

TABLE I
Precision

Sl. No.	Standard %	Per cent		Standard Deviation	
		La	Ce	Nd	Sm
1	1.0	0.98	0.35	0.51	0.16
2	0.5	1.03	0.69	0.74	1.7
3	0.1	3.4	7.7	2.5	7.8
4	0.025	17.1	7.0	9.1	7.7
5	0.01	42.0	37.4	21.1	25.7

TABLE II
Theoretical minimum detection limits (TMDL)

Sl. No.	Element	Back-ground counts N_b	$\sigma = \sqrt{N_b}$	3σ	*Net counts for 100 sec.	TMDL ppm
1	La	9,430	97	291	2,239	32.5
2	Ce	19,419	139	417	3,575	29.2
3	Nd	32,052	179	537	6,148	21.8
4	Sm	25,652	160	480	3,375	35.6

* Net counts are for 250 ppm standard.

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MESOMORPHIC BEHAVIOUR OF SOME NAPHTHALENE SCHIFF BASES: 4-*n*-ALKOXY- 1-NAPHTHYLIDENE-*p*-*n*-BUTOXYANILINES

MESOMORPHISM is exhibited mainly by compounds with relatively rigid, polar, rod-shaped molecules that tend to be oriented with their long axes parallel because of the intermolecular attractive forces. It is generally found that nematic compounds have high melting points, because, the molecular characteristics that are necessary for nematic mesomorphism, also produce stable crystalline lattices. For practical applications

nematic mesophases which exist near room temperature are desirable. Pure low melting mesomorphic compounds can be prepared by the introduction of dissymmetry in the molecule or by the introduction of lateral substitutions in the molecule.

The introduction of a naphthalene nucleus into a potentially mesomorphic compound should affect its mesomorphic behaviour considerably. Dave *et al.* have observed that the introduction of a 1, 4-substituted naphthalene nucleus considerably reduces the mesomorphic properties of the compounds.^{1,2} To further investigate this phenomenon, the following Schiff base compounds of the series 4-*n*-alkoxy-1-naphthylidene-*p*-*n*-butoxyanilines have been synthesized by condensing various 4-*n*-alkoxy-1-naphthaldehydes¹ with *p*-*n*-butoxyaniline³. The mesomorphic properties of these compounds have been investigated under a Leitz Ortholux Polarizing Microscope, equipped with Leitz heating stage. The melting points and transition temperatures of these compounds are given in Table I. The combustion analysis for C, H and N for these compounds agree well with their calculated values.

TABLE I

Compound	Alkyl Group	Solid-nematic	Nematic-Isotropic or Solid-Isotropic	
1	CH ₃	..	91.0	
2	C ₂ H ₅	(70.5)	88.0 ^a	84.0 ^b
3	C ₂ H ₇	(56.5)	80.0	
4	C ₄ H ₉	(70.5)	87.5	
5	C ₅ H ₁₁	(61.5)	80.0 ^a	74.0 ^b

Figures in parenthesis indicate monotropy.
^a, stable modification.
^b, metastable modification.

The compound No. 1 is non-mesomorphic; the rest are monotropic nematic in nature. Compounds No. 2 and 5 exhibit two solid modifications. The metastable solid modification C_{II} is obtained by a sudden cooling of the isotropic liquid. Both the solid forms on heating give the isotropic liquid. The metastable solid modification melts at a lower temperature than the stable solid modification C_I. In both the cases the isotropic liquid cools to give a monotropic nematic phase. These can be represented as follows in Fig. 1.

The non-mesomorphism of compound No. 1 can be attributed to its relatively high melting point. It is observed that the melting points and transition temperatures of these compounds are higher than the corresponding members of the series 4-*n*-alkoxy-1-

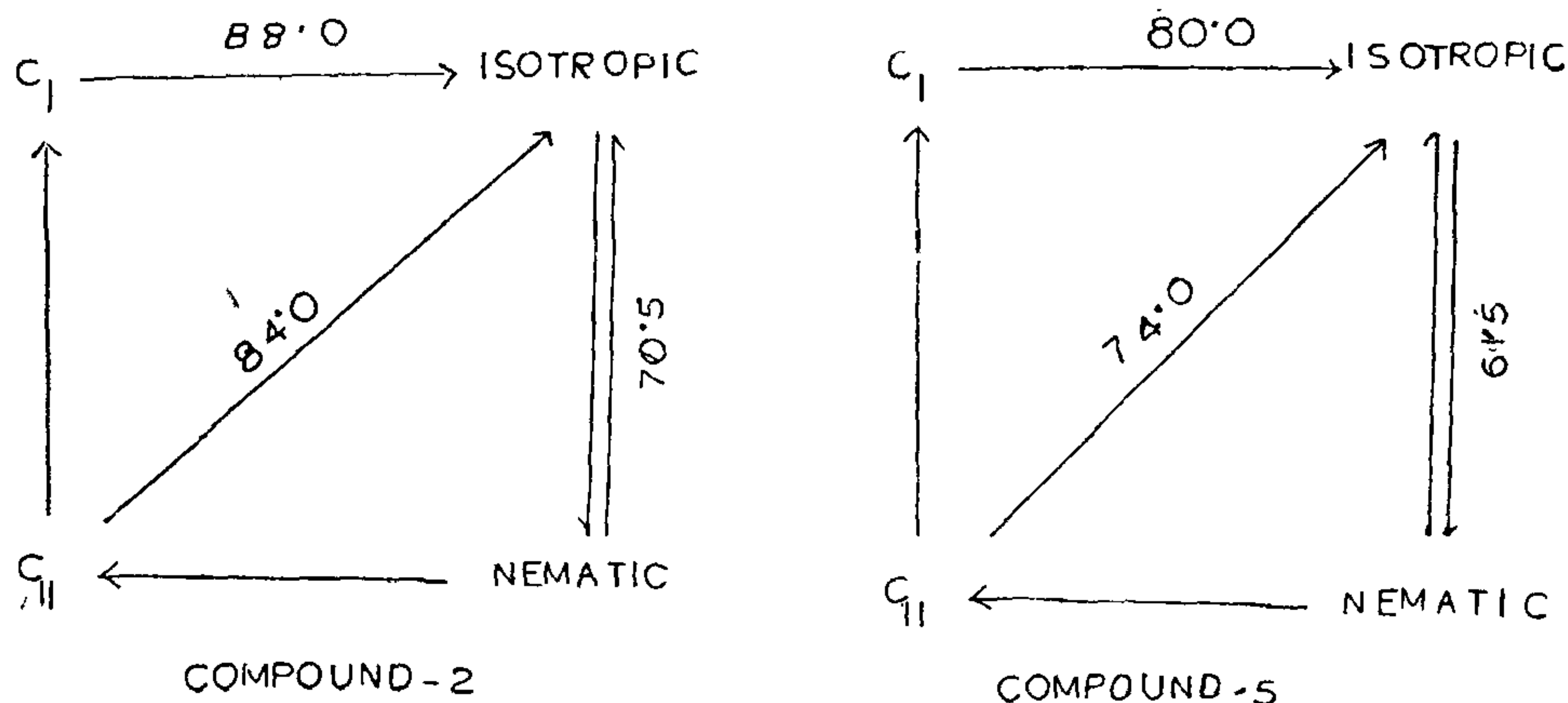


FIG. 1

naphthylidene-*p*-n-amyloxyanilines. This compares with the results of Dave and Patel in their study of the corresponding benzylidene series⁴. Further work is in progress.

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EFFECT OF SOLVENT ON ABSORPTION AND FLUORESCENCE SPECTRA OF ISOMERIC TRIFLUOROMETHYL BENZONITRILE ($C_6H_4CF_3CN$)—ESTIMATION OF DIPOLE MOMENT CHANGE

THE study of solvent effect upon absorption and fluorescence spectra is one of the methods to understand nature of the electronic excited and ground states. In solutions, the position of the fluorescence bands under certain circumstances show marked solvent effect. It is usually the solvent polarity which principally affects the π - π transitions and particularly if such transitions have some mixed intramolecular charge

transfer contribution. If the charge transfer character is great, hydrogen bonding solvent as well as the polar solvent shift fluorescence to longer wavelength¹.

Table I giving the absorption and fluorescence wavelength maxima of isomeric trifluorobenzonitriles ($C_6H_4CF_3CN$) in ethanol, water and cyclohexane shows the effect of solvent on the corresponding spectra. In these molecules the wavelength of fluorescence maxima shows a considerable shift in going from non-polar to polar solvent. It is clear from these results that these molecules become more polar in the excited state than in the ground state showing larger dependency of fluorescence band maxima on solvent than absorption.

TABLE I

Solvent	Wavelength (m μ)					
	Absorption			Fluorescence		
	Ortho	Meta	Para	Ortho	Meta	Para
Cyclohexane	271.0	269.9	270.7	327	329	332
Water	271.4	270.2	272.5	339	342	343
Ethanol	271.5	270.5	272.0	340	342	344

Further, the study of the wavelength of absorption and fluorescence spectra in different solvents can be utilized for an estimation of the order of magnitude of the dipole moment change from the ground state to the first excited singlet state. The relation for such an estimation is given by (using Oshika's theory)^{2, 3}

$$-hc(\nu_f^m - \nu_a^m) \approx \text{constant} + 2(D - 1)/2D + 1 - 2(n^2 - 1)/2n^2 + 1 \times (\mu_e - \mu_g)^2/a^3$$

where ν_f^m and ν_a^m are the fluorescence and absorption frequencies (in wave numbers) of corresponding maxima