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Citation: *The Journal of Chemical Physics* **105**, 4395 (1996); doi: 10.1063/1.472258

View online: <http://dx.doi.org/10.1063/1.472258>

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Electron states of benzene-Br₂ donor-acceptor complex: HeI photoelectron spectroscopy and *ab initio* molecular orbital study

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(Received 30 January 1996; accepted 5 June 1996)

[S0021-9606(96)02534-2]

I. INTRODUCTION

The concept of intermolecular donor-acceptor (D-A) complexes is associated with interaction of molecular orbitals. It is assumed that the D-A bond between two molecules involves charge transfer from a donor to an acceptor. Mulliken^{1,2} has generalized these concepts. Even though benzene-I₂ was the first D-A complex studied,³ exact molecular orbital (MO) description of this complex is still not clear. Bromine which is next to iodine is expected to form D-A complex with benzene. The D-A complex of benzene-Br₂ is not studied by any spectroscopic technique. In the solid phase, a benzene-Br₂ complex is expected to have a structure in a *D*_{6h} symmetry. Recent study on the hydrogen bonded complex of benzene with HCl⁴ predicted a *C*_{6v} symmetry. In an attempt to understand the D-A interaction, a series of molecular complexes have been studied in this laboratory by photoelectron spectroscopy and *ab initio* MO study.⁵ Since the ionization energies of π_g orbitals of I₂ and π orbitals of benzene are about the same at 9.3 eV and that of Br₂ and benzene are well separated, a benzene-bromine D-A complex is chosen for this study. Here we report the first study of the D-A complex of benzene and bromine by ultraviolet photoelectron spectroscopy and *ab initio* MO calculations.

II. EXPERIMENT AND COMPUTATIONAL METHODS

Photoelectron spectroscopy measurements of the molecules and the complex are recorded with a homebuilt spectrometer.⁵ Bromine and benzene obtained commercially are freshly distilled. The samples are taken in glass ampoules. The complex is prepared by co-condensation of equimolar amounts of benzene and bromine vapors. A sample of the complex is warmed to about 50 °C to obtain sufficient vapor pressure of the complex.

Ab initio MO calculations on the monomers and the complex were carried out using a GAUSSIAN 92 system of programs.⁶ Geometry optimization of the complex is carried out at a 3-21G* level. Single point MP2 calculation is done on the 3-21G* optimized structure. The optimized structure was confirmed to be true minima through frequency calculations. The complex is found to have *C*_{6v} symmetry.

III. RESULTS AND DISCUSSION

HeI photoelectron spectra of Br₂ and the complex between Br₂ and benzene are given in Fig. 1. In the inset, the

photoelectron spectrum of benzene is shown. The bromine spectrum has peaks at 10.6, 10.9, 13.1, and 14.3 eV. The first two peaks are due to the spin-orbit split π_g molecular orbitals of bromine. The peaks at 13.1 and 14.3 are due to the π_u and σ_g MOs, respectively. The benzene molecule shows peaks at 9.2, 11.7, 13.7, 15.1, and 16.3 eV. The first peak is from the π -type orbital of benzene which is doubly degenerate. The second peak at 11.7 eV is from the σ orbital of benzene which is also doubly degenerate. The peaks at 13.7, 15.1, and 16.3 eV are due to $a_{2u}(\pi)$, $e_{1u}(\sigma)$, and e_1 type of MOs, respectively. The photoelectron spectra of bromine and benzene obtained here match well with the literature.⁷ The spectrum of the complex given in Fig. 1 is different from that of benzene and bromine with additional peaks at 9.5, 10.0, 10.4, and 12.8 eV which are marked by arrows.

Ab initio MO calculations are done for the complex. Three different geometries of the complex are tried. They are: (a) a structure with two bromine molecules above and below the benzene ring with a *D*_{6h} symmetry; (b) one bro-

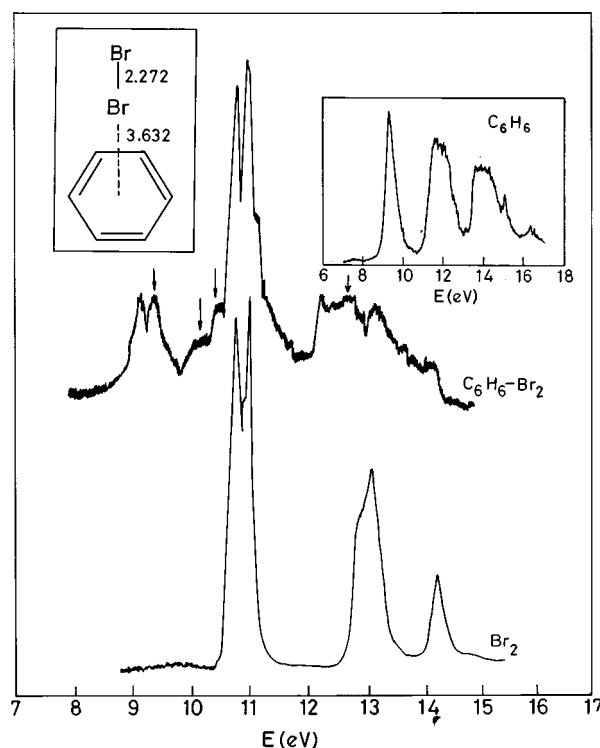


FIG. 1. HeI spectra of bromine, benzene (in the inset), and the complex between benzene and Br₂ and the optimized geometry.

TABLE I. Calculated total energies of the complexes, uncorrected complexation energies, ΔE_b , basis set superposition error, and the counterpoise corrected complexation energies ΔE_b^{cp} .

Complex	Basis set	Total energy (a.u.)	ΔE_b (kcal/mol)	BSSE (kcal/mol)	ΔE_b^{cp} (kcal/mol)
$\text{C}_6\text{H}_6\text{--Br}_2$	3-21G//3-21G	−5 349.508 29	1.01	0.28	0.73
	3-21G*/3-21G*	−5.349.952 26	1.58	0.43	1.15
	MP2//3-21G*/3-21G*	−5.350.725 93	3.06	1.56	1.5

mine molecule parallel to the benzene ring in C_{2v} symmetry; and (c) one bromine molecule in C_{6v} symmetry bonded to the benzene electron cloud. Geometry optimization and frequency calculations predicted that the one with C_{6v} symmetry is a stable and optimized structure. The binding energy of the complex with different basis sets and basis set superposition error correction is given in Table I. Complexation energy is about 1–1.5 kcal/mol. *Ab initio* MO calculations on a benzene– I_2 complex showed that it is stronger than the benzene–bromine with a stabilization energy of 2 kcal/mol. The structure of the complex is that of a weak $\pi \rightarrow \sigma^*$ between the benzene π electron cloud and the bromine. The structure of the complex with bond lengths is given in Fig. 1. The distance between Br and the benzene ring is calculated to be 3.6329 Å. The Br–Br distance 2.2715 Å in the complex is slightly increased compared to the distance 2.2701 Å in the bromine molecule.

The observed photoelectron spectra can be interpreted using *ab initio* orbital energies in conjunction with the Koopmans' theorem.⁸ The computed orbital energies of bromine and benzene are generally consistent with the observed vertical ionization energies and they are given in Table II. The

peak at 9.5 eV in the complex spectrum are due to the π orbital of benzene. The peaks at 10.1 and 10.4 eV are due to the π_g orbitals of bromine. The feature at 12.8 eV is due to the π_u orbital of bromine. The bromine orbitals are shifted to lower binding energy by 0.5 eV whereas the benzene orbital to higher energy by 0.25 eV demonstrating charge transfer from benzene to bromine. The calculated shifts in the binding energies of the benzene and bromine orbitals are in good agreement with the observed vertical ionization energies. The main factors which determine the shifts in the ionization energies and the nature of interaction is the charge transfer. Natural bond orbital analysis⁹ showed that magnitude of charge transfer from the benzene molecule to bromine is about 0.002 indicating that benzene is a donor.

In conclusion we have shown that a weak $\pi \rightarrow \sigma^*$ type D–A complex is formed between benzene and bromine. MO calculations showed that a stronger D–A complex is formed by benzene– I_2 and benzene–ICl as well.

ACKNOWLEDGMENT

Contribution No. 1171 from Solid State and Structural Chemistry Unit.

TABLE II. Vertical ionization energies, calculated orbital energies, and assignments of bromine, benzene, and the complex.

Molecule	I (eV)	$-\epsilon(\text{eV})$ 3-31G(*)	Assignment
Br_2	10.5, 10.9	10.7	π_g
	13.1	13.4	π_u
	14.3	14.4	σ_g
C_6H_6	9.2	9.2	e_{1g}
	11.7	13.4	e_{2g}
	13.7	13.8	a_{2u}
	15.1	16.1	e_{1u}
	16.3	17.0	e_{1g}
C_6H_6 – Br_2	9.5	9.5	e_1
	10.0, 10.4	10.5	$e_1 [\pi_g (\text{Br})]$
	12.8	13.2	$e_1 [\pi_u (\text{Br})]$

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