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X-RAY STUDY AND MOLECULAR MODELLING OF THE MESOGEN 4-PENTYL CYCLOHEXYL-4-(4-PROPYLCYCLOHEXYL) BENZOATE

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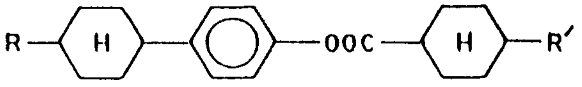
Abstract

X-ray studies of the mesogen 4- pentyl cyclohexyl -4-(4- propyl cyclohexyl) benzoate (HD35) has been conducted at various temperatures both in the aligned and non-aligned phases and molecular length/apparent layer thickness and average inter molecular distances determined. The order parameters in the SmecticB phase have been calculated as function of temperature. The molecular structure and charge density distribution in the minimum energy configuration has been obtained from molecular orbital calculations. This has been used to calculate intermolecular interaction energies using atom-atom potential function. Using a hexagonal type cell to simulate the SmB phase the lattice parameters have been calculated which are in good agreement with experimentally observed values. Using the energy values obtained from the DSC results in the McMillan potential, calculatons have been carried out and phase transition temperatures reproduced.

INTRODUCTION

The mesogen HD35 (supplied by Merck Ltd.), having the molecular formula $C_{27}H_{42}O_2$ and the structural formula as given below



$R = C_3H_7$ $R' = C_5H_{11}$

has been studied by X-ray methods at various temperatures. From differential scanning calorimetry, the exact temperatures of phase transitions are found to be

solid $\xrightarrow{42\,^{0}C}$ Sm1 $\xrightarrow{72.4\,^{0}C}$ Sm2 $\xrightarrow{126.7\,^{0}C}$ nematic $\xrightarrow{193\,^{0}C}$ isotropic

while heating and

solid $\xleftarrow{38\,^{0}C}$ Sm1 $\xleftarrow{63.4\,^{0}C}$ Sm2 $\xleftarrow{120.8\,^{0}C}$ nematic $\xleftarrow{188.2\,^{0}C}$ isotropic

while cooling. The heat transfer in the Sm1 $\longrightarrow$ Sm2 and Sm2 $\longrightarrow$ nematic transitions are 35.67 and 8.14 J/gm respectively. Sm1 and Sm2 phases have been identified to be the SmE and SmB phases respectively from X-ray and texture studies. The present work has been undertaken with a view to corroborate our experimental findings from X-ray studies with theoretically obtained values and thereby to attempt an explanation of the nature of molecule-molecule interaction in the mesophase.

EXPERIMENTAL METHODS

X-ray studies was conducted by taking photographs with a flat plate camera at various temperatures. Measurements on the photographs was done by scanning both linearly and circularly with an optical densitometer (VEB Carl Zeiss Jena Model Microdensitometer 100). In certain photographs where the rings obtained were sharp, a comparator (Rich, Seifert) was used to measure the diameter of the rings. Texture studies were done using a polarizing microscope (Leitz) fitted with hot stage (Mettler FP82HT).

Detailed account of our X-ray studies will be published elsewhere.

COMPUTATIONAL DETAILS

The molecular geometry of the mesogen HD35 was initially built up using the molecular modelling program package DTMM[1]. Of the four possible combinations of the conformations of the two cyclohexane moities, chain conformations for both was considered acceptable as the length of the molecule with such a conformation was in agreement with the experimental value obtained by X-ray diffraction. The molecular geometry thus obtained was subjected to further refinement using AM1 Hamiltonian of MOPAC[2], a semiempirical molecular orbital program using self consistent field (SCF). A realistic model of the mesogen HD35 was simulated assuming packing of the molecules in a dimensionally hexagonal cell, with no imposition of hexagonal symmetry. The minimum potential energy configuration was obtained using non-bonded atom-atom potential eqn(1) of WMIN[3], a program package for modelling molecules and crystals.

$$E=\sum\left(A_{ij}\exp(-B_{ij}R_{ij}) - \frac{Cij}{R_{ij}^{6}} + \frac{q_{ij}}{R_{ij}} \right) \qquad (1)$$

i,j run over all atoms in different molecules. A_{ij}, B_{ij} and C_{ij}s are obtained from Fillipini and Gavezzotti[4] and partial charges were taken from MOPAC calculations. To expedite the convergence, the method of Ewald[5] and Williams[6] was used.

Applying the McMillan[7] potential for the SmA phase to the SmB phase to investigate the SmB-N transition, we note that McMillan potential is given by

$$V(\cos\theta, z) = -V_1\left[\delta\alpha\tau \cos\left(\frac{2\pi z}{d}\right) + \left\{ \eta + \alpha\sigma \cos\left(\frac{2\pi z}{d}\right) \right\} P_2(\cos\theta) \right] \qquad (2)$$

where α, δ are two adjustable parameters, z is the displacement along the layer normal, d is the layer thickness and $\eta=\langle P_2\rangle$ is the orientational order parameter. At the SmB-N phase boundary $\tau=0$, $\sigma=0$ and $\eta=1$ (in the ideal case of perfect alignment) and therefore $V(\cos\theta, z)=-V_0$ at the phase boundary. Again, at the phase boundary of N-I transition we have, from eqn(2), V=0.0. This means that V_0 is the total energy needed by a single particle to undergo a transition from SmB phase to N phase and then from N phase to I phase. From DSC result we see that the energy E needed for such transition is (35.67+8.14)=43.81 J/gm i.e. 17.444 kJ/mol. Using Mcmillan potential and this value of V_0, the phase transition temperatures have been calculated.

RESULTS AND DISCUSSION

Detailed account of the procedure involved in determining the molecular length/ apparent layer thickness 'l', intermolecular distance 'D' and order parameter will be published elsewhere. The variation of 'l' and 'D' with temperature are shown in Figs. 1 and 2. The variation in 'l' in the SmE phase ranges from 24.8Å to 26.0Å and in the SmB phase from 24.7Å to 26.0Å. This finding agrees well with the calculated distance of 24.68Å (including Van der Waal's radii) between two end methyl groups of the molecule from molecular orbital calculations. From molecular orbital calculation the components of dipole moments along the principal axes of the inertia tensor in the single lowest energy conformation were calculated to be $\mu_x=-0.764$, $\mu_y=0.412$ and $\mu_z=1.163$ Debye ($\mu_{total}=1.451$) where the z-axis runs along the molecular length and μ_x, μ_y along the transverse directions. The polarizability is 34.72Å^3. Force calculations showed that the maximum contribution to the dipole moment is due to $-\underset{\underset{O}{\|}}{C}-$ stretching vibration band. The scaled calculated vibrational frequencies match well with the experimental FTIR values.

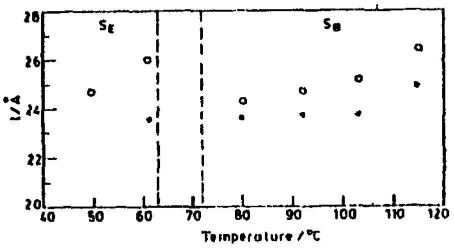


FIGURE 1

Variation of layer spacings (1) with T.
Open circles —— After alignment
Black circles —— before alignment

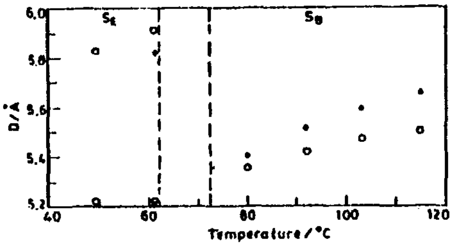


FIGURE 2

Variation of intermolecular distance (D) with T. Open circles —— After alignment
Black circles —— before alignment

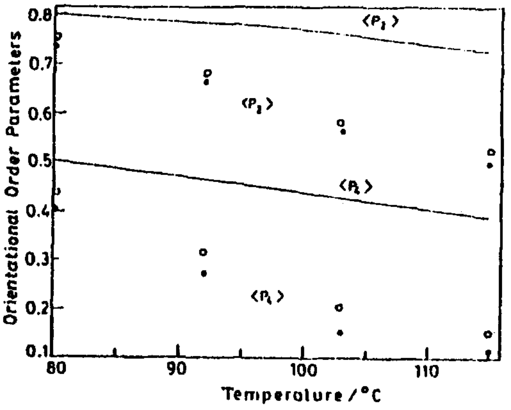


FIGURE 3
Variation of order parameter with T
Solid line - McMillan (δ=.28,α=.47)
Open circles - X-ray data (Leadbetter)
Half filled circles - X-ray data (Vainstein)

From X-ray studies the two 'D' values corresponding to the repeat distances in the SmE phase have been determined to be approximately 5.22Å and 5.85Å. In the SmB phase the value of 'D' increases from approximately 5.4Å to 5.5Å with temperature. The hexagonal packing arrangement to simulate the SmB was refined to yield a=5.94Å and c=25.82Å (from WMIN, discrepancy parameter RDWS=.0214) for the hexagonal cell. The value c=25.82Å agrees well with the average value of the layer thickness 'l' obtained from X-ray studies in the SmB phase and a=5.94Å is a rather close fit to the experimental value of the intermolecular spacing 'D'. The variation of order parameters $<P_2>$ and $<P_4>$ with temperature obtained from X-ray studies in the SmB phase is depicted in Fig.3. $\langle P_2 \rangle$ varies from approximately .75 to .55 over a temperature range of 80^0C to 115^0C. The order parameters calculated in the SmB phase using McMillan potential (Fig.3 solid line), (α=.47,δ=.28) to reproduce the SmB-N and and N-I transition show approximately the same trend as the experimentally determined values. The energy value 17.44 J/mol obtained from the DSC results was used with same α, δ in the calculation of order parameter and produced the SmB-N and N-I transition temperature as 192^0C and 132^0C. These transition temperatures are close to the temperatures determined from DSC studies.Such agreement provides a justification of the theoretical consideration based on which the value of V_0 was adopted.

CONCLUSION

The experimentally obtained values of 'l' and 'D' are in good agreement with those obtained from MOPAC and WMIN calculations. Also the value of 17.44 J/mol as V_0 from the DSC results produce SmB-N and N-I phase transition temperatures which are close to the experimentally observed temperatures. Such close agreement between experimentally determined parameters and those obtained from calculations reveal that calculations not only explain the nature of molecular interaction but may be used to predict molecular properties as well.

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