

THE PHOTOELECTRON SPECTRUM OF BISMABENZENE

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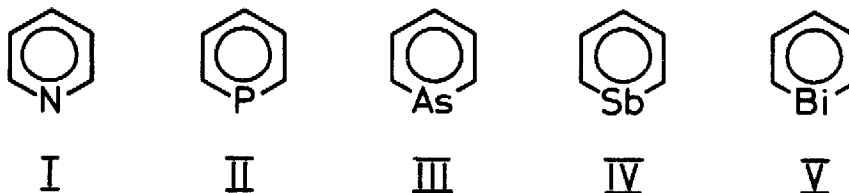
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In this note we report the photoelectron-(PE)spectroscopic data of bismabenzene (V)<sup>1</sup>, which terminates the series pyridine (I), phosphabenzene (II)<sup>2</sup>, arsabenzene (III)<sup>2</sup> and stibabenzene (IV)<sup>3</sup>, the PE-spectra of which have been reported previously<sup>4</sup>.



Bismabenzene V is a very labile compound which undergoes partial rearrangement and/or fragmentation under the conditions prevailing in the inlet systems and in the target chambers of the PE spectrometers used in this investigation. These unidentified compounds yield PE-bands in the region above 10 eV which obliterate those of V and therefore restrict identification of PE-bands due to V to the region  $I < \approx 10.5$  eV. Notwithstanding the above difficulty, the partial He(I)-spectrum shown in figure 1 is reproducible, as has been verified by running spectra from independently synthesized samples on different instruments

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and at different times. We therefore believe that the first three features labeled ①, ②, ③ are genuine PE-bands of V. The maximum of ④ at 10.2 eV, apart from its enhanced intensity, probably represents the position of the fourth PE-band of V. In table 1 are given the "vertical" ionization energies  $I_{V,j}$  of V, calibrated with the rare gases and benzene ( $I_{V,1} = 9.25$  eV), and for comparison those of I to IV<sup>4</sup>, approximated by the positions  $I_{m,j}$  of the respective PE-band maxima:  $I_{V,j} \approx I_{m,j}$ .

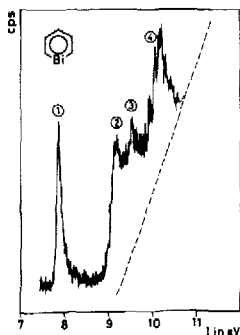


Figure 1. He(I) PE-Spectrum of Bismabenzene (V). The part of the spectrum to the right of the dashed line is obliterated by the superimposed PE-spectra of rearrangement and/or fragmentation product(s) of V.

The 118 electrons of V occupy 59 molecular orbitals which distribute as follows over the four irreducible representations of the symmetry group  $C_{2V}$ :  $A_1$ , 27;  $A_2$ , 5;  $B_1$ , 11;  $B_2$ , 16. Making use of the correlation established previously for I to IV<sup>4</sup> (see figure 2) the four highest occupied molecular orbitals of V are, in order of descending orbital energies  $\epsilon_j$ :  $11b_1(\pi)$ ,  $5a_2(\pi) \approx 27a_1(\sigma)$ ,  $16b_2(\sigma)$ .

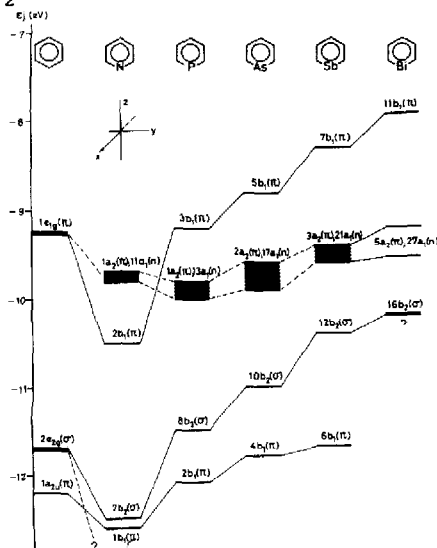


Figure 2. Orbital Correlation Diagram

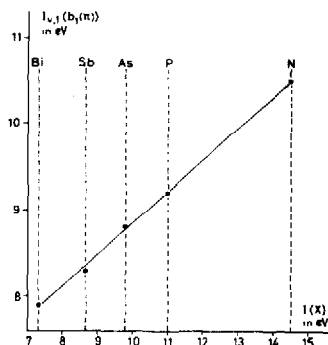


Figure 3. Regression of the Ionization Energies  $I_{V,1}(nb_1(\pi))$  of I to V on the Atomic Ionization Energies  $I(X)$  of the Free Atoms  $X = N$  to Bi.

Table 1. Proposed assignment of the bands in the PE.-spectra of I to V.

The relative sequence of the bracketed pair of orbitals is uncertain on experimental grounds. However the sequence given is that proposed in ref. 6.

	I		II		III		IV		V	
Band	Orbital	$I_V$ (eV)	Orbital	$I_V$ (eV)	Orbital	$I_V$ (eV)	Orbital	$I_V$ (eV)	Orbital	$I_V$ (eV)
①	$1a_2(\pi)$	9.7	$3b_1(\pi)$	9.2	$5b_1(\pi)$	8.8	$7b_1(\pi)$	8.3	$11b_1(\pi)$	7.9
②	$11a_1(\sigma)$	9.8	$1a_2(\pi)$	9.8	$2a_2(\pi)$	9.6	$3a_2(\pi)$	9.4	$5a_2(\pi)$	9.2
③	$2b_1(\pi)$	10.5	$13a_1(\sigma)$	10.0	$17a_1(\sigma)$	9.9	$21a_1(\sigma)$	9.6	$27a_1(\sigma)$	9.6
④	$7b_2(\sigma)$	12.5	$8b_2(\sigma)$	11.5	$10b_2(\sigma)$	11.0	$12b_2(\sigma)$	10.4	$16b_2(\sigma)$	10.2
⑤	$1b_1(\pi)$	12.6	$2b_1(\pi)$	12.1	$4b_1(\pi)$	11.8	$6b_1(\pi)$	11.7		

There is no doubt that the first PE-band ① of V is due to the ejection of an electron from the  $11b_1(\pi)$  orbital. Indeed, if the ionization energies  $I_{V,1}$  of I through V are plotted vs. the ionization energies  $I(X)$  corresponding to the transition  $^4S_{3/2} \rightarrow ^3P_0$  of the free atoms N (14.53 eV), P (11.0 eV), As (9.81 eV), Sb (8.64 eV), and Bi (7.29 eV)<sup>5</sup> the regression shown in figure 3 is obtained.\* A linear least square fit yields:

$$I_{V,1}(b_1(\pi)) = 5.22 \text{ eV} + 0.363 I(X); r = 0.9994 \quad (1)$$

As indicated by the correlation coefficient  $r$  and as can be seen from figure 3 the regression is almost perfect. The benzene  $\pi$ -orbital corresponding to the  $nb_1(\pi)$  orbitals of I to V i.e. the component of the degenerate pair  $1e_{1g}(\pi)$  symmetric with respect to the  $\sigma(xz)$  plane (see figure 2), has an atomic orbital coefficient of  $1/\sqrt{3}$  in position 1. It is an amusing, albeit an unexplained fact, that the slope 0.363 of regression (1) is practically that expected on the grounds of a naive first-order HMO perturbation argument, namely  $(1/\sqrt{3})^2 = 0.333$ .

The Franck-Condon envelope of the expanded PE-band ① shows evidence of vibrational fine-structure which, however, is not well resolved. The suggested vibrational quantum corresponds to a normal mode of  $400 \pm 100 \text{ cm}^{-1}$  of the radical cation  $V^+$  in its electronic doublet ground state. The corresponding first bands in the PE-spectra of II, III and IV<sup>4</sup> also revealed the excitation of a low frequency mode on photoionization of an electron from the  $nb_1(\pi)$  orbital. The magnitude of the frequency suggests that this mode can best be described in terms

of the concerted movement of the ring carbon atoms with respect to the heavy hetero-atom.

In contrast to the PE-spectra of I to IV, bands ② and ③ are now clearly separated by a gap of 0.4 eV in the spectrum of V. Nevertheless, it is not possible to deduce on purely experimental grounds whether the sequence is  $5a_2(\pi)$  above  $27a_1(\sigma)$ , in terms of Koopmans' approximation, or the reverse. Recent ab initio calculations for II, by von Niessen, Diercksen and Cederbaum<sup>6</sup>, which include the effects of electron correlation and rearrangement, indicate that  $1a_2(\pi)$  lies above  $13a_1(\sigma)$ , as originally surmised on the basis of semi-empirical<sup>7</sup> and less sophisticated ab initio models<sup>4</sup>. If this result is extrapolated to the higher members of the series, then  $6a_2(\pi)$  above  $26a_1(\sigma)$  is, presumably, a good working hypothesis for the orbital sequence in V. For a more detailed discussion the reader is referred to that given in ref. 4, which applies also to the present case.

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\* On the basis of the present results we venture the prediction that the analogue to compounds I to V, carrying the element with atomic number 115 in position 1, will have a first ionization energy of  $\approx 7.1 \pm 0.1$  eV.