

Phase Transformation Studies in HeptylCyanobiphenyl with the Help of Positron Lifetime Measurements

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ABSTRACT

Heptylcyanobiphenyl(7CB) is a liquid crystalline compound. It is a member of the family of 4-n-alkyl-4'-cyanobiphenyl homologues. Positron lifetime measurements were carried out during the heating and cooling cycles of this compound. The results of phase transformations study in this liquid crystalline material are presented in this paper. In this compound, the positron lifetime measurements were performed as a function of temperature. The temperature range for the study was chosen from 5°C to 55°C, so that all the phases of compound could be 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 noticeable changes on passing from one phase to another phase. The comparison of the lifetime changes with temperature in heating cycle and cooling cycle strongly support the existence of some memory of more ordered solid phase on passing to the liquid crystal phase. No significant changes observed in o-Ps formation probability I_3 , indicating the fact, that the positronium formation and annihilation may take place at different places. The little variation in the o-Ps pick-off lifetime at lower range of temperature may be attributed to solid crystalline polymorphism in the compound investigated.

Introduction

Positron annihilation spectroscopy has been widely used in investigation of various structural changes taking place in Liquid crystals. Liquid crystalline materials are used in many display devices [1]. These materials are fascinating materials for studying theoretically and experimentally the characteristics of phase transformations near room temperature. Cyanobiphenyls are stable mesogenic compounds [2]. These are often abbreviated as n-CB and n-OCB, where n is the number of carbon atoms in the alkyl chain. The cyanobiphenyls are interesting because they have low temperature mesophases near room temperature and smectic layer spacing (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 super cooling. 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].

Several interesting results have also been reported in these compounds 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 also been employed for the study of some complex molecular motions in liquid crystalline materials [20, 21, 22, 23].

Materials and Methods

Heptylcyanobiphenyls(7CB) used in the present study was procured from BDH chemicals and were of high purity grade. Their transition temperatures measured here in agree well with those accepted for these products. Therefore, used as such without adopting any purification procedure.

Positron lifetime measurements as a function of temperature were carried out using a standard positron lifetime spectrometer, details of this spectrometer 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, approximately, a total of 2×10^5 counts were collected.

Observations and Results

The positron annihilation lifetime spectra recorded in the present investigation were analyzed using the software PC-PATFIT, developed by Riso-National Laboratory, Denmark [26]. All the lifetime spectra were 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 , corresponds 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 free annihilation. This is the annihilation of positrons with electrons of the medium without forming any bound state with them. This component was found to be insensitive to any structural change occurring in the medium. The 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 thus 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 heptylcyanobiphenyl, 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 compound investigated, 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 variation in o-Ps pickoff lifetime τ_3 with temperature, in liquid crystalline heptylcyanobiphenyl compound, is shown in Figure 1. The phase transformation observed in this compound and the corresponding transition temperatures are indicated in the respected plot by arrows on temperature axis. In molecular materials 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. Fig.1 depicts that 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 exhibited by this kind of compounds [4-8]. This kind of bimolecular association is a result of the interaction between the dipoles induced by the powerful electron withdrawing cyano groups to the easily polarizable 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 is observed. However, in the solid phase molecular packing, energy prohibits anti-parallel pairing, resulting in a lower value of τ_3 .

In figure 1 for 7CB, the τ_3 value is almost independent of temperature upto 10°C and then gradually increases approximately upto 14 °C indicating a solid-solid phase transformation. The same trend is repeated at 20 °C, thus exhibiting solid crystalline polymorphism. Such a polymorphism has been reported in various liquid crystalline materials exhibiting different mesogenic phases [8-12]. In 8OCB (octyloxycyanobiphenyl), a similar homologue of alkyloxycyanobiphenyl, solid crystalline 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 diffraction and optical microscopy [29]. However, the solid crystalline polymorphism in 7CB, as observed in the present work, has not previously been reported.

Almost all liquid crystalline compounds of this series exhibit relaxational behaviour. In the liquid crystalline phase adjacent to the solid crystalline phase, τ_3 , is found to increase gradually with increasing temperature, as seen in Fig 1. In this region the rate of increase of τ_3 is not in keeping with the corresponding thermal expansion of the system. This kind of 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 in cooling cycle the τ_3 plot does not retrace the plot obtained in the heating cycle.

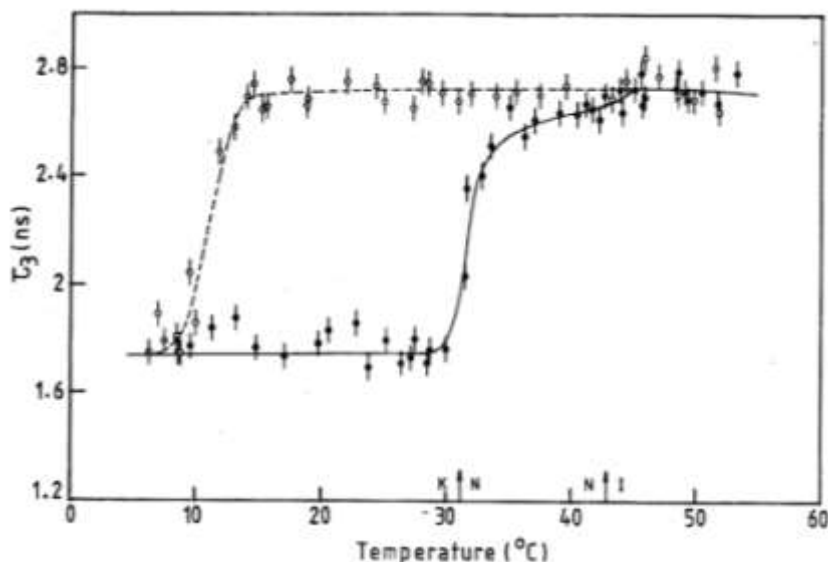


Figure1. Temperature dependence of τ_3 in 7CB: solid circles represent the heating cycle and hollow circles represent cooling cycle. The arrows on the temperature axis represent solid crystalline to liquid crystalline and liquid crystalline to isotropic liquid transitions.

Another interesting feature is revealed in figure 1. It is observed 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 isotropic phase the structure of the nematic phase does not disappear completely but give rise to the formation of cybotactic groups [30]. On heating the size of these cybotactic groups decrease, resulting in a decrease of o-Ps 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.

Temperature dependence of I_3 for the same compound is shown in figure 2. This parameter is somewhat less sensitive, as compared to τ_3 , towards structural changes taking place in the compound investigated. Except for very low range of temperature ($> 10^\circ\text{C}$), it is observed that the average value of I_3 in the solid crystalline phase, liquid crystalline phase and isotropic liquid phase does not show any significant change. It is well known that in a given medium, the positronium formation and the o-Ps 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 as an efficient trap for positronium, the o-Ps pick-off lifetime is determined by the average size of the void.

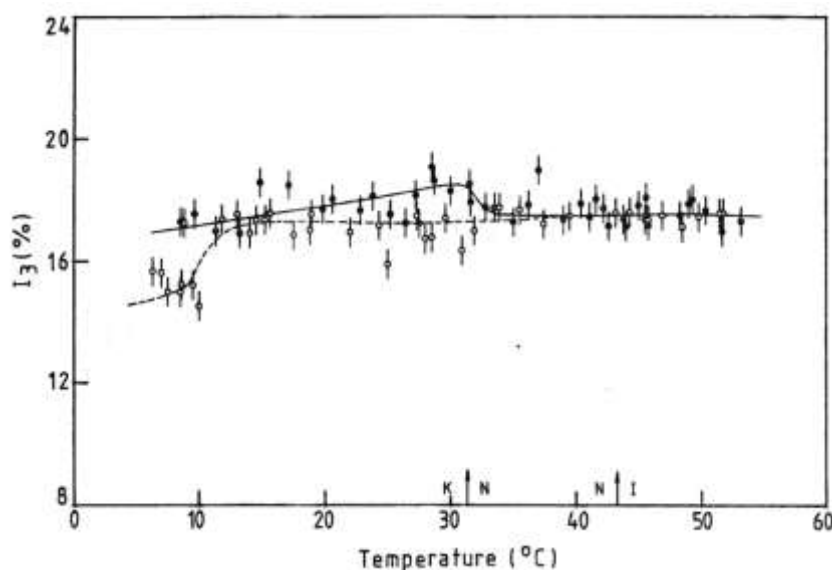


Figure 2: Temperature dependence of I_3 in 7CB. The meaning of the symbols and arrows are the same as in figure 1.

Below 10 °C the value of I_3 in solid crystalline phase is little bit low but after 10 °C, its average value becomes almost similar to that in nematic and isotropic phases. Thus below 10 °C, the behavior of I_3 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 7CB.

Conclusion

The present investigation demonstrates the potentiality and sensitivity of positron annihilation parameters in detecting various phase transformation. Some important features of this cyanobiphenyl compound, like anti-parallel bimolecular association, formation of cybotactic groups and the retention of solid crystalline phase memory in the liquid crystalline phase are also revealed in present study. In isotropic liquid phase the pick-off lifetime remains almost constant indicating that in isotropic liquid phase the availability of free volume is more or less same. 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 7CB provides information on the changes in the molecular packing occurring in this phase.

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