Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Molecular Packing Coefficients of the Homologous Series Cholesteryl Alkanoates

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Version of record first published: 28 Mar 2007.

To cite this article: N. C. Shivaprakash , P. K. Rajalakshmi & J. Shashidhara Prasad (1979): Molecular Packing Coefficients of the Homologous Series Cholesteryl Alkanoates, Molecular Crystals and Liquid Crystals, 51:3-4, 317-322

To link to this article: http://dx.doi.org/10.1080/00268947908084717

Mol. Cryst. Liq. Cryst., 1979, Vol. 51, pp. 317–322

Printed in Holland

Note

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(*Received August 22, 1978; in final form December 21, 1978*)

The properties of cholesterol derivatives are important owing to the involvement of these compounds in a myriad of industrial and biological research areas such as thermography, display devices and the formation in atherosclerosis of arterial deposits containing cholesteryl esters. Molecular structural studies of mesogens in the crystalline state have been carried out in search of a better understanding of the physical properties which lead to mesophase formation. It has been demonstrated previously for a homologous series of nematogens[1] how the molecular packing coefficients of the solid phase vary with increasing chain length and how this throws light upon the variation of other physical properties. Here, we extend this treatment to the cholesteryl alkanoates. Detailed crystal structure analysis is available for only one member of this series: cholesteryl tetradecanoate, which was studied by Craven and de Titta.[2] Prior to this, unit cell dimensions and space groups has been obtained for 13 members by Barnard and Lydon.[3] They found the crystallography of these compounds to be complex. No overall homology of crystal structure was apparent and at least eight different types of crystal structure occur.

The molecular packing coefficient is defined as the ratio of the actual geometric (van der Waals) volume of the molecule to the volume occupied per molecule in the crystal. Values of this ratio have been evaluated for the 14 members of this series for which crystallographic data are available. Using the approach described by Kitaigorodsky[4] the geometric volume of a molecule is given by summing the atomic volume increments, each of which is calculated using the formula:

$$V = \tfrac{4}{3}\pi R^3 - \sum_i \tfrac{1}{3}\pi h_i^2(3R - h_i^2)$$

where R is the van der Waals radius of the atom considered. The h_i values are the heights of the excluded segments of the sphere and are given by the equation:

$$h_i = R - \frac{R^2 + d_i^2 - R_i^2}{2d_i}$$

where the R_i values are the van der Waals radii of the atom to which the atom in question is bonded and the d_i values are the respective bond lengths.

It was assumed that the sterol nucleus remains invariant throughout this series and the bond lengths for it were taken from the work of Craven and de Titta.[2] Bond lengths for the alkyl chains were taken from Kennard and Watson.[5] The van der Waals radii used for hydrogen, carbon and oxygen were respectively 1.17 Å, 1.80 Å and 1.52 Å.

The results listed in Table I and plotted in Figure 1 were obtained from the crystallographic data of Barnard and Lydon[3] and Craven and de Titta.[4] It is apparent that there is an irregular variation of the packing coefficients and that the range of spread of these values is not appreciably greater than their estimated errors. In addition there is no systematic correlation between these packing coefficients and either the melting points or the crystal to mesophase transition enthalpies or entropies.[7–11] However, there does appear to be a significant general trend. From the methanoate to the heptanoate the value of the packing coefficient tends to fall and from the nonanoate to the hexadecanoate it steadily increases. The packing coefficient of the octanoate seems to be unusually high (although this does not appear to be significant in relation to the possible accumulated experimental error). That of the octadeconoate, on the other hand, appears to be unexpectedly low and in the absence of further data it is not possible to say whether this indicates the beginning of a new sequence or whether it is an isolated anomaly. Since the nonanoate marks the appearance of the smectic phase, it would seem that the change of slope shown in Figure 1 is significant and provides a link between the crystallographic data and the thermodynamic parameters. Presumably it marks the appearance of an efficiently packed antiparallel assembly of alkyl chains in both the crystalline solids and the smectic mesophases.

Our previous observations have shown that an odd/even effect in terms of the crystal structures can give rise to a similar effect for the packing coefficients. The crystallographic study of Barnard and Lydon which included only the lower odd homologues does not show any odd/even effect for the

TABLE I

Unit cell volumes, densities, number of molecules per unit cell, geometrical volumes of molecules and packing coefficients of the homologous series, cholesteryl alkanoates and the compound cholesterol methyl carbonate.

	Unit cell volume in Å^3	Z	Crystal class	Densities g/cc	Molecular geometrical volume in Å^3	Packing coefficients
Cholesteryl methanoate	1276.14	2	mono	1.027	440.69	0.691
Ethanoate	2612.24	4	mono	1.023	457.42	0.700
Butanoate	5693.89	8	mono	1.064	490.89	0.690
Pentanoate	2951.52	4	ortho	1.014	507.63	0.688
Hexanoate	1548.78	2	mono	1.028	524.36	0.677
Heptanoate	1621.75	2	mono	1.062	541.10	0.667
Octanoate	1622.11	2	mono	1.034	557.83	0.688
Nonanoate	1717.88	2	mono	1.051	574.56	0.669
Decanoate	3486.65	4	mono	1.001	591.30	0.678
Dodecanoate	3659.82	4	mono	1.023	624.77	0.683
Tetradecanoate	3836.75	4	mono	1.061	658.24	0.686
	7881.548[2]	8	mono			
Hexadecanoate	8018.97	8	ortho	1.103	691.71	0.690
Octadecanoate	4403.82	4	mono	1.086	725.17	0.659
Methyl carbonate	1219.82[6]	2	mono	1.210	466.71	0.765

All of the above data were taken from Barnard and Lydon[3] except for the value for the tetradecanoate obtained from Craven and de Titta[2] and for the Methyl carbonate from Rajalakshmi *et al.*[6]

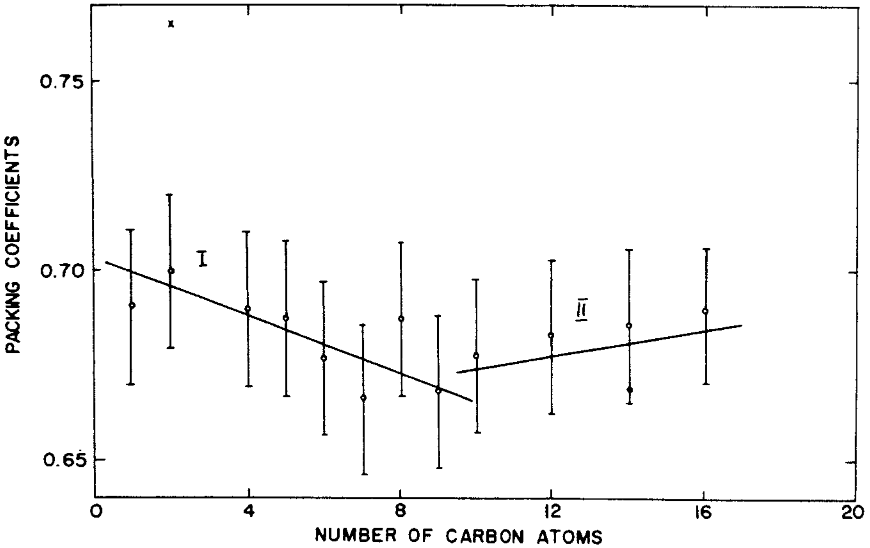

FIGURE 1 The variation of the packing coefficient with alkyl chain length for the cholesteryl alkanoates. Values calculated from the data of Barnard and Lydon (obtained by photographic techniques) are represented by open circles. The error bars were calculated using an estimate of a possible error of 1 % in each unit cell dimension and of 0.5° for the β angles of the monoclinic cells. (We feel that Barnard & Lydon probably overestimated their possible experimental errors and this is a lower figure than they quoted). The value for the tetradecanoate shown as a solid circle was calculated from the data of Craven and de Titta. These workers used a diffractometer and in this case the estimated error for the packing coefficients is less than 0.5 %.

The line lablelled I is the best straight line (given by a least squares fitting) down through the points corresponding to the esters numbered 1, 2, 4, 5, 6 and 7. It has the equation $k = -0.00430n + 0.703$. The line labelled II is the best straight line drawn through the points corresponding to the esters numbered 9, 10, 12, 14 and 16, and it has the equation $k = 0.00169n + 0.657$. The value shown as a cross is for cholesteryl methyl carbonate.

unit cell parameters and as shown in Figure 1 there is no evident odd/even effect for the corresponding packing coefficients either. However, Barrall and Johnson[12] have reported that the familiar odd/even effect does occur for the thermodynamic properties of higher homologues (the nonanoate and subsequent esters) and we would therefore expect it to arise for the packing coefficients also. Kitaigorodsky[13] has made the explicit warning that "the value of k (the packing coefficient) is very sensitive to change in cell parameters: an error in a parameter of 0.5 to 0.6 % alters k by one unit in the second decimal place. One must therefore be careful in selecting material for calculating k". This paper using the preliminary data of Barnard and Lydon suggests that the packing coefficient is a meaningful parameter for mesogenic molecular crystals. However, for conclusions of any weight to be drawn, more accurate unit cell data are clearly necessary and when diffractometer data become available, a recalculation of these packing coefficients would be very informative.

Acknowledgement

The authors would like to thank the referee for his suggestions for the improvement of the paper.

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