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Study of Structural Changes in 4-n-nonyloxy-4'-cyanobiphenyl Employing Positron LifetimeSpectroscopy

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ABSTRACT

Liquid crystals are fascinating state of material. They arebeing used in liquid crystal display devices for the last few decades. Alkyl- and alkyloxy- cyanobiphenyls are liquid crystal forming compounds. 4-n-nonyloxy-4'-cyanobiphenyl, represented as 9OCB or M27,is one of the homologues ofalkyloxycyanobiphenyl series.Positron lifetime measurements have been carried out in M27, both in the heating and cooling cycles of the sample.Positron lifetime parameters were found to be sensitive in detecting some of the interesting features like solid crystalline polymorphism, retention of some memory of more ordered crystalline state in liquid crystalline phase, formation of cybotactic groups and phase transitions taking place in this compound. The temperature range for the study was so chosen as to cover all the phases of compoundM27, i.e., crystalline solid phase, liquid crystalline phase and isotropic liquid phase. In present investigation, the crystalline solid to liquid crystalline phase and liquid crystalline to isotropic liquid phase transitionsare achieved at65 ^{0}C and 76^{0}C respectively. These transition temperatures agree well with those reported in literature for this compound.

Keywords:9OCB, Liquid Crystal, Positron Lifetime, Phase Transformation.

Introduction

The liquid crystal forming compound, M27has very large dipole moment associated with its nitrile bond. Due to this large dipole moment associated, they arrange themselves anti parallel to each other and form a kind of bimolecular association [1-3]. The apparent length of this anti-parallel pair in the liquid crystalline phase is found to be greater than 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 [4]. 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 [1, 2].These small aggregates of molecules are known as cybotactic clusters. The size of these clusters decreases with increasing temperature [5]. Another interesting feature reported to be associated with cyanobiphenyl liquid crystalline materials is the solid crystalline polymorphism [6-8].

Positron annihilation parameters are found sensitive towards various characteristics and micro-structural changes taking place in liquid crystalline materials. A compilation of this work has been done by P.C. Jain [9]. Positron lifetime spectroscopy was used by M. Sharmaand K.C. Singh in the study of complex molecular motions taking place in alkyl- and alkyloxy- cyanobiphenyls [10-13]. The present work describes the potentiality of positron annihilation technique in investigating various characteristic features of M27.

Initial efforts, in investigating various characteristics of this kind of compounds, were made by Malhotra et al [14, 15] and Jain et al [16]. In Present investigation, a systematic temperature-dependent positron lifetime measurements were performed on M27.

Experimental

The radioactive sources with neutron deficient nuclei are generally used as positron sources.In this kind of nuclei, a proton is converted into a neutron by emitting a positron.The positron source used in present investigation was ^{22}Na. The decay scheme of this source is shown in figue1. The benefit of using this source is that, there is almost a simultaneous emission of 1.276 MeV gamma radiation with the birth of positron. So this 1.276 MeV gamma energy radiation provides the birth signal of positron. The positron annihilate with electron by emitting a 0.511 MeV gamma ray. Thus a correlation between 1.276 and 0.511 MeV radiation gives an estimate of positron lifetime in the medium. The principal of lifetime measurement technique is depicted in figure2.

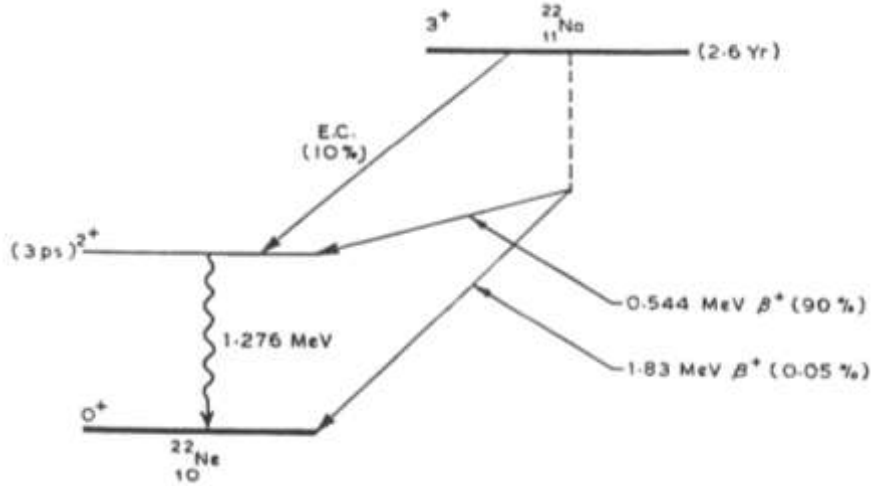

Figure1. Decay Scheme of Positron Source ^{22}Na

The aqueous solution of ^{22}NaCl was used to prepare positron source.The positron source was prepared by evaporating a few drops ^{22}NaClsolution 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 fixed in the grooves of a specially designed glass ampuleand then thisampule was sealed properly. The temperature of the sample was thermostatically maintained constant in every cycle of measurement. In each set of measurement a total of two lakh counts were collected.

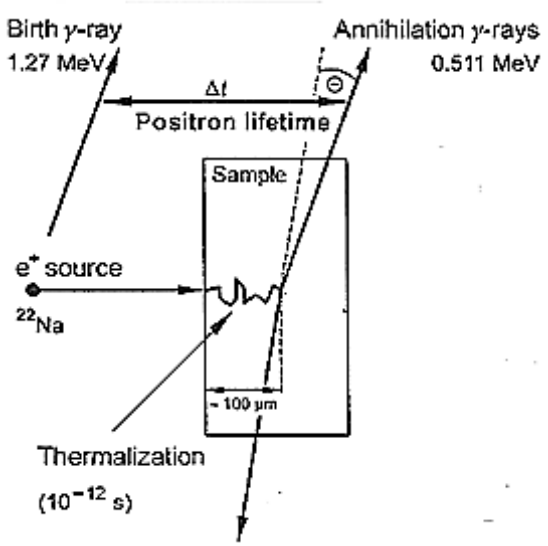

Figure2. Principle of Positron Lifetime Measurement Technique

Positrons emitted by radioactive source, on entering into material media, loss almost all their energy in ionic collisions. The thermalized positrons then eventually annihilate with the electrons of the media. The lifetime of positron is therefore, governed with the state of electron in the media with which it annihilate. The liquid crystalline material used in the present, M27 was procured from British Drug HouseChemicals, UK and was of high purity grade. This was, therefore, used without any further purification.

Results and Discussion

Positrons entering into the material media either annihilate with the free electrons or form bound states with electrons. The annihilation with free electrons is known asfree annihilation. Free annihilation lifetime and its relative intensity are represented by τ_2 and I_2respectively. The bound state of positron isvery much similar to hydrogen atom with proton replaced by positron. It is known as positronium.Positronium may exists in two states either para-positronium (p-Ps) or ortho-positronium (o-Ps). The annihilation of positron, with the electron with which it is bound, is known as self-annihilation. The self-annihilation lifetime ofpara-positroniumis0.125ns and that of ortho-positronium is 140 ns. The p-Ps lifetime and its intensity of formation are represented by τ_1 and I_1 respectively.Due to its long lifetime, instead of self-annihilation, o-Ps generally picks up an electron from surrounding medium and annihilate with it. This is known as pick-off annihilation. Thepick-off annihilation lifetimeof o-Ps is represented asτ_3. 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 o-Ps interaction mechanism is shown in figure3.

Variation ino-Ps pick-off lifetime $\tau_3$with temperature, in liquid crystalline M27, is shown in Figure4. Positron lifetime parameters picked up some of the important features like solid crystalline polymorphism, retention of memory of crystalline state even in passing to liquid crystalline phase, formation of cybotactic groups and relaxational behavior.

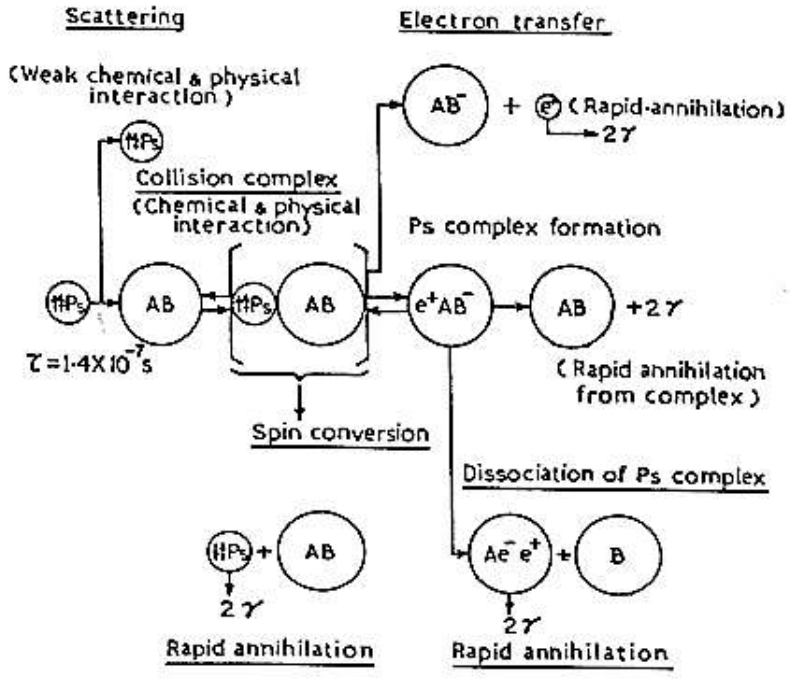

Figure3.Schematic Diagram of Possibleo-Ps Interaction with Matter

Positron annihilation lifetime spectroscopy was used to investigate solid crystalline polymorphism in various liquid crystalline materials [6-8]. Present study provides evidence for the existence of solid crystalline polymorphism in M27. Present positron lifetime studies reveal that Solid K_1 to Solid K_2 transformation takes place at temperature 60^0C.However, the observed temperature range for K2 phase is too short (~4.5^0C) to provide clear evidence about its nature. This transformation is represented by arrow on temperature axis in figure4. Solid crystalline polymorphism, in similar liquid crystalline material M24, has also been reported using Raman spectroscopy [7], ac calorimetry and picosecond time resolved fluorescence [17], and DSC, X-ray diffraction and optical microscopy [18].

Here solid K_1 to solid K_2 transformation arising out of conformational change. 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 60 to 65 ^{0}C, is indicating two possibilities. Either a new crystalline phase K_2 begins to grow at the expense of K_1 phase or growth of liquid crystalline SmA phase which is inter-dispersed in K_1. The first possibility supports the metastable character of K_1 phase. The constancy of τ_3 value over the temperature range 60 to 65 ^{0}Cdoes not support the metastable character of K_1 phase. Hence an early onset of SmA phase inter-dispersed in the crystalline K_1 phase is supported by our observation. As the temperature is raised the content of SmA increases at the expense of K_1. At 65^0C, the SmA content reaches a critical limit and the system completely transforms to SmA phase. At 77^0C, system again transforms its state from smectic to nematic.

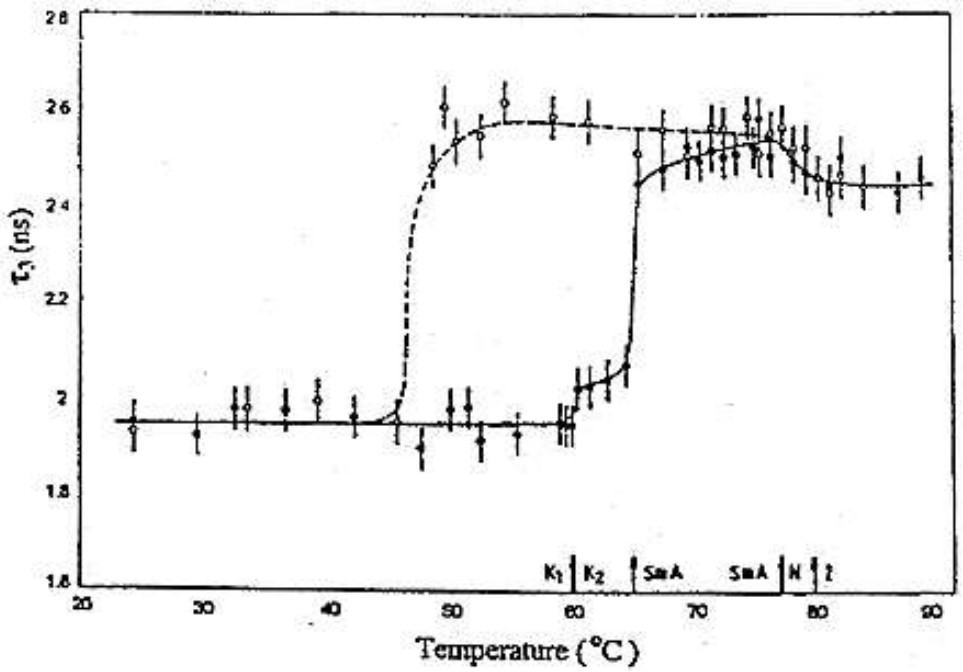

Figure4. Temperature dependence of τ_3 in M27: solid circles represent the heating cycle and hollow circles represent cooling cycle. The arrows on the temperature axis represent solid crystalline to liquid crystalline and liquid crystalline to isotropic liquid transitions.

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 M27, 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 [1-3]. 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 the smectic 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 [19]. Such an anti-parallel pairing in liquid crystalline state, leads to scares availability of free dipolar endings, probable sites for o-Ps pick off to take place. This lowering of ortho-positroniumpick 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 [4].

In liquid crystalline state, adjacent to crystalline solid phase, $\tau_3$is found to increase gradually with increasing temperature. In this region, the rate of increase of τ_3 does 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.

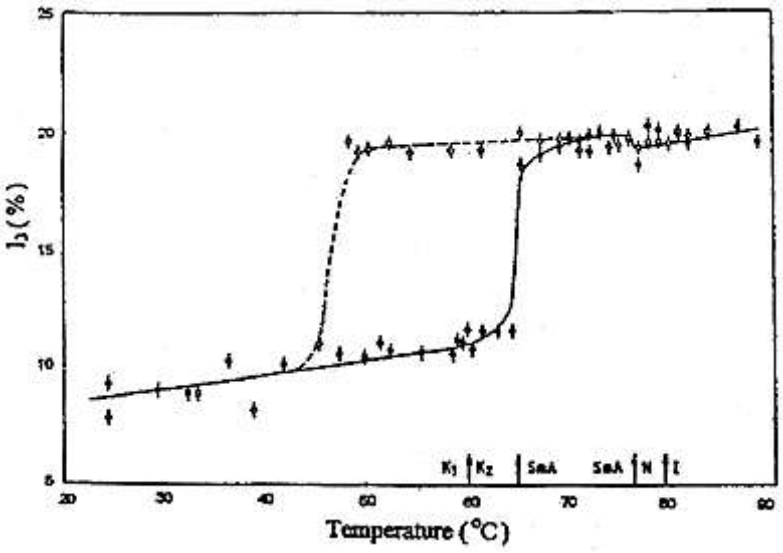

Figure5. Temperature dependence of I_3 in 8OCB.Symbols have the same meanings as in figure1.

It is mentioned previously that the positronium formation probability is represented by I_3. Figure5 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 polymorphish 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. A slight decrease in I_3 value at smectic to nematic transition indicates that there is a lesser positronium formation in nematic phase.

Conclusions

Positron annihilation parameters are found quite sensitive not only in detecting gross features like phase transformations but also to fine structural changes occurring in the liquid crystal forming M27. The positron annihilation lifetime shows 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 M27 indicates a kind of molecular repacking.

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