Conformation Studies by Nuclear Magnetic Resonance Spectroscopy in Nematic Phases: 3-Phenyl-1,2,5-oxa-, -thia-, and -selena-diazole

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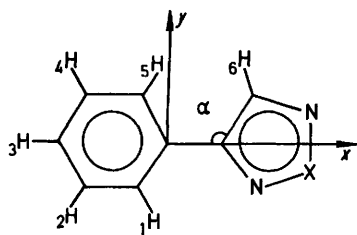
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The 100 MHz n.m.r. spectra of 3-phenyl-1,2,5-oxa- (1), -thia- (2), and -selena-diazole (3) partially oriented in the nematic phase have been obtained and analysed. The spectral analysis affords examples of conformational situation in molecules containing two aromatic rings of six and five members respectively. A preferred twisted conformation around the bond between the two rings has been found, the twisting angle θ ranging from 18 to 21°. The conformation is little influenced by the heteroatom in position 2 and by the solvent. The results are discussed in connection with theoretical EHT calculations.

N.M.R. spectroscopy of molecules partially oriented in nematic solvents has been successfully used to study internal potential and preferred conformations of medium sized molecules.[1] The case of internal rotation in molecules containing two aromatic rings connected by a single bond, like 2,2'-bithienyl,[2] 4,4'-dichlorobiphenyl,[3] 4,4'-bipyridyl [4] and similar molecules, has been discussed by several authors. The nematic phase findings emphasize twisted conformations for some such molecules

X = O, S, Se

FIGURE 1 Structure of molecules (1)—(3) and choice of the Cartesian co-ordinate system (non-systematic numbering used for convenience)

in good agreement with the gas phase data from measurements of microwave and/or electron diffraction spectra, while the same compounds in the solid state are planar, from X-ray diffraction investigations, owing to the flattening effect of the crystalline field.

The present work reports an n.m.r. study of the 3-

phenyl-1,2,5-oxa- (1), -thia- (2), and -selena-diazole (3) (Figure 1) oriented in the nematic phase in order to gain information about their conformational situation in connection with the nature of the heteroatom and with the degree of rigidity of the heterocyclic system.

The effect of the solvent and of the change in molecular shape upon partial orientation of the solute has been tested by studying compound (2) in two different nematic phases at various concentrations and by comparing the n.m.r. data of compounds (2) and (3) obtained under the same experimental conditions.

EXPERIMENTAL

Compounds (1),[5] (2),[6] and (3) [7] were prepared and carefully purified according to literature methods. 100 MHz Spectra were recorded on a JEOL PS 100 spectrometer, in the frequency sweep mode, using a thin capillary tube filled with tetramethylsilane in order to provide the n.m.r. lock. Nematic Phase IV (Merck) was used as nematogen for the three compounds. The spectral parameters are summarized in Table 1. Compound (2) was studied in the Nematic Phase IV at two different concentrations [Table 1, column 2(A) and 2(B)], one of which [2(B)] carefully reproduces the experimental conditions for taking the spectrum of compound (3). Compound (2) was also studied using as nematic solvent p-propoxy-p'-heptyldiphenylacetylene (S.E.A.C.) [Table 1, column 2(C)]. All the spectra were analysed iteratively using the LAOCOONOR program. Indirect spin couplings were taken from the literature;[8] their inclusion in the final iteration afforded vanishingly small modifications in the direct parameters. In Figure 2 the experimental [Table 1, column 2(B)] and simulated spectra of compound (2) are displayed.

[1] J. W. Emsley and J. Lindon, ' N.M.R. Spectroscopy Using Liquid Crystal Solvents,' Pergamon Press, Oxford, 1975.

[2] P. Bucci, M. Longeri, C. A. Veracini, and L. Lunazzi, *J. Amer. Chem. Soc.*, 1975, **96**, 1413.

[3] W. Niederberger, P. Diehl, and L. Lunazzi, *Mol. Phys.*, 1973, **26**, 571.

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

[5] R. A. Olofson and J. S. Michelman, *J. Org. Chem.*, 1965, **30**, 1854.

[6] V. Bertini and A. De Munno, *Gazzetta*, 1967, **97**, 1614.

[7] V. Bertini, A. De Munno, and G. Denti, *Chimica e Industria*, 1972, **54**, 571.

[8] W. Brügel, ' Nuclear Magnetic Resonance Spectra and Chemical Structure,' Steinkopf Verlag, 1967.

RESULTS AND DISCUSSION

Spectral analysis gave nine dipolar couplings (D_{ij}). Assuming a rigid rotor model,[1] six of them can be used to define the molecular orientation and the geometry of the phenyl ring, and the remaining three can then be used to test models for internal rotation. Excluding free

For the rigid part of the molecules the program SHAPE was used, assuming an H(2)–H(3) distance of 2.481 Å. The obtained motional parameters and interproton distance ratios are reported in Table 2. The attempt to use three motional parameters, including a c_{xy} motional constant, leads in every case to a vanishingly small

TABLE 1

Spectral parameters used in the simulation of the 100 MHz spectra of compounds (1)—(3) partially oriented in nematic phase

Parameter	(1)	[2(A)]	[2(B)]	[2(C)]	(3)
			Value (Hz)		
D_{13}	−1 878.3 ± 0.4	−1 710.4 ± 0.5	−1 370.8 ± 0.7	−1 735.0 ± 0.6	−1 380.6 ± 0.9
D_{13}	−239.7 ± 0.4	−219.3 ± 0.4	−175.1 ± 0.9	−222.2 ± 0.7	−178.3 ± 0.8
D_{14}	−6.9 ± 0.3	−5.2 ± 0.4	−5.6 ± 0.5	−5.15 ± 0.5	−4.4 ± 0.7
D_{15}	107.6 ± 0.9	95.7 ± 0.8	76.7 ± 1.0	97.38 ± 0.8	78.3 ± 2.0
D_{16}	−863.6 ± 1.0	−904.6 ± 1.0	−729.4 ± 1.3	−922.9 ± 1.0	−751.2 ± 1.8
D_{23}	−52.0 ± 0.7	−48.9 ± 0.6	−46.6 ± 1.0	−51.3 ± 0.7	−30.1 ± 1.0
D_{24}	102.7 ± 1.0	94.1 ± 0.9	74.2 ± 0.9	95.7 ± 1.0	74.2 ± 1.2
D_{26}	−143.1 ± 0.9	−140.8 ± 1.1	−110.5 ± 1.2	−142.4 ± 1.2	−115.4 ± 1.9
D_{36}	−93.8 ± 0.5	−87.9 ± 0.6	−76.1 ± 1.0	−87.8 ± 0.8	−78.4 ± 1.0
$\nu_3 - \nu_1$	−16.5 ± 1.0	−4.7 ± 1.0	8.2 ± 2.0	−3.2 ± 1.1	10.5 ± 2.0
$\nu_3 - \nu_2$	−44.3 ± 1.2	−42.6 ± 0.9	−26.7 ± 1.5	−41.5 ± 0.9	−37.3 ± 2.2
$\nu_3 - \nu_6$	81.0 ± 1.0	101.7 ± 1.2	107.9 ± 1.8	104.2 ± 1.4	169.2 ± 3.0

Indirect couplings constants used [8] are: J_{12} 7.8, J_{13} 1.3, J_{14} 0.6, J_{15} 1.8, J_{23} 7.8, J_{24} 1.3 Hz.

TABLE 2

N.m.r. ratios of interproton distances and motional parameters from the spectra of samples

Samples	(1)	[2(A)]	[2(B)]	[2(C)]	(3)
r_{12}/r_{23}	0.987 ± 0.003	0.988 ± 0.002	0.988 ± 0.003	0.988 ± 0.003	0.985 ± 0.003
r_{13}/r_{23}	1.717 ± 0.003	1.72 ± 0.002	1.72 ± 0.004	1.72 ± 0.003	1.709 ± 0.004
r_{14}/r_{23}	1.986 ± 0.002	1.989 ± 0.002	1.986 ± 0.002	1.987 ± 0.002	1.984 ± 0.002
r_{15}/r_{23}	1.716 ± 0.004	1.721 ± 0.004	1.717 ± 0.005	1.719 ± 0.004	1.709 ± 0.005
r_{24}/r_{23}	1.730 ± 0.002	1.731 ± 0.002	1.729 ± 0.002	1.729 ± 0.002	1.736 ± 0.002
R.m.s. deviation	0.5	0.05	0.6	0.4	0.6
$c_{3z^2-r^2}$ *	−0.360 ± 0.001 5	−0.330 ± 0.001	−0.264 ± 0.001 6	−0.335 ± 0.001	−0.263 ± 0.002
$c_{x^2-y^2}$ *	0.381 ± 0.000 8	0.351 ± 0.000 7	0.279 ± 0.000 9	0.356 ± 0.000 8	0.281 ± 0.000 9

* r_{12} = 2.481 Å (assumed).

rotation, which has always turned out to be unlikely in molecules containing two aromatic rings,[2–4] and considering the molecular symmetry, two models corresponding
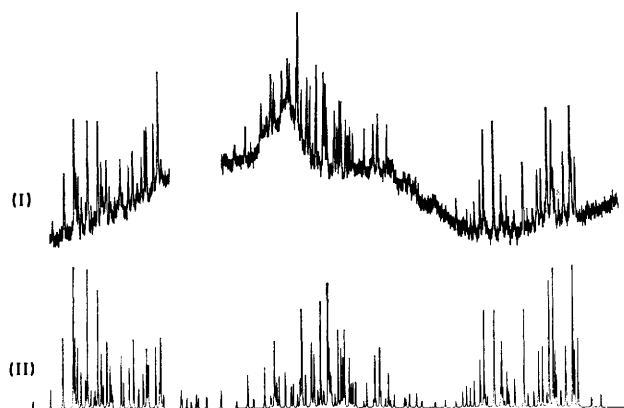

FIGURE 2   Observed (I) and calculated (II) ^{1}H n.m.r. spectra of 3-phenyl-1,2,5-thiadiazole [sample (2B)] partially oriented in Nematic Phase IV (Merck). Temperature 27°; operating frequency 100 MHz

to a planar conformation or to an out-of-plane (twisted) conformation were tested.

value of this parameter showing that an effective C_{2v} mean geometry is created by the internal motion as far as the phenyl ring protons are concerned.

Planar Conformation.—The model of an equilibrium of planar conformations was tested using the motional parameters derived from the analysis of the rigid part of the molecule. As three inter-ring dipolar couplings are available, it was possible to vary the x and y co-ordinates of the proton on the heterocyclic ring [H(6)] to obtain the best fit co-ordinates. However the root mean square (r.m.s.) deviation between the calculated and experimental dipolar couplings, in all the cases studied, did not drop below 5 or 6 Hz, making such solutions unsatisfactory. The best fit geometry, moreover, was quite distorted with respect to the position of H(6) as expected from X-ray and microwave data on similar molecules.[9,10] In the case of the rate of reorientation of the whole molecule being faster than the rate of internal rotation the testing of the planar model should allow for a non-zero value of c_{xy} motional constant as the couplings between phenyl ring and H(6) depends on c_{xy} in that case.[11] However we excluded this possibility on the base of EHT calculations (see below) indicating

[9] S. V. Dobyns and L. Pierce, *J. Amer. Chem. Soc.*, 1963, **85**, 3553.

[10] M. Mellini, Thesis, University of Pisa, Italy, 1974.
[11] K. G. Orrell and V. Sik, *J.C.S. Faraday II*, 1976, 941.

clearly an out-of-plane conformation with a very low barrier to internal motion ($\leqslant 1$ kcal mol^{-1}). It is well known, moreover, that EHT calculations tend to exaggerate the barrier to internal rotation in conjugate systems.

We can safely conclude, therefore, that the planar model is unable to describe the conformation of the title compounds in the nematic solution.

Non-planar Conformation.—To obtain at least a qualitative idea of the intramolecular potential energy
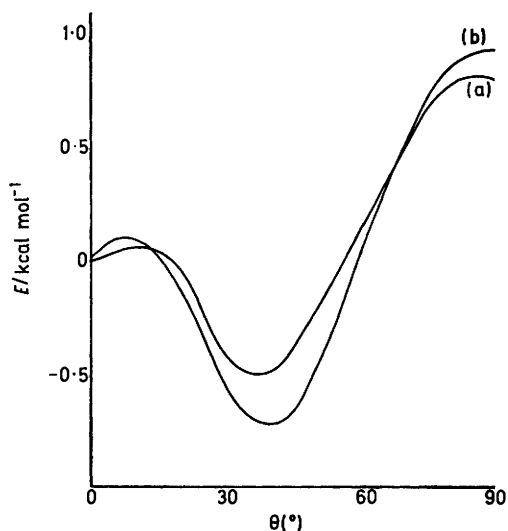

Figure 3 Potential energy for intramolecular rotation *versus* dihedral angle from iterative extended Hückel calculations: (a) 3-phenyl-1,2,5-oxadiazole; (b) 3-phenyl-1,2,5-thiadiazole

curve we carried our an iterative extended Hückel calculation for molecules (1) and (2). In the calculations the geometry of the phenyl ring was assumed to be undistorted while that of the heterocyclic ring was taken by combining the available microwave measurements [9] and X-ray data of 3,4-diphenyl-1,2,5-oxa- and -thiadiazole respectively.[10] The inter-ring distance and the angle α (see Figure 1) were varied to obtain an energy minimum. The energy calculations were made for every 10° twist angle θ except near the minima, where the interval of twist angle was reduced to 5°. In Figure 3 the molecular energy *versus* the twist angle is plotted having assumed as the zero point the planar position ($\theta = 0$). The intramolecular potential energy obtained by fitting the computed values of the potential energy by an analytical function of θ has form (1). In the case

$$V(\theta) = \frac{V_2}{2}(1 - \cos 2\theta) + \frac{V_4}{2}(1 - \cos 4\theta) + \frac{V_8}{2}(1 - \cos 8\theta) \quad (1)$$

under investigation, however, only three D_{ij} couplings are available, and it is not possible to extract from them all the Fourier components of $V(\theta)$, and the best fit co-ordinates of H(6). Therefore an approximate solution for a non-planar conformation was sought by reproducing

the D_{ij} couplings in terms of stable twisted conformers containing a dihedral angle θ between the phenyl and the heterocyclic rings in the molecule. The conformer approximation, used in some cases whenever a more rigorous averaging (*e.g.* with a suitable potential energy) is not allowed,[12] was found to give a good description of the conformational situation in similar molecules and only a very slight modification of twist angle was produced by the inclusion of vibrational averaging.[4] In our case four symmetry related positions are present in the range $0 \leqslant \theta \leqslant 2\pi$ which allowed us to obtain the x, y, and z co-ordinates of H(6) and then to obtain the twist angle θ.

It should be pointed out that, owing to the pronounced orientation of the examined molecules along the x axis, the coupling between H(1) and H(5) of the phenyl ring and H(6) of the diazole ring is very sensitive to θ. In Figure 3 we give as an example the r.m.s. deviation between D_{ij} as calculated on the basis of the best fit co-ordinates and the experimentally determined ones, as a function of θ, for compound (2). Similar results were obtained by calculating the D_{ij} couplings on the basis of a geometry assumed from other sources (X-ray and molecular weight data).[9,10] In Table 3 the best fit

TABLE 3

	(1)	[2(A)]	[2(B)]	[2(C)]	(3)
x	2.061	1.966	1.948	1.960	1.796
y	2.058	2.087	2.065	2.082	2.039
z	0.729	0.698	0.709	0.701	0.803
θ (°)	19.5	18.5	19	18.7	21.5
$\dfrac{c_{x^2-y^2}}{c_{3z^2-r^2}}$	-1.058	-1.063	-1.057	-1.062	-1.068

co-ordinates and twist angle, as well as the ratio $c_{x^2-y^2}/c_{3z^2-r^2}$, are displayed.
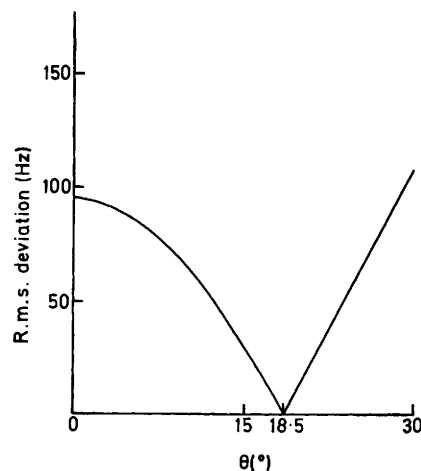

Figure 4 R.m.s. deviation, between experimental and calculated D_{ij} values, as a function of θ for case (2A)

From the results we can conclude that the studied molecules exist in an out-of-plane conformation. Moreover, even if vibrational averaging was not carried out, the results of Tables 2 and 3 can be compared because all

[12] S. A. Spearman and J. H. Goldstein, *J. Magnetic Resonance,* 1975, **20**, 75.

of them were treated at the same level of approximation. The value of the twist angle θ is almost unaffected by the solvent and slightly, but not insignificantly, influenced by the chalcogen atoms. The angle θ for the studied derivatives of selenium, sulphur, and oxygen varies over a range of few degrees, and assumes values not in agreement with a monotonic function of the atomic numbers. The thiadiazole derivative has the lower value of θ suggesting that in such compounds the conjugation between the phenyl and the heterocyclic rings is strongest. Several other series of methyl- or aryl-substituted 1,2,5-oxa-, -thia-, and -selena-diazole derivatives were found to show minimum m.p.s. or b.p.s. for the sulphur compound.[13]

Apart from the present data no other information on the molecular structures of the compounds (1)—(3) are available in the literature for useful comparison. The EHT semiempirical calculations strongly support the twisted structure of the molecules examined even if quantitative results cannot be obtained by this type of calculation.

As far as the motional behaviour is concerned we can see from Table 3 an essential similarity of orientation. The values of the ratio $c_{x^2-y^2}/c_{3z^2-r^2}$ of Table 3 differ only by a fraction of a percent showing that even if the orientation parameters depend on the gross feature of the molecular shape, they are insensitive to minor modifications.

[13] V. Bertini, *Gazzetta*, 1967, **97**, 1870.