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# UV-induced photoisomerization of maleic hydrazide

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## ARTICLE INFO

#### ABSTRACT

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Keywords: Infrared spectroscopy Matrix isolation Photochemistry Maleic hydrazide N-aminomaleimide DFT and QCISD calculations Monomers of maleic hydrazide (3-hydroxypyridazin-6-one) were studied using the experimental matrixisolation technique as well as DFT and QCISD methods of quantum chemistry. The oxo-hydroxy tautomer was theoretically predicted to be the most stable form of the compound. The energies of the dihydroxy and dioxo forms were calculated (at the QCISD level) to be higher by more than 20 kJ mol<sup>-1</sup>. Only the oxohydroxy form was trapped from the gas phase into low-temperature Ar matrices. UV irradiation of matrix-isolated maleic hydrazide induced two isomerization processes: (i) hydrogen-atom transfer converting the oxo-hydroxy form into the dihydroxy tautomer ( $\lambda > 234$  nm and  $\lambda > 200$  nm); (ii) transformation to N-aminomaleimide ( $\lambda > 200$  nm). Both photoproducts were identified by comparison of their experimental FTIR spectra with the spectra theoretically predicted at the DFT level.

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## 1. Introduction

Maleic hydrazide (Scheme 1) can be easily synthesized by condensation of maleic acid (or anhydride) with hydrazine. Maleic hydrazide (MH) is industrially produced in large quantities and widely used as a plant growth regulator [1–10]. It has been suggested, that the molecules of MH can act either as a purine analog forming base pairs with uracil and thymine (nucleoside formation through O atom), or as a pyrimidine analog forming base pairs with adenine (nucleoside formation through N) [11,12].

The crystals of MH were found to exist as three different polymorphs [13-18] and, in all the polymorphs, MH adopts exclusively the oxo-hydroxy form (Scheme 1). Tautomerism of solid maleic hydrazide was studied experimentally using infrared [19,20] and Raman spectroscopies [20]. The structure of MH in a variety of solutions was characterized using UV spectroscopy [21,22], Raman spectroscopy [23], proton magnetic resonance [24,25], and ionization constants [22]. Finally, IR spectra of gaseous MH were characterized in the 1200-4000 cm<sup>-1</sup> range using a UR-10 grating spectrometer [26]. All these studies have invariably concluded that MH, under all the experimental conditions listed above, exists as the oxo-hydroxy tautomer. As far as we know, there are no reports on investigations of monomeric maleic hydrazide isolated in inert low-temperature matrices. Furthermore, no reports on observation of MH tautomers, other than the oxo-hydroxy, are available in the literature.

The structure and tautomerism of maleic hydrazide were also the subject of several computational studies [27–33]. For the monomeric compound, all the theoretical assessments of relative energies of tautomers agree with the experiment and favor the oxo-hydroxy form.

Unimolecular photochemical transformations were previously studied for matrix-isolated heterocyclic compounds such as cytosine, 2-pyridone, 3-pyridazone, 4-pyrimidone and  $\alpha$ -pyrones (see Scheme 2) structurally similar to maleic hydrazide [34–41]. Three basic types of unimolecular photoreactions were observed: (i) UVinduced phototautomerism (hydrogen-atom transfer) [34–38], (ii) ring opening leading to conjugated ketenes or isocyanates [36–41], (iii) Dewar isomer generation [38–41].

These patterns of photochemical behavior were observed for nearly all compounds with a six-membered heterocyclic ring and a carbonyl group directly attached to it. However, some exceptional cases are also known: uracil appeared to be remarkably photostable and none of the phototransformations listed above was observed for this compound.

Regarding the photochemistry of maleic hydrazide, we are aware of only one report describing the photolysis of MH in aqueous solutions. MH dissolved in air-containing or in oxygen-free water was found to decompose into a number of acidic products [42]. Interestingly, the photolysis of the sodium salt of MH in the presence of air was immeasurably slow. It is then a fortunate circumstance that this plant growth regulator is marketed for agricultural use in the form of its sodium salt [42]. To the best of our knowledge, no investigations of unimolecular photochemistry of maleic hydrazide have been reported hitherto. In the current work, we studied the photochemical behavior of MH isolated in

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Scheme 1. Tautomers of maleic hydrazide and atom numbering of the ring.

low-temperature Ar matrices. The pattern of unimolecular phototransformations found for matrix-isolated maleic hydrazide was quite unique and did not directly follow the photochemical patterns observed for other heterocyclic compounds studied so far.

## 2. Experimental and computational methods

Maleic hydrazide used in the present study was a commercial product (99% purity) supplied by Aldrich. To prepare the Ar matrices, a solid sample of MH was heated in a miniature glass oven placed in the vacuum chamber of a helium cooled cryostat. Vapor of MH was deposited, together with large excess of argon (N60, Air Liquide) onto a Csl window (T = 15 K) mounted on the tip of an APD Cryogenics DE-202A closed-cycle refrigerator. Care was taken to keep the guest-to-host ratio in matrices low enough to avoid association. The infrared spectra were recorded using a Thermo Nicolet 6700 FTIR spectrometer equipped with a KBr beam splitter and a DTGS detector. The matrices were irradiated through the outer quartz window of the cryostat with light from a high-pressure xenon–mercury lamp operating at 300 W. The lamp was fitted with a water filter (8 cm long) to absorb heat and appropriate UV-cutoff filters.

The geometries of the chemical structures considered in the current work were optimized at the density functional theory level of approximation with the three-parameter exchange functional [43] and the gradient-corrected correlation functional [44.45] [DFT(B3LYP)] using the standard 6-31++G(d,p) basis set. At the optimized geometries, the DFT(B3LYP) harmonic vibrational frequencies and IR intensities were calculated. For the purpose of modeling IR spectra, the B3LYP/6-31++G(d,p) calculated frequencies were scaled by factors of 0.975 below 3000 cm<sup>-1</sup> and 0.950 above 3000 cm<sup>-1</sup>, the resulting frequencies, together with the calculated intensities, served to simulate the spectra shown in the figures by convoluting each peak with a Lorentzian function having a full width at half-maximum (fwhm) of 2 cm<sup>-1</sup>, so that the integral band intensities correspond to the calculated infrared absolute intensity. Note that the peak intensities in the simulated spectra are several times less (in the arbitrary units of "relative intensity") than the calculated intensity (in km  $mol^{-1}$ ). The theoretical normal modes were analyzed by means of the potential energy distribution (PED) calculations. Transformations of the force constants with respect to the Cartesian coordinates to the force constants with respect to the molecule-fixed internal coordinates allowed the PED analysis to be carried out as described by Schachtschneider and Mortimer [46]. The internal coordinates used in this analysis were defined as recommended by Pulay et al. [47] and are provided in the Supplementary data (Tables S1–S3).

The relative energies of isomeric forms of maleic hydrazide were calculated using the quadratic configuration interaction method [48] with single and double excitations (QCISD) and the standard 6-31++G(d,p) basis set. These calculations were carried out at geometries optimized using the same QCISD/6-31++G(d,p) method. All quantum–mechanical calculations were performed with the GAUSSIAN 03 program [49].



**Scheme 2.** Selected heterocyclic compounds structurally similar to maleic hydrazide: 2-pyridone, 3-pyridazone, 4-pyrimidone, cytosine and uracil (depicted to have the H—N—C=O moiety in the same orientation). Middle column shows the oxoforms. The experimentally found structures of their hydroxy tautomers and openring ketene counterparts (isocyanate for cytosine) are shown in right and left columns, respectively. The open-ring or hydroxy forms of uracil have never been experimentally reported.  $\alpha$ -Pyrone is also shown for comparison. The hydroxy form in  $\alpha$ -pyrone is impossible and the experimentally found Dewar isomer is shown instead.

## 3. Results and discussion

## 3.1. The most stable form of maleic hydrazide

Geometry optimizations carried out in the current work resulted in localization of six minima corresponding to maleic hydrazide isomers differing in prototropic tautomerism and in rotations of the OH groups (see Table 1). The relative energies of these forms were calculated using the QCISD/6-31++G(d,p) method at geometries optimized at the same level of approximation. The electronic

#### Table 1

Relative energies (kJ mol<sup>-1</sup>) of isomeric forms of maleic hydrazide.

	H O N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N		H O N-N H	H_O_L_N_N_N_H		
	Ĭa	Ib	lla	IIb	llc	III
Sym.	Cs	Cs	$C_{2v}$	Cs	C <sub>2v</sub>	C <sub>2</sub>
$\Delta E_{el}$	0.0	24.5	22.0	50.9	81.1	21.9
$\Delta ZPE$	0.0	-1.4	-1.7	-3.2	-4.8	-0.9
$\Delta E_{ m total}$	0.0	23.1	20.3	47.7	76.3	21.0

 $\Delta E_{el}$  relative electronic energy calculated at the QCISD/6-31++G(d,p) level.

 $\Delta$ ZPE relative zero point vibrational energy calculated at the DFT(B3LYP)/6-31++G(d,p) level;

 $\Delta E_{\text{total}} = \Delta E_{\text{el}} + \Delta ZPE$ . The absolute  $E_{\text{el}}$  and ZPE calculated values of **Ia** form are equal to -413.6647286  $E_{\text{h}}$  and 0.085982  $E_{\text{h}}$ , respectively.

energies obtained from QCISD calculations were corrected for zeropoint vibrational energies calculated at the DFT(B3LYP)/6-31++G(d,p) level. The results presented in Table 1 clearly show that the most stable form of maleic hydrazide is the oxo-hydroxy structure **Ia**. The oxo-hydroxy rotamer **Ib** as well as the dihydroxy forms **IIa**, **IIb** and **IIc** were predicted to be higher in energy by 23, 20, 48 and 76 kJ mol<sup>-1</sup>, respectively. For the dioxo tautomer **III**, a relative energy of 21 kJ mol<sup>-1</sup> was calculated. The latter form was predicted to be non-planar, with C<sub>2</sub> symmetry, and optimized values of the H–N–N–H and C6–N–N–C3 dihedral angles are 61.1° (QCISD), 49.6° (DFT) and 29.3° (QCISD), 18.5° (DFT), respectively. The predictions of relative stabilities of maleic hydrazide isomers obtained in the current work are in a qualitative agreement with the previous calculations carried out at the MP4/6-31(d,p) level of theory [31].

The computed substantial energy difference between **Ia** and the second most stable form **IIa** strongly suggests that only the most stable isomer **Ia** should be populated in the equilibrium gas phase. An energy difference of 20 kJ mol<sup>-1</sup> is significantly higher than the usual uncertainty in assessments of relative energies based on

QCISD methods. Previous benchmark calculations [35,50] of relative energies of the oxo and hydroxy tautomers of 2-pyridone (and a series of similar compounds) demonstrated that inaccuracies of QCISD calculations should not exceed 2–3 kJ mol<sup>-1</sup>. That is why **Ia** is expected to be the sole form of MH populated in the gas phase and, as a consequence, trapped in low-temperature matrices.

The infrared spectrum of MH monomers isolated in an Ar matrix is presented in Fig. 1. In this spectrum, the characteristic bands due to the stretching vibrations of the OH, NH and C=O groups were found at 3588, 3441 and  $1708/1707/1699 \text{ cm}^{-1}$ . The presence of these characteristic bands is in line with the expectation that in a low-temperature matrix maleic hydrazide monomers exist as form **Ia**. This interpretation is strongly supported by the good general agreement (see also Table 2) between the experimental IR spectrum and the spectrum theoretically predicted for structure **Ia**.

Why it is so that the oxo-hydroxy tautomer **I** is by far the most stable form of maleic hydrazide? Consideration of the tautomerism in the archetype case of 2-pyridone (existing as a mixture of the



Fig. 1. (a and b) Experimental FTIR spectrum of maleic hydrazide monomers isolated in an argon matrix at 15 K; (c and d) Simulated infrared spectrum of maleic hydrazide isomer Ia. For the full calculated spectrum of Ia see Table 2.

## Table 2

Experimental wavenumbers ( $\tilde{v}$ /cm<sup>-1</sup>) and relative integral intensities (I) of the absorption bands in the spectrum of maleic hydrazide isolated in an Ar matrix, compared with wavenumbers ( $\tilde{v}$ /cm<sup>-1</sup>), absolute intensities (A<sup>th</sup>/km mol<sup>-1</sup>) and potential energy distribution (PED,%) calculated for the oxo-hydroxy ( $C_s$ ) form Ia of maleic hydrazide.

Experimental Ar matrix		Calculated B3LYP/6-31++	-G(d,p)		
v	I <sup>a</sup>	$\tilde{v}^{\mathbf{b}}$	A <sup>th</sup>	Sym.	PED <sup>c</sup> (%)
3588.4	156	3593.3	85.8	A'	v OH (100)
3441.1	108	3433.3	69.6	A'	v NH (100)
		3153.6	0.2	A'	v <sub>s</sub> CH (82), v <sub>a</sub> CH (17)
3113.3	2	3131.6	1.5	A'	v <sub>a</sub> CH (82), v <sub>s</sub> CH (17)
<u>1708.0, 1706.6</u> , 1698.6 <sup>d</sup>	247	1713.9	380.7	A'	vC=0 (60)
1624.7	306	1628.3	305.0	A'	v <sub>a</sub> (N=C/C=C) (62), vC=O (14)
1567.0	6	1565.8	10.2	A'	v <sub>s</sub> (N=C/C=C) (52), v <sub>a</sub> CC (12)
1460.0, 1452.8, 1437.8	74	1446.0	73.5	A'	$\beta_a$ CH(24), vC-O(22), $v_s$ (N=C/C=C)(19), $v_a$ CC(17)
1411.0	10	1409.9	16.4	A'	β NH (72)
<u>1341.3</u> , 1308.4	12	1324.5	7.9	A'	β <sub>a</sub> CH (30), β OH (27), v <sub>s</sub> CC (10)
1272.5, 1264.7	8	1264.0	27.9	A'	β <sub>a</sub> CH(24), v <sub>s</sub> (NN/N–C)(22), v C–O(16), β C=O(10)
1229.5	157	1224.5	136.9	A'	v <sub>a</sub> (NN/N–C) (55), v C–O (12)
1158.4, <u>1150.5</u>	55	1149.9	77.4	A'	β OH (40), β <sub>s</sub> CH (25), v <sub>a</sub> (NN/N–C) (13)
1103.0	47	1099.4	60.4	A′	$\beta_{s}$ CH (50), $v_{a}$ (N=C/C=C) (17), $v_{s}$ (NN/N-C) (12)
		983.2	0.0	Α″	γ <sub>s</sub> CH (118)
984.5	52	975.2	52.6	A'	β R1 (38), v <sub>a</sub> CC (24), v <sub>a</sub> (NN/N–C) (16)
<u>841.9,</u> 840.5	71	835.2	39.6	A″	γ <sub>a</sub> CH (78), γ <sub>a</sub> CO (25)
815.3	38	812.2	31.5	A'	v <sub>s</sub> CC (51), v <sub>s</sub> (NN/N–C) (21)
792.0	12	790.7	10.0	A'	β R1 (37), v C–O(21), v <sub>a</sub> CC(15), v <sub>s</sub> (NN/N–C)(10)
		716.9	0.4	A″	γ <sub>s</sub> CO (63), τ R1 (45)
655.1	95	663.9	79.4	A″	γ NH (81), γ <sub>a</sub> CO (23)
627.1	9	620.9	7.0	A'	β R3 (56), v <sub>a</sub> CC (17), β C–O (12)
526.0, 524.3		525.1	0.3	A″	$\gamma_{a}$ CO (45), $\gamma$ NH (22), $\tau$ OH (13), $\gamma_{a}$ CH (13)
488.3	5	485.3	4.5	A'	$\beta$ R2 (75), $v_s$ (NN/N–C) (10)
473.5, <u>472.4</u>	23	467.1	21.9	A'	β C=O (46), β R3 (30), β C-O (19)
<u>430.3</u> , 427.2	152	447.5	143.0	Α″	τ OH (82)
n.i. <sup>d</sup>		367.1	0.7	A″	τ R2 (90), τ R1 (18)
n.i.		357.3	8.5	A'	β C—O (53), β C=O (24)
n.i.		310.3	4.4	Α″	$ au$ R1 (48), $\gamma_{\rm s}$ CO (34), $ au$ R2 (21)
n.i.		117.1	3.1	Α″	τ R3 (100)

<sup>a</sup> Relative integrated experimental intensities, normalized in such a way that their sum is equal to the sum of the corresponding calculated intensities.

<sup>b</sup> Theoretical frequencies were scaled by a factor of 0.975, except for v OH and v NH, which were scaled by 0.950.

<sup>c</sup> PED's lower than 10% are not included. Definition of symmetry coordinates is given in Table S1.

<sup>d</sup> The underlined values correspond to the most intense peaks in the multiplets; n.i. = not investigated.

hydroxy and oxo forms) [35,37,50,51] does not help answering this question. Formally, uracil is an isomer of maleic hydrazide with switched positions of one pair of NH and C=O groups. Uracil is known [50] to exist exclusively in the dioxo tautomeric form. Structural similarities between uracil and maleic hydrazide do not help to explain the differences in tautomerism of these two compounds either. What is then so special in maleic hydrazide that makes its tautomerism unique? This feature is the presence of two vicinal nitrogen atoms in the pyridazine ring of the MH molecule. The same hybridization at these two nitrogen atoms is strongly destabilizing to the system [52]. In the dihydroxy tautomer II, energy rises due to repulsion of lone electron pairs at both nitrogen atoms. In the dioxo tautomer III, repulsion of the positively loaded hydrogen atoms of the two NH groups strongly destabilizes the system. Only in the oxo-hydroxy form I, the destabilizing repulsive effects (described above) are replaced by an energy-lowering, attractive interaction between the hydrogen atom of the NH group and the lone electron pair of the other nitrogen atom. Due to the same reasons, the oxo tautomer of 3-pyridazone is the only form of the compound populated in the gas phase and in low-temperature matrices [36]. 3,6-Dithiopyridazine (DTP) is structurally similar to maleic hydrazide. Both molecules have two nitrogen atoms in the vicinal positions in the pyridazine ring, but two oxygen atoms, present in the structure of MH, are substituted in DTP by two sulfur atoms. Very recently, we have experimentally demonstrated that the thione-thiol tautomer of DTP (the structural analog of oxo-hydroxy form of MH) is the form that strongly dominates in low-temperature Ar matrices [53].

## 3.2. UV-induced unimolecular transformation of maleic hydrazide

Monomers of maleic hydrazide isolated in an Ar matrix were irradiated with the UV light emitted by a high-pressure Xe-Hg lamp operating at 300 W. The matrix was exposed to UV radiation passing through a series of filters transmitting light with waves longer than a cutoff (defined as 40% of transmission) at  $\lambda$  > 397, 367, 346, 328, 295 and 234 nm. After each irradiation, the matrix was monitored by taking an IR spectrum. Then, a filter was replaced by another one, transmitting at shorter wavelengths. No discernible changes in the spectrum of matrix-isolated MH molecules occurred until the  $\lambda$  > 234 nm transmitting filter was used. Irradiation through this filter resulted in appearance of a new set (set #1) of infrared bands. These spectral changes were very slight and stopped after a few minutes of irradiation. At the next stage of the experiment, the UV cut-off filters were removed and the matrix was irradiated only through the outer quartz window of the cryostat. Upon such UV ( $\lambda$  > 200 nm) irradiation, the initial IR spectrum substantially decreased and a new spectrum of the photoproduct(s) emerged (Fig. 2). The photoproduct bands belonging to set #1 increased in intensity upon changing the cutoff filter  $\lambda$  > 234 nm for  $\lambda$  > 200 nm. However, this increase occurred only at the initial stage of UV ( $\lambda > 200$  nm) irradiation and stopped soon afterwards. Another set of new bands (set #2) appeared and grew continuously with each consecutive UV irradiation ( $\lambda > 200$  nm). The IR spectra of the photoproduced species (both set #1 and set #2) consist of sharp IR absorption bands, as narrow as the bands in the initial IR spectrum. This suggests that the observed



**Fig. 2.** (a) Experimental spectra showing results of UV ( $\lambda > 200$  nm) irradiation of MH isolated in an argon matrix at 15 K. The insets show different stages of the irradiation and demonstrate two different kinetics of the two photoproducts; (b) B3LYP calculated spectra of **Ia** ( $\blacksquare$ ) and **IIa** ( $\bigcirc$ ) MH forms (see Table 1 for the structures), as well as N-aminomaleimide (**NAMI**,  $\triangle$ ).

UV-induced transformation(s) are rather photoisomerization(s) and not photofragmentation of MH molecule. In the latter case, interaction of the fragments in the same matrix cage would lead to broadening of the IR bands. Additionally, the observed changes suggest that the UV-induced transformation of **Ia** into a structure characterized by set #1 of infrared bands is photoreversible. This conversion leads to photostationary states, with the photostationary ratio of the substrate and the product specific for the wavelength of UV light used for irradiation.

If the UV-induced isomerization was the oxo  $\rightarrow$  hydroxy hydrogen-atom transfer (similar to the phototautomerism previously observed for 2-pyridone, 3-pyridazone, 4-pyrimidone, and cytosine; see Scheme 2) [34–38] then the dihydroxy form **IIa** of maleic hydrazide should be photoproduced. According to the DFT calculations, in the IR spectrum of **IIa**, two characteristic bands due to stretching vibrations of the OH groups ( $\nu$  OH) should appear at frequencies lower by some 20 cm<sup>-1</sup> than the spectral position of the  $\nu$  OH band in the spectrum of **Ia**. Taking into account that in the experimental spectrum of **Ia** the *v* OH band was found at 3588 cm<sup>-1</sup>, the *v* OH bands due to photoproduced **IIa** can be expected in the 3575–3560 cm<sup>-1</sup> range. And indeed, in the experimental spectrum recorded after UV ( $\lambda > 234$  nm) irradiation of matrix-isolated MH new bands appeared at 3572 and 3570 cm<sup>-1</sup> (see Fig. 2). These frequencies are similar to those of the *v* OH bands observed in the IR spectra of 2-hydroxypyridine (3576 cm<sup>-1</sup>), 4-hydroxypyrimidine (3563 cm<sup>-1</sup>) and 3-hydroxypyridazine (3558/3553 cm<sup>-1</sup>) [35–38]. Hence, the dihydroxy form **IIa** may be considered as a probable candidate for the photoproduct, being the carrier of the experimentally observed set #1 of IR bands. The phototautomeric reaction transforming the oxo-hydroxy form **Ia** into the dihydroxy form **IIa** would be analogous to the thione–thiol  $\rightarrow$  dithiol phototautomerism recently observed for matrix-isolated DTP [53].

As already mentioned, careful inspection of the progress of the photoreactions consuming **Ia** form of MH (Fig. 2) led to identification of two kinetic patterns of growth of the IR bands due to



**Fig. 3.** (a) The experimental spectrum of the minor photoproduct generated upon UV ( $\lambda > 234$  nm and  $\lambda > 200$  nm) irradiations of maleic hydrazide isolated in an Ar matrix at 15 K; (b) infrared spectrum of MH dihydroxy form **IIa** simulated using Lorentzian functions; (c) infrared spectrum of **IIa** calculated at the B3LYP level. For the full calculated spectrum of **IIa** see Table 3.

photogenerated species. By exploring the differences in the kinetics of the photochemical behavior, it was possible to separate the IR bands emerging upon UV irradiation into set #1 and set #2, each of them characterizing one of the photoproducts.

Within set #1, alongside the high frequency bands at 3572, 3570 cm<sup>-1</sup>, several bands were found at lower frequencies. The fingerprint region of set #1 is dominated by the intense bands observed at 1455 and 1214/1193 cm<sup>-1</sup>. These experimental bands are easily ascribable to the pair of intense bands at 1454 and  $1196 \text{ cm}^{-1}$  in the theoretically predicted spectrum of **IIa** (see Fig. 3). According to the calculations, the experimental band at 1214/1193 cm<sup>-1</sup> should be due to the antisymmetric bending vibration of the OH groups ( $\beta_a$  OH). This band is split, similarly as it was observed for the  $\beta$  OH bands (usually split in several components) in the experimental spectra 2-hydroxypyridine, 4-hydroxypyrimidine and 3-hydroxypyridazine isolated in Ar matrices [36-38]. A good agreement between the experimental and theoretical spectra, presented in Fig. 3, strongly supports the assignment of the dihydroxy structure IIa to the photoproduct characterized by set #1 of IR bands emerging upon UV irradiation. These bands are compared with the calculated infrared spectrum of the dihydroxy form IIa in Table 3. Analysis of this table shows that all bands of form IIa having calculated infrared intensities above  $20 \text{ km mol}^{-1}$  appear in the experimentally observed spectrum of set #1. The only exception is the band due to  $\gamma_a$  CH, predicted for IIa at 833.8  $\text{cm}^{-1}$  (Table 3). It must be obscured by the  $\gamma_a$  CH band of **Ia** (calculated at 835.2 cm<sup>-1</sup>, Table 2). The nonobservation of additional experimental bands in set #1 is consistent with predictions: more than a half of vibrations of form IIa have calculated infrared intensities below 5 km mol<sup>-1</sup> (see Table 3).

The other kinetic behavior was observed for set #2 of IR bands appearing after UV ( $\lambda > 200$  nm) irradiation. This type of kinetics concerned the growth of a number of new bands appearing throughout the spectrum; e.g. the high-frequency band at

#### Table 3

Experimental wavenumbers ( $\bar{\nu}$ /cm<sup>-1</sup>) and relative integral intensities (*I*) of the absorption bands in the spectrum of the minor photoproduct generated upon UV irradiation of maleic hydrazide isolated in an Ar matrix, compared with wavenumbers ( $\bar{\nu}$ /cm<sup>-1</sup>), absolute intensities ( $A^{th}$ /km mol<sup>-1</sup>) and potential energy distribution (PED,%) calculated for the dihydroxy ( $C_{2\nu}$ ) form **IIa** of maleic hydrazide.

Experimental Ar matrix		Calculated B3LYP/6-31++G(d,p)				
ĩ		I <sup>a</sup>	$\tilde{\nu}^{\ b}$	A <sup>th</sup>	Sym.	PED <sup>c</sup> (%)
35	72.1*	250.4*	3572.3	98.1	A <sub>1</sub>	v <sub>s</sub> OH (100)
35	70.0*	*	3570.4	63.6	$B_2$	v <sub>a</sub> OH (100)
			3150.5	0.7	$A_1$	v <sub>s</sub> CH (99)
			3137.1	1.6	B <sub>2</sub>	v <sub>a</sub> CH (100)
			1613.1	1.1	$A_1$	v CC (44), β <sub>s</sub> CH (14), v <sub>s</sub> CN (11),
						v <sub>s</sub> CC (11), β R2 (11)
			1590.9	0.4	B <sub>2</sub>	<i>v</i> <sub>a</sub> CC (44), <i>v</i> <sub>a</sub> CN (23), <i>β</i> <sub>a</sub> OH (11)
14	55.4	508.5	1454.3	581.9	B <sub>2</sub>	<i>v</i> <sub>a</sub> CN (40), <i>β</i> <sub>a</sub> CH (24), <i>v</i> <sub>a</sub> CO (23)
			1432.6	1.4	$A_1$	$\beta_{s}$ OH (33), $v_{s}$ CC (22), $\beta_{s}$ CO (16)
			1324.5	3.5	$A_1$	v <sub>s</sub> CO (41), v <sub>s</sub> CN (28), v CC (23)
			1291.7	8.7	B <sub>2</sub>	$\beta_{a}$ CH (44), $v_{a}$ CO (21), $\beta_{a}$ OH (19),
						β R1 (12)
			1214.9	13.9	$A_1$	v NN (53), v <sub>s</sub> CN (23), β <sub>s</sub> CH (13),
						v <sub>s</sub> CO (11)
12	14.4**	196.9	1196.4	352.9	B <sub>2</sub>	$\beta_{a}$ OH (61), $v_{a}$ CN (14), $v_{a}$ CO (11)
11	93.5**	154.9				
			1151.2	0.3	$A_1$	$\beta_{\rm s}$ OH (52), $v_{\rm s}$ CC (18), $v_{\rm s}$ CN (16),
						β <sub>s</sub> CH (13)
10	93.2	13.4	1095.0	20.3	$A_1$	β <sub>s</sub> CH (57), v CC (16), v NN (13)
10	19.6	28.7	1017.2	35.8	B <sub>2</sub>	β R1 (32), v <sub>a</sub> CC (30), v <sub>a</sub> CN (18),
						β <sub>a</sub> CH (16)
			958.8	0	$A_2$	γ <sub>s</sub> CH (116)
			852.0	10.8	$A_1$	v <sub>s</sub> CC (48), v <sub>s</sub> CO (14), v <sub>s</sub> CN (14),
						β R2 (12)
			833.8	37.4	$B_1$	γ <sub>a</sub> CH (83), γ <sub>a</sub> CO (20)
7	84.1	17.2	779.2	22.7	B <sub>2</sub>	v <sub>a</sub> CO (42), β R1 (40)
			720.1	0	$A_2$	τ R1 (63), γ <sub>s</sub> CO (44)
			641.6	4.6	$B_2$	$\beta$ R3 (70), $\beta_a$ CO (16), $v_a$ CC (11)
5	66.8,	38.2	572.7	71.4	$B_1$	γ <sub>a</sub> CO (56), τ <sub>a</sub> OH (26), γ <sub>a</sub> CH (11)
5	65.4					
			497.9	1.4	$A_1$	β R2 (71), v <sub>s</sub> CO (17)
			497.5	0	$A_2$	τ <sub>s</sub> OH (94)
4	46.7	216.0	466.0	180.4	B <sub>1</sub>	τ <sub>a</sub> OH (74), γ <sub>a</sub> CO (19)
4	56.1	59.3	451.5	56.5	B <sub>2</sub>	β <sub>a</sub> CO (73), β R3 (21)
			429.2	0	$A_2$	$ au$ R2 (68), $ au$ R1 (16), $\gamma_{\rm s}$ CO (14)
			339.7	0.3	$A_1$	β <sub>s</sub> CO (83)
			339.3	0	$A_2$	$ au$ R2 (40), $\gamma_{\rm s}$ CO (38), $ au$ R1 (27)
			140.9	0.4	$B_1$	τ R3 (96)

<sup>a</sup> Relative integrated experimental intensities, normalized in such a way that their sum is equal to the sum of the corresponding calculated intensities.

<sup>b</sup> Theoretical frequencies were scaled by a factor of 0.975, except for  $v_a$  OH and  $v_s$  OH, which were scaled by 0.950.

<sup>c</sup> PED's lower than 10% are not included. Definition of symmetry coordinates is given in Table S2.

<sup>\*</sup> The bands observed at 3572.1 and 3570.0 cm<sup>-1</sup> are merged in the experiment, and the relative experimental intensity (250.4) applies for the pair of bands.

<sup>\*\*</sup> The theoretical band predicted at 1196.4 cm<sup>-1</sup> is assigned to the pair of experimental bands observed at 1214.4 and 1193.5 cm<sup>-1</sup>.

3380 cm<sup>-1</sup> (see Fig. 2). Appearance of set #2 of bands (making the spectrum of a second photoproduct) clearly shows that **IIa** is not the only species generated upon UV-irradiation of **Ia**. The most striking feature of set #2, is the very intense IR absorption observed at 1742 cm<sup>-1</sup>. Of course, a band at such frequency (characteristic of stretching vibrations of C=O groups, v C=O) cannot belong to the spectrum of the dihydroxy form **IIa**. More specifically, a frequency of 1742 cm<sup>-1</sup> indicates a C=O group directly attached to a five-membered ring. Usually, the frequencies of the stretching vibrations of such C=O groups are intermediate between the frequencies (1830–1780 cm<sup>-1</sup>) of vibrations of C=O groups attached to four-membered rings [38–40] and the frequencies (~1700 cm<sup>-1</sup>) of vibrations of C=O groups attached to sixmembered rings (see e.g. the IR spectrum of the initial form **Ia**).



**Fig. 4.** (a) The experimental spectrum of the major photoproduct generated upon UV ( $\lambda > 200 \text{ nm}$ ) irradiation of maleic hydrazide isolated in an Ar matrix at 15 K; (b) infrared spectrum of N-aminomaleimide (NAMI) simulated using Lorentzian functions; and (c) infrared spectrum of NAMI calculated at the B3LYP level. For the full calculated spectrum of NAMI see Table 4.



**Fig. 5.** Relaxed potential energy scan for the amino group *rotation* in N-aminomaleimide calculated at the B3LYP/6-31++G(d,p) level. The dummy atom "X" in the reaction coordinate is located on the axis that goes through the ring nitrogen atom and is perpendicular to the CNC plane (plane of the figure). The "Lp" in the reaction coordinate stands for the "lone pair" of electrons of the amino group and is defined as a second dummy atom located in the plane bisecting the two NNH planes. The relative zero energy level was chosen as the energy of the maleic hydrazide most stable isomer **Ia**.

Several candidate structures were considered in order to identify the second product of maleic hydrazide photoisomerization. The extracted experimental spectrum shown in Fig. 4 was well reproduced only by the theoretical spectrum calculated for N-aminomaleimide. The structure of N-aminomaleimide (NAMI), optimized at the DFT(B3LYP)/6-31++G(d,p) level, has a symmetry plane and the overall C<sub>s</sub> symmetry (see Fig. 5). In this optimized structure, both hydrogen atoms of the NH<sub>2</sub> group are directed to one of the C=O groups. Of course, there is a second, equal by symmetry minimum on the potential energy surface of NAMI (see Fig. 6). The barrier between these minima was calculated, at



**Fig. 6.** Potential energy scan for the amino group *inversion* in N-aminomaleimide calculated at the B3LYP/6-31++G(d,p) level of theory within the  $C_s$  symmetry. The carbon atom that defines the scan coordinate is shown explicitly. The second CNNH angle is symmetrically equal to the scan coordinate (has the same numeric value and the opposite sign). The energy scale in Figs. 5 and 6 is equal.

the DFT(B3LYP)/6-31++G(d,p) level, to be 8.1 kJ mol<sup>-1</sup> (by rotation of the NH<sub>2</sub> group, see Fig. 5) or 17.7 kJ mol<sup>-1</sup> (by inversion of the NH<sub>2</sub> group, see Fig. 6). Then, NAMI is a double-energy-well molecule, with hydrogen atoms of the NH<sub>2</sub> group tunneling from one minimum to the other. Hence, the calculations carried out within a harmonic approximation can predict frequencies and intensities of some bands somewhat poorer than it usually is the case for rigid molecules.

Nevertheless, the juxtaposition of the experimental IR spectrum of the second photoproduct generated from MH with the theoretical spectrum of NAMI (shown in Fig. 4) is quite convincing and strongly supports the identification of the photoproduced species. The experimental position  $(1742 \text{ cm}^{-1})$  of the band due to antisymmetric vibration of the C=O groups is well predicted (1748 cm<sup>-1</sup>) by the DFT(B3LYP) calculations. Similarly, the lowintensity band at 3380 cm<sup>-1</sup>, which is due to the stretching vibrations of the NH<sub>2</sub> group attached to the five-membered ring, is well predicted in the theoretical spectrum (Fig. 2). A characteristic group of four bands observed in the experimental spectrum at 870, 823/821, 730 and 688  $\text{cm}^{-1}$  is nicely reproduced by the theoretical bands at 862, 808, 720 and 674 cm<sup>-1</sup>. These bands correspond to the wagging vibration of the NH<sub>2</sub> group, out-of-plane vibrations of the two CH groups, and to the deformations of the five-membered ring, respectively. Altogether, the general patterns of IR absorptions in the experimental and theoretical spectra are convincingly similar to each other (see Table 4). This allows a reliable assignment of N-aminomaleimide structure to the second species photogenerated from maleic hydrazide.

Several steps are necessary to convert the molecule of maleic hydrazide into N-aminomaleimide: (i) opening of the six-membered ring (by cleavage of the CN bond) and concomitant isomerization of the open-ring product; (ii) closure of the five-membered ring to form N-iminomaleimide; (iii) hydrogenatom transfer to form the  $NH_2$  group (see Scheme 3).

In the first step, the ring-opening reaction within the  $C_s$  symmetry does not yield an open-ring isomer that corresponds to a local energy minimum (see Fig. 7). A similar behavior during the ring-opening reaction was found for  $\alpha$ -pyrone and its sulfur analogs [54]. If the symmetry during the ring-opening reaction is not restricted, an additional local energy minimum appears at the cost of isomerization around the C=C–N=N dihedral angle from *cis* (in **Ia**) to *trans* orientation (see Fig. 8). This isomerization requires an activation energy of about 280 kJ mol<sup>-1</sup> (DFT calculations) and proceeds over the potential energy barrier designated in Fig. 8 as TS1. The resulting open-ring product has a relative energy of about

## Table 4

Experimental wavenumbers ( $\tilde{v}/cm^{-1}$ ) and relative integral intensities (*I*) of the absorption bands in the spectrum of the major photoproduct generated upon UV irradiation of maleic hydrazide isolated in an Ar matrix, compared with wavenumbers ( $\tilde{v}/cm^{-1}$ ), absolute intensities ( $A^{th}/km mol^{-1}$ ) and potential energy distribution (PED, %) calculated for N-aminomaleimide ( $C_s$ ).

Experimental Ar matrix		Calculated B3LYP/6-31++	Calculated B3LYP/6-31++G(d,p)				
ĩ	$I^a$	$\tilde{v}^{\mathbf{b}}$	A <sup>th</sup>	Sym.	PED <sup>c</sup> (%)		
3379.7	15.0	3400.3	11.5	Α″	v <sub>a</sub> NH (100)		
3285.9	2.2	3314.8	1.7	A'	v <sub>s</sub> NH (100)		
		3184.3	0.02	A'	v <sub>s</sub> CH (98)		
		3164.4	0.05	A'	v <sub>a</sub> CH (99)		
1837.3	9.6						
1827.3	9.6						
1790.4	19.4	1802.1	38.4	A'	v <sub>s</sub> C=O (80)		
1765.2	30.9						
1741.8	538.1	1747.8	736.8	A'	v <sub>a</sub> C=O (82)		
1730.3	81.8						
1721.8	29.7						
		1654.2	8.0	A'	$\beta$ NH <sub>2</sub> (62), $\beta_{s}$ NH (35)		
		1605.6	0.9	A'	v C=C (84)		
1423.0, 1420.2, 1415.1	108.1	1406.7	117.1	A'	ν NN (34), v <sub>s</sub> CN (33), β <sub>s</sub> CO (12), β R1 (12)		
		1305.0	3.0	A″	β <sub>a</sub> NH (100)		
		1298.5	1.8	A'	$\beta_a$ CH (74), $v_a$ CC (17)		
1182.1	75.6	1163.4	37.8	A'	v <sub>a</sub> CN (34), v <sub>s</sub> CC (14)		
1147.4, 1137.7	42.2	1126.2	42.1	A'	v <sub>a</sub> CN (25), β <sub>s</sub> CH (17), v <sub>s</sub> CC (16), v NN (15)		
1044.7	8.1	1036.8	17.2	A'	$\beta_{\rm s}$ CH (57), $v_{\rm s}$ CC (11)		
1035.9	2.2	1025.6	3.9	A'	$v_a$ CC(24), $\beta_a$ CO (18), $\beta_a$ CH (13), $\beta$ NN (11)		
		946.1	0.02	A″	γ <sub>s</sub> CH (114)		
870.3	118.9	861.7	111.1	A'	β <sub>s</sub> NH (55), β NH <sub>2</sub> (24)		
822.8, 820.7	80.6	807.9	70.1	A″	γ <sub>a</sub> CH (64), γ <sub>a</sub> CO (35)		
		751.4	0.4	Α″	γ <sub>s</sub> CO (74), τ R1 (29)		
730.1	13.0	720.3	11.1	A'	v <sub>s</sub> CC (38), v <sub>s</sub> CN (27), v NN (26)		
688.4	56.7	674.3	43.0	A'	β R2 (61), v <sub>a</sub> CN (19)		
		591.1	1.6	A'	β R1 (70), v <sub>s</sub> CN (10)		
		589.3	0.2	A″	γ <sub>a</sub> CO (49), γ <sub>a</sub> CH (36), τ R2 (17)		
		562.5	1.4	A'	$\beta_{a}$ CO (51), $v_{a}$ CC (34)		
		363.2	15.6	A'	$\beta_{\rm s}$ CO (65), $v_{\rm s}$ CN (19)		
		290.4	0.4	Α″	τ R1 (85), γ <sub>s</sub> CO (21)		
		280.2	12.0	A'	β NN (69), β <sub>a</sub> CO (21)		
		189.2	47.0	A″	τ NH2 (92), γ NN (11)		
		151.4	0.04	A″	γ NN (92)		
		123.4	14.6	Α″	$ au$ R2 (89), $\gamma_{a}$ CO (14)		

<sup>a</sup> Relative integrated experimental intensities, normalized in such a way that their sum is equal to the sum of the corresponding calculated intensities.

<sup>b</sup> Theoretical frequencies were scaled by a factor of 0.975, except for  $v_a$  NH and  $v_s$  NH, which were scaled by 0.950.

<sup>c</sup> PED's lower than 10% are not included. Definition of symmetry coordinates is given in Table S3.

196 kJ mol<sup>-1</sup> with respect to the closed-ring reactant **Ia**. The subsequent steps are energetically much less demanding. By overcoming TS2 (215 kJ mol<sup>-1</sup>), the ring-closure can yield N-iminomaleimide (202 kJ mol<sup>-1</sup>), which in turn, by overcoming TS3 (228 kJ mol<sup>-1</sup>), may transform into N-aminomaleimide (Fig. 9). It is important that the set of four structures including consecutively (a) the open-ring isomer, (b) TS2, (c) N-iminomaleimide, and (d) TS3 fall in an energy range between 196 and 228 kJ mol<sup>-1</sup>, which is much lower than the activation barrier of 280 kJ mol<sup>-1</sup>. Therefore, both the open-ring product (see the structure shown in Figs. 8 and 9) and N-iminomaleimide are kinetically unstable and unlikely to be trapped in the photolyzed matrix.

A careful inspection of the spectra of irradiated matrices reveals yet another group of bands which cannot be attributed to either of the photoproducts discussed above. These bands start to be discernible only after UV ( $\lambda > 200$  nm) irradiation, and are located around 2150–2100 cm<sup>-1</sup> (see Fig. 10). This spectral range is characteristic of the antisymmetric stretching vibration of the ketene ( $v_a$  C=C=O) group [55,56]. This vibration has inherently very high intensity in infrared, ranging usually above 1000 km mol<sup>-1</sup> [57]. In the present experiment, the intensities of the bands appearing between 2150 and 2100 cm<sup>-1</sup> are two orders of magnitude lower than the strongest (v C=O) band of NAMI (see Fig. 10). Taking also into account that the calculated absolute intensities of the



Scheme 3. UV-induced unimolecular transformations of maleic hydrazide.



**Fig. 7.** Relaxed potential energy scan for the ring-opening reaction in maleic hydrazide isomer **Ia** calculated at the B3LYP/6-31++G(d,p) level of theory within the C<sub>s</sub> symmetry point group. The two atoms that define the scan coordinate are shown in bold. The horizontal dashed line designated as TS1 is explained in the caption of Fig. 8.



**Fig. 8.** Relaxed potential energy scan for the ring-opening/ring-closure reaction connecting the "open-ring" maleic hydrazide isomer (right) with the closed ring **Ia** isomer calculated at the B3LYP/6-31++G(d,p) level of theory. The four atoms that define the scan coordinate are shown in bold. TS1 corresponds to the first order saddle point (top of the barrier) having the CCNN dihedral angle equal to 98.4° and located at the level of 279.7 kJ mol<sup>-1</sup> relatively to the energy of **Ia** isomer. This level is shown in Fig. 7 as the horizontal dashed line. The energy scale in Figs. 7 and 8 is equal.

 $v_a$  C=C=O vibration are much higher than those of v C=O in NAMI, it implies that the total amount of the open-ring ketene trapped in the matrix does not exceed a few tenths of 1% (comparing to NAMI). This confirms the above statement that the ketene intermediate must be produced but is kinetically unstable in the present case. The high conformational mobility of the open-ring ketene derived from **Ia** may result in additional isomerization of a small fraction of this transient species (i.e. around the central C=C bond) and in observation of residual amount of open-ring ketene in a conformation different from that shown in Fig. 9. The likelihood of the conformational isomerization of the open-ring ketene is manifested by the presence of several components in the observed multiplet and by changes in their relative intensity at different stages of the UV irradiation.



**Fig. 9.** Potential energy scan for the ring-closure reaction from the open-ring maleic hydrazide isomer (right) to N-iminomaleimide (top-left) calculated at the B3LYP/6-31++G(d,p) level of theory within the C<sub>s</sub> symmetry. The two atoms that define the scan coordinate are shown in bold. The horizontal dashed line designated as TS1 is positioned at the energy of transition state shown in Fig. 8. TS3 (empty square) corresponds to the transition state between N-iminomaleimide (NIMI) and N-aminomaleimide (NAMI, full square). Note that the isomerization from NIMI to NAMI (via TS3) involves an intramolecular H-atom shift and does not affect much the **CN** distance. The energy scale in Figs. 7–9 is equal.



**Fig. 10.** Results of UV ( $\lambda > 200 \text{ nm}$ ) irradiation of MH isolated in an argon matrix at 15 K, showing changes in infrared spectra in the characteristic regions of the C=C=O antisymmetric stretching and C=O stretching vibrations. Note that the inset shows expansion of the ordinate scale by approximately two orders of magnitude.

Comparison of experimental intensities of IR bands in the spectra of two products of maleic hydrazide leads to the conclusion that N-aminomaleimide is the main photoproduct, whereas the dihydroxy tautomer **IIa** is a lesser populated, minor photoproduct. After 70 min of UV ( $\lambda > 200$  nm) irradiation, the quantity of **Ia** remaining in the matrix was measured directly and amounted to 29%. An approximate branching ratio of the photoreaction converting **Ia** to NAMI and **IIa** was estimated by reducing the experimental integral intensities of the bands due to these species by their theoretically calculated infrared intensities. The amounts of the photoproduced NAMI corresponded to 58%, while the amount of photoproduced **IIa** corresponded to 8% of the initially deposited **Ia**.

The summary of unimolecular phototransformations experimentally observed in this study is presented in Scheme 3. Although none of the elementary photoinduced acts is unusual, the final result of these transformations (conversion of maleic hydrazide into N-aminomaleimide) is unique. For any heterocyclic compound with a structure similar to maleic hydrazide (for example, 3,6-dithiopyridazine) [53], no analogous phototransformation has been reported so far.

## 4. Conclusions

The most stable oxo-hydroxy form of maleic hydrazide was found to be exclusively populated in low-temperature Ar matrices. Upon irradiation with UV light with waves longer than 250 nm this form was photostable. Only upon UV ( $\lambda > 234$  nm) irradiations, providing considerable excitation energy excess, unimolecular photoreactions of maleic hydrazide occurred. Two channels of UV-induced transformations were observed for maleic hydrazide: (i) the oxo  $\rightarrow$  hydroxy phototautomerism similar to that observed for other analogous heterocyclic compounds; (ii) the phototransformation of maleic hydrazide to N-aminomaleimide. Of the two photoreactions of matrix-isolated maleic hydrazide, the latter one was found to be the most efficient. The result of this phototransformation is quite unique, but can be explained in terms of elementary photochemical reactions (ring-opening, isomerization, ring-closure, intramolecular hydrogen shift) reported earlier.

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### Appendix A. Supplementary material

Supplementary data available for the lists of internal coordinates used in the normal mode analyses of MH isomers **Ia** (Table S1), **IIa** (Table S2), and NAMI (Table S3). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.11.051.

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