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 important 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 nBA 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 ($E_{\text{total}}$) is expressed as

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

where $E_{\text{el}}$, $E_{\text{pol}}$, $E_{\text{disp}}$, and $E_{\text{rep}}$ are electrostatic, polarization, dispersion and repulsion energy terms, respectively. The electrostatic energy was calculated up to the dipole-dipole term under the multiconfigured-multipoles expansion scheme as

$$E_{\text{el}} = E_{\text{QQ}} + E_{\text{QMI}} + E_{\text{MIMi}}.$$
where $E_{QQ}$, $E_{QM}$, and $E_{MM}$ are the monopole-mono-
pole, monopole-dipole and dipole-dipole interaction en-
ergy, respectively. The charges and dipole moments are
not reported for brevity, and to focus the attention main-
lly 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 dis-
tance has been chosen to eliminate van der Waals con-
tacts completely and to keep the molecule within the
range of short and medium interactions. In the computa-
tions, one molecule was fixed and the other one was
placed on both sides during stacking, in-plane and ter-
minal 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 struc-
ture can be obtained in most of the cases. Also, since all
possible configurations are scanned, the relative prob-
abilities 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 $n\text{BA}$ ($3 \leq n \leq 9$) 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 mole-
cule.

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 com-
ponent 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
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.

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

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

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

* The total energy corresponds to the sum of atomic as well as electronic energies of all the constituents 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.

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![Fig. 2a](image_url) Fig. 2a. Variation of the energy components of the stacking interaction through the $F_1$ with the number $n$ of the homologue.

![Fig. 2b](image_url) 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.
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 E₂ (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 E₁ 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 E₂, 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.
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 with 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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