# Nematic Phase Nuclear Magnetic Resonance Investigations of Rotational Isomerism. Part IV.[1] Conformational Study on the Rotamers of 3,3'-Bithienyl

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The 220 MHz n.m.r. spectrum of partially oriented 3,3'-bithienyl has been obtained and interpreted. A number of models have been tested in order to determine the molecular conformation in solution on the basis of the observed dipolar couplings. It has been shown that the molecule does not exist as a single species but as an equilibrium between two rotational conformers. The two rotamers are not planar (the twisting angle being ca. 22°) and the SS-trans-like rotamer is the more abundant (ca. 66%). The results agree with previous electron diffraction studies in the gas phase.

THE structure of 3,3'-bithienyl has been so far investigated in the solid and in the gas phase by X-ray[2] and electron[3] diffraction. In both cases evidence has been
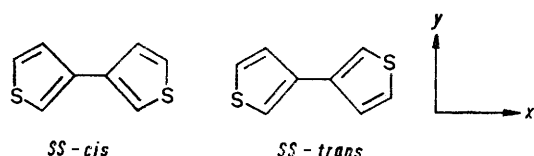
SS - cis SS - trans

found that both the SS-cis- and the SS-trans-conformers are present, the latter in larger amount.

Theoretical investigations also predict that the plot of the total energy as a function of the twisting angle θ has two minima corresponding to two unequally populated conformers.[3,4] Furthermore, contrary to theoretical studies on 2,2'-bithienyl,[3] those concerning the 3,3'-bithienyl agree in indicating that the two rotamers are not planar,[3,4] the twisting angle being ca. 25—30°.

Electron diffraction (e.d.)[3] and u.v.[5] measurements

[1] Part III, P. Bucci, M. Longeri, C. A. Veracini, and L. Lunazzi, J. Amer. Chem. Soc., 1974, **96**, 1305.

[2] G. J. Wisser, G. J. Heeres, J. Wolters, and A. Vow, Acta Cryst., 1968, **B24**, 467.

[3] A. Skancke, Acta Chem. Scand., 1970, **24**, 1389.

[4] V. Galasso and N. Trinajstic, Tetrahedron, 1972, **27**, 4419.

[5] B. Norden, R. Hakansson, and M. Sundbom, Acta Chem. Scand., 1972, **26**, 429.

also seem to confirm that the two rotamers are not planar, whereas they were found to be planar in the crystalline state (X-ray).[2] The latter finding, however, is not unexpected since in analogous cases molecules which are twisted in the gas or in the liquid state (e.g. biphenyl [6,7]) are flattened by the effect of the crystalline field.[8]

In order to gain more detailed information on the conformational properties of the title compound in solution, an n.m.r. study in a nematic solvent has been undertaken: this technique is probably the most reliable method to obtain structural information on organic molecules in solution.[9]

Previous Parts ascertained unambiguously that thiophen-2-carbaldehyde [10] and pyridine-2,6-dicarbaldehyde [11] exist as a single conformer, whereas similar molecules, in particular 2,2'-bithienyl,[1,12] display the two possible rotational isomers.

RESULTS AND DISCUSSION

The 220 MHz n.m.r. spectrum of 3,3'-bithienyl dissolved in a nematic solvent (Licrystal Phase IV [9c]) has been interpreted in terms of chemical shift differences, indirect spin–spin couplings (J_{HH}) and direct dipolar couplings. The experimental and computer simulated

$$D_{ij} = 1/2\ h(2\pi)^{-2}\ \gamma_H^2 \langle (3\cos^2\theta_{ij} - 1)r^{-3} \rangle \qquad (1)$$

spectra are displayed in Figure 1 and the parameters used for the analysis listed in Table 1. From the nine observed D_{ij} couplings, information can be derived upon the conformational preferences of the molecule.[9] A number of models will be discussed: (i) free rotation; (ii) the existence of a single conformer; and (iii) the equilibrium between a cis- and a trans-like conformer.

(i) *Free Rotation.*—The free rotational model has been found to hold only in the cases of groups (such as methyl) which have very low (<1 kcal mol⁻¹) activation energies for the rotational barrier.[13] On the other hand this model always turned out to be unsatisfactory when applied to molecules containing two joined aromatic rings.[6,14,15] When such a model is applied to this molecule an effective cylindrical symmetry is dynamically created along the x axis of Figure 2, which has then to be taken as the axis of maximum symmetry, i.e. it has to be called z axis in the framework of the free rotational model. The root mean square (r.m.s.) deviation between the experimental and computed dipolar couplings is however so high (487 Hz) to deny any meaning to this

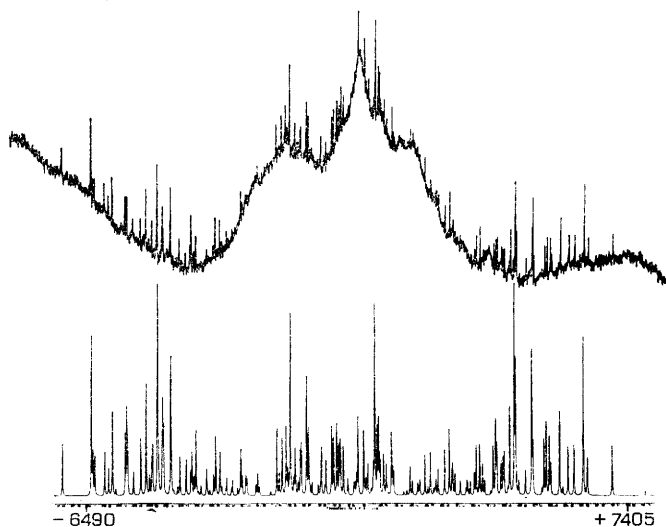model for the 3,3'-bithienyl (the corresponding $c_{3z^2-r^2}$ is −0.215).

FIGURE 1 Experimental (top) and computer simulated 220 MHz n.m.r. spectrum of 3,3'-bithienyl partially oriented in a nematic phase (Licrystal Phase IV [9b,c]). The frequencies refer to an arbitrary point in the central part of the spectrum

TABLE 1

Spectral parameters (Hz) used in the simulation of the 200 MHz spectrum of 3,3'-bithienyl partially oriented in nematic phase

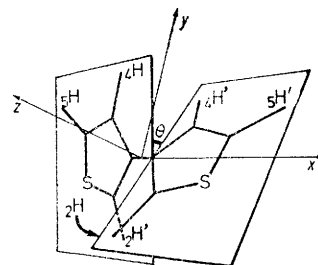|			
$D_{22'}$	−841.6 ± 1.5	$D_{44'}$	−931.6 ± 1.3
D_{24}	+256.2 ± 1.4	D_{45}	−2 399.0 ± 1.2
D_{24}	−1 856.1 ± 1.4	$D_{45'}$	−186.0 ± 1.1
D_{25}	+22.8 ± 1.5	$D_{55'}$	−83.3 ± 1.7
$D_{25'}$	−273.8 ± 1.6	$\nu_5-\nu_2$	−146.0 ± 2.7
		$\nu_4-\nu_2$	+46.1 ± 2.4

FIGURE 2 A representation of the conformation of the SS-cis-like rotamer; the SS-trans is obtained by a ca. 180° rotation

(ii) *Single Conformer.*—Three possible situations have to be tested within the framework of this hypothesis:

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[7] O. Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; O. Bastiansen and M. Traetteberg, *Tetrahedron*, 1962, **17**, 147.

[8] J. Trotter, *Acta Cryst.*, 1961, **14**, 1135; A. Hargreaves and S. Hasan-Rizvi, *ibid.*, 1962, **15**, 365; G. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, *Mol. Phys.*, 1968, **15**, 339.

[9] (a) P. Diehl and C. L. Khetrapal in ' N.M.R. Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer Verlag, New York, 1969, vol. 1, ch. 1; (b) J. W. Emsley and J. C. Lindon, ' N.M.R. Spectroscopy using Liquid Crystal Solvents,' Pergamon, Oxford, 1975; (c) L. Lunazzi in ' Determination of Organic Structures by Physical Methods,' eds. F. C. Nachod, J. J. Zuckermann, and E. W. Randall, Academic Press, New York, 1976, vol. 6, ch. 6.

[10] L. Lunazzi and C. A. Veracini, *J.C.S. Perkin II*, 1973, 1739.

[11] P. L. Barili, M. Longeri, and C. A. Veracini, *Mol. Phys.*, 1974, **28**, 1101.

[12] C. L. Khetrapal and A. C. Kunwar, *Mol. Phys.*, 1974, **28**, 441.

[13] P. Dihel, H. P. Kellerhals, and W. Niederberger, *J. Magnetic Resonance*, 1971, **4**, 352; C. L. Khetrapal and A. Saupe, *ibid.*, 1973, **9**, 275; D. Canet and J. Barriol, *Mol. Phys.*, 1974, **27**, 1705; L. F. Williams and A. A. Bothner-By, *J. Magnetic Resonance*, 1973, **11**, 314.

[14] P. Bucci and C. A. Veracini, *J. Chem. Phys.*, 1972, **56**, 1290; C. A. Veracini, D. Macciantelli, and L. Lunazzi, *J.C.S. Perkin II*, 1973, 751.

[15] J. W. Emsley, D. S. Stephenson, J. C. Lindon, L. Lunazzi, and S. Pulga, *J.C.S. Perkin II*, 1975, 1541.

a planar SS-cis-conformation [model (1a)], a planar SS-$trans$-conformation [model (1b)], and a twisted conformation having an angle θ different from 0 and 180° [model (1c)]. In the first case (1a), two orientational parameters have to be employed owing to the C_{2v} symmetry, whereas three such parameters are required for the other two cases (1b and c) because of the reduced elements of symmetry.[9]

Table 2 reports the proton co-ordinates derived by combining structural data of thiophen as given by microwave investigation [16] with those of the X-ray investigation of the title compound.[2] Table 2 also lists the orientational

TABLE 2

Proton co-ordinates (Å 10 nm) assumed for the planar conformations of 3,3'-bithienyl (see text). The motional constants and the r.m.s. deviations (Hz) best fitting the D_{ij} values of Table 1 are also reported [models (1a and b)]

SS-trans		Atom	SS-cis	
x	y		x	y
—1.13	2.14	2	—1.13	—2.14
—3.64	—1.70	5	—3.64	1.70
—1.06$_5$	—2.16	4	—1.06$_5$	2.16
1.06$_5$	2.16	4'	1.06$_5$	2.16
3.64	1.70	5'	3.64	1.70
1.13	—2.14	2'	1.13	—2.14

Motional constants

—1.117	$c_{3z^2-r^2}$	—1.162
—0.104	$c_{x^2-y^2}$	—0.320
—0.787	c_{xy}	

R.m.s. deviations

411	801

parameters corresponding to the best agreement, as well as the r.m.s. deviations between computed and experimental dipolar couplings. The latter are extremely large for both the SS-cis- and $trans$-rotamers: in the SS-cis case the parameters ($c_{3z^2-r^2}$) even exceed the allowed physical limits.[9] Models (1a and b) are thus discarded.

Using the same structure given in Table 2, the two rings were allowed to be twisted out of the xy plane [model (1c)]; again no reasonable fitting with the experiment can be reached; it has thus to be recognized that model (1c) is also wrong, and that in solution, as in the solid [2] and gas phases,[3] a single isomer (planar or twisted) cannot account for the experimental data of the liquid crystal n.m.r. spectrum.

(iii) *Two Conformers.*—In principle a study involving the presence of two species at equilibrium would require knowledge of the isomer ratio from an independent source and it would also allow for five independent orientational parameters, two for planar SS-cis and three for the planar SS-$trans$. We shall indicate this model as (2a). The geometry of the molecule can again be assumed (see Table 2) since the purpose of the present investigation is not to derive an accurate structure, but rather to have a better insight into the conformational behaviour. Because of the assumption of the geometry, the fitting of the experimental couplings cannot be expected to be better than a few Hz, as deviations in the assumed

proton distances with respect to the real structure have to be taken into account. Having assumed a knowledge of the basic geometry, the nine dipolar couplings can be used to determine the orientational parameters and the twisting angle: the problem is thus overdetermined. As for the assumption of the relative amount of the SS-cis-isomer, very accurate results are not available; a reasonable approach seemed to be to use the average (35%) between the two analogous values reported in the e.d. studies [3] and X-ray investigations.[2]

The results of this model [(2a)] are unsatisfactory in that the r.m.s. deviation is exceedingly large, as shown in Table 3. The r.m.s. deviation turns out to be insensitive

TABLE 3

Motional constants and r.m.s. deviations obtained from a model assuming an equilibrium between two planar conformers with a $trans$: cis ratio (65 : 35) taken from an independent source [2,3] [model (2a), see text], and from a model based on an equilibrium between two twisted (0 22°) cis- and $trans$-like conformers with the same ratio [model (2b), see text]

Model	trans : cis Ratio		Motional constants		R.m.s. deviation (Hz)
			SS-trans	SS-cis	
(2a)	65 : 35	$c_{3z^2-r^2}$	—0.752	0.519	
		$c_{x^2-y^2}$	0.305	0.909	288
		c_{xy}	—0.753		
(2b)	65 : 35	$c_{3z^2-r^2}$	—0.812	0.267	
		$c_{x^2-y^2}$	0.592	0.911	5.5
		c_{xy}	—0.035		

to the isomer ratio when five motional constants are employed; nevertheless, since the error is so large (288 Hz), there is little doubt that an equilibrium between two planar structures can never give an acceptable solution. It may be thus concluded that, if there is an equilibrium between two conformers, they cannot be planar.

Having shown the failure of model (2a), we tested a model where various angles $\theta \neq 0°$ are assumed, all the other conditions being equal. No allowance was made for a potential function, assuming that in both the cis- and $trans$-like rotamers the structures with the tested angles are the only populated species [model (2b)]. When θ is 22° from planar SS-cis (for the rotamer present at 35%), and 22° from planar SS-$trans$ (for the rotamer present at 65%), a reasonable r.m.s. deviation (5.5 Hz) is obtained, as shown in Table 3. Also in this case, as in model (2a), the deviation is independent of the assumed cis : $trans$ ratio. Despite the relatively good agreement between computed and experimental couplings, the real significance of model (2b) is questionable since the two $c_{3z^2-r^2}$ values (*i.e.* that of the cis-like and that of the $trans$-like rotamers) are so different even to be opposite in sign, whatever the cis : $trans$ ratio assumed. On the contrary in this kind of molecule the orientational parameters relative to the z-axis should be very similar, owing to the analogous elongated shapes of the two conformers. Furthermore they are expected to be both negative; a

[16] B. Back, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1961, 7, 58.

positive value for only one of the two rotamers would mean that its z-axis tends to be parallel to the magnetic field, whereas elongated molecules usually have their longest axis (x in this case) parallel to the field (thus $c_{3z^2-r^2}$ is negative). In addition to this general consideration, one cannot easily accept the conclusion that one of these rotamers is oriented in an opposite way to the other.

In order to solve the problems presented by model (2b), the quite reasonable assumption was made that the $c_{3z^2-r^2}$ terms are equal for both conformers [model (2c)]. This model will only have a physical meaning if the two equalized parameters will yield a negative value, according to expectations about the molecular orientation. Indeed (see Table 4) this assumption produces good agree-

TABLE 4

Motional constants obtained considering an equilibrium between two twisted (θ 22°) trans- and cis-like conformers with a ratio (65 : 35) taken from an independent source.[2,3] It has been assumed that both the trans- and cis-like conformers have the same value of $c_{3z^2-r^2}$ [model (2c), see text]

$c_{3z^2-r^2}$ (trans) = $c_{3z^2-r^2}$ (cis)	−0.450
$c_{x^2-y^2}$ (trans)	0.706
$c_{x^2-y^2}$ (cis)	0.688
c_{xy} (trans)	−0.028
R.m.s. deviation (Hz)	6.5

ment with the experimental couplings (r.m.s. deviation 6.5 Hz, for θ 22°), and also a negative value for $c_{3z^2-r^2}$ (−0.450) is obtained. In Table 4 it should be observed that the two parameters $c_{x^2-y^2}$ are also very close: a not unreasonable feature if one considers that the similarity of the shapes of the two rotamers makes likely an analogous orientation within the xy plane. A satisfactory interpretation of the experimental data has been thus obtained with model (2c). The conclusion is that there are two twisted (θ 22°) cis- and trans-like conformers at equilibrium, the latter in larger amount.

Finally a fourth model (2d) has also been tested, based on different assumptions with respect to the previous three.

If the lifetime of the two rotamers is shorter than the time needed for the reorientation of the whole molecule in the liquid crystalline solvent and the two motions are uncorrelated, then only three averaged parameters are required to describe the orientation.[1,9b,14,17] Owing to the quite low energy barrier expected for the rotational process of the title compound,[3,4] this hypothesis does

not seem unreasonable. According to model (2d) the number of unknowns is further reduced since only three orientational parameters instead of four or five are needed. Therefore, in addition to the twisting angle θ, the rotamer ratio too can be treated as an unknown, and a previous knowledge of this quantity from independent sources is not needed any more. Model (2d) turns out to have an r.m.s. deviation strongly dependent upon the twisting angle and the rotamer ratio. The best solution eventually yields θ 22°, SS-trans-like conformer 66.5%, and an r.m.s. of 3.2 Hz (see Table 3). The result parallels that obtained with model (2c).

TABLE 5

Motional constants obtained considering an equilibrium between two twisted (θ 22°) trans- and cis-like conformers. In this model (2d) only three averaged motional constants were considered. The ratio was not assumed and corresponds to that giving the best r.m.s. deviation

trans : cis	66.5 : 33.5
$\bar{c}_{3z^2-r^2}$	−0.451
$\bar{c}_{x^2-y^2}$	0.698
$\bar{c}_{xy}$	−0.024
R.m.s. deviation (Hz)	3.2

Independent of the models employed, the conclusion that two twisted rotamers are present at equilibrium seems inescapable, and also that the trans-like species is the more abundant rotational isomer.

In Figure 2 the twisted conformation of one of the two isomers (SS-cis like) is given, the other being obtained by 180° rotation.

EXPERIMENTAL

The spectra were run on a Varian HR-220 MHz spectrometer at probe temperature (ca. 20 °C) with sample spinning. The whole spectrum was recorded in various overlapping sections each 1 kHz wide with a sweep time of 250 s. The sample contained ca. 10 mol % of the title compound in Merck Licrystal Phase IV.

[17] L. Lunazzi, G. F. Pedulli, M. Tiecco, and C. A. Veracini, J.C.S. Perkin II, 1972, 755.
[18] S. Gronowitz and H. O. Karlson, Arkiv. Kemi., 1960, 17, 89.