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Odd-Even Effects in Homologous Series of 4-Cyano-4'-Alkylbiphenyls (*n*CB): Role of Anisotropic Pair Potential

A quantum mechanical analysis has been carried out to determine the association energy of five homologous of 4-Cyano-4'-Alkylbiphenyls series with alkyl group: propyl (**3CB**); butyl (**4CB**); pentyl (**5CB**); hexyl (**6CB**); hepty (**7CB**) using Rayleigh-Schrodinger perturbation method for different nearest neighbour configurations of interacting pairs. The net atomic charges and dipoles have been computed using the **CNDO/2** method. The complete association energy with all its components has been reported. An attempt has been made to explain the odd-even effects at the molecular level on the basis of these results.

Keywords: mesogens, odd-even effects, pair potential, computer simulation

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Introduction

The majority of mesogenic molecules are composed of an aromatic core to which are attached one or two alkyl chains. The primary roles of the alkyl chain to enhance the liquid crystal range by lowering the melting point. The liquid crystal properties, such as the nematic-isotropic transition temperature and the entropy of transition, are also influenced by the presence of the alkyl chain (FERRARINI et al. 1995). Marcelja argued (MARCELJA, 1974) that the alkyl chains actually take an active part in the anisotropic interaction. He analysed the molecular interactions in terms of a two-component model taking ring part and alkyl chain part separately into consideration. He could not obtain a broad agreement with the trend of odd-even alternations in the nematic to isotropic transition in a homologous series by introducing some adhoc coupling parameters. He explained the reason of this effect as the addition of carbon atom C2 increases the anisotropy of the molecule and helps the ordering process; subsequent addition of C3 hinders the ordering, atom C4 help again, and so on. As the chains become longer, their flexibility makes the effect progressively smaller until, for long end chains, it becomes unnoticeable. These calculations have since been refined by Luckhurst (LUCKHURST, 1986) and used to make successful calculations for compounds having two rigid cyanobiphenyl moieties by flexible spacers.

The primary success of Marcelja and Luckhurst suggests that each component of the mesogenic molecules need individual attention. Also, the short-range interaction involved in molecular packing, should be analysed with a view to develop understanding of mesogenic behaviour. These interactions have been visualised as **(i)** stacking interactions between the planes, **(ii)** in-plane interactions in a layer, and **(iii)** end to end or terminal interactions. Earlier, relative contribution of various intermolecular forces to the interaction energy was

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analysed with respect to variation in intermolecular separation, orientation etc. (OJHA, 2000a; 2000b; 2000c; 2001a; 2001b; OJHA et al. 2000).

Now since it is possible to calculate the intermolecular association energy in detail on the basis of atom-atom potential, it seems important to analyse the energy contribution of molecular pairs of a homologous series with a view to understand the role of various components as well as mesogenic properties such as odd-even effect.

The present work deals with the computations on the five homologous of 4-cyano-4'-alkylbiphenyls series with alkyl group: propyl (**3CB**); butyl (**4CB**); pentyl (**5CB**); hexyl (**6CB**); heptyl (**7CB**). The series has typical liquid crystalline phase sequences depending on the chain length (KURIBAYASHI et al. 1999). Association energy of each homologous has been evaluated in case of stacking, in-plane and terminal interactions. Thus taking into account the anisotropic nature of interactions, including the polar effect if any, nearest neighbour packing energy of a homologue has been estimated. An attempt has been made to understand the odd-even effect at molecular level.

Computational Details

The molecular geometry has been constructed on the basis of published crystallographic data with standard values of bond lengths and bond angles (HAASE et al. 1983; VANI, 1983; HANEMANN et al. 1995; KURIBAYASHI et al. 1999). Net atomic charges and dipoles have been computed using the **CNDO/2** method (POPLE, 1970). Second order perturbation theory as modified for intermediate range interaction (CLAVERIE, 1978) has been used to evaluate the intermolecular interaction energy between pair of molecules. Total interaction energy (E_{total}) is expressed as:

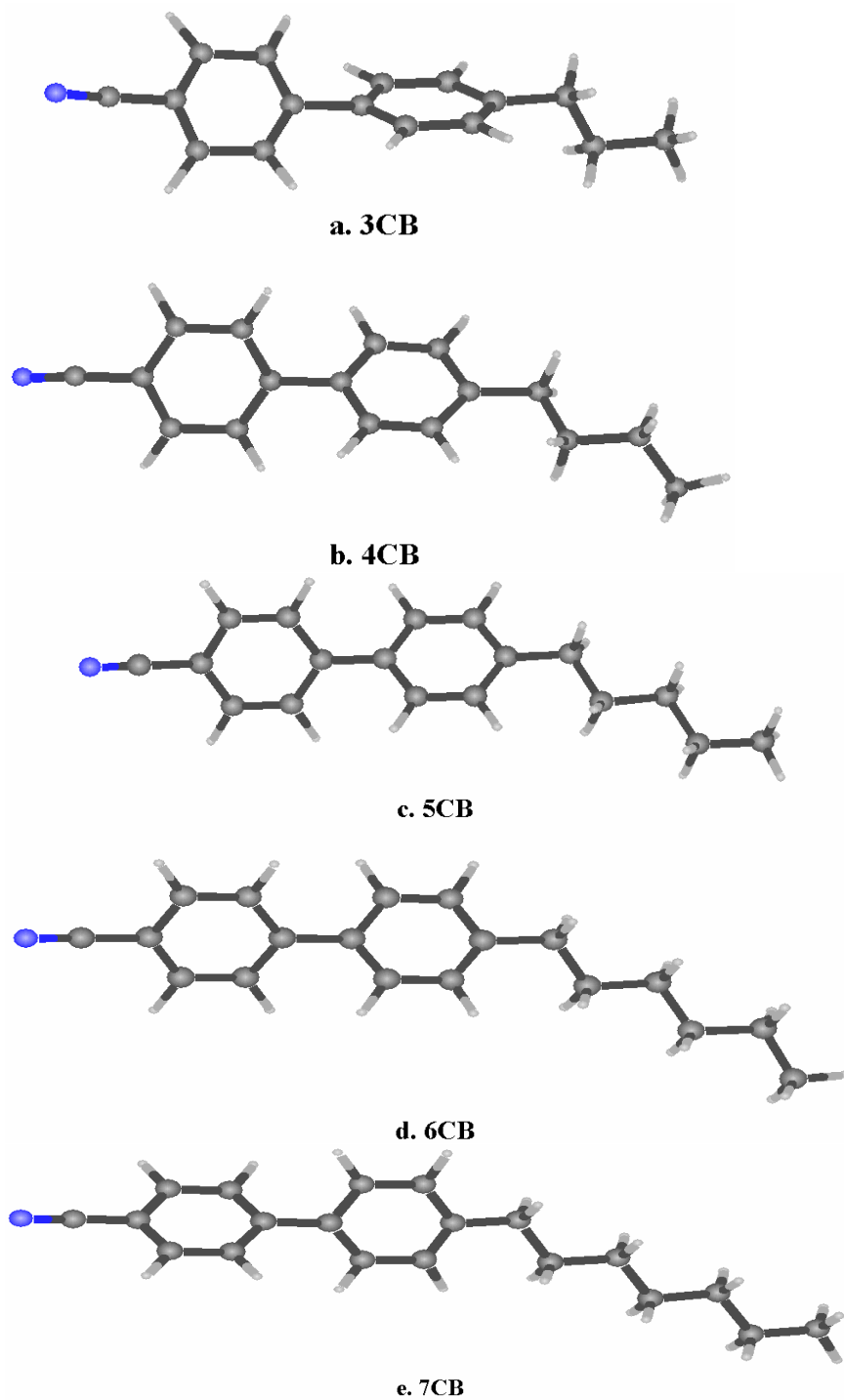
$$E_{\text{total}} = E_{\text{el}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{rep}}$$

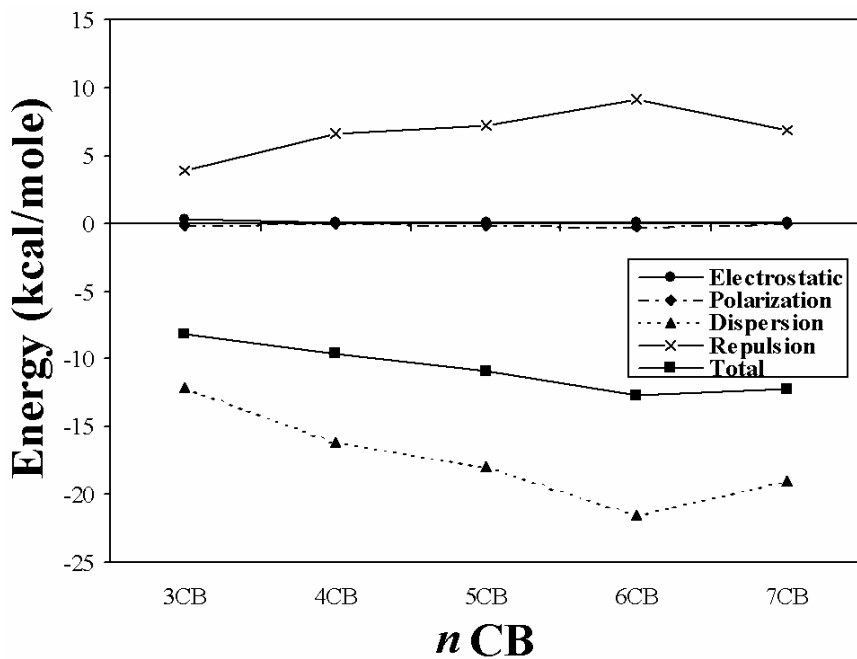
where E_{el} , E_{pol} , E_{disp} and E_{rep} are electrostatic, polarization, dispersion and repulsion energy terms respectively. Electrostatic energy is again calculated upto dipole-dipole term under multicentered-multipole expansion scheme as

$$E_{\text{el}} = E_{\text{QQ}} + E_{\text{QMI}} + E_{\text{MIMI}}$$

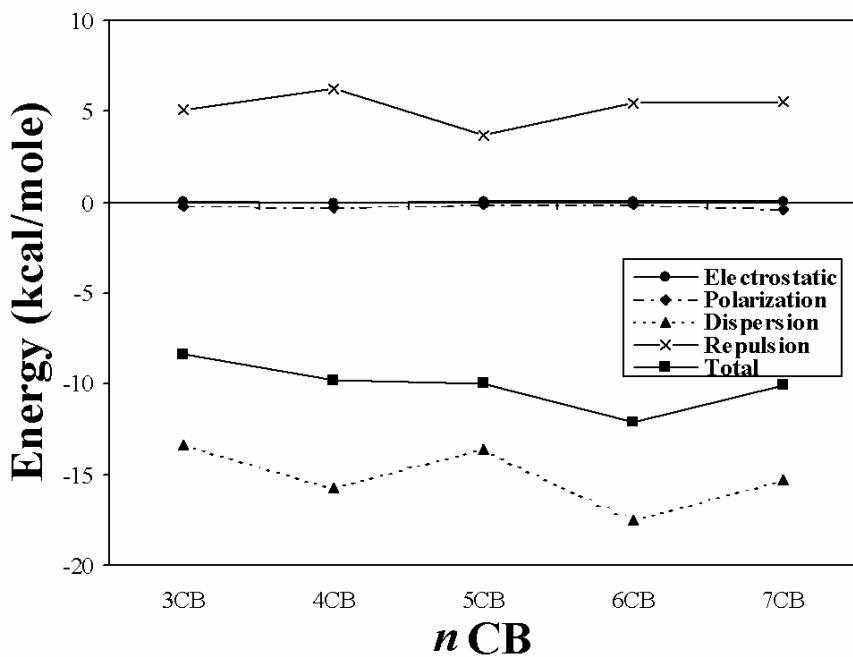
where E_{QQ} , E_{QMI} and E_{MIMI} are monopole-monopole, monopole-dipole and dipole-dipole interaction energy terms respectively. The details methodology is skipped and the values of charges and dipole moment are not being reported for the sake of brevity and to focus the attention mainly to analyse the odd-even effect. The details methodology may be found elsewhere (OJHA, 2001a).

In this case, the origin on an atom has been chosen close to the centre of mass of the molecule. The X-axis has been chosen along the long molecular axis, while the Y-axis lies in the plane of the molecule and Z-axis perpendicular to the molecular plane. The choice of distance has been made to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the short and medium range interactions. Keeping one molecule fixed and placing the other molecule on both sides during stacking, in-plane and terminal interactions have carried out computations. The association energy has been minimized with respect to translation and rotation of the interacting molecule about all the axes. An accuracy of 0.1Å in translation and 1° in rotation has been achieved.

Fig. 1: Molecular geometry of 4-cyano-4'-Alkylbiphenyls (*n*CB)



a)



b)

Fig. 2: a) Variation of stacking interaction energy components with homologue number through interaction face F_1 ; b) Variation of stacking interaction energy components with homologue number through interaction face F_2 .

Application of this method to a variety of molecules (SANYAL et al. 1986; TIWARI et al. 1991; ROYCHOUDHURY et al. 1996) has been established that it is capable of predicting the observed crystal structure in most of the cases. Also, since all possible configurations are scanned, the relative probabilities of observed configurations provide a tool for understanding the molecular tendency of alignment, layer formation and extent of freedom corresponding to rotation, translation etc.

Results and Discussion

The molecular geometry of *n*CB is shown in Figure 1. The calculated total energy, binding energy and total dipole moment are listed in Table 1. As evident from Table 1 that the total energy, binding energy and total dipole moment do not show any alternation with homologue number. This also reveals that the odd-even effect is not the characteristic of electronic structure of the molecule. The results of intermolecular interaction energy calculations are discussed below:

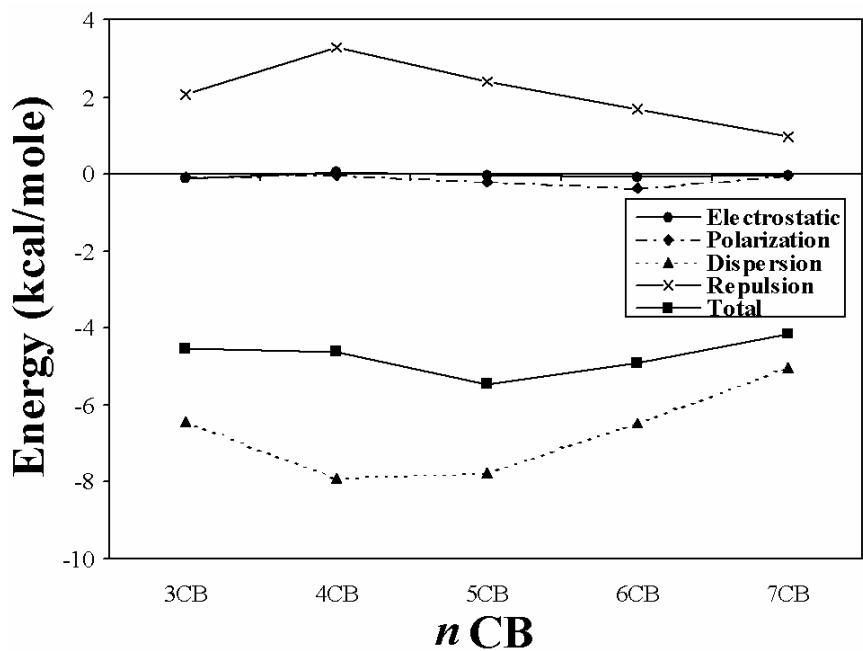
(A) Stacking Interactions

The variation of stacking interactions energy components through face F_1 (i.e. one of the molecules is fixed in X-Y plane while the second has been kept at an intermediate distance along the +Z-axis with respect to fixed molecule) and face F_2 (i.e. one of the molecule is fixed in X-Y plane while the second has been kept at an intermediate distance along the -Z-axis with respect to fixed molecule) with homologue number is shown in Figure 2a and Figure 2b respectively. An observation of Figure reveals that the dominant component of total energy is the dispersion energy. The contribution of electrostatic and polarization energy is negligible. Since stacking side A covers all the components i.e. the cyanogroup, biphenyl and the alkyl group, the total energy is almost constant with homologue number which suggests that there is no role of long alkyl chain in the stacking interaction of face F_1 . Therefore, no odd-even effect has been observed in Figure 2a.

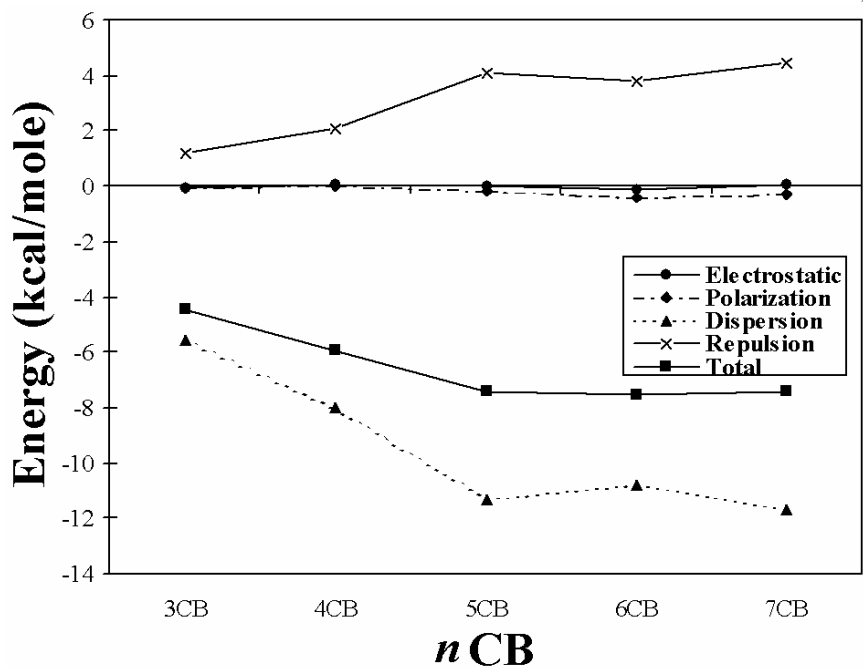
In the stacking interactions through face F_2 , the role of alkyl chain is well distinct (Figure 2b). As the chain is elongated from 4-5, 6-7 the intermolecular separation increases, since even alkyl terminal lies off the molecular axis. The extension of alkyl chain from 3-4, 5-6 increases one bond parallel to the molecular axis. So in each such case interaction energy decreases due to increase of number of atoms at the same intermolecular separation. Further, it is evident that major role in odd-even effect is exhibited by dispersion energy and repulsion energy. The odd-even effect in total energy is the cumulative effect of repulsion as well as dispersion energy. The electrostatic energy and polarization energy have almost no contribution. They slightly increase with increase in the homologue number and become almost constant for longer chain.

(B) In-plane Interactions

The variation of in-plane interactions energy components through side S_1 (i.e. one of the molecules is fixed in X-Y plane while the second has been kept an intermediate distance along +Y-axis with respect to fixed molecule) and side S_2 (i.e. one of the molecules is fixed in X-Y plane while the second has been kept an intermediate distance along -Y-axis with respect to fixed molecule) with homologue number is shown in Figure 3a and Figure 3b.



a)



b)

Fig. 3: a) Variation of in-plane interaction energy components with homologue number through interaction side S_1 ; b) Variation of in-plane interaction energy components with homologue number through interaction side S_2 .

Table 1: Total energy, Binding energy and Total dipole moment of the homologues of *n*CB molecule

Molecule	Total Energy* (a.m.u.)	Binding Energy** (a.m.u.)	Total Dipole Moment (Debyes)
4-cyano-4'-propylbiphenyl (3CB)	-136.53	-17.24	2.41
4-cyano-4'-butylbiphenyl (4CB)	-145.31	-18.57	2.57
4-cyano-4'-pentylbiphenyl (5CB)	-154.03	-19.85	2.58
4-cyano-4'-hexylbiphenyl (6CB)	-162.72	-21.09	2.65
4-cyano-4'-heptylbiphenyl (7CB)	-171.42	-22.35	2.64

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

**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

It is clear from this figure that repulsion energy shows a slight alternation with homologue number, but the dispersion energy shows a compensatory effect. Since the dispersion energy has major contribution in the total energy, the total energy does not show alternation with homologue number.

(C) Terminal Interactions

The variation of terminal interaction energy and its various components has also been studied through end E_1 (i.e. one of the molecules is fixed in X-Y-plane while the second has been kept at an intermediate distance along +X-axis with respect to fixed molecule) and end E_2 (i.e. one of the molecules is fixed in X-Y-plane while the second has been kept at an intermediate distance along -X-axis with respect to fixed molecule). It has been observed that interaction energy is almost constant with homologue number. Since the molecules have bent structure, the terminal interaction energy decreases with increase in homologue number from 5 onwards. A minor alternation of interaction energy between homologue numbers 3 to 5 is due to less pronounced bent structure. Here also the major contribution in total energy comes from the dispersion energy while the repulsion energy shows compensatory effect.

Figure 4 shows the variation of total interaction energy, total stacking, in-plane, terminal and layer (in-plane + terminal) interaction energy with homologue number. It is clear from figure that in-plane interaction is almost constant with increase in homologue number. The total terminal interaction energy increases in homologue number 3 to 4 then decreases with increase in homologue number. At 7th homologue lowering of the terminal interaction energy than the stacking interaction energy are partially due to dimer energy and also due to the increased interaction between the alkyl chains.

The variation of total stacking interactions (face F_1 + face F_2) with homologue number shows distinct odd-even effect. The amplitude of alternation in interaction energy decreases with increase in the homologue number. The total energy reported here corresponds to the association energy with the first neighbour at all sides. This refers only to a local ordering energy. The total energy computed by including next neighbours would probably provide an estimate for vaporizing energy. As we are interested mainly in the breaking of local crystal packing, only the nearest neighbour has been taken into account.

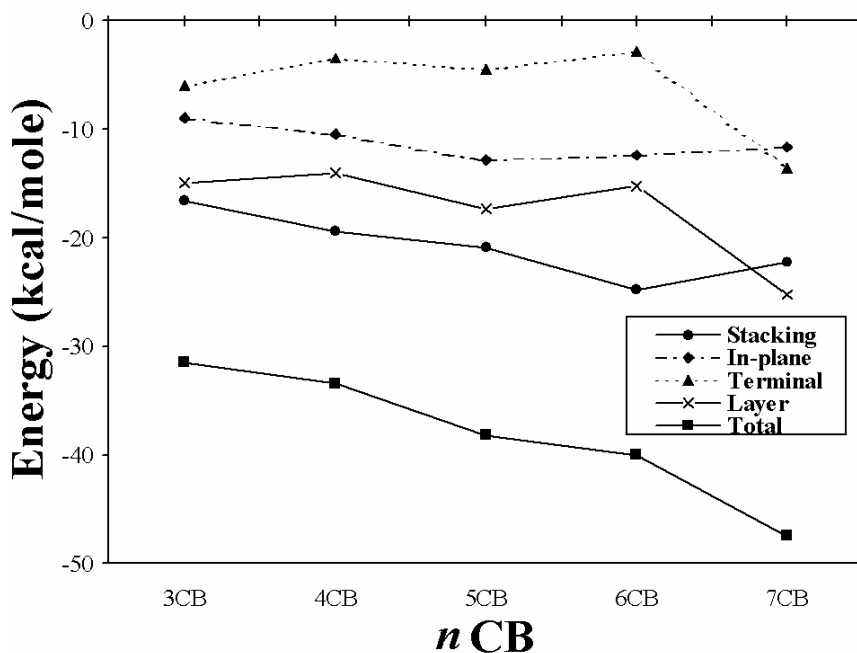


Fig. 4: Variation of energies with homologue number

Conclusion

It may, therefore, be concluded that some well-known effects related to mesogens such as odd-even effect may be addressed by applying these methods.

Acknowledgements

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