

## DFT Studies of Biphenyl Derivatives, Potential Application as Chiral Dopants for Liquid Crystals

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**Summary:** High polarization power may be achieved by designing dopants with chiral cores having polar functional groups that are conformationally more restricted when confined to the zigzag binding site of the (smectic) SmC\* host. Axially chiral biphenyls having conformationally restricted and unrestricted cores were investigated for dipole moment at B3LYP/6-31G(d) method of DFT (density functional theory). It was reflected from the computed data that the dipole moment of conformationally restricted biphenyl cores containing dioxolane and dithiolane bridge was more compared to the conformationally unrestricted biphenyl core. Overall we have investigated the dipole moment of nineteen biphenyl derivatives having substituents at different positions.

Key words: Liquid crystal, Biphenyl, Dipole moment

### Introduction

The liquid crystalline state is considered as the fourth state of matter i.e. observed between the solid and isotropic (liquid) states [1]. In liquid crystal, mainly two phases exist depending upon the positional order of molecules i.e. “nematic phase” molecules have orientational order but no positional order and “smectic phase” molecules possess positional order [2, 3].

Commercially available S-811 dopant is very well known to cause the formation of a left handed helical structure in the nematic mixtures [4]. Now a days chiral dopants have attracted the attention due to the special technological properties [5]. Chiral dopants are normally designed on the principles of molecular recognition phenomena and particularly in the case of ferroelectric SmC\* liquid crystals, those have applications in high-resolution reflective liquid crystal on silicon (LCOS) micro displays. Liquid crystals also have significance in nonlinear optics, chiral sensing and photonics applications. Commercial ferroelectric liquid crystals (FLC) mixtures are normally prepared by mixing together a chiral dopant in an achiral SmC\* liquid crystal host having low viscosity and wide temperature ranges [6]. The properties of ferroelectric liquid crystal devices, like electro optical switching time, second order nonlinear optical (NLO) susceptibility and photo switching threshold, often depend on the magnitude of polarization power ( $P_s$ ) induced by the chiral dopant [7]. Most important aspect of FLC materials research is to understand the relationship between the molecular structure of a chiral dopant and the intensity of the polarization it

induces [8]. Siemensmeyer and Stegemeyer showed that this structure property relationship can be expressed in terms of the polarization power according to eq. 1.

$$\bar{P}_o = \left( \frac{dP_o}{dx_d} \right)_{x_d=0} \quad (1)$$

$x_d$  is the mole fraction of chiral dopant and  $P_o$  is the polarization normalized for variations in tilt angle  $\theta$  according to eq. 2 [9].

$$P_o = P_s / \sin \theta \quad (2)$$

Stegemeyer classified dopants in to two types, as ‘Type I’ dopants (e.g. 1 in Fig. 1) are chiral dopants contain stereogenic centers in one of the side chains. The polarization power of these dopants is more or less invariant of the achiral host structure and ‘Type II’ dopants are dopants having stereogenic centers located in the rigid core (e.g. 2 in Fig. 1) [10].

Stegemeyer demonstrated that the polarization power ( $P_s$ ) of ‘Type II’ dopant varies with the structure of the achiral host. Urbanc and Zeks [11] suggested that the spontaneous polarization ( $P_s$ ) induced by a ‘Type II’ chiral dopant is influenced by steric interactions with the surroundings of host molecules that affects the rotational distribution of the core transverse dipole moment  $\mu_{\perp}$  with respect to the polar axis of the SmC\* phase [10]. The spontaneous polarization is expressed as a function of dipole moment  $\mu_{\perp}$  as shown in eq. 3

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$$P_s = N1\mu \perp \cos\psi_0 \Re \cos\psi > \quad (3)$$

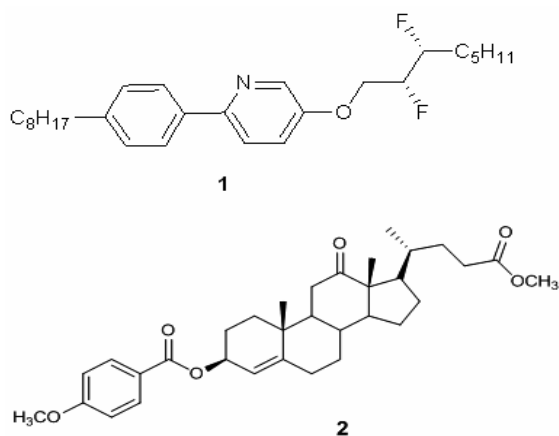


Fig. 1: Examples of dopants, Type I (1) and Type II (2)[9].

First example of chiral dopant containing biphenyl core was reported by Lemieux and co-workers [12]. Hence, it is assumed that it may be possible to achieve high polarization powers by designing dopants with chiral cores having polar functional groups that are conformationally more restricted when confined to the zigzag binding site of the SmC\* host. To prove this hypothesis, In this article we are reporting theoretical measurement of dipole moment of different biphenyl cores having different functional groups at DFT (density functional theory) level. To the best of our knowledge this work is not reported yet by someone else.

## Results and Discussion

Chiral biphenyl dopants, conformationally restricted (1-8) and unrestricted (9-19) biphenyl core were investigated by using DFT studies, the computed data of dipole moment ( $\mu$ ) and dihedral angle between two phenyl rings (Fig. 2 for numbering) is given in the Table-1 and 2. Optimized structures along with dipole moment orientation are shown in Fig. 3 and 4.

Table-1: Dipole moment ( $\mu$ ) and dihedral angle ( $^\circ$ ) in compounds (1-8).

Compound	Dipole Moment ( $\mu$ ) Debyes	Dihedral angle ( $^\circ$ ) (C2-C1-C1'-C2')
1	9.61	54.6°
2	5.86	53.5°
3	5.52	57.0°
4	4.49	53.7°
5	3.76	55.8°
6	4.47	75.5°
7	4.29	75.2°
8	3.72	79.5°

Table-2: Dipole moment ( $\mu$ ) and dihedral angle ( $^\circ$ ) in compounds (9-19).

Compound	Dipole moment ( $\mu$ ) Debyes	Dihedral angle ( $^\circ$ ) (C2-C1-C1'-C2')
9	4.91	84.3°
10	4.84	71.7°
11	3.98	78.9°
12	3.94	90.6°
13	3.39	86.4°
14	3.16	85.5°
15	1.72	82.9°
16	1.60	92.1°
17	1.49	99.1°
18	1.12	83.5°
19	1.08	84.0°

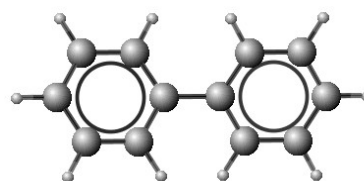


Fig. 2: General scheme of numbering for the biphenyl system.

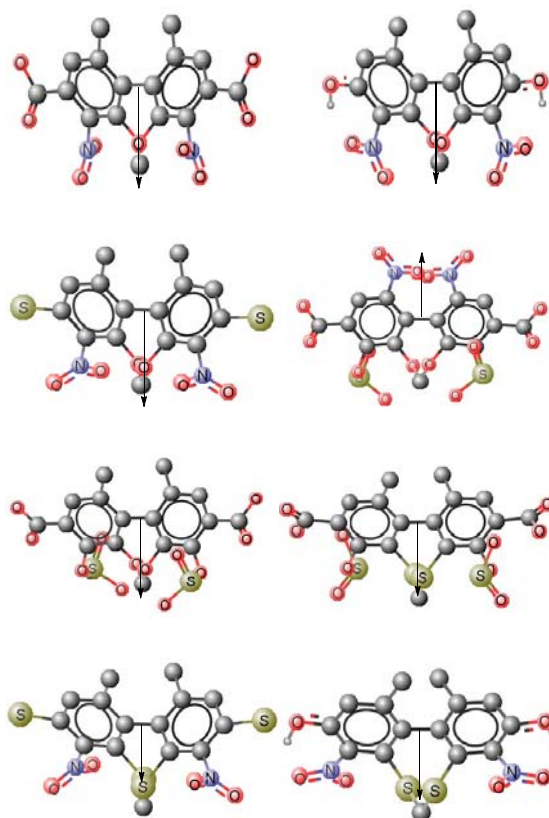


Fig. 3: Optimized structures showing the orientation of dipole moment of conformationally restricted biphenyl dopants (1-8).

Dipole moment of conformationally restricted chiral biphenyl dopant **1** containing methyl, carboxylate and nitro functional groups at positions 2(2 $\neq$ ), 4(4 $\neq$ ) and 5(5 $\neq$ ) respectively, was calculated 9.61 D whereas the dihedral angle between two rings (C2-C1-C1 $\neq$ -C2 $\neq$ ) was found 54.6 $^\circ$  and by comparing it with the reported values of dipole moment of benzene substituted derivatives, this was found very high [13]. The computed data shows that the dipole moment of compound **2** having methyl, hydroxyl and nitro substituent at 2(2 $\neq$ ), 4(4 $\neq$ ) and 5(5 $\neq$ ) was calculated 5.86 D and dihedral angle between two phenyl rings (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 53.3 $^\circ$  (Table-1). It is clear from the optimized structure of biphenyl compound **1** that the orientation of C=O of carboxylate group is in the same direction as the orientation of nitro group, and both of these groups i.e. (carboxylate and nitro) are enhancing the dipole moment. Therefore biphenyl compound **1** has higher dipole moment compared to **2**, which contains hydroxyl at the same position instead of carboxylate, however the orientation of the hydroxyl group is in the plane of biphenyl core instead of the orientation of the nitro group (coming out of the plane) (Fig. 3). Therefore the dipole moment of **2** has little contribution from the hydroxyl group.

The dipole moment of biphenyl compound **3** having thiol functional group at 4(4 $\neq$ ) instead of hydroxyl was 5.52 D and dihedral angle between the two rings (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 57.0 $^\circ$ . Although the thiol group lies in the same plane as the hydroxyl group in **2**, but sulphur is less electronegative and its polarization power is less effective compared to oxygen therefore biphenyl core **3** has a slight decrease in dipole moment. Similarly dipole of conformationally restricted biphenyl core **4** having nitro, carboxylate and sulphonic functional groups at 2(2 $\neq$ ), 4(4 $\neq$ ) and 5(5 $\neq$ ) positions was 4.49 D and dihedral angle (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 53.7 $^\circ$ . In biphenyl compound **4**, although the nitro and carboxylate have strong polarization effects but due to opposite orientation (C=O) of carboxylate and nitro groups the effect of polarization by each group is partially cancelled by the other one. Sulphonic group attached at the position 5(5 $\neq$ ) is oriented in a way that oxygen atoms are oriented out of plane and therefore have less impact on dipole moment as expected. Nitro group attached at position 2,2 $\neq$  has slightly more pronounced effect on polarization, that is also reflected by the orientation of dipole moment (Fig. 2) as well, due this the compound **4** has less dipole moment as compared to **3**. Dipole moment of biphenyl core **5** having methyl, nitro and sulphonic groups at 2,2 $\neq$ , 4,4 $\neq$  and 5,5 $\neq$  was found 3.76 D and

dihedral angle was 55.8 $^\circ$ . Oxygen atoms attached to the sulphonic group are oriented in the opposite directions as compared to the orientation of the dipole moment and minimizing the polarization effect.

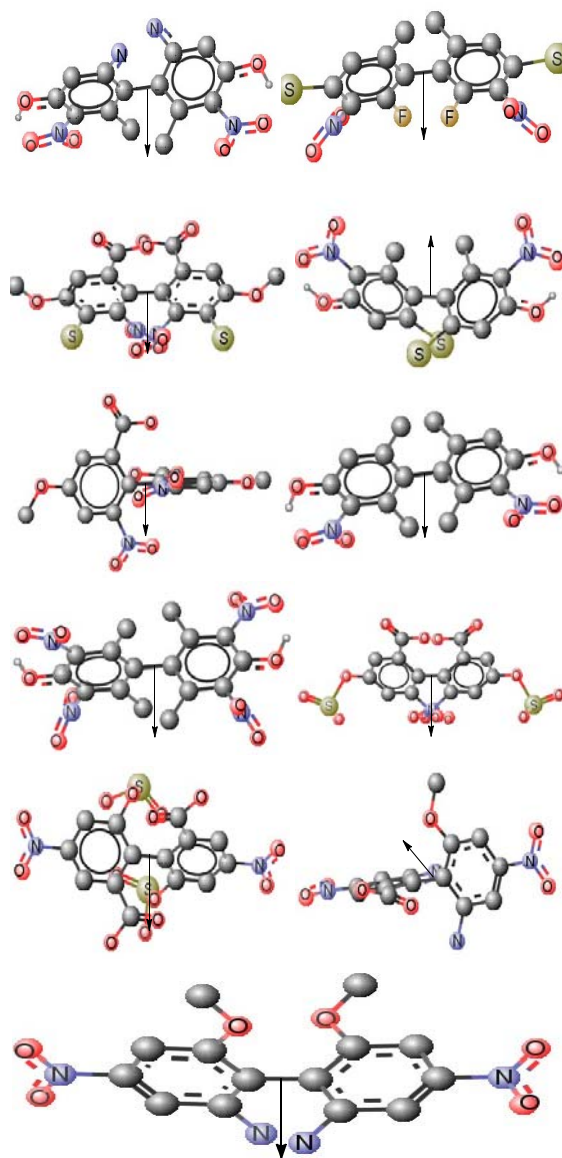


Fig. 4: Optimized structures showing the orientation of dipole moment of free rotating biphenyl dopants (9-19).

In biphenyl cores **6-8**, the oxygen bridge was replaced with sulphur and data shows these were less planar and low dipole moment was observed compared to the biphenyl cores **1-5**, is due the less polarization and more flexibility of sulphur as compare to oxygen. The dipole moment of biphenyl

core **6** having methyl, nitro and sulphonic group at 2(2 $\neq$ ), 4(4 $\neq$ ) and 5(5 $\neq$ ) was 4.47 D and dihedral angle between two phenyl rings was (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 75.5°. The dipole moment of biphenyl compound **7** having methyl, thiol and nitro functional groups at 2(2 $\neq$ ), 4(4 $\neq$ ) and 5(5 $\neq$ ) positions was 4.29 D and dihedral angle between two phenyl rings (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 75.2°, similarly dipole moment of biphenyl core **8** hydroxyl group instead of thiol in compound **7** at position 4(4 $\neq$ ) was 3.72 D and dihedral angle (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 79.5°. Biphenyl compounds (**6-8**) containing the sulphur bridge instead of oxygen has lower dipole moment because these are less planer due to the flexibility of sulphur. The polarization effect of groups attached to the biphenyl core is not too effective.

Conformationally unrestricted biphenyl cores i.e having free rotation of two phenyl rings around C1-C1 $\neq$  (**9-19**) were investigated as well and the computed data are given in Table-2. Dipole moment of biphenyl core **9** having amino, hydroxyl, nitro and methyl groups at the positions 2,2 $\neq$ , 4,4 $\neq$ , 5,5 $\neq$  and 6,6 $\neq$  was 4.91 D and dihedral angle was found 84.3°. Due to free rotation of two phenyl rings along the C1-C1 $\neq$ , polarization effect of attached groups to the phenyl core was not prominent as it was in the case of conformationally restricted (**1-8**) biphenyl cores. Dipole moment of conformationally unrestricted compound **10** having methyl, thiol, nitro and fluoro functional groups at 2(2 $\neq$ ), 4(4 $\neq$ ), 5(5 $\neq$ ) and 6(6 $\neq$ ) was 4.84 D and dihedral angle between two phenyl rings was 71.7°. Biphenyl core **10** was more planer as compare to **9** as reflected by dihedral angle and was due to the steric effects of groups attached to the biphenyl core. Dipole moment of biphenyl core **11** containing carboxyl, methoxy, thiol and nitro substituents at 2(2 $\neq$ ), 4(4 $\neq$ ), 5(5 $\neq$ ) and 6(6 $\neq$ ) positions was 3.98 D and dihedral angle between two phenyl rings (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 71.7°. In biphenyl core **11**, functional groups attached are oriented in the opposite direction of each other and cancelling the polarization effect of each other. Similarly dipole moment of biphenyl core **12** having methyl, nitro, hydroxyl and thiol functional groups at 2(2 $\neq$ ), 3(3 $\neq$ ), 4(4 $\neq$ ) and 6(6 $\neq$ ) was 3.94 D and dihedral angle (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 90.6°. Biphenyl core **13** having carboxylate, methoxy and nitro functional groups at 2(2 $\neq$ ), 4(4 $\neq$ ) and 6(6 $\neq$ ) was investigated and dipole moment was 3.39 D, dihedral angle (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 86.4°. Dipole moment of free rotating biphenyl core **14** having methyl, hydroxyl, nitro and methyl functionalities at 2(2 $\neq$ ), 4(4 $\neq$ ), 5(5 $\neq$ ) and 6(6 $\neq$ ) was 3.16 D, dihedral angle

(C2-C1-C1 $\neq$ -C2 $\neq$ ) was 85.5°. Biphenyl core **15** having methyl, nitro, hydroxyl, nitro and methyl substituents at 2(2 $\neq$ ), 3(3 $\neq$ ), 4(4 $\neq$ ), 5(5 $\neq$ ) and 6(6 $\neq$ ) showed dipole moment 1.72 D as well as dihedral angle (C2-C1-C1 $\neq$ -C2 $\neq$ ) between two phenyl rings was 82.9°. Although the biphenyl core **15** has same substitutes at all positions of two rings, but it's, dipole was due its non-planarity. Dipole moment of compound **16** having bulky substituents like carboxylate, sulphonic and nitro groups at 2(2 $\neq$ ), 4(4 $\neq$ ) and 6(6 $\neq$ ) was 1.60 D and dihedral angle (C2-C1-C1 $\neq$ -C2 $\neq$ ) was 92.1°. Biphenyl core **17** was investigated as well and computed data showed dipole moment 1.49 D and dihedral angle was 99.1°. Similarly dipole moment of biphenyl core **18** was 1.12 D and dihedral angle was found 83.5°. Conformationally unrestricted biphenyl core **19** showed dipole moment 1.08 D, and dihedral angle was 84.0°. In compound **19** nitro group attached was in the plane of biphenyl core as compare to others those have the nitro attached at 6(6 $\neq$ ) position, therefore in **19** the polarization effect of nitro was not effective and dipole moment of compound **19** was the least of all compounds, those were investigated. Optimized structures of all biphenyl cores (**1-19**) showed orientation of dipole moment toward the polar groups and almost in all cases it was oriented toward the nitro group attached to the biphenyl core.

## Experimental

All calculations were performed by using Gaussian 09 [14]. Visualization of the results/optimized geometry was achieved with Marvin view [15]. Geometry optimization of all biphenyl compounds (**1-19**) was carried out at 631+G(d) basis set by using the B3LYP method of DFT. Frequency analysis was performed at the same level of theory to confirm that all optimized geometries as true minima (no imaginary frequencies).

## Conclusion

In conclusion we have investigated the dipole moment of two types of dopants, with conformationally restricted and unrestricted core, as potential chiral dopants for liquid crystalline materials. Compound **1** containing dioxolane type bridge and having methyl, carboxylate and nitro at different positions of skeleton showed maximum dipole moment and was found 9.61 D whereas compound **19** having free rotating biphenyl rings showed the lowest dipole moment (1.08 D). We concluded that the conformationally restricted

biphenyl compound can act as best chiral dopant among all those we have investigated by using DFT studies.

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