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Determination of the r_α-Structure and of Bond Contributions to the Degree of Order of Thiophene by NMR of Partially Oriented Molecules Considering Correlated Deformation

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The solvent effects on the structure of partially oriented thiophene are studied in 7 different liquid crystal solvents. In an analysis of the combined data considering correlated molecular deformation, interaction parameters are determined and a unique solvent independent structure is found which agrees well with MW-results. The interaction parameters allow an assignment of the contributions to the degree of order to parts of the molecule, i.e. to the C—H bonds and to the carbon-sulfur ring.

Keywords: NMR, molecular structure, orienting forces, molecular deformation

I. INTRODUCTION

The structure of thiophene has been previously determined by NMR of partially oriented molecules in several different liquid crystal solvents as well as in solvent mixtures.[1,2] Unusually large solvent effects of the order of 7% in distance ratios and 2.1° in angles were observed. Also the use of a so called "ideal solvent" was suggested in order to minimize solvent effects.[2] In the present publication we have used different solvents and have determined the structures corrected for harmonic vibrations. Again very large solvent effects are detected. In a second approach the theory of correlated molecular deformation[3]

TABLE I

Liquid crystal solvents and spectral parameters used for the solute thiophene

Experiment number	Solvent	Number of Scans	Spectral Width (Hz)	Pulse Width (μs)	Temperature (K)	Wt-% of Thiophene
1	ZLI 1695	6,000	6024	3.5	302	1.7
2	ZLI 1167	3,000	6024	3.5	304	11.3
3	ZLI 1083	6,000	8024	3.5	302	3.8
4	HAB nematic	8,000	6024	3.5	302	5.3
5	HAB smectic	12,000	6024	3.5	295	5.4
6	Phase 4	500	3500	3.5	302	8.0
7	EBBA	12,000	6097	3.5	290	2.8

is used to correct the data and to determine a unique solvent independent r_α-structure. This theory assumes, that the liquid crystal interacts with the solute by applying torques to the bonds which orient the molecule but simultaneously distort it. The torques are characterized by the anisotropy ΔA and the asymmetry η of the mean field interaction tensors. These parameters are determined iteratively together with the solute structure. They allow to interpret the molecular degrees of order in terms of contributions of parts of the molecule.

2. EXPERIMENTAL

Thiophene was dissolved in seven different liquid crystals as summarized in Table I. The ^{1}H-spectra with ^{13}C-satellites were recorded on a Bruker WH90DS FT-spectrometer and analyzed with the program LEQUOR.[4] In the analysis the indirect couplings were used from the literature.[5] The numbering of nuclei is shown on Figure 1. The resulting direct couplings are presented in Table II.

In a first analysis the data of the individual solvents were corrected for harmonic vibration on the basis of a force field from the literature[6] and the structures determined by the program SHAPE.[7] The resulting data are shown in Table III.

In a second run the direct couplings of all the solvents were corrected also for the correlated deformation and fitted in a combined analysis. The experimental errors of direct couplings were increased by 0.2 Hz in order to consider the approximations introduced by the theory of correlated deformation. The final r_α-structure is presented and compared with MW-results in Table IV.

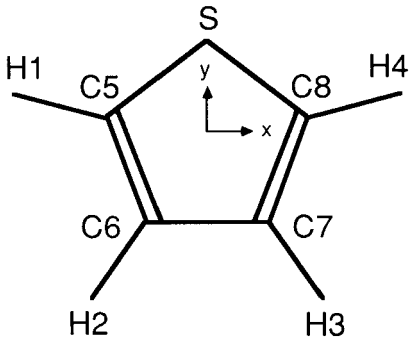

FIGURE 1 Numbering of the nuclei of thiophene and definition of the coordinate axes.

TABLE II

Experimental direct coupling constants (Hz) for thiophene in various liquid crystal solvents

	Experiment number						
	1	2	3	4	5	6	7
D(12)	334.67(8)	193.74(3)	−502.21(4)	−412.69(3)	−454.32(3)	−301.35(2)	−448.24(3)
D(13)	74.16(3)	42.75(3)	−115.32(5)	−71.77(3)	−86.56(4)	−36.35(2)	−25.98(4)
D(14)	64.70(5)	37.36(5)	−102.74(7)	−53.01(6)	−68.91(6)	−16.40(7)	14.04(23)
D(15)	1141.46(6)	656.96(14)	−1801.64(13)	−955.85(9)	−1223.97(12)	−328.46(33)	133.87(29)
D(16)	141.75(6)	81.90(14)	−218.04(14)	−149.09(9)	−173.98(11)	−87.64(13)	−94.43(24)
D(17)	40.15(7)	23.27(17)	−62.83(15)	−36.87(12)	−45.44(15)	−16.24(37)	−5.5(15)
D(18)	34.77(6)	20.03(22)	−55.51(18)	−28.95(14)	−37.25(18)	−9.08(49)	5.9(9)
D(23)	324.90(5)	187.71(5)	−517.46(7)	−271.68(6)	−351.79(6)	−86.46(7)	67.29(24)
D(25)	152.48(6)	88.12(16)	−226.54(15)	−194.09(9)	−210.65(13)	−148.37(30)	−234.82(25)
D(26)	1153.13(5)	664.55(12)	−1747.73(14)	−1291.07(8)	−1464.12(11)	−848.38(12)	−1116.26(31)
D(27)	138.09(8)	79.64(24)	−217.04(17)	−124.53(13)	−155.07(17)	−52.50(38)	−11.1(12)
D(28)	41.10(8)	23.70(20)	−63.53(19)	−41.60(14)	−49.31(18)	−22.94(46)	−20.8(9)

TABLE III

Solvent effects on the structure of thiophene dissolved in various liquid crystal solvents. Distance ratios and angles (in degrees)

	Experiment number						
	1	2	3	4	5	6	7
$r(12)/r(23)$	1.0521(30)	1.0367(62)	1.0686(25)	0.9897(17)	0.9848(22)	0.9944(11)	0.9958(4)
$r(14)/r(23)$	1.7139(6)	1.7151(8)	1.7165(3)	1.7269(6)	1.7244(4)	1.7470(20)	1.7507(10)
$r(15)/r(23)$	0.4070(1)	0.4060(2)	0.4073(1)	0.4081(1)	0.4073(1)	0.4124(1)	0.3836(26)
$r(26)/r(23)$	0.4250(10)	0.4199(21)	0.4302(8)	0.4075(6)	0.4053(8)	0.4140(6)	0.4237(5)
$r(56)/r(23)$	0.5464(15)	0.5393(33)	0.5552(13)	0.5165(10)	0.5142(12)	0.5169(7)	0.5174(13)
$r(67)/r(23)$	0.5409(4)	0.5420(10)	0.5423(4)	0.5411(5)	0.5412(4)	0.5445(7)	0.5534(6)
$<(156)$	128.89(5)	128.77(14)	128.77(16)	127.92(6)	128.01(6)	126.90(5)	130.88(37)
$<(267)$	122.70(8)	123.05(18)	122.14(6)	124.27(6)	124.47(7)	123.38(10)	121.81(8)
$<(567)$	111.31(4)	111.61(11)	111.02(4)	112.68(3)	112.73(4)	112.90(7)	116.12(27)

TABLE IV

Resulting structure of thiophene from the combined analysis of the seven experiments corrected for correlated deformation compared with MW-results (See Ref. 9). Distance ratios and angles (in degrees).

	$r(12)/r(23)$	$r(14)/r(23)$	$r(15)/r(23)$	$r(26)/r(23)$	$r(56)/r(23)$	$r(67)/r(23)$
NMR	0.9964(9)	1.7236(11)	0.4087(6)	0.4084(4)	0.5197(5)	0.5404(3)
MW	1.000(5)	1.715(7)	0.408(1)	0.409(1)	0.519(2)	0.539(3)
	$<(156)$	$<(267)$	$<(567)$			
NMR	128.07(8)	124.24(4)	112.41(5)			
MW	128.68(81)	124.28(7)	112.45(18)			

Table V summarizes the interaction parameters for the C—H bonds and the ring part of the molecule as well as the degrees of order (see the discussion).

3. DISCUSSION

STRUCTURE

The results shown in Table III display very pronounced solvent effects with a maximum of 7% in $r(56)/r(23)$. The effects are particularly large in the liquid crystals ZLI 1695, 1167 and 1083 as well as in EBBA. After the correction for the correlated deformation the solvent-effects disappear. Consequently all the solvent effects must be caused by the neglect of correlated deformation. The question, why this neglect leads to particularly large effects in some solvents, remains to be answered. A detailed study revealed, that in EBBA by coincidence the direction of the C—H bond (15) has a very small degree of order, so that the correlation contribution is 50% of the equilibrium direct coupling. The extreme deviations in the ZLI solvents have a more complex origin. They have to do with the particular mathematical interdependence of direct coupling ratios and distance ratios in systems of four spins with C_{2v} symmetry.[8] For such systems the following relation is valid:

$$(D_{12}/D_{23})(r_{12}/r_{23})^5 - (D_{13}/D_{23})\,[(D_{23}/D_{14})^{1/3} + (r_{12}/r_{23})^2]^{5/2} + (D_{23}/D_{14})^{1/3} = 0 \quad \text{i.e.} \quad (1)$$

$$\alpha \cdot x^5 - \beta\,[\gamma + x^2]^{5/2} + \gamma = 0 \quad (2)$$

TABLE V

Interaction and order parameters of thiophene (in 10^{-22}J) derived from the combined analysis of the seven experiments. Direction of the virtual bond axis representing the ring: C(6)–C(7)

	Experiment number						
	1	2	3	4	5	6	7
ΔA(C8H4)	12.3(17)	6.5(10)	8.7(14)	0.5(8)	1.6(10)	−2.8(4)	−6.2(2)
ΔA(C7H3)	5.0(9)	2.4(6)	3.3(7)	−2.2(5)	−1.8(6)	−3.7(3)	−6.0(5)
ΔA(ring)	5.1(30)	2.3(18)	4.3(24)	9.3(14)	10.1(17)	8.3(6)	9.6(4)
η(ring)	13.2(80)	15(12)	11.2(63)	4.7(8)	4.8(9)	4.0(3)	4.6(2)
S_{yy}	0.10345	0.05980	0.07685	0.06636	0.07188	0.05094	0.08023
S_{xx}	0.10087	0.05821	0.08023	0.04207	0.05443	0.01343	−0.01024

For a fixed molecular geometry (x and γ constant), by choosing different liquid crystals, we measure D-ratios (α,β) which define a straight line in the α,β-plane. If we vary the geometry we find different straight lines which all have a common envelope given by:

$$\beta = (\gamma + \alpha^{-2/3})^{-3/2} \tag{3}$$

For points on the envelope the following relations are valid:

$$\alpha = x^{-3} \text{ and } \beta = (\gamma + x^2)^{-3/2} \tag{4}$$

corresponding to $S_{xx} = S_{yy}$.

If we have used a liquid crystal solvent which by coincidence orients the molecule with $S_x \sim S_y$, the structure becomes particularly sensitive to small changes in the direct couplings. Generally the tangent of the envelope changes its direction most drastically if the point (α,β) moves out of the envelope, whereas the same movements i.e. variation in the D-ratio at a point far from the envelope leaves the tangent direction, i.e. the distance ratio practically invariant.

Also in the ZLI liquid crystals the solvent effects are due to the neglect of correlated molecular distortion (maximum 3% of the direct couplings) but here, the amplification of the error (maximum 7% in a distance ratio) is not due to the small degree of order but to the similarity of the degrees of order independent of their size.

The final r_α-structure shown in Table IV agrees well with MW-results. Its precision is approximately 5 times higher than the one of the MW-data.

Interaction, Degree of order

The carbon-proton structure of thiophene is defined by 6 coordinates with respect to a fixed basis ($r(23)$). The degree of order depends upon the interaction of 5 different bond-types with the liquid crystal mean field. In principle we have 10 interaction parameters for each of the 7 liquid crystals. Therefore in the iterative fit there are 76 unknown parameters to be determined from the 84 measured direct couplings. With the possible interdependence of parameters the system is practically underdetermined. In particular, if certain parts or bonds of the molecule are only very slightly deformed, they contribute exclusively to the degree of order, i.e. there are only two measured parameters (degrees of order) for the determination of their interaction with the solvent. In thiophene it can be shown, that the carbon-sulfur ring part is in fact much more rigid than the C—H bonds. An

analysis without ring-deformation gives virtually identical results. Consequently the interaction parameters of individual C—C and C—S bonds cannot be measured. The ring must be characterized by a virtual bond parallel to the bond C6—C7 with the two parameters $\Delta A = A_{xx} - (1/2)(A_{yy} + A_{zz})$ and $\eta = (A_{yy} - A_{zz})/A_{xx}$. On the contrary the two ΔA's for the different C—H bonds are easily obtained.

The measured interaction parameters shown in Table V for the first time allow to assign order contributions to the individual parts of the molecule.

For a planar molecule the segment n makes the following contributions to the molecular interaction tensor, i.e. the orientation[3]:

$$A^n_{xx} = \Delta A_n [(2/3) - (1 - \eta_n/3) \sin^2\theta_n]$$

$$A^n_{yy} = \Delta A_n [(2/3) - (1 - \eta_n/3) \cos^2\theta_n]$$

$$A^n_{zz} = -(1/3)\Delta A_n (1 + \eta_n)$$

$$A^n_{xy} = (1/2)\Delta A_n (1 - \eta_n/3) \sin 2\theta_n$$

$$A^n_{xz} = A^n_{yz} = 0$$

Here the z-axis is perpendicular to the plane and θ_n is the angle between the bond axis and the molecular x-axis.

If we consider the solvents ZLI 1695, HAB (nematic) and EBBA; we see, that the C—H contributions to the degree of order of the C_2-axis are either small (HAB) or compensate each other so that the decrease from ZLI 1695 to EBBA is caused mainly by the ring contribution.

In the perpendicular direction we have different situations in all the three solvents: In ZLI 1695 the ring contribution is small so that the C—H contribution dominates. In HAB the ring contribution dominates because the C—H contributions are small and in EBBA the interactions are similar but of opposite sign so that we observe a change of sign in the degree of order.

CONCLUSIONS

The fact that the very large solvent effects on the structure of thiophene disappear, if the data are corrected for the correlated molecular deformation, again confirms the merit and necessity of this correction.

The study has shown, that in larger spin systems parts of the molecule (e.g. carbon-carbon or carbon-sulfur rings) may be practically undistorted. For these parts the determination of individual bond interaction parameters is not possible, but a virtual bond representing the sums of the interactions must be introduced.

The discussion of the orientation of thiophene in terms of the interaction parameters demonstrates how complicated and difficult to predict the build up of order parameters from contributions of parts of the molecules must be in general.

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