

Interactions Studies On 1-Bromohexane, 1-Bromodecane, 1-Bromooctane With O-Nitro Phenol In CS₂:- Dft Approach

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Abstract - The molecular interactions between 1-Bromohexane, 1-Bromodecane, 1-Bromooctane with O-Nitro phenol in cs₂ has been studied using density functional theory (DFT). Their nature of interaction to form complexes have been analyzed. The complexes form hydrogen bonding among which Br...H-O bond is most stable than other. The PCM method has been employed to optimize the structures in the carbon di sulfide ($\epsilon = 2.6105$) environment and the solvent effect has been studied. Atom in molecule (AIM) analysis has been done to investigate the hydrogen bonding in the complexes. From the topological analysis an excellent linear correlation is obtained between the hydrogen bond length, electron density [$\rho(r)$] and Laplacian density [$\nabla^2\rho(r)$] at the bond critical points. Also the charge transfer from proton acceptor to the proton donor to an anti orbital of H-bond has been analyzed by natural bonding orbital analysis

Keywords: Density functional theory; O- nitrophenol; NBO

I. INTRODUCTION

Ortho-substituted phenols is a popular model system for studying molecular interactions and widely investigated by experiment and theory [1-14]. This compound posses a common proton donator (O-H group), but the proton acceptors may vary within a range. Hence, these compounds give the information about different kinds of proton acceptors during interactions because of the increasing electronegativity of an oxygen atom. Resulting from the electron donation of the OH group to the aromatic ring [15]. Past decade phenols have been identified to participate in hydrogen bonding[16] many ortho-substituted phenols. e.g., O-nitro phenol or O-hydroxyacetophenone are found as substances forming strong hydrogen bonds. From this interaction study well recognized H bonding acids and bases. In table entries of geometry and energy. However, the interaction strengths range from rather strong hydrogen bonds down to extremely weak interactions that may be considered as H-bond[17]. Although the wide focus on interaction study is on halogen acceptors functioning in an essential system like water and molecules, interactions involving halogen acceptor have been found by scholars and reported [19]. In fact, the first use of the term hydrogen bond is connected with halogen acceptors because halogen acceptor is strong hydrogen bond interaction. As per as halogen group concern fluorine and chlorine are detected hydrogen bond due to large partial negative charges in their compounds but low electronegative heavier halogens bromine and iodine has weaker proton acceptor abilities. And the directionality of the hydrogen bond is ruling by the

electron density distribution around hydrogen and an acceptor. The depletion of the electron density on the opposite side of the donor to hydrogen bond would favour a linear hydrogen bonding. Moreover, the rich electron density acceptor in the direction of the lone pair would prefer for a hydrogen bond such preference has been revealed in the hydrogen bond system. The most comprehensive details about hydrogen bonded structures in the solid phase are the Cambridge structural database (CSD)[20-24]. Many statistical analyses based on CSD appeared for the molecular interactions of Fluorine and chlorine. Even rare data Br and I acceptor did not found of these interactions yet. The purpose of this paper is, therefore, to present to the medicinal chemist of proton donor and proton acceptor ability, the 1-Bromohexane, 1-Bromooctane, 1-Bromodecan as acceptor and O-Nitrophenol as a donor in CS₂ (carbon disulphide) as the solvent. this interactions involve recognition sites for drug design. The present study is to investigate the interaction between o-nitrophenol and 1-bromohexane, 1-bromodecane and 1-bromooctane and the influence of latter on the stability of the complex.

II. COMPUTATIONAL DETAILS

DFT method has been employed by Becke's three parameter exact exchange functional (B3)[25] combined with gradient corrected correlation functional of Lee-Yang-Parr (LYP)[26] in combination with B3LYP 6-311++G** basis set for all the calculations. The solute- solvent interaction studies has been done using self-consistent reaction field theory (SCRF) [28-30] on basis of PCM

(Tomasi's polarized continuum model) in the CS₂ environment ($\epsilon = 2.6105$). all the studies and the complexes were geometry optimized at B3LYP/6-311++G** bond of theory. All the optimized structure were conformed to be in the local minima from frequency analysis. The interaction energy of the complexes were corrected for BSSE using counterpoise method of Boys and Bernardi the topological analysis using AIM and Natural bandorbital analysis (NBO) has been done in order to understand the nature of molecular interaction between the structure. The formation of hydrogen bonding and hence the electrostatic interaction is further conformed from MEP analysis. All the calculation are performed with help of Gaussian 09W programming package[33] and all the structure are constructed using Chemcraft

III. RESULT AND DISCUSSION

3.1. Structure and energetics

The isolated 1-bromohexane, 1-bromodecane, 1-bromooctane and o-nitro phenol and their complexes 1-Bromohexane – O-nitrophenol (BH-ONP), 1-Bromodecane – O-nitrophenol (BD-ONP) and 1-Bromooctane – O-nitrophenol (BO-ONP) were geometry optimized at 6-311++G** level are shown in figure.1 for convenience, the optimized monomer 1-Bromohexane, 1-Bromodecane, 1-Bromooctane and O-Nitro phenol are represented as BH, BD, BO and hereafter BH, BD, BO molecules offer several possible acceptor sites to form hydrogen bonding. The geometrical parameters of all the structures are shown in table1 and table2. In all the complexes ONP is acts as a donor and BH, BD,BO as acceptors. The length of the hydrogen bonds formed for the complexes BH-ONP, BD-ONP, BO-ONP are 2.508Å, 2.505Å and 2.527 Å respectively. Additionally intermolecular hydrogen bonding interfered in ONP. an intermolecular hydrogen bonding between Br of form and H18-O1 of ONP is observed. The geometry optimized complexes are depicted in Fig 2. The analysis of all the optimized complexes clearly predict function of hydrogen bonding at the some points ie Br...H-O and H...O-C. The complexes BH-ONP and BD-ONP possess two equivalent hydrogen bond distances 2.508Å and 2.505Å respectively. The calculated bond angle reflect that the hydrogen bonds formed are almost linear.

Interaction energy is calculated using counterpoise procedure by applying the (BSSE) following equation

$$E_{in}(corr) = E_{AB}(AB) - [E_A(AB) + E_B(AB)]$$

Where $E_{AB}(AB)$ is energy of complex, $E_A(AB)$ and $E_B(AB)$ are the energies of monomers A and B with the full complex basis set by setting the appropriate nuclear charge to zero, which is located at the same intermolecular configuration as in the complex. The calculated interaction energies are presented in Table 3 which reveals that among the three system, the large interaction energy is for BH-ONP with a value of -4.58 kcal/mol followed by BD-ONP and BO-ONP having energies -4.32 and -4.20 kcal/mol

Fig (1 & 2) , Table (1-3)

3.2. Topological analysis

Topological analysis of electron density for one of the conformations for the hydrogen bonds [37, 38] in BH-ONP, BD-ONP and BO-ONP complex. This interaction study of electron density on based topological parameters, as the values of the electron density and Laplacian at the bond critical points (BCP) of H...O-H bond. We have studied the nature of interactions involved in the BH-ONP, BD-ONP and BO-ONP hydrogen bonded complexes within the framework of Bader's topological theory of AIM. A BCP (Point corresponding to $\nabla^2\rho = 0$) is found between each pair of nuclei, which considered to be liked by a chemical bond with two negative curvatures (λ_1 and λ_2) and one positive curvature (λ_3) denoted as the (3, -1) critical point. The bond ellipticity defined in terms of the two negative curvatures λ_1 and λ_2 and more is positive curvature λ_3 as $\epsilon = (\lambda_1/\lambda_2-1)$ reflects the derivation of the charge distribution of a bond path from axial symmetry, thus providing a sensitive measure of the susceptibility of a system to undergo a structural change. The Laplacian of the electron density ($\nabla^2\rho$) indicates whether the electron density is locally concentrated ($\nabla^2\rho < 0$) or depleted ($\nabla^2\rho > 0$) and provides a detailed map for basic and acidic regions of a molecule. It is evident that a quantitative comparison of the nature of bonding involved in BH-ONP, BD-ONP and BO-ONP complex should follow from $\nabla^2\rho$ values at BCP and also from other BCP properties. Thus, a values $\nabla^2\rho < 0$ at BCP is unambiguously related to the covalent character of the bond, indicating a sharing of electrons and known to be shared interactions, while $\nabla^2\rho > 0$ implies closed-shell type interaction found in noble gas repulsive states, ionic bonds, hydrogen bonds, and van der Waals molecules.

The calculated values of electron density (ρ) Laplacian ($\nabla^2\rho$), bond ellipticity (ϵ) at BCP (bond critical point) of O...H bonds at the B3LYP level of theory in BH-ONP, BD-ONP and BO-ONP forms are given in Table 3. From table 3 mention that all values in positive so that the Laplacian of electron density are depletion of electronic charge along the bond path, which is a closed shell interaction like as hydrogen bond. Laplacian electron density at the BCP is to be larger for both BD-ONP and BH-ONP complex with 0.4890 a.u. which observed for Br-H-O interaction. This type of large charge density is due to the localization of charges. Thus the BCP method calculated for electron density and stability predicted by energy minimization. Further, the complex BH-ONP and BO-ONP possess an electron density of 0.16032 a.u and 0.15469 a.u for Br...H-O interactions representing in second and third most stable complex. however, the electron density for H...O-C interactions lies in the range 0.60251, 0.65554 and 0.62001 a.u.as the bond is weak compared to Br...H-O. it is mention that the Br...H-O interaction involved in bonding. The positive values of Laplacian of electron density in Table 3 indication of

depletion of electronic charge along the bond path, which is a properties of closed shell interactions such as hydrogen bonds, it is noteworthy that the Laplacian of electron density at BCP is found to be larger for Br...H-O interaction than H...O-C type interaction. meanwhile correlation between the bond length, electron density, and Laplacian of electron density. The curve corresponding to

the correlation fit is shown in fig. 3 & 4, the correlation coefficient between bond length and electron density is inverse, from the calculated data bond length corresponds to a decrease in the electron density, when the bond length is decreased orbital overlapped because of low electron density along the bond. Similarly, bond length and Laplacian density is also inverse. The correlation coefficient value for the electron density and Laplacian density with Hydrogen bond distance are 0.98706, 0.96838. the value of ellipticity for BO-ONP complex is found as higher value to other interactions, this indicates that higher possibility of structural change.

Table:- 4, Fig (3,4)

3.3. NBO analysis

The natural bond orbital analysis reflect formation of hydrogen bond that certain amount of electron charge transferred from the hydrogen acceptor to hydrogen donor, and arrangement of electron density within each molecule part as well as AIM analysis can give necessary information about strength of hydrogen bond in BH-ONP, BO-ONP and BD-ONP complexes but it cannot provide information on electronic charge transfer. Therefore NBO analysis has been an important tool for hydrogen bond analysis. So that NBO analysis has been done using the DFT method to investigate oh hydrogen bonds. The hydrogen/ carbon atom with lone pair acts as donor Br and oxygen as the acceptor in the strong intermolecular charge transfer interaction. the occupation numbers for the proton donor antibonds (X-H) and for proton acceptor lone pairs n(Y) employed at the B3LYP level of theory are shown in Table 5. NBO result analysis compared in the table the charge is transferred between the interacting orbitals and X-H anti-bonding occupation value of proton donor are found to be high for BD-ONP, BO-ONP complexes. Specifically, the complex BD-ONP large amount of charge transfer (0.058) has occurred from ONP (H26-O1) antibonding orbital to BD (Br1) for Br-H-O interaction and it leads to the elongation of the H26-O1 bond. Hence, the anti-bonding occupation values (H-O) and bond lengths of the proton donor H26-O1 are found to be higher on compare with the monomer. Moreover, a similar amount of charge transfer (0.056 and 0.057) to proton donor (H18-O1) and (H22-O1) has observed for BH – ONP and BO – ONP complexes resulting in the elongation of H-O bond from its corresponding monomer. And few H...O-C interactions which explicitly show that minimum charge transfer has occurred

For every donor and acceptor, the stabilization energy E is associated with i-j delocalization is given by the following equation

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F^2(i,j)}{\epsilon_j - \epsilon_i}$$

Where q_i the i th donor orbital occupancy, ϵ_i , ϵ_j are diagonal elements (orbital energies), and $F(i,j)$ is off diagonal elements, respectively, associated with NBO Fock matrix. The $E^{(2)}$ term corresponding to bonding interactions of total charge transfer energy. the stabilization energy between possible and lone pair electrons of the proton acceptor and anti-bonding orbitals of the proton donor has been examined for various intermolecular hydrogen bonds has formed among the complexes at B3LYP/6-311++ G** level of theory and it is present in Table 5. It is mention that there is a correlation between hydrogen length and stabilization energy $E^{(2)}$, shorter the bond length larger stabilization energy. In the case Br...H-O type interactions in BH-ONP, BD-ONP and BO-ONP. The bond is very strong and hence they are found that large value of stabilization energy . for the complex BD-ONP, the major interaction occurs between lone pair Br1 and the contacting (H26-O1) anti bond and interaction has resulted in the stabilization energy of 5.98 kcal/mol. Similar the lone pairs of the acceptor atom O1 in complexes. BH-ONP and BO-ONP have offered their electrons to the H18-O1 and H22-O1 anti bond and thus have a stabilization energy of 5.66 and 5.77 kcal/mol. Hence it is to be observed that Br...H-O interactions surpass H...O-C interactions. Further. the calculated stabilization energy value predicts BD-ONP to be most the most stable among 3 complexes as confirmed by the electron density values calculated at BCP. In case of H...O-C interactions, it is observed that the stabilization energies of these hydrogen bonds are found to be fairly low (0.35-0.54) which reveals that the minimum charge transfer has occurred. This can be obtained to the larger charge transfer from the lone pair Br atom to the anti-bonding of H-O bond and it is accountable for the high stability of the complex.

The molecular electrostatic potential (MEP) surface[39] of the BH-ONP, BD-ONP and BO-ONP has been carried and plotted in Fig 5. The MEP surface has given a visual method, through different colors to understand, the red color indicates regions of most positive electrostatic potential, blue color represents regions of the most positive potential. As shown in fig 5. for BH-ONP, BD-ONP and BO-ONP complex OH group of donor complex have some electrostatic interaction with BH, BD and BO monomers.

Table:- 5 Fig:- (5)

IV. CONCLUSION

We have studied the three different structures for BH-ONP, BD-ONP and BO-ONP complex using B3LYP level theories employing 6-311++G** level theory. The

structural parameter of BH-ONP, BD-ONP and BO-ONP complex. The total energy values indicate BD-ONP to be the most stable system. This is due to proton donating accepting ability is more than other complexes from ONP because of the presence of an additional hydrogen bond for their higher stability. From the topological analysis results, good linear correlation has been found between hydrogen bond length, electron density and Laplacian electron density. NBO analysis explains stabilization energy during the forming of more hydrogen bonds even though the bond is strong

V. REFERENCES

- [1] A. Simperler, W. Mikenda, *Monatsh. Chem.* 128 (1997) 969.
- [2] M.H. Langoor, J.H. van der Maas, *J. Mol. Struct.* 403 (1997) 213.
- [3] H. Lampert, W. Mikenda, A. Karpfen, *J. Phys. Chem.* 100(1996) 7418.
- [4] H. Lampert, Thesis, University of Vienna, Vienna, 1996.
- [5] K.B. Borisenko, I. Hargittai, *J. Mol. Struct.* 382 (1996) 171.
- [6] K. Rutkowsky, A. Koll, *J. Mol. Struct.* 322 (1994) 195.
- [7] E. Steinwender, W. Mikenda, *Monatsh. Chem.* 125 (1994) 695.
- [8] T. Dziembowska, *Polish J. Chem.* 68 (1994) 1455.
- [9] S.R. Salman, A.R. Kudier, *Spectrochim. Acta* 46A (1990)1147.
- [10] T. Visser, J.H. van der Maas, *J. Chem. Soc. Perkin Trans. 2* (1988) 1649.
- [11] J.W. Lewis, C. Sandorfy, *Can. J. Chem.* 60 (1982) 1727.
- [12] G.L. Carlson, W.G. Fateley, A.S. Manocha, F.F. Bentley, *J. Phys. Chem.* 76 (1972) 1553.
- [13] M. Oki, H. Iwamura, *Bull. Chem. Soc. Jpn* 39 (1966) 470.
- [14] H.H. Freedman, *J. Amer. Chem. Soc.* 83 (1961) 2900
- [15] D. Hadzi, *Hydrogen Bonding*, Pergamon Press, London, 1959
- [16] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1939
- [17] A. Simperler, H. Lampert, W. Mikenda, *J MolStru* 448 (1998) 191- 199
- [18] G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, 1997
- [19] Huggines. M.L., *Angew. Chem. Int. Ed* 10 (1971) 147.
- [20] Murray-Rust. P., Stalling W.C., Monti C.T, Preston R.K., Glusker. J.P., *J. Am. Chem. Soc.* 105 (1983) 3206.
- [21] Shimoni. L., Glusker J.P., *Struct. Chem.* 5 (1994) 383.
- [22] Howard J.A.K., Hoy. V.J., Hagan D. O., Smith G.T., *Tetrahedron* 52 (1996) 12613
- [23] Dunitz. J.D., Taylor. R., *Chem. Eur. J.* 3 (1997) 89
- [24] Van der Berg J.-A., Seddon. K.R., *Cryst. Growth Design* 5 (2003) 643
- [25] Becke A.D., Density-functional exchange-energy approximation with correct asymptotic behaviour, *Phys. Rev. A* 38 (1998) 3098–3100.
- [26] Lee. C., Yang. W., Parr R.G., Development of the Colle–Salvetti correlationenergy formula into a functional of the electron density, *Phys. Rev. B* 37 (1988) 785–789.
- [27] Boys S.F., Bernardi F., Calculation of small molecular interactions by differences of separate total energies – some procedures with reduced errors, *Mol. Phys.* 19 (1970) 553–566.
- [28] Binev I.G. Stamboliyska B.A. Binev Y.I., *J Mol Struct (Theochem)* 378 (1996) 189.
- [29] Abbasi. A., Nadimi. E., Plänitz. P., Radehaus. C., *Surf Sci* 603 (2009) 2502
- [30] Bauer J.D., Haussuhl. E., Winkler. B., Arbeck. D., *Cryst Growth Des* 10 (2010) 3132.
- [31] Bader R.F.W., *Atoms in molecules, A quantum theory*, Clarendon press, Oxford (UK), 1990
- [32] Gledening ED, Reed AE, Carpenter JA, Weinhold F. NBO Version 3.1
- [33] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian03, Revision B.05, Gaussian, Inc., Pittsburgh (PA); 2003
- [34] Konstantin B., Borisenko., Charles.W. Bock., and Istvan Hargittai *J. Phys. Chem.* 1994, 98, 1442-1448
- [35] Grabowski S.J., *Hydrogen bonding New Insights*, Springer, 2006.
- [36] Boys S.F., Bernardi F., Calculation of small molecular interactions by differences of separate total energies – some procedures with reduced errors, *Mol. Phys.* 19 (1970) 553–566
- [37] Karthika. M., Senthil Kumar K. Kanakaraju .R., *Hydrogen bond interactions in hydrated acetylsalicylic acid*, *Comput. Theor. Chem.* 966 (2011) 167–179
- [38] Senthilkumar, L., Ghanty. T.K., Ghosh S.K., Electron density and energy decomposition analysis in hydrogen-bonded complexes of azabenzene with water, acetamide, and thioacetamide, *J. Phys. Chem. A* 109 (2005) 7575–7582

Table:- 1 Geometrical parameters (bond lengths in Å, bond angles in degrees) for BH, BO and BD monomers calculated B3LYP/6-311++G** level theory.

Parameters	BD	BO	BH	Parameters	ONP(Ref) ^a
Br1-C1	1.9916	1.9918	1.9874	N1-O2	1.2210 (1.2082)
C1-H1	1.0889	1.0889	1.0884	N1-O3	1.2277
C1-H2	1.0877	1.0877	1.0884	N1-C4	1.4726 (1.4442)
C1-C2	1.5187	1.5189	1.5178	C2-C4	1.3934
C2-H3	1.1000	1.0999	1.0947	C2-H1	1.0824
C2-H4	1.0952	1.0952	1.0946	C2-C1	1.3874 (1.3984)
C2-C3	1.5308	1.5308	1.5370	C1-H4	1.0835
C3-H5	1.0950	1.0949	1.0975	C1-C3	1.3954 (1.3990)
C3-H6	1.0981	1.0981	1.0975	C3-H2	1.0847 (1.0734)
C3-C4	1.5322	1.5322	1.5327	C3-C5	1.3890 (1.3710)
C4-H7	1.0982	1.0982	1.0978	C5-H3	1.0869 (1.0736)
C4-H8	1.0979	1.0978	1.0977	C5-C6	1.4000 (1.3683)
C4-C5	1.5321	1.5322	1.5322	C6-O1	1.3523(1.3231)
C5-H9	1.0977	1.0978	1.0972	O1-H5	0.9655 (0.9499)
C5-H10	1.0980	1.0980	1.0972	O2-N1-O3	124.95 (123.13)
C5-C6	1.5322	1.5320	1.5302	O2-N1-C4	118.14 (118.25)
C6-H11	1.0981	1.0983	1.0946	O3-N1-C4	116.89
C6-H12	1.0980	1.0982	1.0946	N1-C4-C2	117.39
C6-C7	1.5322	1.5323	1.0936	H1-C2-C4	118.29
C7-H13	1.0980	1.0972	-	C4-C2-C1	120.32
C7-H14	1.0981	1.0973	-	H1-C2-C1	121.38
C7-C8	1.5321	1.5303	-	C2-C1-H4	120.12
C8-H15	1.0983	1.0948	-	H4-C1-C3	120.68
C8-H16	1.0982	1.0947	-	C1-C3-H2	120.19
C8-C9	1.5322	1.0938	-	H2-C3-C5	119.27(120.84)
C9-H17	1.0972	-	-	C3-C5-H3	120.05(119.13)
C9-H18	1.0972	-	-	H3-C5-C6	118.94
C9-C10	1.5304	-	-	C5-C6-O1	122.03(125.70)
C10-H19	1.0948	-	-	C6-O1-H5	110.05
C10-H20	1.0948	-	-	C5-C6-C4	117.83
C10-H21	1.0938	-	-	C6-C4-N1	121.53
Br1-C1-H1	104.87	104.86	105.01	-	-
Br1-C1-H2	104.37	109.33	109.21	-	-
H1-C1-H2	109.32	112.12	112.52	-	-
H1-C1-C2	112.53	113.08	112.12	-	-
H2-C1-C2	112.14	109.44	109.52	-	-
Br1-C1-C2	113.05	106.06	106.53	-	-
C1-C2-H3	106.16	109.35	109.50	-	-
C1-C2-H4	109.43	106.11	106.03	-	-
H3-C2-H4	106.04	109.21	109.52	-	-
C2-C3-H5	109.36	109.50	109.35	-	-
H5-C3-H6	106.09	109.26	109.32	-	-
C2-C3-H6	109.21	109.25	109.30	-	-
C2-C3-C4	112.96	109.29	109.30	-	-
H5-C3-C4	109.56	109.35	111.38	-	-
H6-C3-C4	109.42	109.34	111.37	-	-
H7-C4-C5	109.28	109.25	111.49	-	-
C3-C4-H7	109.49	109.27	107.39	-	-
C3-C4-H8	109.26	111.38	107.50	-	-
C4-C5-H9	109.24	107.37	-	-	-
C4-C5-H10	109.31	-	-	-	-
C5-C6-H11	109.29	-	-	-	-
C5-C6-H12	109.29	-	-	-	-
C5-C6-C7	113.63	-	-	-	-
H9-C5-C6	109.34	-	-	-	-
H10-C5-C6	109.29	-	-	-	-
C6-C7-H13	109.27	-	-	-	-
C6-C7-H14	109.29	-	-	-	-

C6-C7-C8	113.63	-	-	-	-
C7-C8-H15	109.32	-	-	-	-
C7-C8-H16	109.33	-	-	-	-
H13-C7-C8	109.29	-	-	-	-
H14-C7-C8	109.27	-	-	-	-
C8-C9-C10	113.33	-	-	-	-
C8-C9-H17	109.28	-	-	-	-
C8-C9-H18	109.27	-	-	-	-
H17-C9-H18	105.83	-	-	-	-
H17-C9-C10	109.43	-	-	-	-
H18-C9-C10	109.43	-	-	-	-
C9-C10-H19	111.37	-	-	-	-
C9-C10-H20	111.37	-	-	-	-
H19-C10-H20	107.36	-	-	-	-
H19-C10-H21	107.48	-	-	-	-
H20-C10-H21	107.47	-	-	-	-

Taken from Ref [34]

Table:-2 The calculated bond length (Å) bond angle θ (degree), optimized ∇E (kcal/mol) of 1-bromohexane + o-nitro phenol, 1-bromodecane + o-nitro phenol, 1-bromooctane + o-nitro phenol complex at B3LYP/ 6-311++G** level theory

Complex	Type of bond	Bond length (Å)	Bond angle (θ)	∇E kcal/mol
BH - ONP	Br1...H18-O1	2.508	146.33	3.4623
	H3...O1-C12	2.683	145.12	
BD - ONP	Br1...H26-O1	2.505	149.50	3.6263
	H4...O1-C16	2.631	144.15	
BO - ONP	Br1...H22-O1	2.527	155.31	3.5443
	H4...O1-C14	2.681	141.16	

Table:- 3 Interaction energy E_{int} (in kcal/mol) for BH – ONP, BD – ONP and BO-ONP systems calculated at B3LYP/ 6-311++G** level of theory

Complex	E_{AB}	E_A	E_B	I_E	E_{int} (kcal/mol)
BH - ONP	-3322.8201	-2810.6998	-512.1123	-0.0073	-4.5808201
BD - ONP	-3480.1167	-2967.9968	-512.1123	-0.0069	-4.3298163
BO - ONP	-3401.4681	-2889.3481	-512.1123	-0.0067	-4.2043144

Table:-4 The calculated electron density [$\rho(r)$], Laplacian density [$\nabla^2 \rho$] values in atomic units (a.u) at B3LYP/ 6-311++G** level of theory.

Complex	Type of bond	Bond length (Å)	$\rho(r)$	$\nabla^2 \rho$	ϵ
BH - ONP	Br1...H18-O1	2.508	0.16032	0.4890	0.2693
	H3...O1-C12	2.683	0.60251	0.2047	0.4419
BD - ONP	Br1...H26-O1	2.505	0.16187	0.4890	0.3966
	H4...O1-C16	2.631	0.65554	0.2212	0.3136
BO - ONP	Br1...H22-O1	2.527	0.15469	0.4645	0.4092
	H4...O1-C14	2.681	0.62001	0.2106	0.6168

Table:- 5 Bond length (X-H) of proton donor, occupation number of (X-H), bonds of the proton donor, occupancy of the acceptor atom, the stabilization energy (in kcal/mol) values for 1-bromohexane + o-nitro phenol, 1-bromodecane + o-nitro phenol, 1-bromooctane + o-nitro phenol complex at B3LYP/ 6-311++G** level of theory

Complex	Type of bond	Bond length (Å)	Proton Donor $\sigma(X-H)$	Proton Acceptor n(y)	E^2 kcal/mol
BH - ONP	Br1...H18-O1	2.508	0.70	0.056	5.66
	H3...O1-C12	2.682	1.77	0.024	0.40
BD - ONP	Br1...H26-O1	2.505	0.71	0.058	5.98
	H4...O1-C16	2.631	1.77	0.028	0.54
BO - ONP	Br1...H22-O1	2.527	0.71	0.057	5.77
	H4...O1-C14	2.681	1.76	0.022	0.35

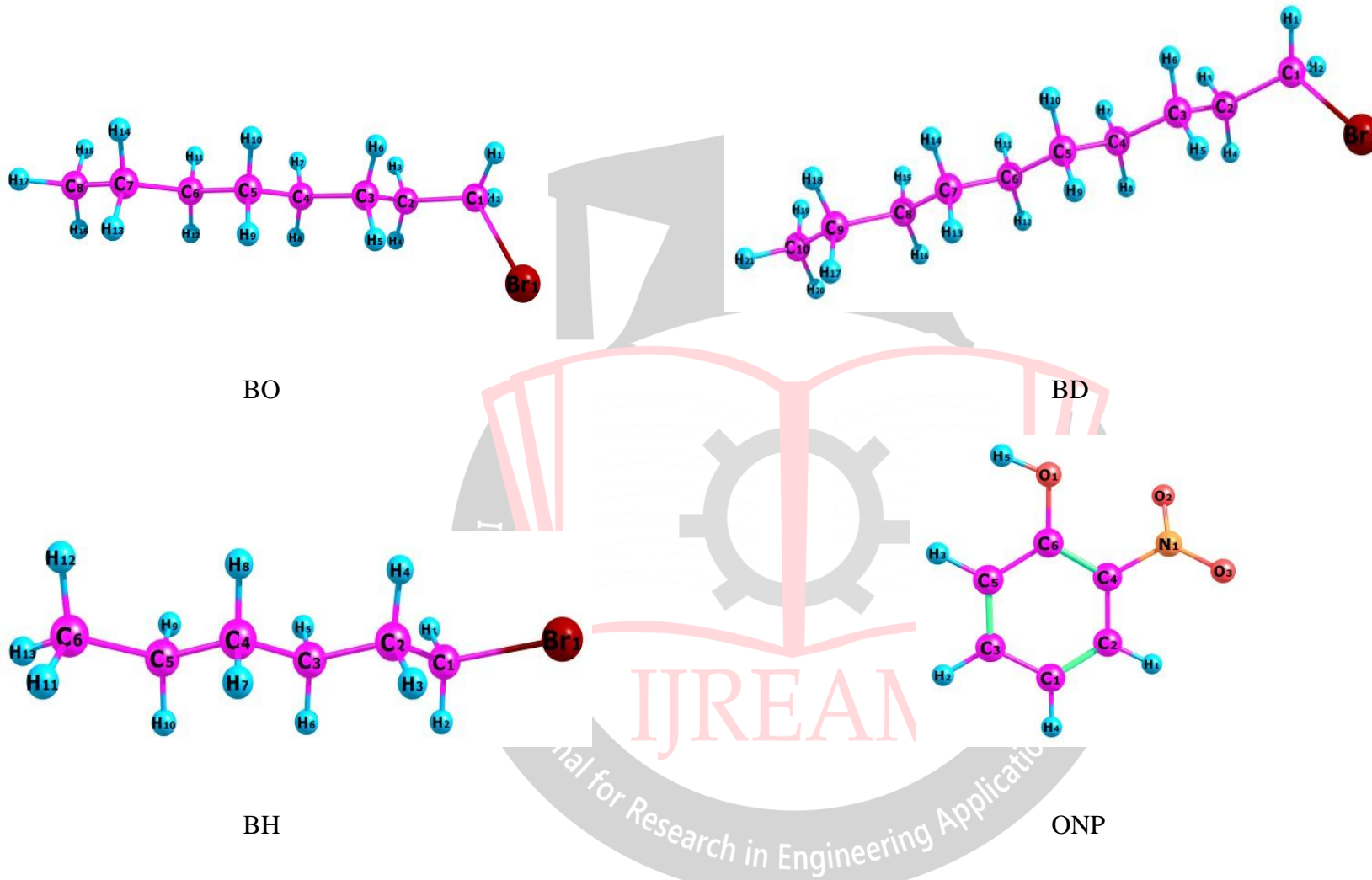


Fig 1. Optimized structure of BH, BD, BO and ONP monomer.

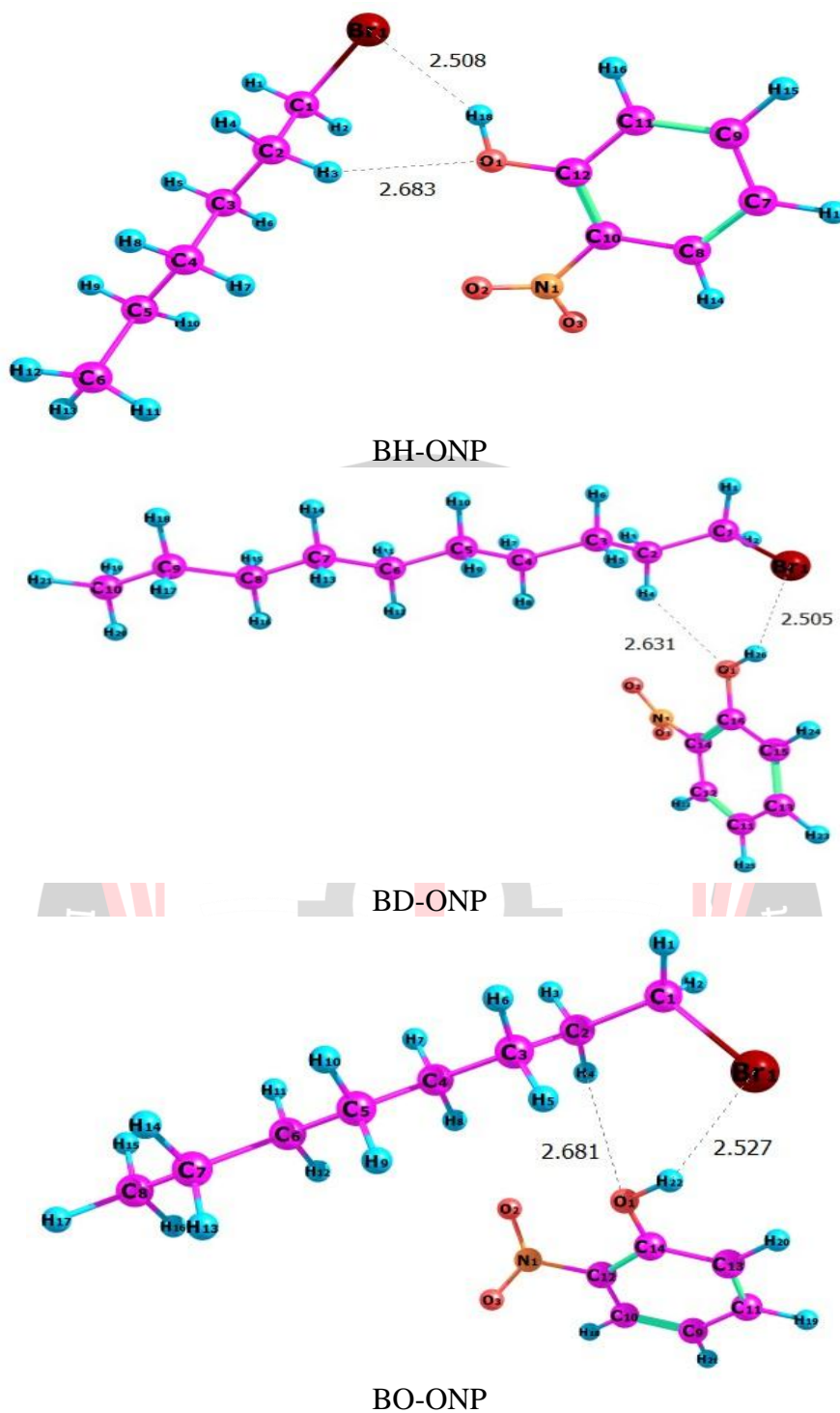


Fig 2. Optimized structure of BH-ONP, BD-ONP and BO-ONP complex

Fig 3. The correlation between electron density and critical point and hydrogen bond distance at B3LYP/6-311++G** level of theory

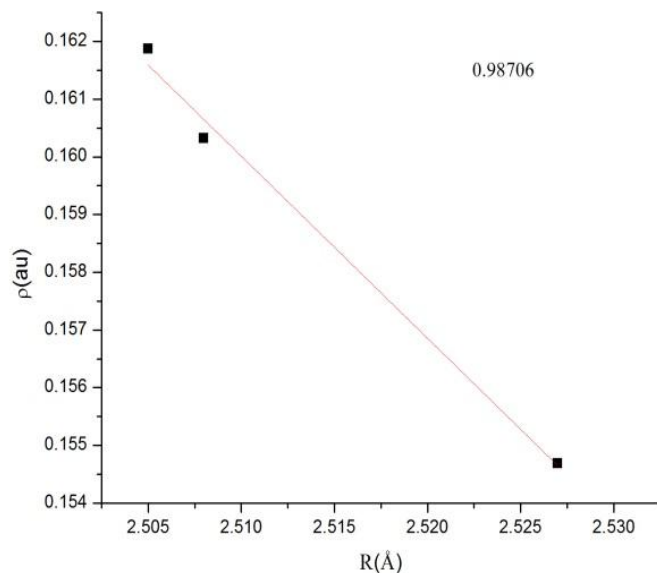


Fig 4. The correlation between Laplacian of electron density and critical point and hydrogen bond distance at B3LYP/6-311++G** level of theory

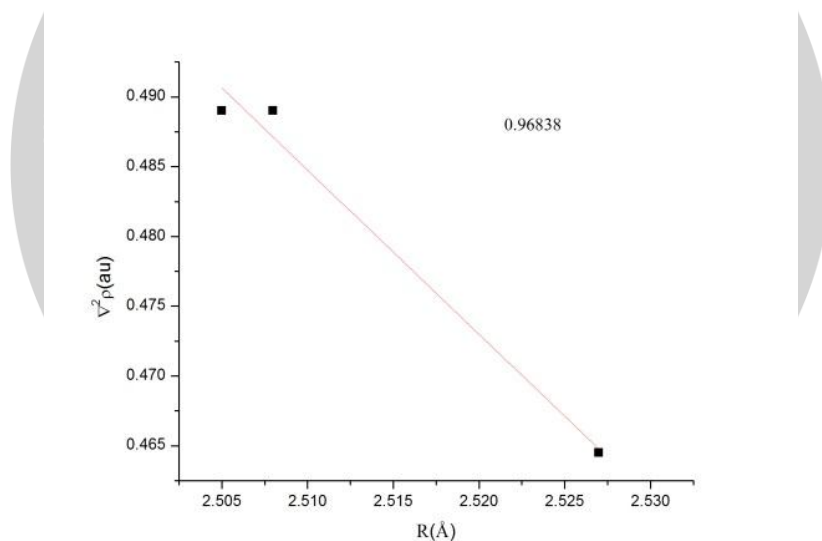
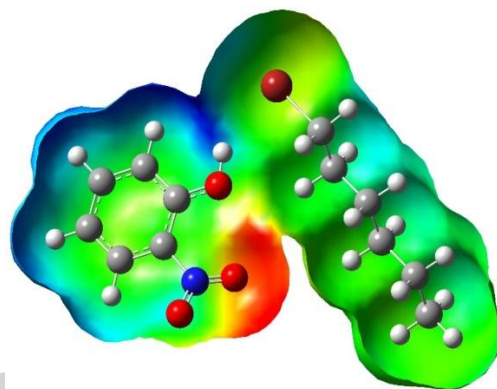


Fig 5. Molecular electrostatic potential surface of BH-ONP, BD-ONP and BO-ONP complexes.

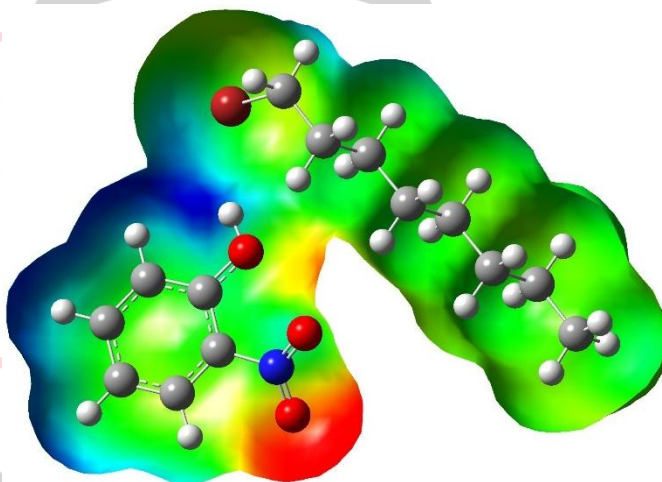
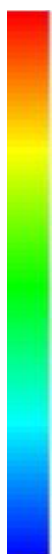
-0.04



+0.04

BH-ONP

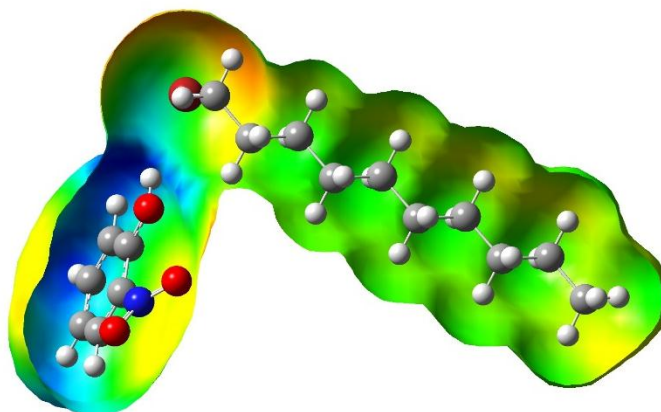
-0.04



BO-ONP

+0.04

-0.02



BD-ONP

+0.04