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Electronic Structure Calculation of Banana-Shaped Liquid Crystals

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With Hückel tight-binding method, we have calculated the electronic structures for banana-shaped liquid crystal 1,3-phenylene bis [4-(4′-nonyloxy) phenylimino-methyl] benzoate, and the effects of the central core, the linkages (–COO– and –CH=N–) and the alkyl tails in the two-branched legs of the banana-shaped liquid crystal on the electronic structures have been discussed. Our results indicate that the energy differences between the lowest unoccupied molecular orbit and the highest occupied molecular orbit are predominantly affected by the central core and the linkages but not too much by the alkyl tails in the two branched legs of the banana-shaped liquid crystal.

Keywords: absorption; banana-shaped liquid crystal; electronic structures; electronic transition; Hückel tight binding method

1. INTRODUCTION

Small-molecular-weight organics have attracted intense attention since Tang and Vanslyke's report on the blue light emission from 8-hydroxyquinoline aluminum in 1987 [1–4]. As a result of the global-wide hunting activities, hundreds of small-molecular-weight organics were found to be highly luminescent in the visible spectral

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region, and some of them are highly luminescent liquid crystals (LCs) [5–10]. Being one novel class of small-molecular-weight LCs, banana-shaped LCs have been intensively investigated because of their ferroelectricity in the absence of molecular chirality [11–14]. In contrast to their well-studied electro-optical properties, their electronic structures and light-emitting properties have attracted little attention. The electronic structures of banana-shaped LCs, however, are critically important for the understanding of the optical absorptions and photoemissions from these banana-shaped LCs.

The aim of this work is to investigate the electronic structures for the firstly reported banana-shaped LC 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate. With Hückel tight-binding method, we have calculated the electronic structures of the banana-shaped LC 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate. The effects of the central core, the linkages (–COO– and –CH = N–) and the alkyl tails in the two branched legs on the electronic structures are to be discussed. Our results indicate that the energy differences between the lowest unoccupied molecular orbit (LUMO) and the highest occupied molecular orbit (HOMO) are predominantly affected by the central core and the linkages but not too much by the alkyl tails in the two-branched legs. On the basis of our calculations, possible electronic transitions are proposed for the banana-shaped LC.

2. COMPUTATION DETAILS

BICON-CEDiT, an extended Hückel band structure and oscillator strength calculation package, was developed by the group of Prof. Gion Calzaferri at University of Berne, Switzerland [15]. It is a set of FORTRAN programs that allow extended-Hückel tight-binding calculations for 1D-3D compounds to get their band structures and density of states. Using the extended Hückel tight binding program, we calculated the electronic structures of the banana-shaped LC in order to give a semi-quantitative description on its optical properties. In order to obtain the optimal molecular structure for the electronic structure calculation, we performed a geometry optimization of an individual molecule of the LC at AM1 level and then extracted the geometry of the molecule. The AM1 program was implemented in the MOPAC package (Quantum Chemistry Program Exchange, Indiana University, USA). The standard Slater parameters for C, H, O, and N atoms were adopted from Ref. [16].

3. RESULTS AND DISCUSSION

To illustrate the effects of the central core, the linkages (–COO– and –CH = N–), and the alkyl tails in the two branched legs on the electronic structures of the banana-shaped LC, we selected three kinds of banana-shaped compounds 1,3-phenylene bis (formic acid methyl ester), 1,3-phenylene bis (formic acid methyl ester), and 1,3-phenylene

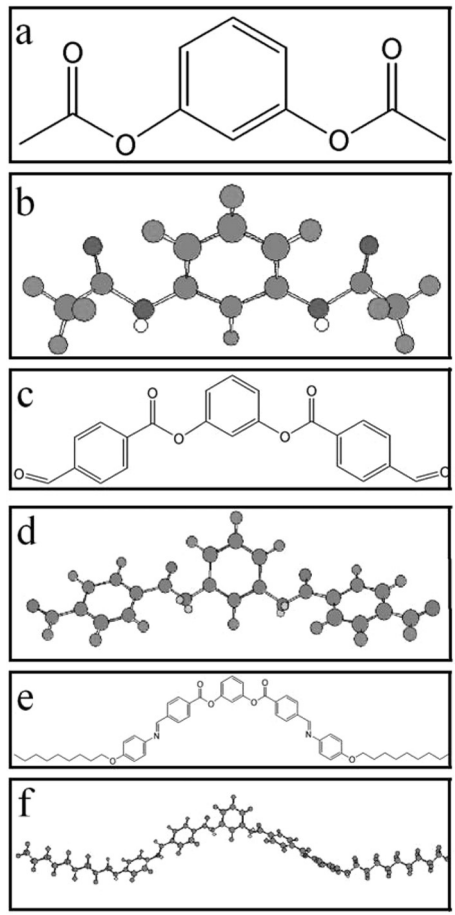

FIGURE 1 Panels (**a**) and (**b**): Molecular structure and cylindrical-bonds model of 1,3-phenylene bis (formic acid methyl ester). Panels (**c**) and (**d**): Molecular structure and cylindrical-bonds model of 1,3-phenylene bis (4-formyl) benzoate. Panels (**e**) and (**f**): Molecular structure and cylindrical-bonds model of 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate.

bis (4-formyl) benzoate for our investigation. Their molecular structures and corresponding cylindrical-bonds models are shown in Figure 1. The panels (**a**) and (**b**) of Figure 1 depict the molecular structure and cylindrical-bonds model of 1,3-phenylene bis (formic acid methyl ester), the panels (**c**) and (**d**) shows the molecular structure and cylindrical-bonds model of 1,3-phenylene bis (4-formyl) benzoate, while the panels (**e**) and (**f**) illustrates the molecular structure and cylindrical-bonds model of 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate. From the top panel (**a**) to the bottom panel (**e**) in Figure 1, the banana-shaped molecule grows progressively with the addition of the functional groups step by step.

Using the extended Hückel tight binding program, we calculated the electronic structures for the banana-shaped compound 1,3-phenylene bis (formic acid methyl ester). Figure 2 shows the energy levels (left panel) and density of states (right panel) of the banana-shaped compound 1,3-phenylene bis (formic acid methyl ester). From the calculated value of the Fermi energy ε_f, we can determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for this banana-shaped compound. The determined LUMO and HOMO are shown in the left panel of Figure 2. Once the LUMO and HOMO are determined, the energy

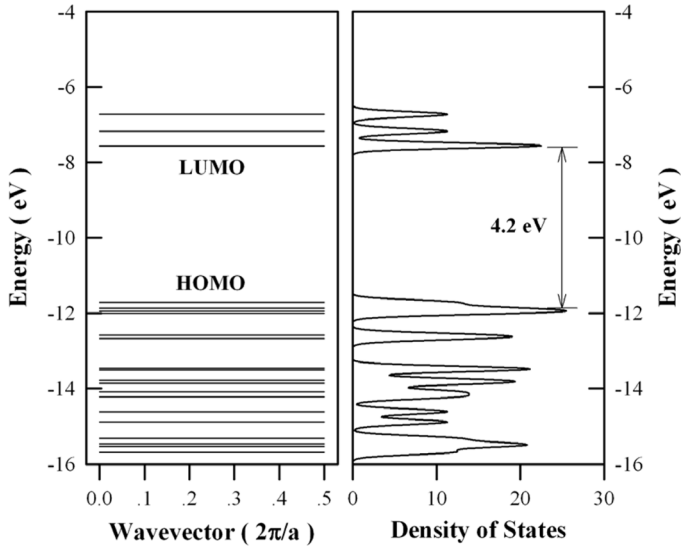

FIGURE 2 Energy levels (left panel) and density of states (right panel) of the banana-shaped compound 1,3-phenylene bis (formic acid methyl ester).

difference between the LUMO and HOMO can be straightforwardly obtained. From Figure 2, the energy difference between the LUMO and HOMO is about 4.2 eV for this banana-shaped compound. Because the energetically favoured electron promotion is from the HOMO to LUMO, the resulted absorption will be located at about 295 nm. Thus, the absorption of 290 nm light renders this substance colourless.

Figure 3 depicts the energy levels (left panel) and density of states (right panel) of the banana-shaped compound 1,3-phenylene bis (4-formyl) benzoate. From Figure 3, the energy difference between the LUMO and HOMO is about 4.0 eV for this banana-shaped compound. Therefore, the optical absorption of this banana-shaped LC will take place at about 300 nm. Such kind of optical absorption at 310 nm light renders this substance colourless. Comparison of the results in Figure 2 to those in Figure 3 reveals that the energy difference between the LUMO and HOMO decreases a little bit. The extended conjugation in the banana-shaped LC should be responsible for the slight decrease in the energy difference because increased conjugation can bring the HOMO and LUMO orbitals closer. It is interesting that an energy level appears at about −9.52 eV in the electronic structures of the banana-shaped compound 1,3-phenylene bis (4-formyl) benzoate. It locates at 2.2 eV above the HOMO but 1.7 eV

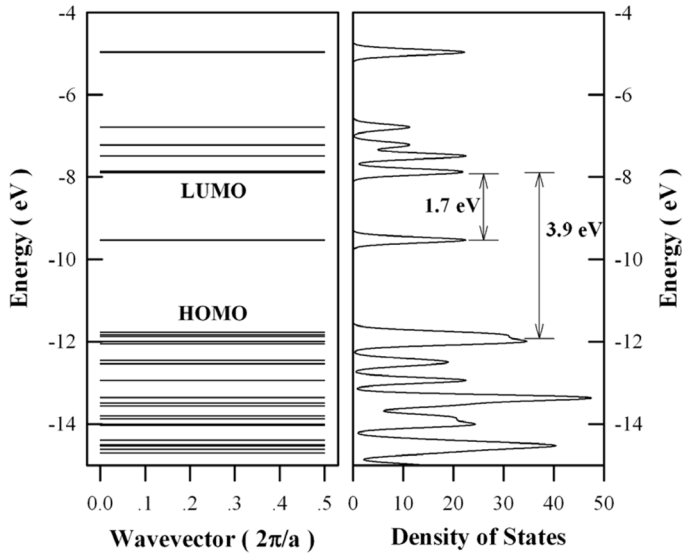

FIGURE 3 Energy levels (left panel) and density of states (right panel) of the banana-shaped compound 1,3-phenylene bis (4-formyl) benzoate.

below the LUMO of the banana-shaped compound. The appearance of this energy level can be assigned to the non-bonding of the lone pairs in the compound. In general, organic compounds containing atoms with lone pairs (non-bonding electrons) are capable of forming non-bonding orbital n. Although the $\pi \rightarrow \pi^*$ transitions make the substance colourless, the $n \rightarrow \pi^*$ transitions at about 1.7 eV possibly renders the compound coloured.

Figure 4 shows the energy levels (left panel) and density of states (right panel) of the banana-shaped compound 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate. Compared to the results in Figure 3, the results in Figure 4 demonstrate that the energy difference between the LUMO and HOMO does not change too much.

The calculated electronic structures are important to understand the optical properties of the banana-shaped LC. For an example, the calculated electronic structures are helpful to predict the electronic transitions and the subsequent optical absorptions in the banana-shaped LC. When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. Figure 5 represents a schematic

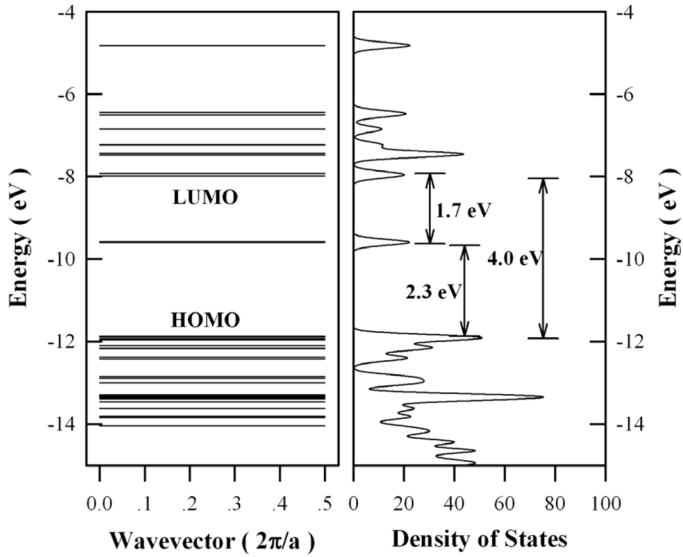

FIGURE 4 Energy levels (left panel) and density of states (right panel) of the banana-shaped compound 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate.

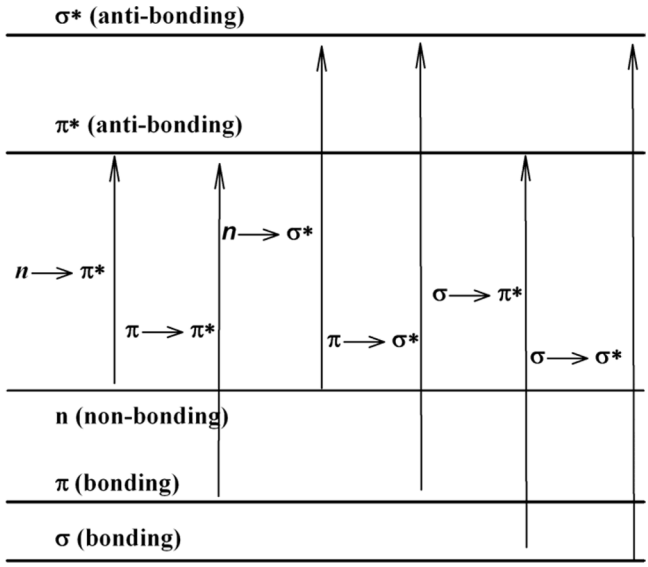

FIGURE 5 Schematic illustration on the various kinds of electronic excitation that may occur in the banana-shaped LC 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate.

illustration of the various kinds of electronic excitation that may occur in the banana-shaped LC 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate. Of the six transitions outlined, only the two lowest energy ones ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$) are often achieved by the energies available in the 200 to 800 nm spectrum. As shown in Figure 4, energetically favoured electron excitation will take place at 4.0 (310 nm) and 1.7 eV (730 nm), respectively, in our banana-shaped LC 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate. Furthermore, electronic structures can find important applications in designing highly efficient photoactive LC devices. For an example, the knowledge on the electronic structures of an azo-containing banana-shaped LC helps to solve the key problem on how much photon energy is required to active the *trans-cis* photochemical isomerization in this substance.

To check the validity of the Gion Calzaferri Hückel tight-binding method, we calculated the electronic structures for our banana-shaped LC by using density functional theory. In the density functional theory calculation, we employed the same molecular conformation as we used in the Gion Calzaferri Hückel tight-binding method, and our calculated energy difference between the LUMO and HOMO was 0.11 eV

larger than that derived from Hückel tight-binding calculation. Therefore, the Gion Calzaferri Hückel tight-binding method is suitable for a preliminary level investigation on the electronic structures of the banana-shaped LC.

In our electronic structure calculations, the solvent effects have not been considered. To investigate the solvent effects on the electronic structures of our banana-shaped LC, we calculated the electronic structures of the banana-shaped LC in solvents of carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and chloromethane (CH_3Cl) by using density functional theory and molecular dynamics simulations. Our preliminary results demonstrate the weak solvent effects on the electronic structures of the banana-shaped LC because the energy differences between LUMO and HOMO decreases a little bit as the solvent polarity increases.

Compared to the weak solvent effect, the torsional degrees of freedom pose significant effects on the electronic structures of the banana-shaped LC. We optimized the geometry of the banana-shaped LC under two different conditions: (i) by optimizing all the degrees of freedom with AM1 program; and (ii) by imposing a fully planar conformation for the conjugated segments in the branched wings where two benzene rings are connected by the Schiff linkage –CH = N–. With extended Hückel tight-binding method, we investigated the impact of the torsional degrees of freedom on the electronic structures of the banana-shaped LC. Our results indicate that the fully relaxed conformation is the most stable and the energy differences between its LUMO and HOMO is lower in energy by 1.8 eV with respect to the planar conformation. It is understandable when the strong steric repulsion between hydrogen atoms in the fully planarized geometry of the banana-shaped LC is taken into consideration.

4. CONCLUSION

In summary, we have calculated the electronic structures for banana-shaped LC 1,3-phenylene bis [4-(4′-nonyloxy) phenyliminomethyl] benzoate with Hückel tight-binding method. One the basis of the calculated electronic structures, the effects of the central core, the linkages (–COO– and –CH = N–) and the alkyl tails of the two branched legs on the electronic structures have been discussed. Our results indicate that the energy differences between the LUMO and the HOMO are predominantly affected by the central core and the linkages but not too much by the alkyl tails in the two-branched legs of the banana-shaped LC. The knowledge on the electronic transitions is helpful to understand the optical properties of the banana-shaped LCs.

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