Spectrochimica Acta, Vol. 46A, No. 7, pp. 1087–1096, 1990
Printed in Great Britain

0584-8539/90 $3.00 + 0.00

Infrared matrix isolation and *ab initio* studies of 3(2H)-pyridazinone and photoproduced 3-hyroxypyridazine

LESZEK LAPINSKI, JAN FULARA, RYSZARD CZERMINSKI and MACIEJ J. NOWAK*
Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland

(*Received* 16 *October* 1989; *accepted* 18 *December* 1989)

Abstract—The infrared spectra of 3(2H)-pyridazinone and its rare tautomeric form, 3-hydroxypyridazine, isolated in an argon matrix are reported and discussed. Only the first tautomer was observed after deposition of the matrix. The second form was photochemically produced after ultraviolet irradiation of the matrix (phototautomeric process). This form has never been observed experimentally before. *Ab initio* 3-21G normal coordinate calculations were carried out for these two forms and on that basis, an assignment of the experimental spectra of both compounds was performed.

INTRODUCTION

THIS WORK is a continuation of our studies on the i.r. spectra and tautomerism of matrix isolated diazinones. In our previous papers we reported the i.r. spectra of matrix isolated 2-hydroxypyrimidine [1], 4(3H)-pyrimidinone [2], cytosine [3] and 5-methylcytosine [4]. We have interpreted the spectra on the basis of *ab initio* calculations performed at the SCF 3-21G level. The same procedure was used in this work for 3(2H)-pyridazinone. In the case of 4(3H)-pyrimidinone [2, 5] and in cytosine [3, 4] we observed a u.v. light induced change of the tautomeric form: from the oxo to the hydroxy form. In this paper we demonstrate that a similar photoreaction for 3(2H)-pyridazinone also occurs.

3(2H)-Pyridazinone exists only in the oxo-form [6, 7] in solutions. As is reported in this paper, 3(2H)-pyridazinone, isolated in a rare gas matrix, exists also only in the oxo form. From this observation one may conclude that in the gaseous state (from which the matrix was formed) the oxo form strongly predominates. The enol form, which has never been observed before, was produced by u.v. irradiation and is stable only if frozen in a low temperature matrix. The exact mechanism (which we suppose is similar in all the above mentioned cases) is not known and it is one of the interests of our future work.

EXPERIMENTAL

The experimental procedure was the same as in our previous works [1–4]. The i.r. spectra were measured on a Perkin–Elmer 580B spectrophotomer working in a mode with 1–3 cm^{-1} spectral resolution. Integral absorptions of the bands were calculated via numerical integration. The preparation of matrices was described in detail in one of our previous papers [8]. 3(2H)-Pyridazinone vapour, obtained from a small glass oven placed in a cryostat vacuum chamber, was mixed with a matrix gas and then deposited on a CsI window placed on the cold finger of the continuous flow helium cryostat. The temperature of the oven during preparation of the matrix was about 350 K. The minimal temperature of the CsI window was about 6–7 K. The matrix gas, argon, which was of spectral grade was obtained from VEB Technische Gase (Leipzig, G.D.R.). 3(2H)-Pyridazinone and 6-methyl-3(2H)-pyridazinone were prepared according to the procedures described elsewhere [9, 10] and 6-hydroxy-3(2H)-pyridazinone as described in Ref. [11]. Ultraviolet irradiation of the matrices was performed (through the CsI window of the cryostat) by the light from the high pressure mercury lamp HBO 200 fitted with a water filter. Irradiation time was 2 h.

Computational details

The SCF and gradient calculations at the Hartree–Fock 3-21G level were performed using the GAMESS [12] program. The molecule was assumed to be planar. As the equilibrium point, we

* Author to whom correspondence should be addressed.

Table 1. Optimized geometries of 3(2H)-pyridazinone and 3-hydroxypyridazine

	3(2H)-Pyridazinone	3-Hydroxypyridazine
Bond lengths		
N1–N2	1.375	1.361
N2–C3	1.377	1.300
C3–C4	1.461	1.401
C4–C5	1.331	1.356
C5–C6	1.442	1.406
C6–N1	1.278	1.308
C3–O7	1.218	1.355
N2–H8	0.998	
O7–H8		0.968
C4–H9	1.069	1.067
C5–H10	1.071	1.070
C6–H11	1.068	1.068
Bond angles		
C6–N1–N2	116.9	119.0
N1–N2–C3	127.3	119.9
N2–C3–C4	112.9	123.7
C3–C4–C5	120.7	116.5
C4–C5–C6	119.6	118.1
C6–C6–N1	122.6	122.8
N2–C3–O7	121.6	118.2
C3–N2–H8	118.3	
C3–O7–H8		110.6
C3–C4–H9	116.3	119.6
C4–C5–H10	121.7	121.6
N1–C6–H11	116.9	116.4

Bond lengths are given in Å and bond angles in degrees. Atom numbering as in Scheme 1. Optimized geometries in cartesian coordinates are available upon request.

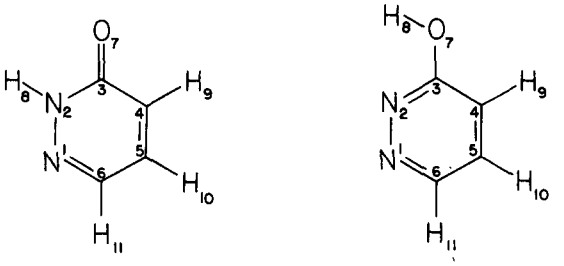
used the geometry optimized in 3-21G. Optimized geometries of both tautomers are given in Table 1. The force constants with respect to the cartesian coordinates were calculated by numerical differentiation of analytical gradient obtained for distorted geometries of the molecule. For each of the cartesian coordinates, two SCF and gradient calculations were performed. The displacements from the reference geometry were ±0.01 a.u. (bohrs) for each cartesian coordinate. Frequencies were obtained by diagonalizing the force constants matrix in mass-weighted cartesian coordinates [13]. Only one scale factor of 0.9 was used to scale down the calculated frequencies. Intensities were obtained from the calculated atomic polar tensors [14]. We chose the internal coordinates in the way recommended by PULAY *et al.* [15]. The list of the in-plane and out-of-plane internal coordinates is given in Table 2. Transformation of the force constant matrix to the internal coordinates was performed and potential energy distribution [16] was calculated for all the normal modes. Potential energy distribution components (PED's) greater than 10% are given in Tables 3 and 4.

RESULTS AND DISCUSSION

Tautomerism and phototautomerism of 3(2*H*)-*pyridazinone*

3(2H)-Pyridazinone may potentially exist in two (oxo and hydroxy) tautomeric forms (see Scheme 1). Tautomerism of 3(2H)-pyridazinone in water solution has been studied by BARLIN *et al.* [6, 7]. They demonstrated by a study of the u.v. spectra and pK properties of the model anhydro base, and also by a study of ^{1}H NMR spectra that only the single (oxo) tautomeric form existed in water solutions.

In our present matrix study, the i.r. spectrum of the argon matrix doped by 3(2H)-pyridazinone molecules exhibits absorption bands which may be attributed only to



Scheme 1.

the oxo form (see next section). No traces of bands which may be assigned to the hydroxy form were found (Fig. 1).

As is known from our earlier investigations [17, 18], the conclusions concerning the proportion of tautomers observed in low-temperature matrices may be extended (with

Table 2. Internal coordinates used in the normal modes analysis for 3(2H)-pyridazinone and 3-hydroxypyridazine

In plane	
Ring stretchings	
$S_1 = r_{1,2}$	r_{N1N2}
$S_2 = r_{2,3}$	r_{N2C3}
$S_3 = r_{3,4}$	r_{C3C4}
$S_4 = r_{4,5}$	r_{C4C5}
$S_5 = r_{5,6}$	r_{C5C6}
$S_6 = r_{6,1}$	r_{C6N1}
Stretchings CH	
$S_7 = r_{4,9}$	r_{C4H9}
$S_8 = r_{5,10}$	r_{C5H10}
$S_9 = r_{6,11}$	r_{C6H11}
Stretching CO	
$S_{10} = r_{3,7}$	r_{CO}
Stretching NH (oxo form)	
$S_{11} = r_{2,8}$	r_{NH}
Stretching OH (hydroxy form)	
$S_{11} = r_{7,8}$	r_{OH}
Ring deformations I, II and III, respectively	
$S_{12} = (6^{-1/2})(\beta_{1,5,6} - \beta_{6,2,1} + \beta_{3,1,2} - \beta_{4,2,3} + \beta_{5,3,4} - \beta_{4,6,5})$	β_{R1}
$S_{13} = (12^{-1/2})(2\beta_{1,5,6} - \beta_{2,6,1} - \beta_{3,1,2} + 2\beta_{2,4,3} - \beta_{5,3,4} - \beta_{4,6,5})$	β_{R2}
$S_{14} = 1/2\ (\beta_{6,2,1} - \beta_{1,3,2} + \beta_{3,5,4} - \beta_{4,6,5})$	β_{R3}
Bending NH (oxo form)	
$S_{15} = (2^{-1/2})(\beta_{3,8,2} - \beta_{1,8,2})$	β_{NH}
Bending OH (hydroxy form)	
$S_{15} = \beta_{3,8,7}$	β_{OH}
Bending CO	
$S_{16} = (2^{-1/2})(\beta_{2,7,3} - \beta_{4,7,3})$	β_{CO}
Bending CH	
$S_{17} = (2^{-1/2})(\beta_{9,3,4} - \beta_{9,5,4})$	β_{CH9}
$S_{18} = (2^{-1/2})(\beta_{10,4,5} - \beta_{10,6,5})$	β_{CH10}
$S_{19} = (2^{-1/2})(\beta_{11,1,6} - \beta_{11,5,6})$	β_{CH11}

Table 2 (*continued*)

Out of plane	
Out of plane O	
$S_{20} = \gamma_{7,2,3,4}$	γ_{CO}
Out of plane CH	
$S_{21} = \gamma_{9,3,4,5}$	γ_{CH9}
$S_{22} = \gamma_{10,4,5,6}$	γ_{CH10}
$S_{23} = \gamma_{11,5,6,1}$	γ_{CH11}
Out of plane NH (oxo form)	
$S_{24} = \gamma_{8,1,2,3}$	γ_{NH}
Torsional OH (hydroxy form)	
$S_{24} = (2^{-1/2})(\tau_{8,7,3,2} + \tau_{8,7,3,4})$	τ_{OH}
Ring OOP deformations **I**, **II** and **III**, respectively	
$S_{25} = (6^{-1/2})(\tau_{6,1,2,3} - \tau_{1,2,3,4} + \tau_{2,3,4,5} - \tau_{3,4,5,6} + \tau_{4,5,6,1} - \tau_{5,6,1,2})$	τ_{R1}
$S_{26} = (1/2)(\tau_{6,1,2,3} - \tau_{2,3,4,5} + \tau_{3,4,5,6} - \tau_{5,6,1,2})$.	τ_{R2}
$S_{27} = (12^{-1/2})(-\tau_{6,1,2,3} + 2\tau_{1,2,3,4} - \tau_{2,3,4,5} - \tau_{3,4,5,6} + 2\tau_{6,1,2,3} - \tau_{5,6,1,2})$	τ_{R3}

Where $r_{i,j}$ is the distance between atoms A_i and A_j, $\beta_{i,j,k}$ is the angle between vectors A_kA_i and A_kA_j, $\gamma_{i,j,k,l}$ is the angle between the vector A_jA_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 A_i, A_j, A_k and the plane defined by A_j, A_k, A_l atoms. Atom numbering as in Scheme 1.

good approximation) to tautomeric equilibrium existing in the gas phase from which the matrix was formed. Therefore, we may postulate that in the gas phase 3(2H)-pyridazinone also exists only in the oxo form. This is in contrast with other similar (isomeric) diazinones, i.e. 4(3H)-pyrimidinone and 2(1H)-pyrimidinone. For these compounds the tautomeric equilibrium strongly depends on the environment. The oxo form (as for 3(2H)-pyridazinone) is the unique one observed in the solid state and in polar solutions (aqueous and nonaqueous) [19], but in the gas phase or noble gas matrix, a considerable percentage of the molecules adopt the hydroxy form. In matrix isolated 4(3H)-pyrimidinone, two forms, oxo and hydroxy are present in comparable amounts while only the hydroxy form of 2(1H)-pyrimidinone could be detected in the matrix.

For several compounds (4(3H)-pyrimidinone [5], 2(1H)-pyridinone, cytosine [2] and 5-methylcytosine [4]) which in low-temperature matrices exist simultaneously in two tautomeric forms: oxo and hydroxy, we observed a change of tautomeric form following the electronic-excitation of the isolated molecules (u.v. irradiation of the matrix). In all cases, the direction of this photoreaction was the same: from the oxo to the hydroxy form ($[O] \xrightarrow{h\nu} [H]$). It was interesting to see if such a photoreaction may be observed for the compound with tautomeric equilibrium (in the ground state) shifted strongly towards the oxo form.

Ultraviolet irradiation of matrix isolated 3(2H)-pyridazinone caused a gradual decrease of all the bands due to the oxo form accompanied by the appearance and increase of a second set of bands (Fig. 1). We attributed this to the appearance of the hydroxy form. We have four reasons to interpret the photoproduct as 3-hydroxypyridazine: first is the appearance of the new absorption at 3553 cm^{-1} where only the band of the OH stretching vibration is expected; second is the similarity of the spectra of the photoproduct and 4-hydroxypyrimidine and 2-hydroxypyrimidine; third is the overall agreement of the i.r. spectrum of the photoproduct with the theoretically predicted spectrum of 3-hydroxypyridazine; and fourth is the similarity of the photoreactions observed for the title compound and for matrix isolated 4(3H)-pyrimidinone and 2(1H)-pyridinone. Hence, we were able to produce in matrix the hydroxy tautomer of 3(2H)-pyridazinone, which does not exist either in the gas phase nor in polar solutions and we demonstrated that the phototautomeric effect may occur even when tautomeric equilibrium is strongly shifted to the oxo form.

Table 3. Experimental wave numbers (ν), integrated absorbances (I) and calculated wavenumbers, integral intensities (A) and potential energy distributions for 3(2H)-pyridazinone in an argon matrix

	Experimental		Calculated		
Nr	ν (cm^{-1})	I (rel.)	ν^* (cm^{-1})	A ($km\ mol^{-1}$)	Assignment (PEDs)
1	3426	111	3439	100	$r_{NH}(100)$
2			3079	1	$r_{C4H9}(79)$, $r_{C5H10}(12)$
3			3069	8	$r_{C6H11}(82)$, $r_{C4H9}(14)$
4			3045	5	$r_{C5H10}(84)$
	1848	7			
	1801	8			
	1760, 1757	11			
	1719, 1716, 1711, 1695, 1687	600	1720	459	$r_{CO}(62)$
	1642	2			
	1621, 1617	10			
	1606, 1602	35			
6			1636	58	$r_{C4C5}(38)$, $r_{C6N1}(26)$, $r_{CO}(10)$
	1589	1			
	1547	2			
7	1538	3	1559	8	$r_{C6N1}(39)$, $r_{C4C5}(24)$, $\beta_{NH}(11)$
	1527	1			
	1442	1			
8	1432	2	1412	3	$\beta_{NH}(30)$, $\beta_{CH10}(25)$, $\beta_{CH9}(16)$
	1412	2			
9	1406	2	1399	0.3	$\beta_{NH}(43)$, $\beta_{CH10}(18)$, $\beta_{CH9}(18)$, $r_{C6N1}(11)$
	1372	2			
10	1360	6	1351	3	$\beta_{CH11}(75)$
	1265	4			
	1260	3			
11	1247, 1243	30	1235	12	$\beta_{CH9}(33)$, $r_{N2C3}(24)$, $r_{C3C4}(15)$
	1226	2			
	1211, 1209	2			
12	1159, 1156	32	1152	37	$\beta_{CH10}(31)$, $r_{N2C3}(24)$, $\beta_{CH9}(15)$
13	1064	3	1096	2	$\gamma_{CH10}(63)$, $\gamma_{CH9}(48)$
14	1109, 1106	21	1057	20	$r_{N1N2}(45)$, $\beta_{R1}(21)$
15	1016	13	995	37	$\beta_{R1}(57)$, $r_{C5C6}(15)$
16			984	2	$\gamma_{CH11}(83)$, $\gamma_{CH9}(21)$
17	989	19	943	20	$r_{C5C6}(53)$, $r_{N2C3}(12)$
	835	1			
	830	3			
18	821	44	881	129	$\gamma_{CO}(37)$, $\gamma_{CH10}(27)$, $\gamma_{CH9}(18)$, $\gamma_{CH11}(15)$
19	811	16	801	56	$\gamma_{NH}(54)$, $\gamma_{CO}(22)$, $\tau_{R1}(12)$, $\gamma_{CH11}(15)$
20			762	2	$r_{C3C4}(46)$, $r_{N2C3}(17)$, $r_{N1N2}(12)$
21	706	90	723	101	$\tau_{R1}(57)$, $\gamma_{NH}(41)$
22	600	5	595	10	$\beta_{R3}(76)$
23	555	14	552	12	$\beta_{R2}(74)$
24	504	14	549	13	$\gamma_{CO}(28)$, $\tau_{R1}(21)$, $\tau_{R2}(16)$, $\tau_{R3}(15)$, $\gamma_{NH}(11)$
25	450	15	439	13	$\beta_{CO}(74)$
26			375	0.1	$\tau_{R2}(78)$, $\tau_{R3}(30)$
27			188	3	$\tau_{R3}(68)$, $\tau_{R1}(21)$, $\tau_{R2}(12)$

* Scaled by 0.9.

For a better comparison of experiment with theory the integrated absorbances of absorption bands are normalized in such a way that the sum of integrated absorbances of all normal modes observed experimentally was equalized to the sum of intensities obtained in calculations.

After u.v. irradiation, an additional band appears in the i.r. spectrum at 2131 cm^{-1} (sub bands at 2150 and 2139 cm^{-1}), which cannot be assigned to the spectrum of the hydroxy form (Fig. 2). Similar bands were found in the spectra of u.v. irradiated matrix isolated 4(3H)-pyrimidinone and 2(1H)-pyridinone. Those bands might be interpreted as due to the =C=O stretching vibration of conjugated ketene (for discussion see Ref. [2]). The relative concentration of the conjugated ketene produced in the matrix after irradiation must be very low since a band of very low intensity is observed at 2131 cm^{-1} (one should take into account its high integral absorption coeficient which is expected to be greater than 1500 km mol^{-1} [2]). So, no other bands due to this species (ketene) are expected to be strong enough to interfere with the spectrum of the hydroxy form of the title compound. TSUCHIYA *et al.* [20] investigated the photoreactions of 3(2H)-pyridazinones in methanolic solution. They proposed the conjugated ketene to be the primary photoproduct but gave no direct proof of its existence. The present study might provide some support for their hypothesis. We also observed similar photoenolization (accompanied by the appearance of the new band near 2130 cm^{-1}) for 6-methyl-3(2H)-pyridazinone, but the rate of this photoreaction was lower than for unsubstituted 3(2H)-pyridazinone. 6-Hydroxy-3(2H)-pyridazinone (which was found in the argon matrix in the oxo–hydroxy form [21]) was unaffected by the u.v. irradiation. In TSUCHIYA'S *et al.* [20] study, the photoreactions in methanolic solution were observed for 3(2H)-pyridazinone and 6-methyl-3(2H)-pyridazinone but for 6-hydroxy-3(2H)-pyridazinone (like in our study) no photoreaction was detected.

Infrared absorption spectra

The survey spectra of argon matrix isolated 3(2H)-pyridazinone are presented in Fig. 1(A). The effect of u.v. irradiation of the matrix and the spectrum of photoproduced 3-hydroxypyridazine is illustrated in Fig. 1(B). The difference spectrum of matrix isolated 3(2H)-pyridazinone before and after u.v. irradiation is shown in Fig. 1(C). In this spectrum it is easier to notice the arising bands of the hydroxy form, especially when they and the bands of the initial spectrum partially overlap. The experimental frequencies and relative integral intensities together with the theoretically obtained results are collected in Table 3 for the oxo, and in Table 4 for the hydroxy tautomers.

3(2H)-Pyridazinone and 4(3H)-pyrimidinone are isomeric species which differ only in the position of one nitrogen atom. Infrared spectra of 4(3H)-pyrimidinone isolated in inert gas matrices (including the argon matrix) were recently studied and are reported in Ref. [2]. Comparison of the experimental and theoretically predicted spectra of both molecules in two tautomeric forms might serve as an additional test of the proposed assignment.

3(2H)-pyridazinone

3600–2800 cm^{-1} region. Only one band is observed in this region in the spectrum of the oxo form. It is placed at 3426 cm^{-1} and we attributed it to the stretching vibration of the NH group. The frequency of this mode is very close to its analogue, observed at 3428 cm^{-1} in the spectrum of 4(3H)-pyrimidinone. In the region between 3200 and 2800 cm^{-1}, the bands due to CH stretchings could be expected. The theoretically predicted intensities of these bands are low and no bands are observed in the experimental spectrum.

1800–1000 cm^{-1} region. The strongest bands in the i.r. spectra of 3(2H)-pyridazinone and 4(3H)-pyrimidinone are placed at 1719 (split due to Fermi resonance) and 1727 cm^{-1}, respectively, and correspond to the CO stretching vibration. Near 1610 and 1540 cm^{-1} in the spectra of the two compounds mentioned above there are bands due to stretchings of the two double bonds in the ring. Frequencies and forms of these two vibrations are similar in both compounds, but the intensities of the bands in the spectrum of 3(2H)-pyridazinone are much lower than those of their counterparts in the spectrum of 4(3H)-pyridazinone. Major contributions to the next three normal modes (1432, 1406 and 1360 cm^{-1}) come from the in-plane bendings of CH and NH. Counterparts of these

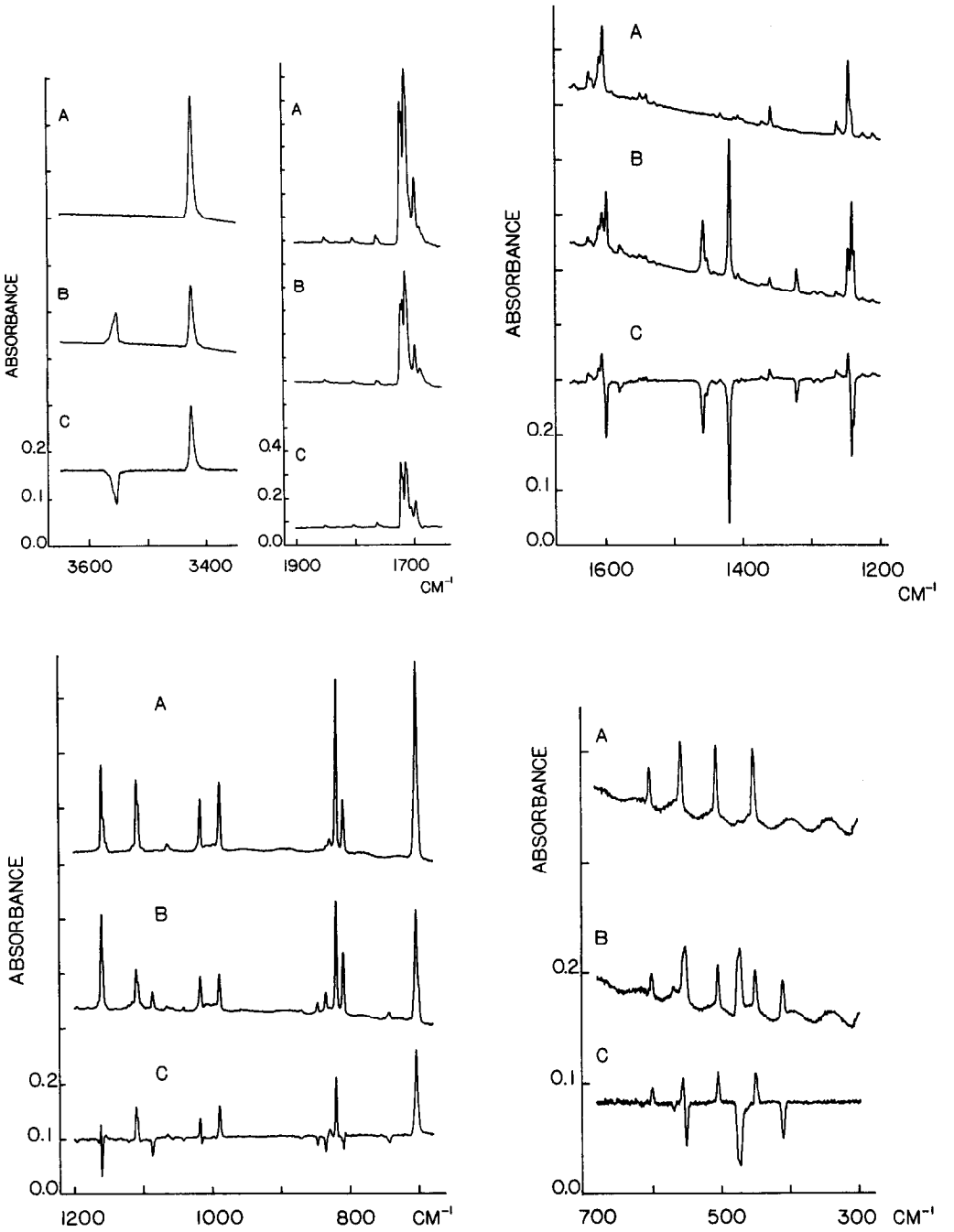


Fig. 1. (A) The i.r. absorption spectrum of argon matrix isolated 3(2H)-pyridazinone, (B) the effect of 2 h u.v. irradiation of the matrix, (C) the difference spectrum, (A) minus (B), where u.v. induced changes in the spectrum are better visualized.

bands might be found in the spectrum of 4(3H)-pyrimidinone at 1434, 1414 and 1366 cm^{-1}. For the other bands in this region, analogy with the spectrum of 4(3H)-pyrimidinone is worse, except for the characteristic band of ring in-plane deformation **I**, which was found at 1016 and 1025 cm^{-1} in the spectra of the title compound and 4(3H)-pyrimidinone, respectively.

1000–200 cm^{-1} region. There are close similarities between the forms of the normal vibrations of 3(2H)-pyridazinone and 4(3H)-pyrimidinone in the region 850–700 cm^{-1}. Three characteristic (relatively strong) bands of CO and CH waggings, NH wagging and ring torsion **I** are found at 821, 811, 706 and at 838, 754, 706 cm^{-1} in the spectra of 3(2H)-pyridazinone and 4(3H)-pyrimidinone, respectively. In the next part of this

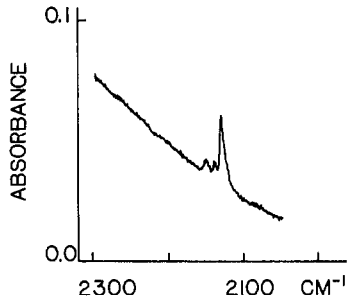


Fig. 2. The new additional band appearing in the spectrum of argon matrix isolated 3(2H)-pyridazinone after 2 h u.v. irradiation.

Table 4. Experimental wavenumbers (ν), integrated absorbances (I) and calculated wavenumbers, integral intensities (A) and potential energy distributions for 3-hydroxypyridazine in an argon matrix

Nr	Experimental ν (cm^{-1})	I (rel.)	Calculated ν^* (cm^{-1})	A (km mol^{-1})	Assignment (PEDs)
1	3558, 3553	152	3496	119	$r_{OH}(100)$
2			3088	0.2	$r_{C4H9}(89)$
3			3069	7	$r_{C6H11}(66)$, $r_{C5H10}(27)$
4			3053	4	$r_{C5H10}(63)$, $r_{C6H11}(33)$
5	1596	45	1598	65	$r_{C4C5}(41)$, $\beta_{CH9}(12)$
6	1576	16	1557	15	$r_{N2C3}(21)$, $r_{C3C4}(18)$, $r_{C5C6}(16)$, $r_{C6N1}(10)$
7	1456, 1451	109	1461	156	$\beta_{CH10}(18)$, $r_{CO}(15)$, $r_{N2C3}(14)$, $\beta_{CH11}(13)$, $r_{C6N1}(12)$, $\beta_{CH9}(11)$
8	1418	200	1402	38	$\beta_{CH11}(28)$, $\beta_{OH}(16)$, $\beta_{CH9}(12)$, $\beta_{CH10}(11)$, $r_{C5C6}(10)$
9	1321	34	1334	12	$\beta_{CH11}(27)$, $r_{CO}(20)$, $\beta_{CH9}(10)$
	1297	7			
	1287	8			
10	1242, 1239	153	1226	128	$r_{C6N1}(36)$, $\beta_{OH}(24)$, $r_{CO}(12)$, $\beta_{CH11}(11)$, $r_{C4C5}(10)$
	1195	4			
	1179	2			
11	1159	81	1167	28	$\beta_{CH9}(40)$, $\beta_{CH10}(33)$
12	1085	24	1113	122	$\beta_{OH}(30)$, $r_{N2C3}(25)$, $r_{C6N1}(23)$, $r_{C3C4}(12)$
13			1078	1	$\gamma_{CH10}(67)$, $\gamma_{CH9}(33)$, $\gamma_{CH11}(17)$
14	1040	4	1050	18	$r_{C4C5}(23)$, $\beta_{R1}(18)$, $r_{N1N2}(18)$, $r_{C5C6}(15)$
15			1010	9	$r_{C5C6}(31)$, $\beta_{R1}(24)$, $r_{N2C3}(12)$, $r_{C3C4}(10)$
16			996	1	$\gamma_{CH11}(68)$, $\gamma_{CH9}(38)$
17			950	8	$r_{N1N2}(39)$, $\beta_{R1}(29)$, $r_{C5C6}(12)$, $r_{CO}(12)$
	871	7			
	848	14			
	836	21			
18	811	38	866	89	$\gamma_{CH10}(32)$, $\gamma_{CH9}(22)$, $\gamma_{CH11}(21)$, $\gamma_{CO}(20)$
19	744	13	792	25	$r_{C3C4}(34)$, $\beta_{R2}(18)$, $r_{N1N2}(17)$, $r_{CO}(13)$
20			777	1	$\tau_{R1}(83)$
21			631	0.3	$\beta_{R3}(86)$
22	551	72	581	49	$\gamma_{CO}(43)$, $\tau_{R1}(16)$, $\tau_{R3}(15)$, $\tau_{R2}(12)$, $\tau_{OH}(12)$
23	568	6	566	4	$\beta_{R2}(64)$, $r_{CO}(19)$
24	472	85	470	162	$\tau_{OH}(84)$, $\tau_{R2}(10)$
25			409	6	$\tau_{R2}(55)$, $\tau_{R3}(48)$
26	410	32	385	30	$\beta_{CO}(81)$
27			236	2	$\tau_{R3}(45)$, $\tau_{R2}(29)$, $\gamma_{CO}(21)$

* Scaled by 0.9.

For a better comparison of experiment with theory the integrated absorbances of absorption bands are normalized in such a way that the sum of integrated absorbances of all normal modes observed experimentally was equalized to the sum of intensities obtained in calculations.

spectral region, two very characteristic bands due to out-of-plane and in-plane deformations of CO are placed at 504, 450 and at 502, 454 cm^{-1} in the spectra of the two considered compounds.

3-hydroxypyridazine

3600–2800 cm^{-1} *region.* After u.v. irradiation, a new band appears at 3553 cm^{-1} which we assigned to the OH stretching vibration. The bands of CH stretchings are not observed in the spectrum of the hydroxy form either.

1800–1000 cm^{-1} *region.* Ring stretchings provide major contributions to the normal modes with frequencies of 1596 and 1576 cm^{-1}. Similar pairs of bands due to ring stretchings were observed at 1607 and 1575 cm^{-1} in the spectrum of 4-hydroxypyrimidine. These bands are strong in the spectrum of 4-hydroxypyrimidine and relatively weak in the spectrum of 3-hydroxypyridazine. Three bands at 1456, 1418 and 1321 cm^{-1} are mainly due to the CH bending vibrations. Their counterparts in the spectrum of 4-hydroxypyrimidine are at 1479, 1395 and 1312 cm^{-1}. In both the compared compounds there is no characteristic band due to OH bending. This vibration contributes considerably to at least two normal modes with frequencies near 1200 and 1100 cm^{-1}.

1000–200 cm^{-1} *region.* Forms of four normal modes of 3-hydroxypyridazine with frequencies in the range 600–400 cm^{-1} are almost the same as those of their counterparts in the spectrum of 4-hydroxypyrimidine. These bands are due to CO wagging, ring bending II, OH torsion and CO bending. The frequencies of the four bands are 551, 568, 472, 410 and 563, 553, 497, 420 cm^{-1} for the two compounds.

Comparison between experimental and theoretically predicted spectra

1800–1000 cm^{-1} *region. Ab initio* calculation predicts this region of the spectra for both oxo and hydroxy tautomers with satisfactory or even good accuracy. Main discrepancies between the experimental and theoretical spectra concern the intensities of the few bands in this region, but most of the frequencies and intensities are predicted correctly. Since the spectrum was not very densely spaced the assignment was not troublesome and seems to be reliable.

1000–200 cm^{-1} *region.* The calculated frequencies and intensities of the bands due to out-of-plane vibrations are often overestimated (which is typical for calculations at the SCF level with split-valence basis set). However, this drawback did not complicate the assignment too much. In the lower frequency region (below 700 cm^{-1}) the bands, especially those due to in-plane vibrations, are well predicted by the calculation. Comparison between experimental and theoretically predicted spectra seems to lead to a reliable assignment of most of the spectra of 3(2H)-pyridazinone and 3-hydroxypyridazine in this region.

Conclusions

3(2H)-Pyridazinone, isolated in an inert matrix, exists only (in the limit of sensitivity of i.r. spectroscopy) in its oxo form.

For this compound, the occurrence of a phototautomeric reaction similar to that observed previously for 4(3H)-pyrimidinone, 2(1H)-pyridinone, cytosine, 5-methylcytosine and some other compounds of similar structure was demonstrated. This

confirms the more general character of that photo-reaction. This reaction always proceeds from the oxo to the hydroxy form independently of the initial relative concentrations of the oxo and hydroxy tautomers. Ultraviolet irradiation allowed us to produce the hydroxy tautomer of the studied compound and then observe its i.r. spectrum.

Ab initio calculations performed at the SCF 3-21G level for both tautomers gave the predicted spectra close to the experimental ones. The obtained assignment seems reasonable for most of the bands in the spectra of both tautomers. Good agreement between the predicted spectrum of 3-hydroxypyridazine and the experimental spectrum of the photoproduct confirms that we really observed the u.v. induced proton transfer reaction of matrix isolated 3(2H)-pyridazinone.

Acknowledgements—This investigation was financed by the Polish Research Programs C.P.B.P. 01.12 and C.P.B.R. 11.5.

REFERENCES

[1] L. Lapinski, R. Czerminski, M.J. Nowak and J. Fulara, *J. Molec. Struct.*, in press.
[2] L. Lapinski, J. Fulara and M. J. Nowak, *Spectrochim. Acta* **46A**, 61 (1990).
[3] M. J. Nowak, L. Lapinski and J. Fulara, *Spectrochim. Acta* **45A**, 229 (1989).
[4] L. Lapinski, M. J. Nomak, J. Fulara, A. Les and L. Adamowicz, *J. Phys. Chem.*, in press.
[5] M. J. Nowak, J. Fulara and L. Lapinski, *J. Molec. Struct.* **175**, 91 (1988).
[6] G. B. Barlin and M. D. Fenn, *Aust. J. Chem.* **32**, 2297 (1979).
[7] G. B. Barlin and A. C. Young, *J. Chem. Soc.*(B), 1261 (1971).
[8] M. Szczesniak, M. J. Nowak, K. Szczepaniak, W. B. Person and D. Shugar, *J. Am. Chem. Soc.* **105**, 5970 (1983).
[9] W. G. Overend and L. F. Wiggins, *J. Chem. Soc.* 239 (1947).
[10] R. F. Homer, H. Gregory and L. F. Wiggins, *J. Chem. Soc.* 2191 (1948).
[11] R. H. Mizzoni and P. E. Spoeri, *J. Am. Chem. Soc.* **73**, 1873 (1951).
[12] M. W. Schmidt, J. A. Boatz, K. K. Baldridge, S. Koseki, M. S. Gordon, S. T. Elbert and B. Lam, *QCPE Bulletin* **7**, 115 (1987).
[13] E. B. Wison Jr, J. C. Decius and P. C. Cross, *Molecular Vibrations*. McGraw-Hill, New York (1955).
[14] W. B. Person and J. H. Newton, *J. Chem. Phys.* **61**, 1040 (1974).
[15] P. Pulay, G. Fogarasi, F. Pang and J. E. Boggs, *J. Am. Chem. Soc.* **101**, 2550 (1979).
[16] S. Califano, *Vibrational States*. Wiley, New York (1976).
[17] M. J. Nowak, K. Szczepaniak, A. Barski and D. Shugar, *J. Molec. Struct.* **62**, 47 (1980).
[18] M. J. Nowak, K. Szczepaniak, A. Barski and D. Shugar, *Z. Naturforsch.* **33c**, 876 (1978).
[19] P. Beak, F. S. Fry Jr, J. Lee and F. Steele, *J. Am. Chem. Soc.* **98**, 171 (1976).
[20] T. Tsuchiya, M. Hasebe, H. Arai and H. Igeta, *Chem. Pharm. Bull.* **22**, 2276 (1974).
[21] G. N. Rodionova and E. S. Levin, *Dokl. Akad. Nauk USSR* **174**, 1132 (1967).