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# THE PHOTOELECTRON SPECTRUM OF DEWAR BENZENE

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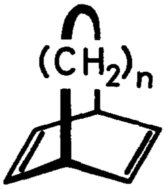
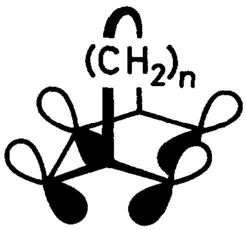
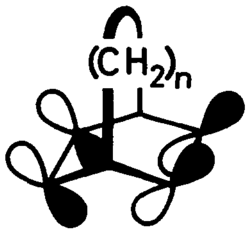
Dewar benzene (I, *n* = 0) terminates the series of bridged bicyclic dienes (I, *n* = 1,2,3,4) whose photoelectron spectra follow a now well understood pattern.[1] As *n* increases from 1 to 4, "through space" interaction becomes increasingly less important than "through bond"[2]; between *n* = 2 and 3, $a_1(\pi)$ replaces $b_2(\pi)$ as the highest occupied molecular orbital.



I(n)



$a_1(\pi)$



$b_2(\pi)$

Whether this pattern also extends back to *n* = 0 is less clear. It has indeed become a matter of some controversy. The photoelectron spectrum of hexamethyl Dewar-benzene convinced Goetz *et al*[3] that $b_2(\pi)$ lies above $a_1(\pi)$; Schrader *et al*[4] favor the opposite assignment.

Although one of these conclusions must necessarily be correct, we find neither set of supporting arguments to be overly convincing. The methyl substituents more than double the number of molecular orbitals and the CNDO/2 model employed in ref 4 is quite inadequate for any such systems[5]. We are convinced that two close-lying states (separated by < 0.5 ev) can never reliably be assigned, within the context of Koopmans' approximation, on the basis of a single spectrum.

We have therefore recorded the photoelectron spectra of Dewar-benzene, of dihydro-Dewar benzene, of tetrahydro-Dewar-benzene and of the three corresponding hexamethyl derivatives.[6] The HeI spectrum of Dewar-benzene (Figure 1) reveals *seven* clearly recognizable bands between 9 and 15 ev, followed by less well resolved ionization.

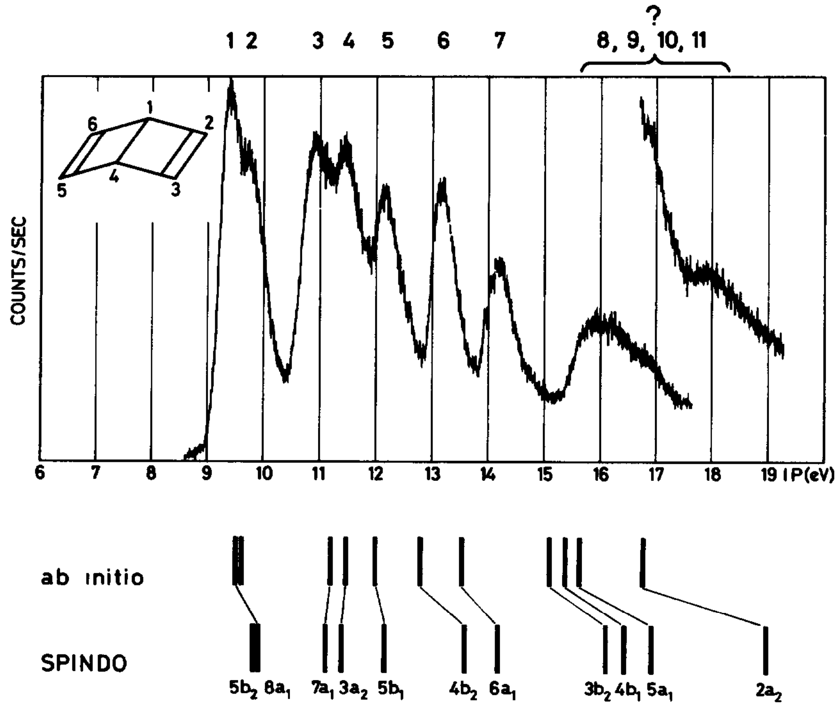


Figure 1: PE-Spectrum of Dewar benzene

Their assignment rests most cogently upon ab initio STO-3G calculations[7], upon the results derived from the SPINDO procedure[8] for the closed shell hydrocarbon, and upon an open-shell STO-3G Hartree-Fock treatment of its radical cation in both the ground and first excited states.

The molecular structure was calculated by minimizing total energy with respect to all internal coordinates (under $\underline{C}_{2v}$) by the MINDO/3 procedure[9]. The interatomic distances and dihedral angle ($\underline{R}_{14}$ = 1.581, $\underline{R}_{12}$ = 1.524, $\underline{R}_{23}$ = 1.352 Å, $\theta$ = 120.6°) agree adequately with those deduced from microwave spectroscopy[10], from electron diffraction of the hexamethyl[11] and hexafluoro[12] derivatives, as well as from earlier ab initio calculations.[13]

To facilitate comparison with observed ionization energies ($I_{v,J}^{obs}$) in Table 1 and Figure 1, the calculated orbital energies ($\varepsilon_j^{ab\ initio}$ and $\varepsilon^{SPINDO}$) were converted to $I_{v,J}^{ab\ initio}$ and $I_{v,J}^{SPINDO}$ using the empirically fitted parameters of eqn (1) and (2)[14].

$$I_{v,j}^{ab\ initio} = 4.63\ \text{eV} - 0.634\ \varepsilon_j^{ab\ initio} \tag{1}$$

$$I_{v,j}^{SPINDO} = -0.57\ \text{eV} - 1.065\ \varepsilon_j^{SPINDO} \tag{2}$$

Table 1. Assignment of Observed and Calculated Ionization Energies ($I_{v,J}$)

| $\underline{J}$ | $\phi_{\underline{J}}$ | Obsd | Ab Initio | SPINDO |
|---|---|---|---|---|
| 21 | $5\underline{b}_2$ | $9.4_0$ | 9.58 | 9.85 |
| 20 | $8\underline{a}_1$ | $9.7_0$ | 9.63 | 9.87 |
| 19 | $7\underline{a}_1$ | $10.9_5$ | 11.19 | 11.11 |
| 18 | $3\underline{a}_2$ | 11.5 | 11.47 | 11.42 |
| 17 | $5\underline{b}_1$ | 12.2 | 12.05 | 12.18 |
| 16 | $4\underline{b}_2$ | 13.2 | 12.86 | 13.62 |
| 15 | $6\underline{a}_1$ | 14.2 | 13.56 | 14.21 |
| 14 | $3\underline{b}_2$ | 15.9 | 15.12 | 16.13 |
| 13 | $4\underline{b}_1$ | (16.2) | 15.37 | 16.45 |
| 12 | $5\underline{a}_1$ | (16.6) | 15.64 | 16.99 |
| 11 | $2\underline{a}_2$ | 17.9 | 16.84 | 19.51 |

It is apparent that the two treatments agree in their orbital sequence. Within their estimated errors, both must regard the two "π-orbitals"; $5b_2(\pi)$ and $8a_1(\pi)$, as being accidentally degenerate; "through space" and "through bond" interactions cancel. The open-shell *ab initio* calculation for the radical cation, which yields $\mathcal{E}(^2\underline{A}_1) - \mathcal{E}(^2\underline{B}_2) = 0.16$ eV, requires a $^2\underline{B}_2$ ground state. In orbital language, this would correspond to $5\underline{b}_2(\pi)$ *above* $8\underline{a}_1(\pi)$.

Alternatively, application of orbital localization techniques[15] to the SPINDO results leads to a self-energy $F_{\lambda,\pi} = -10.37$ eV for the two localized π-orbitals: $\pi_{23}$, $\pi_{56}$. Their "through space" interaction amounts to $F_{\lambda,\pi\pi} = -0.25_5$ eV which yields -10.63 eV and -10.12 eV for the symmetry adapted linear combinations $(\pi_{23} + \pi_{56})/\sqrt{2}$ and $(\pi_{23} - \pi_{56})/\sqrt{2}$ respectively. The appropriate "through bond" interaction parameters[5,16] are then $\tau_+ = 0.83$ eV and $\tau_- = 0.34$ eV. This last figure is hardly negligible.

Obviously, the situation is not as simple and straightforward as previous treatments of the more complicated hexamethyl derivative would suggest. Equally obvious, now, the behavior of $\underline{1}$ (n = 0) deviates from the pattern set by its higher homologues.

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