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Article

Photochemical Generation of Benzoazetinone by UV Excitation of Matrix-Isolated Precursors: Isatin or Isatoic Anhydride

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ABSTRACT: Benzoazetinone was photochemically generated by UV irradiation of isatin isolated in low-temperature Ar matrixes. Upon UV (λ = 278 nm) excitation of isatin, monomers of the compound underwent decarbonylation and the remaining part of the molecule adopted the benzoazetinone structure or the structure of its open-ring isomer α-iminoketene. The same products (benzoazetinone and α-iminoketene) were generated by UV (λ = 278 nm) induced decarboxylation of matrix-isolated monomers of isatoic anhydride. Photoproduced α-iminoketene appeared in the low-temperature matrixes as a mixture of syn and anti isomers. Photoproducts generated upon λ = 278 nm irradiation of matrix-isolated isatin were subsequently exposed to λ = 532 nm light. That irradiation resulted in the shift of the α-iminoketene–benzoazetinone population ratio in favor of the latter closed-ring structure. The next irradiation at 305 nm caused the shift of the α-iminoketene–benzoazetinone population ratio in the opposite direction, that is, in favor of the open-ring isomer. Neither benzoazetinone nor its α-iminoketene open-ring isomer was generated upon UV (λ = 278 nm) irradiation of phthalimide isolated in Ar matrixes. Instead, the UV-excited monomers of this compound underwent such phototransformations as oxo → hydroxy phototautomerism or degradation of the five-membered ring with release of HNCO and CO. The efficiency of these photoconversions was low.
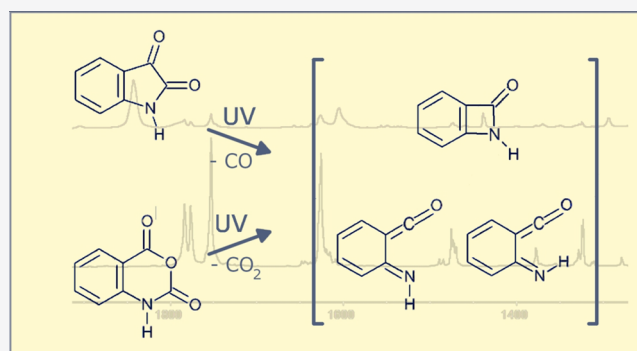
INTRODUCTION

Azetinone molecules are interesting because of the partially antiaromatic character of their four-membered ring.[1,2] The saturated azetidinone moiety is a common structural fragment of natural semisynthetic and synthetic β-lactam anitibiotics.[3,4] It has also been recognized as a building block for the synthesis of many biologically important compounds, such as amino acids, peptides, alkaloids, aminosugars, and others.[5]

Azetinone itself is an extremely unstable compound, even at low temperature. Hence, the attempts to obtain this species were not successful.[1] The azetinone structure, with four-membered ring, is ~50 kJ mol^{-1} less stable than its open-ring α-iminoketene isomer.[2] In contrast to that, the energy of the closed-ring structure of benzoazetinone is lower (by more than 30 kJ mol^{-1}) than that of its open-ring α-iminoketene isomer. Although benzoazetinones are highly reactive and difficult to obtain, there are several reports on successful preparation of benzoazetinone or its derivatives.[6−9] Only some N-alkylbenzoazetinones with tertiary alkyl groups can be stable at room temperature. Pyrolysis of isatoic anhydride, followed by trapping of the products at 77 K, was reported to yield benzoazetinone itself.[6] Similarly, trapping of the products of 1-methyl-1,2,3-benzotriazin-4(1H)-one pyrolysis in a layer of solid argon at 15 K led to stabilization of N-methylbenzoazetinone in an Ar matrix.[7] UV-induced decarbonylation of N-

methoxyisatin isolated in an Ar matrix yielded N-methoxy-benzoazetinone.[8] Recently, N-deuterated benzoazetinone and related deuterated open-ring α-iminoketene were photochemically generated from deuterated 2-formylphenylazide isolated in an Ar matrix.[9] This latter photoconversion occurred via a deuterated 2-formylphenylnitrene diradical, which was the primary photoproduct directly obtained by N_2 detachment from deuterated 2-formylphenylazide.

In the current work, we attempted to generate benzoazetinone by *in situ* UV excitation of matrix-isolated precursors: isatin, phthalimide, or isatoic anhydride (Scheme 1). To convert into benzoazetinone, such precursors need to undergo UV-induced decarbonylation (isatin, phthalimide) or decarboxylation (isatoic anhydride).

In the literature, there are many examples of photodecarboxylation or photodecarbonylation processes,[8,10−12] which occur in molecules having one or more C═O groups
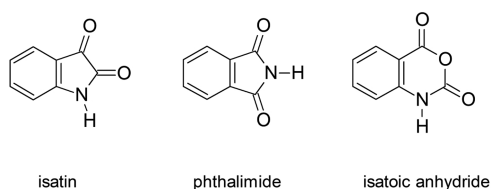
Scheme 1. Chemical Structures of the Most Stable Dioxo Forms of Isatin, Phthalimide, and Isatoic Anhydride

isatin   phthalimide   isatoic anhydride

in the structure (see Scheme S1 in the Supporting Information). Hence, it seemed possible that photodecarbonylation or photodecarboxylation of isatin, phthalimide, or isatoic anhydride might yield benzoazetinone. The experiments carried out within the current work confirmed some of these expectations. We demonstrated that photodecarbonylation of isatin as well as photodecarboxylation of isatoic anhydride yielded benzoazetinone and its open-ring isomer α-iminoketene. It is the first investigation on photochemical transformations of isolated molecules of unsubstituted isatin. Phthalimide molecule, despite the structural similarity to isatin (Scheme 1), did not undergo UV-induced conversion into benzoazetinone and its open-ring α-iminoketene form.

■ EXPERIMENTAL SECTION

The compounds used in the current study as photochemical precursors were commercial products. Phthalimide (purity >99%) was provided by Sigma-Aldrich, and isatin (>98%) and isatoic anhydride (>98%) were purchased from TCI Europe. For each matrix-isolation experiment, a solid sample of the studied compound was placed in a miniature glass oven located inside the vacuum shroud of the cryostat cooled by a Sumitomo SRDK-408D2 closed-cycle helium refrigerator. The cryostat was then evacuated, and the compound was heated (to 400 K for isatin, 430 K phthalimide, 420 K isatoic anhydride) by a resistive wire wrapped around the microoven. The vapor of the compound was deposited, together with a large excess of argon (Linde, 6.0 purity), onto a CsI substrate mounted on the cold (15 K) tip of the cryostat. The infrared (IR) absorption spectra were recorded with 0.5 cm^{-1} resolution in the 4000–400 cm^{-1} range, using a Thermo Nicolet iS50R FTIR spectrometer equipped with a KBr beam

splitter and a DTGS-KBr detector. The spectra in the 690–220 cm^{-1} range were recorded with 1 cm^{-1} resolution using the same spectrometer but equipped with a solid substrate beam splitter and a DTGS-PE detector. Matrix-isolated monomers of isatin, phthalimide, and isatoic anhydride were irradiated with UV (λ_{max} = 278 nm, fwhm = 15 nm) light or with UV (λ_{max} = 305 nm, fwhm = 15 nm) light emitted by 6060 LG Innotek diodes. The optical power of UV light generated by these LEDs was 100 mW. In some experiments, a high-pressure mercury lamp HBO200, fitted with a water filter and cutoff WG295 or WG320 Schott filters, was used as a source of UV light. Matrixes were also irradiated with visible 532 nm light of a green laser pointer (30 mW).

■ COMPUTATIONAL SECTION

The geometries of all structures considered in this work were fully optimized using the density functional method DFT(B3LYP) with the Becke's three-parameter exchange functional[13] and the Lee, Yang, Parr correlation functional.[14] The 6-311++G(2d,p) basis set was applied in these calculations. At the optimized geometries, the harmonic vibrational frequencies and IR intensities were calculated at the same DFT(B3LYP)/6-311++G(2d,p) level. The computed harmonic vibrational wavenumbers were scaled down by a factor of 0.95 for wavenumbers higher than 3000 cm^{-1} and by a factor of 0.98 for wavenumbers lower than 3000 cm^{-1}. All quantum-mechanical computations were carried out with the Gaussian 03 program.[15]

■ RESULTS AND DISCUSSION

4.1. Most Stable Isomeric Forms of Monomeric Isatin, Phthalimide, and Isatoic Anhydride. X-ray studies demonstrated that in the condensed phases the molecules of isatin,[16,17] phthalimide[18] and isatoic anhydride[19] adopt only their dioxo forms. However, in the gas phase, where intermolecular interactions are absent, the relative energies and relative populations of isomeric forms of these compounds may be different.

For monomers of isatin, phthalimide, and isatoic anhydride, the relative energies of different isomeric structures (the dioxo tautomer and the conformers of the oxo-hydroxy tautomer) were calculated at the DFT(B3LYP)/6-311++G(2d,p) level. In
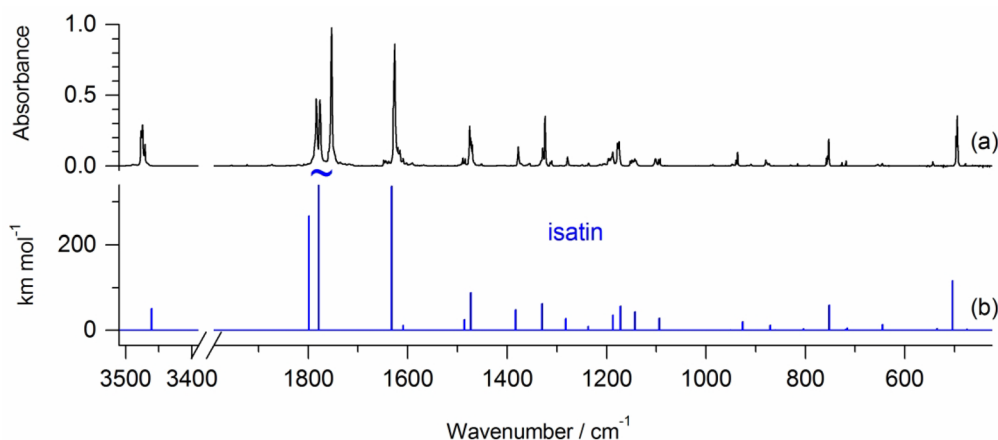

Figure 1. Experimental IR spectrum of isatin monomers isolated in a low-temperature argon matrix at 15 K (a), compared with harmonic wavenumbers and IR intensities calculated for the dioxo tautomer of the compound at the DFT(B3LYP)/6-311++G(2d,p) level (b). The theoretical wavenumbers higher than 3000 cm^{-1} were scaled by a factor of 0.95, whereas those lower than 3000 cm^{-1} were scaled by 0.98.
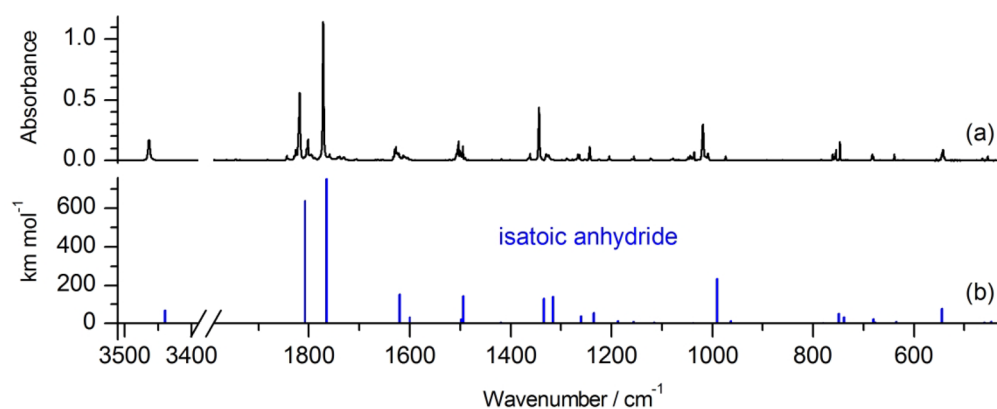
Figure 2. Experimental IR spectrum of isatoic anhydride monomers isolated in a low-temperature argon matrix at 15 K (a), compared with harmonic wavenumbers and IR intensities calculated for the dioxo tautomer of the compound at the DFT(B3LYP)/6-311++G(2d,p) level (b). The theoretical wavenumbers higher than 3000 cm^{-1} were scaled by a factor of 0.95, whereas those lower than 3000 cm^{-1} were scaled by 0.98.
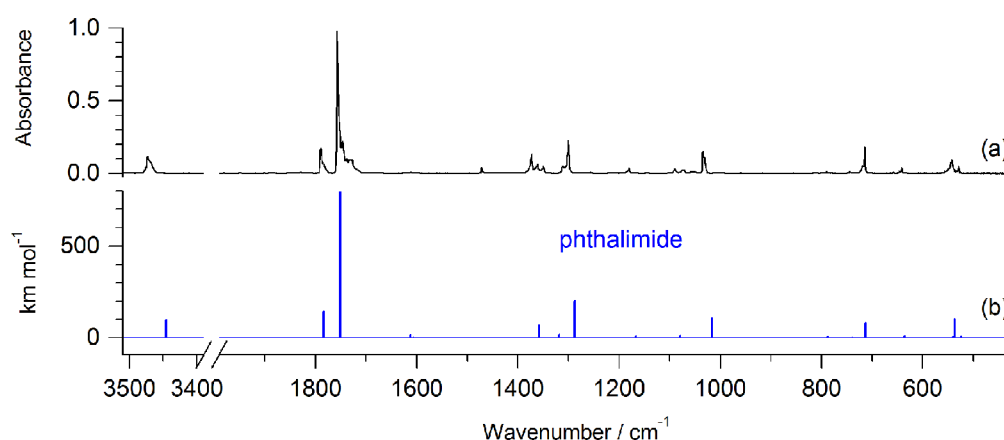

Figure 3. Experimental IR spectrum of phthalimide monomers isolated in a low-temperature argon matrix at 15 K (a), compared with harmonic wavenumbers and IR intensities calculated for the dioxo tautomer of the compound at the DFT(B3LYP)/6-311++G(2d,p) level (b). The theoretical wavenumbers higher than 3000 cm^{-1} were scaled by a factor of 0.95, whereas those lower than 3000 cm^{-1} were scaled by 0.98.

the case of isatoic anhydride, the lowest energy has been obtained for the dioxo tautomer, while the calculated energies of the oxo-hydroxy isomeric forms were higher by more than 45 kJ/mol (Table S1 in the Supporting Information). For isatin and for phthalimide, the dioxo tautomers have also been predicted to be the most stable. For these two latter compounds, the computed difference between the energy of the most-stable dioxo tautomers and other oxo-hydroxy structures is even bigger than it was for isatoic anhydride (see Tables S2 and S3 in the Supporting Information). Big energy gap, substantially larger than the usual inaccuracy of the theoretical DFT(B3LYP) prediction, means that in the gas phase only the molecules in the dioxo form should be expected. Consequently, only the molecules of isatin, phthalimide, and isatoic anhydride in the dioxo tautomeric form should be trapped from the gas phase into the low-temperature argon matrixes. Hence, in the infrared spectra of isatin, phthalimide, and isatoic anhydride isolated in Ar matrixes, only the IR bands due to vibrations of the dioxo structures of these compounds are to be expected.

4.2. Infrared Spectra of Monomeric Isatin, Phthalimide, and Isatoic Anhydride Isolated in Argon Matrixes. The IR spectrum of isatin monomers trapped in a low-temperature argon matrix matches well the spectrum simulated theoretically for the dioxo isomer (Figure 1 and Table S4 in the Supporting Information). The infrared spectra

of monomeric isatoic anhydride and monomeric phthalimide isolated in Ar matrixes (Figures 2 and 3 and Tables S5 and S6) are also accurately reproduced by the spectra theoretically simulated for the dioxo tautomers of these compounds. The most characteristic features in the mid-IR spectra of the three studied compounds are the bands observed at ~3450 cm^{-1}, which are assigned to the stretching vibrations of the N−H group. Other characteristic bands appearing in these spectra near 1800 cm^{-1} are attributed to the coupled stretching vibrations of the C=O groups. Although formally phthalimide and isatin are isomers, the general shape of their IR spectra is different. The spectrum of matrix-isolated phthalimide is simpler than that of isatin. This is due to different symmetry of the two molecules in question. The dioxo tautomer of phthalimide is of higher C_{2v} symmetry, whereas the dioxo tautomer of isatin is of lower C_s symmetry (see Scheme 1).

4.3. Effects of UV (λ = 278 nm) Irradiation of Isatin and Isatoic Anhydride Isolated in Low-Temperature Argon Matrixes. Isatin molecules isolated in an Ar matrix were irradiated with UV light. The first UV (λ > 320 nm) irradiation did not result in any changes in the infrared spectrum of the compound. Next exposure to UV (λ > 295 nm) light caused only extremely small changes in the IR spectrum of isatin. This indicated occurrence of some photochemical processes consuming the isatin precursor, but the yield of these phototransformations was very low. Upon
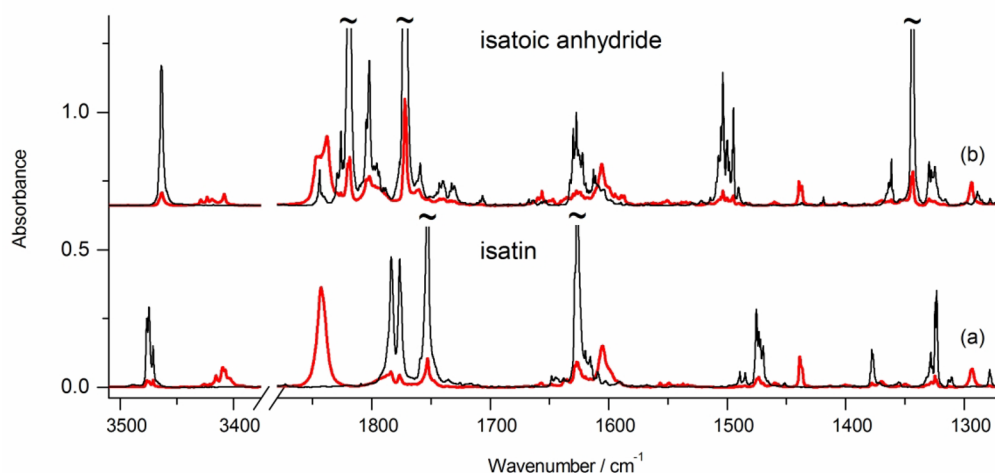
Figure 4. Effects of UV ($\lambda = 278$ nm) irradiation of isatin (a) and isatoic anhydride (b) isolated in Ar matrixes at 15 K. Black traces represent the spectra after deposition of the matrix. Red traces illustrate the spectra after exposure to the UV ($\lambda = 278$ nm) light. Total duration of UV irradiation was 4 h for isatin and 95 min for isatoic anhydride.

subsequent UV ($\lambda = 278$ nm) irradiation, the infrared spectrum of the isatin underwent substantial changes (Figure 4a). After 4 h of UV ($\lambda = 278$ nm) irradiation, the IR spectrum of the initial dioxo tautomer of isatin disappeared nearly totally, reflecting consumption of this form in a photochemical reaction. Concomitantly, a series of new bands due to photogenerated products appeared in the IR spectrum. Also irradiation of isatoic anhydride isolated in an Ar matrix with UV ($\lambda = 278$ nm) light resulted in a conversion of the initial dioxo form of the compound into photoproducts. Upon such irradiation, intensities of IR bands in the initial spectrum due to the dioxo tautomer substantially decreased and a set of new bands appeared (Figure 4b). It is easy to notice that the IR spectrum of the photoproduct(s) generated from isatoic anhydride matches very well the spectrum of the species photogenerated from isatin (compare red traces in both panels of Figure 4). This suggests that the main photoproduct obtained by UV ($\lambda = 278$ nm) irradiation of isatin or isatoic anhydride is the same.

Fragments of the experimental IR spectra of photoproducts, extracted from the spectra recorded after exposure of matrix-isolated isatin and isatoic anhydride to UV ($\lambda = 278$ nm) light, are presented in Figure 5a,b. The most characteristic features of these spectra are the strong absorptions at 1843 or 1846/1838 cm^{-1}. Intense bands appearing in the 1860−1820 cm^{-1} wavenumber range are typical of the stretching (νC=O) vibrations of the carbonyl group attached to a four-membered ring.[7−9,20−22] Hence, benzoazetinone may be treated as one of the obvious candidates for the structure of the main photoproduct generated by photodecarbonylation of isatin or by photodecarboxylation of isatoic anhydride (see Scheme 2).

In the IR spectra of matrix-isolated *N*-methylbenzo-azetinone[7] and N-deuterated benzoazetinone[9] (compounds having the structures similar to that of benzoazetinone), the bands due to the νC=O vibrations were found at 1843 and 1836 cm^{-1}, respectively. The spectral positions of these bands are very close to the positions of the bands observed in the current study in the spectra recorded after UV ($\lambda = 278$ nm) irradiation of isatin and isatoic anhydride. This supports the assumption that the photoproduced species has the benzoa-zetinone structure.
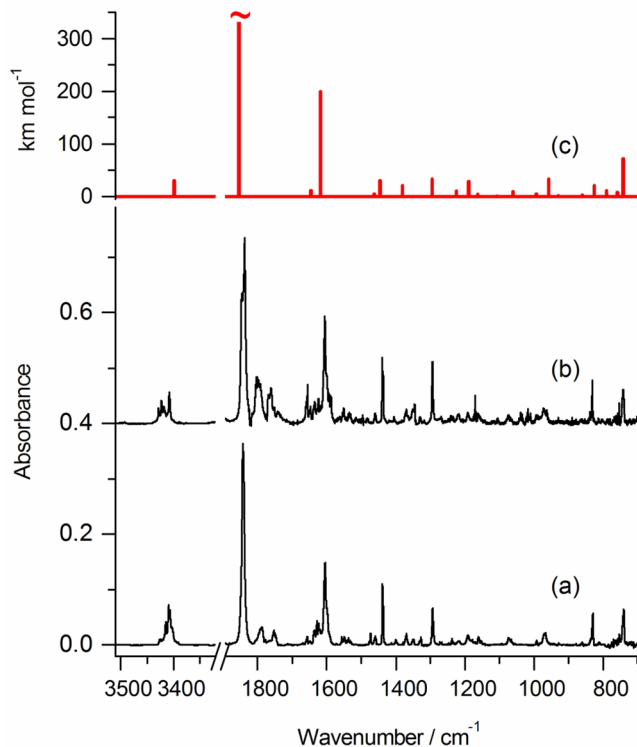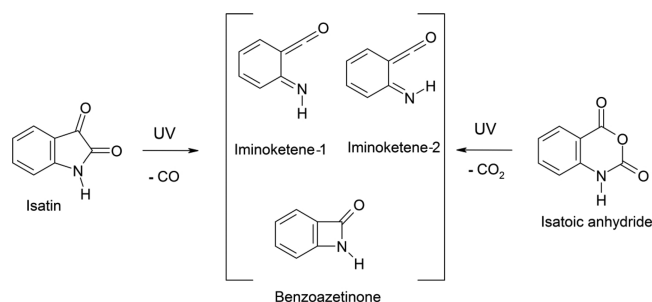

Figure 5. Fragments of the IR spectra of the photoproducts obtained after UV ($\lambda = 278$ nm) irradiation of isatin (a) and isatoic anhydride (b) isolated in low-temperature Ar matrixes, compared with harmonic wavenumbers and IR intensities calculated for benzoazetinone at the DFT(B3LYP)/6-311++G(2d,p) level (c). The theoretical wave-numbers higher than 3000 cm^{-1} were scaled by a factor of 0.95, whereas those lower than 3000 cm^{-1} were scaled by 0.98.

The geometry of benzoazetinone has been theoretically optimized at the DFT(B3LYP)/6-311++G(2d,p) level. The optimized structure of the molecule is not planar, with the angle between the N−H vector and the plane defined by the C5, N, and C7 atoms as large as 42° (see Table S7 for atom numbering). At the optimized geometry, the infrared spectrum of benzoazetinone has been calculated at the same

Scheme 2. Photochemical Reactions Induced by UV (λ = 278 nm) Irradiation of Matrix-Isolated Isatin and Isatoic Anhydride

Figure 6. The 2430–1680 cm^{-1} range of the IR spectra of photoproducts generated upon UV (λ = 278 nm) irradiation of monomeric isatin (a) and monomeric isatoic anhydride (b) isolated in low-temperature Ar matrixes, compared with harmonic wavenumbers calculated at the DFT(B3LYP)/6-311++G(2d,p) level (c) for benzoazetinone (red), isocyanic acid (turquoise blue), and two isomers of iminoketene (green and violet); see Scheme 2. The theoretical wavenumbers were scaled by a factor of 0.98. Arrows at the lower panel indicate spectral positions of the experimental bands due to the stretching vibrations of CO$_2$ (magenta), HNCO (turquoise blue), and CO (blue).

DFT(B3LYP)/6-311++G(2d,p) level. This spectrum (Figure 5c) reproduces well the experimental spectra (Figure 5a,b) of photoproducts obtained upon UV (λ = 278 nm) irradiation of isatin and isatoic anhydride. The agreement between the theoretical and experimental spectra shown in Figure 5 provides convincing evidence that benzoazetinone was photo-produced from isatin as well as from isatoic anhydride isolated in low-temperature Ar matrixes (Table 1 and Table S7 in the Supporting Information).

Carefull analysis of the IR spectra recorded after UV (λ = 278 nm) irradiation of Ar matrixes containing monomers of isatin or isatoic anhydride revealed the presence of the bands that could not be attributed to the spectrum of benzoazetinone. The most characteristic of these bands are those observed in the 2400–2000 cm^{-1} region (Figure 6). The bands indicate that benzoazetinone is not the only product photogenerated from both reactants. In the spectrum recorded after UV (λ = 278 nm) irradiation of the dioxo form of matrix-isolated isatin, alongside the bands due to benzoazetinone (with the most prominent absorption feature at 1843 cm^{-1}, Figure 5a), a group of bands was observed in the 2200–2100 cm^{-1} range (Figure 6a). Within this group, the medium-strong absorptions at 2147 and 2144 cm^{-1} can be assigned to photogenerated CO, released from UV-excited molecule of isatin.[23,24] Two other medium-strong bands appeared at 2126 and 2111 cm^{-1}. These bands have their close counterparts
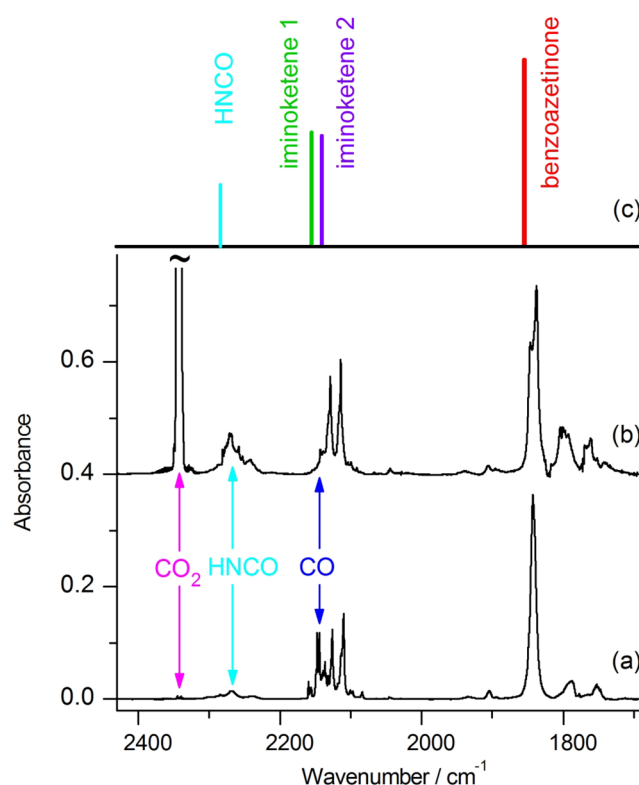
observed at 2129 and 2114 cm^{-1} in the spectrum of UV-irradiated isatoic anhydride (Figure 6 b). The two bands in

Table 1. Approximate Assignment of the Most Pronounced Absorption Bands, Observed in the IR Spectra of Photoproducts Generated upon UV (λ = 278 nm) Irradiation of Isatin and Isatoic Anhydride Isolated in Ar Matrixes, to the Normal Modes Calculated for Benzoazetinone at the DFT(B3LYP)/6-311++G(2d,p) Level of Theory[a]

Ar matrix				calculation		
isatin photoproduct		isatoic anhydride photoproduct		DFT(B3LYP)/6-311++G(2d,p)		
$\tilde{\nu}$ (cm^{-1})	I (rel)	$\tilde{\nu}$ (cm^{-1})	I (rel)	$\tilde{\nu}^b$ (cm^{-1})	A^{th} (km mol^{-1})	approximate description
3415, <u>3409</u>, 3407	124	3424, <u>3408</u>	85	3370	26	ν NH
1843	570	1846, <u>1838</u>	570	1844	570	ν C=O
1606	238	1606	262	1604	190	ν CC
<u>1439</u>, 1437	54	<u>1440</u>, 1437	55	1445	28	β CH
1370	16	1370	16	1361	17	ν CC
1293	55	1294	56	1295	33	β CH
1191 broad	23	1192 broad	25	1181	27	ν CN, ν CC
968	46	971	22	956	27	β R, ν CN, β CH
830	31	831	26	818	21	ν CC
740	68	741	55	737	69	γ CH
497, <u>492</u>	31	493	25	472	108	γ NH

[a]Abbreviations: rel, relative; ν, stretching; β, bending; γ, wagging. Wavenumbers of the strongest bands in a multiplet are underlined. [b]The theoretical wavenumbers higher than 3000 cm^{-1} were scaled by a factor of 0.95, whereas those lower than 3000 cm^{-1} were scaled by 0.98.
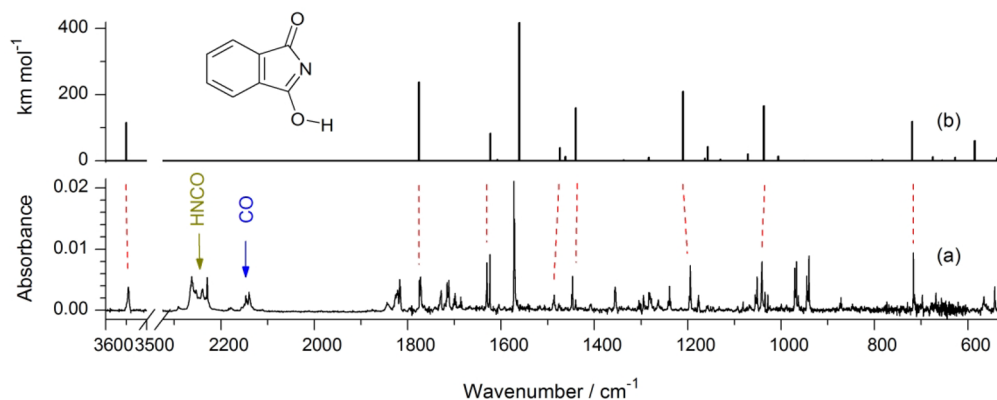
Figure 7. Fragments of the IR spectra of the photoproducts obtained upon UV (λ = 278 nm) irradiation of phthalimide isolated in low-temperature Ar matrixes (a), compared with harmonic wavenumbers and IR intensities calculated for the oxo-hydroxy tautomer of phthalimide at the DFT(B3LYP)/6-311++G(2d,p) level (b). The theoretical wavenumbers higher than 3000 cm^{-1} were scaled by a factor of 0.95, whereas those lower than 3000 cm^{-1} were scaled by 0.98.

question appeared in the spectral region, where the infrared absorptions due to "antisymmetric" C=C=O stretching vibrations of various open-ring ketenes were previously observed.[7−9] Therefore, these bands can be treated as the spectral indications of two anti and syn isomers (iminoketene-1 and iminoketene-2; see Scheme 2) of an open-ring isomer (6-imino-2,4-cyclohexadien-1-ketene) of benzoazetinone. This interpretation is strongly supported by a close match between the spectral positions of the lower-wavenumbers bands (2111 and 2114 cm^{-1}) and the wavenumber (2110 cm^{-1}) at which a band of iminoketene-2 was previously observed.[25] Small differences between the wavenumbers given above are easily understandable, taking into account the presence of different partners (CO, CO$_2$, and N$_2$) in the same matrix cage with the *in situ* generated iminoketene product.

The spectral positions of the bands due to "antisymmetric" stretching vibrations of the iminoketene-1 and iminoketene-2 structures have been theoretically calculated at the DFT(B3LYP)/6-311++G(2d,p) level. Although the theoretically computed wavenumbers 2147 and 2132 cm^{-1} differ slightly from the experimentally observed spectral position (the shift between theory and experiment is a mere result of the applied scale factor), the predicted spectral distance ($\Delta\nu$ = 15 cm^{-1}) between the band due to iminoketene-1 and the band due to iminoketene-2 is exactly the same as the spectral distances within the pairs of the experimentally observed bands (2126 and 2111 cm^{-1}, Figure 6a) or (2129 and 2114 cm^{-1}, Figure 6b). All this spectral evidence speaks in favor of the intepretation of the bands observed in the 2130−2110 cm^{-1} spectral range in terms of two iminoketene-1 and iminoketene-2 open-ring isomers of benzoazetinone. Moreover, this assignment has been further supported by the results of the experiments on ring-opening/ring-closure photoinduced transformations, which are described in section 4.5.

The most intense band, present in the spectrum recorded after UV (λ = 278 nm) irradiation of matrix-isolated isatoic anhydride, is the very strong IR absorption at ∼2343 cm^{-1} (Figure 6b). This band is split into several components. It appears only in the spectrum of UV-irradiated isatoic anhydride; no analogous strong IR absorption appears in the spectrum of UV-irradiated isatin. The very characteristic frequency[26,27] and huge intensity strongly suggest that this band must be due to the antisymmetric stretching vibration of

the CO$_2$ molecule, which has been released from the UV excited isatoic anhydride. All the experimental observations and their interpretations described above combine into a consistent picture (Scheme 2) of photoreactions occurring for isatin and isatoic anhydride monomers trapped in Ar matrixes and irradiated with UV (λ = 278 nm) light.

4.4. Effects of UV (λ = 278 nm) Irradiation of Phthalimide Isolated in Low-Temperature Argon Matrixes. The photochemical behavior of phthalimide, the formal isomer of isatin, appeared to be quite different. Photo-transformations of phthalimide monomers isolated in an Ar matrix and irradiated with UV (λ = 278 nm) light were slow but noticeable. After 5.5 h of UV irradiation at 278 nm, the bands initially present in the IR spectrum of the dioxo form of phthalimide diminished by ∼20%, while a set of new IR bands emerged.

Extracted IR spectrum of the photogenerated product(s) is presented in Figure 7. In this spectrum, one of the new IR absorption bands appeared at 3545 cm^{-1}, where IR bands due to O−H stretching vibrations are expected. The presence of this band suggests that one of the photogenerated products has an O−H group in its structure. One of the most probable candidates for such a photoproduced species is the oxo-hydroxy tautomer of phthalimide. The oxo-hydroxy tautomer may be formed by UV-induced migration of hydrogen atom from nitrogen to one of the vicinal oxygen atoms of the dioxo form of phthalimide. The comparison of the experimental spectrum of the photoproducts generated upon UV (λ = 278 nm) irradiation of matrix-isolated phthalimide with the spectrum theoretically simulated for the oxo-hydroxy form of the compound is presented in Figure 7 and Table S8 in the Supporting Information. The theoretical IR bands predicted for the hydroxy tautomer of phthalimide have their counterparts in the experimental spectrum of the photogenerated species. Good agreement between these two sets of bands suggests that the oxo-hydroxy form of phthalimide is indeed photoproduced (Scheme S2 in the Supporting Information). Analogous oxo → hydroxy phototautomerizations in systems without intramolecular hydrogen bonds are well-known. The oxo → hydroxy phototransformation was first observed for 4(3H)-pyrimidinone[28,29] and later for a number of other matrix-isolated compounds containing lactam groups.[30−34] Therefore, occurrence of this type of phototautomerization may be expected also for phthalimide.

Other characteristic bands, appearing upon UV (λ = 278 nm) irradiation in the spectrum of matrix-isolated phthalimide, are those found in the 2300−2100 cm^{-1} region; see Figure 7. The split absorption at 2265−2225 cm^{-1} can be attributed to the stretching vibrations of HNCO,[35−37] whereas absorption bands at 2147 and 2140 cm^{-1} are due to the CO stretching vibration of carbon monoxide.[23,24] The presence of these bands in the spectra of phthalimide isolated in an Ar matrix and exposed to UV (λ = 278 nm) light could indicate the decomposition of the five-membered (maleimide) ring of the compound into HNCO and CO fragments. The remaining fragment of the molecule, with a six-membered ring, might adopt the o-benzyne structure. But no experimental IR absorptions, appearing in the spectrum of photoproducts generated from phthalimide, were assigned to o-benzyne. This may be related to very low intensities theoretically predicted for IR bands of this species.[38] Hence, photogeneration of o-benzyne from UV-excited phthalimide was not spectroscopically supported; see Scheme S2 in the Supporting Information.

4.5. Photoreversible Conversions between Closed-Ring Benzoazetinone and Open-Ring α-Iminoketene. Monomers of isatin isolated in an Ar matrix and irradiated with UV (λ = 278 nm) light were subsequently irradiated with green (λ = 532 nm) light (Figure 8). Upon this irradiation the IR bands at 2126 and 2111 cm^{-1} (due to two isomers of α-iminoketene) decreased in intensity (Figure 8b), whereas the intensity of the band at 1843 cm^{-1} (due to closed-ring

benzoazetinone) increased. The observed intensity changes are the spectral signatures of the photoinduced conversion transforming the open-ring α-iminoketene into benzoazetinone, where the four-membered ring is closed. Analogous ring-closure conversions, occurring upon irradiation of matrix-isolated α-iminoketene with visible (λ = 500 nm) light, were observed for compounds structurally similar to benzoazetinone: N-methylbenzoazetinone[7] and N-deuterated benzoazetinone.[9] In the current study, both iminoketene-1 and iminoketene-2 isomers are consumed in the ring-closure photoprocess. That implies that excitation with green (λ = 532 nm) light also induces the syn−anti photoisomerization converting one α-iminoketene isomer into the other.

The argon matrix containing isatin isomers subjected to irradiations at λ = 278 nm and then at λ = 532 nm was subsequently irradiated with λ = 305 nm light generated by an UV LED. Upon this latter irradiation, the intensity of the band at 1843 cm^{-1} (due to closed-ring benzoazetinone) decreased, whereas the intensities of the bands at 2126 and 2111 cm^{-1} (due to two isomers of α-iminoketene) increased (Figure 8c). This is a clear indication of the ring-opening photoconversion that occurs upon λ = 305 nm irradiation and transforms the closed-ring benzoazetinone into two isomers of α-iminoketene. The effects of irradiation at 532 and 305 nm allowed separation of the IR spectra of benzoazetinone and its opening-ring α-iminoketene isomers (Figure 9). The experimental IR bands assigned to the α-iminoketene product are listed in Table S9 in the Supporting Information.
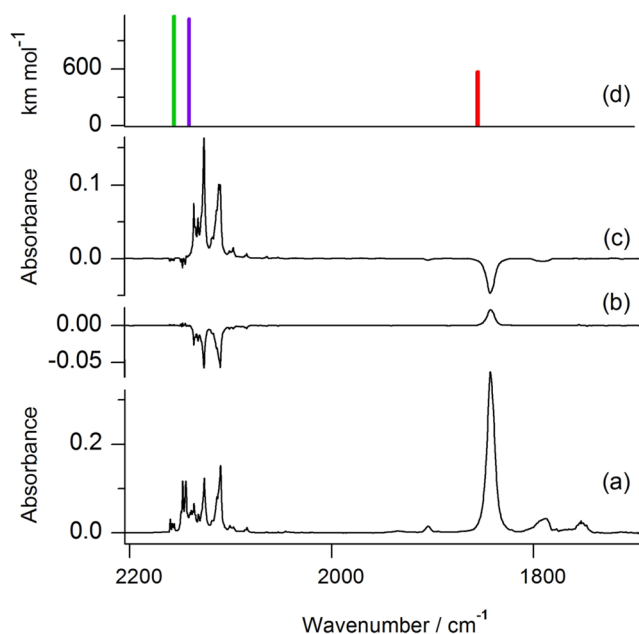

Figure 8. Experimental spectra of photoproducts generated from isatin isolated in an Ar matrix and subjected to a series of irradiations: the spectrum recorded after the first irradiation with UV (λ = 278 nm) light (a); the spectrum recorded after subsequent irradiation of the matrix with green (λ = 532 nm) light *minus* the spectrum recorded before this irradiation (b); the spectrum recorded after three consecutive UV (λ = 278, 532, and 305 nm) irradiations *minus* the spectrum recorded before the last irradiation at 305 nm (c). The experimental spectra are compared with harmonic wavenumbers and IR intensities calculated at the DFT(B3LYP)/6-311++G(2d,p) level (d) for benzoazetinone (red) and two isomers of iminoketene (green and violet); see Scheme 2. The theoretical wavenumbers were scaled by a factor of 0.98.
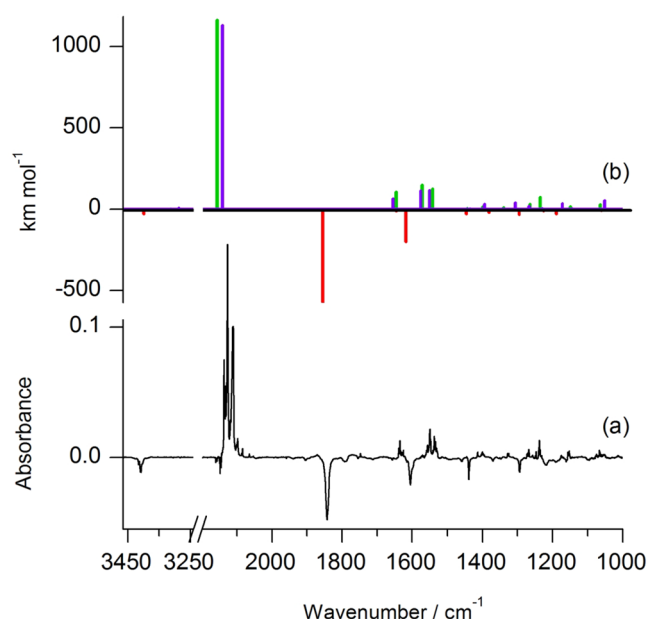

Figure 9. Fragments of experimental difference spectrum obtained by subtraction of the spectrum recorded after irradiation of matrix-isolated isatin with UV (λ = 278 nm) light and subsequently with green (λ = 532 nm) light, from the spectrum recorded after three consecutive UV (λ = 278, 532, and 305 nm) irradiations (a). The experimental spectrum is compared with harmonic wavenumbers and IR intensities calculated at the DFT(B3LYP)/6-311++G(2d,p) level (b) for benzoazetinone (red) and two isomers of iminoketene (green and violet), Scheme 2. The theoretical wavenumbers higher than 3000 cm^{-1} were scaled by a factor of 0.95, whereas those lower than 3000 cm^{-1} were scaled by 0.98.

The intensity changes of the IR bands at 2126/2111 cm^{-1} (due to α-iminoketene isomers) and at 1843 cm^{-1} (due to benzoazetinone), reflecting ring-closure transformation occurring upon irradiation at 532 nm, were quantitatively measured. Upon this irradiation, the intensity of the bands at 2126/2111 cm^{-1} diminished by ~40%, whereas the intensity of the band at 1843 cm^{-1} increased by 5%, with respect to the intensities of these bands in the spectrum recorded after the initial irradiation at 278 nm. (Figure 8a,b) The intensity changes, reflecting the ring-opening transformation occurring upon the subsequent irradiation at 305 nm (the third irradiation, following exposure of the matrix to λ = 278 nm and λ = 532 nm light), were also quantitatively measured. Upon this latter irradiation at 305 nm, the intensity of the bands at 2126/2111 cm^{-1} increased by 50%, while the intensity of the band at 1843 cm^{-1} decreased by 7%, with respect to the intensities of these bands in the spectrum recorded after the initial irradiation at 278 nm (Figure 8a,c). These data show that after a prolonged UV (λ = 278 nm) irradiation (consuming nearly all of the isatin precursor), the amount of benzoazetinone is ~7.5 times larger than the combined amount of both isomers of open-ring α-iminoketene, produced upon the same irradiation at λ = 278 nm.

A similar ratio of closed-ring benzoazetinone and open-ring α-iminoketene was generated (Figure 6a,b) upon a prolonged UV (λ = 278 nm) irradiation that consumed nearly all of the isatoic anhydride precursor. In spite of low population, the IR spectral signature of photoproduced α-iminoketene was clearly seen in the spectra recorded after λ = 278 nm irradiation. This was possible mainly because of the very high (>1000 km mol^{-1}) absolute intensity of the IR band due to the "antisymmetric" stretching vibration of the C=C=O fragment.

■ CONCLUSIONS

In the current work, photochemical behavior of isolated molecules of unsubstituted isatin has been studied for the first time. The study demonstrated that monomers of the compound, isolated in Ar matrixes and excited with UV (λ = 278 nm) light, undergo photodecarbonylation. The main molecular fragment remaining after release of CO adopts either the closed-ring benzoazetinone structure or the open-ring structure of α-iminoketene. Benzoazetinone and its open-ring isomer α-iminoketene were also obtained as the products of UV (λ = 278 nm) induced photodecarboxylation of isatoic anhydride. Thus, in the present paper, we provide the first report on photogeneration of unsubstituted and nondeuterated benzoazetinone and on the IR spectrum of this compound (see Table 1 and Table S7 in the Supporting Information). Our identification of the products of the investigated photo-transformations was based on the analysis of the IR spectra recorded after UV (λ = 278 nm) irradiation of matrix-isolated isatin and isatoic anhydride. The assignment of benzoazetinone and α-iminoketene structures to the photogenerated products was further supported by the observation of the photoinduced ring-closure and ring-opening conversions transforming the open-ring (α-iminoketene) and closed-ring (benzoazetinone) products into each other.

Interestingly, phthalimide molecules isolated in Ar matrixes and excited with UV (λ = 278 nm) light did not phototransform to benzoazetinone and its open-ring α-iminoketene isomer. Instead, matrix-isolated molecules of phthalimide underwent a photoinduced dioxo → oxo-hydroxy conversion, leading to generation of the oxo-hydroxy tautomer

of the compound; see Scheme S2 in the Supporting Information. HNCO and CO were also detected as minor products of the UV-induced transformations of phthalimide.

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c02562.

> Calculated relative energies of different isomers of isatin, isatoic anhydride, and phthalimide; tabulated infrared spectra of isatin, isatoic anhydride, phthalimide, benzoazetinone, and α-iminoketene; effects of UV irradiation of phthalimide; schemes of photochemical reactions (PDF)

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

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■ REFERENCES

(1) Olofson, R. A.; Morrison, D. S.; Banerji, A. Azetinones Revealed. *J. Org. Chem.* **1984**, *49*, 2652−2653.

(2) George, L.; Bernhardt, P. V.; Netsch, K. P.; Wentrup, C. Imidoylketene Dimerization and Rearrangement. *Org. Biomol. Chem.* **2004**, *2*, 3518−3523.

(3) Donowitz, G. R.; Mandell, G. L. Beta-Lactam Antibiotics. *N. Engl. J. Med.* **1988**, *318*, 419−426.

(4) Drawz, S. M.; Bonomo, R. A. Three Decades of β-Lactamase Inhibitors. *Clin. Microbiol. Rev.* **2010**, *23*, 160−201.

(5) Deshmukh, A. R. A. S.; Bhawal, B. M.; Krishnaswamy, D.; Govande, V. V.; Shinkre, B. A.; Jayanthi, A. Azetidin-2-ones, Synthon for Biologically Important Compounds. *Curr. Med. Chem.* **2004**, *11*, 1889−1920.

(6) Chiu, S. J.; Chou, C. H. Facile Synthesis of Reactive Benzoazetione by Flash Vacuum Pyrolysis of Isatoic Anhydride. *Tetrahedron Lett.* **1999**, *40*, 9271−9272.

(7) Dunkin, I. R.; Lynch, M. A.; Withnall, R.; Boulton, A. J.; Henderson, N. The Thermal Decomposition of 1-Methyl-1,2,3-benzotriazin-4(1*H*)-one: Matrix Isolation of the Reactive Intermediates. *J. Chem. Soc., Chem. Commun.* **1989**, 1777−1778.

(8) Tomioka, H.; Ichikawa, N.; Komatsu, K. Photochemistry of 2-(Methoxycarbonyl)phenyl Azide Studied by Matrix-Isolation Spec-

troscopy. A New Slippery Energy Surface for Phenylnitrene. *J. Am. Chem. Soc.* **1993**, *115*, 8621−8626.

(9) Nunes, C. M.; Reva, I.; Kozuch, S.; McMahon, R. J.; Fausto, R. Photochemistry of 2-Formylphenylnitrene: A Doorway to Heavy-Atom Tunneling of a Benzazirine to a Cyclic Ketenimine. *J. Am. Chem. Soc.* **2017**, *139*, 17649−17659.

(10) Chapman, O. L.; McIntosh, L. C.; Pacansky, J.; Calder, G. V.; Orr, G. Photochemical Transformations. XLIX Benzpropiolactone. *J. Am. Chem. Soc.* **1973**, *95*, 4061−4062.

(11) Itoh, T.; Tatsugi, J.; Tomioka, H. Photolysis of Indan-1,2-dione Derivatives in Oxygen-Doped Argon Matrix at Low Temperature. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 475−481.

(12) Jarmelo, S.; Reva, I. D.; Lapinski, L.; Nowak, M. J.; Fausto, R. Matrix-Isolated Diglycolic Anhydride: Vibrational Spectra and Photochemical Reactivity. *J. Phys. Chem. A* **2008**, *112*, 11178−11189.

(13) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic-Behavior. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098−3100.

(14) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron-Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(16) Goldschmidt, G.; Llewellyn, F. J. The Crystalline Structure of Isatin. *Acta Crystallogr.* **1950**, *3*, 294−305.

(17) Palmer, M. H.; Blake, A. J.; Gould, R. O. [14]N Nuclear Quadrupole Coupling in Cyclic Amides and Thioamides. Ab Initio Simulations of the Solid State Environment as Interpretation of the NQR Spectra of 2-Pyridinone, Isatin and Benzothiazole-2-one. A New X-Ray Structure for Isatin. *Chem. Phys.* **1987**, *115*, 219−227.

(18) Matzat, E. Die Kristallstruktur des Phtalimids (Kladnoit). *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 415−418.

(19) Kashino, S.; Nakashima, S.; Haisa, M. The Crystal and Molecular Structures of 2H- 1,3-Benzoxazine-2,4(3H)-dione (CSA) and 2H-3,l-Benzoxazine-2,4(1H)-dione (ISA). *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2191−2195.

(20) Breda, S.; Reva, I.; Lapinski, L.; Fausto, R. Matrix Isolation FTIR and Theoretical Study of α-Pyrone Photochemistry. *Phys. Chem. Chem. Phys.* **2004**, *6*, 929−937.

(21) Breda, S.; Lapinski, L.; Reva, I.; Fausto, R. 4,6-Dimethyl-α-Pyrone: A Matrix Isolation Study of the Photochemical Generation of Conjugated Ketene, Dewar Valence Isomer and 1,3-Dimethyl-Cyclobutadiene. *J. Photochem. Photobiol., A* **2004**, *162*, 139−151.

(22) Breda, S.; Lapinski, L.; Fausto, R.; Nowak, M. J. Photo-isomerization Reactions of 4-Methoxy- and 4-Hydroxy-6-Methyl-α-Pyrones; An Experimental Matrix Isolation and Theoretical Density Functional Theory Study. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4527−4532.

(23) Barnes, A. J.; Lasson, E.; Nielsen, C. J. Molecular Complexes of Nitric Acid with N_2, CO and NO studied by Matrix Isolation IR Spectroscopy. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3111−3116.

(24) Loewenschuss, A.; Givan, A.; Nielsen, C. J. CO-Water Interactions in Argon Matrices and in Porous Ices. *J. Mol. Struct.* **1997**, *408/409*, 533−537.

(25) Nunes, C. M.; Knezz, S. N.; Reva, I.; Fausto, R.; McMahon, R. J. Evidence of a Nitrene Tunneling Reaction: Spontaneous Rearrangement of 2-Formyl Phenylnitrene to an Imino Ketene in Low-Temperature Matrixes. *J. Am. Chem. Soc.* **2016**, *138*, 15287−15290.

(26) Irvine, M. J.; Mathieson, J. G.; Pullin, D. E. The Infrared Matrix Isolation Spectra of Carbon Dioxide. II Argon Matrices: the CO_2 Monomer Bands. *Aust. J. Chem.* **1982**, *35*, 1971−1977.

(27) Vigasin, A. A.; Schriver-Mazzuoli, L.; Schriver, A. An Attempt to Systematize the Vibrational Shifts in CO_2 Monomers and Dimers Trapped in Various Matrices. *J. Phys. Chem. A* **2000**, *104*, 5451−5456.

(28) Nowak, M. J.; Fulara, J.; Lapinski, L. IR Spectra and Phototautomerism of Matrix Isolated 4-Oxopyrimidine. *J. Mol. Struct.* **1988**, *175*, 91−96.

(29) Lapinski, L.; Nowak, M. J.; Les, A.; Adamowicz, L. Ab Initio Calculations of IR Spectra in Identification of Products of Matrix Isolation Photochemistry: Dewar Form of 4(3H)-Pyrimidinone. *J. Am. Chem. Soc.* **1994**, *116*, 1461−1467.

(30) Lapinski, L.; Reva, I.; Nowak, M. J.; Fausto, R. Five Isomers of Monomeric Cytosine and Their Interconversions Induced by Tunable UV Laser Light. *Phys. Chem. Chem. Phys.* **2011**, *13*, 9676−9684.

(31) Lapinski, L.; Reva, I.; Rostkowska, H.; Fausto, R.; Nowak, M. J. Near-IR-induced, UV-induced and Spontaneous Isomerizations in 5-Methylcytosine and 5-Fluorocytosine. *J. Phys. Chem. B* **2014**, *118*, 2831−2841.

(32) Gerega, A.; Lapinski, L.; Nowak, M. J.; Furmanchuk, A.; Leszczynski, J. Systematic Effect of Benzo-Annelation on Oxo-Hydroxy Tautomerism of Heterocyclic Compounds. Experimental Matrix-Isolation and Theoretical Study. *J. Phys. Chem. A* **2007**, *111*, 4934−4943.

(33) Gerega, A.; Lapinski, L.; Nowak, M. J.; Rostkowska, H. UV-Induced Oxo → Hydroxy Unimolecular Proton-Transfer Reactions in Hypoxanthine. *J. Phys. Chem. A* **2006**, *110*, 10236−10244.

(34) Nowak, M. J.; Lapinski, L.; Fulara, J.; Les, A.; Adamowicz, L. Matrix Isolation IR Spectroscopy of Tautomeric Systems and Its Theoretical Interpretation. 2-Hydroxypyridine/2(1H)-Pyridinone. *J. Phys. Chem.* **1992**, *96*, 1562−1569.

(35) Raunier, S.; Chiavassa, T.; Allouche, A.; Marinelli, F.; Aycard, J. P. Thermal Reactivity of HNCO with Water Ice: an Infrared and Theoretical Study. *Chem. Phys.* **2003**, *288*, 197−210.

(36) Sałdyka, M.; Mielke, Z. Photodecomposition of Formohydroxamic Acid. Matrix Isolation FTIR and DFT Studies. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4790−4797.

(37) Maier, G.; Bothur, A.; Eckwert, J.; Reisenauer, H. P.; Stumpf, Th. Isofulminic Acid − Phantom or Reality? *Liebigs Ann.* **1997**, *1997*, 2505−2517.

(38) Radziszewski, J. G.; Hess, B. A., Jr.; Zahradnik, R. Infrared Spectrum of *o*-Benzyne: Experiment and Theory. *J. Am. Chem. Soc.* **1992**, *114*, 52−57.