

Multiple liquid crystals and NMR

C L KHETRAPAL

Sophisticated Instruments Facility, Indian Institute of Science, Bangalore 560012, India

Abstract. The use of more than one liquid crystal solvents to determine molecular structure and conformation is discussed. Liquid crystals of similar and opposite signs of diamagnetic anisotropies are considered separately since they lead to different novel applications. Advantages of such experiments over those employing single solvents are pointed out with illustrative examples.

Keywords. Liquid crystals; NMR; diamagnetic anisotropy; chemical shift anisotropy; direct dipolar couplings; indirect spin-spin couplings; hetero nuclei.

1. Introduction

The use of liquid crystals as solvents in NMR experiments providing the structure and conformation of dissolved molecules is well known (Diehl and Khetrpal 1969; Emsley and Lindon 1975; Khetrpal *et al* 1975; Khetrpal and Kunwar 1977, 1983). The information for molecules with spin $\frac{1}{2}$ nuclei in diamagnetic materials is derived from the direct dipolar couplings (D_{ij} 's), the chemical shifts ($\nu_i - \nu_j$'s) and the indirect spin-spin couplings (J_{ij} 's) where i and j are the interacting nuclei. For successfully employing the technique to structural problems, therefore, precise evaluation of these parameters is essential. To derive geometrical information from dipolar couplings, the number of D_{ij} 's must not be less than the sum of the geometrical and orientational parameters in the system so as to obtain the information without having to make assumption. The use of multiple liquid crystals in NMR is a step forward in making the technique as a routine method in structural chemistry (Diehl *et al* 1980; Dombi *et al* 1980; Ambrosetti *et al* 1981; Jokissari *et al* 1981; Khetrpal *et al* 1980; Khetrpal and Kunwar 1981a, b, 1982, 1984). The experiments under different orientation conditions have been used to obtain information which would not be possible from a single experiment. Also the use of multiple liquid crystals of opposite diamagnetic anisotropies has been employed to derive the information. A few such applications are reported in the present paper. Multiple liquid crystals as media for different orientations and the use of solvents with opposite diamagnetic anisotropies are discussed separately since they both lead to different novel applications.

2. Multiple liquid crystals as media for different orientations

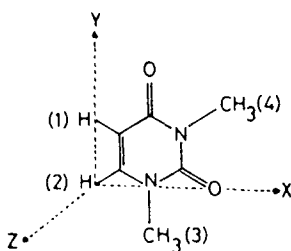
As pointed out in §1, the number of direct dipolar couplings obtained for a system must be larger than or equal to the number of geometrical and orientational parameters to be determined. If, however, the number of derived dipolar couplings (N) is less than the sum of the geometrical (P) and orientational (A) parameters to be derived, performing experiments under different orientation conditions *i.e.* the use of more than one liquid crystal solvents is quite informative. In such a case, one has to perform a minimum of

$P/(N - A)$ experiments under different orientation conditions. If $P/(N - A)$ is not an integer, the minimum number is the next higher integer. It is clear that this procedure is based on the assumption that the molecular geometry is invariant from one experiment to the other. Such applications to systems such as N,N-dimethyl uracil (Khetrpal and Kunwar 1982, 1984) (μ -butatriene) hexacarbonyl diiron (Arumugam *et al* 1984) complex are reported in this section.

2.1 N,N-dimethyl uracil

The analysis of the proton NMR spectrum of N,N-dimethyl uracil (structure 1) in a single liquid crystal provides 8 HH dipolar couplings. If it is assumed that (i) axes of the methyl group rotations are along the respective N-CH₃ bonds, (ii) the methyl groups themselves are rigid, (iii) the influence of molecular vibrations are neglected, (iv) the distance between the protons 1 and 2 (r_{12}) is used as a scaling distance (2.30 Å), (v) the molecule has a plane of symmetry and (vi) the motions of the two methyl groups are not correlated, 8 geometrical parameters define the proton positions for specific modes of rotations of the methyl groups. Under such conditions, the number of order parameters for each experiment is 3. The 8 geometrical and 3 order parameters cannot be determined from a single experiment providing a total of 8 HH dipolar couplings. If, however, the experiments are performed in two different liquid crystals, the total number of 6 orientational (3 for each experiment) and 8 geometrical (assuming that the molecular geometry is invariant with solvent) can be derived from the 16 direct dipolar couplings using a least square fit procedure.

N,N-dimethyl uracil has been investigated in two liquid crystals, namely N-(*p*-methoxybenzylidene)-*p*'-*n*-butylaniline (MBBA) and *p*-*n*-butyl-*p*'-methoxyzobenzene (Merck Phase IV) (Khetrpal and Kunwar 1982, 1984). From the interpretation of the data, parameters as given in table 1 were derived. These are with respect to a right-handed Cartesian coordinate system for which the origin is at proton position 2 and the positive Y-axis lies along the line joining proton 2 to 1 with XY-plane being the molecular plane of symmetry. The derived parameters are: (i) the angle α_1 between the Y-axis and the N-CH₃ bond axis of the methyl group marked (3) in structure 1, (ii) the angle α_2 between the X-axis and the N-CH₃ bond axis of the methyl group marked (4), (iii) the (X, Y) coordinates of the centres of the equilateral triangles formed by each of the two methyl group protons—they are referred to as (X_3, Y_3) and (X_4, Y_4) for the groups (3) and (4) respectively in structure 1, (iv) (r_{HH})₃ and (r_{HH})₄, the distances within the methyl protons marked (3) and (4) respectively, and (v) two sets of order parameters denoted by S_{XX}, S_{YY}, S_{XY} and S'_{XX}, S'_{YY} and S'_{XY} for experiments in MBBA and Merck Phase IV respectively.



Structure 1. N,N-dimethyl uracil

Table 1. Geometrical and order parameters in N,N-dimethyluracil

Parameter	Mode of rotation of methyl groups				X-ray values*
	E3, E4	E3, S4	E3, P4	E3, F4	
α_1 (degrees)	2.7	2.7	2.7	2.7	1.4
α_2 (degrees)	25.5	24.4	25.0	25.0	26.2
X_3 (Å)	1.88	1.82	1.85	1.85	1.95
Y_3 (Å)	-1.85	-1.83	-1.84	-1.84	-1.95
X_4 (Å)	4.78	4.84	4.81	4.81	4.76
Y_4 (Å)	2.50	2.44	2.47	2.47	2.48
$(r_{HH})_3$ (Å)	1.77	1.77	1.77	1.77	
$(r_{HH})_4$ (Å)	1.82	1.82	1.82	1.82	
S_{XX}	0.0014	-0.0008	0.0003	0.0003	
S_{YY}	0.1287	0.1287	0.1287	0.1287	
S_{XY}	0.0143	0.0199	0.0171	0.0171	
S'_{XX}	0.0093	0.0065	0.0078	0.0078	
S'_{YY}	0.1885	0.1885	0.1885	0.1885	
S'_{XY}	0.0298	0.0337	0.0337	0.0337	
RMS error (Hz)	0.08	0.10	0.09	0.09	

* Based on an average value of the methyl C-H distance and the tetrahedral value for the methyl HCH bond angles.

The above parameters were derived for each of the following modes of rotation of the methyl group(s). For the methyl group (3), (i) a free rotation (designated as F3) about the N-C bond, (ii) three energetically equivalent conformers each with a C-H bond of the methyl group pointing towards or away from the adjacent C=O group (denoted as E3 or S3 respectively), and (iii) three equivalent conformers each with a C-H bond of the methyl group perpendicular to the molecular plane of symmetry (referred to as P3) were considered. Similar possibilities were also considered for the methyl group (4) and are designated as F4, E4, S4 and P4 respectively. In this case, E4 or S4 means that one C-H bond of the methyl group (4) points towards or away from the carbonyl bond adjacent to the methyl group (3). All the combinations of the various possibilities were considered and the root-mean-square (r.m.s.) errors between the observed and the best fit calculated dipolar couplings were determined. It was observed that the r.m.s. error is larger by about an order of magnitude for all the P3 possibilities and hence they are considered less favourable. It is thus concluded that the conformation with a C-H bond of the methyl group (3) being orthogonal to the ring plane is not favoured. Table 1, therefore, does not include such possibilities. Similarly for the S3-possibilities, the r.m.s. error was nearly twice as large as for some other modes of methyl group rotations reported in table 1. Furthermore, for such cases the geometrical parameters are in complete disagreement with those obtained from x-ray data reproduced in table 1 for ready comparison. Deviations upto 0.4 Å were observed in some of the derived parameters in such cases. Hence, such conformers are also considered less favoured and the results have not been included in table 1. The F3 possibilities provided r.m.s. error comparable to that for the possibilities reported in table 1 but the derived geometrical data were in complete disagreement with x-ray crystallographic data. Consequently, the free rotation of the CH₃ group (3) is also not favoured. The r.m.s. error is minimum

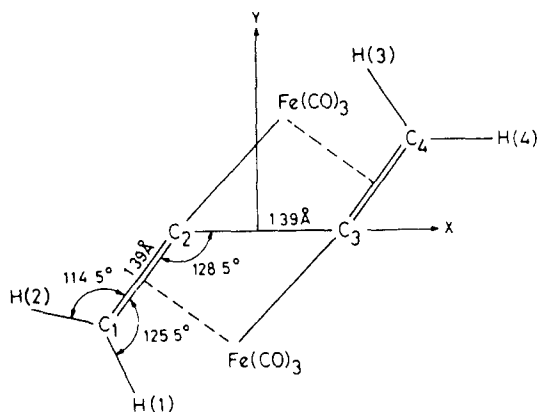
(0.08–0.10 Hz) for the E3 possibilities irrespective of the mode of rotation of the methyl group (4).

The results, therefore, indicate that the preferred conformation of N,N-dimethyl uracil is the one where one C–H bond of the methyl group (3) is the ring plane and points towards the adjacent C=O group. The results are not very sensitive to the mode of rotation of the methyl group (4). The results can be interpreted in terms of the bond polarization hypothesis (Khetrapal and Becker 1981). The C–H and the C=O bonds have opposite polarizations ($C^{\delta-} - H^{\delta+}$ and $C^{\delta+} - O^{\delta-}$) and due to electrostatic attraction, the conformer with a C–H bond of the methyl group (3) pointing towards the adjacent C=O group is preferred. On the other hand for the CH_3 (4) group, the presence of C=O groups on either side at about equal distances makes it hard for either the E4 or S4 conformer to be preferred. The results, therefore, are not very sensitive to the mode of rotation of CH_3 (4).

The geometrical data derived from NMR and x-ray studies are in reasonable agreement with each other indicating thereby that the structure does not change in going from the liquid state to the solid.

2.2 Conformation of (μ -butatriene) hexa carbonyl diiron complex:

The title compound (structure 2) provides 4 proton-proton dipolar couplings from the analysis of the spectrum in a single solvent. Since 3 of the dipolar couplings are used up for the determination of molecular order, only one item of geometrical information can be derived from the study in a single solvent. However, a study in 3 different liquid crystals permits the evaluation of the 9 order parameters (3 corresponding to each experiment) and the conformational angles θ and ϕ between the two CH_2 planes and the dihedral angle between the four carbons of the (μ -butatriene) moiety, respectively under the assumption of the reasonable bond lengths and the bond angles. A study in the three solvents, namely (i) N-(*p*'-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA), (ii) Merck Phase IV and (iii) ZLI-1167 (a ternary eutectic mixture of propyl-, pentyl- and heptyl bicyclohexyl carbonitrile) has been undertaken (Arumugam *et al* 1984) and the values of the angles θ and ϕ determined as 44° and 46° respectively.



Structure 2. (μ -butatriene) hexa carbonyl diiron

3. Multiple liquid crystals of opposite diamagnetic anisotropies

Khetrpal and Kunwar (1981) noticed that a mixture of liquid crystals with opposite diamagnetic anisotropies leads to novel application of NMR. The D_{ij} values change gradually with relative concentrations of the two solvents until at a critical concentration and temperature, they jump abruptly to twice or half with opposite signs depending upon the direction of approach of the critical point. A typical behaviour for acetonitrile and the ortho protons of benzene is shown in figure 1. A close examination of the results in the vicinity of the critical point reveals the coexistence of two types of spectra at a particular temperature with dipolar couplings in one being twice with opposite sign to those in the other as shown in figure 2. They correspond to two types of orientations of the liquid crystal optic axis, one being preferentially parallel and the other perpendicular to the magnetic field. Though the behaviour is theoretically well understood (Sinha *et al* 1983a, b, c), the question whether the two spectra near the critical point arise from certain inhomogeneities (temperature, concentration) in the sample or whether there is a "true" coexistence of the two phases, is still open. However, the experiments lead to the following novel applications: (i) determination of chemical shift anisotropy ($\Delta\sigma$) without the use of a reference or change of experimental conditions; (ii) separate determination of the indirect spin-spin and direct dipolar couplings between heteronuclei; (iii) determination of diamagnetic anisotropy of liquid crystals; (iv) precise determination of spectral parameters; and (v) determination of molecular structure with minimal distortions. These are discussed individually with illustrative examples in the following sections:

3.1 Determination of ($\Delta\sigma$) without the use of a reference or change of experimental conditions

The use of NMR spectroscopy of oriented molecules for the determination of chemical shift anisotropy is well known. It involves determination of the chemical shift difference

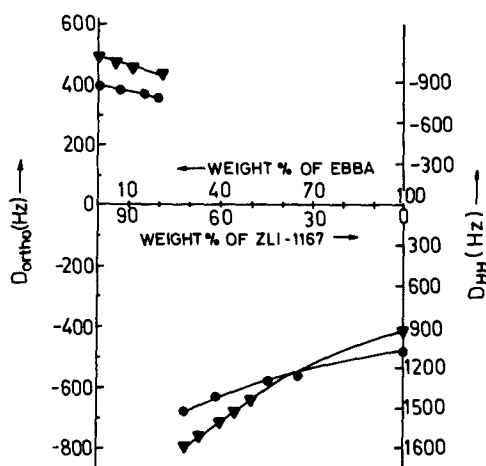


Figure 1. Dipolar couplings between methyl protons (D_{HH}) in acetonitrile (●) and those between ortho protons (D_{ortho}) in benzene (▼) as functions of relative concentration of EBBA and ZLI-1167.

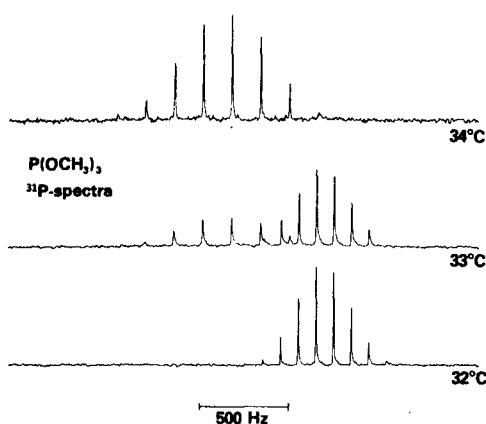


Figure 2. ^{31}P NMR spectra of trimethyl phosphite oriented in a 0.3:1 (by weight) mixture of EBBA:ZLI-1167. At 33°C, the two spectra corresponding to those at 32 and 34°C coexist.

between isotropic and anisotropic media and the order parameter. The use of equation (1) then, for a system with a 3-fold or higher axis of symmetry provides $\Delta\sigma$

$$\sigma_a = \sigma_i + \frac{2}{3} \cdot \Delta\sigma \cdot S_{C_3}, \quad (1)$$

where σ_a and σ_i are the chemical shifts in the nematic and the isotropic phases and S_{C_3} is the order parameter of the symmetry axis. In actual practice, however, the real problem lies in the precise determination of the shift difference ($\sigma_a - \sigma_i$) due to different solvent effects arising from change of experimental conditions and the need of an internal or external reference.

On the other hand, the use of mixed liquid crystals of opposite diamagnetic anisotropies near the critical point where the "coexistence" of two spectra is observed, permits evaluation of the chemical shift anisotropy without using a reference or changing the experimental conditions. Equation (2) is valid for a molecule with 3-fold or higher axis of symmetry

$$\Delta\sigma = (\sigma_{\parallel} - \sigma_{\perp}) / (S_{C_3}), \quad (2)$$

where σ_{\parallel} and σ_{\perp} are the chemical shifts for the orientations corresponding to $\Delta\chi > 0$ and $\Delta\chi < 0$ respectively and (S_{C_3}) is the order parameter of the symmetry axis for the orientation with $\Delta\chi > 0$.

The method has been used to obtain proton as well as carbon-13 chemical shift anisotropies (Khetrapal and Kunwar 1981b; Raghothama 1984). An interesting comparison of the values of the chemical shift anisotropies determined using various methods has been made (Diehl *et al* 1982a). It has been concluded that this method proposed by Khetrapal and Kunwar (1981) and named as NEMIX method (Diehl *et al* 1982a) provides most satisfactory results. Although the NEMIX method provides satisfactory results, the "local effects" on the chemical shifts are present even for this method and they may at times lead to unrealistic results (Khetrapal *et al* 1984a, b) if such effects are not taken into account. Theoretical calculations to estimate such effects have yet to be made.

3.2 Separate determination of indirect and direct dipolar couplings between heteronuclei

It is well known that the nuclear spin Hamiltonian for oriented systems contains the sum $(J_{AX} + 2D_{AX})$ when A and X are heteronuclei. Consequently, individual determination of the direct dipolar and the indirect spin-spin couplings is not possible in such cases. In order to obtain precise value of D_{AX} for accurate evaluation of molecular geometry, J_{AX} must be known. Since J_{AX} may be temperature and solvent-dependent specially when heavy nuclei are involved, it may be appropriate to obtain its value in the nematic phase itself without changing experimental conditions. This can be achieved conveniently from the coexistence of the two spectra near the critical point in mixed liquid crystals of opposite diamagnetic anisotropies. The quantities $(J_{AX} + 2D_{AX})$ and $(J_{AX} - D_{AX})$ (where D_{AX} is the dipolar coupling for the orientation corresponding to $\Delta\chi > 0$; the value for $\Delta\chi < 0$ near the critical point is $-\frac{1}{2}D_{AX}$) provide J_{AX} and D_{AX} individually.

The first demonstration of this application was made for acetonitrile (Khetrapal and Kunwar 1981) where the indirect and the direct couplings between protons and ^{13}C and ^{15}N in the natural abundance have been determined. Subsequently, the values for phenyl selenyl chloride and bromide (Suryaprakash *et al* 1983a,b), trimethyl phosphate (Khetrapal *et al* 1984) and trimethyl phosphite (Subburam 1984) have been obtained and the molecular geometries determined.

3.3 Determination of diamagnetic susceptibility anisotropy of liquid crystals

A direct consequence of the experiments in mixed liquid crystals of opposite diamagnetic anisotropies is that the macroscopic diamagnetic anisotropy of the system at the critical point vanishes *i.e.*

$$p(\Delta\chi)_{\parallel} + (1-p)(\Delta\chi)_{\perp} = 0, \quad (3)$$

where p is the mole-fraction of the solvent with $\Delta\chi > 0$ and $(\Delta\chi)_{\parallel}$ and $(\Delta\chi)_{\perp}$ are the diamagnetic susceptibility anisotropies of the components with $\Delta\chi > 0$ and $\Delta\chi < 0$ respectively. Both $(\Delta\chi)_{\parallel}$ and $(\Delta\chi)_{\perp}$ are related to molar susceptibility anisotropy $(\Delta\chi_a)$ by the relation $\Delta\chi = S_{\text{LC}} \cdot \Delta\chi_a$ where S_{LC} is the order parameter of the liquid crystal. This method has been proposed and used by Diehl and Jokisaari (1982) using a solute as the probe molecule. Relative diamagnetic anisotropies of a number of liquid crystals have been thus obtained.

3.4 Precise determination of spectral parameters

When the number of observed transitions in a nuclear spin system is not very large compared to the number of spectral parameters to be derived, it may sometimes turn out that the derived spectral parameters suffer from large uncertainties. Such a situation was actually encountered for the proton NMR spectra of the type AB_2 in 2,6-dichlorophenol (Lakshminarayana *et al* 1985). The system was studied in a mixture of EBBA and ZLI-1167 and the spectra were analysed above and below the critical point. Values of the indirect coupling J_{AB} determined from the two spectra were -7.3 and $+10.1$ Hz. On the other hand, near the critical point where the two orientations "coexist", values of the dipolar couplings are related by a factor -2 . Using this condition and analysing the spectra near critical point provides $J_{AB} = 8.3$ Hz which is identical to the value determined from the analysis of the spectrum in an isotropic medium.

3.5 Determination of molecular structure with minimal distortions

There has recently been a great interest in the study of solvent effects on the structure of molecules derived from NMR studies of oriented systems. A systematic study of benzene in various liquid crystals has been undertaken and it has been concluded that the distortions are minimal in liquid crystals such as ZLI-1167 with no aromatic rings (Diehl *et al* 1979). On the other hand, in thiophene largest distortions have been observed in the solvent ZLI-1167 (Diehl *et al* 1983). Similarly in N-methyl pyrrole, the distortions are less in the solvent ZLI-1167 (Suryaprakash *et al* 1984) whereas they are quite large in the same solvent for benzo(b)selenophene (Suryaprakash *et al* 1985). A study of acetonitrile in various liquid crystals has been undertaken and the distortions in molecular structure have been correlated to the diamagnetic anisotropy of the solvent (Diehl *et al* 1982b). Since the macroscopic diamagnetic susceptibility anisotropy vanishes at the critical point, it is concluded that the distortions are minimal when the studies are performed near the critical point. It has actually been demonstrated to be so in systems such as methane (Jokisaari and Hiltunen 1983) and N-methyl pyrrole also.

It is, therefore, concluded that the NMR studies of molecular structure using liquid crystal solvents should be performed around the critical point in mixed liquid crystals of opposite diamagnetic anisotropies in order to derive the molecular geometry with minimal distortions.

4. Conclusions

It is demonstrated that the NMR studies of molecules oriented in more than one solvent provide more information on molecular structure than single liquid crystals. When the multiple liquid crystals are of opposite diamagnetic anisotropies, they lead to novel applications of NMR. Furthermore, mixed liquid crystals of opposite diamagnetic anisotropies provide media with minimal distortions in molecular structure.

References

- Ambrosetti R, Catalano D, Veracini C A, Chidichimo G and Longeri M 1981 *J. Mol. Struct.* **73** 203
Arumugam S, Kunwar A C and Khetrapal C L 1984 *J. Organomet. Chem.* **265** 73
Diehl P, Bösiger H and Zimmermann H 1979 *J. Mag. Res.* **31** 113
Diehl P, Dombi G and Bösiger H 1980 *Org. Mag. Res.* **14** 280
Diehl P, Moia F and Bösiger H 1980 *J. Mag. Res.* **41** 336
Diehl P and Jokisaari J 1982 *Chem. Phys. Lett.* **87** 494
Diehl P, Jokisaari J and Moia F 1982a *J. Mag. Res.* **49** 498
Diehl P, Jokisaari J and Moia F 1982b *J. Mol. Struct.* **96** 107
Diehl P, Jokisaari J, Müller S and Väänänen T 1983 *Org. Mag. Res.* **21** 143
Diehl P and Khetrapal C L 1969 *NMR—Basic principles and progress* (Berlin, Heidelberg: Springer Verlag) Vol. 1
Dombi G, Amerin J and Diehl P 1980 *Org. Mag. Res.* **13** 224
Emsley J W and Lindon J C 1975 *NMR spectroscopy using liquid crystals solvents* (Oxford: Pergamon)
Jokisaari J and Hiltunen Y 1983 *Mol. Phys.* **50** 1013
Jokisaari J, Räisänen K and Väänänen T 1981 *J. Mag. Res.* **42** 396
Khetrapal C L and Becker E D 1981 *J. Mag. Res.* **43** 8
Khetrapal C L, Chatterjee C L and Yeh H J 1980 *Chem. Phys. Lett.* **76** 553
Khetrapal C L, Govil G and Yeh H J C 1984 *J. Mol. Struct.* **116** 303
Khetrapal C L and Kunwar A C 1977 *Adv. Mag. Res.* **9** 301

- Khetrapal C L and Kunwar A C 1981a *Chem. Phys. Lett.* **82** 170
Khetrapal C L and Kunwar A C 1981b *Mol. Cryst. Liq. Cryst.* **72** 13
Khetrapal C L and Kunwar A C 1982 *J. Phys. Chem.* **86** 4815
Khetrapal C L and Kunwar A C 1983 *Adv. Liq. Cryst.* **6** 173
Khetrapal C L and Kunwar A C 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* **93** 1215
Khetrapal C L, Kunwar A C and Lakshminarayana M R 1984a *Liq. Cryst. Ordered Fluids* **4** 1033
Khetrapal C L, Kunwar A C and Lakshminarayana M R 1984b *Mol. Cryst. Liq. Cryst.* **111** 189
Khetrapal C L, Kunwar A C, Tracey A S and Diehl P 1975 *NMR—Basic principles and progress* (Berlin, Heidelberg: Springer Verlag) Vol. 9
Lakshminarayana M R, Kunwar A C and Khetrapal C L 1984 *J. Mag. Res.* **60** 184
Raghothama S 1984 *J. Mag. Res.* **57** 294
Sinha K P, Subburam R and Khetrapal C L 1983a *Chem. Phys. Lett.* **96** 472
Sinha K P, Subburam R and Khetrapal C L 1983b *Mol. Cryst. Liq. Cryst.* **94** 375
Sinha K P, Subburam R, Kunwar A C and Khetrapal C L 1983c *Mol. Cryst. Liq. Cryst.* **101** 283
Subburam R 1984 *Oriented molecules—Theoretical studies on mixed liquid crystals of opposite diamagnetic anisotropies and experimental NMR results in individual and mixed liquid crystals* Ph.D. Thesis, Indian Institute of Science, Bangalore
Suryaprakash N, Kunwar A C and Khetrapal C L 1983a *J. Mag. Res.* **54** 502
Suryaprakash N, Kunwar A C and Khetrapal C L 1983b *J. Organomet. Chem.* **252** 301
Suryaprakash N, Kunwar A C and Khetrapal C L 1984 *Chem. Phys. Lett.* **107** 333
Suryaprakash N, Raghothama S, Kunwar A C, Khetrapal C L, Baiwir M and Llabres G 1984 *J. Organomet. Chem.* **277** 359