

Positron Annihilation Spectroscopy as a Tool to Study Phase Transformation in Octyl Cyanobiphenyl

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Abstract

Liquid crystal forming compound Octyl cyanobiphenyl (8CB) is a member of the family of 4-n-alkyl-4'-cyanobiphenyl homologues. The results of phase transformations carried out in this liquid crystalline material, using positron annihilation spectroscopy, are presented in this paper. In this compound, the positron lifetime measurements were performed as a function of temperature. A systematic study of positron lifetime measurements were carried out during heating and cooling cycle of the sample. The temperature range for the study was chosen from 5°C to 55°C, so that all the phases of compound investigated i.e., solid crystalline, liquid crystalline and isotropic liquid can be covered. The positron annihilation parameters are found to exhibit strong dependence on temperature. It is found that the ortho-positronium (o-Ps) pick-off lifetime shows changes which strongly support the existence of some memory of more ordered solid phase on passing to the liquid crystal phase. The changes were also observed in o-Ps formation probability I_3 , indicating a systematic transformation of the solid phase from a close-pack structure to an open-pack structure. Solid crystalline polymorphism was also observed in the compound investigated.

Keywords: Positron lifetime, liquid crystals, Phase transformation, 8CB

Introduction

Liquid crystals are fascinating materials for studying theoretically and experimentally the characteristics of phase transformations near room temperature. Alkyl cyanobiphenyls and alkyloxy cyanobiphenyls are stable mesogenic compounds [1], widely used in liquid crystal displays [2]. These are often abbreviated as nCB and nOCB, where n is the number of carbon atoms in the alkyl chain. The cyanobiphenyls are interesting because they have low temperature mesophases and smectic layer spacings (or in nematics, layer like correlation) about 1.4 times the molecular lengths [3, 4]. These compounds are electrically highly polar. Due to very large dipole moment associated with the nitrile bond they form antiparallel bimolecular association [5-8]. In the mesophase, these materials are highly viscous and exhibit the phenomenon of supercooling. Other characteristic features associated with these types of cyanobiphenyls are solid crystalline polymorphism [9-14] and the presence of cybotactic groups in the nematic phase [4].

In these compounds several interesting results have also been reported from other techniques such as specific heat measurements [15], Raman spectroscopy [16, 17], NMR studies [18] and scanning tunneling microscopy [19]. Positron annihilation technique has been employed for the study of some complex molecular motions in liquid crystalline materials [20, 21, 22, 23].

Materials and Methods

The cyanobiphenyls used in the present study were procured from BDH chemicals and were of high purity grade. Their transition temperatures measured here agree well with those accepted for these products.

Positron lifetime measurements as a function of temperature were carried out using a standard positron lifetime spectrometer, details of which are described elsewhere [24, 25]. 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 ($\sim 10\mu\text{g cm}^{-2}$). It was then covered 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 Mylar film thickness used was such that less than 5% of the positrons were annihilated in it. Appropriate correction for these annihilations was applied when analyzing the data. The ring diameter and the source positions were such that no positrons annihilated in the ring. 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.

Observations and Results

The lifetime spectra recorded in the present work were analysed using the software PC-PATFIT, developed by Riso-National Laboratory, Denmark [26]. All the lifetime spectra could be resolved into three components. The shortest component, τ_1 , was constrained to 0.125ns, the para-positronium (p-Ps) lifetime. The longest component, τ_3 , is ascribed to pick-off annihilation of o-Ps with electrons bound to the molecules of the surrounding medium. This pick-off annihilation lifetime, τ_3 , exhibits considerable temperature dependence and sensitivity to structural changes occurring in the medium. The intermediate component, τ_2 , has been attributed to the annihilation of positrons with electrons of the medium without forming any bound state with them, usually termed as free annihilation. This component was found to be insensitive to any structural change occurring in the medium. The relative intensities I_1 , I_2 and I_3 of these components therefore represent the relative probabilities of the three annihilation processes. The intensities I_1 and I_3 therefore, represent the relative proportion of p-Ps and o-Ps formed in the medium and hence is expected to be in proportion 1:3. In a material medium p-Ps and o-Ps formed on interacting with the electrons belonging to that medium undergo pick-off annihilation. As a consequence of pick-off process, the o-Ps lifetime is considerably modified, however the p-Ps lifetime is not affected by this process as it cannot become lower than its free annihilation lifetime 0.125ns. Since the p-Ps lifetime does not undergo any modification with environmental changes and I_1 and I_3 provide complementary information. In the later discussion only the behaviours of τ_3 and I_3 were considered. Both these parameters exhibit considerable temperature dependence and sensitivity to structural changes taking place in the medium.

In the compound investigated, the observed change in τ_3 at the solid to liquid crystalline phase transition is not commensurate with the corresponding changes in free volume. Such an abnormally large change can be ascribed to the phenomenon of anti-parallel molecular pairing exhibited by this kind of compounds.

In the cyanobiphenyl studied, during the heating cycle, the τ_3 value exhibits an increasing trend with temperature in the mesophase, immediately following a solid crystalline phase. The rate of increase in τ_3 is not commensurate with the corresponding changes in density observed in this region. Thus the system tends to retain some memory of its previous state in passing from a state of higher order to that of lower order.

Discussion

The temperature dependence of τ_3 in octyl cyanobiphenyl compound is shown in Figure 1. The phase transformation observed in this compound and the corresponding transition temperatures are indicated in the respected plot. In molecular materials, generally, the changes observed in τ_3 at a phase transition are attributed to the corresponding change in free volume density. But in the compound studied this is not true. As seen in Fig.1, the change in τ_3 values at the solid to liquid crystalline

transition is about 70% whereas the corresponding change in its density is reported to be less than 10%. Such an abnormally large change can be ascribed to the phenomenon of anti-parallel molecular pairing [4-8] exhibited by this kind of compounds. Such a bimolecular association occurs as a result of the interaction between the dipoles induced by the powerful electron withdrawing cyano groups to the easily polarisable phenyl groups. The formation of anti-parallel molecular pairing reduces the availability of free dipolar ending; the probable sites for o-Ps pick-off to take place. This results in a low o-Ps pick-off rate and hence a higher τ_3 value in the liquid crystalline phase. However, in the solid phase molecular packing, energy prohibits anti-parallel pairing, resulting in a lower value of τ_3 . In the plot for temperature dependence of τ_3 for 8CB (figure1), the τ_3 value is almost independent of temperature upto about 16 °C and then increases abruptly indicating a solid-solid phase transformation (K_1 to K_2). Thus exhibiting solid crystalline polymorphism. Such a polymorphism has been reported in various liquid crystalline materials exhibiting different mesogenic phases [8-12]. In 8OCB (octyloxy cyanobiphenyl), a similar homologue of alkyloxy cyanobiphenyl, solid cryastalline polymorphism has been observed using different techniques such as Raman spectroscopy [27], ac calorimetry and picoseconds time-resolved fluorescence [28], differential scanning calorimetry, x-ray diffusion and optical microscopy [29]. However, the solid crystalline polymorphism in 8CB, as observed in the present work, has not previously been reported.

Another common characteristic shown by these types of liquid crystalline compounds is relaxational behaviour. In the liquid crystalline phase adjacent to the crystalline phase, τ_3 , is found to increase gradually with increasing temperature, as seen in Fig1. In this region the rate of increase of τ_3 is not in keeping with the corresponding thermal expansion of the system. This behaviour could be ascribed to retention of some memory of the 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 the cooling cycle. During the cooling cycle the material passes from a less ordered state to a state with a higher degree of molecular order and therefore, there is no constraint of any memory of the previous phase thus not retracing the plot obtained in the heating cycle.

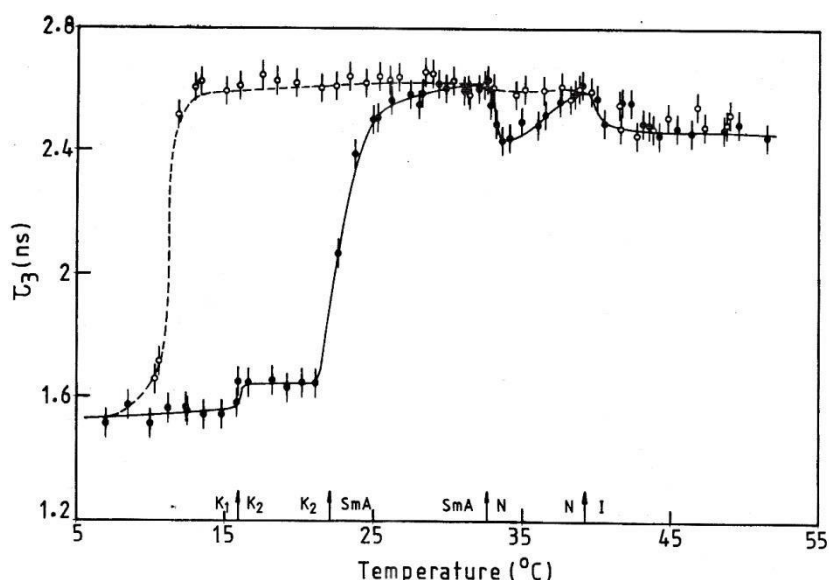


Figure 1 Temperature dependence of τ_3 in 8CB: \bullet denotes the heating cycle and \circ denotes the cooling cycle. The arrows on the temperature axis indicate the locations of solid 1 (K_1) \rightarrow solid 2 (K_2), solid 2 \rightarrow smectic A, smectic A \rightarrow nematic and nematic \rightarrow isotropic liquid transitions.

In figure 1 another interesting feature can be noticed. It is seen that during the heating cycle, in the nematic phase, the τ_3 value gradually increases with increasing temperature. This can be attributed to

the fact that during heating cycle and on passing into the nematic phase the interdigitated layered structure of the smectic phase does not disappear completely but give rise to the formation of cybotactic groups [30]. On heating the size of these cybotactic groups decreases, resulting in a decrease in the o-Pos pick-off rate and hence an increase in τ_3 . This view is strongly supported by the absence of such behavior during the cooling cycle. This is due to the fact that during the cooling cycle the system enters the nematic phase from the isotropic phase where cybotactic groups are practically non-existent.

Figure2 depicts the temperature dependence of I_3 for the same compound. It is observed that, as compared to τ_3 , this parameter is somewhat less sensitive towards structural changes taking place in the compound investigated. It can be noted from figure2 that much greater positronium formation takes place in solid phase as compared to smectic and nematic phases. It is an observation contrary to general behavior. Normally there is a lesser extent of positronium formation in the solid phase compared to the liquid crystalline phase. It is observed that I_3 exhibit temperature dependence in solid crystalline phase while the average value of I_3 in the liquid crystalline as well as in isotropic liquid phase does not show any significant change. It is well known that in a given medium, the Positronium formation and the o-Pos pick-off lifetime are intimately connected with the availability of free volume (number of voids) and its distribution (average void size) respectively. Positronium formation probability is linked with the total free volume available or the number of voids. Since a void acts an efficient trap for positronium, the o-Pos pick-off lifetime is determined by the average size of the void.

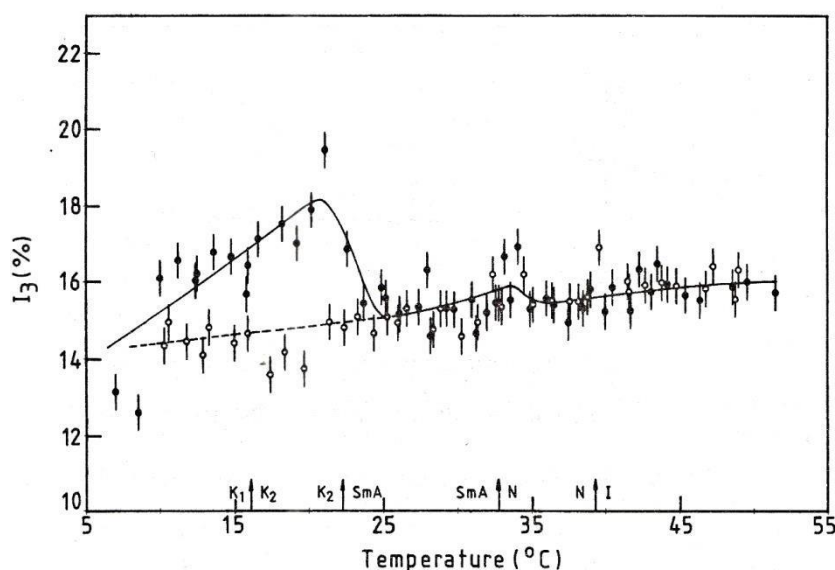


Figure 2 Temperature dependence of I_3 in 8CB. The meaning of the symbols and arrows are the same as in figure1.

The larger value of I_3 in solid crystalline phase suggests a kind of molecular repacking. The system begins to transform from a close-pack solid to an open-pack solid. With increasing temperature, a greater and greater fraction of the close-pack structure transforms to an open-pack structure. This kind of transformation is here suggested for the first time. To confirm this assertion, a detailed temperature dependent X-ray diffraction study is required. It is worthwhile to mention that the present study can give an added advantage in revealing the subtle nature of structural changes taking place in the solid phase of 8CB.

Conclusions

The present work demonstrate the usefulness and sensitivity of positron annihilation parameters in detecting various phase transformation and some features of the cyanobiphenyls, like anti-parallel

bimolecular association, formation of cybotactic groups and the retention of solid crystal order in the liquid crystalline phase. In isotropic liquid phase the pick-off lifetime again decreases to a very little extent. This indicates although the isotropic liquid phase is more open structured but the availability of free volume decreases as one passes from liquid crystalline to isotropic liquid phase. The changes were also observed in o-Ps formation probability I_3 in the solid phase, indicating a systematic transformation of the solid phase from a close-pack structure to an open-pack structure. The peculiar behavior of I_3 in the solid phase of 8CB provides information on the changes in the molecular packing occurring in this phase.

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