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

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The formation of charge transfer (CT) complexes is effectively explained through stabilization of the highest occupied orbital of a donor molecule and destabilization of the lowest unoccupied orbital of an acceptor molecule in the molecular orbital diagram. Extensive density functional theory (DFT) calculations have been carried out to indicate the variation in structure, stability and charge transfer of CT complexes formed by homologous series of donors. The formation and structure of CT complexes of iodine with aromatic compounds are deduced. The excitation energy of CT complexes is also calculated by time-dependent DFT.

Keywords: Absorption spectra, aromatic compounds, charge transfer complexes, excitation energy, iodine.

BENESI and Hildebrand[1] showed that the colour of iodine in aromatic hydrocarbons is brown in contrast to violet in saturated hydrocarbons and vapour phase. Various kinds of donors and acceptors form charge transfer (CT) complexes, which have been studied for the last 70 years[2–12]. This gives the closest relation between the structure of a donor–acceptor complex and its stability. The halogen molecules generally act as acceptors because they have an unfilled antibonding orbital. The π-donors like aromatic hydrocarbons or n-donors like alcohols, ethers, thiols, sulphides and amines have excess electrons and can donate electron density from the highest occupied orbital. A review of the microscopic interactions of halogens with water reveals the importance of CT complexes[13]. The formation and structure of the iodine–water CT complex are well understood by our previous study[14]. There are many theoretical works related to CT complexes[15,16]. However, variation in the properties of CT complexes of iodine with homologous series of n- or π-donors has not been studied in detail. So, it is worthwhile to revisit to understand the CT complexes and their interactions better.

The present study aims to understand the structure, stability and behaviour of CT complexes formed by iodine

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with a homologous series of donors. The molecular orbital (MO) diagram is the best tool to understand the excitation and electronic properties of CT complexes. The first-principles density functional theory (DFT) calculation is performed to obtain the structural variations in CT complexes. Here, we report in detail the structure and interactions of CT complexes formed by iodine with n-donors like oxygen, sulphur, and nitrogen donors, and π-donors like aromatic hydrocarbons.

## Experimental and theoretical methods

Absorption spectra were recorded using a UV spectrometer (Labman, India) in a quartz cell from 190 to 1100 nm with a resolution of 1 nm. The calculations were based on first-principles DFT, as implemented in the QUANTUM ESPRESSO code with the generalized gradient approximation exchange-correlation potential parameterized by Perdew–Burke–Ernzerhof[17]. Every chemical species was determined 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 in the neighbouring cell. The Kohn–Sham wave functions (density) were represented on a plane-wave basis with an energy cut-off of 30 Ry (240 Ry). Every structural optimization was carried out until the energy converged to an accuracy of 10^{-8} eV.

Results and discussion

Absorption spectra of CT complexes

We obtained the molecular iodine spectrum with n-hexane as the solvent. Figure 1 a shows the absorption spectrum of iodine in n-hexane. The visible band of iodine is observed at 523 nm, which can be assigned to the π^* to σ^* transition. The absorption spectra of iodine with oxygen donors were obtained by directly dissolving it in the respective donors (Figure 1 a–e). So, the absorption spectra of only the CT complexes were obtained. The visible iodine band had shifted to lower wavelengths in all cases. The energy difference between the molecular iodine band in n-hexane
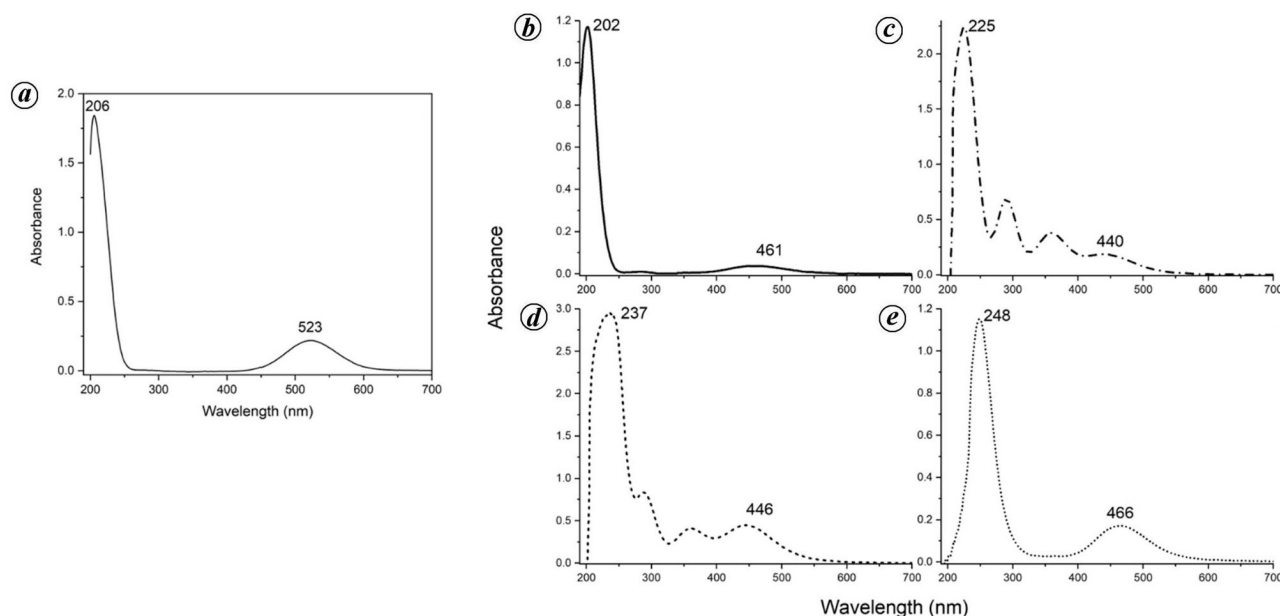
Figure 1. Absorption spectra of iodine in (**a**) *n*-hexane, (**b**) water, (**c**) methanol, (**d**) ethanol and (**e**) diethyl ether.
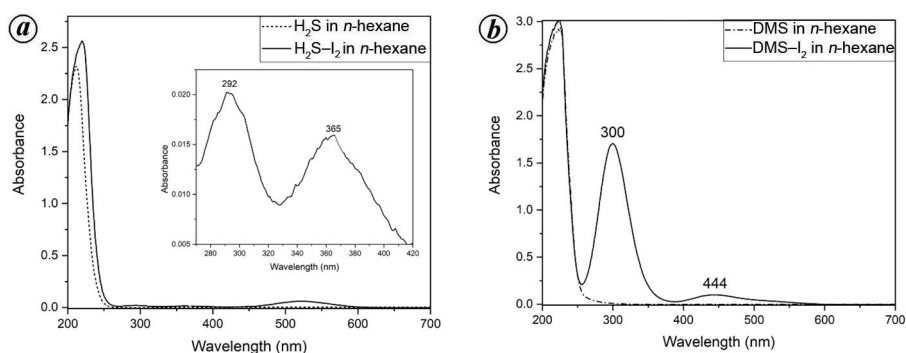
Figure 2. Absorption spectra of iodine with (**a**) H_2S and (**b**) dimethyl sulphide in *n*-hexane.

and the donors gives the shifting energy. The shifting in the case of methanol (0.45 eV) and ethanol (0.41 eV) was more compared to water (0.32 eV) and diethyl ether (0.29 eV).

Molecular iodine undergoes chemical transformation in protic solvents and forms triiodide anions. So, there are two additional bands near 350 and 290 nm in the case of iodine in water, methanol and ethanol. A distinct, intense peak in the ultraviolet (UV) 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).

Figure 2 shows the absorption spectra of iodine with sulphur donors in an *n*-hexane solvent. In the case of pure H_2S and $H_2S–I_2$, a band near 210 nm corresponds to H_2S. A band at 365 nm was found as a shifted iodine band. A pure iodine band near 523 nm was also observed because of noninteracting iodine. An additional band at 292 nm

was attributed to CT transition. Pure dimethyl sulphide (DMS) and $DMS–I_2$ showed similar bands near 220 nm corresponding to DMS. The visible iodine band had shifted to 444 nm, and the charge transfer band was observed at 300 nm. The shifted energy in the case of H_2S was more (1.03 eV) than DMS (0.42 eV), hence the interaction.

Figure 3 shows the absorption spectra of iodine with nitrogen donors in an *n*-hexane solvent. The shifted iodine band was observed at 446 and 414 nm for NH_3 and triethylamine respectively. The energy of shifting was higher in the case of iodine with NEt_3 (0.63 eV) than NH_3 (0.41 eV). A band near 520 nm was also observed corresponding to pure iodine, which had not interacted with the donor. Apart from the donor bands, additional bands at 227 nm for NH_3 and 276 nm for NEt_3 were observed to be attributed to charge transfer transition.

Figure 4 shows the absorption spectra of iodine with aromatic compounds recorded by dissolving it in the respective donor as solvent. The energy of shifting was 0.12 eV
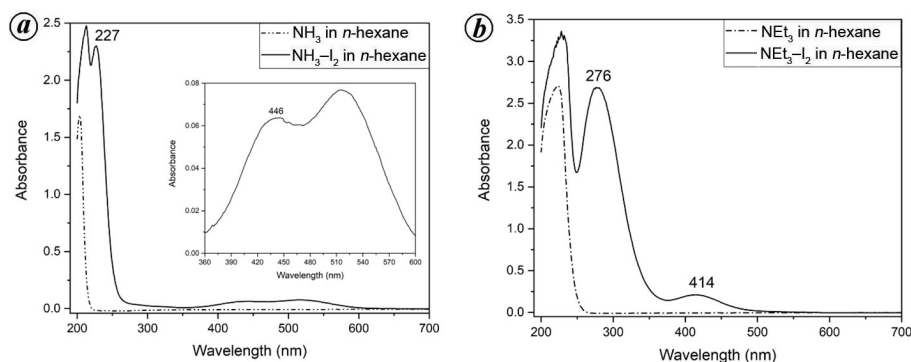
Figure 3. Absorption spectra of iodine with (*a*) NH$_3$ and (*b*) NEt$_3$ in *n*-hexane.
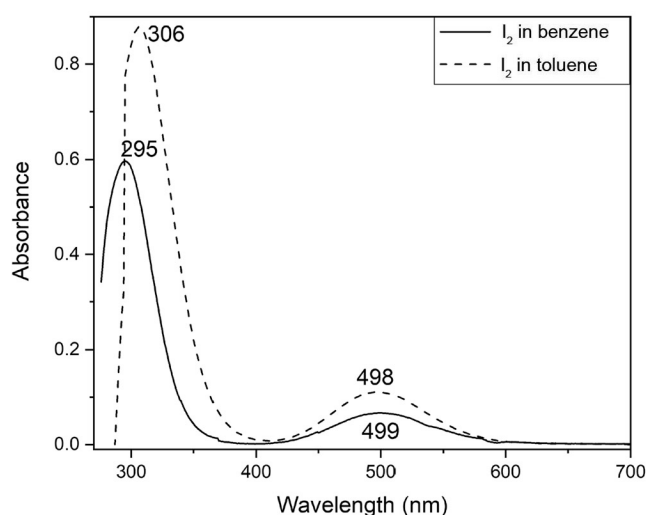
Figure 4. Absorption spectra of iodine in benzene and toluene.

in the case of iodine with benzene as well as toluene. The charge transfer band was observed at 295 nm for benzene and 306 nm for toluene. From the spectral analysis, non-bonding electron donors such as oxygen, sulphur and nitrogen interacted more with iodine than π-donors such as benzene and toluene.

Molecular orbital diagrams of CT complexes

The MO diagram of the CT complexes was studied to better understand the absorption spectra and electronic structure. The MO diagram of the CT complexes was constructed using 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 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 will destabilise them by 0.1 eV. Therefore, by taking the π^* orbital, we fixed the σ^* orbital of iodine in the CT complex. Using σ^* orbital and CT band energy, we fixed the highest occupied molecular orbital (HOMO) of the donor molecule. HOMO of oxygen, sulphur, nitrogen and π-donors are denoted as n_o, n_s, n_N and π_g respectively.
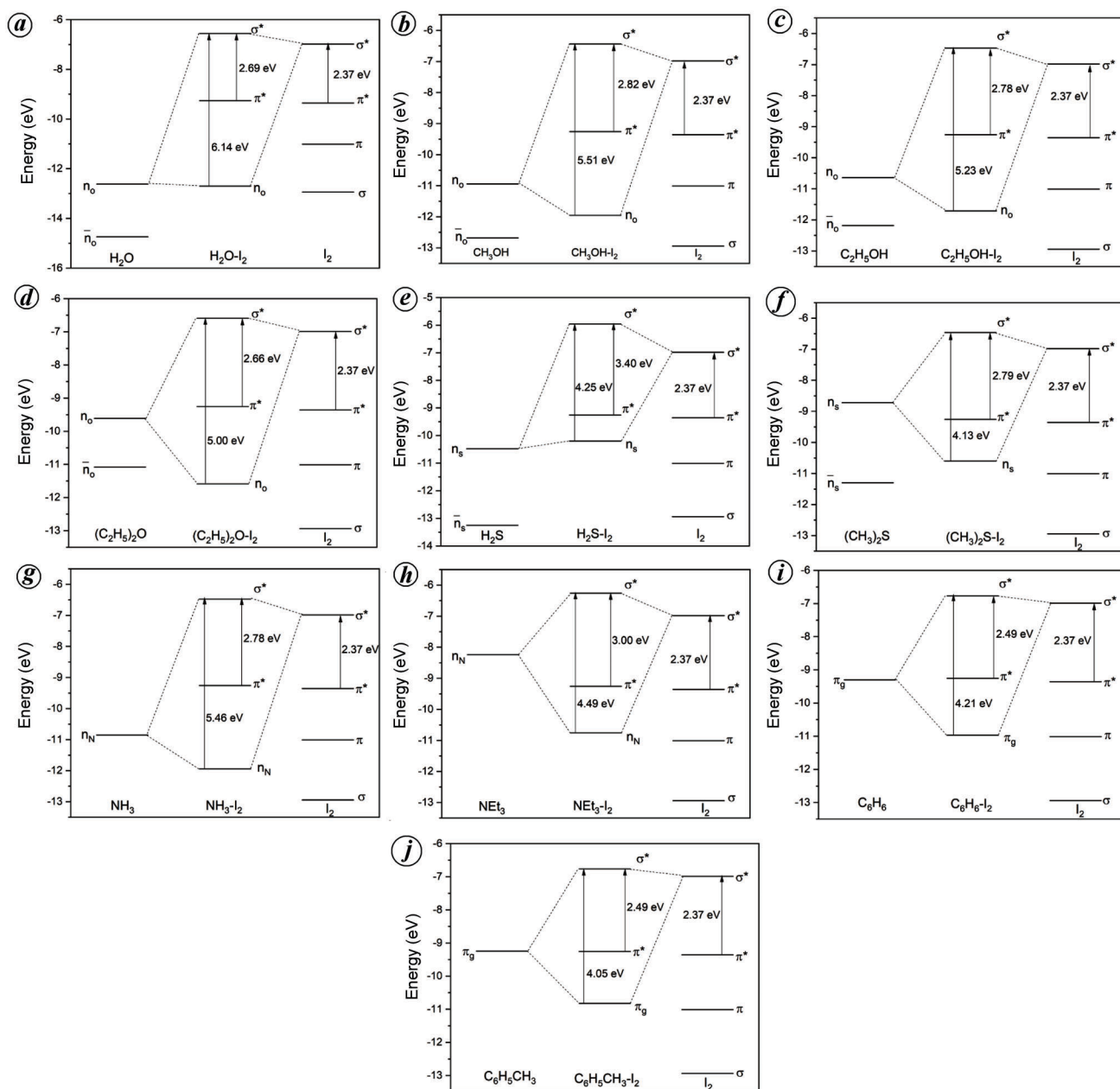
Figure 5 shows the MO diagrams of CT complexes of iodine with various donors. The major charge transfer is from the donor HOMO to the σ^* orbital of iodine in the CT complex. So, the σ^* orbital will be destabilized by getting the electron density. However, the HOMO of the donor molecules will donate electron density and stabilizes. The energy of stabilization of the n_o orbital in the H$_2$O–I$_2$ complex is 0.08 eV, while that of methanol, ethanol and diethyl ether is 1.01, 1.07 and 1.98 eV respectively. So, the energy of stabilization of the n_o orbital increases with the electron-donating substitutes. This trend is similar for both sulphur as well as nitrogen donors with iodine.

DFT calculations on CT complexes

The structural optimization of the iodine molecule was carried out with an I–I bond length of 2.69 Å. The formation energy of the CT complexes was calculated using the formula: energy of formation = energy of CT complex – (energy of I$_2$ molecule + energy of donor). The optimized geometry from DFT was visualized using the software XCrySDen[20].

CT complexes of iodine with n-donors

Optimized geometry of water was obtained with an O–H bond length of 0.97 Å and an HOH bond angle of 104.9°. The alcohols had similar geometries with an O–H bond length of 0.97 Å. There was 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 was 1.43 Å, for secondary alcohols was 1.44 Å and for tertiary alcohols 1.45 Å. The CÔH bond angle in every alcohol was almost

Figure 5. 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*) $C_6H_5CH_3$.

the same (108°). The C–O bond distance in both the ethers was the same (1.42 Å). The CÔC bond angle in dimethyl ether was 112°, and that in diethyl ether was 113°.

The oxygen donors contained two lone pairs, one perpendicular and the other parallel to the plane. Surprisingly, iodine in the CT complex had an orientation between parallel and perpendicular positions (Figure 6 *a*). The angles between iodine and the plane of the donor were in the order of 104° to 110°. The IÔH angle in the H_2O–I_2 CT complex was 104.4°, nearly equal to the HÔH bond angle. The IÔC angle in the $(CH_3)_2O$–I_2 CT complex was 110°, comparable with the bond angle in sp^3 hybridization. The angle of

iodine with alcohols was distributed between 104° and 110°. This will provide a clue for nearly the sp^3 hybridization in oxygen with a lone pair at 105° interacting with iodine and the other at 255° on another side of the plane not interacting. The I–I bond distance after the formation of the CT complex increased by 1–2% with oxygen donors. The C–O bond length was 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 remained unaltered.

Table 1 shows the formation energy and net charge transfer of the CT complexes of iodine with oxygen donors. The energy of formation of H_2O–I_2 was the least in oxygen

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	$(CH3)_2CHCH_2OH–I_2$	–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
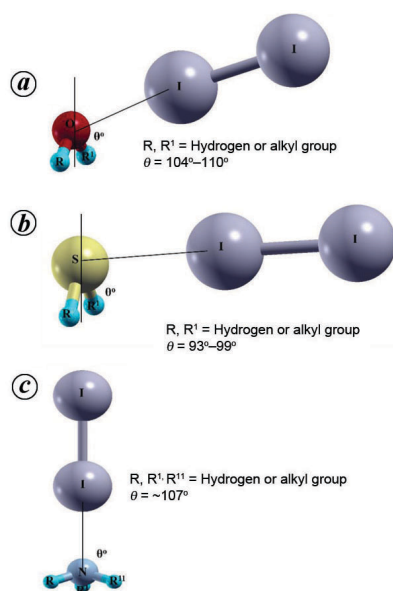
Figure 6. Geometry of CT complexes of iodine with (*a*) oxygen, (*b*) sulphur and (*c*) nitrogen donors.

donors, which was 5.67 kcal/mol. The rest were almost the same, with ~7 kcal/mol. However, diethyl ether was exceptional, with less energy (–6.42 kcal/mol). With the increase in the inductive effect due to the addition of more alkyl groups, the net charge transferred should also increase. However, the net charge transferred from all the oxygen donors to iodine was almost the same (0.1 e). This indicates that the charges are redistributed in both lone pairs of donors due to hybridization. Therefore, substituting the alkyl group will not increase the energy of formation and net charge transferred to the CT complexes of iodine and oxygen donors.

H_2S was also bent with an $\hat{HSH}$ angle of 92° and S–H bond distance of 1.35 Å. The S–H bond distance in thiols was the same as in H_2S. The C–S bond length was 1.82 Å in all cases, except in dimethyl sulphide, which is 1.80 Å. The $\hat{CSH}(C)$ bond angle increased from 97° in the case of thiols to 99° for alkyl sulphides. The N–H bond distance in

ammonia and the rest of the cases was the same (1.02 Å). The HNH bond angle in ammonia was 107°, and in the case of primary amines, it was 111°. However, in the case of dimethylamine, the CNH angle was 110°, and that of CNC was 113°. The CNC bond angle for tertiary amines was 111°, similar to primary amines. The C–N and C–C bond distances in all the cases were the same, at 1.46 and 1.52 Å respectively.

Unlike in the oxygen donors, the orientation of iodine with sulphur was mostly perpendicular to the plane (Figure 6 *b*). The bond angle was between 93° and 99° from the plane, indicating no hybridization. The nitrogen donors contained only one lone pair, so there was only one possibility that is iodine is above the nitrogen, like ammonium ion (Figure 6 *c*). The angle was about 107° in all the cases. The angle increased with the substitution of the alkyl group than with hydrogen in the case of oxygen and sulphur donors. This is because of steric hindrance by the bulk alkyl moieties. However, this trend was 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, the S–H, N–H, C–S and C–C bond distances did not change. The I–I bond length increased by 2–5% in sulphur and nitrogen donors. The C–N bond distance increased by 0.01 Å in the amines. The $\hat{HSH}(C)$ bond angles did not change in H_2S, as well as in thiols. However, C–C increased by 1° in the case of alkyl sulphides. The $\hat{HNH}$ bond angle increased by 2.5° in the case of ammonia. In the case of primary amines, the $\hat{HNH}$ bond angle decreased by 2.5° and the $\hat{HNC}$ bond angle by 1°. On the contrary, both the $\hat{HNH}$ and $\hat{HNC}$ bond angles increased by 1° in the case of dimethylamine. The $\hat{CNC}$ bond angle with trimethylamine was 112°, and that of triethylamine was 111°.

Table 2 shows the results of PWScf calculation of the CT complexes of iodine with sulphur and nitrogen donors. As expected, the energy of formation increased with an increase in the substituents in the CT complexes of iodine with sulphur donors. This was partially true in the case of iodine with nitrogen donors. The net charge transferred

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

Entry	CT complex	Energy of formation (kcal/mol)	Net charge transferred (e)	S-I/N-I distance (Å)
1	$H_2S–I_2$	−7.05	0.18	3.03
2	$CH_3SH–I_2$	−10.16	0.23	2.93
3	$CH_3CH_2SH–I_2$	−11.03	0.24	2.92
4	$(CH_3)_2S–I_2$	−13.63	0.27	2.86
5	$(CH_3CH_2)_2S–I_2$	−14.89	0.29	2.83
6	$NH_3–I_2$	−12.04	0.19	2.63
7	$CH_3NH_2–I_2$	−14.81	0.23	2.59
8	$CH_3CH_2NH_2–I_2$	−14.71	0.24	2.60
9	$(CH_3)_2NH–I_2$	−15.82	0.25	2.58
10	$(CH_3)_3N–I_2$	−15.51	0.25	2.59
11	$(CH_3CH_2)_3N–I_2$	−14.16	0.27	2.63
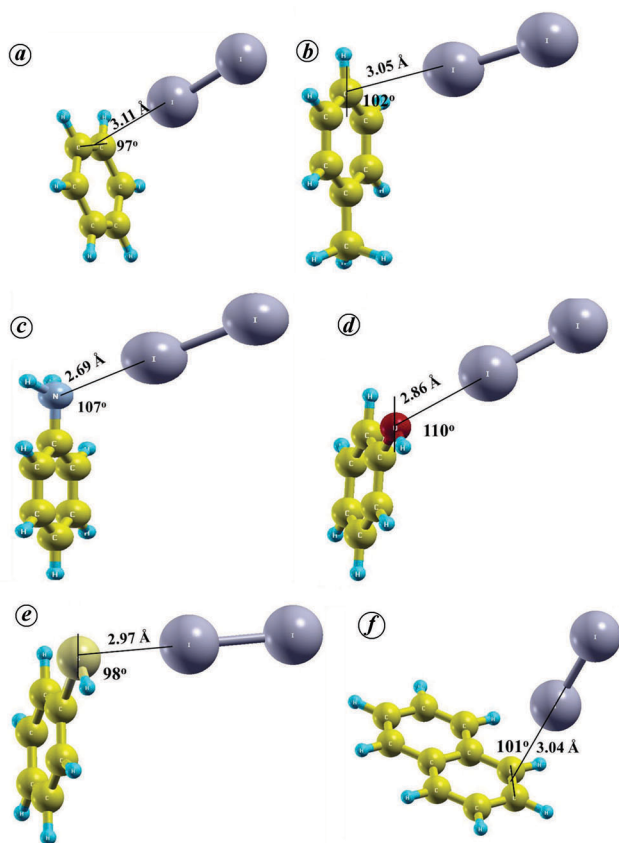
Figure 7. Optimized geometry of CT complex of iodine with (*a*) benzene, (*b*) toluene, (*c*) aniline, (*d*) phenol, (*e*) thiophenol and (*f*) naphthalene.

increased with an increase in the alkyl group substitution. This clearly demonstrates the inductive effect of the alkyl substituents attached to the sulphur and nitrogen donors. As expected, the S–I distance with sulphur donors was more than the O–I and N–I distance in oxygen and nitrogen donors respectively.

CT complexes of iodine with aromatic compounds

The optimized geometry of benzene was 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 were simulated by placing iodine in various sites. The energetically feasible complex is having iodine situated on one of the C–C bonds with 97° with respect to the plane of the benzene (Figure 7 *a*). However, the energy of formation (E_f) is less, which was −3.39 kcal/mol with 0.07 e net transferred.

The Ph–CH_3 bond length was 1.50 Å, and the PhĈH bond angle was 111° while that of HĈH was 107°. Iodine on para carbon position in toluene was energetically favourable with E_f of −3.70 kcal/mol (Figure 7 *b*). The I–I bond distance with both benzene and toluene was the same (2.73 Å). The C–C bond length increased by 0.01 Å in both cases.

The optimized C–C bond length of aniline, phenol and thiophenol was the same as in benzene. The C–X bond length in aniline was 1.39 Å, phenol was 1.38 Å and thiophenol 1.77 Å. The X–H bond distance was similar to their aliphatic analogues. The CN̂H bond angle was 117° and HN̂H bond angle was 114° in aniline. The CÔH bond angle was 108° in phenol, and the CŜH bond angle was 97° in thiophenol.

The orientation of iodine in aniline was similar to aliphatic amines (Figure 7 *c*). Unlike benzene and toluene, the energy of formation of the aniline–I_2 CT complex was high, at −9.66 kcal/mol. Similarly, phenol and thiophenol formed CT complexes with iodine like their aliphatic analogues (Figure 7 *d* and *e*). The energy formation of the CT complex with phenol was −6.18 kcal/mol, and with thiophenol, it was −8.47 kcal/mol. The net charge transferred in the case of phenol (0.07 e) was less than that of water. The net charge transferred to iodine from aniline was 0.20 e, and from thiophenol was 0.21 e, which was comparable with their aliphatic analogues. The donor–iodine distance in benzene, toluene and thiophenol was about 3 Å each, and that of aniline and phenol was 2.69 Å and 2.86 Å respectively.

After the formation of CT complexes, C–C and X–H bonds had changed in all the cases. However, C–X changed by 0.01 Å with phenol, 0.02 Å with aniline, and it remained the same with thiophenol. The I–I bond distance with phenol was 2.72 Å, and with aniline was 2.77 Å, similar to $H_2O–I_2$ and $NH_3–I_2$ complexes respectively. The I–I distance with

thiophenol was 2.78 Å. The $C\hat{X}H$ bond angle remained unaltered with phenol and thiophenol. In the case of aniline, the $C\hat{N}H$ and $H\hat{N}H$ bond angles decreased by 3° each.

The optimized C–C bond length in naphthalene was 1.42 Å, but the C_1–C_2 bond distance was 1.38 Å. The $C\hat{C}C$ bond angle was 121°, but the $C\hat{C}C$ bond angle associated with the fused C-atoms was 119°. The orientation of iodine in the CT complex was on the C_1–C_2 bond of the first and second carbon atoms at 101° to the plane with a distance of 3.04 Å (Figure 7f). After the formation of the CT complex, the C_1–C_2 bond distance increased by 0.01 Å, the I–I bond by 0.05 Å while the other bonds remained unaltered. The energy of formation was –4.24 kcal/mol, and the net charge transferred was 0.10 e. Time-dependent density functional theory (TDDFT) calculations were done to obtain the excitation energy that matched well with the experiments (Supplementary Information).

Conclusion

Thus, the stabilization and destabilization of corresponding orbitals were well understood using the MO diagram. DFT was employed effectively to explain the formation, structure and stability of the CT complex. The effect of substitution of the alkyl group to the donor molecule in the CT complex was studied. TDDFT calculations were also carried out.

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