Asian Journal of Chemistry; Vol. 33, No. 2 (2021), 338-344

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23006

ab initio Study on the π-π Stacking and Halogen Interaction in Chlorobenzene Systems in Comparison to Chloro Substituted Ethenes

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Received: 29 September 2020; *Accepted*: 9 November 2020; *Published online*: 15 January 2021; AJC-20218

This study emphasizes on the π-π stacking and halogen interaction among chlorobenzene in comparison to the interactions in chloro substituted ethene systems. Studies of the stacked chlorobenzene systems, reveal that the π-π stacking interactions energy of the staggered conformation (dihedral angle 120º) gives much more stable stacked model than that of others. We have also studied the variation of π-π stacking interaction in chloro substituted ethene systems (monochloroethene, dichloroethene, trichloroethene and tetrachloroethene) to compare the change in interaction energy values. Among all the chloro substituted ethene systems, stacked tetrachloroethene monomer gives more stable conformation with more negative interaction energy value.

Keywords: Stacking and halogen interaction, Substituted chlorobenzene, Dihedral angle.

INTRODUCTION

Non-covalent halogen-bonding interactions (short or long range) are strongly directive and they show vast number of applications in crystal engineering, material chemistry, solid state synthesis and drug discovery of various organic molecules in the area of supramolecular chemistry [1-6]. Halogen bonding and hydrogen-bonding have many properties in common, both physical and chemical, for example, the type and kind of halogen bonding greatly depends on many different factors and substances altogether, producing an effect greater than the sum of the individual effects, also known as cooperative or synergetic effects [7-11]. These effects can regulate the strength and stability of the biological and chemical systems consisting of halogen bonding and provide them with desired functions and properties.

The size and polarizability are the two main properties of halogen bonds that differentiate them from other hydrogen bonds. The halogens are much larger in size and more polarizable than hydrogen; thus halogen bonding complexes are effectively stabilized by dispersion forces of interactions. The most commonly studied halogen bond types usually arise between a carbon bounded halogen along with an electronegative atom, such as oxygen, nitrogen, or sulphur [12]. Halogen bonds involve sigma-hole, *i.e.* halogen bonds requires an electrostatic attraction around the vicinity of the positive charge situated along the carbon-halogen bond and a negatively charged atom (*i.e.* C---X···Z; X = Cl/Br/I; Z = O/N/S [13]. Thus, in this case the bound halogen is also known as the halogen bond donor and the electronegative atom with which the halogen interacts is called the halogen bond acceptor. The sigma-hole of a halogen bond is mainly dependent on few factors that control its size and charge; thus varying the strength of a halogen bond interaction. Literature studies reveal that the larger size of the halogen (X), greater the sigma-hole hence greater is the probability of the atom or molecule to form a halogen bond (I > Br > Cl > F) [14,15].

Halogen bond is often found in nature as R---X, where the halogen atom (X) acts as the Lewis acid and the other end of the halogen bond acts as a Lewis base (hereafter denoted as X) possessing at least one lone pair of electron. Halogen bonds can commonly be viewed as short range type of interactions; usually depicted as R---X---Y---Z, where X is a halogen (typically Cl/Br/I) which is a part of the molecule R---X. On the other hand, Y---Z is a Lewis base (where Y is typically O/N/S) [16]. Recently, much effort has been given to study the significance of cooperative effects that occur between different halogen bonding interactions or sometimes between a halogen bond and other types of intermolecular interaction in complexes where these interactions coexist. Theoretically, it has been observed that such attractive interaction in halogen bonds happen from the terminal part of positive electrostatic potential (ESP), known as sigma-hole, of covalently bound halogens along the direction of the R---X bonds [17]. The strength and stability of the R---X---Y---Z halogen bond is purely dependent on the group adjacent to X. This non-covalent interaction strengthens when the X atom is connected to an electron withdrawing atom or group and Y atom is joined with an electron-donating atom or group. In several studies C---X---Y (Y= O, N, *etc*.) were found to be mainly linear systems because the halogen atom is covalently bonded with the carbon atom. Moreover, it has a strong tendency to act as Lewis acid [18,19]. This directional behaviour of halogen-bonding can be explained by using the anisotropic concept of distribution of electron density around the halogen nuclei. This anisotropy character of charge distribution in halogen atoms was observed experimentally in the mid-1980s and recently the study has been established theoretically for unperturbed carbon-bonded halogen atoms [20-23]. The anisotropy behaviour of halogen atom has another important outcome; which is, the overabundance of electron charge density in a direction perpendicular to C---X bond. Due to this reason, the halogen atom might also act as the Lewis base, for example when it plays the role of proton acceptor in H-bonding. Thus halogens show dual behaviour; this dual character of the halogen atoms was revealed during the analysis of H-bonded and X-bonded complexes where the halogens act as the Lewis base and Lewis acid, respectively [24,25]. Therefore, it can be anticipated that the halogen atom acquires the potential to play a significant role of both the Lewis acid and Lewis base at the same time, through H-bond and X-bond in one complex and as a result of this, additional stabilization of the complex can also be considered.

The structure and existence of molecules in the π-systems, has been well studied giving rise to typical halogen or hydrogen bond interactions [26]. The X---π type of interactions give rise to weak but directional packing pattern, which assists in the evaluation and stabilization of molecular assemblies [27]. Moreover, π-π interactions undoubtedly play an important role in the X----π and halogen-bonding interactions and it also helps in determining the appropriate molecular conformations, geometries, assemblies and structure of large biomolecules [28,29]. The π-systems with halo atoms form different interaction sites and can interact in various geometrical arrangements, for example, face-to face, offset and point-to-face arrangement. Thus, this has been found to be a useful tool for handling molecular components in crystals [30,31].

COMPUTATIONAL METHODS

ab initio Calculations have been shown useful for studying the non-bonded interactions of aromatic molecules. The present studies focus how the interaction energies can be improved with the inclusion of diffused functions in MP2 level of calculations. Present results show that the interaction energies do not considerably vary with the inclusion of more diffuse functions in the basis set. The interaction energies obtained from MP2/6-311++G(d,p) calculations are found much better than any other computational methods. All the electron correlation energies for chlorobenzene and chloro substituted ethene systems have been calculated by *ab initio* level of theory. The Gaussian09 program was used for the *ab initio* molecular orbital calculations to evaluate total interaction energies. Electron correlation was accounted for the MP2 level and the basis set 6-311++G(d,p) has been implemented in the Gaussian program. Geometries of isolated molecules were optimized at the MP2/6-311++G(d,p) level and used for the calculations of interaction energies of chlorobenzene and chloro substituted ethene systems. The minimized stacked structures were obtained by MP2 method which shows the most favoured geometry. All the calculations were performed with the Gaussian09 software package and the visualization was done by GaussView 5.0 and Arguslab [30].

The interaction energy for the stacked geometry can directly be calculated by the following equation:

$$\text{Interaction energies} = E_{st} - 2 \times E_{us}$$

where, E_{st} = energy of stacked model, E_{us} = energy of unstacked model.

Construction of models: The eclipsed conformation of stacked chlorobenzene and chloro substituted ethene systems show exact sandwich form at a dihedral angle of 0º. On the other hand, the staggered conformation for stacked phenolic dimers may also suitably stacked at different dihedral angles, *viz.* 60º, 120º and 180º. The individual models in a stacked conformation of stacked chlorobenzene dimers are separated at a fixed vertical separation of 3.6 Å, while for chloro substituted ethenes, the separation is at 3.0 Å which are found to be the most favoured separations between two chlorobenzene and chloro substituted ethenes, respectively. The -Cl group of the chlorobenzene ring and chloro substituted ethene plays an important role in the stability of stacking interaction in the stacked dimers. Therefore, during the construction of stacked models, -Cl group of the two rings may be placed either in same or opposite direction. Here, we have constructed the stacked models to study the stacking interactions of following systems:

Stacked models	Dihedral angle (°)
Chlorobenzene-chlorobenzene	0°, 60°, 120° and 180°
Dichlorobenzene-dichlorobenzene	0° and 60° (0°~180° and 60°~120°)
Chlorobenzene-dichlorobenzene	0° and 60° (0°~180° and 60°~120°)
Mono, di, tri and tetra-chloroethene	0° and 90°

RESULTS AND DISCUSSION

In this current investigation, the π-π stacking interaction of chlorobenzene, dichlorobenzene (1,3-dichlorobenzene and 1,4-dichlorobenzene) and chloro substituted ethene systems have been studied for various stacked conformers of a dimer in gas phase. All the stacked models for chlorobenzene stacked systems were prepared with different dihedral angles of 0º, 60º, 120º and 180º, respectively. But, chloro substituted ethene systems were stacked at dihedral angles of 0º and 90º only. The eclipsed conformation of chlorobenzene (with dihedral angle 0º), has been prepared by placing one ring horizontally over the other ring with a constant vertical separation of 3.6 Å, which gives the favourable stacking interaction. Then one ring has been simultaneously shifted from +*x* to –*x* direction along *x*-axis, keeping the other ring at constant position, so as to obtain the most stable minima for the stacked chlorobenzene and dichlorobenzene models. The parallel shifting for the

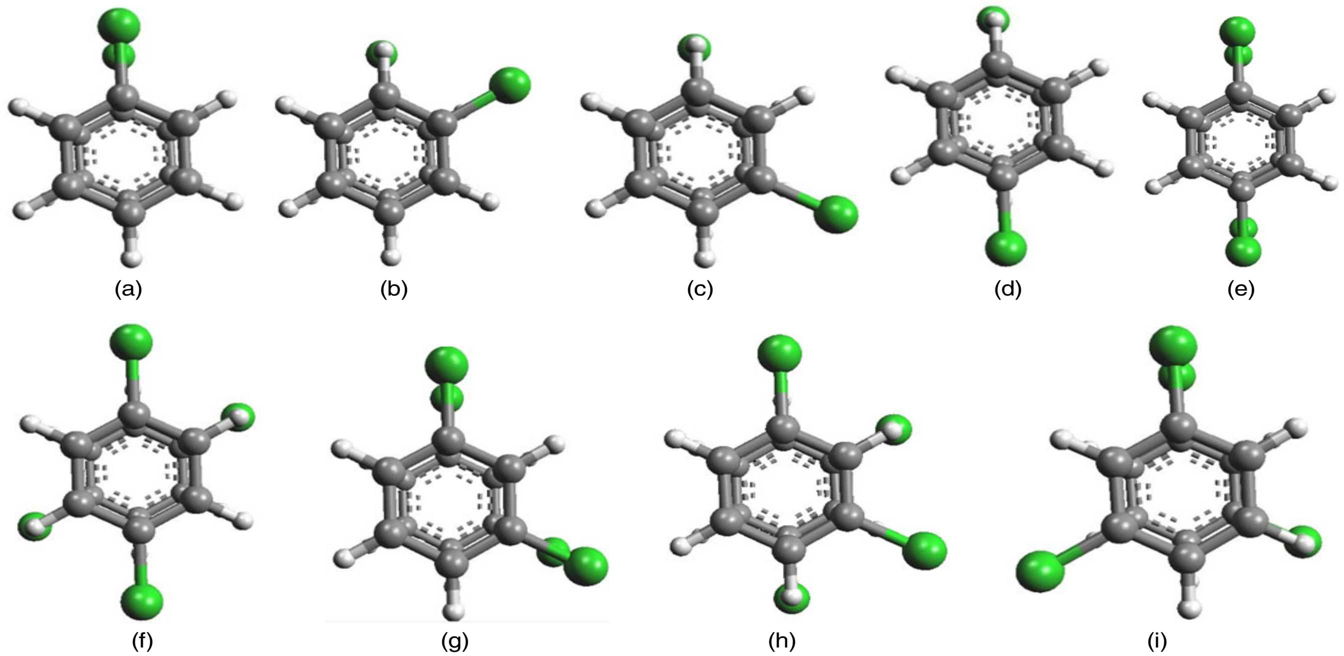
(a) (b) (c) (d) (e) (f) (g) (h) (i)

Fig. 1. Possible stacked models of **chlorobenzene (a-d):** eclipsed (0°), staggered (60°), staggered (120°), staggered (180°); **1,4-dichlorobenzene (e-f):** eclipsed (0°), staggered (60º); **1,3-dichlorobenzene (g-i):** eclipsed (0°), staggered (60°) and staggered (120°)

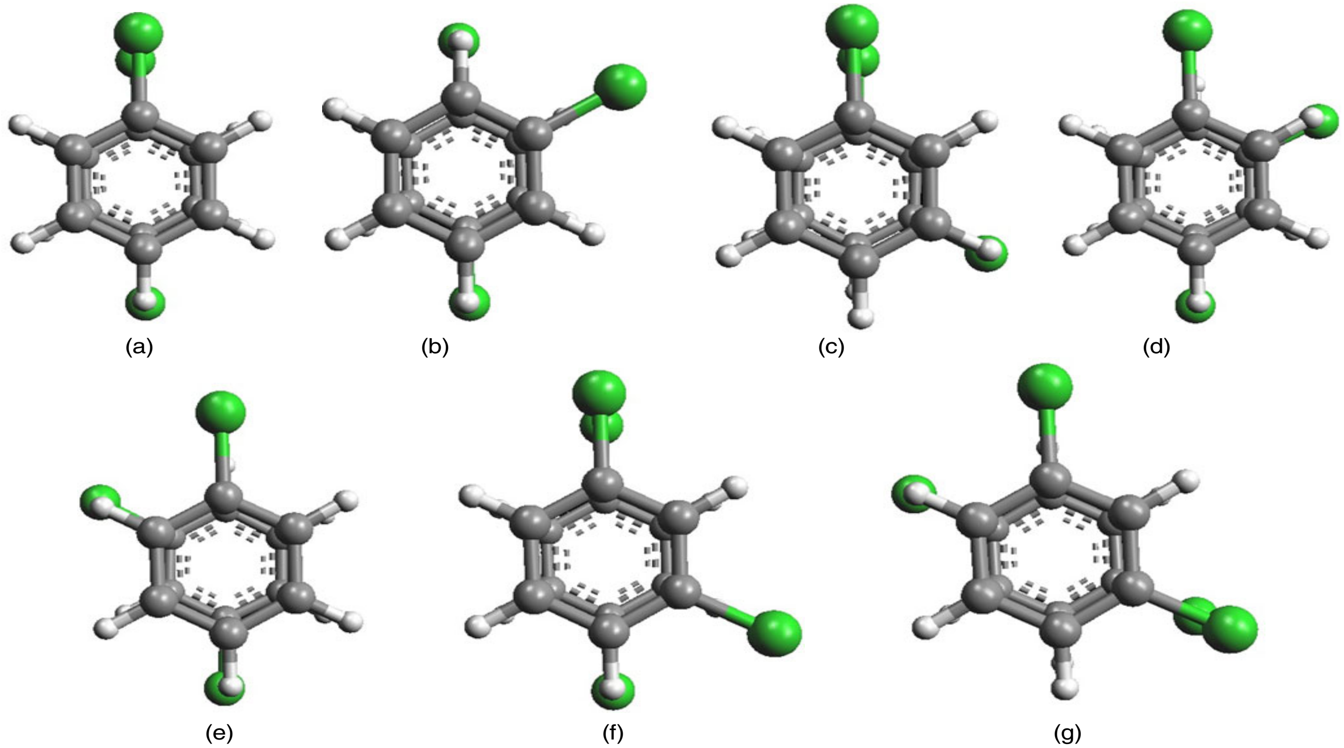
(a) (b) (c) (d) (e) (f) (g)

Fig. 2. Possible models of **chlorobenzene stacked with 1,4-dichlorobenzene (a-b):** eclipsed (0°), staggered (60°); **chlorobenzene stacked with 1,3-dichlorobenzene (c-e):** eclipsed (0°), staggered (60°), staggered (120°); **1,3-dichlorobenzene stacked with 1,4-dichlorobenzene (f-g):** eclipsed (0°) and staggered (60°)

stacked models have been carried out from –3 to +3 Å along *x*-axis. Similarly, all the staggered conformations for the stacked models were prepared with dihedral angles of 60º, 120º and 180º, respectively (Fig. 1). The same procedure was carried out for the different stacked conformations of chloro substituted ethene systems *viz.* mono-, di-, tri- and tetrachloroethene in gas phase; with an internal vertical separation of 3.0 Å (which gives the favourable stacking interaction) (Fig. 2). The eclipsed (0º) and staggered (90º) conformations were prepared and the parallel shifting has been done from -2 to +2 Å along *x*-axis to calculate the stacking interactions.

The relative changes for the π-π stacking interaction energies in gas phase, with MP2 methods for different stacked chlorobenzene, dichlorobenzene and the chloro substituted ethene conformations are shown in Figs. 3-5 and certain stable structures are located from the local minima in the potential energy curves (figures not shown). The stacked conformations with different intermolecular rotations/dihedral angles (0º and 90º) of ethene and substituted chloroethene was studied just to compare the stacking interaction of stacked systems of chlorobenzene and dichlorobenzene. The intermolecular separation between the stacked models play an important role in the

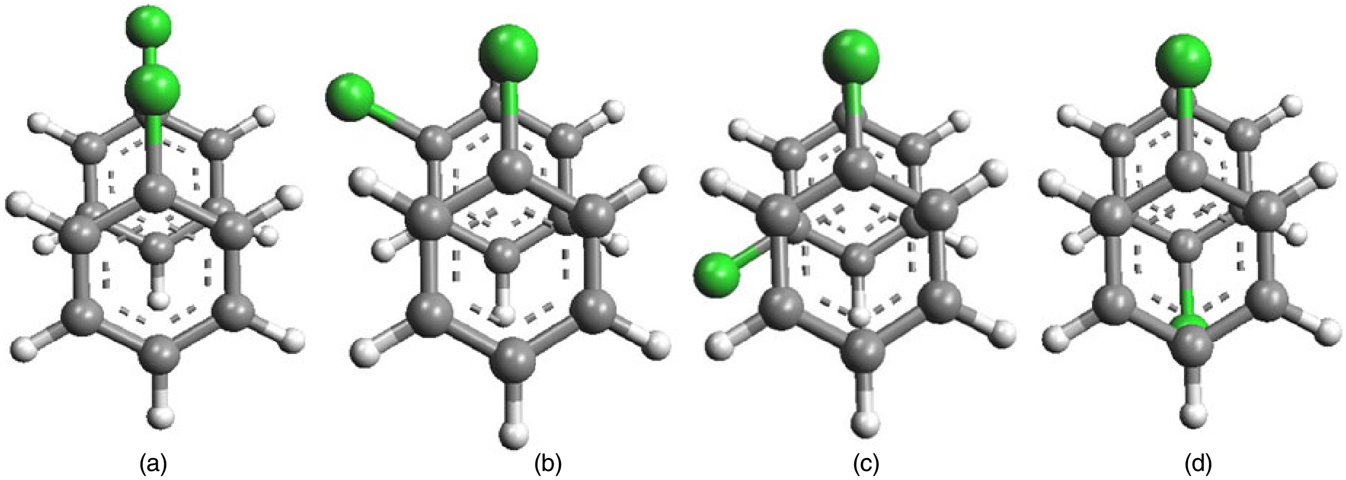

Fig. 3. Minimized stable stacked models of chlorobenzene (a-d): eclipsed (0°), staggered (60°), staggered (120°) and staggered (180°)

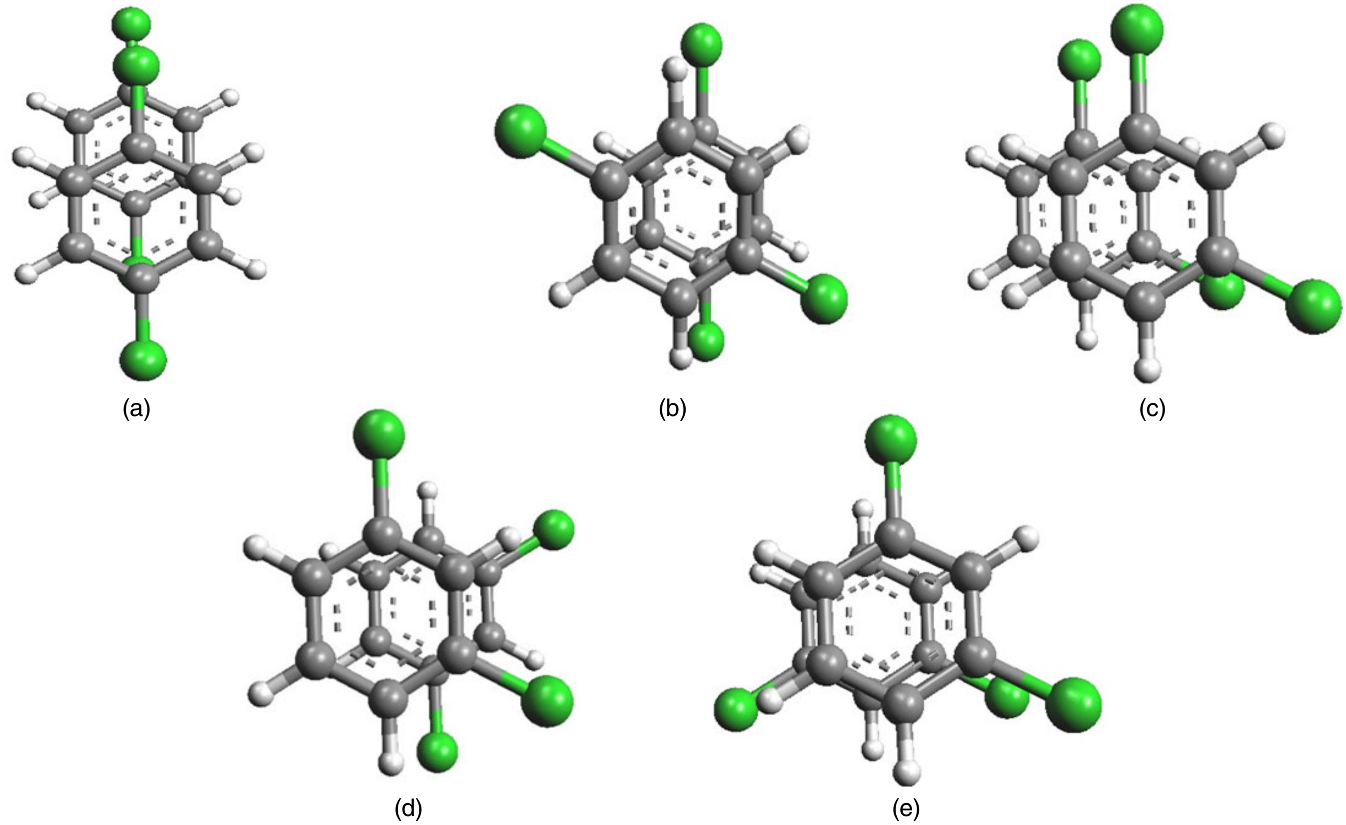

Fig. 4. Minimized stable stacked models of **1,4-dichlorobenzene (a-b):** eclipsed (0°), staggered (60°); **1,3-dichlorobenzene stacked with chlorobenzene (c-e):** eclipsed (0°), staggered (60°) and staggered (120°)

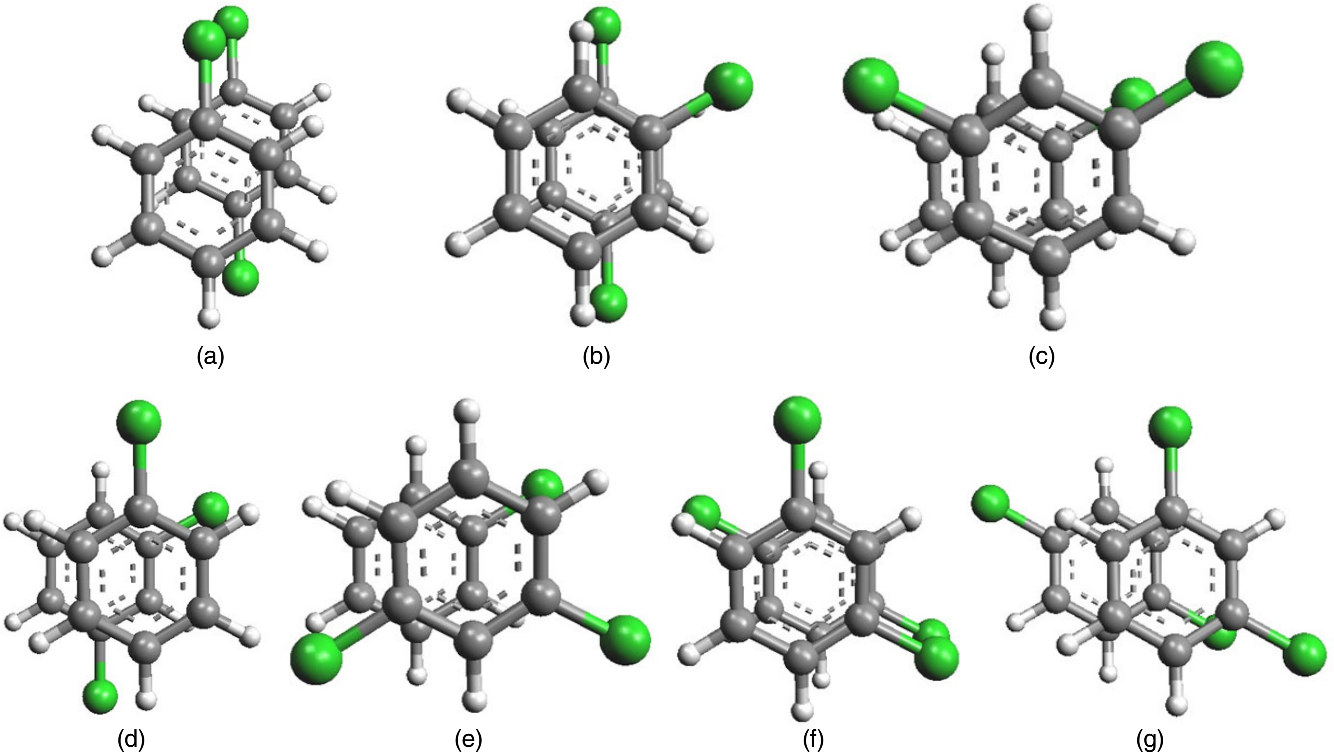

Fig. 5. Minimized stable stacked models of chlorobenzene stacked with **1,4-dichlorobenzene (a-b):** eclipsed (0°) and staggered (60°); **chlorobenzene stacked with 1,3-dichlorobenzene (c-f):** eclipsed (0°), staggered (60°), staggered (120°); **1,3-dichlorobenzene stacked with 1,4-dichlorobenzene (g-h):** eclipsed (0°) and staggered (60°)

calculation of effective π-π stacking interaction energy. The π-π stacking is found to be more feasible when the separation between the stacked molecules are being changed for a certain intermolecular distance (Å); where it is said to be well stacked. In this study, the separation between the stacked models were kept on increasing from 2.8 to 3.6Å and the standard intermolecular separation between the stacked conformations were taken as 3.6 Å for chlorobenzene and dichlorobenzene systems and 3.0Å for the chloro substituted ethene systems, which has given the most favoured stacked models as shown in Figs. 6 and 7. The results of MP2 level of theories reflect the extent of dispersion energies accounted in all these calculations. Indeed, the electron correlations included in MP2 level with diffused function in the basis set could estimate more negative stacking energies, where the increase of diffuse function in the basis set provides little change in the energy values.

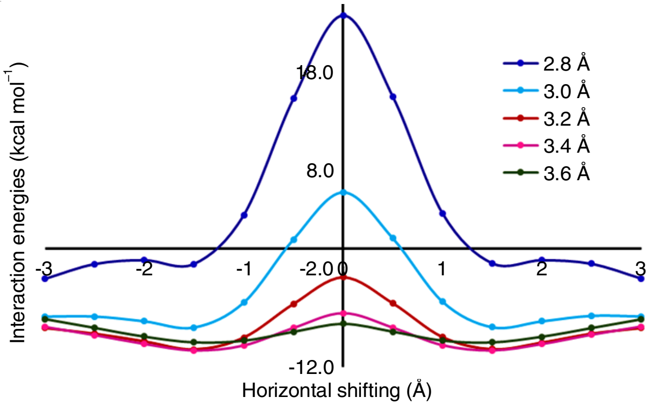

Fig. 6. Plot of interaction energies (MP2 single point) *versus* stacking positions (Å) of chlorobenzene with different vertical separation

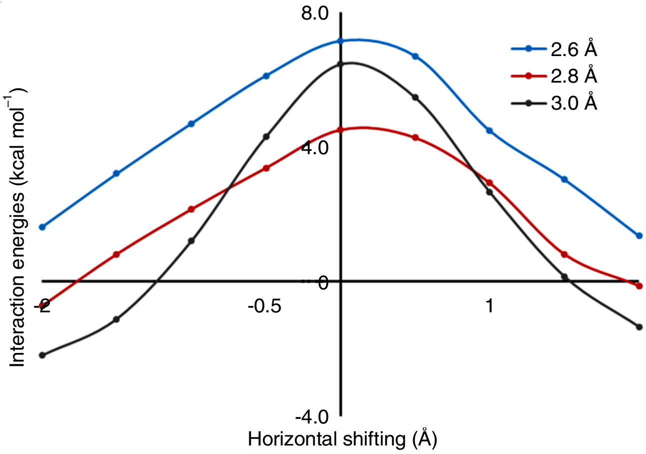

Fig. 7. Plot of interaction energies (MP2 single point) *versus* stacking positions (Å) of chloroethene with different vertical separation

In gas phase, among all the stacked models of chlorobenzene systems, it has been observed that the π-π stacking interaction energy of stacked chlorobenzene-chlorobenzene model with a staggered conformation (dihedral angle = 120°) is found to have the most negative value (-10.539 kcal/mol) and gives more favourable model (Table-1). The more negative stacking interaction energy values (kcal/mol) represent the effective calculation of electron-electron correlation and dispersion forces. On the other hand, between 1,3-dichlorobenzene and 1,4-dichlorobenzene, 1,3-dichlorobenzene gives

TABLE-1
STACKING INTERACTION ENERGIES FOR MINIMIZED STACKED MODELS OF
MIXED CHLORO AND DICLOROBENZENE WITH THE BASIS SET MP2/6-311++G(d,p)

Stacked systems	Interaction energies (kcal/mol)			
	0°	60°	120°	180°
Chlorobenzene-chlorobenzene	-9.512	-9.937	-10.539	-10.455
1,4-Dichlorobenzene-1,4-dichlorobenzene	-14.173	-15.188	–	–
1,3-Dichlorobenzene-1,3-dichlorobenzene	-12.412	-13.965	-13.400	–
Chlorobenzene-1,4-dichlorobenzene	-12.111	-12.943	–	–
Chlorobenzene-1,3-dichlorobenzene	-11.565	-11.991	–	-12.319
1,3-Dichlorobenzene-1,4-dichlorobenzene	-14.071	-14.064	–	–

more favoured structure at a dihedral angle of 60º, with an interaction energy value of -14.064 kcal/mol. Moreover, the π-π stacking interaction energies for mixed stacked systems such as 1,3-dichlorobenzene stacked with 1,4-dichlorobenzene and chlorobenzene stacked with 1,4-dichlorobenzene were also investigated. Herein, it is observed that for both the stacked systems, the minimized stacked models were obtained at a dihedral angle of 60º. But interestingly we have found that chlorobenzene stacked with 1,3-dichlorobenzene gives favoured model at a dihedral angle of 180º with an interaction energy value of -12.319 kcal/mol (Table-1).

If we study the variations among the different chloro substituted ethene systems, it is observed that stacked chloroethene-chloroethene model gives the most favoured conformer for model IV (Table-2). It is because of the minimum repulsion at a vertical separation of 3.0 Å. But among the different stacked chloro substituted ethene systems, 4-chloroethene---4-chloroethene stacked system gives more favoured stacked model, with an interaction energy value of -8.966 kcal/mol; due to the presence of four chlorine atoms which shows strong halogen-π interaction (Table-3). Even with an intermolecular rotation of 90º, 4-chloroethene---4-chloroethene gives the most negative interaction energy value of -9.479 kcal/mol (Table-4). The relative changes of the interaction energies of different stable stacked models of stacked chlorobenzene and chloro substituted ethene molecules and certain stable stacked structures are located from the minima in the interaction energy plots (Tables 1-4) *i.e.* it gives the most favoured and stable stacked models. Although the π-π stacking interaction is quite common in all the aromatic systems but in chlorobenzene systems, both π-π and halogen-π interactions are effectively observed. Therefore, the π-π stacking interaction energy for chlorobenzene system with different intermolecular rotations give more negative interaction energy value than that of non-halogen aromatic stacked systems. On the other hand, due to the presence of four chlorine atoms in tetrachloroethene, the halogen-π interaction is much more effective than that of π-π interaction, which results the most negative interaction energy values and thus it gives most favoured minimized model than that of other chloro substituted ethene systems (Table-4).

TABLE-2
STACKING INTERACTION ENERGIES FOR
MINIMIZED STACKED MODELS OF mono, di, tri AND TETRA-
CHLOROETHENE WITH THE BASIS SET MP2/6-311++G(d,p)

Stacked systems	Interaction energies (kcal/mol)			
	Model I	Model II	Model III	Model IV
C_2H_3Cl-C_2H_3Cl	-2.191	-2.042	-2.696	-2.876
$C_2H_2Cl_2$-$C_2H_2Cl_2$	-2.366	-4.156	-6.261	–
C_2HCl_3-C_2HCl_3	-6.628	-6.700	–	–
C_2Cl_4-C_2Cl_4	-8.966	–	–	–

TABLE-3
STACKING INTERACTION ENERGIES FOR MINIMIZED
STACKED MODELS OF TETRACHLOROETHENE
WITH THE BASIS SET MP2/6-311++G(d,p)

Stacked systems	Interaction energies (kcal/mol)
C_2Cl_4-C_2H_3Cl	-8.970
C_2Cl_4-$C_2H_2Cl_2$	-8.966
C_2Cl_4-C_2HCl_3	-6.841
C_2Cl_4-C_2Cl_4	-8.966
C_2Cl_4-C_2H_4	-3.677

TABLE-4
STACKING INTERACTION ENERGIES FOR MINIMIZED
STACKED MODELS OF mono, di, tri AND TETRA-
CHLOROETHENE STACKED WITH 90° DEHDRAL
ANGLE WITH THE BASIS SET MP2/6-311++G(d,p)

Interaction energies (kcal/mol)			
C_2H_3Cl-C_2H_3Cl	$C_2H_2Cl_2$-$C_2H_2Cl_2$	C_2HCl_3-C_2HCl_3	C_2Cl_4-C_2Cl_4
-2.432	-3.777	-4.358	-9.479

Conclusion

From the above studies, it has been observed that the π-π stacking in chlorobenzene systems results in more negative interaction energy values than that of other aromatic systems due to the presence of both π-π and halogen-π interaction. Among the different stacked chlorobenzene systems, it has been observed that minimized π-π stacking interaction energy of the staggered conformation (dihedral angle 120°) gives more negative interaction energy values as shown in Table-1. The staggered conformation gives more negative interaction energy values due to less repulsive forces. It has been observed that both 1,3-dichlorobenzene and 1,4-dichlorobenzene systems give effective π-π stacking interaction (since both the stacked models give negative stacking interaction energies). Moreover, we have studied the variation of π-π stacking interaction in chloro substituted ethene systems (monochloroethene, dichloroethane, trichloroethene and tetrachloroethene) to compare the change in interaction energy values. Among all the chloroethene systems, stacked tetrachloroethene shows strong halogen-π interaction and gives the most stable conformations.

ACKNOWLEDGEMENTS

The authors are highly grateful to the AICTE-TEQIP-3 fund and Ministry of Human Resource Development (MHRD), New Delhi for providing research assistance.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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