C06

Investigating the Reactivity and Stability of Halogenated Fullerene C60: Study of Regiochemistry

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ABSTRACT

This paper explores the reactivity and stability of halogenated fullerene C_{60}, focusing on its potential applications in various chemical reactions. The unique structure of C_{60} with 30 reactive 6-6 double bonds offers a vast "workspace" for addition reactions, leading to a multitude of regioisomeric fullerene adducts. Computational methods utilizing Gaussian09 software at the B3LYP / 6-31G (d) level based on density functional theory (DFT) were employed to characterize the electronic structure and optimize the molecules.

Keywords: Density Functional Theory (DFT); Fullerene Adduct; Halogenated Fullerene, Regioisomeric; Electronic Structure

METHODS

The study investigates the impact of halogenation on the reactivity and stability of C_{60}, particularly comparing bromides to fluorides. Structural stability analysis was conducted to assess the effects of varying distributions of halogen on the fullerene surface. Quantum computational methods using Density Functional Theory (DFT) at the level of B3LYP 6-31G (d) were employed to calculate different halogenation levels (n = 2, 4, 6, 8) and analyze regiochemistry influences on halogen release. The calculations were performed using Gaussian 09 software. Experimental observations regarding iodine's non-reactivity with fullerenes were made to corroborate findings from computational methods.

RESULTS AND DISCUSSION

Result of Comparison between C_{60}-Br_2, C_{60}-Cl_2, and C_{60}-F_2

When comparing the computational data for C_{60}-Br_2, C_{60}-Cl_2, and C_{60}-F_2, several differences emerge that reflect distinct characteristics of these halogenated complexes.

1. Energy (RB3LYP)
   - C_{60}-Br_2: -7429.57855992 atm
   - C_{60}-Cl_2: -3206.54915630 atm
   - C_{60}-F_2: -2485.83002830 atm

The energy values indicate stable formations for all three complexes. However, C_{60}-Br_2 exhibits the lowest energy, followed by C_{60}-Cl_2 and then C_{60}-F_2. This suggests a trend where the bond strength decreases with decreasing atomic size of the halogen, with bromine forming the strongest bonds and fluorine the weakest.

2. Dipole Moment

- C_{60}-Br_2: 2.1375 Debye
- C_{60}-Cl_2: 2.7437 Debye
- C_{60}-F_2: 2.5304 Debye

The dipole moments vary among the complexes, with C_{60}-Cl_2 having the highest value, followed by C_{60}-F_2 and then C_{60}-Br_2. This suggests a trend where the polarity of the bond increases with increasing electronegativity of the halogen, with chlorine being more polar than fluorine and bromine.

3. Thermal Corrections

The thermal corrections to energy, enthalpy, and Gibbs free energy are comparable among the complexes, indicating similar stability at finite temperatures.

4. RMS Gradient Norm and Point Group

- C_{60}-Br_2: RMS gradient norm of 0.00002687 a.u, Point Group C1
- C_{60}-Cl_2: RMS gradient norm of 0.00005160 a.u, Point Group C1
- C_{60}-F_2: RMS gradient norm of 0.00010905 a.u, Point Group C1

All three complexes exhibit convergence in the calculations and possess the same point group, indicating similar structural characteristics.

The differences observed among C_{60}-Br_2, C_{60}-Cl_2, and C_{60}-F_2 have significant implications for their reactivity, stability, and potential applications:

- The decreasing trend in bond strength and increasing trend in bond polarity with decreasing halogen size (Br > Cl > F) suggest that smaller halogens may lead to weaker and more polar bonds with the fullerene surface.
- This trend could impact the reactivity and selectivity of these complexes in various chemical reactions. For example, C_{60}-Br_2 may be more suitable for reactions requiring strong bond formation, while C_{60}-F_2 may exhibit higher reactivity due to its greater polarity.
- Understanding these differences enables the rational design and optimization of halogenated fullerene derivatives for specific applications, such as in materials science, catalysis, or drug delivery.

5. Raman and IR Spectra

Below are images showing the Raman and IR spectra of C_{60}-Br_2, C_{60}-Cl_2, and C_{60}-F_2, illustrating their differences in vibrational modes and spectral signatures. These spectra provide additional insights into the structural characteristics and bonding environments of these halogenated fullerene complexes.

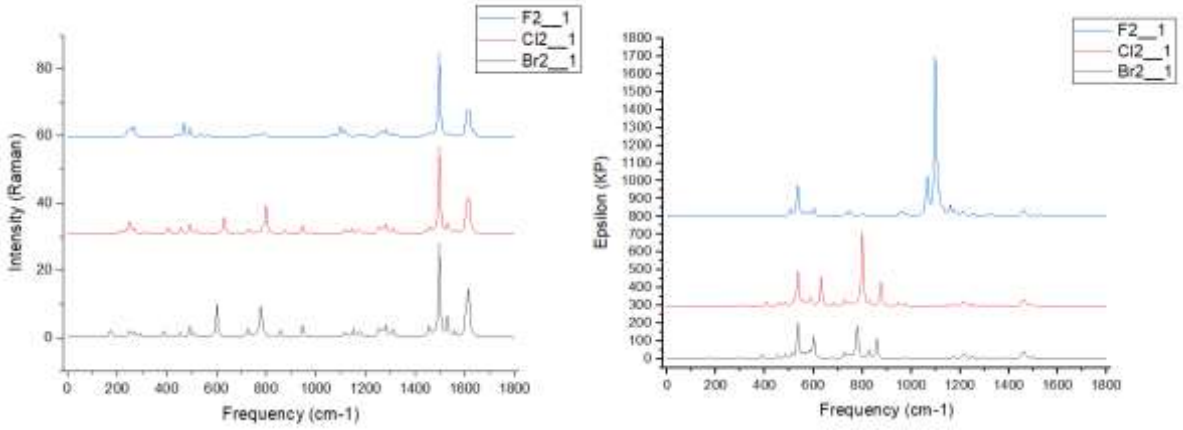

Figure – Raman Spectra (*left*) and IR Spectra (*right*)

The study reveals a general stereochemical pattern where larger diameter halogen atoms (F, Cl, Br) require lower energies for C-X bond formation. Additionally, the presence of halogen atoms influences the minimum energy required for adduct release, with more halogenated atoms correlating to lower energy thresholds. Analysis of varying distributions of halogen on the fullerene surface suggests that different configurations affect stability differently. Furthermore, the proximity of halogenated compounds to C_{60} influences the energy required for adduct release, with atoms placed on different sides of the fullerene requiring less energy compared to those within the same hexane. These findings contribute to a deeper understanding of fullerene reactivity and stability, with implications for various chemical applications.

In addition to the examination of C_{60}-Br_2, C_{60}-Cl_2, and C_{60}-F_2, the study also encompasses experimental data on C_{60}-X_4, C_{60}-X_6, and C_{60}-X_8. This comprehensive analysis reveals a specific stereochemical pattern where larger diameter halogen atoms (F, Cl, Br) mostly necessitate lower energies for C-X bond formation across all halogenation levels examined. Furthermore, the presence of halogen atoms significantly influences the minimum energy required for adduct release, with a clear trend observed where higher halogenation levels correlate with lower energy thresholds.

The structural analysis further elucidates that varying distributions of halogen on the fullerene surface affect stability differently. Notably, the proximity of halogenated compounds to C_{60} emerges as a critical factor in determining the energy required for adduct release. Atoms positioned on different sides of the fullerene necessitate less energy for adduct release compared to those within the same hexane.

These findings contribute to a nuanced understanding of fullerene reactivity and stability, offering valuable insights into the impact of halogenation patterns on chemical properties. By elucidating the underlying mechanisms governing halogenated fullerene behavior, this study provides a solid foundation for the development of fullerene-based materials and chemical processes.

CONCLUSION

In conclusion, this study sheds light on the reactivity and stability of halogenated fullerene C60, demonstrating the influence of halogenation patterns on chemical properties. The insights gained contribute to the development of fullerene-based materials and chemical processes, with implications for various scientific and technological applications.

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