

Positron Annihilation Spectroscopy as a Tool to Investigate Phase Transformation and Complex Structural Changes in 8OCB

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ABSTRACT

Cyanobiphenyl liquid crystalline compounds have been the materials of interest for various studies. Most of them exhibit liquid crystalline phase near room temperature. Octyloxycyanobiphenyl (8OCB) is one of the homologues of alkyloxycyanobiphenyl family. The phase transitions in 8OCB were investigated employing positron lifetime spectroscopy. Temperature dependent positron lifetime measurements have been performed in this compound; both in the heating and cooling cycles of the sample. Positron annihilation technique was found to be capable of detecting some of the interesting characteristics like solid crystalline polymorphism, retention of some memory of more ordered crystalline state in liquid crystalline phase, anti-parallel bimolecular association and 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 8OCB changes to liquid crystalline phase at 54°C and liquid crystalline phase changes to isotropic liquid phase at 80°C which exactly matches with the transition temperatures reported in the literature for this compound.

Keywords: Liquid Crystal, octyloxycyanobiphenyl, Positron Lifetime, Phase Transformation.

Introduction

The Molecular shape and structure of liquid crystal forming material, 8OCB, is shown in figure 1. The dashed line in the figure represents long molecular axis of the molecule. This compound is one of the homologues of alkyloxycyanobiphenyl series. It is electrically highly polar. Due to very large dipole moment associated with the nitrile bond of this kind of compounds, they form 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 as one approaches isotropic phase [7]. Some of the members of this series exhibit layered smectic phase characterized with interdigitated semi-bilayer structure. If on heating such a smectic phase, a nematic phase is obtained, then small aggregates of this interdigitated structure persists even in nematic phase [4, 5]. These small aggregates of molecules are known as cybotactic clusters. The size of these clusters decreases with increasing temperature [8]. Another interesting feature reported to be associated with cyanobiphenyl liquid crystalline materials is the solid crystalline polymorphism [9-14].

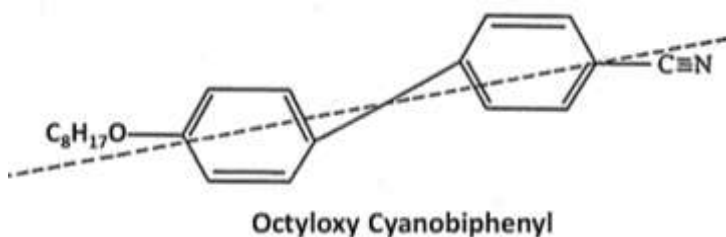


Figure1. Molecular Shape and Structure of 8OCB

The structural and micro-environmental changes taking place in liquid crystalline materials are picked up sensitively by positron annihilation parameters. A compilation of this work has been done by P.C. Jain [15]. Positron lifetime spectroscopy was also found sensitive towards the complex molecular motions taking place in alkyl- and alkyloxy-cyanobiphenyls [16-19]. The present work describes the usefulness of positron annihilation technique in investigating various characteristics of 8OCB. Initial efforts in investigating various characteristics of this kind of compounds were made by Malhotra et al [20, 21] and Jain et al [22]. Present investigation presents a systematic temperature-dependent positron lifetime measurements performed on 8OCB.

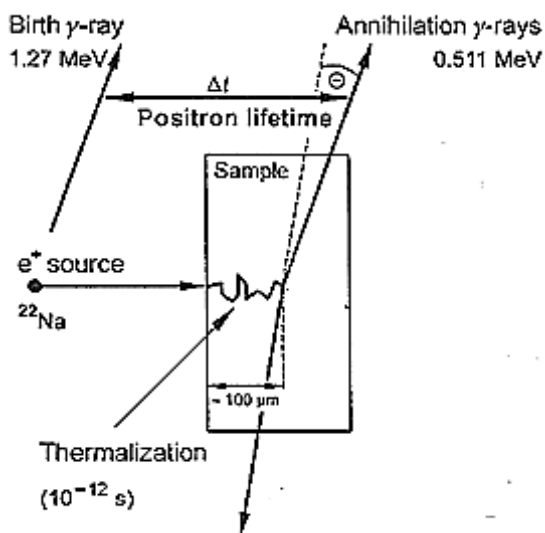


Figure2. Principle of Positron Lifetime Measurement Technique

Experimental Details

Positrons emitted by positron source enter into material media. They lose almost all their energy in thermalisation. The thermalized positrons then eventually annihilate with the electron of the media. A correlation between gamma rays emitted at the time of birth and annihilation gives an estimate of positron lifetime. The lifetime of positron is therefore, governed with the state of electron in the media with which it annihilates. Principle of positron lifetime measurement technique is depicted in figure 2. The liquid crystalline material used in the present study was 8OCB. It was procured from British Drug House Chemicals, UK and was of high purity grade. This was, therefore, used without any further purification.

Generally the source with neutron deficient nuclei is used as positron source, because in neutron deficient nuclei, a proton is converted into a neutron by emitting a positron. The positron source used in present investigation 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 smooth, concentric, tightly fitting stainless steel rings. It was then placed in the sample contained in a cylindrical glass case and then the glass ampule 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 two lakh counts were collected.

Observations and Discussion

The lifetime spectra associated with most of the molecular materials are composed of the sum of several exponential decaying terms. All the lifetime spectra could be resolved into three components. Software PC-PATFIT, developed by Riso-National Laboratory, Denmark was used to analyze the lifetime spectra recorded [23]. The shortest component, τ_1 , was constrained to 0.125ns, 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 changes occurring in the medium.

Temperature dependence of τ_3 in liquid crystalline 8OCB is shown in Figure 3. Some of the important features about this compound, picked up by the lifetime parameter τ_3 are; solid crystalline polymorphism, retention of memory of crystalline state even in passing to liquid crystalline phase, anti-parallel bimolecular association and relaxational behavior. These phenomena picked by positron annihilation studies are summarized below.

Solid crystalline polymorphism has been previously reported in various liquid crystalline materials [9-14]. Present study provides evidence for the existence of solid crystalline polymorphism in 8OCB. For convenience, the crystalline phase in 8OCB is divided into three parts; Solid K_1 , Solid K_2 , Solid K_3 . Present positron lifetime studies reveal that Solid K_1 to Solid K_2 transformation takes place at temperature 46°C and Solid K_2 to Solid K_3 transformation takes place at temperature 51.5°C . These transformations are represented by arrows on temperature axis in figure 3. Solid crystalline polymorphism in 8OCB has also been reported using Raman spectroscopy [10], ac calorimetry and picosecond time resolved fluorescence [24], and DSC, X-ray diffraction and optical microscopy [25].

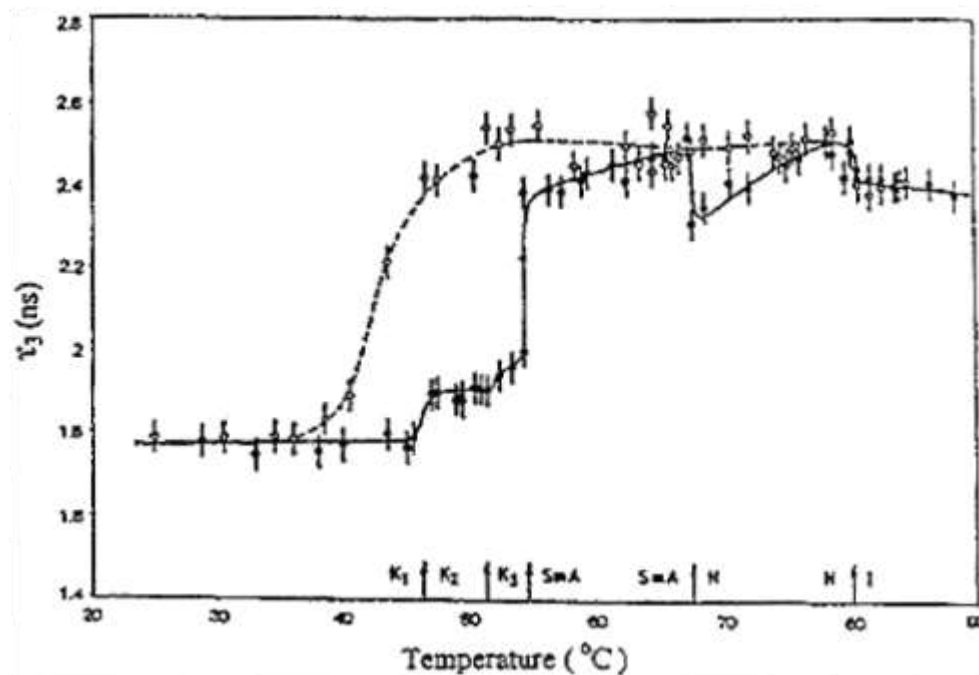


Figure3. Temperature dependence of τ_3 in 8OCB: solid circles represent the heating cycle and hollow circles represent cooling cycle. The arrows on the temperature axis represent solid crystalline to liquid crystalline and liquid crystalline to isotropic liquid transitions.

Here solid K_1 to solid K_2 transformation arising out of conformational change while solid K_2 to solid K_3 transformation is rather complex. At this temperature, τ_3 begin to increase gradually indicating the growth of a new structure. The nature of this new structure is not very well understood. A gradual increase in τ_3 value in temperature range 51.5 to 54 °C is indicating two possibilities. Either a new crystalline phase K_3 begins to grow at the expense of K_2 phase or growth of liquid crystalline SmA phase which is inter-dispersed in K_2 . The first possibility supports the metastable character of K_2 phase. The constancy of τ_3 value over the temperature range 46 to 51.5 °C does not support the metastable character of K_2 phase. Hence an early onset of SmA phase inter-dispersed in the crystalline K_2 phase is supported by our observation. As the temperature is raised the content of SmA increases at the expense of K_2 . At 54°C, the SmA content reaches a critical limit and the system completely transforms to SmA phase.

Generally, the changes observed in τ_3 values at a phase transition are attributed to the corresponding changes in free volume or density. However, in the investigated compound 8OCB, the observed change in τ_3 at solid to liquid crystalline phase transition is not in keeping with the corresponding change in free volume. In present study, 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. This kind of pairing is reported in literature by similar compounds [1-6]. This 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. 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 [26]. 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 lowering of ortho-positronium pick off rate increases 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].

As seen in figure 3, in liquid crystalline state adjacent to crystalline solid phase, τ_3 is found to increase gradually with increasing temperature. In this region, the rate of increase of τ_3 does not commensurate 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, τ_3 maintain 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.

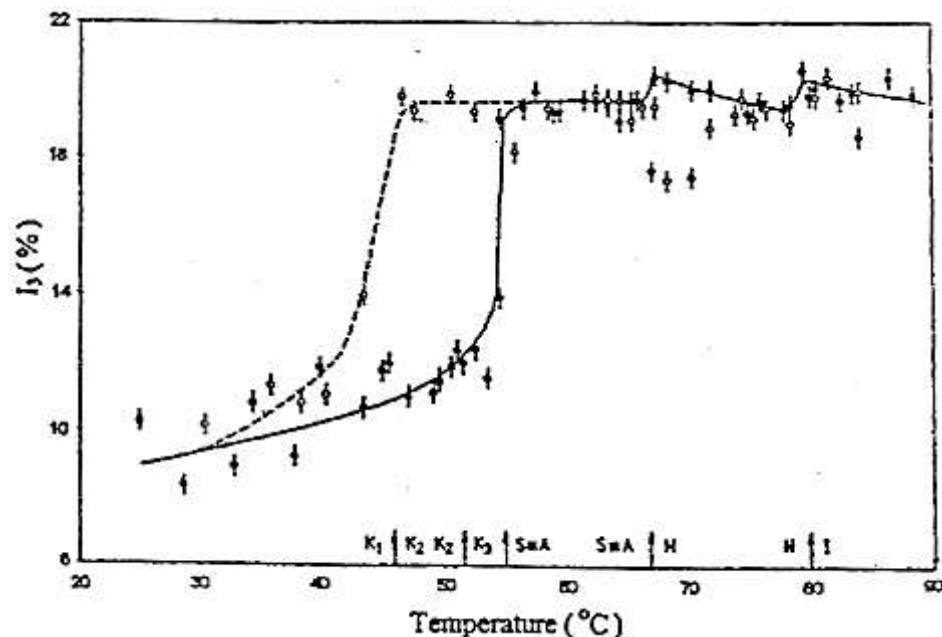


Figure 4. Temperature dependence of I_3 in 8OCB. Symbols have the same meanings as in figure 1.

It is mentioned previously that the positronium formation probability is represented by I_3 . Figure 4 represents the temperature dependence of I_3 in the compound investigated. This parameter is not as sensitive as ortho-positronium lifetime τ_3 , in detecting solid crystalline polymorphisms and formation of cybotactic groups. Normally due to the compactness of the structure, a lower positronium formation is expected in solid phase as compared to liquid crystalline phase. The same trend is obtained in the compound investigated.

Conclusions

Present investigation reveals that positron annihilation technique is not only sensitive enough in detecting gross features like phase transformations but also to fine structural changes occurring in the compound investigated. The positron annihilation parameters show considerable variations for phenomena like solid crystalline polymorphism, anti-parallel bimolecular pairing, formation of cybotactic groups 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, an increasing trend in I_3 value with temperature in solid phase 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 8OCB indicates a kind of molecular repacking.

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