UV-Induced Photochemistry of 1,3-Benzoxazole, 2-Isocyanophenol, and 2-Cyanophenol Isolated in Low-Temperature Ar Matrixes

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ABSTRACT: The monomers of 1,3-benzoxazole isolated in a cryogenic argon matrix were characterized by infrared spectroscopy. The photochemistry of matrix-isolated 1,3-benzoxazole, induced by excitation with a frequency-tunable narrowband UV light, was investigated. Irradiation at 233 nm resulted in a nearly quantitative conversion of 1,3-benzoxazole into 2-isocyanophenol. The individual photochemical behavior of the in situ produced 2-isocyanophenol was studied upon excitations at 290 nm, where 1,3-benzoxazole does not react. The photochemistry of isomeric matrix-isolated 2-cyanophenol was also studied. The photoreactions of 2-substituted (cyano- or isocyano-) phenols were found to have many similarities: (i) OH bond cleavage, yielding a 2-substituted (cyano- or isocyano-) phenoxyl radical and an H-atom, (ii) recombination of the detached H-atom, resulting in an oxo tautomer, and (iii) decomposition leading to fulvenone, together with HCN and HNC. In another photoprocess, 2-cyanophenol undergoes a [1,5] H-shift from the hydroxyl group to the cyano group yielding isomeric ketenimine. The analogous [1,5] H-shift from the hydroxyl group to the isocyano group must have also occurred in 2-isocyanophenol; however, the resulting nitrile ylide isomer is kinetically unstable and collapses to benzoxazole. All photoproducts were characterized by comparing their observed infrared spectra with those computed at the B3LYP/6-311++G(d,p) level. The mechanistic analysis of the photochemistry occurring in the family of the title compounds is presented.

INTRODUCTION

1,3-Benzoxazole 1 (also known as benzo[d]oxazole or benzoxazole) consists of an oxazole ring fused to a benzene ring (Scheme 1). It is the nucleus of numerous compounds with important biological, pharmacological, and photophysical properties.1-4 Its isomeric 1,2-benzisoxazole 2 (also known as benzo[d]isoxazole or benzisoxazole) has an isoxazole ring fused to a benzene ring (Scheme 1). They differ by the relative position of the oxygen and nitrogen atoms: in oxazole, the two heteroatoms are separated by a carbon atom, while in isoxazole, they are bound directly. This key structural difference renders a weak N–O bond in benzisoxazole, making it much more reactive6,8 and consequently more prone to undergo chemical transformations than benzoxazole.

Interestingly, photoexcitation of 1,2-benzisoxazole 2 in polar solvents affords 1,3-benzoxazole 1, whereas the photochemistry of 2 in non-polar solvents leads mainly to its open-ring isomer 2-cyanophenol 3 (Scheme 1).7-10 The thermal reaction (single-pulse shock-tube experiments, T > 1200 K) of 2 results in its complete isomerization to 3 (Scheme 1) prior to fragmentation.11 Data from luminescence measurements and from sensitization and quenching studies suggest that the lowest singlet excited state of benzisoxazole in non-polar solvents is the \((\pi,\pi)^*\) state, which undergoes intersystem crossing (ISC) to a triplet state, leading to 3. On the contrary, in polar solvents, the lowest singlet excited state of 2 is the \((\pi,\pi)^*\) state, which leads to faster conversion of the compound into 1 than ISC to the triplet manifold.10 Nevertheless, the photochemistry of benzisoxazole is still puzzling. Low-temperature (−77 and −196 °C) studies of 2 in neat films or in ionic (KBr) matrices showed that under those conditions, the compound photoisomerizes to 2-cyanophenol 3 and 2-isocyanophenol 4. Upon heating to 0 °C, 4 undergoes thermal cyclization to benzoxazole 1 (Scheme 1).6,10 Our previous study on the photochemistry of monomeric benzisoxazole 2 isolated in cryogenic Ar matrixes revealed isomeric spiro-2H-azirine and ketenimine (see below) as key intermediates in the isomerization to 2-cyanophenol 3. No signs of 4 or 1 were spectroscopically detected. Supported by studies on the chemistry of simple isoxazoles,13,14 it was postulated that the photochemical mechanism of matrix-isolated benzisoxazoles is initiated by the N–O bond cleavage and formation of a vinylnitrile intermediate.5,15 This fascinating nitrene species, having a monovalent nitrogen

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atom and a triplet ground state,\textsuperscript{16,17} was proposed to dictate the subsequent chemistry and explains the observation of different photoproducts found in the low-temperature matrixes.

In contrast to benzisoxazole, the photochemistry of benzoxazole has been much less explored. In polar solvents under air-saturated conditions, UV excitation of 1 was found to result in dehydrodimerization, yielding the 2,2\textsuperscript{'}-dibenzoazole dimer, with yields up to 90%.\textsuperscript{16} However, in the absence of oxygen, this dimer was not formed. Likewise, in non-polar inert solvents, such as methylcyclohexane, UV excitation of 1 only leads to trace amounts of the 2,2\textsuperscript{'}-dibenzoazole dimer. However, the studies performed at −40 °C (in methylcyclohexane) seemed to indicate the formation of a different photoproduct, 2-isocyanophenol 4, which promptly decayed back to 1 upon heating to room temperature.\textsuperscript{15} The thermal reaction of benzoxazole under single-pulse shock-tube conditions was also studied.\textsuperscript{16} Under those conditions, the main isomerization product was 2-cyanophenol 3, which subsequently decomposed to cyano-cyclopentadiene and CO.

Herein, we report on the photochemistry of benzoxazole 1 isolated in a low-temperature Ar matrix. Aiming to find out whether there is any pathway connecting benzoxazole 1 and benzisoxazole 2, this study is also extended to their isomeric 2-cyanophenol 3 and 2-isocyanophenol 4. As far as we are aware, the narrowband UV-induced photochemistry of monomeric 1, 3, and 4 has never been reported hitherto and is addressed in this work for the first time. The three starting compounds (1, 3, and 4) isolated in solid Ar at 12 K, as well as their photoproducts, were characterized experimentally by IR spectroscopy and computationally with the aid of density functional theory (DFT) calculations.

### RESULTS AND DISCUSSION

#### Photochemistry of Matrix-Isolated Benzoxazole Induced by Irradiation at 270 nm

The IR spectrum of benzoxazole 1, recorded immediately after isolating the monomer of this compound in an Ar matrix at 12 K, is presented in Figure S1a. The spectrum is dominated by the absorptions centered at 1525, 1452, 1239, 1106, 1070, 779, 764, and 748/745 cm\textsuperscript{−1}. Strong bands at approximately the same positions have been previously identified in the vapor-phase infrared and Raman spectra of this compound, respectively, at 1529, 1454, 1240, 1107, 1074, 778, 764, and 746 cm\textsuperscript{−1} (infrared)\textsuperscript{20,21} and at 1528, 1453, 1237, 1107, 1072, 777, 764, and 748 cm\textsuperscript{−1} (Raman).\textsuperscript{20,21} The B3LYP/6-311+ +G(d,p)-computed IR spectrum of 1 is shown in Figure S1b. The most intense infrared modes (with IR intensities above 10 km mol\textsuperscript{−1}) are predicted at 1535, 1451, 1234, 1105, 1062, 781, 750, and 742 cm\textsuperscript{−1}, all of them correlating well with the positions of the dominant bands observed in the Ar matrix experimental spectrum. The most intense infrared modes (with IR intensities above 10 km mol\textsuperscript{−1}) are predicted at 1535, 1451, 1234, 1105, 1062, 781, 750, and 742 cm\textsuperscript{−1}, all of them correlating well with the positions of the dominant bands observed in the Ar matrix experimental spectrum.

The monomers of benzoxazole 1 isolated in solid Ar at 12 K were irradiated with a frequency-tunable UV laser light generated in an optical parametric oscillator (OPO). The photochemical studies were initiated by searching the lowest energy (or the longest wavelength) of UV photons that would induce a photochemical reaction. As a reference, we used the wavelength of the origin of the first electronic transition (0→0 of S\textsubscript{1}→S\textsubscript{0} transition) observed at 274 nm for the compound in the gas phase.\textsuperscript{22,23} As anticipated, when the OPO output was tuned in the 300 > λ > 277 nm range, the UV irradiations of 1 did not lead to any spectral changes. This observation is important for the mechanistic analysis presented below. When the OPO was tuned at λ = 270 nm, near the origin of the first electronic transition of 1 in the gas phase, the IR bands of matrix-isolated 1 started to decrease, and new bands due to photoproducts appeared in the spectrum, most prominently in the range near 2100 cm\textsuperscript{−1}. The intense IR band centered at 2138 cm\textsuperscript{−1} is likely to be associated with the characteristic antisymmetric stretching vibration \([v_a(C\equiv C\equiv O)]\textsuperscript{24,25}\) of a ketene moiety assigned to fulvenone\textsuperscript{26} as will be explained later in the paper. As it is shown below, the ketene species responsible for this absorption is not directly formed from 1 but rather from photodecomposition of 2-isocyanophenol 4. Under conditions of irradiation at λ = 270 nm, 4 is produced from 1 and undergoes prompt photodecomposition. Large-scale generation and subsequent capture of 2-isocyanophenol 4 in a low-temperature Ar matrix could only be observed upon UV excitation of 1 at shorter wavelengths (see the discussion below). A similar photochemical behavior was observed for matrix-isolated isoxazole.\textsuperscript{13} During irradiations near its first electronic transition origin, isoxazole underwent decomposition (to ketene H\textsubscript{2}C\textequiv C\equiv O plus hydrogen cyanide HCN), while irradiations at shorter wavelengths resulted in the ring-opening reaction, followed by photoisomerizations involving various H-atom shifts.\textsuperscript{13}

#### Photochemistry of Matrix-Isolated Benzoxazole Induced by Irradiation at 233 nm

The most significant spectral changes were observed when matrix-isolated 1 was exposed to a UV laser light tuned at λ = 233 nm. In fact, ~18 min of irradiation at this wavelength resulted in consumption of half of the initial amount of the compound. Concomitantly, various new bands were observed in the IR spectrum registered after the irradiation. Owing to the good correspondence between the IR spectrum of the emerging photoproduct and that simulated for 2-isocyanophenol, these bands were reliably assigned to 4, as shown in Figure 1. The rearrangements observed in this photoproduct involves cleavage of the C2=O1 bond in 1 and H-shift from C2 to O1. It should be noted here that 4 may adopt two conformations, differing by the orientation of the OH group (cis or trans) in relation to the isocynano (−N≡C) group. However, we have recently demonstrated that the less stable trans form of 4, once photogenerated in a cryogenic Ar matrix,
quickly relaxes into the most stable cis form by means of H-atom quantum mechanical tunnelling,27 following the same behavior previously reported for the other 2-substituted phenols isolated in solid Ar.28–30 Consequently, all the observed bands of 4 are due to the most stable cis conformer.

The \( \text{I} \rightarrow \text{4} \) isomerization is by far the dominating, nearly quantitative, transformation induced by the irradiation at \( \lambda = 233 \text{~nm} \). Therefore, we were able to accumulate a significant amount of 4 in the Ar matrix, which allowed its subsequent detailed spectroscopic characterization. All the 18 vibrations in the 2200–400 cm\(^{-1}\) range with predicted IR intensities above 2 km mol\(^{-1}\) were identified in the experiment, as we have recently reported elsewhere.27 The main spectral signatures of matrix-isolated 4 are the bands found at 3584 and 2118 cm\(^{-1}\), ascribed to the \( \nu(\text{OH}) \) and \( \nu(\text{N} \equiv \text{C}) \) stretching modes, respectively (see Figure 1). Previously, only the bands due to these two modes of 4 were detected at 3350 and 2130 cm\(^{-1}\), respectively, after photoproduction of 4 from 1 at \(-196\) and \(-77^\circ\text{C}\) in a KBr matrix or in a neat film.10

It is worth to comment on the different photochemical behaviors of benzoxazole 1 upon irradiation at 233 and 270 nm. Toward this end, we used time-dependent DFT (TD-DFT) and computed vertical excitation energies of the low-lying electronic excited states of all relevant species (Table S1). It is known that TD-DFT allows reproduction of the absorption band shapes with good to excellent accuracy.31 However, many authors point out to systematic overestimation of the TD-DFT computed transition energies, as compared to the experimental results.32,33 The overestimates reported by different authors range from 0.2 eV,34 can reach 0.4 eV,35 and more—about 0.5 eV.35 With this information in mind, the predicted UV spectra of 1 and 4, simulated based on the TD-DFT computed data and presented in Figure S2, qualitatively explain very well the observed photochemistry of 1 and 4. In fact, we can postulate that the photoreactivity of 1 is the same at 270 or 233 nm, that is, formation of isocyanophenol 4. What changes is that at 270 nm, isocyanophenol 4 has a very high absorption (compared to 1) and 4 quickly decomposes (see the discussion below), whereas at 233 nm, the absorption of 1 is several times higher than that of 4, and isocyanophenol 4 is allowed to accumulate.

**Photochemistry of Matrix-Isolated 2-Isocyanophenol Induced by Irradiation at 290 nm.** After the *in situ* photoproduction of 4, subsequent narrowband UV irradiations were conducted with the objective of inducing transformations in this species. These irradiations were carried out at \( \lambda = 290 \text{~nm} \), very close to the wavelength of absorption maximum of 4 measured in ethanol at \(-77^\circ\text{C} \) (\( \lambda_{\text{max}} = 288 \text{~nm} \)).10 It is important to note that 1 does not absorb UV-light above 277 nm, as established above, and hence, the presence of 1 in the matrix does not interfere with the photochemistry of 4 induced at 290 nm. Irradiations at 290 nm resulted in an appreciable consumption of 4, accompanied by an increase of the bands due to precursor 1, demonstrating that under such conditions, 4 photoisomerizes back to 1 (see Figure 2).

It is likely that the \( \text{4} \rightarrow \text{1} \) photoisomerization proceeds through a two-step mechanism, involving an initial [1,5] H-atom shift from the hydroxyl group to the isocyano group, originating the nitrile ylide derivative 6, followed by cyclization of this intermediate to form 1. The energy profile for the conversion of nitrile ylide 6 to benzoxazole 1 is presented in Figure 3. It was computed by tracing the corresponding potential energy profile as a function of the distance between the carbon and oxygen atoms (shown in blue in Figure 3). As it can be seen in Figure 3, the barrier height for the \( \text{6} \rightarrow \text{1} \) conversion in the ground state is very low, amounting to only 3 kJ mol\(^{-1}\) at the B3LYP/6-311++G(d,p) level of theory and can be easily surmounted in an Ar matrix at 15 K. Therefore, as 6 is photoproduced, it should immediately collapse into 1, impeding its possible detection in the Ar matrix. In a previous study performed in our laboratory,44 an acetyl nitrile ylide derivative was identified in an Ar matrix as an intermediate in the photoisomerization of 3,5-dimethylisoxazole to 2,5-dimethylxazole. Acyclic acetyl nitrile ylide derivatives

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**Figure 1.** UV generation of 2-isocyanophenol 4 from benzoxazole 1: (a) Extracted IR spectrum of the photoproduct generated after irradiation at \( \lambda = 233 \text{~nm} \) (18 min, \~10 mW) of 1 isolated in an Ar matrix at 12 K. The bands due to reactant 1 were nullified, only a few negative bands due to 1 (marked with asterisks) remain in the difference spectrum. The dotted lines (below the baseline) show the spectral positions of bands due to other photoproducts (8—green, 9—red, and 10—blue), which do not appear at this stage; (b) simulated IR spectrum of 4. See the Experimental Section for scaling factors and other details of simulation.
have been computed to exhibit two conformers (cis and trans), regarding the mutual orientation of the carbonyl (−C═O) and nitrile ylide (−C−N⁺CH) groups with respect to the central C−C bond (see Scheme S1). Only the trans acetyl nitrile ylide conformer was captured and spectroscopically characterized (the trans → cis conformational isomerization barrier was estimated to be 54.5 kJ mol⁻¹). The energy barrier of 10 kJ mol⁻¹ from the cis acetyl nitrile ylide to 2,5-dimethyloxazole was found to be not high enough to allow the capture of cis acetyl nitrile ylide. The benzannulated nitrile ylide 6 (belonging to the present work) can exist exclusively as a cis isomer, regarding the relative orientation of the carbonyl and nitrile ylide groups (see Figure 3). It must undergo easy thermal relaxation to 1, over the low energy barrier in the ground state (3 kJ mol⁻¹ only, see the inset in Figure 3) even at cryogenic temperatures.

The reverse 4 → 1 transformation takes place with only about one half of the yield compared with the forward 1 → 4 photoprocess (Figure 2), that is, only one half of 4 existing in the matrix converts back to 1. This suggests that the remaining half of 4 is converted to other photoproducts. These are fulvenone 8 (cyclopenta-2,4-dienylidenemethanone) plus HCN and HNC, resulting from direct decomposition of 4, and the isomeric species 1-oxo-2-isocyano-2,5-cyclohexadiene 10, which is a result of a radical recombination process involving 2-isocyanophenol radical 9 as the intermediate (see below). The proton stretching modes of matrix-isolated HNC and HCN were identified in this work at 3620/3610 [ν(NH)] and 3301 cm⁻¹ [ν(CH)], respectively (Figure 4). The position of the ν(N≡C) band of HNC observed at 2037 cm⁻¹ (Figure 5) matches well with the computed value of 2041 cm⁻¹ (Table 1) of experimental values in a good match with those reported earlier at 3620 cm⁻¹ for ν(NH) of HNC,37,38 at 3306/3303 cm⁻¹ for ν(CH) of HCN,38–41 as well as with the theoretical wavenumbers computed at 3610 [ν(NH)] and at 3315 cm⁻¹ [ν(CH)] for HNC and HCN, respectively (see Table 1). Other bands of HNC and HCN observed in this work also agree with the spectra reported previously for these compounds isolated in the Ar matrix.7,7–43
Table 1. Experimental and Computed Infrared Absorptions of Selected Photoproducts Generated by Irradiation at $\lambda = 290$ nm of 2-Isocyanophenol 4 Isolated in an Ar Matrix at 12 K

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$^a$ Bands emerging in the IR spectrum upon 6 min of irradiation of matrix-isolated 4 at $\lambda = 290$ nm.

$^b$ Wavenumbers (cm$^{-1}$) and absolute IR intensities (A$^a$, km mol$^{-1}$) computed in harmonic approximation at the B3LYP/6-311+G(d,p) theory level. The computed wavenumbers were scaled by 0.948 [$\nu$(NH)], 0.960 [$\nu$(CH)], 0.974 [$\nu$(N≡C) and $\nu_{as}$(C≡C=O)], or 0.983 (all other modes, below 1800 cm$^{-1}$). $^d$ Assignment based on the computed wavenumbers and the symmetry of the molecule.
and the experimental values 2032 and 2031 cm\(^{-1}\) reported previously.\(^{42,43}\) The \(\delta\) (HCN) band of hydrogen cyanide was reported earlier\(^{13}\) to appear at 727/725 cm\(^{-1}\), but in the present experiment, it must overlap with an intense IR band of other species (8, see Table 1).

In the 3700–3200 cm\(^{-1}\) spectral range (Figure 4), the three species (4, HNC, HCN) have well-defined non-overlapping bands. From their integrated intensities, weighted by respective computed IR intensities (Table 1), extension of the photodecomposition can be estimated. Considering that about a half of 4 converts back to 1 (Figure 2), the next major photoreaction channel consists in elimination of HNC (12%) plus HCN (24%), making up to about one-third of consumed 4 (Figure 4). The immediate corollary is that the irradiated matrix is likely to contain a detectable photoproduct resulting from decomposition of 4, with a formula up to \(C_6H_4O\).

The absorption centered at 2138 cm\(^{-1}\), which appears during the irradiation of 1 at \(\lambda = 270\ \text{nm}\), also grows in the course of the irradiations at \(\lambda = 290\ \text{nm}\) (Figure 5), thus confirming that a ketene species responsible for this absorption results indeed from photodecomposition of 4. Cyclopenta-2,4-dienylidenemethanone 8, also known as fulvenone,\(^{44,45}\) was identified as the product giving rise to this band. Fulvenone 8 has been previously characterized as a major product of the photochemistry of 2-chlorophenol\(^{29}\) and 2-bromophenol\(^{30}\) isolated in low-temperature Ar matrixes. In those studies, besides a very strong IR band at 2140/2130 cm\(^{-1}\) due to the characteristic \(\nu_{\text{as}}(\text{C} = \text{C} = \text{O})\) ketene mode, other bands were assigned to matrix-isolated 8 generated from 2-halophenols (e.g., bands at 1447, 1404, 1327, 896, and 729 cm\(^{-1}\)).\(^{29}\) As
shown in Table 1 and Figure 6, bands at nearly the same positions were observed in the IR spectrum recorded after irradiation of matrix-isolated 4 at \(\lambda = 290\) nm. All nine fundamental modes of 8 with computed IR intensities over 10 km mol\(^{-1}\) are nicely reproduced in the present experiment. Additionally, it should be noted that the bands of 8 do not appear in the spectrum upon irradiation at \(\lambda = 233\) nm, as can be seen in Figure 1, the dotted vertical green lines below the baseline. All these data support fulvenone 8 as a product of photodecomposition of 4 at \(\lambda = 290\) nm (Scheme 2).

Consistent with the expectation, fulvenone 8, formed together with HCN and HNC, has the molecular formula C\(_6\)H\(_4\)O. The formation of fulvenone 8 from 2-halophenols has been proposed to occur through Wolff-type rearrangement of a singlet ketocarbene 7 (2-oxocyclohexa-3,5-dienylidene) intermediate.\(^{29,46-48}\) A similar mechanism is expected for the 4 \(\rightarrow\) 8 photoreaction, as illustrated in Scheme 2. Experimental evidence of ketocarbene 7 was previously obtained by time-resolved UV–vis spectroscopy upon photolysis of 2-chlorophenol at \(\lambda = 266\) nm in hexane and methanol at room temperature, with measured lifetimes of 23 and 5 ps, respectively.\(^{48}\)

The experimental observation of HNC and HCN resulting from 4 is the proof that 2-isocyanophenol undergoes cleavage of both the single O–H and C(2)–N bonds under \(\lambda = 290\) nm UV irradiation. However, as pointed out by Garcia-Garibay and co-authors, C–C (and C–N) bond cleavages do not usually lead to products in crystals unless a second bond cleavage takes place that yields stable products.\(^{49-53}\) A similar situation can be expected to happen in the case of argon matrixes because radical pairs tend to recombine faster than they can escape;\(^{54}\) however, H is a notorious exception to this rule.\(^{55,56}\) Under these conditions, two possible mechanisms leading to formation of fulvenone 8 can be postulated: (a) concurrent intramolecular H atom shift and C(2)–N bond cleavage, generating HNC and NCH and carbene 7 directly, or (b) initial photocleavage of the OH phenolic bond to produce the hydrogen atom, followed by cleavage of the C(2)–N bond and prompt recombination to yield HCN and HNC and carbene 7. In both (a) and (b) cases, formation of the transient carbene 7 is followed by its rearrangement to fulvenone 8. Though both possibilities are compatible with the spectroscopic data and expected chemistry,\(^{49-53}\) hypothesis (b) seems to be more plausible in view of the experimental detection of the 2-isocyanophenoxyl radical 9.

The proposed mechanisms are also in agreement with the fact that no band was observed in our experiments that could be ascribed to the CN radical. The vibrational fundamental of the free radical CN isolated in argon matrixes has been reported to appear at 2046.0 cm\(^{-1}\),\(^{37}\) as a doublet between 2043 and 2048 cm\(^{-1}\),\(^{57}\) or as a small band at 2050.8 cm\(^{-1}.\)\(^{58}\) No such band was found in our experiments. Moreover, 2-hydroxyphenyl radical 5 (Scheme S2) was previously generated in argon matrixes by photolysis (\(\lambda > 280\) nm) of 2-iodophenol.\(^{59,60}\) The strongest infrared bands of 5 were reported at 1448, 1440, 1233, 1163, 820, and 728 cm\(^{-1}.\)\(^{59}\) Even if some of these spectral positions are near absorptions of other photoproducts, some other non-overlapping bands with characteristic frequencies (e.g., 1233 and 820 cm\(^{-1}\)) do not appear in our experiments, suggesting that the 2-hydroxyphenyl radical is in fact not formed (see Scheme 2).

The cleavage of only the O–H bond should give rise to 2-isocyanophenoxyl radical 9 and H-atom. The H atom is invisible in infrared spectra, but 2-isocyanophenoxyl radical 9,
formed by hydrogen detachment from the OH group of 4 (Scheme 2), was unequivocally identified based on a set of nine bands appearing in the IR spectrum recorded after the performed irradiations (Table 1). The stronger ones were found at 2101 [ν(N=≡C)], 1559 [ν(CC)], 1517 [ν(CC); δ(CH)], and 772 cm⁻¹ [γ(CH)] (Figures 5 and 6). All these nine bands belong to the set of bands with computed IR intensities over 10 km mol⁻¹ and correlate well with the computed wavenumbers of this radical. These bands of 9 do not appear in the spectrum upon irradiation at λ = 233 nm, as demonstrated by the dotted vertical red lines below the baseline in Figure 1. It is worth mentioning that the band observed at 1458 cm⁻¹ (Figure 6), which is assigned to the ν(CO) mode of 9, appears at a much higher frequency than the band assigned to the equivalent vibrational mode observed for 4 (1261 cm⁻¹).²⁷ Such an accentuated shift to higher frequency (+197 cm⁻¹) indicates that the CO bond acquires a considerable double-bond character in radical 9, as confirmed by the values of the natural bond orders computed for both the CO bond within the parent pair, and the order of CO bond involving the O–H bond cleavage, yielding in this case a cyanoenol radical 11 and the corresponding oxo tautomer 12 (1-oxo-2-cyano-2,5-cyclohexadiene). The identification of these three photoproducts was based on (i) the good agreement between the computed and experimental IR bands emerging in the spectra recorded after the UV irradiations (Figure 7 and Table S2); (ii) spectral data for analogous products resulting from the photochemistry of 4; (iii) previous IR spectroscopic characterization of 11 in Ar matrix captured upon photolysis of 3-chloro-1,2-benzisoxazole.¹⁵

Photochemistry of Matrix-Isolated 2-Cyanophenol Induced by Irradiation at 280 nm. The photochemistry of matrix-isolated 2-cyanophenol 3 was also investigated by irradiating monomers of the compound trapped in an Ar matrix (15 K) at λ = 280 nm. This wavelength was chosen to directly reproduce the UV irradiation conditions of 3 with those implemented for UV irradiation of 2 in the earlier study.⁵ Also, this wavelength is not far from the origin of the first electronic transition found for this compound (294 nm) under supersonic jet conditions.⁷⁰,⁷¹ Two of the reaction pathways identified above for 4 were also observed for 3 (see Scheme 2): one leading to the formation of fulvenone 8 and the other involving the O–H bond cleavage, yielding in this case a cyanophenoxyl radical 11 and the corresponding oxo tautomer 12 (1-oxo-2-cyano-2,5-cyclohexadiene). The identification of these three photoproducts was based on (i) the good agreement between the computed and experimental IR bands emerging in the spectra recorded after the UV irradiations (Figure 7 and Table S2); (ii) spectral data for 4(100%) → 1(50%) + HCN(24%) + HNC(12%) + 9(7%)(7%)

Figure 7. (a) Difference IR spectrum showing the changes after irradiation of 2-cyanophenol 3 at λ = 280 nm (1 min, ~30 mW) in an Ar matrix at 15 K. Positive bands are due to photoproducts 8 (green squares), 11 (solid red circles), 12 (open blue circles), and 13 (purple triangles). The negative bands (truncated) are due to the consumed reactant 3. (b) Simulated IR spectra of 3 (black, truncated, intensity multiplied by ~1), 8 (green), 11 (red), 12 (blue), and 13 (purple). The computed B3LYP/6-311++G(d,p) wavenumbers below 1800 cm⁻¹ were scaled by 0.983, and the IR intensities of 8, 11, 12, and 13 were not scaled. See the Experimental Section for other details of the simulation.
of vapors of 1 or 3 with an excess of the matrix host gas (argon N60, obtained from Air Liquide) onto the CsI optical substrate cooled down to 15 K. 2-Isocyanophenol 4 was photogenerated in situ from 1 isolated in solid Ar at 15 K, as described in ref 27. The matrix-isolated compounds were then irradiated with narrowband (fwhm < 1 cm\(^{-1}\)) UV light from the 290–233 nm range, generated in an OPO pumped with a nanosecond-pulsed (pulse frequency 10 Hz) Nd:YAG laser. The progress of the phototransformations was monitored by infrared spectroscopy. Details of the experimental setup, methodology for the preparation of the cryogenic matrices, laser UV irradiations, and acquisition of IR spectra can be found elsewhere.20

All computations were carried out using the Gaussian 09 software package (Revision D.01).72 The geometries of all relevant species were fully optimized by employing the DFT(B3LYP) method27 combined with the standard 6-311+G(d,p) basis set.73–75 The Cartesian coordinates of the optimized geometries are provided in Table S3, and the corresponding electronic energies, without and with the zero-point vibrational energy correction, are collected in Table S4. Harmonic vibrational calculations were then performed at the same level of theory on the optimized geometries. With the aim of comparison with the experimental spectra and vibrational assignment, the computed harmonic wavenumbers were scaled. The computed vibrational fundamentals appearing in the 3700–3330 cm\(^{-1}\) spectral range \(\nu(\text{OH})\) and \(\nu(\text{NH})\) modes were scaled by 0.948, as in the preceding work.77 The computed wavenumbers of \(\nu(\text{CH})\) modes (appearing in the 3330–2900 cm\(^{-1}\) spectral range) were scaled by 0.960, with the scaling factor obtained for this range using data on various monoterpenes that are very abundant with CH groups.79 The computed vibrational fundamentals appearing in the 2300–2000 cm\(^{-1}\) spectral range \(\nu(N=\text{C})(\text{C})\), \(\nu(N=\text{C})(\text{N})\), \(\nu(N=\text{C})(\text{C}=\text{N})\), and \(\nu(N=\text{C})(\text{C}=\text{N})\) modes were scaled by 0.974, a factor providing the best match with experiments. Finally, a factor of 0.983 was applied for all modes below 1800 cm\(^{-1}\). It was obtained from least-squares linear fit of the experimental vs B3LYP/6-311+G(d,p) computed harmonic wavenumbers of 2-isocyanophenol (see ref 27 for details). The computed scaled wavenumbers and infrared intensities are provided as the Supporting Information (Table S5). These data were used to simulate the IR spectra using the ChemCraft software (version 1.8).80 The peaks centered at the scaled wavenumbers were convoluted with Lorentzian functions having fwhm = 2 cm\(^{-1}\) and peak heights equal to the computed infrared intensities.

A natural bond orbital (NBO) analysis was performed for selected species at the B3LYP/6-311+G(dp) level using the NBO 6.0 program.11 Vertical excitation energies of the low-energy electronic excited singlet states (Table S1) were calculated at the B3LYP/6-311+G(dp) level using TD-DFT.82,83 For the graphical representation, each calculated peak was convoluted with a Lorentzian function having a half width at half-maximum equal to 0.124 eV (1000 cm\(^{-1}\)). The resulting simulated UV spectra of 1 and 4 are presented in the Supporting Information (Figure S2).

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02970.

Experimental IR spectrum of 1 isolated in an Ar matrix vs B3LYP/6-311+G(dp)-computed IR spectrum of 1; natural bond orders computed for 9 and 4; natural spin densities computed for 9; predominant resonance structures of 9 resulting from NRT analysis; simulated UV spectra of 1 and 4 obtained from TD-DFT calculations; experimental and computed IR spectra of the photoproducts resulting from UV irradiations of matrix-isolated 3; electronic energies, optimized geometries, wavenumbers, and IR intensities extracted from the harmonic B3LYP/6-311+G(dp) vibrational calculations for all relevant species; and wavelengths and
oscillator strengths of the low-energy electronic excited singlet states obtained from TD-DFT calculations at the B3LYP/6-311++G(d,p) level (PDF)

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Notes
The authors declare no competing financial interest.

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(36) Note that HNC or HCN are not produced during irradiation of ClNC+, and BrCN+ trapped in solid neon.

(37) Milligan, D. E.; Jacox, M. E. Spectroscopic Study of the Vacuum-Ultraviolet Photolysis of Matrix-Isolated HCN and Halogen Cyanides. Infrared Spectra of the Species CN and XNC. Benzoxazole at 233 nm (blue spectrum in Figure 4a), and appear only during the subsequent irradiation at 290 nm (red spectrum in Figure 4a), at the cost of isocyanophenol.


(65) One of the products complementary to HCN and HNC is fulvenone 8. The net production of 8 is about 8% of the reacted 4, which is less than 36% (the sum of yields of HCN and HNC). This can be explained by the fact that once HCN and HNC are formed, they remain stable in the matrix, because their lowest-energy electronic transitions are situated in the vacuum-UV region of spectrum, below 190 nm (see refs 66−68). However, fulvenone 8 can be simultaneously produced and consumed by UV-irradiation at 290 nm, because the electronic absorption spectrum of 8 extends to wavelengths longer than 300 nm (see ref 69 and Table S1). A possible photoproduce of 8 is carbon monoxide, which cannot be identified unequivocally in the experiment because the only infrared absorption of CO appears at exactly the same frequency (2138 cm−1) as the much more intense infrared band of 8. It is known that fulvenone decomposes thermally to cyclopentadienylidene and CO (see ref 26).


