



Dipole moment calculation in solution for some liquid crystalline molecules



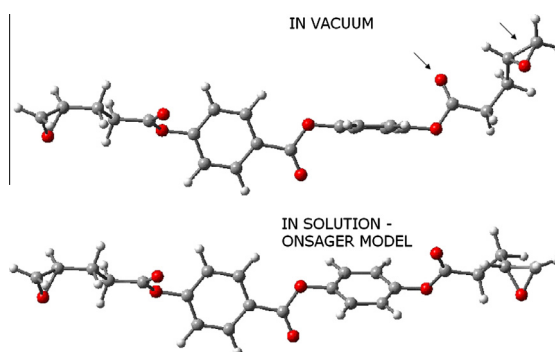
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HIGHLIGHTS

- We computed geometry and dipole moment of four LC compounds in non-polar solvent.
- For highly polar molecules, PCM model is closer to experiment than Onsager model.
- Orientation of symmetric terminal polar groups affects the direction of dipole moment.
- Adding polar terminal groups changes the dielectric anisotropy in the LC phase.

GRAPHICAL ABSTRACT



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ABSTRACT

Theoretical and experimental studies were used to determine the dipole moment for four liquid crystalline materials. *Ab initio* calculations in vacuum led to elimination of a few potential conformers in each molecule. These results were used as initial data to obtain the geometry of the molecules in non-polar solvent according to Onsager's or PCM model. After employing both models, slight increase of the dipole moment was noticed for all the molecules. The results are similar for both the models, with one exception for the strongly polar molecule where the Onsager's model led to much higher dipole moment. The dipole moment was also determined experimentally for all the materials. The experimental data were compared with the results from calculations. For the nematic materials, the theoretically predicted sign of the dielectric anisotropy was compared with experimental results.

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1. Introduction

Connecting theoretical computations of molecular structure with experiment is a constant subject of scientific interest [1–3]. Recent theoretical studies also consider changes in the molecular structure resulting from interactions with the surrounding medium (e.g. a solvent) [3–6]. One group of materials in which the molecular structure as well as the interactions between the molecules have large impact on the physical properties in the condensed phase

are liquid crystals [7–10]. The fundamental parameters describing a liquid crystal are the temperatures of phase transitions and the type of the mesophase [11–13], which are also related to the structure of the molecules. Thus, precise determination of the parameters describing internal structure of the investigated material may help to predict some physical properties of the mesophase. A very important property of compounds used in devices based on electrostatic control of molecular orientation (mainly nematics) is also the dielectric anisotropy, which determines the character and speed of changes in the molecular alignment in response to the applied electric field [7,8]. The Maier–Meier equations successfully provide qualitative explanation of the observed changes in the electric

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permittivity of nematic liquid crystals built of polar molecules. The best example is the relation between dielectric anisotropy $\Delta\epsilon$ and the angle β between the direction of the dipole moment and the long axis of the molecule. When $3\cos^2\beta = 1$ ($\beta \approx 55^\circ$), the contributions of the dipole moment to ϵ_{\parallel} and ϵ_{\perp} are equal. $\Delta\epsilon$ is then determined by (positive) anisotropy of molecular polarizability. The dipolar contribution to $\Delta\epsilon$ is positive for $\beta < 55^\circ$ and negative for $\beta > 55^\circ$. In the latter case, the actual sign of $\Delta\epsilon$ will depend on the absolute values of contributions from the anisotropy of molecular polarizability $\Delta\alpha$ and the orientational polarization [7]. Qualitative analysis based on Maier–Meier equations may be useful for initial estimation of the dielectric anisotropy of a given material, based on the dipole moments of functional groups building up the compound. For instance, starting with a non-polar compound with small positive dielectric anisotropy and substituting one of the functional groups with a group having strong dipole moment roughly parallel to the long molecular axis, one may expect the dielectric anisotropy to increase significantly due to the large growth of ϵ_{\parallel} . If the introduced functional group has small dipole moment which makes a large angle with the long axis of the molecule then a small increase of ϵ_{\parallel} may be expected, due to the component μ_{\parallel} and increased polarizability in the direction of the long axis. However, since the component ϵ_{\perp} will also increase due to the appearance of the perpendicular component of the dipole moment, the dielectric anisotropy may be expected to remain unchanged or even decrease slightly. A behavior qualitatively consistent with this description has been observed e.g. in some derivatives of azobenzene [7]. This means that by knowing the value of the dipole moment and the angle between its direction and the long molecular axis in a nematic material it is possible to predict the sign of the dielectric anisotropy and therefore determine how the ordering of the given material will change in an external electric field. The quantum–mechanical calculations can be used to determine the dipole moment and its inclination angle to the long axis. In earlier theoretical studies we used *ab initio* calculations in vacuum to determine basic conformers and their dipole moments for four of the compounds investigated in the present paper [14]. In the present work, the molecular geometry obtained from those calculations was used as a starting point for further optimization, using also the RHF method with 6-31G* basis set, but including the interaction between the molecules and the solvent (benzene) according to Onsager's model of polar molecules in solution [15] and PCM model [16]. The theoretically determined dipole moments of the investigated compounds were compared with the dipole moments obtained from the experiment. For the nematic materials, the sign of the dielectric anisotropy predicted by the calculations was compared with the experimental data.

2. Materials

The general structure of the monomers investigated in this work consists of a rigid central segment and two flexible endings. The central segments are typical for mesogenic compounds. Indeed, five of these six monomers appear in liquid crystalline state in a wide temperature range. The molecular structure of the monomers is shown below, along with the acronyms introduced for greater clarity of the text (Fig. 1).

The compounds were synthesized recently and were subjected to detailed analysis, including confirmation of the molecular structure (FTIR, NMR, and elemental analysis) and determination of phase transitions and type of mesophase (DSC, optical observations, and X-ray diffraction studies). The results of these investigations have been presented elsewhere [17–19]. It has been established that the compound B1 has no mesophase, BU1 exhibits two smectic phases at cooling: SmB and – in a narrow temperature

range – SmE. The compounds M1, MU1 exist in the nematic phase in a wide temperature range (115–72 °C), both at heating and cooling [17].

3. Experimental

Dielectric measurements in low frequency range were carried out using a Novocontrol system containing a high-resolution Alpha dielectric analyzer. The refractive index was measured with Carl-Zeiss Abbe refractometer with sodium vapor lamp as the light source. The investigated materials were dissolved in benzene at room temperature and the solutions with different concentration were studied. The measurements of the dielectric anisotropy of the compounds were made with a Solartron 1260 Impedance Analyser. The samples were placed inside a flat capacitor made of glass plates covered with a conducting ITO layer, and oriented in a magnetic field of 1T.

Ab initio calculations of molecular structures and dipole moments were performed using the *Gaussian 03* program suite on a PC workstation [20]. Molecular energies and wavefunctions were computed by closed-shell Hartree–Fock method (RHF) with standard basis set 6-31G*. Structural parameters of the studied molecules were determined by means of the Berny algorithm of geometry optimization, using a program developed by Schlegel with later modifications [21]. As a final step, single-point energy calculations were performed for all the optimized geometries, using the RHF/6-31G* model with second-order Møller–Plesset (MP2) energy correction for electron correlation. The dipole moments were computed as first derivatives of energy with respect to the applied electric field. Furthermore, interactions between the molecules and the non-polar surrounding medium (solvent) were included in the calculations, according to Onsager model [15] and polarizable continuum model (PCM) [16]. As in the earlier cases, the molecular energy was calculated using restricted Hartree–Fock (RHF) method with 6-31G* basis set. The electric permittivity of the solvent was taken from literature data for benzene.

4. Results

4.1. Theoretical study

Earlier theoretical studies on the structure of the monomers, using *ab initio* calculations in vacuum [14], resulted in determining basic conformers and their dipole moments. In the course of the calculations the molecules were split into three segments (one central part and two identical endings) in a view to enable detection of more than one possible structure. Indeed, it has been found that the central segment of the monomers B1/BU1 may exist in at least two forms, which have substantially different dipole moments but very close values of energy. Consequently, two structural isomers were found for B1 and BU1 compounds and possible conformers of M1 and MU1 molecules were also presented. In addition, possible existence of several conformations differing in the mutual orientation of segments was discussed [14].

In our previous paper [14], a two-step method for geometry optimization of the monomers was proposed. In the first step, the investigated structures were split into three segments: the central part and the two endings (cf. Fig. 1), which were optimized as if they were separate molecules. In the next step, the optimized segments were used to reconstruct the original molecules, taking into account several possible orientations of the terminal segments with respect to the central segment, and these structures were further optimized. Based on the results of the calculations, which were carried out for four of the compounds studied in the present paper, possible co-existence of several isomers in real materials

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