

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 [$\tau_1(\text{OCOC}) \sim 60^\circ$, $\tau_2(\text{COCC}) \sim 270^\circ$] and ethyl esters [$\tau_1(\text{OCOC}) \sim 45^\circ$, $\tau_2(\text{COCC}) \sim 240^\circ$] 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 $\tau_1(\text{OCOC})$ and $\tau_2(\text{COCC})$ for propargyl esters and ethyl esters are qualitatively similar.

Acknowledgment. The authors are grateful to Professor E. Bright Wilson of Harvard University for the use of his microwave spectrometer supported by NSF Grant GP-37066X. Calculations were carried out at the University of Connecticut Computer Center.

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.

References and Notes

- (1) Paper 4 of this series: N. S. True and R. K. Bohn, *J. Mol. Struct.*, **36**, 173 (1977).
- (2) N. S. True and R. K. Bohn, *J. Am. Chem. Soc.*, **98**, 1188 (1976).
- (3) J. M. Riveros and E. B. Wilson, *J. Chem. Phys.*, **46**, 4605 (1967).
- (4) N. S. True and R. K. Bohn, 31st Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1976, Abstract WB'1.
- (5) D. G. Scroggin, J. M. Riveros, and E. B. Wilson, *J. Chem. Phys.*, **60**, 1376 (1974).
- (6) D. G. Lister, N. L. Owen, and P. Palmieri, *J. Mol. Struct.*, **31**, 411 (1976).
- (7) G. I. L. Jones, D. G. Lister, and N. L. Owen, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1330 (1975).
- (8) R. A. Nyquist, *Spectrochim. Acta, Part A*, **28**, 285 (1972).
- (9) W. E. Steinmetz, *J. Am. Chem. Soc.*, **96**, 685 (1974).
- (10) M. S. Farag and R. K. Bohn, *J. Chem. Phys.*, **62**, 3946 (1975).
- (11) N. S. True and R. K. Bohn, *J. Chem. Phys.*, **62**, 3951 (1975).
- (12) F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *J. Am. Chem. Soc.*, **72**, 1254 (1950).
- (13) S. Nakanishi, T. C. Meyers, and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 3099 (1955).
- (14) W. Giud, W. W. Nussler, and K. Keller, German Patent 592 539 (1934).
- (15) E. Hirota, T. Oka, and Y. Morino, *J. Chem. Phys.*, **29**, 444 (1958).
- (16) See paragraph at the end of the article concerning supplementary material.

Molecular Motion of Fluorocinnamates

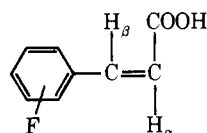
J. T. Gerig,* B. A. Halley, and J. A. Reimer

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. Received November 1, 1976

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 dy-



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

namical 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.

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

3.5 g of *p*-fluorobenzoic acid (25 mmol, Aldrich) with 1.0 g of lithium aluminum deuteride (24 mmol, Merck, Sharpe, and Dohme) in 60 mL of dry tetrahydrofuran. The deuteride was dissolved in 25 mL of THF and added over a period of 1.5 h; the reaction mixture was then heated at reflux for 24 h. Upon cooling, the mixture was quenched with water (40 mL) and acidified with HCl. A separation of phases took place and the aqueous phase was extracted with 25 mL of ether. The ether extract and THF layer were combined, washed with 10% sodium bicarbonate solution and saturated sodium chloride solution, and then dried over sodium sulfate. Removal of the organic solvent in vacuo afforded 2.5 g (78%) of the product which was distilled, bp 104–105 °C (5 mm). The ¹H NMR spectrum was as expected and showed the lack of the benzylic protons.

α -Deuterio-*p*-fluorobenzaldehyde was obtained by oxidation of α,α -dideuterio-*p*-fluorobenzyl alcohol. Potassium dichromate (2.0 g, 6.8 mmol) was dissolved in 60 mL of glacial acetic acid. Under a nitrogen atmosphere and with stirring of the dichromate solution, 2.5 g of the dideuterated alcohol dissolved in 20 mL of acetic acid was added. The progress of the reaction was monitored by GLC and at the appropriate time (10–30 min), the reaction mixture was poured into 500 mL of water and extracted with three 50-mL portions of methylene chloride. The combined organic extracts were washed with water and, after drying with sodium sulfate, the solvent was removed by evaporation in vacuo. The residue, representing a 64% yield, was usually used directly in the condensation reaction with malonic acid.

The deuterated fluorocinnamic acids were repeatedly recrystallized from hot water, giving products with the same melting point as the nondeuterated analogues.² ¹H NMR spectra showed no detectable signals in the spectral regions characteristic of the deuterated positions, indicating that the extent of deuteration was probably >97%. In both *o*-fluoro- and *p*-fluorodeuteriocinnamic acids, the ¹H NMR signal for the remaining vinyl proton was a broad triplet, $J_{HD} = 2.45$ Hz. This corresponds to $J_{HH} = 16$ Hz and demonstrates that the specifically deuterated compounds exist in the *trans* configuration, as was found with the nondeuterated forms of these molecules.²

All buffer salts were reagent grade materials; deuterium oxide (>99.6% D) was obtained from Stohler Isotope Chemicals. Sample pH was determined with a Radiometer PHM 52 digital pH meter and a Radiometer micro combination electrode; pH values reported are meter readings and are not corrected for the presence of deuterium in the solution.

Methods. Samples for the relaxation studies were prepared in deuterium oxide solution in 0.2 M phosphate buffer containing 2 mM ethylenediaminetetraacetic acid (EDTA) and were carefully degassed by at least three freeze–thaw cycles before sealing under vacuum. The apparent sample pH was between 7 and 8 typically; experiments showed that there was no detectable variation in relaxation rates with pH over this range.

Fluorine-19 spectra at 94.133 MHz were obtained with a Varian Associates XL-100 spectrometer coupled with a Nicolet Technology Corp. TT-100A Fourier transform accessory. Proton decoupling was achieved by use of a General Radio 1061 frequency synthesizer, Hewlett-Packard 3722A noise generator, and ENI 320L power amplifier coupled to the Varian V4412 probe through a locally designed double-tuning network.³ Under conditions of proton irradiation typical 90° pulse widths were 16–20 μ s for a 12-mm insert. R_1 values at this frequency were obtained by the “homospoil” technique⁴ and/or the 180°– τ –90° inversion–recovery sequence.

Fluorine relaxation data at 22.8 and 51 MHz were obtained by the inversion–recovery method with a Bruker BKR-321S spectrometer as described previously.⁶ On both instruments temperature control in the sample probe was achieved with Varian controllers and is believed to be accurate to ± 1 °C; temperatures were determined with a 5-mm o.d. thermometer supplied by Kontes Glass Co. immersed, where possible, in unsealed sample tubes containing the same volume of buffer as sealed samples.

Carbon-13 spectra were taken with a Varian Associates CFT-20 spectrometer. The inversion–recovery method was used for R_1 determinations. Ambient probe temperature with full proton decoupling was 36–37 °C, but no regulation of sample temperature is possible with the current configuration of the instrument.

Fluorine and carbon nuclear Overhauser effects were obtained using gated proton decoupling;⁷ at least 5 T_1 s separated each data acquisition.⁸ During NOE determinations the carbon sample temperature was 33 \pm 1 °C.

Proton spectra were obtained with the XL-100 using an internal capillary of hexafluorobenzene to provide a fluorine lock signal. Spectra were recorded with and without deuterium decoupling; the line width of the vinyl singlet of the decoupled spectra was taken as the instrumental line width. Theoretical line shapes for a proton coupled to a deuterium atom were prepared by a computer program based on the equations of Kintzinger et al.⁹ The experimental values for the instrumental line width were included in the calculations as an effective transverse relaxation rate ($R_2^* = 1/T_2^* = \pi w_{1/2}$); the deuterium spin–lattice relaxation time was adjusted until a good visual comparison of observed and calculated spectra resulted.

Results

Fluorine-19 Relaxation. Table I records fluorine-19 spin–lattice relaxation rates (R_1) for the fluorine nucleus of the fluorocinnamates under a variety of conditions. Data were obtained at field strengths of 0.569 T, 1.27 T, and 2.35 T, corresponding to fluorine resonance frequencies of 22.8, 51.0, and 94.1 MHz. No detectable field dependence was noted. The effect of solute concentration on the fluorine R_1 of each fluorocinnamate was checked over the range 20–100 mM and no concentration dependence beyond experimental error was detected. Replacement of the deuterium oxide solvent with normal water produces a substantial change in R_1 , leading to an average decrease in relaxation rate of 0.07 s^{–1}.

Most of the data in Table I were collected at 25 °C. However, a few fluorine relaxation experiments were carried out at 37 °C; these indicate that temperature effects on the relaxation rates are <25% over this (small) temperature range, slightly greater than the estimated experimental uncertainty ($\pm 15\%$).

In order to determine the extent of the fluorine relaxation due to intramolecular dipole–dipole interactions with nearby hydrogen nuclei, ¹⁹F {¹H} nuclear Overhauser effects were determined. In the small molecule–rapid motion limit the fractional enhancement of the fluorine signal intensity upon irradiation of protons is given by¹⁰

$$f_F(H) = 0.5(\gamma_H/\gamma_F)f = 0.532f \quad (1)$$

where γ_H and γ_F are the gyromagnetic ratios of ¹H and ¹⁹F, respectively, and f is the fraction of the total fluorine relaxation due to proton–fluorine dipole interactions. The Overhauser effects (fractional enhancements) reported in Table I were obtained under conditions of simultaneous irradiation of all protons and, since a small amount of residual protium in the solvent was unavoidable, represent minimum values.

It became apparent early in this work that the hydrogen nuclei of the vinyl group in the fluorocinnamate structure were involved in the relaxation of the fluorine nucleus of *o*-fluorocinnamate. To elucidate these interactions, several deuterated derivatives were prepared. Replacement of both vinyl hydrogens by deuterium significantly decreased the fluorine relaxation rate in Ia and study of monodeuterated analogues showed that, within experimental error, all of this change originates with the deuterium at the β position (Table I). Thus, in *o*-fluorocinnamate about 57% of the proton dipolar relaxation of the fluorine arises from interaction with the aromatic protons, and 43% is due to the β -vinyl hydrogen.

Carbon-13 Relaxation. Carbon relaxation times appear to be especially useful in providing details of the anisotropy of molecular motion^{1b,1d} and we therefore determined the carbon spin–lattice relaxation rates for the proton-bearing carbons of the fluorocinnamates. Because of poor sensitivity, the solute concentration was increased to 0.2 M for these experiments; data collected from 0.1 M samples gave relaxation rates in essential agreement with values obtained at the higher concentration, but were less reliable because of poorer signal-to-noise ratios.

Assignment of the carbon signals according to the structure

Table I. Fluorine-19 NMR Parameters for Fluorocinnamates^a

Parameter	Solvent	Rf, MHz	o-Fluoro				m-Fluoro	p-Fluoro
			Full H	α,β -di-D	α -D	β -D		
$\delta,^b$ ppm	H ₂ O		41.45				38.55	36.60
R_1, s^{-1}	H ₂ O	22.8						0.16
R_1, s^{-1}	H ₂ O	51.0	0.32	0.23	0.26	0.22		0.18 ^c
R_1, s^{-1}	D ₂ O	22.8	0.20				0.14	0.12
R_1, s^{-1}	D ₂ O	51.0	0.20			0.14	0.14	0.11 ^d
$R_1, s^{-1 e}$	D ₂ O	94.1	0.20	0.12	0.30	0.15	0.17	0.12
$R_1, s^{-1 e,f}$	D ₂ O	94.1	0.26	0.15			0.15	0.12
$f_c(H)[NOE]^g$	D ₂ O	94.1	0.33	0.37	0.28	0.29	0.38	0.28
$R_1^{DD}, s^{-1 h}$	D ₂ O	94.1	0.13	0.084	0.16	0.082	0.12	0.063
$R_1^{other}, s^{-1 i}$	D ₂ O	94.1	0.08	0.04	0.14	0.07	0.05	0.06

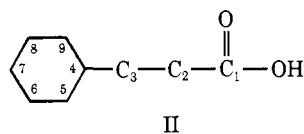
^a Samples were approximately 0.1 M and were run at 25 ± 1 °C, pH 7. Samples contained 2 mM EDTA. Relaxation rates estimated to be accurate to $\pm 15\%$. ^b Chemical shifts relative to internal trifluoroacetate (0.5 mM). In D₂O the chemical shift was 0.07 and 0.05 ppm to higher field for the ortho and meta isomers, respectively. There was no detectable change in the position of the fluorine signal for the para isomer in D₂O. ^c R_1 was invariant over concentration range 0.01–0.10 M. ^d Transverse relaxation rate, R_2 , determined by the Carr–Purcell–Meiboom–Gill method. ^e R_1 determined with proton decoupling. ^f Sample temperature was 37 ± 1 °C. ^g Estimated accuracy $\pm 10\%$. ^h Estimated accuracy $\pm 25\%$. ⁱ Estimated accuracy $\pm 40\%$.

Table II. Carbon-13 NMR Parameters for Fluorocinnamates^a

Carbon	δ, ppm^c	J_{CF}, Hz^d	$R_1, s^{-1 b}$
o-Fluoro			
2	61.90	2.8	0.45
3	66.30	3.5	0.31
6	49.30	22.3	0.50
7	64.55	8.7	0.67
8	60.20	4.8	0.37
9	58.05	3.4	0.46
m-Fluoro			
2	59.10	<0.1	0.30
3	72.75	2.2	0.25
5	47.15	22.3	0.37
7	49.45	21.5	0.91
8	64.00	8.6	0.35
9	59.25	2.5	0.40
p-Fluoro			
2	57.50	<0.1	0.32
3	73.00	<0.1	0.37
5, 9	63.00	8.2	0.44
6, 8	49.15	21.6	0.39

^a Determined at 20 MHz. Samples were 0.1–0.2 M cinnamate, pH 8, containing 2 mM EDTA, degassed by four freeze–thaw cycles, and sealed under vacuum. Probe temperature was 37 °C. ^b Estimated error $\pm 15\%$. ^c Downfield from 1% internal dioxane; estimated error ± 0.05 ppm. ^d Estimated error ± 0.4 Hz.

II was aided by the characteristic magnitudes of carbon–fluorine coupling constants¹¹ and ample precedent.¹² Table II



presents the carbon relaxation rates for the fluorocinnamate, obtained with complete proton decoupling at 37 °C. (Data could be obtained only at 37 °C because our instrumentation currently lacks variable-temperature capability.) Under the conditions used, carbons 1 and 4 and the carbon directly bonded to the fluorine were barely visible due to their very long relaxation times and no attempt was made to obtain data for these nuclei.

Carbon–hydrogen nuclear Overhauser effects were estimated and, in all cases, were within experimental error ($\pm 10\%$)

Table III. Comparison of Observed and Calculated Spin–Lattice Relaxation Rates in Fluorocinnamates

	Nucleus	$R_1(\text{calcd}), R_1(\text{obsd}),$ s^{-1}	
		s^{-1}	$s^{-1 a}$
o-Fluoro $D_{\parallel} = 1.8, D_{\perp} = 0.46^b$	F	0.06	0.083
	C(2)	0.42	0.45
	C(3)	0.42	0.31
	C(6)	0.42	0.50
	C(7)	0.75	0.67
	C(8)	0.42	0.37
	C(9)	0.42	0.46
	² H(β)	9.7	10, 5.6
	² H(α)	9.7	10, 5.6
m-Fluoro $D_{\parallel} = 2.6, D_{\perp} = 0.42^b$	F	0.12	0.12
	C(2)	0.37	0.30
	C(3)	0.37	0.25
	C(5)	0.37	0.37
	C(7)	0.90	0.90
	C(8)	0.37	0.35
	C(9)	0.37	0.40
	² H(β)	9.5	9.5, 5.9
	² H(α)	9.5	9.5, 5.9
p-Fluoro $D_{\parallel} = 2.1, D_{\perp} = 0.46^b$	F	0.068	0.063
	C(2)	0.40	0.32
	C(3)	0.40	0.37
	C(5), C(9)	0.40	0.44
	C(6), C(8)	0.40	0.39
	² H(β)	9.5	9.5, 5.9
	² H(α)	9.5	9.5, 5.9

^a Experimental data from Table I and Table II. The fluorine data were obtained at 25 °C, the carbon data at 37 °C, and the deuterium relaxation rates at 25 (first value) and 37 °C (second value). In the deuterium experiments the concentration of cinnamate was 0.01 M; the estimated accuracy of the deuterium rate is $\pm 20\%$. ^b Diffusion coefficients, $\times 10^{-10} s^{-1}$.

of the theoretical maximum value ($f_c(H) = 1.99$).¹³ Within the detection limits of our experiments, all carbons with directly bonded protons thus relax by the ¹H–¹³C dipolar mechanism.

Deuterium Relaxation. The close similarity of the spin–lattice relaxation rates of the vinyl carbons and the protonated aromatic carbons in the fluorocinnamates suggests that these nuclei are relaxed by the same molecular motions. An implication of this observation is that the rotation of the vinyl group relative to the aromatic ring must be slower than the overall tumbling rate of the molecule. To provide further confirmation of this conclusion, the spin–lattice relaxation rate for a deuterium atom bound to the β -carbon (carbon 3 of structure II) was determined. The method used was analysis of the line shape of the remaining vinyl proton; this line shape varies from

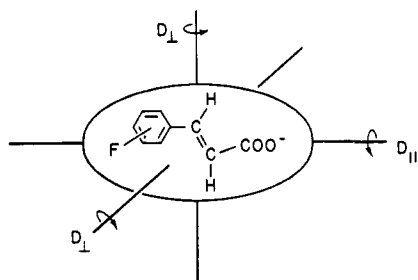


Figure 1. Ellipsoid of revolution model assumed for motion of fluorocinnamates.

a triplet to a singlet depending upon R_1 for the deuterium nucleus.⁹ Good correspondence between theory and experiment could be obtained in the line shape analysis. Table III includes the deuterium R_1 values for specifically deuterated *o*- and *p*-fluorocinnamates. An experimental error of $\pm 20\%$ in these relaxation rates is estimated by consideration of the sensitivity of the calculated line shapes to the deuterium spin-lattice relaxation rate.

Data Analysis. The same molecular motions are involved in the relaxation of the fluorine, carbon, and deuterium nuclei of a given fluorocinnamate. It was assumed that these molecules can be represented by an ellipse of revolution oriented in such a way that the major axis of the ellipse corresponds to the "length" of the cinnamate ion (Figure 1). This admittedly simplified picture is characterized dynamically by two diffusion coefficients, one for motion about the symmetry axis, D_{\parallel} , and one for motion perpendicular to the symmetry axis (D_{\perp}).¹⁴ The same model has been applied to the motion of monosubstituted benzenes.^{1b}

Experimentally we observe little temperature effect on the fluorine relaxation rates and so assumed that R_1^{DD} , the proton-hydrogen dipolar contribution to fluorine relaxation in the fluorocinnamates, determined at 25 °C could be compared directly to the carbon relaxation data obtained necessarily at 37 °C. For each isomer of I, a set of values of D_{\parallel} and D_{\perp} was sought which would give calculated fluorine, carbon, and deuterium relaxation rates that agreed with experiment. A computer program was used to minimize the function

$$A = \sum_n (1 - R_1^n(\text{calcd})/R_1^n(\text{obsd}))^2$$

where $R_1^n(\text{calcd})$ is a calculated relaxation rate and $R_1^n(\text{obsd})$ is the corresponding experimental quantity.¹⁵ In computing the dipolar relaxation contributions the structure of fluorobenzene¹⁶ was used to estimate internuclear distances in the fluorocinnamates. A deuterium quadrupolar coupling constant (e^2qQ/h) of 194 kHz was used in the deuterium relaxation calculations.^{17,18} (The deuterium relaxation rates at 37 °C seemed anomalously low and were not included in the data fitting.) Table III records the values of D_{\parallel} and D_{\perp} found to give optimum agreement with the experimental relaxation data; the diffusion coefficients could be varied by 10% from the values given in Table III and still afforded calculated relaxation rates within the estimated accuracy of the experimental data. The agreement between calculated and observed relaxation rates for the *m*-fluoro and *p*-fluoro isomers is excellent, but is not so satisfactory in the case of the ortho isomer.

The data analysis confirms that the relaxation of nuclei in the acrylate part of the fluorocinnamate structures can be described reasonably well by the *same* diffusion coefficients which describe the motion of the aromatic ring.

Discussion

Solvent plays a significant role in the relaxation of the fluorine nuclei of the fluorocinnamates in H_2O , with about 30%

of the observed spin-lattice relaxation rate in water being derived from interactions with water molecules. This contribution to fluorine relaxation should be reduced by 42-fold when the solvent protons are replaced by deuterium. However, even under these conditions, a substantial contribution to fluorine relaxation arises from sources other than the H-F dipole-dipole interactions in these materials. These contributions are reflected in R_1^{other} , listed in Table I and, because of the lack of concentration dependence of the relaxation rates, likely are not due to intermolecular interactions. Although chemical shift anisotropy (csa) can lead to an important relaxation mechanism for aryl-bound fluorine,¹⁹ this effect is dependent on the applied magnetic field. We see no field dependence of the fluorine relaxation data over a fourfold variation in magnetic field and it is likely that the csa contribution to relaxation is not more than a few percent at the highest field used.

The R_1^{other} terms could be the result of a spin-rotation relaxation mechanism; spin-rotation appears to be an important relaxation process for fluorine in fluorobenzene.²⁰⁻²² However, additional evidence such as an extended study of the temperature dependence of R_1^{other} is needed to substantiate the suggestion that spin-rotation interactions are responsible for this term.

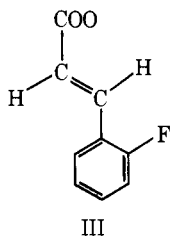
Dipolar relaxation in coupled multispin systems can be strongly nonexponential²³ and in the fluorocinnamate systems exponential spin-lattice relaxation is expected only under conditions of full proton decoupling. We have compared fluorine R_1 relaxation curves at 94.1 MHz obtained under conditions of continuous proton decoupling and also with proton decoupling only during data acquisition. In the former case single exponential relaxation is followed nicely to better than 4 half-lives. In the latter experiment some deviation from simple exponential behavior was observed, but the initial relaxation rates in both cases were, as expected, identical. We found no evidence for deviations from simple exponential relaxation of fluorine at 22.8 and 51 MHz. In these cases the signal-to-noise ratio is less than that obtained at the higher frequency. Calculations suggest that any nonexponential character in the relaxation curves at these frequencies would not be apparent until ~ 3 half-lives and by this time the uncertainty in the experimental data would have obscured effects of this kind.

Internal rotation about the C(3)-C(4) bond in the fluorocinnamates appears not to contribute detectably to the relaxation of the carbon nuclei of the vinyl group and the rate of this motion must therefore be less than the rate of molecular tumbling in the parallel direction, as quantified by D_{\parallel} . Behr and Lehn²⁴ have concluded from deuterium and carbon-13 relaxation studies of *p*-methyl- and *m*-methylcinnamate that the acrylate side chain and the phenyl ring in these molecules are dynamically strongly coupled, in agreement with the implications of our results. Presuming that the vinyl group has a diffusion constant, D_i , that is descriptive of internal rotation and that the rate constant, k_r , for internal rotation is $2D_i$,²⁵ our results require that

$$k_r \leq 4 \times 10^{10} \text{ s}^{-1}$$

Therefore, the free energy barrier to rotation is $> \sim 3$ kcal/mol. There have been no determinations of this rotational barrier, but infrared and NMR evidence show that the corresponding torsional barriers in the fluorine-substituted benzaldehydes range between 3.6 and 7.3 kcal/mol.^{12b,26} Contrastingly, the barrier to rotation in styrene, which ranges between 1.6 and 2.2 kcal/mol depending upon the experimental method used,²⁷ is substantially lower than this. It is difficult to know whether styrene or the aldehydes are better models for the conformational properties of the cinnamates, but in any event the rotational barrier required to account for our results, as well as those of Behr and Lehn, is not unreasonable.

Deuterium substitution shows that a significant part of the fluorine relaxation in Ia must arise from dipolar interactions with the β -vinyl hydrogen. Taking the contribution of the β -hydrogen to relaxation ($R_1 \approx 0.062$) and the values for D_{\parallel} and D_{\perp} found for *o*-fluorocinnamate, we estimate that the average distance between this hydrogen and the *o*-fluorine must be about 2.2 Å. This is essentially the proton-fluorine distance which obtains when the molecule is in the conformation shown in III, and since any other orientation about the carbon-carbon bond which holds the acrylate group to the *o*-fluorophenyl ring increases this distance, we must conclude that structure III



represents the only significantly populated conformation of *o*-fluorocinnamate. It may be recalled that *o*-fluorobenzaldehyde exists exclusively as the rotamer analogous to III.^{12b} Description of the molecular tumbling of the fluorocinnamates in terms of two diffusion coefficients is reasonably successful, although possibly a more complete model is needed to account for the relaxation data of Ia. The anisotropy of motion ($D_{\parallel}/D_{\perp} = 4-6$) is greater with these compounds than with more simply monosubstituted benzenes¹ ($D_{\parallel}/D_{\perp} \sim 1.3-1.8$) as would be expected given the relative molecular dimensions or the likely association of the anions with solvent. Although it is clear that solvent molecules can influence the relaxation of nuclei on the periphery of the fluorocinnamates, more data are needed to define the role of solvent effects in the molecular dynamics of these species.

Acknowledgments. This work was supported by the National Science Foundation (Grant CHE73-05209) and, in part, by the National Institutes of Health (Grant CA-11220). Purchase of the XL-100 and CFT-20 spectrometers was made possible

by a grant from the National Science Foundation (MPS75-06292). J.A.R. was a NSF Undergraduate Research Participant during the summer of 1975. J.T.G. is a Research Career Development Awardee of the National Institutes of Health (Grant GM-70373).

References and Notes

- (1) (a) Ch. Brevard, J. P. Kintzinger, and J. M. Lehn, *Tetrahedron*, **28**, 2429 (1972); (b) G. C. Levy, J. D. Cargioli, and F. A. L. Anet, *J. Am. Chem. Soc.*, **95**, 1527 (1973); (c) J. P. Kintzinger and J. M. Lehn, *Mol. Phys.*, **27**, 491 (1974); (d) S. Berger, F. R. Kreissl, D. M. Grant, and J. D. Roberts, *J. Am. Chem. Soc.*, **97**, 1805 (1975); (e) G. C. Levy, T. Holak, and A. Steigel, *ibid.*, **98**, 495 (1976).
- (2) (a) J. T. Gerig, B. A. Halley, and C. E. Ortiz, *J. Am. Chem. Soc.*, submitted for publication; (b) J. T. Gerig and R. S. McLeod, *Can. J. Chem.*, **53**, 513 (1975).
- (3) G. B. Matson, *J. Magn. Reson.*, in press.
- (4) G. G. McDonald and J. S. Leigh, Jr., *J. Magn. Reson.*, **9**, 358 (1973).
- (5) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).
- (6) J. T. Gerig, G. B. Matson, and A. D. Stock, *J. Magn. Reson.*, **15**, 382 (1974).
- (7) G. A. Gray, *Anal. Chem.*, **47**, 546A (1975).
- (8) S. J. Opella, D. J. Nelson, and O. Jardetzky, *J. Chem. Phys.*, **64**, 2533 (1976).
- (9) J. P. Kintzinger, J. M. Lehn, and R. L. Williams, *Mol. Phys.*, **17**, 135 (1969).
- (10) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect", Academic Press, New York, N.Y., 1971, p. 49.
- (11) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p. 362.
- (12) (a) V. Wray and D. N. Lincoln, *J. Magn. Reson.*, **18**, 374 (1975); (b) T. Drakenberg, R. Jost, and J. M. Sommer, *J. Chem. Soc., Perkin Trans. 2*, 1682 (1975).
- (13) K. F. Kuhlmann and D. M. Grant, *J. Am. Chem. Soc.*, **90**, 7355 (1968).
- (14) D. E. Woessner, *J. Chem. Phys.*, **37**, 647 (1962).
- (15) This form of weighted least-squares analysis was chosen so that all experimental values were represented by quantities (R_1 , (calcd)/ R_1 (obsd)) of similar magnitudes.
- (16) L. Nygaard, I. Bojesen, T. Pederson, and J. Rastrup-Andersen, *J. Mol. Struct.*, **2**, 209 (1968).
- (17) J. A. Glasel, *J. Am. Chem. Soc.*, **91**, 4569 (1969).
- (18) W. T. Huntress, Jr., *Adv. Magn. Reson.*, **4**, 1 (1970).
- (19) W. E. Hull and B. D. Sykes, *J. Mol. Biol.*, **98**, 121 (1975).
- (20) D. K. Green and J. G. Powles, *Proc. Phys. Soc.*, **85**, 87 (1965).
- (21) M. Chien and C. G. Wade, *J. Chem. Phys.*, **54**, 3562 (1971).
- (22) R. A. Assink and J. Jonas, *J. Chem. Phys.*, **57**, 3329 (1972).
- (23) L. G. Werbelow and D. M. Grant, *J. Chem. Phys.*, **63**, 4742 (1975).
- (24) J. P. Behr and J. M. Lehn, *J. Am. Chem. Soc.*, **98**, 1743 (1976).
- (25) Reference 10, p. 28.
- (26) F. A. Miller, W. G. Fately, and R. E. Witkowski, *Spectrochim. Acta, Part A*, **23**, 891 (1967).
- (27) T. Schaefer and W. J. E. Parr, *J. Mol. Spectrosc.*, **61**, 479 (1976).

A Theoretical Study of the Structure of Cyclobutadiene

H. Kollmar* and V. Staemmler

Contribution from the Lehrstuhl fuer theoretische Chemie, Abteilung fuer Chemie, Ruhr-Universitaet-Bochum, D-4630 Bochum, West Germany. Received September 24, 1976

Abstract: Ab initio calculations both on the SCF level and with electronic correlation have been performed for the square singlet and triplet and the rectangular singlet states of planar cyclobutadiene. In the square geometry the singlet turns out to be more stable than the triplet by about 7 kcal/mol. This violation of Hund's rule is explained as an effect of "dynamic spin polarization". Distortion of the square geometry to a rectangular structure stabilizes the singlet state further. The equilibrium structure of cyclobutadiene shows long C-C single bonds of 1.57 Å and normal double bonds, similar to the bond lengths observed experimentally for substituted cyclobutadienes. The energy difference between the rectangular and the square structure of singlet cyclobutadiene is estimated to be 14 kcal/mol.

I. Introduction

The structure of cyclobutadiene is still a vividly discussed subject.^{1,2} Most experiments seem to be in favor of a square structure of the unsubstituted cyclobutadiene in its ground state.¹ For an alkyl-substituted cyclobutadiene, however, the

rectangular singlet structure is well established by x-ray structural analysis.³ In a recent paper Borden² presented theoretical arguments favoring a square singlet to be the ground state of cyclobutadiene.

Previous ab initio calculations,⁴⁻⁶ on the other hand, do not support a square structure to be a minimum of the singlet