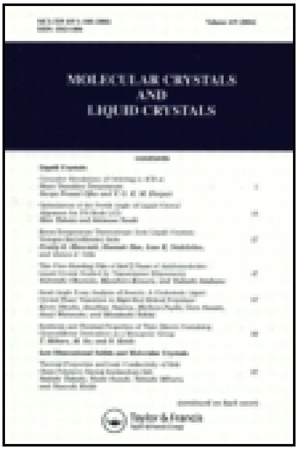

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Quantum Modeling of Geometric Electronic Structures of Some Mesogenic Systems

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To cite this article: Wacław Witko & Renata Tokarz-Sobieraj (2008): Quantum Modeling of Geometric Electronic Structures of Some Mesogenic Systems, Molecular Crystals and Liquid Crystals, 480:1, 219-228

To link to this article: http://dx.doi.org/10.1080/15421400701826605

Mol. Cryst. Liq. Cryst., Vol. 480, pp. 219–228, 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701826605

Quantum Modeling of Geometric and Electronic Structures of Some Mesogenic Systems

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Standard Density Functional Theory calculations for two mesogenic species (phenylbenzoate derivatives with the terminal and lateral –CN group) are performed in order to study the interaction between two molecules of each derivative. Two steps investigations are done: for isolated molecules and for pair of molecules for each of derivatives. Results of calculations (involving geometry optimization), which are carried out for isolated species, indicate the similar geometries (except –CN groups position) although different electronic structures of molecules of both derivatives. Examination of the interaction energy of molecule pairs allows one to get their mutual orientation. It is found that for two parallel molecules with terminal –CN group the interaction energy reaches minimum when they are shifted mutually ca. *0.32 nm. On contrary, for two molecules with lateral –CN group the energy minimum is obtained such a mutual geometry in which atoms of both species can be projected to each other; the molecules do not show tendency to shift. This may serve as indication for existing nematic and smectic A phases, which are observed macroscopically for phenylbenzoate derivatives with terminal and lateral –CN groups, respectively.*

Keywords: conformational analysis; DFT calculations; phenyl benzoate derivatives

1. INTRODUCTION

Macroscopic properties and polymorphism of mesogenic compounds are strongly influenced by molecular electronic and geometric structures.

This work was supported in part by Polish Ministry of Science and Informatization as the research grant No 1 P03B 060 28.

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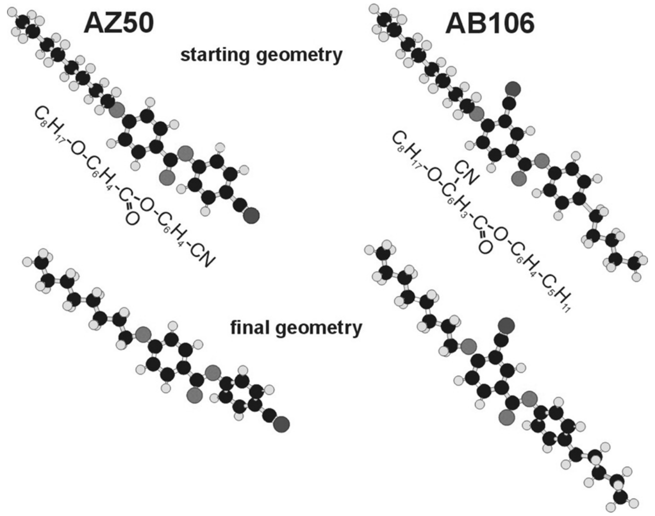

FIGURE 1 Starting geometric structures and final optimized structures of studied AZ50 and AB106 molecules.

Unfortunately it is impossible to predict their molecular properties directly from the chemical formula even analyzing many of them (currently more than 90,000 mesogenic compounds are known [1]). Therefore, it seems interesting to use quantum chemical approach to understand the molecular properties of these species and to indicate their macroscopic consequences. Such an approach was until recently almost impossible, but the rapid development of computers made the calculations feasible.

There are many different approaches possible basing on quantum, atomistic, coarse-grained or continuum modeling as was reviewed by Wilson [2]. Recently we published the results of calculations on molecular orbitals level for some cyanobiphenyl derivatives [3]. Basing upon these calculations we discussed the optimal molecular conformations, bond orders and lengths, electrostatic potentials as well as molecular interactions.

Present article focuses on two phenylbenzoates with −CN group substituent; abbreviated as AZ50 and AB106 (see Fig. 1), which are chosen for analysis from quantum chemical point of view. These two compounds, which have identical molecular cores (two phenyl rings bridged by carboxyl group and one terminal octyloxy chain) and differ by the position of cyano group (terminal in AZ50, lateral in AB106) and the additional pentyl chain in AB106, have completely different macroscopic properties, namely AZ50 forms nematic phase whereas AB106 smectic A phase. Using the results of calculations done for pair of isolated molecules the prediction of the influence of molecular properties on the macroscopic properties is provided.

In our recent calculations [4] different conformations of both above mentioned molecules were examined. Two steps optimization were done for each isolated molecule. First, different groups of atoms (for example C_6H_4 phenyl ring) were defined in each molecule and positions of these groups with respect to each other were calculated. By such an optimization the preferable conformations, with different mutual orientations of rings, chains, and carboxyl group were found. As a next step, for the selected conformations, which were energetically preferable, full optimization procedure, was performed where all atoms of molecule were allowed to move leading to final geometry of each species, which is characterized by the lowest energy. The systematic studies of all various conformations showed the energy differences for particular conformations and illustrated the changes in electronic structure of studied molecules.

2. COMPUTATIONAL DETAILS

The molecules taken into account (see Fig. 1a) are built of two phenyl rings linked together *via* carboxyl $-C(=O)-O$ group. In the first (abbreviated as AZ50) one ring is terminated by $O-C_8H_{17}$ alkoxy chain, whereas the second ring is terminated with cyano group $-CN$ (both terminal groups are in *para* position). The second species (of AB106 acronym) has the same central moiety with two chains attached to it. At first phenyl ring there is the same $-O-C_8H_{17}$ alkoxy chain, whereas the second ring is connected directly to shorter $-C_5H_{11}$ alkyl chain; the cyano $-CN$ group is substituted in *ortho* position of the phenyl ring linked with alkoxy chain.

The electronic and geometric structures of studied AZ50, AB106 molecules are calculated by means of the DFT framework [5,6], implemented in the StoBe code [7]. All electrons are described by a Gaussian basis set (CGTO) of double-zeta quality with polarization functions [8–10]. Calculations are performed within the Local Density Approximation using the Vosko-Wilk-Nusair (VWN) correlation functional [11], which was proven to be successful in describing the structural ground-state properties of different molecules and sufficiently accurate for geometry optimizations in various systems [12–14]. Geometry optimization is carried out according to the Broyden-Fletcher-Goldfarb-Shanno algorithm [15] with the energy gradient threshold of 10^{-4} Hartree/Å.

Basing upon optimal geometry of each molecule that was obtained in paper [4] a systematic examination of interactions of two isolated molecules of the same kind (i.e., either two AZ50 or two AB106) is carried out. First, the equilibrium distance between two molecules is found, and then the possibility of mutual translation of molecules is checked.

The geometric structure of the given molecule is determined by a set of bond lengths and torsional angles. In addition, Mayer bond orders indices [16], contours characterizing HOMO and LUMO orbitals as well as maps of electrostatic potential are analyzed to describe electronic properties of studied mesogenic molecules.

3. RESULTS AND DISCUSSION

3.1. Isolated Molecules

Systematic studies on the rotation of rings with respect one to another and on the rotation of terminal chains with respect to the attached rings, lead to final geometrical structures presented in Figure 1(b) that are similar for AZ50 and AB106 molecules.

In both molecules hydrocarbon chain always prefers the position, where its frame is located in plane of an adjacent ring. In AZ50 molecule the least stable conformation (higher in energy *ca.* 5.6 kcal/mole) is the starting one; rotation of the terminal chain by 45, 135, 225, 315 degrees results in the less stable geometries (higher of about 4.4 kcal/mole) with respect to "final" structure. In analogy, in AB106 molecule the differences in conformation energies are also about 4.3 kcal/mole (for different rotation angles mentioned above) and 5.6 kcal/mole for starting geometry. Rotation of shorter $-C_5H_{11}$ chain leads to the energy changes in the range of 0.25–0.77 kcal/mole.

For both AZ50 and AB106 molecules having energetically favorable geometries the plane of carboxyl group coincides with the plane of phenyl ring that is close to long $-C_8H_{17}$ chain. Location of $-C(=O)-O$ group plane perpendicular to phenyl ring increases the energies *ca.* 10 kcal/mole.

The phenyl ring connected to cyano group (in the case of AZ50 molecule) or attached to $-C_5H_{11}$ chain (in the case of AB106 molecule) prefers to be tilted with respect to another one by *ca.* 38 degrees. In the AZ50 molecule the energy gain is 3.0 kcal/mole compared to geometry with the parallel phenyl rings or 1.4 kcal/mole with regard to geometry where both phenyls rings are perpendicular. For the AB106 molecule the energy difference between conformations with perpendicular rings and tilted rings is smaller (0.6 kcal/mole) however between tilted and parallel equals to 2.9 kcal/mole.

TABLE 1 Selected Bond Lengths [Å] and Mayer Bond Order Indices (in brackets) for Optimized Geometries of AZ50 and AB106 Molecules

	Bonds lengths [Å] and bond order indices	
Bonds	AZ50	AB106
C≡N	1.17 (2.94)	1.17 (2.93)
C–CN	1.43 (1.08)	1.43 (1.10)
C=O (in COO)	1.22 (1.95)	1.22 (1.94)
C–O (in COO)	1.38 (1.07)	1.38 (1.12)
O (from COO)–C(C_6H_4)	1.38 (1.16)	1.38 (1.20)

Table 1 summarizes the bond lengths and bond order indices for AZ50 and AB106 molecules. Results of the calculations show that in both species the crucial bond lengths are identical and typical for organic fragments. Also the bond order indices underline the similarity between both studied molecules and in agreement with chemical intuition they reflect the bond strength in typical organic and inorganic groups. For example triple bond in cyano group is described by bond order equal to 2.9 and the double C=O in carboxyl group is characterized by bond order that amounts to 1.9.

The results of calculations show that the position of cyano –CN group (terminal in AZ50 or lateral in AB106) does not influence geometric structure of studied systems. This may suggest that the differences in physical properties are probably due to the differences in electronic structures of these species. Therefore, in the following maps of electrostatic potential and characteristic of valence molecular orbitals are given.

The maps of electrostatic potential, which are calculated from wave functions, for both mesogenic molecules are shown at Figure 2. They reflect the influence of activating ($-C_8H_{17}$, $-C_5H_{11}$) and inactivating (–CN, –COO) substituent in both aromatic rings. The activating substituent donates the electrons to the ring and its role relays mostly on stabilization of resonance structures. The inactivating fragment attracts electron from the ring and the effect is connected with the presence of atom (C, N), which from one side is bound to carbon atom from the ring and from another one with strongly electronegative element (O, N) by a multiple bond. Such electronegative atoms (nitrogen from the cyano group or oxygen from carboxyl group) attracts electrons from the multiple π C≡N or C=O bonds, and as a result, the carbon atoms from

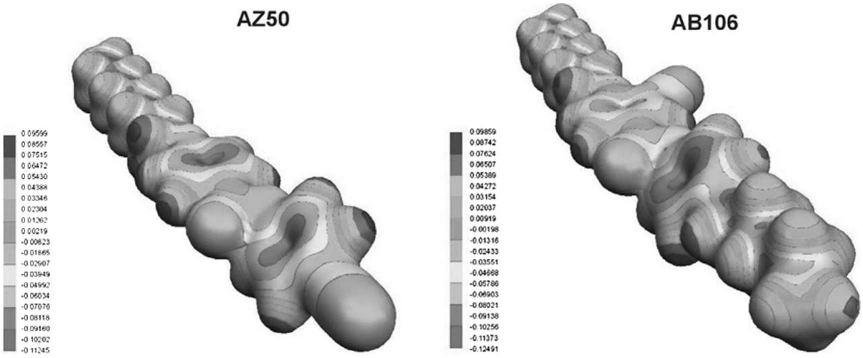

FIGURE 2 Maps of electrostatic potential for AZ50 and AB106 molecules.

cyano/carboxyl fragments becomes poorer in electrons. To compensate that lack, the electrons from the attached aromatic ring are moved to the appropriate group.

Comparing the phenyl ring, which is terminated by $-$CN group in AZ50 and by $-C_5H_{11}$ chain in AB106 molecule, one can notice that the ring is less nucleophilic in AZ50 than in AB206. This effect is a consequence of activating role of $-C_5H_{11}$ chain rather than inactivating properties of $-$CN group.

Inactivating effect of substituent is seen in a very pronounced way when considering the second phenyl ring connected to $-$C(=O)$-$O group through oxygen (AZ50) or linked to two inactivating species $-$C(=O)$-$O and $-$CN (AB106). In the last case two inactivating groups are bonded to aromatic ring through carbon, which binds either to oxygen or nitrogen *via* multiple bonds (double or triple, respectively). Here synergetic effect of both groups leads to the decrease of nucleophilic character of that aromatic fragment.

The differences between both studied molecules are also visible from the character of HOMO (Highest Occupied Molecular Orbitals) and LUMO (Lowest Unoccupied Molecular Orbitals) orbitals. The discussed orbitals for both species are depicted at Figure 3. In both molecules the HOMO orbitals are localized at carboxyl group and that of the aromatic rings, which is far from cyano group. So, in the case of AZ50 molecule it is the phenyl ring attached to C_8H_{17} hydrocarbon chain, whereas in the case of AB106 molecule the aromatic ring bound with shorter C_5H_{11} hydrocarbon chain. In both molecules the second aromatic ring together with cyano group participates in LUMO orbital.

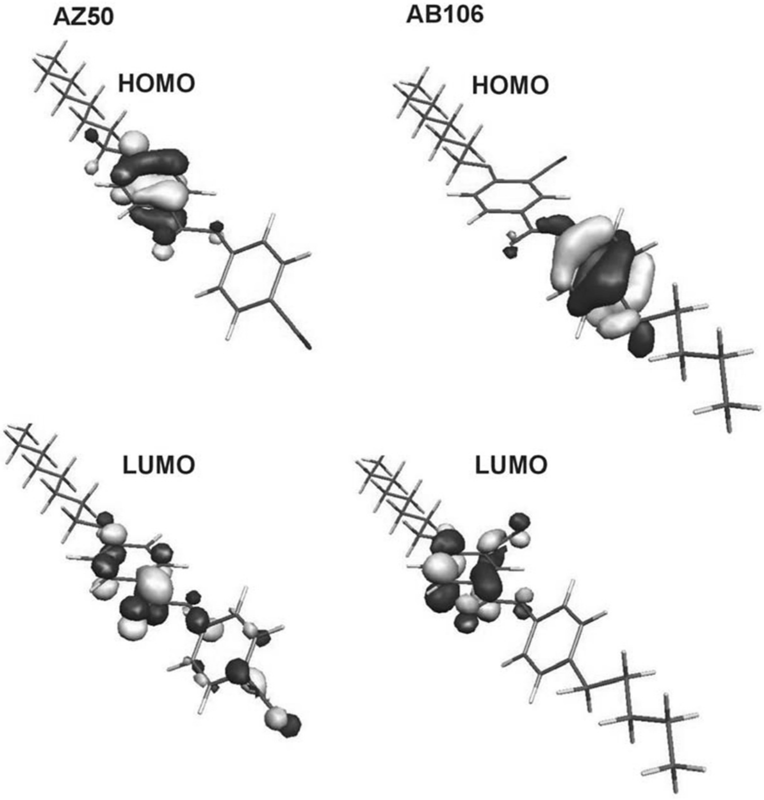

FIGURE 3 The character of HOMO and LUMO orbitals for AZ50 and AB106 molecules.

3.2 Pairs of Molecules

The results of calculations obtained for both isolated molecules suggest that the observed physical properties of mesogenic compounds are strongly influenced by their electronic structures. Therefore as the next step, the interactions of two isolated molecules of the same type (both being AZ50 or both AB106) are studied. These studies may give hints towards a preferred ordering of macroscopic sample.

The interactions inside pair of molecules are considered systematically in several steps. At first the interactions of two parallel molecules are checked taking into account two possibilities: parallel where long hydrocarbon chain of one molecule is located exactly above the long hydrocarbon chain of the second one and anti-parallel in which

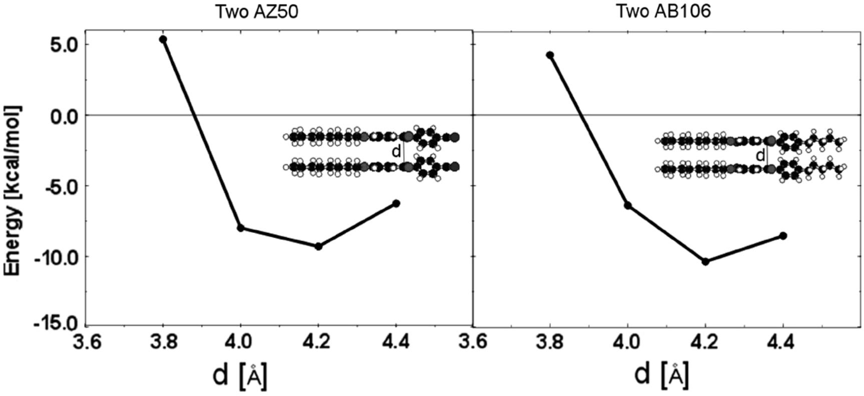

FIGURE 4 The interaction energy as a function of distance between two AZ50 or two AB106 molecules (d – distance between carbon atoms from the carboxyl groups of each molecule) together with the equilibrium geometries of isolated appropriate molecules.

long hydrocarbon chain of one molecule is positioned above the cyano group (AZ50) or above the shorter hydrocarbon chain (AB106). For both molecules the first mutual conformation is energetically favorable, and as such is shown in Figure 4.

Next, the equilibrium distance between two molecules, which is connected with the minimum of the interaction energies (defined as a difference between the energies of two interacting molecules and sum of energies of two isolated molecules) is calculated. Figure 4 summarizes results of these studies. One can see that in both systems, no interaction between two AZ50 or between two AB106 occurs for the distance between the molecules smaller than 3.9 Å. The interaction energy is larger than energies of isolated two AZ50 or AB106 molecules that are shown as horizontal lines. For both mesogenic molecules the equilibrium distance between two molecules are found to be 4.2 Å. At this distance the interaction energies for both molecules are close to the 10 kcal/mole.

Finally, the lateral mutual displacement in two opposite directions of two molecules in each pair is taken into account. Here, the position of one molecule exactly above the second one is assumed to be a starting point. The results of these studies are presented in Figure 5, where the starting mutual position is shown as vertical dotted line.

In AZ50 case the energetically favorable mutual displacement of both molecules is found to be 2.3 Å. Molecules tend to change their mutual position. On contrary, in case of two AB106 molecules, the assumed starting geometry appears to be energetically the most stable

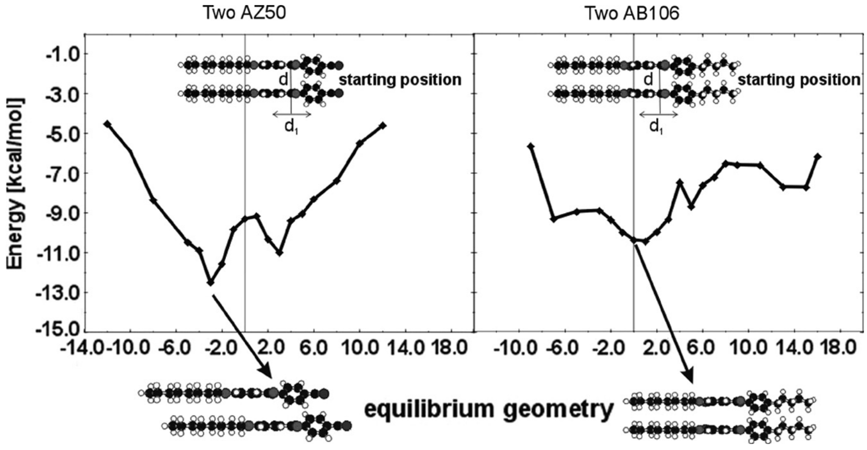

FIGURE 5 The interaction energy as a function of lateral mutual displacement of two AZ50 or two AB106 structures. Starting (above the pictures) and equilibrium (below the picture) geometries are shown.

one, which means that the molecules do not want to relocate. These results may be directly connected with the experimental observation. Experimentally AZ50 forms nematic phase, where molecules quite easy perform translational movements. Contrary to this, the AB106 molecule exists in smectic A phase and there are some spatial hindrances which make such translations more restricted.

4. CONCLUSIONS

Based upon quantum chemical DFT calculations performed for isolated molecules and pairs of molecules it is shown that detailed information on electronic and geometrical structure of simple models, which are mimicking the macroscopic system, may help to predict physical properties of the whole system.

Theoretical studies on geometries and electronic properties of isolated AZ50 and AB106 species show the similarities and the differences between these molecules. The detailed analysis of geometric structure of both molecules show that despite the differences in −CN group positions and differences in number of terminal chains, both molecules have very similar geometry structure, i.e., the important bond lengths and what follows bond orders are almost the same. Contrary to geometry, the electronic structure of both molecules is totally different and depends on the position of −CN group within molecule. In addition, the synergetic effect following from the binding of carboxy and cyjano groups to the same aromatic ring is found. Electronic structure can be characterized by electrostatic potential as well as HOMO and LUMO characterization. Maps of electrostatic potential are perceived to serve as a starting point to indicate the mutual orientation between molecules in pairs, which can be looked for in a very systematic way.

Results of basic quantum chemical calculations carried out for two mesogenic species (phenylbenzoate derivatives with the terminal and lateral −CN group) for isolated species, indicate the similar geometries (except −CN groups position) although different electronic structures of both derivatives. Examination of the interaction energy of molecule pairs lead to the conclusion that for two parallel molecules with terminal −CN group tend to be shifted mutually *ca.* 0.32 nm. On contrary, for two molecules, with lateral −CN group, do not incline to relocate. This may serve as indication for existing nematic and smectic A phases, which are observed macroscopically for phenylbenzoate derivatives with terminal and lateral −CN groups, respectively.

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