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Molecular orbital calculations for iodine complexes
2. Ammonium iodine and pyridine iodine

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Calculations of $H_3N{\cdot}I_2$ and $PY{\cdot}I_2$ using the INDO method with single and double-zeta Slater atomic orbital basis are reported. It is found that polarization and charge transfer play a fundamental role in stabilizing the complex. Interaction between donor and acceptor molecules involves the highest occupied as well as the inner molecular orbitals of the constituent molecules. 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 — Ammonium iodine — Pyridine iodine

1. Introduction

Theoretical calculations of the wave functions and energies of charge transfer (CT) complexes are usually based on Mulliken's resonance structure theory [1]. The CT complexes may also be considered as super molecules and treated by SCF MO methods. Recently the INDO method with single and double-zeta Slater atomic orbital basis has been applied in a structural study of $C_2H_4{\cdot}I_2$ and $C_6H_6{\cdot}I_2$, representative of what is known as π–π complexes [2]. This method predicted the correct structures of these complexes which turned out to be more of a π–σ than a π–π type. It also revealed that the polarization and charge transfer play an important role in stabilizing the complex in the ground state. The present paper, second in a series of two ([2] is the first of this series), contains also the results of similar calculations on n–σ type complexes, namely: ammonium iodine ($H_3N \cdot I_2$) and pyridine iodine ($PY \cdot I_2$). It is assumed that these complexes are, in the gas-phase, one to one complexes even though the situation may be different in solution, especially when an excess of pyridine exists [3]. The INDO method is used with single-zeta Slater orbital basis sets on H, C and N atoms, while on iodine a single and double-zeta Slater orbital basis is utilized. More detail about the method of calculation is given in [2].

The calculations showed that the polarization and charge transfer are also responsible for the complex stability. The polarization is the result of lowering the level of symmetry of I_2, which makes possible the formation of polarized molecular orbitals. In general, the complex molecular orbitals (CMO's) are of two sorts: those which are practically localized on the constituent molecules, and those which are spread over the entire complex. The orbitals localized on the I_2-end are polarized. The direction of polarization differs from one such orbital to another, but the over-all result is an accumulation of negative charge on the outer iodine atom. The CMO's that are localized on the donor molecule end of the complex and their energies are also quite perturbed as compared with the corresponding orbitals and energies of the free donor molecule. More details about the CMO's are given in the following sections.

2. Geometry and binding energy

A search for an optimal geometry of each complex is done in a simplified way. The experimental geometry of the donor molecule (H_3N and PY) was kept constant. The iodine molecule was made to approach the donor with their main symmetry axes coinciding with each other. During this approach, the bond length of I_2 was allowed to relax. This procedure was followed until a minimum total energy value was obtained. Both complexes were found to be stable. Figures 1 and 2 show the resulting geometries and charge distributions at equilibrium of $H_3N \cdot I_2$ and $PY \cdot I_2$ respectively. The numbers in parentheses are the net atomic charges of the complex, while the numbers in brackets are the charges of the corresponding free molecules. The complexation causes a transfer of a net electronic charge ΔQ from the donor to the acceptor (I_2). ΔQ is equal to 0.210 in $H_3N \cdot I_2$ and to 0.238 in $PY \cdot I_2$. The atoms in the donor molecule, in both $H_3N \cdot I_2$ and $PY \cdot I_2$, become more positive upon complex formation. Negative charges are

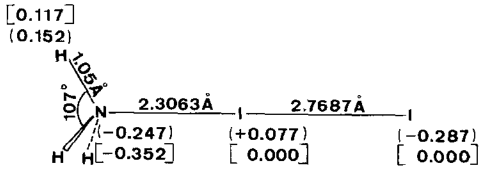

Fig. 1. Geometry and charge density distribution of the $H_3N \cdot I_2$ complex. Numbers in parenthesis are the atomic charges of the complex, and numbers in brackets are the corresponding charges of the free molecules

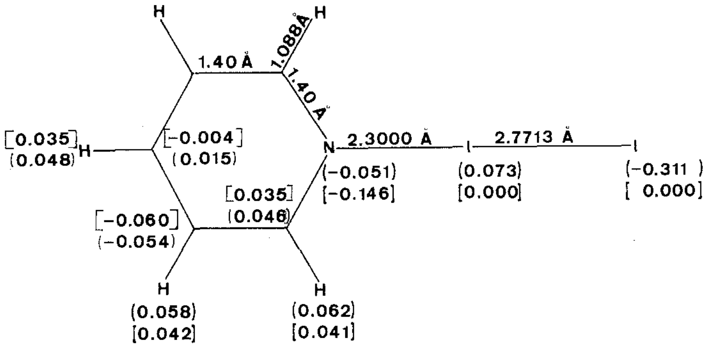

Fig. 2. Geometry and charge density distribution of PY·I_2 complex. Numbers in parenthesis are atomic charges of the complex, and numbers in brackets are the corresponding charges of the free molecules

withdrawn in different proportions from all these atoms toward the acceptor molecule.

The iodine-iodine distance, in both complexes, is slightly larger than in the free I_2 molecule (2.66 Å) (see Figs. 1 and 2).

The binding energy ΔE of the complex is defined as equal to the difference between the energy of the complex at equilibrium and the sum of energies of the separate constituent molecules. It is found that ΔE is equal to: −31.0 kcal/mole and −33.9 kcal/mole for $H_3N{\cdot}I_2$ and PY·I_2, respectively. Although experimental data in the gas phase are, to our knowledge, lacking, the calculated binding energies could be slightly exaggerated. This judgement is based on the fact that measurements on sulfide-iodine complexes gave values for the internal energy change, $\Delta E'$, of complexation ranging between 7.1 and 8.3 kcal/mole [4]. It should be noted, however, that the comparison between calculated binding energies and $\Delta E'$ values is not straightforward. The relationship between these quantities involves partition functions. For example, there are six more vibrational modes in the complex than in the separate fragments, which are expected to be activated to a varying extent upon complexation. Therefore, the experimental $\Delta E'$ may be expected to be less (in absolute value) than the binding energy by a few kcal/mol.

3. $H_3N{\cdot}I_2$

This complex belongs to the C_{3v} point group. Figure 3 shows its molecular orbital energy diagram. The MO energy levels of the separate NH_3 and I_2 are also included for comparison. The MO's are labeled according to the corresponding irreducible representation. Table 1 also lists the CMO's of the complex in the same order as in Fig. 3, with the lowest energy orbital given the number 1. In this table, % I_2 indicates the percentage contribution to the CMO from the basis

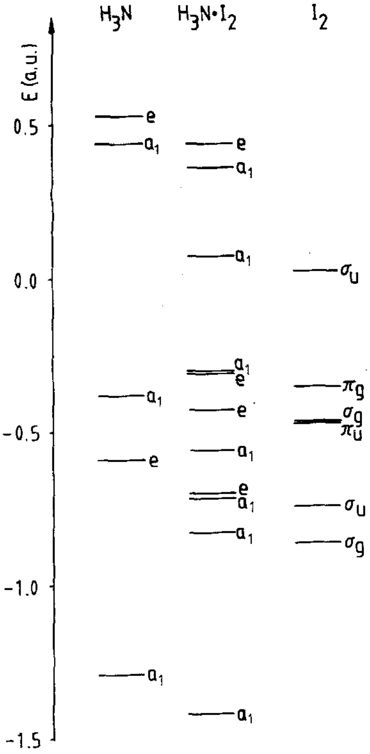

Fig. 3. Molecular orbital energy diagram of $H_3N{\cdot}I_2$, H_3N and I_2.

Table 1. The complex molecular orbitals (CMO's) of $H_3N{\cdot}I_2$. *e*-type orbitals are degenerate. For more explanation see text

No	CMO	% I_2	Aspect
1	a_1	4.4	$a_1(NH_3)$
2	a_1	97.4	$\sigma_g(I_2)$
3	a_1	86.0	$\sigma_u(I_2)+a_1(H_3N)$
4	e	3.4	$e(H_3N)$
5	a_1	57.5	$\sigma_g(I_2)+\sigma_u(I_2)+a_1(H_3N)$
6	e	97.0	$\pi_u(I_2)$
7	e	99.5	$\pi_g(I_2)$
8	a_1	65.3	$a_1(H_3N)+\sigma_g(I_2)$
9	a_1	87.9	$\sigma_u(I_2)+a_1(H_3N)$
10	a_1	1.5	$a_1(H_3N)$
11	e	0.0	$e(H_3N)$

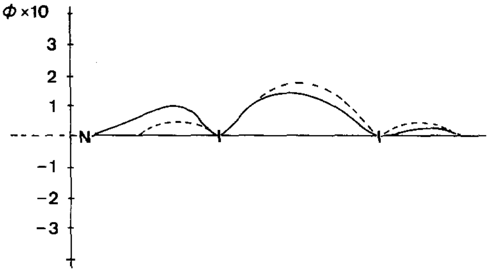

Fig. 4. ——: variation of the orbital $\phi = 2a_1$ of $H_3N{\cdot}I_2$; - - -: variation of the unperturbed orbital $\phi = \sigma_g$ of I_2 molecule, along the symmetry axis

atomic orbitals on iodine atoms. This contribution is defined as equal to: $100 \sum_l c_{li}^2$, where the c_{li}'s are the coefficients in the LCAO expansion of the ith CMO corresponding to the atomic orbitals located on I_2 (see [2]). The aspect of the CMO (Table 1) implies that a CMO may be considered as a combination of, not pure but rather distorted, molecular orbitals of the separate molecules. For example, the $2a_1$, which is practically localized on I_2, may be considered a $\sigma_g(I_2)$ polarized toward NH_3. Figure 4 shows the variations of the orbitals $2a_1$ of the complex and the unperturbed $\sigma_g(I_2)$ along the symmetry axis. Similar remarks apply to orbitals $1a_1$, $6e$ and $7e$ (Table 1), with $1a_1$ slightly polarized toward I_2, $6e$ polarized toward H_3N and $7e$ polarized away from H_3N.

Figures 5, 6 and 7 represent the variations of the delocalized complex orbitals $3a_1$, $5a_1$ and $8a_1$ (Table 1) and the corresponding charge densities along the symmetry axis between the nitrogen and iodine atoms. Orbitals $3a_1$ and $5a_1$ are bonding between the H_3N and I_2 segments. Even though orbital $8a_1$ has a nodal surface between H_3N and I_2, it has a relatively high electronic charge density near the nitrogen and opposite to a positively charged iodine. It may therefore contribute to bonding through electrostatic attraction. The polarization of the orbitals is accompanied by a charge transfer from H_3N toward I_2. The % I_2-analysis of the orbitals (see Table 1) indicates that the transfer of charge takes place mainly through the interaction of σ-type MO's of I_2 with a-type MO's of H_3N. This interaction also results in the polarization which, in turn, has a net stabilizing effect on the entire complex. This may be recognized from the energy

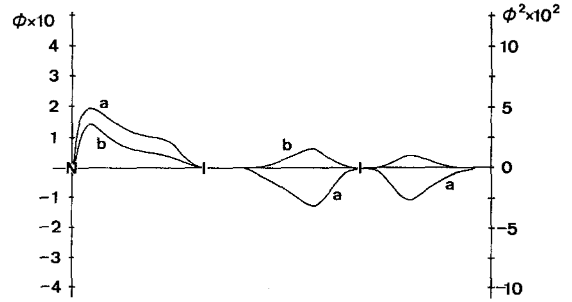

Fig. 5. Variation, along the symmetry axis between the nitrogen and iodine atoms of: **a** the orbital $\phi = 3a_1$, and **b** its charge density ϕ^2

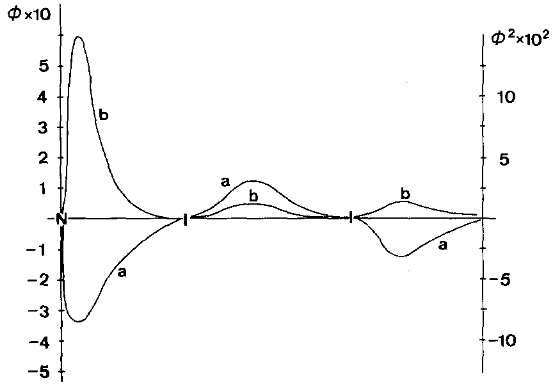

Fig. 6. Variation, along the symmetry axis between the nitrogen and iodine atoms of: **a** the orbital $\phi = 5a_1$, and **b** its charge density ϕ^2

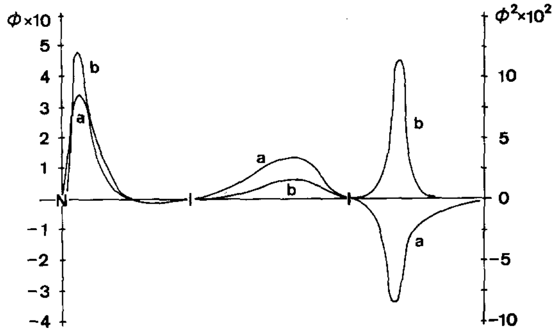

Fig. 7. Variation, along the symmetry axis between the nitrogen and iodine atoms of: **a** the orbital $\phi = 8a_1$, and **b** its charge density ϕ^2

level diagram (Fig. 3). The MO energy levels of the donor and acceptor molecules are all perturbed considerably by the complex formation. This is apparently a general aspect of the n-σ and π-σ type complexes (see [2]).

4. PY·I_2

The pyridine iodine complex belongs to the C_{2v} point group. Its molecular energy diagram is presented in Fig. 8. Table 2 lists the complex molecular orbitals (CMO's) in the same order as in Fig. 8 with the lowest energy orbital given the number 1. The first twenty-two orbitals are occupied in the ground state. The general aspect of the orbitals is similar to what was found in the case of ammonium iodine. The orbitals localized on the PY moiety are more or less polarized toward the I_2 molecule. The delocalized orbitals are of two symmetry types, a_1 and b_2. They result from the interaction of σ-type orbitals of I_2 with a_1-type orbitals of pyridine, and π-type orbitals of I_2 with the b_2-type of PY. Figures 9 and 10 display schematically the main atomic orbitals (with coefficient $c_i \geq 0.1$) contributing to the delocalized CMO's. The hydrogen-1s orbitals are omitted to avoid making the figures cumbersome. Only occupied CMO's are considered. Orbitals

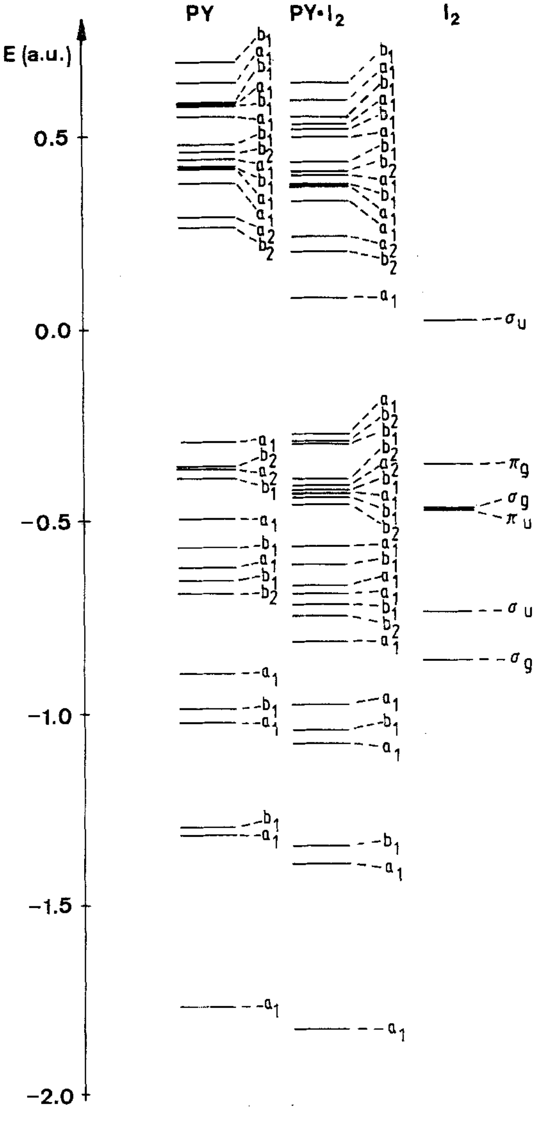

Fig. 8. Molecular orbital energy diagram of pyridine iodine, pyridine and iodine molecules

$19b_2$ and $22a_1$ have a nodal surface between the pyridine and I_2 segments, and may be considered antibonding. The rest of the delocalized orbitals are bonding.

The calculated change in charge density caused by complexation at the nitrogen and 2-, 4- and 6-carbons of the pyridine segment (see Fig. 2) agrees with the NMR measurements on pyridine iodine [5]. The change at 3- and 5-carbons, being smaller in magnitude, has an opposite sign to what is predicted by NMR measurement. Apart from this minor discrepancy, the general trend of the charge density variations and the direction of the charge transfer agree with experimental

Table 2. The complex molecular orbitals (CMO's) of PY·I_2. For more explanation see text

No	CMO	% I_2	Aspect
1	a_1	0.5	$a_1(\mathrm{PY})$
2	a_1	2.7	$a_1(\mathrm{PY})$
3	b_1	0.1	$b_1(\mathrm{PY})$
4	a_1	1.1	$a_1(\mathrm{PY})$
5	b_1	0.7	$b_1(\mathrm{PY})$
6	a_1	8.6	$a_1(\mathrm{PY})+\sigma_g(\mathrm{I}_2)+\sigma_u(\mathrm{I}_2)$
7	a_1	95.5	$\sigma_g(\mathrm{I}_2)$
8	b_2	0.9	$b_2(\mathrm{PY})$
9	b_1	1.3	$b_1(\mathrm{PY})$
10	a_1	81.4	$\sigma_u(\mathrm{I}_2)+a_1(\mathrm{PY})+\sigma_g(\mathrm{I}_2)$
11	a_1	0.5	$a_1(\mathrm{PY})$
12	b_1	0.6	$b_1(\mathrm{PY})$
13	a_1	35.5	$a_1(\mathrm{PY})+\sigma_u(\mathrm{I}_2)+\sigma_g(\mathrm{I}_2)$
14	b_2	50.7	$b_2(\mathrm{PY})+\pi_u(\mathrm{I}_2)$
15	b_1	1.8	$b_1(\mathrm{PY})$
16	a_1	37.5	$a_1(\mathrm{PY})+\sigma_g(\mathrm{I}_2)$
17	b_1	95.8	$\pi_u(\mathrm{I}_2)$
18	a_2	0.0	$a_2(\mathrm{PY})$
19	b_2	50.7	$b_2(\mathrm{PY})+\pi_u(\mathrm{I}_2)$
20	b_1	99.6	$\pi_g(\mathrm{I}_2)$
21	b_2	97.5	$\pi_g(\mathrm{I}_2)$
22	a_1	48.9	$a_1(\mathrm{PY})+\sigma_g(\mathrm{I}_2)$
23	a_1	86.1	$a_1(\mathrm{PY})+\sigma_u(\mathrm{I}_2)$
24	b_2	0.2	$b_2(\mathrm{PY})$
25	a_2	0.0	$a_2(\mathrm{PY})$
26	a_1	0.96	$a_1(\mathrm{PY})$
27	a_1	0.3	$a_1(\mathrm{PY})$
28	b_1	0.0	$b_1(\mathrm{PY})$
29	a_1	0.1	$a_1(\mathrm{PY})$
30	b_2	0.0	$b_2(\mathrm{PY})$
31	b_1	0.0	$b_1(\mathrm{PY})$
32	a_1	0.4	$a_1(\mathrm{PY})$
33	b_1	0.0	$b_1(\mathrm{PY})$
34	a_1	0.0	$a_1(\mathrm{PY})$
35	b_1	0.0	$b_1(\mathrm{PY})$
36	a_1	0.0	$a_1(\mathrm{PY})$
37	b_1	0.0	$b_1(\mathrm{PY})$

findings even though the geometry of PY was not allowed to relax during the energy optimization process.

5. Conclusion

It appears, from the results of calculations reported in this paper and in [2], that polarization and charge transfer play a fundamental role in stabilizing the CT complexes. The maximum overlap between the highest occupied orbital of the donor and the lowest unoccupied orbital of the acceptor does not seem to be a

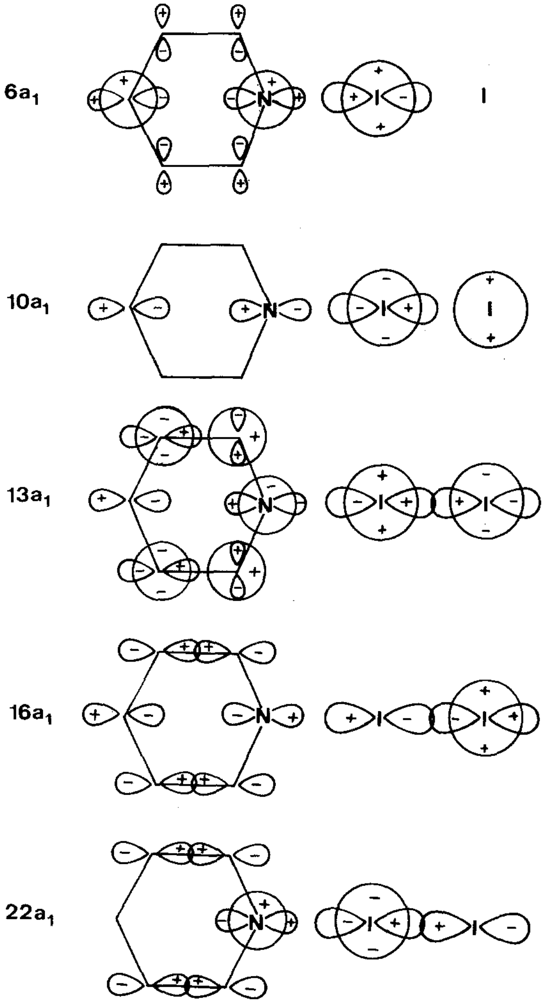

Fig. 9. The main atomic orbitals contributing to the delocalized, a_1-type complex molecular orbitals of PY·I_2

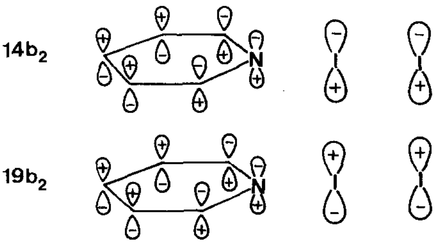

Fig. 10. The main atomic orbitals contributing to the delocalized, b_2-type complex molecular orbitals of PY·I_2

justified criterion for complex formation [7]. The interaction between the donor and acceptor molecules involves not only the frontier but also the inner molecular orbitals. The stable structure of the complex is the one that permits enough polarization of the molecular orbitals to stabilize the complex. It is also interesting to note that our calculations support, in general, the "Bond-Length Variation" rules formulated by Gutmann [6].

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