This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 23 February 2013, At: 03:04
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Average Orientation of Molecules Dissolved in Nematic Liquid Crystals of Opposite Diamagnetic Anisotropies

C. L. Khetrapal [a b c] & A. C. Kunwar [a]
[a] Raman Research Institute, Bangalore, 560080, India
[b] Bangalore NMR Facility, Indian Institute of Science, Bangalore, 560012, India
[c] National Institutes of Health, Bethesda, Maryland, 20205, USA
Version of record first published: 21 Mar 2007.

To cite this article: C. L. Khetrapal & A. C. Kunwar (1981): Average Orientation of Molecules Dissolved in Nematic Liquid Crystals of Opposite Diamagnetic Anisotropies, Molecular Crystals and Liquid Crystals, 72:1, 13-16

To link to this article: http://dx.doi.org/10.1080/01406568108084031

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:04 23 February 2013

Mol. Cryst. Liq. Cryst. Vol. 72 (Letters), pp. 13-16
0140-6566/81/7201-0013$06.50/0
©1981, Gordon and Breach, Science Publishers, Inc.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:04 23 February 2013

AVERAGE ORIENTATION OF MOLECULES DISSOLVED IN NEMATIC LIQUID CRYSTALS OF OPPOSITE DIAMAGNETIC ANISOTROPIES

C.L.KHETRAPAL[1,2,3] and A.C.KUNWAR[1]

[1]Raman Research Institute, Bangalore 560080, India

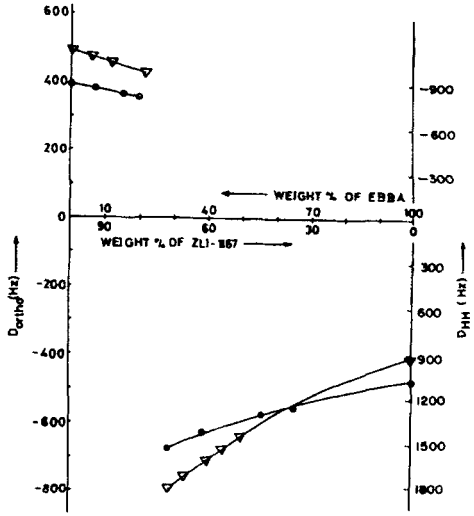
[2]Bangalore NMR Facility, Indian Institute of Science, Bangalore 560012, India

[3]National Institutes of Health, Bethesda, Maryland-20205, USA

(Submitted for Publication May 19, 1981)

ZLI-1167 is a ternary mixture of nematic liquid crystals with negative diamagnetic anisotropy. It has, therefore, been used as a solvent where the spinning of the samples around the vertical axis in the conventional electromagnets without destroying the orientation of the dissolved molecules is possible in NMR experiments. This results in sharp lines with widths up to 1 Hz in the spectra.[1,2] In an NMR system using a superconducting magnet (where the magnetic field direction is along the axis of spinning of the sample), it is possible to use even the nematic liquid crystals with positive diamagnetic anisotropy such as N-(p'-methoxybenzylidene)-p-n-butylaniline (MBBA) or N-(p'-ethoxybenzylidene)-p-n-butylaniline (EBBA) to obtain the spectra with sample spinning with equally sharp lines.[3] The orientational behaviour of the dissolved molecules as a function of relative concentrations of the two solvents is investigated and the results are reported in the present communication.

Proton NMR spectra of acetonitrile, benzene and 2,1,3-benzoselenadiazole were studied on a Bruker WH-270 FT-NMR spectrometer at 21°C. One hundred free induction decays were accumulated in each case and Fourier transformed with the help of a 20K core memory BNC-12 computer. Nearly 3 weight per cent solutions of acetonitrile, benzene and 2,1,3-benzoselenadiazole in EBBA and ZLI-1167 were first studied. Known amounts of the solution in EBBA (I) was then added to the solution in ZLI-1167 (II) and the spectra recorded. The concentration of (I) was gradually increased and the spectra were obtained at each concentration. The spectra of benzene and 2,1,3-benzoselenadiazole were analysed iteratively with the help of the LAOCOONOR programme.[4] Typical derived parameters namely the chemical shifts ($\nu_i - \nu_j$), the direct (D_{ij}) and the indirect (J_{ij}) coupling constants between nuclei i and j for 2,1,3-benzoselenadiazole are reported in table 1. A typical plot of the dipolar coupling



Dipole couplings between methyl protons (D_{HH}) in acetonitrile (O) and those between ortho protons (D_{ortho}) in benzene (▽) as a function of relative concentrations of EBBA and ZLI-1167.

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:04 23 February 2013

TABLE 1. Spectral parameters for 2,1,3-selenadiazole oriented in the nematic phases of ZLI-1167 and EBBA

Weight per cent of ZLI-1167	Parameters (Hz)[a]				
	D_{12}	D_{13}	D_{14}	D_{23}	$(\nu_1 - \nu_2)$[b]
100	1108	38	-30	-266	-187
90	1033	40	-23	-208	-185
80	978	42	-18	-164	-186
70	-1752	-88	21	191	36
0	- 759	-63	-15	-129	- 45

[a] Assumed J-values: J_{12}=9.12, J_{13}=1.19, J_{14}=0.87, J_{23}=6.40 Hz.

[b] at 270 MHz

between the methyl protons in acetonitrile obtained directly from the triplet due to such protons against the relative weight percentages of the liquid crystals is given in fig.1. The figure also includes the dipolar coupling between ortho protons in benzene as a function of relative concentrations of the two nematic solvents. It is observed from fig. 1 that the dipolar couplings first decrease gradually by the addition of (I) until at a critical concentration, the values abruptly change to twice with opposite signs. A further increase in the concentration of (I) changes the coupling constants smoothly. The behaviour of the various dipolar couplings as a function of the relative concentrations of the the two solvents in 2,1,3-benzoselenadiazole which needs two independent parameters to describe the molecular order is reproduced in the table. The resulting change of the direct couplings $[D(3\cos^2\alpha - 1)]$, from D to -2D is attributed to a change of the angle (α) between the applied magnetic field

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:04 23 February 2013

and the liquid crystal optical axis from 90^{o} in ZLI-1167 to 0^{o} in EBBA. The results are also confirmed by the relative signs of the direct and the indirect coupling constants in the two solvents. It is interesting to mention that the switch-over of the orientations in all the cases occurs when the weight per cent of ZLI-1167 is nearly 77%. The behaviour of the mixed solvents in the vicinity of the critical concentration is being investigated more closely as a function of temperature.

The method may be used to determine the chemical shift anisotropy without referring to the isotropic value of the chemical shift. One has to determine the chemical shifts close to the critical concentration. It may also be used for the determination of the dipolar couplings between heteronuclei which normally cannot be determined as the splittings are dependent upon $|J+2D|$.

The results suggest a simple experiment to change the angle between the liquid crystal optic axis and the magnetic field direction from 90^{o} to 0^{o} with the result that the anisotropic parameters change from -0.5 to 1.0 times the original value. A similar observation has been reported earlier with the help of simultaneous application of the electric and magnetic fields[5] orthogonal to each other.

REFERENCES

1. P.Diehl, H.Bosiger and H.Zimmerman, J.Magn.Reson. 31, 113 (1979).
2. A.Saupe (Private communication)
3. C.L.Khetrapal and A.C.Kunwar, Specialist Periodical Reports, NMR (The Royal Society of Chemistry), London, Vol.9 (1980).
4. P.Diehl, C.L.Khetrapal and H.P.Kellerhals, Mol. Phys., 15, 333 (1968).
5. P.Diehl, C.L.Khetrapal, H.P.Kellerhals, U.Lienhard and W.Niederberger, J.Magn.Reson., 1, 527 (1969).

Our sincere thanks are due to Dr. E.D. Becker for critical comments.

Downloaded by [Tomsk State University of Control Systems and Radio] at 03:04 23 February 2013