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Solution Structure and Preferred Orientation of 3,7-Dichloro-10*H*-phenothiazine Dissolved in Nematic Liquid Crystal†

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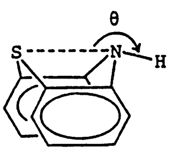
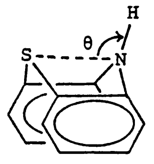
^{1}H NMR spectrum of the title compound was measured in a nematic liquid crystal ZLI1167 and analyzed utilizing modified versions of the LAOCN program. Direct couplings obtained were interpreted on the basis of a folded structure of tricyclic framework. The results show that the dihedral angle between the two benzene rings is 153.1±2.0° and the angle of S⋯N–H is 170.9±6.7°. Hence a "H-intra" conformation is dominant in a mobile state dissolved in the nematic liquid crystal. The preferred orientation of this molecule in ZLI1167 is discussed by comparing the results with those of the dibromo analogue reported previously and by comparing the principal axes of the order tensor with those of the moment of inertia. The chlorine and bromine atoms are supposed to exert a special steric effect on the ordering of these molecules.

We have studied the solution structure and orientation of 3,7-dibromo-10*H*-phenothiazine dissolved in a thermotropic liquid crystal in a previous report of this series.1) In that work the "H-intra" conformation was evidenced in a mobile state in conformity with a theoretical prediction2) and crystal data3) for 10*H*-phenothiazine. The dihedral angle between two benzene rings was observed to be smaller by ca. 10° than that reported for crystal of the unsubstituted compound. With regard to the orientation of solute in liquid crystal, bromine atoms were suggested to exert a steric effect in 3,7-dibromo-10*H*-phenothiazine.



"H-intra" form

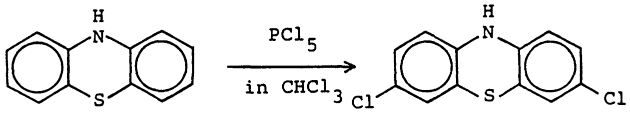


"H-extra" form

Hitherto, several factors have been reported to be responsible for the orientation of molecules in liquid crystal, i.e., the dispersion force,4–7) the electric dipole-dipole interaction,4,5) and the Lewis acid-base interaction8) between solute and solvent molecules, and further the molecular shape and the moment of inertia of solute.9) The steric effect of substituent is also pointed out as one of these factors.10) To investigate further the effect of substituent on the solution structure as well as on the preferred orientation, 3,7-dichloro-10*H*-phenothiazine is synthesized and analyzed in the present study. The results are discussed by comparison with those for the dibromo derivative.

Experimental

3,7-Dichloro-10*H*-phenothiazine was synthesized by the chlorination of 10*H*-phenothiazine.11) The raw product was recrystallized from benzene after decolorizing by sodium dithionite $Na_2S_2O_4$. The final pale-green product melts at 227—229°C (lit., 227 °C11)).



The liquid crystal ZLI1167 from Merck was used without further purification. The solute was dissolved in this solvent at a concentration of 6.7 wt%. ^{1}H NMR spectrum was measured on a Varian XL-200 NMR spectrometer operating at 200 MHz, and the prove temperature was 34.1 °C. 5000 fids were accumulated using a 40° pulse (4 μs). The acquisition time was 0.4 s over a spectral width of 8000 Hz. The data were Fourier transformed to obtain a convolution difference spectrum for 16k data points (CD=0.05 and CCD=1.0). The resulting line width was ca. 10 Hz in the center and ca. 20 Hz in the edges of the spectrum. A small amount of 1,10-phenanthlorine was added to suppress the extraordinary line broadening observed in preliminary measurements. Such broadening was probably induced by a trace amount of paramagnetic impurity. The normal spectrum in isotropic solution was measured on a Hitachi R-22 NMR spectrometer in the CW mode at 90 MHz and at 34.1 °C. Solvent used was a mixture of dimethyl sulfoxide and carbon tetrachloride (20/80 vol%), in which a better separation in chemical shift was obtained.

Analysis of the NMR spectrum observed in ZLI1167 was made by the use of programs LAO3D9 and LAO3D9D which are versions of LAOCN3 modified by the authors.1) A program SHAPE12) was used to calculate structural and order parameters from the experimental direct couplings. Only the diagonal terms (variances) were input for the error analysis in this program. The principal axes of moment of inertia were determined by utilizing a program XYZ.13)

All the above calculations were done on NEAC S-1000 and SX-1 computers at the Computation Center in Osaka University.

Results and Discussion

The indirect couplings of 3,7-dichloro-10*H*-phenothiazine measured in the isotropic medium were J_{12}=8.25 and J_{23}=2.25 Hz, other couplings being very small. The spectrum in ZLI1167 was simulated using direct couplings obtained previously for the dibromo deriv-

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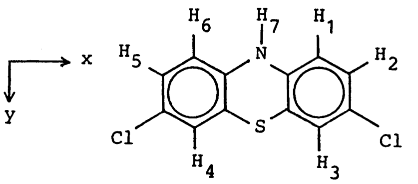

ative as an initial set of parameters.[1] Although the spectrum in the present case resembles to that in the previous report, simulation could not be accomplished straightforwardly. Therefore, some difference in orientation or in solution structure was expected between the two derivatives. NMR parameters reached at the completion of spectral analysis are given in Table 1. Sixty-one lines were assigned and the final rms error was 1.47 Hz in the LAOCN calculation. The experimental and the simulated spectra are depicted in Fig. 1. We analyzed the experimental direct couplings to derive the solution structure and preferred orientation of solute in liquid crystal. The inversion rate of tricyclic framework was assumed to be slower than the rate of whole molecular reorientaion. In the previous study[1] we did not find any significant difference in the structural and ordering parameters for the two limiting models of a fast inversion and a slow one. The results of the present analysis are listed in Table 2. The weighted rms error between experimental and recalculated direct couplings was 0.202 Hz. This is a little larger than the error usually encountered in the NMR study using liquid crystal solvents. But such an error would be inevitable in the present case because experimental direct couplings contain larger errors coming from the line broadening in NMR spectrum observed especially in the edges. Such broadening may be due to a residual trace amount of paramagnetic impurity as stated above. In Table 2 structural parameters are also listed for the dibromo derivative[1] together with the crystal data of 10*H*-phenothiazine.[3] Dihedral angle (ϕ_0) and angle of S ··· N-H (θ) are both smaller in the dihalogeno derivatives as compared to those in unsubstituted 10*H*-phenothiazine. For further quantitative discussion of these angles, systematic work by the NMR spectroscopy would be necessary for other derivatives including 10*H*-phenothiazine itself.

Table 1. NMR Parameters of 3,7-Dichloro-10*H*-phenothiazine Dissolved in Nematic Phase ZLI1167

Direct coupling/Hz:			
D_{12}	733.81±0.18	D_{34}	84.90±0.33
D_{13}	74.64±0.32	D_{37}	60.97±0.33
D_{14}	32.52±0.34		
D_{15}	40.88±0.22	Chemical shift/Hz:[a]	
D_{16}	137.07±0.56	1	105.73±0.40
D_{17}	882.98±0.20	2	180.40±0.37
D_{23}	116.91±0.30	3	180.06±0.58
D_{24}	22.95±0.32	7	466.81±0.65
D_{25}	19.82±0.38		
D_{27}	117.16±0.31		

a) Given in Hz at 200 MHz. Positive toward the low field side.

The order parameters of S_{zz} and S_{yz} are larger for the dichloro derivative as compared to those for the

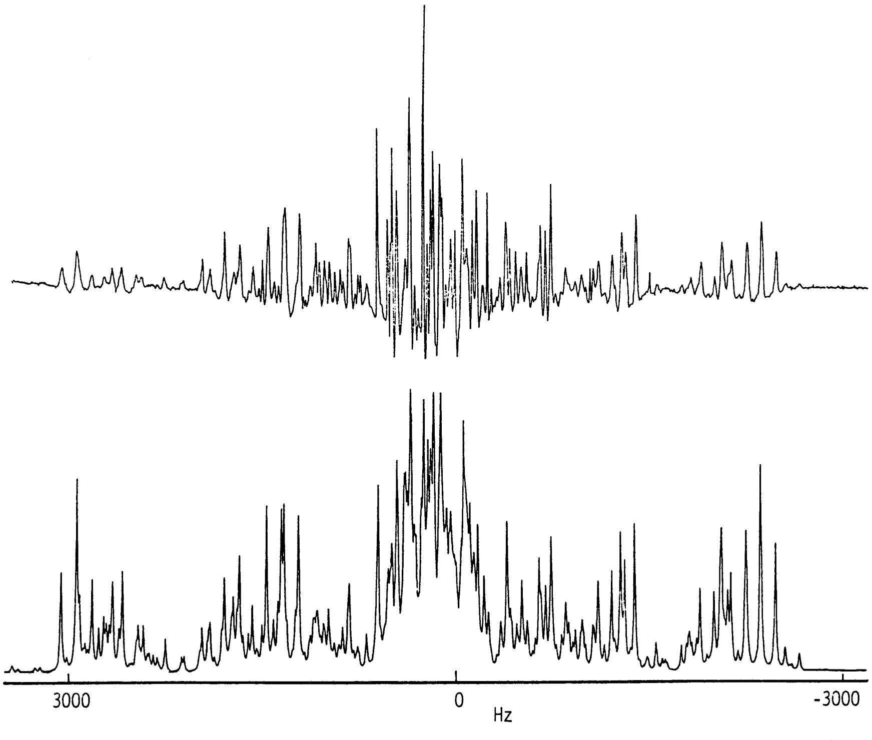

Fig. 1. Experimental (upper) and simulated (lower) ^{1}H NMR spectra of 3,7-dichloro-10*H*-phenothiazine dissolved in a nematic liquid crystal ZLI1167.

Table 2. The Structural and Order Parameters of 3,7-Dihalogeno-10*H*-Phenothiazine Dissolved in ZLI1167

	Dichloro[a)]	Dibromo[b)]	10*H*-Phenothiazine[c)]
	Distance ratios		
r_{13}/r_{12}	2.109±0.048	2.092±0.013	1.979
r_{14}/r_{12}	3.010±0.029	2.958±0.013	2.860
r_{15}/r_{12}	2.923±0.027	2.854±0.025	2.835
r_{16}/r_{12}	1.983±0.022	1.904±0.018	1.902
r_{17}/r_{12}	1.037±0.014	1.003±0.013	0.969
r_{23}/r_{12}	1.946±0.031	1.952±0.045	1.750
r_{24}/r_{12}	3.554±0.035	3.525±0.055	3.368
r_{25}/r_{12}	3.805±0.040	3.753±0.036	3.697
r_{27}/r_{12}	1.963±0.020	1.929±0.020	1.858
r_{34}/r_{12}	2.325±0.025	2.296±0.041	2.240
r_{37}/r_{12}	2.225±0.049	2.175±0.027	2.248
	Angles/degree		
ϕ_o[d)]	153.1±2.0	149.1±2.5	158.5
θ[e)]	169.6±6.7	169.3±3.4	181.9
	Order parameters[f)]		
S_{xx}	−0.1162±0.0007	−0.1223±0.0009	
S_{zz}	0.1922±0.0070	0.1834±0.0013	
S_{yz}	0.0692±0.0158	0.0659±0.0234	

a) 3,7-Dichloro-10*H*-phenothiazine(this work). b) 3,7-Dibromo-10*H*-phenothiazine.[1)] c) Crystal data.[3)] d) The dihedral angle. e) The angle of S---N-H. f) r_{12}=2.356 Å assumed.

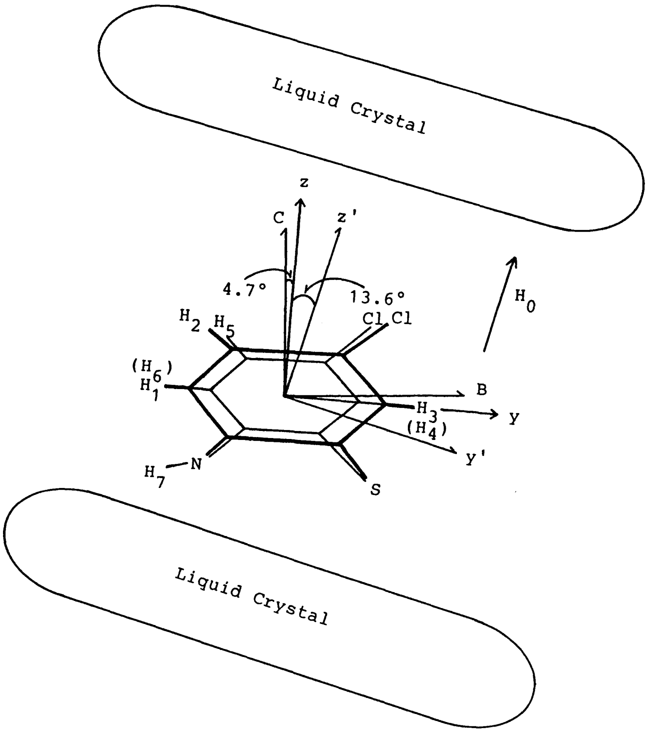

Fig. 2. Principal axis systems for the order tensor (x', y', z') and for the moment of inertia (A, B, C) in 3,7-dichloro-10*H*-phenothiazine (side view). The x' and A axes coincide with the x axis from the C_s symmetry, but these three axes are abbreviated for simplicity in the Figure. The x, y, and z axes are defined so as to place protons of H_1, H_3, H_4, and H_6 on the xy plane. The angles of rotation are −13.6° for y' and z' and 4.7° for B and C with respect to the y and z axes. H_0 denotes the direction of external magnetic field.

dibromo analogue. The absolute value of S_{xx} is, however, smaller for the dichloro derivative. This is a reason why the NMR spectrum of the dichloro derivative is not simply similar to that of the dibromo derivative. Such a decrease in S_{xx} means lowering of orientational order along x axis. This is in accordance with a shortening in diameter along the x direction for the chlorine derivative as compared to the bromine derivative. The positive large values of S_{zz} for both the dichloro and dibromo derivatives indicate that the molecule is most liable to orient with its z axis parallel to the external magnetic field. This leads to the most preferred orientaion of tricyclic plane perpendicular to the long axis of solvent which also orients perpendicular to the external magnetic field.[14)] Such orientational behavior is better understood by considering the principal values of the order parameter. The principal axes of the order parameter(x', y', and z') can be obtained by rotating y and z axes anticlockwise around the x axis by an angle of ω which satisfies a relation: $\mathrm{TAN}(2\omega)=2S_{yz}/(S_{yy}-S_{zz})$.[1)] From this equation $\omega=-13.6°$ is obtained, and the principal values turn out to be $S_{x'x'}=S_{xx}=-0.1162$ and $S_{z'z'}=\sin^2\omega S_{yy}+\cos^2\omega S_{zz}-\sin(2\omega)S_{yz}=0.2090$. Therefore, z' axis orients most preferrably perpendicular to the solvent molecule as shown in Fig. 2. The principal axes of the moment of inertia (A, B, and C) are also depicted in Fig. 2 (I_A=406.4, I_B=3068.6, and I_C=3371.1 amu Å^2). By comparing Fig. 2 with Fig. 2 in Ref. 1, following tendency is noticed: substitution of Cl atoms for Br atoms makes z' and C axes inclined much toward the Cl atoms in conformity with the smallness in size and weight of the Cl atoms, also it reduces slightly the discrepancy between the two principal axis systems determined for the order tensor and for the moment of inertia. Such a steric effect of substituent was already observed in cases of the stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane.[10)] The absolute value of $S_{x'x'}/S_{z'z'}$ is equal to 0.56 for the dichloro derivative, which is smaller than the value of 0.61 for the dibromo derivative. This is in accordance with the trend in size of the substituents.

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