRMW Spectral Data of Ethyl Chloroformate

	^{35}Cl		^{37}Cl	
$J+1$	ν, MHz	$B+C$, MHz	ν, MHz	$B+C$, MHz
	Extended Conformer			
7	19 745	2820.7	19 335	2762.2
8	22 560	2816.3	22 100	2762.5
9	25 385	2820.6	24 870	2763.4
Av $B+C$	2819 ± 3		2762 ± 3	
κ^a	−0.91 ± 0.01		−0.91 ± 0.01	
Estimated $B_0 + C_0{}^a$	2813 ± 4		2756 ± 4	
	Compact Conformer			
6	18 370	3061.7		
7	21 425	3060.7	20 905	2986.4
8	24 495	3061.9	23 925	2990.7
Av $B+C$	3061 ± 3		2989 ± 3	
κ^a	−0.94 ± 0.02		−0.94 ± 0.02	
Estimated $B_0 + C_0{}^a$	3057 ± 5		2984 ± 5	
	Intermediate Conformer			
7	20 685	2955.0	20 110	2872.8
8	23 620	2952.2	23 080	2885.0
9			26 070	2896.7
Av $B+C$	2954 ± 5		2885 ± 17	
κ^a	−0.91 ± 0.02		−0.92 ± 0.02	
Estimated $B_0 + C_0{}^a$	2947 ± 7		2879 ± 20	

[a] See footnotes to Table I.

species. Corresponding effective $B_0 + C_0$ values for these series were calculated from eq 2 and are 2813 ± 4 MHz (2756 ± 4 MHz), 3057 ± 5 MHz (2984 ± 5 MHz), and 2947 ± 7 MHz (2879 ± 20 MHz). The spectral data of ethyl chloroformate are summarized in Table III. The relative intensities of the series are markedly temperature dependent. The intensity ratios are 1:0.4:0.8 at 25 °C and 1:0.7:0.3 at ca. − 63 °C for the extended, compact, and intermediate band series, respectively. Relative energies were calculated using the procedure described above for ethyl trifluoroacetate. The relative energies of the extended, compact and intermediate species are 0, −0.6 ± 0.7 kcal/mol, and 1.7 ± 0.5 kcal/mol. The bandwidths of the intermediate conformer of ethyl chloroformate are not appreciably larger than those of the extended and compact conformers nor are the band positions temperature dependent.

Ethyl Cyanoformate. Ethyl cyanoformate produced the low-resolution K-band spectra at 25 and ca. −63 °C shown in Figure 4. Again three series of a-type bands are present. They yield $B + C$ values of 2752 ± 2, 2954 ± 5, and 2870 ± 2 MHz. The corresponding $B_0 + C_0$ values are 2754 ± 4, 2950 ± 8, and 2863 ± 5 MHz. The spectral data of ethyl cyanoformate are summarized in Table IV. The intensities of the bands vary dramatically with temperature. The relative intensities of the bands corresponding to the extended, compact, and intermediate species vary from 1:0.6:3 at 25 °C to 1:0.6:1 at ca. −63 °C. Relative energies were determined using the method described above and are 0, −0.2 ± 0.3, and 1.7 ± 0.4 kcal/mol for the extended, compact, and intermediate conformers, respectively (Table II).

Discussion

Characterization of the configurations of the various conformations is done by matching the observed $B + C$ values with those calculated from models. Molecular parameters consistent with A_0, B_0, and C_0 were reported in high-resolution microwave studies of methyl trifluoroacetate,[17] methyl chloroformate,[13] methyl cyanoformate,[11] and ethyl formate.[18] Direct coupling of these geometries for the carboxyl fragments with that suggested for the ethoxyl moiety in the planar form of ethyl formate[18] (Figure 5a) yielded calculated $B_0 + C_0$ values differing by several percent from the values observed in this work for the ethyl esters. We determined carboxyl group geometries which reproduce the reported methyl ester rotational constants and which simultaneously reproduce the observed value of $B + C$ for each extended species when coupled with the ethoxyl geometry of ethyl formate. These carboxyl group models differ only slightly from those originally reported and are shown in Figure 5.

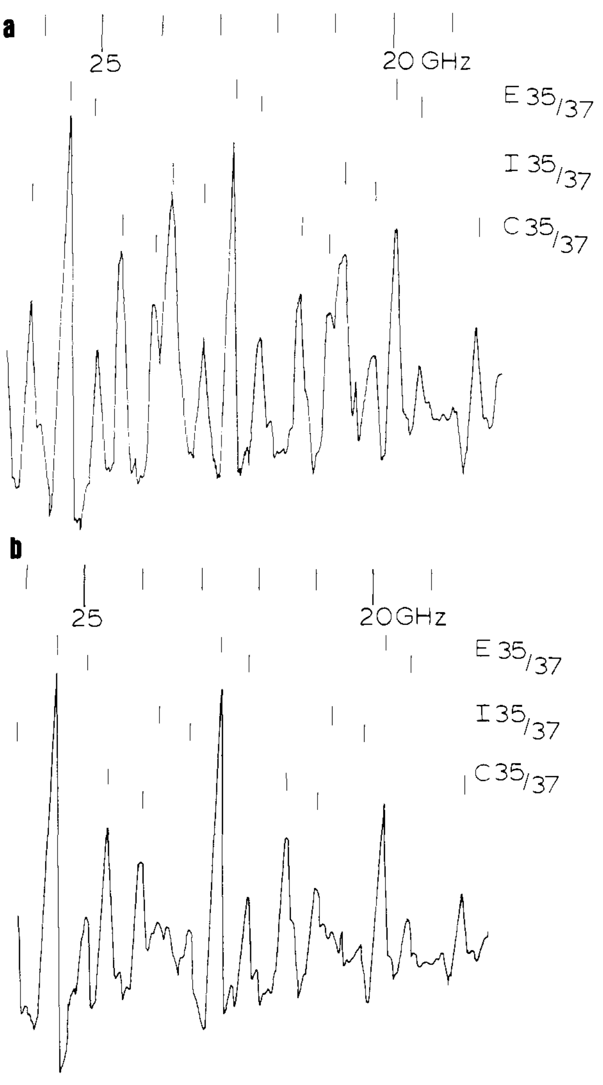

Figure 3. LRMW spectra of ethyl chloroformate. (a) K-band spectrum at 20 °C scanned at 10 MHz/s with a 1-s time constant. The band markers are calculated from $(J + 1)(B + C)$ with $B + C$ = 2819 (2762), 3061 (2989), and 2954 (2885) MHz for the extended (E), compact (C), and intermediate (I) species, respectively The values in parentheses are for the ^{37}Cl species. (b) Same as (a) except the temperature is ca. −63 °C.

Thus, the geometries of each of the ethyl esters have been adjusted to match the observed rotational constants for the extended species. That the observed and calculated $B + C$ values can be brought into agreement is still support that the extended species has the cis-trans configuration shown in Figure 1b. Uncertainties estimated for each of the structural parameters (Figure 5) used in calculating $B + C$ values correspond to an uncertainty of ~1.5% or 30 MHz in $B + C$ for ethyl trifluoroacetate. $B + C$ increases from the value calculated for a planar cis-trans rotamer if the molecule becomes nonplanar. Thus there is no other configuration with reasonable structural parameters which can match the observed $B + C$ value.

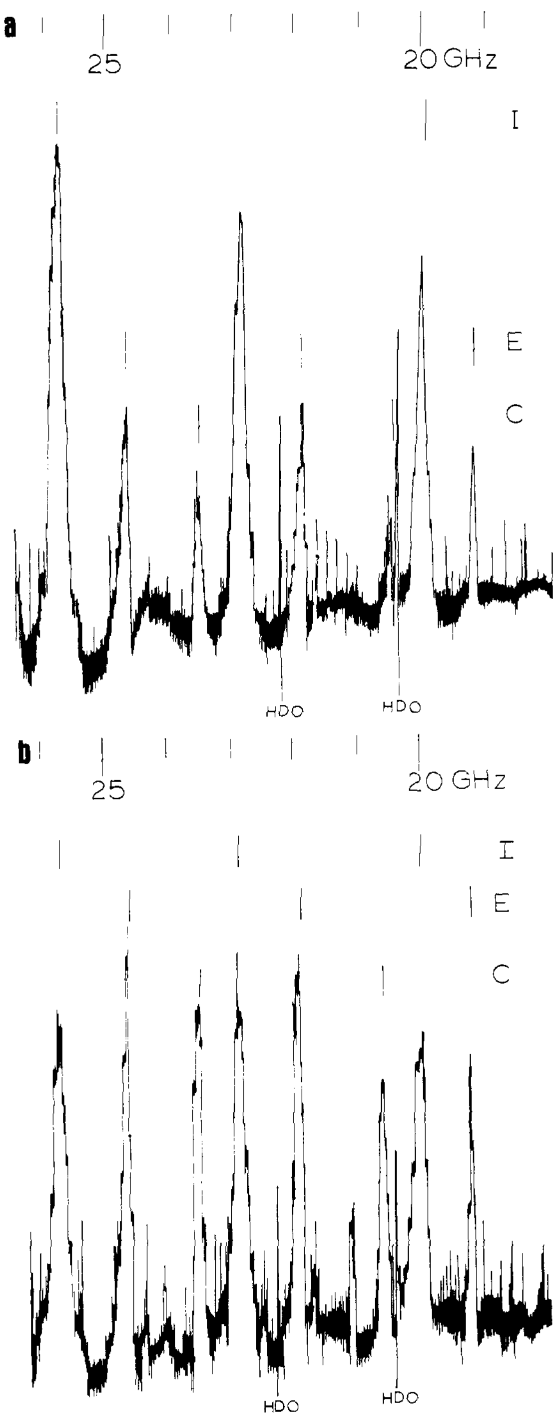

Figure 4. LRMW spectra of ethyl cyanoformate. (a) K-band spectrum at 25 °C scanned at 10 MHz/s with a 0.3-s time constant. The band markers are calculated from $(J + 1)(B + C)$ with $B + C = 2752$, 2954, and 2870 MHz for the extended (E), compact (C), and intermediate (I) species, respectively. (b) Same as (a) except the temperature is ca. −63 °C.

To characterize the structures of the compact and intermediate species $B_0 + C_0$ values were calculated at 30° intervals of the two torsional angles, τ_1(O=COC) and τ_2(COCC) with all other geometrical parameters held constant. These results for ethyl trifluoroacetate are summarized in the contour diagram of Figure 6. The calculated values of $B_0 + C_0$ are indicated by the contours shown at 100-MHz intervals as functions of the two torsional angles. From the discussion above the calculated values are accurate to about 1.5% due to the uncertainties in the assumed structural parameters. This uncertainty has been arbitrarily assigned to the observed value for easy visualization and models consistent with 1839 ± 30, 1944 ± 30, and 1900 ± 30 MHz are those lying within the hatched areas. The diagram has a center of symmetry so that only conformations corresponding to the lower half of the figure will be discussed. In order to produce a LRMW band spectrum a molecule must be a near prolate rotor ($A > B \sim C$) with a large dipole moment along the a principal axis.[22] Dipole moments for the various rotational isomers were simultaneously calculated from a vector model using the following bond dipoles: C ← H, 0.30 D; C → 0, 0.86 D; C → F, 1.51 D; C → =0, 2.40 D; C → N, 3.6 D; C → Cl, 1.56 D.[24] For all the structures calculated the dipole moment was estimated to be sufficient to produce the large Stark shifts necessary to observe band spectra. κ values were also calculated. It is estimated that κ must be less than −0.65 to obtain LRMW band spectra for polar compounds such as those studied in

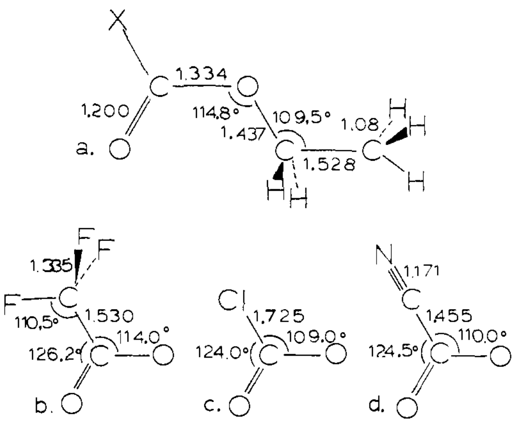

Figure 5. Structural parameters for ethyl esters. (a) Values used from ethyl formate[18] and values derived from studies of (b) methyl trifluoroacetate,[17] (c) methyl chloroformate,[15] and (d) methyl cyanoformate.[11]

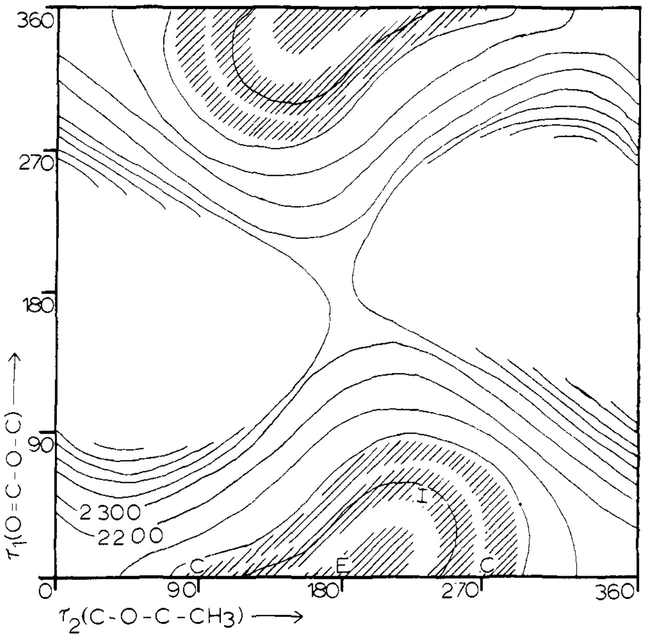

Figure 6. Contour diagram of $B_0 + C_0$ for ethyl trifluoroacetate as a function of the torsional angles, τ_1(O=COC) and τ_2(COCC). The diagram has a center of symmetry. The cross-hatched regions cover those conformations consistent with the observed $B + C$ values. The labels E, C, and I locate the most probable configurations of the extended, compact, and intermediate species, respectively. The blank regions correspond to models too asymmetric to produce LRMW band spectra and therefore unobservable by the technique.

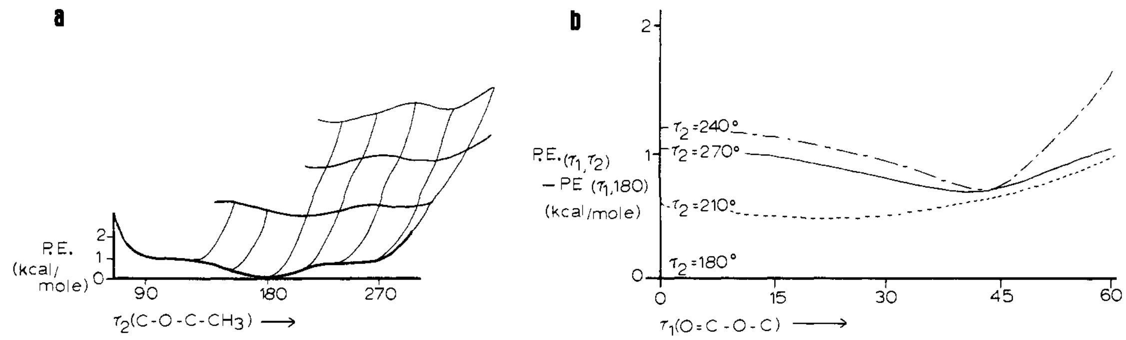

Figure 7. (a) Ab initio potential energy surface of ethyl formate. The heavy cross section corresponds to τ_1(O=COC) = 0°, and the succeeding cross sections correspond to τ_1 = 30, 45, and 60°, respectively. Potential energy minima lie at 0°,180° (0 kcal/mol) and 0°,90° (1.0 kcal/mol, 0.186 ± 0.06 kcal/mol, observed value[18]). The oblique cross sections are at 30° intervals of τ_2(COCC) spanning 120° $\leq \tau_2 \leq$ 300°. (b) Differences between τ_1, τ_2 = constant cross section and τ_1, τ_2 = 180° cross section. The dip at 45°,240° indicates that the side of the potential energy valley is relatively less steep here than in nearby regions.

Table IV. LRMW Spectral Data of Ethyl Cyanoformate

$J + 1$	ν, MHz	$B + C$, MHz
	Extended Conformer	
7	19 250	2750.0
8	22 020	2753.7
9	24 765	2751.7
10	27 545	2754.0
11	30 290	2753.6
12	33 040	2753.3
13	35 790	2753.1
14	38 485	2748.9
Av $B + C$	2752 ± 2	
κ^a	−0.90 ± 0.01	
Estimated $B_0 + C_0{}^a$	2745 ± 4	
	Compact Conformer	
7	20 645	2949.2
8	23 635	2954.4
9	26 590	2954.4
10	29 540	2954.0
11	32 480	2952.7
12	35 445	2953.7
13	38 485	2960.4
Av $B + C$	2954 ± 5	
κ^a	−0.94 ± 0.02	
Estimated $B_0 + C_0{}^a$	2950 ± 8	
	Intermediate Conformer	
7	20 090	2870.0
8	22 960	2870.0
9	25 830	2870.0
10	28 700	2870.0
11	31 535	2868.6
12	34 435	2869.6
13	37 330	2871.5
Av $B + C$	2870 ± 2	
κ^a	−0.91 ± 0.04	
Estimated $B_0 + C_0{}^a$	2863 ± 5	

[a] See footnotes to Table I.

this work. The contours were terminated where the value of κ rose above −0.65 so that blank regions of Figure 6 correspond to configurations unobservable to LRMW spectroscopy.

Similar surfaces were calculated for ethyl chloroformate and ethyl cyanoformate using the geometrical parameters of Figure 5. Because these molecules have larger $B_0 + C_0$ rotational constants, they are more sensitive to structural changes and the gradients of the surfaces are steeper. The topography of the $B_0 + C_0$ surfaces for ethyl trifluoroacetate, ethyl chloroformate, and ethyl cyanoformate is qualitatively similar. The three rotational isomers in each case have $B_0 + C_0$ values which are compatible with the same ranges of τ_1(O=COC) and τ_2(COCC). For a given conformation ethyl chloroformate is more nearly a symmetric rotor than ethyl trifluoroacetate and thus a somewhat greater range of configuration is observable by LRMW than is shown in Figure 6. In particular the trans-trans structure ($\tau_1 = \tau_2$ = 180°, Figure 1d) has a κ value of about −0.70 and would have been observed had it been present in significant concentration, perhaps 20%. In contrast, ethyl cyanoformate is generally less symmetric than ethyl trifluoroacetate and the κ value for the trans-trans configuration is −0.53 and not likely to be observable.

As can be seen from Figure 6, the low-resolution $B + C$ rotational constant does not, by itself, give an unambiguous conformational determination of a molecule with two torsional degrees of freedom except for the extended species. On the other hand, it is also clear that the conformational properties of the three ethyl formates are qualitatively similar and therefore not strongly dependent upon the nature of the substituent on the carboxyl group. A potential energy surface for ethyl formate was determined from ab initio calculations using an STO-3G minimal basis set.[25] It is assumed that this potential energy surface is similar to those for ethyl trifluoroacetate, chloroformate, and cyanoformate. The potential energy was calculated at 15 or 30° intervals of τ_1 and τ_2 covering the hatched region of Figure 6 and is shown in Figure 7a. Structural parameters reported by Riveros and Wilson[18] were used. The potential energy surface is characterized by a long, relatively flat valley with τ_1 = 0° and 60° < τ_2 < 300°. The absolute minimum occurs at 0°,180° with a secondary minimum (1.0 kcal/mol) at 0°,90° or 0°,270° which are equivalent structures. A similar result was obtained from a CNDO/2 calculation.[26] These minima correspond to the cis-trans and cis-gauche structures (Figures 1b,c) characterized in ethyl formate. Experimentally the gauche form is 186 ± 60 cal/mol less stable than the planar form.[18] The compact species of ethyl trifluoroacetate, chloroformate, and cyanoformate are thus characterized to have cis-gauche configurations, τ_1 = 0° and $\tau_2 \sim$ 90°. Using the structural parameters fitted for the cis-trans species, $B_0 + C_0$ values calculated with τ_1 = 0° and τ_2 = 90° agree satisfactorily (within 1%) with the observed $B_0 + C_0$ values of the compact series of each of the three ethyl esters.

The remaining intermediate species cannot have τ_1 = 0° for two reasons. The theoretical calculations indicate no other minima than those already assigned. Furthermore, if τ_1 were 0°, then the intermediate species would correspond to $\tau_2 \sim$ 120°. The potential energy surface would have to undulate from a minimum of 0.2 kcal.mol at τ_2 = 90° over a barrier and into a minimum at τ_2 = 120° at an energy of ~2 kcal/mol for ethyl trifluoroacetate. That undulation alone would require a very large 12-fold component to the barrier to internal rotation of the ethyl group, an unreasonable condition. The latter argument suggests that the intermediate configuration should be that configuration still compatible with the calculated $B_0 + C_0$ values and most distant from the cis-trans and cis-gauche forms in the space of τ_1 and τ_2. From Figure 6 this model would correspond to $\tau_1 \sim 45°$ and $\tau_2 \sim 240°$. The potential energy surface of ethyl formate shows no minimum in this region but is relatively flatter in this region than in its surroundings. That flattening is barely visible in Figure 7a but is evident in Figure 7b which displays cross sections of the potential energy surface for fixed τ_2 values relative to the cross section at $\tau_2 = 180°$. For example, the cross section for $\tau_2 = 210°$ is seen to lie consistently about 0.5 kcal/mol higher than the 180° cross section for $0 < \tau_1 < 45°$. For $\tau_2 = 240°$, the cross section falls relative to the 180° cross section at about $\tau_1 = 45°$ indicating that the potential energy surface is somewhat flatter here. This structure is shown in Figure 1e. A high-resolution microwave study of the three conformers of ethyl cyanoformate has been initiated to better characterize the configurations.

A brief search for a third conformation in ethyl formate using LRMW spectroscopy was unsuccessful. For this light, relatively nonpolar molecule, band spectra were obtained from the extended conformer only. Riveros and Wilson[18] found no evidence for a third species in their study although the presence of small populations of another species was not ruled out.

A final observation which demands interpretation is the unusually large intensities of the bands of the intermediate species, especially of ethyl trifluoroacetate and ethyl cyanoformate. In the case of ethyl trifluoroacetate at ca. −63 °C the intermediate bands are still five times as intense as the bands of the more stable series even though the Boltzmann factor, $\exp(-1900/RT)$, is 0.01 for this species. Estimated dipole moments of the various species differ relatively little as do the asymmetry parameters and thus cannot explain the intensities. The strong intensities of the intermediate species' bands, their great width, and the temperature dependence of the band positions for ethyl trifluoroacetate suggest that these features are due to the superposition of bands of excited species populating an unusually dense manifold of vibrational states in the vicinity of the potential minimum of the intermediate forms. That is, the intermediate species has one or more fundamental vibrations with considerably lower frequencies than found in the more stable rotamers.

Summary

The esters ethyl trifluoroacetate, ethyl chloroformate, and ethyl cyanoformate each display LRMW band spectra from three conformers: a planar cis-trans (0°,180°) configuration, a cis-gauche (0°,∼90°) configuration, and a less stable gauche-gauche (∼45°,∼240°) configuration. The cis-trans and cis-gauche form are nearly equally stable and the gauche-gauche form is less stable (1-2 kcal/mol higher energy). Spectral features suggest that the least stable configuration has one or several normal vibrations of considerably lower frequency than the more stable forms.

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