Nematic Phase Nuclear Magnetic Resonance Investigations of Rotational Isomerism. Part II.† Evidence for the *SO-cis*-Conformation in Thiophen-2-carbaldehyde

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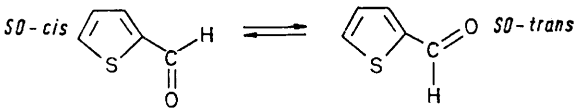
The 100 MHz ^{1}H n.m.r. spectrum of thiophen-2-carbaldehyde partially oriented in the nematic phase of a liquid crystalline solvent has been obtained and interpreted. It has been shown that only the *SO-cis*-conformer is present whereas the *SO-trans*-form, an equilibrium between the two rotamers, and free rotation of the formyl group can be unambiguously excluded. The *SO-cis*-conformation has been found to be planar or very nearly so and the orientational parameters of the molecule with respect to the magnetic field have been determined. Self consistent molecular orbital calculations (CNDO/2) indicate that the *SO-cis*-conformation is more stable by 2 kcal mol^{-1} than the *SO-trans*, in agreement with the experimental findings. The differences in the conformational behaviour of furan- and thiophen-2-carbaldehyde are discussed in terms of different electronic distribution.

WHETHER thiophen-2-carbaldehyde exists as a mixture of the *SO-cis*- (I) and *SO-trans*- (II) conformers in rapid equilibrium or as a single rotational isomer is a problem which has been long investigated but not yet unambiguously settled. Whereas substituted furan and pyrrole derivatives do show rotational isomerism (in the n.m.r. time scale) at low temperatures,[1-4] this is not the case for thiophen-2-carbaldehyde[3] or other thiophen derivatives. This could be due either to a fast rotation averaging the signals of the two species or to the existence of a single isomer. Since the barrier to the rotation[5] is expected to be larger than the value required for an averaging process to occur,[3] the second alternative seems more likely. Indirect support for this hypothesis also came from a number of investigations which indicate *SO-cis* as the only rotational isomer.[6-14] Recently however both isomers were detected in the radical anion[15] and this might be evidence for the existence of both species in the neutral molecule also. Some thiophen derivatives actually shows analogous conformational preferences in both cases.[14,16,17]



(I) (II)

A method which would offer, in principle, a conclusive answer on the conformation of thiophen-2-carbaldehyde in solution is n.m.r. spectroscopy in the nematic phase of a liquid crystalline solvent. As this technique allows an accurate determination of interproton distances[18] it is possible to decide whether a single isomer or a more complex system has to be considered. In the first case an unambiguous assignment of the conformation can be obtained whereas in the second an approximate determination of the ratios and structures of isomers can still be achieved given a number of assumptions.[14,17,19,20]

RESULTS AND DISCUSSION

The 100 MHz of thiophen-2-carbaldehyde obtained at room temperature as a solute in a nematic solvent (Figure) has been interpreted in terms of four chemical shifts and six D_{ij} dipolar couplings by using, as customary, the J_{HH} values reported for an isotropic solution.[21]

In the basic equation linking the experimental D_{ij}

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† Part I, ref. 19.

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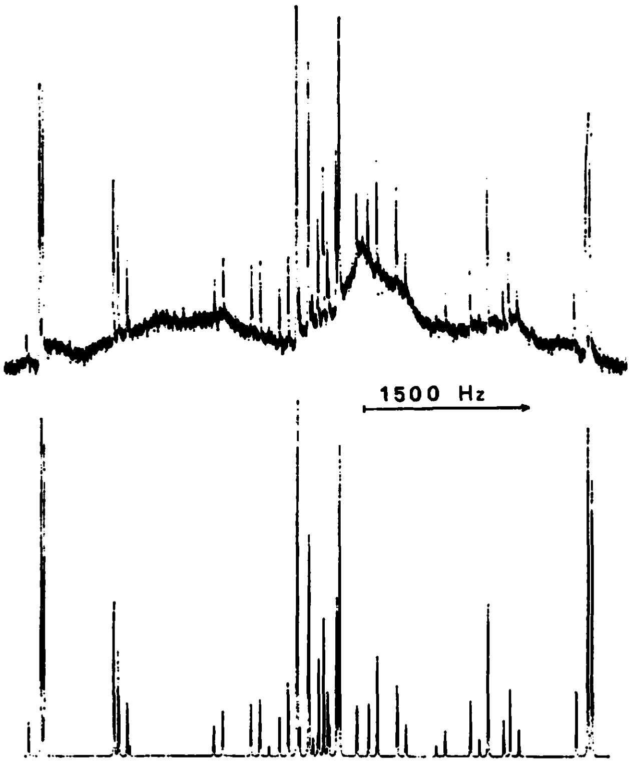


Experimental and computed 100 MHz ^{1}H n.m.r. spectrum of thiophen-2-carbaldehyde partially oriented in a nematic solvent

values to the proton co-ordinates[22] three motional constants have to be used as the molecule possesses only a plane of symmetry (C_{1h} point group). The geometry of thiophen is known from a microwave investigation[23] and was used here to determine the co-ordinates of the hydrogen atoms in positions 3—5 with the assumption that their values are not significantly affected by the presence of the formyl group. The C(2)–CHO bond length (1·45 Å), the formyl CH bond (1·11 Å) and the $\widehat{\text{C(2)–CO–H}}$ angle (117°) were taken from the geometry of appropriate derivatives.[11,24] As far as the $\text{C(3)–}\widehat{\text{C(2)}}\text{–CHO}$ angle is concerned there are only indications[13,25] that its value lies within 125—134°; therefore we considered this angle as the fourth unknown in addition to the three motional constants. Since six D_{ij} couplings are available the problem is overdetermined, so that if the experimental D_{ij} values are matched assuming either the *SO-cis*- or the *SO-trans*-conformation we can assign without ambiguity the structure of the rotamer. On the other hand if neither of the structures reproduces the experimental data an equilibrium may exist between the two conformational isomers, as observed in the case of furan-2-carbaldehyde.[19] From Table 1 it is evident that the *SO-cis*-conformer accounts satisfactorily for the experimental data thus allowing us to exclude either a fast *cis–trans*-equilibrium or a single isomer having the *SO-trans*-structure. The latter assumption in fact leads to a r.m.s. deviation larger by two orders of magnitude than that of the *SO-cis*-conformation. The $\text{C(3)–}\widehat{\text{C(2)}}\text{–CHO}$ angle was 126° using the previously mentioned assumptions, well within the range typical for 2-substituted five-membered rings. The final proton co-ordinates are in Table 2.

TABLE 1

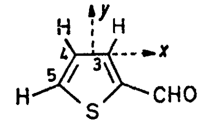
Experimental and computed parameters (Hz) of the nematic phase 100 MHz spectrum of thiophen-2-carbaldehyde

The J_{HH} couplings ($J_{\text{CHO-H(3)}}$ 0, $J_{\text{CHO-H(4)}}$ 0·1, $J_{\text{CHO-H(5)}}$ 1·2, $J_{\text{H(3)-H(4)}}$ 3·85, $J_{\text{H(3)-H(5)}}$ 1·25, and $J_{\text{H(4)-H(5)}}$ 4·85 Hz) were taken from ref. 21. The chemical shifts (ν_{CHO} −238 ± 3, $\nu_{\text{H(3)}}$ 32 ± 3, $\nu_{\text{H(4)}}$ −33 ± 3) were determined relative to $\nu_{\text{H(5)}} = 0$

		Computed		
	Experimental	*SO-cis*	*SO-trans*	Free rotation
$D_{\text{CHO-H(3)}}$	−2371 ± 5	−2370·7	−1988·8	−2149·5
$D_{\text{CHO-H(4)}}$	−340 ± 4	−344·0	−763·9	−539·2
$D_{\text{CHO-H(5)}}$	−130 ± 7	−127·6	−465·6	−153·7
$D_{\text{H(3)-H(4)}}$	−1653 ± 4	—1653·2	−1670·6	−1702·2
$D_{\text{H(3)-H(5)}}$	−9 ± 2	−9·8	+526·1	+544·4
$D_{\text{H(4)-H(5)}}$	+364 ± 4	+364·0	+232·7	+299·2
R.m.s. deviation		2	352	259
$c_{3z^2-r^2}$		−0·335	−0·828	−0·606
$c_{x^2-y^2}$		0·133	−0·148	−0·014
c_{xy}		−0·249	−0·952	−0·628

TABLE 2

Co-ordinates of the hydrogen atoms (Å) for the *SO-cis*- (I) and *SO-trans*- (II) conformations of thiophen-2-carbaldehyde



SO-cis (I)			*SO-trans* (II)	
x	y		x	y
$3{\cdot}36_4$	$-0{\cdot}76_5$	H (formyl)	$2{\cdot}90_2$	$-\ 2{\cdot}68_7$
$1{\cdot}31_9$	$0{\cdot}89_2$	H(3)	$1{\cdot}31_9$	$0{\cdot}89_2$
$-1{\cdot}31_9$	$0{\cdot}89_2$	H(4)	$-1{\cdot}31_9$	$0{\cdot}89_2$
$-2{\cdot}25_9$	$-15{\cdot}6_7$	H(5)	$-2{\cdot}25_9$	$-1{\cdot}56_7$

We also checked whether the liquid crystal n.m.r. spectra, unlike those in isotropic solvents, were able to rule out free rotation of the formyl group. Such an occurrence is unlikely as the energy barrier should be[5] at least 10 kcal mol^{-1} and the deviation between experimental and calculated couplings becomes extremely large (259 Hz) when the free rotation model is assumed.

A planar structure for thiophen-2-carbaldehyde accounts for the experimental data: thus an attempt has been made to determine the sensitivity of the

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method to deviations from planarity,[26] with the reasonable assumption that the only geometrical variable is the out-of-plane angle. To study out-of-plane conformations five motional constants are, in principle, required as there is no element of symmetry. On the other hand it is likely that oscillations of the CHO plane between two equivalent forms above and below the thiophen ring will occur faster than the reorientation of the molecule in the liquid crystal. Within the framework of this second hypothesis the original plane of symmetry is not on the average destroyed[27] and three motional constants will still describe the orientation.

In the first case (five c values) the deviation around planarity is rather large ($\pm 20°$) but when the sounder hypothesis of three c values is employed the error is reduced to $<10°$.

The orientational parameters (Table 1) indicate that the molecule has its plane of symmetry mainly oriented along the applied magnetic field (the angle between the z-axis and the direction of B_0 being 61°) and owing to the presence of the formyl group the x-axis of the molecule is oriented in the direction of B_0 much more than the y-axis. This reverses the situation observed in the unsubstituted thiophen[28] where the ratio $S_{xx} : S_{yy}$ is smaller than unity (0·415) while now it is larger (5·402). The direction of the largest molecular dimension in the xy-plane also orients preferentially along the magnetic field vector ($c_{xy} = -0{\cdot}249$) in agreement with the fact that molecular shape is one of the main factors determining the orientation in a nematic medium.*

An attempt has been made to explain the reasons for the different behaviour of the conformation of thiophen-2-carbaldehyde than that of the analogous furan-2-carbaldehyde. It has been suggested[6] that the presence of *OO-trans*-rotamer in the latter molecule is due to an electrostatic repulsion between the two oxygen atoms which would reduce the stability of the *OO-cis*-conformation and allow the existence of the more sterically hindered *OO-trans*-structure. On the other hand attractive forces between a supposed positive sulphur and a negative carbonyl oxygen atom would be responsible for the absence of the *SO-trans*-isomer in thiophen-2-carbaldehyde.[6] Theoretical calculations (CNDO and INDO) gave quantitative support[12] to this hypothesis in the case of the furan derivative. Thus we carried out the same kind of study on thiophen-2-carbaldehyde.

The geometry of the thiophen ring as well as the bond lengths involved were kept unchanged whereas the total energy was approximately minimized with respect to $\mathrm{C(3)}\text{–}\widehat{\mathrm{C(2)}}\text{–}\mathrm{CHO}$ and $\mathrm{C(2)}\text{–}\widehat{\mathrm{CH}}\text{–}\mathrm{O}$ angles. The first turned out to be 123°, in reasonable agreement with the experimental value of 126° while the second, which was not needed in the nematic phase investigation, was found to be 129°. The CNDO/2 calculations indicated the *SO-cis*-conformation to be more stable than the *SO-trans* by $2{\cdot}1_5$ kcal mol^{-1}. Accordingly the amount of the latter is expected to be less than 3% in agreement with the experimental observation of only the *SO-cis*-conformation. The computed dipole moment for the latter conformer ($3{\cdot}2_1$ D) also matches the experimental value (3·45 D)[9] thus allowing us to regard with some degree of confidence the charge distribution calculated by the CNDO/2 method. In the *SO-cis*-isomer the charge density on sulphur was negligible ($-0{\cdot}02$) with respect to that of the carbonyl oxygen atom ($-0{\cdot}24$) and we conclude that the suggested[6] electrostatic interaction between sulphur and oxygen should not be present: it is not, in any case, required to explain the greater stability of the *SO-cis*-conformer. The above hypothesis should thus be modified to state that the absence of electrostatic repulsion is sufficient to prevent the existence of the *SO-trans*-conformation in thiophen-2-carbaldehyde. However, it should be realized that the good agreement between calculation and experiment might be in part accidental as the dispersion forces operating in the liquid crystal were not taken into account in the theoretical approach.

EXPERIMENTAL

The 100 MHz spectrum (JEOL PS 100 spectrometer) of thiophen-2-carbaldehyde was recorded in a 4-n-butyl-4′-methoxyazoxybenzene (Merck Licristal Phase IV) solution in the externally locked field sweep mode. The experimental frequencies and intensities were interpreted by means of the LAOCOON program[29] modified in order to include the anisotropic part of the Hamiltonian.[30] All the observed 42 lines were employed in the iterative process and their frequencies were matched with a r.m.s. deviation of 6 Hz. The simulated patterns were obtained by means of a plotter subroutine using a Lorentzian line shape with an half height width of 4·0 Hz. The CNDO/2 program is that of Pople and Beveridge[31] run on a CDC 6600 computer.

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* The relationship between S and c values is given in ref. 22.

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