1(ii), dotted lines for the halobenzenes represent the pressure dependence of ring proton resonance corrected for the $\Delta\sigma_E(P)$ contribution, that is the pressure dependence which might be related exclusively to the steric effect of the substituent ortho to the resonating proton. It can be seen that the dotted line for the ortho proton of bromobenzene-*3,5-d_2* behaves almost identically with that for the ring proton of 1,4-dibromobenzene. This is consistent with the foregoing aspect that the meta substituent does not contribute to the $\Delta\sigma_w(P)$ term and constitutes further support for the validity of present estimations on the $\Delta\sigma_E(P)$ contribution. Since the quadrupole moments of 1,4-dialkylbenzenes and the dipole moment of 4-*tert*-butyltoluene are extremely small, the $\Delta\sigma_E(P)$ contributions in these molecules become even much smaller and may be safely neglected.

We thus arrive at the view that the observed $\delta\Delta$ for the ortho proton is largely accounted for in terms of the contribution of σ_w, which varies depending on the extent of the substituent steric effect to hinder the approach of the medium molecule to the resonating proton. In this respect, the measurement of the $\delta\Delta$ is expected to offer a means of experimentally establishing a measure of the "steric effect" of the ortho substituent, quantitative evaluation of which might otherwise be really difficult.

The present observation of the substituent steric effect on the σ_w contribution at high pressure indicates that a similar effect must basically exist even at the ordinary pressure (δ_1 in Figure 2) and suggests that this effect, in studying the ortho substituent effect on the ring proton resonance,[3,13] should be taken into account as an additional factor in the SCS (substituent chemical shift) other than the electronic (polar) as well as the magnetic anisotropy effect of the substituent.[14]

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Low Resolution Microwave Spectroscopy. 5. Rotational Isomerism of Propargyl Cyanoformate, Propargyl Trifluoroacetate, Propargyl Fluoroformate, and Propargyl Chloroformate[1]

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Abstract: Low resolution microwave spectra of propargyl cyanoformate and propargyl trifluoroacetate each display three *a*-type band series characterized by $B + C$ values of 1935 (3), 2253 (1), and 2142 (1) MHz for propargyl cyanoformate and 1342 (2), 1507 (1), and 1467 (3) MHz for propargyl trifluoroacetate, associated with three conformational forms designated extended, compact, and intermediate. Propargyl fluoroformate and chloroformate display band spectra from two conformational forms with $B + C$ values of 2515 (1) and 3175 (1) MHz for the fluoroformate and 1938 (2) and 2280 (2) (2235 (2), ^{37}Cl) for the chloroformate, designated extended and compact. For each compound the extended species is consistent with a syn-anti [τ_1(OCOC) = 0°, τ_2(COCC) = 180°)] heavy atom planar structure and the compact species with a syn-gauche [τ_1(OCOC) = 0°, τ_2(COCC) $\sim$ 90°)] structure. The intermediate forms of propargyl cyanoformate and trifluoroacetate are both consistent with a gauche-gauche [τ_1(OCOC) $\sim$ 60°, τ_2(COCC) $\sim$ 270°] structure. The extended and compact forms are of nearly equal energy in all cases. The intermediate forms of propargyl cyanoformate and trifluoroacetate are approximately 1–2 kcal/mol higher in energy. These results parallel previous findings for ethyl esters, demonstrating that the potential functions for internal rotation in ethyl and propargyl esters are similar.

Three conformers in ethyl trifluoroacetate, ethyl chloroformate, and ethyl cyanoformate have been observed and characterized using low resolution microwave (LRMW) spectroscopy.[2] The two most stable forms of each ester, designated extended and compact, have the syn-anti [τ_1(OCOC) = 0°, τ_2(COCC) = 180°] and syn-gauche [τ_1 (OCOC) = 0°,

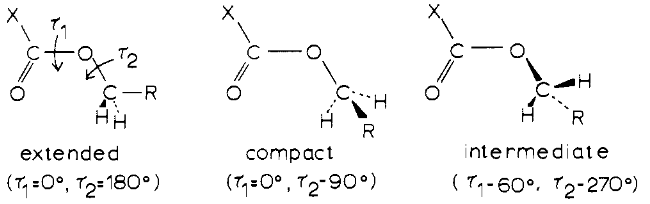

Figure 1. Conformers of propargyl (R = C≡C–H) and ethyl (R = CH_3) esters.

τ_2(COCC) ~ 90°] structures, respectively, shown in Figure 1. The third conformer, designated intermediate, has a nonplanar configuration around τ_1 [τ_1(OCOC) ~ 40°, τ_2(COCC) ~ 240°]. For each molecule the intermediate form is ca. 1–2 kcal/mol higher in energy than the extended and compact forms which are of comparable stability. The intermediate forms of ethyl trifluoroacetate and ethyl cyanoformate produce the most intense bands in each spectrum, even at ~−63 °C. The extended and compact conformers of ethyl formate,[3] ethyl fluoroformate,[4] and ethyl nitrate,[5] have been assigned to the τ_1(OCOC) = 0°, τ_2(COCC) = 180° and τ_1(OCOC) = 0°, τ_2(COCC) ~ 90° structures using high resolution microwave spectroscopy. For ethyl formate, fluoroformate and nitrate the energy differences between the two forms are 186 ± 60, 0 ± 144, and 143 ± 200 cal/mol, the extended form being the more stable in the formate and nitrate.

Propargyl esters are similar to ethyl esters with the methyl group replaced by an acetylene moiety. An ab initio SCF study of rotational isomerism in ethyl formate[2,6] and propargyl formate[6] calculated energy minima at the extended and compact structures for both molecules. A recent infrared study of propargyl formate concluded that two rotamers of equal stability are present in the liquid phase.[7] The extended conformer of propargyl formate was characterized by microwave spectroscopy. Other conformational species were not assigned, but their presence was not ruled out.[7] An infrared and Raman study of propargyl chloroformate concluded that this molecule exists in two conformational forms, both having C_s symmetry.[8]

LRMW spectroscopy is ideally suited for characterizing conformational isomerism of gaseous polar, prolate molecules of moderate complexity.[1-2,9-11] This study was undertaken to resolve the ambiguity regarding the conformational preferences of propargyl esters and to compare the internal rotation potential functions for ethyl and propargyl esters. This study determines the conformational species present and their relative stabilities in gas phase samples of propargyl cyanoformate, trifluoroacetate, fluoroformate, and chloroformate.

Experimental Section

All microwave measurements were made on a Hewlett-Packard Model 8460A microwave spectrometer. Spectra of propargyl trifluoroacetate were obtained from 18 to 37 GHz. Spectra of propargyl cyanoformate and chloroformate were obtained from 26.5 to 37 GHz. Spectra of propargyl fluoroformate were obtained from 26.5 to 40 GHz. All spectra were recorded at two temperatures; room temperature and with the sample cells packed in dry ice. In all cases the Stark voltage was 3200 V/cm, the scan rate was 10 MHz/s with a 1-s detector time constant.

Samples were distilled into the wave guide to pressures of 30–70 mTorr. In order to minimize errors in intensity measurements, the sample pressure and detector crystal current were kept constant while each spectrum was being recorded. Frequency measurements are frequencies of the band maxima averaged over forward and reverse scans. Frequency accuracy, which is dependent on the shape and width of the bands, ranges from about 5 to 50 MHz for the samples studied.

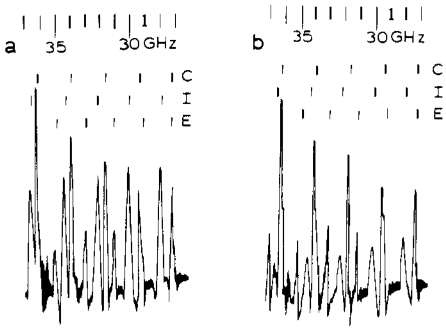

Figure 2. LRMW spectra of propargyl cyanoformate: (a) R-band spectrum from 26.5 to 37 GHz at 25 °C scanned at 10 MHz/s with a 1-s time constant. The band markers are calculated from $(J + 1)(B + C)$ with $B + C$ = 1935, 2253, and 2142 for the extended (E), compact (C), and intermediate (I) species, respectively. (b) Same as (a) except temperature is ca. −63 °C.

Table I. $B + C$ Values (MHz) of the Conformers of Propargyl Cyanoformate, Propargyl Trifluoroacetate, Propargyl Fluoroformate, and Propargyl Chloroformate

	Extended	Compact	Intermediate
	Propargyl Cyanoformate		
(v,v') = (0,0)	1935 (3)	2253.0 (1.0)	2142 (1)
(v,v') = (1,0)		2241.1 (4)	
(v,v') = (2,0)		2228.4 (8)	
(v,v') = (3,0)		2212.3 (3)	
(v,v') = (1,1)		2244.9 (6)	
(v,v') = (2,1)		2232.2 (3)	
(v,v') = (3,1)		2216.9 (6)	
	Propargyl Trifluoroacetate		
$v = 0$	1342 (2)	1507 (1)	1467 (3)
	Propargyl Fluoroformate		
$v = 0$	2515 (1)	3175 (1)	
$v = 1$	2522 (1)	3144 (1)	
$v = 2$		3112 (1)	
$v = 3$		3074 (1)	
	Propargyl Chloroformate (^{35}Cl/^{37}Cl)		
$v = 0$	1938 (2)/—	2280 (2)/2235 (2)	

A sample of propargyl trifluoroacetate was prepared from propargyl alcohol and trifluoroacetic anhydride by a method previously discussed.[2] Propargyl chloroformate was prepared from the alcohol and phosgene by the method of Strain et al.[12] The reaction was carried out at 0 °C. The product was washed with sodium bicarbonate and fractionally distilled at reduced pressure to remove unreacted propargyl alcohol and propargyl carbonate formed as a side product. Propargyl fluoroformate was prepared by direct exchange between propargyl chloroformate and thallium fluoride using the procedure of Nakanishi et al.[13] Propargyl cyanoformate was synthesized from propargyl chloroformate and sodium cyanide using the method of Giuud et al.[14] All samples were fractionally distilled under reduced pressure prior to use. They were characterized by their ^{1}H NMR and infrared spectra and their purity was established to be in excess of 98% by gas–liquid chromatography on a 6 ft SE-30 column with 5–10-min retention times.

Results

Propargyl Cyanoformate. Low resolution R band spectra of propargyl cyanoformate at 25 and at ~−63 °C are shown in Figure 2. Three band series corresponding to three conformational species are present. The band series are all a-type and obey the relationship

$$\nu_a = (B + C)(J + 1) \tag{1}$$

Values of $B + C$ for the three band series are 1935 (3), 2253 (1), and 2142 (1) MHz. Based on the similarity to ethyl esters,[2] these series are designated extended, compact, and intermediate, respectively. The $B + C$ values are summarized in Table I.

Table II. Relative Energies of the Conformational Isomers of Propargyl Cyanoformate, Trifluoroacetate, Fluoroformate, and Chloroformate

Propargyl ester	Extended, kcal/mol	Compact, kcal/mol	Intermediate, kcal/mol
Cyanoformate	0	0.0 ± 0.6	1.7 ± 0.8
Trifluoroacetate	0	~0	~2
Fluoroformate	0	~0	
Chloroformate	0	~0	

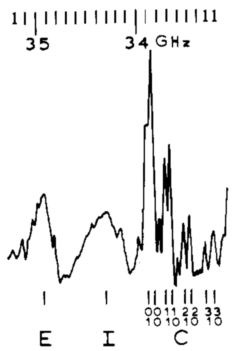

Figure 3. LRMW spectrum of ethyl cyanoformate from 33.2 to 35.2 GHz recorded at −63 °C. The bands correspond to the $J + 1 \leftarrow J$ $18 \leftarrow 17$, $15 \leftarrow 14$, and $16 \leftarrow 15$ transitions of the extended (E), compact (C), and intermediate (I) conformers. Vibrational quantum numbers label satellites of the compact band.

The relative intensities of the three series at 25 °C are 1:2.6:3.6 for the extended, compact, and intermediate species and at ~−63 °C they are 1:2.4:1.1. From the temperature variation of the intensities the relative energies of the species are calculated to be 0, 0 ± 0.6, and 1.7 ± 0.8 kcal/mol, respectively, see Table II.

There are striking qualitative differences among the three band series as can be seen in Figure 3. The bands of the compact species are very narrow, since it is accidentally very nearly a symmetric rotor. Ray's asymmetry parameter, κ, is calculated to be ~−0.98. The compact bands display a multiplet structure which is reproduced with each value of J. Figure 3 displays this structure for the $15 \leftarrow 14$ band. Each component can be assigned to an a-type R-branch series with excellent precision as the data in Table III[16] indicate. The series of diminishing intensity bands extending to lower frequency from the band maximum can reasonably be assigned to the $v = 0, 1, 2$, and 3 states of a single vibrational mode. The smooth variation of $B + C$ with v, the direction and magnitude of the $B + C$ shifts, and an estimated frequency of ~50 cm^{-1} for this vibration based on relative intensities indicate that this mode is the torsion of the propargyl group about the O-C bond (τ_2). Completely analogous properties have been found for the vibrational satellite pattern of the ethyl group torsion in ethyl fluoroformate which was assigned using conventional high resolution microwave techniques.[4] Displaced 50–100 MHz toward higher frequency of each of the satellites assigned above is another set of satellites which we assign to the $v' = 1$ state of another vibrational mode. The $v' = 2$ state of this mode appears above the noise level for a few bands. The band frequencies and assignments of this second excited mode are listed in Table III. From the magnitude and direction of the shift of $B + C$ with v' and the estimated frequency of the vibration, this mode is probably the torsion about the carbonyl C to ether O bond (τ_1). Resolvable satellite spectra are not apparent for the broader bands of the extended and intermediate forms (Figure 3). The intermediate form displays smooth structureless bands at both room and dry ice temperatures which are approximately 300–500 MHz wide, in contrast to the bands of the extended and compact species which are ~200 and <100 MHz wide, respectively.

Propargyl Trifluoroacetate. Low resolution K and R band spectra of propargyl trifluoroacetate display a-type band spectra from three conformational species. $B + C$ values are 1342 (2), 1507 (1), and 1467 (3) MHz for the extended, compact, and intermediate species, respectively. 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 1:2:7 at room temperature to 1:2:2 at ~−63 °C. The extended and compact species have roughly equal energies, while the intermediate form is approximately 2 kcal/mol higher in energy. The high degree of overlap in the spectrum, which is especially severe for the extended and intermediate species, makes a quantitative determination of the relative energies of the three conformers impossible. The intermediate form of propargyl trifluoroacetate produces wide (ca. 500 MHz) structureless bands, whereas the extended and compact species produce bands about 200-MHz wide. There is no characteristic fine structure in the compact bands of propargyl trifluoroacetate which are broader than the compact bands of the cyanoformate. Spectral data of propargyl trifluoroacetate are summarized in Tables I and II.

Propargyl Fluoroformate. Low resolution R-band spectra of propargyl fluoroformate display two intense series of narrow (~100 MHz wide) bands which show repeating resolvable fine structure displaced up to 2 GHz from the main bands. The $B + C$ values for these series are 2515 (1) and 3175 (1) MHz. The corresponding conformers are designated extended and compact, respectively. No bands corresponding to an intermediate conformer are present in the spectrum. The relative intensities of the extended and compact species are ~1:1 at both 25 and ~−63 °C, indicating that the conformers are of approximately equal energy. The fine structure in the spectrum corresponds to rotational band spectra of vibrational satellites of the extended and compact conformers. One satellite of the extended species having a $B + C$ value of 2522 (1) MHz is apparent. The $v = 1$, $v = 2$, and $v = 3$ satellites of the compact species have $B + C$ values of 3144 (1), 3112 (1), and 3074 (1) MHz, respectively. The smooth variation of $B + C$ as a function of vibrational quantum number indicates that these satellites correspond to the same vibrational mode. The frequency of this mode is ca. 60 cm^{-1}, based on relative intensity measurements. For both the extended and compact species, the observed satellites most likely correspond to a torsional motion around τ_2(COCC) based on analogous variations of B and C with the vibrational state, reported for this torsion for ethyl fluoroformate.[4] It is clearly the same mode as that in propargyl cyanoformate, which displayed several vibrationally excited states. There is a suggestion of an excited state of another mode, but the spectral resolution is not sufficient for a conclusive identification. Spectral data of propargyl fluoroformate are summarized in Tables I and II.

Propargyl Chloroformate. Propargyl chloroformate produced weak dense spectra at both 25 and ~−63 °C. Three band series can be unambiguously assigned. They have $B + C$ values of 1938 (2) and 2280 (2)/2235 (2) MHz and correspond to the ^{35}Cl isotope of the extended species and the ^{35}Cl and ^{37}Cl isotopes of the compact species, respectively. The spectrum is not consistent with appreciable quantities of a third conformational species. It is estimated that a third species would have to compose ~20% of the total sample in order to be observed in this noisy spectrum. The extended and compact species are of approximately equal intensity at both 25 and ~−63 °C. Spectral data of propargyl chloroformate are summarized in Tables I and II.

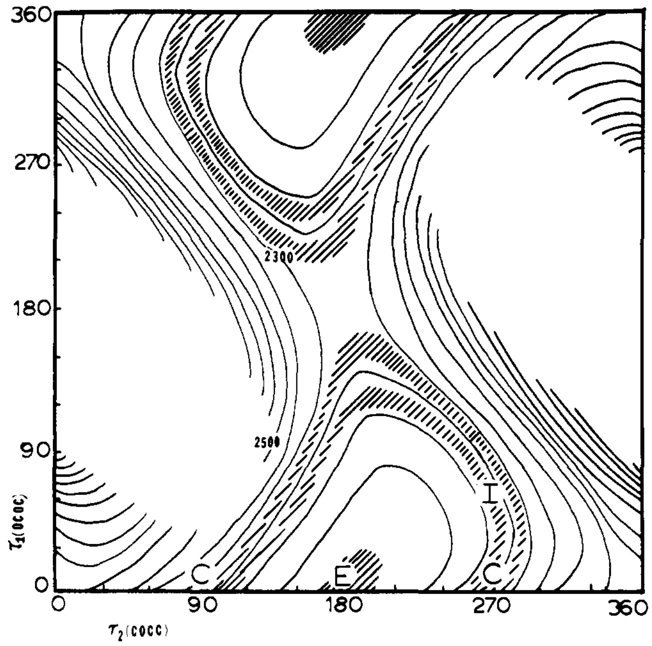

Figure 4. Contour diagram of $B + C$ for propargyl cyanoformate as a function of the torsional angles, τ_1(OCOC) and τ_2(COCC). The diagram has a center of symmetry. The hatched regions cover those conformations consistent with the observed $B + C$ values. The labels E, C, and I locate the most probable 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 this technique.

Discussion

For each molecule, values of $B + C$ were calculated as functions of τ_1(OCOC) and/or τ_2(COCC), defined in Figure 1, using geometrical parameters reported for the corresponding ethyl formates[2,4] coupled with the geometry reported for the propargyl group in propargyl chloride.[15] An OCC angle of 109.5° was used in these calculations. This geometry reproduces the experimental $B + C$ values for the extended form of each propargyl ester to within 1.5% when $\tau_1(\mathrm{OCOC}) = 0°$ and $\tau_2(\mathrm{COCC}) = 180°$. To characterize the conformations of the compact and intermediate forms, $B + C$ values were calculated at 30° intervals of τ_1(OCOC) and τ_2(COCC) holding all other geometrical parameters constant. For propargyl cyanoformate, the results of these calculations are displayed graphically in Figure 4. The calculated values of $B + C$ are indicated by the contours shown at 100-MHz intervals as functions of the two torsional angles. The calculated values are accurate to about 2% due to uncertainties in the assumed structural parameters. This uncertainty has been arbitrarily assigned to the observed values for easy visualization and models consistent with 1935 ± 40, 2253 ± 45, and 2142 ± 45 MHz are those lying within the hatched areas. The contour 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 nearly symmetric rotor. Ray's asymmetry parameter, $\kappa = (2B - A - C)/(A - C)$, is a measure of this symmetry and ranges from -1 to 1 for the limiting prolate and oblate cases, respectively. The blank regions correspond to conformers having calculated values of $\kappa > -0.65$ which are not observable to LRMW spectroscopy.[10]

A similar surface was calculated for propargyl trifluoroacetate. Since this molecule is heavier than propargyl cyanoformate, $B + C$ is less sensitive to conformational changes and the gradient of the surface is less steep. The overall topography of the two surfaces is the same and the three rotational isomers in each case have $B + C$ values which are compatible with the same range of τ_1(OCOC) and τ_2(COCC).

For propargyl cyanoformate and trifluoroacetate the compact conformer is compatible with a range of structures including the syn-gauche [$\tau_1(\mathrm{OCOC}) = 0°$, $\tau_2(\mathrm{COCC}) \sim 90°$] structure observed for all the ethyl formates[2-5] that have been characterized. The compact conformers of propargyl cyanoformate and propargyl trifluoroacetate are assigned to this structure based on analogy to the ethyl ester results and the similarity between the ethyl and propargyl formate ab initio potential functions.[7] $B + C$ was calculated as a function of τ_2(COCC) for propargyl fluoroformate and chloroformate holding $\tau_1(\mathrm{OCOC}) = 0°$ and all other geometrical parameters constant. The experimental values of $B + C$ for the compact species of both the fluoroformate and chloroformate are compatible with the syn-gauche [$\tau_1(\mathrm{OCOC}) = 0°$, $\tau_2(\mathrm{COCC}) \sim 90°$] structure. For propargyl fluoroformate $B + C$ is extremely sensitive to τ_2(COCC), varying from a minimum of 2490 MHz for the extended syn-anti ($\tau_1(\mathrm{OCOC}) = 0°$, $\tau_2(\mathrm{COCC}) = 180°$] structure to a maximum of 4050 MHz for the syn-syn [$\tau_1(\mathrm{OCOC}) = 0°$, $\tau_2(\mathrm{COCC}) = 0°$] structure. This large variation in $B + C$ as a function of τ_2(COCC) allows an estimate of τ_2(COCC) for the compact species of 95 ± 7° for the fluoroformate, allowing for a 2% uncertainty in assumed structural parameters. The unusually narrow band widths of the compact species of each ester, which allowed for the enhanced resolution of the satellite spectra of the compact species of the cyanoformate and the fluoroformate, are further support for this structure.[9] The syn-gauche [$\tau_1(\mathrm{OCOC}) = 0°$, $\tau_2(\mathrm{COCC}) \sim 90°$] structure for all the propargyl esters has a calculated κ value of -0.98 to -0.99, extremely close to the prolate limit. Calculated κ values for the syn-anti [$\tau_1(\mathrm{OCOC}) = 0°$, $\tau_2(\mathrm{COCC}) = 180°$] structure range from -0.94 to -0.96 for the propargyl esters studied and their band widths are correspondingly greater.

The intermediate conformer of propargyl cyanoformate and propargyl trifluoroacetate, although compatible with a syn-gauche [$\tau_1(\mathrm{OCOC}) = 0°$, $\tau_2(\mathrm{COCC}) = 120°$] structure, cannot have the syn ($\tau_1(\mathrm{OCOC}) = 0°$) structure, as this would put unreasonable constraints on the potential function for internal rotation around τ_2(COCC). This argument is discussed in a previous paper on ethyl esters.[2] If we assume that the configuration of the intermediate conformer of propargyl cyanoformate and trifluoroacetate are identical, one can superimpose Figure 4 for the cyanoformate and an equivalent diagram for the trifluoroacetate and determine that point in τ_1,τ_2 space which simultaneously matches the observed $B + C$ value of the intermediate conformer of both compounds. That point is $\tau_1 \sim 60°$ and $\tau_2 \sim 270°$. In analogy with the ethyl esters, the structure of the intermediate conformer is believed to be that which is farthest removed from the syn-anti and syn-gauche forms in the space of τ_1 and τ_2 and still has compatible B + C values. The $\tau_1 \sim 60°$, $\tau_2 \sim 270°$ structure suggested above is consistent with this argument. In the case of ethyl esters the intermediate conformation was estimated to have the configuration $\tau_1 \sim 45°$, $\tau_2 \sim 240°$.[2] The authors do not consider these structures significantly different.

A striking result of this study is the similarity between the conformational properties of propargyl and ethyl esters. In all cases the syn-anti and syn-gauche structures are present and are of roughly equal stability. In ethyl esters, the bands of the intermediate conformer are very intense for the trifluoroacetate and cyanoformate, of comparable intensity to the extended and compact bands for the chloroformate, and absent in the fluoroformate and nitrate, qualitatively paralleling the results for propargyl esters. As was the case for the ethyl esters, the calculated dipole moments and asymmetry parameters of the extended, compact, and intermediate forms of each propargyl ester are very similar and cannot account for the intensity anomalies. If the intermediate conformer had the same vibrational partition functions as the extended and compact conformers, the expected intensity ratio would be 1:2:0.08 for the extended, compact, and intermediate species at room temperature, assuming the energy of the intermediate form to be 2 kcal/mol higher than the extended and compact species. Since this is not the case, it is believed that the intensity of the intermediate bands is due to the superposition of bands of excited species populating an unusually dense manifold of vibrational states. The variation of intensity of the intermediate form with formyl substituent provides qualitative support for this. The heavier esters, propargyl trifluoroacetate and propargyl cyanoformate, have small internal rotation constants, and accordingly, the energy levels within their vibrational potential functions should be lower and more closely packed than those of their lighter counterparts such as propargyl fluoroformate. Thus the intensities of the intermediate forms of esters should be enhanced as a function of their mass and complexity.

The similar values of τ_1 and τ_2 for the intermediate forms of propargyl esters [$\tau_1(\mathrm{OCOC}) \sim 60°$, $\tau_2(\mathrm{COCC}) \sim 270°$] and ethyl esters [$\tau_1(\mathrm{OCOC}) \sim 45°$, $\tau_2(\mathrm{COCC}) \sim 240°$] indicates that substitution of an acetylene group for a methyl group has little effect on the shape of the potential surface for internal rotation near the intermediate minimum. This study demonstrates that the potential functions for internal rotation around τ_1(OCOC) and τ_2(COCC) for propargyl esters and ethyl esters are qualitatively similar.

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Supplementary Material Available: Tables (III-VI) of band frequencies, $J + 1$, and $B + C$ values for propargyl cyanoformate, trifluoroacetate, fluoroformate, and chloroformate (8 pages). Ordering information is given on any current masthead page.

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Molecular Motion of Fluorocinnamates

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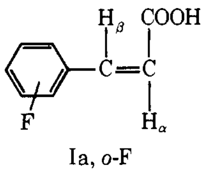
Abstract: Fluorine, carbon, and deuterium relaxation rates have been used to diagnose the anisotropy of molecular motion in three monofluorocinnamate ions in aqueous solution. The fluorine and carbon data were obtained by direct observation, while proton line shapes were used to estimate the deuterium relaxation rates. An ellipse of revolution was used to approximate the shape of each molecule and analysis showed that the available relaxation data were consistent with motion about the symmetry axis of the ellipse being four to six times more facile than motion perpendicular to this axis. Nuclei of the vinyl group in these structures appear to be relaxed by the overall tumbling motions of the molecules. Specific deuterium labeling shows that the β-vinyl hydrogen contributes appreciably to relaxation of an o-fluorine atom.

The relaxation of nuclear moments is sensitive to the details of molecular motion in the structures which hold them. Theoretical underpinnings for the interpretation of nuclear relaxation rates in terms of molecular motion are securely in place and a number of studies of the anisotropy of molecular motions by NMR techniques have been reported.[1]

The action of the proteolytic enzyme, α-chymotrypsin, is effectively inhibited by the various monofluorocinnamate anions (I)[2] and, as part of a study of chymotrypsin–fluorocinnamate complexes, we have examined in detail the dynamical properties of these ions. Because of the constraints imposed by the protein system all experiments have been carried out at fairly low solute concentrations (0.02–0.2 M) in aqueous solution, in contrast to previous studies of motional anisotropy which employed concentrated solutions in organic solvents or neat liquids. The results described below provide background information needed for the interpretation of our studies with the enzyme and may also help illuminate the role of solvent in molecular tumbling in solution.



Ia, *o*-F
b, *m*-F
c, *p*-F

Experimental Section

Materials. *o*-Fluoro-, *m*-fluoro-, and *p*-fluorocinnamic acids were synthesized as described previously.[2b] The deuterated fluorocinnamic acids were synthesized by condensation of the appropriate specifically deuterated benzaldehyde with malonic acid. For α,β-dideuterio-o-fluorocinnamic acid, α,α'-dideuteriomalonic acid was used in the condensation reaction. The following procedures are typical of those used to prepare the deuterated aldehydes.

α,α-Dideuterio-p-fluorobenzyl alcohol was prepared by reducing