Odd-even Effect in a Homologous Series of 4-*n*-Alkylbenzoic Acids: Role of Anisotropic Pair Potential

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A computational analysis based on quantum mechanics has been carried out to determine the association energy of seven homologues of the 4-*n*-alkylbenzoic acid series ($n = 3$, 4, 5, 6, 7, 8, and 9), using the Rayleigh-Schrödinger perturbation method for various nearest neighbour configurations of interacting pairs. The net atomic charges and dipoles have been computed using the **CNDO/2** method. An attempt is made to explain the odd-even effects at the molecular level on the basis of these results.

Key words: Mesogens, Odd-even Effects, Pair Potential, Computer Simulation.

Introduction

Mesogens or liquid crystals are important due to their many applications [1]. The majority of mesogenic molecules are composed of an aromatic core, to which one or two alkyl chains are attached. The primary role of the alkyl chain is to widen the liquid crystal range. 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 [2]. Marcelja [3] analysed the molecular interactions in terms of a two-component model taking the ring part and the alkyl chain part separately into consideration. He did not reach a broad agreement with the trend of odd-even alternations in the nematic to isotropic transitions of a homologous series, however his calculations have since been refined by Luckhurst [4] and used to make successful calculations for compounds having two rigid cyanobiphenyl moieties.

The initial success of Marcelja and Luckhurst suggests that each component of a mesogenic molecule needs individual attention. Also, the short-range interaction involved in the molecular packing should be analysed in order to understand the mesogenic behaviour. These interactions can be classified as (**i**) stacking interactions between the planes, (**ii**) in-plane interactions in a layer, and (**iii**) end to end or terminal interactions. The contribution of various intermolecular forces to the interaction energy was analysed in [5 – 10].

Since it is possible to calculate the intermolecular association energy in detail on the basis of atom-atom potentials, it seems inportant to analyse the energy contributions of molecular pairs of a homologous series in order view to understand the odd-even effect.

The present work deals with computations on the odd-even effect in a series of seven homologues of 4-*n* alkylbenzoic acid ($n = 3$, 4, 5, 6, 7, 8, and 9). The association energy of each pair of homologues has been evaluated in for stacking, in-plane and terminal interactions. An attempt has been made to understand the odd-even effect.

Methodology

The molecular geometry of ***n*BA** has been constructed on the basis of published crystallographic data with standard values of bond lengths and bond angles [11]. Net atomic charges and dipoles have been computed using the **CNDO/2** method [12]. Second order perturbation theory, as modified for intermediate range interaction [13], has been used to evaluate the intermolecular interaction energy of pairs of molecules. The 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. The electrostatic energy was calculated upto the dipole-dipole term under the multicentered-multipole expansion scheme as

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

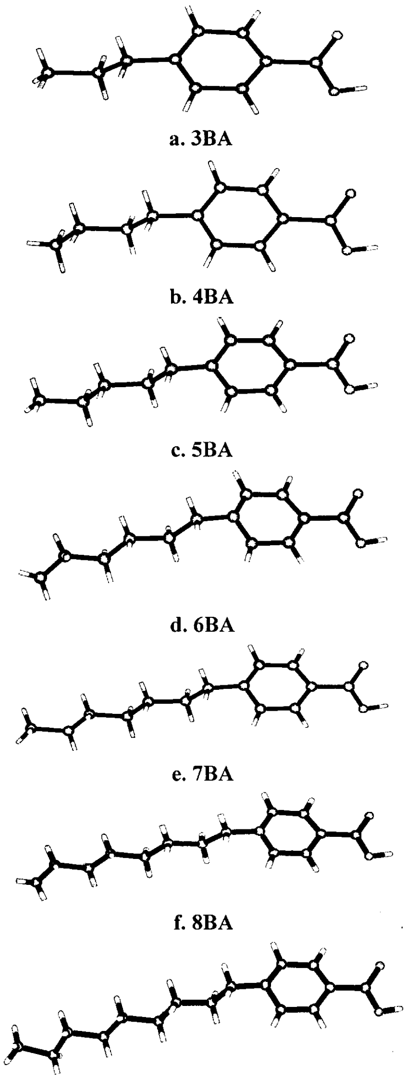
where E_{QQ}, E_{QMI}, and E_{MIMI} are the monopole-monopole, monopole-dipole and dipole-dipole interaction energy, respectively. The charges and dipole moments are not reported for brevity, and to focus the attention mainly to analyse the odd-even effect. Details of the method may be found in [8].

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

Application of this method to a variety of molecules [14–16] has established that the observed crystal structure can be obtained in most of the cases. Also, since all possible configurations are scanned, the relative probabilities of the observed configurations provide an understanding of the tendencies for alignment, layer formation, freedom of rotation, translation, etc.

Results and Discussion

The molecular geometry of ***n*BA** ($3 \leq n \leq 9$) 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, the total energy, binding energy, and total dipole moment do not change with the number of the homologue. This reveals that the odd-even effect is not characteristic for the electronic structure of the molecule.



a. 3BA

b. 4BA

c. 5BA

d. 6BA

e. 7BA

f. 8BA

g. 9BA

Fig. 1. Geometry of seven 4-*n*-Alkylbenzoic Acid **(*n*BA)** molecules.

A. Stacking Interactions

The variation of the stacking-interaction-energy-components through the face F_1 (i.e. one molecule is fixed in the *X*-*Y* plane while the other one is kept at an intermediate distance from the fixed one along the +*Z*-axis and the face F_2 (i.e. one molecule is fixed in the *X*-*Y* plane while the other one is kept at an intermediate distance from the fixed one along the –*Z*-axis) with the number of the homologue is shown in Figs. 2a and 2b, respectively. The Figures reveal that the dominant component of the total energy is the dispersion energy. The contributions of the electrostatic and polarization energy are negligible. In the stacking through face F_1 the role of the alkyl chain is distinct (Fig. 2a). As the chain is elongated from 3 to 4 and 7 to 8, the intermolecular separation increases, since the even alkyl terminal lies off the molecular axis. The extension of the alkyl chain from 4 to 5 and 6 to 7 elongates one bond parallel to the molecular axis. So in each such case the interaction

Table 1. Total energy*, binding energy**, and total dipole moment of the homologues of ***n*BA**.

Molecule	Total Energy (a.m.u.)	Binding Energy (a.m.u.)	Total Dipole Moment (Debyes)
4-*n*-propylbenzoic acid **(3BA)**	−116.845	−11.366	1.088
4-*n*-butylbenzoic acid **(4BA)**	−125.517	−12.596	1.123
4-*n*-pentylbenzoic acid **(5BA)**	−134.157	−13.793	1.114
4-*n*-hexylbenzoic acid **(6BA)**	−142.812	−15.006	1.087
4-*n*-heptylbenzoic acid **(7BA)**	−151.440	−16.192	1.107
4-*n*-octylbenzoic acid **(8BA)**	−160.126	−18.637	1.139
4-*n*-nonylbenzoic acid **(9BA)**	−168.770	−18.637	1.139

* The total energy corresponds to the sum of atomic as well as electronic energies of all the constitutions of the molecule in the equilibrium geometry.

** The 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.

energy decreases due to the increase of the number of atoms at the same intermolecular separation. Further, it is evident that the major role in the slight odd-even effect is played by the dispersion and repulsion energy. The odd-even effect in the total energy is due to both the repulsion and dispersion energy. The electrostatic and polarization energy do almost not contribute. They slightly increase with increasing number of the homologue and become almost constant for longer chains.

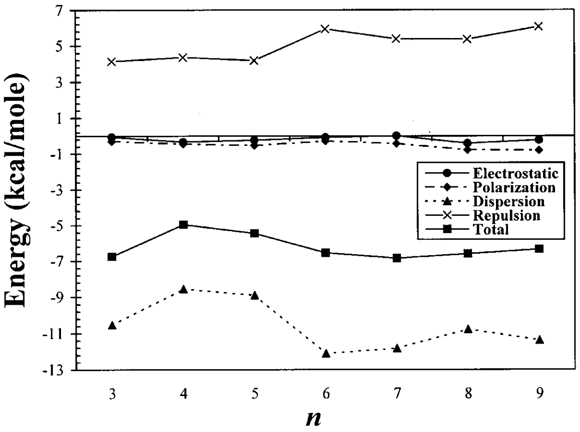


Fig. 2a. Variation of the energy components of the stacking interaction through the F_1 with the number *n* of the homologue.

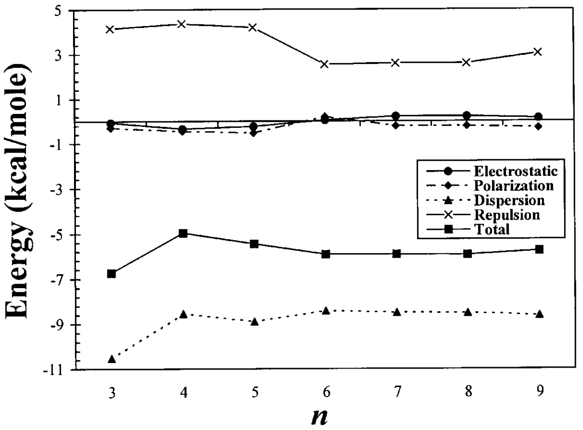


Fig. 2b. Variation of the energy components of the stacking interaction through the F_2 with the number *n* of the homologue.

In the stacking interactions through face F_2 cover all the components, i.e. the COOH group, benzene ring and alkyl group. The total energy is almost independent of the number of the homologue, which suggests that the length of the alkyl chain plays no role in the stacking interaction of face F_1. Therefore, no odd-even effect occurs in Figure 2b.

B. In-plane Interactions

The variation of the in-plane-interaction-energy-components through the side S_1 (i.e. one molecule is fixed in the *X*-*Y* plane while the other one is kept at an intermediate distance from the fixed one along the +*Y*-axis) and the side S_2 (i.e. one molecule is fixed in the *X*-*Y* plane while the other one is kept at an intermediate distance from the fixed one along the –*Y*-axis) with the number of the homologue is shown in Figs. 3a and 3b respectively. It is clear from Fig. 3a that the repulsion energy shows a slight alternation with the number of the homologue, but this is partly compensated by the dispersion energy. Since the dispersion energy contributes to the total energy, the total energy does not show an alternation with the number of the homologue through side S_1. However, for side S_2 situation is quite different, and the role of the alkyl chain is distinct. Therefore a slight odd-even effect is observed in Figure 3b.

C. Terminal Interactions

The variation of the terminal interaction energy and its various components through the end E_1 (i.e. one

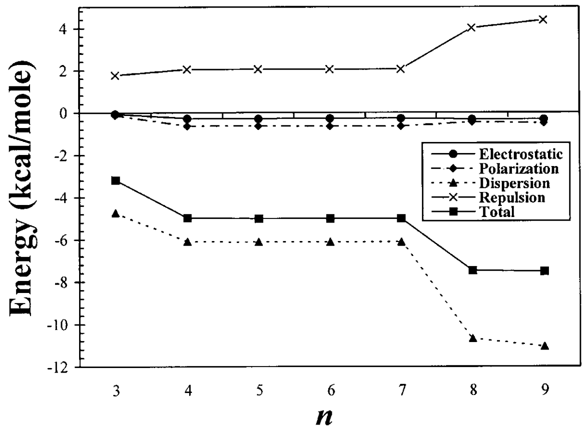


Fig. 3a. Variation of in-plane interaction energy components through the interaction side S_1 with the number *n* of the homologue.

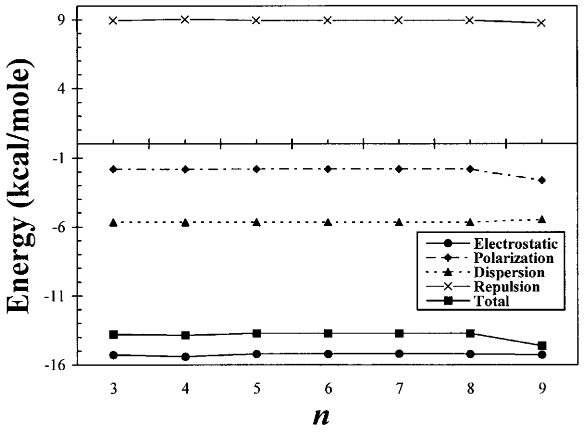


Fig. 4a. Variation of terminal interaction energy components through the interaction end E_1 with the number *n* of the homologue.

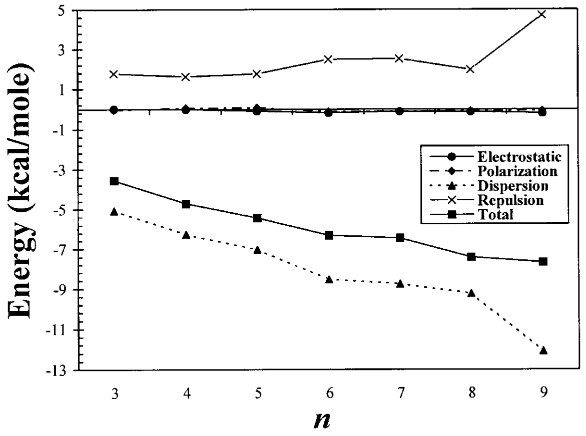


Fig. 3b. Variation of in-plane interaction energy components through the interaction side S_2 with the number *n* of the homologue.

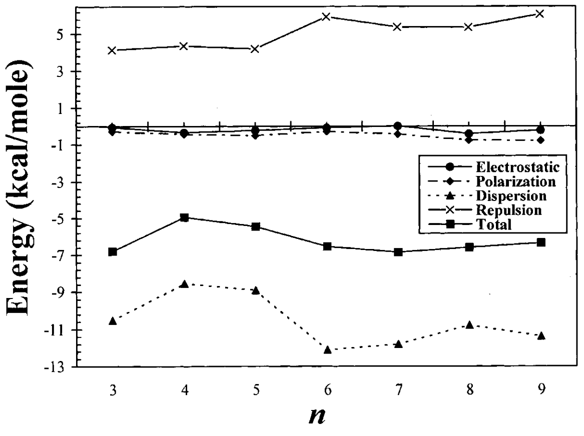


Fig. 4b. Variation of terminal interaction energy components through the interaction end E_2 with the number *n* of the homologue.

molecule is fixed in the *X*-*Y*-plane while the other one is kept at an intermediate distance from the fixed one along the +*X*-axis) and the end E_2 (i.e. one molecule is fixed in the *X*-*Y*-plane while the other one is kept at an intermediate distance from the fixed one along the –*X*-axis) is shown in Figs. 4a and 4b, respectively. The interaction through end E_1 shows the tendency of forming a dimer with double hydrogen bonding. It is also evident from Fig. 4a that the interaction energy is almost independent of the homologue number. Here the major contribution to the total energy comes from the electrostatic energy, which shows that the molecules have a strong tendency to form hydrogen bonding.

In the terminal interaction through the end E_2, the alkyl chains interact. Since the molecules are bent, the terminal interaction energy decreases for $n > 4$. A minor alternation of the interaction energy between the homologues 5 to 7 is due to the less pronounced bent structure. Here also the major contribution to the total energy comes from the dispersion energy, while the repulsion energy shows a compensatory effect.

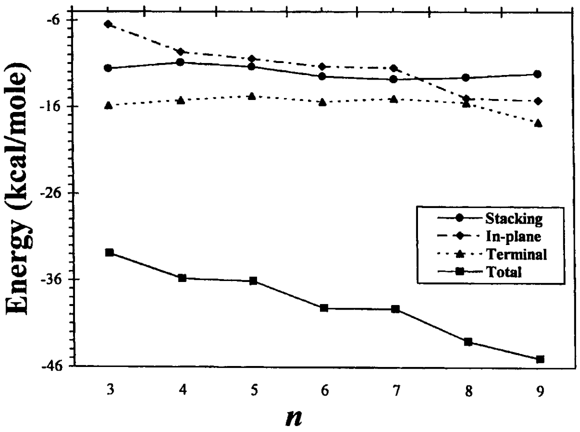


Fig. 5. Variation of the energies with the number *n* of the homologue.

In the Fig. 5 the energies of the three modes of interaction (total stacking; total in-plane, and total terminal) and their sum are shown as function of *n*. Evidently the in-plane interaction is almost independent of *n*. The total terminal interaction energy increases in homologous number 3 to 5 and then decreases with increase of the homologous number. At the 9th homologous, the lowering of the terminal interaction energy below the stacking interaction energy is partially due to the dimer energy and also due to the increased interaction between the alkyl chains.

The variation of the total interaction energy with *n* shows a distinct odd-even effect (see Fig. 5), the amplitude of the alternation decreasing withe increasing *n*. The total energy reported here corresponds to the association energy with the first neighbour. The total energy, computed by including next neighbours, would probably provide an estimate for the vaporizing energy. As we are interested mainly in the breaking of local crystal packing, only the nearest neighbour has been taken into account.

Conclusion

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

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