

# Ab Initio Calculations of IR Spectra in Identification of Products of Matrix Isolation Photochemistry: Dewar Form of 4(3H)-Pyrimidinone

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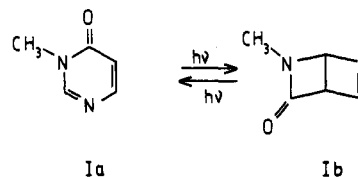
**Abstract:** *Ab initio* calculations of the infrared spectrum of the Dewar isomer of 3-methyl-4(3H)-pyrimidinone have been carried out at the MP2/6-31G\*\* and SCF/6-31G\*\* levels of theory. These were compared with the experimental spectrum of the photoproduct that emerged upon UV (308 nm) irradiation of 3-methyl-4(3H)-pyrimidinone isolated in a low-temperature argon matrix. The agreement between the spectrum simulated at the MP2 level and the experimental spectrum was remarkable and enabled positive assignment of the photoproduct structure. Photoreactions of matrix-isolated 4(3H)-pyrimidinones not methylated at the N3 nitrogen atom have also been studied. For these compounds, three types of photoreactions were observed, *i.e.*, phototautomerism, ring opening, and Dewar structure formation. The relative probabilities of the three competing reaction directions and their dependencies on ring substitutions have been investigated, and results are presented.

## Introduction

One of the fundamental problems of matrix-isolation photochemistry is the identification of the structures of photoproducts on the basis of their IR spectra. In the vast majority of matrix photochemistry experiments, photoproducts have been characterized by means of IR absorption spectroscopy. The simple identification procedure based on searching the spectra of unknown species for the IR bands with frequencies characteristic for specific groups of atoms is rarely a sufficient tool for analyzing the new products isolated in the low-temperature matrix. A more reliable way is to base the assignment on the *ab initio* calculations of vibrational spectra, which has been demonstrated for a number of small, unstable species isolated in matrices.<sup>1</sup> For photoproducts with more than 10 atoms, the IR spectra become closely spaced and the identification becomes more complicated, mandating more accurate theoretical prediction of the spectra. For such systems, higher orders of theoretical sophistication need to be used in predicting the IR frequencies and intensities to avoid misassignments and to enable positive structure determination. In the case of some photoproducts, it seems necessary to include electron correlation effects in the theoretical calculations due to strained bonds and angles.

The purpose of the present work was to demonstrate that an assignment procedure that combines the *ab initio* calculations with the matrix-isolation IR spectroscopy can be very effective in identifying the photoproducted species of medium size (10–20 atoms). As a test example, we consider here the Dewar isomer produced from 3-methyl-4(3H)-pyrimidinone upon UV irradiation (Scheme 1). The Dewar 4(3H)-pyrimidinone was first postulated by Takahashi *et al.*,<sup>2</sup> who studied the results of UV irradiation of 2,3,6-trialkyl-substituted 4(3H)-pyrimidinones in alcoholic solutions. Their assumption that the Dewar form was

Scheme 1. Photoreaction of 3-Methyl-4(3H)-pyrimidinone (Ia) to 6-Methyl-2,6-diazabicyclo[2.2.0]hex-2-en-5-one (Ib)



the primary product was based on the analysis of the secondary thermal reactions of the photoproducts with the solvent<sup>2a</sup> and subsequent isolation of the Dewar 4-pyrimidinone in crystalline form from a cooled ammonia–ether solution.<sup>2b</sup>

In previous works<sup>3,4</sup> on unsubstituted 4(3H)-pyrimidinone isolated in low-temperature matrices, we observed the UV-induced phototautomeric reaction leading to conversion of the oxo form into the hydroxy form. In order to inhibit the photoautomerism reaction and to observe other reaction channels, in particular the formation of the Dewar isomer, we considered in the present work the photoreactions of 3-methyl-4(3H)-pyrimidinone. We have chosen this molecule for the following reasons: first, the competing phototautomeric reaction cannot occur for this compound; second, the moderate size of this molecule makes good quality theoretical calculations feasible; and third, one could expect that the IR spectra of both the parent compound and its Dewar isomer should be relatively uncomplicated, enabling positive assignment of the spectra and subsequent structure determination.

Following successful spectral characterization of the Dewar isomer of 3-methyl-4(3H)-pyrimidinone, we repeated the experiment with unsubstituted 4(3H)-pyrimidinone. Upon re-

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examination of the spectrum and comparison of it with the spectrum of the methylated compound, we noticed that three competing photoreactions take place, *i.e.*, phototautomerism, ring opening, and Dewar structure formation. The same reactions were also observed for 4(3*H*)-pyrimidinone methylated in the 2- and 6-positions in the ring; however, the relative probabilities of the reactions changed with the methylation. In the second part of this paper, our spectroscopical study of the photochemistry of unmethylated and methylated 4(3*H*)-pyrimidinone is described.

### Experimental Section

The general procedure of matrix preparation was the same as that described elsewhere.<sup>5</sup> Matrices were deposited on the CsI window, mounted on the cold finger of a continuous flow helium cryostat. The temperature of the cold window was 6–7 K, and the temperature of the oven, from which the sample sublimated, was 325 K for 3-methyl-4(3*H*)-pyrimidinone and 400 K for 4(3*H*)-pyrimidinone, 6-methyl-4(3*H*)-pyrimidinone, and 2,6-dimethyl-4(3*H*)-pyrimidinone. Argon of spectral grade was purchased from VEB Technische Gase, Leipzig, Germany. Infrared spectra were recorded on a Perkin-Elmer 580B spectrometer. Band intensities were obtained by means of numerical integration. Samples of 4(3*H*)-pyrimidinone and 2,6-dimethyl-4(3*H*)-pyrimidinone were obtained from Aldrich Chemical Co., Inc. 3-Methyl-4(3*H*)-pyrimidinone was prepared according to the procedures given in ref 6. A sample of 6-methyl-4(3*H*)-pyrimidinone was kindly supplied to us by Dr. K. Felczak (Institute of Biochemistry and Biophysics, Polish Academy of Sciences, Warsaw, Poland). Prior to the experiments, the samples were purified by vacuum sublimation. The matrices were irradiated with the 308-nm (XeCl) line of the LPX 100 Lambda Physik excimer laser (pulse energy 75 mJ, repetition rate 50 Hz). In some cases, matrices were additionally irradiated with the light from a 200-W high-pressure mercury lamp (HBO 200) passed through a water filter and an appropriate cutoff filter.

**Theoretical Calculations.** The IR spectra of the species considered in this work were calculated with the use of the SCF and MP2 analytical derivative procedures incorporated in the GAUSSIAN 92 program.<sup>7</sup> All calculations were performed on a CONVEX C220 computer. The geometrical coordinates of the 6-methyl-2,6-diazabicyclo[2.2.0]hex-2-en-5-one molecule, which is the Dewar isomer of 3-methyl-4(3*H*)-pyrimidinone, optimized at SCF/6-31G\*\* and MP2/6-31G\*\* levels of theory, are available from the authors of this paper upon request. Atom numbering and internal coordinates characterizing the bent ring of the Dewar form are given in Table 1.

The relative stabilities of the Dewar forms with respect to planar ring isomers were estimated for 4(3*H*)-pyrimidinone and 3-methyl-4(3*H*)-pyrimidinone at the MP2 level using the standard 6-31G\*\* basis set. Results of these calculations are presented in Table 2.

The following procedure was applied in the analysis of the theoretical spectra of the Dewar form of 3-methyl-4(3*H*)-pyrimidinone. The calculated wavenumbers of all normal modes were scaled down by 0.90 for the SCF calculation and by 0.96 for the MP2 calculation. This is a commonly used procedure to approximately correct the results for the anharmonicity of the vibrations and, in the case of SCF calculations, for electronic correlation contributions. To express the normal modes in the molecule's fixed coordinate system, we defined a set of internal coordinates (Table 3). The force constant matrices expressed in terms of Cartesian coordinates were transformed into internal coordinates, and the potential energy distribution matrices were calculated. The potential energy distribution components (PEDs) of the normal modes greater than 10% are reported in Table 4.

### Results and Discussion

**1. Identification of the Dewar Form of 3-Methyl-4(3*H*)-pyrimidinone.** The survey IR spectrum of 3-methyl-4(3*H*)-pyrimidinone isolated in argon matrix is presented in Figure 1A.

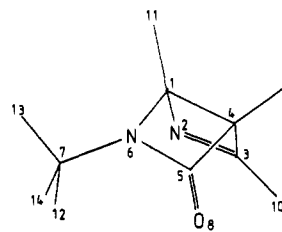
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**Table 1.** Bond distances, bond angles in four-membered rings, and torsional angles between the rings at the geometry optimized at the MP2/6-31G\*\* level for

6-Methyl-2,6-diazabicyclo[2.2.0]hex-2-en-5-one (the values optimized at SCF/6-31G\*\* level are given in parentheses); atom numbering is shown below



Bond Distances (Å)			
C1–N2	1.5173 (1.4872)	C5–O8	1.2162 (1.1855)
C1–C4	1.5470 (1.5380)	C1–H11	1.0865 (1.0787)
C1–N6	1.4506 (1.4438)	C4–H9	1.0853 (1.0786)
N2–C3	1.3041 (1.2630)	C3–H10	1.0853 (1.0780)
C3–C4	1.5091 (1.5151)	C7–H12	1.0877 (1.0814)
C4–C5	1.5486 (1.5374)	C7–H13	1.0884 (1.0837)
C5–N6	1.3884 (1.3673)	C7–H14	1.0910 (1.0858)
N6–C7	1.4475 (1.4413)		
Bond Angles <sup>a</sup> (deg)			
N6–C4–C1	89.30 (88.80)	N2–C4–C1	90.22 (89.55)
C1–C5–C4	84.48 (84.56)	C1–C3–C4	80.45 (79.98)
C4–N6–C5	91.55 (91.68)	C4–N2–C3	100.77 (99.77)
C5–C1–N6	94.25 (94.71)	C3–C1–N2	88.45 (90.66)
Torsional Angles <sup>b</sup> (deg)			
N6–C4–C1–N2	114.25 (114.72)	C5–C1–C4–C3	111.89 (112.44)

<sup>a</sup> A–B–C is the angle between bonds A–C and B–C. <sup>b</sup> A–B–C–D is the dihedral angle between the plane defined by atoms A, B, and C and the plane defined by atoms B, C, and D.

**Table 2.** Total Electronic and Nuclear Vibration Energies of 4(3*H*)-Pyrimidinone and 3-Methyl-4(3*H*)-pyrimidinone in Their Planar and Dewar Isomers<sup>a</sup>

	4(3 <i>H</i> )-Pyrimidinone	
	planar	Dewar
SCF/6-31G**	–337.578 935	–337.487 231
SCF + MP2/6-31G**	–338.575 336	–338.493 733
0.9 × ZPE/6-31G**	0.084 441	0.083 098
total	–338.490 895	–338.410 635
cumulative Relative Stability (kJ/mol)	0.0	210.9
	3-Methyl-4(3 <i>H</i> )-pyrimidinone	
	planar	Dewar
SCF/6-31G**	–376.611 276	–376.522 608
SCF + MP2/6-31G**	–377.754 506	–377.673 808
0.9 × ZPE/6-31G**	0.112 452	0.105 464
total	–377.642 054	–377.568 344
cumulative Relative Stability (kJ/mol)	0.0	193.7

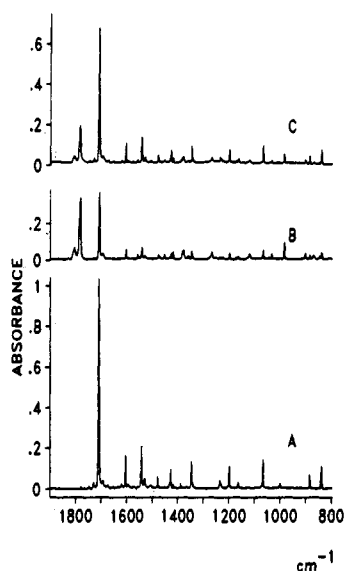
<sup>a</sup> All calculations performed on geometry-optimized molecules at the SCF/6-31G\*\* level. Energies in hartrees, relative energies in kJ/mol.

The effect of 4 h of irradiation of this compound with light from the XeCl excimer laser ( $\lambda = 308$  nm) is shown in Figure 1B. After such irradiation, about 65% of the initial amount of 3-methyl-4(3*H*)-pyrimidinone was converted into a photoproduct. In the infrared spectrum of the photoproduct, the most pronounced feature was a strong band at 1784  $\text{cm}^{-1}$ . This band could be assigned to a stretching vibration of the C=O group attached to a smaller (four- or three-membered) ring, because its frequency is much higher than that of the  $\nu$  C=O vibration (1709  $\text{cm}^{-1}$ ) in the six-membered ring substrate molecule. Upon subsequent irradiation of the matrix with the light from a high-pressure mercury lamp fitted with cutoff filters, we observed a decrease of the intensities of the bands due to the photoproduct and an

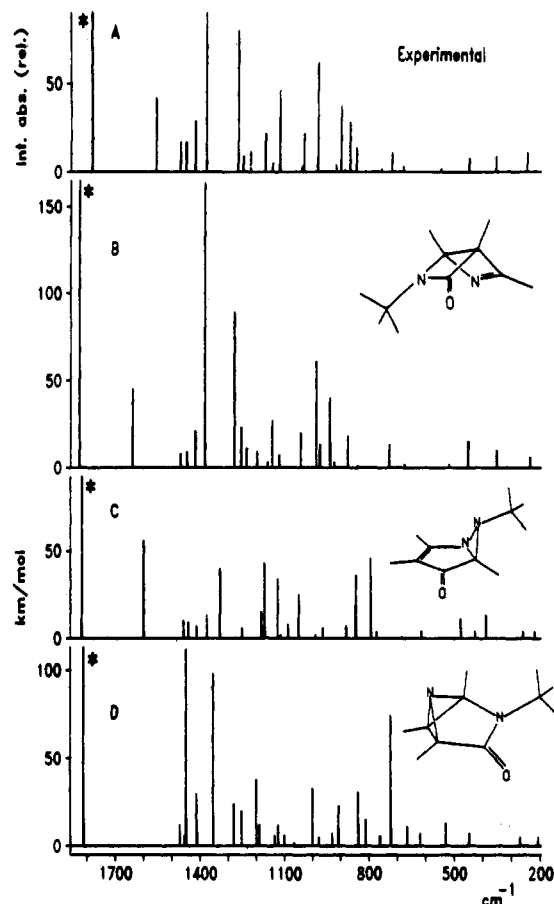
**Table 3.** Internal Coordinates Used in the Normal Modes Analysis for 6-Methyl-2,6-diazabicyclo[2.2.0]hex-2-en-5-one (atom numbering as in Table 1)

$S_1 = r_{1,2}$	$\nu$ C1N2
$S_2 = r_{2,3}$	$\nu$ N2C3
$S_3 = r_{3,4}$	$\nu$ C3C4
$S_4 = r_{4,5}$	$\nu$ C4C5
$S_5 = r_{5,6}$	$\nu$ C5N6
$S_6 = r_{6,1}$	$\nu$ N6C1
$S_7 = r_{1,4}$	$\nu$ C1C4
$S_8 = r_{5,8}$	$\nu$ CO
$S_9 = r_{1,11}$	$\nu$ C1H
$S_{10} = r_{3,10}$	$\nu$ C3H
$S_{11} = r_{4,9}$	$\nu$ C4H
$S_{12} = r_{6,7}$	$\nu$ N6C7
$S_{13} = (3^{-1/2})(r_{7,12} + r_{7,13} + r_{7,14})$	$\nu$ Me1
$S_{14} = (6^{-1/2})(2r_{7,12} - r_{7,13} - r_{7,14})$	$\nu$ Me2
$S_{15} = (2^{-1/2})(r_{7,13} - r_{7,14})$	$\nu$ Me3
$S_{16} = (1/2)(\beta_{1,5,6} - \beta_{6,4,5} + \beta_{5,1,4} - \beta_{4,6,1})$	$\beta$ R1
$S_{17} = (1/2)(\beta_{4,2,3} - \beta_{3,1,2} + \beta_{2,4,1} - \beta_{1,3,4})$	$\beta$ R2
$S_{18} = (2^{-1/2})(\beta_{8,6,5} - \beta_{8,4,5})$	$\beta$ CO
$S_{19} = (2^{-1/2})(\beta_{10,4,3} - \beta_{10,2,3})$	$\beta$ C3H
$S_{20} = (2^{-1/2})(\beta_{7,1,6} - \beta_{7,5,6})$	$\beta$ N6C7
$S_{21} = \beta_{9,1,4}$	$\beta$ C4H
$S_{22} = \beta_{11,4,1}$	$\beta$ C1H
$S_{23} = (6^{-1/2})(\beta_{12,13,7} + \beta_{12,14,7} + \beta_{13,14,7} + \beta_{13,6,7} - \beta_{13,6,7} - \beta_{14,6,7})$	$\beta$ Me1
$S_{24} = (6^{-1/2})(2\beta_{13,14,7} - \beta_{12,13,7} - \beta_{12,14,7})$	$\beta$ Me2
$S_{25} = (6^{-1/2})(2\beta_{12,6,7} - \beta_{13,6,7} - \beta_{14,6,7})$	$\beta$ Me3
$S_{26} = (2^{-1/2})(\beta_{12,13,7} - \beta_{12,14,7})$	$\beta$ Me4
$S_{27} = (2^{-1/2})(\beta_{13,6,7} - \beta_{14,6,7})$	$\beta$ Me5
$S_{28} = (1/2)(\tau_{1,6,5,4} - \tau_{6,5,4,1} + \tau_{5,4,1,6} - \tau_{4,1,6,5})$	$\tau$ R1
$S_{29} = (1/2)(\tau_{4,3,2,1} - \tau_{3,2,1,4} + \tau_{2,1,4,3} - \tau_{1,4,3,2})$	$\tau$ R2
$S_{30} = (6^{-1/2})(\tau_{13,7,6,5} + \tau_{13,7,6,1} + \tau_{14,7,6,5} + \tau_{14,7,6,1} + \tau_{12,7,6,5} + \tau_{12,7,6,1})$	$\tau$ Me
$S_{31} = (2^{-1/2})(\tau_{11,1,4,5} + \tau_{11,1,4,3})$	$\tau$ C1H
$S_{32} = (2^{-1/2})(\tau_{9,4,1,6} + \tau_{9,4,1,2})$	$\tau$ C4H
$S_{33} = (2^{-1/2})(\tau_{6,1,4,3} - \tau_{5,4,1,2})$	$\tau$ R1R2
$S_{34} = \gamma_{7,5,6,1}$	$\gamma$ N6C7
$S_{35} = \gamma_{8,4,5,6}$	$\gamma$ CO
$S_{36} = \gamma_{10,2,3,4}$	$\gamma$ C3H

<sup>a</sup>  $r_{ij}$  is the distance between atoms  $A_i$  and  $A_j$ .  $\beta_{ij,k}$  is the angle between vectors  $A_kA_i$  and  $A_kA_j$ .  $\gamma_{i,j,k,l}$  is the angle between the vector  $A_kA_i$  and the plane defined by atoms  $A_j, A_k, A_l$ .  $\tau_{i,j,k,l}$  is the dihedral angle between the plane defined by atoms  $A_i, A_j, A_k$  and the plane defined by atoms  $A_j, A_k, A_l$ .

**Figure 1.** (A) IR absorption spectrum of argon matrix-isolated 3-methyl-4(3H)-pyrimidinone (1900–800  $\text{cm}^{-1}$ ). (B) Effect of 4 h of excimer laser UV ( $\lambda = 308$  nm) irradiation of the matrix. (C) Effect of subsequent 1 h irradiation with high-pressure mercury lamp ( $\lambda > 250$  nm).

increase in the bands due to the substrate (it is best seen on the two  $\nu$  C=O bands of the product at 1784  $\text{cm}^{-1}$  and the substrate at 1709  $\text{cm}^{-1}$  in Figures 1B and 1C). These changes were

**Figure 2.** Comparison of the experimental IR spectrum of the photoproduct emerging upon UV irradiation of 3-methyl-4(3H)-pyrimidinone (A) with the IR spectra theoretically calculated (at the SCF/6-311G\*\* level) for three likely photoproduct structures: the Dewar isomer (B), the [3.1.0] bicyclic isomer (C), and the benzvalene-like isomer (D). Trace A presents in the “stick” form the spectrum obtained by subtracting the bands due to the planar form (Figure 1A) from the spectrum obtained after irradiation (Figure 1B), see also Figure 3. The bands marked with asterisks are very intense. For trace A; the relative integral absorbance is 441. For traces B, C, and D, the absolute intensities are 671, 493, and 526  $\text{km/mol}$ , respectively.

apparently caused by the back reaction leading to partial consumption of the photoproduct and to recovery of starting material. After 1 h of continuous irradiation, photostationary states emerged, which were different for different filters transmitting light with  $\lambda > 270$  and  $\lambda > 250$  nm. The photostationary state established upon irradiation with light  $\lambda > 250$  nm is shown in Figure 1C. Occurrence of the back reaction suggests that the photoproduct does not result from a photodecomposition of 4-pyrimidinone but rather from photoinduced isomerization.

Taking into account the results of Takahashi *et al.*,<sup>2</sup> who found that the primary products of the photochemical reactions of 4-pyrimidinones in solution are Dewar structures, we might anticipate that the same photoproducts would appear in photochemical reactions of matrix-isolated 3-methyl-4(3H)-pyrimidinone (Scheme 1). In order to test this prediction, we followed the “ideal procedure” for comparing experimental and theoretical IR spectra proposed by Hess *et al.*<sup>1a</sup>. The procedure required that besides the spectrum of the Dewar isomer of 3-methyl-4(3H)-pyrimidinone, we also calculated theoretically the infrared spectra of two other, more plausible isomers of this compound, *i.e.*, the [3.1.0] bicyclic isomer structure known from the studies of photochemistry of linearly conjugated cyclohexadienones and the benzvalene-like isomer. The IR spectra of these structures were predicted theoretically at the SCF/6-311G\*\* level. They are compared with the experimental spectra of the photoproduct in Figure 2.

**Table 4.** Experimental Wavenumbers ( $\bar{\nu}$ ), Integral Intensities ( $I$ ), and Assignments to the Normal Modes (Q) of the Bands Observed in Ar Matrix Compared with the Theoretically Calculated Wavenumbers, Absolute Intensities ( $A^{\text{th}}$ ), and Potential Energy Distribution (PED) of the Absorption Bands of 6-Methyl-2,6-diazabicyclo[2.2.0]hex-2-en-5-one<sup>a</sup>

mode no.	experimental Ar matrix		calculated			
	$\bar{\nu}$ (cm <sup>-1</sup> )	$I$ (rel)	$\bar{\nu}^b$ (cm <sup>-1</sup> )	$A^{\text{th}}$ (km/mol)	PED (%)	SCF/6-31G**
Q1			3121	16	$\nu$ C3H (67), $\nu$ C4H (31)	3015 21 $\nu$ C3H (91)
Q2			3118	5	$\nu$ Me2 (95)	2973 9 $\nu$ Me 2 (95)
Q3			3110	11	$\nu$ C4H (66), $\nu$ C3H (32)	2995 14 $\nu$ C4H (76), $\nu$ C1H (16)
Q4			3093	18	$\nu$ C1H (96)	2986 26 $\nu$ C1H (83), $\nu$ C4H (17)
Q5			3089	18	$\nu$ Me 3 (94)	2934 36 $\nu$ Me 3 (97)
Q6			2997	33	$\nu$ Me 1 (97)	2873 47 $\nu$ Me 1 (93)
Q7	1784	441	1780	404	$\nu$ CO (82)	1845 631 $\nu$ CO (85)
Q8	1806					
	1558	28	1518	16	$\nu$ N2C3 (80), $\beta$ C3H (15)	1658 44 $\nu$ N2C3 (90)
	1549					
	1544					
Q9	1472	11	1504	5	$\beta$ Me 2 (85)	1479 7 $\beta$ Me 2 (78), $\beta$ Me 3 (10)
Q10	1452	11	1481	7	$\beta$ Me 4 (93)	1455 8 $\beta$ Me 4 (92)
Q11	1419	20	1423	12	$\beta$ Me 1 (90)	1427 23 $\beta$ Me 1 (75), $\beta$ Me 4 (10)
	1381					
Q12	1378	60	1375	101	$\nu$ N6C7 (28), $\nu$ C5N6 (27)	1394 165 $\nu$ C5N6 (26), $\nu$ N6C7 (23), $\beta$ Me 1 (17)
	1358					
Q13	1267	53	1271	47	$\beta$ C3H (38), $\nu$ N2C3 (11), $\nu$ N6C1 (10)	1289 88 $\beta$ C3H (32), $\nu$ N6C1 (10), $\tau$ C1H (10)
Q14	1248	6	1251	17	$\beta$ Me3 (22), $\nu$ N6C1 (18), $\tau$ C1H (16), $\beta$ C3H (14)	1262 23 $\beta$ Me3 (23), $\nu$ N6C1 (21), $\tau$ C1H (10)
Q15	1223	8	1227	13	$\tau$ C1H (69), $\beta$ C3H (10)	1247 11 $\tau$ C1H (61), $\beta$ C3H (13)
	1172					
Q16	1165	15	1177	14	$\tau$ C4H (43), $\nu$ C1C4 (15)	1211 8 $\tau$ C4H (41), $\nu$ C1C4 (13), $\beta$ C1H (10)
Q17	1144	3	1154	3	$\beta$ C1H (48), $\beta$ C3H (18)	1172 2 $\beta$ C1H (33), $\beta$ C3H (25), $\tau$ C3H (15), $\nu$ C1C4 (14)
Q18	1119	31	1127	24	$\beta$ Me 5 (52), $\beta$ C4H (23)	1125 7 $\beta$ Me 5 (88)
Q19	1130	3	1122	7	$\beta$ Me5 (35), $\beta$ C4H (26), $\tau$ C4H (13)	1156 26 $\beta$ C4H (56), $\beta$ C1H (15), $\nu$ C1C4 (11)
	1040	2				
Q20	1033	15	1023	30	$\nu$ C4C5 (28), $\beta$ CO (16), $\nu$ C5N6 (14), $\beta$ R1 (10)	1053 20 $\nu$ C4C5 (25), $\beta$ CO (14), $\beta$ R1 (12), $\nu$ C5N6 (11)
Q21			988	37	$\nu$ C3C4 (19), $\nu$ N6C1 (18), $\beta$ Me3 (15), $\gamma$ C3H (14)	995 59 $\beta$ Me 3 (31), $\nu$ N6C1 (29), $\nu$ C5N6 (10)
Q22	984	41	976	11	$\nu$ C3C4 (33), $\nu$ N6C1 (18), $\beta$ Me3 (14)	982 13 $\gamma$ C3H (35), $\nu$ C3C4 (29), $\nu$ C1N2 (17)
Q23	919	3	913	7	$\gamma$ C3H (47), $\beta$ R2 (25)	944 39 $\nu$ C1N2 (42), $\tau$ R1 (13), $\gamma$ C3H (11), $\beta$ R2 (10)
Q24	902	25	893	27	$\nu$ C1N2 (42), $\tau$ R1 (13), $\gamma$ C3H (10), $\beta$ R2 (10)	930 3 $\beta$ R2 (34), $\gamma$ C3H (24), $\nu$ C3C4 (13), $\tau$ C4H (12)
	887	1				
Q25	870	19	869	6	$\nu$ C1C4 (29), $\beta$ C1H (24), $\beta$ C4H (17), $\beta$ R2 (11)	883 16 $\beta$ C1H (20), $\nu$ C3C4 (15), $\beta$ R2 (13), $\nu$ C1C4 (12)
Q26	847	9	842	11	$\nu$ C1N2 (31), $\beta$ R2 (18), $\beta$ C4H (13)	850 2 $\nu$ C1C4 (29), $\beta$ C4H (27)
Q27	758	1	759	1	$\nu$ C4C5 (25), $\nu$ C5N6 (14), $\beta$ R1 (10)	776 0.5 $\nu$ C4C5 (20), $\nu$ C5N6 (14), $\beta$ R1 (13)
Q28	721	7	702	8	$\beta$ R2 (20), $\beta$ R1 (19), $\beta$ CO (16), $\nu$ N6C7 (11)	730 14 $\gamma$ CO (21), $\beta$ R2 (16), $\beta$ CO (16)
Q29	681	2	662	3	$\gamma$ CO (45), $\beta$ R1 (12), $\nu$ N6C7 (10)	679 2 $\nu$ N6C7 (24), $\gamma$ CO (23), $\beta$ CO (19)
Q30	548	1	500	2	$\beta$ R1 (19), $\tau$ R1R2 (18), $\tau$ R2 (18)	520 2 $\tau$ R2 (21), $\tau$ R1 (20), $\tau$ R1R2 (18)
Q31	450	5	447	11	$\tau$ R1R2 (29), $\beta$ CO (23)	453 15 $\tau$ R1R2 (29), $\beta$ CO (24), $\nu$ N6C1 (10)
Q32	356	6	339	7	$\tau$ R2 (48), $\nu$ C4C5 (13), $\beta$ CO (12), $\tau$ R1R2 (12)	354 11 $\tau$ R2 (44), $\tau$ R1R2 (14), $\nu$ C4C5 (13), $\beta$ CO (13)
Q33	248	7	228	5	$\beta$ N6C7 (70), $\beta$ CO (13)	238 6 $\beta$ N6C7 (72), $\beta$ CO (13)
Q34			160	5	$\tau$ R1 (65), $\gamma$ CO (21)	165 7 $\tau$ R1 (66), $\gamma$ CO (21), $\tau$ R1R2 (10)
Q35			135	0.2	$\tau$ Me (92)	117 0.2 $\tau$ Me (90)
Q36			127	10	$\gamma$ N6C7 (81), $\tau$ R1R2 (11)	129 11 $\gamma$ N6C7 (82)

<sup>a</sup> PEDs lower than 10% not included. Abbreviations:  $I$ , integral absorbances of absorption bands normalized in such a way that the observed intensity sum of all modes is equal to the MP2 calculated intensity sum of all modes;  $A^{\text{th}}$ , calculated intensities; rel, relative;  $\nu$ ,  $\beta$ ,  $\tau$ ,  $\gamma$  are defined in Table 3. <sup>b</sup> Theoretical positions of absorption bands scaled by the factor 0.96 (MP2 calculation) or 0.90 (SCF calculation).

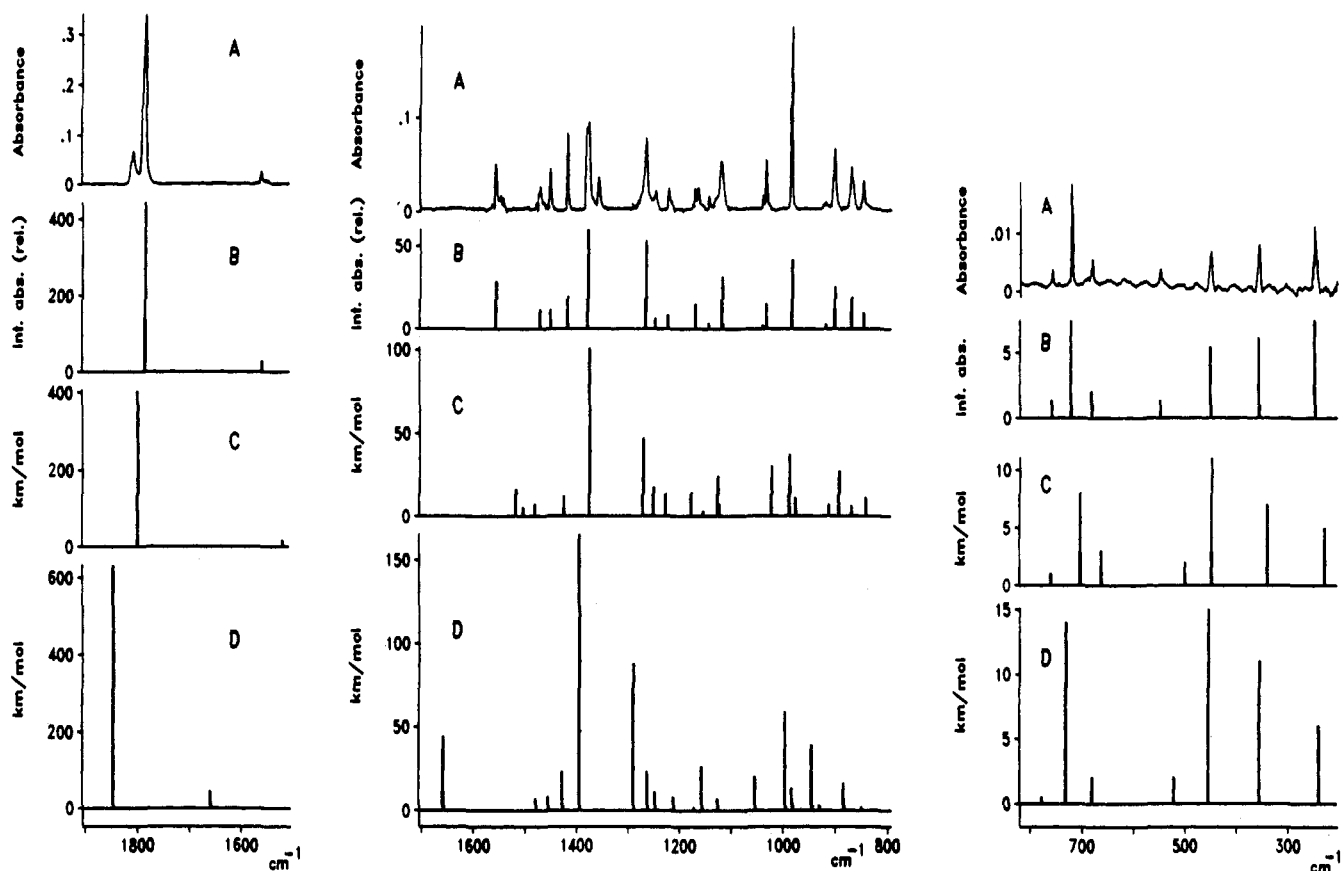
From this comparison, one notices that the spectrum predicted for the Dewar structure fits in better with the experimental spectrum than the spectra predicted for the two other photoisomers.

In order to test whether our theoretically predicted IR spectrum of the Dewar form is sufficiently converged in terms of the quality of the basis sets, geometry optimizations and the frequency calculations were repeated at SCF/6-311G(2d,p) and SCF/6-31G\*\* levels of theory. In both cases, the obtained spectral patterns were virtually the same as that obtained with 6-311G\*\* basis set, indicating that the results cannot be much improved by extending the basis set and that the 6-31G\*\* basis set is quite sufficient at the SCF level of theory. There can be, however, a significant error due to lack of the electronic correlation effects in the SCF calculation. In molecules with strained bonds and angles, one can expect a particularly sizeable contribution from nondynamical electronic correlation. Therefore, we anticipated that the MP2 method should provide a better prediction of the IR spectra of the Dewar isomer than the SCF method. The spectra predicted at MP2/6-31G\*\* and SCF/6-31\*\* levels of

theory are compared with the experimental spectrum in Figure 3. The remarkable agreement between the spectrum predicted at the MP2/6-31G\*\* level and the experimental spectrum of the photoproduct seems to support our expectation as to the size of the correlation contribution and provides a sufficient basis for positive assignment of the Dewar isomer. This result indicates that the theoretically predicted infrared spectrum, if generated at an appropriately high level of theory, offers a very viable tool for identification of medium-size photoproducts trapped in low-temperature matrices.

The agreement of the spectral pattern predicted at the SCF level with the experimental spectrum is somewhat less apparent than that for the spectrum obtained at the MP2 level of theory. The main difference between the spectra predicted at the SCF and MP2 levels can be observed in the region 950–800 cm<sup>-1</sup> (see Figure 3 and Table 4). The four bands present in this region are most adequately reproduced in the MP2 calculation.

At both the SCF and MP2 levels, the frequency of the normal mode due to the stretching vibration of the double bond N2=C3 seems to be less accurately predicted than the frequencies of



**Figure 3.** Comparison between the experimental and *ab initio* predicted IR spectra of 6-methyl-2,6-diazabicyclo[2.2.0]hex-2-en-5-one (**IIb**). (A) The experimental spectrum of the photoproduct obtained by subtracting the bands due to the planar form (Figure 1A) from the spectrum obtained after irradiation (Figure 1B). (B) The same spectrum presented in "stick" form. (C) Theoretical spectrum of **1b** calculated at the MP2/6-31G\*\* level. (D) Theoretical spectrum of **1b** calculated at the SCF/6-31G\*\* level. The split bands (probably due to the "matrix effect") including those at 1806, 1784, and 1381, 1378, 1358  $\text{cm}^{-1}$ , are presented in trace B as single sticks. Their heights correspond to the sum of the intensities of the components.

other modes. At the SCF level, the frequency of the  $\nu$  N2C3 mode is overestimated by 100  $\text{cm}^{-1}$ , and at the MP2 level it is underestimated by 40  $\text{cm}^{-1}$ . Fortunately, the corresponding experimental band at 1558  $\text{cm}^{-1}$  is placed in the region, in which there are no other bands, and because of that its assignment caused no problems (see Figure 3). The large difference between the SCF and MP2 values of the N2C3 bond length indicates that there is a significant contribution of nondynamical electron correlation to the wave function near this bond. It would, undoubtedly, require inclusion of higher order correlation corrections to obtain a convergence value for the lengths of this bond as well as to obtain a better agreement of the calculated frequency of the  $\nu$  N2C3 mode with the experimental frequency.

The three bands, with frequencies between 1500 and 1400  $\text{cm}^{-1}$ , are due to the bending vibrations of the methyl group and are well predicted at both SCF and MP2 levels of theory. In the lower frequency region, the PED analysis of the calculated normal modes indicate that the vibrations are not localized in any particular group of atoms in the molecule. It seems worth noting that the experimental spectral pattern at the lowest frequencies (below 800  $\text{cm}^{-1}$ ) is well predicted at both MP2 and SCF levels of theory.

**2. Photochemistry of 4(3H)-Pyrimidinones.** For 4(3H)-pyrimidinones not methylated at the N3 atom, the formation of the Dewar structure upon irradiation may compete with the phototautomeric reaction (oxo  $\rightarrow$  hydroxy) described in our previous works.<sup>3,4,8-10</sup> The third phototautomeric reaction,  $\alpha$ -bond cleavage, leading to formation of conjugated ketenes, may also

be anticipated. Such a ring-opening reaction was previously observed and widely studied for 2,4-cyclohexadienones,<sup>11-13</sup>  $\alpha$ -pyrones,<sup>14-16</sup> 2(1H)-pyridinone,<sup>8</sup> 4(3H)-pyrimidinone,<sup>4</sup> and 3(2H)-pyridazinone<sup>9</sup> frozen in low-temperature matrices. The three photoreactions that may occur for nonsubstituted 4(3H)-pyrimidinones are presented in Scheme 2.

The results of UV irradiation of matrix-isolated 4(3H)-pyrimidinone (**IIa**) were reported previously.<sup>3,4</sup> Upon closer examination of these results, we noticed that simultaneously with the most pronounced photochemical processes, phototautomerism, and a photoreversible ring opening, another side reaction takes place. The only sign of this process is the appearance in the spectrum of a new very weak band at 1812  $\text{cm}^{-1}$  (see Figure 4B). The effects of UV (308 nm) irradiation of unsubstituted 4(3H)-pyrimidinone are shown in Figure 4. The spectrum obtained just after deposition is composed of two sets of bands due to two tautomeric forms: oxo and hydroxy in similar amounts (Figure 4A).<sup>3,4</sup> The spectrum after UV irradiation is shown in Figure 4B. The dominance of the phototautomeric reaction (**IIa**  $\rightarrow$  **IIc**) is striking for this compound. The bands due to the oxo form become weaker, whereas the bands due to the hydroxy form increase (see Figure 4). In the course of irradiation, a new band appears at 2139  $\text{cm}^{-1}$ . It subsequently increases and after

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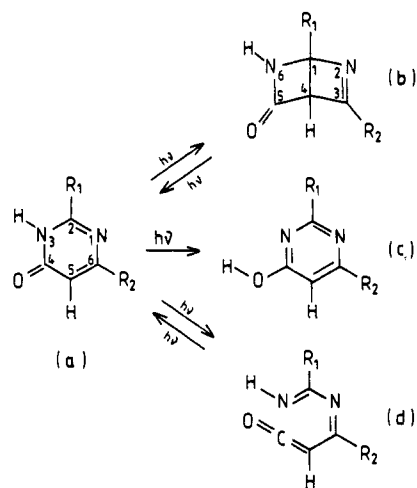
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**Scheme 2.** Photoreactions of 4(3*H*)-Pyrimidinone (**IIa**; R<sub>1</sub> = H, R<sub>2</sub> = H), 6-Methyl-4(3*H*)-pyrimidinone (**IIIa**; R<sub>1</sub> = H, R<sub>2</sub> = CH<sub>3</sub>), and 2,6-Dimethyl-4(3*H*)-pyrimidinone (**IVa**; R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = CH<sub>3</sub>) to Respective Dewar Forms **IIb**, **IIIb**, and **IVb**, Hydroxy Tautomers **IIc**, **IIIc**, and **IVc**, and Conjugated Ketenes **IIId**, **IIIId**, and **IVd**



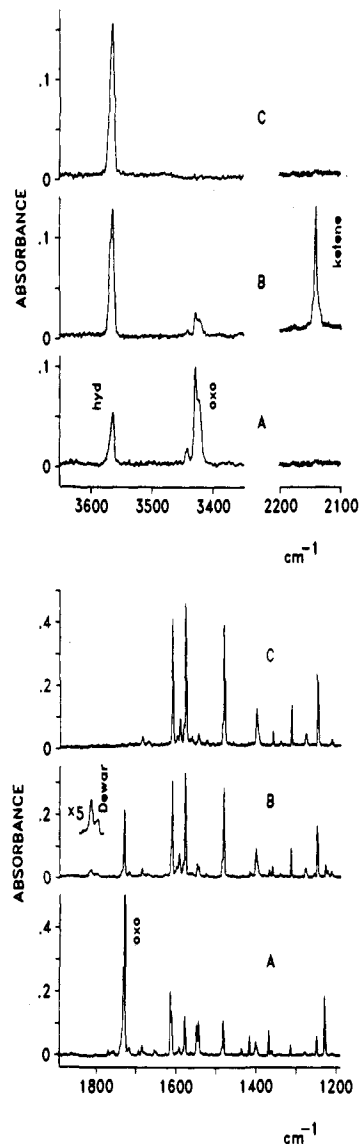
prolonged irradiation decreases. We interpret this band<sup>4</sup> as due to the  $\nu$ -C=C=O antisymmetric stretch of a conjugated ketene (**IIId**).

In this case, the Dewar form (**IIb**) is produced only in trace amounts; so little, in fact, that the most intense band of this form,  $\nu$  C=O, is barely noticeable at 1812  $\text{cm}^{-1}$ . After prolonged UV (308 nm) irradiation, the conjugated ketene, the Dewar form, and the oxo tautomer disappear totally and all the molecules convert to the hydroxy tautomeric form (**IIc**) (Figure 4C).

For 6-methyl-4(3*H*)-pyrimidinone (**IIIa**), the UV-induced (308 nm) change of the tautomeric form (**IIIa**  $\rightarrow$  **IIIc**) is still the most pronounced photoreaction, but the Dewar structure (**IIIb**), with its  $\nu$  C=O band clearly visible at 1810, 1800  $\text{cm}^{-1}$  (split into two components), is produced in larger amounts than that for unsubstituted 4(3*H*)-pyrimidinone (**IIa**). At the stage of the photoreaction when all the planar oxo form of 6-methyl-4(3*H*)-pyrimidinone was consumed (Figure 5B), we observed in the high-frequency region (at 3438 (3450 sh)  $\text{cm}^{-1}$ ) a band due to stretching vibration of the NH group in the Dewar form (**IIIb**). Upon subsequent irradiation with UV light ( $\lambda > 250$  nm), the decrease of the population of the Dewar isomer and partial recovery of the starting planar 6-methyl-4(3*H*)-pyrimidinone was observed. The recovering population of the oxo form was in turn reduced in the phototautomeric reaction, leading to a further increase in the population of the hydroxy form (**IIIc**). As for 4(3*H*)-pyrimidinone, the photoreversible ring-opening reaction was observed for 6-methyl-4(3*H*)-pyrimidinone too. The strongest split band at 2139 and 2132  $\text{cm}^{-1}$  of the conjugated ketene (**IIIId**) is shown in Figure 5B. Intensities of the  $\nu$ -C=C=O antisymmetric stretching band (that near 2140  $\text{cm}^{-1}$ ), presented in Figures 4 and 5, correspond to that stage of the photoreaction when the concentration of the ketene was at maximum. After prolonged irradiation, the concentration of the ketene declined to vanished completely.

Irradiation with UV light (308 nm) of 2,6-dimethyl-4(3*H*)-pyrimidinone (**IVa**) caused much more pronounced production of the Dewar form (**IVb**). About two-thirds of the starting planar oxo form was converted into the Dewar isomer, while only one-third was transformed to the hydroxy tautomer (see Figure 6). The opened ring isomer (**IVd**) was observed only in very tiny quantities—its  $\nu$ -C=C=O “antisymmetric” stretching band of very low relative intensity is shown in Figure 6B. At no stage of this photoreaction was the ketene concentration any higher.

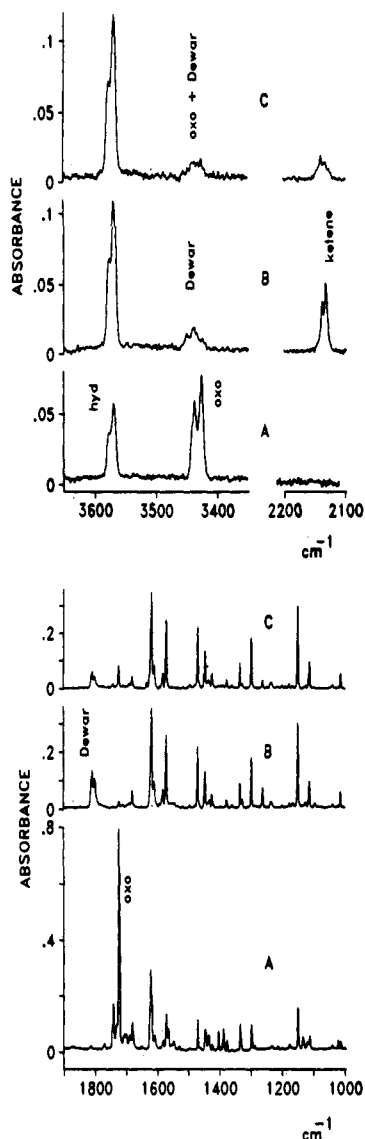
There is, hence, a clear relation between the number of methyl substituents in the ring and the predominant direction of the



**Figure 4.** (A) IR absorption spectrum of argon matrix-isolated 4(3*H*)-pyrimidinone before irradiation (only the lower absorbance half of the band at 1727  $\text{cm}^{-1}$  is shown—absorbance in maximum was 0.95). (B) Effect of 15 min of excimer laser UV ( $\lambda = 308$  nm) irradiation of the matrix. (C) Effect of further 15 min of UV ( $\lambda = 308$  nm) irradiation. photoreaction. The more methyl substituents, the more pronounced the photoinduced Dewar isomer formation becomes and the more suppressed phototautomeric and ring-opening reactions are.

Hydrogen abstractions by the carbonyl in the excited state are commonly believed to be classical examples of photochemistry of excited  $n\pi^*$  states.<sup>17</sup> Also, the  $\alpha$ -splitting reactions (Norrish type I) of excited carbonyl compounds are considered as originating from the  $n\pi^*$  excited states.<sup>17</sup> On the other hand, the Dewar structure formation is believed to result in a disrotatory electrocyclic reaction of the excited  $\pi\pi^*$  state. On the basis of the observed behavior of the three compounds **IIa**, **IIIa**, and **IVa** upon UV irradiation, it seems that, indeed, the phototautomeric (a  $\rightarrow$  c) and the ring opening (a  $\rightleftharpoons$  d) reactions represent the photochemistry characteristic for the excited states with pronounced  $n\pi^*$  characters and the reaction of the Dewar isomer formation (a  $\rightleftharpoons$  b) represents a structural transformation passing via an excited state with a more pronounced  $\pi\pi^*$  character. It has been demonstrated<sup>13,18</sup> for the compounds with electronic structures similar to those studied in the present work that alkyl

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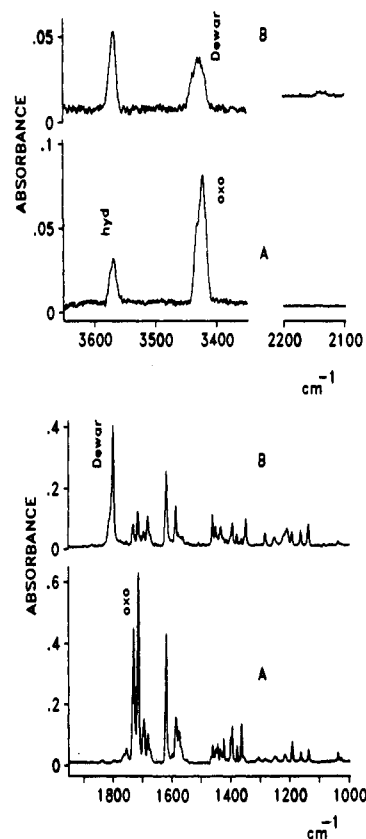


**Figure 5.** (A) IR absorption spectrum of argon matrix-isolated 6-methyl-4(3H)-pyrimidinone before irradiation. (B) Effect of 30 min of excimer laser UV ( $\lambda = 308$  nm) irradiation of the matrix. (C) Effect of further 30-min irradiation with high-pressure mercury lamp ( $\lambda > 250$  nm).

substitutions in the ring diene group cause a red shift of the excited  $\pi\pi^*$  state. Hence, increasing the number of the alkyl substituents in the ring should promote the  $\pi\pi^*$  photochemistry and suppress the photoreactions of the excited  $n\pi^*$  states. The results presented here show that this is the case for 4(3H)-pyrimidinones.

### Conclusions

(1) The IR spectrum simulated theoretically at the MP2/6-31G\*\* level for the Dewar form of 3-methyl-4(3H)-pyrimidinone reproduces the experimental spectrum of this species obtained



**Figure 6.** (A) IR absorption spectrum of argon matrix-isolated 2,6-dimethyl-4(3H)-pyrimidinone before irradiation. (B) Effect of 3 h of excimer laser UV ( $\lambda = 308$  nm) irradiation of the matrix.

upon UV irradiation of the planar 3-methyl-4(3H)-pyrimidinone well enough to allow for a positive identification of the photoproduct. It seems, hence, that the combination of the theoretical calculations with the IR spectroscopy offers a viable tool for identification of medium-size photoproducts trapped in low-temperature matrices.

(2) For matrix-isolated 4(3H)-pyrimidinones not substituted at the N3 atom, three photoreactions compete, *i.e.*, (i) Dewar isomer formation, (ii) phototautomerism (oxo  $\rightarrow$  hydroxy), and (iii) photochemical ring-opening. The first reaction seems to represent the  $\pi\pi^*$  photochemistry and the remaining two reactions the  $n\pi^*$  photochemistry of 4(3H)-pyrimidinones.

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