

COMMUNICATION

A study of the vacuum pyrolysis of 11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,9-diene. The HeI ultraviolet photoelectron spectrum of 1,2-cyclohexadiene

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Abstract: A newly developed ultraviolet photoelectron spectrometer – CO₂ laser apparatus that utilizes a 50-watt CW CO₂ laser as a directed heat source is used to study the vacuum pyrolysis of 11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,9-diene (**4**). We report the HeI photoelectron spectrum of the strained cyclic allene 1,2-cyclohexadiene (**1**) that correlates with the HAM/3 ionization energies calculated with the optimized C₂ equilibrium structure obtained with AM1 and the molecular orbital energies of the optimized C₂ equilibrium structure calculated at the ab initio HF/6-31G** level of theory.

Key words: 11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,9-diene, vacuum pyrolysis, HeI ultraviolet photoelectron spectrum, 1,2-cyclohexadiene.

Résumé : On a utilisé un spectromètre photoélectronique ultraviolet à laser au CO₂ de 50 watt CW développé récemment comme source de chaleur dirigée pour d'étudier la pyrolyse sous vide du 11-oxatricyclo[6.2.1.0^{2,7}]undéca-2,9-diène (**4**). On a déterminé le spectre photoélectronique HeI du cyclohexa-1,2-diène (**1**), un allène cyclique tendu; il existe une bonne corrélation entre ce spectre expérimental et les énergies d'ionisation HAM/3 calculées en utilisant une structure en équilibre C₂ optimisée obtenue avec AM1 ainsi que les énergies d'orbitales moléculaires de la structure en équilibre C₂ optimisée calculée au niveau ab initio HF/6-31G** de la théorie.

Mots clés : 11-oxatricyclo[6.2.1.0^{2,7}]undéca-2,9-diène, pyrolyse sous vide, spectre photoélectronique ultraviolet HeI, cyclohexa-1,2-diène.

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Studies that combine ultraviolet photoelectron spectroscopy (pes) and calculations of molecular orbital (MO) energies and orbital coefficients at the semi-empirical or ab initio levels of theory provide fundamental information about the structures and bonding of stable compounds and transient species that is obtained by no other technique. In the past, transient species studied with pes generally were prepared by vacuum pyrolysis of compounds using electrically heated furnaces centimetres in length (1, 2). To facilitate the study of highly reactive transients in the gas phase, we developed a CW CO₂ laser – pes apparatus (the laser is used as a directed heat source to produce a hot zone that is 1–2 mm in length) and

used it successfully to study the vacuum pyrolysis of a number of substrates (3–5).

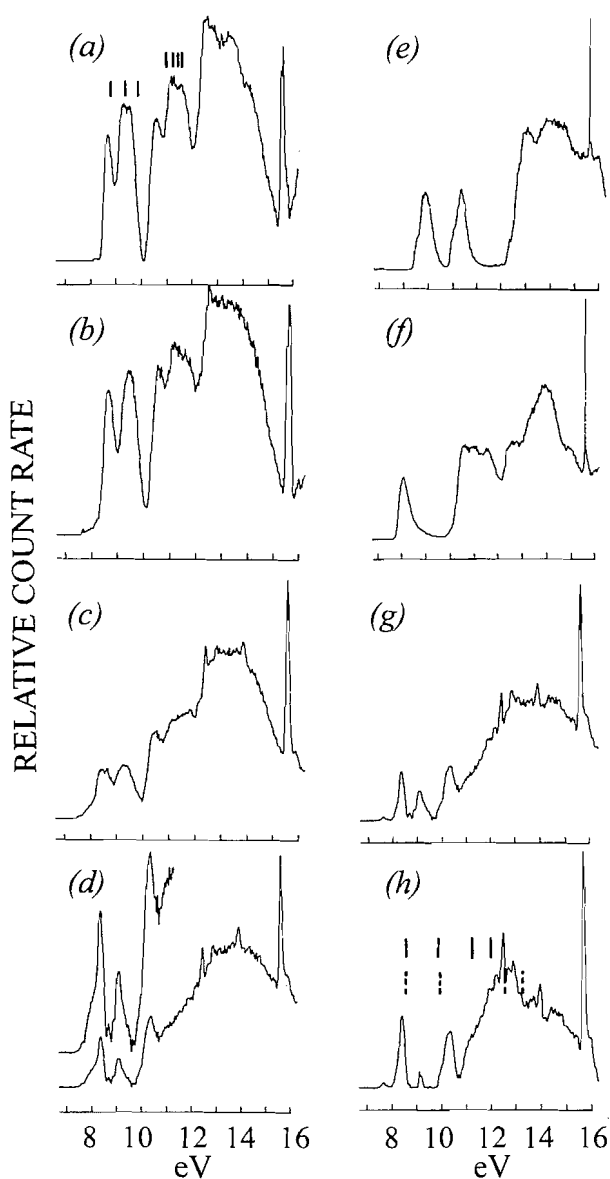
Because of its unique structure and kinetic reactivity, the highly strained cyclic allene, 1,2-cyclohexadiene (**1**), has been the focus of studies by experimentalists and theoreticians for some time (6). When generated from a wide range of precursors in solution it is trapped with reactive dienes and hydroxylic solvents or it dimerizes and tetramerizes. And, there have been two reports of attempts to prepare and study **1** with the matrix isolation technique. Wentrup et al. pyrolyzed bicyclo[3.10]hexane-6-carbonyl chloride (**2**) at 1073 K and obtained infrared spectroscopic data that indicated the successful trapping of **1** in an Ar matrix at 11 K (7). Runge and Sander subsequently challenged the conclusions reached in this paper on the basis of the results they obtained by pyrolyzing 6-bromo-6-(trimethylstannyl)bicyclo[3.10]hexane (**3**) at 873 K and trapping the pyrolysate at 10 K (8). Given these findings and the fact that (a) there have been no reports of the pe spectrum of **1** and (b) we wished to establish the scope and limitations of studying transient species with our newly devel-

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Fig. 1. (a) HeI photoelectron spectrum of **4** obtained at ambient temperature (the vertical lines mark the HAM/3 IEs calculated with the AM1 optimized equilibrium structure); (b) HeI photoelectron spectrum of **4** obtained at a laser power level of 26 W; (c) HeI photoelectron spectrum of the pyrolysate of **4** obtained at a laser power level of 46 W; (d) spectrum obtained by subtracting (b) from (c); (e) HeI photoelectron spectrum of furan obtained at a laser power level of 47 W; (f) HeI photoelectron spectrum of 1,3-cyclohexadiene obtained at a laser power level of 47 W; (g) spectrum obtained by subtracting (f) from (d); (h) spectrum obtained by subtracting (e) from (g) (the solid vertical lines mark the HAM/3 IEs calculated with the AM1 optimized equilibrium structure; the broken lines correspond to the negative of the MO energies calculated for the HF/6-31G** optimized equilibrium structure).

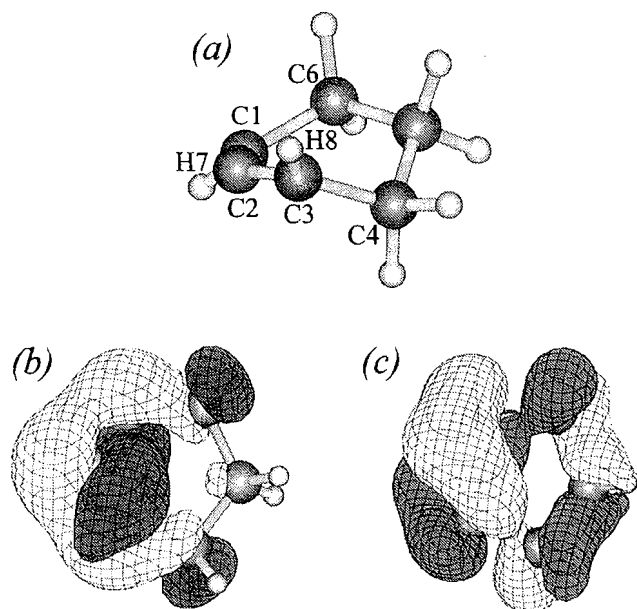


oped pes – CW CO₂ laser apparatus, we undertook to prepare **1** in the gas phase and obtain its pe spectrum. In this communication, we report the results of a study on the pyrolysis of 11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,9-diene (**4**).

We chose to prepare and study **4** (**9**) with the expectation that its pyrolysis in a 1–2 mm hot zone of a quartz nozzle (3–5) would yield **1** and furan, a stable product that would be easily identified by photoelectron spectroscopy. The photoelectron spectra of **4** along with its pyrolysate obtained at two laser power levels are displayed in Fig. 1. Figure 1 (a) is the pe spectrum of **4** obtained at ambient temperature. The seven lowest ionization energies (IEs) (8.98, –9.54, 10.02, 11.06, 11.26, 11.53, and 11.69 eV) calculated with HAM/3 (10) — the equilibrium optimized structure of **4** obtained with AM1 (11) was used in this case — are marked on the spectrum as solid lines, indicating that this combination of computational methods yields the IEs with good accuracy and allowing the molecular orbitals of **4** to be characterized. Spectra (b) and (c) were obtained at laser power levels of 26 W (the tip of the nozzle is 550 ± 50°C) and 47 W (850 ± 50°C), respectively. It is seen that the latter one differs significantly from spectrum (a). Spectrum (b) (scaled by 0.7, not (a), was subtracted from (c) to obtain the difference spectrum (d)². In this way, the effect of potential changes in the spectrum of **4** induced by the high temperature would be minimized although the signals due to **1** and furan would be reduced to some extent as well. Spectra of authentic samples of furan and 1,3-cyclohexadiene — the latter compound is formed from **1** via a 1,3-hydrogen shift (8) — were also obtained at 47 W and are displayed as spectra (e) and (f), respectively. Spectrum (g) is obtained by subtracting (f) (scaled by 0.28) from spectrum (d). This operation reduces the shoulder at 8 eV of the lowest IE peak found in (d) and brings out the lowest IE bands of furan at 9.00 and 10.38 eV, respectively. Spectrum (h) is obtained by subtracting the spectrum of furan (e), scaled by 0.4) from (g). There are no sharp bands centered at 9.60 eV in spectra (g) and (h) that are characteristic of the pe spectrum of 1-buten-3-yne (12), indicating that the retro Diels–Alder reaction of **1** observed by Runge and Sander (8) does not occur to a significant extent under the experimental conditions employed in this study. That **1** does not dimerize is indicated by the fact that spectra (g) and (h) do not exhibit a band at 9.6 eV, a peak seen in the spectrum (not shown; obtained at 47 W) of an authentic sample of **5** (13) that exhibits two low-IE bands of equal intensity at 8.40 and 9.60 eV. That the experimental pe spectrum (the vertical IEs of the two low-lying bands are 8.4 and 10.4 eV) obtained in this study correlates with the HAM/3 IEs (the four lowest ones at 8.60, 9.89, 11.40, and 12.00 eV calculated with the AM1 optimized C₂ structure are indicated with solid lines) and the negative of the energies of the four highest occupied MOs (8.64, 9.96, 12.61, and 13.12 eV, shown as broken lines) of the optimized C₂ structure obtained at the HF/6-31G** level of theory (a) indicates that **1** is obtained from **4** and (b) provides support

² We recognize that care should be exercised when difference spectra are obtained, especially when fairly featureless spectra are involved. Because the spectra acquired in this study differed in intensity, scaling was required to obtain the difference spectra. When spectrum (d) was obtained by subtracting (b) from (c), special attention was paid to the region at 10 eV to ensure that the subtraction did not yield a negative baseline. This criterion was also used in the other cases. That the low-IE band of furan is cleanly recovered in the difference spectrum (d) and the two low-IE bands of spectrum (h) are roughly equal in area, in our view, validates the process.

Fig. 2. (a) Optimized equilibrium structure of **1** obtained at the HF/6-31G** level of theory; (b) a display of the HOMO of **1**; (c) a display of the HOMO-1 of **1**.



that **1** is a chiral allenic singlet species (6). The optimized equilibrium C_2 structure calculated at the ab initio HF/6-31G** level of theory using Gaussian 94 (14) is displayed as Fig. 2(a). As seen from a comparison of several selected geometrical parameters, the ab initio and AM1 optimized C_2 structures of **1** are similar (HF/6-31G**: C1—C2 1.306 Å, C3—C4 1.526 Å, C4—C5 1.572 Å, \angle C1-C2-C3 133.9°, \angle H7-C1-C2-C3 141.4°, \angle C6-C1-C2-C3 -26.0°; AM1: C1-C2 1.320 Å, C1—C6 1.504 Å, C4—C5 1.542 Å, \angle C1-C2-C3 134.8°, \angle H7-C1-C2-C3 151.3°, \angle C6-C1-C2-C3 -23.4°) with the largest difference seen in the H7-C1-C2-C3 dihedral angles. The C6-C1-C3-C4 dihedral angles of the structures obtained at the HF/6-31G** and AM1 levels of theory are -47.8° and -43.7°, respectively, approximately half the angle expected for an allene. Thus, the twist angles for the double bonds of the HF/6-31G** and AM1 structures are 20.7° and 22.8°, well within the value required to maintain effective overlap of adjacent p orbitals. The HOMO and HOMO-1 of **1** calculated with AM1 and visualized with HyperChem³ are displayed as Figs.

2(b) and 2(c), respectively. The HOMO/HOMO-1 gap of **1** is surprisingly large (calculated 1.3 eV, experimental 2 eV) given that 2,3-pentadiene optimized with the C2-C3-C4 angle fixed at 134° exhibits a HOMO/HOMO-1 gap of 0.15 eV. This study also indicates that **4** may be useful for generating **1** in matrix isolation experiments.

Acknowledgement

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³ HyperChem Version 4.0. Hypercube Inc., 419 Philip St., Waterloo, ON N2L 2X2, Canada.