Density functional theory study on the conformational behaviour of substituted banana-shaped mesogens with a central 1,3-phenylene unit

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Abstract

In the present study, the influence of the direction of ester linkage groups on the structural and electronic properties of the three-ring bent-core, bis(4-subst.-phenyl) 2-methyl-iso-phthalates molecules with a central 1,3-phenylene unit including 4-n-alkanoyl, 4-n-alkaoxyl and 4-n-alkayl terminal chains have been studied by density functional theory (DFT) calculations. The BP86/SVP level of theory has been adopted for all the computations. These computations were performed on the conformational behavior of the three-ring bent-core compounds in a systematic way. The relaxed rotation barrier with respect to the torsion angles $\varphi_1$and φ_2 where calculated. Moreover, replacement of terminal chains, alkanyl group by alkayloxy and alkayl groups, results a small rotational barrier with a difference of about 0.2-0.8 kcal.mol^{-1} in the height of the barriers, suggesting that the terminal chain have no effect on the relaxed barriers for these isomers. The dipole moment with respect to the torsion angle φ_1 was also studied. The large differences in the dipole moments, can be seen as signs of their different phase behaviour and mesophase stability.

Keywords:- banana liquid crystals; bent-core mesogens, molecular structure and DFT calculations.

استخدام نظرية دالة الكثافة في دراسة سلوك وضعيات المركبات البلورية الشبية بالموز مع وحدة 1،3-فينيلين المركزية

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الخلاصة

في الدراسة الحالية تمت دراسة تأثير اتجاه مجاميع الاستر الرابطة بين الحلقات الاروماتية ester linkage (groups) على الخصائص التركيبية والالكترونية للمركب ثلاثي الحلقات المائل bis(4- subst.-phenyl) 2-methyl- iso-phthalates مع وحدة مركزية 1,3-phenylene ومجاميع طرفية معوضة بالالكوكسايل 4-n-alkaoxyl الالكانويل 4-n-alkanoyl والالكايل 4-n-alkayl باستخدام نظرية دالة الكثافة (DFT). تم استخدام طريقة BP86/SVP في جميع الحسابات. تضمنت هذه الحسابات دراسة السلوك الوضعي للمركب ثلاثي الحلقات المائل بطريقة منهجية. كما تمت دراسة حاجز استرخاء الدوران كدالة لزوايا الالتواء φ_2, φ_1. فضلا عن ذلك، تم أستبدال سلسلة الالكانويل الطرفية بمجاميع الالكوكسايل والالكايل وقد اظهرت النتائج ان مقدار التغير في حاجز الدوران هو صغير جدا بحوالي 0.2-0.8 kcal.mol^{-} معللة عدم تاثير المجاميع الطرفية على حاجز الدوران. كما تمت دراسة ثنائي القطب كدالة لزاوية الالتواء φ_1. ان الاختلاف الكبير في عزم ثنائي القطب ادى الى تغير في ظهور الاطوار البلورية السائلة ومدى استقراريتها.

الكلمات المفتاحية: البلورية الشبية بالموز، الخصائص التركيبية والالكترونية للمركب ثلاثي الحلقات المائل

1. Introduction

A banana-shaped (Bent-core) mesogens characterize an important field in liquid crystal research and supramolecular chemistry. The significant interest of this mesogens is their ability to generate supramolecular chirality from a chiral molecules **[1]**. Surprisingly, it open the way to new materials can exhibit interesting and peculiar properties as optical properties and anti-ferroelectric behaviour, making them potentially suitable for electro-optical applications like liquid crystalline Displays (LCD) **[2, 3]**. The unusual properties are correlated with the bent-core shape of the molecules. In the last few year a number of classes of Bent-core molecules have been synthesized and the largest part of them containing a central 1,3-phenylene unit **[4–8]**. These compounds were characterized by using different tools such as Nuclear Magnetic Resonance (NMR) spectroscopy **[9–12]**, X-ray diffraction **[1, 13]** and electro-optical experiments **[14, 15]**. Substituents connected to both onto the central 1,3-phenylene unit and the legs of these molecules alter the dipole moment, shape and flexibility of the molecules and have very strong influence on the formation or suppression of banana phases **[16]**. The objective of this work is to examine the molecular conformations and calculate relaxed Potential Energy Surface (PES) scans for substituted bent-core systems with a central 1,3-phenylene unit, as illustrated in Fig. 1,**[17]** including torsion angles (relaxed rotational barriers) using DFT. The influence of substituents groups on the torsion angles were considered in order to study the flexibility of different terminal chains and different terminal group. The effect of substituents on the polarity of banana shaped mesogens was investigated by analysis of the magnitude and direction of the dipole moment and its components in relation to the long axis of the molecules.

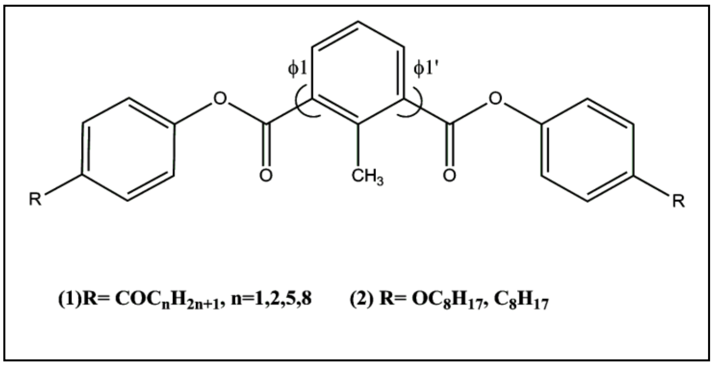

Figure 1: General formula of laterally methyl-substituted three-ring- bent-core mesogens.

2. Computational methods

All calculations were performed using the BP86 functional **[18]** with the Gaussian03 series of programs **[19]**. All atoms were described using the SVP basis set of Ahlrichs and co-workers **[20]**. Full geometry optimizations with no restrictions were carried out in each case, and stationary points were confirmed to be genuine minima or transition states by analytical calculation of their harmonic vibrational frequencies.

3. Results and Discussion

3.1 Relaxed Rotational Barriers

For a systematic study on the conformational behavior of the three -ring-bent-core molecules (fig.2), the relaxed rotational barriers were calculated for significant torsion angle ϕ1 and ϕ2.

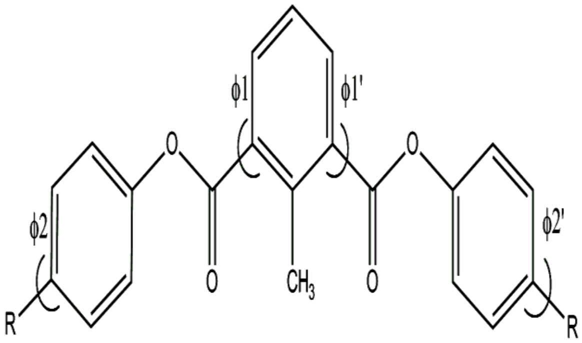

Figure 2: General formula of laterally methyl-substituted three-ring bent-core mesogens.

A serious of three ring bent-core mesogen such as bis (4-n-alkanoyl phenyl) 2-methyl isophthalatec prepared by Weissflog group **[17]** was studied (fig. 3) and the mesophase was presented in table 1.

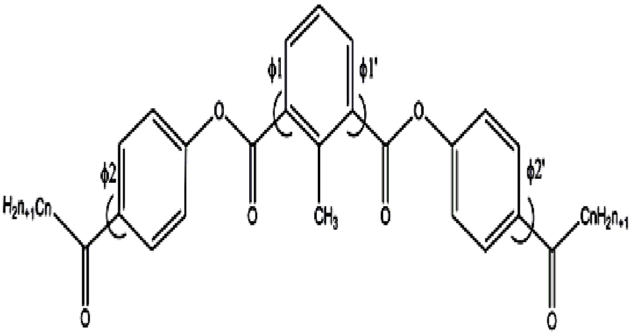

Figure 3: General formula of laterally methyl-substituted three-ring bent-core mesogens bis (4-n-alkanoylphenyl) 2-methylisophthalates **1a–1d**.

Table 1: Transition temperatures C°, for monotropic of the bis (4-n-alkanoylphenyl) 2-methylisophthalates **1a–1d** [17].

No.	n	Cr	SmA	N
1a	1	202.6	-	92
1b	2	229.7	-	-
1c	5	159	-	90
1d	8	101.7	114.7	-

The energetically preferred structures were obtained by a full optimization from different starting structures including twisted and planar ones in order to understand the conformational change for the compounds in more detail, the one- and two-fold potential energy surface (PES) scans were generated by fixing the corresponding torsion angles, calculated every 30^0, and a complete optimization of the other parameters in a stepwise manner.

3.1.1. Relaxed rotational barriers for noyl bent-core system

The relaxed rotation with respect to the torsion angle φ_1 for **1a** compound shows four stable minima and three barriers with a maximum energy barrier of about 2.5 kcal mol^{-1} as shown in figure 4. The preferred conformers are characterized by a torsion angles 90 and 180. The preferred conformers, with coplanar arrangement of the carbonyl group and the adjacent phenyl ring (φ_1=180), is in agreement with conformational studies on other bent-core systems including ester connecting groups **[21].**

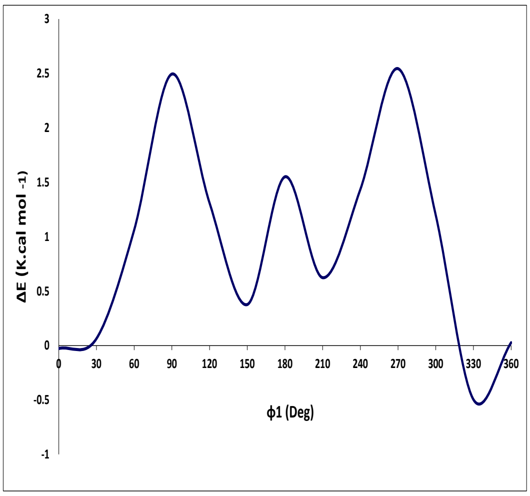

Figure 4: Relaxed rotational barriers related to the torsion angle ϕ_1 for compound **1a**.

The relaxed rotational barriers with respect to the torsion angle φ_2 is illustrated in Figure 5 for the bent-core molecules **1a**. The potential energy curve of compound **1a** consist of two barriers and one stable minima. In contrast to φ_1, the one-fold PES scans related to φ_2 shows a rather limited conformational degree of freedom (φ_2= 90) with a barrier of about 6.5 kcal mol^{-1}.

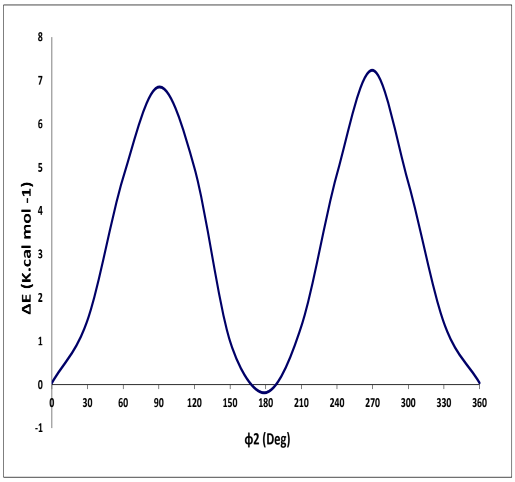

Figure 5: Relaxed rotational barriers related to the torsion angle ϕ_2 for compound **1a**

3.1.2. Effect of chain lenghts in the external phenyl rings

In order to investigate the influence of chain lenghts substituents at *para*-positions of the external phenyl rings on the conformational behavior, the relaxed rotational barriers of the isomers **1b-1c** were calculated with respect to the torsion angles φ_1 and φ_2 (Figures 6 and 7). Similar conformational behaviour were found in the systems **1b** (ethanoyl group), **1c** (pentanoyl group) and **1d** (octanoyl group). Clearly, the terminal chain lengths have no effect on the relaxed barriers for these isomers.

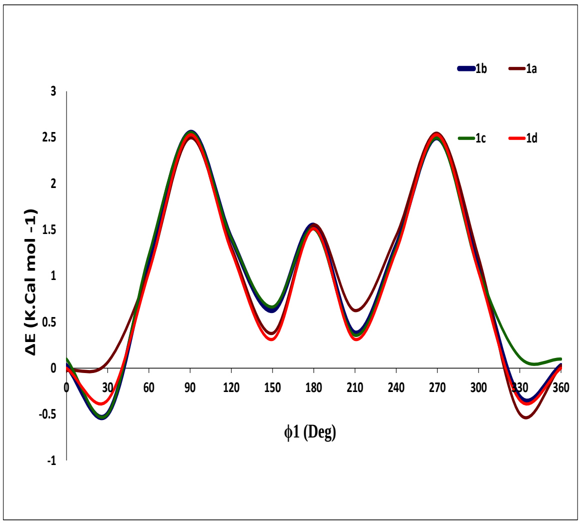

Figure 6: Relaxed rotational barriers related to the torsion angle **ϕ_1** for compound **1a-1d**

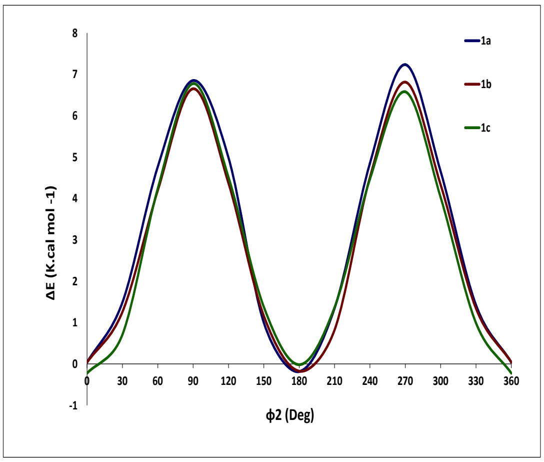

Figure 7: Relaxed rotational barriers related to the torsion angle **ϕ_2** for compound **1a-1c**

3.1.3. Effect of substituents in the external phenyl rings

In order to investigate the influence of the wing-groups substituents at external phenyl rings on the potential energy surfaces of the liquid crystal mesogen with respect to the angle φ_1, the aliphatic acyl chains (octanoyl group) replaced by octayloxy and octayl groups for compound **2** and **3** respectively, as shown in figure 1[17] and the transition temperature of mesogenes are presented in table 2 .

Table 2: Transition temperatures C°, for monotropic of the bis (4-n-octaylox phenyl) 2-methylisophthalates 2 and bis (4-n-octayl phenyl) 2-methylisophthalates 3**[17]**.

No	R	Cr	N
2	OC_8H_{17}	73.7	71.9
3	C_8H_{17}	48.9	39

The three compounds **1d**, **2** and **3** essentially show three different types of barriers for **ϕ_1** as presented in figures 6 and 8. If the terminal chain group is connected by an oxygen atom (octayloxy chain) to the terminal phenylene unit (O–C bond), compound **2**, it results a marginally lower barrier of about 2.36 Kcal/mol^{-1}. Similar trends are also obtained for the curve of the compound **3**, the terminal group is connected by a carbon atom to external phenyl rings (C–C bond), it originates a rather small barrier of about 1.77 kcal mol^{-1} like in compound **2** which corresponds to a high flexibility for this segment of the molecule. In contrast to the octanoyl compounds **1d**, which exhibit a semectic A phase at 114.7 C°, the compound **2** and **3** exhibit nematic phases at 71.9 C° and 39 C°, respectively. Therefore, different types of terminal chain with a high flexibility can influence the phase behaviour [**22**].

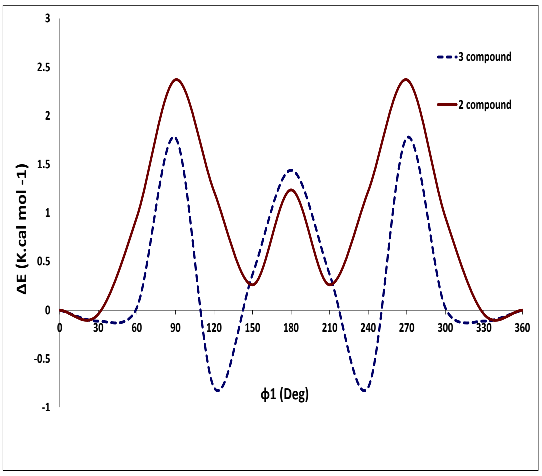

Figure 8: Relaxed rotational barriers related to the torsion angle ϕ_1 for compound **2** and **3**.

3.2. Dependency of the dipole moment on conformers with constraints to the torsion angle

The dependency of the dipole moment μ to the polarity is important properties of banana-shaped compounds. The curves for the dependency of μ on conformers with constraints to the torsion angle ϕ_1 show a significantly different trend for **1a**, **1b**, **1c** and **1d** systems. For these systems the magnitude of the dipole moment μ vary in a rather large range of about 4-7 Debye, as presented in figure 9.

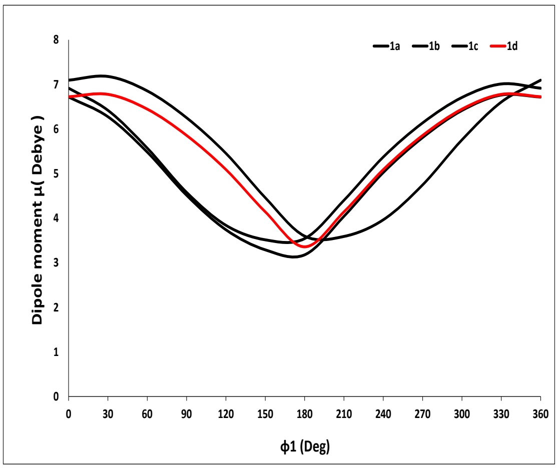

Figure 9: One-fold scans related to the torsion angle ϕ_1 and dipole moment **μ** for compounds **1a-1d**.

Moreover, replacement of terminal chains by octayloxy and octayl groups results in a lower value of the dipole moment :2.5-4 Debye and 1-2.5 Debye, respectively (figure 10). The large differences in the dipole moments, especially in compounds **2** and **3**, can be seen as signs of their different phase behaviour, and mesophase stability, effected by their various global polarity [**23**].

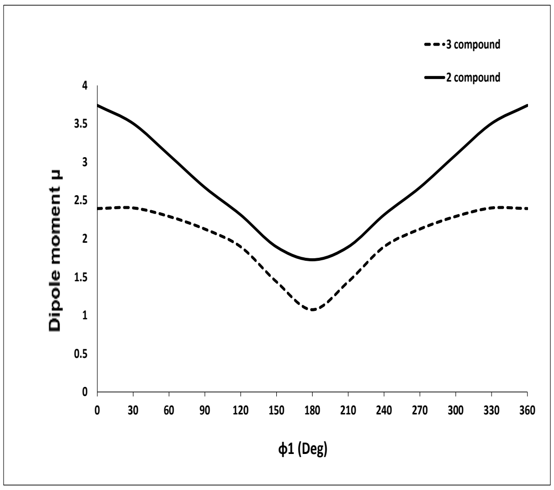

Figure 10: One-fold scans related to the torsion angle ϕ_1 and dipole moment μ for compounds **2, 3**.

4. Conclusions

A DFT study, using BP86/SVP method, was performed on three-ring bent-core bis (4-subst.-phenyl) 2-methyl-iso-phthalates molecules with a central 1, 3-phenylene unit and ester linkage groups in different orientations including 4-n-alkanoyl, 4-n-alkaoxyl and 4-n-alkayl terminal chains. The relaxed rotation with respect to the torsion angle φ_1 for compound **1a** exhibit preferred conformers with torsion angles 90 and 180, showing four stable minima and three barriers with a maximum energy barrier of about 2.5 kcal mol^{-1}. Whereas, the potential energy curve related to φ_2, consist of two barriers and one stable minima, show a rather limited conformational degree of freedom (**φ_2= 90**) with a barrier of about 6.5 kcal mol^{-1}. Similar conformational behaviour was found in the systems **1b-1c**, which the terminal chain lengths have no effect on the relaxed barriers for these isomers. Moreover, the influence of replacement of terminal chains, alkanyl group by alkayloxy and alkayl groups results, on the rotational barrier is small with a difference of about 0.2-0.8 kcal.mol^{-1} in the height of the barriers. The large differences in the dipole moments, especially in compounds **1a-d**, can be seen as a signs of their different phase behaviour and mesophase stability.

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