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Pyrolysis and UV photoelectron spectroscopy of bicyclo[3.2.0]hept-6-en-2-one; preparation and detection of cyclohepta-2(*Z*),4(*E*)-dien-1-one

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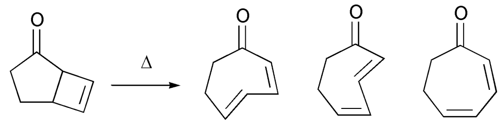
Flash vacuum pyrolysis of bicyclo[3.2.0]hept-6-en-2-one (1) in the source chamber of a UV photoelectron (PE) spectrometer using a CW CO_2 laser as a directed heat source facilitated an electrocyclic ring expansion to yield the transient species cyclohepta-2(*Z*),4(*E*)-dien-1-one (2), the PE spectrum of which was compared to that of an authentic sample of cyclohepta-2(*Z*),4(*Z*)-dien-1-one (4) and confirmed a conrotatory ring opening of 1 that obeys the Woodward–Hoffmann rules.

Ultraviolet photoelectron spectroscopy in conjunction with *ab initio* calculation[†] of molecular orbital eigenvalues and eigenvectors provides information about the electronic structure and bonding of stable and transient species that is provided by no other experimental technique. Our ultraviolet PE spectrometer is interfaced with a CW CO_2 laser that has been successfully used as a directed heat source in gas phase pyrolysis experiments.[†1*d*,*e*,2–4] This unique experimental setup allows the generation of transients and strained molecules directly in the source chamber of the spectrometer. The laser is focused on the tip of a quartz nozzle generating a 1 mm hot zone that is 10 mm away from the ionization beam and eliminates the need for an external electric furnace that is normally several centimeters in length. In this way, strained molecules and transient species may be generated and detected in real time.

The electrocyclic ring opening of cyclobutene has received considerable attention, mostly directed at photochemical study.[5] The Woodward–Hoffmann rules predict that the thermal reaction undergoes a conrotatory ring opening while the photochemical process exhibits a disrotatory ring opening. If the substituents on the cyclobutene ring are another ring, that joins the two saturated carbons of the cyclobutene, a thermal reaction should generate a *trans* double bond in the newly formed ring. In the case of bicyclo[6.2.0]deca-9-ene the ring is large enough to accommodate a *trans* double bond in the thermal product, cycloocta-1(*Z*),3(*E*)-diene.[6] When the second ring joining the two bridge heads of the cyclobutene is small, such as in the case of bicyclo[3.2.0]hept-6-ene, the product of the thermal ring expansion is cyclohepta-1(*Z*),3(*Z*)-diene which indicates that this process unexpectedly appears to follow the thermally forbidden disrotatory pathway.[7] We decided to investigate the thermal ring opening of bicyclo[3.2.0]hept-6-en-2-one (**1**)[8,9] using PE spectroscopy, which in principle can yield dienones **2**, **3**, and **4**.

We found that, bicyclo[3.2.0]hept-6-en-1-one (**1**), when pyrolysed, undergoes a ring opening to the transient dienone, cyclohepta-2(*Z*),4(*E*)-dien-1-one (**2**), and not **3** or **4**. The first and the second IP bands of **1** at 8.98 and 10.14 eV and are only 0.25 and 0.36 eV higher in energy then the predicted Becke3LYP values as shown in Table 1. The PE spectrum of ketone **1** is shown in Fig. 1(a) and the simulated PE spectrum of **1** is shown in Fig. 1(d). Although the calculated and experimental IP_vs differ slightly, the agreement in the features of the experimental and simulated spectra is excellent.



The pyrolysis of **1** in the PE spectrometer allowed us to record the PE spectrum of **2** as shown in Fig. 1(b). This thermal reaction of **1** follows a conrotatory ring opening of the cyclobutene moiety. A disrotatory ring opening, which is thermally forbidden, would generate cyclohepta-2(*Z*),4(*Z*)-dien-1-one (**4**). We synthesized an authentic sample of **4**[10] and

Table 1 Experimental and calculated vertical IPs (eV) of **1**, **2** and **4**

1	Becke3LYP	IP_v	8.73	9.78	—
	Exp.	IP_v	8.98	10.14	—
2	Becke3LYP	IP_v	8.65	9.08	10.19
	Exp.	IP_v	8.36	9.06	10.18
4	Becke3LYP	IP_v	8.84	8.96	10.93
	Exp.	IP_v	9.36		11.16

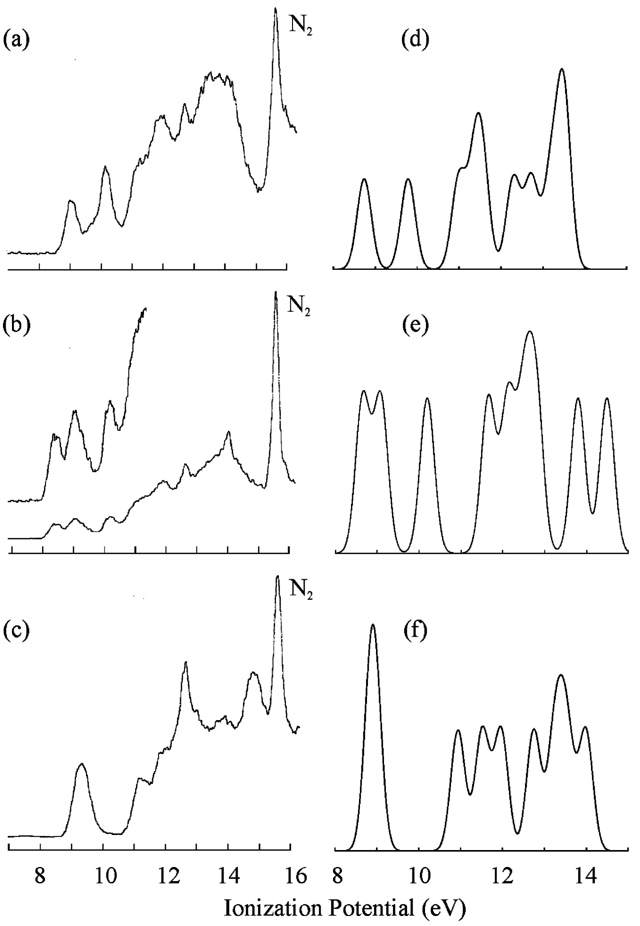


Fig. 1 Experimental PE spectra: (a) **1**, (b) pyrolysis of **1**, (c) **4**. Simulated Becke3LYP/6-31+G(d) PE spectra: (d) **1**, (e) **2** and (f) **4**.

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recorded its PE spectrum for comparison as shown in Fig. 1(c).

Although one could expect two possible products from the conrotatory ring opening, namely dienones **2** or **3**, transition state calculations at Becke3LYP/6-31+G(d) indicate that **2** should be the product. A transition state, which would lead to **4**, could not be located. The PE spectra of **2** and **4** are very distinct. The photoelectron spectrum of the pyrolysate can clearly be assigned to the cyclohepta-2(*Z*),4(*E*)-dien-1-one (**2**) based on the calculated Becke3LYP IPs (Table 1) as well as the simulated spectrum (Fig. 1e). The first and second bands in the PE spectrum of the transient dienone **2** are separated by 0.7 eV, while the second and third bands are separated by 1.1 eV. The three IP bands in **2** are observed at 8.36, 9.06, and 10.18 eV while the predicted Becke3LYP IPs are at 8.65, 9.08, and 10.19 eV. The difference between the first experimental and calculated IP_v is only 0.29 eV, while the second and third IP_vs show a difference of 0.02 and 0.01 eV, confirming an excellent correlation between experiment and theory. Remarkable correlation is also observed between the experimental and simulated spectra of **4**, which are shown in Fig. 1(c) and 1(f). A single large IP band is observed in the experimental as well as in the simulated spectrum at 9 eV.

At the Becke3LYP/6-31+G(d) level the conrotatory ring opening of **1** has a barrier of 131.9 kJ mol^{-1}. The transition state was confirmed by a frequency calculation, which had one negative eigenvalue with a single negative frequency. Visualization of this vibrational mode showed that the newly forming double bond at position C4 in the product is the *trans* double bond. This thermal reaction, in principle, could lead to two different products, where both would be the result of a conrotatory ring opening. In the first case, a transition state that leads to **2** was found. The transition state that would link **1** and **3** was also found at the Becke3LYP/6-31+G(d) level of theory with the energy barrier being 185.9 kJ mol^{-1}. Therefore it is clear that the PE spectrum observed upon the pyrolysis of **1** is that of **2**. The computational and experimental evidence shows that neither **3** nor **4** can be generated in the thermal rearrangement of **1**. The difference of 54.0 kJ mol^{-1} in the activation energy between the two processes clearly indicates that the rearrangement of **1** to **2** is favored. The calculations also predict that **2** is 24.7 kJ mol^{-1} more thermodynamically stable than **3**. The calculated total and relative energies of **1–4**, radical cations (RC) and transition states **Ta** and **Tb** are shown in Table 2. Calculated first vertical ionization potentials were obtained by the calculational method of Muchall and Werstiuk.[1d]

Our pyrolysis experiments on **1** have shown that this bicyclic enone undergoes a thermal ring opening that obeys the Woodward–Hoffmann rules and follows the conrotatory path. This generated the transient dienone **2** and its photoelectron spectrum was recorded for the first time. The product of the pyrolysis was confirmed by recording an authentic PE spectrum of **4** which was also recorded for the first time and has allowed us to differentiate between the two isomers. The possibility of **3** as the product of the pyrolysis was eliminated based on transition state calculations, which have shown that the transition state that links **1** and **3** is 54.0 kJ mol^{-1} higher in energy than the transition state linking **1** and **2**. Work is currently underway in our laboratory to re-examine the gas phase pyrolysis of bicyclo[3.2.0]hept-6-ene.

Table 2 Becke3LYP/6-31+G(d) total and relative energies of **1–4**, radical cations (RC) and transition states **Ta** and **Tb**

	E_T/hartrees	Relative energy/kJ mol^{-1}	Ionization potential/eV
1	−346.733 976	0.0	8.73
1–RC	−346.413 253	—	
Ta[a]	−346.683 808	131.9	
2	−346.705 326	75.4	8.65
2–RC	−346.387 364	—	
3	−346.695 937	100.1	8.75
3–RC	−346.695 937	—	
Tb[a]	−346.663 182	185.9	
4	−346.763 673	−77.9	8.84
4–RC	−346.763 673	—	

[a] **Ta**-transition state between **1** and **2**. **Tb**-transition state between **1** and **3**

Notes and references

† Becke3LYP[1a] calculations were performed on IBM RS/6000 model 39H, 350, 350, SGI Octane and Intel dual processor PC computers with Gaussian 94[1b] and Gaussian 98.[1c] Becke3LYP/6-31+G(d) optimized geometrical structures were used in single point radical cation calculations performed at the same level of theory and with the same bases set. The interpretation of PE spectra was based on a recently developed[1d,e] and successfully applied[1f,g] routine based on Becke3LYP theory. The simulated PE spectra of all compounds were obtained from MO results using a Fortran program PESPEC.[1h] Gaussian line shape with a full width at half height (FWHH) and a temperature set to 300 K was used to simulate the partial PE spectra with ten eigenvalues (HOMO to HOMO-9, B3LYP/6-31+ G(d)).

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