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Phase transformations in some homologues of 4-n-alkyl-4'-cyanobiphenyls investigated by positron annihilation spectroscopy

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Abstract

The results of phase transformation studies carried out in four homologues of 4-n-alkyl-4'-cyanobiphenyls, using positron annihilation spectroscopy, are presented. The homologues investigated are, hexyl-, heptyl-, octyl- and decyl-cyanobiphenyls (6CB, 7CB, 8CB and 10CB). In these compounds, the positron lifetime measurements were performed as functions of temperature. The positron annihilation parameters are found to exhibit strong dependence on temperature. It was found that the *ortho*-positronium pick-off lifetime shows changes which strongly support (i) a gradual disappearance, instead of an abrupt one, of some memory of the more ordered solid phases on passing to the liquid crystalline phases, (ii) the strong tendency for the molecules in the mesophases to undergo anti-parallel bimolecular association and (iii) the formation of cybotactic groups of a smectic phase in a nematic medium. Changes were also observed in the *ortho*-positronium formation probability which apparently indicate a systematic transformation of the solid phase from a close-pack structure to an open-pack structure as one goes from a lower to a higher homologue of the compounds investigated. Solid crystalline polymorphism has been observed in 8CB. A change in molecular packing in the solid phase of 10CB has been observed.

1. Introduction

Liquid crystals are fascinating materials for studying theoretically and experimentally the characteristics of phase transitions near room temperature. 4-n-alkyl-4'-cyanobiphenyls are stable mesogenic compounds [1], widely used in liquid crystal displays [2]. They are

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often abbreviated as n CB, 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 the case of nematics, layer-like correlations) about 1.4 times the molecular lengths [3, 4], which might be described as a modified bilayer structure. The molecules of this series of compounds have large dipole moments. In each molecule, a nitrile group, with a dipole moment of about 4 debye, is attached at one end practically parallel to the long axis of the molecule. In such a case, correlation amongst the neighbouring molecules of these cyanocompounds leads to the formation of anti-parallel bimolecular associations [4–10]. 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 [11–16] and the presence of cybotactic groups in the nematic phase [4]. About these compounds, several interesting results have also been reported from other techniques such as specific heat measurements [17], Raman spectroscopy [18, 19], NMR studies [20] and scanning tunnelling microscopy [21].

Here, we present our results of positron lifetime measurements carried out for pure hexyl-, heptyl-, octyl- and decyl-cyanobiphenols (6CB, 7CB, 8CB and 10CB) during the heating and cooling cycles. Positron annihilation has been investigated in several liquid crystalline materials. Jain [22] has compiled this work. The present work describes the usefulness of the positron annihilation technique in investigating various characteristics of these cyanocompounds. Initial efforts in this direction were made by Malhotra and co-workers [23, 24] and Jain *et al* [25]. But no thorough study has so far been made in these compounds.

2. Experiment

The cyanobiphenyls used in the present study were procured from BDH Chemicals. Samples were used directly from the sealed containers and their transition temperatures measured herein agree well with those accepted for these products. Therefore, no further purification was attempted. Positron lifetime measurements, as a function of temperature, were carried out using a standard positron lifetime spectrometer, details of which are described elsewhere [26, 27]. The 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 Mylar film thickness used was such that less than 5% of the positrons were annihilated in it. Appropriate correction for these annihilations was applied while analysing the data. Putting it between two concentric, tightly fitting, stainless-steel annular rings then sealed the source sandwich. The ring diameter and the source positions were such that no positrons annihilated in the ring. It was then placed in the sample contained in a cylindrical glass ampoule. The sample was degassed using the conventional freeze–thaw technique and after degassing 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

All lifetime spectra recorded in the present work were analysed using the software PC-PATFIT, developed by Risø-National Laboratory, Denmark [28]. Two-, three- and four-component fits were tried; a three-component fit gave the least value of χ^2 . The shortest component, τ_1 , was attributed to the annihilation of the *para*-positronium (*p*-Ps) and the intermediate component, τ_2 , was ascribed to the annihilation of positrons with the electrons of the medium

without forming any bound state with them; this is generally termed as free annihilation. The longest component, τ_3 , was ascribed to the pick-off annihilation of the *ortho*-positronium (*o*-Ps). 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 proportions of *p*-Ps and *o*-Ps formed in the medium and hence are expected to be in a proportion of 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 the 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, 0.125 ns. Keeping these facts in mind, to get a better understanding of positronium formation and interaction in the medium under investigation, a three-component analysis with different constraints was carried out. Three different procedures were adopted; (i) a free three-component fit without any constraint, (ii) a three-component fit with a constraint on the intensities I_1 and I_3 , fixing them in a proportion of 1:3 and (iii) constraining the shortest component to the *p*-Ps lifetime, 0.125 ns, and I_1 and I_3 in the proportion of 1:3. The constrained analysis adopting procedure (iii) provided the best fit to all lifetime spectra. The annihilation parameters, τ_1 , τ_3 , I_1 and I_3 , therefore, characterize positronium formation and interaction in the medium under investigation. 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. The component τ_2 did not show any significant temperature dependence and was found to be insensitive to any structural changes taking place in the medium.

Figures 1–4 depict the temperature dependence of τ_3 in the cyanobiphenyl compounds investigated. The phase transformations observed in these systems and the corresponding transition temperatures are indicated in the respective plots.

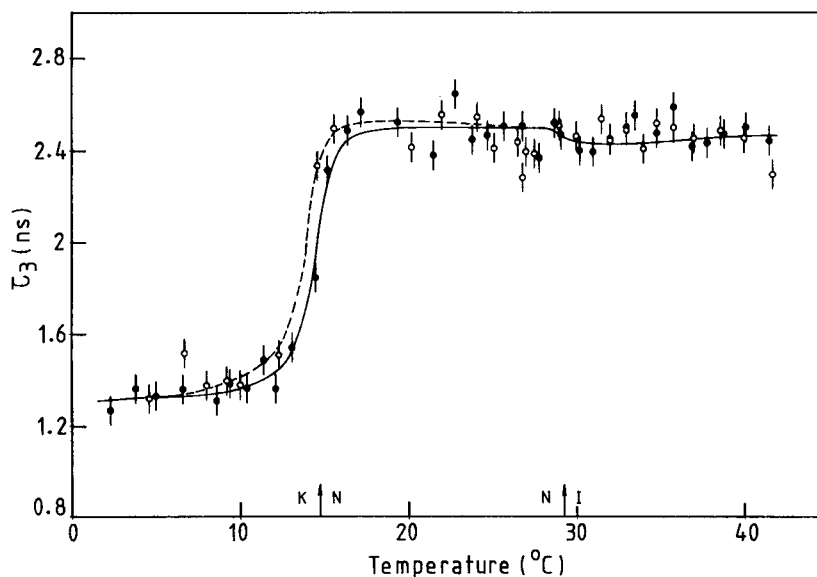


Figure 1. Temperature dependence of τ_3 in 6CB: \blacklozenge denotes the heating cycle and \circ denotes the cooling cycle. The arrows on the temperature axis indicate the locations of crystal \rightarrow nematic and nematic \rightarrow isotropic liquid transitions.

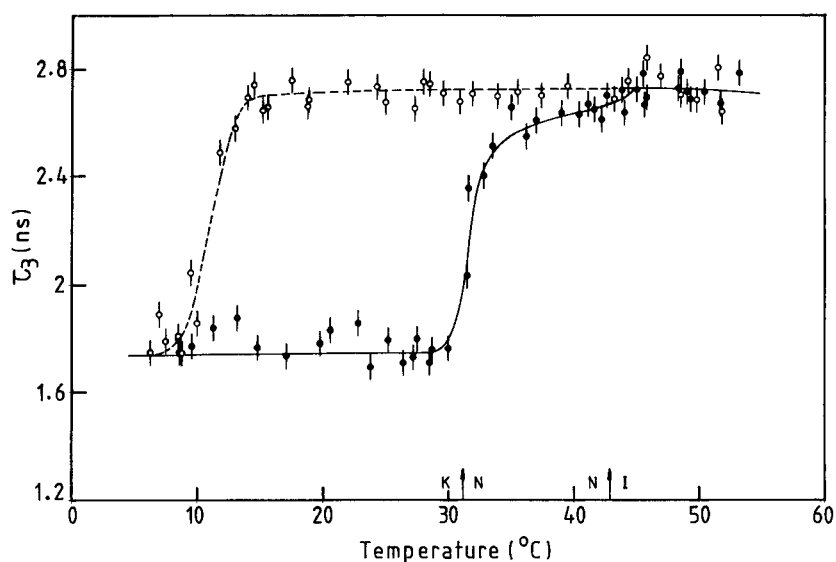


Figure 2. Temperature dependence of τ_3 in 7CB; The meaning of the symbols and arrows are the same as in figure 1.

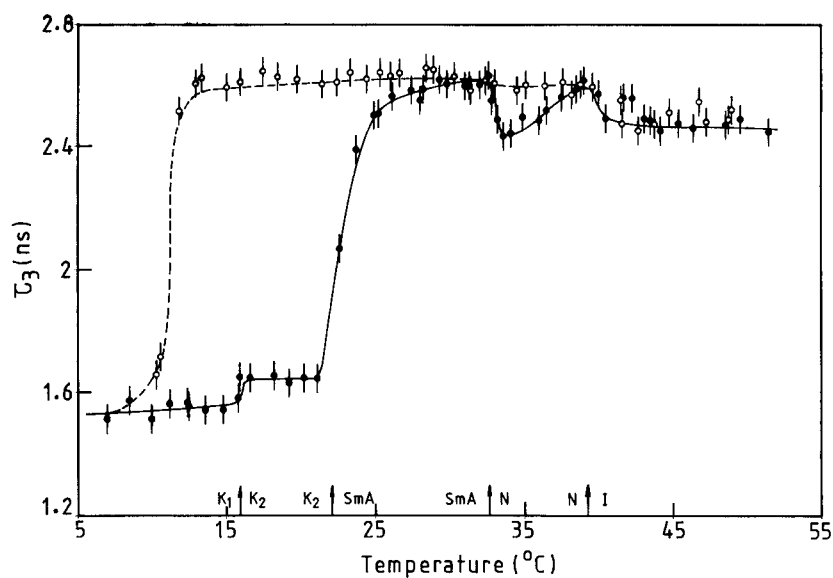


Figure 3. Temperature dependence of τ_3 in 8CB: \blacklozenge denotes the heating cycle and \circ denotes the cooling cycle. The arrows on the temperature axis indicate the locations of solid 1 (K_1) \rightarrow solid 2 (K_2), solid 2 \rightarrow smectic A, smectic A \rightarrow nematic and nematic \rightarrow isotropic liquid transitions.

A common observation shared by all the compounds investigated in the present work is that the change in τ_3 at the solid to liquid crystalline phase transition is much larger than the corresponding change in free volume. In the case of 6CB, the average value of τ_3 in the solid phase is ~ 1.35 ns and that in the nematic phase is ~ 2.50 ns, a change of over 70% (figure 1).

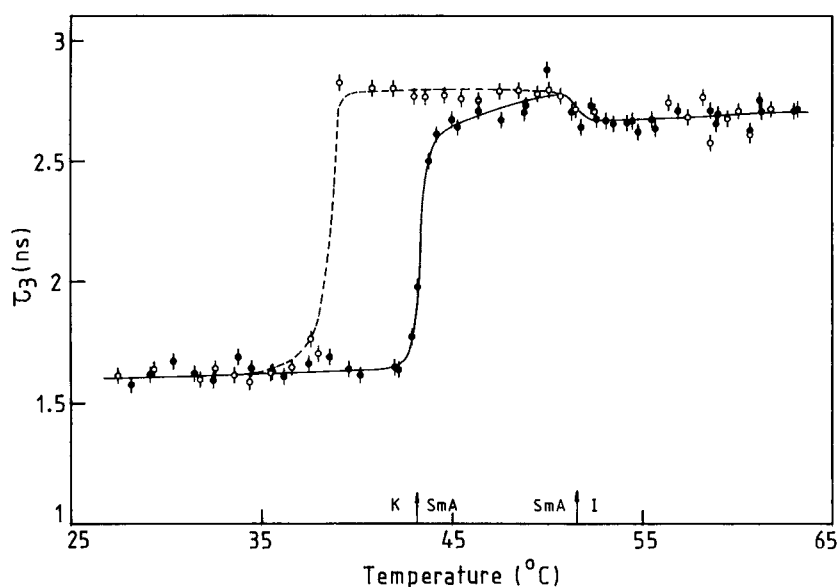


Figure 4. Temperature dependence of τ_3 in 10CB: \blacklozenge denotes the heating cycle and \lozenge denotes the cooling cycle. The arrows on the temperature axis indicate the crystal \rightarrow smectic A and smectic A \rightarrow isotropic liquid transitions respectively.

Such a large change in τ_3 is not commensurate with the corresponding change in density, which is less than 10%. Such an abnormally large change observed in all the cyanocompounds studied can be ascribed to the phenomenon of anti-parallel molecular pairing [4–10] exhibited by them in their respective liquid crystalline phases. In these polar compounds, the formation of anti-parallel molecular pairing reduces the availability of free dipolar endings; the probable sites for *o*-Ps pick-off to take place. This thus 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 .

As seen in figure 3, a plot for the temperature dependence of τ_3 for 8CB, in the solid phase the τ_3 value is independent of temperature up to about 16 °C and then increases abruptly indicating a solid \rightarrow solid phase transformation ($K_1 \rightarrow K_2$). Thus exhibiting solid crystalline polymorphism. Such a polymorphism has been reported in various liquid crystalline materials exhibiting different mesogenic phases [9–14]. In 8OCB (octyl-alkyloxy cyanobiphenyl), a similar homologue of the alkyloxy cyanobiphenyls, solid crystalline polymorphism has been observed using different techniques such as Raman spectroscopy [29], ac calorimetry and picosecond time-resolved fluorescence [30], differential scanning calorimetry, x-ray diffraction and optical microscopy [31]. However, the solid crystalline polymorphism in 8CB, as observed in the present work, has not previously been reported.

In all the cyanocompounds studied, as indicated in figures 1–4, it is observed that in the mesophase, immediately following a solid crystalline phase and during the heating cycle, the τ_3 value exhibits an increasing trend with temperature. The rate of increase is not commensurate with the corresponding changes in density observed in this region. This behaviour indicates that in passing from a state of higher order to that of lower order the system tends to retain some memory of its previous state. In the liquid crystalline phase, as the temperature is increased the extent of this memory gradually decreases and ultimately disappears. This view is supported by

the results obtained during the cooling cycle. It is observed that during the cooling cycle, unlike the heating cycle, the τ_3 value in the liquid crystalline phase does not exhibit any significant temperature dependence. On cooling, 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 operating on the system. Hence in this case no relaxation effect, as seen during the heating cycle, is observed.

In figure 3 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 the heating cycle and on passing into the nematic phase the interdigitated layered structure of the smectic phase does not disappear completely but gives rise to the formation of cybotactic groups [5]. On heating, the size of these cybotactic groups decreases, resulting in a decrease in the *o*-Ps pick-off rate and hence an increase in τ_3 . This view is strongly supported by the absence of such behaviour 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.

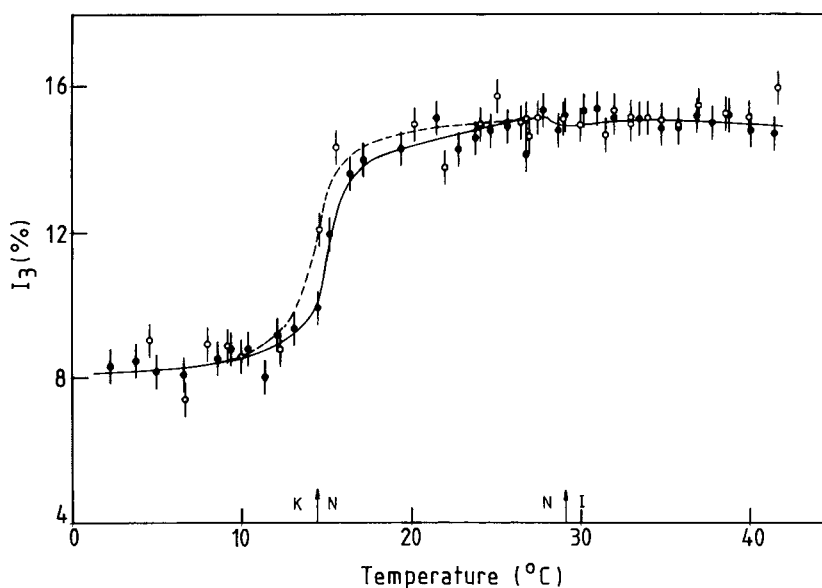


Figure 5. Temperature dependence of I_3 in 6CB. The meaning of the symbols and arrows are the same as in figure 1.

Figures 5–8 exhibit the temperature dependence of I_3 for the same set of cyanocompounds. It is observed that, as compared to τ_3 , this parameter is somewhat less sensitive to any structural changes taking place in a system. However, the temperature dependence of I_3 exhibits a systematic change as one moves from a lower to a higher homologue, a feature not exhibited by τ_3 . As seen in figure 5, the average I_3 value in the solid phase of 6CB is less than its corresponding value in the liquid crystalline phase. However, a reverse trend is observed in case of 10CB. These results are better depicted in figure 9. In this figure the average value of I_3 in a given phase is plotted as a function of the number of carbon atoms in the alkyl chain of a homologue. It is observed that the average value of I_3 in the liquid crystalline phase of all the alkyl cyanobiphenyls investigated in the present work does not show any significant change. However, in the solid phase the I_3 value exhibits a strong dependence on

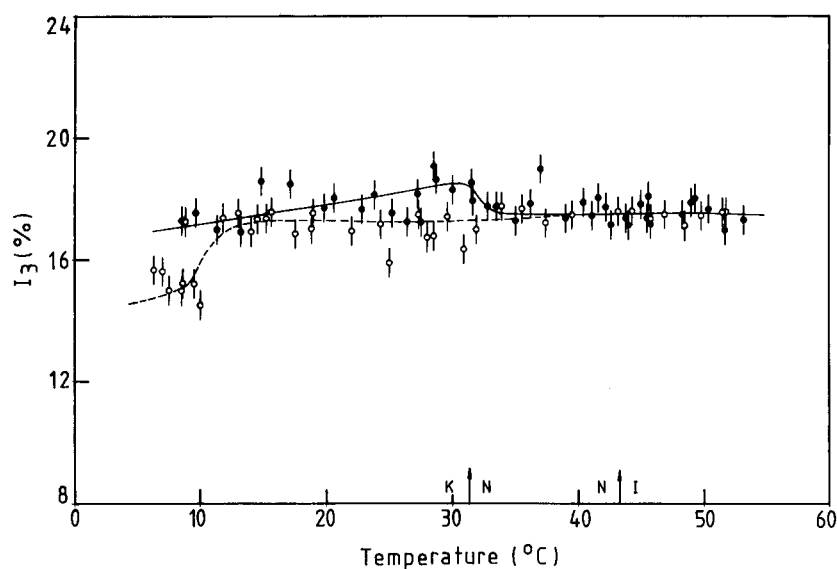


Figure 6. Temperature dependence of I_3 in 7CB. The meaning of the symbols and arrows are the same as in figure 1.

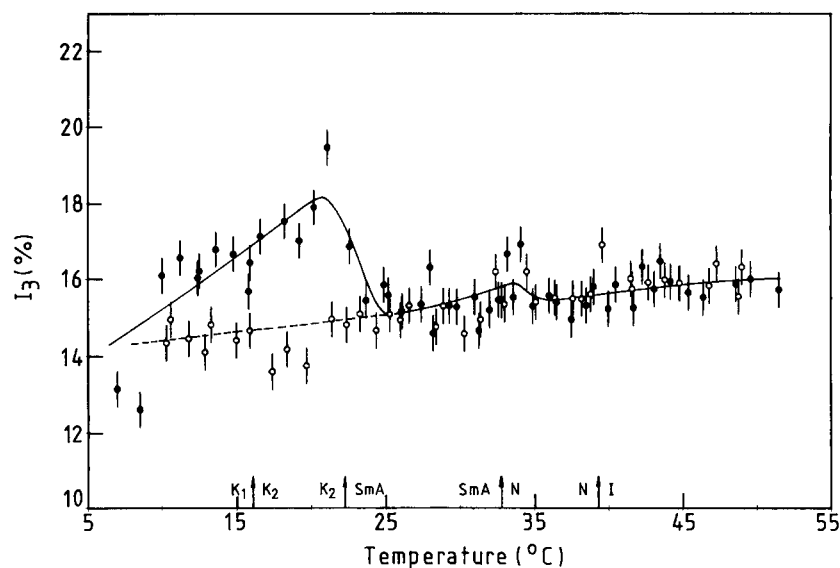


Figure 7. Temperature dependence of I_3 in 8CB. The meaning of the symbols and arrows are the same as in figure 3.

the length of the alkyl chain. On the other hand, τ_3 does not exhibit such behaviour. It can, however, be seen (figures 1–4) that the average value of τ_3 in the solid crystalline phase of 6CB is ~ 1.4 ns, and has nearly the same value, ~ 1.6 ns, in the solid crystalline phases of the other three alkyl cyanobiphenyls investigated in the present work. 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

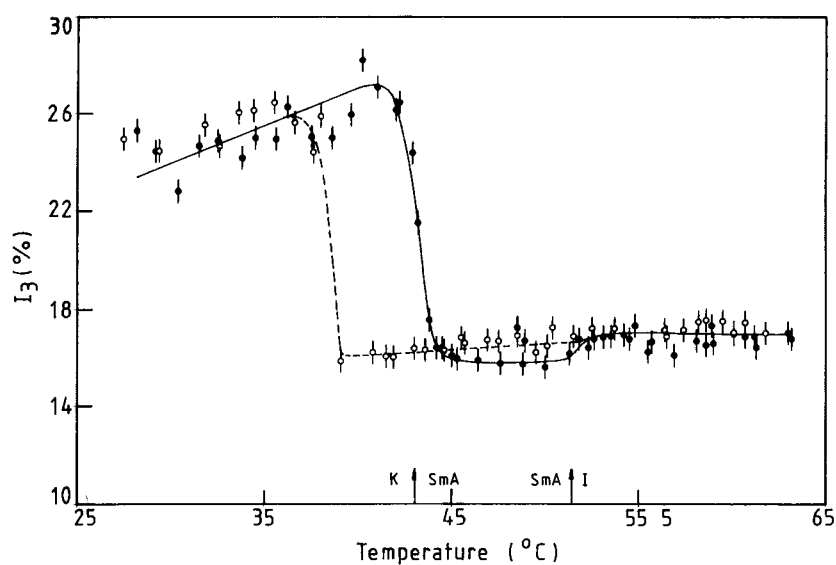


Figure 8. Temperature dependence of I_3 in 10CB. The meaning of the symbols and arrows are the same as in figure 4.

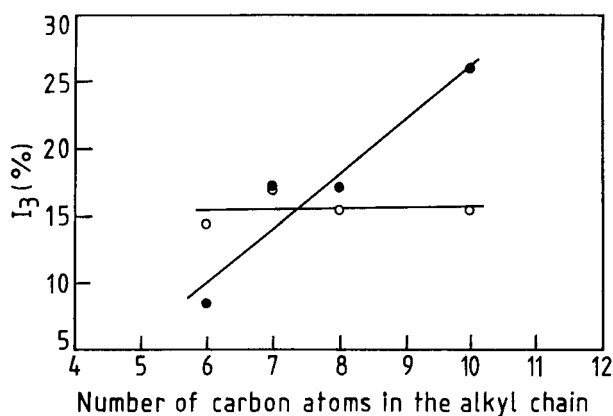


Figure 9. Variation of I_3 with the number of carbon atoms in the alkyl chain: ● denotes the solid phase and ○ denotes the liquid crystalline phase.

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 the positroniums, the *o*-Ps pick-off lifetime is determined by the average size of a void. The observed fact that the I_3 value in the liquid crystalline phase remains the same in all the cyanocompounds investigated, therefore, suggests that the average size of voids and their number density is more or less same in these compounds. This indicates that in the liquid crystalline phase the spatial packing of the molecules in all these compounds is similar. However, the significant variation in I_3 values in the solid crystalline phases, as shown in figure 9, indicates that in this phase there is an appreciable change in the spatial arrangement of the molecules as one goes across the successive homologues of these compounds. The results suggest that in 6CB

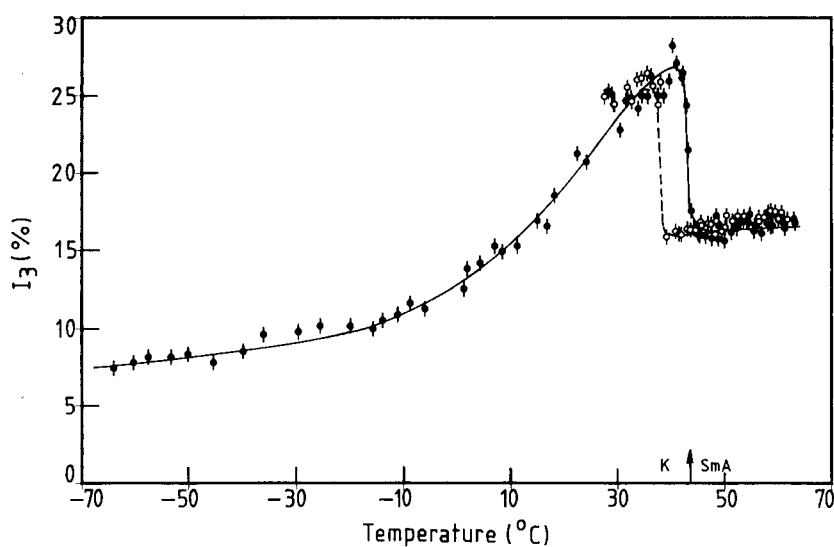


Figure 10. Temperature dependence of I_3 in 10CB extended to low temperatures: \blacklozenge denotes the heating cycle and \blacklozenge denotes the cooling cycle.

the solid crystalline phase is a close-packed structure and with increasing alkyl chain length the structure becomes more open-packed. Furthermore, a lower average value of τ_3 in the solid crystalline phase of 6CB suggests a smaller average void size in this phase. Similarly, a higher value of τ_3 in the solid phases of the other three alkyl cyanobiphenyls suggests the formation of larger voids in these materials. This conclusion is in conformity with that arrived at earlier. Furthermore, it can be noted that in 10CB, as compared to the smectic phase much greater positronium formation takes place in the solid phase (figure 8). It is an observation contrary to the general behaviour. Normally, there is lesser extent of positronium formation in the solid phase compared to the liquid crystalline phase. To understand this abnormality, in this sample positronium formation was further investigated by extending our measurements to low temperatures (down to -70°C). The results of this study are depicted in figure 10. It is observed that with increasing temperature the positronium formation increases, at first slowly and then rapidly. In the temperature range, -70 to -10°C , the increase in positronium formation is commensurate with the thermal expansion of the crystal lattice. However, in the region, -10 to 30°C the change is rather rapid, suggesting the initiation of some 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. Thus, with increasing temperature the proportion of the open-pack solid increases at the expense of the close-pack solid. 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 10CB

4. Conclusions

The present work demonstrates the usefulness of positron annihilation parameters in detecting various features of the cyanobiphenyls, including anti-parallel bimolecular association, solid

crystalline polymorphism and the formation of cybotactic groups in the nematic phase and the retention of solid crystal order in the liquid crystalline phase. The formation of solid crystalline polymorphs in 8CB as reflected in the present work, has not previously been reported. It is also observed that τ_3 is a more sensitive parameter than I_3 in its response to the various structural changes occurring in the system. However, a systematic change observed in the I_3 values in the solid crystal phase as a function of the alkyl chain length provides a better picture of the molecular packing. The peculiar behaviour of I_3 in the solid phase of 10CB provides information on the changes in the molecular packing occurring in this phase.

Acknowledgments

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