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Technical Note

Molecular Packing Coefficients and Thermal Stabilities in Some Cholesterol Derivatives

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INTRODUCTION

Many derivatives of cholesterol form cholesteric liquid crystal phases and these have wide application in medicine and technology. In particular the straight chain alkyl esters of cholesterol occur in arterial fatty deposits and a knowledge of the crystalline forms and mesophases of these compounds may explain the conditions of formation of the deposits and ultimately lead to preventative measures.[1–4]

Preliminary crystallographic studies have been carried out for a number of cholesteryl esters but a full crystal structure determination has been carried out only for a small number of cases.[5–7]. In view of this, we have undertaken a project to obtain further crystallographic data on these compounds and to relate various physical properties of the crystalline state to the molecular packing arrangements.[8–10]

It has been shown in our earlier papers[11,12] that the molecular packing coefficient is a meaningful parameter for mesogenic molecular crystals in providing a link between crystallographic data and thermodynamic parameters; when the principal forces holding the molecules together in the crystal are of a non-directional van der Waals type, the more compact the molecular packing, the higher the temperature required to overcome the molecular adhesion and disrupt the structure. Our previous paper[11] dealt with the cholesteryl alkanoates and this paper extends our studies to the cholesteryl halides, methyl and ethyl carbonates and the benzoate.

CALCULATION OF PACKING COEFFICIENTS

The molecular packing coefficient is defined as the ratio of the geometric (van der Waals) volume of the molecule to the volume of the phase per molecule. The geometric volume was calculated by summing the volume increments for each atom using the formula of Kitaigorodsky[13] as described in our previous papers.[11,12]

It was assumed that the geometry of the sterol nucleus remained invariant and the bond lengths for it were taken from the work of Craven and de Titta.[7] The van der Waals radii used for hydrogen, carbon, oxygen, chlorine, bromine and iodine were respectively: 1.17 Å. 1.80 Å, 1.52 Å, 1.78 Å, 1.95 Å and 2.10 Å. Bond lengths for the alkyl chains were taken from Kennard and Watson.[14] Values for V_0 were calculated from crystallographic data from a variety of sources[8–10,15–17] which are tabulated in Table I. Table II gives the packing coefficients which we have calculated and the upper temperature limit of existence of the crystalline phases.

DISCUSSION

As we progress along the series of cholesteryl halides from the chloride to the bromide and then the iodide there are two principal factors which one might expect to affect the value of the packing coefficient. The first of these is the increase in size of the halogen atom and the second is the decrease

TABLE I

Unit cell dimensions of the cholesteryl halides, cholesteryl alkyl carbonates and cholesteryl benzoate

	a(Å)	b(Å)	c(Å)	β(°)	V(Å^3)
Cholesteryl chloride	[a]10.60	7.55	21.70	132	1290.58
	[b]16.333	7.553	10.691	102.95	1285.33
Cholesteryl bromide	[a]11.00	7.55	21.60	134	1290.41
Cholesteryl iodide	[a]11.00	10.42	21.80	149	1286.93
	[c]12.57	9.04	21.89	149	1281.12
Cholesteryl methyl carbonate	[d]16.50	7.43	10.22	103.2	1219.82
Cholesteryl ethyl carbonate	[e]17.89	11.34	13.11	105.2	2566.62
Cholesteryl benzoate	[f]10.14	10.06	26.00	—	2652.22

[a] Bernal *et al.*[15]
[b] Ohrt *et al.*[16]
[c] Carlisle *et al.*[17]
[d] Rajalakshmi *et al.*[8]
[e] Shivaprakash *et al.*[9]
[f] Shivaprakash *et al.*[10]

TABLE II

Unit cell volumes, number of molecules per unit cell (Z), crystal class, densities, melting points, geometrical volumes of molecules and packing coefficients of cholesteryl chloride, bromide, iodide, methyl carbonate, ethyl carbonate and benzoate.

	Unit cell volume† in Å^3	Z	Crystal class	Densities (g/cc)‡	Melting points in °C	Geometrical volume in Å^3	Packing coefficients
Cholesteryl chloride	1290.58	2	Mono	1.042	95	425.43	0.659 ± 0.01
	1285.33	2	Mono	1.047	95	425.43	0.662 ± 0.01
Cholesteryl bromide	1290.41	2	Mono	1.157	98	432.26	0.670 ± 0.01
Cholesteryl iodide	1286.93	2	Mono	1.281	106	440.09	0.684 ± 0.01
	1281.12	2	Mono	1.287	106	440.09	0.687 ± 0.01
Cholesteryl methyl carbonate	1219.82	2	Mono	1.210	110	466.71	0.765 ± 0.01
Cholesteryl ethyl carbonate	2566.62	4	Mono	1.187	83	483.78	0.754 ± 0.01
Cholesteryl benzoate	2652.22	4	Ortho	1.228	148	505.21	0.762 ± 0.01

† The estimated errors in the unit cell parameters are 0.5%.
‡ The estimated errors of the densities are 2%.

in electronegativity. The preliminary X-ray investigation of Bernal *et al.*[15] suggested that the molecules lie in an antiparallel, head to tail array in the crystal and this would imply that a decrease in electronegativity and hence a decrease in the dipole moment of the molecules should be accompanied by a decrease in the lateral forces holding the molecules together and hence a decrease in the compactness of the crystal packing.

It appears that this reasoning is not valid. In spite of the size difference between the halogen atoms, the unit cell dimensions are virtually identical and the packing coefficients therefore increase rather than decrease. It is possible that the decrease of negative charge on the halogen atom actually reduces the strength of some other interactions that were tending to keep the molecules apart. However, the most obvious explanation is that the molecules are packed in a pattern which leaves plenty of room available for the halogen atom. The relatively small chlorine atom lies in a cavity too large for it and as we progress to the bromide and the iodide the halogen atoms merely fill more of the void. Whatever the explanation, it appears significant that the increase of the packing coefficient is coupled with an increase in the transition temperature. A similar phenomenon occurs for the two cholesteryl alkyl carbonates studied here but note that this does not

occur when the cholesteryl alkyl carbonates are compared with the cholesteryl alkanoates. The considerable difference in the densities of the two families of compounds must mean that the packing pattern are radically different.

CONCLUSION

The molecular packing coefficients has been further shown to be a useful parameter when discussing the relationship between the structures and the thermal stabilities of molecular crystals. However, it must be used with circumspection and, whilst it appears that the direct relationship between packing coefficient and upper temperature limit holds within a homologous series or for very closely related compounds, it is not universally valid and does not hold for even molecules as similar as the cholesteryl alkanoates and the alkyl carbonates.

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