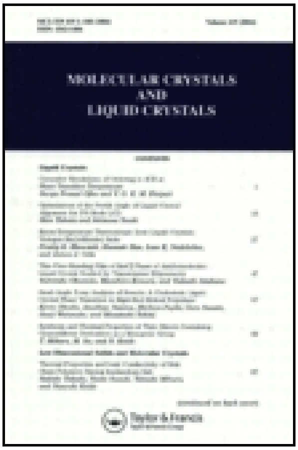

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Structure and Conformation of N, p-Chlorophenylmaleimide in a Nematic Solvent by Proton Magnetic Resonance

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Structure and Conformation of *N,p*-Chlorophenylmaleimide in a Nematic Solvent by Proton Magnetic Resonance

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PMR studies of *N,p*-chlorophenylmaleimide in a nematic solvent have been undertaken. The structural and the conformational informations are derived.

The distance-ratios of the phenyl protons show significant distortions from corresponding values in benzene. The data indicate that the molecule has a twisted conformation with C_2-symmetry and that an exchange between energetically equivalent conformations takes place. Assuming a rigid conformation the angle θ between phenyl and maleimide moieties is estimated to be 54.5°C.

The data can also be interpreted by an exchange between planar ($\theta = 0, 180$) and perpendicular ($\theta = \pm 90$) conformations. This possibility is discarded on the basis of theoretical considerations of the stability of conformations.

1 INTRODUCTION

NMR spectroscopic studies related to the structure of bicyclic compounds were first undertaken for "rigid" systems with C_{2v}-symmetry.[1,2] In these cases, two parameters are sufficient for defining the molecular order. Later on, the method was extended to several other bicyclic compounds including "non-rigid" ones like bithiophenes,[3–5], biphenyls,[6,7] bis-iso-oxazoles[8] and bipyrimidine.[9] However, in all the studies reported thus far, the "non-rigidity" arises from the motion of two identical moieties about the C—C bond. The interpretation of the spectrum of such a system is simpler than that of the one where two different types of moieties are present in the "non-rigid" system. The results for one such system, namely, *N*,*p*-chlorophenylmaleimide are reported in the present paper.

2 EXPERIMENTAL

A 10 mole percent solution of commercially available *N*,*p*-chlorophenylmaleimide was prepared in a 5 mm NMR sample tube in a mixture of 80% 4-ethoxybenzylidene-4-*n*-butylaniline (a) and 20% O-carbobutoxy-4-oxybenzoic acid ethoxyphenyl ester (b) and kept in the horizontal position for a

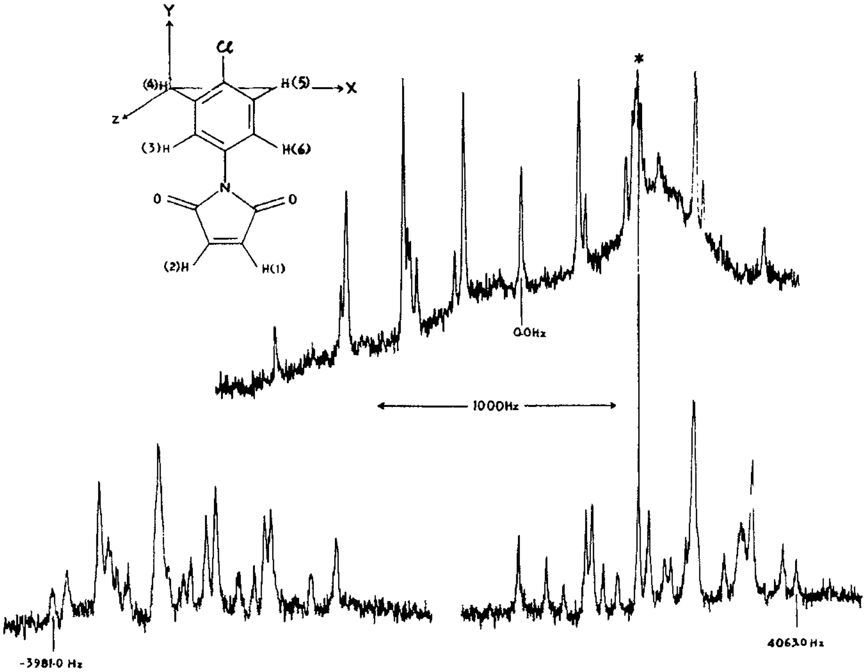

FIGURE 1 PMR spectrum of *N*,*p*-chlorophenylmaleimide dissolved in nematic phase of (a) + (b). Lower trace is due to the phenyl protons and the upper one arises from the protons of the maleimide ring.

Solute concentration:	10 mole %
Temperature:	30°C
Spectrometer frequency:	100 MHz

[(*) indicates the position of the "lock-signal."]

few days to achieve concentration uniformity. The spectrum recorded on a Varian XL-100 NMR spectrometer† at 30°C is shown in Figure 1. The sweep width and the sweep time used were 5000 Hz and 2500 s respectively. The most intense line in Figure 1 (marked *) provided the "lock-signal". The average linewidth was 12 Hz and the maximum error in the measurement of any line position was 4.0 Hz. The position of 70 lines could be measured experimentally.

3 SPECTRAL ANALYSIS

The spectrum was analyzed iteratively on a CDC-3600 computer using the LAOCOONOR program.[10] The definitions of the chemical shift ($\nu_i - \nu_j$) and the direct and the indirect coupling constant (D_{ij} and J_{ij} respectively) are the same as in the LAOCOONOR program. During the analysis, iterations were carried out only on the chemical shifts and the direct dipolar couplings; the indirect spin–spin couplings being kept fixed as given in Table I. All the 70 lines were assigned for spectral analysis. The r.m.s. error between the observed and the calculated line positions was 1.3 Hz with a maximum error in the position of any line being 2.9 Hz. The derived parameters are given in the table. Errors of the parameters in the table are those given by the LAOCOONOR program.

TABLE I

Spectral, geometrical and order parameters for *N,p*-chlorophenyl-maleimide oriented in the nematic phase of (a) + (b). Numbering of the protons and the coordinate system with respect to which the *S*-values are reported are defined in the figure.

Parameter	Value	Parameter	Value
D_{12}	328.2 ± 0.1 Hz	$\nu_4 - \nu_1$	37.7 ± 1.2 Hz
$D_{13} = D_{16} = D_{23} = D_{26}$	−181.0 ± 0.2 Hz	r_{45}/r_{36}	1.015
$D_{14} = D_{15} = D_{24} = D_{25}$	−71.9 ± 0.2 Hz	r_{34}/r_{36}	0.583
$D_{34} = D_{56}$	−2296.4 ± 0.1 Hz	Y_1/r_{36}	−1.645
$D_{35} = D_{46}$	23.9 ± 0.1 Hz	θ	54.5°
D_{36}	202.3 ± 1.1 Hz	S_{xx}	−0.1339
D_{45}	193.6 ± 1.1 Hz	S_{yy}	0.2997
$\nu_3 - \nu_1$	50.6 ± 1.2 Hz	S_{xz}	−0.1131

Assumed: *J*-values (Hz): $J_{34} = 8.5$, $J_{35} = 0.5$, $J_{45} = 1.5$, $J_{36} = 1.5$. J_{12} does not influence the spectrum. All other *J*-values equal to zero. $r_{36} = 4.3$ Å. $r_{12} = 2.6$ Å.

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4 MOLECULAR STRUCTURE AND CONFORMATION

The table shows that seven different direct dipolar couplings are obtained in *N*,*p*-chlorophenylmaleimide and $D_{13} = D_{23} = D_{16} = D_{26}$ and $D_{14} = D_{24} = D_{15} = D_{25}$. This means that the symmetry of the Hamiltonian is such that the two rings are orthogonal (or "effectively so") to each other on the NMR time scale.

The four dipolar couplings within the phenyl protons provide the distance ratios r_{45}/r_{36} and r_{34}/r_{36} using standard equations.[11] The values are given in the table. They are significantly different from the corresponding ratios in benzene. If we assume a Cartesian coordinate system for which the X and Y-axes lie along the lines joining protons 4 and 5 and the C—Cl bond respectively, the direct dipolar couplings within the phenyl protons also provide two independent elements of the order matrix as: $S_{xx} = -0.1339$ and $S_{yy} = 0.2997$.

For discussion of the conformation of the maleimide plane with respect to the phenyl ring, we assume that these two rings make an angle θ with each other. We consider an exchange between energetically equivalent conformations of C_2-symmetry. For such a case, 3 independent S-values, vis., S_{xx}, S_{yy} and S_{xz} define the problem. The 3 coupling constants, namely, D_{12}, D_{13} and D_{14} provide Y_1/r_{36}, θ and S_{xz} as given in the table where Y_1 is the Y-coordinate of proton 1. The value of Y_1/r_{36} is in reasonable agreement with that estimated from standard bond lengths.

We have also considered a superposition of the conformations for which the phenyl and the maleimide rings (1) are orthogonal ($\theta = 90°$) and (2) lie in the same plane ($\theta = 0°, 180°$) with an exchange between energetically equivalent conformations. In this case, two S-values are needed for each conformation. The product of the relative weights of the individual conformers and the corresponding order parameters have been derived as: $wS^{p}_{xx} = 0.0104$, $wS^{p}_{yy} = 0.092$, $(1 - w)S^{o}_{xx} = -0.1442$ and $(1 - w)S^{o}_{yy} = 0.2026$ where w is the weight fraction of the "planar" conformer and the superscripts p and o refer to "planar" and "orthogonal" conformations. The geometrical information for the phenyl ring protons thus derived remains the same as described in the earlier case. Y_1/r_{36} thus obtained is 1.651. It deviates only little from the result obtained with the twisted conformation.

On the basis of a mean field approach and with some assumptions on the interactions in nematics, it is possible to estimate that the relative weight planar to perpendicular conformation is about 1 : 3. However, it seems unlikely that the two conformations correspond to energy minima as necessary for this model. The repulsive steric interaction reaches a sharp maximum for $\theta = 0$, for $\theta = 90°$ on the other hand conjugation is completely interrupted. Both conformations will therefore in fact correspond to energy maxima.

The results, indicate that the favored conformation of *N*,*p*-chlorophenylmaleimide is indeed twisted with an equilibrium angle between the two rings of 54.5°. The neglection of the angular vibration around the C—N bond makes the value of the angle somewhat uncertain and we cannot give an error estimate.

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