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Analysis and Comparison of Experimental and Computational Study of 4-(2-2,6-bis (2-carbamothionylhydrazone) Cyclohexylidene)hydrazinyl) Benzoic Acid

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Abstract

In this work a comprehensive study of 4-(2-2,6-bis (2-carbamothionylhydrazone) cyclohexylidene) hydrazinyl) benzoic acid was conducted using theoretical first principle. The ligand was chosen due to its crucial importance as hormone for neurotransmitting process in the animal body. Many bases set and functional were used for the optimization of the compound to attain stability and find the suitable energy point for the overall calculations. The theoretical result was then compared with the experimental result to obtain the accuracy of the calculations. Due to the changes in the electronic properties the spectroscopic method was applied. The spectroscopic methods include determination of the bandgap energy, nuclear magnetic resonance (NMR) and infrared spectroscopy (IR) and ultraviolet spectroscopy (UV).

Keywords: Dopamine, DFT, Hartree-Fock, Bandgap, Humo-Lumo and spectroscopy

1. Introduction

One of the main function of 4-(2-2,6-bis (2-carbamothionylhydrazone) cyclohexylidene) hydrazinyl) benzoic acid in animals especially human beings is the neuro transmitting process which is the ability to send signals from brain to nerves cells and vice versa [1, 2]. Some researchers suggested that dopamine serve as a memory storage in the brain, control incoming noise to the body and regulate human character [3]. Majority of the diseases associated with the brain and nervous system is related to the malfunction of dopamine in the body. Such diseases include Parkinson disease (PD) resulted from improper or insufficient release of dopamine in the brain and Schizophrenia disease (SD) which is resulted from the change in the level of dopamine the body system of the body [4-7].

2. Methods

2. Computational procedure

The 4-(2-2,6-bis (2-carbamothionylhydrazone) cyclohexylidene) hydrazinyl) benzoic acid figure was drawn using gauss view 9.0 and two methods were applied to optimized the structure (DFT and Hatree-Fock) using eight basis set and functionals to achieve convergence and stability of the molecule[7]. The method was implemented by different papers to describe geometries and energies of a noncovalent systems. The ground state geometry optimization of the ligand was done with DFT using hybrid functional B3LYP at various basis set; STO-3G, 3-21G, 6-31G, 6-31G*, 6-311G, LanL2MB, LanL2DZ, SDD. The frequency calculation was determined using the optimized structure to obtain the minimum on the potential energy surface [7]. Furthermore, the UV is also determined using the optimized structure. The plotting of the three dimensional mapping of the molecular orbitals is done by the B3LYP/6-311G basis set [8-9]. At the B3LYP/6-311G basis sets, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies are calculated. All calculations in this paper are performed using the Gaussian 09 program [12-14]. During the stability check there is appearance of resonance in the benzene ring instead of conjugated cyclic double bond. This indicate that there is a strong bond between the atoms of the molecule after optimization.

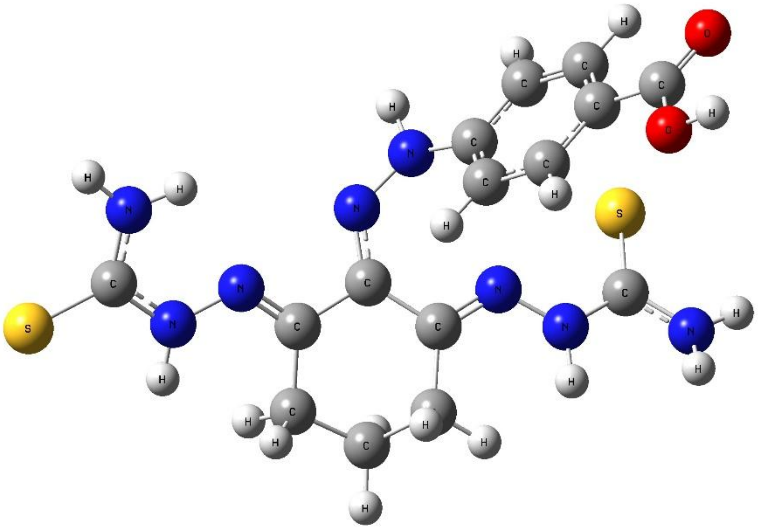
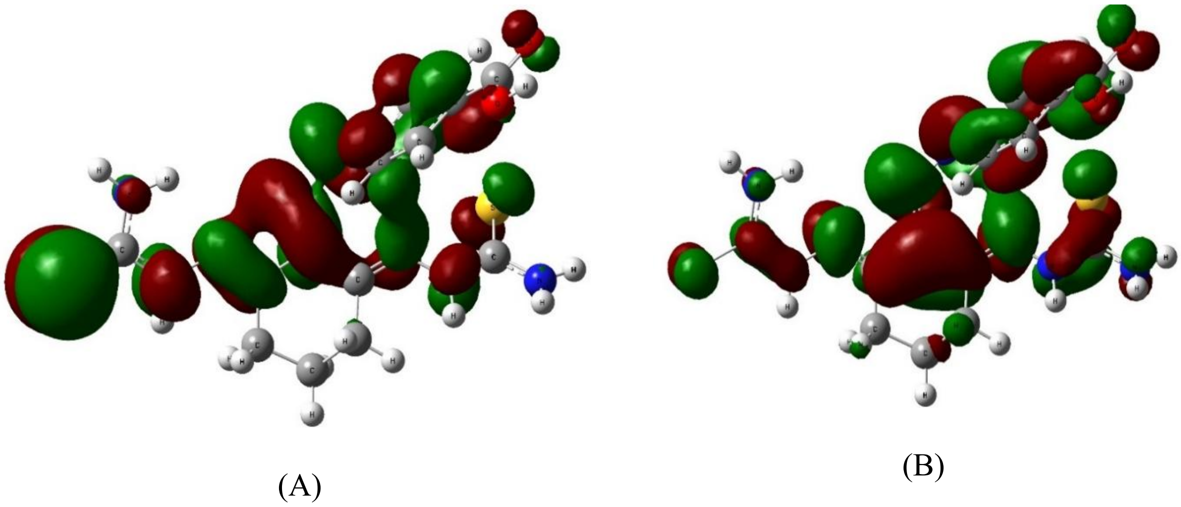


Figure 1. Optimized molecular structure of 4-(2-2,6-bis (2-carbamothionylhydrazone) cyclohexylidene) hydrazinyl) benzoic acid



(A)

(B)

Figure 2. Frontier molecular orbital of 4-(2-2,6-bis (2-carbamothionylhydrazone) cyclohexylidene) hydrazinyl) benzoic acid

3. Result and discussion

The dopamine figure was drawn using gauss view 9.0 and two methods were applied to optimized the structure (DFT and Hatree-Fock) using eight basis set and functionals to achieve convergence and stability of the molecule. During the stability check there is appearance of resonance in the benzene ring instead of conjugated cyclic double bond. This indicate that there is a strong bond between the atoms of the molecule after optimization.

3.1 Fourier transform infrared spectroscopy (FT-IR)

The vibrational frequencies of the dopamine molecule in this work were analyse using DFT/B3LYP along with 6-311G basis set. Gauss-view molecular visualization software was initially use to plot the infrared then Origin graphing and analysis software is used to plot the fourier transform infrared spectroscopy vibrational band. The comparison between the normal dopamine and then doped with members of halogen group can be observe from figure 4.

The benzene ring present in the dopamine molecule can be investigated from the bonds of C-H, C-C and C=C ring vibrational modes. The C-H stretching vibrations of dopamine occurs about 3000 cm^{-1} and there is also a present of weak to moderate bands (multiplicity) when compared with normal C-H stretching [17-19]. In this work, the vibrational modes were calculated theoretically in the range 3065-3124 cm^{-1}. This shows an excellent and precise agreement with experimental results.

The normal aliphatic C-H stretching was detected theoritically at about 2867-2973 cm^{-1} [20]. In the work, C-H stretching in ascorbic acid was calculated at 2979-3046 cm-1 for B3LYP while 1259, 1193 and 1147 cm^{-1} bands are for C-H in-plane bending vibration in the dopamine molecule. The theoretical results obtained from the B3LYP model are close to the true value which is the indication of the accuracy of the model.

The C-C stretching vibration in the ring has different values due to the nature of the ring but in most cases it ranges from 1600-1350 cm^{-1} [18]. The value has little increase due to the DFT methods approximation in this work and was found to at 1680, 1444 and 1365 cm^{-1}.

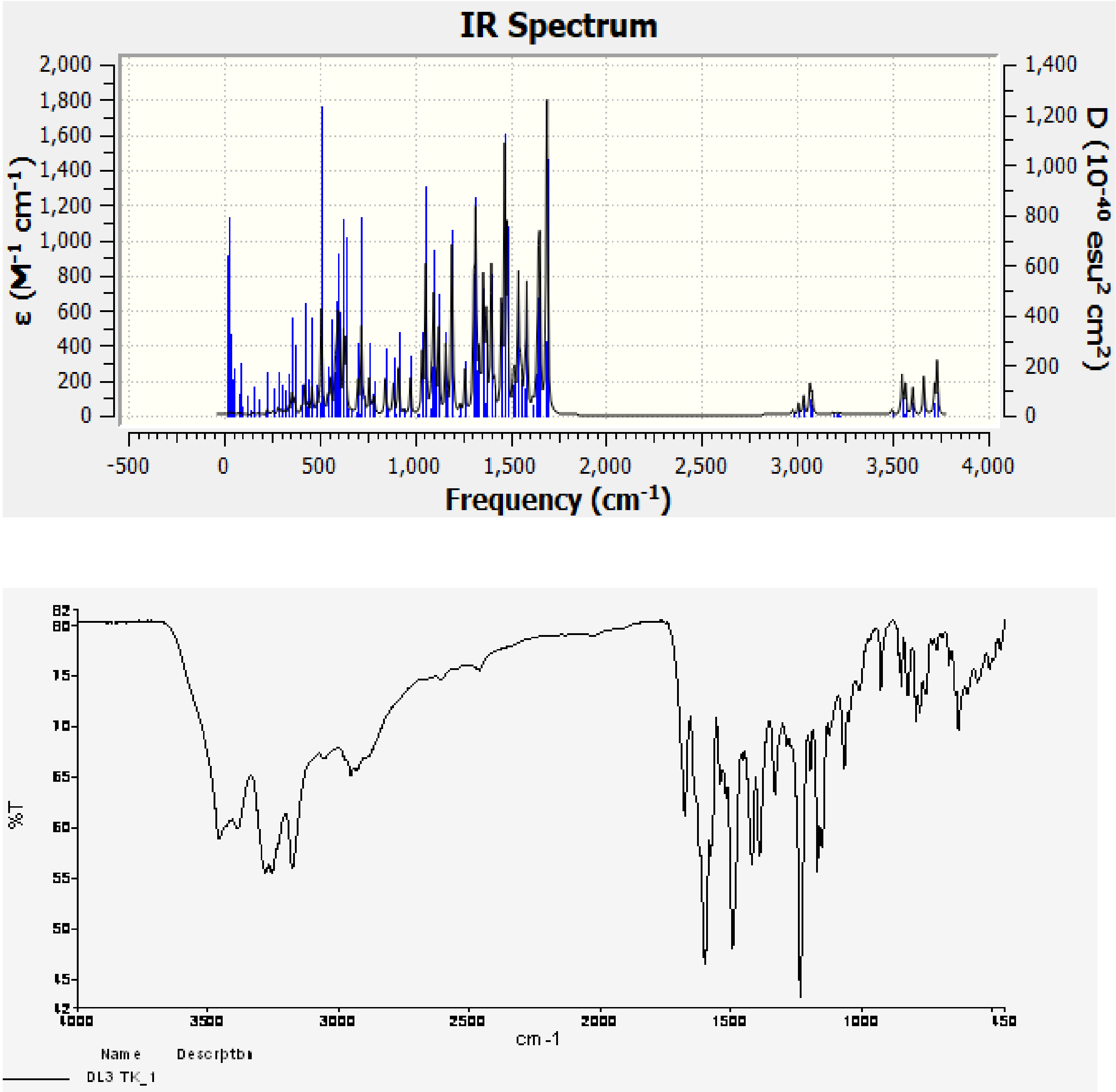


Figure 3. Comparison of FT-IR absorbance spectra of 4-(2-2,6-bis (2-carbamothionylhydrazone) cyclohexylidene) hydrazinyl) benzoic acid between theoretical and experimental results.

3.2 Proton magnetic resonance (1H-NMR)

Proton nuclear magnetic resonance (NMR) is a spectroscopic technique use to determine the chemical enviroment of the protons present in the molecule under considerations. The two auto protons have peak at around 7.88-8.01 ppm due to the closeness with carboxylic acid carbon while the two meta protons absorbed at around 7.05 ppm as result of distance with the carboxylic carbon. The single proton attached to the bridged nitrogen atom has a peak at around 10.98ppm due to the electronegative properties of the nitrogen. 8.09-8.65ppm peak belongs to the two protons attached to the nitrogen atom (NH_2) attached to hexane group. The peak at 14.86-13.12 ppm is attributed to the single attached to the nitrogen atom of the hexane molecule.

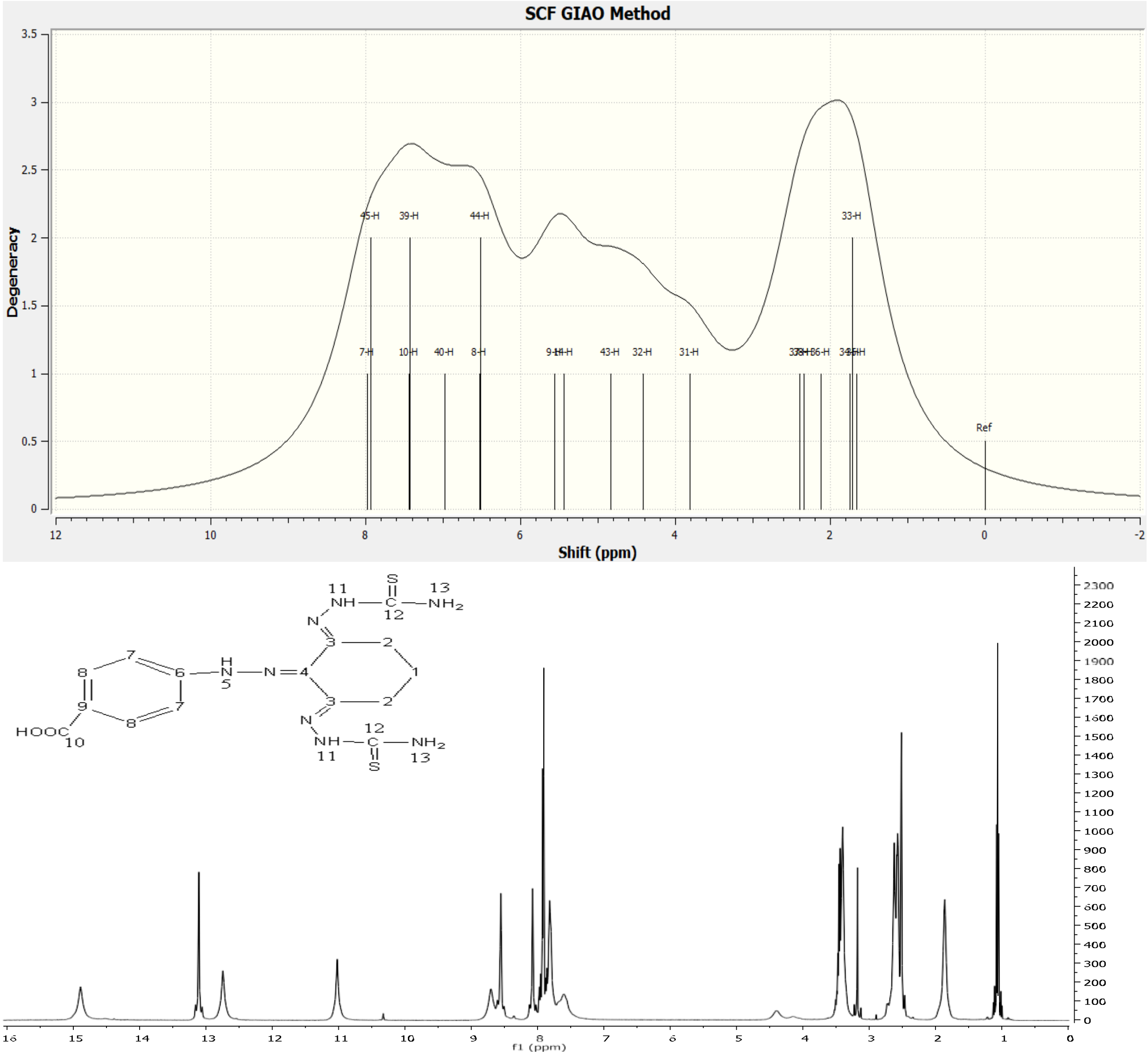


Figure 4. Comparison of ^{1}H-NMR of 4-(2-2,6-bis (2-carbamothionylhydrazone) cyclohexylidene) hydrazinyl) benzoic acid between theoretical and experimental results

3.2 Carbon nuclear magnetic resonance (^{13}C-NMR)

Just like proton NMR, proton nuclear magnetic resonance (NMR) is a spectroscopic technique use to determine the chemical enviroment of the protons present in the molecule under considerations. The peak at 166.88 ppm is attributed to the carboxylic acid carbon atom. The peak at the 131.12 is the peak of the two auto carbon atom on the benzene ring while the peak at 115.09ppm is attributed to meta carbon atom on the benzene ring and 124ppm belongs to para carbon atom. 148.74-146.63 ppm is the peak that is result as a result of absorbtion of auto carbon in the hexane ring while 26.71-33.48 ppm belong to meta carbon and 19.18 belongs to para carbon on the hexane molecule. Due to the electronegative nature of nitrogen and sulphur atom, 182.02-178.63 ppm belong to carbon that is bonded to two nitrogen and double bonded to sulphur atom.

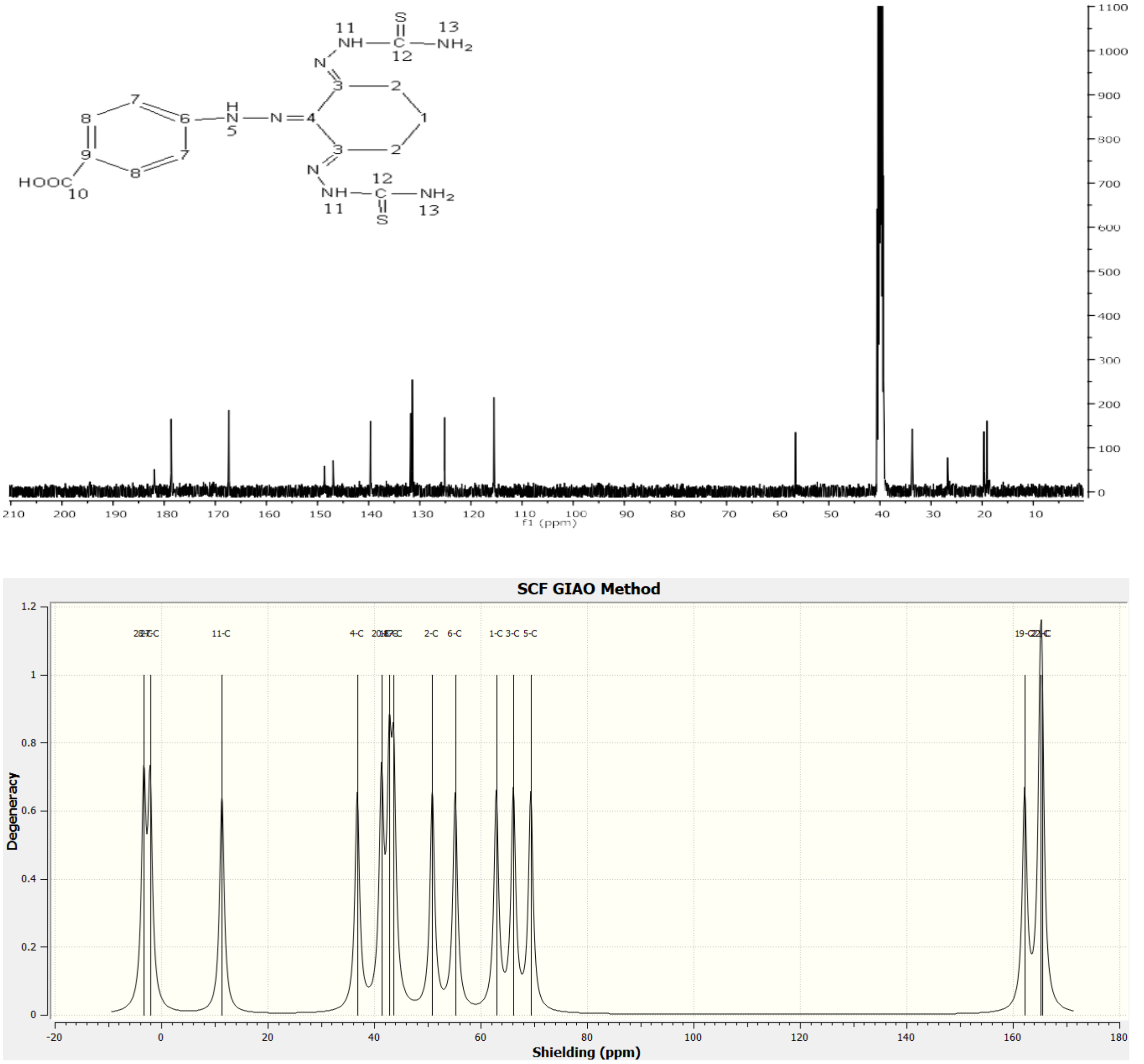


Figure 5. Comparison of ^{13}C-NMR of 4-(2-2,6-bis (2-carbamothionylhydrazone) cyclohexylidene) hydrazinyl) benzoic acid between theoretical and experimental results

4. Conclusion

This research analyse the basic properties of dopamine (including bandgap, density of states and spectroscopic properties) and it is then doped with the first three members of halogen group to compare the change in electronic and other spectroscopic parameters. Different basis set in DFT and Hatree-Fock were used in the optimization process to determine the lowest energy and suitable basis set for the whole calculation of the ascorbic acid, then later the compound was doped with the first three halogens members separately. Spectroscopic properties were determined such as uv-vis and NMR for both the doped and the undoped dopamine. Finally, the FTIR spectra of the dopamine with different doping with halogens group was investigated by theoretical method. It was found that the bandgap is sensitive to the doping as we moved down the group members (the bandgap depends on the electronegativity of the halogens members).

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