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On the Molecular Structure, Packing Coefficients and Thermal Stabilities of the Homologous Series p-Methoxy-XY-p′-Alkyl Tolanes

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Note

On the Molecular Structure, Packing Coefficients and Thermal Stabilities of the Homologous Series *p*-Methoxy-XY-*p'*-Alkyl Tolanes

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Molecular structural aspects of liquid crystalline materials in the solid state are quite useful in explaining the bulk physical properties of the liquid crystalline phase itself. In an earlier paper (1) it has been demonstrated how thermal stabilities in the mesogenic homologous series *p*-*p*-ethoxy phenylazo phenyl alkanoates could be nicely explained with the help of molecular packing coefficients without the actual conformation of the molecules in the crystalline state. The idea has now been extended to the case of *p*-methoxy-XY-*p'*-alkyl tolanes. Detailed crystal structure analysis of the above homologous series has been undertaken by Cotrait *et al.*[2] to obtain the molecular arrangement in the solid state and to relate alkyl chain lengths with the macroscopic properties of the materials. With the solution of the structures of the first two members of the series which are not mesogenic, the authors have come to the conclusion that unidirectional three dimensional arrangement of molecules to be one of the main requirements for the formation of the mesophase. The reasoning for their conclusion stems from the fact that there is a transition from bidirectional to unidirectional arrangement as one goes up to the second member. This result is not in conformity with the detailed structural data for the series *p*-*p*-ethoxy phenylazo phenyl alkanoates,[3,4,1] wherein one finds unidirectional and bidirectional arrangements with layer like stacking arrangements for the mesogenic crystals in an arbitrary disposition as one goes up the higher members of the series. It has been shown that the macroscopic properties, such as thermal stabilities, could be very well explained by the changes in the angle between the phenyl groups in the molecules, as one goes up the series, and independently by a knowledge

of the molecular packing coefficients. Molecular packing coefficients, defined to be the ratio of the volume of a molecule (geometric volume) to that of the volume per molecule in the crystal, have been evaluated for the series *p*-methoxy-XY-*p'*-alkyl tolanes by calculating the volume increments for atomic combinations using the formula (5)

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

where R is the intermolecular radius of the atom considered, the R_i's are intermolecular radii of the atoms that are valence bonded with this atom, and are positioned at distances d_i from this atom, and the height of the cut-off segment is

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

and using the crystallographic data of Cotrait *et al.*[2] The intermolecular radii used for hydrogen, carbon, oxygen and nitrogen are respectively 1.17, 1.80, 1.52 and 1.58 Å. Bond lengths have been taken from the work of Cotrait *et al.* and Kennard and Watson.[6] The results obtained are tabulated in Table I.

In the case of *p-p*-ethoxy phenylazo phenyl alkanoates, it was shown that the packing coefficient gradually decreases as one goes up the homologs, the thermal stabilities of which also gradually decrease. In the series studied earlier, all the members were mesogenic. In the present case, the first two members are not mesogenic whereas the other higher members are. We see that the packing coefficient decreases, as it should, for the nonmesogenic members but increases when the member which begins to show the mesogenic state is encountered. Unlike the earlier case, we have a case where the

TABLE I

Unit cell volumes, densities, number of molecules per unit cell, the melting points, geometrical volumes of molecules and packing coefficients for the homologous series *p*-methocy-XY-*p'*-alkyl tolanes (CH_3—O—ϕ—C≡C—ϕ—R)

R	CH_3	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}
Volume in Å^3	1275.33	1420.24	1475.46	3236.68	—
Z	4	4	4	8	—
Crystal class	Ortho	Mono	Tri	Mono	—
Densities	1.173	1.125	1.11	1.084	—
Geometrical volume in Å^3	223.34	241.01	258.11	275.21	—
Melting points in °C	124.3	72.8	61–66	42.5–49.5	45.2–57
Packing coefficients	0.70	0.68	0.70	0.68	—

packing coefficient monotonically decreases as we increase the length of the alkyl chain, thereby accounting for the decrease in stability and suddenly increases at the onset of the mesogenic member and then again decreases accounting for the thermal stability decrease within the mesogenic materials. The varying differences between packing coefficients of the neighbouring members with differences in their thermal stabilities are taken care of by the relationship between symmetry and packing coefficient—a crystal moves into a crystal class of lower symmetry provided the packing coefficient increases. Thus we see how with the help of packing coefficients we can account for the thermal stabilities fairly well.

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