

Intermolecular energy calculations on 4'-nitrophenyl, 4-hexyloxybenzoate—a mesogenic compound

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Abstract. Intermolecular interaction energies between a pair of 4'-nitrophenyl, 4-hexyloxybenzoate (NPHB) molecules, have been calculated. CNDO/2 method has been employed to compute the net atomic charge and atomic dipole components at each atomic centre. A second order perturbation theory with multicentered-multipole approximation has been used to evaluate the energies corresponding to the stacked and in-plane lateral interactions between a pair of the molecules. An attempt has been made to discuss the results in the light of experimental evidences.

Keywords. Mesomorphism; intermolecular energy; stacking interaction; multicentered-multipole.

1. Introduction

Role of molecular forces and conformational properties on mesomorphic behaviour have attracted the attention of a large number of workers (Gray 1962; Chandrasekhar *et al* 1970; Photinos 1979; de Gennes 1975; Dong *et al* 1981; Tokita *et al* 1981; Berges and Perrin 1981; Perrin and Berges 1981, 1982). The successful application of quantum mechanical methods for discussion of the liquid crystalline behaviour of anisaldehydeazine (Sanyal *et al* 1984) and biphenyls (Sanyal *et al* 1985) encouraged us to examine the validity of these methods for other systems. 4'-nitrophenyl, 4-hexyloxybenzoate (NPHB) has been chosen from the homologous series of 4'-nitrophenyl, 4-*n*-alkoxybenzoates. In this series, homologues upto pentyloxy are pure nematogenic, except the first two members, while homologues after octyloxy are all pure smectogenic (Griffin *et al* 1978). Therefore, it is pertinent to study this model system as it shows both the smectic and nematic mesophases. During the heating cycle, NPHB shows crystal to nematic transition at 55°C and nematic to isotropic at 57.5°C, while in the cooling cycle nematic to smectic transition takes place at 40°C (Griffin *et al* 1978). The molecular geometry has been constructed on the basis of the published crystallographic data (Kaiser *et al* 1980). The CNDO/2 method (Pople and Beveridge 1970) has been employed to compute net atomic charge and dipole at each atomic centre. Using this quantum mechanical charge distribution and second order perturbation treatment with multicentered-multipole approximation (Rein 1978; Claverie 1978), the stacking as well as in-plane interaction energy values have been evaluated. In this paper, only the lowest energy configurations have been reported and used to discuss molecular ordering, mesomorphic behaviour and related parameters of NPHB molecules.

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2. Method

Second order perturbation theory as modified by Caillet and Claverie (1974, 1975) and Caillet *et al* (1976) for intermediate range interactions has been used to evaluate the intermolecular interaction energy between a pair of NPHB molecules. The total interaction energy (E_{TOT}) is expressed as

$$E_{TOT} = E_{EL} + E_{POL} + E_{DISP} + E_{REP}$$

where E_{EL} , E_{POL} , E_{DISP} and E_{REP} are electrostatic, polarization, dispersion and repulsion energy terms respectively. Electrostatic energy (Rein 1973) is again calculated upto dipole-dipole term as

$$E_{EL} = E_{QQ} + E_{QMI} + E_{MIMI}$$

where E_{QQ} , E_{QMI} and E_{MIMI} are monopole-monopole, monopole dipole and dipole-dipole interaction energy terms respectively. The details of the formalism may be found elsewhere (Sanyal *et al* 1984). Net atomic charges and dipoles have been computed by the CNDO/2 method (Pople and Beveridge 1970).

Minimum energy configuration between a pair of NPHB molecules has been obtained by varying the position of one molecule along the rectangular coordinate axes with a simultaneous rotation keeping the other fixed. The same process has been repeated after inversion of the molecule. Accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to the other has been achieved. The stacking and in-plane configurational interaction energies have been minimized separately.

All the computations have been carried out on a CDC 'Cyber' computer at TIFR, Bombay.

3. Results and discussion

The molecular geometry of the NPHB molecule is shown in figure 1 while the net charge and dipoles at each atomic centre are listed in table 1. The total dipole moment, its components and the binding energy of the molecule are given in table 2. The lowest energy configurations obtained for stacking and in-plane interactions have been shown in figures 2 and 3 respectively. The corresponding energies and various contributing terms are listed in table 3.

Figure 2 shows two molecules of NPHB which are stacked one above the other 4.20 Å apart with one molecule inverted in its plane and laterally displaced with respect to the

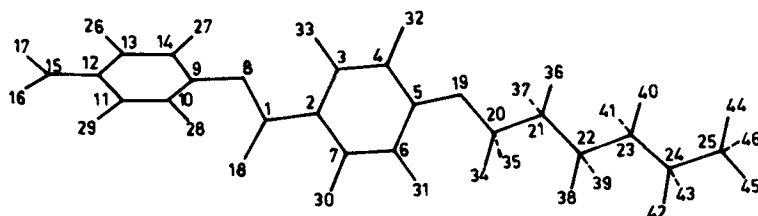


Figure 1. Molecular geometry of NPHB molecule with various atomic index numbers.

Table 1. Atomic charges and dipoles of NPHB molecule.

Atom	No.	Charge	Atomic dipole moments		
			X	Y	Z
C	1	0.400	-0.232	0.167	-0.002
C	2	-0.073	0.056	-0.023	-0.018
C	3	0.053	0.048	-0.131	-0.003
C	4	-0.063	-0.090	-0.162	-0.008
C	5	0.210	0.201	0.028	-0.006
C	6	-0.067	-0.068	0.154	0.004
C	7	0.056	0.083	0.124	0.000
O	8	-0.264	-0.809	-0.977	-0.030
C	9	0.203	0.162	-0.020	-0.008
C	10	-0.032	-0.102	0.117	-0.155
C	11	0.038	0.090	0.098	-0.183
C	12	0.022	-0.189	0.038	-0.012
C	13	0.039	0.033	-0.122	0.180
C	14	-0.038	-0.139	-0.070	0.142
N	15	0.467	-0.026	0.049	-0.054
O	16	-0.352	0.728	0.408	-1.123
O	17	-0.321	0.516	-0.641	1.145
O	18	-0.320	0.777	1.133	0.043
O	19	-0.226	-0.678	-1.140	0.202
C	20	0.153	-0.085	0.235	-0.036
C	21	-0.001	-0.055	-0.120	0.034
C	22	0.021	0.004	0.111	-0.045
C	23	0.019	-0.026	-0.076	0.042
C	24	0.024	0.040	0.083	-0.045
C	25	-0.007	-0.163	-0.030	0.033
H	26	0.025	0.000	0.000	0.000
H	27	0.019	0.000	0.000	0.000
H	28	0.023	0.000	0.000	0.000
H	29	0.028	0.000	0.000	0.000
H	30	0.003	0.000	0.000	0.000
H	31	0.008	0.000	0.000	0.000
H	32	0.014	0.000	0.000	0.000
H	33	-0.000	0.000	0.000	0.000
H	34	-0.016	0.000	0.000	0.000
H	35	-0.017	0.000	0.000	0.000
H	36	0.008	0.000	0.000	0.000
H	37	0.005	0.000	0.000	0.000
H	38	-0.007	0.000	0.000	0.000
H	39	-0.006	0.000	0.000	0.000
H	40	-0.007	0.000	0.000	0.000
H	41	-0.005	0.000	0.000	0.000
H	42	-0.008	0.000	0.000	0.000
H	43	-0.008	0.000	0.000	0.000
H	44	0.001	0.000	0.000	0.000
H	45	-0.003	0.000	0.000	0.000
H	46	0.001	0.000	0.000	0.000

Table 2. Dipole moment distribution, total^a and binding^b energy of NPHB molecule.

Components	X	Y	Z
Densities	3.64	-0.38	0.05
<i>sp</i> *	0.08	-0.77	0.10
<i>pd</i> *	0.00	0.00	0.00
Total	3.72	-1.15	0.15

Total energy = -255.095017 atomic unit.

Binding energy = -23.060098 atomic unit.

Total dipole moment = 3.89374 debyes.

^a Total energy corresponds to the sum of atomic as well as electronic energies of all the constituents of the molecule in the equilibrium geometry.

^b Binding energy of a molecule is the difference between the total energy of the equilibrium molecular geometry and the sum of the atomic energies of the constituent atoms.

* *sp* hybridization moment.

** *pd* hybridization moment.

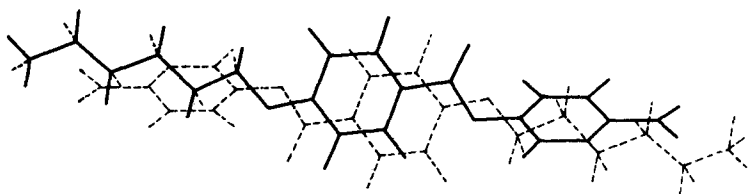
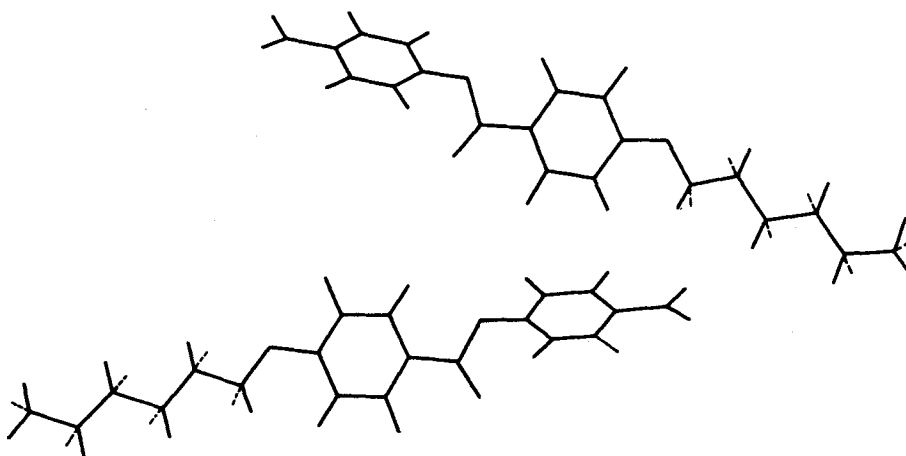
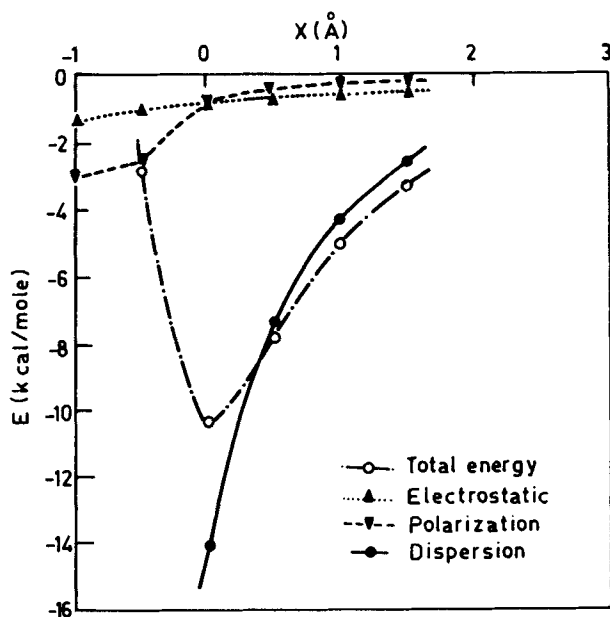
**Figure 2.** Lowest energy stacked complex of two antiparallel NPHB molecules having energy -12.25 kcal/mole and inter-planar separation of 4.20 Å.**Figure 3.** Lowest energy configuration of two NPHB molecules during in-plane interactions with energy -6.51 kcal/mole.

Table 3. Stacking and in-plane interaction energy values between a pair of NPHB molecules (energy in kcal/mole).

Energy terms	Stacking energy	In-plane energy
E_{QQ}	0.40	-0.59
E_{QMI}	0.00	-0.33
E_{MIMI}	-0.33	-0.24
$E_1 (= E_{QQ} + E_{QMI} + E_{MIMI})$	0.07	-1.16
E_{POL}	-0.75	-0.79
E_{DISP}	-19.96	-8.17
$E_2 (= E_{POL} + E_{DISP})$	-20.70	-8.96
E_{REP}	8.38	3.61
$E_{TOT} (= E_1 + E_2 + E_{REP})$	-12.25	-6.51

**Figure 4.** Variation of stacking energy values with intermolecular separation (X). Various components have been plotted corresponding to increasing (+ve) and decreasing (-ve) intermolecular separation with reference to equilibrium point (0) which corresponds to 4.50 Å.

other. The energy for this configuration is -12.25 kcal/mole which is mainly due to the dispersive forces (table 3). Figure 4 shows the variations of stacking energy values with respect to intermolecular separation. Since the stacked complex of NPHB molecules selects its minimum energy value at an intermolecular separation of 4.50 Å, this has been chosen as the reference point and the deviations have been marked as the positive and negative numbers. The positive sign stands for increasing intermolecular

separation from the reference point corresponding to minimum energy configuration while the negative sign represents the decreasing separation. It is clear that as the intermolecular separations are increased from the equilibrium value, polarization and electrostatic energies maintain more or less constant values but the contribution of these forces are very small. The total stacking energy curve shows that the energy decreases with inter-molecular separation upto the equilibrium position but on lowering the separation it suddenly increases and ultimately becomes repulsive. A deep and sharp minimum is obtained in the energy curve corresponding to the equilibrium position and the interaction energy for this position has been further recalculated using further refinement. A careful look at the dispersion energy curve suggests that as the overlapping of the molecules increases, the energy always decreases but beyond equilibrium, the repulsive energy which arises due to short range interactions becomes so high that it leads to an increase in the total energy. Hence, it may be inferred that the stacking interactions which play a major role in mesomorphic stability, are mainly due to dispersion forces. Figure 3 shows the in-plane lateral interaction energy configuration where one molecule has been rotated by 180° about its long axis and then translated along an axis perpendicular to the long molecular axis. This corresponds to the lowest energy configuration among all the possible in-plane lateral interaction energy configurations. The corresponding energy is -6.51 kcal/mole which is also mainly due to dispersion forces as observed in the stacking interactions. These configurations are in agreement with those obtained from crystallographic studies. Since NPHB molecules are associated with two highly polar groups ($O16 = -0.352e$ and $O17 = -0.321e$) at one end and a long alkoxychain at the other; terminal (end to end) attractions seem to be improbable due to the non-availability of any proton preventing the formation of any conventional bond. Hence, the present calculations have been restricted to stacking and in-plane interactions. It may be noted that the in-plane lateral energy corresponds to -6.51 kcal/mole which is comparable with the stacking energy (-12.25 kcal/mole) but is higher in comparison with those of other pure nematic liquid crystals (Sanyal *et al* 1984, 1985).

The interaction energy calculations for all the possible configurations show that in closed packed structures, dispersion forces play a key role in stabilizing both the stacking and in-plane lateral interactions as observed in several other cases (Mishra and Tyagi 1973; Baran and Les 1979).

4. Conclusion

It may be concluded, therefore, that inter-molecular interaction energy studies are helpful in understanding the role of molecular forces in accounting for the mesomorphism.

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