

POSITRON LIFETIMES IN LIQUID  
CRYSTALLINE COMPOUNDS

by

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## CHAPTER I

### INTRODUCTION

In 1949 Shearer and Deutsch<sup>1</sup> investigated the annihilation of positrons in a variety of gases. Their results showed that the annihilation rate was not proportional to the gas pressure (as expected if positrons annihilate as free particles), and further, that the decay rate contained several components. To explain these results it was assumed that some of the positrons were annihilating from some type of bound state.

Mohorovicic<sup>2</sup> had earlier referred to a bound state between a positron and an electron, and Ruark<sup>3</sup> named such a system positronium. Wheeler<sup>4</sup> was first to discuss its theory.

After the work on the annihilation of positrons in gases, several groups, notably de Benedetti and Richings<sup>5</sup> and Bell and Graham,<sup>6</sup> were led to study this process in solids and liquids. Pond,<sup>7</sup> during this

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<sup>1</sup>J. W. Shearer and M. Deutsch, *Phys. Rev.* 76, 642 (1949).

<sup>2</sup>S. Mohorovicic, *Astron. Nachr.* 253, 94 (1934).

<sup>3</sup>A. E. Ruark, *Phys. Rev.* 68, 278 (1945).

<sup>4</sup>J. A. Wheeler, *Ann. N. Y. Acad. Sci.* 48, 219 (1946).

<sup>5</sup>S. de Benedetti and H. J. Richings, *Phys. Rev.* 85, 377 (1952).

<sup>6</sup>R. E. Bell and R. L. Graham, *Phys. Rev.* 90, 644 (1953).

<sup>7</sup>T. A. Pond, *Phys. Rev.* 85, 489 (1952).

same period, estimated that about one-quarter to one-third of all positrons annihilating in most gases formed positronium. Assuming that positronium was formed in, or quickly decayed to, the 1s state, one-quarter would be in the singlet state (parapositronium), which would annihilate with the emission of two quanta in about  $1.25 \times 10^{-10}$  sec, and the other three-quarters would be in the triplet state (orthopositronium), which would annihilate by three-quantum emission with a lifetime of  $1.4 \times 10^{-7}$  sec.<sup>8</sup>

Wallace<sup>9</sup> has summarized the early experiments of positron annihilation rates in solids as follows: (a) in metals, ionic crystals, and valence crystals, there was found a single lifetime for annihilation, surprisingly constant from material to material and of the same order as that for singlet positronium; (b) in a wide variety of organic, amorphous, or "molecular" materials, two decay lifetimes were discovered, a short lifetime  $\tau_1$  of the same order as in (a), and a longer lifetime  $\tau_2$  of the order of  $10^{-9}$  sec, which in most cases accounted for something of the order of 30% of the annihilations.

A possible explanation of the  $\tau_2$  component has been given as follows:<sup>9</sup> Positrons, upon entering a substance, rapidly slow down to a few electron volts of energy as a result of the mechanisms of ionization and/or electronic excitation of the molecules of the material. After slowing down, triplet positronium is formed by a certain fraction of the positrons. This state of positronium is assumed to be con-

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<sup>8</sup>A. Ore and J. L. Powell, Phys. Rev. 75, 1696 (1949).

<sup>9</sup>P. R. Wallace, Solid State Phys. 10, 1 (1960).

tinually scattered by the molecules of the sample until the positron experiences a collision with an electron whose spin state relative to it is singlet. When such a collision occurs, the positron annihilates with this electron by the so called "pickoff" process<sup>10</sup> giving a lifetime which is of the order of a few nanoseconds.

One of the least understood effects observed for the first time by Bell and Graham is the strong dependence of  $\tau_2$  in sintered Teflon and in ice on temperature.<sup>11</sup>  $\tau_2$  varied almost directly with temperature. They were led to conclude that the appearance and changes of the  $\tau_2$  component were related to the order-disorder property of the solid. Landes, Berko, and Zuchelli<sup>12</sup> performed a melting experiment on naphthalene to check this correlation.  $\tau_2$  increased from 1.3 to 2.6 nsec as the melting point was passed. Cottini, Fabri, Gatti, and Germagnoli<sup>13</sup> performed a melting experiment on anthracene, and, except for the fact that  $\tau_2$  was absent in the solid form of this substance and appeared only on melting, reported similar results. In the same paper, this group reported a complex decay in the solid specimens of anthracene which had been irradiated with neutrons. Both effects were ascribed to the influence of disorder on the lifetime of positrons.

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<sup>10</sup>M. Dresden, Phys. Rev., 93, 1413 (1954).

<sup>11</sup>S. Berko and F. L. Hereford, Revs. Modern Phys. 28, 299 (1956).

<sup>12</sup>H. S. Landes, S. Berko, and A. J. Zuchelli, Phys. Rev. 103, 828 (1957).

<sup>13</sup>C. Cottini, G. Fabri, E. Gatti, and E. Germagnoli, J. Phys. Chem. Solids 17, 65 (1960).

Brandt, Berko, and Walker<sup>14</sup> assumed that the temperature and phase dependences of  $\tau_2$  in molecular substances were primarily "free volume" effects, in that the overlap between the positronium and lattice wave functions decreases with increasing lattice spacing. This theory was tested experimentally for the cases of glycerol, polytetrafluoroethylene, and water. The theory fitted the experimental data for glycerol and polytetrafluoroethylene, as well as those of naphthalene referred to previously. However, an anomalous behavior was found for the ice-water transition, where  $\tau_2$  increased significantly despite the contraction of water on melting. Liu and Roberts<sup>15</sup> suggested, after trying unsuccessfully to fit their  $\tau_2$  data in gaseous, liquid, and solid hydrogen to this theory, that phase was a factor in the annihilation rate in hydrogen as well as in water.

Bisi, Fasana, Gatti, and Zappa<sup>16</sup> studied  $\tau_2$  in a number of polymers. This group divided these polymers into two general classes: (a) non-polar polymers which have no permanent dipole moments, and (b) polar polymers which have permanent dipoles in their structures. They found that two polymers, one polar and one non-polar, with the same average electron density exhibited different lifetimes. The greater  $\tau_2$  was observed in the non-polar polymer. Their conclusion was that the presence of these polar groups would create large electric

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<sup>14</sup>W. Brandt, S. Berko, and W. W. Walker, Phys. Rev. 120, 1289 (1960).

<sup>15</sup>D. C. Liu and W. K. Roberts, J. Phys. Chem. Solids 23, 1337 (1962).

<sup>16</sup>A. Bisi, A. Fasana, E. Gatti, and L. Zappa, Nuovo Cimento 22, 266 (1961).

fields on a microscopic scale. The positronium would come under a polarization force which would attract it to the surface of the atoms leading to an electron density at the positron that would be greater than the average. This in turn would lead to a faster pickoff rate.

Solid-solid transitions have also been found to give rise to variations in  $\tau_2$ . Clarke and Hogg<sup>17</sup> observed a change in the slope of  $\tau_2$  versus temperature in cyclohexane at the cubic-monoclinic transition near  $-110^\circ\text{C}$ . Recently, Fabri, Germagnoli, and Randone<sup>18</sup> reported that  $\tau_2$  nearly doubled in unsintered Teflon when the temperature crossed the interval of the triclinic-hexagonal lattice transition. This transition occurred near room temperature. No further changes in  $\tau_2$  were observed in the sample until the hexagonal structure broke down at about  $275^\circ\text{C}$ .

The present experimental work was undertaken to obtain some data on the lifetime of orthopositronium, as a function of temperature, in five organic substances which exhibit turbid states above or below their respective melting points. These data were utilized to attribute changes in the annihilation rate of orthopositronium to certain variations which occurred, during phase transitions, as the temperature of these compounds was increased or decreased.

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<sup>17</sup>H. C. Clarke and B. G. Hogg, *J. Chem. Phys.* 37, 1898 (1962).

<sup>18</sup>G. Fabri, E. Germagnoli, and G. Randone, *Phys. Rev.* 130, 204 (1963).

## CHAPTER II

### EXPERIMENTAL APPARATUS

The electronic apparatus used for the lifetime determinations was similar to that described by Green and Bell,<sup>19</sup> with the exception of the time-to-amplitude converter which was of the transistorized type designed by Simms.<sup>20</sup> A block diagram of the electronics is shown in Figure 1.

Measurements were made using a Na<sup>22</sup> positron source of approximately 2- $\mu$ C activity, which was deposited between "Mylar" films of 0.87 mg/cm<sup>2</sup> thickness. The sample surrounded the source with more than sufficient thickness (i.e., > 181 mg/cm<sup>2</sup>) to stop the positrons which have a maximum energy of 0.56 Mev. When the positron was emitted from Na<sup>22</sup>, a 1.28-Mev gamma ray was emitted from the daughter nucleus Ne<sup>22</sup> within < 10<sup>-11</sup> sec. The positron annihilated in the sample material producing two quanta of 0.51 Mev. The source and sample were placed between the two scintillation counters. One counter detected the nuclear gamma ray, and the other counter detected one of the annihilation photons. The lifetimes of positrons in the substance being studied were determined by measuring the delay of the pulses due to the annihilation quanta relative to the Ne<sup>22</sup> gamma rays.

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<sup>19</sup>R. E. Green and R. E. Bell, Nuclear Instruments 3, 127 (1958).

<sup>20</sup>P. C. Simms, Rev. Sci. Instr. 32, 894 (1961).

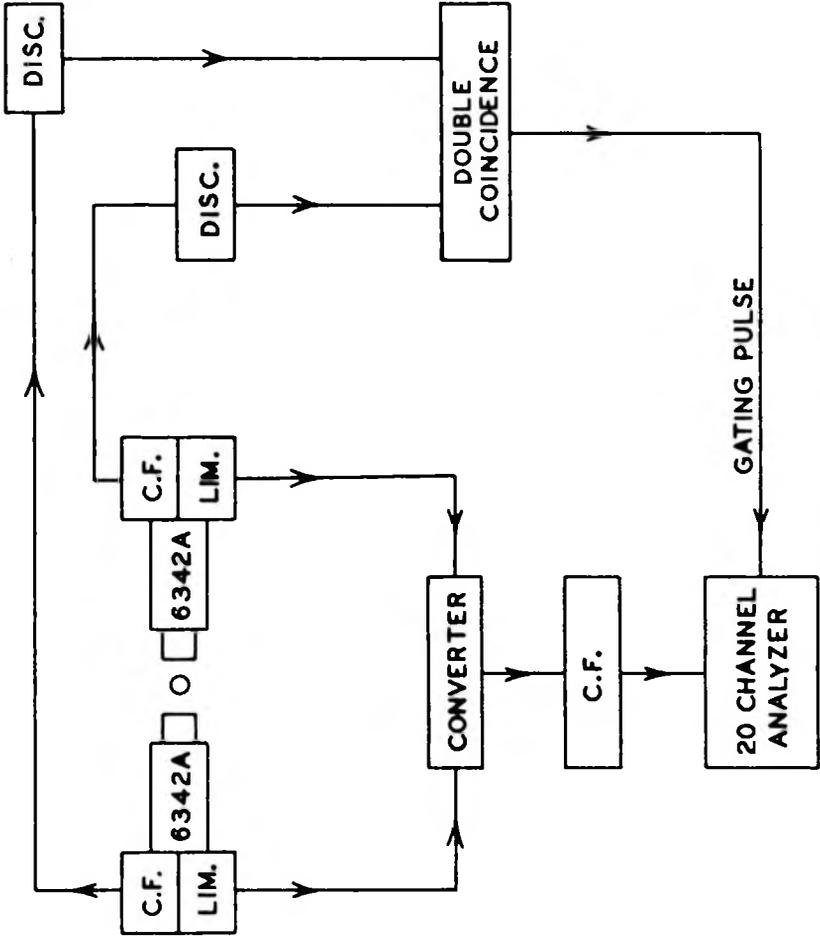


Figure 1. Coincidence System.

The scintillation counters consisted of plastic phosphors (Nuclear Enterprises NE 102) 1" diameter x 3/4" long with magnesium oxide reflector coating on the top and sides coupled optically with DC 200 silicone fluid to RCA 6342A photomultipliers which were operated at 2100 volts. An output was taken from the ninth dynode of each counter and fed through a cathode follower to an integral discriminator. One discriminator was set to accept only those pulses whose corresponding energies were higher than 0.51 Mev. The other discriminator was set to accept all pulses above noise. Thus, the first discriminator accepted only the 1.28-Mev nuclear gamma ray which established the time of creation of a positron while the second discriminator accepted the annihilation radiation as well. The result of accepting the 1.28-Mev gammas by both discriminators increased the chance coincidence rate, but, for sources of the activity used in these measurements, this was a small correction which was easily determined experimentally. The outputs of these discriminators were fed to a slow (2.0  $\mu$ sec) double coincidence circuit (Radiation Instrument Development Laboratory, Model 412). The output of this coincidence circuit was used to gate the 20 channel pulse height analyzer (Atomic Instruments, Model 520).

The anode of each photomultiplier was coupled by a capacitor to the grid of a 6AK5 operated as a limiter. The output of the limiter was set at one volt by adjusting the screen voltage of the 6AK5. The limited pulse was then shaped to a width of 32 nsec by a shorted 4 meter coaxial cable before entering the time-to-amplitude converter. The delay cables, as well as the clipping stubs, were 125 ohm coaxial cables (RG-63/U). The propagation constant for this type of cable is

0.84c. Therefore, one meter of the cable is equivalent to four nano-seconds of delay.

A diagram of the time-to-amplitude converter is shown in Figure 2. In the quiescent state, the two input transistors  $T_1$  and  $T_2$  were conducting, and the output transistor  $T_3$  was cut off. The resistor  $R_1$  served as a constant current source. When either of the input transistors was cut off by a positive pulse, all of the current  $I$  flowing through  $R_1$  was carried by the other input transistor and  $T_3$  remained cut off. When both  $T_1$  and  $T_2$  were cut off (i.e., a coincidence), the current  $I$  was switched into  $T_3$ . This current was integrated at the collector of  $T_3$ . Therefore, the amplitude of the output was given by

$$V = \frac{I}{C_s} \Delta t \quad . \quad (1)$$

$C_s$  was the stray capacitance at the collector of  $T_3$ , and  $\Delta t$  was the period of time that both  $T_1$  and  $T_2$  were cut off.<sup>20</sup>  $I$  and  $C_s$  were kept constant, and thus  $V$  was directly proportional to the time overlap of the two input pulses. The output pulse was fed through a cathode follower to the input of a 20 channel pulse height analyzer.

To obtain fast switching action, the switching transistors  $T_1$  and  $T_2$  were balanced. This was done by reducing the bias on  $T_3$  with  $R_5$  until single input pulses were observed at the output. Then  $R_8$  was varied until the amplitude of the output pulse was approximately the same with either input cable removed.<sup>20</sup> After  $T_1$  and  $T_2$  were balanced, the bias on  $T_3$  was raised until no single pulses were observed.

The calibration of the circuit was obtained by inserting different

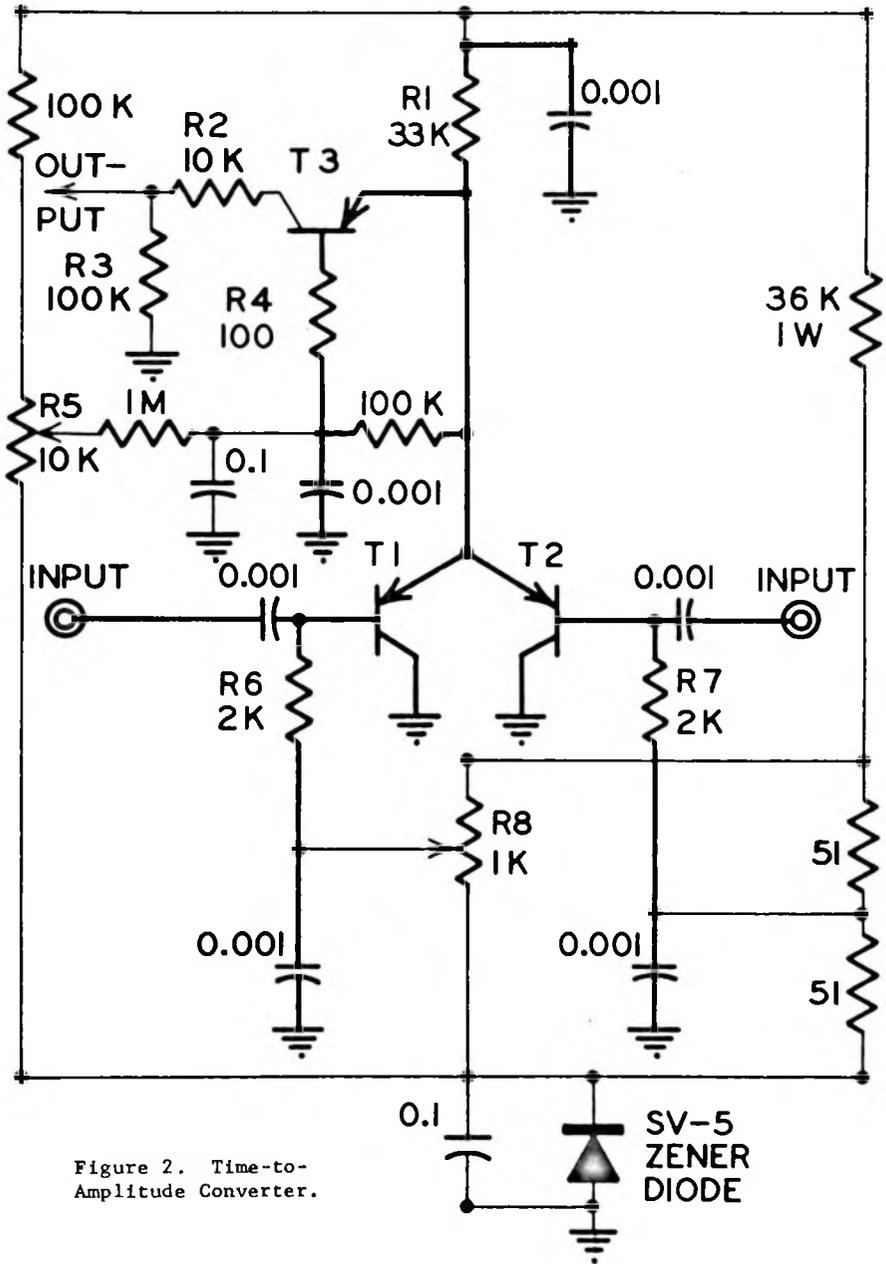


Figure 2. Time-to-Amplitude Converter.

lengths of RG-63/U cable between the limiters and the time-to-amplitude converter. A typical curve showing the variation of the peak channel of the amplitude distribution from the time converter as a function of relative delay between the two detectors is shown in Figure 3. Linearity was found to be poor for complete overlap and minimum overlap. With input pulses of 32 nsec in width, there was a range of 14 to 15 nsec that was linear. All measurements were made with the circuit operating in this range. The slope of the curve in the linear region was used for time calibration of the system.

Figure 4 shows the sample and source holders. The "Mylar" films, with the positron source deposited between them, were supported by a thin aluminum frame. The frame was made to fit in the center of the copper sample chamber. A Lucite cover on the sample container allowed visual observation of the sample during each experiment. The 2" x 5/8" x 2" copper sample container was removable from the 8" x 5/8" x 2" copper base. The sample was heated with a 1" x 2" heating tape (192 watts) which was wrapped around the base of the sample holder. The temperature was varied and held constant with very good accuracy by changing the current through the tape. Temperature measurements were made with a copper-constantan (30 B. & S. Ga.) thermocouple placed near the positron source. A new container and a new thermocouple were used for each sample.

The scintillation counters were placed near the sample holder to maintain a good counting rate. The plastic phosphors were cooled by placing a copper water jacket around each phosphor.

Performance of the electronics was checked using the gamma-gamma

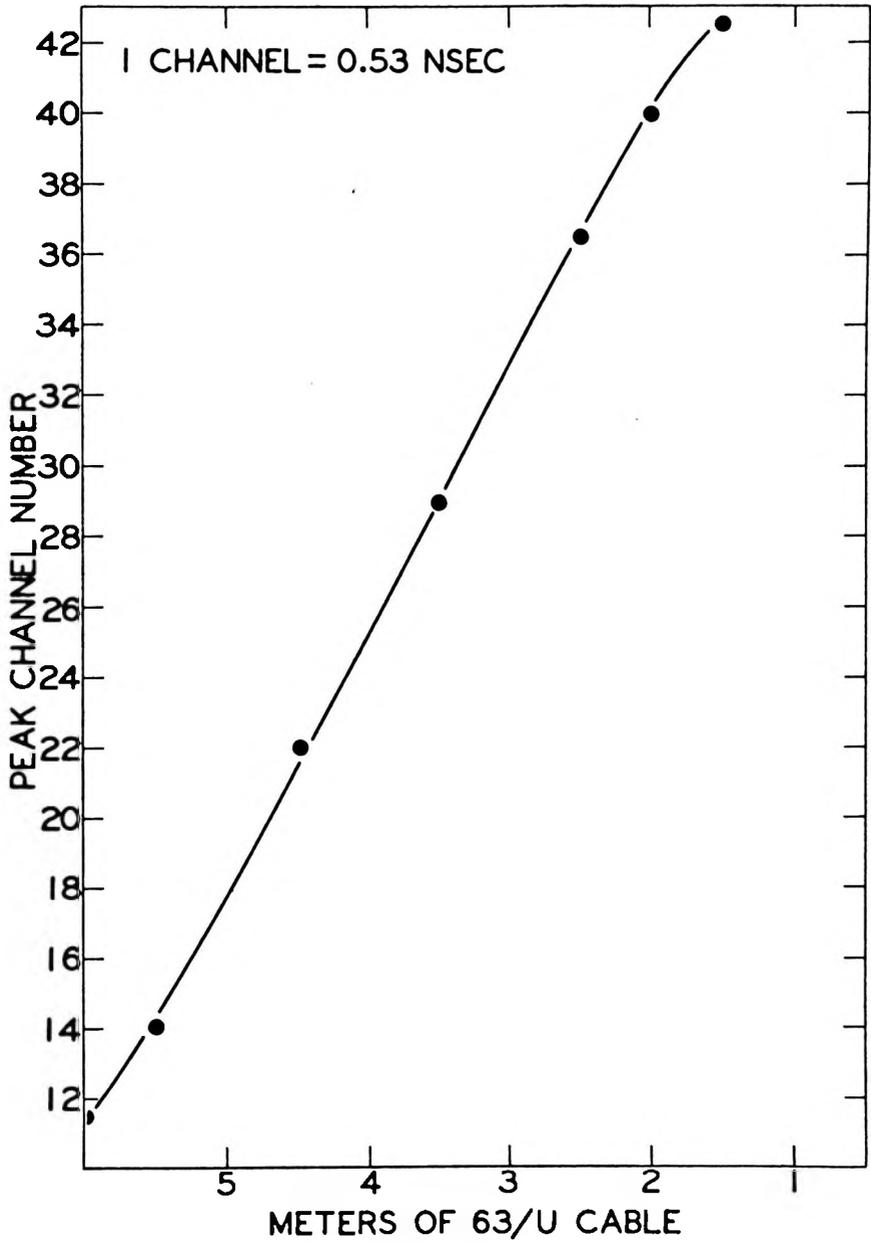


Figure 3. Variation of Peak Channel as a Function of Delay.

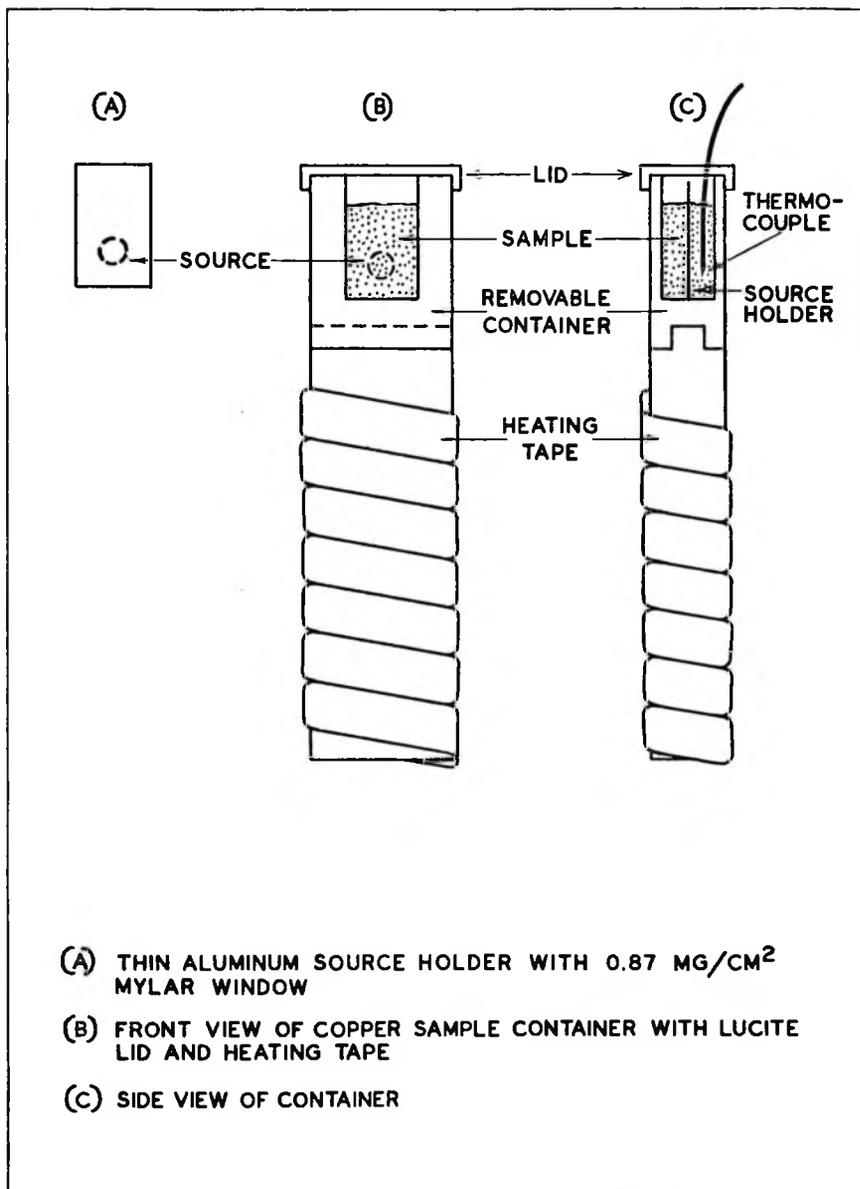


Figure 4.

coincidence from a  $\text{Co}^{60}$  source. The prompt resolution curve obtained in this manner had a full width at half maximum of 1.4 nsec, and a slope corresponding to a half life of 0.19 nsec. Time calibration was checked periodically during the measurements.

## CHAPTER III

### EXPERIMENTAL PROCEDURE AND TREATMENT OF DATA

A positron source was prepared for each sample as described in Chapter II. The source holder was then sandwiched between two aluminum plates which were thick enough to stop all the positrons emitted from  $\text{Na}^{22}$ . This assembly was then placed between the two scintillation counters. The output of the time-to-amplitude converter was fed to the 20 channel pulse height analyzer to obtain the prompt time spectrum. The gain of the analyzer linear amplifier was set so that the largest number of counts was obtained in the first ten channels. With this setting the peak counting rate was registered in the fifth or sixth channel of the analyzer.

After the circuit was time calibrated, several timed (one hour) runs, with the positrons annihilating in aluminum, were conducted for each source using the above gain setting. The counts in each channel were recorded. The base line of the pulse sorter unit was then increased by approximately 15 channels to eliminate true coincidences. Accidental coincidences were obtained in this manner over a timed interval of three to six hours. The accidentals in each channel, which were always nearly constant, were recorded and an average per channel per hour was computed. This average was compared with the peak coincidence counting rate. For the sources used in these measurements, it was found that the accidental rate per channel was always less than

one-thousandth of the coincidence rate in the peak channel.

Following the determination of the accidentals rate, the source was sandwiched between two pieces of commercial Teflon. Teflon has a large  $\tau_2$  component ( $3.5 \pm 0.4$  nsec) which may be used as a precautionary check of the time calibration of the circuit. The experimental time spectrum displayed on the multichannel analyzer was plotted, after the accidentals were subtracted out, on a semi-logarithmic paper. The lifetime of the  $\tau_2$  component was obtained from the slope of the "tail" of this delayed coincidence resolution curve following the analysis of Newton.<sup>21</sup> Newton has shown that if a prompt coincidence resolution curve is represented by  $P(x)$  and if a delayed coincidence resolution curve is represented by  $F(x)$  then,

$$F(x) = \lambda e^{-\lambda x} \int_{-\infty}^x e^{\lambda y} P(y) dy, \quad (2)$$

where the mean life is  $\tau = 1/\lambda$ . Differentiation of (2) gives

$$\frac{dF(x)}{dx} = \lambda [P(x) - F(x)] \quad (3)$$

and

$$\frac{d}{dx} [\ln F(x)] = -\lambda \left[ 1 - \frac{P(x)}{F(x)} \right]. \quad (4)$$

At delays great enough so that  $F(x) \gg P(x)$ , equation (4) becomes

$$\frac{d}{dx} [\ln F(x)] = -\lambda. \quad (5)$$

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<sup>21</sup>T. D. Newton, Phys. Rev. 78, 490 (1950).

Integration from  $x = A$  to  $x = B$  gives

$$\lambda = \frac{\ln \left[ \frac{F(A)}{F(B)} \right]}{B - A} \quad (6)$$

or, since  $\tau = 1/\lambda$ ,

$$\tau = \frac{B - A}{\ln \left[ \frac{F(A)}{F(B)} \right]} \quad (7)$$

In practice A and B were always chosen so that  $F(A)/F(B) = 2$ , reducing equation (7) to the simple relation

$$\tau = \frac{T_{\frac{1}{2}}}{\ln 2} \quad (8)$$

where  $T_{\frac{1}{2}}$  was the half life.

When several Teflon curves were analyzed and found to be satisfactory, the source holder was placed in a sample container and the sample was packed around the source. A Lucite cover, with a small hole drilled near the center, was placed over the container. The thermocouple was positioned in the sample by passing the wires through the hole of the lid. Cementing the thermocouple to the cover prevented its movement while the measurements were being taken.

Each time spectrum required approximately a one to two hour period depending on the counting rate. Typical curves are shown in Figure 5. A run was discarded if there was any observable drift in the electronics. Drift was not a problem as long as the temperature of the laboratory was kept constant. Acceptable spectra were plotted and  $\tau_2$  was computed before the temperature of the sample was changed. All  $\tau_2$  variations

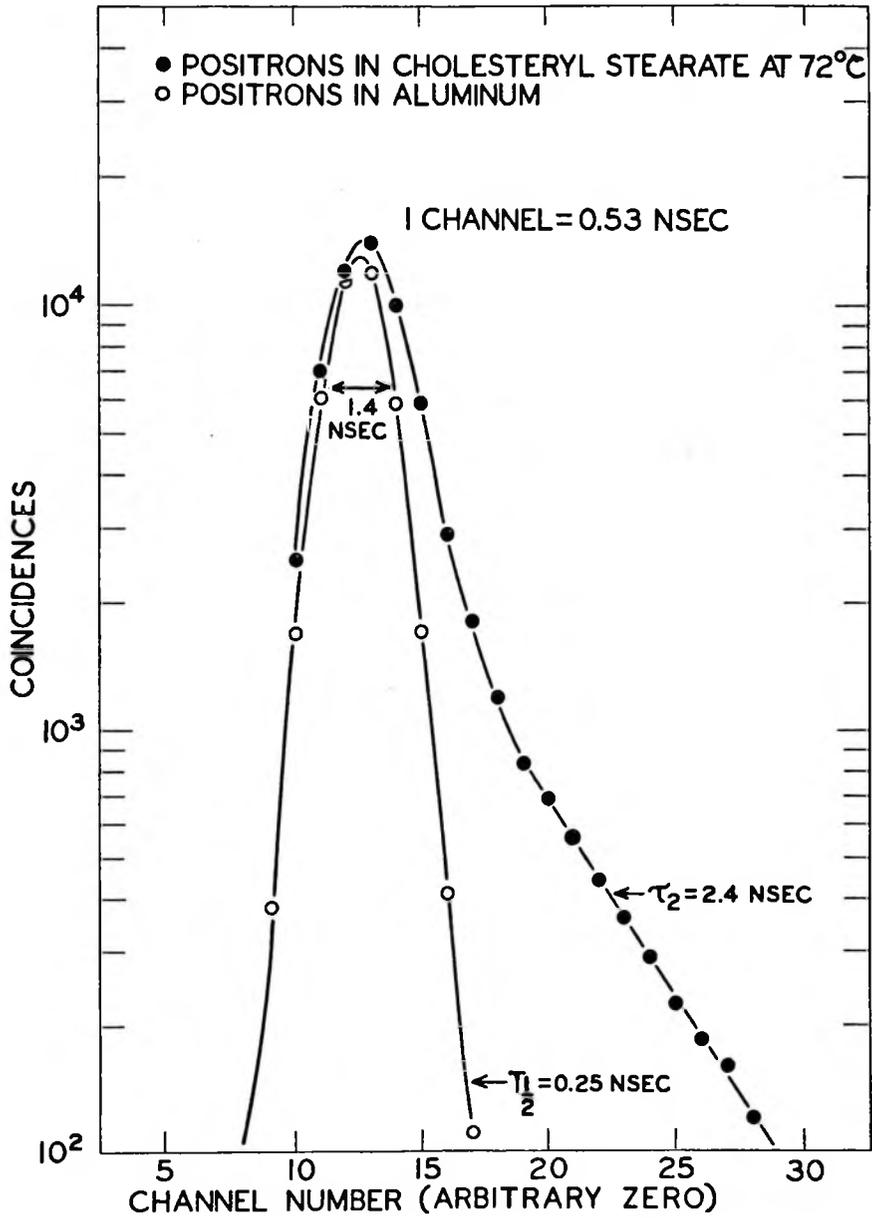


Figure 5.

were checked two or more times to ascertain their validity.

The intensity  $I_2$  was evaluated according to the method proposed by Green and Bell.<sup>22</sup> The straight line representing the  $\tau_2$  component was extrapolated back to the point where the center of a prompt resolution curve would lie. The value of  $I_2$  was taken to be the area under the  $\tau_2$  line to the right of the point of intersection, divided by the area of the entire delayed coincidence curve.

Observable phase transition temperatures of each sample were checked by heating a small quantity of the compound in a melting point capillary tube. The results obtained using this technique served as a guide to the properties (which are described in Chapter IV) of the substance, and as an indication of sample purity.

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<sup>22</sup>R. E. Green and R. E. Bell, Can. J. Phys. 38, 398 (1957).

## CHAPTER IV

### LIQUID CRYSTALS

Towards the end of the nineteenth century (in 1888) Reinitzer prepared a number of esters of cholesterol in which he observed a new and peculiar melting phenomenon.<sup>23</sup> When some of these substances were heated they did not pass directly into the liquid state, but instead adopted a structure which had properties intermediate between those of a true crystal and those of a true liquid. On reaching a certain temperature these solids underwent a transformation into a turbid condition that was both birefringent and fluid. At a higher temperature the turbid condition was converted into an isotropic liquid, and as the liquid was cooled the changes took place in reverse order.

Lehmann was the first to suggest the name "liquid crystal" for those substances which are liquid in their mobility and crystalline in their optical properties.<sup>24</sup> Friedel<sup>25</sup> proposed the term "mesophase" to stress the intermediate nature of these states of matter. In the literature these terms are used interchangeably.

Friedel<sup>25</sup> distinguished three types of mesophases. They are

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<sup>23</sup>G. W. Gray, Molecular Structure and the Properties of Liquid Crystals, (Academic Press, New York, 1962), p. 8.

<sup>24</sup>G. H. Brown and W. G. Shaw, Chem. Rev. 57, 1049 (1957).

<sup>25</sup>G. Friedel, Ann. Physique 18, 273 (1922).

referred to as the smectic, nematic, and cholesteric mesophases. A brief description of each type follows:

(a) The smectic mesophase is a turbid, viscous state with certain properties reminiscent of those found for soaps.<sup>26</sup> The special feature of this structure is its stratification. In each stratum the molecules are arranged side by side, the thickness of a stratum being approximately the length of the molecule.<sup>24</sup> For example, the thickness of the layers of ethyl p-azoxybenzoate in the smectic phase, as determined by x-ray diffraction, is  $19.9 \text{ \AA}$ , while in the solid crystal the spacing is  $16.2 \text{ \AA}$ .<sup>27</sup> The difference is due to the inclination of the molecules in the solid as compared to the approximately perpendicular arrangement in the smectic state. This implies that a smectic liquid crystalline state is likely to be obtained from a layer crystal lattice. The x-ray work by Bernal and Crowfoot<sup>28</sup> makes this assumption fairly certain. The change that occurs at the solid-smectic transition is then probably due to a weakening of the molecular attractions between the ends of the molecules. That is, the intermolecular lateral attractions must be considerably greater than the terminal attractions.<sup>29</sup> The stronger lateral forces hold the molecules together forming the smectic structure, and allow these layers to move as a two-dimensional fluid.

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<sup>26</sup>Gray, *op. cit.*, p. 4.

<sup>27</sup>E. Friedel, *Compt. rend.* 180, 269 (1925).

<sup>28</sup>J. D. Bernal and D. Crowfoot, *Trans. Faraday Soc.* 29, 1032 (1933).

<sup>29</sup>Gray, *op. cit.*, p. 165.

(b) The nematic mesophase is a turbid but mobile state. The nematic structure has no stratification but does possess some degree of molecular arrangement. According to the swarm hypothesis, the molecules in the mesomorphic structure are not oriented in the same direction throughout the whole medium but are grouped in aggregates or swarms.<sup>30</sup> The molecules in the swarm lie approximately parallel, but the swarms are distributed at random with respect to each other. Quantitative experiments on orientation give the number of molecules per swarm to be of the order of  $10^5$ . However, these groups do not remain constant in size. Due to the mobility of the molecules they are constantly exchanging molecules with each other, and with the isotropic part of the phase. Whether the swarm hypothesis is accepted or not, it can be concluded that the substance owes its mobility to the facility with which the molecules can be drawn past one another while retaining a strong tendency to acquire or retain a parallelism between the long dimensions of the molecules, and the direction of the drawing.<sup>24</sup> For this reason, the nematic liquid crystal is said to exist in one-dimensional order.

(c) The cholesteric mesophase is a turbid and mobile mesophase. The majority of compounds exhibiting this type of mesophase are derived from cholesterol or other sterol systems.<sup>31</sup> The molecular orientation of this liquid crystal is unknown. It is optically negative, while smectic and nematic structures are optically positive. When illuminated

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<sup>30</sup>L. S. Ornstein and W. Kast, *Trans. Faraday Soc.* **29**, 931 (1933).

<sup>31</sup>Gray, *op. cit.*, p. 5.

with white light, the most striking property of the cholesteric state is that of scattering the light to give vivid colors. The color of the scattered light at a particular angle to the surface of the film is dependent on the substance, the temperature, and the angle of the incident beam.<sup>24</sup> Friedel<sup>25</sup> suggested that the cholesteric mesophase is a special kind of nematic structure. His main point of argument was as follows: Some mesomorphic substances show both the smectic and nematic structures; some show both the cholesteric and smectic; but no substance has been found to exhibit both cholesteric and nematic. Such observations appear to be of little help as long as the molecular arrangement in the cholesteric state is unknown. Less work has been done with cholesteric systems, and it is difficult to say whether this mesophase should be regarded as a modification of the smectic or nematic mesophases, or whether it is a separate type of liquid crystal.

Liquid crystals are usually observed when the compound is heated to a temperature which is above the stability temperature of the crystal lattice. Using the capillary method for determining melting points the following observations may be made:

(a) If the organic compound is not mesomorphic it will melt at a particular temperature giving a clear isotropic liquid with a meniscus.

(b) If the substance is smectogenic the crystal will collapse at the melting point and give a turbid, viscous melt which adheres to the capillary walls.<sup>31</sup> At a higher temperature, this mesophase will flow and give the isotropic liquid.

(c) If the compound gives a nematic state the crystal will melt

and give a flowing turbid fluid which has a meniscus. The turbidity disappears at a higher temperature giving the isotropic liquid.

(d) If the substance is cholesteric it resembles the nematic mesophase. The same changes occur, but characteristic iridescent colors may be observed in the cholesteric mesophase.<sup>32</sup>

Many compounds exhibit both a smectic and a cholesteric (or nematic) mesophase. The smectic structure occurs at the lower temperature. If the mesomorphic transitions are reversible in opposite order on cooling, then the substance is associated with enantiotropic mesomorphic states.

Quite frequently a mesophase may be monotropic with respect to the crystalline solid or to another mesophase. In this case the crystals may melt normally to give the isotropic liquid at  $T_1$ , but when the isotropic liquid is cooled, supercooling may occur, and the temperature may fall to considerably less than  $T_1$  before crystallization occurs. If a mesophase has a stable range of existence just below the melting point, then under these conditions, the mesophase may appear at  $T_2 < T_1$ . Such a mesophase is therefore observed only on cooling, but if the temperature can be raised before crystallization occurs, the isotropic liquid will be obtained at  $T_2$ .<sup>32</sup>

From this brief review it can be seen that the melting process (or solidification) takes place in stages in mesomorphic compounds. For enantiotropic substances the three-dimensional order of the crystal lattice changes to two- and/or one-dimensional order before the zero-

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<sup>32</sup>Gray, op. cit., p. 6.

dimensional order of the isotropic liquid is reached. If the substance is monotropic with respect to the solid, then solidification occurs in stages on cooling from the zero-dimensional order of the isotropic liquid to the final three-dimensional order of the crystalline solid.

Chapters V and VI contain additional information on liquid crystalline compounds.

## CHAPTER V

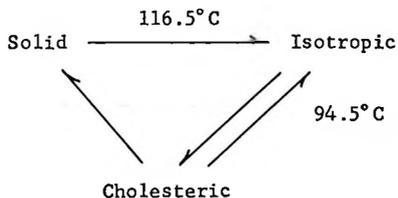
### EXPERIMENTAL RESULTS

#### A. Introduction

The study of positronium decay was conducted in four esters of cholesterol (acetate, benzoate, stearate, and myristate) and p-azoxyanisole (see Table 1). These esters were chosen because of their smectic and/or cholesteric properties. The p-azoxyanisole was used because it exhibits a nematic mesophase. All measurements were carried out to determine the dependence of the  $\tau_2$  lifetime on temperature, particularly in the regions of phase transitions.

#### B. Positronium Decay in Cholesteryl Acetate

Cholesteryl acetate exhibits two liquid phases. These are (a) the isotropic liquid and (b) the cholesteric mesophase. The sequence of changes of state for this compound, according to Gray,<sup>23</sup> is:



At 116.5°C the crystalline solid melts producing an isotropic liquid. When this liquid is cooled, supercooling may occur, and the temperature

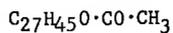
Table 1

## Chemical Formulae

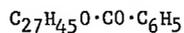
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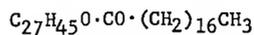
1. Cholesteryl Acetate



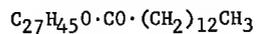
2. Cholesteryl Benzoate



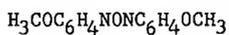
3. Cholesteryl Stearate



4. Cholesteryl Myristate



5. p-Azoxyanisole



may fall to considerably less than 116.5°C before crystallization occurs. Under these conditions, cholesteryl acetate has a cholesteric mesophase. This isotropic-cholesteric transition occurs at 94.5°C.

Three different samples of cholesteryl acetate were used for these measurements, two of these being obtained from Distillation Products Industries (at least 98% purity, with the only impurity being cholesterol itself),<sup>33</sup> and the third from Nutritional Biochemicals Corporation. Since all samples showed the same behavior, no distinction between samples is made in the data points shown in Figure 6.

The first change in  $\tau_2$  ( $1.5 \pm 0.1$  to  $2.4 \pm 0.1$  nsec) occurred in the interval 63°-66°C. No visible change was observed in the sample, and, as is indicated by the measuring cycle, this transition was found to be irreversible. The second increase in  $\tau_2$  ( $2.4 \pm 0.1$  to  $3.2 \pm 0.1$  nsec) occurred as the temperature was varied from 104° to 111°C. The sample was a clear liquid at the latter temperature.  $\tau_2$  decreased ( $3.2 \pm 0.1$  to  $2.4 \pm 0.1$  nsec) on the second downward cycle between 87.5° and 84°C. Solidification was observed in this interval.

The large, irreversible change in  $\tau_2$  near 63°C may possibly be explained if it is assumed that an irreversible crystalline modification occurred at that temperature. Qualitative examination of x-ray diffraction patterns shown in Figure 7 lends support to this assumption. Further, differential thermal analysis showed a very strong endothermic reaction in this range.<sup>34</sup> Chistyakov<sup>35</sup> has referred to two

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<sup>33</sup>C. Kuimjian, private communication (1963).

<sup>34</sup>A. F. Findeis, private communication (1963).

<sup>35</sup>I. G. Chistyakov, Soviet Phys.-Cryst. 5, 917 (1961).

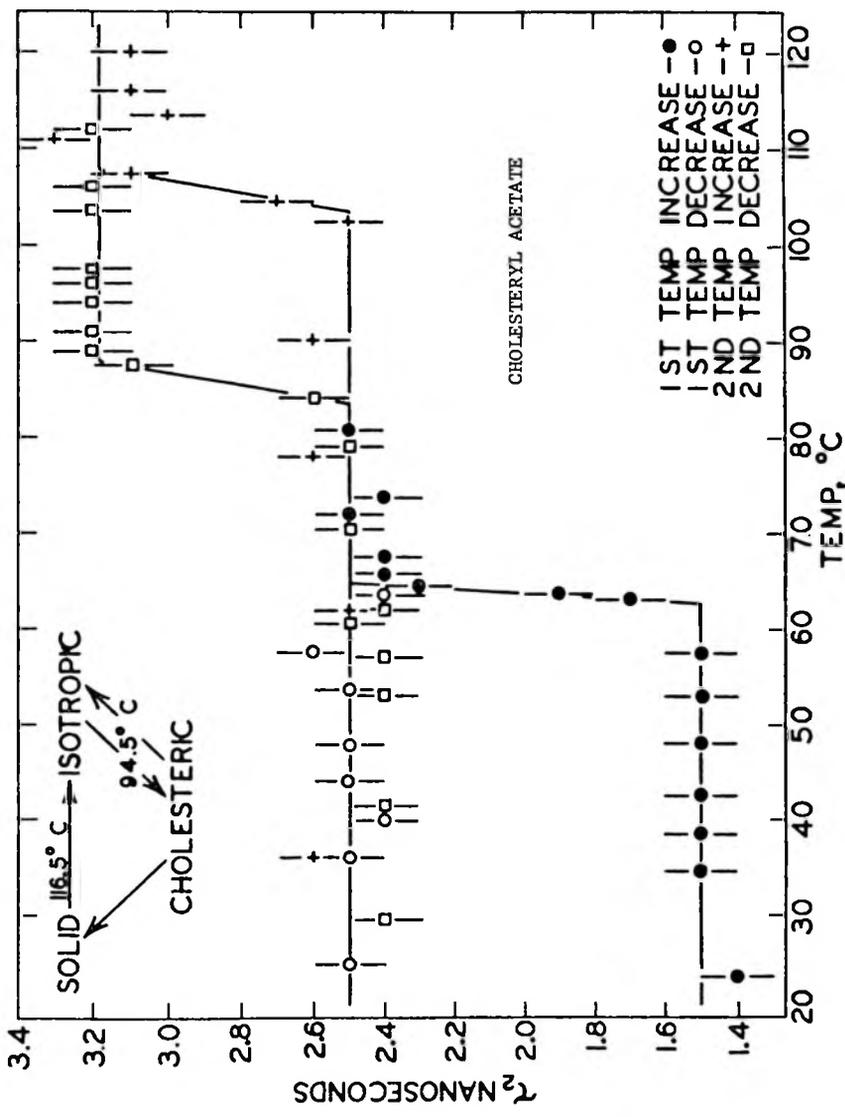


Figure 6.

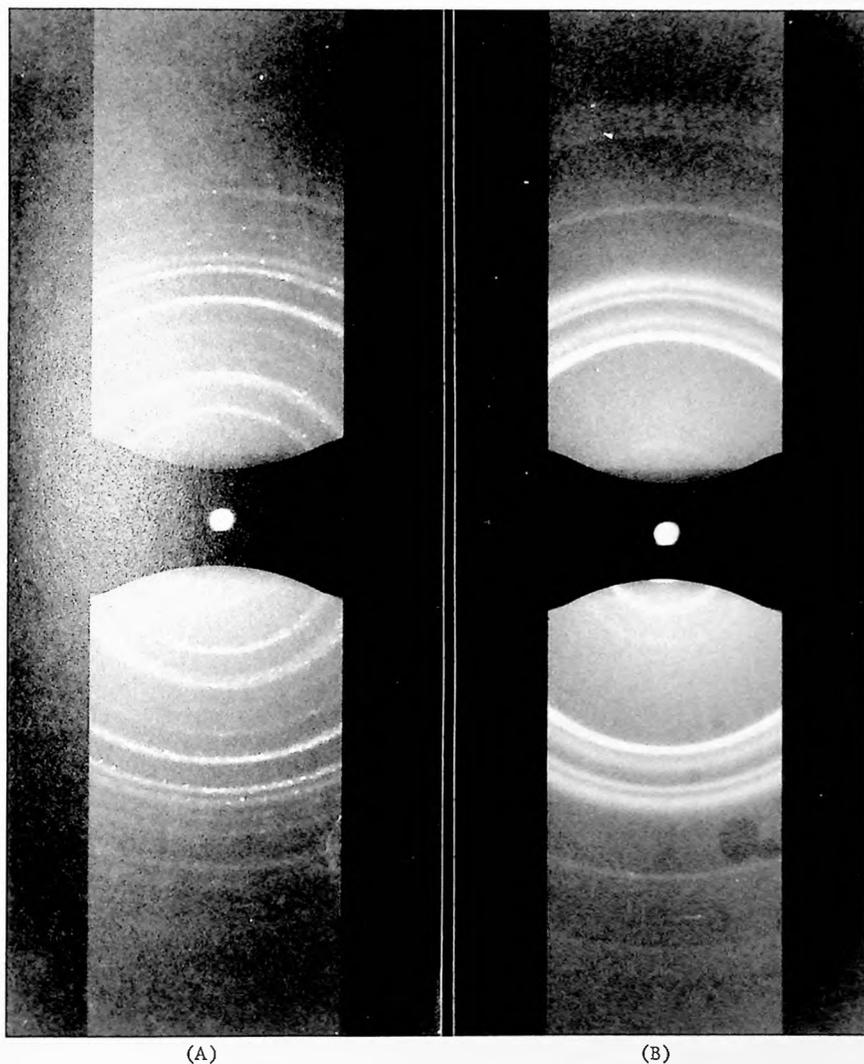


Figure 7. (A) X-ray powder diffraction pattern of cholesteryl acetate before heating.

(B) X-ray powder diffraction pattern of cholesteryl acetate after heating for 24 hours at 70°C.

solid forms of cholesteryl acetate and Kofler<sup>36</sup> has reported three solid forms of this compound.

The second increase in  $\tau_2$  was not unexpected, since similar behavior has been observed in other compounds at their melting points. However, the fact that  $\tau_2$  did not change at the isotropic-cholesteric transition is significant, because the cholesteric mesophase is supposed to possess a certain degree of order relative to the isotropic liquid.

The fraction of annihilations in  $\tau_2$  decay,  $I_2$ , was of the order of  $(30 \pm 5)\%$  in each phase studied.

#### C. Positronium Decay in Cholesteryl Benzoate

Cholesteryl benzoate exhibits a cholesteric mesophase. Gray<sup>37</sup> has found that the solid-cholesteric transition occurs at 145.5°C and the cholesteric-isotropic transition occurs at 178.5°C. Each of these transitions is reversible. The sequence of changes of state may be indicated in the following diagram:



Two samples from Sigma Chemical Company were used to obtain these data. Results were the same for each sample.

<sup>36</sup>A. Kofler, Arch. Pharm. 281, 8 (1943).

<sup>37</sup>Gray, op. cit., p. 2.

Reference is made to Figure 8.  $\tau_2$  increased ( $1.3 \pm 0.1$  to  $3.1 \pm 0.1$  nsec) in the interval from  $122^\circ$  to  $137^\circ\text{C}$ . The sample was observed to be a turbid liquid at  $144^\circ\text{C}$  and remained in this phase until it was near  $175^\circ\text{C}$ . After the initial increase in  $\tau_2$ , no further changes occurred as the temperature was increased to  $185^\circ\text{C}$ . Upon cooling  $\tau_2$  decreased ( $3.1 \pm 0.1$  to  $1.8 \pm 0.1$  nsec) in the interval from  $134^\circ$  to  $117^\circ\text{C}$ . The value of  $\tau_2$  at the latter temperature did not change significantly as the substance was cooled to room temperature.

The first change in  $\tau_2$  demonstrated the reverse of the cholesteric-solid transition which was observed to give a decrease in  $\tau_2$  in cholesteryl acetate. The absence of a change in  $\tau_2$  at the cholesteric-isotropic transition (and vice-versa) gives further evidence that the  $\tau_2$  lifetime is not influenced to any greater extent by the order which is associated with the cholesteric mesophase than it is by the order of the isotropic liquid.

The failure of  $\tau_2$  to return to its original value at room temperature is most probably due to oxidation of the sample. Hoyer and Nolle<sup>38</sup> reported that cholesteryl benzoate gave evidence of decomposition in their sample chamber, even in the presence of nitrogen, when heated for a long period of time.

The intensity,  $I_2$ , was found to be of the order of  $(30 \pm 5)\%$  in each state of the compound.

#### D. Positronium Decay in Cholesteryl Stearate

Cholesteryl stearate exhibits a smectic and a cholesteric

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<sup>38</sup>W. A. Hoyer and A. W. Nolle, J. Chem. Phys. 24, 803 (1956).

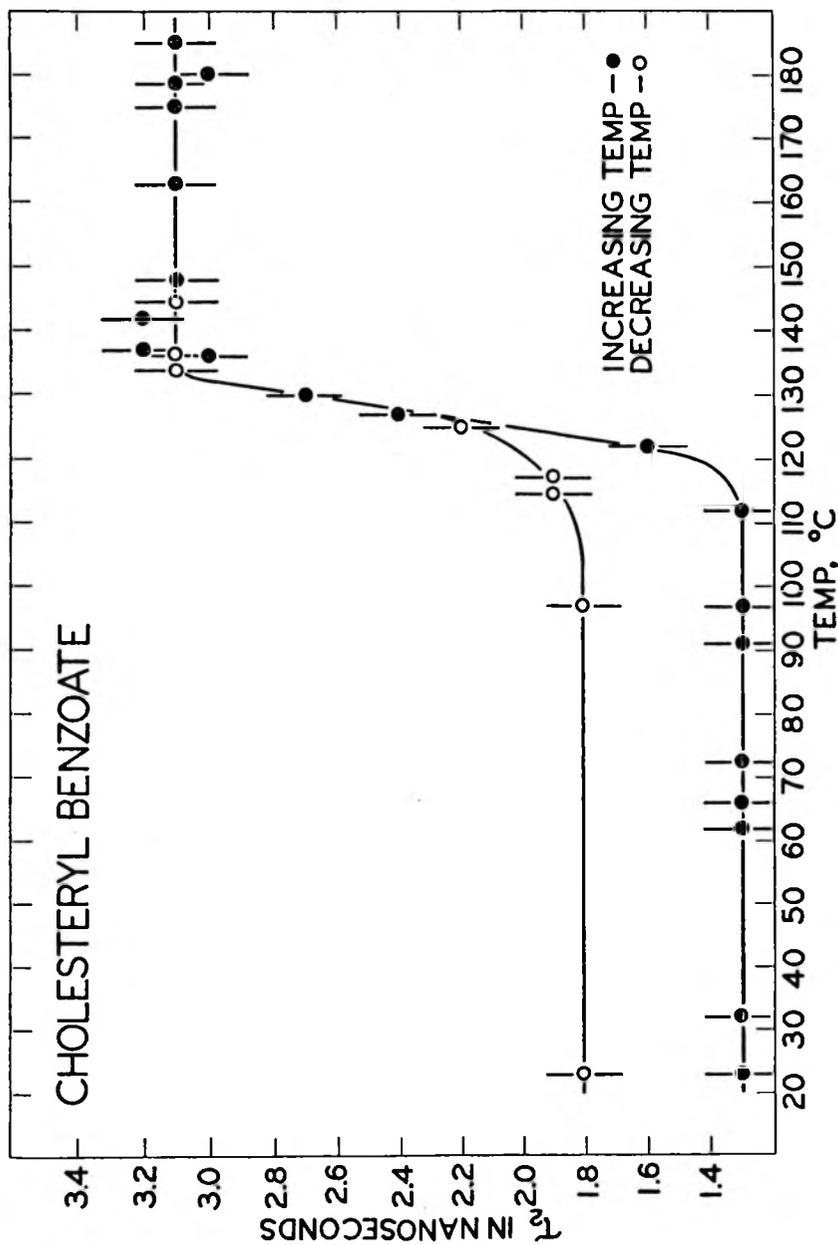
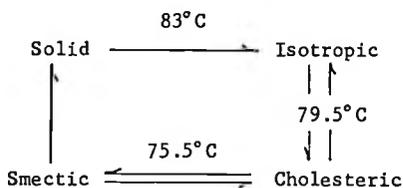


Figure 8.

mesophase.<sup>39</sup> These mesophases are monotropic with respect to the solid, and can only be obtained by supercooling the isotropic liquid. This ester melts at 83°C giving a clear liquid. As the liquid is cooled the cholesteric phase appears at 79.5°C, and at 75.5°C the cholesteric-smectic transition occurs. The sequence of phase changes is illustrated below:



One sample, prepared by General Biochemicals, was used for the measurements. The measuring cycle was repeated three times. Each cycle showed the same behavior; therefore, no distinction is made in the data points which are shown in Figure 9.

Significant changes occurred in  $\tau_2$  ( $1.9 \pm 0.1$  to  $2.8 \pm 0.1$  nsec) as the temperature was increased from 73.5° to 80.5°C. The compound was a clear liquid at 82°C. No further changes were observed as the temperature of the sample was increased to 100°C. The temperature was then decreased slowly. The first  $\tau_2$  change ( $2.8 \pm 0.1$  to  $2.4 \pm 0.1$  nsec) in this part of the cycle was found at 75°C. However, when the sample was cooled from 73.5° to 72°C,  $\tau_2$  did not vary. A second decrease in  $\tau_2$  ( $2.4 \pm 0.1$  to  $1.9 \pm 0.1$  nsec) was observed at 71.5°C. Solidification was observed at the latter temperature. The compound

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<sup>39</sup>Gray, *op. cit.*, p. 41.

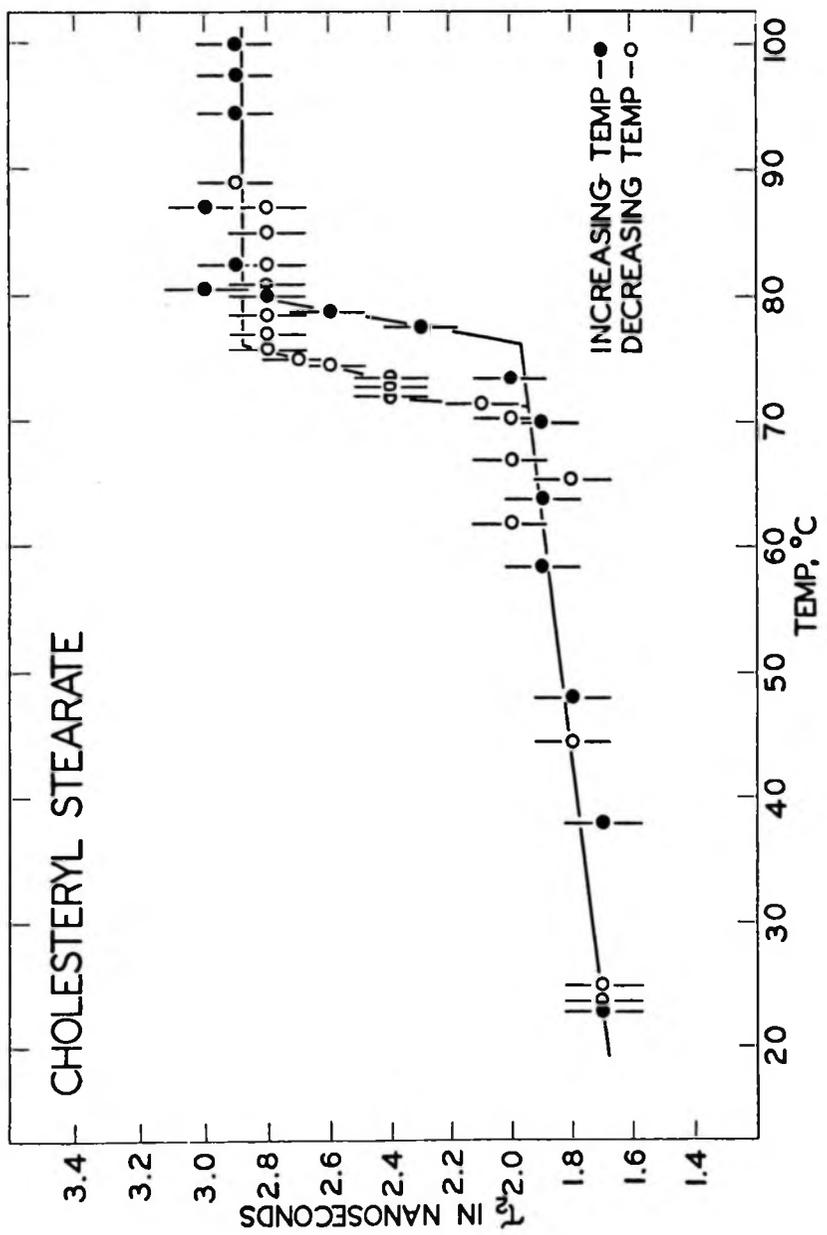


Figure 9.

was then cooled slowly to room temperature with the lifetime returning to its original value of  $1.7 \pm 0.1$  nsec.

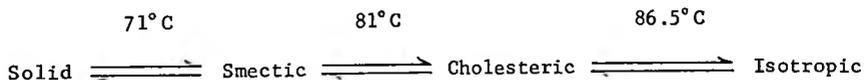
As in the case of cholesteryl acetate, the increase in  $\tau_2$  near the melting point was not unexpected, and the isotropic-cholesteric transition showed no change in  $\tau_2$ .

There was a definite decrease in  $\tau_2$  at the cholesteric-smectic transition. The lifetime remained constant over a range of approximately 1.5 degrees in the smectic state before the smectic-solid transition occurred causing a further decrease in  $\tau_2$ . The former change implies that the positron is influenced by the greater degree of order that is associated with the smectic mesophase as opposed to the order of the cholesteric liquid crystal.

$I_2$  was of the order of  $(30 \pm 5)\%$  at room temperature, and did not change over the region measured.

#### E. Positronium Decay in Cholesteryl Myristate

Cholesteryl myristate<sup>40</sup> melts at 71°C forming a smectic liquid crystal. At 81°C a smectic-cholesteric transition occurs giving a cholesteric mesophase that is transformed to an isotropic liquid at 86.5°C. These transitions are reversible with respect to each other as is indicated below:




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<sup>40</sup>G. W. Gray, J. Chem. Soc. 3733 (1956).

One sample was used for these measurements. It was prepared by Distillation Products Industries. The measurements were repeated three to four times above and below all transition regions.

The first change in  $\tau_2$  ( $1.9 \pm 0.1$  to  $2.9 \pm 0.1$  nsec) was observed in the region from  $69.5^\circ$  to  $73^\circ\text{C}$  as is shown in Figure 10. The lifetime remained constant over a range of approximately seven degrees, as the temperature was raised, with a second increase ( $2.9 \pm 0.1$  to  $3.2 \pm 0.1$  nsec) occurring in the interval from  $79^\circ$  to  $82^\circ\text{C}$ . No further changes in  $\tau_2$  occurred as the temperature of the sample was increased to  $95^\circ\text{C}$ . Upon cooling the compound, the first lifetime decrease ( $3.2 \pm 0.1$  to  $2.9 \pm 0.1$  nsec) occurred in the region of  $82^\circ$  to  $79^\circ\text{C}$ , and the second decrease (to  $1.9 \pm 0.1$  nsec) was observed at  $66^\circ\text{C}$  as the sample changed back to a solid form.

The large reversible change in  $\tau_2$  that began at  $69.5^\circ\text{C}$  must be associated with the solid-smectic transition.  $\tau_2$  did not vary in the smectic mesophase. This is in agreement with constant value of  $\tau_2$  observed in the smectic region of cholesteryl stearate.

The second variation in the positron lifetime occurred near the smectic-cholesteric transition temperature. The increase was sharp, but much less than the first variation. This change demonstrated the reverse of the cholesteric-smectic transition which was found to give a decrease in  $\tau_2$  in cholesteryl stearate.

The absence of a variation in the lifetime of the positron at the cholesteric-isotropic transition gives further evidence that the positron annihilated in an average environment that was approximately

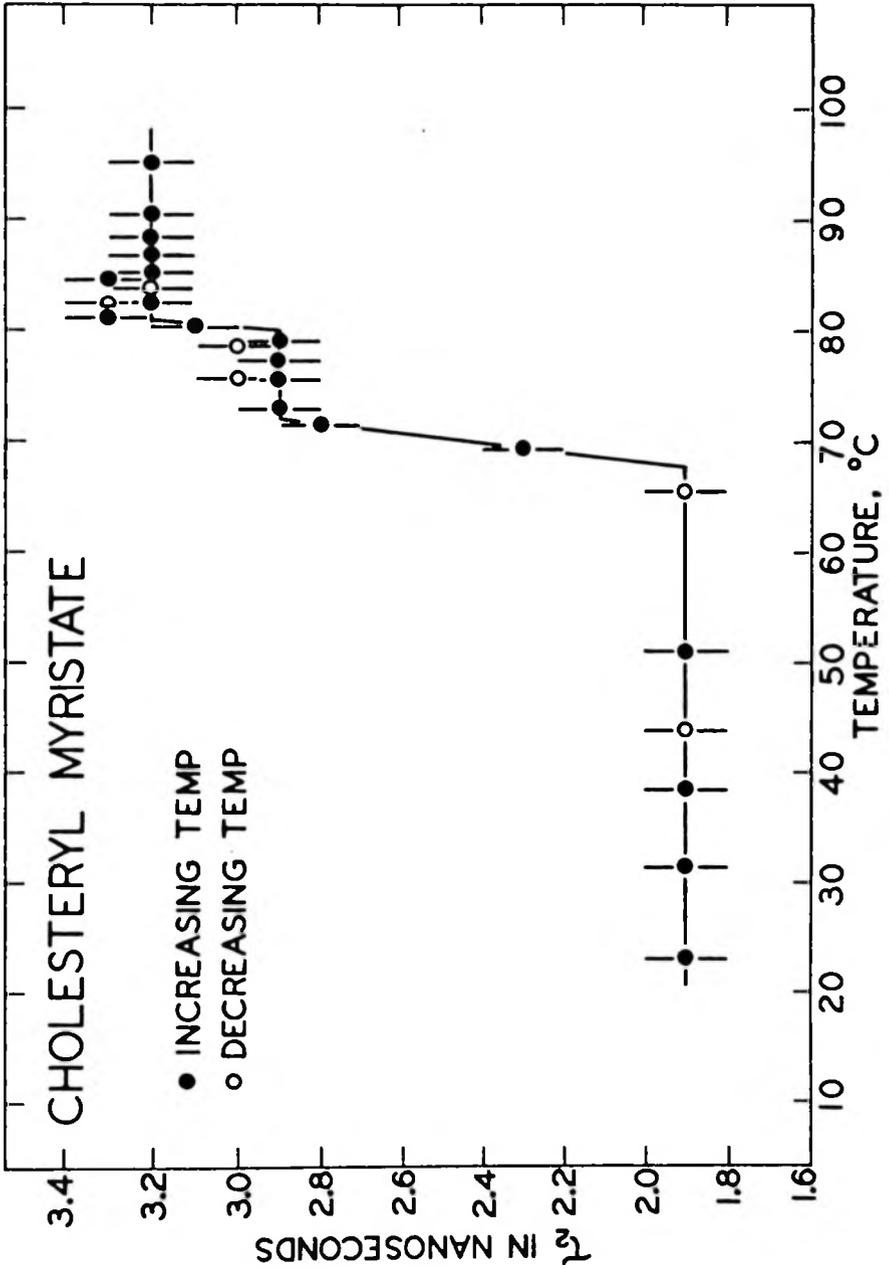


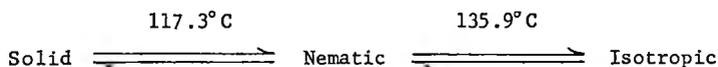
Figure 10.

the same<sup>41</sup> in each of these liquid states.

$I_2$  was of the order of  $(23 \pm 5)\%$  throughout the measuring cycle.

#### F. Positronium Decay in p-Azoxyanisole

p-Azoxyanisole has been studied more thoroughly than any other liquid crystalline compound. This compound has an enantiotropic nematic mesophase with a crystalline-nematic transition temperature at  $117.3^\circ\text{C}$ , and a nematic-isotropic transition which takes place at  $135.9^\circ\text{C}$ .<sup>42</sup> The former transition is extremely sharp. These phase changes are illustrated below:



The compound was obtained from Columbia Organic Chemicals Company, Inc.

Figure 11 shows that there was no measurable  $\tau_2$  component from room temperature to approximately  $116^\circ\text{C}$ . The first measurable value of  $\tau_2$  was of the order of  $1.0 \pm 0.1$  nsec, and occurred near  $117^\circ\text{C}$ . The sample was observed to be a yellow turbid liquid at the latter temperature.  $\tau_2$  did not vary from its initial value as the temperature was increased to  $150^\circ\text{C}$ . The liquid was not turbid at  $136^\circ\text{C}$ . When the sample was cooled the lifetime remained constant until solidification

<sup>41</sup>R. K. Wilson, P. O. Johnson, and R. Stump, Phys. Rev. 129, 2091 (1963).

<sup>42</sup>G. W. Gray, Molecular Structure and the Properties of Liquid Crystals, (Academic Press, New York, 1962), p. 116.

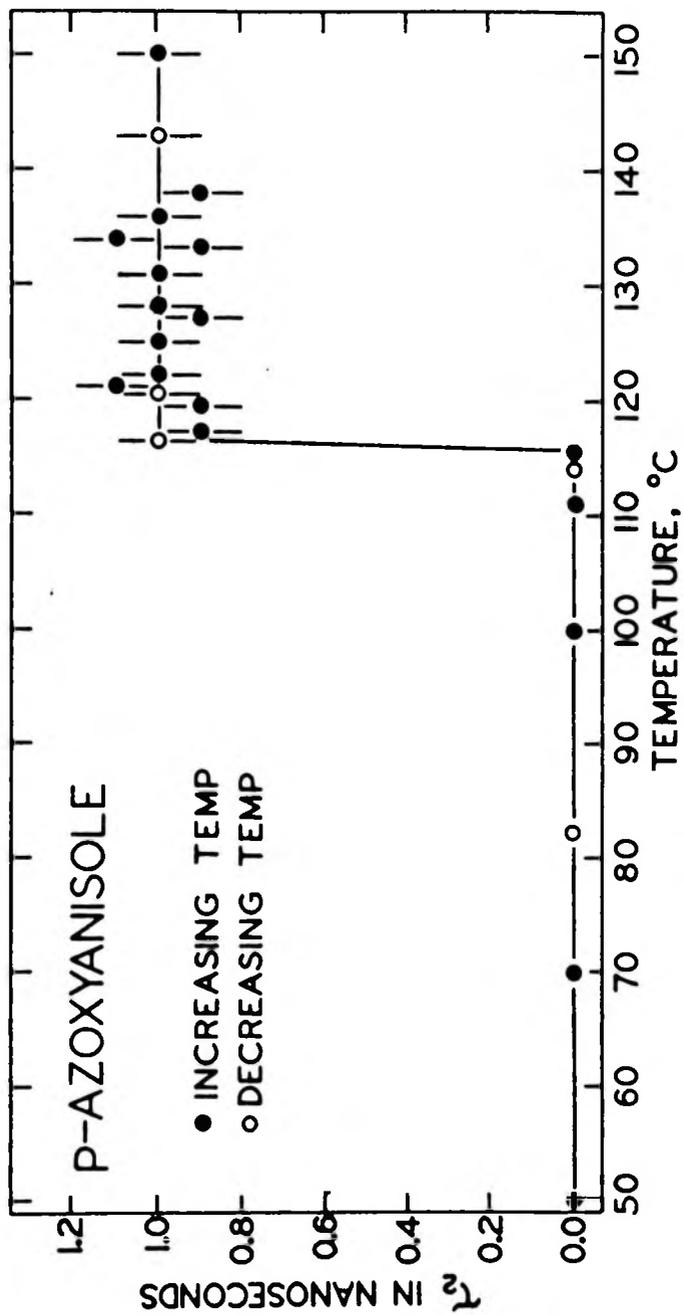


Figure 11.

occurred at approximately 115°C. At the latter temperature  $\tau_2$  was too small to measure if it existed at all.

The failure of a change in  $\tau_2$  at the nematic-isotropic transition is significant since a one-dimensional order has been fairly well established for the nematic mesophase. This result does not necessarily mean that this mesophase is not ordered. The implication is that the positronium atom annihilated in the same average environment in both the nematic liquid crystal and isotropic liquid.

The intensity of the  $\tau_2$  component was approximately (35 ± 5)%.

Pederson<sup>43</sup> gives the following results for the work that was done on p-azoxyanisole at McGill University:

<u>State</u>	<u>Temperature</u>	<u><math>\tau_2</math></u>	<u><math>I_2</math> (%)</u>
Liquid	147 - 153°C	3.6 ± 1.0 nsec	17 ± 5
Nematic	129 - 132°C	2.1 ± 0.5 nsec	20 ± 5
Solid	20°C	----	< 1

The time distribution curves given in Pederson's thesis are extremely poor, and from the above data it is clear that the temperature was not controlled with any degree of accuracy. Due to the poor quality of these results the measurements were repeated in greater detail for this paper.

Porter and Johnson<sup>44</sup> observed a density decrease in p-azoxyanisole

<sup>43</sup>E.C.B. Pederson, Ph.D. thesis, McGill University, 1960 (unpublished).

<sup>44</sup>R. S. Porter and J. F. Johnson, J. Appl. Phys. 34, 51 (1963).

of only 0.1% at the solid-nematic transition, whereas the decrease in density at the nematic-isotropic transition was 0.36%. It is quite apparent that the free volume approach of Brandt, Berko, and Walker<sup>14</sup> would have difficulty in explaining the behavior of  $\tau_2$  at the solid-nematic transition where the density change is so small.

## CHAPTER VI

### DISCUSSION OF INTERMOLECULAR FORCES AND X-RAY DIFFRACTION DATA

#### A. Introduction

Four sub-topics of this chapter are devoted to information which is needed to substantiate the final arguments and the conclusions of this experimental work.

#### B. Intermolecular Attractions

Intermolecular forces may be divided into three classes:<sup>45,46</sup>

1. Dipole-dipole attractions--the direct interactions between permanent dipoles in the molecules;
2. Induced dipole attractions arising from the mutual polarization of the molecules by their permanent dipole moments;
3. Dispersion forces--the attractions between instantaneous dipoles produced by spontaneous oscillations of the electron clouds of the molecules.

In the solid state, the intermolecular attraction between polar molecules is due to the combined attractions of the three classes of forces described above. However, the contribution of each type of force depends primarily on the molecular arrangement within the solid.

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<sup>45</sup>Gray, op. cit., p. 148.

<sup>46</sup>Y. K. Syrkin and M. E. Dyatkina, Structure of Molecules and the Chemical Bond, (Butterworths, London, 1950) pp. 262-291.

### C. Mesomorphic Components

Many factors are involved in the construction of a potentially mesomorphic system. The molecules are generally long and narrow. Each system must contain groups of atoms with which are associated permanent dipole moments, and the molecule itself must be highly polarizable.<sup>47</sup> Hence, molecules which incorporate properly arranged (linearity of the system is necessary in most cases) aromatic rings and unsaturated linkages are more inclined toward mesomorphism than those molecules without these constituents. In fact, the majority of organic mesomorphic compounds are aromatic in character and frequently contain additional double or even triple bonds.<sup>47</sup>

The above requirements for the formation of liquid crystalline states are generally satisfied in each of the substances studied in this paper. The cholesterol derivatives each contain a polar ester group as well as a double bond in the second ring of the cholesterol radical, with the benzoate ester having in addition the highly polarizable benzene ring as a part of its structure. p-Azoxyanisole is constructed with an azoxy group, two ether groups, and two benzene rings properly associated to give good mesomorphic characteristics.

### D. Thermal Stabilities of Smectic and Nematic States

Gray<sup>48</sup> summarized the results of a large amount of experimental

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<sup>47</sup>Gray, op. cit., p. 149.

<sup>48</sup>Gray, op. cit., pp. 239-298.

work concerning substituent effects with respect to smectic and nematic thermal stabilities. Different polar and polarizable groups were substituted (or added) in a variety of positions in a number of liquid crystalline compounds. Relating these substitutions and additions to changes of mesomorphic stability the following conclusions were drawn:

1. Intermolecular attractions arising from dispersion forces are augmented in the smectic liquid crystal by attractions which depend upon the permanent dipolar properties of the molecules;
2. Dipole-dipole and induced dipole interactions do not contribute significantly to the intermolecular attractions in the nematic melt. That is, dispersion forces arising from molecular polarizability effects must account for the intermolecular attractions which maintain the essentially parallel arrangement of the molecules within the nematic swarms.

The latter conclusion seems reasonable since the molecules form a parallel imbricated arrangement in the nematic state. With this orientation, dipole-dipole attractions are less likely to occur because (a) the distance between dipoles will be as often as not too great, and (b) dipoles in nearby molecules will lead to repulsion as often as attraction rendering a rather low average dipole-dipole interaction in the nematic melt.

#### E. X-ray Diffraction

Stewart<sup>49</sup> made an extensive study of p-azoxyanisole in the nematic and isotropic states using x-ray diffraction. These observations

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<sup>49</sup>G. W. Stewart, Trans. Faraday Soc. 29, 982 (1933).

showed a distinct semi-orderly molecular array which was practically the same in the liquid crystal and clear liquid. From these results the assumption was made that the isotropic liquid is composed of cybotactic groups of molecules (100 to 1000 per group). The alignment of these smaller cybotactic groups makes up the larger swarms found in the nematic mesophase.

Bernal and Crowfoot<sup>28</sup> made a thorough x-ray study of p-azoxyanisole in the solid state. The structure is monoclinic and the cell dimensions are:

$$a = 11.0 \text{ \AA} \quad b = 8.10 \text{ \AA} \quad c = 14.95 \text{ \AA} \quad \beta = 107^\circ 30'$$

Each cell contains four molecules which are parallel but do not lie in layers. The ether group at the end of one molecule lies very close to the azoxy-group of the nearest neighbor molecule giving an imbricated structure.

DeWolff<sup>50</sup> gives two monoclinic structures for cholesteryl acetate. Their cell dimensions are:

$$(I) \quad a = 17.68 \text{ \AA} \quad b = 16.48 \text{ \AA} \quad c = 9.236 \text{ \AA} \quad \beta = 91.74^\circ$$

$$(II) \quad a = 17.65 \text{ \AA} \quad b = 9.532 \text{ \AA} \quad c = 16.54 \text{ \AA} \quad \beta = 106.40^\circ$$

According to Kofler<sup>36</sup> the first structure is stable above 58°C and the second structure is stable below this temperature.

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<sup>50</sup>DeWolff, Tech. Phys. Dienst, Delft, Holland (X-Ray Powder Data File, American Society for Testing Materials, Philadelphia, Pa. (1962) No. 7-740 and No. 7-741).

X-ray diffraction data are not available on the cholesteric mesophase. However, following the liquid model given by Frenkel,<sup>51</sup> the isotropic liquid of each ester will be assumed to be made up of a number of microcrystallites which give a certain degree of local ordering to the liquid state.

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<sup>51</sup>J. Frenkel, Kinetic Theory of Liquids, (The Clarendon Press, Oxford, 1946), p. 305.

## CHAPTER VII

### SUMMARY AND CONCLUSIONS

The only variation in the molecular structure of each cholesteryl ester is due to a change of the chemical radical which is attached to the ester group. Each change of this radical varies the length of the molecule. If the length of the molecule is greatly increased, as in the cases of cholesteryl stearate and cholesteryl myristate, the terminal attractions between molecules in the solid will decrease. This is evidenced by the fact that both of these substances exhibit smectic mesophases. At the same time, because of the increase in polarization due to the increased chain length, the dispersion forces will increase. However, since the melting point and mesophase transition temperatures are comparatively low in these compounds, the lateral attractions must decrease to some extent also. If the lateral attractions decrease in the presence of an increase in the dispersion forces, then this will require a decrease in the permanent dipolar interactions between molecules.  $\tau_2$  was observed to be relatively large in the crystalline state of these two esters.

In cholesteryl benzoate, the increase in the length of the molecule, relative to cholesteryl formate, is brought about by substitution of a phenyl group for the hydrogen atom which is attached to the ester group. This substitution contributes strongly to the intermolecular attractions. The solid-cholesteric transition temperature is much

higher than the other esters studied, and the cholesteric thermal stability is greater. The high melting point suggests that the permanent dipolar attractions are enhanced by the presence of this phenyl group. The lowest  $\tau_2$  lifetime in the esters studied was obtained in the solid state of cholesteryl benzoate.

It is interesting to note that in the crystalline state  $\tau_2$  varied approximately linearly with the melting point of the benzoate, stearate, and myristate esters. The largest lifetime occurred in the ester with the lowest melting point, and the smallest value of  $\tau_2$  in the ester with the highest melting point.

Only those phase transitions which can be associated with variations in the dipole-dipole interactions gave a change in the annihilation rate of orthopositronium. For example, p-azoxyanisole exhibits strong dipole-dipole interactions in the solid state as well as strong interactions due to dispersion forces. No measurable value of  $\tau_2$  was obtained in the solid, but  $\tau_2$  did appear at the solid-nematic transition. In the preceding chapter it was pointed out that dipole-dipole interactions do not contribute significantly to the intermolecular attractions in the nematic melt. Hence, this transition is associated with a decrease in the permanent dipolar attractions. In addition, smectic transitions are connected with decreases (or increases) in the dipole-dipole interactions between molecules. Table 2 shows that  $\tau_2$  always varied with these transitions, and that the positron lifetime in the smectic region was intermediate between the solid and cholesteric states. Further, it is possible to explain the irreversible solid-solid transition which occurred in cholesteryl

Table 2  
Lifetime of Orthopositronium in Nanoseconds

Substance	State				
	Solid	Smectic	Nematic	Cholesteric	Isotropic
Cholesteryl acetate	1.5 ± 0.1	---	---	3.2 ± 0.1	3.2 ± 0.1
Cholesteryl benzoate	1.3 ± 0.1	---	---	3.1 ± 0.1	3.1 ± 0.1
Cholesteryl stearate	1.7 ± 0.1	2.4 ± 0.1	---	2.8 ± 0.1	2.9 ± 0.1
Cholesteryl myristate	1.9 ± 0.1	2.9 ± 0.1	---	3.2 ± 0.1	3.2 ± 0.1
p-Azoxyanisole	zero	---	1.0 ± 0.1	---	1.0 ± 0.1

acetate in terms of a decrease in the dipole-dipole intermolecular attractions. Examination of the cell structures of form (I) and form (II) indicates that a rotation of the molecules about their major axes changes (II) to (I). The volume per unit cell of form (I) is approximately 2.7% greater than form (II). Such a small increase in volume would not be expected to give rise to large variations in dispersion attractions, but a molecular rearrangement could reduce the interaction between permanent dipolar groups. The value of  $\tau_2$  in form (I) of cholesteryl acetate was 79% greater than in form (II).

Reference to Table 2 shows that the lifetime of positronium was relatively constant in the cholesteric mesophase from ester to ester. That is,  $\tau_2$  did not vary significantly with the thermal stability of this mesophase. Although the limits involved are unknown, it is apparent that variations in the dispersion forces, which determine thermal stability, have only a small measurable effect on the decay rate of positronium.

The lack of a change in  $\tau_2$  at the nematic-isotropic transition indicates that the annihilation of the positrons occurred in an environment which was similar in each of these two states. Similar environments occur in the nematic swarms and in the isotropic cybotactic groups. Therefore, it may be concluded that the annihilations most likely occurred within these locally ordered groups. It is felt that this same approach is applicable to the cholesteric-isotropic transition.

Finally, it may be concluded, from the preceding discussion,

that changes in the intermolecular interactions, particularly dipole-dipole attractions, were the primary factors involved in the variations of positronium decay rates in the substances examined.

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