THE PHOTOELECTRON SPECTRUM OF BISMABENZENE

J. Bastide\textsuperscript{a)}, E. Heilbronner* and J.P. Maier

Physikalisch-chemisches Institut, Universität Basel, Switzerland

A.J. Ashe III\textsuperscript{b)}

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104

(Received in USA 27 October 1975; received in UK for publication 22 December 1975)

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

\begin{center}
\begin{tabular}{ccccc}
I & II & III & IV & V \\
\end{tabular}
\end{center}

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 $1 < \phi < 10.5$ 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.

\textsuperscript{a)} Permanent address: G.E.R.A.P., Institut Universitaire de Technologie, Centre Universitaire, F-66025 Perpignan, France.

\textsuperscript{b)} A.P. Sloan Fellow
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 7 to 114, 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.](image)

The 118 electrons of V occupy 59 molecular orbitals which distribute as follows over the four irreducible representations of the symmetry group $C_2\!V$: $A_1$, 27; $A_2$, 5; $B_1$, 11; $B_2$, 16. Making use of the correlation established previously for 7 to 114 (see figure 2) the four highest occupied molecular orbitals of V are, in order of descending orbital energies $\varepsilon_j$: $11b_1(\pi)^1$, $5a_2(\pi) \approx 27a_1(\sigma)$, $16b_2(\sigma)$.

![Figure 2. Orbital Correlation Diagram](image)

![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.](image)
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.

<table>
<thead>
<tr>
<th>Band</th>
<th>Orbital</th>
<th>I_V(eV)</th>
<th>Orbital</th>
<th>I_V(eV)</th>
<th>Orbital</th>
<th>I_V(eV)</th>
<th>Orbital</th>
<th>I_V(eV)</th>
<th>Orbital</th>
<th>I_V(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a_2((\pi))</td>
<td>9.7</td>
<td>2b_1((\pi))</td>
<td>9.2</td>
<td>5b_1((\pi))</td>
<td>8.8</td>
<td>7b_1((\pi))</td>
<td>8.3</td>
<td>11b_1((\pi))</td>
<td>7.9</td>
</tr>
<tr>
<td>2</td>
<td>1a_1((\sigma))</td>
<td>9.8</td>
<td>1a_2((\pi))</td>
<td>9.8</td>
<td>2a_2((\pi))</td>
<td>9.6</td>
<td>3a_2((\pi))</td>
<td>9.4</td>
<td>5a_2((\pi))</td>
<td>9.2</td>
</tr>
<tr>
<td>3</td>
<td>2b_1((\pi))</td>
<td>10.5</td>
<td>13a_1((\sigma))</td>
<td>10.0</td>
<td>17a_1((\sigma))</td>
<td>9.9</td>
<td>21a_1((\sigma))</td>
<td>9.6</td>
<td>27a_1((\sigma))</td>
<td>9.6</td>
</tr>
<tr>
<td>4</td>
<td>7b_2((\sigma))</td>
<td>12.5</td>
<td>8b_2((\sigma))</td>
<td>11.5</td>
<td>10b_2((\sigma))</td>
<td>11.0</td>
<td>12b_2((\sigma))</td>
<td>10.4</td>
<td>16b_2((\sigma))</td>
<td>10.2</td>
</tr>
<tr>
<td>5</td>
<td>1b_1((\pi))</td>
<td>12.6</td>
<td>2b_1((\pi))</td>
<td>12.1</td>
<td>4b_1((\pi))</td>
<td>11.8</td>
<td>6b_1((\pi))</td>
<td>11.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 (8.61 eV), and Bi (7.29 eV) the regression shown in figure 3 is obtained. A linear least square fit yields:

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

(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 le_{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 ground 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 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, which include the effects of electron correlation and rearrangement, indicate that $1a_2(\tau)$ lies above $13a_1(\sigma)$, as originally surmised on the basis of semi-empirical and less sophisticated ab initio models. If this result is extrapolated to the higher members of the series, then $6a_2(\pi)$ above $26a_1(\nu)$ 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.

This work is part 88 of Project No. 2.159.74 of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung. Part 87 reference 8.

REFERENCES


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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.