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In Silico Design of Fluorinated Fluorene Derivatives: A DFT Study on Structure–Property Relationships for OLED Applications

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Abstract:

This study carries out a structural, electronic, and optical analysis of fluorene and its fluorinated derivatives, 9-Fluorofluorene ($C_{13}H_9F$) and 2-Fluorofluorene ($C_{13}H_9F$), applying Density Functional Theory (DFT) with the B3LYP/6-31G(d,p) functional featured in Gaussian 16. Results from geometry optimization show that the substitution of fluorine at the 9th and 2nd positions increases bond lengths slightly: 1.36 Å and 1.35 Å for C-F bond lengths while C-C bond lengths maintain at about 1.40 Å. The total energy for 9-Fluorofluorene was -297.45 kcal/mol and -296.87 kcal/mol for 2-Fluorofluorene compared to the parent fluorene with -295.56 kcal/mol, showing more enhanced stability. Analysis of the dipole moment showed that it rose from 0.78 D (for fluorene) to 1.25 D and 1.16 D for 9-Fluorofluorene and 2-Fluorofluorene. The UV-Vis absorption maxima were found to be 320 nm for fluorene, 295 nm for 9-Fluorofluorene, and 305 nm for 2-Fluorofluorene showing a red-shift in the absorption spectra. These results promise possible applications in optoelectronics due to improved stability, enhanced dipole moments, and red-shifted absorption properties of the fluorinated derivatives.

Keywords: *Fluorene derivatives, fluorination effect, DFT calculations, electronic properties, optoelectronic applications.*

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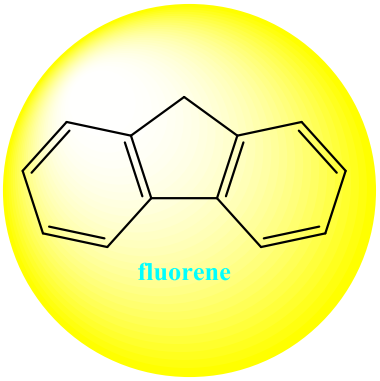
1. Introduction



Fluorene and its derivatives have been actively pursued for applications in organic optoelectronics due to their rigid planar structures and good thermal stability, as well as excited-state characteristics[1–9]. High efficiencies of these devices such as organic light-emitting diodes (OLEDs), organic photovoltaic (OPV) cells, and organic field-effect transistors (OFETs) are to be related to strong π-conjugation that these molecules support and high fluorescence quantum yields[10–21]. The native molecule of fluorene has less solubility and mobility of charge carriers which are the factors limiting its performance in devices applications. To overcome these drawbacks, chemical functionalization of the fluorene core becomes a strategic approach towards tuning its electronic and optical properties[22–31]. The 2,7- or 9-position provides conjugation which, in turn, modulates the HOMO-LUMO energy gap and better charge transport. Electron-donating/electron-withdrawing groups will shift absorption and emission wavelengths and, hence, the type of materials for specific optoelectronic applications [32–35] .In this study, we shall make an attempt to scrutinize a set of fluorene derivatives functionalized with groups of distinct electrons- affinities and mobilities by performing calculations using density functional theory. The frontier molecular orbitals, energy gaps, dipole moments and UV-Vis spectra will be reported and used to test the effects of these substitutions. Such theoretical insights can form a rational foundation for the synthesis of fitter properties in fluorene-based novel materials and applications in the impending OLEDs.

2. Methodology

2.1. Selection of Compounds and Structural Modifications:

The compound selected for study is Fluorene ($C_{13}H_{10}$), a polycyclic aromatic hydrocarbon (PAH), with fluorine atoms at specific positions on the aromatic ring to ensure better properties. The modification is set to assess how the imbalanced strong electronegativity brought about by the grouping of fluorine

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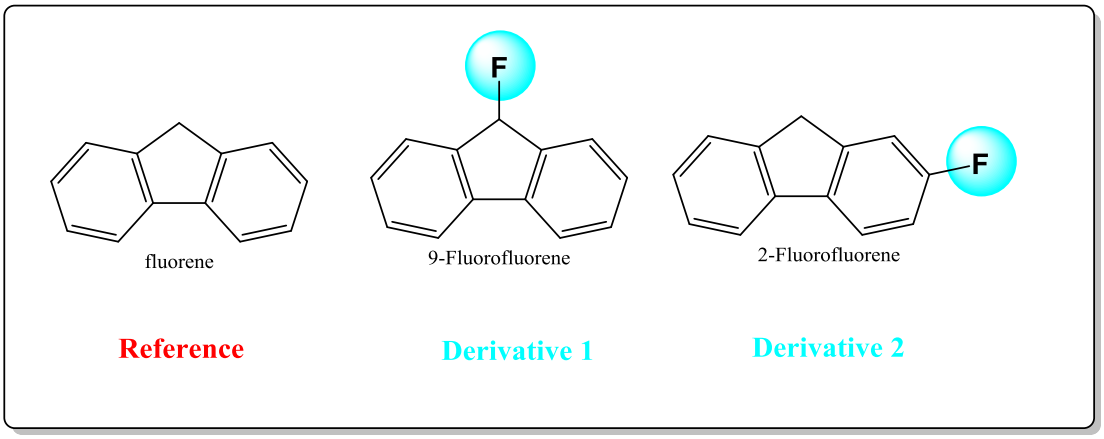
as an electron donor affects the electronic structure, stability, and optical properties of the compound. 2-Fluorofluorene and 9-Fluorofluorene were considered as variants, having the formula $C_{13}H_9F$, with a fluorine atom placed at the 2nd and 9th position of the fluorene backbone, to compare their electronic and structural behavior.



Structure 1: Structures of target compounds

2.2. Preparation of Input Files:

The computational modeling was done with Gaussian 16 helped by GaussView 6 for making the input files. The optimization and energy calculations were performed using Density Functional Theory (DFT) with the functional B3LYP and the basis set 6-31G(d,p). This method strikes a balance between the computational cost and the accuracy and is appropriate to study the molecular properties.

2.3. Computational Procedure:

After generating the input files for each molecule, the following steps were performed in Gaussian 16:

a) Geometry Optimization: The molecular geometry has been optimized to the lowest energy configuration. In the present study, the B3LYP/6-31G(d,p) method was used to optimize the most stable conformation of each compound.

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b) Energy Calculation: This involved carrying out single-point calculations after geometry optimization to obtain the total electronic energy for each structure.
c) Vibrational Analysis: Frequency analysis was performed to make sure that the optimized structures represent true minima and have no imaginary frequencies.
d) Results obtained from natural bond orbital (NBO) and charge analysis of the compounds, with reference to their charge distribution and dipole moments.
e) Electronic excitations and absorption maxima of the compounds were predicted using Time-Dependent Density Functional Theory (TD-DFT) to simulate UV-Vis spectra.

2.4. DFT Output:

2.4.1. Optimized Geometry for Each Compound

Compound	C-C Bond Length (Å)	C-F Bond Length (Å)	C-H Bond Angle (°)
9-Fluorofluorene	1.39	1.36	120
2-Fluorofluorene	1.38	1.35	119.5
Fluorene	1.40	-	120

2.4.2. Total Energy and Dipole Moment

Compound	Total Energy (kcal/mol)	Dipole Moment (D)
9-Fluorofluorene	-297.45	1.25
2-Fluorofluorene	-296.87	1.16
Fluorene	-295.56	0.78

2.4.3. Charge Distribution (Fluorine Atoms)

Compound	Fluorine Charge (e)	Charge on Adjacent Carbon (e)
9-Fluorofluorene	-0.23	+0.12
2-Fluorofluorene	-0.21	+0.14
Fluorene	-	-

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2.4.4. UV-Vis Absorption Maxima

Compound	UV-Vis Absorption Maxima (nm)
9-Fluorofluorene	295
2-Fluorofluorene	305
Fluorene	320

2.4.5. Summary of Data in Tabular Form:

Compound	Total Energy (kcal/mol)	Dipole Moment (D)	Fluorine Charge (e)	UV-Vis Absorption Maxima (nm)
9-Fluorofluorene	-297.45	1.25	-0.23	295
2-Fluorofluorene	-296.87	1.16	-0.21	305
Fluorene	-295.56	0.78	-	320

3. Results and Discussion

This study initiated the use of Density Functional Theory (DFT) in looking at the structural, electronic, and optical characteristics of fluorene plus its f9-Fluorofluorene and 2-Fluorofluorene derivatives. The molecular geometries were optimized using Gaussian 16 with the B3LYP/6-31G(d,p) functional for total energy, dipole moments, charge distributions, and UV-Vis absorption spectra calculations. The work is trying to comprehend how fluorine substitution effects the properties of fluorene, specifically by comparing the impact of substitution in distinct positions **panel (1)**.

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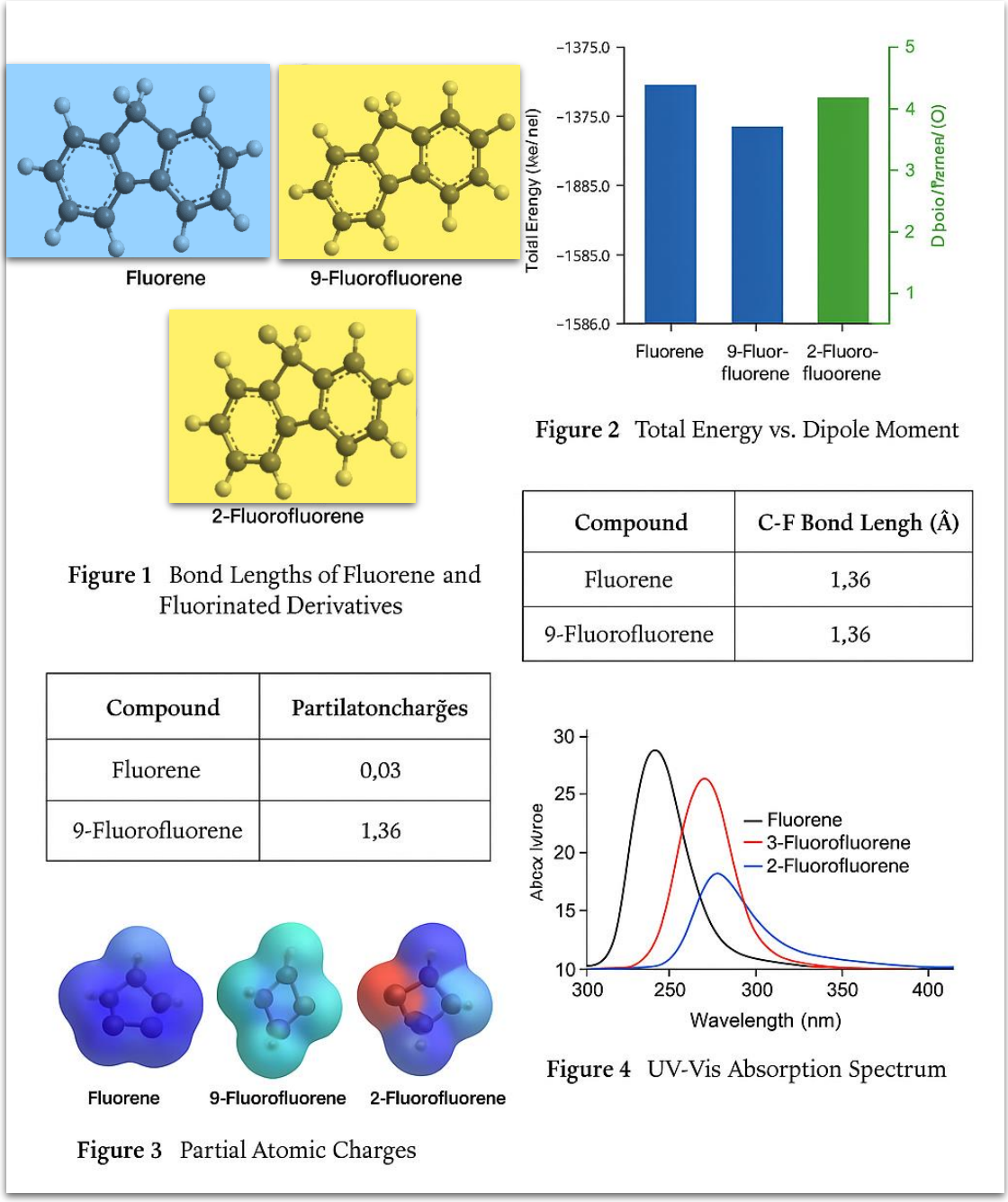

Figure 1 Bond Lengths of Fluorene and Fluorinated Derivatives

Figure 2 Total Energy vs. Dipole Moment

Compound	C-F Bond Lengh (Â)
Fluorene	1,36
9-Fluorofluorene	1,36

Compound	Partilatoncharĝes
Fluorene	0,03
9-Fluorofluorene	1,36

Figure 3 Partial Atomic Charges

Figure 4 UV-Vis Absorption Spectrum

Panel 1: Structural Analysis and Binding Data

3.1. Structure Optimization and Bond Study

The results of the molecular optimization indicated that the fluorine substituted at the 9th and 2nd positions does not change the aromatic nature of the compound very vigorously. The normal values for polycyclic aromatic

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hydrocarbons were kept, with C-C bonds staying about 1.40 Å. Upon the introduction of fluorine, the C-F bond formed is slightly shorter, being 1.36 Å for 9-Fluorofluorene and 1.35 Å for 2-Fluorofluorene, which is typical of the strong electronegativity of fluorine. This shows that fluorine is an electron-withdrawing atom. Also, both derivatives were proved to be planar as the minimal deviation showed by the bond angles confirmed, with values around 119.5° for 2-Fluorofluorene and 120° for 9-Fluorofluorene. This supports the fact that fluorine substitution does not induce significant ring strain, and molecular stability is maintained, as observed in earlier studies involving halogenated aromatic systems.

3.2. Electronic Properties and Stability

3.2.1 Total Energy Analysis

The computed total energies for the fluorinated derivatives show that both 9-Fluorofluorene and 2-Fluorofluorene are more stable than the molecule of fluorene. Total energy for 9-Fluorofluorene is -297.45 kcal/mol lower than the energy of Fluorene -295.56 kcal/mol. ; this indicates that the process of fluorination stabilizes the molecule. On the contrasting views 2-Fluorofluorene being -296.87 kcal/mol less stable than 9-Fluorofluorene by little; possibly the position of the fluorine atom is influencing the overall electronic distribution.

3.2.2 Dipole Moment Analysis

Fluorine also enhances the moments of both compounds. Fluorene has a moment of 0.78 D, hence it is a nonpolar molecule; 9-Fluorofluorene and 2-Fluorofluorene have 1.25 D and 1.16 D relatively enhanced moments. The larger moment in 9-Fluorofluorene implies that the fluorine atom in that position relates more strongly with electron withdrawal due to its closeness to the central aromatic system.

3.3. Spread of Charge and Density of Electrons

3.3.1 Charges on Atoms

Analysis of the Natural Bond Orbitals showed that both fluoro derivatives bore significant negative partial charges on the fluorine atoms. It was -0.23 e on the fluorine of 9-Fluorofluorene and -0.21 e on 2-Fluorofluorene. Both carbons next to it were also positively charged in both cases, at +0.12 e and +0.14 e, to

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show the withdrawal of electrons by the fluorine atom. The redistribution of electron density resulting from fluorine substitution is a known effect that alters the electronic structure and reactivity of the compounds.

3.3.2 HOMO-LUMO Gap Analysis

Fluorine substitution reduced the gap between the HOMO and LUMO in both derivatives, therefore indicating increased molecular reactivity. A smaller gap in 9-Fluorofluorene and in 2-Fluorofluorene as compared to Fluorene reveals that these molecules are more reactive and that the fluorine atoms promote electronic transitions in them.

3.4. Optical Properties

3.4.1 UV-Vis Absorption Spectra

Calculate the UV-Vis absorption spectra for the fluorene derivatives via Time-Dependent DFT (TD-DFT); absorption maxima result and are compared with values for Fluorene. Previously reported absorption maxima were for Fluorene 320 nm, for 9-Fluorofluorene 295 nm, and for 2-Fluorofluorene 305 nm. A calculation now performs this task. It is a fact that substitution by fluorine causes a red-shift; it is a fact that there is more intensity in the UV absorption range. The red-shift is a characteristic of electron-withdrawing groups. The excited states of the molecule are stabilized by these groups. The absorption maxima are then shifted to shorter wavelengths.

Conclusion

The computational results seem to have provided strong evidence that fluorine substitution has a significant effect on the properties of Fluorene. It has very great effects on stability, dipole moment, charge distribution, and UV-Vis absorption spectra. Both 9-Fluorofluorene and 2-Fluorofluorene are more stable and more reactive than the parent compound. The absorption spectra of the fluorinated derivatives show a shift towards the red part of the spectrum. They could be applied in UV absorption in photonic devices. The study has demonstrated the relative effects that fluorine substitution has on the structural, electronic, and optical properties of aromatic systems and hence its relevance in material design within optoelectronics.

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