



TEMPERATURE DEPENDENT PHASE TRANSFORMATION STUDIES IN HEXYLOXY CYANOBIHENYL EMPLOYING POSITRON ANNIHILATION TECHNIQUE

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ABSTRACT

Hexyloxycyanobiphenyl (6OCB) is one of the homologues of alkyloxycyanobiphenyl family. The phase transitions in 6OCB were investigated employing positron lifetime spectroscopy. In this compound, temperature dependent positron lifetime measurements have been carried out, both in the heating as well as cooling cycles of the sample. Besides detecting many interesting features like anti-parallel biomolecular association, retention of some memory of more ordered crystalline state in nematic phase, positron annihilation parameters have been able to reveal anomalous structural changes taking place in this compound. The temperature range for the study was chosen from 20°C to 90°C, so that all the phases of compound could be investigated. In present investigation, the crystalline solid phase of 6OCB changes to liquid crystalline phase at 57 °C and liquid crystalline phase changes to isotropic liquid phase 76 °C which exactly matches with the transition temperatures reported in the literature for this compound.

Keywords: Positron Lifetime, Liquid Crystals, Phase Transition, 6OCB

1. INTRODUCTION

6OCB is liquid crystal forming material. Like most of the liquid crystalline materials, this compound is also electrically highly polar. Very large dipole moment of approximately 4.5 Debye is associated with the nitrile bond of this compound. Thus, similar to other members of alkyloxycyanobiphenyl family, 6OCB also forms anti-parallel bimolecular association [1-6]. The apparent length of anti-parallel pair in the liquid crystalline phase is found to be 1.4 times the actual molecular length. As per the dielectric study performed in this compound, it has been shown that the extent of antiparallel pairing decreases in



isotropic phase [7]. Some members of alkyloxy series exhibit liquid crystalline smectic phase characterized with interdigitated semi-bilayer structure. On heating such a smectic phase, a nematic phase is obtained. This interdigitated structure persists in small aggregates of molecules even in nematic phase [4, 5]. These small aggregates of molecules are known as cybotactic clusters. The size of these clusters decrease as the temperature in nematic phase is increased [8]. Another interesting feature reported to be associated with other members of alkyloxycyanobiphenyl series is the solid crystalline polymorphism [9-14].

Positron annihilation parameters have been demonstrated to be extremely sensitive towards structural and micro-environmental changes taking place in liquid crystalline materials. A compilation of this work has been done by P.C. Jain [15]. Positron lifetime spectroscopy was employed for the study of complex molecular motions of alkyl- and alkyloxy- cyanobiphenyls [16-19]. The present work describes the usefulness of positron annihilation technique in investigating various characteristics of 6OCB, a member of alkyloxy series. Initial efforts in this direction were made by Malhotra et al [20, 21] and Jain et al [22]. In this paper we report the temperature-dependent studies, using positron lifetime spectroscopy, performed on 6OCB.

2. EXPERIMENTAL

The material used in the present study, namely, 6OCB was procured from British Drug House Chemicals, UK and were of high purity grade. They were, therefore, used without any further purification.

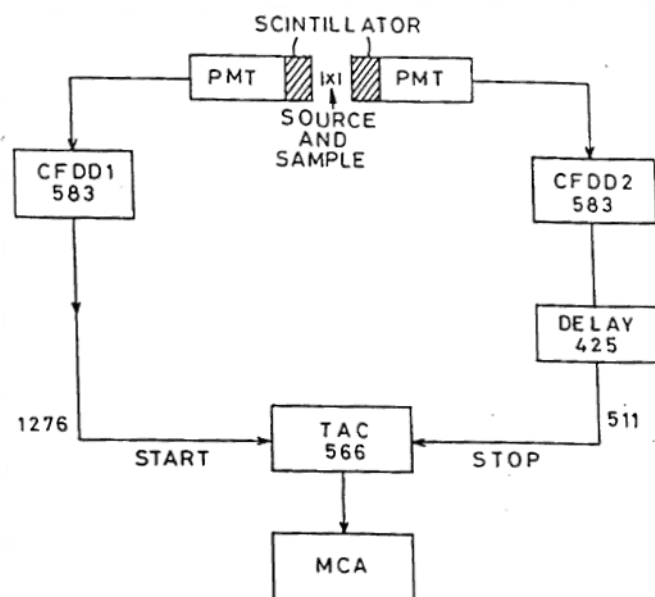


Figure1: Block diagram of experimental set up used for positron annihilation lifetime measurements.

The schematic representation of standard lifetime spectrometer used in the present work is shown in figure1. Positron lifetime measurements as a function of temperature were carried out in the sample. The radiation detectors used consisted of 1"x1" plastic scintillators coupled to RCA 8575 photomultiplier tubes. The photomultiplier tubes were operated typically at -2.5 kV. For driving timing signals two, EG&G ORTEC Model 583, constant fraction differential discriminators (CFDD) were employed. Each of these devices provides an energy discriminated signals in the form of a rectangular pulse of 30 ns duration. The start signal was provided by the discriminator CFDD1, which was set for 1276 keV gamma ray. The stop signal provided by discriminator CFDD2, which was set for 511 keV gamma ray. In case of ^{22}Na positron source, the emission of gamma ray having energy 1276 keV is simultaneous with the emission of a positron. Time correlation between these two signals then provides information about the positron lifetime in a given medium. To get this information, these two signals are then fed to EG&G ORTEC Model 566; time to pulse height convertor. This unit converts the time difference between the start and stop signals into a proportionate pulse height. Thus the time correlation between these signals is converted into a pulse height distribution which is recorded in a multichannel analyzer (MCA).



Positron source used was ^{22}Na . It was prepared by evaporating a few drops of aqueous solution of $^{22}\text{NaCl}$ on a thin Mylar film and then covering it with another similar film. The source sandwich was sealed by putting it in between two concentric tightly fitting stainless steel rings. It was then placed in the sample contained in a cylindrical glass ampoule. The sample was degased using conventional freeze-thaw technique and after degasing, the glass ampoule was sealed. The temperature of the sample was maintained, thermostatically at each step, to a constancy of $\pm 0.1^\circ\text{C}$. In each set of measurement a total of 2×10^5 counts were collected.

3. RESULTS AND DISCUSSION

The lifetime spectra recorded in the present work were analyzed using the software PC-PATFIT, developed by Riso-National Laboratory, Denmark [23]. The lifetime spectra associated with most of the molecular materials are composed of the sum of several exponential decaying terms. The knowledge of the constant γ_i of the spectral components and their relative weights I_i is the aim of spectrum analysis, which is usually made by fitting a model curve to raw experimental data.

All the lifetime spectra could be resolved into three components. The shortest component, τ_1 , was constrained to 0.125 ns, the para-positronium (p-Ps) lifetime. The ratio of the relative intensities of the longest and shortest components, I_3/I_1 , was fixed at 3. This constrained analysis gave best fit to all lifetime spectra. The longest component, τ_3 , is ascribed to pick-off annihilation of ortho-positronium (o-Ps) with electrons bound to the molecules of the surrounding medium. The relative intensity, I_3 , of this component is, therefore, proportional to positronium formation. Both these parameters exhibit considerable temperature dependence and sensitivity to structural changes occurring in the medium. The intermediate component, τ_2 , has been attributed to annihilation of positrons with electrons of the medium without forming any bound state with them, usually termed as free annihilation. This component did not show any significant temperature dependence and was found to be insensitive to any structural change occurring in the medium.



3.1 The Ortho-Ps Pick-off Lifetime, τ_3

Figure 2 depicts the temperature dependence of τ_3 in the cyanobiphenyl compound investigated. Some of the important features about this compound, picked up by the lifetime parameter τ_3 are summarized here.

3.1.1. Antiparallel Pairing

In molecular materials, generally, the changes observed in τ_3 at a phase transition are attributed to the corresponding changes in free volume or density. However in the compound 6OCB investigated, the observed change in τ_3 at solid to liquid crystalline phase transition is not in keeping with the corresponding change in free volume. As seen in figure 2, the change in τ_3 value at solid to liquid crystalline phase transition is about 70%, whereas the corresponding change in its density is reported to be 5-10%. Such a large change in τ_3 can be attributed to the phenomenon of anti-parallel molecular pairing exhibited by these kinds of compounds [1-6]. This kind of bimolecular association occurs as a result of interaction between the dipoles induced by powerful electron withdrawing cyano groups and the easily polarizable phenyl groups. In solid crystalline state this interaction is also assumed to be responsible for dimer formation. However, in this state molecular packing energy prohibits large overlapping.

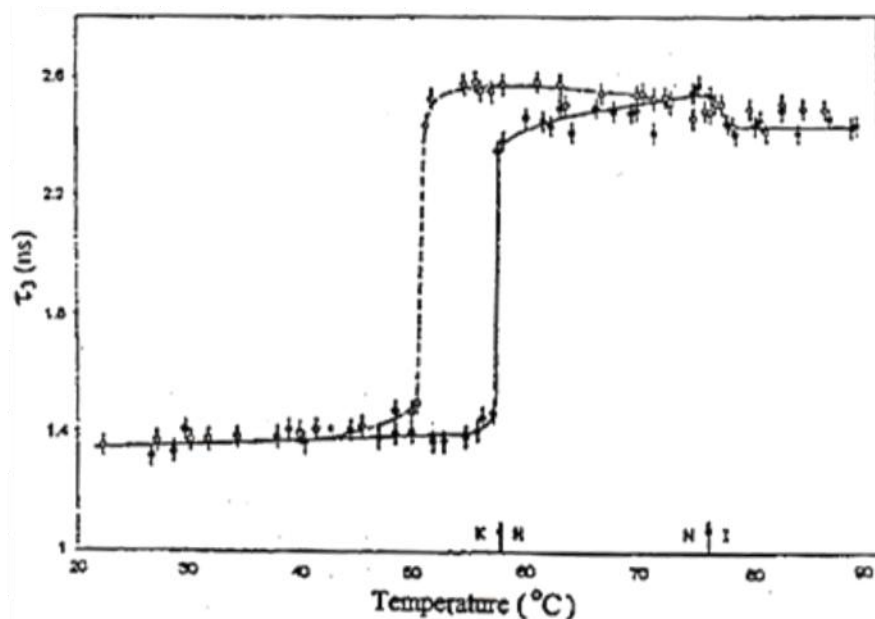


Figure 2. Temperature dependence of τ_3 in 6OCB: solid circles represent the heating cycle and hollow circles represent cooling cycle. The arrows on the temperature axis represent solid crystalline to liquid crystalline and liquid crystalline to isotropic liquid transitions.

In the nematic phase intermolecular attractive forces relax due to increased thermal energy and the large overlapping is achieved. This can be achieved only by a shift of the molecules with respect to each other along the crystal axis. The transition thus is of displacive type [24]. Such an anti-parallel pairing in liquid crystalline state, leads to scarce availability of free dipolar endings, probable sites for o-Ps pick off to take place. This results in significant lowering of ortho-positronium pick off rate and in turn increasing τ_3 value in liquid crystalline phase. A small decrease in τ_3 value at liquid crystalline to isotropic liquid state transition could also be attributed to a decrease in the extent of anti-parallel pairing as reported in dielectric studies [7].

3.1.2. Relaxational Behaviour

Another common behavior shared by alkyl cyanobiphenyls and alkyloxycyanobiphenyls is that, in liquid crystalline state, adjacent to crystalline solid phase, τ_3 is found to increase



gradually with increasing temperature. This behavior of the compound investigated is shown in figure2. In this region, the rate of increase of τ_3 is not in keeping with the thermal expansion of the system. This behavior could be attributed to retention of some memory of higher ordered crystalline phase and its gradual disappearance as the temperature in this region is increased. This view is supported by the results obtained during cooling cycle. During the cooling cycle, in the liquid crystalline phase, the temperature dependence of τ_3 maintains a near constant level instead of retracing the plot obtained in heating cycle. On cooling, the material passes from a less ordered state of liquid crystalline phase to a higher degree ordered state of crystalline phase and therefore, there is no constraint of any memory of previous phase. Hence in this case no relaxational effect, as seen during heating cycle, is observed.

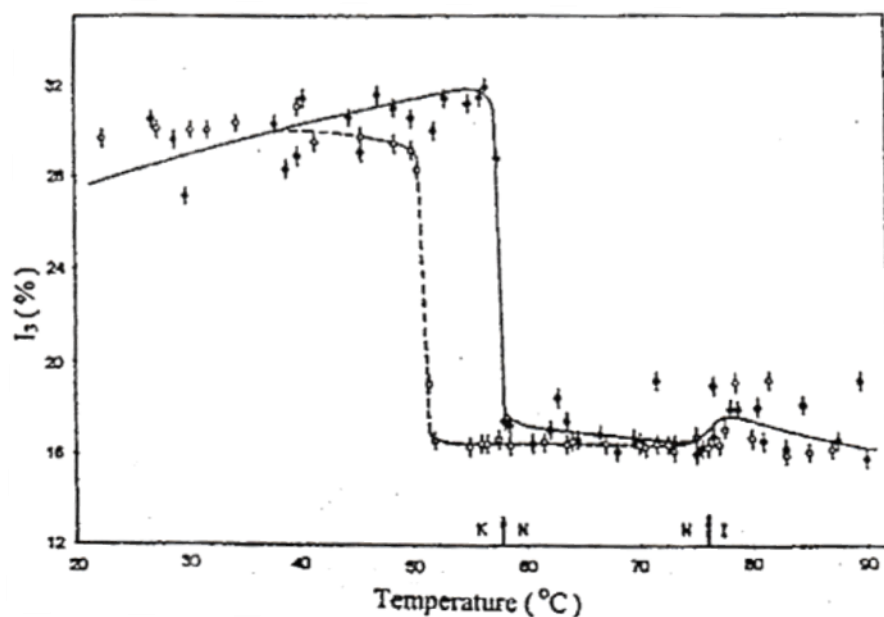


Figure 3. Temperature dependence of I_3 in 6OCB. Symbols have the same meanings as in figure1.

3.2 Positronium Formation, I_3

Temperature dependence of positronium formation probability, I_3 , in the compound investigated, is shown in figure 3. This parameter is not as sensitive as ortho-positronium lifetime τ_3 to structural and micro environmental changes occurring in system under



investigation. It is seen that in 6OCB, the I_3 values in solid phase are higher as compared to those in liquid crystalline phase. A reverse trend is observed in most of the homologues of this series. Normally due to the compactness of the structure, a lower positronium formation is expected in solid phase. However, this does not seem to apply to 6OCB for which the solid phase appears to be more favourable to positronium formation as compared with liquid crystalline phase. The solid phase in 6OCB appears to possess a more-open packed structure in comparison to solid phase of other homologues of this family.

4. CONCLUSIONS

Present work has demonstrated the sensitiveness of positron annihilation parameters not only to gross features like phase transformations but also to fine structural changes occurring in the compound investigated. The present study has revealed phenomena like anti-parallel bimolecular pairing and retention of solid crystal order in liquid crystalline phase. It is observed that τ_3 is more sensitive parameter than I_3 in its response to various characteristic changes occurring in the system. However, a small increasing trend in I_3 value with temperature in solid phase upto 55⁰C reveals the fact that system transforms from a closely packed to open pack structure. Thus the peculiar behavior of I_3 in the solid phase of 6OCB represents a kind of molecular repacking occurring in this phase.

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