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COMPUTER SIMULATIONS OF ORDERING IN A HOMOLOGOUS SERIES OF *p-n*-ALKOXYCINNAMIC ACIDS (*n*OCAC) AT PHASE TRANSITION TEMPERATURE—ROLE OF DIELECTRIC MEDIUM

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Computer simulations of ordering in three nematogenic acids (nOCAC) having two, four, and six carbon atoms in the alkyl chain was carried out on the basis of quantum mechanics and intermolecular forces. The evaluation of atomic charges and dipole moment at each atomic center was carried out through an all-valence electron (CNDO/2) method. The configurational energy has been computed using the Rayleigh-Schrodinger perturbation method. The total interaction energy values obtained through these computations were used to calculate the probability of each configuration in a dielectric medium (i.e., noninteracting and nonmesogenic solvent, benzene) at phase transition temperature using the Maxwell-Boltzmann formula. It was observed that in dielectric medium the energies/probabilities are redistributed and there is considerable rise in the probability of interactions, although the order of preference remains the same. An attempt has been made to develop a new and interesting model of nematogenic acids in dielectric medium. The present investigation provides theoretical support to the experimental observations.

Keywords: computer simulations; nematogens; quantum chemistry; *n*OCAC

INTRODUCTION

Research in the field of liquid crystals has focused considerable effort on phase transitions involving one- and two-dimensional ordering [1,2]. The phase transitions in liquid crystals are often accompanied by interesting changes in their properties. Several techniques/methods are employed to

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investigate phase transitions, depending on the nature of liquid crystals and properties of interest. Such studies are not only of academic value in understanding the structural and mechanistic aspects of phase transitions but can also be of technological importance [3,4].

The proper understanding of liquid crystalline behavior requires an adequate theoretical background as precursor to application of new developments and to account for abnormal properties in materials. The liquid crystalline materials are known for their anomalous physical properties near the phase transitions, and they maintain orientational order in mesophase. The phase transitions of these liquid crystals are primarily governed by the intermolecular interactions acting between sides, planes, and ends of a pair of molecules. The potential energy of interaction of two molecules is considered as a prime requirement in the theoretical investigation on molecular interactions. This interaction determines the physical properties of liquid crystals, as well as the type of kinetics of physical and physicochemical process taking place in these substances [5]. Furthermore, the computer simulation of liquid crystals is occupying an increasingly influential role in placing empirical structure–property relationship on firm theoretical foundations [6–8].

The role of intermolecular forces in mesomorphic behavior has attracted the attention of several workers based on the Rayleigh-Schrodinger perturbation method [5,9,10]. These studies were aimed to compute interaction energy between a molecular pair to study the variation of interaction energy with respect to angle and distance between two molecules, but their attempts were directed towards explaining the aligned structure, or at best correlating the minimum energy with observed crystal structure. It has been observed that the interaction energies for a pair of mesogens indicate the preference of a particular configuration over the other depending on their energy values, which are not directly related quantities. Furthermore, it is difficult to have direct correlation between pair energy and liquid crystallinity. It is not straightforward even if one takes the relative probabilities into account. It is, therefore, necessary to identify the characteristic features of liquid crystallinity in terms of pair energy or configurational probabilities. Hence, in order to obtain a quantitative measure for the relative preference, authors have evaluated the relative probability of occurrence of each configuration. Since mesogenic properties are related to molecular aggregation in a specific manner, the probability calculations based on energy distribution results can provide valuable information in this respect.

In the present article we report the characteristic features of *p-n*-alkoxycinnamic acids having two (2OCAC), four (4OCAC), and six (6OCAC) carbon atoms in the alkyl chain in dielectric medium (i.e., the noninteracting and nonmesogenic solvent benzene, the average dielectric

constant of which has been taken to be 2.25 for the entire temperature range) fully for a molecular pair at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å was kept for terminal interactions. The choice of distance was made to eliminate the possibility of van der Waals contacts and to keep the molecule within the short- and medium-range interactions. Furthermore, instead of finding the exact minimum energy configuration an attempt was made to elucidate the general behavior of the molecules surrounding a fixed molecule in a particular frame of reference.

An examination of thermodynamic parameters reveals that the molecules show nematic–isotropic transition temperatures as [11] 2OCAC at 471 K, 4OCAC at 460.5 K, and 6OCAC at 452 K.

COMPUTATIONAL DETAILS

The molecular geometry of 2OCAC, 4OCAC, and 6OCAC has been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles [11]. The chains have the all-*trans* extended conformation, and the molecules exist in the crystal as planar hydrogen-bonded dimers. The dimers are arranged in end-to-end fashion in parallel rows. Similarly, side-to-side packing of pairs of dimers is found in each crystal structure, giving a good fit between adjacent aromatic cores [11]. The calculations have been carried out in three stages as outlined below.

Computation of Atomic Net Charges and Dipole Moments

The simplified formula for interaction energy calculations requires the evaluation of atomic net charges and dipole moment components at each atomic center through an all-valence-electron method. In the present computation, the CNDO/2 method [12] was employed to compute the net atomic charge and dipole moment at each atomic center of the molecule. A revised version QCPE No. 142 program, which is an extension of the original program QCPE No. 141 for the third-row elements of periodic table, was used. The program language is FORTRAN IV.

Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on simplified formula provided by Claverie [13] for the evaluation of interaction energy between a molecular pair was used to calculate the energy for fixed configuration. The computer program INTER, originally developed by Claverie and later on modified at Chemical Physics Group, Tata Institute of Fundamental Research, Bombay,

India by Govil and associates has been used for this purpose with further modifications. According to the second-order perturbation theory as modified for intermediate range interactions [13], the total pair interaction energy of molecules (U_{pair}) is represented as sum of various terms contributing to the total energy:

$$U_{pair} = U_{el} + U_{pol} + U_{disp} + U_{rep},$$

where U_{el}, U_{pol}, U_{disp}, and U_{rep} are the electrostatic, polarization, dispersion, and repulsion energy terms, respectively.

Again, electrostatic term is expressed as

$$U_{el} = U_{QQ} + U_{QMI} + U_{MIMI} + \cdots\cdots,$$

where U_{QQ}, U_{QMI}, U_{MIMI}, etc. are monopole–monopole, monopole–dipole, and dipole–dipole terms, respectively. In fact, the inclusion of higher order multipoles does not significantly affect the electrostatic interaction energy, and the calculation only upto dipole–dipole term gives satisfactory results [14]. The computation of electrostatic term has, therefore, been restricted only upto dipole–dipole energy term.

In the present computation, the dispersion and short-range repulsion terms are considered together because several semiemperical approaches, viz. the Lennard-Jones or Buckingham type approach, actually proceed in this way. Kitaigorodskii introduced a Buckingham formula whose parameters were later modified by Kitaigorodskii and Mirskay for hydrocarbon molecules, and several other molecules, and finally gave the expression [15]

$$U_{disp} + U_{rep} = \sum_{\lambda}^{(1)} \sum_{\nu}^{(2)} U(\lambda, \nu),$$

$$U(\lambda, \nu) = K_\lambda K_\nu (-A/Z^6 + B\, e^{-\gamma Z}),$$

where $Z = R_{\lambda\nu}/R^0_{\lambda\nu}$; $R^0_{\lambda\nu} = [(2R^w_\lambda)\ (2R^w_\nu)]^{1/2}$, where R^w_λ and R^w_ν are the van der Waals radii of atoms λ and ν, respectively. The parameters A, B, and γ do not depend on the atomic species, but $R^0_{\lambda\nu}$ and factor $K_\lambda\ K_\nu$ allows the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [15].

An orthogonal coordinate system is considered to facilitate the above calculation. The origin on an atom was chosen close to the center of mass of the molecule. The x axis is along the long molecular axis, while the y axis, lies in the plane of the molecule and the z axis is perpendicular to the molecular plane.

Computation of Configurational Probabilities

The total interaction energy values obtained through these computations were used as input to calculate the probability of occurrence of a particular configuration i using the Maxwell-Boltzmann formula [16] in order to obtain a better insight:

$$P_i = \frac{exp(-\beta\varepsilon_i)}{\sum_i exp(-\beta\varepsilon_i)},$$

where P_i stands for probability, $\beta = 1/kT$, k is the Boltzmann constant, T is the absolute temperature, and ε_i represents the energy of the configuration i relative to the minimum energy value for which the probability distribution is computed.

RESULTS AND DISCUSSION

The molecular geometry of p-n-alkoxycinnamic acids having two, four, and six carbon atoms in the alkyl chain is shown in Figure 1. Calculated net atomic charges and dipole moments at each atomic center are listed in Table I. The results of probability distribution based on interaction energy during the different modes of interactions in dielectric medium are discussed below.

Stacking Interactions

In a molecular pair, one of the interacting molecules is fixed in x-y plane, while the second has been kept at a separation of 6 Å along z axis with respect to fixed one. The variation of probability with respect to rotation about the z axis is shown in Figure 2, corresponding to configuration X(0°)Y(0°) at nematic–isotropic transition temperature. The figure reveals that the maximum probability among the molecules corresponds to 4OCAC at an equilibrium position. The minimum energy so obtained in each molecule is then taken as the starting point, and the entire process is repeated for smaller intervals. The energy has been minimized with respect to translation and rotation about all axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to other has been achieved. It is important to note here that the path of minimization strictly depends on the objective of computation. The global search for minimum energy configuration or the study of variation of interaction energy under preselected conditions will have a completely different path and, therefore, one has to careful in choosing the specific route.

The variation of probability with respect to translation along the long molecular axis (x axis) corresponding to configuration Y(0°)Z(180°) is

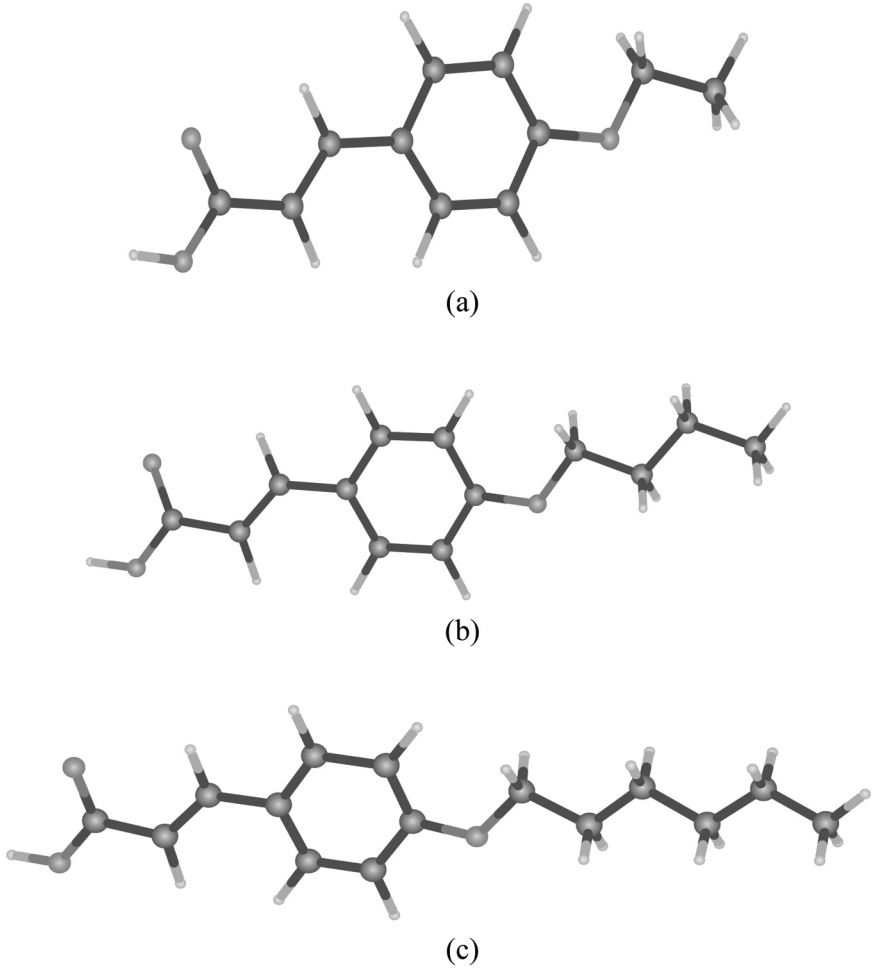

FIGURE 1 Molecular geometry of *p*-*n*-alkoxycinnamic acids (*n*OCAC): (a) 2OCAC, (b) 4OCAC, and (c) 6OCAC.

shown in Figure 3 for 2OCAC, 4OCAC, and 6OCAC molecules. It may be observed that the configuration shows a sharp preference towards the minimum energy point at nematic–isotropic transition temperature. The variation of probability is almost constant in the region of $-1.6\,\text{Å} \pm 0.4\,\text{Å}$, which shows that sliding one molecule over the other is energetically for a small range, which might be correlated with the fluidity of compound maintaining its alignment in mesophase.

TABLE I Calculated Atomic Net Charge and Dipole Moments Using the CNDO/2 Method for the Molecules 2OCAC, 4OCAC, and 6OCAC

S. no	Atom	Charge	Atomic dipole components		
			μ_X	μ_Y	μ_Z
2OCAC($C_{11}H_{12}O_3$)					
1	C	0.005	0.010	0.046	−0.008
2	C	0.031	−0.057	0.110	0.002
3	C	−0.034	−0.172	0.014	−0.003
4	C	0.175	0.114	0.077	0.009
5	C	−0.049	0.114	−0.138	−0.003
6	C	0.026	0.132	0.008	0.002
7	O	−0.228	−1.351	0.248	−0.001
8	C	0.187	0.187	−0.224	−0.002
9	C	−0.035	−0.130	−0.101	−0.003
10	C	0.064	0.064	−0.065	−0.001
11	C	−0.082	−0.106	0.073	0.002
12	C	0.405	0.023	−0.318	0.008
13	O	−0.372	1.352	−0.179	0.034
14	O	−0.258	−1.192	0.365	−0.043
15	H	−0.011	0.000	0.000	0.000
16	H	0.011	0.000	0.000	0.000
17	H	0.012	0.000	0.000	0.000
18	H	−0.004	0.000	0.000	0.000
19	H	−0.037	0.000	0.000	0.000
20	H	−0.037	0.000	0.000	0.000
21	H	0.014	0.000	0.000	0.000
22	H	0.007	0.000	0.000	0.000
23	H	0.014	0.000	0.000	0.000
24	H	0.008	0.000	0.000	0.000
25	H	0.013	0.000	0.000	0.000
26	H	0.174	0.000	0.000	0.000
4OCAC($C_{13}H_{16}O_3$)					
1	C	−0.008	0.003	0.044	0.006
2	C	0.033	−0.054	0.116	−0.004
3	C	−0.050	−0.163	0.010	0.001
4	C	0.199	0.131	0.141	−0.008
5	C	−0.064	0.100	−0.135	0.003
6	C	0.036	0.118	0.013	0.007
7	O	−0.226	−1.341	0.101	0.004
8	C	0.154	0.154	−0.205	0.001
9	C	0.003	−0.127	0.045	−0.001
10	C	0.029	0.109	−0.062	0.001
11	C	−0.012	−0.119	−0.114	0.011
12	C	0.072	0.052	−0.057	0.016
13	C	−0.092	−0.109	0.087	−0.005
14	C	0.401	0.128	−0.315	0.049

(*Continued*)

TABLE I (*Continued*)

S. no	Atom	Charge	Atomic dipole components		
			μ_X	μ_Y	μ_Z
15	O	−0.338	1.336	−0.218	0.184
16	O	−0.248	−1.225	0.237	−0.153
17	H	−0.008	0.000	0.000	0.000
18	H	0.008	0.000	0.000	0.000
19	H	0.006	0.000	0.000	0.000
20	H	−0.008	0.000	0.000	0.000
21	H	−0.018	0.000	0.000	0.000
22	H	−0.019	0.000	0.000	0.000
23	H	0.006	0.000	0.000	0.000
24	H	0.005	0.000	0.000	0.000
25	H	−0.007	0.000	0.000	0.000
26	H	−0.007	0.000	0.000	0.000
27	H	0.004	0.000	0.000	0.000
28	H	−0.001	0.000	0.000	0.000
29	H	0.004	0.000	0.000	0.000
30	H	0.006	0.000	0.000	0.000
31	H	0.013	0.000	0.000	0.000
32	H	0.169	0.000	0.000	0.000
6OCAC($C_{15}H_{20}O_3$)					
1	C	0.009	−0.034	0.024	0.004
2	C	0.029	−0.059	0.112	0.000
3	C	−0.035	−0.161	0.000	0.001
4	C	0.193	0.138	0.115	−0.006
5	C	−0.076	0.128	−0.105	0.001
6	C	0.018	0.157	−0.017	0.002
7	O	−0.227	−1.339	0.163	−0.034
8	C	0.148	0.131	−0.252	0.010
9	C	0.009	−0.094	0.092	−0.005
10	C	0.024	0.097	−0.114	0.005
11	C	0.021	−0.070	0.080	−0.000
12	C	0.035	0.107	−0.043	−0.022
13	C	−0.003	−0.141	−0.106	0.004
14	C	0.066	0.059	−0.064	−0.005
15	C	−0.090	−0.111	0.085	−0.001
16	C	0.403	0.139	−0.315	−0.041
17	O	−0.374	1.357	−0.166	−0.060
18	O	−0.248	−1.237	0.187	0.093
19	H	−0.010	0.000	0.000	0.000
20	H	0.007	0.000	0.000	0.000
21	H	0.008	0.000	0.000	0.000
22	H	0.005	0.000	0.000	0.000
23	H	−0.019	0.000	0.000	0.000
24	H	−0.019	0.000	0.000	0.000

(*Continued*)

TABLE I (*Continued*)

S. no	Atom	Charge	Atomic dipole components		
			μ_X	μ_Y	μ_Z
25	H	0.001	0.000	0.000	0.000
26	H	0.001	0.000	0.000	0.000
27	H	−0.010	0.000	0.000	0.000
28	H	−0.009	0.000	0.000	0.000
29	H	−0.007	0.000	0.000	0.000
30	H	−0.007	0.000	0.000	0.000
31	H	−0.013	0.000	0.000	0.000
32	H	−0.012	0.000	0.000	0.000
33	H	0.000	0.000	0.000	0.000
34	H	−0.006	0.000	0.000	0.000
35	H	−0.001	0.000	0.000	0.000
36	H	0.005	0.000	0.000	0.000
37	H	0.015	0.000	0.000	0.000
38	H	0.168	0.000	0.000	0.000

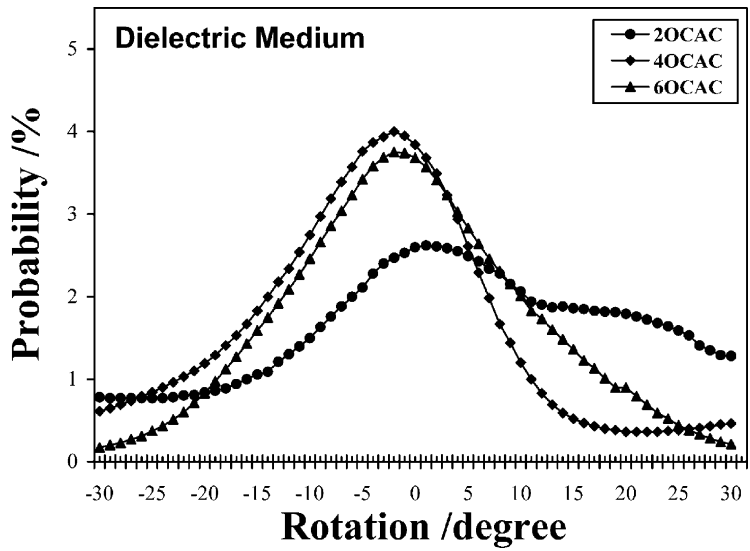

FIGURE 2 Variation of probability with respect to rotation about z axis during stacking interactions at nenmatic–isotropic transition temperature (2OCAC at 471 K, 4OCAC at 460.5 K, and 6OCAC at 452 K).

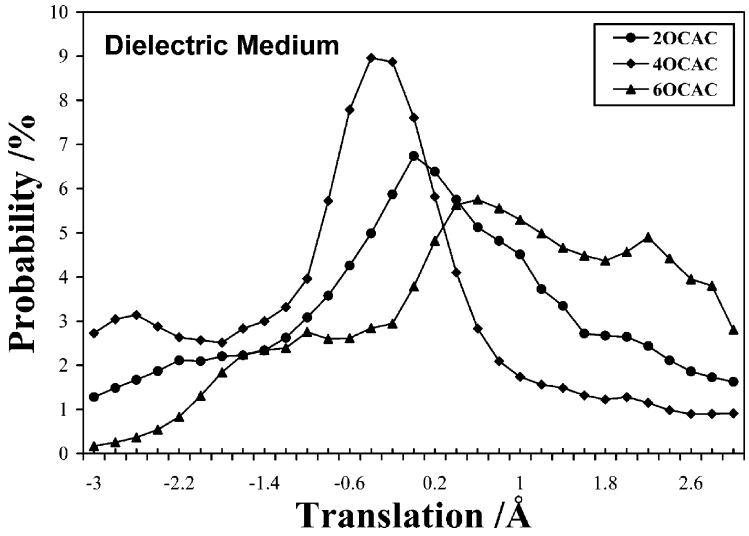

FIGURE 3 Variation of probability with respect to translation along x axis during stacking interactions at nematic–isotropic transition temperature (2OCAC at 471 K, 4OCAC at 460.5 K, and 6OCAC at 452 K).

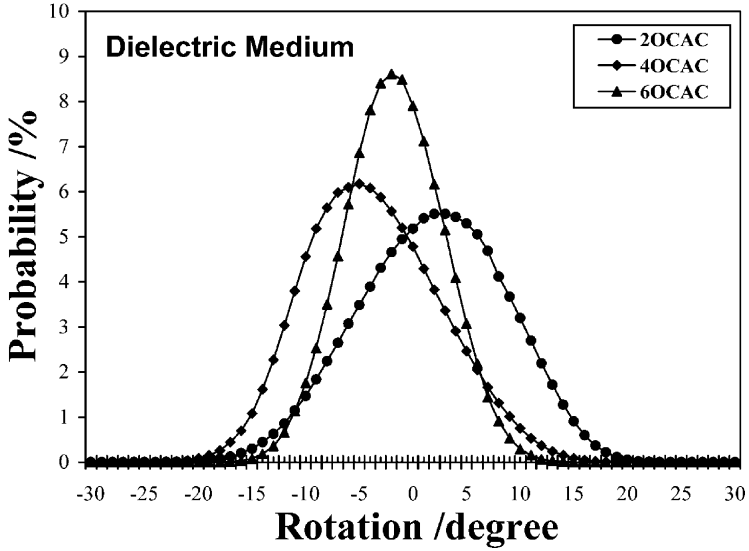

FIGURE 4 Variation of probability with respect to rotation about x axis during stacking interactions at nematic–isotropic transition temperature (2OCAC at 471 K, 4OCAC at 460.5 K, and 6OCAC at 452 K).

Figure 4 shows the variation of probability with respect to rotation about x axis corresponding to configuration Y(0°) at nematic–isotropic transition temperature. The maximum probability corresponds to 6OCAC at $-3°$ rotations, while the maximum probability for 2OCAC and 4OCAC is at a different position, indicating a slight preference for aligned structure of this configuration. Furthermore, it may be observed that the rotational rigidity about the long molecular axis is less at nematic–isotropic transition temperature. At room temperature (300 K) the observed value indicates a strong binding, but with the increase of temperature the molecules obtain sufficient freedom to rotate about the long molecular axis.

In-plane Interactions

The interacting molecule has been kept at a separation of 8 Å along y axis with respect to fixed one to avoid the possibility of van der Waals contacts and similar calculations being performed for in-plane interactions. The effect of translation along x axis corresponding to configuration Y(0°) is shown in Figure 5 for 2OCAC, 4OCAC, and 6OCAC molecules at nematic–isotropic transition temperature. Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation

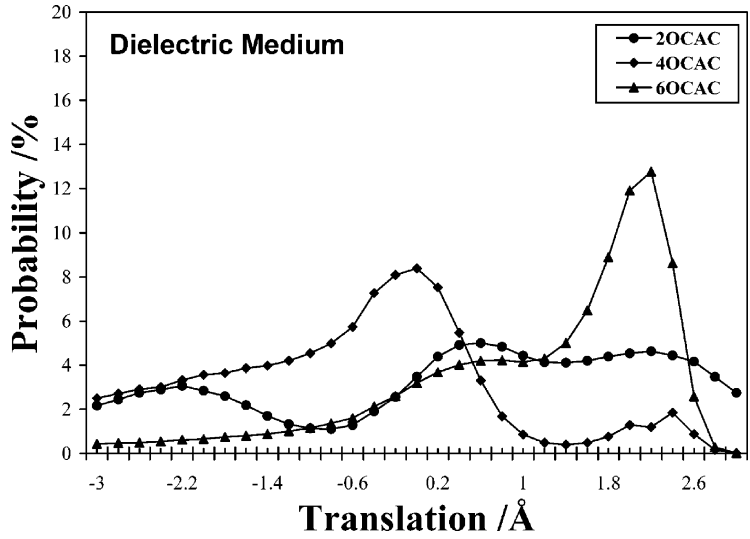

FIGURE 5 Variation of probability with respect to translation along x axis during in-plane interactions at nematic–isotropic transition temperature (2OCAC at 471 K, 4OCAC at 460.5 K, and 6OCAC at 452 K).

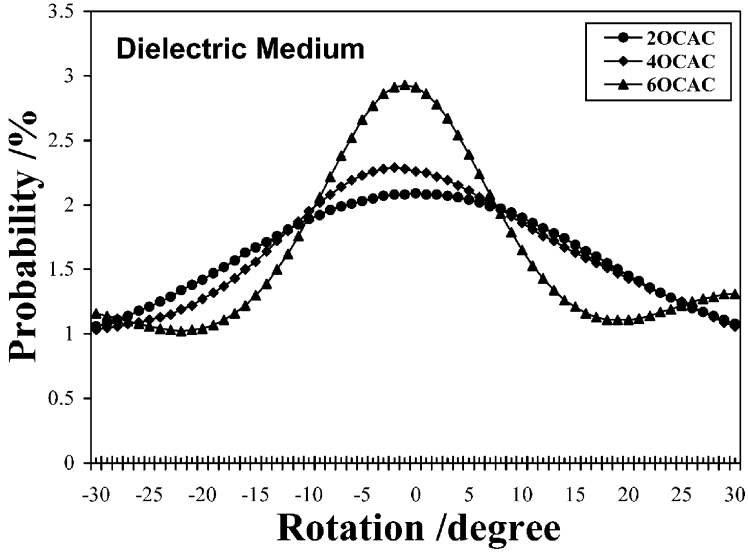

FIGURE 6 Variation of probability with respect to rotation about x axis during in-plane interactions at nematic–isotropic transition temperature (2OCAC at 471 K, 4OCAC at 460.5 K, and 6OCAC at 452 K).

is observed. It is evident from the figure that the maximum probability occurs at an equilibrium position.

Figure 6 shows the variation of probability with respect to rotation about x axis corresponding to configuration Y(0°). A pronounced peak exists at an equilibrium point for 6OCAC at nematic–isotropic transition temperature, and all the remaining regions have negligible probability as compared to this configuration. Thus, generally molecules may be assumed to be capable of free rotations where the molecules prefer being in the same plane. Further, it may observe that the rotational freedom is much more pronounced as compared to stacking interactions.

Having refined the interacting configuration with respect to rotation about x axis at equilibrium condition, the energy is brought down and the probability is further investigated with respect to rotation about y axis corresponding to configuration X(180°). It has been observed that rotation about y axis does not alter the configurational probability drastically.

Terminal Interactions

The end-to-end interactions are weakest but become important when the molecule possesses polar group at either or both ends or if there is a possibility

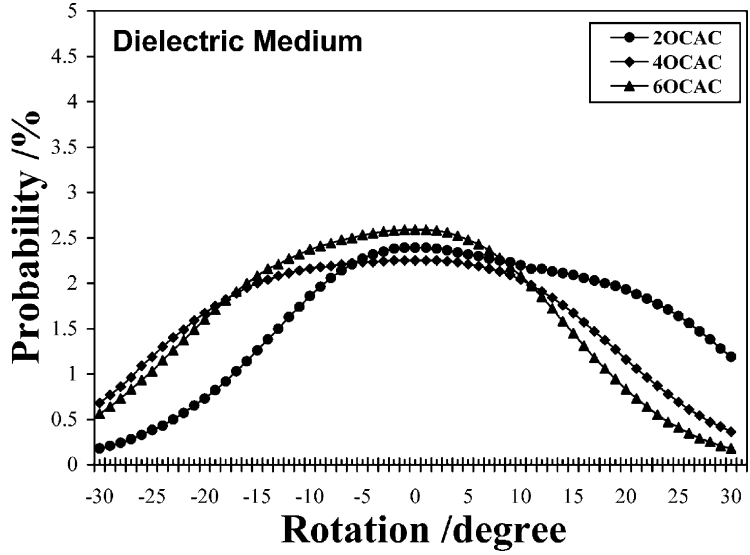

FIGURE 7 Variation of probability with respect to rotation about x axis during terminal interactions at nematic–isotropic transition temperature (2OCAC at 471 K, 4OCAC at 460.5 K, and 6OCAC at 452 K).

of hydrogen bonding. To investigate the terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the x axis by 22 Å. The terminal interactions are much weaker than the stacking and in-plane interactions. Rotations about the x axis (Figure 7) show no preference for any angle, i.e., the molecules are completely free to rotate about their long molecular axis.

Table II shows the relative probabilities of different minimum energy configurations calculated in vacuum and dielectric medium during the different modes of interactions. It may be observed that in dielectric medium the energies/probabilities are redistributed and there is considerable rise in the probabilities of interaction, although the order of preference remains the same. This provides theoretical support to the experimental observations [17]. Further, all possible geometrical arrangements between a molecular pair of 2OCAC, 4OCAC, and 6OCAC have been considered for stacking, in-plane, and terminal interactions. The most favorable stacked configuration of pairing has been obtained for 4OCAC, with 38.10% probability (see Table II) in dielectric medium at room temperature (300 K).

It is clear from the above discussion that in a molecular assembly a number of local minimum energy configurations exist. Each of them has its own importance; as in the case of closed molecular packing, any molecule,

TABLE II Relative Probabilities of Different Minimum Energy Configurations Obtained During Stacking, In-plane, and Terminal Interactions in Vacuum and in Dielectric Medium, Benzene

Configuration	Energy in vacuum kcal/mole	Energy in dielectric medium kcal/mole	Probability (%) at different temperature					
			300 K		471 K*		500 K	
			A	B	A	B	A	B
2OCAC								
X(0°)Y(0°)	–11.920	–5.298	40.58	35.99	38.02	33.82	37.73	33.09
Y(0°)Z(180°)	–11.862	–5.292	36.81	35.60	35.70	33.59	35.58	32.85
Y(0°)	–11.572	–5.143	22.60	27.71	26.19	28.65	26.56	29.45
Y(0°)	–5.584	–2.481	0.00	0.28	0.03	1.65	0.03	1.91
X(180°)	–5.947	–2.643	0.00	0.39	0.03	1.96	0.07	2.28
Y(0°)	–2.163	–0.961	0.00	0.00	0.00	0.30	0.00	0.39
			300 K		460.5 K*		500 K	
			A	B	A	B	A	B
4OCAC								
X(0°)Y(0°)	–12.786	–5.682	44.62	38.10	40.73	35.29	40.11	34.68
Y(0°)Z(180°)	–12.636	–5.616	34.67	34.10	34.54	32.82	34.45	32.43
Y(0°)	–12.329	–5.479	20.70	27.09	24.68	28.23	25.31	28.26
Y(0°)	–6.237	–2.772	0.00	0.26	0.00	1.44	0.04	1.83
X(180°)	–6.824	–3.032	0.00	0.41	0.00	1.94	0.08	2.39
Y(0°)	–2.769	–1.230	0.00	0.00	0.00	0.24	0.00	0.38
			300 K		460.5 K*		500 K	
			A	B	A	B	A	B
6OCAC								
X(0°)Y(0°)	–13.603	–6.045	43.19	37.56	39.88	34.68	39.26	34.71
Y(0°)Z(180°)	–13.211	–5.871	22.33	28.02	25.76	28.54	26.42	29.12
Y(0°)	–13.469	–5.986	34.47	33.99	34.34	32.46	34.27	32.69
Y(0°)	–6.956	–3.091	0.00	0.26	0.00	3.12	0.07	1.77
X(180°)	–6.460	–2.871	0.00	0.15	0.00	1.00	0.00	1.38
Y(0°)	–2.979	–1.324	0.00	0.00	0.00	0.17	0.00	0.31

*Nematic → isotropic transition temperature.
A, probability in vacuum; B, probability in dielectric medium.
Average dielectric constant of benzene = 2.25.

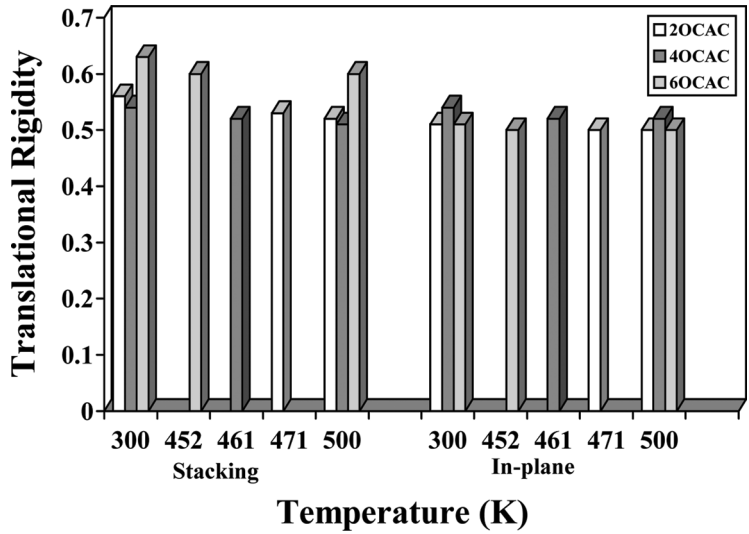

FIGURE 8 Translational rigidity of 2OCAC, 4OCAC, and 6OCAC molecules as a function of temperature during stacking and in-plane interactions. (See COLOR PLATE I)

depending on its own spatial position, may be forced to assume a local minimum energy configuration. The global minimum is, however, of paramount importance because while coming down from very high temperature where the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy and the others have a sequential preference depending on their individual relative probabilities.

CORRELATION OF THE RESULTS

The investigation of a physical parameter in homologous series of compounds is useful to understand the mesomorphic behavior of the system. The nematic character of liquid crystal is generally manifested by its translational freedom along the long molecular axis. Therefore, for stacking and in-plane interactions, translations have been allowed an interval of 0.2 Å and corresponding change in probabilities has been reported.

Figure 8 shows the translational rigidity[1] as a function of temperature during stacking and in-plane interactions. Evidently, the translational rigidity along the long molecular axis is 0.53 for 2OCAC at nematic–isotropic

[1]This has been defined as the ratio of probability being at maximum probable point having ±2 Å displacement along the long molecular axis.

transition temperature (471 K). However, at room temperature (300 K), the value is 0.56, indicating more binding at low temperature. With increase of temperature the molecules obtain sufficient freedom to slide along the long molecular axis. Similar to the case discussed above for 2OCAC, the gross nature of rigidity also remains unchanged for 4OCAC and 6OCAC molecules. Such translational freedom is much more pronounced in planar interactions. Thus, even at room temperature this value is 0.51 for 2OCAC, which reduced to 0.50 at nematic–isotropic transition temperature. It may be noted that although the freedom is considerable for smaller translation, longer translations are not permitted in general. Thus, small movements of molecules are only possible in the mesomorphic range. However, the comparable values in both the cases (i.e., stacking and in-plane interactions) show that the molecules 2OCAC, 4OCAC, and 6OCAC do not show extra-ordinary preference in forming the stacked layers, hence the nematic character is justified.

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