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THE ELECTRONIC STRUCTURE OF BENZVALENE

PHOTOELECTRONSPECTROSCOPIC STUDIES

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Abstract—The photoelectron(PE)spectrum of tricyclo[3.1.0.$0^{2,6}$] hex-2-ene(benzvalene, **1**) has been recorded. The first four bands in the PE spectrum of **1** can be assigned to transitions to $^2B_2$, $^2A_1$, $^2A_2$ and $^2B_1$ states of 1^+. This assignment is discussed in terms of the results of semiempirical and *ab initio* calculations on **1**. Furthermore the highest occupied MO's of **1** are derived qualitatively from an interaction diagram between a distorted bicyclobutane and an ethylene moiety.

The electronic structure and the high reactivity of tricyclo[3.1.0.$0^{2,6}$] hex-2-ene (benzvalene, **1**) has attracted the interest of many chemists since the unsubstituted compound was detected a decade ago.[1] Its convenient synthesis[2] makes this compound available to any organic chemist interested in its chemical or spectroscopic properties. Surprisingly enough, its PE spectrum has not yet been reported, although the PE data are of great value in checking the various theoretical predictions given in the literature.[3-5]

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We wish to report these data along with results obtained by various theoretical treatments applied to the ground state molecule. The PE spectrum of **1** is shown in Fig. 1, and the vertical ionisation potentials $I_{v,j}$ are collected in Table 1 and compared with the predicted values, assuming the validity of Koopman's theorem,[6] i.e. $I_{v,j} = -\epsilon_j$.

RESULTS

The spectrum shows three distinct peaks in the low energy region followed by a pattern of strongly overlapping bands with higher transition energies. The first band at 8.55 eV, corresponding to the transition of the molecule to the radical cation in its electronic ground state clearly reveals vibrational fine structure with a mean spacing of 833 cm^{-1}. The striking feature of this first peak is its enormous intensity as compared with the following bands in the spectrum. Similar unexplained differences in cross sections have been reported for other systems, where double bonds are conjugated with cyclopropyl groups.[12]

All calculations agree with experiment in so far as three well separated orbitals (i.e. within Koopmans' theorem[6] three electronic states of the cation with quite different energies) are predicted, followed by a manifold of close lying orbitals. All methods except CNDO/2[9] predict the four lowest states of the cation to be $^2B_2$, $^2A_1$, $^2A_2$ and $^2B_1$ in order of increasing energy, while the latter two are predicted to be interchanged with the CNDO/2 method.

Benzvalene can be regarded as a bicyclobutyl fragment symmetrically bridged by a double bond. Various theoretical studies[1-5,13] have adopted this point of view and it is suggestive to fit the experimental PE data into a simple ZDO model of this type. However, this latter procedure is complicated by the strongly distorted geometry of the bicyclobutyl part in **1** as compared to the unsubstituted bicyclobutane. The dihedral angle θ between the cyclopropyl rings in **1** is 105°,[14] while in the unsubstituted bicyclobutane this angle is reported to be 121.7°.[15] The energies of the highest occupied MO's of bicyclobutane[16] are highly dependent upon this angle. This is illustrated in Fig. 2, where the orbital energies of bicyclobutane calculated by the MINDO/3 method are shown as functions of θ. The values of θ corresponding to those in benzvalene and bicyclobutane are indicated by the arrows **D** and **A**, respectively. The following tendencies are apparent: As the angle θ becomes smaller, the orbitals $7a_1$ and $3b_2$ are shifted towards lower energies, while $1a_2$ and $4b_1$ show the opposite trend. The same behaviour is predicted by the extended Hückel(EH)[8] method as well as by an *ab initio* Hartree–Fock calculation on the STO-3G level.[11] The latter calculation was performed only to obtain the derivatives of the orbital energies by finite differences at the point $\theta = 121.7°$, corresponding to the equilibrium structure of bicyclobutane.[15] Qualitatively these trends are expected and most simply explained by the nodal properties of the wavefunctions inducing the irreducible representations given above. To visualize the situation, we shall refer to Fig. 3, which shows a projection of bicyclobutane onto the x,y-plane of the coordinate system. In this projection, carbon atoms C^1 and C^4[17] are positioned on the y axis. The nodal properties of the wave functions can be deduced from Fig. 3.

Enlarging the dihedral angle θ simply moves C^1 and C^4 further apart. Since any function of A_2 and B_1 symmetry

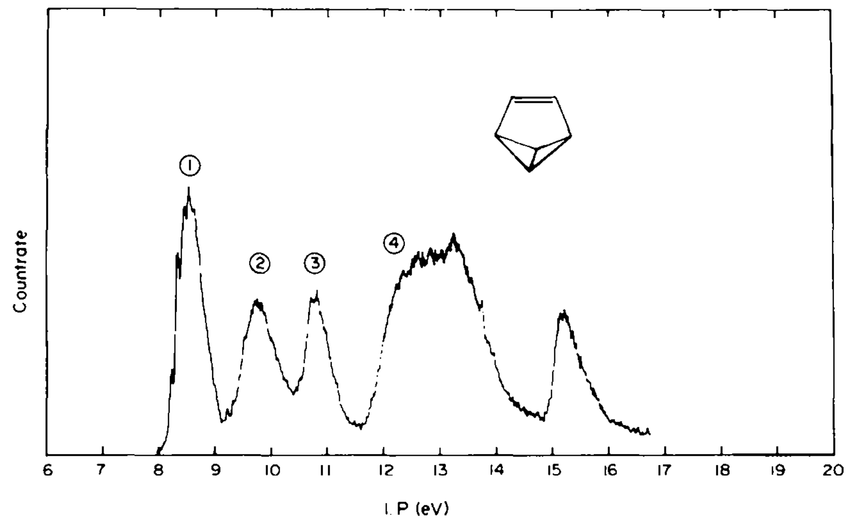


Fig. 1. Photoelectron spectrum of benzvalene between 8 and 16 eV.

Table 1. Comparison between measured vertical ionization energies $I_{v,J}$ and orbital energies ϵ_J (all values in eV)

band	$I_{V,J}$ (exp)	assignment	MINDO/3 [7]	EH [8]	CNDO/2 [9]	SPINDO [10]	STO-3G [11]
①	8.55	$4b_2$	-8.43 ($4b_2$)	-11.96 ($4b_2$)	-11.22 ($4b_2$)	-9.59 ($4b_2$)	-7.61 ($4b_2$)
②	9.75	$10a_1$	-9.10 ($10a_1$)	-12.28 ($10a_1$)	-13.25 ($10a_1$)	-10.15 ($10a_1$)	-9.16 ($10a_1$)
③	10.83	$1a_2$	-9.87 ($1a_2$)	-13.14 ($1a_2$)	-14.62 ($6b_1$)	-10.59 ($1a_2$)	-9.90 ($1a_2$)
④	12.18	$6b_1$	-11.06 ($6b_1$)	-13.86 ($6b_1$)	-15.60 ($1a_2$)	-12.11 ($6b_1$)	-12.48 ($6b_1$)
			-11.40 ($5b_1$)	-13.99 ($5b_1$)	-16.65 ($5b_1$)	-12.28 ($5b_1$)	-12.82 ($5b_1$)

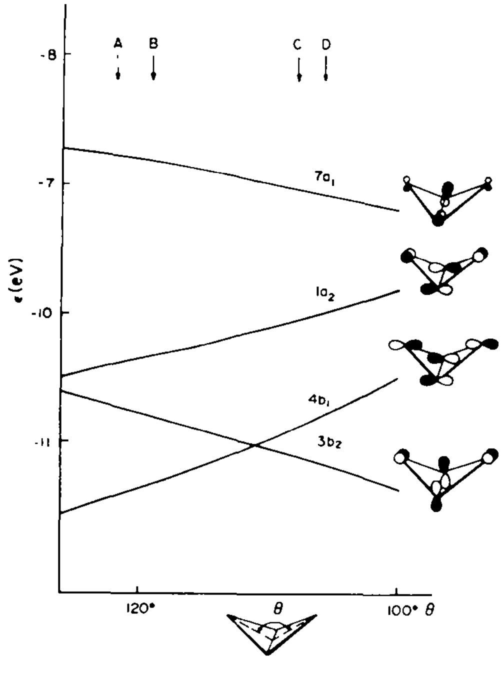
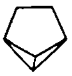


Fig. 2. Orbital energies of bicyclobutane as a function of the dihedral angle θ according to MINDO/3. For the meaning of **A**, **B**, **C** and **D** see text.

is antibonding with respect to the "bond" C^3–C^4, the corresponding orbitals are stabilized while the functions of A_1 and B_2 symmetry must show the opposite behaviour as has been worked out for the specific orbitals in detail above (Fig. 2).

To "check" these predictions experimentally we compare the PE spectra of two additional bicyclobutyl derivatives,[18] namely tricyclo[3.1.0.$0^{2,6}$] hexane (**2**) and



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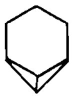

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tricyclo[4.1.0.$0^{2,7}$] heptane (**3**). These compounds provide further checkpoints on the reaction coordinate θ. The measured vertical ionization potentials of **2** and **3** are listed and compared with calculated orbital energies in Table 2.

Since the structures of **2** and **3** are not experimentally known, their geometries have been optimized by MINDO/3 yielding a θ value of 119.0°(**3**) and 107.7°(**2**). Optimization of **1** yields 105°. Since the predicted structure of **1** compares very well with experiment,[14] the experimentally unknown θ values for **2** and **3** are expected to be reasonably well predicted by the values given above. Again the corresponding points are indicated in Fig. 2 by arrows **B** for **3** and **C** for **2**.

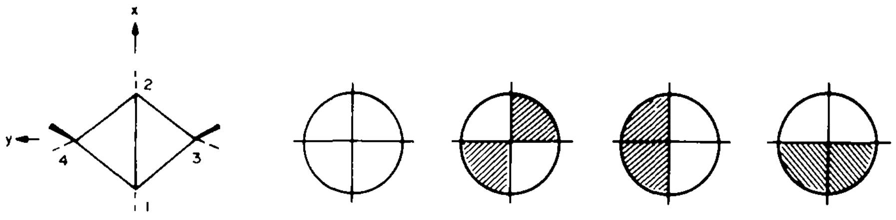


Fig. 3. Projection of the bicyclobutane molecule in the x-y plane (left). General nodal properties of any wave function transforming according to A_1, A_2, B_1 and B_2 symmetry. Shaded and white areas indicate regions of different signs of the corresponding wave functions.

Table 2. Comparison between measured vertical ionization energies $I_{v,J}$ of **2** and **3** and orbital energies ϵ_J (all values in eV)

compound	band	$I_{v,J}$ (exp)	assignment	MINDO/3 [7]
2	①	9.43	$10a_1$	$-9.03(10a_1)$
	②	10.23	$2a_2$	$-9.44(2a_2)$
	③	11.53	$4b_2$	$-10.22(4b_2)$
3	①	8.72	$12a_1$	$-8.66(12a_1)$
	②	10.45	$2a_2$	$-9.85(2a_2)$
	③	10.8	$5b_2$	$-10.03(5b_2)$

The interpretation of the experimental data is now straight forward. The somewhat larger inductive effect of the trimethylene bridge in **3** as compared with the dimethylene bridge in **2** acts parallel with the "geometrical effect" outlined above upon the highest occupied MO in **3**. The large shift towards lower energy between the first band in **3** as compared to the first band in **2** ($\Delta = -0.71$ eV) can hardly be a consequence of the inductive shift alone.

A comparison between the second band of **2** and **3** reveals a shift towards higher energy ($\Delta \geq 0.22$ eV) for **3** as compared to **4**. This is opposite to what is expected from the inductive effect and is clearly an indication that the change of θ is the dominant perturbation of the system.

After this discussion we are now capable of estimating the basis orbital energies of the bicyclobutane system under the geometrical constraints present in benzvalene. If we assume that the shifts of the first levels of bicyclobutane caused by changing θ are about equal in magnitude (Fig. 2), we can work out that the highest occupied a_2 and a_1 orbitals are shifted inductively 0.2 eV more in **3** than in **2** due to the additional CH_2 group. As a result of the larger dihedral angle in **3** (119°) compared to 107.7° in **2** both orbitals (a_2 and a_1 mentioned above) are shifted by 0.5 eV. Taking this value we can calculate the shift which is due to an angle of 16°, the difference in dihedral angles between **1** and bicyclobutane:

$$\Delta\epsilon(a_1) = -\Delta\epsilon(a_2) = 0.5 \cdot \frac{16.0}{11.3} = 0.71\ \text{eV}. \qquad (1)$$

The ionization potentials of bicyclobutane corresponding to the ejection of an electron out of the $7a_1$ and $1a_2$ orbitals are[3,18]

$$\epsilon(7a_1) = -9.14\ \text{eV}$$

and (2)

$$\epsilon(1a_2) = -11.23\ \text{eV}.$$

With (1) and (2) we obtain for the basis orbital energies for the bicyclobutane part in **1**:

$$\epsilon(a_1) = -9.14 - 0.71[\text{eV}] = -9.85\ \text{eV}$$

$$\epsilon(a_2) = -11.23 + 0.71[\text{eV}] = -10.52\ \text{eV}.$$

Note that these values need to be corrected for the inductive effect of the unsaturated bridge in benzvalene; such an effect should destabilize both levels by about 0.1 eV. The second band in the PE spectrum of **1** appears in about the estimated region while the third ionization potential found for **1** is evidently higher as expected by approximately 0.3 eV (Fig. 4).

This is most likely due to the circumstance that both levels are not influenced equally in magnitude by changing θ.[19] Additionally the $1a_2$ level may be stabilized relative to the $10a_1$ level by interaction with the $a_2(\pi^*)$ orbital of the ethylene bridge.[5]

Values for the basis orbital energies of the b_1 and b_2 levels of the bicyclobutane unit can only be estimated roughly. Using the orbital diagram of Fig. 2 and perturbation theory as a guide we estimate both basis orbital energies between 11.5 and 12.3 eV. This is indicated at the right of Fig. 4.

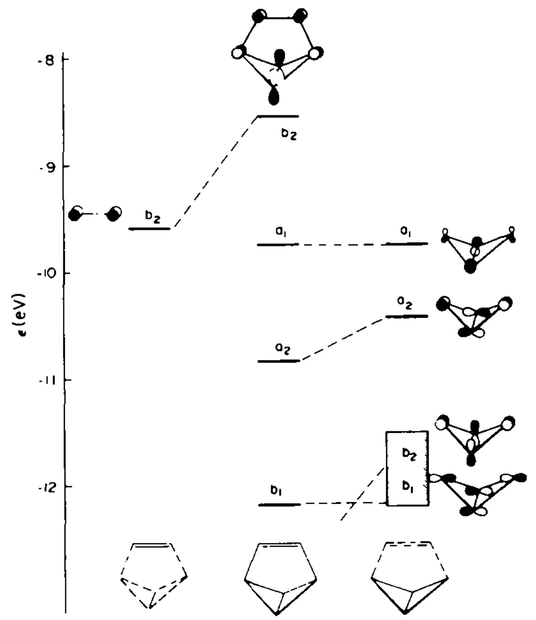


Fig. 4. Correlation diagram between the basis orbitals of a double bond in **1** and those of bicyclobutane to yield the orbital energies of **1**.

For the basis orbital energy of the double bond of **1** we adopt the same value as for the double bond in tricyclo[3.3.0.0^{2,6}]octene $\epsilon_\pi = -10.5 + 0.9$ [eV] $= -9.6$ eV as discussed recently.[20] This value is indicated at the left of Fig. 4.

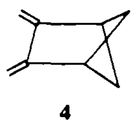
From these basis orbital energies we have constructed the qualitative interaction diagram given in Fig. 4 which demonstrates the anticipated large interaction between the $b_2(\pi)$ and the corresponding bicyclobutane orbital.

CONCLUSIONS

The assignment of the first four bands in the PE spectrum of **1** is unambiguous and yields the sequence $^2B_2$, $^2A_1$, $^2A_2$ and $^2B_1$ for the lowest lying Koopmans' states of the radical cation.

The observation that $I_V(10a_1)$ is higher in energy in **1** than $I_V(7a_1)$ in bicyclobutane while $I_V(1a_2)$ is lower in energy than $I_V(1a_2)$ in bicyclobutane has an important consequence. It clearly shows that the geometrical distortion of the bicyclobutyl moiety in benzvalene has a large impact upon its electronic structure and cannot be disregarded. The importance of this effect has apparently not been fully recognized before.

A second corollary can be deduced by comparing the basis orbital energies of the a_2 level of the bicyclobutane moiety in **1** and **5** (~ -10.5 eV) and the a_2 level of the cyclobutane ring in **4**. The latter a_2 level should be close to the value derived for tricyclo[3.3.0.0^{2,6}]octene (-12.0 eV).[20] This large energy difference leads to a strong destabilization of the highest occupied $a_2(\pi)$orbital of **5** but only a minor destabilization of the highest occupied $a_2(\pi)$orbital of **4**. This is in line with the observed reactivity difference between **4** and **5** towards dienophiles.[5,21]



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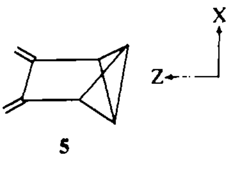

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EXPERIMENTAL

Benzvalene has been synthesized using the method described in the literature.[2] The sample used was purified by gas chromatography.

The spectrum was recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield, England) of the type described by Turner.[22] To avoid the known rapid rearrangement to benzene,[2] the sample was cooled to 0° during the time its spectrum was recorded. As apparent from its PE spectrum, no contamination by benzene was observed.

Calculations. The results of the calculations reported in Table 1 were all carried out using the experimentally determined geometry[14] of **1** except for the MINDO/3[7] calculation. Here the geometry was optimized by means of the Fletcher Powell algorithm.[23] Analogously the geometries of **2** and **3** were optimized with the MINDO/3 method.

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