Conformational analysis of N_2F_4 inside C_{60} and C_{80} Fullerenes

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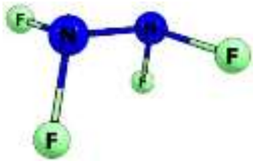
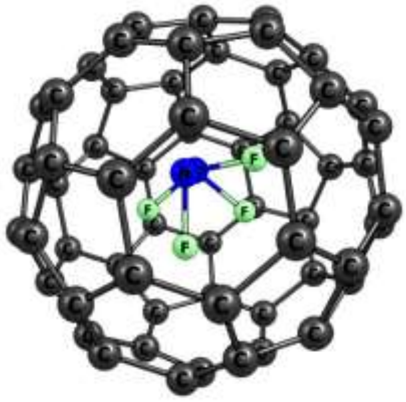
Abstract

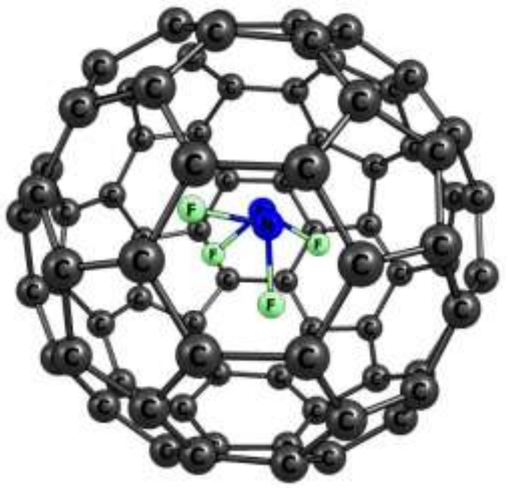
Investigation of structural properties of the tetrafluorohydrazine molecule inside C_{60} and C_{80} fullerenes using the hybrid DFT method. PBE/3ζ revealed in the contraction of the N–N and N–F bond length, decreasing the N–N–F angle and a noticeable increase in the rotation barrier about the N–N bond. The gauche conformer was found to be minimum inside both fullerenes unlike the free N_2F_4 which prefers anti-form, the molecular parameters. The rotations energies for all conformers were calculated, reported and investigated. The quantum chemical properties such as E_{HOMO}, E_{LUMO}, the energy gap (E_g), ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η) softness (S) were also reported.



Free N_2F_4



C_{60} Capsule



C_{80} capsule

Keywords: N_2F_4, DFT, Conformational analysis, Fullerenes, Priroda software.

Introduction

Tetrafluorohydrazine is an organic compound with N_2F_4 formula, the determination of its structure was first done by Lide and Mann[1] using microwave spectroscopy, and found to be in a gauche form with N-N and N-F bond length of 147 pm and 137 pm respectively and the bond angles were F-N-F=108° and F-N-F=65°. These values were corrected later by Gilbert[2] and became N-N 1.492Å, N-F 1.372Å, F-N-F 64°, and N-N-F 101.4°. Lide and Mann[1] also calculated the rotational barrier to be approximately 3.00 kcal mol^{-1} with the presence of 10% of gauche conformer at 200K. Infrared spectroscopy and electron diffraction and found that the anti-form is more stable than gauche by 0.7-1.2 kcal mol^{-1}. ^{19}F-NMR study in non-polar solvent shows coexistence of both[5]. Tetrafluorohydrazine dissociates readily in the gas and liquid phase to NF_2.[6] In recent years the study of small molecules behaviors encapsulated inside fullerenes and nanotubes gained a great interest. A notable change in the rotational barrier and structure parameter was found for ethane[7], hydrazine[8], dimethyl ether[9] and 1,1,1-trifluoroethane.[10]

Attempting to determine the influence of encapsulation on the N_2F_4 molecule inside fullerenes, density functional theory (DFT) computational approach was used to determine the physical properties and energies of the N_2F_4 encapsulated inside C_{60} and C_{80} fullerenes and the impact of these fullerenes on the conformations and structural parameters of the N_2F_4 molecule.

Computational Methods

All calculations were conducted using Priroda-04[11] and Hyperchem software[12], molecule was optimized first at AM1 semi-empirical approximation using Hyperchem, and then density functional theory was used by Perdew et al[13] in hybrid function and triple zeta (3ζ) basis set (Priroda-04), a scanning of F–N–N–F dihedral by 60 steps with 6° for each step and 360° in total. Chemcraft[14] software was used to visualize the results. Internal energy, activation energy, Gibes free energy, enthalpy change, and partial charges were reported. One imaginary frequency distinguished all transition states. The electronic properties of all system such as E_{HOMO}, E_{LUMO}, the energy gap between LUMO and HOMO, the ionization potential ($I=-E_{HOMO}$), electron affinity ($A=-E_{LUMO}$), global hardness ($\eta=I-A/2$), electronegativity ($\chi=I+A/2$), electronic chemical potential ($\mu=-(I+A)/2$), electrophilicity ($\omega=\mu2/2\eta$), chemical softness ($S=1/\eta$) were calculated.[15]

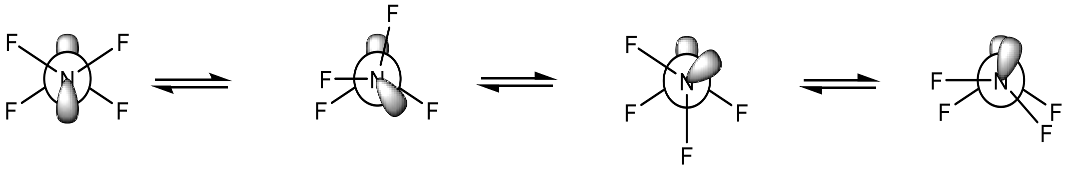
Results and Discussion

Tetrafluorohydrazine was studied previously both experimentally[4] and theoretically at different levels of theories [16]. N_2F_4 has two possible conformations around the N-N bond anti and gauche forms, the transformation between these two forms goes via eclipsed transition state. Previous studies include only the rotation of the N-N bond with 180° and found that the gauche rotamer is more stable by 3.4 kcal mol^{-1}.[16] Figure 1 shows the possible rotamers of tetrafluorohydrazine.

The current calculations were carried out at the PBE/3ζ level of theory, the obtained results form this level of theory such as bond angle and dihedral angle are in good agreement with the previously obtained results at MP2/6-31g* level and the experimental results. The PBE/3ζ calculations show a deviation in bond length by about 0.027Å and 0,093Å for F-N and N-N bonds respectively compared with the experimental results. Table 1 shows the N_2F_4 parameters of the PBE/3ζ results compared with the MP2/6-31G* levels[17] and the experimental results.[2]

A conformational analysis around the N-N bond followed by the analysis of the stationary points on the potential energy surface led to identifying the anti-conformer structure as minimal. Figure 2 shows the structure of the anti-conformer of tetrafluorohydrazine calculated at PBE/3ζ levels.

The potential surface scan of the N-N bonds shows five stationary points(I-V), analysis of this points led to identifying of point II and IV as stable conforms. Points I, II, and V are transition states conformers. Conformer IV which is the minimal global conformer was found to be in the anti-form. Conformer II, on the other hand, is local minima with 0.52 kcal mol^{-1} energy difference comparing to conformer IV. Conformer I is global maxima with 6.50 kcal mol^{-1} energy difference compared with the global minima conformer IV, the other conformers III and V are local maxima with almost equal energies difference of 3.1 kcal mol^{-1} related to conformer IV (global minima). The reason that conformers III and V are more stable than conformer I is because the repulsion between the two lone pairs in conformer I is unfavorable compared with the bond-pair lone-pair repulsion presence in conformers III and V. Table 2 shows the energies of all conformers; figure 3 shows the potential energy surface of the rotation around the N-N bond.



Anti Eclipsed Gauch syn

Figure 1: Conformers of Tetrafluorohydrazine.

Table 1
Bond length(Å), bond angle (°) and dihedral angle (°) for N_2F_4 molecules

	F-N	**N-N**	**F-N-F**	**F-N-N**	**F-N-N-F**
PBE/3ζ	1.401	1.585	102.8	99.2	179.7
MP2/6-31G*	1.374	1.507	103.2	99.8	179.9
Experimental	1.372	1.492	102.9	100.6	180.0

Table 2
Calculated (PBE/3ζ) energies for N_2F_4 conformers

Form	**ΔE (kcal mol^{-1})**	**ΔH (kcal mol^{-1})**	**ΔG (kcal mol^{-1})**	**ΔS (cal mol-1K-1)**	**∠FNNF degree**
I	0.52	0.42	0.50	-0.26	-175.71
II	6.50	5.70	6.65	-3.18	-108.46
III	3.11	2.40	3.42	-3.45	19.93
IV	0.00	0.00	0.00	0.00	74.953
V	3.10	2.38	3.41	-3.44	129.98

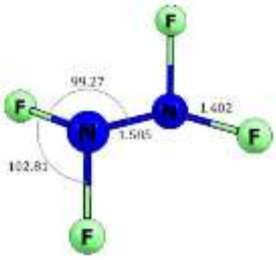


Figure 2: The minimal structure of N_2F_4

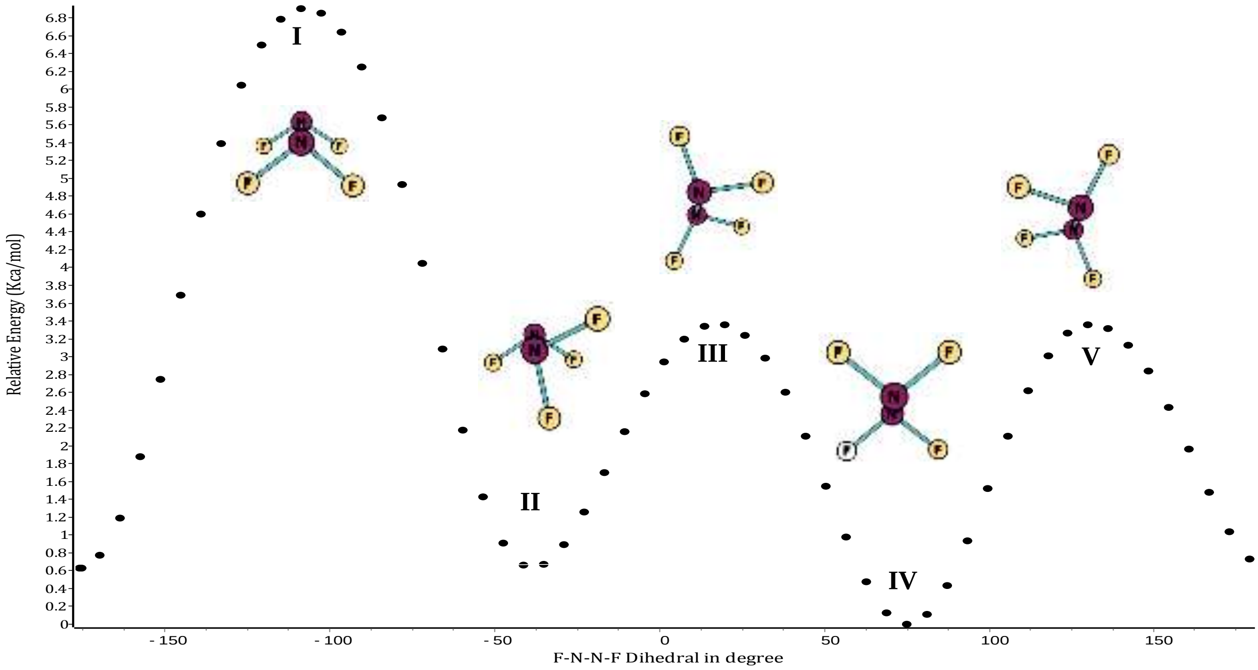


Figure 3: The relative energy of N_2F_4 as a function of F-N-N-F dihedral angle

Calculations at PBE/3z level show that the fullerene cavities of C_{60} and C_{80} have a high impact on the parameters of the N_2F_4 structure, C_{60} cavity is smaller than C_{80}, and hence the C_{60} has more impact on the N_2F_4 structural parameters. Inside the C_{60} the F-N bonds length decreased by 0.052Å and the N-N bond contracted by about 0.176Å. A decrease in the F-N-F and F-N-N bonds by 4.15° and 4.21° was also noted, the dihedral angle of the structure changed from the anti-form ϕ=179.7° into the gauche form ϕ= -51.4°.

On the other hand, the C_{80} fullerene has a lower impact on the N_2F_4 parameters, the F-N and N-N bond lengths were reduced by 0.019Å and 0.208 respectively, C_{80} impact on the F-N-F and the F-N-N angle was also small and can be neglected. The preferable conformer inside C_{80} was found to be gauche like the C_{60} capsule. Table 3 shows the parameters for free N_2F_4 and N_2F_4 encapsulated inside C_{60} and C_{80}.

The rotational barrier of N_2F_4 inside C_{60} changed dramatically. The energy required for N-N rotation changed from 6.50 kcal mol^{-1} in case of free N_2F_4 into 42.56 kcal mol^{-1} inside the C_{60}. Six conformers were found inside the C_{60} (Figure 4) with two global minima conformers, one local minima conformer, and three conformers represent a transition states. The rotation from gauche conformer II into its equivalent conformer IV threw conformer III as a transition state and required 13 kcal mol^{-1}, conformers I and V are transition states between two gauche forms (IV and VI). The energy required for this rotation was extremely high 42.56 kcal mol^{-1} as the structures of conformers I and V have a large volume and will not be favorable inside the C_{60} cavity, conformer III has dihedral angle of ϕ=0.00 and the two lone pairs on nitrogen are eclipsed to each other, typically this conformer is highly unfavorable, unexpectedly inside the C_{60} found to be more stable than the bond-pair lone-pair gauche transition state conformers(I and V) with about 30 kcal mol^{-1} energy difference. Table 4 presents the energies of all conforms of N_2F_4 inside the C_{60}.

The scaffold of C_{80} nanotube has influenced the N_2F_4 parameter as well; the potential energy surface shows six stationary points I, II, III, IV, V, and VI. Conformers I and III are identical and represent a global minimum, while structures IV and VI represent global maximum. The rotation energy around the N-N bond decreased by approximately 30 kcal mol^{-1} compared to C_{60} capsule and doubled the required energy for free molecules. Again and similar to the C_{60} the gauche conformer was found to be the global minima and about 8 kcal mol^{-1} is required to rotate conformer I into conformer III, this rotation goes via syn transition state with lone pair perpendicular to each other and dihedral angle of ϕ=0.5. The anti conformer inside the C_{80} was found to be local minima with a dihedral angle of ϕ=174 and 7.6 kcal mol^{-1} higher than the gauche conformer. Table 5 shows the relative energies of the founded conformers. Figure 5 represents the potential energy surface for N-N rotation inside C_{80} fullerene.

Table 3
Bond length(Å), bond angle (°) and dihedral angle (°) for N_2F_4 conformers

	F-N	N-N	F-N-F	F-N-N	∠F-N-N-F
Free N_2F_4	1.402	1.585	102.81	99.20	179.7
C_{60} Capsule	1.350	1.409	98.66	94.99	-51.4
C_{80} Capsule	1.383	1.477	102.8	98.62	-56.9

Table 4
Calculated (PBE/3ζ) energies for C_{60} capsule conformer

Form	ΔE (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔG (kcal mol^{-1})	ΔS (cal mol^{-1}K^{-1})	∠F-N-N-F degree
I	40.05	38.92	39.87	-3.17	-132.2
II	0.00	-0.01	-0.13	0.39	-51.4
III	13.00	12.31	13.01	-2.37	0.0
IV	0.00	0.00	0.00	0.00	52.6
V	42.56	40.81	42.61	-6.05	137.8
VI	30.28	29.92	30.12	-0.68	-179.9

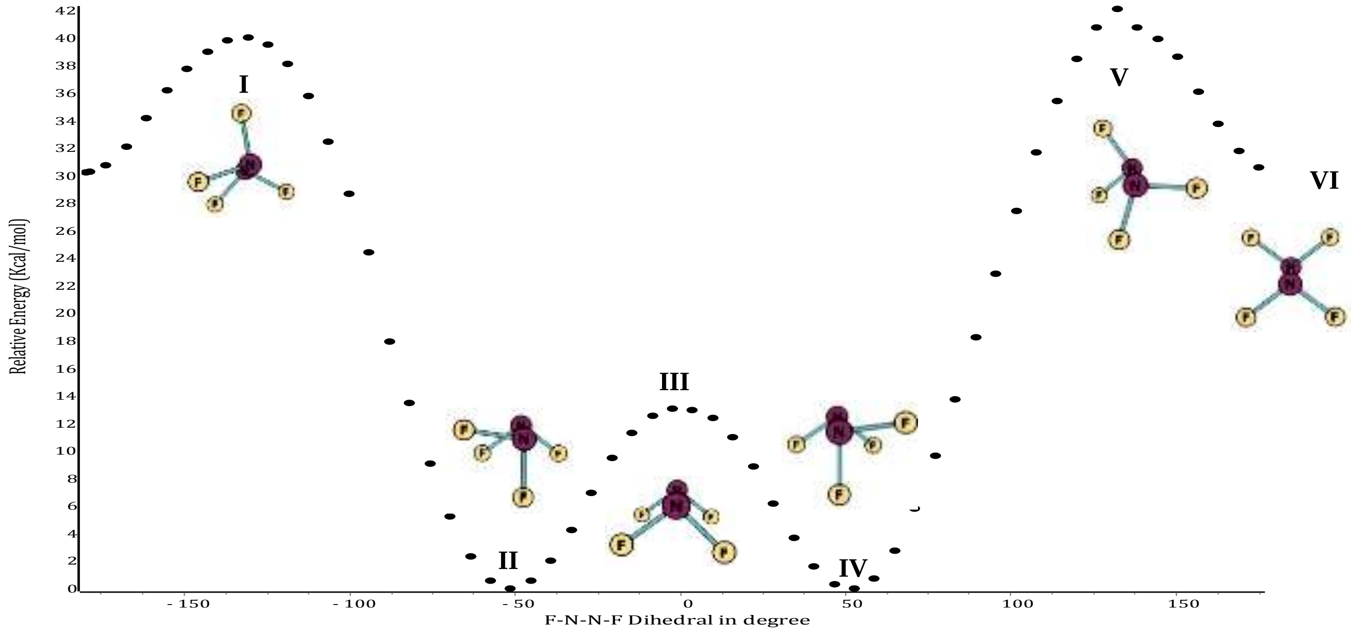


Figure 4: The relative energy of N_2F_4 as a function of F-N-N-F dihedral angle inside C_{60}

Table 5
Calculated (PBE/3ζ) energies for C_{80} capsule conformer

Form	ΔE (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔG (kcal mol^{-1})	ΔS (cal mol^{-1}K^{-1})	F-N-N-F angle
I	0.00	0.00	0.00	0.00	-56.9
II	8.40	6.91	9.31	-8.04	0.5
III	0.17	0.10	-1.61	5.73	59.1
IV	12.93	10.36	16.77	-21.50	131.8
V	7.62	6.89	8.75	-6.24	174.6

The charges of the of encapsulated molecules are found to be affected by the wall of the fullerene scaffold. Table 6 shows the charges change in each system, C_{60} and C_{80} fullerene have impacts on the N_2F_4 molecule, the positive charge on nitrogen atom has decreased by 0.05 and the negative charge on the fluorine atoms increased by 0.03, which indicates the donation of electrons from the fullerenes toward the N_2F_4 molecule. On energetical point of view using equation 1, the capsulation systems were found to be highly unfavored, the energies differences were found to be 173.05 kcal mol^{-1} and 32.13 kcal mol^{-1} for C_{60} and C_{80} respectively, the high energy in the C_{60} capsule is due to small cavity compared to C_{80} capsule. Table 7 shows the energies of both systems.

Finally the E_{HOMO}, E_{LUMO}, the energy gap between LUMO and HOMO, the ionization potential (I=-E_{HOMO}), electron affinity (A=-E_{LUMO}), global hardness (η=I-A/2), electronegativity (χ=I+A/2), electronic chemical potential (μ=-(I+A)/2), electrophilicity (ω=μ2/2η), and chemical softness (S=1/η) were listed in table 8. The energy of HOMO is directly related to the ionization potential (I) while the energy of LUMO is related to the electron affinity (A). The global hardness (η) corresponds to the energy gap between HOMO and LUMO. A molecule with a small energy gap has high chemical reactivity, low kinetic stability and is a soft molecule, while a hard molecule has a large energy gap.

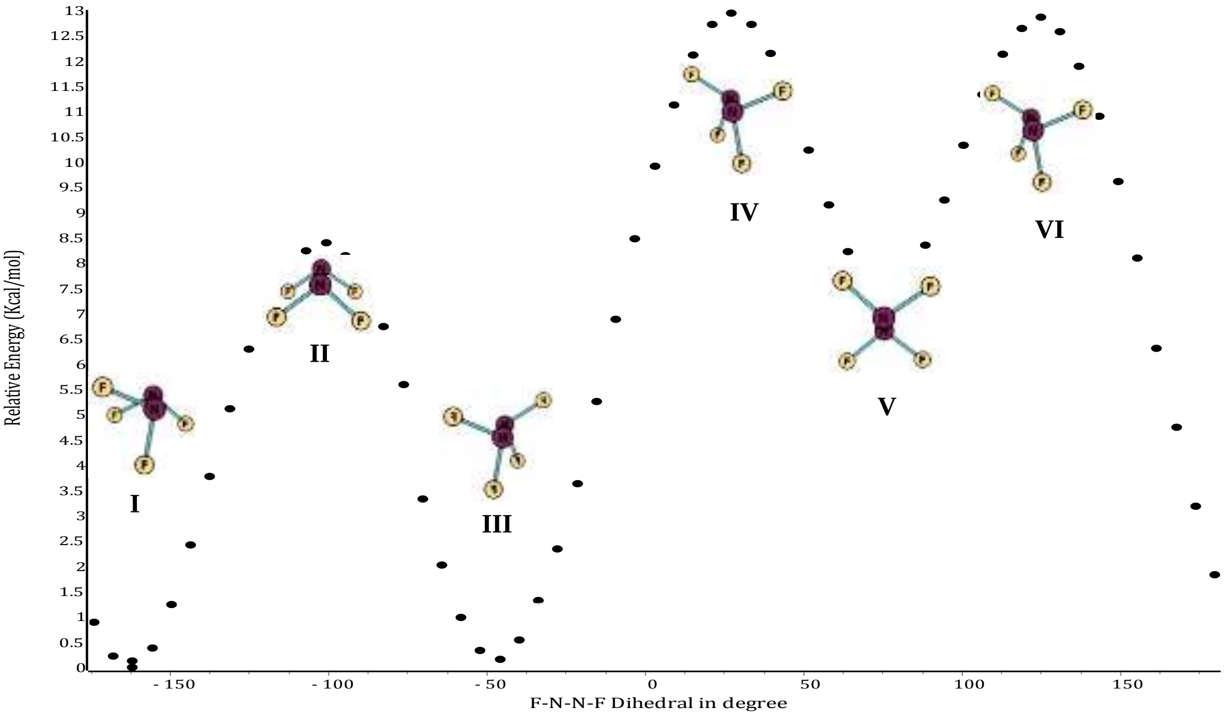


Figure 5: The relative energy of N_2F_4 as a function of F-N-N-F dihedral inside C_{80}

Table 6
Calculated charges for N_2F_4 in different systems

	N1	N2	F1	F2	F3	F4
Free	0.2764	0.2762	-0.1379	-0.1384	-0.1380	-0.1383
C_{60}	0.2244	0.2245	-0.1715	-0.1752	-0.1716	-0.1752
C_{80}	0.2610	0.2615	-0.1787	-0.1969	-0.1795	-0.1965

$E_{encapsulation}$ = [$E_{capsule}$] - [E_{N2F4} + $E_{empty-fullerene}$]

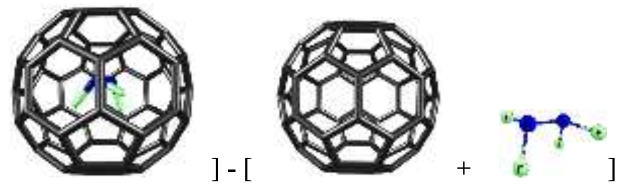

$E_{encapsulation}$ = [ ] - [+] (1)

Figure 6: Encapsulation equation

Table 7
Calculated encapsulation energies for C_{60} and C_{80} systems

	E (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔG (kcal mol^{-1})	S (cal mol^{-1} K^{-1})
N_2F_4	-318983.51	8949.41	-5431.28	76.86
Empty-C_{60}	-1433417.08	153714.41	127944.79	137.74
C_{60} Capsule	-1752227.54	161466.23	131886.12	158.10
Encapsulation C_{60}	**173.05**	**-1197.60**	**9372.61**	**-56.50**
Empty-C_{80}	-1911295.46	203409.21	171556.27	170.25
C_{80} Capsule	-2230246.83	212820.29	174811.66	203.15
Encapsulation C_{80}	**32.13**	**461.66**	**8686.68**	**32.90**

	N_2F_4 eV	**C_{60} eV**	**C_{80} eV**
LUMO	-2.46	-4.48	-5.26
HOMO	-7.98	-5.97	-5.40
E_g	5.522	1.493	0.1467
I	7.98	5.97	5.40
A	2.46	4.48	5.26
η	2.76	0.75	0.07
χ	5.22	5.22	5.33
μ	-5.22	-5.22	-5.33
ω	4.93	18.27	193.75
S	0.36	1.34	13.63

Conclusion

The size of the fullerene substantially affects the conformational properties of the encapsulated molecule, leading to the changes in bond lengths, bond and torsion angles together with significant variations in the relative stability of possible conformations in comparison with a free molecule. The Gauche conformer was found to be more stable than anti conformer inside both fullerenes, a notable change in rotation energy around N-N bond inside the fullerenes compared to free molecules, and both C_{60} and C_{80} capsule were found to be energetically unfavored.

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