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Conformational behavior of tetrafluorohydrazine inside C_{60} fullerene

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Abstract

The conformational behavior of tetrafluorohydrazine was studied inside C60 fullerene using density functional theory with PBE_3ζ basis set, a notable change in bond length, bond angle, and the dihedral angle was detected, the required energy for rotation about F-N-N-F also changed. The molecular parameter and rotation energy for all conformers were calculated, reported and investigated.

Keywords: DFT, Conformational analysis, fullerenes, PRIRODA.

1. Introduction

Tetrafluorohydrazine is an organic compound with N_2F_4 formula, the first determination of its structure was done by Lide using microwave spectroscopy (Lide Jr and Mann, 1959), and found to be in a gauche form, with N-N and N-F bond length of 147 pm and 137 pm respectively. The bond angles were also calculated and were F-N-F=108^o, F-N-F=65^o. Lide also calculated the rotational barrier to be approximately 3 Kcal/mol. F^{19} nuclear magnetic resonance (Colburn et al., 1965), infrared spectroscopy (Koster and Miller, 1968) and electron diffraction(Cardillo and Bauer, 1969) found that the *trans* conformer is more stable than gauche by 0.3-0.5 Kcal. In recent years the study of small molecules behaviors encapsulated inside fullerenes and nanotubes gain a great interest. A notable change in rotational barrier and structure parameter were found for Ethane(Kuznetsov, 2016b), Hydrazine (Kuznetsov, 2016c), dimethyl ether(Kuznetsov, 2016a) and 1,1,1-Trifluoroethane(Kuznetsov, 2017). The main aim of this work is to study the structure and rotational barrier of tetrafluorohydrazine inside $C_{60.}$

2. Computational methods

All calculations were conducted using PRIRODA-04(Laikov and Ustynyuk, 2005) and hyperchem software(HyperChem, 2002), the molecules was optimized first at AM1 semi-empirical approximation sing hyperchem, and then density functional theory was used at Perdew–Burke–Ernzerhof (Perdew et al., 1996) hybrid function and triple zeta (3ζ) basis set (Priroda-04), a scanning of F–N–N–F dihedral by 60 steps with 3° for each step and 180° in total. Chemcraft (Zhurko and Zhurko, 2009) software was used to visualize the results. Internal energy, activation energy, Gibes free energy and enthalpy change were reported. All transition states were distinguished by one imaginary frequency.

3. Result and discussion

Teterafluorohydrazine was studied previously both experimentally(Cardillo and Bauer, 1969) and theoretically at different levels of theory(Jursic, 1998) Figure 1.

Figure 1: Structure of Tetrafluorohydrazine.

Table 1 shows the N_2F_4 parameters of the current study compared with the MP2/6-31G* levels result and experimental result.

The PBE_3ζ result for the bond angle and dihedral angle are in good agreement with both the MP2 and the experimental result, but the PBE_3ζ shows deviation in bond length by about 0.026 Å Figure 2, shows the change in energy as the F-N-N-F dihedral change, the global minimal structure was at 74.95° and it's found to be trans conformer, whereas the gauche conformer is a local minimum with -175.71° dihedral angle, on the other hand, the highest energy was an eclipsed conformer with -108.4 dihedral angle and it is found to be a transition state, another conformer was also found to be a transition state with a dihedral angle of 19.93º, this conformer also in eclipsed conformation, in total the rotation about F-N-N-F required about 6.50 Kcal/mol. table 2 shows the relative energies, enthalpies, and entropies for all conformers.

The energy profile of tetrafluorohydrazine inside the C_{60} Fullerene has been changed widely table 3. The energy profile of C_{60} capsule is presented in figure 3. A minimal structure was found inside the capsule with a dihedral angle of -51.4°. At -179.9° dihedral angle another stable conformer was found with 29.9 Kcal/mol energy difference from the minimal conformer. The rotation inside the C_{60} fullerene goes via two transition states; the first transition states is an eclipse conformer where the lone pair of nitrogen is eclipse with N-F bond and requires about 10 kcal/mol to rotate the molecules from the trans conformer into the gauche form. The second transition state is in a full eclipse form in which the lone pairs of the nitrogen and all the bonds are facing each other. Table 4 shows the energies of C_{60} capsule.

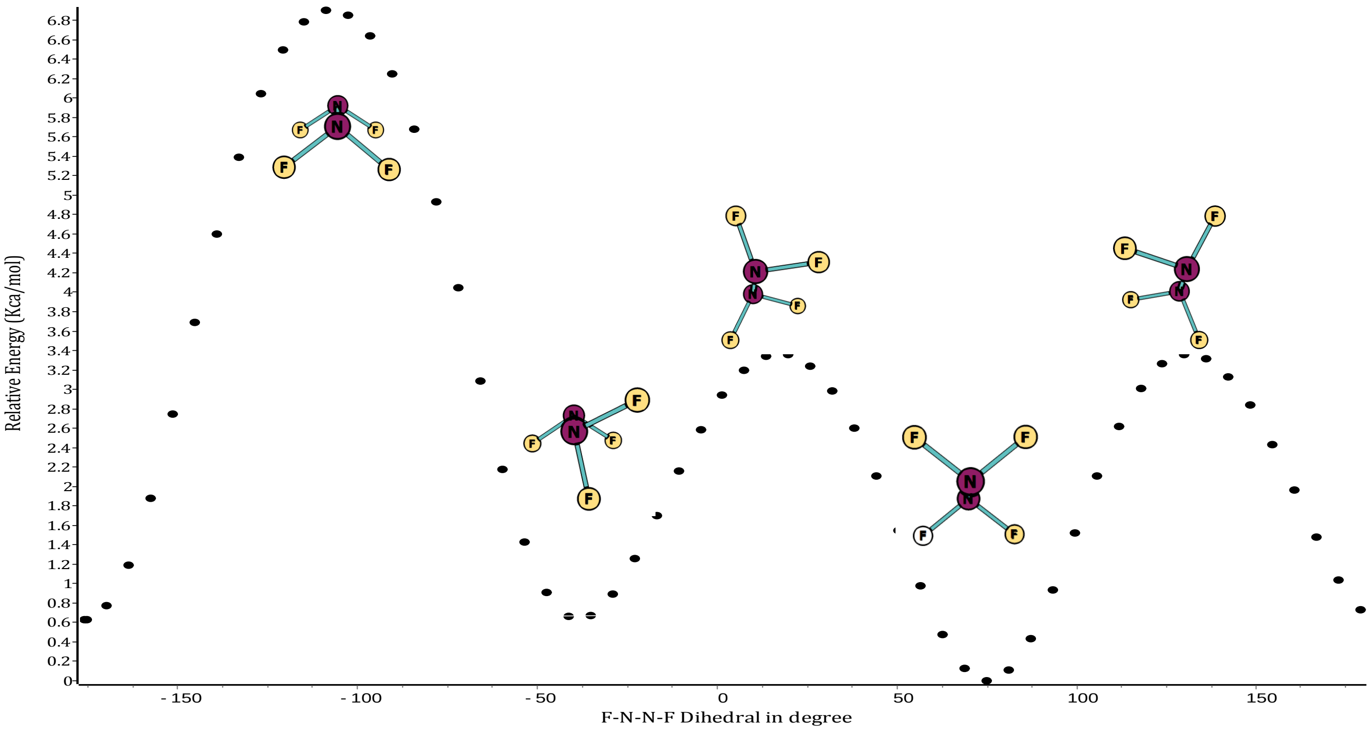

Figure 2: Relative energy of N_2F_4 as a function of F-N-N-F dihedral

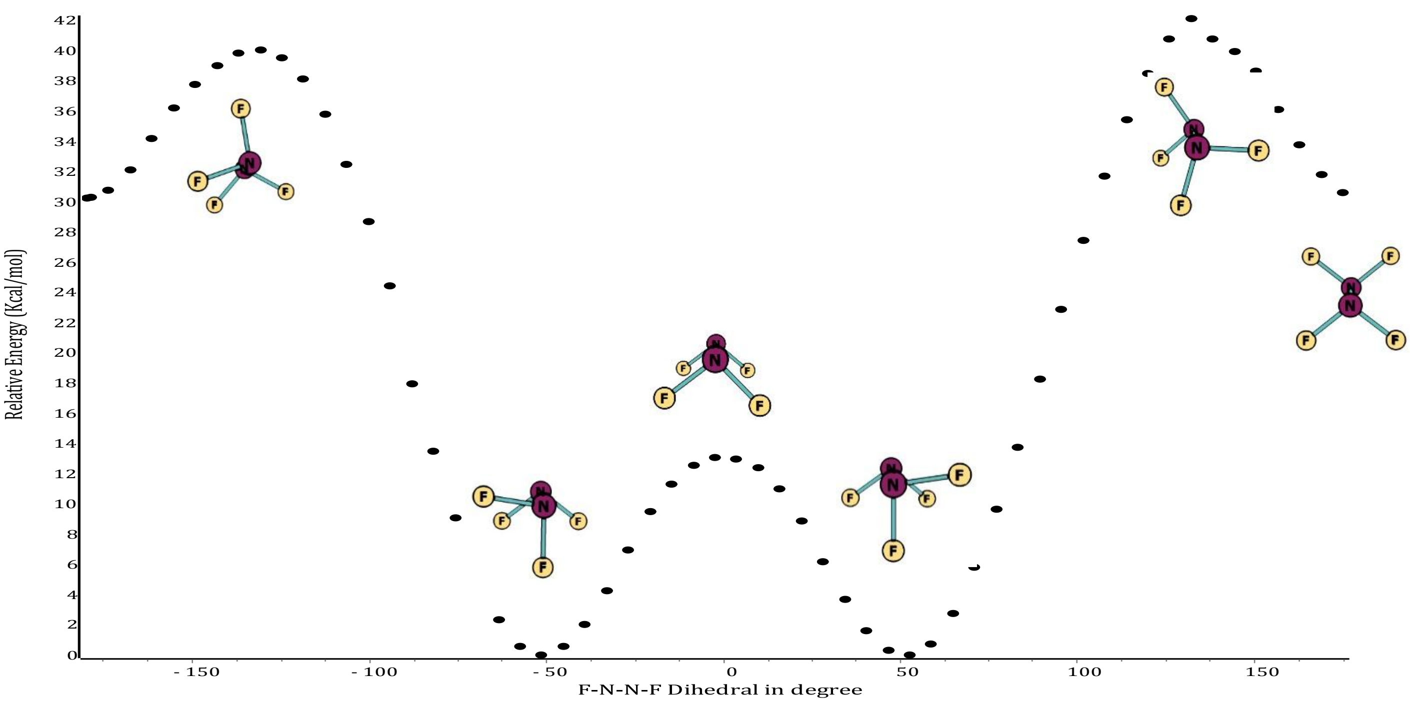

Figure 3: Relative energy of N2F4 as a function of F-N-N-F dihedral inside C_{60}

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

	F – N	N – N	F-N-N	F-N-N	F-N-N-F
PBE_3ζ	1.401	1.585	102.8	99.270	179.7
MP2/6-31G*	1.374	1.507	103.2	99.8	179.9
Experimental	1.375	1.489	102.9	100.6	180.0

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

F-N-N-F angle	ΔE (kcal/mol)	ΔH (kcal/mol)	ΔG (kcal/mol)	ΔS (cal/mol*K)
-175.71	0.52	0.42	0.50	-0.26
-107.19	6.50	5.70	6.65	-3.18
- 35.09				
18.55	3.11	2.40	3.42	-3.45
74.953	**0.00**	**0.00**	**0.00**	**0.00**
131.077	3.10	2.38	3.41	-3.44

Table 3. Bond length(Å), bond angle (°) and dihedral angle (°) for N_2F_4 and C_{60} capsule

	F – N	N – N	F-N-N	F-N-N	F-N-N-F
Free N2F4	1.401	1.585	102.8	99.270	179.7
C_{60} Capsule	1.372	1.411	98.9	95.28	-151.4

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

F-N-N-F angle	**ΔE (Kcal/mol)**	**ΔH (kcal/mol)**	**ΔG (kcal/mol)**	**ΔS (cal/mol*K)**
-179.27	**29.97**	**29.62**	**29.94**	**-1.07**
-132.23	**39.39**	**38.27**	**39.34**	**-3.57**
-51.204	**0.00**	**0.00**	**0.00**	**0.00**
0.00	**12.73**	**12.05**	**12.87**	**-2.76**
52.287	**0.03**	**0.04**	**0.15**	**-0.39**

4. CONCLUSION

In this study, comparisons were made between the behaviors of the N_2F_4 molecule, in free form and inside C_{60}. Meaningful changes were found in bond angle, bond length, and dihedral angle. The F-F and N-N bonds inside C_{60} were shorter than that for free N_2F_4 as results of the repulsions with the fullerenes walls. The same reflections were observed with the F-N-N bond angle. Moreover, there were variations in the conformational behavior of free and encapsulated N_2F_4. The global minimal structure for free N_2F_4 was at 74.95^o. While they were at -51.434^o for encapsulated N_2F_4 in C_{60}. The rotation barriers were found to be 6.50 Kcal/mol. For the free N_2F_4molecule and 41.69 Kcal/mol. for the C_{60} capsule.

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