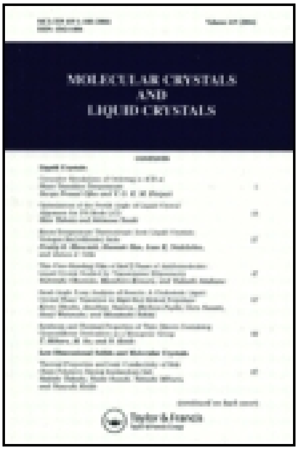

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Proton Magnetic Resonance in Nematic Liquid Crystals: Acetoxybenzal-*p*-Anisidine, Acetoxybenzal-*p*-Aminoazobenzene, and Anisal-*p*-Aminoazobenzene

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Abstract—Proton magnetic resonance has been investigated in three nematic liquid crystals—acetoxybenzal-*p*-anisidine, acetoxybenzal-*p*-aminoazobenzene and anisal-*p*-aminoazobenzene, using a broad line PMR spectrometer. The results show that the five-line pattern in the first two compounds is due to the hindered rotation of the acetoxy group. The degree of order parameter S has been evaluated for the three liquid crystals from line separations and second moment measurements. These calculations also confirm the hindered rotation of the acetoxy group.

Since the pioneering work of Spence and his coworkers,(1) several investigators made use of proton magnetic resonance in liquid crystals to investigate the structural problems of the mesophase. The nematic phase is known to give a multiplet proton spectrum superposed on a broad line. The inherent ordering in the phase and the influence of the magnetic field contribute to the breadth of the line, while the multiplet structure is a consequence of the intramolecular dipole–dipole interactions. The contribution of the intermolecular interactions is usually considered as negligible due to the large separations and the rotational and translational motions of molecules within the phase. Thus, the structure of the proton spectrum offers useful information about the intramolecular motions.

The proton magnetic resonance (PMR) spectrum of the liquid crystal anisalaminophenyl acetate (AAPA)(2,3) has been found to give five lines. The source of the outer doublet has not been well understood. In order to improve our understanding of this problem, three liquid crystals—(i) acetoxybenzal-*p*-anisidine (ABPA), (ii) Acetoxybenzal-*p*-aminoazobenzene (ABPAAB) and (iii) anisal-*p*-aminoazobenzene (APAAB)—have been investigated in the present work. The first one is similar to AAPA, except for interchange of positions by acetoxy and methoxy groups. The other two are similar in their proton structure. The acetoxy group of ABPAAB is replaced by the methoxy group in APAAB.

1. Experimental

The compounds ABPA and ABPAAB were prepared by condensing the respective amines with acetoxybenzaldehyde, which was, in turn, prepared by refluxing the commercially available *p*-hydroxybenzaldehyde with acetic anhydride for 2 to 3 hr and distilling the product under reduced pressure as suggested by W. Richter⁽⁴⁾ and J. S. Dave *et al.*⁽⁵⁾ The compound APAAB was prepared by condensing commercially available anisaldehyde and *p*-aminoazobenzene. The crude samples were repeatedly recrystallized from ethanol till pure samples were obtained. The transition temperatures are as follows: (i) ABPA: 112–119 °C, (ii) ABPAAB: 154–200 °C and (iii) APAAB: 152–184 °C. The spectra were recorded using a low level Robinson type oscillator operating at a frequency of 16 MHz. A Varian 12 in. magnet supplied the required 3800 G field. The samples were heated by hot air blown past the sample coil. The temperature was measured with the help of a copper-constantan thermocouple placed in the sample and the accuracy was up to ± 1 °C.

2. Results and Discussion

ABPA, which is similar to AAPA, gives a five-line proton spectrum above the solid–nematic transition point. The outer components are separated by 4.92 G, while the inner doublet separation is 2.5 G at 113 °C. As the nematic phase in this compound exists only for 7 °C, the line separations rapidly decrease and the outer peaks vanish quickly with increase in temperature. ABPAAB also gives five lines. At 160 °C the outer doublet separation is 6.81 G and the

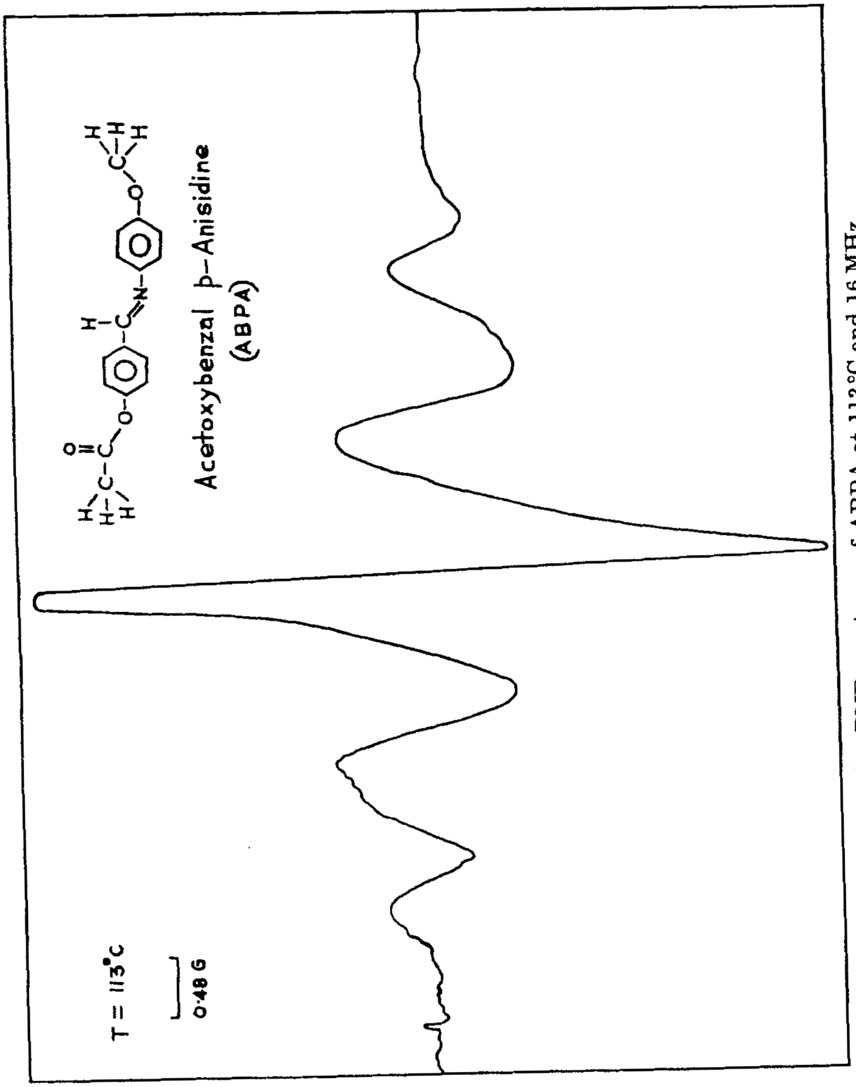

Figure 1. PMR spectrum of ABPA at 113 °C and 16 MHz.

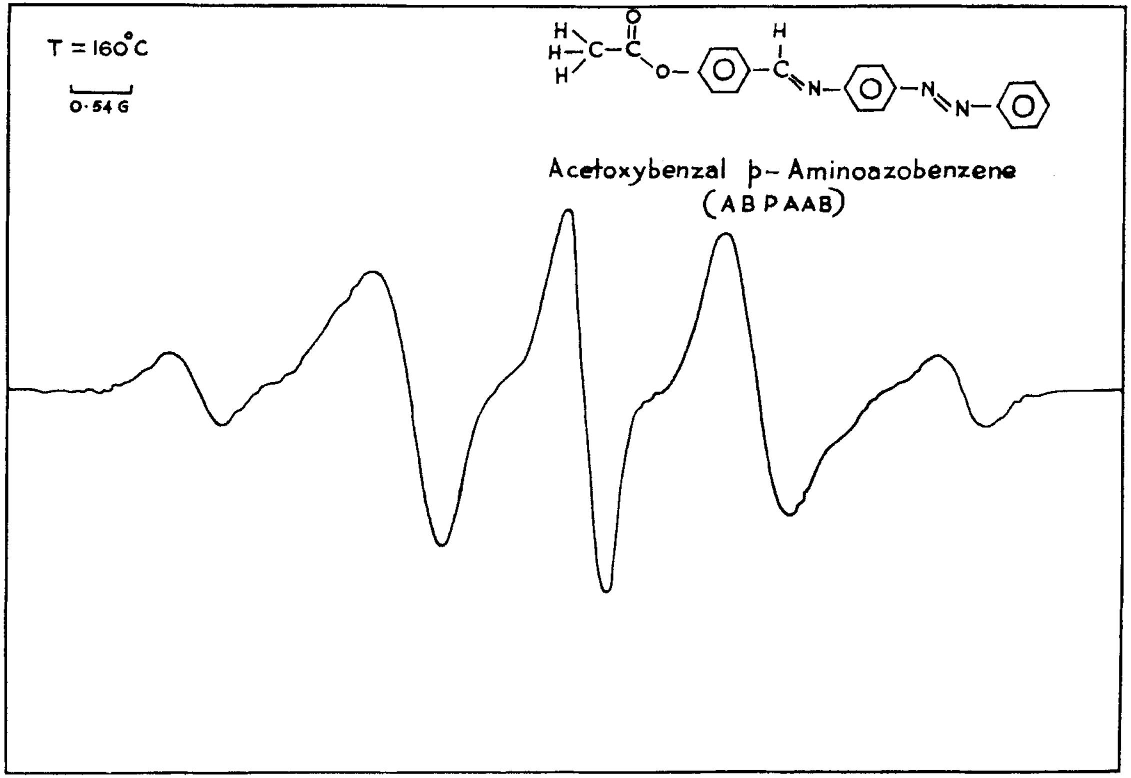

Figure 2. PMR spectrum of ABPAAB at 160 °C and 16 MHz.

inner component separation is 3.06 G. In APAAB, we observe only three lines and the separation of the satellites is 2.82 G at 154 °C. The recorded derivative curves with the corresponding molecular structures for ABPA and ABPAAB are given in Figs. 1 and 2.

In the case of APAAB, the three-line pattern can be understood following the earlier workers,⁽¹⁾ by assuming that the methoxy group rotates freely and contributes only to the central line while the aromatic protons give rise to the satellites. In the case of the other two compounds, the observed five line pattern has been explained by two different approaches. Carr *et al.*⁽²⁾ suggested that the outer doublet is due to the hindered rotation of the acetoxy group while the lone proton of the amino group contributes to the central line. Christman *et al.*⁽³⁾ suggested that the outer peaks are due to the interaction of the lone proton with the phenyl ring protons. Both however agree that the inner lines are due to the phenyl ring protons.

In the present work, an attempt has been made to decide between these two alternate approaches, employing line intensity calculations, second moment analysis and the evaluation of degree of order parameter S for the three liquid crystals.

I. LINE INTENSITY CALCULATIONS

Detailed calculations of the relative weights of each line, which depends on the number of protons contributing to that line, are carried out for ABPA only. In ABPA, three different cases have been considered:

(i) The end groups are assumed to be completely free and the rest of the molecule rigid. As the lone proton is nearly midway from the protons of the phenyl rings and separated by almost equal distance as ortho protons, triplet interaction is taken into account. It is realized that it is rather a crude model. This case is not considered for the other two compounds.

(ii) The end groups are assumed to have freedom of rotation while the triplet interaction is neglected. This means possible rotation of the phenyl rings on their *p*-axes; and

(iii) The phenyl rings are assumed to have rotational freedom about their *p*-axes, which means the lone proton is isolated while the acetoxy group is assumed to have hindered rotation on its O—C bond. This does not arise in APAAB because of methoxy group.

The calculated and the experimental intensities are given in Table 1.

TABLE 1 Calculated and Observed Line Intensities

Molecule	Intensity Ratios			
	Experimental	Calculated		
		Case i	Case ii	Case iii
1. Acetoxybenzal-*p*-anisidine (ABPA)	*1 : 5 : 9*	*1 : 4.2 :10.7*	*1 : 7 : 14*	*1 : 5.3 : 7.3*
2. Acetoxybenzal-*p*-aminoazobenzene (ABPAAB)	1 : 9.3 : 7	—	1 : 7.7 : 5.3	1 : 8 : 4.7
3. Anisal-*p*-aminoazobenzene (APAAB)	1 :1	—	1.2 : 1	—

In the case of ABPA, the experimental values seem to be nearer to those calculated on the basis of triplet interaction and the hindered rotation of acetoxy group (cases (i) and (iii)). However Bravo *et al.*⁽⁶⁾ convincingly demonstrated that the phenyl rings rotate freely on their *p*-axes. Hence the triplet interaction arising out of the lone proton of the amino group with the aromatic protons can be ruled out. The outer doublet therefore should arise due to the hindered rotation of the acetoxy group in ABPA. However, in ABPAAB we cannot choose between cases (ii) and (iii). For APAAB, the slight disagreement between the experimental and theoretical values may be due to probable decomposition of the sample while heating.

II. SECOND MOMENT ANALYSIS

Second moment analysis has been carried out using Weber's⁽⁷⁾ formula applicable for the liquid crystal phase. This formula due to Weber is

$$(\overline{\Delta H^2})_{\text{theor.}} = \mu_L S^2 M = \mu S^2 \qquad (1)$$

S represents the inherent micro-ordering of the phase while M is the macro-ordering brought about by the external magnetic field. At high field strength M is independent of temperature and can be taken as 4. μ_L is given by

$$\mu_L = \frac{3(I+1)\mu_P{}^2}{2IN}\left(\tfrac{3}{2}\cos^2\phi - \tfrac{1}{2}\right)^2 \sum_{j>k} \frac{\overline{\left(\tfrac{3}{2}\cos^2\gamma_{jk} - \tfrac{1}{2}\right)^2}}{r_{jk}^6}\,. \qquad (2)$$

The terms have their usual significance.

The evaluation of the second moment now consists in finding out the average value of $(\frac{3}{2}\cos^2\gamma_{jk} - \frac{1}{2})^2$ over all possible rotations of the internuclear vector r_{jk} about the p axis of the molecule. The neglect of intermolecular dipole–dipole interactions in the liquid crystal phase permits the separate evaluation of the contributions of the individual pairs of nuclei within a molecule to the second moment. All these contributions are added up and compared with the experimental values. Two possibilities have been considered:

(i) Free rotation of both methoxy and acetoxy groups; and
(ii) Free rotation of methoxy and hindered rotation of acetoxy groups.

The second moments calculated for these two cases are given in Table 2 together with the experimental values. The experimental values of the second moment are obtained for $S = 0.45$ which has been obtained from line separation measurements.

TABLE 2 Calculated and Experimental Second Moments

Molecule	$\mu_{\text{theor.}} = 4\mu_L$		$\mu_{\text{exp.}}$
	Free	Rigid	
1. Acetoxybenzal-*p*-anisidine (ABPA)	4.56 G^2	8.95 G^2	7.19 G^2
2. Acetoxybenzal-*p*-aminoazobenzene (ABPAAB)	5.35 G^2	9.22 G^2	9.86 G^2
3. Anisal-*p*-aminoazobenzene (APAAB)	6.72 G^2	—	7.33 G^2

ABPA and *p*-azoxyanisole (PAA) are similar in their general proton structure and also in the structure of the terminal groups. PAA has two methoxy groups while ABPA has one acetoxy and one methoxy group. In the absence of any hindrance to acetoxy group, the two compounds should have nearly the same second moment.

Similarly, ABPAAB and APAAB are identical in their proton structures and as such should have the same second moment, if the acetoxy group has rotational freedom. But, however the second moments are considerably different. The $\mu_{\text{expt.}}$ of PAA is 4.3 G^2 only, for $S = 0.45$ and $\mu_{\text{theor.}} = 5.3\ \mathrm{G}^2$. In calculating the theoretical second moments for APAAB, three models with different freedoms of rotation of the methoxy group were assumed. The model, in which methyl protons are assumed to be freely reorienting on the O—C bond, while the bond itself remains rigid, gave a μ value nearer to the experimental value. Hence, that μ is used in the present work. The calculated μ values on the basis of rigid acetoxy group are in fair agreement with the experimental values. The higher second moments of ABPA and ABPAAB compared to those of PAA and APAAB respectively are only due to the hindered acetoxy group. It may be pointed out that in this analysis the contribution of the lone proton is neglected.

III. EVALUATION OF " DEGREE OF ORDER " PARAMETER *S*

The order parameter S can be evaluated in two ways from PMR data. It can be obtained from proton line separations using the formula

$$\delta H = 6\mu_p r_{jk}^{-3}(\tfrac{3}{2}\cos^2\phi - \tfrac{1}{2})(\tfrac{3}{2}\cos^2\gamma_{jk} - \tfrac{1}{2})S. \qquad (3)$$

TABLE 3 " Degree of Order " S at Different Temperatures

Molecule	T °C	S From δH	S From $\overline{\Delta H^2}$
1. Acetoxybenzal-*p*-anisidine (ABPA)	113	0.45	0.40
2. Acetoxybenzal-*p*-aminoazo-benzene ABPAAB)	160	0.55	0.53
	172	0.51	0.52
	178	0.45	0.47
	184	0.39	0.38
3. Anisal-*p*-aminoazobenzene (APAAB)	154	0.51	0.52
	165	0.45	0.47
	170	0.42	0.45
	175	0.38	0.41
	180	0.36	0.38

Alternately, Eq. (1) can be employed to obtain S from the experimental second moment values. In using Eq. (3) the amino proton interaction with aromatic protons is neglected. For ABPA and ABPAAB, rigid structure values are taken for μ in using Eq. (1). In Table 3 are given the S values obtained in these two methods at different temperatures.

The agreement obtained for S by these two methods is not very satisfactory. The discrepancy may partly be attributed to the assumptions made in evaluation of $\mu_{\text{theor.}}$. For example, it is assumed that the phenyl rings are coplanar, while they are generally considered to be out of plane to the extent of 40–60° with one another. However, it may be mentioned that S values obtained on the basis of free rotation of acetoxy group are much larger than the S values obtained from line separations, which are generally considered more accurate. On this basis the acetoxy group can be considered as having hindered rotation only.

In conclusion, the present work, using line intensities, second moments and degree of order parameter calculations, shows that the acetoxy group has hindered rotation about its O—C bond and is responsible for the outer doublet in the five line spectrum observed in ABPA, ABPAAB and AAPA. The lone proton of the amino linkage contributes to the central line and is not responsible for the outer doublet as suggested by Christman *et al.*(3)

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