A Computational Study of the Electronic Properties of Heterocirculenes: Oxiflowers and Sulflowers

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ABSTRACT: This study investigated the relationship of electronic properties with some structural parameters of two circulene classes: Sulflowers and Oxiflowers. It is found that correlations between the HOMO-LUMO gap and some electronic properties of these circulenes are opposite to those of linear conjugated structures. Moreover, a new hybrid molecule, called an Oxisulflower, is proposed to be a potential structure for synthesizing as Sulflower. Also, a brand-new descriptor, namely, the "degree of non-planarity," is evaluated with excellent correlations with the HOMO-LUMO gap of molecules in Oxiflower and Sulflower classes. The correlations have also shown that the steric characteristic of a structure can be controlled to modulate its band gap for studying the prediction science of the electronic properties in developing organic semiconductors.

1. INTRODUCTION

Thiophene-based materials have been used in commercial applications of organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) because of their chemical versatility and favorable electrical and optical properties.1,2 Specifically, sulfur atoms could form two-dimensional (2D) and three-dimensional (3D) structures via intermolecular S···S interaction that enhances transport properties, which are essential in the design of these electronic materials.3

Octathio[8]circulene (C16S8) in Figure 1 first successfully synthesized by Nenajdenko et al. in 2006 had a unique set of electronic and thermal dynamics properties in thin films and was found to be a potentially good electron donor.4 Another name of the circulene is “Sulflower”—a combination of “sulfur” and “flower” as given by the authors.

This finding has motivated a number of studies about [8]circulenes for many years subsequently. Different elements such as nitrogen, oxygen, selenium, tellurium, and even silicon were used in place of sulfur in the circulene ring, and their physical and chemical properties were also reported in a number of reports.5−9 For instance, the aromaticity of planar hetero[8]-circulenes and their charged ions were studied by nucleus-independent chemical shift and gauge-including magnetically induced current methods. Similarly, a study of the aromaticity and photophysical properties of unsymmetrical azatrioxa[8]-circulenes was also reported.6,10 Regarding the thiophene-based compounds, a study depicted that underlying the approximations, time-dependent density functional theory (TD-DFT) gave qualitatively incorrect results of electronically excited states.11 Moreover, Maeda et al. synthesized azahelicenes and diaza[8]circulenes through the intramolecular Scholl reaction.12 Another study of interest was to make a comparison between the Selenosulflower (tetraselenotetrathio[8]circulene) and the Sulflower. It was expected that the Selenosulflower exhibited higher charge mobility in the solid state as selenium was a more polarizable element than sulfur and less stable under oxidizing agents.13 Thus, it was investigated if an appearance of an oxygen element would lead to desired physical properties or not. Moreover, there is a lack of studies about oxygen completely replacing the sulfur atoms in the Sulflower, although a furan ring is comparable with a thiophene ring in electronic and aromatic properties.14,15

Figure 1. 2D structure of a Sulflower.

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Almost all published papers studied molecules whose frameworks were built in different types of fused rings such as pyrrole, thiophene, and furan around the inner eight-membered cyclooctatetraene (COT) ring. However, Christoph et al. suggested that the biggest circulene with 20 rings of hydrocarbon components can be synthesized,\textsuperscript{25} or a [4]circulene molecule with a bowl-shaped structure was successfully prepared.\textsuperscript{1}\textsuperscript{1} Therefore, it is necessary to discover new structures, especially structures having various numbers of fused rings and also different types of heterocycles joined together. These structures are needed to be proven stable for synthesis, and valuable properties should be studied for the preparation of semiconductor materials.

In this study, a survey is established to assess correlations between electronic properties and several structural parameters of the Sulflower class (thiophene ring-circulated) and Oxiflor class (furan ring-circulated). Consequently, an Oxiflor and an OxiSulflower are new potential structures suggested to be synthesized by experimentalists with their promising electronic characters to be discovered in the future. Along with the “degree of π-orbital overlap”, a quantity related to the planarity of linear and angular polycyclic aromatic hydrocarbons that was published in our previous papers, a new descriptor—called the “degree of non-planarity”—also can be quantified with excellent correlations with the HOMO-LUMO gap.

2. COMPUTATIONAL DETAILS

2.1. Computational Methods. A frontier orbital energy gap is an important value to study the charge transport of the structures and the related physical properties in solid and liquid states.\textsuperscript{20,21} In this study, for each molecule in data sets, the 3D structures are fully optimized at the level of theory B3LYP/6-31+G(d,p) DFT method\textsuperscript{9,22} by using the GAUSSIAN\textsuperscript{99} program.\textsuperscript{2} The B3LYP method is chosen for its rather accurate predictions in calculating the HOMO-LUMO gap of heterocycles, especially thiophene and furan derivatives in dye compounds.\textsuperscript{25,26} Since these classes contain conjugated systems such as thiophene- and furan-based materials (lone pairs), the basis set is often added to diffuse functions to calculate more accurately the optimization and polarizability properties.\textsuperscript{25,26}

In this study, there are two sets of molecules formed. First, a ring-annulated set is composed by annulated oligo-furans and oligo-thiophenes (C\textsubscript{2}-C\textsubscript{m}X\textsubscript{n}H\textsubscript{4}; X: O and S; m = 1–5); this set is used to re-assess the possibility of the basis set of B3LYP/6-31+G(d,p) for collecting the strain energy parameter, compared to the PBE method in a previous study. Second, another one is the ring-circulated set consisting of circulated rings of furans (C\textsubscript{n}O), with n from 11 to 16 corresponding to the numbers of fused furan rings in the Oxiflor class and circulated rings of thiophenes (C\textsubscript{n}S), with n from 6 to 11 in the Sulflower class (Figure 2). All their structural parameters and electronic properties are presented in Tables S1 and S2 in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Relationship of the Number of Fused Rings and Structural Properties. 3.1.1. Relationship of the Number of Fused Rings and Strain Energies of Circulenes. In the previous paper, the Sulflower molecule was predicted by using the PBE method before synthesizing.\textsuperscript{27} In order to get the agreement between the two papers, there is a comparison of the trend of the strain energies of the two methods: B3LYP and PBE. The results are shown Figure S1 in the Supporting Information. This comparison confirms that the B3LYP method is suitable to be performed in the whole study because the PBE method calculates electronic properties less accurately than the B3LYP method.\textsuperscript{28}

To determine the strain energies of Oxiflowers, the same process as the calculation of the strain energies of Sulflowers is applied. Figure 3 shows that there is also a similar trend that presents the relationship between the number of fused rings and the strain energies of Oxiflowers. The 13-furan-fused molecule has the least strain energy in the Oxiflor class, which is a little bit lower than the 14-furan-fused ring. However, the Oxiflor with 14 fused rings is suggested to be synthesized as it has an even number of fused rings, which is more conveniently approached from symmetric fragments.

3.1.2. Relationship of the Number of Fused Rings and Frontier Orbital Energies. Figure 4A,B shows that the opening of the gaps along with the increase in the number of fused rings results from ascending LUMO levels, while the HOMO values of flowers almost do not change significantly. This is an unusual change and is rarely observed with the opening of the conjugated system. The gaps have close values at three points: from 13 to 15 furan-fused rings in the Oxiflor and from 8 to 10 thiophene-fused rings in the Sulflower. In general, the structure with more rings fused together has a larger band gap.
structure. Normally, for simple molecules, the structure with a small band gap has a high polarizability and the one with a larger band gap has a lower polarizability. The importance of this property was investigated by Kamada et al., who conducted a study of a correlative comparison of polarizabilities of furan homologues: furan (C₄H₄O), thiophene (C₄H₄S), selenophene (C₄H₄Se), and tellurophene (C₄H₄Te) by the Ab Initio Molecular Orbital Method. In a study of electronic correlations in oligo-acene and oligo-thiophene organic molecular crystals, it was shown that the polarizability per unit volume around a molecule increased with the opening of the conjugated system.

In Figure 5, the plot shows that there is an excellent correlation between the increase in the size of the conjugated structures such as Oxlowers and also Sulflowers. Both the R² values of the two classes are 0.99.

### 3.2. Relationship of HOMO-LUMO Gaps and Structural Properties

#### 3.2.1. Relationship of HOMO-LUMO Gaps and Strain Energy

Before investigating the relationship of HOMO-LUMO gaps and structural parameters, the aromaticity indices, namely, the harmonic oscillator model of aromaticity (HOMA)/harmonic oscillator model for heterocycle electron delocalization (HOMHED) values, were suggested to be potential indices that could be correlated to the physical and chemical properties of the aromatic compounds. However, after plotting these indices with the HOMO-LUMO gaps, there were no clear correlations.

Another assessment is the plot of the strain energies of Oxlowers and Sulflowers with the HOMO-LUMO gaps in Figure 6. There are fair correlations between the gaps of Sulflowers and Oxlowers and strain energies with R² = 0.65 and R² = 0.58, respectively.

#### 3.2.2. Relationship of HOMO-LUMO Gaps and Polarizability

In a paper, when comparing fluorobenzene to iodobenzene structures, the more polarizable halogenobenzene had a lower HOMO-LUMO gap. Particularly, the most polarizable molecule—iodobenzene—had the smallest gap. Similarly, the more fused ring added into a linear polycyclic aromatic hydrocarbon was known to increase polarizability, also corresponding to a lower band gap. However, in the circulene class, there is an opposite trend compared to previous papers in Figure 7. From six- to eight-fused-ring Sulflowers, the flower having a larger HOMO-LUMO gap interestingly possesses a higher polarizability. There is also a similar trend in the case of 11- to 14-fused-ring Oxlowers. This result suggests an additional conclusion for the relationship between the HOMO-LUMO gap and the polarizability in the circulene class, which is different from the linear molecules used in works published before.

### 3.3. Degree of Non-planarity Descriptor

#### 3.3.1. Determination of the Degree of Non-planarity

Preliminary studies have shown that the planarity of a structure in a conjugated system affects the delocalization of electrons, leading to a considerable change in HOMO-LUMO gaps. However, there is a lack of documents reporting about a factor that quantifies the
planarity of a molecule and assesses the planarity with electronic properties. Based on the trend of the bond of molecules in Figure 8, that factor is called the “degree of non-planarity” (DNP). The DNP is defined to be an average of the different angles that are formed between the bonds that fused two rings and the plane going through most atoms in the core of the structure, and its unit is angular degree, shown in Figure 9. The value of the degree of non-planarity is determined by the following steps.

Step 1. Determine the C—C bond fusing the rings together, which is in bold in Figure 10.

Step 2. (a) A reference point is established at the center of the ring. When the rings that have all carbon atoms in the core are on “an absolute plane”, it is easy to find the point. However, in the case that the core carbons are not planar together, the point is on another plane. The new plane goes through most carbon atoms, so it is called “a relative plane”, like the cases of the 16-furan-ring Oxiower and 11-thiophene-ring Sulfower. (b) After determining the reference point in part (a), every angle that is formed by the C—C bonds (bold in Figure 10) with an absolute/relative plane (Figure 9) is calculated.

Step 3. After calculating each angle of the specific C—C fused bond, the average of the angle values is taken. Note that all angles are absolute values, or a positive number. Eventually, the average value is subtracted by 180° and the final value is called the degree of non-planarity. Its unit is angular degree. The structure having a larger DNP is the more non-planar molecule.

3.3.2. Relationship of the Degree of Non-planarity with HOMO-LUMO Gaps. In Figure 11, it is surprisingly observed that there are excellent correlations between the degree of non-planarity and the HOMO-LUMO gaps in both Oxiower and Sulfower classes. Particularly, in each class, the structure having a larger degree of non-planarity has a smaller HOMO-LUMO gap, meaning that the more non-planar structure has a lower gap. This trend is opposite to the normal in which a more planar structure often has the lower band gap. In previous papers, non-planarity was a reason that our previous rule to predict the band gap through the degree of $\pi$-orbital overlap value was broken; specifically, many non-planar structures were out of the trend.18,19 This is the first time that a quantity of non-planarity is introduced in a strong correlation to the gap, supporting the idea that the HOMO-LUMO gap of a structure can be correlatively modulated by controlling the steric factor.

In Figure 4A, when the HOMO levels are insignificantly different, the LUMO orbital levels are considered a reason for the unusual trend of the gap with non-planarity. For example, the LUMO values of the 12-fused-ring Oxiower and six-fused-ring Sulfower are lower than those of the 14-fused-ring Oxiower and eight-fused-ring Sulfower. As can be seen, in Figure 12, there is a higher overlap between the lobes of the LUMO orbital in a bowl-shaped molecule due to a closer space, leading to a lower level of the LUMO orbital. However, the lobes in planar molecules are more separated, making less overlap. Thus, the variation of LUMO shape reasons that the more non-planar flower has a lower HOMO-LUMO gap.
3.4. Suggestion of a New Structure: Oxisulfowers.
Along with the degree of non-planarity descriptor, there is a new structure that is suggested in this paper, namely, an Oxisulfower. Before creating a new molecule, the Selenosulfower, Selenoflower, and Sulffower were screened, and they were found to be planar at eight-fused-ring size. Then, the Selenosulfower was formed with a staggering fusion of four thiophene rings and four selenophene rings and also got a planar structure at the same number as its parent rings. From the same idea, a new structure is created from a new couple: a Sulfower with 8 fused rings and an Oxiower with 14 fused rings. The selection of the Oxiower with 14 furan rings instead of the 13-fused-ring Oxiower for synthetic reason is due to the even number of fused rings and a little smaller DNP than the previous Oxiower. Thus, the suggested molecule contains totally 10 fused rings with alternate five thiophene rings and five furan rings. While structures with 8 and 12 fused ring structures are largely bent, the proposed flower with 10 fused rings is potentially planar, shown in Figure 13.

Several properties of the hybrid structure Selenosulfower were different from its parent circulenes. For example, the LUMO energies decreased slightly in the order of Selenosulfower, Selenoflower, and Sulffower, and also the change in band gap between these flowers came mainly from the HOMO level. Meanwhile, the Oxisulfower’s electronic properties and its polarizability are approximately average values of the parents, compared to the Oxiower with 14 furans and the Sulfowers with 8 thiophenes, shown in Table 1.

Table 1. A Comparison of Electronic Properties between the Oxiower with 14 Fused Rings, Oxisulfower with 10 Fused Rings, and Sulfower with 8 Fused Rings

| property          | Oxiower | Oxisulfower | Sulfower |
|-------------------|---------|-------------|----------|
| band gap (eV)     | 5.62    | 4.99        | 4.42     |
| ionization potential (−eHOMO) (eV) | 6.42 | 6.04        | 5.89     |
| electron affinity (−eLUMO) (eV) | 0.80 | 1.05        | 1.47     |
| polarizability (Å³) | 50.44  | 47.57       | 48.41    |

Second, one of the most important properties studied in the flower class is the charge distribution. There are three common approaches to calculate this quantity: Mulliken, CHELPG, and NPA methods. However, the charge distribution value can be varied through different methodologies and the basis sets of the level of theory. For a more reliable value and consistency, a higher basis set, 6-311++G(d,p), is set up for finding the distribution of charge for the below molecules. In particular, NPA analysis is suggested to be the most consistent method, shown Figure 14. The eight-fused-ring Sulfower was forecasted to be an electron donor, whose distribution of the partially

Figure 12. HOMO and LUMO plots of several Sulfowers (isovalue = 0.02) and Oxisulfowers (isovalue = 0.01).

Figure 13. A comparison between the 10-fused-ring Oxiower and its homologous structures: 8 fused ring and 12 fused ring molecules.

Figure 14. NPA charge distribution of heteroflowers. Fresh red and green colors present the negative charge and positive charge, respectively; dark red and dark green are nearly neutral.
positive charge is located on the sulfur atoms and the partially negative charge is on the carbon atoms. Oppositely, in an Oxiflower, the negative charge is on oxygen atoms and the positive one is on the neighboring carbon atoms, so the Oxiflower can be considered as an electron acceptor. Interestingly, the Oxisulfower can be both an electron donor and acceptor due to the positive charge located on the sulfur atoms and the negative charge on the oxygen atoms, which is a mixture from its parents. Although there are some differences between the methods for calculating the charge distribution, especially in Mulliken and CHELPG in Figures S3 and S4, they still show that the charge on atoms in the Oxisulfower is a mixed distribution from the Oxiflower and the Sulfower. It is necessary to be confirmed by the success of the Oxisulfower synthesis for more reliable conclusions.

Moreover, the IR spectrum of the Oxisulfower is also a hybridization of the typical signals of the parents shown in Figure 15. The spectra are a data set for experimentalists used to discover the new structure, the Oxisulfower. Particularly, in the Oxisulfower, at 772 cm\(^{-1}\), the \(\nu_{C=C}\) is an asymmetric stretching vibration of carbon atoms in the core of the ring. At 920 cm\(^{-1}\), there is an asymmetric vibration of a C–S bond in the structure, which is lower than the same vibrating peak at 958 cm\(^{-1}\) of the original Sulfower. The highly intense peak at 1212 cm\(^{-1}\) in the hybrid structure is the frequency of a typical asymmetric stretching of C–O bonds, but this type of vibration is also smaller when compared to the original peak of the 14-fused-ring Oxiflower at 1322 cm\(^{-1}\). Overall, the typical signals of IR spectroscopy of the Oxisulfower are lower than those of its parents.

4. CONCLUSIONS
This study presents an analysis of the correlations between electronic properties and structural parameters of Oxiflower and Sulfower classes. The strain energy is shown to be fairly correlated with the HOMO-LUMO gap in both Oxiflower and Sulfower classes. Especially, there are two unusual correlations of the circulene classes, opposite with the single and linear-fused ring structures. First, a correlation between the polarizability and the HOMO-LUMO gap shows that the more polarizable structure generally has a larger gap. Second, a new descriptor, the “degree of non-planarity”, has an excellent correlation with the gap, proposing that the more non-planar structure has a lower HOMO-LUMO gap. Hence, the non-planarity has been supported as a quantitative descriptor, which is promisingly developed to modulate the band gap in quantitative-structure–property-relationship models for organic semiconductor materials. Finally, there are two new structures suggested: the Oxiflower with 14-furan-fused rings and the hybrid flower Oxisulfower with five furan and five thiophene rings. They are proposed to be synthesized and studied for their chemical and physical properties by experimentalists in the future.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04882.

Structural parameters and electronic properties of Oxiflowers and Sulfowers and strain energy calculations (PDF)

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**ABBREVIATIONS**
OLED, organic light-emitting diodes; OFET, organic field-effect transistors; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; RMSD, root mean square difference; HOMA, harmonic oscillator model of aromaticity; HOMHED, harmonic oscillator model for heterocycle electron delocalization

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