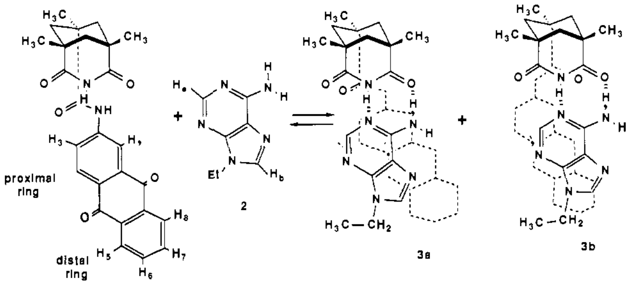
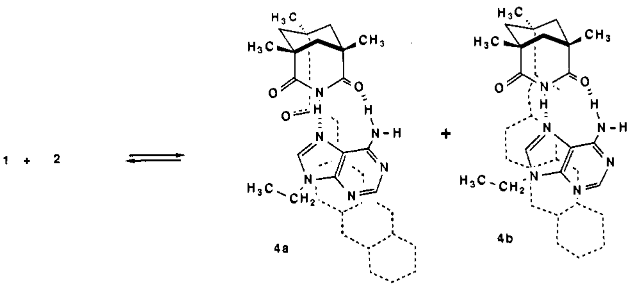
of 9-ethyladenine.[5] Selective irradiation of the methylene group of 9-ethyladenine resulted in enhancements of the proton signals in both the proximal and distal rings of the anthraquinone surface. Two conformations, **3a** and **3b** (eq 3), can be conceived for Watson–Crick base pairing and these are related by rotations around the nitrogen aryl bond. While one seems more favorable to overall aromatic contacts of the van der Waals sort, the NOE's observed in this experiment 3.3% and 3.9%, for $H_{5,8}$ and $H_{6,7}$, respectively, indicate that both conformations contribute to the structure of the Watson–Crick type complex.[6]



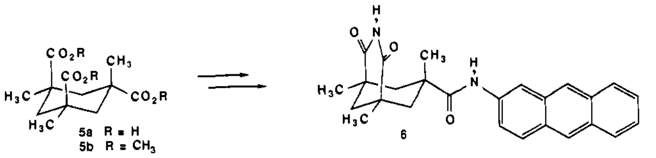
(3)

In the same experiment, NOE's were also observed for protons in the proximal ring, specifically H_1 and H_3, showing a 3% enhancement on irradiation of the methylene of **2**. This result cannot be rationalized on the basis of exclusive Watson–Crick base pairing but is nicely accommodated by the Hoogsteen[7] base pairings **4a** and **4b** shown in eq 4.



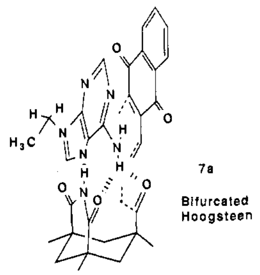
(4)

Parallel experiments with the cis/trans isomer[8] (eq 5) provide a series of control experiments. In structure **6**, both intermolecular forces are available but cannot act simultaneously. Indeed, no such intermolecular NOE's were observed between the methylene of **2** and the aromatic surface of **6** in its complex ($K_a = 60\ M^{-1}$).

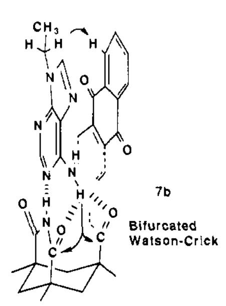


(5)

In heteronuclear experiments, irradiation of the NH bond of the adenine derivative **2** led to enhancements of the ^{13}C signals of both imide carbonyls (20%) as well as the amide carbonyl (24%) indicated in **7a** and **7b**. The simplest explanation would invoke bifurcated hydrogen bonds in which the amino NH is in simultaneous contact with both carbonyls as suggested in the structures. Again, parallel experiments involving **6** in the complexes of **1** showed only enhancements of the imide carbonyl (11%). A bifurcated hydrogen bond appears preferred in the complex as of **1** even though a near perfect match in the Watson–Crick sense is presented by the imide portion.[9] The bifurcation in this system could be reinforced by the natural tendency of A–T base pairs to undergo a propellerlike twist in double-stranded DNA.[1]


7a

Bifurcated Hoogsteen


7b

Bifurcated Watson-Crick

In summary, the model system permits direct observation of Watson–Crick, Hoogsteen, and bifurcated hydrogen bonds, and the relative contributions of each can now be assessed.[10] It is our intent to use these new systems as a probe with intact nucleic acids in more biologically relevant media.[11]

Acknowledgment. We thank the National Science Foundation for support of this research.

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Infrared Spectroscopy of Matrix-Isolated Propadienone

Orville L. Chapman,* Michael D. Miller, and
Steven M. Pitzenberger†

Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, California 90024-1459

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Traditional valence bond theory predicts that propadienone ($H_2C{=}C{=}C{=}O$) should possess a linear heavy atom chain and that it should resemble formaldehyde more closely than ketene in its physical and chemical properties.[1] Since propadienone was first detected in 1976,[2,3] lively debate has ensued about its geometric and electronic structure.[4-8] Results from microwave spectroscopy contradict the valence bond predictions and show that the heavy atom chain is bent.[6-8] Calculations agree with this

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† Present address: Merck Sharp & Dohme Research Laboratories, West Point, PA 19486.

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Scheme I

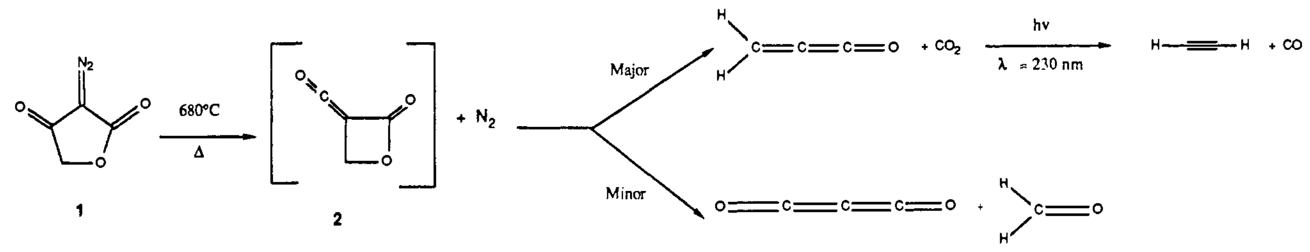

Table I. Experimental Frequencies and Relative Intensities for Propadienone

argon matrix		nitrogen matrix	
freq[a]	intensity[b]	freq[a]	intensity[b]
3049	1.37	3037	1.18
3024		3026	
2978	1.62	2978	1.16
2974		2968	
2603	0.58	2604	0.51
2177	14.21	2172	6.17
2125	72.06	2124	82.93
2079	0.83	2075	0.95
1959	0.68	1973	0.33
1690	1.16	1685	0.87
1444	0.65	1457	0.17
1046	3.44	1047	2.25
980	2.51	988	2.40
903	0.40	910	0.15
668	*c*	674	0.27
473	0.77	479	0.65

[a] Frequencies are in cm^{-1}. [b] Intensities are average values of integrated intensities for a series of experiments normalized to 100. [c] Peak detected as a shoulder on the 667 band of CO$_2$.

result, but only when performed above the Hartree–Fock level.[9-11] In order to more fully characterize this unique and highly reactive molecule, we undertook a study of the infrared spectrum of matrix-isolated propadienone.

Thermal cracking of acrylic anhydride is reported to be an efficient method for preparing propadienone in the gas phase.[12] Although propadienone prepared by this method can be trapped in a low-temperature matrix, the method is not suited to observing the infrared spectrum of propadienone because of interference from the residual starting material and the acrylic acid byproduct.

Propadienone for infrared strudies is conveniently prepared by gas-phase pyrolysis of 3-diazo-2,4(5*H*)-furandione (**1**, diazotetronic acid).[13] The diazo compound is sublimed at 0 °C and 10^{-5} torr through a quartz tube with a 5-cm hot zone (680 °C), and the resulting pyrolysate is codeposited with either argon or nitrogen onto a 14K CsI window (Figure 1). The pyrolysis proceeds cleanly and results in complete destruction of the diazo compound. Presumably diazotetronic acid undergoes a thermal Wolff contraction to lactoketene **2**[16] followed by fragmentation to propadienone and carbon dioxide (Scheme I). Small quantities (<10%) of formaldehyde and carbon suboxide are also formed via an alternate fragmentation. The absorption bands of these minor byproducts are easily recognized and do not interfere with the observation of propadienone. Propadienone prepared by this route is spectroscopically identical with propadienone prepared by the acrylic acid route.

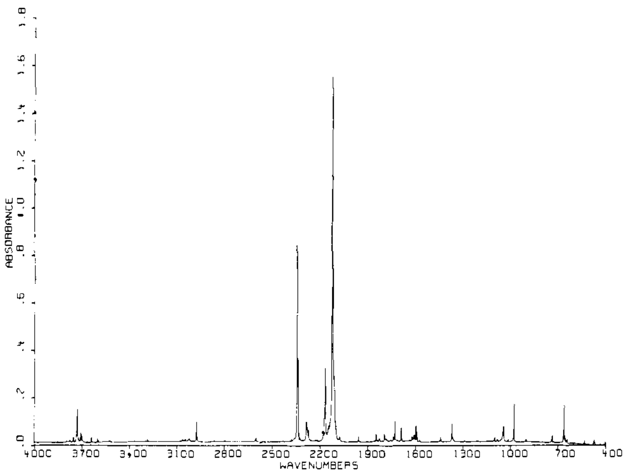

Figure 1. Infrared spectrum of propadienone and byproducts (see Scheme I) in argon at 14K generated by pyrolysis of diazotetronic acid.

The absorption bands observed for matrix-isolated propadienone (from the diazotetronic acid route) are listed in Table I. The degree of isolation, and therefore the quality of the IR data, depends strongly on the temperature of the CsI window on which the matrix is deposited. Thus, the cummulenic stretch ν_2 appears as a single intense band at 2125 cm^{-1} when the matrix is deposited at 14K. The band splits with a decrease in the observed frequency (2125, 2115, and 2105 cm^{-1}) when the matrix is deposited at 22K. At 30K, the ν_2 mode consists of three peaks of approximately equal intensity centered at 2100 cm^{-1}. The splitting of the ν_2 mode reflects various states of aggregation between propadienone and carbon dioxide (corresponding frequency changes are observed in the 649-cm^{-1} band of carbon dioxide) and possibly with itself. Annealing studies, which eliminate site effects, are consistent with this explanation. The 2100-cm^{-1} band previously reported[1] for propadienone is therefore due to complexed propadienone.

Irradiation of propadienone (λ = 230 ± 10 nm) gives acetylene and carbon monoxide as the only observable photoproducts. Acetylene is presumably formed via 1,1-ethenylidene, although this intermediate was not observed. Propargyl aldehyde and cyclopropanone, possible photorearrangement products, were not formed under these conditions.

Warming a matrix containing propadienone or thermal deposition directly onto the CsI window in the absence of argon produces a white insoluble polymer, which has not been characterized.

In conclusion, pyrolysis of diazotetronic acid (**1**) provides clean propadienone suitable for infrared studies. Our spectroscopic studies of deuteriated and alkylated propadienones and the related ethenylidenes as well as high-level ab initio calculations for detailed analysis continue.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (Grant CHE84-04994); the IBM Corporation provided a predoctoral fellowship (1986–1987) for Michael D. Miller; Merck Sharp & Dohme Research Laboratories provided a grant for publication costs.

Registry No. 1, 98026-98-3; propadienone, 61244-93-7; formaldehyde, 50-00-0; carbon suboxide, 504-64-3; acetylene, 74-86-2; carbon monoxide, 630-08-0.

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