

Conformational Analysis of Bithienyl Derivatives: a Liquid Crystal Nuclear Magnetic Resonance Approach †

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The conformational analysis of three substituted 2,2'-bithienyl derivatives has been accomplished by means of the liquid crystal n.m.r. spectroscopy. The interpretation of the spectral data allows the possibility of free rotation as well as the existence of a single planar or twisted conformation to be ruled out. Models of an equilibrium between the *S-trans* (=78%) and *S-cis* (=22%) rotamers were in agreement with the experimental data. The results also agree with previous e.s.r. experiments and with the predictions of theoretical calculations.

THE n.m.r. spectra of molecules partially oriented in the nematic phase of liquid crystal solvents allow the detection of those terms of the spin Hamiltonian (D_{ij}) that are averaged to zero in isotropic solvents because of rapid molecular tumbling.¹ Since the D_{ij} couplings depend upon magnetic interactions between the nuclear dipoles, fairly accurate information can be obtained on molecular shapes.² These investigations, however, may be complicated by the effects of internal molecular motions such as vibrations and rotations. The effects of vibrations have been discussed in some detail,³ while cases of molecules exhibiting slower internal motions have been only recently examined.⁴⁻⁸ The main problem which has to be clarified concerns the re-orientation times of the molecules dissolved in the mesophase: this has been discussed in previous papers⁵⁻⁷ and although definite conclusions have not been reached so far, the use of a reduced number of motional constants seems to give not unreasonable results.⁵⁻⁸

Even though no accurate measurements have been yet obtained on the reorientation rates of molecules dissolved in liquid crystal solvents, the values are believed to be^{7,9} of the same order of magnitude as those in isotropic liquids (10^{10} s⁻¹) or less. According to the Arrhenius equation, at the temperature of many liquid crystal experiments (*ca.* 80 °C), the internal molecular motions have the same or faster rates when the activation energies are equal to or smaller than 5 kcal mol⁻¹, provided the frequency factor has the 'normal'¹⁰ value of 10^{13} s⁻¹. The energy barrier for the *cis-trans* interconversion of the 2,2'-bithienyl has been

estimated¹¹ as <5 kcal mol⁻¹. Nevertheless we approached the problem by considering either that internal rotation was faster than reorientation, or by analysing the approximations involved in assuming the opposite situation.

The study of 2,2'-bithienyl derivatives (I)—(III) (Figure 1) offers a useful way to test the liquid crystal

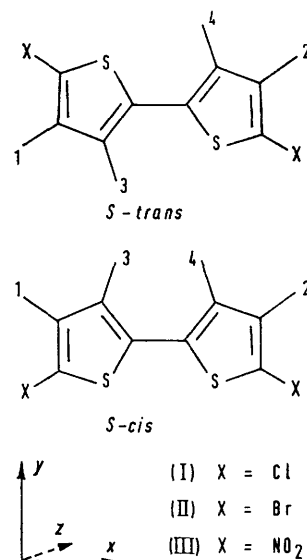


FIGURE 1 *S-trans* and *S-cis* conformations of 5,5'-dichloro- (I), 5,5'-dibromo- (II), and 5,5'-dinitro-2,2'-bithienyl (III)

approach to conformational analysis since e.s.r. experiments on the unsubstituted derivative ascertained the existence of two rotational isomers¹² and X-ray

† Part of this work was presented at the 4th International Symposium on Magnetic Resonance, Rehovot-Jerusalem, 24-31 August, 1971.

¹ A. D. Buckingham and K. A. McLachlan, *Progr. N.M.R. Spectroscopy*, 1967, **2**, 63; G. R. Luckhurst, *Quart. Rev.*, 1968, **22**, 179; A. Saupe, *Angew. Chem. Internat. Edn.*, 1968, **7**, 97; S. Meiboom and L. C. Snyder, *Science*, 1968, **162**, 1337; P. Diehl and C. L. Ketrpal, *N.M.R. Basic Principles and Progr.*, 1969, **1**, 1.

² L. C. Snyder, *J. Chem. Phys.*, 1965, **43**, 4041.

³ L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, 1966, **44**, 4057; N. J. D. Lucas, *Mol. Phys.*, 1971, **22**, 147; S. Meiboom and L. C. Snyder, *Account Chem. Res.*, 1971, **3**, 81; J. Bulthuis and C. MacLean, *J. Magnetic Resonance*, 1971, **4**, 148.

⁴ A. D. Buckingham, E. E. Burnell, and C. A. de Lange, *Mol. Phys.*, 1969, **16**, 521; P. Diehl, P. M. Henrichs, and W. Niederberger, *ibid.*, 1971, **20**, 139; 1971, **21**, 377; P. Diehl, H. P. Kellerhals, and W. Niederberger, *J. Magnetic Resonance*, 1971, **4**, 352.

⁵ P. Diehl, P. M. Henrichs, and W. Niederberger, *Org. Magnetic Resonance*, 1971, **3**, 243; P. Diehl and P. M. Henrichs, *ibid.*, p. 791.

⁶ P. Bucci, C. A. Veracini, *J. Chem. Phys.*, 1972, **56**, 1291.

⁷ L. Lunazzi, G. F. Pedulli, M. Tiecco, and C. A. Veracini, *J.C.S. Perkin II*, 1972, 751, 755.

⁸ I. J. Gazzard and N. Sheppard, *Mol. Phys.*, 1971, **21**, 169; T. N. Huckerby, *Tetrahedron Letters*, 1971, 3497.

⁹ S. A. Brooks, G. R. Luckhurst, G. F. Pedulli, and J. Roberts, to be published; R. Y. Dong, *J. Magnetic Resonance*, 1972, **7**, 60.

¹⁰ B. G. Gowenlock, *Quart. Rev.*, 1960, **14**, 133.

¹¹ M. J. S. Dewar and N. Trinajstić, *J. Amer. Chem. Soc.*, 1970, **92**, 1453; V. Galasso and N. Trinajstić, *Tetrahedron*, 1972, **28**, 4419.

¹² P. Cavaliere d'Oro, A. Mangini, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Tetrahedron Letters*, 1969, 4179.

diffraction gave the geometrical parameters of the more stable structure (*S-trans*) in the solid state.¹³

EXPERIMENTAL

The spectra of (I) and (II) were recorded on a JEOL PS 100 spectrometer using solutions *ca.* 20% molar either in 4,4'-di-*n*-hexyloxyazoxybenzene or in Merck Phase 4 at the temperatures reported in Tables 2 and 3; because of the poor solubility the spectrum of (III) could be only recorded in saturated solutions of 4,4'-di-*n*-hexyloxyazoxybenzene at much higher temperatures than the other derivatives. The spectra were run in the field sweep mode with external lock and analysed by means of the iterative computer program (LOACONOR) modified to include the anisotropic terms of the Hamiltonian.

The derivatives 5,5'-dichloro- (I), 5,5'-dibromo- (II), and 5,5'-dinitro-2,2'-bithienyl (III) were prepared by standard methods.¹⁴

RESULTS AND DISCUSSION

The spectra of 5,5'-dichloro- (I), 5,5'-dibromo- (II), and 5,5'-dinitro-2,2'-bithienyl (III) are AA'BB' systems and so four D_{ij} values have to be determined. Information on the molecular geometry could have been obtained only in the particular case of a 100% *S-cis* conformation which has the required C_{2v} symmetry.¹ To discuss the problem from a more general point of view knowledge of the basic geometry is therefore required; X-ray data are available for 2,2'-bithienyl¹³ and were used as a basic set with the additional assumption that the C-H bonds (1.08 Å) approximately bisect the thiophen ring angles. The dependence of the results on the geometry has been tested by modifying the angles by 2 or 3°, as larger deviations are not expected to occur between the solid and the liquid state. The variations observed do not affect the conclusions of the work and the results are almost independent of minor uncertainties of the molecular structure. In Table 1 the final

TABLE I

Co-ordinates of the hydrogen atoms (Å) used for the derivatives (I)–(III)

<i>S-cis</i>			<i>S-trans</i>	
x	y	Nuclei	x	y
-3.79 ₆	1.32 ₁	1	-3.79 ₆	-1.32 ₁
3.79 ₆	1.32 ₁	2	3.79 ₆	1.32 ₁
-1.33 ₉	2.19 ₀	3	-1.33 ₉	-2.19 ₀
1.33 ₉	2.19 ₀	4	1.33 ₉	2.19 ₀

co-ordinates for the hydrogen atoms are reported. The data obtained from the spectrum of the 5,5'-dichloro-2,2'-bithienyl (I) in 4,4'-di-*n*-hexyloxyazoxybenzene at 79 °C (Figure 2) will be discussed in the following sections. There are three possible situations that in principle can be expected, namely free rotation, the existence of one single conformation, an equilibrium between the *S-cis* and *S-trans* rotamers.

(a) *Free Rotation*.—The hypothesis of the two thiophen rings rotating with a negligible potential barrier is not

¹³ G. J. Visser, G. J. Heeres, J. Wolters, and A. Vos, *Acta Cryst.*, 1968, **24B**, 467.

very realistic as the detection of the two rotamers¹² in the e.s.r. spectrum of the radical anion of 2,2'-bithienyl seems to exclude the occurrence of unrestricted motion. However, if free rotation should occur, only one motional constant ($c_{3z^2-r^2}$) need be used in interpreting the spectrum since effective cylindrical symmetry is created. This value should obviously be the same, irrespectively of the D_{ij} value from which is calculated. Four different values (0.972, 1.379, 0.875, and 1.341 from D_{12} , D_{13} , D_{14} , and D_{34} respectively) were obtained, thus confirming that the problem cannot be solved without taking into account the existence of conformations having a minimum of energy.

(b) *Single Conformation*.—For this model we first calculated the D_{ij} couplings for the two planar *S-cis* and *S-trans* forms; as reported in Table 2 the results are

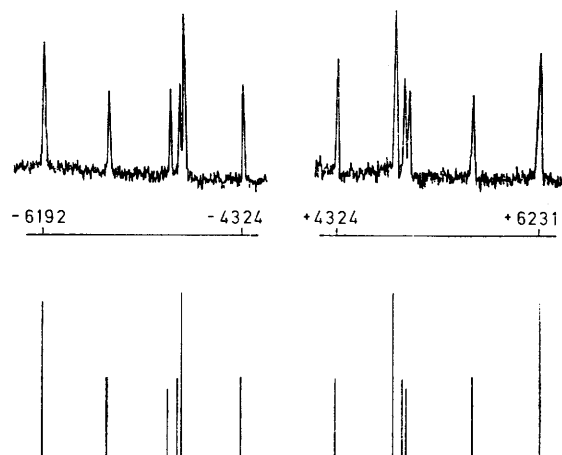


FIGURE 2 Experimental (upper) and computed n.m.r. spectrum (100 MHz) of 5,5'-dichloro-2,2'-bithienyl (I) in 4,4'-di-*n*-hexyloxyazoxybenzene at 79 °C. The scale is given in Hz relative to the middle point of the two central peaks

completely unrealistic both as regards the values of the motional constants, which greatly exceed their physical limits, and the values of the computed dipolar couplings, whose deviations are much greater than the experimental uncertainty. It can be nevertheless inferred that the *S-trans* conformation, having a smaller deviation than the *S-cis*, should be the more stable of the two planar rotamers, in agreement with the finding for the solid state.¹³

As a second step we also investigated whether a twisted form would account for the experimental D_{ij} couplings and accordingly examined all the possible situations with dihedral angles between the heterocyclic rings ranging from 0 to 180°. None of the structures was found to match the experimental data satisfactorily, except the conformation twisted by 102° from the *S-trans* form (Table 2); however, the corresponding motional constants exceed the theoretical limits, thus denying any physical meaning to this solution.

(c) *Rotamers in Equilibrium*.—A more likely possi-

¹⁴ J. H. Ulenbroek and J. D. Bijlos, *Rec. Trav. chim.*, 1960, **79**, 1181; C. Carpanelli and G. Leandri, *Ann. Chim. (Italy)*, 1961, **51**, 181.

bility is the existence of a rapid equilibrium between the two planar rotamers *S-cis* and *S-trans*. In this model, however, if reorientation is faster than internal rotation no information can be obtained on the ratio of rotamers, as different motional constants have to be assigned to each isomer, thus exceeding the number of experimental

It is found (Figure 4) that the solution, whose r.m.s. deviation is expected to be zero because of the equal number of equations and unknowns, is obtained for *S-trans* = 78% which only just exceed the upper limit: furthermore at 77.5%, which is still within the expected range, the deviation of the couplings are almost within

TABLE 2

Experimental and calculated parameters (Hz) of the 100 MHz spectrum of 5,5'-dichloro-2,2'-bithienyl (I) in 4,4'-dihydroxyazoxybenzene at 79 °C. Column (a) gives data calculated on the assumption of internal rotation slower than reorientation in the liquid crystal, column (b) reports data for the reverse situation. See text for the different physical meaning of the *c* value in the two cases

Experimental	Calculated					
	(a) <i>S-trans</i> = 77.5%	(b) <i>S-trans</i> = 78.1%	<i>S-trans</i>	<i>S-cis</i>	Twisted (102°)	
$\Delta\nu$	91.4 ± 1.7					
$D_{1,2}$	-202.3 ± 2.9	-204.9	-212.4	-127.9	-65.9	-202.7
$D_{1,3}$	-6964.4 ± 0.6	-6964.3	-6964.1	-6964.9	-6964.9	-6951.8
$D_{1,4}$	-383.9 ± 0.6	-381.0	-376.3	-425.2	-371.7	-383.3
$D_{3,4}$	-1495.1 ± 2.9	-1495.2	-1497.2	-1487.2	-1502.3	-1495.8
R.m.s. error		2.0	6.4	42.7	68.6	1.4
$c_{3z^2-r^2}$		-1.104	-1.096	-3.486	-8.446	-2.226
$c_{x^2-y^2}$		0.708	0.762	-1.274	-4.566	-0.240
c_{xy}		-0.286	-0.283	-0.483		0.730

D_{ij} couplings. On the other hand, under the hypothesis of an internal rotation faster than the reorientation in the mesophase, only three averaged parameters, $\bar{c}_{3z^2-r^2}$, $\bar{c}_{x^2-y^2}$, and \bar{c}_{xy} , are required and the problem can thus be approached. Some investigations have recently been reported in which analogous problems were dealt with in this way.^{6-8,15} Even for the case of reorientation faster than internal rotation, however, some simplifying assumptions allow an estimate of the ratio of conformers; in at least one case the results were essentially equal using both the slow and the fast reorientation hypotheses.⁷ To make use of the hypothesis of internal rotation slower than reorientation we have to reduce the number of motional constants. This can be done by assuming that the terms $c_{3z^2-r^2}$ and $c_{x^2-y^2}$ are equal for both the *S-cis* and *S-trans* isomers while c_{xy} is different from zero only for the *S-trans*. The assumption of near equivalence of the first two motional constants seems to be a rough approximation; however at least one case has been reported¹⁶ where structural isomers actually had almost equal values for these terms. When such an approximation is employed it appears that for *S-trans* values smaller than 74.7 and larger than 77.6% the terms $c_{x^2-y^2}$ and $c_{3z^2-r^2}$ respectively exceed their theoretical limits, as in Figure 3 where these motional constants are reported as function of the molar fraction of the *S-trans* rotamer. This indicates that in order to have a physical meaning the solution has to be found within this range, or at least sufficiently close to avoid the deviation of the computed D_{ij} couplings largely exceeding the experimental values. Such a situation, due to the very large degree of alignment of these molecules in the nematic solvent, is very useful in testing the internal consistency of the approximation involved.

¹⁵ P. L. Barili, L. Lunazzi, and C. A. Veracini, *Mol. Phys.*, 1972, **24**, 673.

experimental error (Table 2), and therefore the value represents an acceptable solution to the problem.

According to the fast rotation model a weighted average of the *S-cis* and *S-trans* forms was considered

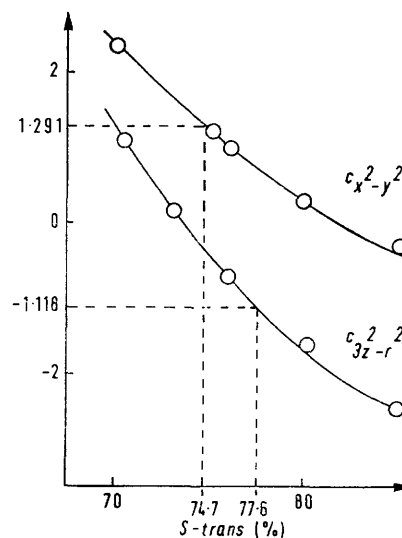


FIGURE 3 The values of the two motional constants $c_{3z^2-r^2}$ and $c_{x^2-y^2}$ (slow rotation hypothesis) as function of the amount of *S-trans* rotamer. The values -1.118 and 1.291 represent, respectively, the lower and the upper physical limits² of $c_{3z^2-r^2}$ and $c_{x^2-y^2}$. The corresponding allowed range for the amount of *S-trans* rotamer is given on (77.6%—74.7%)

and the D_{ij} couplings computed for various ratios of the rotamers. In this case the upper and lower limits for $\bar{c}_{3z^2-r^2}$ and $\bar{c}_{x^2-y^2}$ correspond to *S-trans* = 76.0 and 78.2% respectively. The exact solution (r.m.s. error = 0) is found at 79.5% which is only slightly above the upper

¹⁶ C. T. Yim and D. F. R. Gilson, *Canad. J. Chem.*, 1969, **47**, 1057.

limit, and at 78.1% the deviation from the experimental data is small enough to be considered an acceptable solution (see Table 2). In order to establish that these results are not due to a fortuitous coincidence we repeated the experiments at other temperatures, solvents,

fact that free rotation, the planar, or any other twisted form give D_{ij} values either in disagreement with the experiment or motional constants exceeding the allowed physical limits. The assumption of an interconversion between two unequally populated stable conformers

TABLE 3

Spectral parameters (100 MHz) of derivatives (I)—(III) in various solvents at different temperatures. Chemical shifts ($\Delta\nu$) and dipolar couplings (D_{ij}) are given in Hz. The amount of *S-trans* isomer and the c values reported in columns (a) represent data obtained assuming internal rotation slower than reorientation in the mesophase; columns (b) report data obtained assuming rotation faster than reorientation. See text for the different physical meaning of the motional constants in the two cases

Compound	(I)		(II)		(II)		(III)	
Solvent	Merck Phase 4		Merck Phase 4		4,4'-Di-n-hexyloxyazoxy-benzene		4,4'-Di-n-hexyloxyazoxy-benzene	
Temperature	30°		49°		79°		108°	
$\Delta\nu$	79.4 ± 1.9		87.0 ± 3.9		116.6 ± 3.0		63.6 ± 3.4	
$D_{1,2}$	-169.4 ± 3.3		-127.4 ± 6.9		-178.4 ± 5.3		-193.3 ± 16.6	
$D_{1,3}$	-6674.8 ± 0.6		-4606.5 ± 1.3		-6682.9 ± 1.1		-7978.8 ± 3.0	
$D_{1,4}$	-326.2 ± 0.6		-233.6 ± 1.3		-354.5 ± 1.1		-327.8 ± 3.1	
$D_{3,4}$	-1209.1 ± 3.2		-891.2 ± 6.7		-1394.5 ± 5.2		-1455.2 ± 16.2	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
$c_{3z^2-r^2}$	-1.082	-0.933	-0.860	-0.924	-1.108	-1.029	-1.033	-1.012
$c_{xz^2-y^2}$	0.604	0.779	0.343	0.326	0.608	0.728	0.843	0.954
c_{xy}	-0.350	-0.335	-0.225	-0.230	-0.328	-0.317	-0.552	-0.546
<i>S-trans</i>	80%	80%	80%	81%	77.5%	78%	77%	78%

and substituents. Table 3 reports the results for (I) at 30 °C, for (II) at 49 and 79 °C, and for (III) at 108 °C in different nematic phases. The relative amount of the

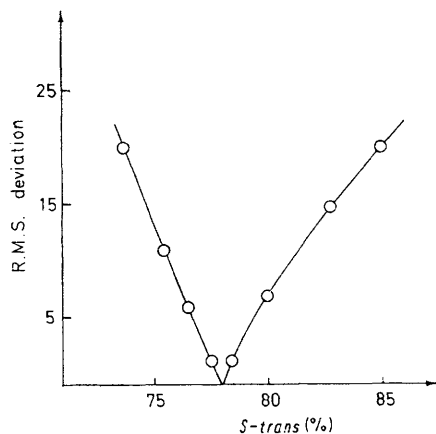


FIGURE 4 Dependence of the r.m.s. deviation between experimental and computed D_{ij} dipolar couplings upon the amount of the *S-trans* rotamer in the slow rotation hypothesis

two rotamers is essentially constant, irrespectively of the approximations employed.

Conclusions.—The n.m.r. liquid crystal investigations of molecules which, like bithienyl derivative, may exist in different conformations allow the unambiguous exclusion of some conformations. We have shown in

having a rate of transition faster or slower than molecular reorientation leads, on the other hand, to a consistent interpretation of all the experimental findings; moreover this interpretation holds for different solvents and compounds (Table 3). The comparison with the ratio of rotamers reported in the e.s.r. experiment is satisfactory since in the 2,2'-bithienyl radical anion the amount of the more stable species was *ca.* 80%^{12,17} which compares favourably with the present values (77—81%). This may largely be accidental because of the differences between the systems compared; however the liquid crystal investigation clearly shows, at least, that the *S-trans* conformation is more stable than the *S-cis*, thus proving that the tentative assignment performed on the radical anion¹⁷ was correct.

The limits of this investigation lie in the small number of available experimental couplings that somewhat reduce the accuracy of the final result. On the other hand it constitutes a good starting point for interpreting the spectrum of 2,2'-bithienyl. Extension of the work to the unsubstituted derivative is in progress.

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¹⁷ L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazzetta*, 1971, **101**, 10.