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Phase Transition Studies in *p*-Nitrobenzylidene-*p*-*n*-Alkoxy Anilines

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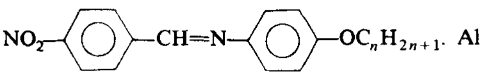
Phase transition studies have been carried out in four members (n = 7, 8, 10 and 12) of a homologous series  $NO_2-C_6H_4-CH{=}N-C_6H_4-OC_nH_{2n+1}$. All these compounds exhibit mesomorphism. Principle techniques used were DSC and positron annihilation (PAT). Transition temperatures and the associated changes in enthalpy have been measured. On rapid cooling (> 16 K/min), two members of this series (n = 7 and 8) exhibit super cooling of the mesophase. In these cases, formation of a metastable solid phase has also been observed. *p*-nitrobenzylidene-*p*-*n*-heptyloxyaniline, on annealing in the solid phase undergoes transformation into a solid phase which in turn transforms to the mesomorphic phase at a higher temperature. In the same compound, PAT results in cooling cycle indicate formation of yet another solid phase not observed by DSC. In this series the thermal stability of the mesomorphic phase is found to increase with increasing chain length.

1. INTRODUCTION

Recently great interest has been shown in mesogens having positive dielectric anisotropy because of their extensive application in electro-optical display devices.[1] Such a property is normally shown by lath

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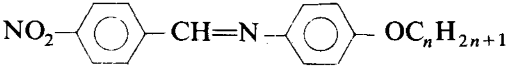
like organic compounds having a highly polar terminal substituents like —NO_2 or —CN. A number of homologous series with positive dielectric anisotropy have been reported.[2-7] In the present work a simple homologous series of *p*-nitrobenzylidene-*p*-*n*-alkoxy anilines  has been investigated. The synthesis of these compounds has been reported elsewhere.[8] Only the higher homologue ($n > 6$) of this series exhibit mesomorphism. A detailed study of phase transitions in four such members ($n = 7$, 8, 10 and 12) has been undertaken. Principal techniques used in this study are the differential scanning calorimetry (DSC) and the positron annihilation technique (PAT). Use of the latter technique for such studies is now well established.[9] Here we present the results of this investigation.

2. EXPERIMENTAL

2.1 Samples

Compounds used in the present investigation were synthesized as described elsewhere.[8] They were recrystallized from ethanol until constant transition temperatures were obtained. All these compounds gave satisfactory elemental analysis.

2.2 Differential scanning calorimetry

Differential scanning calorimetry was carried out using Perkin-Elmer Differential Scanning Calorimeter Model DSC-1B. The calorimeter was calibrated using standard references. Transition temperature and the associated change in enthalpy were determined from the position of the peak and the area under it. For such determinations a heating rate of 4 K/min was always used. Necessary correction for any super heating effect was always applied. To study super cooling of the mesophase and formation of metastable solid phase in various samples, different heating and cooling rates were employed.

2.3 Positron annihilation technique

Positron annihilation studies consisted of measuring the positron lifetimes in a sample as a function of temperature. These measurements were carried out using a standard timing spectrometer details of which are described elsewhere.[10] It had a time resolution of 325 ps (fwhm) at ^{22}Na energies. A ^{22}Na-radioactive source was used as a source of positrons. Such a source was prepared by evaporating aqueous solution of ^{22}NaCl on a thin Mylar film and covering it with another similar film. The source was sealed from all sides to avoid any leakage of radioactivity into the sample. Sample and the sealed source were contained in a copper cell, details of which are described elsewhere.[11] In the sample cell the sealed source was placed in such a manner so that it was surrounded by sufficient sample thickness as to ensure complete absorption of positrons emitted by the source within the sample. Sample temperature was maintained thermostatically to a constancy of ± 0.1 K.

Measurements were carried out as a function of temperature so as to cover various phase transitions exhibited by a sample. At each temperature the lifetime data were accumulated over a 10–15 hour period to give at least 10^6 counts in a time spectrum.

3. RESULTS AND DISCUSSION

Results obtained in this investigation are given in Tables I and II. The thermodynamic data related to various transitions observed are given in Table I. The smectic mesophases exhibited fan shaped texture which suggests that the mesophase is of the smectic A type. The positron annihilation parameters in various phases are given in Table II. Some of the typical results are described below.

In *p*-nitrobenzylidene-*p*-*n*-heptyloxy aniline (NBHOA) ($n = 7$), the nematic–smectic transition is found to be monotropic. On the basis of DSC measurements, various phase transitions during heating and cooling cycles can be represented as follows:

$$\begin{tikzcd}
\text{Solid} \arrow[rr, "333\text{ K}"] & & \text{Nematic} \arrow[rr, "350\text{ K}", leftrightarrow] \arrow[dl, "326\text{ K}"] & & \text{Isotropic} \\
& \text{Smectic} \arrow[ul, "315\text{ K}"] & & &
\end{tikzcd}$$

The DSC curve for the heating cycle of a fast cooled sample (32 K/min) shows an exothermic peak at ~ 290 K which can be attributed to the crystallization of the upper cooled smectic phase. Such a peak is not observed for cooling rates lower than 16 K/min. Similar super cooling of the mesophase has also been observed in NBOOA ($n = 8$). A typical DSC curve for the heating cycle of a NBOOA sample prepared by cooling rapidly (32 K/min) from the isotropic liquid phase is shown in Figure 1. In this case two exothermic broad

TABLE I

Thermodynamic data of the phase transitions observed in *p*-nitrobenzylidene-*p*-*n*-alkyloxyanilines

Material	Phase Transition		Transition temperature DSC (K)	PAT (K)	Change in in enthalpy Kcal mol^{-1}	Change in entropy cal mol^{-1} K^{-1}
NBHOA	Solid	Nematic	333.0	328.5	14.3	42.8
	Nematic	Isotropic Liquid	350.0	348.0	0.11	0.32
NBOOA	Nematic	Smectic	326	331.5	—	—
	Smectic	Solid	315	315	—	—
	Solid	Smectic	336.0	334.5	7.4	21.9
	Smectic	Nematic	347.5	345.0	0.06	0.17
	Nematic	Isotropic Liquid	357.0	356.5	0.13	0.37
NBDOA	Solid	Smectic	336.0	339.0	7.3	21.7
	Smectic	Isotropic Liquid	367.0	368.0	0.32	0.88
NBDDOA	Solid	Smectic	330.1	335.0	4.35	13.2
	Smectic	Isotropic Liquid	369.5	370.5	0.22	0.6

TABLE II

Positron annihilation parameters in *p*-nitrobenzylidene-*p*-*n*-alkyloxyanilines

	Phase	τ_1(ns)	τ_2(ns)	I_2(%)	$\Delta\tau_2$(ns)
NBHOA	Solid	0.289 ± 0.005	0.98 ± 0.01	3.6 ± 0.83	
	Nematic	0.291 ± 0.002	0.69 ± 0.01	3.7 ± 0.49	0.29
	Isotropic	0.304 ± 0.005	0.64 ± 0.01	4.0 ± 0.83	0.05
NBOOA	Solid	0.289 ± 0.005	0.85 ± 0.01	3.2 ± 0.47	
	Smectic	0.291 ± 0.002	0.64 ± 0.01	5.2 ± 0.92	0.21
	Nematic	0.295 ± 0.005	0.55 ± 0.01	6.0 ± 1.05	0.09
	Isotropic	0.304 ± 0.005	0.50 ± 0.01	6.5 ± 0.87	0.05
NBDOA	Solid	0.273 ± 0.005	0.82 ± 0.01	4.1 ± 0.82	
	Smectic	0.274 ± 0.006	0.63 ± 0.01	4.5 ± 1.91	0.19
	Isotropic	0.273 ± 0.005	0.60 ± 0.01	4.0 ± 1.79	0.03
NBDDOA	Solid	0.274 ± 0.007	0.83 ± 0.01	3.9 ± 0.54	
	Smectic	0.264 ± 0.004	0.63 ± 0.01	4.3 ± 0.85	0.20
	Isotropic	0.264 ± 0.001	0.61 ± 0.01	4.2 ± 1.12	0.02

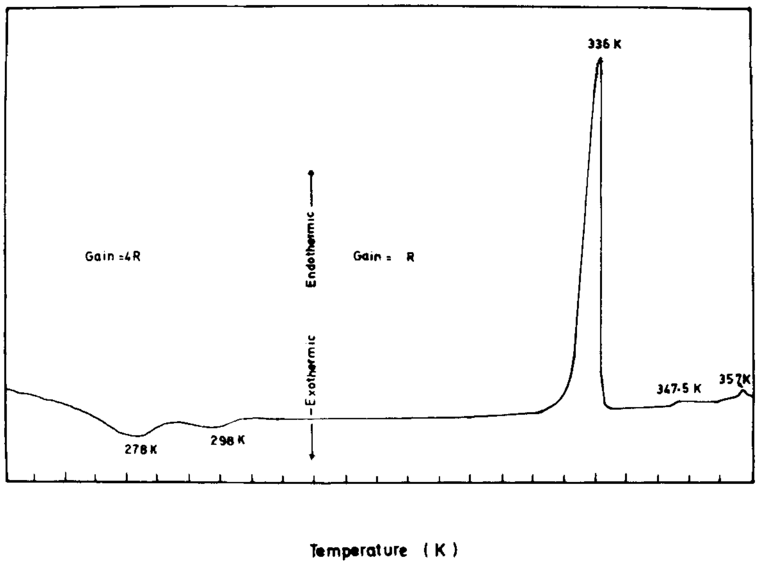


FIGURE 1 DSC Curve for the heating cycle of NBOOA sample which has been cooled from the isotropic phase at a rate of 32 K/min (Heating rate − 8 K/min).

peaks are seen at temperatures ~ 278 and ~ 298 K, respectively. On decreasing the cooling rate the area under the higher temperature peak decreases and is not perceptible at cooling rates lower than 8 K/min. However, the lower temperature peak is seen even at still lower cooling rates. The appearances of these two peaks could be interpreted in terms of super cooling of the smectic phase and a possible formation of a metastable solid modification. No super cooling was observed in case of the other two members (n = 10 and 12) of this series.

In case of NBHOA, on annealing the sample in the solid phase, the thermal analysis reveals formation of newer solid modification. On annealing this material at a temperature closer to the melting point for different times and then cooling (4 K/min) the sample to room temperature, a heating run (8 K/min) showed an additional endothermic peak at 339 K (Figure 2). The area under this peak is found to depend on the annealing time. However, the sum of the areas under the peaks at 333 K and 339 K is found to be independent of the annealing time. Thus on annealing, a fraction of the material undergoes a solid modification which goes to smectic phase at a higher temperature. This interpretation is supported by the X-ray diffraction results shown in Figure 3(a) and 3(b). These figures show the X-ray

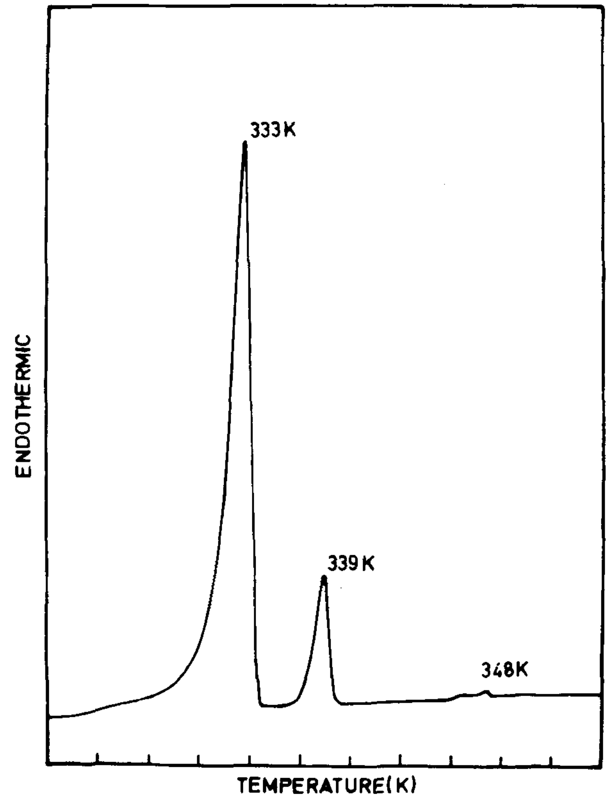


FIGURE 2 DSC curve for the heating cycle of a NBHOA sample annealed at 332 K.

diffractograms of unannealed and annealed samples, respectively. The annealing was carried out by keeping the sample at 332 K for 6 hours. The normalized peak intensities for various reflections in these two samples are given in Table III. It is clearly seen that some of the reflections on annealing get weakened while others get enhanced.

The positron lifetime data were analysed using a computational method developed by Tao.[12] Measured lifetime spectra could be fitted with two components, τ_1 and τ_2. Results of this analysis are given in Table II which gives average values of the annihilation parameters in various phases. The shorter component, τ_1, is attributed to the free annihilation of positron with the electrons belonging to the medium with a very small contribution from the decay of para-positronium. This component is in a way a measure of the average electron density in the medium. The longer component, τ_2, is due to the pick-off annihilation of the ortho-positronium. It is very sensitive to the environmental conditions. It is seen from Table II that the shorter component shows lesser susceptibility to a phase transition as compared to the longer component, τ_2. The intensity I_2 of the long lived component, which is a measure of the positronium formation probability in the medium, is found to be low (~ 4%). This could be attributed to the positronium inhibiting action of the $-NO_2$ group in the molecule. In each sample the long lived component τ_2 is found to decrease in going from a phase of higher degree of molecular order to that of a lesser degree of molecular order. This behaviour could be understood in terms of the changes in pick-off crossection due to different degrees of end to end linking of dipoles.

Temperature dependence of the positron annihilation parameters in NBHOA as obtained in the present study is shown in Figure 4. The

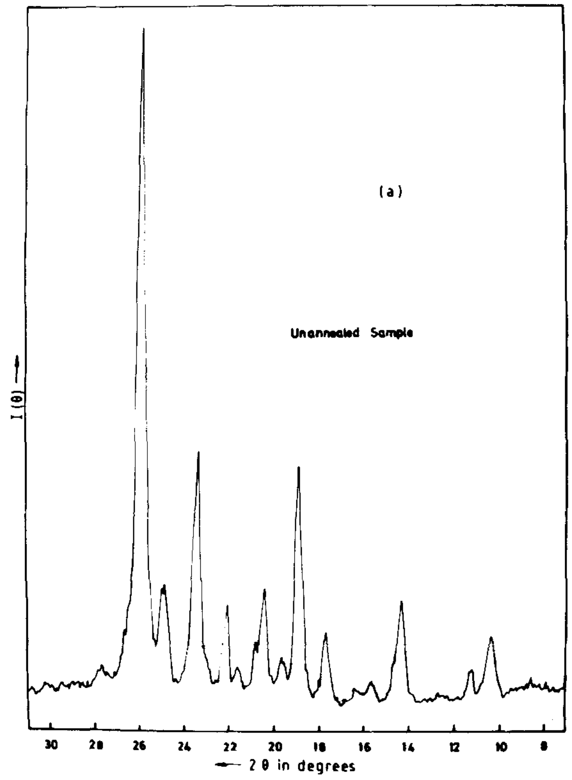


FIGURE 3 X-ray diffractograms of (a) unannealed and (b) annealed NBHOA samples.

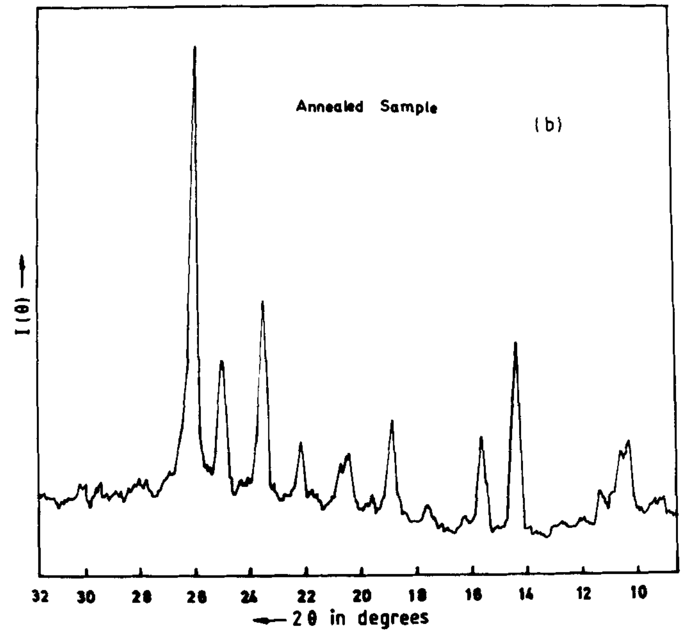


FIGURE 3 *Continued*

TABLE III

Normalised intensities (%) of the diffraction peaks observed in the diffractograms of unannealed and annealed samples

2θ(°)	I(θ) Unannealed sample	I(θ) Annealed sample
26.4	36.8	25.1
25.3	6.1	7.7
23.8	11.1	10.3
22.5	3.4	2.6
21.0	5.1	4.0
10.2	10.8	3.4
16.0	3.0	4.9
14.7	5.7	10.6
10.7	3.4	5.4

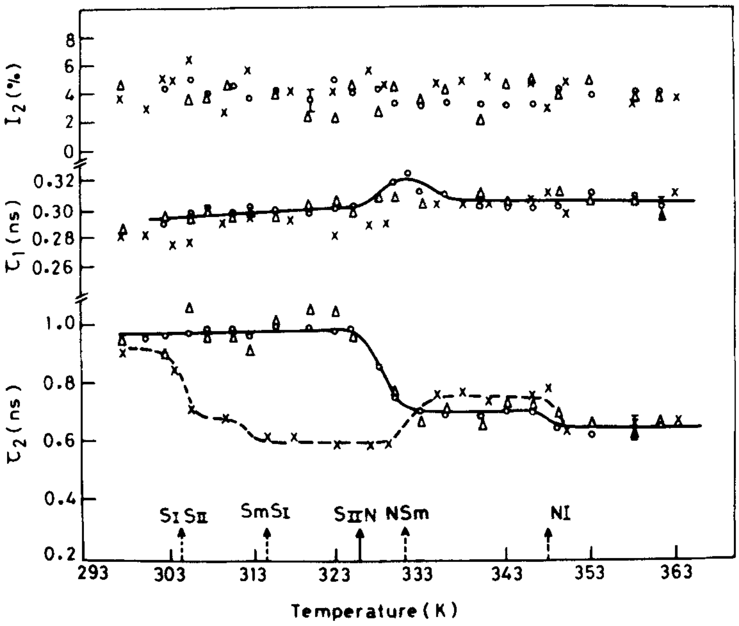
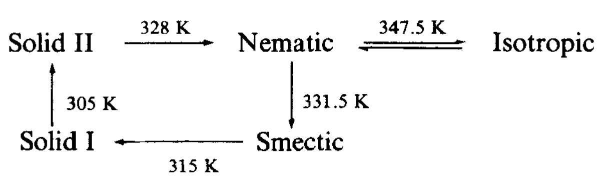


FIGURE 4 Temperature dependence of the positron annihilation parameters in NBHOA; heating cycle —O—, cooling cycle —×— and heating cycle of a quenched from the isotropic phase —△—.

phase transitions observed during heating cycle are similar to those observed by DSC. However, in the cooling cycle an additional solid phase (solid I) is observed. The existence of this phase has been confirmed by optical microscopy on the basis of textural changes when viewed in polarized light. The various phase transitions in this compound can now be represented by the following flow chart.



A comparison of the DSC and PAT results in case of this compound demonstrates the sensitivity of the later technique to phase transitions involving very little or no change in enthalpy but large changes in electronic environment to which positron annihilation is very sensitive.

The nematic (or smectic) → isotropic transition temperatures, determined by DSC given in Table I are lower than those reported in Ref. (8). This difference originates in the use of two different techniques, DSC and hot stage polarised microscopy, and different heating rates involved. Super heating effects are quite prominent in these materials. Further, a comparison between the DSC and PAT results reveals that the transition temperatures obtained by these two techniques are also different. This may be attributed to basic difference between them, one senses the enthalpic changes (DSC) while the other senses the changes in electronic environment (PAT). DSC is a dynamic technique, transition temperatures obtained by it depend on the heating rate, true thermodynamic transition temperatures are obtained only in the limiting case when the heating rate tends to zero. PAT on the other hand is a static technique, the results obtained by it are closer to thermodynamic values.

The data on transition temperatures given in Table I and in Ref. (8) do not show any definite odd-even effect. Similar to thermodynamic parameters, the positron annihilation parameters also do not reveal any definite odd-even effect. However, as seen from Table II, the τ_2 value in a given phase does show some weak odd-even effect. In any case the data is meagre to draw any definite conclusion.

It is interesting to note that contrary to general observation the mesophase to isotropic liquid transition temperature is found to increase with increasing chain length of the alkyl group. Such a behaviour can be understood in terms of the molecular structure of these compounds. These compounds are trans and acoplanar.[13] When two aromatic nuclei are not coplaner, it is possible for the termini of one molecule to interact strongly with one of the rings of another molecule, causing additional attractions and a more thermally stable mesophase as the terminus grows in length,[14,15] such a conclusion is supported by the positron annihilation results. In these compounds, the orthopositronium pick-off annihilation rate is found to increase with a decreasing degree of molecular order in the system. Orthopositronium undergoes pick-off annihilation preferentially at the negative end of the dipole. Therefore an increase in the ortho-posotronium pick-off annihilation rate indicates a corresponding increase in the availability of free dipole ends. Hence in a more ordered state like the solid phase, the positron annihilation results suggest that there is a lesser number of free dipole endings as compared to a disordered state like the isotropic liquid phase. Such a picture is in conformity with the possibility of the termini of one molecule interacting strongly with one of the rings of another molecule and thus decreasing the availability of free dipole endings with increasing degree of molecular order.[16]

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References

1. M. Schadt and W. Helfrich, *Appl. Lett.*, **18**, 127 (1971).
2. Patent No. 76, 136,630 Kokai (Japan); *Chem. Abstr.*, **87**, 1 (1971).
3. G. W. Gray, K. J. Harrison and A. Nash, *Electronics Lett.*, **9**, 130 (1973).
4. A. S. Orahovats, T. Zh. Radeva and S. L. *Spassov*, *Compt. Rend.*, **26**, 663 (1973).
5. B. K. Sadashiva, *Mol. Cryst. Liq. Cryst.*, **35**, 205 (1976).
6. J. Billard, J. C. Dubois and A. Zann, *J. Physique Colloq.*, **36**, C1–355 (1975).
7. G. W. Gray, J. *Physique Colloq.*, **36**, C1–337 (1975).
8. R. A. Vora and N. Dixit, in Liquid Crystals, ed. S. Chandrasekhar, Heyden, London (1980) p. 585.
9. P. C. Jain, in Proceedings of 2nd National Symposium on Positron Annihilation, Madras (1982) (in print).
10. P. C. Jain, S. Bhatnagar and A. Gupta, *J. Phys., C.*, **65**, 2156 (1972).
11. S. R. S. Kafle, Ph.D. Thesis, Delhi University (1981).
12. S. J. Tao, *IEEE Trans. Nucl. Sci.*, **15**, 175 (1968).
13. S. L. Arora, J. L. Fergason and T. R. Taylor, *J. Org. Chem.*, **35**, 4055 (1970).
14. V. I. Minkin, Y. A. Zhdanov, E. A. Madyantzeva and Y. A. Ostroumov, *Tetrahedron*, **23**, 3651 (1967).
15. H. B. Burgi and J. D. Dunitz, *Helv. Chim. Acta*, **54**, 1255 (1971).
16. P. C. Jain, S. R. S. Kafle, in Positron Annihilation, eds. P. G. Coleman, S. C. Sharma and L. M. Diana, North Holland Publishing Co., Amsterdam (1982), p. 748.