Computational and Theoretical Chemistry 1068 (2015) 117–122

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

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

Computational study on aromaticity and resonance structures of substituted BODIPY derivatives

Nurettin Menges *

Yüzüncü Yil University, Pharmacy Faculty, Van 65080, Turkey

ARTICLE INFO

Article history:
Received 28 January 2015
Accepted 29 June 2015
Available online 6 July 2015

This study was dedicated to Prof. Dr. Paul von Rague Schleyer.

Keywords:
NICS
DFT
Azafulvene
Pyrrole

ABSTRACT

We have developed a systematic study for the investigation of resonance structures of the substituted BODIPYs. Aromaticity of two rings of BODIPY were calculated by means of NICS (Nucleus independent chemical shift) values and these values gave us an insight to predict dominant resonance structure between two different resonance forms of BODIPYs. Furthermore, bond order comparisons were utilized to specify dominant forms of the resonance structures. BODIPYs substituted with electron donating (EDG) or withdrawing groups (EWG) at different positions were analyzed and it was observed that character of substituents affected the aromaticity as well as dominant resonance structure. Substituent positions were also investigated and some important points were yielded from these calculations. We further extended the study to aromaticity of pyridine or benzene[b]-fused BODIPYs.

1. Introduction

The 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene derivatives (boronodipyrro-methene or BODIPY) were first discovered by Treibs and Kreuzer (Fig. 1) [1]. Since then, there is a great tendency to explore its different features such as optical properties [2].

BODIPYs are excellent fluorescent dyes and have been used in various research fields as labeling reagent, fluorescent switches, photosensitizer, chemosensors, light-harvesting systems, dye-sensitized solar cells because of their advantageous photophysical properties, such as photostability, high absorption coefficients, high fluorescence quantum yields [3a–g].

BODIPY is a polycyclic system, which has three π-delocalized rings. One of these rings is pyrrole and the others are azafulvene and diazaborinin-type ring systems (Fig. 2). Azafulvene ring is a common motif in some of natural products such as prodigiosin [4a], tambjamine [4b] and porphyrin structure [4c,d]. It has different reactivity than pyrrole and can be substituted by nucleophiles [5]. For instance, formylation of pyrrole gives an azafulvene intermediate which is extremely susceptible to nucleophilic attack to form 2-formyl pyrrole via Vilsmeier–Haack reaction.

According to structure of parent BODIPY, it is assumed that there are two equivalent resonance forms resulting in forming of two rings named azafulvene and pyrrole. Pyrrole is aromatic whereas azafulvene is a quinoid-type ring which is less aromatic than pyrrole. Parent BODIPY has two resonance forms between azafulvene and pyrrole rings but these resonance forms cannot be distinguished. On the other hand, unsymmetric BODIPYs have resonance forms whose contributions might be different between these rings. Therefore, we have desired to see the contribution between these rings when changed electronic state of it and to say that which resonance form will be dominant upon different electronic structure and aromaticity. In fact, it is very important to know dominant resonance form of BODIPY since it specifies nucleophilic substitution of BODIPY structure [6a–c]. Although there is an extremely wide literature on BODIPY chemistry, the aromaticity of them has been rarely studied and those examples have not included information in detail [12]. Aromaticity is a concept with a great importance in physical organic chemistry [7,9,10]. It has been very useful in the rationalization of the structure, stability, and reactivity of many molecules. In heteroaromatic chemistry, the degree of aromaticity has a particular importance in guiding our understanding of reactivity [8a,11]. Aromaticity relates fundamentally to chemical reactivity from both the thermodynamic and kinetic standpoints [8b]. In this study, we aimed to study aromaticity of unsymmetric BODIPYs by quantum chemical techniques and to confirm their dominant resonance structures.

* Tel.: +90 432 2251025 (1088).
E-mail address: nurettinmenges@yyu.edu.tr

http://dx.doi.org/10.1016/j.comptc.2015.06.031
2210-271X/

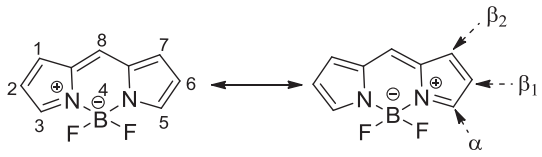


Fig. 1. The structure of BODIPY.

2. Theoretical methods

Geometric optimizations were performed by using Gaussian 09 [15] through Gaussview 5.0.9. and the method of DFT/B3LYP/6-31 G (d) which is well reproduced by the crystal structure of a BODIPY derivative [12]. Absolute values of NMR shielding were calculated by using the Gauge-Independent Atomic Orbital (GIAO) method with the restricted closed shell formalism employing DFT/B3LYP/6-31 G(d,p) basis set over DFT/B3LYP/6-31 G(d) optimized geometries (see Table 1). NICS values were obtained by calculating absolute NMR shielding at different points of the rings. Calculation of bond orders was done by using Multiwfn suit software [16a,b] through Mayer [17], Fuzzy [18], and Lablacian [19] bond order theories. The normal mode analyses for each structure have yielded no imaginary frequencies for the 3*N*_6 vibrational degrees of freedom, where N is the number of atoms in the system, which indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface.

3. Result and discussion

To calculate aromaticity of BODIPYs, a widely used aromatic index, the nucleus-independent chemical shift (NICS), was applied [13]. It is defined as the negative value of the absolute shielding was observed at a ring center or at some other interesting points of the system, usually above the ring center. Rings with large negative NICS values indicate strong aromatic character. The more negative the NICS values, the more aromatic the rings. In this study, NICS technique has been chosen as a valuable probe to determine the aromaticity of any desired ring of polycyclic aromatic molecules.

Firstly, parent BODIPY was calculated as a control compound and it was shown that NICS values of parent BODIPY were sense to basis sets and theoretical methods which were applied [20]. We have chosen NICS(0) values of B3LYP/6-31 G(d,p) method since it is more prevalent owing to same values for both rings and more economic method than the others. Pyrrole and azafulvene rings of parent BODIPY are equivalent with each other in the ring plane, NICS(0), (Table 1) [12].

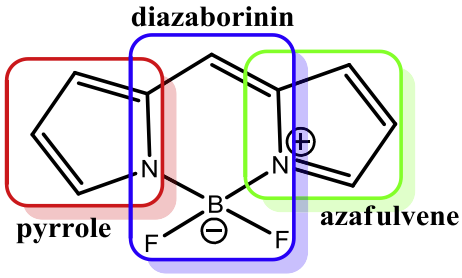


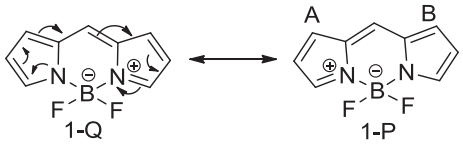
Fig. 2. Different π-delocalized rings of BODIPY.

After proving the concept with parent BODIPY and verifying the applied method, we have extended our focus to some electron donating groups such as Me, NH_2, OMe, $(Ph)_2N$, $(Ph)_2P$. The NICS(0) values of amine substituted BODIPY **4** showed that amine substituted ring gained more quinoid character than unsubstituted one (Scheme 1). Accordingly, it is proposed that **4-Qa** or **4-Qb** resonance forms are dominant in which positive charge stays on nitrogen of amine (**4-Qa**) or amino substituted azafulvene ring (**4-Qb**) where electron drawing feature of them might stabilize the positive charge on nitrogen atom of the azafulvene ring (Scheme 1). Bond length is 1.347 Å between amine and its adjacent carbon and 1.344 Å between nitrogen atom of azafulvene ring and its adjacent carbon. These distances are longer than C=N double bond (1.294 Å) and shorter than C—N single bond (1.470 Å) and indicate that there is also a resonance form between amine group and azafulvene ring (Scheme 1).

The NICS(0) values of Me, OMe, $(Ph)_2N$, and $(Ph)_2P$ substituted BODIPYs showed that substituted rings were less aromatic than unsubstituted one. This is because of the fact that positive charge of nitrogen atom of azafulvene ring is stabilized by electron donating groups. Consequently, it is clear that **Q** resonance forms of **2**, **3**, **5** and **6** which are substituted with electron donating groups are more dominant (Scheme 2).

Aromaticity difference between the rings of amine substituted BODIPY **4** is 2.9 ppm whereas aromaticity difference between the rings of diphenylamine substituted BODIPY **2** is 1.5 ppm. Compound **3** mirrors increasing of aromaticity according to parent BODIPY but shows the lowest difference between the rings. Hence, we have assumed that nucleophilic character of substituent influences aromaticity degree of the rings.

Table 1
NICS values of parent BODIPY with different theoretical methods.



Methods	NICS(0)	NICS(0.5)	NICS(1)	NICS(1.5)	Ring
RHF/6-311 G d,p	−9.8	−10.4	−9.9	−6.9	A
RHF/6-311 G d,p	−9.8	−10.2	−9.4	−6.9	B
RHF/6-311+G d,p	−9.1	−9.6	−9.2	−6.3	A
RHF/6-311+G d,p	−9.1	−9.4	−8.6	−6.2	B
B3LYP/6-31 G d,p	−7.0	−8.1	−8.3	−5.9	A
B3LYP/6-31 G d,p	−7.0	−7.7	−7.7	−5.8	B
B3LYP/6-311+G d,p	−6.4	−7.4	−7.6	−5.4	A
B3LYP/6-311+G d,p	−6.4	−6.9	−6.9	−5.2	B