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Effect of Intermolecular Forces on the Annihilation of Positrons in a Nematic Liquid Crystal

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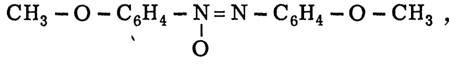
Lifetime spectra have been measured for positrons annihilating in the liquid-crystal p-azoxyanisole. Four lifetime components appear when positrons annihilate in either the nematic mesophase or in the isotropic liquid phase, but in solid p-azoxyanisole the longest-lived component is absent. No abrupt changes in either lifetimes or intensities are observed across the nematic-isotropic transition; however, the solid-nematic transition produces changes in all annihilation parameters which are unattributable to the accompanying 0.1% density change. Annihilation mechanisms are proposed to account for the observed positron lifetime components and their dependence on phase. The degree of molecular orientation appears to have little direct influence on annihilation behavior, but the nature and strength of the intermolecular forces in different phases can greatly affect the positron lifetimes and intensities.

INTRODUCTION

Lifetime measurements of positrons annihilating in the liquid-crystal p-azoxyanisole as a function of temperature are reported here. Before discussing these results, we will first consider some of the physical characteristics of this material which might influence positron annihilation. p-azoxyanisole, whose chemical formula is



$$\mathrm{CH_3-O-C_6H_4-\underset{\underset{\displaystyle O}{|}}{N}=N-C_6H_4-O-CH_3}\ ,$$

consists of elongated rod-like molecules. The molecular weight is 258.27. The presence of the N-O group, which makes an angle of 57°31′ with the long axis of the molecule, produces a molecular electric-dipole moment of 2.48 D.[1] In addition to the solid and isotropic liquid phases, p-azoxyanisole exhibits a nematic mesophase. The sequence of transitions between the phases is indicated in the following diagram:

$$\text{Solid} \xleftrightarrow{116\,^{\circ}\text{C}} \text{Nematic} \xleftrightarrow{136\,^{\circ}\text{C}} \text{Isotropic}\ .$$

The transition from the solid phase to the nematic mesophase is accompanied by a change in density of only 0.1%. The density change across the nematic-to-isotropic-liquid transition is 0.35%.[2]

The nematic mesophase of p-azoxyanisole is characterized by a nearly parallel alignment of the molecular axes, but with the molecular centers of gravity arranged randomly. This is shown schematically in Fig. 1(b). This arrangement permits almost complete freedom of translational molecular movement, but only rotational movement about the long molecular axis is likely. p-azoxyanisole in the solid phase has a monoclinic structure with each cell containing four molecules in an imbricated parallel arrangement, as is indicated in Fig. 1(c).[3] The cell dimensions are

$$a = 15.776\ \text{Å}, \quad b = 8.112\ \text{Å}, \quad c = 11.018\ \text{Å},$$

$$\beta = 114.57^{\circ}.$$

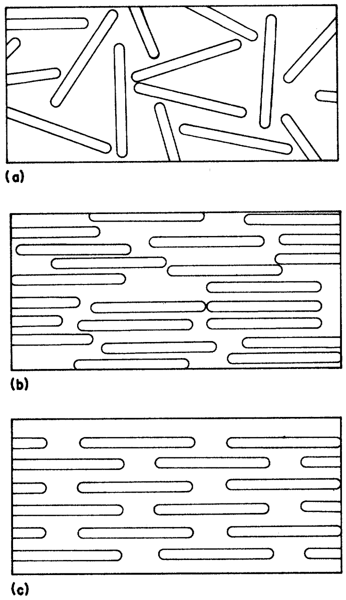
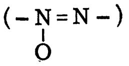


FIG. 1. Schematic representation of the molecular orientation in (a) isotropic liquid, (b) nematic, and (c) solid p-azoxyanisole.

The ether (CH_3-O-) groups at the ends of each molecule are positioned opposite the azoxy



$$(-\underset{\underset{\displaystyle O}{|}}{N}=N-)$$

groups of the nearest-neighbor molecules.

In addition to the change in the degree of molecular order which accompanies the solid-to-nematic transition, it has been shown that there is a corresponding change in the nature of the predominant intermolecular forces.[4] In the solid state, intermolecular attraction is primarily due to strong dipole-dipole and dipole-induced dipole forces. The parallel, but less-ordered, molecular arrangement found in the nematic mesophase results primarily from dispersion forces. Dipole-dipole and dipole-induced dipole forces do not contribute significantly to the intermolecular attractions in either the isotropic or the nematic phase.

EXPERIMENTAL

The annihilation-lifetime spectra were measured with a standard type of timing spectrometer utilizing a time-to-amplitude conversion range of 50 nsec. Measurements of a ^{60}Co prompt spectrum yielded a full width at half-maximum of 0.49 nsec and a logarithmic slope corresponding to a mean life of 0.12 nsec. The positron lifetime spectra were resolved into components by a weighted nonlinear least-squares computer fit.[5]

The p-azoxyanisole, which was obtained from K & K Laboratories, Inc., had a purity certified to be between 98 and 99%. No further purification was attempted. The positron source, which consisted of about 6.9 μC of high-specific-activity ^{22}NaCl sealed between sheets of 1.3-mg/cm^2 Mylar, was surrounded by sufficient p-azoxyanisole to ensure the annihilation of all positrons within the liquid crystal. A stainless-steel and Teflon assembly, designed to apply an external electric field, was located in the liquid crystal beyond the positron range. This assembly was not used in this experiment. The p-azoxyanisole was contained in a Pyrex test tube which was suspended in a temperature-controlled oil bath. Prior to assembly, all materials were thoroughly cleaned to minimize contamination of the liquid crystal. The deviation of temperature due to all causes was estimated to be less than 0.5 °C.

RESULTS

The lifetime spectra of positrons annihilating in liquid p-azoxyanisole can be resolved into four components. In order of increasing lifetime, the mean lives and relative intensities of these components will be labeled τ_1, τ_2, τ_3, τ_4 and I_1, I_2, I_3, I_4, respectively. The computer program determined the optimum fit to the data corresponding to the three longest-lived components and returned the values τ_4, I_4, τ_3, I_3, and τ_2. For each spectrum, the logarithmic slope of the data which remained after subtraction of the three longest-lived components corresponded to a mean life only slightly larger than that of the ^{60}Co prompt spectrum (0.12 nsec). No accurate determination of τ_1 was therefore possible, and the relative intensities I_1 and I_2 could not be unambiguously resolved. In solid p-azoxyanisole, the longest-lived component was absent.

The measured positron mean lives in p-azoxyanisole are presented in Figs. 2 and 3 as a function of temperature over the temperature range 23–146 °C. Statistically weighted least-squares fits to the data are shown as solid lines. Within experimental error, τ_4 remains constant with a statistically weighted average value of

$$\tau_4 = 2.2 \pm 0.1 \text{ nsec} \tag{1}$$

throughout the measured nematic and isotropic temperature ranges. The τ_3 values, which appear to be independent of phase changes, are found to fit a linear function of

$$\tau_3 = (0.74 \pm 0.05) + (0.0034 \pm 0.0007)T, \tag{2}$$

where τ_3 is in nsec and T is the temperature in °C. The mean life τ_2 appears to be sensitive only to the solid-nematic transition; the values fit linear functions of

$$\tau_2 = (0.32 \pm 0.01) + (0.00016 \pm 0.00004)T \tag{3}$$

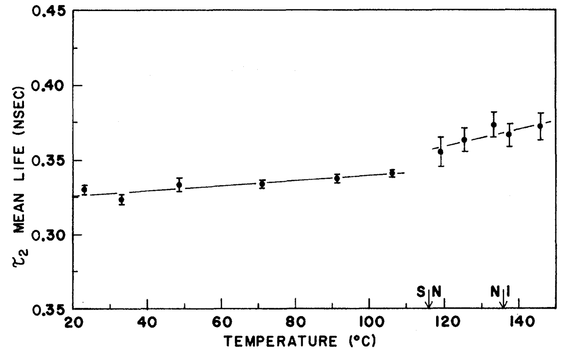


FIG. 2. τ_2 mean life as a function of temperature in *p*-azoxyanisole. The error bars represent statistical standard deviations. The solid-nematic and nematic-isotropic transition temperatures are indicated by arrows.

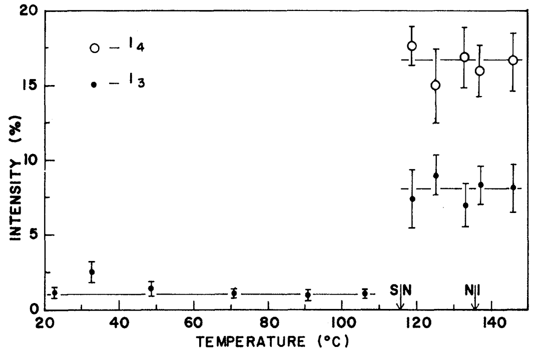


FIG. 4. Relative intensities I_3 and I_4 as a function of temperature in *p*-azoxyanisole. The error bars represent statistical standard deviations. The solid-nematic and nematic-isotropic transition temperatures are indicated by arrows.

in the solid phase, and

$$\tau_2 = (0.29 \pm 0.06) + (0.0006 \pm 0.0004)T \qquad (4)$$

throughout the nematic and isotropic phases.

The relative intensities I_3 and I_4 also appear insensitive to the nematic-isotropic transition, but exhibit marked changes at the solid-nematic transition. These intensities, which are presented in Fig. 4, are approximately constants within the measured solid- and liquid-temperature ranges and have the following statistically weighted average values:

$$I_3 = (1.1 \pm 0.1)\% , \quad I_4 = 0\% \qquad (5)$$

in the solid phase, and

$$I_3 = (8.0 \pm 0.7)\%, \quad I_4 = (16.7 \pm 0.8)\% \qquad (6)$$

in the nematic and isotropic phases.

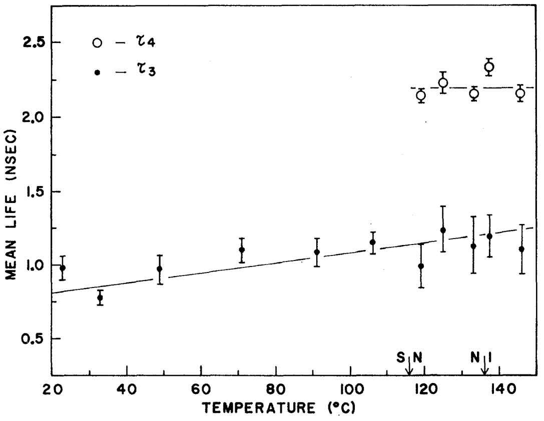


FIG. 3. Mean lives τ_3 and τ_4 as a function of temperature in *p*-azoxyanisole. The error bars represent statistical standard deviations. The solid-nematic and nematic-isotropic transition temperatures are indicated by arrows.

No measurable changes in mean lives or intensities were observed after subjecting the *p*-azoxyanisole to several thermal cycles. A second sample of *p*-azoxyanisole, measured in a differently designed container, gave identical values for the above annihilation parameters.

DISCUSSION

The long-lived component, with mean life $\tau_4 = (2.2 \pm 0.1)$ nsec and relative intensity $I_4 = (16.7 \pm 0.8)\%$, results from the process of electron pickoff by positrons bound in orthopositronium (*o*-Ps) atoms. Our results agree with those of Pederson[6] and those of Cole and Walker[7] in that this component is observed only in the nematic and isotropic phases. In the nematic phases our values are similar to Pederson's, who reported on *o*-Ps component with a mean life of (2.1 ±0.5) nsec and an intensity of (20 ± 5)%. Cole and Walker, however, reported a lower value for the nematic *o*-Ps mean life, (1.0 ± 0.1) nsec, with an intensity of (35 ± 5)%. In the isotropic phase, Pederson reported an increase in mean life to (3.6 ± 1.0) nsec, while our results and those of Cole and Walker remained the same as in the nematic mesophase. These authors measured only the long-lived component.

With the assignment of the τ_4 component to the annihilation of *o*-Ps atoms, the τ_1 component observed in the liquid phases must result from the annihilation of parapositronium (*p*-Ps) atoms. Lacking definite τ_1 and I_1 values, the possibility exists that this component also contains contributions from other modes of annihilation characterized by mean lives less than, or of the order of, that of *p*-Ps. However, in view of the difficulty of envisioning the required annihilation mechanisms, it will be assumed in the following that such anni-

TABLE I. The I_1 and I_2 values in percent calculated from Eqs. (5)–(10). Case (a) is shown in the text to represent the correct lifetime assignment.

Phase	I_1	I_2
(a) τ_2 is taken as the free-positron mean life		
Solid	0.4	98.5
Liquid	8.2	67.0
(b) τ_3 is taken as the free-positron mean life		
Solid	24.7	74.2
Liquid	23.0	52.3

hilation modes do not exist.

In solid p-azoxyanisole, the τ_4 component is absent from the lifetime spectra. The τ_1 component, however, is still present with reduced relative intensity. This implies the continued formation of positronium in the solid phase, with either the τ_2 or the τ_3 component resulting from the decay of o-Ps. The remaining component must result from the annihilation of free positrons, i.e., those positrons which do not form positronium.

The low I_3 values suggest that the τ_2 component results from free-positron annihilations. If this is so, then the statistics of positronium formation prescribe that

$$I_1 = \tfrac{1}{3} I_{o\text{-Ps}} = \tfrac{1}{3}(I_3 + I_4) \ , \tag{7}$$

$$I_2 = 100\% - 4I_1 \, . \tag{8}$$

If, however, the τ_3 component is attributed to the annihilation of free positrons, then

$$I_1 = \tfrac{1}{4}(100\% - I_3), \tag{9}$$

$$I_2 = 3I_1 - I_4 \ . \tag{10}$$

The I_1 and I_2 values calculated from Eqs. (5)–(10) are given in Table I.

Although exact values were not obtainable, the changes in the I_1 and I_2 intensities across the solid-liquid transition can be roughly estimated from the areas under the experimental curves. It is found that when p-azoxyanisole melts, I_2 is reduced by a factor of roughly $\frac{1}{3}$ and I_1 is *increased* by a factor which is at least 2 but could be considerably larger. Comparison with the values in Table I indicates that the τ_2 component most likely does represent free-positron annihilation.

Further support for this interpretation results from calculations of Z_{eff}, the effective number of electrons per molecule which are available for annihilation with free positrons.[8] Z_{eff} is determined from the equation

$$\lambda = (\pi r_0^2 c)(\rho/M) Z_{\text{eff}}, \tag{11}$$

where λ is the free-positron annihilation rate, r_0 is the classical electron radius, c is the speed of light, and ρ and M are the molecular density and mass, respectively, of the material. Using the p-azoxyanisole densities reported by Maier and Saupe,[2] the following Z_{eff} values were obtained:

$$Z_{\text{eff}} = 142 \pm 1 \tag{12}$$

for the solid phase, and

$$Z_{\text{eff}} = 136 \pm 2 \tag{13}$$

for the nematic and isotropic phases. Linear least-squares fits to both the solid and liquid λ_2-vs-ρ data points yielded zero-density intercepts which were within one standard deviation of $\lambda_2 = 0$.

Cova and Zappa developed a method for predicting Z_{eff} in molecular substances by assuming that each atom in the molecule contributes to the annihilation of free positrons an amount which is typical of that type of atom and is independent of the structural properties of the molecules and of the material.[9] Their results predict a Z_{eff} for p-azoxyanisole of 132.9 ± 4.4 which agrees reasonably well with our experimental values.[10]

It remains to discuss the mechanisms responsible for the appearance of the two o-Ps annihilation components described by the parameters (τ_3, I_3) and (τ_4, I_4). p-azoxyanisole, being a strongly polar material, is characterized by the presence of intense electric fields on a microscopic scale. Owing to the permanent dipole interactions, these fields would be particularly strong in the solid phase. The dipole regions would act as strongly attractive centers for polarized o-Ps atoms.[11] After sufficient thermalization, o-Ps atoms would become localized in the vicinity of the azoxy group in the p-azoxyanisole molecules. The pickoff electron density near such localized o-Ps atoms would be considerably enhanced over that sampled by nonlocalized o-Ps atoms. We attribute the τ_3 component to the annihilation of such localized o-Ps atoms and the τ_4 component to the annihilation of o-Ps atoms which remain nonlocalized.

The imbricated parallel molecular arrangement of solid p-azoxyanisole ensures that all o-Ps atoms, wherever they are formed in the lattice,[12] can never be far removed from an attractive center. It is thus reasonable to assume that all o-Ps formed in the solid will annihilate from a localized state. In the liquid phases, where the absence of permanent dipole interactions and the resulting decrease in the degree of molecular order apparently favor positronium formation, o-Ps atoms may well form in regions where they are much less influenced by the now randomly oriented dipole fields and annihilate from nonlocalized states.

Finally, a similar mechanism can explain the observed increase in free-positron lifetime across the solid-to-nematic transition, the higher-intensity electric fields in the solid more strongly attracting free positrons to molecular regions of higher than average electron density.

In conclusion, it is apparent from these measurements that caution must be exercised in attributing changes in annihilation lifetimes and intensities across a phase transition solely to density effects. Although the degree of molecular orientation appears to have little direct influence, e.g., across the nematic-isotropic transition, the nature and strength of the intermolecular forces in the two phases can greatly affect the observed annihilation behavior.

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