An experimental and first-principles DFT study on the charge transfer complexes of iodine with homologous series of donors

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Abstract

The formation of CT complex is effectively explained through stabilization of the highest occupied orbital of the donor molecule and destabilization of the lowest unoccupied orbital of the acceptor molecule in MO diagram. Extensive DFT calculations are carried out to show the variation in the structure, stability, and charge transfer of the CT complexes formed by homologous series of donors in detail. The formation and structure of CT complexes of iodine with aromatic compounds are deduced. The excitation energy of the CT complexes is also calculated by TDDFT.

Keywords: Absorption spectra, CT band, CT complex, first-principles DFT.

1 Introduction

Ever since Benesi and Hildebrand showed the color of iodine in aromatic hydrocarbons is brown in contrast with the violet in saturated hydrocarbons and vapor phase[1]. Various kinds of donors and acceptors form CT complexes which have been studied for the last 70 years[2-12]. This gives the closest relation between the structure of the donor-acceptor complex with their stability. The halogen molecules generally act as acceptors because they are having an unfilled

antibonding orbital. The π-donors like aromatic hydrocarbons or n-donors like alcohols, ethers, thiols, sulfides, and amines have excess electrons and can donate some electron density from the highest occupied orbital. A review of the microscopic interactions of halogens with water provides the importance of charge transfer complexes[13]. The formation and structure of the iodine-water charge transfer complex are well understood by our previous study[14]. There are many theoretical works related to CT complexes reported[15-16]. But the variation in the properties of CT complexes of iodine with homologous series of n or π donors is not studied in detail. So, it is worthwhile to revisit for a better understanding of the CT complexes and their interactions.

We aim to understand the structure, stability, and behavior of CT complexes formed by iodine with homologous series of donors. The molecular orbital diagram is the best tool to understand the excitation and electronic properties of the CT complexes. The first-principles DFT calculation is performed to get the structural variations in the CT complexes. We report the structure and interactions of CT complexes formed by iodine with n-donors like oxygen, sulfur, and nitrogen donors and π-donors like aromatic hydrocarbons in detail.

2 Experimental and theoretical methods

Absorption spectra are recorded in a Labman UV spectrometer in a quartz cell from 190 nm to 1100 nm with a 1 nm resolution. The calculations are based on the first principle DFT, as implemented in the QUANTUM ESPRESSO code with the GGA exchange-correlation potential as parameterized by PBE[17]. Every chemical species was calculated by placing it in a supercell of $15.87 \times 15.87 \times 15.87 Å^3$, so there will be no interaction between successive chemical species present in the neighbor cell. Kohn-Sham wave functions (density) were represented with a plane wave basis with an energy cut-off of 30 Ry (240 Ry). The structural

optimizations of each of them were carried out until the energy converged to an accuracy of 10^{-8} eV.

3 Results and discussions

3.1 Absorption spectra of charge transfer complexes

We obtained the molecular iodine spectrum with n-hexane as the solvent. The absorption spectrum of iodine in n-hexane is given in Fig. 1a. The visible band of iodine is observed at 523 nm which can be assigned for the π^* to σ^* transition. The absorption spectra of iodine with oxygen donors are obtained by dissolving it in the respective donors directly (Fig. 1a-1e). So, the absorption spectra of only the charge transfer complexes are obtained. The visible iodine band is shifted to lower wavelengths in all cases. The energy difference between the molecular iodine band in n-hexane and donors will give the shifting energy. The shifting in the case of methanol (0.45 eV) and ethanol (0.41 eV) is more compared to water (0.32 eV) and diethyl ether (0.29 eV).

The molecular iodine undergoes chemical transformations in protic solvents and forms triiodide anions. So, there are two additional bands near 350 nm and 290 nm in the case of iodine in water, methanol, and ethanol. A distinct intense peak in the ultraviolet region of the spectra shows the charge transfer band of iodine with the donors. The energy of the charge transfer band of iodine with water (6.14 eV) is more than methanol (5.51 eV), ethanol (5.23 eV), and diethyl ether (5 eV).
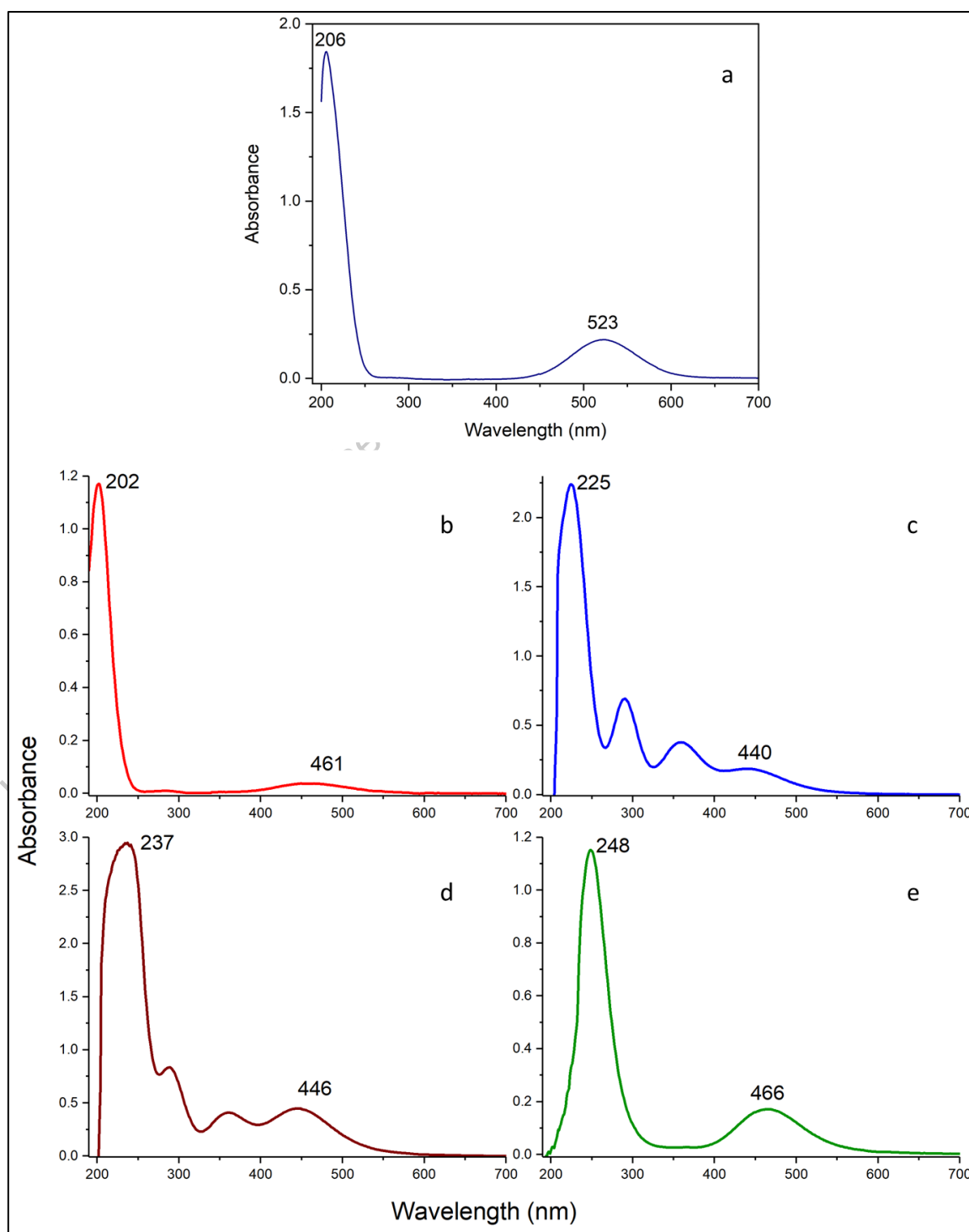
Fig. 1: Absorption spectra of iodine in (a) n-hexane (b) water, (c) methanol, (d) ethanol, and (e) diethyl ether.

The absorption spectra of iodine with sulfur donors are carried out in an n-hexane solvent (Fig. 2). In the case of both pure H_2S and H_2S-I_2, there is a band near 210 nm that corresponds to H_2S. A band at 365 nm was found as shifted iodine band. A pure iodine band near 523 nm was also observed because of noninteracting iodine. An additional band at 292 nm is found attributed to charge transfer transition. Pure dimethyl sulfide (DMS) and DMS-I_2 show a similar band near 220 nm corresponding to DMS. The visible iodine band is shifted to 444 nm and the charge transfer band is observed at 300 nm. The shifted energy in the case of H_2S is more (1.03 eV) than DMS (0.42 eV) and hence the interaction.
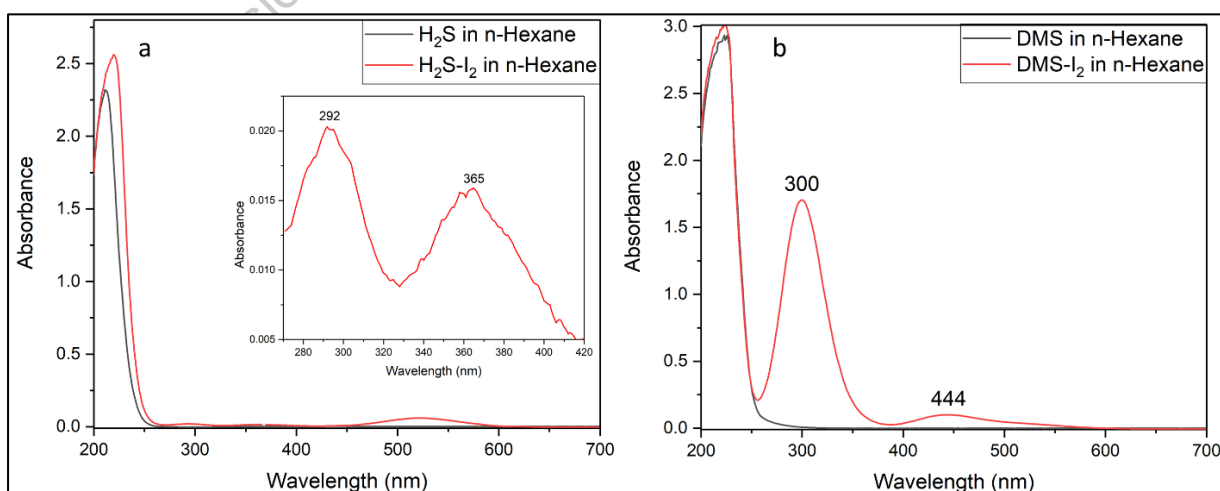

Fig. 2: Absorption spectra of iodine with (a) H_2S and (b) dimethyl sulfide in n-hexane.

The absorption spectra of iodine with nitrogen donors are also carried out in an n-hexane solvent (Fig. 3). The shifted iodine band is observed at 446 nm and 414 nm for NH_3 and triethylamine respectively. The energy of shifting is more in the case of iodine with NEt_3 (0.63 eV) is more than that of NH_3 (0.41 eV). A band near 520 nm is also observed corresponding to pure iodine which has not interacted with the donor. Apart from the donor bands, an additional

band at 227 nm for NH_3 and 276 nm for NEt_3 was observed attributed to charge transfer transition.
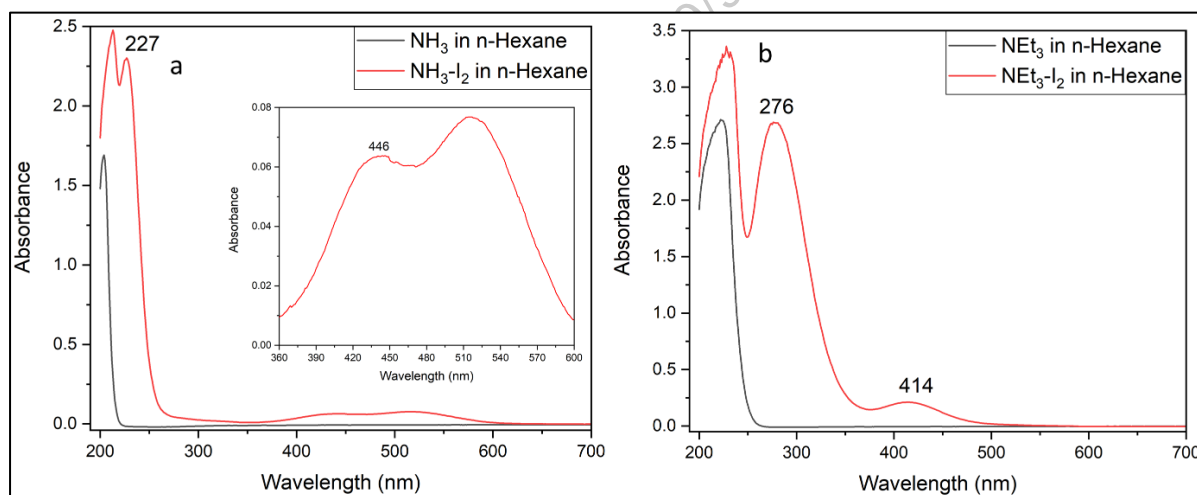

Fig. 3: Absorption spectra of iodine with (a) NH_3 and (b) NEt_3 in n-Hexane.

The absorption spectra of iodine with aromatic compounds are recorded by dissolving iodine in the respective donor as a solvent (Fig. 4). The energy of shifting is 0.12 eV in the case of iodine with benzene as well as toluene. The charge transfer band is observed at 295 nm for benzene and 306 nm for toluene. From the spectral analysis, non-bonding electron donors such as oxygen, sulfur, and nitrogen donors are more interactive with iodine than π-donors such as benzene and toluene.
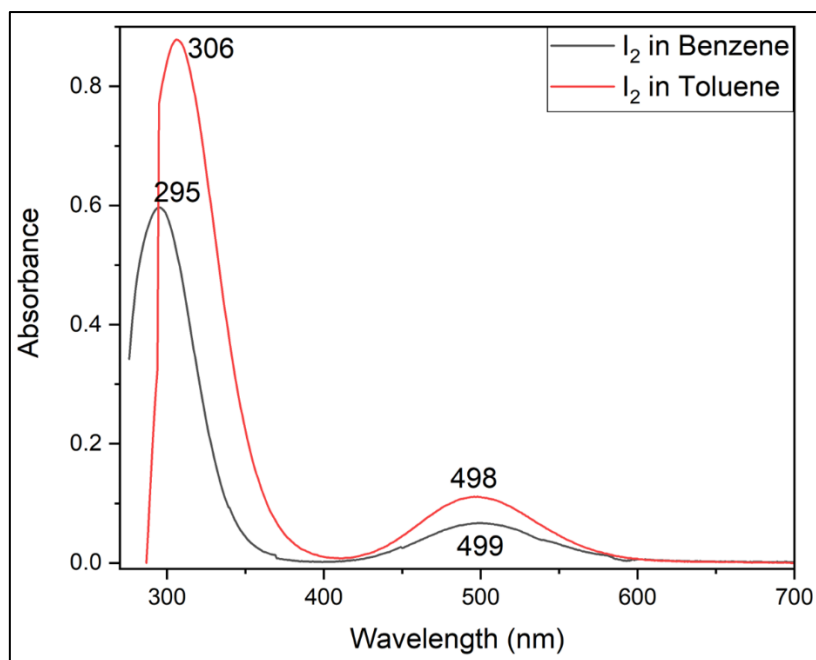
Fig. 4: Absorption spectra of iodine in benzene and toluene.

3.2 Molecular orbital diagrams of CT complexes

The molecular orbital (MO) diagram of the CT complexes is studied for a better understanding of the absorption spectra and electronic structure. The MO diagram of the CT complexes is constructed by the photoelectron spectroscopy (PES) of pure iodine and donors and absorption spectra of CT complexes[18-19]. The outer electronic configuration of molecular iodine is $\sigma(5p)^2$, $\pi(5p)^4$, $\pi^*(5p)^4$. The antibonding orbital energy of iodine ($\sigma^*(5p)$) is found by adding the transition energy of the visible iodine band (523 nm) to the π^* energy level. From the PES study of the diethyl ether-iodine complex, it is clear that only interacting orbitals are changing their position in the complex. So, non-interacting orbitals like π^* will not change much and they will be destabilized by 0.1 eV. Therefore, by taking the π^* orbital, we fixed the σ^* orbital of iodine in the CT complex. By using σ^* orbital and CT band energy, we fixed the highest occupied molecular orbital (HOMO) of the donor molecule. The HOMO of oxygen donors, sulfur donors, nitrogen donors, and π-donors are denoted as n_o, n_s, n_N, and π_g respectively.

The MO diagrams of the CT complexes of iodine with various donors are given in Fig. 5. The major charge transfer is from the donor HOMO to the σ^* orbital of iodine in the CT complex. So, the σ^* orbital will be destabilized by getting the extra electron density. But the HOMO of donor molecules will lose the electron density and stabilizes. The energy of stabilization of n_o orbital in the H_2O-I_2 complex is 0.08 eV. But that of methanol, ethanol, and diethyl ether is 1.01, 1.07, and 1.98 eV respectively. So, the energy of stabilization of n_o orbital increases with the electron-donating substitutes. This trend is also similar for both sulfur as well as nitrogen donors with iodine.
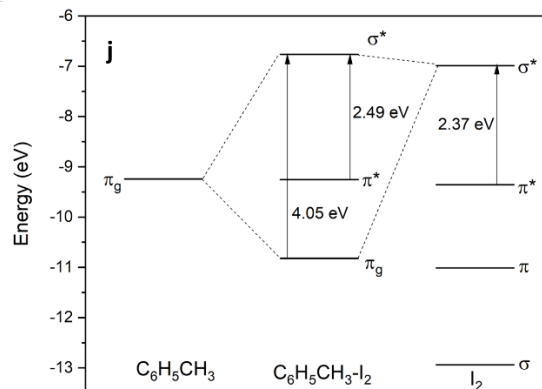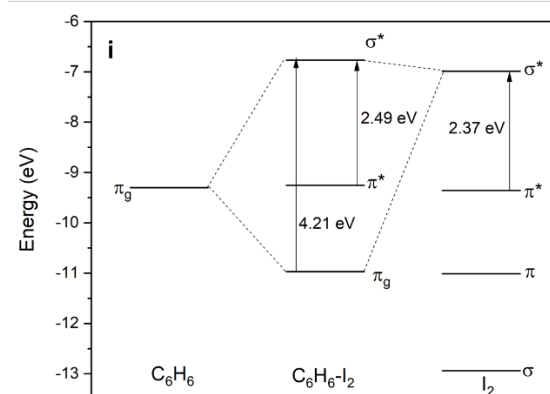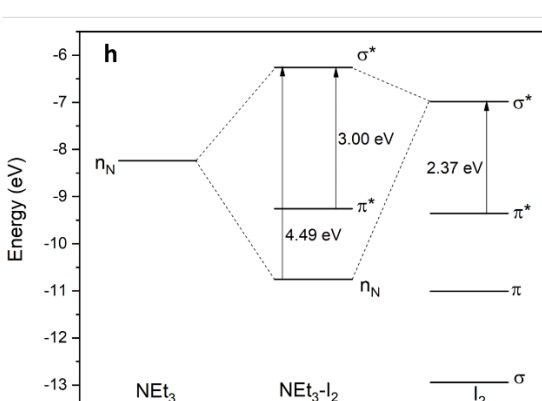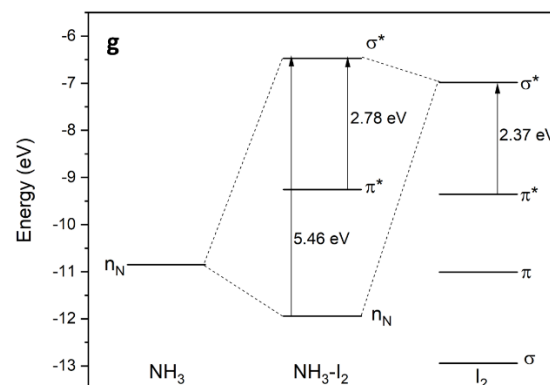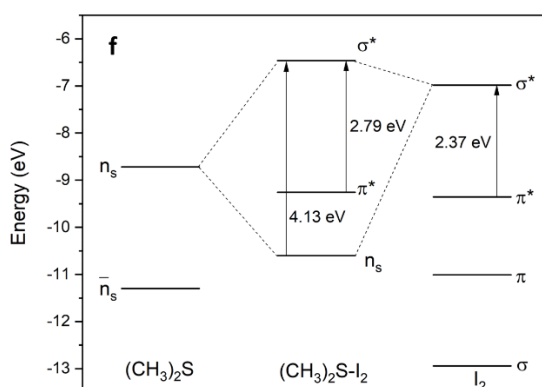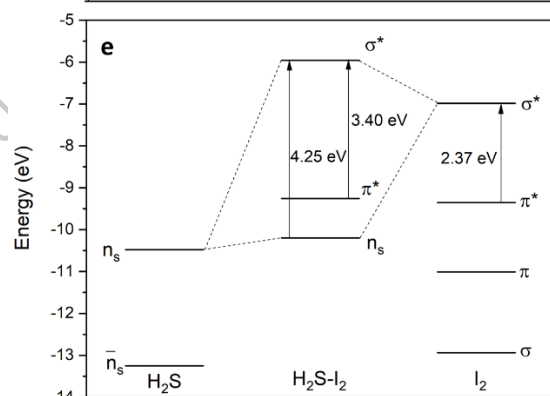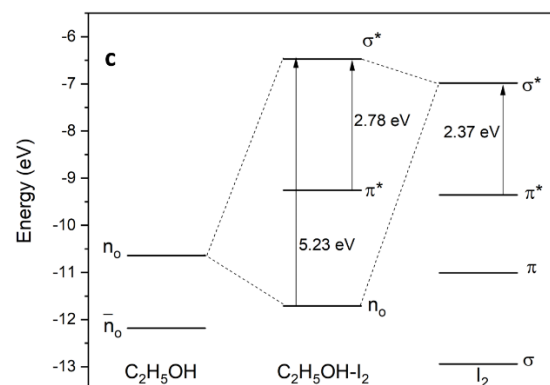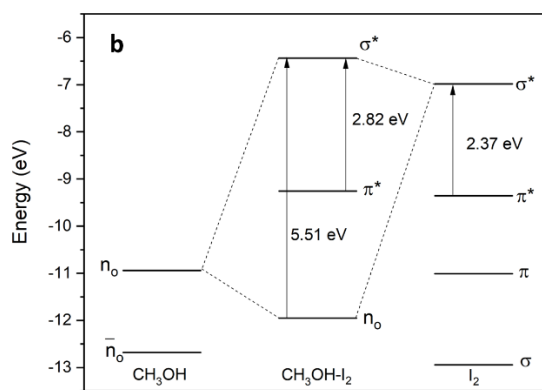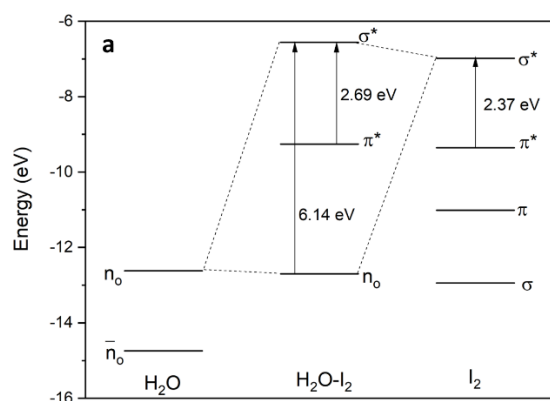
Fig. 5: The experimental MO diagrams of CT complexes of I_2 with (a) H_2O, (b) CH_3OH, (c) C_2H_5OH, (d) $(C_2H_5)_2O$, (e) H_2S, (f) $(CH_3)_2S$, (g) NH_3, (h) NEt_3, (i) C_6H_6, and (j) $C_6H_5CH_3$.

3.3 DFT calculations on CT complexes

The structural optimization of the iodine molecule is carried out with an I-I bond length of 2.69 Å. The formation energy of the CT complexes is calculated by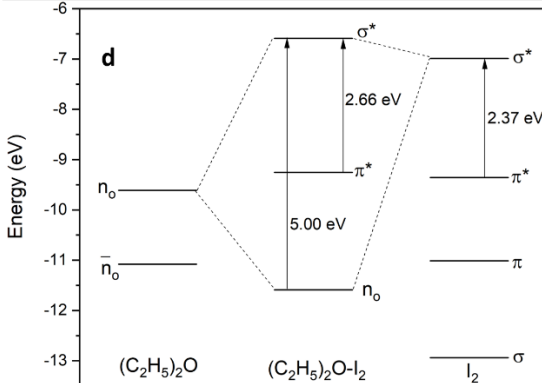 using the formula: Energy of formation = Energy of CT complex − (Energy of I_2 molecule + Energy of donor). The optimized geometry from the DFT is visualized by the software XCrySDen[20].

CT complexes of iodine with n-donors

Optimized geometry of the water is obtained with an O-H bond length of 0.97 Å and an HOH bond angle of 104.9°. The alcohols are having similar geometries with an O-H bond length of 0.97 Å. There is a slight increase in the C-C bond length from 1.51 Å for ethanol to 1.53 Å for hexanol. The C-O bond length for, primary alcohols is 1.43 Å, for secondary alcohols is 1.44 Å, and that of tertiary alcohols is 1.45 Å. The CÔH bond angle in every alcohol is almost the same (108°). The C-O bond distance in both the ethers is the same, which is 1.42 Å. The CÔC bond angle in dimethyl ether is 112° and that in diethyl ether is 113°.

The oxygen donors contain two lone pairs of which one is perpendicular and the other parallel to the plane. Surprisingly, iodine in the CT complex takes the orientation in between parallel and perpendicular positions (Fig. 6a). The angles between iodine and the plane of the donor are in the order of 104° to 110°. The IÔH angle in the H_2O-I_2 CT complex is 104.4° which is nearly equal to the HÔH bond angle. The IÔC angle in the $(CH_3)_2O$-I_2 CT complex is 110° which is comparable with the bond angle in sp^3 hybridization. The angle of iodine with alcohols

is distributed between 104° to 110°. This will provide the clue for nearly the sp^3 hybridization in oxygen with a lone pair at 105° interacting with iodine and the other at 255° at another side of the plane not interacting. The I-I bond distance after forming the CT complex is increased by 1-2% with oxygen donors. The C-O bond length is slightly increased by 0.02 Å with alcohols and 0.01 Å with ethers. The C-C and O-H bonds and CÔH bond angles have stayed unaltered.

The formation energy and net charge transfer of the CT complexes of iodine with oxygen donors are given in Table 1. The formation energy of H_2O-I_2 is the least in oxygen donors which is 5.67 kcal/mol. The rest of them are almost the same with ~ 7 kcal/mol. But, diethyl ether is exceptional with less energy of -6.42 kcal/mol. As the increase in the inductive effect of the addition of more alkyl groups, the net charge transferred should increase. But the net charge transferred from all the oxygen donors to iodine is almost the same which is 0.1 e. This means charges are redistributed in both lone pairs of donors due to hybridization. Therefore, the substitution of the alkyl group will not increase the energy of formation and net charge transferred with CT complexes of iodine and oxygen donors.

Table 1: PWScf calculation of CT complexes of iodine with oxygen donors.

Entry	CT complex	Energy of formation (kcal/mol)	Net charge transfer (e)	O-I length (Å)
1	H_2O-I_2	-5.61	0.08	2.77
2	CH_3OH-I_2	-6.87	0.10	2.72
3	$CH_3CH_2OH-I_2$	-7.06	0.11	2.70
4	$CH_3CH_2CH_2OH-I_2$	-6.96	0.10	2.73
5	$(CH_3)_2CHOH-I_2$	-7.10	0.10	2.71

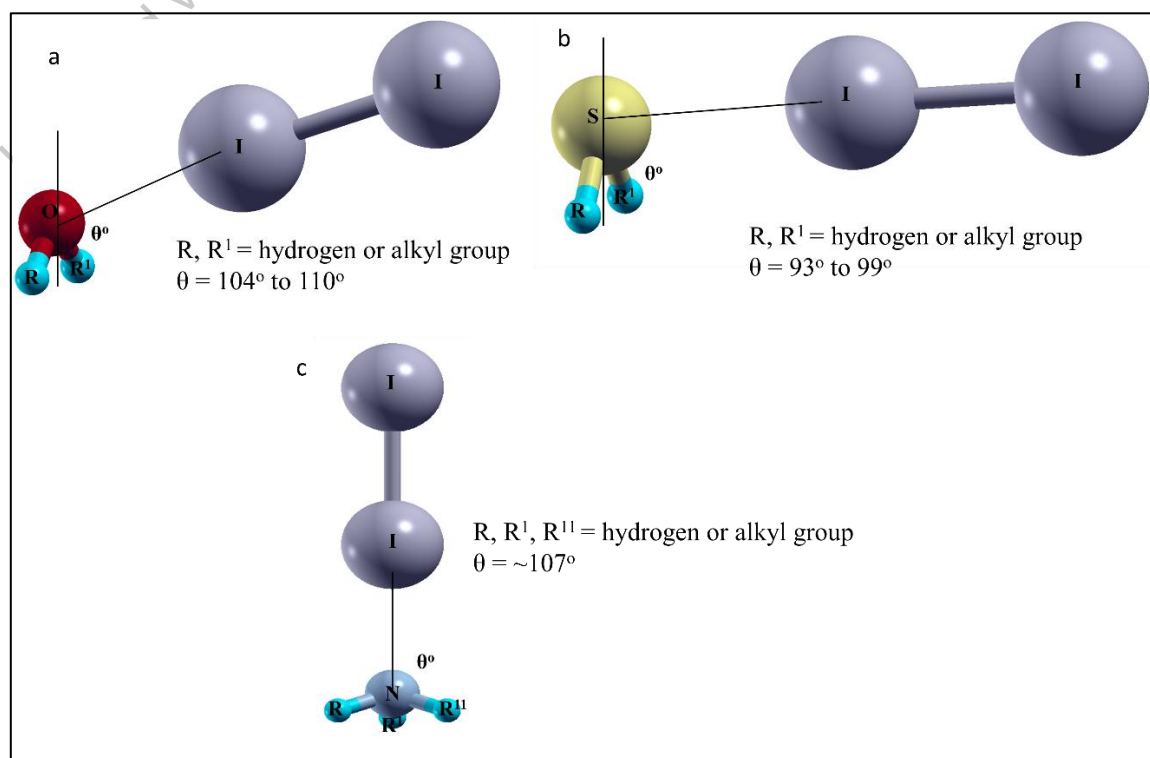| 6	$CH_3CH_2CH_2CH_2OH-I_2$	-7.14	0.11	2.70
7	$(CH_3)_2CHCH_2OH-I_2$	-6.98	0.10	2.71
8	$CH_3CH_2CH(CH_3)OH-I_2$	-7.19	0.11	2.69
9	$(CH_3)_3COH-I_2$	-7.21	0.11	2.70
10	$CH_3CH_2CH_2CH_2CH_2OH-I_2$	-7.04	0.11	2.69
11	$CH_3CH_2CH_2CH_2CH_2CH_2OH-I_2$	-6.97	0.11	2.71
12	$(CH_3)_2O-I_2$	-6.90	0.10	2.69
13	$(CH_3CH_2)_2O-I_2$	-6.42	0.11	2.73

Fig. 6: Geometry of CT complexes of iodine with (a) oxygen, (b) sulfur, and (c) nitrogen donors.

The H$_2$S is also bent shape with an HŜH angle of 92° and an S-H bond distance of 1.35 Å. The S-H bond distance in thiols is the same as in H$_2$S. The C-S bond length is 1.82 Å in all cases except in dimethyl sulfide, which is 1.80 Å. The CŜH(C) bond angle increases from 97° in the case of thiols to 99° for alkyl sulfides. The N-H bond distance in ammonia and the rest of all the cases is the same, which is 1.02 Å. The HNH bond angle in ammonia is 107° and that in the case of primary amines is 111°. But in the case of dimethylamine, the CNH angle is 110° and that of CNC is 113°. The CNC bond angle in the case of tertiary amines is 111° similar to primary amines. The C-N and C-C bond distances in all the cases are the same with the value of 1.46 Å and 1.52 Å respectively.

Unlike in the oxygen donors, the orientation of iodine with sulfur is mostly perpendicular to the plane (Fig. 6b). The bond angle will be between 93° to 99° from the plane, indicating no such hybridization. The nitrogen donors contain only one lone pair, so there is one possibility that is above nitrogen, like ammonium ion (Fig. 6c). The angle is about 107° in all the cases. The angle increases with the substitution of the alkyl group than with hydrogen in the case of oxygen and sulfur donors. This is because of the stearic hindrance by the bulk alkyl moieties. But, this trend is not observed in the case of nitrogen donors because of the proper spatial separation of iodine and donor molecules in the CT complex.

After the formation of the CT complex S-H, N-H, C-S, and C-C bond distances are not changed. The I-I bond length increased by 2-5% in both sulfur and nitrogen donors. The C-N bond distance is increased by 0.01 Å in the amines. The HŜH(C) bond angles are not changed in H$_2$S as well as thiols. But CŜC is increased by 1° in the case of alkyl sulfides. The HNH bond angle is increased by 2.5^o in the case of ammonia. But in the case of primary amines HNH bond angle decreased by 2.5^o and the HNC bond angle increased by 1°. On the contrary, both the HNH and HNC bond angles increased by 1° in the case of dimethylamine. The CNC bond angle with trimethylamine is 112° and that of triethylamine is 111°.

The results of the PWScf calculation of CT complexes of iodine with sulfur and nitrogen donors are given in Table 2. As expected the formation of energy increases with an increase in the substituent in the CT complexes of iodine with sulfur donors. This is partially true in the case of iodine with nitrogen donors. The net charge transferred increases with an increase in the alkyl group substitution. This is a clear demonstration of the inductive effect of the alkyl substituents attached to the sulfur and nitrogen donors. As expected, the S-I distance with sulfur donors is more than the O-I and N-I distance in oxygen and nitrogen donors respectively.

Table 2: PWScf calculation of CT complexes of iodine with sulfur and nitrogen donors.

Entry	CT complex	Energy of formation (kcal/mol)	Net charge transferred (e)	S-I/N-I distance (Å)
1	$H_2S\text{-}I_2$	-7.05	0.18	3.03
2	$CH_3SH\text{-}I_2$	-10.16	0.23	2.93
3	$CH_3CH_2SH\text{-}I_2$	-11.03	0.24	2.92
4	$(CH_3)_2S\text{-}I_2$	-13.63	0.27	2.86
5	$(CH_3CH_2)_2S\text{-}I_2$	-14.89	0.29	2.83
6	$NH_3\text{-}I_2$	-12.04	0.19	2.63
7	$CH_3NH_2\text{-}I_2$	-14.81	0.23	2.59
8	$CH_3CH_2NH_2\text{-}I_2$	-14.71	0.24	2.60
9	$(CH_3)_2NH\text{-}I_2$	-15.82	0.25	2.58
10	$(CH_3)_3N\text{-}I_2$	-15.51	0.25	2.59
11	$(CH_3CH_2)_3N\text{-}I_2$	-14.16	0.27	2.63

CT complexes of iodine with aromatic compounds

The optimized geometry of benzene is obtained with a C-C bond length of 1.39 Å and a CĈC bond angle of 120°. The CT complexes of iodine with benzene are simulated by placing iodine in various sites. In that, iodine on one of the C-C bonds with 97° slanted on the plane of benzene is feasible energetically (Fig. 7a). But, the energy of formation (E_f) is very less which is -3.39 kcal/mol with 0.07 e net transferred.

The Ph-CH$_3$ bond length is 1.50 Å and PhĈH bond angle is 111° and that of HĈH is 107°. Iodine on para carbon position in toluene is energetically favorable with E_f of -3.70 kcal/mol (Fig. 7b). The I-I bond distance with both benzene and toluene is the same (2.73 Å). The C-C bond length is increased by 0.01 Å in both cases.

The optimized C-C bond length of aniline, phenol, and thiophenol is the same as in benzene. The C-X bond length in aniline is 1.39 Å, phenol is 1.38 Å, and thiophenol is 1.77 Å. The X-H bond distance is similar to their aliphatic analogs. The CNH bond angle is 117° and the HNH bond angle is 114° in aniline. The CÔH bond angle is 108° in phenol and the CŜH bond angle is 97° in thiophenol.

The orientation of iodine in aniline is similar to aliphatic amines (Fig. 7c).Unlike benzene and toluene, the formation energy of the aniline-I$_2$ CT complex is high, which is -9.66 kcal/mol. Similarly, phenol and thiophenol form CT complexes with iodine like their aliphatic analogs (Fig. 7d & 7e). The formation energy of the CT complex with phenol is -6.18 kcal/mol and with thiophenol is -8.47 kcal/mol. But, the net charge transferred in the case of phenol (0.07 e) is less than that of water. The net charge transferred to iodine from aniline is 0.20 e and from thiophenol is 0.21 e which is comparable with their aliphatic analogs. The donor-iodine distance in benzene, toluene, and thiophenol is about 3 Å and that of aniline and phenol is 2.69 Å and 2.86 Å respectively.

After the formation of CT complexes, C-C and X-H bonds are changed in all the cases. But, C-X changed by 0.01 Å with phenol, 0.02 Å with aniline and it remains the same with thiophenol. The I-I bond distance with phenol is 2.72 Å and with aniline is 2.77 Å similar to H_2O-I_2 and NH_3-I_2 complexes respectively. The I-I distance with thiophenol is 2.78 Å. The CXH bond angle remains unaltered with phenol and thiophenol. But in the case of aniline, the CNH and HNH bond angles decreased by 3°.

The optimized C-C bond length in naphthalene is 1.42 Å but the C_1-C_2 bond distance is 1.38 Å. The $C\hat{C}C$ bond angle is 121° but the $C\hat{C}C$ bond angle associated with the fused C-atoms is 119°. The orientation of the iodine in the CT complex is on the C_1-C_2 bond of 1st and 2nd carbon atoms at 101° to the plane with a distance of 3.04 Å (Fig. 7f). After the formation of the CT complex, the C_1-C_2 bond increased by 0.01 Å, I-I bond distance increased by 0.05 Å and the other bonds are remaining unaltered. The formation energy is -4.24 kcal/mol and the net charge transferred is 0.10 e. The TDDFT calculations are also calculated to get the excitation energy that matches well with the experiments (Supporting information).
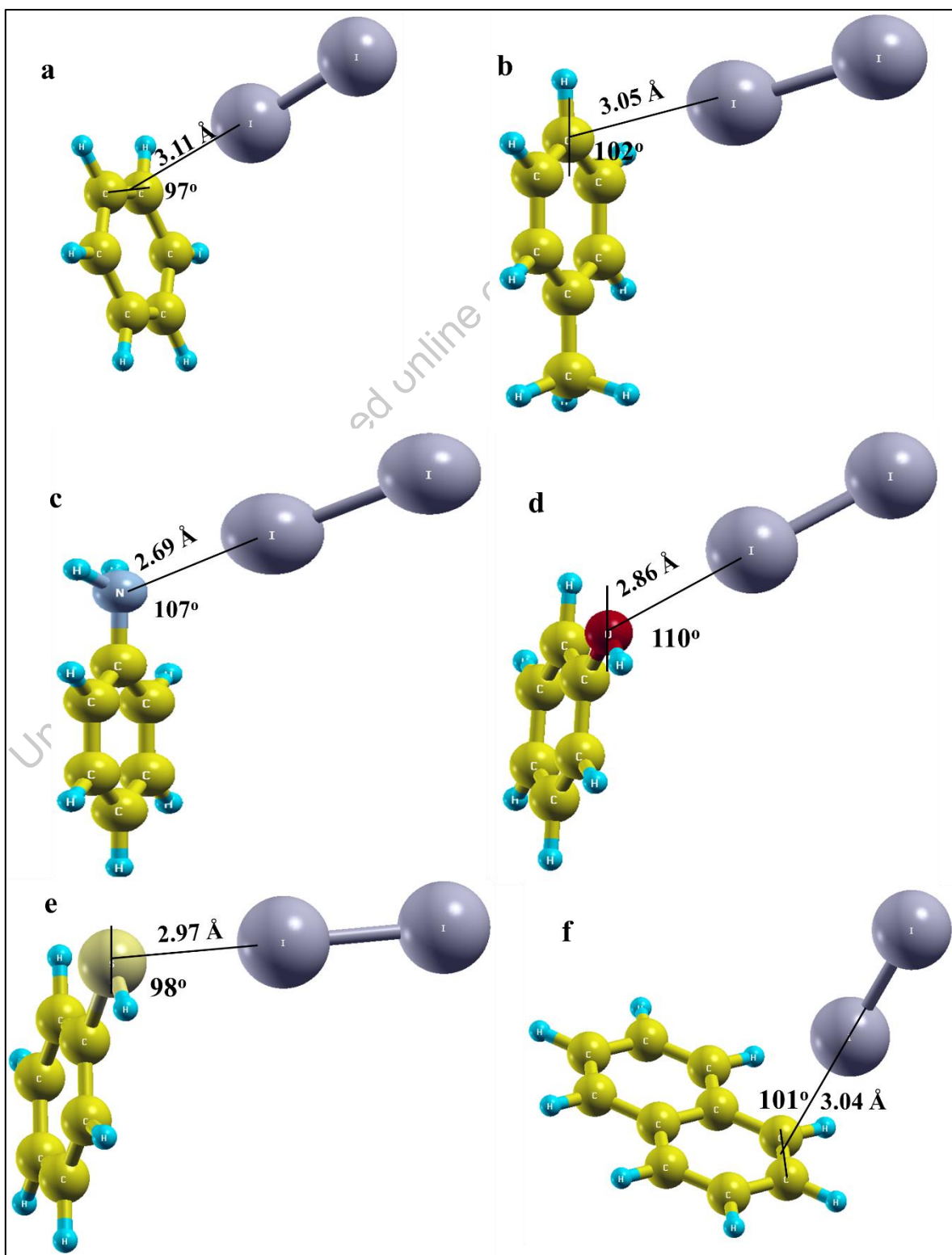
Fig. 7: Optimized geometry of the CT complex of iodine with (a) benzene, (b) toluene, (c) aniline, (d) phenol, (e) thiophenol, and (f) naphthalene.

4 Conclusion

The stabilization and destabilization of corresponding orbitals were well understood by using the molecular orbital diagram. The density functional theory was employed effectively to explain the formation, structure, and stability of the CT complex. The effect of the substitution of the alkyl group to the donor molecule in the CT complex was studied. The time-dependent DFT calculations are also carried out.

5 Acknowledgment

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