Molecular orbital calculations for iodine complexes: $C_2H_4 \cdot I_2$ and $C_6H_6 \cdot I_2$

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The INDO method is used with single and double-zeta Slater atomic orbital basis to calculate the wave functions and binding energies of ethylene iodine and benzene iodine which are treated as "super" molecules. The relative stability of the resting and axial structures of these complexes is investigated. It is found that the axial structure forms a stable bound state while the resting structure is rather unstable. Both, the polarization and charge transfer forces seem to play a more important role in the formation of the axial structure than in the resting one. A detailed description of the complex molecular orbitals is presented.

Key words: INDO calculation for iodine complexes—binding energy of iodine complexes—structure of iodine complexes—ethylene iodine—benzene iodine

1. Introduction

The most stable geometry of the benzene-iodine, $C_6H_6 \cdot I_2$ complex presents an interesting question. Two geometrical structures may be considered energetically favorable: The resting structure where the iodine molecule is parallel to the plane of benzene molecule, and the axial structure where the iodine aligns itself along the main symmetry axis of benzene (see Fig. 5). The distinction between these two possible geometries on the basis of Mulliken's simple resonance structure theory is not straightforward [1a]. The early prediction based on a symmetry argument implied that the resting geometry would be more favorable than the axial one [1b]. The experimental study of the structure of a similar complex, $C_6H_6 \cdot Br_2$, in solid state revealed that the axial structure is the stable one [1a].

Even though the situation in the gas phase could be different, Mulliken and Person suggested that the axial configuration in the gas phase is the most likely configuration for $C_6H_6 \cdot Br_2$ and the analogous $C_6H_6 \cdot I_2$ complex [1a]. This implies that the formation of these complexes would involve low lying molecular orbitals in addition to the highest occupied ones. More recently, Engdahl and Nelander [2] analyzed the infrared and visible spectra of the benzene iodine complexes in solid matrices. They confirmed that the axial structure is the stable one.

In the present work, the relative stability of the resting and axial structures of $C_2H_4 \cdot I_2$ and $C_6H_6 \cdot I_2$ complexes is investigated. The INDO method [3] is used for studying the variation of the binding energy of the complex as a function of the separating distance between the component molecules. The complex is treated as a "super" molecule with varying geometry.

In the INDO method a minimal Slater atomic orbital basis is usually used [3]. However, in order to obtain reasonable optimal bond lengths in iodine-containing compounds, it was found more suitable to use a double-zeta basis of s and p Slater-type orbitals on the iodine atom, as explained in Sect. 2.

In both of the complexes studied, the axial structure was found to be considerably more stable than the resting structure. In fact, the latter is barely stable with a rather flat-minimum energy curve. In addition, the molecular orbitals (MO's) of the complexes at the optimal separation between the constituent molecules, are analyzed. It is seen that the lower MO's in the resting complexes remain localized on their respective component molecules. Only one MO of I_2 (π_u in the case of $C_2H_4 \cdot I_2$, and π_g in the case of $C_6H_6 \cdot I_2$) mixes with the highest occupied MO of hydrocarbon (e_{1g} MO in the case of C_6H_6 and b_{3u} MO in the case of C_2H_4). This mixing, or interaction, yields a pair of "complex" molecular orbitals (CMO) which extend over the whole complex. One CMO is bonding in the sense that is forms a bond between the iodine and the hydrocarbon, and the other CMO is antibonding. In the case of the axial structure, the HOMO's as well as some of the low lying MO's mix together and form complex molecular orbitals (CMO).

In the following sections, the method of calculation is briefly described, and the results are analyzed in detail.

2. Method of calculation

The INDO method [3] is used in this work for calculating the wave functions and energies in the ground states of the complexes under consideration. For this purpose the INDO program developed by Ridley and Zerner, and Bacon and Zerner [4] is utilized.

It is found that, in the framework of the INDO method, the use of a minimal basis of atomic orbitals in the treatment of iodine containing compounds yields, in general, relatively short bond lengths. It was realized that the reason for this lies in the fact that in this method the equilibrium bond length is determined mainly by the derivatives, with respect to the bond distance R of the core-core

interaction energy, and the two-center coulomb integrals, γ, and by the quantity:

$$\sum_{\mu,\lambda} \bar{\beta}_{AB} \frac{\partial}{\partial R} (P_{\mu\lambda} \cdot S_{\mu\lambda}) \tag{1}$$

where μ and λ refer to atomic orbitals on the bonded atoms A and B (μ on A and λ on B), and $P_{\mu\lambda}$, $S_{\mu\lambda}$ and $\bar{\beta}_{AB} = \frac{1}{2}(\beta_A^0 + \beta_B^0)$ are respectively the density matrix elements, the overlap integrals, and the average of the β^0 parameters. The larger the value of expression (1) the smaller the bond length between A and B. Therefore, a steep variation of $P_{\mu\lambda} \cdot S_{\mu\lambda}$ (i.e. large value of the derivative) in the bonding region leads to a short equilibrium bond length. This happens when the overlaps $S_{\mu\lambda}$ vary steeply in the bonding region. To obtain a better bond length, either the values of the parameters β^0 have to be reduced, or an extended atomic orbital basis must be utilized. The reduction of the β^0's values however has an adverse effect on the MO's energies. The use of an extended atomic orbital basis is preferable. A similar situation has, in fact, been encountered in different methods of approximation. For example, in CNDO/2 method, it was recognized that the inclusion of d orbitals in the AO's basis gave better geometries of iodine containing compounds [5a]. In other methods, double zeta basis or single zeta plus polarization basis sets are used [5b]. In the present work a scheme due to Andersen, Edwards, and Zerner is adapted, where single zeta Slater orbital basis sets are used on all atoms except on iodine. The S and P orbitals on this atom are expanded in terms of STAO's, $5s$ and $5P$ as follows [6]:

$$S = 0.618030 \times (5s; \zeta = 3.34077) + 0.458166 \times (5s; \zeta = 2.04555) \tag{2a}$$

$$P = 0.591824 \times (5p; \zeta = 2.92046) + 0.506777 \times (5p; \zeta = 1.67111). \tag{2b}$$

The zeta values are quoted from Ref. [7], and the coefficients in Eqs. 2 are chosen in such a way as to insure normalization of the resulting orbitals S and P, and to maintain the same ratio as the corresponding coefficients given in Ref. [7]. The basis set given in Eq. 2 is used in fact only in calculating the over-lap integrals and the one-electron matrix elements. In calculating the coulomb and exchange integrals, single zeta Slater-type orbitals are used. For iodine, the following zetas are adapted:

$$\zeta(s) = 2.6712, \quad \zeta(p) = 2.1949.$$

For other atoms (C and H) Slater's zetas are used.

The parameter β^0 of iodine was then determined in such a way as to produce the experimental bond length ($R = 2.66$ Å) of I_2 molecule. The value $\beta^0 = -13.0$ e.V. satisfied this requirement. Using Koopman theorem, the 1st ionization potential of I_2 is found equal to 9.41 e.V. as compared to the experimental value 9.7 e.V. [8]. As a further checking, the optimal bond length of the molecule $H-I$, and the bond length $C-I$ in CH_3I and C_6H_5I are calculated. Table 1 shows the results.

The binding energy, ΔE, of the complex is defined as the difference between the energy, $E(C)$, of the complex, and the sum of the energies of the separate

Table 1. Bond lengths, in angstroms, of some iodine containing compounds

Compound	I_2	HI	CH_3I	C_6H_5I
bond	I—I	H—I	C—I	C—I
cal.	(2.67)[a]	1.63	2.14	2.08
exp.	2.66[b]	1.65[b]	2.13[c]	2.09[d]

[a] This value was used to obtain the value of β^0.
[b] Ref. [8].
[c] Ref. [5a].
[d] This value is the bond length of C—I in C_6I_6, as quoted from Ref. [9]

constituent molecules:

$$\Delta E = E(C) - [E(I_2) + E(x)] \tag{3}$$

where $x = C_2H_4$ or C_6H_6. All energies are calculated using the same AO basis sets as described above. In studying the relative stability of the resting and axial structures, ΔE is calculated simply as a function of the separation R between the component molecules. In the following discussion, R is always the distance between the centers of symmetry of the hydrocarbon and iodine molecules.

3. $C_2H_4 \cdot I_2$

The resting and axial structures of this complex are depicted in Fig. 1.

The variations of the binding energy ΔE (Eq. 3) as a function of R are summarized in Table 2. In this table CT is the net charge on I_2. It is equal to the amount of charge that is transferred from C_2H_4 to I_2. The charge densities are calculated from the diagonal elements of the bond order matrix. Although these charge densities were, in general, smaller (in absolute value) than the Mulliken population densities, the net charge transfer CT was very close to the one calculated from Mulliken population densities.
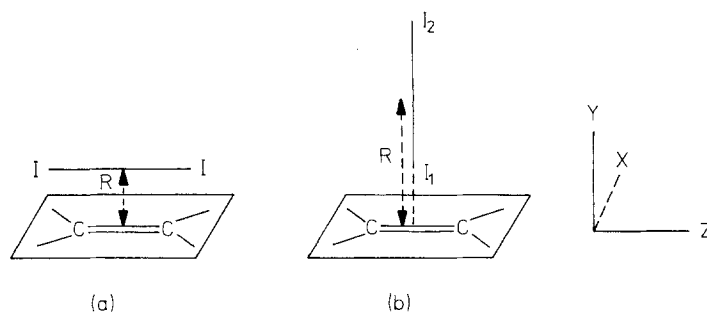
Fig. 1. The resting (a) and the axial (b) structures of $C_2H_4 \cdot I_2$

Table 2. Calculated binding energy, ΔE (kcal/mole) and charge transfer CT in $C_2H_4 \cdot I_2$ as functions of R

Resting structure			Axial structure		
$R(\text{Å})$	ΔE	CT^a	$R(\text{Å})$	ΔE	CT^a
4.000	−0.25	0.000	4.000	−33.5	−0.125
3.720	−0.55	0.000	3.720	−44.5	−0.191
3.500	−0.93	0.004	3.698^b	−44.8	−0.196
3.188^b	−1.52	0.010	3.500	−38.3	−0.238
2.900	−0.72	0.024	3.000	+211.4	−0.230
2.500	+14.19	0.060			

^{a} CT is the net charge on I_2. It is equal to the charge transferred from C_2H_4 to I_2.
A positive CT means that the charge is transferred from I_2 to C_2H_4.
^{b} Optimal distance

It is obvious from Table 2 that the axial configuration of $C_2H_4 \cdot I_2$ forms a bound state corresponding to an equilibrium value of R equal to 3.698 Å and a binding energy of 44.8 kcal/mole. The resting configuration, on the other hand, has an optimal value of R equal to 3.188 Å and a binding energy of only 1.52 kcal/mole.

During the approach of I_2 molecule from C_2H_4 in the resting geometry, and at certain values of $R > 3.5$ Å, I_2 was rotated in the YZ plane (Fig. 1) around its midpoint, to bring the resting structure into the axial one. It was found that this rotation had practically no energy barrier. It may be therefore concluded that the axial structure is much more favorable than the resting one.

To have an insight into the molecular orbital structure of both geometries, the MO's are closely analyzed. Fig. 2 shows a diagram of the occupied MO's energies of the complex $C_2H_4 \cdot I_2$ at its equilibrium geometries and the separate C_2H_4 and I_2 molecules. The MO's are labeled according to the corresponding irreducible representations of the proper point groups and are numbered in an increasing order of energy.

Since the molecular orbitals of the complex are, in general, linear combinations of atomic orbitals located on both components of the complex, they can be considered as sums of two linear combination-parts:

$$\psi_i = \sum_1 x_1 c_{1i} + \sum_k x_k c_{ki} \tag{4}$$

where the index 1 runs over the atomic orbitals x_1 on iodine molecule and k runs over the atomic orbitals x_k on the hydrocarbon molecule. The percent contributions to ψ_i from I_2 and the hydrocarbon are put equal to: $100 \sum_1 c_{1i}^2$ and $100 \sum_k c_{ki}^2$ respectively. Table 3 shows the percent contributions from I_2 molecule (denoted $\% I_2$) to the molecular orbitals of $C_2H_4 \cdot I_2$. The analysis of the symmetry properties of the different MO's made it easy to identify the main molecular orbitals of I_2 and ethylene that contribute to each of the complex molecular orbitals. This is indicated in the columns headed "Cont. MO's" in Table 3.
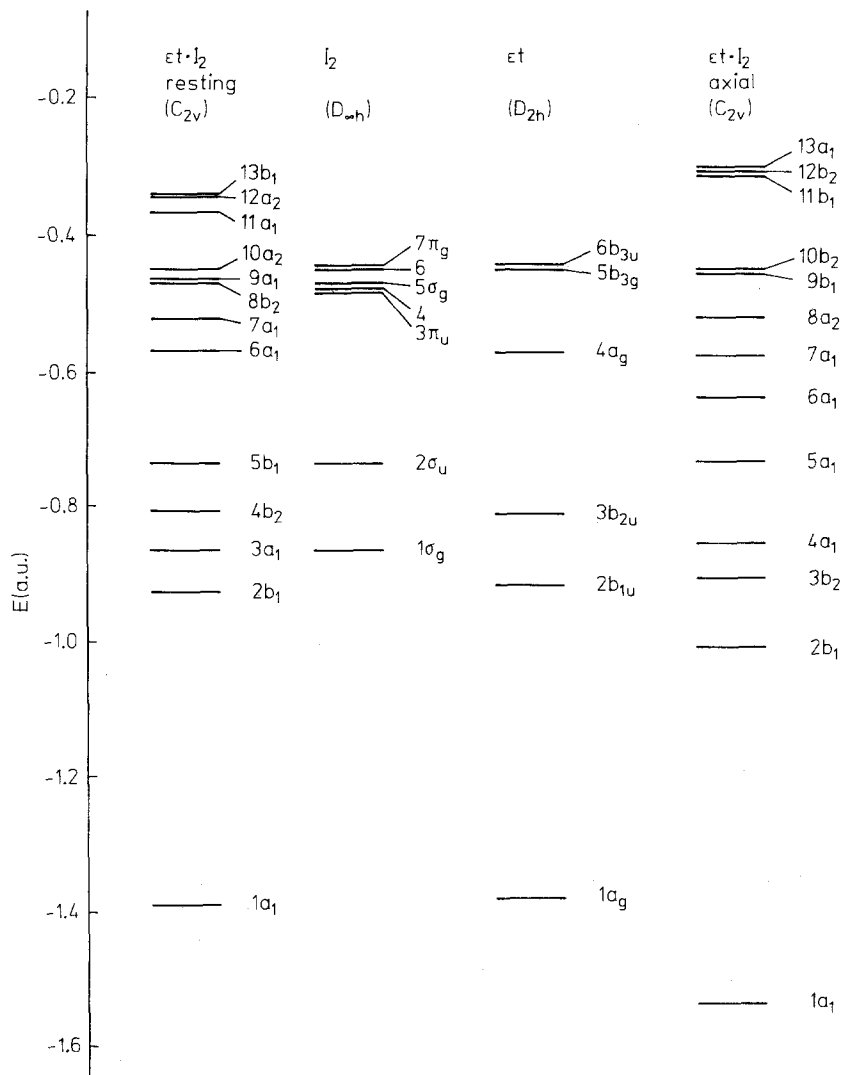
Fig. 2. Molecular orbital energy diagram of ethylene iodine (Et.I_2), iodine (I_2) and ethylene (Et). For explanation see text

In the resting structure of $C_2H_4 \cdot I_2$, most of the MO's of I_2 and C_2H_4 practically remain localized on their respective molecules without much alteration. Only the HOMO, b_{3u} of ethylene and the orbital π_u of iodine mix together appreciably yielding two CMO's: one bonding, $7a_1$, and one antibonding, $11a_1$. Fig. 3 shows schematically the main atomic orbitals that constitute these two CMO's. In each of these CMO's a small fraction of negative charge moves from I_2 to C_2H_4 creating a small positive charge on I_2. The total net charge on I_2 is CT $= 0.010$ (Table 2).

Table 3. Percent contributions from iodine, denoted as %I_2, to the molecular orbitals of $C_2H_4 \cdot I_2$. The main contributing MO's of I_2 and C_2H_4 are indicated

	Resting geometry[a]			Axial geometry[a]	
MO	%I_2	Cont. MO's	MO	%I_2	Cont. MO's
$1a_1$	1.5	a_g(Et)	$1a_1$	7.6	a_g(Et)
$2b_1$	2.2	b_{1u}(Et)	$2b_1$	2.8	b_{1u}(Et)
$3a_1$	98.5	σ_g(I_2)	$3b_2$	3.0	b_{2u}(Et)
$4b_2$	0.5	b_{2u}(Et)	$4a_1$	94.5	σ_g(I_2)
$5b_1$	98.7	σ_u(I_2)	$5a_1$	75.7	b_{3u}(Et)$+\sigma_u$(I_2)$+\sigma_g$(I_2)
$6a_1$	0.1	a_g(Et)	$6a_1$	0.4	a_g(Et)
$7a_1$	48.0	b_{3u}(Et)$+\pi_u$(I_2)	$7a_1$	63.4	b_{3u}(Et)$+\sigma_u$(I_2)$+\sigma_g$(I_2)
$8b_2$	99.5	π_u(I_2)	$8a_2$	0.0	b_{3g}(Et)
$9a_1$	96.3	σ_g(I_2)	$9b_1$	96.1	π_u(I_2)
$10a_2$	1.7	b_{3g}(Et)	$10b_2$	97.4	π_u(I_2)
$11a_1$	42.3	b_{3u}(Et)$+\pi_u$(I_2)	$11b_1$	98.9	π_g(I_2)
$12a_2$	98.3	π_g(I_2)	$12b_2$	99.5	π_g(I_2)
$13b_1$	98.5	π_g(I_2)	$13a_1$	70.4	σ_g(I_2)$+b_{3u}$(Et)

[a] The columns headed "Cont. MO's" indicate the main molecular orbitals of I_2 and ethylene (Et) that contribute to the corresponding complex molecular orbitals

The situation in the axial $C_2H_4 \cdot I_2$ is rather more complicated. It is seen from Fig. 2 that the MO's energies of this complex are more spread apart than in the case of the resting complex. This indicates a relatively stronger interaction between C_2H_4 and I_2. Table 3 also shows that two MO's from I_2, σ_u and σ_g, mix with the HOMO b_{3u} of ethylene yielding three CMO's. Two of them, namely $5a_1$ and $7a_1$, are bonding and one, $13a_1$, antibonding. Fig. 4 shows the main atomic orbital components of these orbitals. From the signs distribution on Fig. 4 it can be seen that orbital $13a_1$ has a nodal surface between atom I_1 and C_2H_4, while the other two orbitals don't have such a surface. It should be noted here that in separate I_2 molecules σ_u and σ_g orbitals do not mix with one another because of a symmetry restriction. In the complex $C_2H_4 \cdot I_2$, which has a lower symmetry, this restriction is removed, and it is possible for σ_u and σ_g to mix together. In fact, the mixing of such orbitals (bonding and antibonding) in the complex is responsible for the

(a)   (b)

$7a_1$ $11a_1$
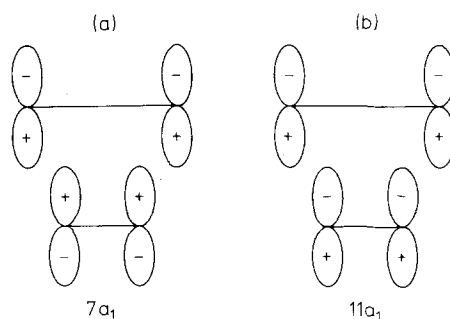
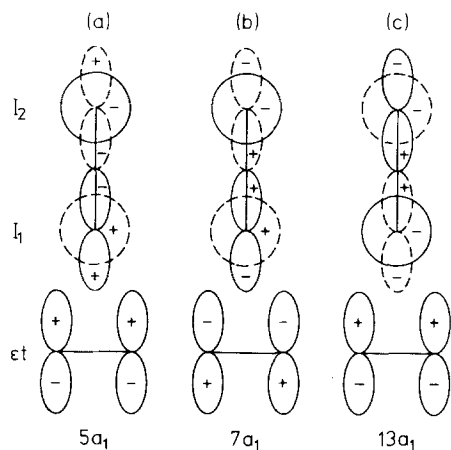**Fig. 3.** The bonding, $7a_1$, and antibonding $11a_1$, molecular orbitals of resting ethylene iodine

Fig. 4. The complex molecular orbitals of the axial ethylene iodine at equilibrium. Orbitals $5a_1$ and $7a_1$ are bonding, and $13a_1$ is antibonding.

polarization of I_2 segment. The charge on atom I_1 is equal to $q_1 = +0.147$ and on atom I_2, $q_2 = -0.343$. The net charge on I_2 molecule is $CT = -0.196$. The amount of polarization of I_2 indicates that, in addition to the charge transfer forces, the polarization forces play an important role in stabilizing the axial structure of $C_2H_4 \cdot I_2$.
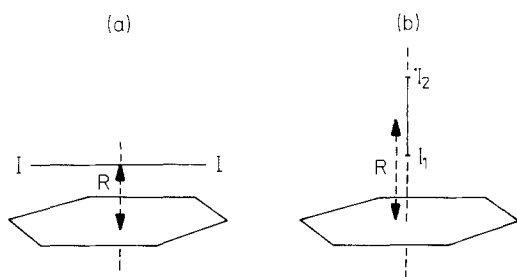

Fig. 5. The resting (a) and axial (b) geometries of benzene iodine

Table 4. Calculated binding energy, ΔE (cal/mole) and charge transfer CT in $C_6H_6 \cdot I_2$ as functions of R

	Resting structure			Axial structure	
$R(\text{Å})$	ΔE	CT^a	$R(\text{Å})$	ΔE	CT^a
4.500	−0.02	0.000	4.300	−12.28	−0.033
4.000	−0.05	0.000	4.000	−17.61	−0.062
3.914[b]	−0.06	0.000	3.945[b]	−18.09	−0.068
3.850	−0.05	0.000	3.700	−14.24	−0.098
3.500	+0.13	0.002	3.000	+231.2	−0.245
3.000	+3.85	0.006			

[a] CT is the net charge on I_2. It is equal to the charge transferred from benzene to iodine
[b] Optimal distance

4. $C_6H_6 \cdot I_2$

This complex is studied in a similar manner to the ethylene iodine. Fig. 5 represents its resting and axial geometries, and Table 4 shows the variations of the binding energy (Eq. 3) as a function of the distance R between the centers of the iodine and benzene molecules. It is seen that the resting configuration is barely stable
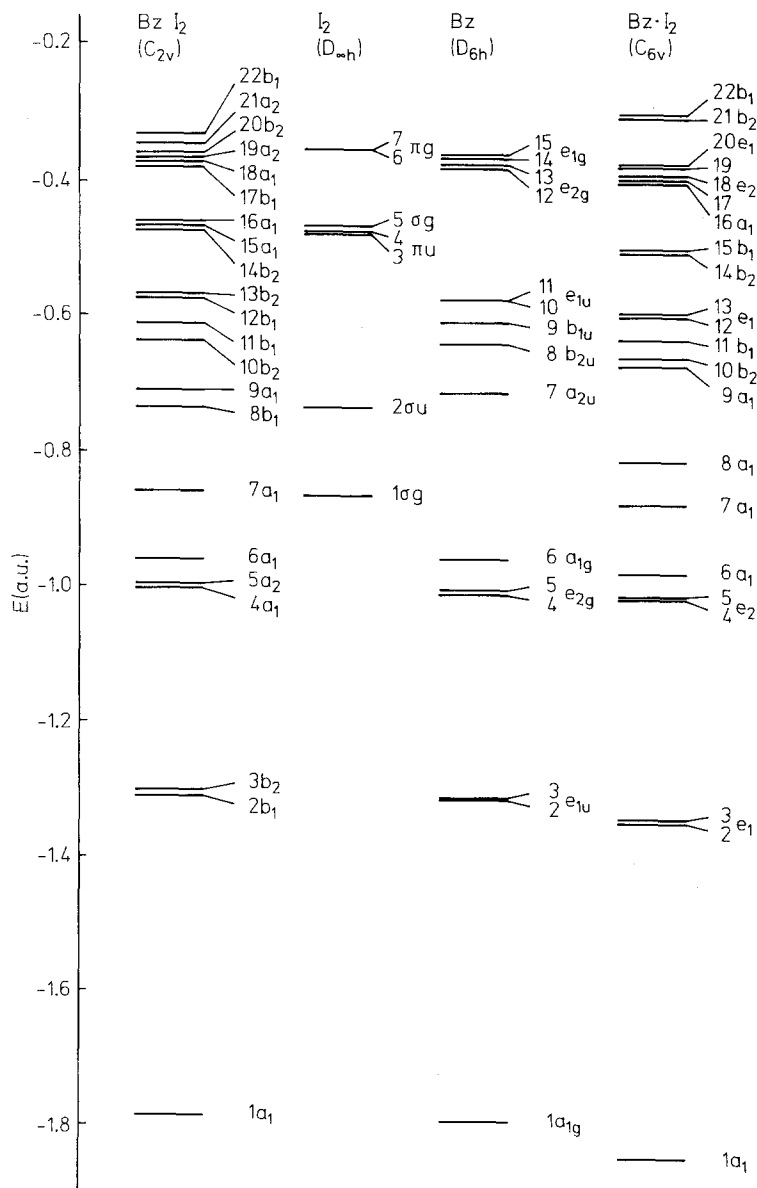

Fig. 6. Molecular orbital energy diagram for benzene iodine complex in resting (C_{2v}) and axial (C_{6v}) geometries, and for iodine (I_2) and benzene (Bz) molecules

with an optimal value of R equal to 3.914 Å and a negligibly small binding energy of 0.06 kcal/mole. Neither a transfer of charge nor a polarization occurs at the equilibrium. The axial configuration, on the other hand, appears to be quite stable with an optimal value of R equal to 3.945 Å and a binding energy of 18.1 (kcal/mole). A net charge equal to CT $= -0.068$ is transferred from benzene to iodine. Besides, I_2 is polarized with a net charge on atom I_1, equal to $q_1 = +0.092$ and a charge on atom I_2 equal to $q_2 = -0.160$. Fig. 6 shows a diagram of the MO's energies of the resting (C_{2v} point group) and axial (C_{6v} point group) structures at equilibrium. For comparison, the MO's levels of the separate C_6H_6 and I_2 are also included in the same diagram. The MO's are labeled according to the irreducible representations of the point group of each compound, and are numbered in an increasing order of energy.

The composition of the complex molecular orbitals and the percent contributions to them from I_2 are shown in Table 5.

In the resting structure, only the HOMO e_{1g} of benzene and the HOMO π_g of iodine mix appreciably together and form two CMO's: one bonding, $17b_1$, and one antibonding, $22b_1$. Fig. 7 schematizes the main atomic orbital components

Table 5. Percent contributions from iodine, denoted as $\% I_2$, to the molecular orbitals of $C_6H_6 \cdot I_2$. The main contributing MO's of I_2 and C_6H_6 are indicated under the heading: Cont. MO's

| Resting geometry (C_{2v})			Axial geometry (C_{6v})		
MO	$\% I_2$	Cont. MO's[a]	MO	$\% I_2$	Cont. MO's[a]
$1a_1$	0.1	$a_{1g}(Bz)$	$1a_1$	2.9	$a_{1g}(Bz)$
$2b_1$	0.1	$e_{1u}(Bz)$	$2e_1$	0.8	$e_{1u}(Bz)$
$3b_2$	0.0	$e_{1u}(Bz)$	$3e_1$	0.8	$e_{1u}(Bz)$
$4a_1$	0.0	$e_{2g}(Bz)$	$4e_2$	0.0	$e_{2g}(Bz)$
$5a_2$	0.0	$e_{2g}(Bz)$	$5e_2$	0.0	$e_{2g}(Bz)$
$6a_1$	0.0	$a_{1g}(Bz)$	$6a_1$	0.4	$a_{1g}(Bz)$
$7a_1$	99.1	$\sigma_g(I_2)$	$7a_1$	79.8	$\sigma_g(I_2) + a_{2u}(Bz)$
$8b_1$	99.1	$\sigma_u(I_2)$	$8a_1$	56.6	$\sigma_g(I_2) + a_{2u}(Bz)$
$9a_1$	3.5	$a_{2u}(Bz)$	$9a_1$	76.1	$\sigma_u(I_2) + a_{2u}(Bz)$
$10b_2$	0.0	$b_{2u}(Bz)$	$10b_2$	0.0	$b_{2u}(Bz)$
$11b_1$	0.0	$b_{1u}(Bz)$	$11b_1$	0.0	$b_{1u}(Bz)$
$12b_1$	0.0	$e_{1u}(Bz)$	$12e_1$	1.0	$e_{1u}(Bz)$
$13b_2$	0.0	$e_{1u}(Bz)$	$13e_1$	1.0	$e_{1u}(Bz)$
$14b_2$	99.0	$\pi_u(I_2)$	$14b_2$	71.6	$\pi_u(I_2) + e_{1g}(Bz)$
$15a_1$	99.0	$\pi_u(I_2)$	$15b_1$	72.3	$\pi_u(I_2) + e_{1h}(Bz)$
$16a_1$	97.2	$\sigma_g(I_2)$	$16a_1$	87.4	$\sigma_g(I_2) + a_{2u}(Bz)$
$17b_1$	35.9	$\pi_g(I_2) + e_{1g}(Bz)$	$17e_2$	0.2	$e_{2g}(Bz)$
$18a_1$	0.0	$e_{2g}(Bz)$	$18e_2$	0.0	$e_{2g}(Bz)$
$19a_2$	0.0	$e_{2g}(Bz)$	$19e_1$	61.3	$\pi_u(I_2) + e_{1g}(Bz)$
$20b_2$	0.0	$e_{1g}(Bz)$	$20e_1$	61.5	$\pi_g(I_2) + e_{1g}(Bz)$
$21a_2$	99.9	$\pi_g(I_2)$	$21b_2$	65.2	$\Pi_g(I_2) + e_{1g}(Bz)$
$22b_1$	64.1	$\Pi_g(I_2) + e_{1g}(Bz)$	$22b_1$	64.5	$\Pi_g(I_2) + e_{1g}(Bz)$

[a] Bz refers to benzene and I_2 to iodine

(a)

17b₁

(b)
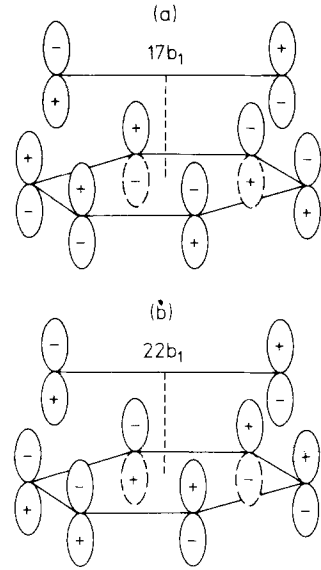
22b₁

Fig. 7. The bonding, $17b_1$, and antibonding, $22b_1$, molecular orbitals of the resting benzene iodine
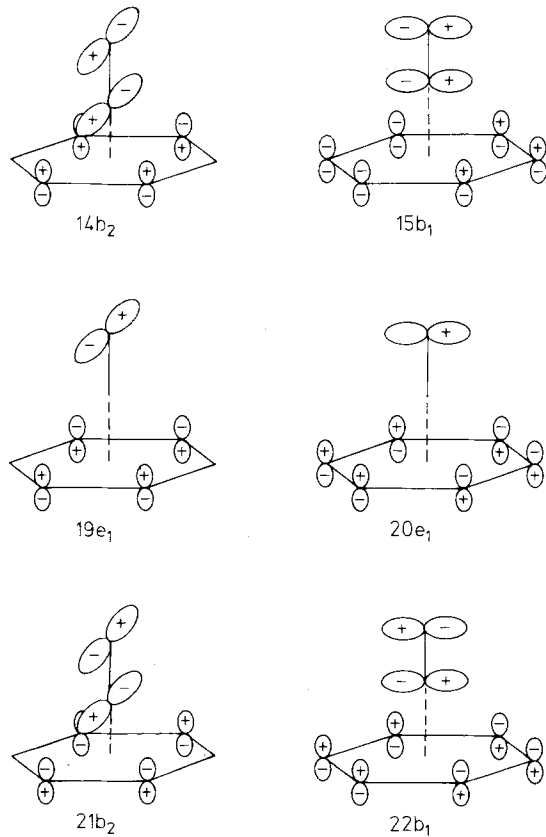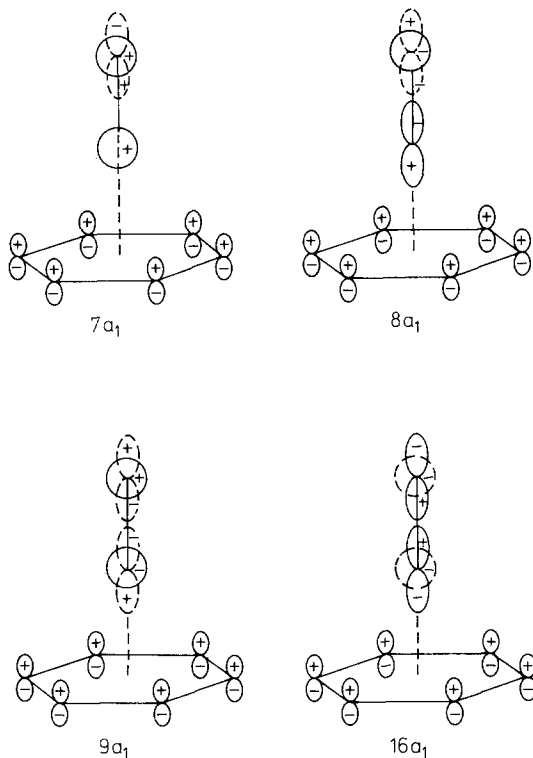
14b₂

15b₁

19e₁

20e₁

Fig. 8. The $(\pi$-$\pi)$-type molecular orbitals of the axial benzene iodine. Orbitals $14b_2$, $15b_1$ are bonding. The rest of the orbitals are antibonding

21b₂

22b₁

Fig. 9. The $(\pi\text{-}\sigma)$-type molecular orbitals of the axial benzene iodine. Orbitals $7a_1$ and $8a_1$ are bonding. The rest of the orbitals are antibonding

of these CMO's. It can be seen from the signs distribution on Fig. 7, that orbital $22b_1$ has a nodal surface between C_6H_6 and I_2, while orbital $17b_1$ has two bonding regions on both sides of the vertical plane of symmetry perpendicular to the I—I bond. It is also observed that these orbitals are polarized in opposite directions along the C_2 axis of the complex. In $17b_1$ there is a negative charge of -0.1411 on the benzene end, while in $22b_1$ there is a charge of -0.1413 on the iodine end. As a result, the net charge transfer is practically null.

In the axial structure of $C_6H_6 \cdot I_2$, practically all of the seven occupied MO's of I_2 mix with the π-type orbitals, a_{2u} and e_{1g} of benzene. Together, these orbitals (ten in number) form ten complex molecular orbitals. The resulting CMO's may be classified in two groups. One contains π-π type CMO's and the other π-σ type. Figs. 8 and 9 show the main atomic orbitals that constitute these CMO's. Even though the complex is stable, as indicated by the value of the binding energy, it has only four bonding CMO's against six antibonding ones! This is evidently an unusual situation. The stability of this complex could be explained by the fact that the lower localized MO's of benzene, such as a_{1g} and e_{1u} orbitals, are stabilized indirectly due to the presence of polarized I_2, and the net effect of the stabilization of the MO's outweighs the destabilizing effect of the antibonding CMO's. This points out, once more to the importance of the polarization forces in stabilizing the axial structure.

5. Conclusion

It has become quite evident, from the INDO calculation described above, that the axial structure of either $C_2H_4 \cdot I_2$ or $C_6H_6 \cdot I_2$ complex forms a stable bound state. The polarization and charge transfer forces appear to be responsible for the stability of this structure. It is also interesting to note that in the case of $C_6H_6 \cdot I_2$ the CMO's are of two types: $(\pi\text{-}\pi)$-, and $(\pi\text{-}\sigma)$-types, while in $C_2H_4 \cdot I_2$ are only of $(\pi\text{-}\sigma)$-type. In addition, the I_2 component is polarized with the negative charge on the farthest iodine atom from the hydrocarbon.

The resting structure, on the other hand, has a very small binding energy, and the polarizatin forces don't seem to be effective in this case.

References

1. a) Mulliken, R. S., Person, W. B.: Molecular complexes. New York: Wiley-Interscience, 1969
   b) Mulliken, R. S.: J. Am. Chem. Soc. **74**, 811 (1952)
2. Engdahl, A., Nelander, B.: J. Chem. Phys. **78**, 6563 (1983)
3. Pople, J. A., Beveridge, D. L., Dobosh, P. A.: J. Chem. Phys. **47**, 2026 (1967)
4. Ridley, J., Zerner, M.: Theoret. Chim. Acta (Berl.) **32**, 111 (1973); Bacon, A. D., Zerner, M. C.: Theoret. Chim. Acta (Berl.) **53**, 21 (1979)
5. a) Scharfenberg, P.: Chem. Phys. Letters, **65**, 304 (1979); b) Straub, P. A., McLean, A. D.: Theoret. Chim. Acta (Berl.) **32**, 227 (1974)
6. Anderson, W., Edwards, W. D., Zerner, M. C.: to be published
7. Clementi, E., Roetti, C.: Atomic data and nuclear data tables, Vol. **14**, 177 (1974)
8. Herzberg, G.: Spectra of diatomic molecules. Amsterdam: Van Nostrand, 1950
9. Steer, R. J., Watkins, S. F., Woodward, P.: J. Chem. Soc. C, 403 (1970)