Organic Electronics 59 (2018) 196–201

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Structure-property relationships of coronene in external electric field

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ARTICLE INFO

Keywords:
External electric fields
Coronene
NBO charge
NLO
Aromaticity

ABSTRACT

Coronene as the smallest molecular approximation of polycyclic aromatic hydrocarbon (PAH) has large π-conjugated orbital. In the present work, under the action the external electric fields (E_{ext}, perpendicular to molecular plane), the geometric structure of **Coronene** from plane to "bowl" and "curly". Interestingly, there is a redistribution of orbitals in E_{ext} would give rise to significant effect on the NBO charge, which the main negative charge is gradually concentrated in the center-six-membered with the increasing E_{ext}. The distinct charge transfer phenomenon brought about a remarkable nonlinear optical (NLO) property and changed the location of the main aromaticity. Surprisingly, the irregular phenomena of these properties would be happened in same E_{ext} range: 5.00×10^{-2} to 6.00×10^{-2} au, which is respond to the structural change. We hope present work can provide a new strategy to design the high-performance electro-optical materials for large π-conjugated centrosymmetric system.

1. Introduction

Coronene is a representative π-conjugated peri-condensed polycyclic aromatic hydrocarbon (PAH) with a highly planar D_{6h} symmetry in which all C-C bonds of the central ring are shared with the peripheral rings, which occurs in nature as the mineral carpathite; at the same time, **Coronene** can be considered as the smallest molecular approximation of a graphite sheet [1] because of its structure; it is an important building block for the construction of novel optoelectronic materials. On the other hand, large PAHs such as **Coronene** are components of the interstellar medium [2] and possibly plays a basic role in interstellar extinction [3,4]; in addition, PAHs have received wide research interest because of their interesting properties, such as self-organization behaviors [5–8], high thermal conductivity [9], high mechanical stability [10], and unusual electronic properties [11–14] etc., which make them promising candidates for use in organic semiconducting devices including organic field-effect transistors (OFETs) [11,15–17], organic photovoltaics (OPVs) [18], and organic light-emitting diodes (OLEDs) [19].

On the other hand, applied external electric fields (E_{ext}) are often used to create new types of materials by control and modulate the electronic properties method, such as, organic conductors [20], hydrogen bonding complexes [21], carbon nanotubes [22,23], and graphene [20,24,25]. But beyond that, it is the E_{ext} effect that is widely applied to probe fundamental properties of matter and to provide important information about molecular structure [26], molecular dynamics [27–29], optical properties [30], conformational and tautomeric equilibria [31].

Most recently, Prof. Hashemianzadeh et al. investigated the influence of a transverse electric field on mechanical properties, electronic and mechanical properties of carbon, boron nitride, and silicon carbide nanotubes, which shown that the nanotubes exposed to the electric field have more effective stiffness in comparison to the similar case in the off-field condition [32]. Nakano group have shown that the static external electric field is applied to enhance the second hyperpolarizability in singlet diradical molecules [33,34]. The electric field induced nonlinear optical (NLO) switch of a push–pull bisboronate chromophore has been reported by Pascal G. Lacroix et al. [35]. In addition, our group has investigated the electrostatic interaction response of phenalenyl π-Dimer under external electric field [36] and the second-order NLO response of HArF system optimized after different external electric field [37].

The goal of present work is to reveal the effect of E_{ext} on electronic property of large π-conjugated centrosymmetric system. In this work, the deformations of **Coronene** in E_{ext} have been investigated, which the various E_{ext} is applied along Z-axis direction of **Coronene** (Scheme 1).

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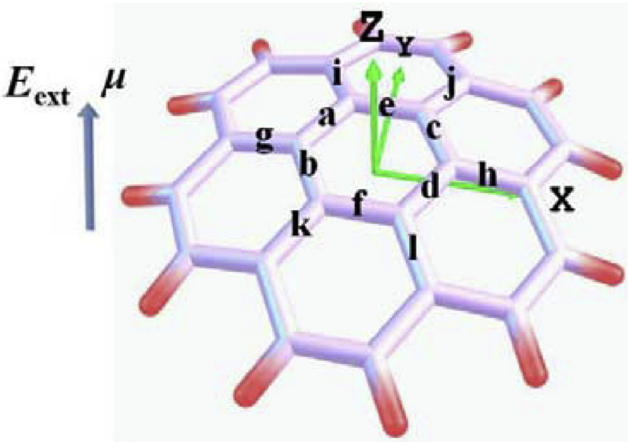
https://doi.org/10.1016/j.orgel.2018.05.013
Received 16 March 2018; Received in revised form 9 May 2018; Accepted 9 May 2018



Scheme 1. Illustration of **Coronene** at the E_{ext}.

Furthermore, the orbitals analysis has been carried out by us. It is noteworthy that the change of orbitals in E_{ext} caused a series of changes in chemical property, e.g. the natural bond orbital (NBO) charge, NLO properties and aromaticity. We hope present work can provide a new strategy to design the high-performance electro-optical materials for large π-conjugated centrosymmetric system.

2. Computational details

The E_{ext} was applied along Z-axis direction which is perpendicular to molecular plane (Scheme 1). The optimized geometric structures of **Coronene** with all real frequency in a series of E_{ext} 1.00×10^{-2} to 6.00×10^{-2} au (1 au = 5.142×10^{9} V/cm) were obtained at the level of B3LYP/6-31G*. The optimized geometric structures were carried out structural analysis and the electric dipole moment analysis. Next, the NBO analyses were performed at the B3LYP/6-31G* level. In addition, the selected coulomb-attenuated hybrid exchange-correlation density functional (CAM-B3LYP) method with 6-311 + G* basis set was used for the calculations of the static first hyperpolarizability (β_0) values [38–43] for **Coronene**, because of the CAM-B3LYP can good explore the long-range interaction and charge-transfer excitation systems recently [44,45]. The selected BHandHLYP/6-311 + G* and M062X/6-311 + G* method have been used for the further calculations of β_0 values under E_{ext} for all molecules. At the same time, the aromaticity of all molecules has been to made an estimate by using the nucleus-independent chemical shifts (NICS) values scan method at the B3LYP/6-31G* level, which the ghost atom (Bq) has serve as the NICS probe along Z-axis direction and the distance of probes is 8 Å perpendiculars to the plane with a step size of 0.2 Å. All calculations are performed based on density functional theory (DFT) with the Gaussian 09 program [46].

3. Results and discussion

3.1. The structural of Coronene in external electric field

3.1.1. The geometric structures of Coronene in external electric field

In order to explore the effect of E_{ext} on deformation for **Coronene**, the geometric structures for **Coronene** were optimized using the B3LYP/6-31G* method from $E_{ext} = 1.00 \times 10^{-2}$ to $E_{ext} = 6.00 \times 10^{-2}$ au at a 1.00×10^{-2} au step, which the E_{ext} along Z-axis direction and perpendicular to molecular plane. The selected structural parameters of **Coronene** in E_{ext} have been listed in Table 1. **Coronene** presents an obvious plane structure with inerratic bond length in the off-E_{ext} condition, in which $r_{c\text{-}c}$ (a-f) and $r_{c\text{-}c}$ (g-l) (Scheme 1) is isometric, respectively. Significantly, the increasing E_{ext} do distort the molecular plane. When E_{ext} gradually increase from 0.00×10^{-2} to 5.00×10^{-2} au, the

Table 1
Variation in bond lengths (Å), bowl depth (Å) and electric dipole moments (Debye) of **Coronene** at the B3LYP/6-31G* level in various field strengths (au).

$E_{ext} \times 10^{-2}$	$r_{c\text{-}c}$ (a-d)	$r_{c\text{-}c}$ (e-f)	$r_{c\text{-}c}$ (g-h)	$r_{c\text{-}c}$ (i-l)	Bowl depth	μ
0.00	1.427	1.427	1.422	1.422	0.00	0.00
1.00	1.428	1.428	1.422	1.422	0.07	2.11
2.00	1.428	1.428	1.422	1.422	0.14	4.28
3.00	1.430	1.430	1.423	1.423	0.23	6.58
4.00	1.432	1.432	1.425	1.425	0.34	9.11
5.00	1.436	1.436	1.429	1.429	0.47	11.97
5.10	1.437	1.437	1.429	1.429	0.49	12.28
5.20	1.437	1.437	1.429	1.429	0.50	12.60
5.21	1.438	1.437	1.429	1.429	–	12.63
5.23	1.438	1.437	1.429	1.430	–	12.70
5.30	1.438	1.437	1.429	1.430	–	12.95
5.40	1.439	1.437	1.429	1.430	–	13.46
5.50	1.440	1.436	1.428	1.431	–	14.10
5.60	1.440	1.434	1.427	1.431	–	14.83
5.70	1.441	1.433	1.426	1.431	–	15.58
5.80	1.442	1.432	1.426	1.432	–	16.37
5.90	1.443	1.431	1.424	1.432	–	17.18
6.00	1.444	1.429	1.423	1.433	–	18.00

$r_{c\text{-}c}$ (a-f) is gradually elongated from 1.427 to 1.436 Å (Fig. 1a and Table 1) and the $r_{c\text{-}c}$ (g-l) (Scheme 1) is gradually elongated from 1.422 to 1.429 Å (Fig. 2a and Table 1). Surprisingly, the isometric $r_{c\text{-}c}$ (a-f) and $r_{c\text{-}c}$ (g-l) were split in $E_{ext} = 5.00 \times 10^{-2}$ ~ 6.00×10^{-2} au (Figs. 1b and 2b). $r_{c\text{-}c}$ (a-d) and $r_{c\text{-}c}$ (i-l) elongation to 1.444 and 1.433 Å, while $r_{c\text{-}c}$ (e-f) and $r_{c\text{-}c}$ (g-h) shrink to 1.429 and 1.423 Å, respectively (Table 1). The isometric bond length suggests that the geometric structure of **Coronene** from plane to "bowl" with the E_{ext} increasing to 5.00×10^{-2} au, while the unequal bond length happened in $E_{ext} = 5.00 \times 10^{-2}$ ~ 6.00×10^{-2} au indicates that the geometric structure of **Coronene** from "bowl" to "curly". At the same time, the change further indicates that there is an electric field threshold for the deformation between the $E_{ext} = 5.00 \times 10^{-2}$ and $E_{ext} = 6.00 \times 10^{-2}$ au.

In order to explore the electric field threshold, the geometric structures for **Coronene** are optimized using the B3LYP/6-31G* method from $E_{ext} = 5.00 \times 10^{-2}$ to $E_{ext} = 6.00 \times 10^{-2}$ au at a 0.10×10^{-2} au step. We can observe from Fig. 1b that the obvious electric field threshold for $r_{c\text{-}c}$ (a-f) is 5.21×10^{-2} au, which $r_{c\text{-}c}$ (a-d) is 1.438 Å and $r_{c\text{-}c}$ (e-f) is 1.437 Å. Curiously, the electric field threshold for $r_{c\text{-}c}$ (g-l) is 5.23×10^{-2} au, which $r_{c\text{-}c}$ (g-h) is 1.429 Å and $r_{c\text{-}c}$ (i-l) is 1.430 Å (Fig. 2b). The different electric fields threshold for unequal bond length indicate that there are three deformations for **Coronene** in $E_{ext} = 0.00 \times 10^{-2} \sim E_{ext} = 6.00 \times 10^{-2}$ au: (1) when $0.00 \times 10^{-2} < E_{ext} < 5.21 \times 10^{-2}$ au, the geometric structure of **Coronene** from plane to "pure bowl" with a gradually deepening bowl depth from 0.00 to 0.50 Å; (2) when $5.21 \times 10^{-2} < E_{ext} < 5.23 \times 10^{-2}$ au, the geometric structure of **Coronene** is between "bowl" and "curly"; (3) when $E_{ext} > 5.23 \times 10^{-2}$ au, the geometric structure of **Coronene** is "pure curly".

3.1.2. The molecular orbital of Coronene in external electric field

Coronene as the smallest molecular approximation of polycyclic aromatic hydrocarbon (PAH) has large π-conjugated orbital. **Coronene** presents obvious degenerate molecular orbital energies of (HOMO, HOMO-1) pair, (HOMO-2, HOMO-3) pair, (LUMO, LUMO + 1) pair and (LUMO + 2, LUMO + 3) pair in the off-E_{ext} condition (Fig. 4a). We have found from Fig. 4a that the four-pair molecular orbital energies continue to preserve degeneracy with a steady decrease with the increasing E_{ext}. Significantly, as well as the unequal bond length, the non-degenerate molecular orbital energies pairs would happen in $E_{ext} = 5.00 \times 10^{-2}$ ~ 6.00×10^{-2} au with increasing molecular orbital energies except LUMO + 2. At the same time, the drastic effect of