

signals at τ 9.10 (d, 3 H, $J=6$ Hz, CHCH_3), τ 8.33 (s, 3 H, $\text{CH}_3\text{COCH}_2-$), τ 7.82 (s, 3 H, NCH_3 or $\text{CH}_3\text{CO}-$), τ 7.77 (s, 3 H, NCH_3 or $\text{CH}_3\text{CO}-$), τ 7.55 (d, 2 H, $J=5$ Hz, $-\text{COCH}_2\text{CH}-$), τ 6.48 (t, 1 H, $J=5$ Hz, $-\text{COCH}_2\text{CHN}$), τ 5.38 (s, 1 H, OH, concentration dependent) and τ 2.2–2.9 (m, 5 H, phenyl group). Two olefinic protons exhibits an ABX₂ pattern with τ_A 3.82 and τ_B 3.14 ($J_{AB}=16$ Hz, $J_{AX_2}=1.1$ Hz, $J_{BX_2}=6$ Hz) indicating the $-\text{CH}_2-\text{CH}_B=\text{CH}_A-\text{CO}-$ system. The large AB coupling implies a *trans* configuration for these protons.

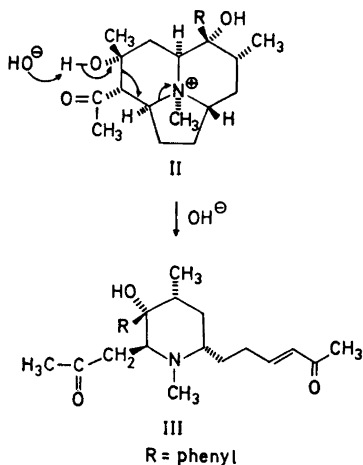


Fig. 3. Alkaline degradation of crepidine methiodide (II).

A full report on the isolation and structural determination of the alkaloids found in *D. crepidatum* will be published later.

Acknowledgements. We are indebted to Dr. Björn Luning for his interest in this work. A fellowship from *Stiftelsen Bengt Lundqvists Minne* to one of us (K.L.) is gratefully acknowledged. This work was supported by the *Tri-Centennial Fund of the Bank of Sweden* and the *Swedish Natural Science Research Council*.

1. Granelli, I. and Leander, K. *Acta Chem. Scand.* **24** (1970) 1108.
 2. Elander, M., Leander, K., Rosenblom, J. and Ruusa, E. *Unpublished results*.
 3. Pilotti, A.-M. *Acta Cryst.* (1971). *In press*.
- Received november 17, 1970.

Acta Chem. Scand. **24** (1970) No. 10

Solute Alignment in the Nematic Mesophase

GEOFFREY R. LUCKHURST and
FRANCISKA SUNDHOLM*

*Department of Chemistry, The University,
Southampton, SO9 5NH, England*

The anisotropy in the solute-solvent intermolecular potential results in the partial alignment of non-spherical solutes by nematogenic solvents. The nature of the anisotropic potential is conveniently studied by measuring the ordering matrix $\bar{\rho}$ which describes the solute alignment.^{1,2} The elements of the matrix are defined by

$$\bar{\rho}_{ij} = \frac{3\overline{l_i l_j} - \delta_{ij}}{2}$$

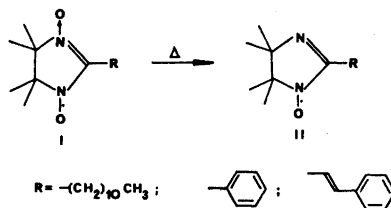
where the bar denotes an ensemble average and l_i is the direction cosine between the i th molecular axis and the optic axis of the mesophase.³ When the solute is paramagnetic the ordering matrix may be determined from the electron resonance spectra of the solute, both above and below the nematic-isotropic transition point.⁴ The resulting shifts in the g factor and coupling constants are directly related to the elements of the ordering matrix by

$$\delta g = \sum_{i,j} g'_{ij} \bar{\rho}_{ij}$$

and

$$\delta a = \sum_{i,j} A'_{ij} \bar{\rho}_{ij}$$

where g' and A' are the anisotropic g and hyperfine tensors.⁴ In this communication we report such measurements for 2-substituted 4,4,5,5-tetramethyl-1,3-dioxymidazolines (I) which were prepared by employing the synthesis described by Osiecki and Ullman.⁵



* Permanent address: Department of Chemistry, University of Helsinki, Helsinki, Finland.

Table 1.

Paramagnetic probe	Isotropic nitrogen coupling constant (MHz)			Hyperfine shifts (MHz)		Nitrogen anisotropic hyperfine tensor A'_{33} (MHz)	Degree of alignment	
	Toluene	4,4'-Dimethoxy-azoxybenzene	Vari-Light VL 462-N	4,4'-Dimethoxy-azoxybenzene	Vari-Light VL 462-N		4,4'-Dimethoxy-azoxybenzene	Vari-Light VL 462-N
I R=undecyl	20.80	20.66	20.86	-0.31	-0.17	31.18	-0.0098	-0.0052
II R=undecyl $\left\{ \begin{array}{l} 1 \\ 3 \end{array} \right.$	26.25	26.31	26.14	-1.04	-1.04	35.39	-0.0293	-0.0291
	11.23	11.23	11.12	-0.70	-0.70	22.00	-0.032	-0.032
I R=styryl	21.06	21.42	21.42	-4.15	-3.87	32.88	-0.127	-0.118
II R=styryl $\left\{ \begin{array}{l} 1 \\ 3 \end{array} \right.$	26.25	26.33	25.97	-4.74	-4.55	38.89	-0.121	-0.116
	12.02	11.93	11.93	-3.51	-2.95	21.97	-0.159	-0.134
I R=phenyl	21.0	21.0	21.0	-3.6	-3.4	32.3	-0.11	-0.11
I R=phenyl $\left\{ \begin{array}{l} 1 \\ 3 \end{array} \right.$	25.63	26.31	25.63	-4.38	-3.87	35.31	-0.124	-0.109
	11.93	11.59	11.93	-2.47	-2.44	22.39	-0.110	-0.109

The electron resonance spectra of all the radicals were measured in both a high- and low-temperature nematic liquid crystal. One, 4,4'-dimethoxyazoxybenzene, has a nematic-isotropic transition point of 135°C, whereas that of the other (VL-462-N) is about 35°C. The low-temperature nematogen was purchased from the Vari-Light Corporation and is thought to consist largely of *N*-(4-methoxybenzylidene)-4-butylaniline which in the pure state has a nematic-isotropic transition temperature of 47°C. The presence of impurities in the solvent will not, however, effect the comparison of the solute alignment provided such comparisons are made at the same reduced temperature.⁶ By the reduced temperature we simply mean the ratio of the temperature to the nematic-isotropic transition point. The electron resonance spectra of the solutes in the two mesophases were measured at a reduced temperature of 0.97. The first paramagnetic probe to be studied was 2-undecyl-4,4,5,5-tetramethyl-1,3-dioxyimidazoline. Its spectrum consists of a quintet splitting from the two equivalent nitrogen nuclei and a triplet from the two α -protons in the alkyl chain. We were surprised to discover that the nitrogen hyperfine shift in both nematogens was only about 0.3 MHz. To see if this small shift corresponds to an equally small degree of solute alignment

the components of the nitrogen hyperfine tensor are required. As expected, the tensor is cylindrically symmetric about an axis 3 perpendicular to the plane of the imidazoline ring. The component A'_{33} was determined from the spectrum of the radical in a toluene glass and is given in Table 1, together with the shifts. Since the hyperfine tensor is cylindrically symmetric the shift in the coupling constant is directly proportional to the component e_{33} along the symmetry axis:

$$\delta a = A'_{33} e_{33}$$

Accordingly, the nitrogen shifts, for this and all other nitroxides which were studied, can only give the degree of alignment for the 3-axis, perpendicular to the ring. This degree of alignment e_{33} , given in the table, is seen to be about -0.007, an extremely small value.

The dioxyimidazolines were found to be thermally unstable and decomposed to another paramagnetic species whose electron resonance spectrum is in accord with structure (II), a 2-substituted 4,4,5,5-tetramethyl-1-oxyimidazoline. Its spectrum was also measured in both mesophases, and the shifts for the two nitrogen splittings are in the table. The anisotropic nitrogen hyperfine tensors in (II) are both cylindrically symmetric and the components along the symmetry axis were

determined from the spectrum in frozen toluene. These components are given in the table, together with the degree of alignment ρ_{33} which is slightly larger than for (I), but still extremely small. Our observations might indicate an unusually low anisotropy in the solute-solvent intermolecular potential,² which would be consistent with the adoption of a spherical configuration by the alkyl chain.

We have attempted to test this hypothesis by synthesising solutes containing rigid substituents in the 2 position. The hyperfine shifts measured in both solvents are given in the table, together with the components of the anisotropic nitrogen hyperfine tensors. When R is a styryl group the degree of alignment, ρ_{33} , is found to be about -0.1 and a similar alignment was found for the product of thermal decomposition (II). The radical (I) with a phenyl group in the 2 position is unstable in the nematogens, and we were not able to measure the shifts with the same accuracy for this compound. However, the degree of alignment for radicals (I) and (II) was again found to be about -0.1.

The marked difference in ρ_{33} between aliphatic and aromatic substituted radicals might indicate a largely spherical configuration for the flexible alkyl chain. However, our observation of high degrees of alignment for other alkyl-substituted solutes makes us believe that the explanation for this difference lies elsewhere. In the case of aromatic substituents the long axis of the substituent is parallel to the plane of the imidazoline ring, and so ρ_{33} corresponds to one of the principal components of the ordering matrix. Let us now suppose that the alkyl substituent is also rigid and adopts an elongated configuration. If this is so, then the 5.61 MHz splitting observed in (I) and 4.46 MHz splitting in (II) for the α -protons in the alkyl-chain, shows that they are symmetrically placed below the plane of the ring with the back-bone of the chain, the z-axis, making an angle of $144^\circ 44'$ with this plane. Accordingly, the 3-axis no longer corresponds to a principal axis of the ordering matrix. Because of the length of the alkyl chain, in comparison with the dimensions of the ring, the ordering matrix will be approximately cylindrically symmetric about the z-axis. The ordering matrix transforms like a second rank tensor³ and so ρ_{33} is related to the principal components of ρ by

$$\rho_{33} = \sum_i l_{i3} l_{i3} \rho_{ii}$$

which reduces to

$$\rho_{33} = \frac{(3l_{z3}^2 - 1)}{2} \rho_{zz}$$

for an ordering matrix with cylindrical symmetry. By analogy with the other solutes the component, ρ_{zz} along the symmetry axis should be about 0.2. Molecular models of the alkyl substituted nitroxides show that the angle between the 3 and z axes is approximately 55° . The estimated value of ρ_{33} , for an elongated chain, is then -0.002, which is in good agreement with the experimental values. This theoretical analysis suggests, therefore, that the alkyl chain adopts an elongated configuration in the mesophase.

We wish to draw attention to two other features of the results given in the table. Firstly, the degree of alignment of all solutes in 4,4'-dimethoxyazoxybenzene is greater than in N-(4-methoxybenzylidene)-4-butylaniline (VL-462-N). This is in keeping with the notion that the order in a nematogenic mesophase increases with the nematic-isotropic transition temperature.⁷ Secondly, the alignment of solutes (I) and (II) with the same substituent are comparable. Presumably the gross molecular shape is important in determining the solute-solvent intermolecular potential rather than the details of the electronic structure.

We are grateful to the *Science Research Council* for a grant towards the cost of the Varian E-3 spectrometer used to make these measurements. We also wish to thank the *Royal Society* for the award of a Fellowship to F.S.

1. Saupe, A. *Mol. Cryst.* **1** (1966) 527.
2. Chen, D. H., James, P. G. and Luckhurst, G. R. *Mol. Crystals and Liq. Crystals* **8** (1969) 71.
3. Saupe, A. *Z. Naturforsch.* **19A** (1964) 161.
4. Luckhurst, G. R. *Mol. Cryst.* **2** (1967) 363.
5. Osiecki, J. H. and Ullman, E. F. *J. Am. Chem. Soc.* **90** (1968) 1078.
6. Chen, D. H. and Luckhurst, G. R. *Trans. Faraday Soc.* **65** (1969) 656.
7. Luckhurst, G. R. and Ockwell, J. N. *To be published.*

Received November 18, 1970.