

ably rather coarse but lead to results internally consistent, at least in a qualitative point of view. Theoretical calculations performed on the same molecule¹² are also in agreement with the present results; they indicate a s-trans-s-cis ratio of 68:32 and a barrier of 4 kcal/mol.

Although one cannot rule out the possibility of an accidental coincidence for what concerns the numerical values, little doubt is left that s-trans is the more stable conformer, as indicated by the present investigation; X-ray diffraction shows that in the solid this is the only observable species,⁵ and in solutions of the radical anion (at -80°) two conformers with an 80:20 ratio were detected.⁸ Such a ratio seems to fit surprisingly well our results since, if ΔS° is taken equal to 0 as usual for internal rotations, the value at room temperature becomes 70:30.

As observed in other cases,^{4a,13} the radical anions seem to have conformational preferences similar to those of the corresponding neutral molecules (allowing also for the different experimental conditions), whereas

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the energy barrier is probably much higher. This might explain the similar results obtained on the isomers ratio as well as the possibility of observing, in the esr time scale, locked rotational isomers which on the contrary rapidly interconvert in the neutral molecule (nmr time scale).

Experimental Section

The spectra of 2,2'-bithienyl as solute in *p*-*n*-butyl-*p*'-methoxyazoxybenzene (Merck Licristal phase IV) were recorded at 100 (JEOL PS 100) and at 220 MHz (Varian HR 220) at room temperature. Spectral analyses were carried out by means of a program (Athena) which iterated the intensity of the lines and cross checked with the LAOCOONOR program.

At 100 MHz, 147 lines were detected and all were iterated with a rms deviation of 5.3 Hz; in the 220-MHz spectrum, 149 lines were detected and iterated with a rms deviation of 5.1 Hz. In both cases, the same line width was observed and the computed spectrum (Figure 1) was obtained using a line shape made by a linear combination (4:1) of a Lorentzian and Gaussian curve with a line width of 4 Hz.

The chemical shifts in ppm satisfy, within the errors, the requirements of the 220:100 ratio.

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The Carbon-13 Nuclear Magnetic Resonance Chemical Shifts of the Fluoroallenes. A Comparison between Theory and Experiment

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Abstract: The five possible fluoroallenes have been prepared and their ¹³C chemical shifts measured. The experimental data for mono- and difluoroallenes are compared with the results of *ab initio* SCF perturbation theory calculations using a slightly extended set of gauge-invariant atomic orbitals. The overall agreement between theory and experiment is good.

An important objective of a theory of magnetism of diamagnetic molecules is the quantitative estimation of ¹³C and ¹H nmr chemical shifts in organic molecules. This goal has often seemed remote due to problems associated with the gauge of the vector potential describing the magnetic field.² However, preliminary applications^{3a} of a recent gauge-invariant *ab initio* theory of magnetic shielding^{3b} have given results for ¹³C and ¹H chemical shifts which are in good agreement with experiment. To further document the performance of this method it is important to test it against experimental information for a variety of molecules. If sufficient consistent success is obtained, this will allow some confidence to be acquired in its predictive power.

It is also important that the experimental systems chosen for the initial studies be inherently simple with

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(3) (a) R. Ditchfield, *Chem. Phys. Lett.*, **15**, 203 (1972); (b) R. Ditchfield, *J. Chem. Phys.*, **56**, 5688 (1972).

respect to their structure and number of atoms and yet exhibit the major types of substituent effect on shielding at carbon nuclei (*e.g.*, inductive and mesomeric effects). A class of compounds which is particularly attractive from this point of view is the fluorocarbons. We have recently reported preliminary results for the ¹³C chemical shifts of the fluoromethanes,⁴ CH_nF_{4-n}, *n* = 0 and 4, fluoroethylenes,⁵ C₂H_nF_{4-n}, *n* = 0 and 4, and fluoroacetylene.⁵

In this work we report extensions of this study to a comparison of the measured ¹³C chemical shifts of the fluoroallenes C₃H_nF_{4-n}, *n* = 0 and 4, with calculated values obtained from the gauge-invariant *ab initio* theory. This series contains examples of one, two, and three bond (α , β and γ , respectively) substituent effects on the carbon atoms forming the cumulated double-bond system of the allene molecule.

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Quantum Mechanical Method

The quantum mechanical method used is SCF perturbation theory. In this method the wave functions Ψ describing the molecule both in the absence and in the presence of a uniform, external magnetic field \mathbf{H} are written as single determinants of molecular orbitals $\psi_j(\mathbf{H})$

$$\Psi(\mathbf{H}) = |\psi_1(\mathbf{H})\overline{\psi_1(\mathbf{H})} \dots \psi_n(\mathbf{H})\overline{\psi_n(\mathbf{H})}| \quad (1)$$

where a bar indicates a β spin function. The molecular orbitals are written as linear combinations of gauge-invariant atomic orbitals (GIAO)⁶ $\chi_\mu(\mathbf{H})$

$$\psi_j(\mathbf{H}) = \sum_{\mu} c_{\mu j}(\mathbf{H})\chi_{\mu}(\mathbf{H}) \quad (2)$$

where

$$\chi_{\mu}(\mathbf{H}) = \exp\{-i/c\mathbf{A}_{\mu} \cdot \mathbf{r}\}\phi_{\mu} \quad (3)$$

In eq 3, ϕ_{μ} is an atomic orbital in the absence of the external magnetic field, \mathbf{A}_{μ} is the vector potential describing the magnetic field at the nucleus on which ϕ_{μ} is centered, and \mathbf{r} is a distance vector from some arbitrary origin. SCF perturbation theory is then used to evaluate the screening fields at the nuclei in the molecule. For this study we have taken the geometries of all systems to be those defined by the standard geometrical model presented by Pople and Gordon.⁷ All the calculated chemical shift values reported here were obtained as outlined above using a slightly extended basis set (4-31G)⁸ of atomic functions ϕ_{μ} , appropriately modified by exponential gauge factors.

Experimental Section

Synthetic Procedures. Tetrafluoroallene has previously been prepared by Bauer and Jacobs⁹ and also by Banks, Haszeldine, and Taylor.¹⁰ Tetrafluoroallene was prepared in our laboratory by a somewhat different procedure; 273 g of dibromodifluoromethane 2.9 g of benzoyl peroxide, and 19.2 g of 1,1-difluoroethylene were placed in a stainless steel bomb. The bomb was then placed in an oven at 110–120° for 5–6 hr. The product obtained was 1,3-dibromo-1,1,3,3-tetrafluoropropane and was purified by distillation at 52° and 130 mm of pressure. The propane was then dehydrobrominated (-2HBr) with molten potassium hydroxide at 140°, the gaseous product being swept into liquid nitrogen traps on a standard high-vacuum line with helium. The crude tetrafluoroallene obtained was then distilled on a low-temperature fractionation column.¹¹ The purity of the tetrafluoroallene obtained was checked from previously reported infrared data.⁹

1,1-Difluoroallene has been prepared by Blomquist and Longone¹² and Knoth and Coffman.¹³ 1,1-Difluoroallene was prepared in a manner analogous to that of tetrafluoroallene. Dibromodifluoromethane (272 g), ethylene (8.4 g), and benzoyl peroxide (5 g) were placed in a bomb at 110° for 5 hr. The product, 1,3-dibromo-1,1-difluoropropane, was purified by distillation at 62° and 86 mm pressure to give 42 g (59% conversion of ethylene) of propane. The propane was then decomposed with (-2HBr) molten potassium hydroxide at 140°. The product was swept into liquid nitrogen traps in the same manner as tetrafluoroallene. The crude 1,1-difluoroallene was then distilled on a low-temperature

fractionation column.¹¹ The distillation yielded 3.2 g of 1,1-difluoroallene (24% conversion of propane). The purity of the 1,1-difluoroallene was checked from infrared data reported by Blomquist and Longone.¹²

Trifluoroallene has not previously been cited in the literature. It was synthesized in our laboratory by dehydrobromination (-2HBr) of 1,3-dibromo-1,1,3-trifluoropropane. The propane used in this reaction was synthesized by the method described by Tarrant, Lovelace, and Lilyquist.¹⁴ The 1,3-dibromo-1,1,3-trifluoropropane prepared by the above method was dehydrobrominated (-2HBr) with 300 g of potassium hydroxide in 150 ml of water at 60 to 80°. The gaseous product formed in this reaction was first swept by an ice-water cooled condenser and then into liquid nitrogen traps on a standard high-vacuum line. The crude product was distilled on a low-temperature fractionation column¹¹ yielding 0.6 g of trifluoroallene (16% conversion of propane for 10.20 g of propane decomposed). The infrared data of trifluoroallene are listed in Table I. Mass spectral data showed a parent peak cor-

Table I. Fluoroallene Infrared Data^a

Trifluoroallene		
3475 w	2040 vs	1180 m
3060 w	1820 w	1080 vs
2850 w	1700 w	840 s
2550 w	1595 w	720 w
2480 m	1475 s	610 m
2160 m	1240 (broad) vs	590 m
1,3-Difluoroallene		
3380 w	1980 vs	990 m
3050 w	1660 w	860 (broad) w
2950 w	1420 w	810 (broad) w
2500 w	1310 m	650 m
2280 w	1210 m	520 (broad) w
2060 m	1080 vs	
Monofluoroallene		
3320 w	2020 m	1170 vs
3080 w	1970 m	1000 vs
3010 w	1920 m	900 m
2340 w	1460 s	830 m
2170 w	1340 s	

^a Infrared spectra were taken with a Perkin-Elmer Model 337 instrument using a 10-cm gas cell: w = weak, m = medium, s = strong, vs = very strong. The units used in the above table are reciprocal centimeters.

responding to a mass charge ratio of 94. Trifluoroallene has a vapor pressure of 11 mm at Dry Ice-acetone bath temperature.

1,3-Difluoroallene was prepared for the first time by the dehydrobromination of 1,3-dibromo-1,3-difluoropropane. 1,3-Dibromo-1,3-difluoropropane was prepared by placing 230 g of fluorodibromomethane (prepared by the method of Swarts),¹⁵ 2.8 g of benzoyl peroxide, and 13.8 g of fluoroethylene in a bomb at 120° for 5 hr. The product 1,3-dibromo-1,3-difluoropropane was distilled at 69° and 68 mm of pressure to give 13 g of propane (18% conversion of fluoroethylene). The 1,3-dibromo-1,3-difluoropropane was then dehydrobrominated in the same manner as 1,3-dibromo-1,1,3-trifluoropropane in the synthesis of trifluoroallene to yield 1.1 g of 1,3-difluoroallene (27% conversion of propane) after distillation on a low-temperature fractionation column.¹¹ 1,3-Difluoroallene infrared data are listed in Table I. Mass spectral data indicate a parent peak with a mass to charge ratio of 76. The vapor pressure of 1,3-difluoroallene at Dry Ice-acetone temperature was 3 mm.

Monofluoroallene has not been previously mentioned in the literature. It was prepared by the dehydrobromination of the corresponding propane, 1,3-dibromo-1-fluoropropane. The propane was prepared analogously to the above procedure for the synthesis of 1,3-difluoroallene except that 8.4 g of ethylene was substituted for fluoroethylene. Distillation of 1,3-dibromo-1-fluoropropane at 85° and 80 mm of pressure yielded 20 g of product (30% conversion of ethylene). The propane was dehydrobrominated with molten potassium hydroxide at 140° and swept by an ice-water condenser into liquid nitrogen traps on a high-vacuum line. Low-tempera-

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Table II. ^{13}C Chemical Shifts of Allene and the Fluoroallenes^a

Compd	C_α		C_β		C_γ	
	Measured	Calcd	Measured	Calcd	Measured	Calcd
$\text{H}_2\text{C}=\text{C}=\text{CH}_2$	0.0 ^b	0.0 ^b	0.0 ^c	0.0 ^c	0.0 ^b	0.0 ^b
$\text{HFC}=\text{C}=\text{CH}_2$	-55.0	-47.7	13.3	8.1	-19.1	-15.7
$\text{HFC}=\text{C}=\text{CFH}$	-57.4	-52.1	37.0	26.1	-57.4	-52.1
$\text{F}_2\text{C}=\text{C}=\text{CH}_2$	-81.4	-73.8	32.1	24.9	-30.0	-25.0
$\text{F}_2\text{C}=\text{C}=\text{CFH}$	-71.0		63.7		-59.0	
$\text{F}_2\text{C}=\text{C}=\text{CF}_2$	-65.8		95.4		-65.8	

^a The various ^{13}C chemical shifts are reported in ppm with respect to the corresponding carbon in allene. Negative values indicate shifts to lower shielding. ^b The measured chemical shift of C_α is -77.1 ppm relative to CH_4 or -74.8 ppm relative to TMS. The calculated chemical shift of C_α is -76.2 ppm relative to CH_4 . ^c The measured chemical shift of C_β is -215.8 ppm relative to CH_4 . The calculated chemical shift of C_β is -227.5 ppm relative to CH_4 .

ture fractional distillation of the crude product gave 0.3 g of monofluoroallene (6% conversion of the propane). Monofluoroallene infrared bands are listed in Table I. Mass spectral information indicates a parent peak of 58 mass to charge units. The vapor pressure of monofluoroallene in a Dry Ice-acetone bath was 12.5 mm.

Nmr Measurements. The measured and calculated values for the ^{13}C chemical shifts of allene and the fluoroallenes are presented in Table II. The ^{13}C spectra were obtained on a Varian XL-100-15 nmr spectrometer operating in the Fourier transform mode at 25.2 MHz. All samples were run in 5-mm nmr tubes as solutions of the fluoroallene in dibromodifluoromethane and TMS in the approximate ratio 1:1:1 by volume. The TMS provided the ^{13}C and ^1H reference signals and the dibromodifluoromethane provided the ^{19}F chemical shift reference. The sample temperature was kept at or below the boiling point of each sample. The experimental precision in the measurement of the chemical shifts reported here is approximately 0.1 ppm.

Results and Discussion

From Table II it is clear that there is good overall agreement between experimental and theoretical values. Some measure of this agreement is given by the mean absolute deviation of 6.5 ppm. Shielding at substituted and unsubstituted terminal carbon atoms is described very well for all the molecules considered here. The chemical shifts of the central carbon are also fairly well described although the value in 1,3-difluoroallene appears to be somewhat underestimated.

It is of interest to compare these results with those for the methyl allenes reported by Crandall and Sojka.¹⁶ These workers found that the chemical shifts of the central carbon of the allene system were additive with respect to the number of methyl groups, with a value of 3 ppm per methyl group. As might be expected, the shifts of the central carbon resonance in the fluoroallenes are much larger than those in the methyl allenes. Furthermore, there is no apparent additivity with respect to the number of fluorine substituents. To provide some understanding of this lack of additivity, we have examined the calculated diagonal elements of the central carbon magnetic shielding tensor σ (using the coordinate system illustrated in Table II). It has been found in other systems¹⁷ that such elements are often far more sensitive to substituent effects than are isotropic values. On going from allene to monofluoroallene the xx and yy elements are shielded by 37.3 and 15.1 ppm, respectively, while the zz element is deshielded by -28.3 ppm. Thus, we see here large changes in

individual elements, but since these are of opposite sign the isotropic chemical shift ($=1/3[\sigma_{xx} + \sigma_{yy} + \sigma_{zz}]$) is fairly small. The changes in the same elements when a second H atom is replaced by F to give 1,1-difluoroallene are 50.4, 17.2, and -17.1 ppm, respectively. Thus, although substituent effects on the yy element are close to being additive, those for the xx and zz elements are not. As a result the overall shielding effect at the central carbon atom due to a CF_2 group differs from twice the isotropic shielding effect associated with a C-F bond.

Comparing 1,3-difluoroallene with monofluoroallene we find the following changes in the central atom magnetic shielding tensor: 14.7 (xx), 36.9 (yy), and 2.4 (zz) ppm. If the effects of fluoro substitution are additive, these values should be 15.1, 37.3, and -28.3 ppm, respectively (the first two values are switched from the set presented above to account for the fact that CHF groups at different ends of the molecule lie in orthogonal planes). Thus, for a 1,3-substitution pattern there is a close additivity for the xx and yy elements but not for the zz element. In this respect it should be noted that the π_x -type and the π_y -type molecular orbitals of the allene system which are different in monofluoroallene are equivalent in 1,3-difluoroallene.

We next consider the terminal carbon atoms. There are two changes which must be considered in going from allene to monofluoroallene. First, there are variations for the substituted terminal atom C_α and second, the modifications for the unsubstituted atom C_γ . The changes in the chemical shift tensor C_α are -26.4 (xx), -61.2 (yy), and -55.5 (zz) ppm. In going from monofluoroallene to 1,1-difluoroallene, the corresponding changes are -16.1 , -25.7 , and -36.7 ppm, respectively. Clearly, the effects of fluorosubstitution on the substituted terminal carbon atom are not additive. It is worth noting that similar nonadditivity is evident in the fluoroethylene series.⁵

The changes in the diagonal elements of the C_γ chemical shift tensor which result from the introduction of a fluoro substituent at C_α are -17.0 , 1.1, and -31.1 ppm, respectively. The corresponding changes between monofluoroallene and 1,1-difluoroallene are -10.2 , 1.4, and -19.1 ppm, respectively. A striking feature of these results is the constant value of the yy element which shows little change in going from allene to 1,1-difluoroallene. The effect on the xx element is approximately additive, but the results for the zz element

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show moderate deviations from additivity. To determine if the shielding effect of a fluoro substituent on a C_γ atom depends on the atoms bonded to the C_γ atom, we compare results for 1,3-difluoroallene with those for monofluoroallene. The changes in the C_α magnetic shielding tensor between these two systems are -13.7 (xx), -1.2 (yy), and 1.9 (zz) ppm. Thus, here also there is reasonable additivity for substituent effects on the xx and yy elements but not for effects on the zz element. This comparison suggests that it is mainly the lack of additivity of substituent effects on the zz component of the magnetic shielding tensor which is responsible for the different γ substituent effects obtained for the isotropic chemical shifts in the 1,1- and 1,3-difluoroallene substitution patterns.

We are currently continuing this study in an attempt to relate the nonadditive shielding effects of fluoro substituents to various features of molecular electronic structure.

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Nuclear Magnetic Relaxation Behavior of Lecithin Multilayers¹

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Abstract: In an effort to elucidate the state of molecular motion in the lamellar liquid crystalline phase of lecithin, the nuclear magnetic relaxation properties of unsonicated lecithin multilayers have been investigated. A previously noted field dependence of the proton magnetic resonance line width is shown to be accounted for by the chemical shift differences among the various kinds of protons. Spin-lattice relaxation rates have been measured for these protons as a function of temperature and frequency, and these data have been interpreted in terms of models for the segmental motion of the choline head groups and the hydrocarbon chains. The influence of spin diffusion on the relaxation behavior of the various protons is also discussed.

The current interest in understanding the details of structure and function of biological membranes has prompted studies of model membrane systems. The lamellar liquid crystalline phase of lecithin and water increasingly is being used as a model for biological membranes.³⁻⁷ Evidence that the liquid crystal phase is a close structural analog to real biomembranes comes from differential scanning calorimetry,^{8,9} X-ray diffraction,¹⁰⁻¹² and spin label studies,^{13,14} all of which have detected this phase in real biomembranes.

Coarse aqueous liquid crystal dispersions can be irradiated ultrasonically to produce bilayer vesicles

which are useful models for studying membrane function, especially transport.^{3,15} However, there is strong evidence that, at the molecular level, the vesicle bilayer is significantly disordered because of the high curvature of these small particles.^{16,17} For this reason, coarse aqueous dispersions of lamellar liquid crystals, hereafter referred to as "multilayers," are better models of membrane structure, though they are not suitable for transport studies because of the absence of a well-defined inside and outside.

Nuclear magnetic resonance (nmr) is a method of established usefulness for studying molecular interactions. Furthermore, nmr is sensitive to the details of molecular motion. For these reasons, there is much interest in using nmr to investigate membrane systems. Lipid model membranes,¹⁸⁻²⁴ as well as erythrocyte²⁵ and

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