Electronic Structures of Meso-ionic Azapentalenes Studied by X-Ray Photoelectron Spectroscopy

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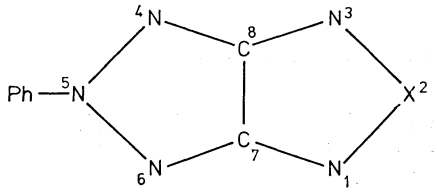
X-Ray photoelectron spectra of meso-ionic azapentalenes were observed in the solid phase. The charge distributions in these molecules were investigated by using the observed chemical shifts of core-electron levels, employing Siegbahn's electrostatic potential model and the results of CNDO/2 calculations.

Pentalene is very unstable because of 8π electron system, and pentalene itself has not yet been synthesized.[1] If a carbon atom in the five-membered ring is replaced by a hetero atom with 2π electrons, the resulted molecule has aromaticity and would be stabilized. As shown in Fig. 1, a series of hetero aza-pentalenes, namely, 2,5-diphenyl[1,2,3]triazolo[4,5-*d*][1,2,3]triazole (I), and 5-phenyl-5*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]-oxadiazole (II), -thiadiazole (III), and -selenadiazole (IV) are expected to be stable compounds since the introduction of a hetero atom at position 2 and a nitrogen atom at position 5, provides 2π electrons to the pentalene skeleton so as to form 10π electron system. In effect, they have recently been synthesized by one of the authors (M.Y.) and his coworkers, and turned to be very stable solid. Syntheses and some properties of these compounds were published elsewhere.[2,3] As readily guessed from Fig. 1, these compounds have meso-ionicity and are expected to have large electronic polarization. It is therefore of great interest to investigate to what extent electronic charges are polarized in these molecules.



(I) X=N–Ph, (II) X=O, (III) X=S, (IV) X=Se

Fig. 1. Molecular structure of azapentalenes.

Recently, X-ray photoelectron spectroscopy (XPS) has proved to be a powerful means for the study of charge distribution in a molecule, having been successfully applied to a number of organic molecules.[4,5] The purpose of this paper is to elucidate charge distributions in the above-described compounds by the measurement and analyses of the chemical shifts of core electron levels with the aid of Siegbahn's electrostatic potential model and CNDO/2 calculation. In addition, a geometry optimization technique in the framework of the CNDO/2 method was used to predict the molecular geometries of these compounds, since they have not yet been determined experimentally.

X-Ray photoelectron spectra of the compounds studied were measured with a McPherson ESCA 36 electron spectrometer, by employing Al $K\alpha$ radiation. Each sample, purified by recrystallization in advance, was coated on an aluminium plate. Core electron binding energies were calibrated by using the Au $4f_{7/2}$ (84.0 eV) peak of a thin gold film deposited onto the sample surface.

TABLE 1. CORE ELECTRON BINDING ENERGIES OF HETEROAZAPENTALENES (eV)

	C 1s	N 1s	$\Delta E_{\text{splitting}}$ (N 1s)	O 1s	S $2p_{3/2}$	Se $3p_{3/2}$
I	(287.1) 284.2	(402.0) 399.3	2.7			
II	(286.1) 284.2	(402.0) 399.2	2.8	532.2		
III	(286.1) 284.2	(401.8) 398.9	2.9		164.0	
IV	(287.1) 284.2	(401.9) 398.7	3.2			160.5

A shoulder and/or a weaker peak is listed in the parenthesis.

Determined core electron binding energies are listed in Table 1. All of C 1s spectra have a small shoulder in the higher binding energy side of the main peak. The C 1s binding energy of the main peak is consistently the same for all compounds, so that it can be assigned to the phenyl carbons. The small shoulder is possibly associated with carbons in the pentalene ring. Figure 2 shows N 1s spectra of these compounds. We can see well-resolved two peaks except for compound (II), in which case the main peak is a little broader than the others. The intensity ratio of the two peaks in compound (I) is 1 : 1.9, so that the stronger peak at the lower binding energy side is easily assigned to the nitrogen atoms at the positions 1, 3, 4, 6 and the weaker peak is to the nitrogen atoms at positions 2 and 5. On the other hand, in compounds (II), (III), and (IV), intensity ratios of two peaks are nearly 1 : 4, so that the stronger peak has the same origin as compound (I), and the weaker peak is due to the nitrogen atom at position 5. These spectra show clearly that the nitrogen atom at position 5 has a less negative charge than the nitrogen atoms at positions 1, 3, 4, and 6. It is to be noted that the splitting of N 1s peaks is larger as the atomic number of the substituent atom is higher, as listed in the fourth column of Table 1.

XPS chemical shift is influenced not only by the charge density of the ionizing atom, but also by those of atoms surrounding it. Siegbahn and his coworkers have proposed the following equation for interpreting chemical shifts:[6]

$$\Delta E_{\text{A}} = kq_{\text{A}} + \sum_{\text{B}\neq\text{A}}^{\text{molecule}} \frac{e^2 q_{\text{E}}}{R_{\text{AB}}}, \qquad (1)$$

where k is a constant characteristic of atom, q_{A} and q_{B}

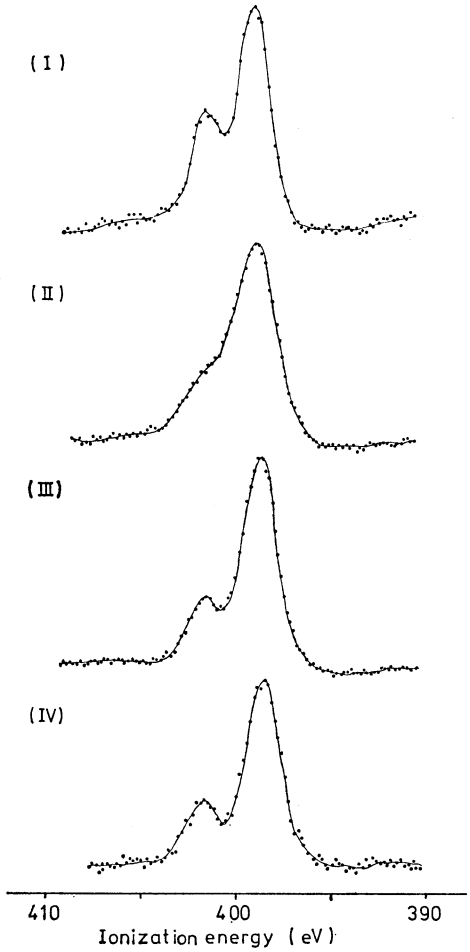


Fig. 2. N 1s spectra of azapentalenes.

are charge densities of atom A and B, respectively, and R_{AB} is the distance between them. For a variety of molecules containing carbon, nitrogen, and oxygen, the chemical shifts of core-electron levels have been successfully interpreted with Eq. 1, by use of CNDO/2 charge densities.

In the present compounds, molecular geometries have not yet been determined experimentally, so that it is difficult to obtain reliable charge densities by MO calculation since they would be influenced more or less by the molecular geometry. Accordingly, geometry optimization has been carried out for these molecules within the scheme of CNDO/2 formulation. The geometry for the CNDO/2 total-energy minimum was searched by using the differentiation of two-center integral terms. Since molecule (I) or (II) is too complex to be calculated with CNDO/2, the simplified model, in which the phenyl group is replaced by a hydrogen atom, was used for the geometry optimization. Such simplification would not affect the interpretation of N 1s chemical shifts. The model compounds are denoted as (I') and (II'), and so on. A regular pentagon structure with a bond length of 1.35 Å was used as the initial geometry for each molecule. Furthermore, the molecular symmetry, D_{2h} for (I') and C_{2v} for (II') and (III'), was retained throughout the geometry optimization. Determined geometries of (I') and (II') are shown in Fig. 3. The N–N or N–O bond length is smaller than the C–N

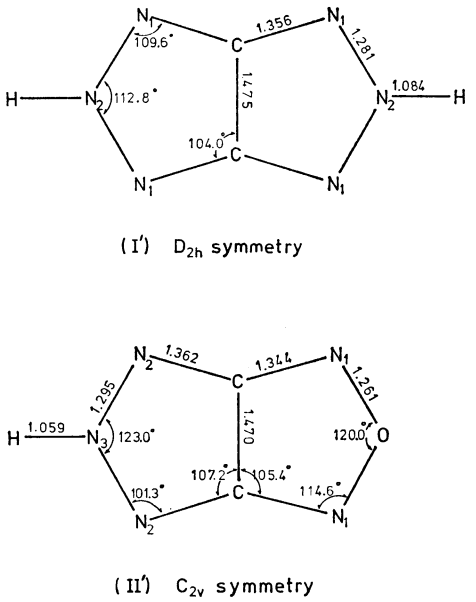


Fig. 3. Optimized geometries of molecules (I') and (II').

TABLE 2. TOTAL CHARGE AND π ELECTRON DENSITIES OF MOLECULES (I') AND (II')

	(I') D_{2h} symmetry			(II') C_{2v} symmetry	
Atom[a)]	Total charge density	π electron density	Atom[a)]	Total charge density	π electron density
C	0.086	−0.043	C	0.090	−0.016
N_1	−0.161	−0.275	N_1	−0.085	−0.233
N_2	0.149	0.592	N_2	−0.163	−0.295
H	0.088		N_3	0.190	0.677
			O	0.032	0.409
			H	0.095	

a) Refer to Fig. 3 about atomic species.

bond length. The C–C bond is much longer than that in benzene and has a character of single bond to large extent. These results seem to be plausible from the comparison with geometries of the related compounds whose structures have already been determined.[7] CNDO/2 charge densities in molecules (I') and (II') are listed in Table 2. In molecule (I'), the total charge density of N_1 atom is negative and that of N_2 is positive. This is in accord with the conclusion derived from the N 1s chemical shift. This tendency is much stronger in the π electron charge distribution as indicated in Table 2. By using calculated charge densities and a k value of 21.5 eV/unit charge as proposed by Siegbahn *et al.*,[6] we obtained 2.9 eV for the N 1s splitting in molecule (I'), which is very close to the observed spliting, 2.7 eV. This would mean that the calculated charge distribution in this molecule is reliable. Similar results are obtained for molecule (II'), in which there are three kinds of nitrogen atom. Calculated shifts are −0.96 eV, −0.92 eV, and 2.41 eV for N_1, N_2, and N_3, respectively. ΔE *fwhm* of the N 1s main peak of compound (II) is 2.5 eV, which is broader than the N 1s peaks of other compounds by about 0.5 eV. The main N 1s peak of compound (II) is composed of the two components,

which are due to N_1 and N_2, respectively. Consequently, its broadening can be understood as that arising from the splitting of the two components by chemical shift. The chemical shift of the N 1s level of N_3 is a little overestimated by MO calculations as compared with the observed result. We tried to carry out the geometry optimization also for molecule (III'), which contains a sulfur atom. In general, CNDO/2 method gives less reliable results for molecules containing second row atoms. In fact, the optimized geometry of molecule (III') shows an unusually long N–S bondlength, 1.8 Å. The charge densities calculated for this geometry could not explain the observed N 1s chemical shifts of compound (III).

We tried to estimate the charge distribution in molecule (III') from the observed N 1s binding energies for compound (III), using the procedure called "ACHARGE" analysis.[5,8] Since the number of obtained experimental values is too limited to give the whole charge distribution, the following assumptions were adopted to carry out the ACHARGE analysis; first, the geometry of molecule (III') was assumed to be the same as molecules (II'), and, second, the charge densities on C and H atoms were assumed to be the same as those in (II'), since they are likely to be small and relatively independent of the substitution of a hetero atom. Resulted charge densities are $-0.17e(N_1)$, $-0.16e(N_2)$, $0.15e(N_3)$, and $0.23e(S)$. They are almost the same as those in molecules (I') and (II'). From the above-described analyses of XPS chemical shifts, it can be concluded that in these molecules the nitrogen at position 5 and the hetero atom at position 2 have positive charges, while the nitrogen atoms at positions 1, 3, 4, and 6 have negative charges, and that the degree of charge polarization in these molecules is not so large, although they have been regarded as meso-ionic compounds.

References

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7) For example, molecular structures of 1,2,4,5-tetrazine, 5-amino-2-methyltetrazole, and adenine hydrochloride hemihydrate have been determined. (See "Tables of Interatomic Distances and Configuration in Molecules and Ions" compiled by H. J. M. Bowen *et al.*, The Chemical Society, London (1958)).
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