



Understanding molecular properties of halogenated cyclohexane – A DFT study



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ABSTRACT

In this work, using density functional theory (DFT) method, halogenated cyclohexane isomers have been studied in order to understand the influence of halogens (F, Cl, Br) on the molecular properties. The substitution of halogens has induced significant changes in the geometrical parameters of cyclohexane ring. Relative energy values suggest that the isomer epsilon in HFCH/HCICH, and isomer theta in HBrCH are the most stable structures. The 1,3 diaxial interactions are present in all the isomers irrespective of the halogen substituents. Fluorination of cyclohexane enhances HOMO–LUMO gap and chemical hardness, which subsequently indicates low reactivity of the HFCH isomers. The principle of maximum hardness (MHP) and the minimum electrophilicity fails to predict stability order of isomers.

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1. Introduction

Cyclohexane ring occupies a pivotal position in organic chemistry as being the only cyclic hydrocarbon, which is completely strain-free and most commonly found in nature, viz., some alkaloids, steroids and terpenoids. The strain free cyclohexane ring assumes shape in the form of either chair or boat. While both the boat and the chair forms of cyclohexane are equally strain free in the classical sense (tetrahedral valency angles of carbon), however, the interaction of neutral non-bonded atoms are mainly repulsive. Therefore, the most stable conformation of the cyclohexane is actually the chair form, in which the distance between the non-bonded atoms is at a maximum. X-ray crystallographic investigation [1,2] of the symmetrical compounds β -hexachlorocyclohexane and β -hexabromocyclohexane provides strong evidence for the chair-form of cyclohexane ring. Eventually, Hassel and Viervoll established that the most stable conformation of cyclohexane is the chair conformation [3] by examining it in the vapor phase using electron diffraction involving the rotating sector technique [4]. The chair conformation of cyclohexane has all bonds on adjacent carbons staggered. Each carbon has an axial bond and an equatorial bond, which are in opposite directions. The bonds, which are nearly parallel to the principal molecular axis are the axial bonds, written as vertical lines, which point up and down alternately. The other six bonds known as the equatorial bonds

are nearly perpendicular to the axial bonds and are directed away from the ring. The conformations can be interconverted by “flipping” the ring. Substituents on cyclohexane can, in principle, occupy either axial or equatorial positions and the stereochemistry of cyclohexane is widened by substituting cyclohexanes.

Compounds with halogen substitution are an important class of chemicals, which are widely distributed in all areas of the environment such as aqueous, atmospheric, and biosphere. Many halogenated and poly halogenated aliphatic and aromatic hydrocarbons belong to a category of chemical carcinogens [5,6] and so its presence becomes more important in the environment [7]. The hexachlorocyclohexane isomers are one of the most widely used and most widely detected organochlorine pesticides in environmental samples. The gamma hexachlorocyclohexane isomer (Lindane) is an insecticide belonging to the group of persistent organic pollutants and has been produced by chlorination of benzene under UV light. This gamma isomer has three neighbouring axial and three equatorial chlorine atoms attached to the cyclohexane ring [6,8] and the laboratory studies, have indicated that the gamma isomer can be isomerized to the alpha form by UV radiation although this has not been proven in an environmental setting. The properties of hexachlorocyclohexanes are largely dictated by the axial and equatorial positions of the chlorine atoms on each molecule.

From the above discussion, we see that there are few studies on the axial and equatorial preferences for mono and disubstituted cyclohexanes [9], however, the hexasubstituted cyclohexanes and their relative stability [10] has not attracted so much attention.

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Thus, it is of interest to search for possible conformers of various hexasubstituted halo cyclohexanes, which could provide information on its structural form. The results obtained subsequently may be useful for the analysis of a carbon–halogen and halogen–halogen interactions. Further, the results of this study will also be useful to analyse the structural features of novel systems like graphene which have a similar carbon atom arrangement, with strong application in material science.

2. Computational details

Density functional theory (DFT) method is employed to obtain the geometries and energetics of hexafluorocyclohexane (HFCH), hexachlorocyclohexane (HCICH) and hexabromocyclohexane (HBrCH) isomers. The geometry optimization has been performed by the DFT method at M06-2X/6-311++G (d, p) level of theory in the gas phase. The frequency calculations carried out confirm that all the optimized structures correspond to true minima as no negative vibration frequency was observed. The substitution effect in the isomers has been studied with the help of DFT [11] derived global descriptors such as chemical hardness, chemical potential and electrophilicity index. The chemical hardness (η) and chemical potential (μ) were calculated using the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies at the above level of theory. Gibbs free energy has been calculated for all the isomers. All calculations were performed using the Gaussian 09W computational package [12].

3. Results and discussions

The optimization of cyclohexane and its halo substituted isomers i.e., hexafluorocyclohexane (HFCH), hexachlorocyclohexane (HCICH) and hexabromocyclohexane (HBrCH) were performed at M06-2X/6-311++G (d, p) level of theory in the gas phase. Seven isomers, each for HFCH, HCICH and HBrCH were obtained and are named as alphaX (α X), betaX (β X), gammaX (γ X), deltaX (δ X), epsilonX (ϵ X), etaX (η X) and thetaX (θ X) (where X = Cl, F, Br). The seven isomers, each differ based on the arrangement of substituents in axial (a) and equatorial (e) positions, i.e., alpha (aaaaee), beta (eeeeee), gamma (aaae), delta (ae), epsilon (aeae), eta (aeae) and theta (aeae) [13]. Figs. 1 and 2 presents the molecular arrangement and labelling of atoms for cyclohexane and its halo substituted isomers respectively.

3.1. Geometrical parameters

The selected bond lengths and bond angle value of cyclohexane along with that of isomers HFCH, HCICH and HBrCH are given in Table 1. In cyclohexane, the average C–H bond lengths for the

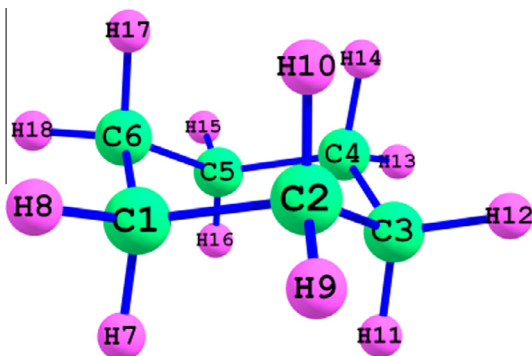


Fig. 1. Optimized structure of cyclohexane calculated using M06-2X/6-311++G (d, p) level of theory.

hydrogen atom in the equatorial and axial positions are 1.095 Å. On the substitution of halogens, for fluorine atom irrespective of its position, there is a negligible change in the C–H bond length values (range 1.092–1.095 Å). However, for the chlorine and the bromine substitution at the carbon atoms, there is a significant change in the C–H bond length values. The C–H bond length in HCICH and HBrCH isomers are in the range 1.088–1.092 Å and 1.087–1.090 Å respectively (Table 1). From the above results we see that the increase in the atomic radii of the halogens from fluorine to bromine, affects the hydrogen atom, thereby leads to the decrease in C–H bond length values. Among all the halogen substitutions (HFCH, HCICH and HBrCH), the isomer alpha possesses minimal C–H bond length value.

The substitution of halogens in cyclohexane results in the carbon–halogen bond (C–X, where X = F, Cl, Br). The C–F bond length is in the range 1.373–1.379 Å. The minimum and maximum C–F bond length corresponds to the isomer theta (1.373 Å) and isomer alpha (1.379 Å) respectively. Similarly, in C–Cl bond, the value of the minimum bond length (1.784 Å) corresponds to the isomer theta and the maximum bond length (1.795 Å) to isomer alpha. Also, the isomer epsilon possesses the minimum C–Br bond length (1.951 Å), while the isomer alpha possess the maximum C–Br bond length (1.962 Å). From the above results as expected C–F bonds are shorter compared with C–Cl and C–Br bonds. Further, the averaged X···X (X = F, Cl and Br) distances of the neighbouring atoms have also been determined and are given in Table 1. Isomer delta in all the three substitutions possesses the maximum halogen···halogen distance, while isomer alpha corresponds to minimum X···X distance in HFCH and isomer theta corresponds to minimum X···X distance in chlorine and bromine substituents. Overall, the halogen···halogen distances determined, follows the order: Br···Br > Cl···Cl > F···F [14]. It is evident from Table 1, that the X···X distances considered here are shorter than the sum of van der Waals radii of X and X. However, it is important to mention here that these short distances between halogens does not refer to the existence of attractive or repulsive interaction between the halogens, which is rather dependent only on the interaction energies of the intramolecular contacts [15,16]. Besides the above, the C–C bond, which forms the backbone of the cyclohexane structure, is also found to be affected by the halogen substitution. The fluorine atoms substituted at both the equatorial and axial positions of the carbon atom strengthens the carbon–carbon bond by 0.009–0.013 Å. This has led to the shortening of C–C bond lengths (1.518–1.522 Å), when compared with the C–C bond length before substitution (1.531 Å, Table 1). Thus, in fluorine substituted isomers, minimum C–C bond length corresponds to isomer beta and maximum to isomer alpha. In contrast, the chlorine and bromine substitution in cyclohexane does not affect the C–C bond. There is no appreciable change in the C–C bond lengths of the isomers of HCICH and HBrCH (Table 1).

The cyclohexane ring tends to assume certain non-planar conformations, which have all the angles closer to 109°. The carbon–carbon bonds along the cyclohexane ring are sp^3 hybrid orbitals, which have tetrahedral symmetry and therefore angles between bonds of a tetravalent carbon atom has a preferred value of $\sim 109.5^\circ$. In our study, from Table 1, the \angle CCC in cyclohexane structure is 111.11° . For the fluorine substituted isomers, the average value of \angle CCC is in the range 110.3° – 111.9° , which shows the minimal effect of the fluorine substitution. However, considerable strain in \angle CCC is observed for HCICH and HBrCH isomers. The bond angle \angle CCC in HCICH and HBrCH isomers varies from 110.3° to 112.6° and 110.3° to 112.8° respectively. Of all the isomers under study, the minimum bond angle value corresponds to isomer epsilon. In all the three substitutions, the isomer alpha (aaaaee) possesses the maximum \angle CCC and this may be due to the number of axial substituents. In general, the \angle CCC bond angle of all the

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