Conformational Studies of Molecules Partially Oriented in Nematic Phase: Nuclear Magnetic Resonance and Theoretical Investigation of 2,2′-Bifuryl

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The 100 MHz spectra of 2,2′-bifuryl partially oriented in the nematic phase of a liquid crystalline solvent (Merck nematic phase IV) have been obtained and interpreted. The values of direct dipolar couplings D_{ij} show that the molecule exists neither in a single planar form nor in a non-planar one. A number of models taking into account the existence of rapid *cis–trans*-equilibrium are discussed. It is shown that the *O-trans*-form is the more stable conformer (78 ±2%). The hindering internal rotation has been also investigated by means of quantum mechanical calculations using the SCF-MO-LCAO *ab initio* method. The overall results are compared with previous experimental and theoretical results.

THE n.m.r. spectra of molecules partially oriented in nematic solvents can give valuable information on molecular structure and conformation.[1] In this paper a study of 2,2′-bifuryl partially oriented in a liquid crystal solvent is presented. In this molecule the possibility of intramolecular motion of large amplitude exists and problems about reorientational and rate of internal motion arise.[2] On the other hand the technique of n.m.r. in liquid crystal solvent has been found very useful either to exclude or confirm the existence of a single conformer (twisted or planar) as well as to investigate the possibility of free rotation.[3] Moreover, for molecules having the same symmetry of 2,2′-bifuryl, it has been shown recently that, provided reasonable assumptions regarding motional parameters are advanced, a satisfactory solution of conformational problem can be obtained.[4] The results are compared with theoretical calculations and a comparison of the motional parameters of 2,2′-bifuryl and 2,2′-bithienyl is made.

Recently, *ab initio* SCF-MO-LCAO investigations of the internal rotation of medium-size organic molecules have been extensively performed.[5] In this paper we use the well known STO-3G basis set [6] which represents a good compromise between the necessary computational effort and the reliability of the results. It gives in effect a reasonable description of the rotation around C–C single bonds relative to experimental findings.[7]

EXPERIMENTAL

2,2′-Bifuryl prepared and purified as already described [8] was transferred under vacuum and sealed under nitrogen in a sample tube containing nematic phase IV (Merck) as solvent. The solute concentration was 18 mole %. Although 2,2′-bifuryl is a very unstable compound, in solution under nitrogen it showed no apparent decomposition. The spectra (A) were recorded at 27 °C on a JEOL PS 100 spectrometer in the frequency sweep mode using tetramethylsilane in an external capillary tube to provide the lock signal. The average line width was <4 Hz. Line position for 80 lines was determined with a frequency meter as a mean of three spectra with a mean deviation <1 Hz. A sample spectrum is reported in Figure 1. Two additional spectra (B and C) were also recorded using the same nematogen and a solute concentration of 20 mole % at probe temperature for B and 5 °C for C.

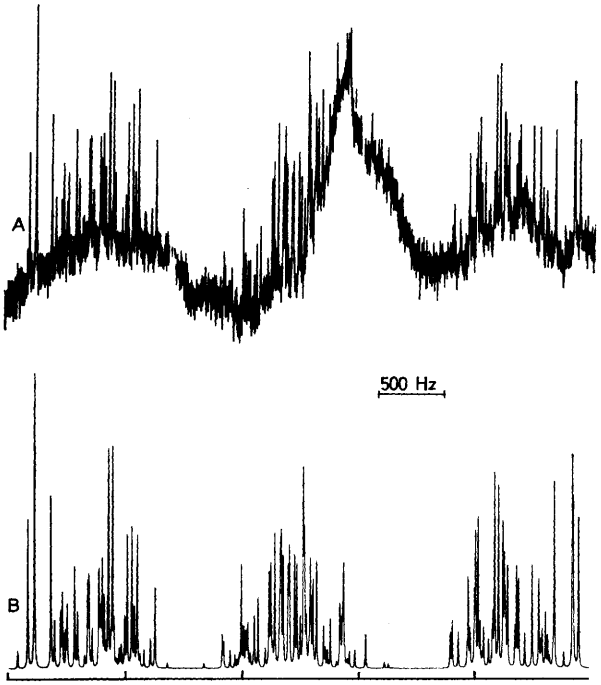

FIGURE 1 Observed (A) and calculated (B) ^{1}H n.m.r. spectrum of 2,2′-bifuryl partially oriented in nematic phase IV. Concentration 18 mole %, temperature 27 °C, operating frequency 100 MHz

RESULTS AND DISCUSSION

Analysis of Spectra.—The iterative computer program LAOCOONOR was used on an IBM 370/67 computer for spectral analysis. The spectra were interpreted in

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[1] (*a*) P. Diehl and C. L. Khetrapal, ' N.M.R. Basic Principles and Progress,' Springer–Verlag, Berlin, 1969, vol. 1; (*b*) J. W. Emsley and J. C. Lindon, ' N.M.R. Spectroscopy Using Liquid Crystals Solvents,' Pergamon Press, Oxford, 1975.

[2] P. Diehl, P. M. Henrichs, and W. Niederberger, *Org. Magnetic Resonance*, 1971, **3**, 243.

[3] P. Bucci and C. A. Veracini, *J. Chem. Phys.*, 1972, **56**, 1290.

[4] P. Bucci, M. Longeri, C. A. Veracini, and L. Lunazzi, *J. Amer. Chem. Soc.*, 1974, **96**, 1413.

[5] A. Veillard, in ' Internal Rotation in Molecules,' ed. W. J. Orville-Thomas, Wiley, New York, 1974, p. 385.

[6] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* 1969, **51**, 2657.

[7] L. Radom and J. A. Pople, in ' Physical Chemistry Series One,' vol. 1 (Theoretical Chemistry), eds. A. D. Buckingham and W. Byers Brown, Butterworths, London, 1972, p. 71.

[8] M. Bambagiotti, A. E. Castellucci, and G. Sbrana, *Spectrochim. Acta*, 1974, **30A**, 1413.

terms of three chemical shifts and nine D_{ij} dipolar couplings. The indirect dipolar couplings were taken from the literature[9] and iterated upon in a final iteration. A calculated spectrum is shown below the observed spectrum in Figure 1. The derived parameters for A—C, together with their standard errors are given in Table 1.

Molecular Structure and Conformation.—The nine D_{ij} coupling constants arising from spectrum analysis are insufficient to determine all geometrical and orientational parameters of the molecule. Therefore the geometry of the rings was taken from microwave measurements[10] assuming that the geometry of the protons does not differ from that in furan. Moreover an inter-ring C–C bond length of 1.48 Å was assumed and that the C–C–C angle containing the inter-ring bond does not change on passing from the *cis*- to the *trans*-conformation. The angle θ was treated as a variable parameter varying its value in 0.5° steps around 132 ± 2.0°. With these assumptions the dipolar couplings can be used to determine the motional constants and the preferred conformation. Accordingly, the equation system linking the proton co-ordinates to the experimental D_{ij} couplings[11] was solved for various model conformations and the motional constants best fitting experiment were obtained. Two possibilities were considered: (*a*) rigid conformers; (*b*) rotamers in equilibrium.

TABLE 1

Results of spectral analysis of the 100 MHz spectrum of 2,2′-bifuryl partially oriented in nematic phase (for experimental conditions see text)

Parameter	Value (Hz) A	B	C
D_{45}	209.2 ± 0.5	175.7 ± 0.3	260.0 ± 0.3
D_{35}	−27.1 ± 0.5	−27.4 ± 1.0	−22.8 ± 1.1
$D_{35'}$	−194.7 ± 0.4	−174.0 ± 0.8	−223.9 ± 0.9
$D_{45'}$	−63.0 ± 0.5	−55.3 ± 0.8	−71.5 ± 0.8
$D_{55'}$	−56.3 ± 0.6	−49.8 ± 0.3	−63.3 ± 0.3
D_{34}	−1 018.2 ± 0.6	−909.1 ± 0.7	−1 143.1 ± 0.8
$D_{34'}$	−95.0 ± 0.6	−86.1 ± 0.4	−105.7 ± 0.4
$D_{44'}$	−47.3 ± 0.5	−43.5 ± 1.2	−54.2 ± 1.2
$D_{33'}$	−244.2 ± 0.5	−218.0 ± 0.9	−258.2 ± 1.0
$\nu_4-\nu_5$	87.2 ± 0.5	74.8 ± 0.9	78.4 ± 1.0
$\nu_3-\nu_5$	89.8 ± 0.6	82.4 ± 1.1	87.0 ± 1.2

Indirect coupling constants used[9] are $J_{4,5}$ 3.5, $J_{3,4}$ 1.8, and $J_{3,5}$ 0.8 Hz.

Rigid conformers. As can be seen from Table 2 neither the *O-trans*- (1) nor the *O-cis*-conformation (2) accounts satisfactorily for the experimental couplings. The deviations are so large that no reasonable values for proton co-ordinates allow a satisfactory solution. It can nevertheless be inferred from the three sets of data that the *O-trans* conformer (1) which has smaller deviations than the *O-cis* (2) should be the more stable of the two forms if an equilibrium of planar conformers is present.

TABLE 2

Root mean square deviations for the *O-cis*- and *O-trans*-conformations of 2,2′-bifuryl. For the geometrical assumptions see text

	R.m.s. deviation (Hz) A	B	C
O-cis	200.4	178.4	230.3
O-trans	67.1	59.5	70.7

We also investigated whether a twisted conformation would account for the experimental D_{ij} values. For twisted structures, given the C_2 axis of symmetry, three motional constants were used and the D_{ij} values were calculated by varying the dihedral angle containing the rings in the range 0—180° in steps of 2°. None of these structures was found to match the experimental data.

Rotamers in equilibrium. The possibility of free rotation could also be tested; it was excluded, however, on the basis of theoretical calculations (see below) predicting a double minimum intramolecular potential with minima in the *cis*- and *trans*-positions. This conformational situation can be tested by considering a weighted average of the two *O-trans*- (1) and *O-cis*-rotamers (2) in equilibrium.[3,4] In order to determine which is the more stable of the two conformers and to define their relative populations it was necessary to solve the basic equation system[11] taking into account a number of motional constants depending on relative intramolecular rotation–molecule reorientation rates[2,3] and one isomer ratio. Moreover, whilst EHT calculations point to a high barrier to internal rotation (*ca.* 8 kcal mol^{-1}), more reliable SCF-MO-LCAO *ab initio* calculations and i.r. and Raman results in the liquid state[8] suggest a low barrier allowing for a rapid conformer equilibrium. Therefore the problem was treated by considering both slower and faster internal rotation with respect to molecular reorientation even though fast internal rotation is more probable in this case.

(*a*) Slower internal rotation. In this model five motional parameters are needed (three for the *O-trans*- and two for the *O-cis*-conformers). Nine dipolar couplings are available and it is possible to derive from them the products of the weights of conformers and the order parameters.[2] Moreover, under the assumptions of geometry previously made, it is possible to obtain, for each value of the conformer ratio, the value of the motional constants best fitting the experimental dipolar couplings, the calculated dipolar couplings, and their r.m.s. deviation with respect to the experimental ones. In Table 3 the proton co-ordinates we used are given, while in Table 4 are the results for the spectra A—C, as a function of *p*, the weight of the *trans*-form in the *cis–trans*-equilibrium. Table 4 shows that the r.m.s. deviations are rather small for all isomer ratios. We suppose this happens because with six parameters (five motional constants and the *cis–trans*-ratio) it would be possible to fit almost any result. In Figure 2 the order parameters obtained in the case of A (curves a) are plotted as a function of *p*. The motional parameters

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[9] K. I. Dahlqvist and S. Forsén, *J. Phys. Chem.*, 1965, **69**, 4062.

[10] B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Mygaard, J. B. Rastrup-Andersen, and M. Schottlander, *J. Mol. Spectroscopy*, 1962, **9**, 124.

[11] L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, 1967, **47**, 1480.

when a slightly different geometry of the molecule is assumed are also plotted (curves b). We can see that the curves a and b are practically coincident for $C_{x^2-y^2}$ order parameters, while they are fairly different for $C_{3z^2-r^2}$ ones. However, at the limits of the high uncertainties in the $C_{3z^2-r^2}$ values, the crossing points of the separate pairs of motional constants have $p = \bar{p}$ indicating that an average orientation of the two conformers may exist. From the trends of curves in Table 3 we can safely conclude that for 95% $< p <$ 30% the $C_{3z^2-r^2}$ parameters are outside their physical limits ($C_{3z^2-r^2} \leqslant -1.118$). Similar results can be derived from the other two sets of data (B and C) and the conformational problem is indeterminate for a wide range of p.

TABLE 3

Co-ordinates (Å) of the hydrogen atoms of 2,2′-bifuryl

O-trans *x*	*O-trans* *y*	Hydrogen	*O-cis* *x*	*O-cis* *y*
−3.345	1.898	5	−3.345	−1.898
−3.944	−0.77	4	−3.944	0.77
−1.492	−2.035	3	−1.492	2.035

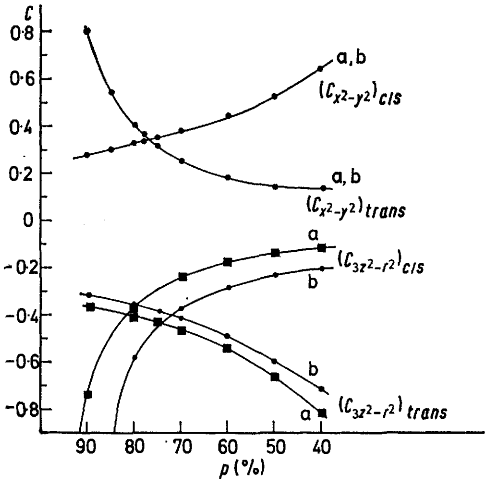


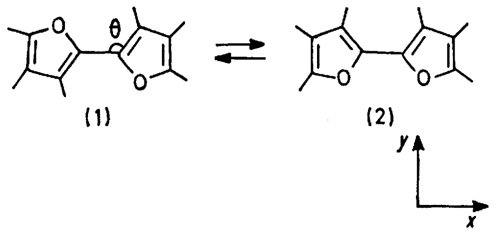
FIGURE 2 Motional parameters of 2,2′-bifuryl as a function of % *trans*-conformer (for calculations see text)

TABLE 4

Motional parameters for 2,2′-bifuryl (calculated as described in the text)

Spectra	% of *O-trans*-conformer	Motional constants *O-trans* $C_{3z^2-r^2}$	*O-trans* $C_{x^2-y^2}$	*O-trans* C_{xy}	*O-cis* $C_{3z^2-r^2}$	*O-cis* $C_{x^2-y^2}$	R.m.s. deviation
	0.7	−0.47 ± 0.05	0.37 ± 0.03	0.036 ± 0.02	−0.24 ± 0.18	0.27 ± 0.09	1
A	0.8	−0.41 ± 0.04	0.32 ± 0.03	0.048 ± 0.02	−0.36 ± 0.27	0.41 ± 0.11	1
	0.9	−0.36 ± 0.07	0.28 ± 0.03	0.041 ± 0.02	−0.73 ± 0.6	0.82 ± 0.24	1
	0.7	−0.43 ± 0.06	0.34 ± 0.03	0.046 ± 0.02	−0.24 ± 0.2	0.22 ± 0.08	2
B	0.8	−0.38 ± 0.05	0.28 ± 0.03	0.042 ± 0.02	−0.40 ± 0.3	0.37 ± 0.12	2
	0.9	−0.34 ± 0.06	0.25 ± 0.04	0.038 ± 0.02	−0.59 ± 0.6	0.75 ± 0.27	2
	0.7	−0.54 ± 0.05	0.41 ± 0.03	0.062 ± 0.03	−0.24 ± 0.3	0.28 ± 0.1	1
C	0.8	−0.46 ± 0.06	0.38 ± 0.03	0.054 ± 0.02	−0.36 ± 0.35	0.44 ± 0.12	1
	0.9	−0.41 ± 0.07	0.33 ± 0.04	0.044 ± 0.02	−0.72 ± 0.6	0.88 ± 0.3	1

In order to overcome this indeterminacy some physical assumptions constraining the motional parameters have to be made. In particular the molecular shape is the main factor affecting the molecular orientation.[12] For this reason, in the absence of specific solute–solvent interactions, the $C_{3z^2-r^2}$ and $C_{x^2-y^2}$ motional constants are expected to be nearly equal for both conformers since they have no great difference in molecular shape. Moreover, it has been shown recently that differences between corresponding motional constants of geometrical isomers having the same symmetry as (1) and (2) are of the order of a few percent.[4] Therefore an approximate solution was attempted by assuming $C_{3z^2-r^2}$ and $C_{x^2-y^2}$ to be equal for the two conformers (1) and (2). With such an assumption only three motional constants have to be determined: $(C_{3z^2-r^2})_{cis,trans}$, $(C_{x^2-y^2})_{cis,trans}$, and $(C_{xy})_{trans}$.



Data analysed on the basis of this assumption using the geometry of Table 3 are given in Table 5. In cases *A* and *B* the use of a reduced number of motional parameters give a sharp minimum r.m.s. deviation for the *trans*-conformer with p 78%. Spectrum C recorded at 5 °C lead to a value of p of 80% as was expected on the basis of a simple Boltzmann weighting. The motional parameters obtained in this analysis show high internal consistency. We point out, moreover, that considering Figure 2, a much less stringent condition on the $C_{x^2-y^2}$ order parameter is needed in order to obtain the ratio of conformers; it is in fact sufficient to require that the $C_{x^2-y^2}$ parameters of the two conformers do not differ by more than 50% to have the *trans*-conformer fixed in the range 85% $> p >$ 65%.

(*b*) *Faster internal rotation*.—In the case of faster internal rotation the problem is well determined as only three motional parameters are needed to describe the molecular orientation.[4] Therefore, at the limits of the rigid rotor approximation, a suitably truncated expansion of the intramolecular potential energy can be used in order to average the D_{ij} couplings over the

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[12] J. C. Robertson, C. T. Yim, and D. F. R. Gilson, *Canad. J. Chem.* 1971 **49**, 2345.

internal rotation [equation (1)]. As shown earlier, a good fit between the observed and calculated couplings

$$V(\tau) = \sum_{n=1}^{3} V_n(1 - \cos n\tau)/2 \qquad (1)$$

has been obtained using two planar conformers. The planar conformer model fixes with precision $(V_1 + V_3)$ and implies that in (1) $(\frac{1}{2}V_1 + V_2 + \frac{1}{2}V_3)$ is infinite. In this section we change the model by allowing a finite value of V_2. In this model the normalized probability of a rotation angle $\tau, P(\tau)$, can be calculated solving the Schrödinger equation of the rotor and weighting the rotational states by a Boltzmann distribution. The wavefunction was expanded in the harmonic series and reduced to 25 terms, while only the first 40 rotational states were considered. In the calculation a reduced moment of inertia I_{red} of 27 a.m.u. Å^2 was used and the geometry was slightly relaxed. With a suitable computer program a best fit of the experimental D_{ij} values was made (only the data of spectrum A were treated in this approximation). However, as previously[4] the r.m.s. deviation is not greatly influenced by the barrier to internal rotation (essentially determined by V_2) and therefore the uncertainty for this parameter is quite large. Table 6 reports the best fit V_1—V_3 values while in Table 7 the recalculated dipolar couplings, r.m.s. deviations, and motional parameters are reported. In Table 7 the ratios of the interproton distances derived from the geometry used are also given together with the values from microwave data for furan. The weight of *trans*-form calculated from the V_1—V_3 is 78.7%.

TABLE 5

Calculated dipolar couplings for 2,2′-bifuryl in the conformer equilibrium approximation

	A	B	C
D_{45}	209.2	173.3	259.6
D_{35}	−27.2	−26.3	−21.9
$D_{35'}$	−195.3	−173.9	−225.2
D_{45}	−62.3	−55.5	−71.0
D_{55}	−54.7	−48.5	−63.4
D_{34}	−1 018.3	−909.4	−1 144.0
$D_{34'}$	−94.6	−84.4	−107.0
$D_{44'}$	−48.7	−43.4	−53.4
$D_{33'}$	−244.0	−218.1	−256.8
p (% *trans*-conformer)	78	78	80
R.m.s. deviation (Hz)	0.85	0.8	1.2
$C_{3z^2-r^2}$	−0.399 4	−0.360	−0.444 6
$C_{x^2-y^2}$	0.337 4	0.297 8	−0.391 2
C_{xy}	0.041 4	0.027 2	0.040 4

TABLE 6

Parameters of the intramolecular potential curve (cm^{-1})

	Computed from the best fit of dipolar coupling	Extracted from the theoretical intramolecular potential
V_1	230 ± 10	199 (194)
V_2	2 100 ± 350	1 455 (1 432)
V_3	75 ± 10	91 (87)
V_4		−28

Motional Parameters.—Although for the solution of the conformational problem we were forced to make assumptions about the motional behaviour of the molecule (at least in the slower internal rotation hypothesis), these assumptions have ***a posteriori*** support from a comparison of the motional parameters of 2,2′-bifuryl (sample A) and of 2,2′-bithienyl,[4] partially oriented under the physical conditions and in the solvent given in Table 8. Since an accidental coincidence of numerical values is improbable the results of Table 5 show that the parameter $C_{3z^2-r^2}$ is weakly sensitive not only to conformation (a *trans–cis*-ratio of 70 : 30 was found for 2,2′-bithienyl) but also to structural changes which do not greatly modify, however, the molecular shape.

TABLE 7

Parameters for the faster internal rotation model of 2,2′-bifuryl

Parameter	Value	Parameter	Value 2,2′-bifuryl (*trans*-form)	Furan[10]
D_{45}	209.3	r_{45}/r_{34}	0.98	0.994
D_{35}	−27.2	r_{35}/r_{34}	1.54	1.571
$D_{35'}$	−194.6	$r_{35'}/r_{34}$	1.71	
$D_{45'}$	−64.0	$r_{45'}/r_{34}$	2.64	
$D_{55'}$	−55.4	$r_{55'}/r_{34}$	2.72	
D_{34}	−1 017.9	$r_{34'}/r_{34}$	2.20	
$D_{34'}$	−95.8	$r_{44'}/r_{34}$	2.91	
$D_{44'}$	−48.1	$r_{33'}/r_{34}$	1.80	
$D_{33'}$	−244.8			
R.m.s. deviation (Hz)	0.6			
$C_{3z^2-r^2}$ [a]	−0.397			
$C_{x^2-y^2}$ [a]	0.343			
C_{xy} [a]	0.023 8			

[a] r_{34} 2.66 Å (assumed).

TABLE 8

Motional constants of 2,2′-bithienyl[4] and 2,2′-bifuryl partially oriented in the nematic phase

	2,2′-Bithienyl	2,2′-Bifuryl
$C_{3z^2-r^2}$	−0.40	−0.399
$C_{x^2-y^2}$	0.386	0.337
C_{xy}	0.039	0.041

Theoretical Calculations.—Theoretical investigation of the internal rotation of 2,2′-bifuryl has been performed by computing the *ab initio* SCF wave function (STO-3G basis set) for five values of the dihedral angle τ between the two furan planes: τ = 0, 45, 90, 135, and 180° (τ = 0° for the *O-O-trans*-rotamer). Owing to the computational time required it was impossible to examine the relaxation of the molecular geometry: values of 1.48 Å and 132° have been assumed for the inter-ring C–C bond length and for the C–C–C bond angles containing the inter-ring bond respectively. The microwave values of furan[10] have been used for the other geometrical parameters.

The internal rotation potential has two minima which correspond to the *cis*- and *trans*-rotamers: the preferred conformation is *trans* and the energy of the *cis*-form is greater by 0.8 kcal mol^{-1} than the absolute *trans*-minimum. The computed barrier for the *cis–trans*-interconversion, corresponding to orthogonal rearrangement of the two furan planes, is 3.7 kcal mol^{-1}. The computed values of the potential energy have been fitted to a Fourier series of the form (2). Table 6

$$V(\tau) = \sum_{n=1}^{N} V_n(1 - \cos n\tau)/2 \qquad (2)$$

reports the values of V_n for $N = 4$ and the best fit to the computed values for $N = 3$ (in parentheses).

For the solution of the Schrödinger equation of the hindered rotor in the field of the potential energy, we have computed for five molecular conformations the reduced moment of inertia I_{red}. By assuming $N = 3$ in equation (2) and a mean value of I_{red} of 27.3 a.m.u. Å^2 (I_{red} slowly varies over the range of τ considered) we obtain a *trans*-population of 77.5 and 75.7% at 278 and 300 K respectively which corresponds to a value of -0.7 kcal mol^{-1} for $\Delta G°$ for the *cis–trans*-interconversion at both temperatures.

The solvent effect of nematic phase IV on the rotational isomerism seems to be negligible: the correction to $\Delta G°$, computed by means of classical reaction-field theory, is <0.1 kcal mol^{-1}.'

The results, besides excluding various conformational possibilities, suggest that 2,2'-bifuryl exists in the liquid crystal phase as a mixture of *O-cis-* and *O-trans*-conformations, with the *trans*-form predominating. These results are in close agreement both with a previous i.r. and Raman investigation of the molecule in the liquid state and with the present results of theoretical calculations. As far as the theoretical results are concerned it can be pointed out that in order to perform a correct investigation of the problem of the internal rotation in 2,2'-bifuryl, the use of *ab initio* molecular wave functions seems to be necessary. Several well known semiempirical methods give incorrect answers. We have computed the internal rotation potential of this compound by means of the CNDO/2 and PCILO methods: the *ortho*-barrier is of the right magnitude, 5.1 and 5.0 kcal mol^{-1}, but the CNDO *cis-* and *trans*-minima are equivalent in energy and the *cis*-rotamer is preferred by 0.4 kcal mol^{-1} with respect to the *trans* in the PCILO approximation. Partial relaxation of the molecular geometry increases this deficiency of the PCILO method. Optimization for both the *cis-* and *trans*-forms of the inter-ring C–C bond length and C–C–C bond angle stabilizes the *cis*-conformer by 0.9 kcal mol^{-1}. Semiempirical EHT calculations give even larger errors.

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