

DFT Studies of Halogen Bonding Abilities of Nitrobenzene with Halogens and Chlorofluorocarbons

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Summary: Chlorofluorocarbons are being used as coolants since the last more than fifty years, and their increasing concentration in atmosphere causes the ozone layer depletion, therefore to develop a sensor for detection of chlorofluorocarbons is environmentally significant. In this article the halogen bonding abilities of nitrobenzene along with halogens and different chlorofluorocarbons have been investigated theoretically at the B3LYP/6-31+G(d) method of DFT. All physical properties such as binding energy, equilibrium distance and dipole moment showed halogen bonding formation. Our investigations revealed that that electron rich nitrobenzene can be used as good sensor for the sensing of halogens (Cl₂, Br₂ and F₂) and different chlorofluorocarbons (CFCs).

Key words: Halogen bonding, Chlorofluorocarbons, Nitrobenzene.

Introduction

Non-covalent interactions are fundamental to supramolecular chemistry [1-3], among all non-covalent interactions, hydrogen bonding is the one that has been studied extensively [4-7], but since last one decade halogen bonding has got considerable attention due to its very important role in biology [8-9], crystal engineering [10-12] as well as in molecular recognition systems [13]. Halogen bonding is directly related to electron donation of lewis bases to halogen atoms and can be defined as the non-covalent interaction of halogens with halogens or lewis bases [14-16]. Halogen bonding is generally weaker than hydrogen bonding (5-30 kJ/mol) [17-19]. Halogen bonding reduces internuclear distances up to twenty percent as compared to the all Van der waals distances [20]. Generally halogen bonding is of two types, (i) halogen halogen interaction X---X which is due to anisotropic distribution of electron density among halogen atoms, (ii) halogen lewis base interaction X---AX. An anisotropic distribution of electron density in chlorofluorocarbons (CFCs), make them suitable lewis base acceptors.

Chlorofluorocarbons are strong candidate for halogen bonding since multiple halogen atoms are available. Chlorofluorocarbons are being used in refrigerators and in cooling industry since more than fifty years as coolants [21], the most common example is freon. Chlorofluorocarbons produce chlorine and other reactive species on photolysis, which cause the ozone layer depletion [22]. Due to ozone layer depletion intensity of UV radiations increases on the earth surface, which may cause some eye diseases (Pterygium, Cataract Ocular melanoma), skin diseases like melanoma skin cancer, UV induce skin allergy and UV-induced immunosuppression [23]. A quick method to sense the chlorofluorocarbons is the need of time; we thought that a sensor for the detection of chlorofluorocarbons

(CFCs) can be designed based on halogen bonding ability of CFCs toward strong bases. Nitro group attached to a benzene ring acts as a very strong lewis base due to high electron density on oxygen and the electron withdrawing inductive and resonance effect of nitro group [24].

As a result of these properties it can act as a potential candidate for the halogen bonding and here the main focus of this study was to investigate the halogen bonding ability of different halogens (Cl₂, Br₂ and F₂) and chlorofluorocarbons with nitrobenzene theoretically. To the best of our knowledge halogen bonding ability of chlorofluorocarbons and nitrobenzene is not reported yet (Fig. 1)

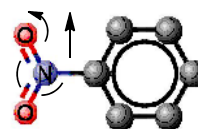


Fig. 1: Optimized Structure of Nitrobenzene.

Results and Discussion

Optimized complexes of nitrobenzene with chlorine, bromine, fluorine and chlorofluorocarbons (2-7) are shown in Fig. 2. Complexation energies (uncorrected and BSSE corrected) along with equilibrium distance and dipole moment are given in the Table-1. Geometrical characters of all halogen nitrobenzene complexes (2-4) were found almost similar, and all three halogens (chlorine, bromine and fluorine) interact with nitrobenzene in the same fashion. Bond angle of O-N-O and C-N-O bond angle in nitrobenzene (before complexation) were 123-124° and 117-118.5°, respectively. Similarly N-O and C-N bond lengths in nitrobenzene were 1.23-1.25 Å and 1.46-1.48 Å, respectively.

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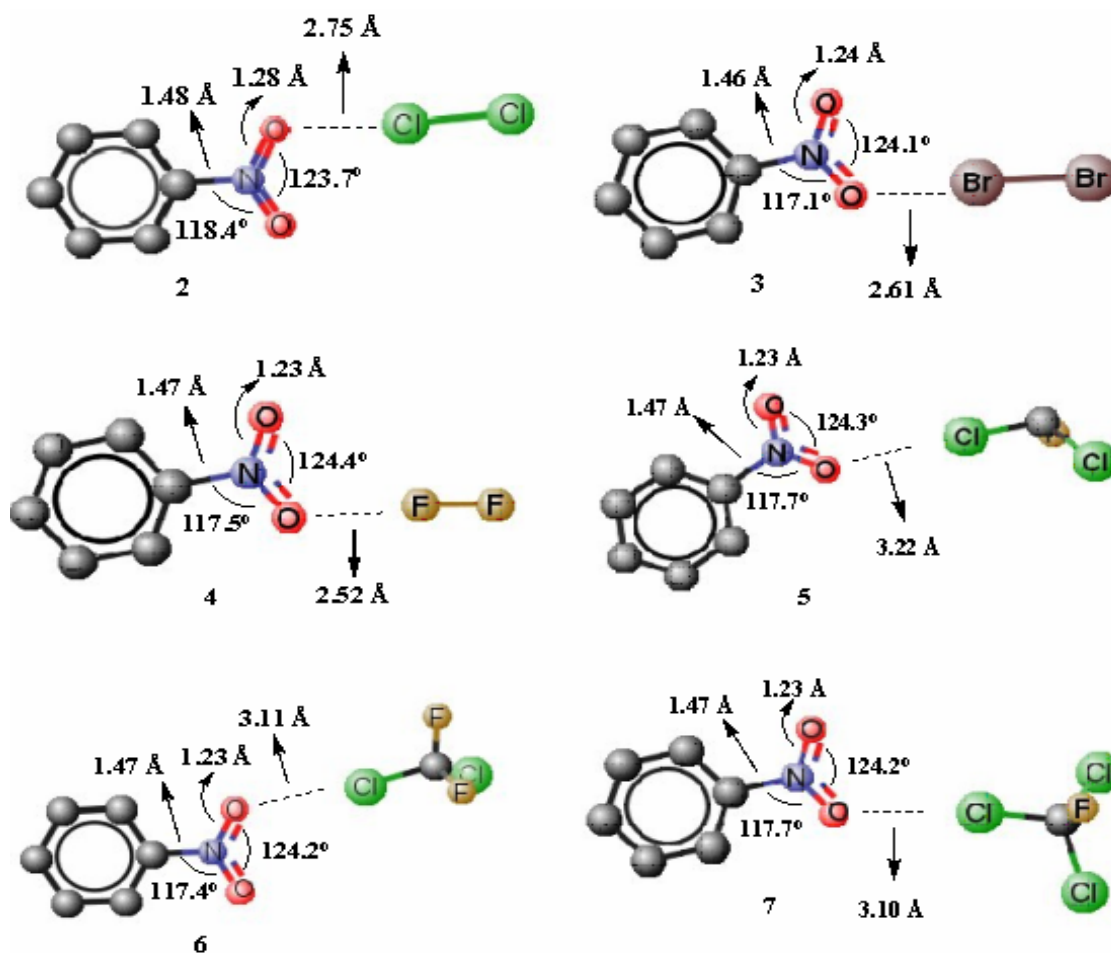


Fig. 2 Optimized structure of complexes 2-7.

Computed binding energy of chlorine---nitrobenzene complex **2** was 2.24 kcal/mol, the BSSE corrected energy was 1.87 kcal/mol (large difference in BSSE corrected energy is normal and is according with values already reported by C. Garau *et al* [25], and same trend follows in case of halogen bonding specially for bromine [26]. Equilibrium distance of nitrobenzene and chlorine in complex **2** was 2.75 Å and dipole moment of the complex **2** was 6.40 D (higher the value of dipole moment, more strong the complexation will be [27]). Decrease in energy, equilibrium distance and dipole moment of complex **2** clearly showed strong interaction between nitrobenzene and chlorine molecule and revealed that the complex was more stable than the isolated molecules, and also a clear evidence for strong halogen bonding formation. Complexation energy of bromine---nitrobenzene complex **3** was 6.82 kcal/mol, while as BSSE corrected energy was 2.68 kcal/mol. Equilibrium distance in bromine---nitrobenzene complex **3** was 2.61 Å and dipole moment was 7.43 D. Computed data showed that

binding was more favorable in case of bromine as compare to chlorine. While as the complexation energy for fluorine---nitrobenzene complex **4** was 0.95 kcal/mol, BSSE corrected energy was 1.26 kcal/mol, equilibrium distance was 2.52 Å and dipole moment was 5.69 D. Computed data showed that binding is less favorable as compared to chlorine and bromine complexes. All physical properties like binding energy, equilibrium distance and dipole moment, those we have described above clearly showed the halogen bonding formation between the nitrobenzene and different halogens and followed the order $\text{Br}_2 > \text{Cl}_2 > \text{F}_2$, that was in close agreement with the reported data in literature [28]. The optimized parameters are consistent with typical "head on halogen bonding interaction", All the optimized bond distances in complexes (**2-4**) are within the range of van der Waals radii (Table-1) which reveals the existence of halogen bonding, and by comparing these values with the reported data (Table-2) values reported here are better, therefore nitrobenzene could be as better sensor material [26].

Table-1: Computational energies with and without BSSE correction (E and E_{BSSE} , kcal/mol), equilibrium distances (\AA) computed for complexes (2-7) and dipole moment (D).

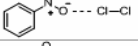
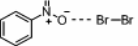
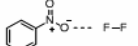
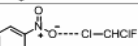
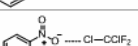
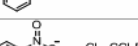
Complex (2-7)	E (kcal/mol)	E_{BSSE} (kcal/mol)	Equilibrium distance (\AA)	Dipole moment (D)
	-2.24	-1.87	2.75	6.40
	-6.82	-2.68	2.61	7.43
	-1.26	-0.95	2.52	5.69
	-0.71	-0.47	3.22	4.69
	-1.19	-0.94	3.11	6.04
	-1.15	-0.88	3.10	5.93

Table-2: Computational energies reported by W. J. Jin and co-workers [26] at different levels CBr_4 with different neutral molecules.

Complexes	E (kcal/mol) B3PW91	E (kcal/mol) MP2
CBr_4 + methanol	-1.6	-2.27
CBr_4 + ethanol	-1.76	-2.13
CBr_4 + ether	-0.26	-0.46
CBr_4 + THF	-5.13	-5.6
CBr_4 + dioxane	-1.86	-2.16

Nitrobenzene and chlorofluorocarbons (dichlorofluoromethane, dichlorodifluoromethane and trichlorofluoromethane) complexes (5-7) showed interactions in the same fashion i.e through single oxygen of nitrobenzene and chlorine atom of chlorofluorocarbons, was very similar as we observed in case of all halogen complexes. No changes were observed in bond angle and bond lengths of isolated molecules and complexes. N-O bond length in all isolated molecules and complexes was found in the range of 1.23-1.28 \AA and N-C bond length was in the range of 1.43-1.48 \AA . Similarly O-N-O bond angle in all complexes 5-7 and isolated molecules was in the range of 123.7 $^\circ$ -124.4 $^\circ$. Binding energy in nitrobenzene---dichlorofluoromethane complex 5 was 0.71 kcal/mol and BSSE corrected energy was 0.47 kcal/mol. Equilibrium distance was 3.22 \AA and dipole moment was 4.69 D. Binding energy for nitrobenzene---dichlorofluoromethane complex 6 was 1.19 kcal/mol, BSSE corrected energy was 0.94 kcal/mol. Computed Equilibrium distance in complex 6 was 3.11 \AA and dipole moment was 6.04 D. Computed binding for complex 7 was 1.15 kcal/mol and BSSE corrected energy was 0.88 kcal/mol, equilibrium distance was 3.10 \AA and dipole moment found was 5.93 D. Computed data for all chlorofluorocarbons complexes (5-7) clearly indicated the halogen bond formation in nitrobenzene and chlorofluorocarbons. Attempts were made to optimize complexes of compounds (5-7) through the fluorine atom with nitrobenzene, however all such attempts were met with failure. Such complexes may exist on shallow potential energy surface which on complete optimization deliver complexes where chlorine is bound to nitrobenzene, Reason for this behavior may

be attributed to the higher affinity of chlorine for halogen bonding compare to fluorine [28].

Experimental

All calculations were performed with Gaussian 09 [29]. Visualization of the results /optimized geometry was achieved with GABEDIT [30] and Marvin view [31]. Geometry optimization of all compounds and complexes (2-7) was carried out at 631+G(d) basis set by using the B3LYP method of DFT. Frequency analysis was performed at the same level of theory to confirm all optimized geometries as true minima (no imaginary frequencies). Energies of the optimized complexes were counterpoise corrected (BSSE) at the same level of the theory B3LYP/6-31+G(d). Normally by using this method, the type of interaction between the host and guest molecule can also be predicted from the amount of interaction energy [32-33]. The interaction can be hydrogen bonding, vander Wall's or Ion dipole (electrostatic) interaction. Normally two methods are in employed, one is the calculation of simple interaction energy (equation 1) and the second is the counter poise corrected energy (BSSE equation 2). With the use of finite basis set, superposition error (BSSE) occur (basis functions of atoms overlap) when atoms of interacting molecules approach one another. Counter poise method corrects this energy. An equation to shown on how to calculate BSSE is given the equation (2)

$$\Delta E_{\text{int}} = E_{\text{Reactant 1}} + E_{\text{Reactant 2}} - E_{\text{Product}} \quad (1)$$

$$\Delta E_{\text{int,CP}} = \Delta E_{\text{int}} - E_{\text{BSSE}} \quad (2)$$

Conclusion

In conclusion we have investigated the halogen bonding ability of nitro group attached with benzene toward halogens (Cl₂, Br₂ and F₂) and different chlorofluorocarbons. Nitrobenzene---bromine complex was found more stable as compare to other complexes of halogens. Different chlorofluorocarbon complexes were also computed and found stable through halogen bonding. Studies with iodine (I₂) and iodine containing compounds are in progress by using the different basis set, because 631G(+)d did not work for heavy atoms.

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References

- S. Park, S. Y. Lee, K-M. Park and S. S. Lee, *Account of Chemical Research*, **45**, 391 (2012).
- V. O. Gelmboldt, E. V. Ganin and M. S. Fonari, *Journal of Fluorine Chemistry*, **135**, 15 (2012).
- C. S. Yun, Y. too and H. B. Ji, *Chinese Journal of Organic Chemistry*, **32**, 686 (2012).
- V. Bianco, S. Iskrov and G. Franzese, *Journal of Biological Physics*, **38**, 27 (2012).
- J. Bonin, C. Costentin, M. Robert, J. M. Savéant and C. Tard, *Account of Chemical Research*, **43**, 372 (2012).
- G. J. Zhao and K. L. Han, *Account of Chemical Research*, **45**, 404 (2012).
- W. Plass, *Co-ordination Chemistry Reviews*, **255**, 2378 (2011).
- E. I. Eger, D. D. Koblin, R. A. Harris, J. J. Kendig, A. Pohorille, M. J. Halsey and J. R. Trudell, *Anesthesia and Analgesia*, **84**, 915 (1997).
- N. P. Franks and W. R. Lieb, *Nature*, **274**, 339 (1978).
- A. K. Przybył and M. Kubicki, *Journal of Chemical Crystallography*, **42**, 685 (2012).
- H. Y. Gao, Q. J. Shen, X. R. Zhao, X. Q. Yan, X. Pang and W. J. Jin, *Journal of Material Chemistry*, **22**, 5336 (2012).
- R. Lo, A. Ballabh, A. Singh, P. Dastidar and B. Ganguly, *Crystal Engineering Communication*, **14**, 1833 (2012).
- P. Metrangolo and G. Resnati, *Chemistry A-Euorpean Journal*, **7**, 2511 (2001).
- M. Erdelyi, *Chemical Society Reviews*, **41**, 3547 (2012).
- M. Fourmigue, *Current Opinion in Solid State and Material Science*, **13**, 36 (2009).
- M. G. Chudzinski, C. A. McClary and M. S. Taylor, *Journal of American Chemical Society*, **133**, 10559 (2011).
- G. B. Piland and P. G. Jasien, *Computational and Theoretical Chemistry*, **988**, 19 (2012).
- A. Kovacs and Z. Varga, *Co-ordination Chemistry Reviews*, **250**, 710 (2006).
- J. S. Murray, Z. P. Shields and P. Politzer, *International Journal of Quantum Chemistry*, **110**, 2823 (2010).
- A. Bondi, *Journal of Physical Chemistry*, **68**, 441 (1964).
- Y. Deng, N. Sun, S. Zheng, C. Zhuang and W. Li, *Indian Journal of Geo-marine Sciences*, **41**, 295 (2012).
- Q. B. Lu, *Physics Reports*, **487**, 141 (2010).
- M. Norval, R. M. Lucas, A. P. Cullen, F. R. de Gruijl, J. Longstreth, Y. Takizawa and J. C. van der Leun, *Photochemical and Photobiological Sciences*, **10**, 199 (2011).
- C. M. Kinart, A. Cwiklinska, A. Bald and Z. Kinart, *the Journal of Chemical Thermodynamics*, **50**, 37 (2012).
- C. Garau, A. Frontera, P. Ballester, D. Quinonero, A. Costa and P. M. Deya, *European Journal of Chemistry*, **179** (2005).
- W. S. Zou, J. Han and W. J. Jin, *Journal of Physical Chemistry A*, **10125**, 113 (2009).
- B. Acemioglu, M. Arik, H. Efeoglu and Y. Onganer, *Journal of Molecular Structure (THEOCHEM)*, **548**, 165 (2001).
- P. Metrangolo, H. Neukirch, T. Pilati and G. Resnati, *Account of Chemical Research*, **38**, 386 (2005).
- Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
- A. R. Allouche, Gatedit-2.2.6, 20 09, ht tp://gatedit.sourceforge.net/.
- Marvin 5.11.0, 2012, ChemAxon (<http://www.chemaxon.com>).
- S. S. Liu, L. J. Bian, F. Luan, M. T. Sun and X. X. Liu, *Synthetic Metal*, **862**, 162 (2012).
- J. Casanovas, M. Canales, C. A. Ferreira and C. Alemán, *Journal of Physical Chemistry A*, **8795**, 113 (2009).