

# Nematic Phase Nuclear Magnetic Resonance Investigations of Rotational Isomerism. III. Conformational Preferences and Interconversion Barrier of 2,2'-Bithienyl<sup>1</sup>

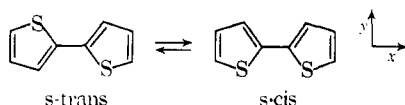
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**Abstract:** The 100- and 220-MHz nmr spectra of 2,2'-bithienyl partially oriented in the nematic phase of a liquid crystalline solvent have been obtained and interpreted. The values of the direct dipolar couplings ( $D_{ij}$ ) were found in disagreement with the presence of solely the s-trans or the s-cis conformation; a number of models taking into account the existence of a rapid equilibrium between the two forms have been discussed. It has been shown that the s-trans is the more stable conformer ( $70 \pm 5\%$ ) and the energy required for the s-trans, s-cis interconversion is about  $5 \pm 2$  kcal/mol. The results agree with the conclusions of theoretical calculations and are consistent with X-ray and esr experimental evidences.

Information on the structures and conformations of molecules with internal motions has been gained by means of the nmr spectroscopy of partially oriented molecules in liquid crystalline solvents.<sup>3,4</sup> The possibility of using this technique for conformational analysis appears very interesting but must be tested with many examples in order to know the advantages and the limits of its applications.

In the case of some bithienyl derivatives<sup>4b</sup> it has been possible to show that neither the free rotation nor the existence of a single conformer (twisted or planar) accounts for the parameters obtained from the nematic phase nmr spectrum. By allowing for some approximations it was possible to infer that both the s-trans and s-cis isomers are present with different populations,



the former being the more stable. However, when symmetrically substituted derivatives of 2,2'-bithienyl are examined,<sup>4b</sup> the number of observable parameters is rather small so that the results cannot be very accurate; furthermore, no data are available for studying the barrier to the internal rotation.

(1) Parts I and II: *Mol. Phys.*, **24**, 673 (1972); *J. Chem. Soc., Perkin Trans. 2*, in press.

(2) (a) Università della Calabria; (b) University of Pisa; (c) University of Bologna.

(3) A. D. Buckingham, E. E. Burnell, and C. A. de Lange, *Mol. Phys.*, **16**, 521 (1969); S. Meiboom and L. C. Snyder, *J. Amer. Chem. Soc.*, **89**, 1038 (1967); *J. Chem. Phys.*, **52**, 3857 (1970); I. J. Gizzard and N. Sheppard, *Mol. Phys.*, **21**, 169 (1971); P. Bucci, P. F. Franchini, A. M. Serra, and C. A. Veracini, *Chem. Phys. Lett.*, **8**, 421 (1971); P. Diehl, P. M. Heinrichs, and W. Niederberger, *Mol. Phys.*, **20**, 139 (1972); K. C. Cole and D. F. R. Gilson, *J. Chem. Phys.*, **56**, 4362 (1972); A. d'Annibale, L. Lunazzi, C. Boicelli, and D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2*, 1396 (1973); W. Niederberger, P. Diehl, and L. Lunazzi, *Mol. Phys.*, **26**, 571 (1973).

(4) (a) P. Bucci and C. A. Veracini, *J. Chem. Phys.*, **56**, 1290 (1972); L. Lunazzi, G. F. Pedulli, M. Tiecco, and C. A. Veracini, *J. Chem. Soc., Perkin Trans. 2*, 755 (1972); P. L. Barili, L. Lunazzi, and C. A. Veracini, *Mol. Phys.*, **24**, 673 (1972); (b) C. A. Veracini, D. Macciantelli, and L. Lunazzi, *J. Chem. Soc., Perkin Trans. 2*, 751 (1973).

In order to obtain more accurate conclusions about this conformational problem and with the purpose of estimating the energy required for the trans, cis interconversion, an nmr investigation of the unsubstituted 2,2'-bithienyl partially oriented in the nematic phase of a liquid crystalline solvent was undertaken.

## Results and Discussion

The partially oriented spectrum of 2,2'-bithienyl at 100 (Figure 1) and 220 MHz was interpreted as that of an AA'BB'CC' system in terms of three chemical shifts and nine dipolar couplings ( $D_{ij}$ ), using as is customary the  $J_{HH}$  values of the isotropic spectrum.

As the basic geometry of the rings is known from X-ray diffraction,<sup>5</sup> the dipolar couplings can be used to determine the orientational parameters and the conformational preferences. Accordingly, the equation linking the protonic coordinates to the experimental  $D_{ij}$  couplings<sup>6</sup> was solved and the motional constants best fitting the experiment obtained. (It can be seen in Tables IV and V that neither the s-trans nor the s-cis conformation accounts for the experimental couplings; the deviations are so large that no reasonable set of protonic coordinates allows for a satisfactory solution.<sup>7</sup>)

It is thus confirmed that in solution both isomers are likely to exist in rapid equilibrium, on the contrary of what was observed in the solid where only the s-trans structure was detected.<sup>5</sup> This also agrees with the esr observation of the two rotamers in the corresponding radical anion.<sup>8</sup> In order to determine which is the more stable of the two conformers and to define their relative population, it is required to solve the basic equation<sup>6</sup> considering five motional constants (three

(5) G. J. Visser, G. J. Heeres, J. Wolters, and C. A. Vos, *Acta Crystallogr., Sect. B*, **24**, 467 (1968).

(6) L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, **47**, 1480 (1967).

(7) Twisted structures and free rotation can also be dismissed on the basis of the previous investigations of 5,5'-substituted derivatives (see ref 4b).

(8) P. Cavaliere d'Oro, A. Mangini, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Tetrahedron Lett.*, 4179 (1969); L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazz. Chim. Ital.*, **101**, 10 (1971).

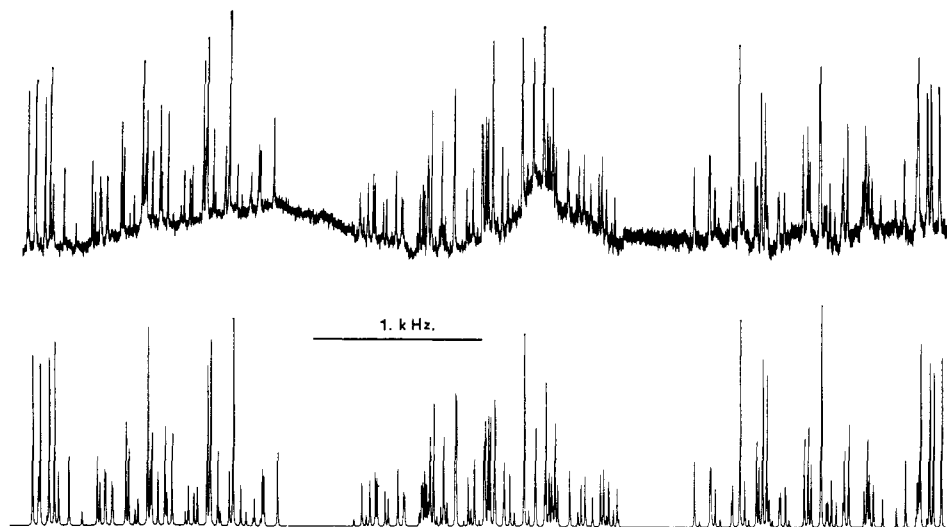


Figure 1. Experimental and simulated 100-MHz nmr spectrum of 2,2'-bithienyl partially oriented in the nematic phase.

for the s-trans and two for the s-cis) and one isomer ratio. If the coordinates of the protons are derived from the 2,2'-bithienyl structure, assuming the CH bonds (1.08 Å) as approximately bisecting the thiophen ring angles, six unknowns have to be determined (Table I).

Table I. Coordinates of the Hydrogen Atoms (Å) of 2,2'-Bithienyl Used in the Present Investigation

s-trans		H atom	s-cis	
x	y		x	y
-4.041	+1.220	5	-4.841	-1.220
-3.821	-1.286	4	-3.821	+1.286
-1.339	-2.189	3	-1.339	+2.189

Since nine  $D_{ij}$  couplings are available, the problem is in principle determined. It was found, however, that some of the experimental couplings are almost insensitive to variations of the s-trans-s-cis ratio, so that a solution allowing for a simultaneous determination of orientation and ratio of the conformers cannot be obtained for 2,2'-bithienyl. Actually, the  $D_{ij}$  values calculated in this way reproduce the experimental data with the same root mean square deviation ( $\sim 4$  Hz) whatever the conformers ratio employed; obviously, the sets of five motional constants corresponding to the various ratios largely differ from each other. When the amount of the s-cis rotamer is assumed to largely exceed that of s-trans, however, some of the constants do not lie within their physical limits.<sup>6</sup> However, even for isomer ratios that give motional constants lying in their physical limits a positive value of  $C_{3z^2-r^2}$  for the s-cis rotamer should be regarded as unrealistic.

(The motional constants for the s-trans-s-cis ratio equal to 0.5, 0.6, and 0.7 are reported as an example in Table II.)

The motional constants of Table II arise from the actual indeterminacy of the problem (standard deviations, not reported in Table II, are of the order of the calculated motional constants). Moreover, such large differences in the corresponding motional constants of the two isomers have no physical meaning. It is well known, in fact, that the molecular shapes is the main

Table II. Motional Constants for 2,2'-Bithienyl Calculated as Described in the Text

s-trans-s-cis isomer ratio	s-cis		s-trans			Rms error
	$C_{3z^2-r^2}$	$C_{x^2-y^2}$	$C_{3z^2-r^2}$	$C_{x^2-y^2}$	$C_{xy}$	
0.5	0.142	0.406	-0.912	0.353	-0.047	4.3
0.6	0.187	0.514	-0.754	0.296	-0.036	3.6
0.7	0.231	0.673	-0.651	0.252	-0.034	4.5

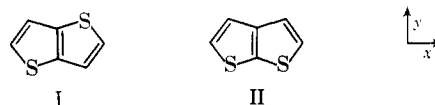
factor affecting the molecular orientation,<sup>9</sup> and the  $C_{3z^2-r^2}$  and  $C_{x^2-y^2}$  parameters are expected, for this reason, to be nearly equal for both conformers since they have no great difference in the overall molecular shape. Some examples of cis-trans geometrical isomers exhibiting similar motional constants can be found in the literature.<sup>10</sup> To give, however, an example as close as possible to 2,2'-bithienyl, we give in Table III preliminary results of a study of motional constants

Table III. Motional Constants of Thienothiophenes I and II Partially Oriented in the Nematic Phase<sup>a</sup>

	I	II
$C_{3z^2-r^2}$	-0.336	-0.341
$C_{x^2-y^2}$	0.068	0.069
$C_{xy}$	0.060	

<sup>a</sup> The proton geometry used for calculations of motional parameters was obtained from X-ray diffraction data for I (E. G. Cox, R. J. Gillat, and G. A. Jeffrey, *Acta Crystallogr.*, **8**, 356, (1949)) with the assumption that the C-H bonds (1.08 Å) approximately bisect the thiophene ring angles.

of the two cis-trans isomers thienothiophenes I and II.<sup>11</sup> The motional constants in Table III were ob-



(9) P. Diehl and C. L. Khetrapal, "NMR Basic Principles and Progress," Vol. 1, Springer-Verlag, Berlin, 1969.

(10) C. T. Yim and D. F. R. Gilson, *Can. J. Chem.*, **47**, 1057 (1969).

(11) C. A. Veracini and L. Lunazzi, to be submitted for publication.

**Table IV.** Experimental and Computed Values (Hz) of the 100-MHz Spectrum of 2,2'-Bithienyl in the Nematic Phase<sup>a</sup>

Exptl	Computed				
	s-trans	s-cis	70% s-trans		
			<i>b</i>	<i>c</i>	
$D_{45}$	+454.1 ± 1.8	+417.1	+401.6	+454.8	+454.1
$D_{35}$	-58.6 ± 2.5	-66.7	-33.0	-64.8	-59.4
$D_{35'}$	-131.3 ± 1.2	-285.8	-41.0	-137.9	-140.3
$D_{45'}$	-51.2 ± 1.2	-85.8	-27.0	-53.7	-54.3
$D_{55'}$	-41.5 ± 1.0	-44.1	-33.1	-44.4	-45.1
$D_{34}$	-1267.2 ± 0.8	-1264.4	-797.5	-1265.4	-1266.6
$D_{34'}$	-118.1 ± 0.8	-189.1	-116.8	-111.4	-112.1
$D_{44'}$	-52.2 ± 2.2	-92.6	-39.3	-53.1	-54.1
$D_{33'}$	-470.7 ± 2.0	-193.9	-911.6	-473.0	-470.0
Rms deviation, Hz		118	218	4.1	4.0
$C_{3z^2-r^2}$		-0.703	-0.2035	-0.388	-0.400
$C_{x^2-y^2}$		+0.481	+0.259	+0.381	+0.386
$C_{xy}$		-0.425		-0.033	-0.039

<sup>a</sup> With respect to  $\nu_5$  taken = 0,  $\nu_4$  is  $-24.5 \pm 1.3$  and  $\nu_3$  =  $-15.1 \pm 1.2$ . The  $J_{HH}$  couplings used are 5.0, 1.3, and 3.8 Hz for  $H_4H_5$ ,  $H_3H_5$  and  $H_3H_4$ , respectively. <sup>b</sup> First approximation (see text). <sup>c</sup> Second approximation (see text).

**Table V.** Experimental and Computed Values (Hz) of the 220-MHz Spectrum of 2,2'-Bithienyl as Solute in Nematic Phase<sup>a</sup>

Exptl	Computed					
	s-trans	s-cis	69% s-trans <sup>b</sup>	70% s-trans <sup>c</sup>	64% s-trans <sup>d</sup>	
$D_{45}$	+454.4 ± 1.8	+417.8	+401.8	+455.0	+454.3	
$D_{35}$	-59.7 ± 2.5	-64.6	-32.1	-65.3	-57.9	
$D_{35'}$	-130.8 ± 1.1	-281.9	-40.5	-135.7	-126.1	
$D_{45'}$	-50.2 ± 1.1	-84.4	-26.9	-53.0	-52.7	
$D_{55'}$	-41.8 ± 0.9	-43.7	-32.8	-44.0	-46.9	
$D_{34}$	-1257.1 ± 0.8	-1254.8	-788.8	-1255.3	-1258.0	
$D_{34'}$	-115.5 ± 0.8	-185.9	-115.6	-109.1	-118.8	
$D_{44'}$	-51.3 ± 1.9	-91.3	-38.8	-52.1	-53.7	
$D_{33'}$	-462.5 ± 1.8	-189.5	-902.2	-465.1	-462.5	
Rms deviation, Hz		116	217	3.6	2.9	
$C_{3z^2-r^2}$		-0.690	-0.200	-0.380	-0.392	-0.398
$C_{x^2-y^2}$		+0.477	+0.257	+0.378	+0.382	+0.384
$C_{xy}$		-0.415		-0.026	-0.034	-0.040

<sup>a</sup> With respect to  $\nu_5$  taken = 0,  $\nu_4$  is  $-54.4 \pm 1.4$  and  $\nu_3$  =  $-28.2 \pm 1.3$ . The  $J_{HH}$  couplings are the same as in Table II. <sup>b</sup> First approximation (see text). <sup>c</sup> Second approximation (see text). <sup>d</sup> Values obtained making use of the potential function (see text).

tained by analyzing spectra of a 20% molar solution of equal amounts of I and II oriented in nematic phase IV (Licristal Merck) in order to ensure identical conditions of solution and temperature.

As we can see from Table III the differences in corresponding motional constants are less than 2%. Therefore, the approximation of assuming equal  $C_{3z^2-r^2}$  and  $C_{x^2-y^2}$  motional constants for the cis and trans isomers of 2,2'-bithienyl seems quite reasonable. Under such an assumption only three motional constants have to be determined, thus lifting the insensitivity on the isomer ratio.

A second method might also be taken into account, but its validity is restricted to the case that in 2,2'-bithienyl the internal rotation of the rings takes place in a time shorter than the reorientation of the whole molecule in the liquid crystal. For energy barriers around 5 kcal/mol, the interconversion rate at room temperature (according to the Arrhenius equation with a "normal" frequency factor of  $10^{13} \text{ sec}^{-1}$ ) has values ( $10^{9.5} \text{ sec}^{-1}$ ) which could be faster than the reorientation of a large molecule in the viscous crystalline medium. Obviously, the lower the energy barrier, and thus the faster the rotation rate, the more acceptable this hypothesis will become. In this case, three averaged motional constants will describe the orientation of the whole system. From a mathematical point of view the different physical meaning of the two methods as ap-

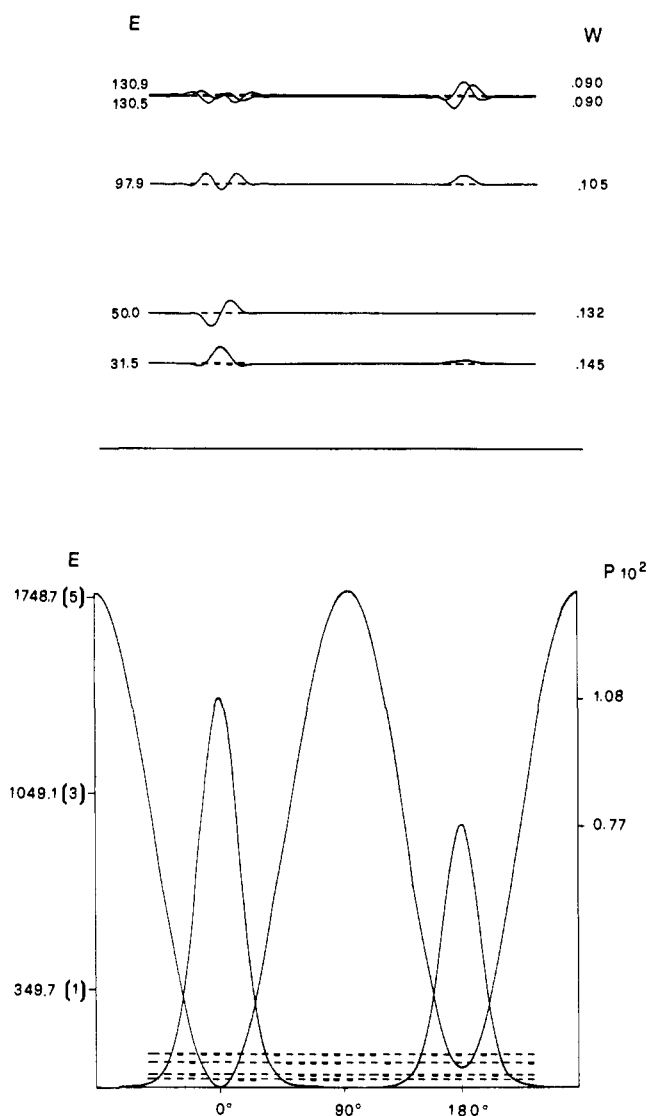
plied to 2,2'-bithienyl only affects the term containing the  $C_{xy}$  element.

These two ways of approaching the problem have already been discussed and tested on a number of derivatives;<sup>4</sup> however, as no definite conclusion could be reached on this argument, both approaches were used to study the 2,2'-bithienyl.

The results are summarized in Tables IV and V where both the 100- and 220-MHz data were used to avoid the possibility that the good fitting is due to an accidental coincidence. The results are substantially equal for both spectra and only minor differences are observed in the two approximations employed. The s-trans conformer is the more stable species, its amount being about 70% at room temperature.

The sensitivity of the results to the geometry has also been tested by making a number of reasonable changes on the protonic coordinates, although for different values slightly worse rms deviations have been obtained, the rotamer ratio is little affected, the amount of the s-trans varying in the cases examined by less than plus or minus 5%.

The conformational results are not in disagreement with the conclusions previously obtained from the 5,5'-substituted derivatives,<sup>4b</sup> although the present figures should be regarded with more confidence, as they fit a larger number of independent equations. It is also interesting to observe that the lack of substituents makes



**Figure 2.** Lower trace: energy levels ( $E$ ) and angular probability density ( $P$ ) for the intramolecular rotation of 2,2'-bithienyl. The scale of the energy (left) is in  $\text{cm}^{-1}$  and the corresponding kcal/mol are given in parentheses. The  $0^\circ$  angle corresponds to the s-trans and  $180^\circ$  to the s-cis conformation. Upper trace: here are reported in expanded scale the first five rotational levels with the corresponding eigenfunctions. The energy values ( $E$ ,  $\text{cm}^{-1}$ ) are on the left, whereas on the right are reported the weights ( $W$ ) according to the Boltzmann distribution.

this molecule much less oriented than those of ref 4b; the absolute values of the motional constants are therefore very different and so are their relative values. If the assumption of taking equal motional constants belonging to different conformers had been completely incorrect, a very different isomer ratio would have been obtained in the two cases. The fact that a substantially similar amount of s-trans and s-cis has been derived (as one must expect from such closely related derivatives) indicates that the approximations involved are not unrealistic.

In this kind of investigation the implicit assumption has been made that the rotamers only populate the state with the lowest energy. On the other hand, if the population distribution over the whole pathway of the ring interconversion is taken into account, it should be possible to determine the energy barrier for the rotation.

The potential function for a rotating system is usually given by

$$V(\alpha) = \sum_n V_n/2(1 - \cos n\alpha)$$

In the case of 2,2'-bithienyl with two positions of minimal energy the equation becomes

$$V(\alpha) = V_1/2(1 - \cos \alpha) + V_2/2 \times (1 - \cos 2\alpha) + V_3/2(1 - \cos 3\alpha)$$

If the two rings rotate rigidly around the central bond, the probability distribution with respect to the dihedral angle ( $\alpha$ ) is obtained by solving the Schrödinger equation for the rotor. The wave function was expanded in the harmonic series and the expansion truncated at the 23 term. As the Hamiltonian is totally symmetric, the matrix could be factored in a symmetric and in an asymmetric part. Finally, the rotational angular probability, which allows the calculation of the average  $D_{ij}$  values, was obtained by weighting with a Boltzmann type distribution the first 40 rotational states. As in the previous approaches, the coordinates of the hydrogen atoms were assumed (see Table I) and, on this basis, a moment of inertia of 105.84 au  $\text{A}^2$  was employed.

The values of  $V_1$ ,  $V_2$ , and  $V_3$  best fitting the experimental data were obtained; the recalculated  $D_{ij}$  values are reported in Table III using the figures for the 220-MHz spectrum, as no appreciable differences were observed in the two sets of data. The results are summarized in Figure 2 where the potential is given as a function of the angle between the two thiophen rings. The angle  $\alpha = 0^\circ$  corresponds to the s-trans conformation and  $\alpha = 180^\circ$  to the s-cis. At  $V_1 = 205 \text{ cm}^{-1}$  and  $V_3 = -130 \text{ cm}^{-1}$ , the energy difference ( $V_1 + V_3$ ) is  $75 \text{ cm}^{-1}$  (0.21 kcal/mol) and the corresponding amount of the s-trans species turns out to be 64%.

The barrier to the internal rotation is given by  $V_1/2 + V_2 + V_3/2$ , and its best value was found for  $1800 \text{ cm}^{-1}$  (5.1 kcal/mol). The root mean square deviation, however, is not very sensitive to the height of the potential barrier (essentially determined by  $V_2$ ), and therefore the uncertainty for this value is rather large; only for variations of at least 2 kcal/mol around the best solution do the deviations between calculated and experimental couplings become exceedingly large, and we can thus restrict to  $5 \pm 2 \text{ kcal/mol}$  the determination of the barrier.

The values of  $V_1$  and  $V_3$  are defined with better accuracy, as the rms deviation is much more sensitive to these parameters; the per cent of s-trans is thus known with an error of only a few per cent around 64% for the given geometry of 2,2'-bithienyl. The result is not in disagreement with the value determined without taking into account the potential function.

## Conclusions

The use of the nmr spectroscopy in the nematic phase cannot give very accurate results when applied to conformational analysis but allows us to obtain a satisfactory knowledge of conformational preferences and interconversion barriers for molecules, such as 2,2'-bithienyl, where the nmr in isotropic solvents does not yield reliable information.

The approximations which had to be used are prob-

ably rather coarse but lead to results internally consistent, at least in a qualitative point of view. Theoretical calculations performed on the same molecule<sup>12</sup> 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,<sup>5</sup> and in solutions of the radical anion (at  $-80^\circ$ ) two conformers with an 80:20 ratio were detected.<sup>8</sup> Such a ratio seems to fit surprisingly well our results since, if  $\Delta S^\circ$  is taken equal to 0 as usual for internal rotations, the value at room temperature becomes 70:30.

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

(12) V. Galasso and N. Trinajstić, *Tetrahedron*, **28**, 4419 (1972).

(13) L. Lunazzi and C. A. Veracini, *J. Chem. Soc., Perkin Trans. 2*, 1739 (1973).

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 <sup>13</sup>C 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 <sup>13</sup>C and <sup>1</sup>H 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.<sup>2</sup> However, preliminary applications<sup>3a</sup> of a recent gauge-invariant *ab initio* theory of magnetic shielding<sup>3b</sup> have given results for <sup>13</sup>C and <sup>1</sup>H 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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(2) For a recent review see W. N. Lipscomb, *Advan. Magn. Resonance*, **2**, 137 (1966).

(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 <sup>13</sup>C chemical shifts of the fluoromethanes,<sup>4</sup> CH<sub>n</sub>F<sub>4-n</sub>, *n* = 0 and 4, fluoroethylenes,<sup>5</sup> C<sub>2</sub>H<sub>n</sub>F<sub>4-n</sub>, *n* = 0 and 4, and fluoroacetylene.<sup>5</sup>

In this work we report extensions of this study to a comparison of the measured <sup>13</sup>C chemical shifts of the fluoroallenes C<sub>3</sub>H<sub>n</sub>F<sub>4-n</sub>, *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 ( $\alpha$ ,  $\beta$  and  $\gamma$ , respectively) substituent effects on the carbon atoms forming the cumulated double-bond system of the allene molecule.

(4) R. Ditchfield and P. D. Ellis, to be submitted for publication.

(5) R. Ditchfield and P. D. Ellis, *Chem. Phys. Lett.*, **17**, 342 (1972).