

# Nuclear Magnetic Resonance Spectroscopy. Rotational Isomerism in $\alpha,\beta$ -Unsaturated Acyl Fluorides

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**Abstract:** Low-temperature fluorine nuclear magnetic resonance spectroscopy has been used to investigate the conformational equilibria and rates of equilibration of acryloyl fluoride, crotonyl fluoride, cinnamoyl fluoride, and *p*-methoxycinnamoyl fluoride. Interconversions of the *s*-trans and the *s*-cis conformers of these  $\alpha,\beta$ -unsaturated acyl fluorides were stopped on the nmr time scale at low temperatures. Rate constants for conversion of the *s*-trans to the *s*-cis conformers were determined at each temperature by analyses of the <sup>19</sup>F nmr lineshapes. Activation parameters and the conformational energy differences for the *s*-trans and the *s*-cis conformers have been determined. The effects of structural changes on activation parameters and free energy differences are discussed. The magnitude of the values of the leading three terms in the rotational potential function for acryloyl fluoride are also reported.

The possibility that 1,3-butadiene- and acrolein-type molecules may exist in more than one stable rotational conformer was recognized many years ago.<sup>2</sup> Recently a variety of experimental techniques have been applied to the study of rotational isomerism of these conjugated diene and enone systems. Electron-diffraction<sup>3</sup> and infrared<sup>4</sup> studies on 1,3-butadiene itself gave evidence that the planar *s*-trans conformer is the dominant (though not necessarily the exclusive) form at room temperature. Microwave studies of 1,1-difluorobutadiene<sup>5</sup> by Beaudet, and 2-fluorobutadiene<sup>6</sup> and isoprene<sup>7</sup> by Lide failed to reveal the presence of the *s*-cis (or skew) conformer. On the other hand, 2,3-di-*tert*-butyl-1,3-butadiene was reported to exist in a nontransoid conformation as a result of steric interactions of the bulky *tert*-butyl groups.<sup>8</sup> By infrared and Raman studies, chloroprene, 2,3-dichloro-1,3-butadiene, and isoprene have been found to exist predominantly in the *s*-trans conformation, while hexachloro-1,3-butadiene exists in a preferred nonplanar conformation.<sup>9a</sup> The photoelectron spectrum of hexafluorobutadiene suggests that the carbon skeleton of this molecule is nonplanar.<sup>9b</sup>

Nmr studies of the substituted 1,3-butadienes by Bothner-By and coworkers have pointed to the possibility that the stable nontransoid form may adopt a skew conformation.<sup>10,11</sup> Based on the magnitude and sign of the four-bond H-H coupling constants, and some uv data, they deduced that 2-bromo-1,3-butadiene and 2-iodo-1,3-butadiene exist practically completely in the *s*-trans conformation, while 1,1,3-trichloro-1,3-butadiene and 1,1,3-tribromo-1,3-butadiene

are predominantly in a skew conformation.<sup>10</sup> Furthermore, 1,1-dichloro-3-fluoro-1,3-butadiene and 1,1-dibromo-3-fluoro-1,3-butadiene were also reported to exist as a mixture of the *s*-trans and the skew conformers.<sup>11</sup> From nmr, microwave, ir, and dipole moment studies, Servis and Roberts<sup>12</sup> concluded that 1,1,4,4-tetrafluoro-1,3-butadiene exists in the *s*-trans conformation. Based on the relatively small magnitude of the five-bond F-F coupling obtained from an analysis of the complex <sup>19</sup>F nmr spectrum of hexafluoro-1,3-butadiene, Manatt and Bowers<sup>13</sup> suggested that this molecule may not be in a planar form.

In the case of acrolein, studies in the near ultraviolet,<sup>14,15</sup> and in the far ir<sup>16</sup> have given values of the torsional frequencies of *s*-trans acrolein, but no spectrum of any other form has been detected. The structure of acrolein was determined more recently by microwave<sup>17</sup> and electron diffraction<sup>18,19</sup> methods and the results were in accord with the occurrence of the *s*-trans conformation. It was concluded from a microwave study of *trans*-crotonaldehyde that this molecule also exists only in the *s*-trans conformation.<sup>20</sup> In a number of recent papers, studies of rotational isomerism in  $\alpha,\beta$ -unsaturated acyl halides have been reported.<sup>21-25</sup> A low-temperature <sup>19</sup>F nmr study of perfluoroacrolein was carried out by Brey and Ramey.<sup>22</sup> The molecule showed an averaged spectrum at room temperature but had two nmr-distinguishable conformers at -105° as a result of restricted rotation about the central C<sub>1</sub>-C<sub>2</sub> bond of the conjugated system.<sup>22</sup>

- (1) Alfred P. Sloan Research Fellow, 1969-1971.
- (2) H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 691 (1951), and references therein.
- (3) A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).
- (4) D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, **17**, 163 (1962).
- (5) R. A. Beaudet, *J. Chem. Phys.*, **42**, 3758 (1965).
- (6) D. R. Lide, Jr., *ibid.*, **37**, 2074 (1962).
- (7) D. R. Lide, Jr., and M. Jen, *ibid.*, **40**, 252 (1964).
- (8) H. Wynberg, A. DeGroot, and D. W. Davies, *Tetrahedron Lett.*, 1083 (1963).
- (9) (a) G. J. Szasz and H. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953); (b) C. R. Brundle and M. B. Robin, *J. Amer. Chem. Soc.*, **92**, 5550 (1970).
- (10) A. A. Bothner-By and D. Jung, *ibid.*, **90**, 2342 (1968).
- (11) A. A. Bothner-By and D. F. Koster, *ibid.*, **90**, 2351 (1968).

- (12) K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1339 (1965).
- (13) S. L. Manatt and M. T. Bowers, *ibid.*, **91**, 4381 (1969).
- (14) J. C. D. Brand and D. G. Williamson, *Discuss. Faraday Soc.*, **35**, 184 (1963).
- (15) J. M. Hollas, *Spectrochim. Acta*, **19**, 1425 (1963).
- (16) R. K. Harris, *ibid.*, **20**, 1129 (1964).
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- (18) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, **1**, 463 (1967).
- (19) M. Traetteberg, *Acta Chem. Scand.*, **24**, 373 (1970).
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- (21) D. F. Koster, *J. Amer. Chem. Soc.*, **88**, 5067 (1966).
- (22) W. S. Brey, Jr., and K. C. Ramey, *J. Chem. Phys.*, **39**, 844 (1963).
- (23) J. E. Katon and W. R. Fearheller, Jr., *ibid.*, **47**, 2248 (1967).
- (24) G. L. Carlson, W. G. Fateley, and R. E. Witkowski, *J. Amer. Chem. Soc.*, **89**, 6437 (1967).
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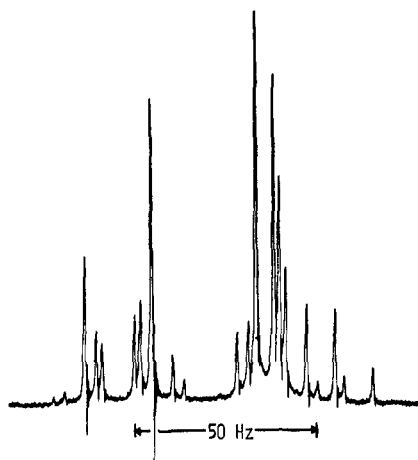


Figure 1. The 100-MHz nmr spectrum of acryloyl fluoride in carbon tetrachloride solution.

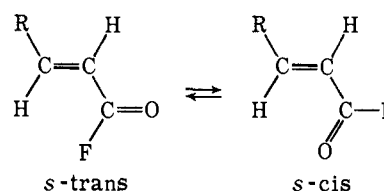
From a study of the infrared spectra of acryloyl chloride, Katon and Fearheller<sup>23</sup> concluded that two discrete rotational conformers coexist in the vapor and liquid states. The energy difference of the two conformers could not be determined because of severe band overlap, but a gas-phase value of 600 cal/mol was suggested.<sup>23</sup>

For acryloyl fluoride, Koster<sup>21</sup> examined the temperature dependence (+85 to -95°) of the <sup>1</sup>H nmr spectra. The averaged three-bond H-F coupling constants were measured at high temperatures. By a least squares treatment, the *s*-trans conformer was calculated to be 800 ± 250 cal/mol more stable than the *s*-cis conformation of acryloyl fluoride. On the other hand, Carlson, Fateley, and Witkowski<sup>24</sup> in an infrared and Raman study of acryloyl fluoride found adsorption bands at 978 and 998 cm<sup>-1</sup> and assigned them to the *s*-trans and the *s*-cis conformers, respectively. From an investigation of the intensity of these bands over the temperature range +28 to -99°, they determined the energy difference between the two forms of acryloyl fluoride to be 150 ± 100 cal/mol in carbon disulfide solution and about the same for the neat liquid. A microwave study of acryloyl fluoride was carried out by Keirns and Curl.<sup>25</sup> The ground-state energy difference between the planar *s*-trans and the planar *s*-cis conformers of acryloyl fluoride was reported to be 90 ± 100 cal/mol, with the *s*-trans conformation being more stable.

It is difficult to measure the rotational barriers of 1,3-butadiene and acrolein with good accuracy since the corresponding *s*-cis (or nonplanar) conformers can not be detected by spectroscopic methods. However, from the result of ir<sup>24</sup> and microwave<sup>25</sup> studies, acryloyl fluoride seemed to be a suitable, tractable molecule for low-temperature nmr work. Low-temperature <sup>19</sup>F nmr studies were undertaken to determine the structural and dynamic properties of α,β-unsaturated acyl fluorides. It was hoped that the analysis of the temperature-dependent nmr spectra of α,β-unsaturated acyl fluorides would give the values of the rotational barriers and the conformational energy differences of the two possible conformers. The possible effects of structural changes on activation parameters and equilibrium constants were also of interest.

## Results

The four conjugated acyl fluorides (I-IV) studied



- I, R = H  
 II, R = CH<sub>3</sub>  
 III, R = C<sub>6</sub>H<sub>5</sub>  
 IV, R = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>

were prepared according to the procedures reported in the literature.<sup>26,27</sup>

The 100-MHz pmr spectrum of acryloyl fluoride in carbon tetrachloride solution, as shown in Figure 1, is best described as resulting from the ABC part of an ABCX spin system. In Table I are summarized the

Table I. The 100-MHz Pmr Parameters for Acryloyl Fluoride in Carbon Tetrachloride Solution

Chemical shifts, Hz	Coupling constants, Hz	
$\nu_2 - \nu_3 = 9.3 \pm 0.1$	$J_{1,2} = 8.4 \pm 0.1$	$J_{2,3} = 10.5 \pm 0.1$
$\nu_3 - \nu_4 = 38.4 \pm 0.1$	$J_{1,3} = 3.0 \pm 0.1$	$J_{2,4} = 17.3 \pm 0.1$
	$J_{1,4} = -0.3 \pm 0.1$	$J_{3,4} = 0.8 \pm 0.1$

nmr parameters obtained by analysis of the spectrum using the computer program LAOCOON III.<sup>28</sup> The nmr parameters we have obtained for acryloyl fluoride are in good agreement with Koster's reported values.<sup>21</sup> The 94.1-MHz fmr spectrum of acryloyl fluoride dissolved in vinyl chloride at ambient temperature was a symmetrical multiplet, as illustrated in Figure 2, centered at a chemical shift 23.9 ppm downfield from internal fluorotrichloromethane, with  ${}^3J_{\text{HF}}^{\text{av}} = 8.4$  Hz (see Table II). Profound changes occurred in the fmr spectrum of acryloyl fluoride as a result of cooling a

Table II. Fluorine Chemical Shifts and Coupling Constants of the α,β-Unsaturated Acid Fluorides at Ambient Temperature

	$\nu^a$	${}^3J_{\text{HF}}^b$
Acryloyl fluoride, I	23.94 <sup>c</sup>	8.43
Crotonyl fluoride, II	23.93 <sup>c</sup>	7.82
Cinnamoyl fluoride, III	24.63 <sup>d</sup>	6.87
<i>p</i> -Methoxycinnamoyl fluoride, IV	24.03 <sup>e</sup>	6.80

<sup>a</sup> In ppm, downfield from internal CCl<sub>3</sub>F. <sup>b</sup> In Hz, uncertainties ±0.1 Hz. <sup>c</sup> In vinyl chloride solution. <sup>d</sup> In 40% CHF<sub>2</sub>Cl and 60% vinyl chloride solution. <sup>e</sup> In 30% acetone and 70% vinyl chloride solution.

- (26) W. Brugel, *Z. Elektrochem.*, **64**, 1149 (1960).  
 (27) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **89**, 2694 (1967).  
 (28) (a) A. A. Bothner-By and S. M. Castellano, *J. Chem. Phys.*, **41**, 3863 (1964); (b) A. A. Bothner-By and S. M. Castellano, "Quantum Chemistry Program Exchange," No. 111, LAOCOON III, Chemistry Department, Indiana University, Bloomington, Ind.

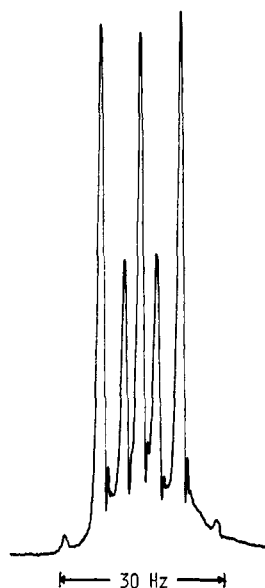


Figure 2. The ambient temperature 94.1-MHz fmr spectrum of acryloyl fluoride in vinyl chloride solution.

vinyl chloride solution of the sample, as shown in Figure 3. As the temperature was progressively lowered, the spectrum became increasingly broadened, and a wide hump was observed at  $-135^\circ$ . When the temperature was lowered down to  $-161^\circ$ , two distinct absorptions with a population ratio of 76 to 24 and well separated by 2075 Hz were observed. A coupling constant of 19.2 Hz associated with the more populated absorption (at higher field) was measured at this low temperature. These two nmr absorptions at very low temperature were attributed to the *s*-trans and the *s*-cis conformations of acryloyl fluoride. The most reasonable explanation for the observed temperature-dependent nmr spectra is that on the nmr time scale interconversion of the two conformers is rapid at room temperature but slow at very low temperature. We have assigned the more intense signal (at higher field) to the *s*-trans conformer and the less intense signal (at lower field) to the *s*-cis conformer. The coupling constant of  $\pm 19.2$  Hz was assigned to be the three-bond H-F coupling of the *s*-trans conformer of acryloyl fluoride.

Due to the extensive spin-spin couplings between the fluorine atom and the other three vinylic protons, the *s*-cis signal was observed to be a broad peak. In order to estimate the magnitude of the three-bond H-F coupling constant of the *s*-cis conformer,  $^3J_{\text{HF}}^{\text{s-cis}}$ , we employed eq 1, where *P* is the population of the *s*-trans

$$^3J_{\text{HF}}^{\text{av}} = P^3J_{\text{HF}}^{\text{s-trans}} + (1 - P)^3J_{\text{HF}}^{\text{s-cis}} \quad (1)$$

conformer and it is further assumed that the energy difference between the two forms was independent of temperature. A value of  $\mp 7.5$  Hz was obtained for  $^3J_{\text{HF}}^{\text{s-cis}}$ . The chemical shifts, coupling constants, populations, and the energy difference for acryloyl fluoride at  $-161^\circ$  in vinyl chloride solution are given in Table III.

A series of theoretical spectra was generated<sup>29</sup> corresponding to different values of the rate constant

(29) (a) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969); (b) G. Binsch and D. A. Kleier, "Quantum Chemistry Program Exchange," No. 140, DNMR Computer Program, Chemistry Department, Indiana University, Bloomington, Ind.

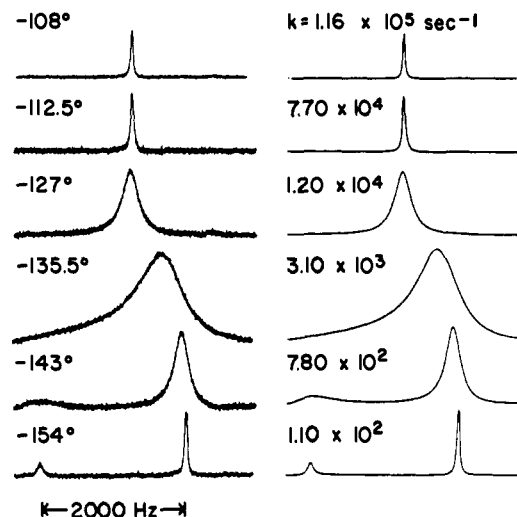


Figure 3. Experimental (left) and calculated (right) 94.1-MHz fmr spectra of acryloyl fluoride in vinyl chloride solution.

Table III. Chemical Shifts, Coupling Constants, Relative Populations, and  $\Delta G$  Values for Equilibrium of the Four Acyl Fluorides Studied at Low Temperatures

	Relative population <sup>a</sup>	$\nu^b$	$^3J_{\text{HF}}^c$
(i) Acryloyl Fluoride (R = H) at $-161.5^\circ$ in Vinyl Chloride Solution ( $\Delta G = 253 \pm 67$ cal/mol)			
<i>s</i> -trans	0.76	1548	19.2
<i>s</i> -cis	0.24	3623	-7.5
(ii) Crotonyl Fluoride (R = CH <sub>3</sub> ) at $-136^\circ$ in Vinyl Chloride Solution ( $\Delta G = 215 \pm 63$ cal/mol)			
<i>s</i> -trans	0.69	1556	21.5
<i>s</i> -cis	0.31	3321	-11.6
(iii) Cinnamoyl Fluoride (R = C <sub>6</sub> H <sub>5</sub> ) at $-130.5^\circ$ in 60% vinyl Chloride and 40% Chlorodifluoromethane Solution ( $\Delta G = 95 \pm 58$ cal/mol)			
<i>s</i> -trans	0.58	1400	19.4
<i>s</i> -cis	0.42	3410	-7.8
(iv) <i>p</i> -Methoxycinnamoyl Fluoride (R = <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub> ) at $-142^\circ$ in 70% Vinyl Chloride and 30% Acetone Solution ( $\Delta G = 112 \pm 54$ cal/mol)			
<i>s</i> -trans	0.61	1376	20.4
<i>s</i> -cis	0.39	3407	-9.6

<sup>a</sup> Uncertainty,  $\pm 0.03$ . <sup>b</sup> All chemical shifts are reported in Hz downfield from internal fluorotrichloromethane. The uncertainties are  $\pm 5$  Hz. <sup>c</sup> In Hz, the uncertainties for *s*-trans values are  $\pm 0.5$  Hz; the calculated *s*-cis values have greater uncertainties, estimated to be  $\pm 2$  Hz.

for *s*-trans to *s*-cis conversion, using the DNMR2 computer program, written by Binsch and Kleier.<sup>29</sup> Comparison of the theoretical spectra with the experimental spectra permitted the correlation of temperatures with the exchange rate constant. A least squares analysis<sup>30</sup> of the variation of these rate constants with temperatures yielded the Arrhenius activation energy ( $E_a$ ) for

(30) (a) D. F. DeTar, *J. Chem. Educ.*, **44**, 759 (1969); (b) D. F. DeTar "Quantum Chemistry Program Exchange," No. 79, ACTENG Program, Chemistry Department, Indiana University, Bloomington, Ind.

**Table IV.** Free Energies of Activation at  $-100^\circ$  ( $\Delta G^\ddagger_{-100^\circ}$ ), Arrhenius Activation Energies ( $E_a$ ), Ground-State Free Energy Differences ( $\Delta G$ ), Entropies of Activation ( $\Delta S^\ddagger$ ), Enthalpies of Activation  $\Delta H^\ddagger$ , and Frequency Factors ( $A$ ) of the  $\beta,\alpha$ -Unsaturated Acyl Fluorides

Fluorides	Acryloyl <sup>d</sup>	Crotonyl <sup>d</sup>	Cinnamoyl <sup>e</sup>	<i>p</i> -Methoxycinnamoyl <sup>f</sup>
$\Delta G^\ddagger_{-100^\circ}$ <sup>a</sup>	$5.62 \pm 0.07$	$6.69 \pm 0.05$	$7.13 \pm 0.07$	$7.32 \pm 0.08$
$E_a$ <sup>a</sup>	$6.60 \pm 0.07$	$6.99 \pm 0.05$	$7.34 \pm 0.07$	$8.21 \pm 0.08$
$\Delta G^\ddagger$ <sup>b</sup>	$253 \pm 67$	$215 \pm 63$	$95 \pm 58$	$112 \pm 54$
$\Delta S^\ddagger$ <sup>c</sup>	$0.93 \pm 0.4$	$-0.25 \pm 0.30$	$-0.88 \pm 0.34$	$2.98 \pm 0.43$
$\Delta H^\ddagger$ <sup>a</sup>	$5.78 \pm 0.07$	$6.65 \pm 0.05$	$6.98 \pm 0.07$	$7.84 \pm 0.08$
$A$	$(1.30 \pm 0.28) \times 10^{13}$	$(0.85 \pm 0.10) \times 10^{13}$	$(0.68 \pm 0.11) \times 10^{13}$	$(4.81 \pm 0.04) \times 10^{13}$

<sup>a</sup> In kcal/mol. <sup>b</sup> In cal/mol. <sup>c</sup> In eu. <sup>d</sup> In vinyl chloride solution. <sup>e</sup> In 60% vinyl chloride and 40% chlorodifluoromethane solution. <sup>f</sup> In 70% vinyl chloride and 30% acetone solution.

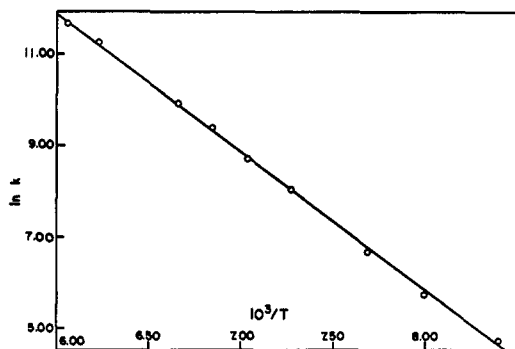


Figure 4. Arrhenius plot for acryloyl fluoride.

the conversion of the *s*-trans conformer to the *s*-cis conformer as  $6.06 \pm 0.07$  kcal/mol. The activation parameters are summarized on Table IV. Representative spectra and the Arrhenius plot are shown in Figures 3 and 4.

The 94.1-MHz fmr spectra of crotonyl fluoride, cinnamoyl fluoride, and *p*-methoxycinnamoyl fluoride at ambient temperature are all very similar and exhibit a doublet with the three-bond H-F coupling constants of 7.82, 6.78, and 6.80 Hz, respectively. The nmr parameters at ambient temperature are summarized in Table II.

As the temperature was progressively lowered, the fmr spectra of crotonyl, cinnamoyl, and *p*-methoxycinnamoyl fluorides underwent changes similar to that for acryloyl fluoride except that the corresponding coalescence temperatures were individually different. The chemical shifts, coupling constants, and relative populations of these acyl fluorides at low temperatures are given in Table III. Representative spectra are shown in Figures 5-7. The corresponding Arrhenius plots are shown in Figures 8-10. The activation parameters are summarized in Table IV.

## Discussion

The magnitude and sign of the H-F coupling constants from the low-temperature fmr spectra of acryloyl fluoride provides information on which to base conformational assignments. A three-bond H-F coupling constant of  $\pm 19.2$  Hz was associated with the more intense higher field signal and a three-bond H-F coupling constant of  $\mp 7.5$  Hz was calculated for the less intense lower field signal. The signs of the two coupling constants are clearly opposite to each other. The absolute sign of the larger coupling constant is assumed to be positive.<sup>31</sup> Modified Karplus equations<sup>32</sup> are useful

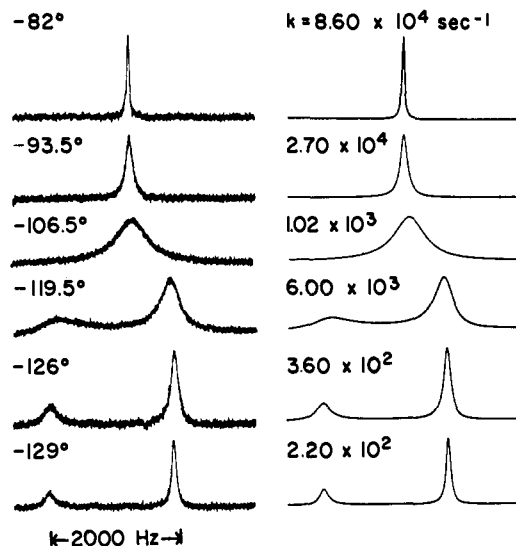


Figure 5. Experimental (left) and calculated (right) 94.1-MHz fmr spectra of crotonyl fluoride in vinyl chloride solution.

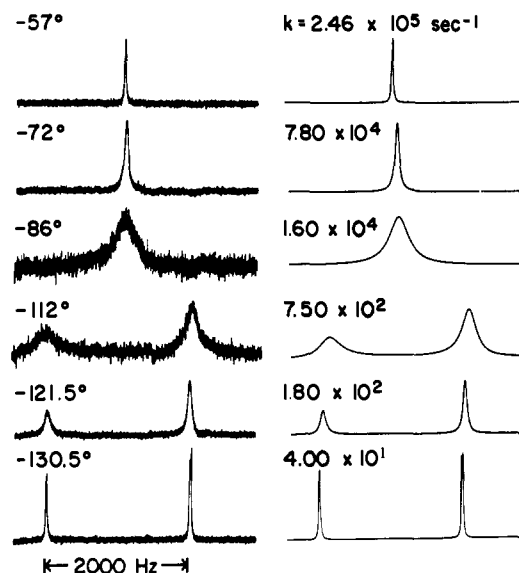


Figure 6. Experimental (left) and calculated (right) 94.1-MHz fmr spectra of cinnamoyl fluoride in 60% vinyl chloride and 40% chlorodifluoromethane solution.

in describing the dihedral angle dependence of vicinal coupling constants. Such equations have been suc-

(31) A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, **87**, 3445 (1965).

(32) M. Karplus, *ibid.*, **85**, 2870 (1963).

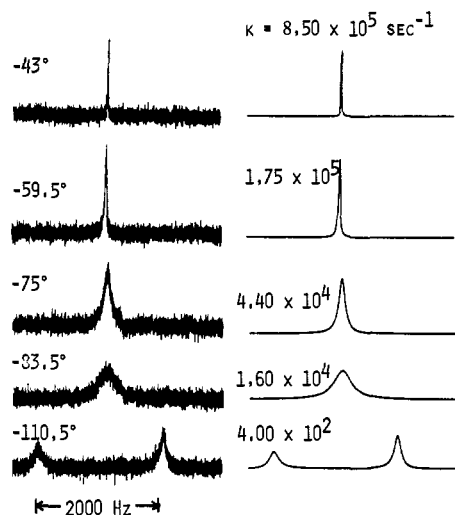


Figure 7. Experimental (left) and calculated (right) 94.1-MHz fmr spectra of *p*-methoxycinnamoyl fluoride in 70% vinyl chloride and 30% acetone solution.

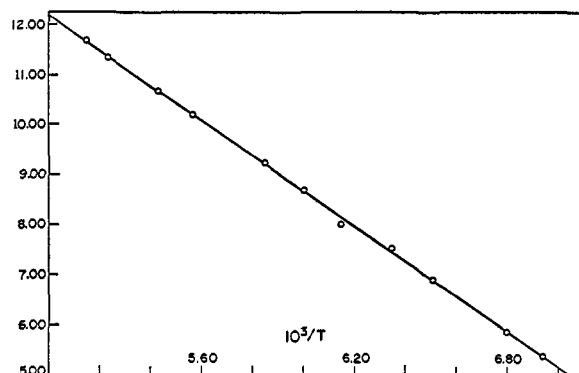
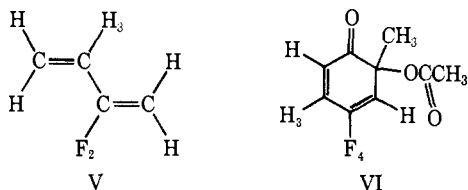


Figure 8. Arrhenius plot for crotonyl fluoride.

cessfully applied not only to the ethane- and the allylic-type systems, but also to conjugated systems.<sup>33,34</sup>

Williamson<sup>35</sup> has also shown that the angular dependence of vicinal H-F coupling constants is similar to those of H-H coupling constants. Hence, one would expect three-bond H-F couplings across a single bond to be greater in *s*-trans than in *s*-cis conformations. This is indeed observed experimentally. In 2-fluorobutadiene (V), which is known to be in the *s*-trans conforma-



tion,<sup>6</sup> the three-bond H-F coupling across the C-C single bond,  ${}^3J_{\text{H}_1\text{F}_2}^{s\text{-trans}}$ , was reported to be 25.15 Hz.<sup>31</sup> While in the near *s*-cis butadiene-type compound (VI), the three-bond H-F coupling  ${}^3J_{\text{H}_1\text{F}_4}^{s\text{-cis}}$  was reported to be  $|7|$  Hz.<sup>33</sup>

(33) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964).

(34) A. A. Bothner-By and E. Moser, *J. Amer. Chem. Soc.*, **90**, 2347 (1968).

(35) K. L. Williamson, Y. F. Li, F. H. Hall, and S. Swager, *ibid.*, **88**, 5678 (1966).

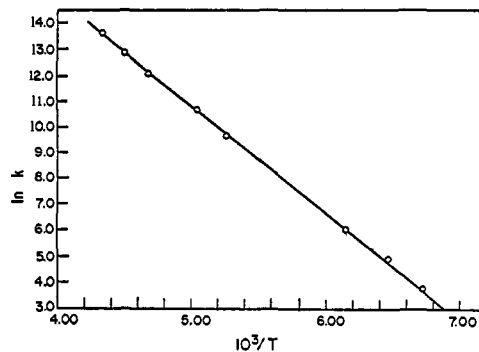


Figure 9. Arrhenius plot for cinnamoyl fluoride.

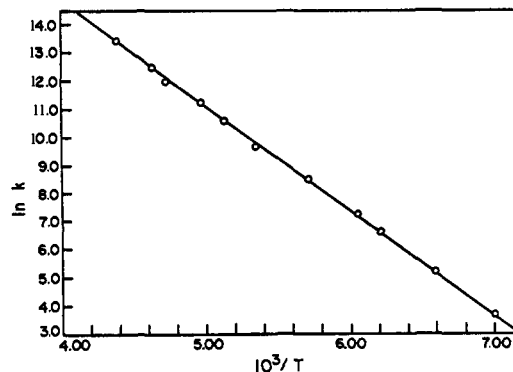


Figure 10. Arrhenius plot for *p*-methoxycinnamoyl fluoride.

We have, therefore, assigned the signal exhibiting  ${}^3J_{\text{HF}} = 19.2$  Hz to the *s*-trans conformation, and the signal with  ${}^3J_{\text{HF}} = -7.5$  Hz to the *s*-cis conformation. Since the coupling constant of  $+19.2$  Hz is associated with the more intense signal in the low-temperature fmr spectrum, the *s*-trans conformer of acryloyl fluoride must be more stable than the *s*-cis analog. By integration at low temperature, the equilibrium ratio of the two conformers was determined. The energy difference between the two conformers was found to be  $253 \pm 67$  cal/mol.

From a microwave study<sup>25</sup> the ground-state energy difference between the two forms was reported to be  $90 \pm 100$  cal/mol, with the *s*-trans thought to be the more stable conformer. The moments of inertia were reported to be virtually identical for the two forms (3.26 and 3.21 D for the *s*-trans and the *s*-cis conformers, respectively) and consequently there was some uncertainty whether the spectra have been correctly assigned to *s*-trans and *s*-cis.<sup>25</sup> However, the value of  $\Delta H = 800 \pm 250$  cal/mol obtained by the analysis of the temperature dependence of  ${}^3J_{\text{HF}}^{s\text{v}}$  for acryloyl fluoride in fluorotrichloromethane solution is too high. In other cases the values derived from the nmr method developed by Gutowsky, Belford, and McMahon<sup>36</sup> have proven to be inaccurate.<sup>37</sup> For example, in 1,1,2-trichloro-1,2,2-trifluoroethane ( $\text{CF}_2\text{Cl}-\text{CFCl}_2$ ), the  $\Delta H$  value of 2000–2760 cal/mol is an order of magnitude different from that measured from vibrational spectra ( $350 \pm 150$  cal/mol).<sup>36</sup> Newmark and Sederholm<sup>37a</sup> “froze out”

(36) H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).

(37) (a) R. A. Newmark and C. H. Sederholm, *ibid.*, **39**, 3131 (1963); (b) G. Govil and H. J. Bernstein, *ibid.*, **47**, 2818 (1967).

the conformers in CF<sub>2</sub>Br-CFBrCl and found that the coupling constants of the conformers did not agree with those found by Gutowsky, *et al.* Govil and Bernstein<sup>37b</sup> had investigated the rotational isomerism on 1,1,2,2-tetrabromofluoroethane (CHBr<sub>2</sub>-CFBr<sub>2</sub>) using low-temperature <sup>1</sup>H and <sup>19</sup>F nmr spectra and found that the values of Δ*H* and coupling constants obtained from the Gutowsky method and the "froze out" method were completely different. The reasons for these discrepancies were discussed by Bernstein.<sup>37b</sup> The similarly obtained value of Δ*H* for acryloyl fluoride may also be incorrect for similar reasons.

The nature of the potential energy barrier restricting rotation around a carbon-carbon single bond between sp<sup>2</sup>-type hybridized carbon atoms has been the subject of great interest to chemists recently.<sup>38,39</sup> Generally, the rotational potential energy function of such a conjugated system, *V*(*θ*), can be expressed as the Fourier cosine series<sup>38</sup>

$$V(\theta) = \sum_{n=1}^{\infty} \frac{1}{2} V_n (1 - \cos n\theta) \quad (2)$$

where *θ* is the angle of internal rotation between the two conjugated double bonds. It is generally true that the higher terms (more than threefold rotational barrier) are small and the series can be terminated after cos 3*θ*. The cos 2*θ* term can be ascribed to the traditional resonance effect and has minima at *θ* = 0 and 180°. The term *V*<sub>2</sub> can be associated with the "resonance energy," since it indicates the additional stability gained from the maximum π-orbital overlap of the two double bonds. The cos 3*θ* term is a rotational potential similar to that in ethane or propylene. The inclusion of *V*<sub>3</sub> term in conjugated diene or enone system is readily accounted for if the double bond is regarded as two bent single bonds as proposed by Pauling.<sup>40</sup> The cos *θ* term identifies the most stable conformer. Obtaining sufficient data to disentangle *V*<sub>1</sub>, *V*<sub>2</sub>, and *V*<sub>3</sub> becomes a major problem.

It can be shown that if 4*V*<sub>2</sub> > *V*<sub>1</sub> + 9*V*<sub>3</sub>, then the non *s*-trans form will be in the *s*-cis conformation, and the following simple expression holds:

$$V(\pi) - V(0^\circ) = V_1 + V_3 \quad (3)$$

The energy difference between the two forms then gives an indication of the relative importance of the *V*<sub>1</sub> and *V*<sub>3</sub> terms in eq 3. From our low-temperature fmr investigation, we found that Δ*G* = 0.25 ± 0.07 kcal/mol, and Δ*H*<sup>‡</sup> = 5.78 ± 0.07 kcal/mol for acryloyl fluoride. We have also established that the two equilibrium conformations are *s*-trans and *s*-cis, with the former being more stable. Thus, eq 4 applies. The rotational

$$V_1 + V_3 = 250 \text{ cal/mol} \quad (4)$$

potential energy barrier can be taken as the enthalpy of activation for *s*-trans to *s*-cis interconversion.

$$V(\theta_{\max}) = \Delta H^\ddagger = \frac{1}{2}(V_1 + V_2 + V_3) - \frac{1}{2}(V_1 \cos \theta_{\max} + V_2 \cos 2\theta_{\max} + V_3 \cos 3\theta_{\max}) \quad (5)$$

where *θ*<sub>max</sub> is the angle of internal rotation at the transition state. In order to find *θ*<sub>max</sub> value, one sets the

(38) L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

(39) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965).

(40) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 130-142, 292.

derivative of *V* with respect to *θ* equal to zero and then determines the roots of the following equation:

$$12V_3 \cos^2 \theta_{\max} + 4V_2 \cos \theta_{\max} + V_1 - 3V_3 = 0 \quad (6)$$

We have three equations (4, 5, and 6) yet there are four unknowns (*V*<sub>1</sub>, *V*<sub>2</sub>, *V*<sub>3</sub>, and *θ*<sub>max</sub>) to be solved. Additional information is needed in order to solve for all the unknowns.

At this point, we want to examine the dependence of *V*<sub>1</sub>, *V*<sub>2</sub>, and *V*<sub>3</sub> values on the different values of *θ*<sub>max</sub>. Using eq 4-6 and the assumed values of *θ*<sub>max</sub>, values for *V*<sub>1</sub>, *V*<sub>2</sub>, and *V*<sub>3</sub> are calculated, as shown in Table V.

Table V. Values of *V*<sub>1</sub>, *V*<sub>2</sub>, and *V*<sub>3</sub> at Different Values of *θ*<sub>max</sub>

<i>θ</i> <sub>max</sub> , <sup>a</sup> deg	<i>V</i> <sub>1</sub> <sup>b</sup>	<i>V</i> <sub>2</sub> <sup>b</sup>	<i>V</i> <sub>3</sub> <sup>b</sup>
85	-325	5735	575
88	-15	5773	265
89	85	5778	165
90	187	5780	63
91	289	5778	-39
92	389	5773	-139
95	698	5735	-448

<sup>a</sup> *θ*<sub>max</sub> is the angle of internal rotation at the transition state.

<sup>b</sup> In cal/mol.

The *V*<sub>3</sub> term is a rotational potential similar to that in acetaldehyde<sup>41</sup> or propylene<sup>42</sup> and is expected to be small for conjugated systems. Miyazawa and Pitzer<sup>43</sup> reported that *V*<sub>1</sub> = 2.1, *V*<sub>2</sub> = 9.9, and *V*<sub>3</sub> = -0.1 kcal/mol for formic acid. For acrolein in the gas phase, *V*<sub>3</sub> was reported<sup>39</sup> to be small and negative (and also somewhat uncertain). In evaluating the rotational potential function for substituted benzaldehydes, the *V*<sub>3</sub> term was ignored.<sup>44</sup> If the torsional frequency of acryloyl fluoride in the liquid phase can be ascertained by infrared spectroscopy, then the needed information can be obtained from the following equation<sup>24</sup>

$$V^* = V_1 + 4V_2 + 9V_3 = \bar{\nu}^2/F \quad (7)$$

where *ν* is the 0 → 1 torsional transition frequency, and *F* is the reduced moment of inertia constant.

Carlson, *et al.*,<sup>24</sup> reported that *ν*<sub>g</sub> = 115 cm<sup>-1</sup> and *V*<sub>g</sub><sup>\*</sup> = *V*<sub>1</sub> + 4*V*<sub>2</sub> + 9*V*<sub>3</sub> = 18.65 kcal/mol for acryloyl fluoride in the gas phase. It is unfortunate that the torsional frequency (*ν*<sub>l</sub>) of acryloyl fluoride in the liquid phase was not measured. Usually, the values differ appreciably (20-25%) in the different phases.<sup>39</sup> The torsional frequencies of acrolein were reported to be *ν*<sub>g</sub> = 157 cm<sup>-1</sup> and *ν*<sub>l</sub> = 182 cm<sup>-1</sup> for the gas phase and the liquid phase, respectively. The torsional frequency of acryloyl fluoride in the liquid phase (*ν*<sub>l</sub>) has been estimated by multiplying *ν*<sub>g</sub> values by a factor of 182/157. Hence, one obtains the approximate values of *ν*<sub>l</sub> = 133 cm<sup>-1</sup> and *V*<sub>l</sub><sup>\*</sup> = 21.6 kcal/mol for acryloyl fluoride in the liquid phase. Using the estimated *V*<sub>l</sub><sup>\*</sup> value of 21.6 kcal/mol coupled with eq 4-6, one obtains *V*<sub>1</sub> = 400 cal/mol, *V*<sub>2</sub> = 5640 cal/mol, and *V*<sub>3</sub> = -150 cal/mol. As expected, the *V*<sub>3</sub> term is

(41) R. W. Kilb, C. C. Lin, and E. B. Wilson, *J. Chem. Phys.*, **26**, 1695 (1957).

(42) D. R. Herschbach and L. C. Krischer, *ibid.*, **28**, 728 (1958).

(43) T. Miyazawa and K. S. Pitzer, *ibid.*, **30**, 1076 (1959).

(44) F. A. Miller, W. G. Fateley, and R. E. Witkowski, *Spectrochim. Acta, Part A*, **23**, 891 (1967).

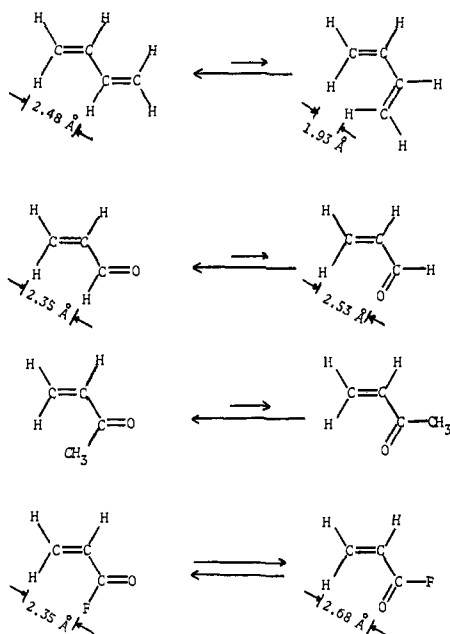
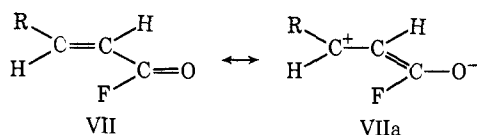


Figure 11. The conformations of 1,3-butadiene, acrolein, methyl vinyl ketone, and acryloyl fluoride.

small.<sup>45</sup> If the  $V_3$  term is completely ignored, then one has  $V_1 = 250$  cal/mol,  $V_2 = 5655$  cal/mol, and  $\theta_{\max} = 90.6^\circ$ . This analysis indicates that the  $V_2$  term contributes more than 90% of the total rotational energy barrier.

The twofold barrier arises mainly from the overlap between the  $\pi$  orbitals of the conjugated double bonds and was expected to be the major term in the potential function. A dipolar resonance structure can be drawn for  $\alpha,\beta$ -unsaturated acyl fluorides. The stabilization of the dipolar form, VIIa, due to the substituent R group,



will tend to increase the contribution of the resonance form VIIa to the ground state of the acyl fluorides. This increase in contribution from the dipolar form will increase the double bond character of the  $C_1$ - $C_2$  single bond, and hence should result in an increased rotational barrier. This explains the fact that the free energy of activation for the four acyl fluorides studied increases in the order acryloyl < crotonyl < cinnamoyl < *p*-methoxycinnamoyl fluoride.

Our values of the conformational energy differences ( $\Delta G$ ) between the *s*-cis and the *s*-trans forms of the substituted  $\alpha,\beta$ -unsaturated acyl fluorides are much lower than that of acrolein,<sup>17</sup> 1,3-butadiene,<sup>18,38</sup> and methyl vinyl ketone,<sup>46</sup> all of which exist predominantly in the *s*-trans forms (Figure 11). Assuming the same bond angles and bond distances as are found for the *s*-trans forms<sup>18</sup> of 1,3-butadiene, the calculated *cis,cis* H-H distance in the *s*-cis form of 1,3-butadiene is 1.93 Å. In the case of acrolein, the distance between *cis*- $C_3$ -H and

(45) The use of the gas-phase value of  $V^*$  would not alter this conclusion. The use of eq 7 for the liquid phase may not be entirely justified. The resulting uncertainty resides largely in  $V_1$  and  $V_3$ .

(46) P. D. Foster, V. M. Rao, and R. F. Curl, Jr., *J. Chem. Phys.*, **43**, 1064 (1965).

the oxygen atom in the *s*-cis conformation is 2.53 Å. The van der Waals radii for H, O, and F are 1.21, 1.40, and 1.35 Å, respectively.<sup>47</sup> Steric repulsion may account for part of the destabilization of the non *s*-trans form, but may not be the determining factor. It is questionable whether nonbonded H-H repulsion in the *s*-cis form of 1,3-butadiene could produce the necessary 2.0 kcal/mol destabilization.<sup>38</sup> The instability of the non *s*-trans metastable conformers of 1,3-butadiene, acrolein, and methyl vinyl ketone must be due to the increased contributions of  $V_1$  and  $V_3$  terms to the potential functions. The metastable forms will be *s*-cis if  $4V_2 - V_1 - 9V_3 > 0$ ; or the metastable forms will be nonplanar (skew) if  $4V_2 - V_1 - 9V_3 < 0$ . A recent self-consistent molecular orbital calculation of 1,3-butadiene was reported by Radom and Pople.<sup>38</sup> They adopted a flexible rotor model (*i.e.*, allow the widening of the CCC angle in the *s*-cis form) in the calculation, and the results reveal that the metastable conformer is in the planar *s*-cis form.

Qualitatively, from an electrostatic point of view, the interactions between  $\pi$ -electron clouds of two C=C bonds or one C=C bond and one C=O bond linked by a C-C single bond are repulsive in nature. The repulsion should be maximum when the two double bonds are eclipsed ( $\theta = 180^\circ$ ), and minimum when they are trans ( $\theta = 0^\circ$ ) to each other. The electrostatic repulsions between these double bonds will be much greater than the interaction between a C=C bond and a C-H bond. In fact, all the available evidence indicates that both the C=O and C=CH<sub>2</sub> bond prefer to be eclipsed by an adjacent single bond.<sup>41,42</sup> Consequently, it is possible that the interaction between two eclipsed double bonds renders all the non *s*-trans forms of acrolein, 1,3-butadiene, and methyl vinyl ketone unstable.

In the case of acryloyl fluoride, both the *s*-trans and the *s*-cis forms were found to exist in comparable amounts (about 60 to 40, respectively, at room temperature) from our low-temperature nmr study. Apparently, the interaction between a C=C moiety and C-F moiety becomes comparable to the interaction between a C=C moiety and a C=O moiety, with the latter slightly greater in magnitude. It is possible that the C-F bond may possess some double bond character in the conjugated acyl fluoride system. One may note that the fluorine atom has six nonbonded electrons and is just slightly smaller than the oxygen atom in size.

## Experimental Section

Acryloyl fluoride was prepared by refluxing acryloyl chloride with antimony trifluoride under a nitrogen atmosphere.<sup>26</sup> Crotonyl fluoride was obtained by treatment of crotonic acid with benzoyl fluoride.<sup>27</sup> Cinnamoyl fluoride and *p*-methoxycinnamoyl fluoride were prepared by treating the corresponding acyl chlorides with hydrogen fluoride in polyethylene bottles.<sup>27</sup> All the acyl fluorides prepared had satisfactory nmr and ir spectra.

Nuclear magnetic resonance spectral measurements were made on about 15% (v/v) of acyl fluorides in vinyl chloride (and other mixed solvents). A small amount of  $CFCl_3$  was added as an internal standard and for homogeneity adjustments. The sample tube was then sealed under vacuum. Spectra were recorded on a Varian As-

(47) Reference 40, p 260. However, the hydrogen van der Waals radius value of 1.21 Å has been disputed. It is felt that 1.5-1.6 Å is probably a more realistic value.<sup>48,49</sup>

(48) N. L. Allinger, M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, *J. Amer. Chem. Soc.*, **89**, 4345 (1967).

(49) J. B. Hendrickson, *ibid.*, **89**, 7036 (1967).

sociates HA-100 spectrometer with a variable temperature accessory. The ambient-temperature spectra were recorded in the frequency-sweep mode using an internal lock. The low-temperature fmr spectra were recorded in HR mode and sweep widths were calibrated by the sideband technique using a Hewlett-Packard Model 200AB audio oscillator and Model 5512A frequency counter. At low temperature, the sample was thermostated with precooled nitrogen gas passing through a vacuum-jacketed Dewar into the probe. The temperatures were measured immediately after recording spectra by inserting a calibrated thermocouple to the bottom of a dummy nmr tube containing the solvents and measuring the potential relative to a second thermocouple in ice water. Temperatures were reproducible to better than  $0.5^\circ$  but systematic error<sup>30</sup> probably reduced the accuracy to  $\pm 1-2^\circ$ . In order to ensure that true Lorentzian lineshapes were actually observed in our lineshape analysis, precautions were made to avoid the saturation of the nmr signals, and to use minimum filtering of noise.

All computer calculations were performed on an IBM 360/65 computer equipped with a University Computing Co. (UCC) digital incremental plotter. The computer program, DNMR2, used for calculation of the theoretical curves for the intramolecular exchange process, was written by Binsch and Kleir.<sup>29</sup> The program simulates

(50) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3165 (1966).

complex exchange-broadened nmr spectra from chemical shifts, coupling constants, effective relaxation times, rate constants, populations, and certain scaling parameters. The effective transverse relaxation time (in seconds) was obtained from the line width at half-height ( $W_{1/2}$ ) of the internal fluorotrichloromethane reference signal by the relationship  $T_2 = 1/(\pi W_{1/2})$ . In most cases, only two nuclei (the fluorine and the  $C_2$  proton) were included in the calculation, since no difference was observed for the two- and four-nuclei calculations for the range of rate constants reported. By placing the theoretical spectrum on top of the experimental spectrum, the line-shapes of the two spectra could be compared. The exchange rate constant at the particular sample temperature was obtained from the calculated spectrum considered to be in best agreement with the experimental spectrum. The rate constants so obtained were considered to have uncertainty less than 5%.

Activation parameters were calculated by a program ACTENG, written by DeTar.<sup>30</sup> The calculations are based on a weighted least squares treatment which allows the use of data of different precision.

**Acknowledgments.** Funds for purchase of the Varian HA-100 were provided through an institution grant from the National Science Foundation to the University of Southern California. Partial support of this research by a grant from the Research Corporation is gratefully acknowledged.

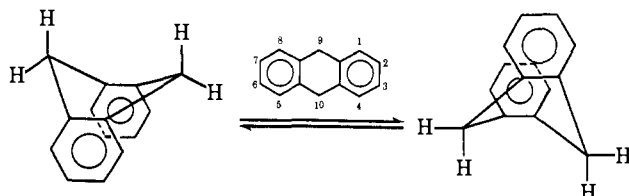
## Stereochemistry of 9,10-Dihydroanthracenes. Preferred Conformations in *cis*-9,10-Dialkyl Derivatives<sup>1,2</sup>

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**Abstract:** The preferred orientation of alkyl groups in *cis*-1,4-dimethyl-9,10-dialkyl-9,10-dihydroanthracenes (and 1,4-dimethoxy) is shown to be diaxial with the alkyl groups rotated away from the 1 and 4 blocking groups. This produces some interesting nmr spectra as a result of diamagnetic anisotropy effects from the aromatic rings. For example, with diisopropyl derivatives, a methyl doublet appears upfield of the tetramethylsilane reference signal.

The conformational analysis of the 1,4-cyclohexadiene ring system has been the subject of a substantial number of investigations.<sup>3-9</sup> Unfortunately, the conformational preference of the parent 1,4-cyclohexadiene (planar *vs.* boat or equilibrating boats) remains a matter of controversy. On the other hand, 9,10-dihydroanthracene (**1**) has been shown by X-ray diffraction<sup>10</sup> to be nonplanar, and is presumed to undergo rapid ring inversion (nmr time scale) even at very low temperatures.<sup>11</sup> Only one report has appeared con-



cerning the effect of aryl ring substitution on the ring inversion, and these authors<sup>12</sup> claimed that methoxy substituents inhibited this process. However, a reinvestigation of one of these compounds (2,3,6,7-tetramethoxy-9,10-dihydroanthracene) in our laboratories<sup>13</sup> suggests that this claim is untrue, and that substituents distant from the central ring do not affect the inversion process (as might be expected).

Controversy has also existed concerning the conformational preferences of 9-substituted 9,10-dihydroanthracenes (**2**). Earlier nmr results led some authors<sup>14-16</sup> to conclude that the conformation in which

(1) This investigation was supported, in part, by a grant from the Eli Lilly Co., Indianapolis, Ind.

(2) A preliminary account of this work has been presented; P. W. Rabideau and J. W. Paschal, Abstracts of Papers, Third Central Regional Meeting of the American Chemical Society, Cincinnati, Ohio, 1971.

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