Generation, Direct Observation under Matrix Isolation Conditions, and ab Initio Calculations for 2-Azacyclopenta-2,4-dien-1-one

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Flash vacuum pyrolysis of a mixture of argon and 5-acetoxy-1,5-dihydro-2*H*-pyrrol-2-one at 350 °C and condensation of the pyrolysate onto a cold plate at 12 K produces acetic acid and 2-azacyclopenta-2,4-dien-1-one (2*H*-pyrrol-2-one, 2), identified by IR spectroscopy. Ab initio calculations for 2 and cyclopentadienone at the MP2/6-31G** level successfully reproduce the observed IR spectra. Photochemically 2 is converted to acetylene, HCN, and CO. Attempts to chemically trap 2 have so far been unsuccessful.

Introduction

Cyclopentadienone (1) has been generated by a number of methods and has been observed under matrix isolation conditions. However it is an extremely unstable compound and



readily dimerizes at temperatures greater than 38 K.¹ Much less work has been reported on aza and diaza derivatives of cyclopentadienone.² We are interested in how substitution of CH by N affects the structure and reactivity of cyclopentadienone. As part of this research effort, we report the IR spectrum and photochemistry of 2-aza-2,4-cyclopentadienone (2) generated under matrix isolation conditions. In addition, the structures, energies, and vibrational spectra calculated using ab initio molecular orbital theory are reported for cyclopentadienone and 2-azacyclopentadienone. The computational results are compared with experiment.

Results and Discussion

Synthesis of 2-azacyclopentadienone (2) was accomplished by flash vacuum pyrolysis of 5-acetoxy-1,5-dihydro-2H-pyrrol-2-one (4). This substrate was prepared by mild acetylation of



the known³ 5-hydroxy compound **3** with acetic anhydride. Acetate **4** is a colorless crystalline substance, with IR, ¹H-NMR, and ¹³C-NMR spectra in good agreement with the indicated structure. Its structure was confirmed by single-crystal X-ray analysis.⁴

Flash vacuum pyrolysis of acetate 4 at 350 °C and 1×10^{-5} Torr and codeposition of the pyrolysate with a large excess of argon or nitrogen onto a cesium iodide window cooled to 20 K produced the IR spectrum shown in Figure 1. No starting material is present in this spectrum, as determined by comparison with the IR spectrum produced by deposition of 4 without pyrolysis. In addition to peaks that are assigned to acetic acid (A), the major bands are assigned to 2-azacyclopentadienone (C). Bands that can be assigned to 2 appear at 3055 w, 1765 vs, 1607 w, 1525 s, 1317 s, 1091 s, 1070 w, 915 w, 825 m, and 817 s cm^{-1} . These bands can be destroyed by irradiation of the matrix with 360 nm light from a monochromator. Alternatively, broad band irradiation with a medium pressure mercury arc through Pyrex ($\lambda > 280$ nm) accomplishes the same end. The decrease in the intensities for all of the bands attributed to 2 occurs at approximately the same rate. As the bands assigned to 2 disappear, new bands appear at 3280, 3228, 2153, 2147, 2139, 1722, 1707, 1117, 966, 755, 740, and 714 cm^{-1} . The band at 2139 cm⁻¹ can be assigned to carbon monoxide. The bands at 3280, 3228, 755, and 740 cm^{-1} are attributed to acetylene and HCN as an aggregate with a molecule of carbon monoxide.



This assignment is based on similar results reported by Maier and Schafer⁵ during the matrix isolation photochemistry of 1,2,4-triazene (5), which produced nitrogen, HCN, and acetylene.



These workers assigned absorbances at 3283, 3232, 755, 750, and 745 cm⁻¹ to HCN and acetylene. Dilute mixtures of acetylene/argon (1:600) at 12 K have bands at 3285 and 731 cm⁻¹ while dilute mixtures of HCN/argon (1:600) have bands at 3300 and 720 cm⁻¹. While Maier and co-workers did not comment on the origin of the band shifts, it is tempting to speculate that they are due to a 1:1 complex of acetylene and HCN which is generated under the matrix isolation conditions. An analogous result has been observed in the formation of the dimer of HCN from photolysis of 1,2,4,5-tetrazine under matrix isolation conditions.⁶

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Figure 1. IR spectrum obtained by flash vacuum pyrolysis of 5-(acetyloxy)-1,5-dihydro-2*H*-pyrrol-2-one at 350 °C in argon and deposition at 12 K. The bands marked A are assigned to acetic acid. The bands marked C are assigned to 2-azacyclopentadienone.

The acetylene/HCN dimer has been observed in the gas phase and calculations have been reported.⁷ The lowest energy structure is a T-shaped one of $C_{2\nu}$ symmetry with the hydrogen end of HCN pointed toward the acetylene π system (6). It is also known that acetylene and carbon monoxide form a 1:1 linear dimer (7). Calculations have been reported for this species.⁸ On the basis of these previous findings, it is possible that the trimer complex 8 is formed during the photolysis of 2 under the matrix conditions, although we have no evidence.



Gaviña and co-workers^{2b} previously obtained evidence for the existence of 2 in solution generated from an insoluble polymeric precursor. They found that 2 could act as a diene or dienophile in Diels-Alder reactions. Our attempts to chemically trap 2 with cyclopentadiene or dimethyl acetylenedicarboxylate by cocondensation from the gas phase were not successful using a variety of conditions. Small amounts of insoluble polymer as well as substantial amounts of recovered 4 were obtained. Attempted removal of the material from the cold window for further identification was not successful. We have so far been unable to divert the reaction of 2 from something other than the simple readdition of acetic acid. The facile addition of weak nucleophiles to the imine double bond of a related indolone has been reported.⁹

Ab Initio Calculations

Remarkably, little previous computational work has been reported for cyclopentadienone (1). The best quality calculations were done at the geometry-optimized HF/6-31G* level of theory and included only the optimized geometry and dipole moment.¹⁰



Figure 2. MP2/6-31G** geometry-optimized structures for cyclopentadienone and 2-azacyclopentadienone. Distances in angstroms, angles in degrees.

No previous theoretical work on 2-azacyclopentadienone (2) has appeared in the literature. The geometry-optimized structures for 1 and 2 were determined at the MP2 (frozen core) level of theory with the 6-31G** basis set using the Gaussian92 code.¹¹ This level of theory usually gives very good agreement with experimentally determined structures.¹² The MP2optimized geometries are shown in Figure 2. Both molecules are predicted to be planar. The carbon-oxygen bond in 2 is slightly shorter than that in 1 while the remaining bonds are approximately the same for the two structures. The dipole moment calculated for 2-azacyclopentadienone (4.25 D) is substantially larger than that calculated for cyclopentadienone (2.89 D). This is due to the reinforcement of the molecular dipole moment of 1 by the C=N bond dipole in 2. Experimentally,¹³ a dipole moment of 3.10 D has been measured for cyclopentadienone and is in good agreement with our calculated value.

The infrared spectra for cyclopentadienone (1) and 2-azacyclopentadienone (2) were determined analytically at the MP2-(frozen core)/6-31G** level of theory. The vibrational frequencies and intensities obtained are listed in Tables 1 and Table

TABLE 1: Calculated Infrared Spectrum of Cyclopentadienone (MP2(frozen core)/ $6-31G^{**}$) Compared with That Observed in Argon at 10 K^a

		0		
calc freq	calc int	scaled freq	obs freq	obs int
3341.2	1(1)	3151		
3339.2	1(1)	3149		
3308.0	5(6)	3120		
3298.0	7(8)	3111		
1767.0	80(100)	1690	1727	100
1664.7	0(0)	1595		
1595.5	0(0)	1531		
1394.6	23(29)	1344	1332	42
1345.8	6(7)	1299		
1184.8	41(51)	1150	1136	30
1122.4	6(7)	1092	1068	8
1120.2	0(0)	1090		
997.7	0(0)	976		
935.1	1(1)	918		
901.2	0(0)	886		
875.4	1(1)	862		
805.6	76(99)	798	822	67
753.7	1(1)	749		
720.9	0(0)	719		
663.0	0(0)	665		
638.9	18(22)	643	632	26
459.9	5(6)	477	458	8
426.3	0(0)	446		
197.0	1(1)	233		

^a Frequencies in inverse centimeters, intensities in kilometers per mole. Intensities in parentheses are scaled relative to the highest intensity band of 100. The bands were scaled using eq 1 (see text). Observed intensities were obtained from relative peak heights.

 TABLE 2: Calculated Infrared Spectrum of

 2-Azacyclopentadienone (MP2(frozen core)/6-31G**)

 Compared with That Observed in Argon at 12 K^a

calc freq	calc int	scaled freq	obs freq	obs int
3350.3	1(1)	3159		
3319.4	2(2)	3130		
3271.4	15(18)	3086	3055	1
1804.9	88(100)	1725	1766	100
1663.1	4	1593	1607	
1577.0	13(15)	1514	1525	22
1373.1	37(43)	1324	1317	47
1335.2	3(3)	1289		
1133.2	75(85)	1102	1091	53
1110.5	13(15)	1081	1070	
980.9	1(1)	960		
945.2	8(9)	927		
916.0	1(1)	900		
845.8	12(13)	835	825	19
809.8	57(64)	801	817	43
792.4	4(4)	785		
694.0	1(1)	694		
663.2	3(3)	665		
489.4	2(2)	504		
467.9	0(0)	484		
190.4	0(0)	227		

^a Frequencies in inverse centimeters, intensities in kilometers per mole. Intensities in parentheses are scaled relative to the highest intensity band of 100. The bands were scaled using eq 1 (see text). Observed intensities were obtained from relative peak heights.

2. Figure 3 is a plot of the calculated frequencies for both 1 and 2 compared with the experimentally observed ones. Bands for cyclopentadienone in argon are observed at 1727, 1724, 1332, 1136, 1068, 822, 632, and 458 cm^{-1.1} The 18 experimental frequencies observed for 1 and 2 and the corresponding MP2(fc)/6-31G** calculated values can be fit using eq 1.

$$\nu_{\rm obs} = (0.928)\nu_{\rm calc} + 50 \,\rm cm^{-1} \tag{1}$$

The degree of agreement between the observed and scaled frequencies is very good (average error = 18 cm^{-1}) and



Figure 3. Plot of observed versus MP2(fc)/6-31G** calculated infrared vibrational frequencies for cylopentadienone and 2-azacyclopentadienone.

reinforces our assignment of 2. Typically a single scaling factor with a zero offset¹² or, alternatively, two different scaling factors¹⁴ have been used to bring calculated harmonic frequency values into closer agreement with the anharmonic experimental ones. We have found that eq 1 can be applied to a variety of other molecules with equally good results.¹⁵

The UV/vis spectra for 1 and 2 were calculated using the CIS (configuration interaction singles) method which employed the MP2/6-31G**-optimized geometries with the 6-31G** basis set. With this method, 1 is calculated to have its long wavelength absorption at 321 nm and that of 2 is calculated to be at 314 nm. Maier and co-workers have assigned a $\lambda_{max} =$ 360 nm to 1 trapped in argon.¹ While we were unable to experimentally observe a corresponding UV/vis maximum for 2, the fact that irradiation at 360 nm destroys the molecule provides evidence for its absorption in this region of the UV/vis spectrum.

Summary

Flash vacuum pyrolysis of 4 generates 2-azacyclopentadienone (2), which can be trapped and observed in an argon matrix at 12 K. The experimentally observed IR spectrum of 2 matches that based on ab initio calculations very well. Likewise, the calculated IR spectrum for cyclopentadienone (1) matches that observed by previous workers. Photochemically, 2 is converted to acetylene, hydrogen cyanide, and carbon monoxide. Attempts to trap 2 in Diels-Alder reactions have so far been unsuccessful.

Experimental Section

General. The low-temperature matrix isolation and irradiation apparatus has been described previously.¹⁶

1,5-Dihydro-5-hydroxy-2H-pyrrol-2-one (3). This compound, mp 100-101 °C (lit. mp 102 °C) was prepared according to the procedure of Fariña et al.³

5-Acetoxy-1,5-dihydro-2H-pyrrol-2-one (4). To a suspension of 20 mg of hydroxy compound 3 in 1 mL of anhydrous ether, held at 0 °C under N₂, were added 100 mg (4.4 equiv) of triethylamine and 46 mg (2.2 equiv) of acetic anhydride. The reaction mixture was stirred at 0 °C for 1 h and then held one day at room temperature. The reaction mixture was diluted with ethyl acetate and then washed with saturated aqueous NH₄Cl solution. The aqueous wash was extracted twice with a small volume of ethyl acetate. The organic layers were mixed, dried with anhydrous magnesium sulfate, and then evaporated at

reduced pressure. The solid residue (16 mg, 56%) was nearly pure acetate 4 (some unreacted alcohol remains in the aqueous layer). Recrystallization from ethyl acetate gave pure 4, mp 126-129 °C dec.

Acetate 4 showed a single broadened carbonyl peak in the IR (CDCl₃ solution) at 1720–1730 cm⁻¹; the ¹H-NMR (300 MHz, CDCl₃) exhibited signals at δ 7.02 (1H, dd, J = 5.8, 1.2 Hz, H-4), 6.48 (1H, bs, NH), 6.31 (1H, bs, H-5), 6.25 (1H, δ , J = 5.8 Hz, H-3), 2.14 ppm (3H, s, CH₃). The ¹³C-NMR showed signals at δ 172.06, 170.65, 143.80, 129.54, 79.99 and 20.41 ppm. A single-crystal X-ray diffraction analysis confirmed the structural assignment. The results are available as supporting information.

Matrix Isolation of 2-Azacyclopenta-2,4-dienone (2). Argon (150 Torr) from a 2.5 L ballast was allowed to flow through a U-trap containing freshly sublimed (60 °C, 100 mtorr) **4** over the course of 2 h, and the mixture was passed through a Pyrex tube (1.2×28 cm) heated to 350 °C. The pyrolysate was collected onto a CsI salt plate held at 23 K. At the completion of the deposition, the temperature of the window was lowered to 12 K and the IR spectrum recorded (Figure 1). Under these pyrolysis conditions all of the starting material was completely consumed and bands for acetic acid and 2-azacyclopentadiene were observed. Bands assigned to acetic acid: 3561, 3550, 1777, 1438, 1383, 1379, 1259, 1091, 1047, 988, 985, 662, 637, 584, 580, 554, and 534 cm⁻¹. Bands assigned to **2**: 3055, 1765, 1607, 1525, 1317, 1091, 1070, 915, 825, and 817 cm⁻¹.

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Supporting Information Available: Results of singlecrystal X-ray structural analysis of compound 4 (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead for ordering information and Internet access instructions.

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