

DFT conformational study of five-ring bent-core mesogens with a central 1,3-phenylene unit

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Abstract: The potential energy surfaces of the five-ring bent-core molecules with a central 1,3-phenylene unit, including azobenzene with alkyloxy as terminal chains, has been investigated by using density functional theory (DFT). The PBE1PBE/6-31G(d,p) level of theory has been used for some computations in addition to the BP86 function, where used to study the influence of rotation of the connection groups. These computations were performed on the conformational behavior of the connection groups, included ester linkage group, N=N group and terminal OR group, of the five-ring bent-core compound in a systematic way. The relaxed rotation barrier with respect to the six torsion angles (φ_1 , φ_2 , φ_3 , φ_4 , φ_5 and φ_6) were calculated. It is interesting to note that the oxygen atoms of the linkage group, which are directly connected to the rings, give banana-shaped compounds with energy barrier by about 0.9 kcal mol⁻¹ and high flexibility, whereas the ester group connected to phenyl ring by a carbon atom shows a high energy barrier by about 10.2 kcal mol⁻¹ and a relatively limited conformational degree of freedom. The dependency of the Dipole moment on conformers with constraints to the torsion angle was studied.

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

1. Introduction

In the last few years, a banana-shaped (Bent-core) mesogens have been achieved significant importance in the field of liquid crystal research and supramolecular chemistry. The main aspect for the interest on such 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 unusual properties as optical properties and anti-ferroelectric behavior, making them potentially suitable for electro-optical applications like liquid crystalline displays (LCD) [2]. The unusual properties are correlated with the bent-core shape molecules. These bent-core molecules prefer to pack in the bent direction leading to a long-range correlation of the lateral dipole moments and then to a macroscopic polarization of the smectic layers. Recently, particular attention has been dedicated to synthesis these types of molecules and the

largest part of them containing a central 1,3-phenylene unit [3–5]. 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 [6]. Different tools were used to characterize these types of molecules such as nuclear magnetic resonance (NMR) spectroscopy [7–9], X-ray diffraction [10] and electro-optical experiments [11, 12]. The objective of this work is to shed light on molecular conformations and calculate relaxed potential energy surface (PES) scans for five bent-core systems with a central 1,3-phenylene unit including torsion angles (relaxed rotational barriers) using DFT. The compound chosen is taken from the series of azobenzene derivatives synthesized by Tschierske group [13] and shows different mesophase characters as shown in Figure 1 and Table 1.

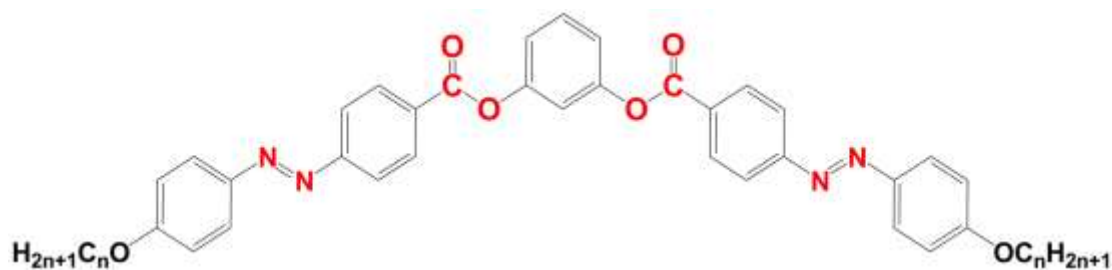


Figure 1: General formula of five ring bent-core mesogen.

Table 1: Transition temperatures C°, for five ring bent-core mesogen [13].

NO.	n	Temperature (°C)
1	8	-
2	10	Cr 147 I
3	12	I 136 Cr
4	14	I 128 B1 126 Cr
5	16	I 129 B1 123 Cr

2. Computational Method

All calculations were performed using the pbe1pbe and Bp86 functions [14] and 6-31G* basis set [15] with the Gaussian09 series of programs[16]. The crystal structures of the series of five-ring bent-core compounds, were obtained by full optimization from different starting

conformations with no restrictions were carried out in each case, and stationary points were confirmed to be genuine minima by analytical calculation of their harmonic vibrational frequencies. The BP86 function and 6-31G* basis set was used to study the influence of rotation of the connection group.

3. Results and Discussion

3.1. Relaxed Rotational Barriers

For a systematic study on the conformational behavior of the five -ring-

bent-core molecules (Figure 1), the relaxed rotational barriers were calculated for six significant torsion angles ϕ_1 , ϕ_2 , ϕ_3 , ϕ_4 , ϕ_5 and ϕ_6 .



Fig.(1): General formula of five-ring bent-core mesogens.

The energetically preferred structures were obtained by a full optimization from different starting structures to understand the conformational change for the compounds in more detail, the one- fold potential energy

surface (PES) scans were generated by fixing the corresponding torsion angles, calculated every 30° , and a complete optimization of the other parameters in a stepwise manner.

3.1.1. Relaxed Rotational Barriers for Ester Group

The relaxed rotational barriers were calculated for ester group with three significant torsion angles ϕ_1 , ϕ_2 and ϕ_3 as shown in Figure 2.

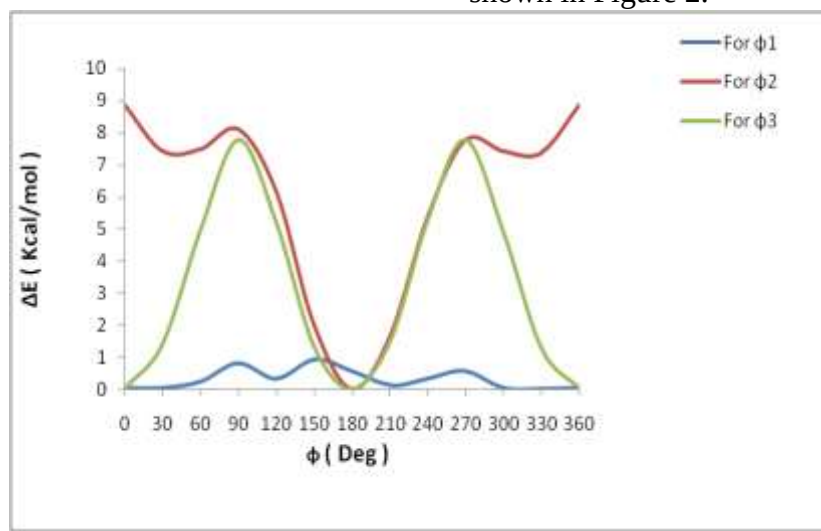


Fig. (2): Relaxed rotational barriers with respect to the torsion angle ϕ_1 , ϕ_2 and ϕ_3 for compound 1.

The relaxed rotational with respect to the torsion angle ϕ_1 for compound **1** show two stable minima at 120° and 210° , and three maximum at 90° , 150° and 270° with energy barrier of about $0.9 \text{ kcal mol}^{-1}$, which corresponds to a high flexibility for this segment of the molecule. These results are in agreement with conformational studies on other bent-core systems including ester group, connecting by an oxygen atom to the central 1,3-phenylene unit, which the energy barrier is lower than $2.4 \text{ kcal mol}^{-1}$ [17]. In contrast to ϕ_1 , the relaxed rotation with respect to the torsion angle ϕ_2 consists of one stable minima at 180° , and two maximum at 90° and 270° with energy barrier of about 8 kcal mol^{-1} as illustrated in Figure 3. The preferred conformer is characterized by a coplanar arrangement ($\phi_2=180^\circ$) of the carbonyl group and the central phenyl ring.

These results are in agreement with the literature[18]. Comparing with the torsion angle ϕ_1 , the energy barrier is higher showing a rather limited conformational degree of freedom.

The relaxed rotational barriers with respect to the torsion angle ϕ_3 is illustrated in Figure 3 for the bent-core molecules **1**. This potential energy curve consists of one stable minima at 180° , and two maximum at 90° and 270° , showing a rather limited conformational degree of freedom with a barrier of about $7.9 \text{ kcal mol}^{-1}$. Interestingly, this energy barrier is higher than the energy barrier with respect to the torsion angle ϕ_1 . Otherwise, if the ester group is connected phenyl ring by a carbon atom (C–C bond) it originates a rather high energy and the conformational degree of freedom is decreased[17].

3.1.2. Relaxed Rotational Barriers for N=N Group

The relaxed rotational barriers for azo group with two significant torsion angles ϕ_4 and ϕ_5 were calculated as shown in Figure 3.

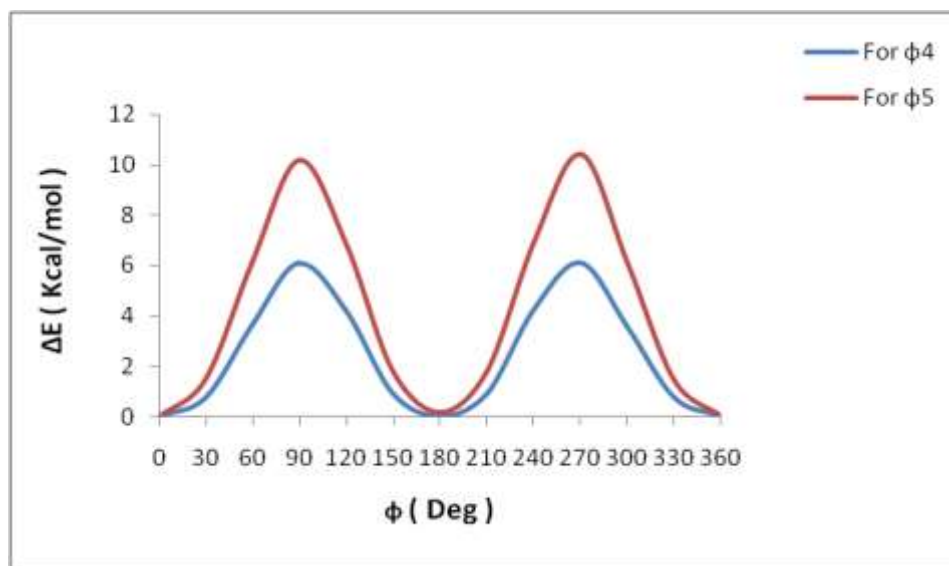


Fig.(3): Relaxed rotational barriers with respect to the torsion angle ϕ_4 and ϕ_5 for compound 1.

The potential energy curve with respect to the torsion angle ϕ_4 consist of one stable minima at 180° , and two maximum at 90° and 270° with energy barrier of about 6 kcal mol⁻¹. Similar to the torsion angle ϕ_4 , the potential energy curve with respect to the

torsion angle ϕ_5 for the bent-core molecule **1** consists of one stable minima at 180° , and two maximum at 90° and 270° . The barrier is increased to 10.2 kcal mol⁻¹ showing a relatively limited conformational degree of freedom.

3.1.3. Relaxed Rotational Barriers for OR Group

In the banana shaped liquid crystal molecules, the conformational degree of freedom of the terminal chains (OR) exerts

influence on the aggregation of these molecules. Therefore, we have carried out a potential energy surface related to the torsion angle ϕ_6 (Figure 4) for compound **1**.

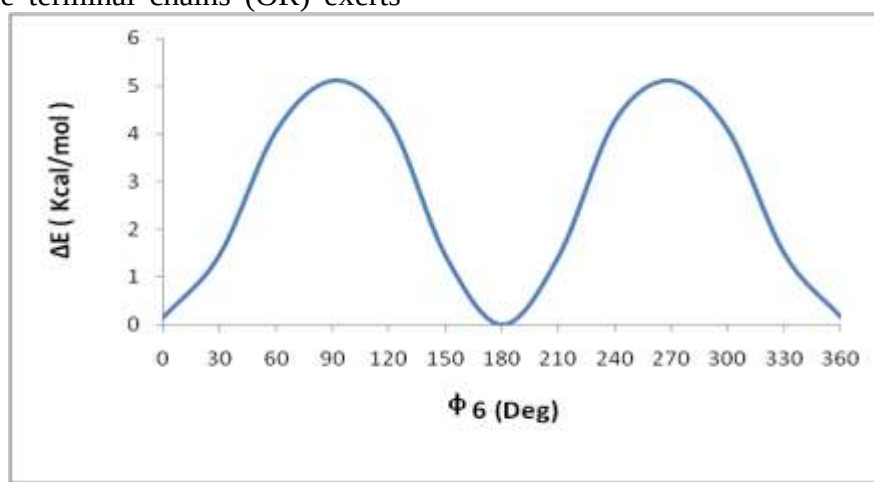


Figure 4: Relaxed rotational barriers with respect to the torsion angle ϕ_6 for compound 1.

This potential energy surface consist of one stable minima at 180° , and two maximum at 90° and 270° with energy barrier of about 5 kcal mol⁻¹. This is in agreement

with conformational studies on other bent-core liquid crystal molecules including ester group[17]. As mentioned above, the barrier is decreased where the external phenyl ring is

bound by an oxygen atom to the terminal chain. It is interesting to note that the numbers of oxygen atoms of the linkage group, which are directly connected to the rings, give banana-shaped compounds with high flexibility. In some way, bent-core

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 property of banana-shaped molecules. The curve for the dependence of μ on conformers with

liquid crystal compound with higher flexibility of the wings show mostly a smectic phases, whereas the compounds with a lower conformational degree of freedom prefer to form columnar phases [17].

constraints to the torsion angle φ_1 of compound **1** is shown in Figure 6. These conformers show a relatively small angle dependency of μ with values of about 4.5 Debye. This result is in line with few research in literature [17].

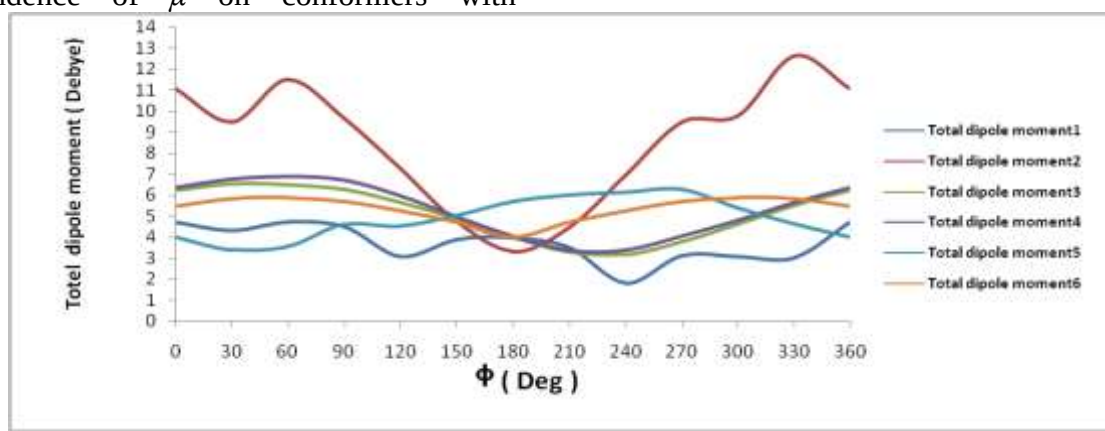


Fig.(5): One-fold scans related to the torsion angles φ and dipole moments μ for compound **1.**

According to torsion angle φ_2 , the values of μ vary in a rather large range of about 3–11 Debye. The magnitude of the dipole

moment varies by about 3–6.5 Debye with variation of the torsion angle φ_3 , φ_4 , φ_5 and φ_6 systems.

4. Conclusion

The functions and basis set used with density functional theory, PBE1PBE and BP86 functions with 6-31G (d,p) basis set, are suitable for calculating a potential energy surfaces and describing the five-ring bent-core molecules with a central 1, 3-phenylene unit. The relaxed rotation with respect to the torsion angle φ_1 for compound **1** exhibit preferred conformers with torsion angles 120° and 210° , whilst the relaxed rotation with respect to the other five torsion angles

(φ_2 to φ_6) for compound **1** exhibit preferred conformers with torsion angle 180° . The bent-core liquid crystal compound with higher flexibility of the wings, with energy barrier by about $0.9 \text{ kcal mol}^{-1}$, shows mostly smectic phases, whereas the compounds with a lower conformational degree of freedom, with energy barrier by about $10.2 \text{ kcal mol}^{-1}$, prefer to form columnar phases. The dependency of the dipole moment on conformers with constraints to the torsion angle was investigated.

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