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CORRELATION BETWEEN POSITRON LIFETIME PARAMETERS AND CRYSTALLOGRAPHIC DATA FOR SOME ESTERS OF CHOLESTEROL

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ABSTRACT: Positron lifetimes have been measured in fifteen n-alkanoate esters of cholesterol. These data reveal five sequences of esters having similarities in their lifetime parameters. Comparison with sequences determined from crystallographic data shows good agreement.

The importance of crystal structure in the formation and annihilation characteristics of positronium (Ps) in organic compounds is well known.[1] The present research is an investigation of possible correlations between positron lifetime parameters and crystal structure in a series of cholesteryl esters. Ideally one might hope to be able to relate positron lifetimes and intensities to the type of lattice and the lattice parameters. However, due to the presence of other factors besides crystal structure which may influence Ps formation and annihilation, this possible correlation is expected to have many exceptions. Our specific aim here has been to determine whether or not those esters of cholesterol which are known to be isostructural also exhibit similarities in their positron lifetime data.

We have recently observed such a correlation among the even-numbered n-alkanoate esters of cholestanol having $n \geq 8$. Those esters are known[2] to form an isostructural series with a and b dimensions of the monoclinic unit cell remaining constant in the series while dimension c increases about 2.5 Å with the addition of each pair of methylene groups to the alkyl chain. Positron lifetime parameters for these esters were found[3] to be identical within experimental error.

Bernard and Lydon[4] were the first to study the crystallography of a large number of the n-alkanoate esters of

cholesterol for the purpose of seeking a correlation between the crystal structures and the mesogenic properties. Although they found no overall structural pattern for this series, they did observe that small groups of esters appear to have structural similarities. For $n \geq 6$ they reported the following limited sequences: C_6, C_7, C_8, and C_9; C_{10} and C_{12}; and C_{14}, C_{16}, and C_{18}.

Later studies by Craven and co-workers[5-11] have found the following sequences of structural homologs: C_6, C_7, C_8, and C_9(II); C_9(I), C_{10}, C_{11}, and C_{12}; and C_n with $n \geq 14$. The notation C_9(I) and C_9(II) represent two solid polymorphs of the nonanoate ester. Guerina and Craven[6] summarize these crystal structures by the following classification: the short-chain acids (C_6 to C_8, later[11] modified to include one polymorph of C_9) have monolayer type II structures; those with medium length chains (C_9 to C_{12})have monolayer type I structures, and those with long chains (C_{14} and longer) have the bilayer type structure. They point out that this does not take into account possible polymorphism in C_6, C_{11}, C_{12}, and C_{16}.

The apparatus used in obtaining the positron lifetime data has been described previously.[14] These data were analyzed by a computer program[15] into two components, where τ_2 and I_2 represent the lifetime and intensity of the longer-lived component resulting from annihilation of orthopositronium (o-Ps). All positron data were obtained at room temperature. The cholesteryl esters were supplied by Nu Chek Prep, Elysian, MN and had purity >99%.

Shown in Table 1 are the positron lifetime data obtained for fifteen esters of cholesterol. The number of carbons in the alkyl chain is represented by n. The grouping of esters in Table 1 is based on similarities in their τ_1, τ_2, and I_2 values.

Table 2 gives a summary of the crystallographic data which have been previously reported in the literature for these esters of cholesterol. All data shown are for monoclinic lattices and Z represents the number of molecules per unit cell. Lattice parameters a and c from references 4 and 6 have been interchanged in Table 2 to make comparison easier. No lattice parameters are given here for C_{16} since the only values available are for an orthorhombic form of this ester. Bernard and Lydon[4] observed their single crystal sample of C_{16} to be orthorhombic while their powder photographs of this ester were similar to C_{14} and C_{18}, which are monoclinic.

Examination of the ester groupings determined from the positron data reveals good agreement with the assignments which are based on x-ray studies. It is not at all clear why the particular values of τ_2 and I_2 occur for the different structural types (i.e., why type II monolayer structures

cause τ_2 to be significantly shorter than does the type I monolayer). Although there are no published data on the crystal structure of C_{13}, C_{15}, C_{17}, C_{19}, and C_{20}, similarities in the positron data suggest that these esters also have the bilayer structure. Since the I_2 value is associated with the probability of positronium formation, the smaller I_2 values of the esters with bilayer structure might be interpreted to mean that in this case there is more efficient packing of the molecules, leaving less free volume available for Ps formation.

The assignment of the nonanoate ester (C_9) to two different isostructural sequences resolved an earlier conflict created when Guerina and Craven[6] reported that the crystal structures of C_8 and C_9 are quite different while Bernard and Lydon[4] found that these two esters have quite similar unit cell dimensions. The obvious explanation is that these investigators had studied different solid polymorphs of C_9. In the positron measurements this dimorphism was first noticed when τ_2 values differing by about 25% were found for C_9 samples obtained from Fastman and from Nu Chek Prep. This difference was unusual in that other esters obtained from these two sources gave results which agreed within about 4%.

The rather large variation in positron lifetime parameters found for these esters of cholesterol emphasizes the fact that Ps formation and annihilation in solids are far less dependent on similarities in molecular structure than on similarities in crystal structure. This is quite reasonable since the electronic environment encountered by free positrons or Ps in solids is expected to be strongly influenced by crystal structure. The present study as well as the study previously reported for some esters of cholestanol were both chosen so that effects other than those due to crystal structure were minimized. From the results of both studies it is clear that some correlation between crystal structure and positron lifetime parameters does indeed exist. Furthermore, one might speculate that the small variations which occur among members of each isostructural group are due to the presence of vacancy defects which have been shown to play a noticeable role in positron lifetime behavior in molecular crystals.[16-17]

TABLE 1 Summary of positron lifetime data.

n	τ_1(±.004)ns	τ_2(±.02)ns	I_2(±0.7)%
6	.325	1.78	38.6
7	.337	1.65	34.7
8	.343	1.62	33.4
9(II)	.332	1.64	34.4
9(I)	.329	2.06	38.9
10	.323	1.95	37.6
11	.319	1.94	38.5
12	.316	1.98	38.1
13	.343	1.96	28.5
15	.347	1.91	26.8
17	.351	1.89	25.8
14	.374	1.82	22.0
16	.371	1.84	19.5
18	.377	1.84	21.3
19	.353	2.05	25.7
20	.359	2.04	23.1

TABLE 2 Summary of previously published monoclinic lattice parameters.

n	a(Å)	b(Å)	c(Å)	β(°)	Z	Ref.
6	12.19	9.30	13.67	92.0	2	4
7	12.54	9.23	14.02	92.0	2	4
8	12.67	9.20	13.95	94.0	2	4
	12.80	9.20	14.12	93.81	2	5
9(II)	12.81	9.33	14.44	95.5	2	4
9(I)	13.96	9.183	27.24	91.95	4	6
10	12.85	9.05	30.00	92.0	4	4
	12.931	9.066	30.22	91.14	4	7
11	13.008	9.006	31.063	90.60	4	10
12	12.92	8.92	31.80	93.0	4	4
	12.989	9.008	32.020	91.36	4	8
	12.995	9.013	34.25	110.97	4	12
14	10.18	7.50	50.30	92.5	4	4
	10.260	7.596	101.43	94.41	8	9
18	10.20	7.55	57.50	96	4	4
	10.23	7.6	110.0	94.23	8	13

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