*J. Am. Chem. Soc.* **2000,** *122,* 5849−5855

# Photochemistry of 1*H*-Benzotriazole in Aqueous Solution: A Photolatent Base

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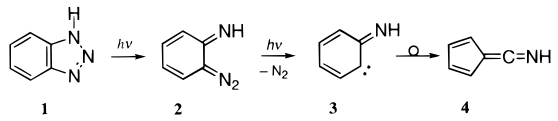
*Received December 21, 1999. Revised Manuscript Received April 22, 2000*

**Abstract:** Flash photolysis of 1*H*-benzotriazole (**1**) has shown that N−N bond fission occurs within a few picoseconds of excitation (248 nm) giving 6-diazo-2,4-cyclohexadien-1-imine (**2**), $\lambda_{max} = 430$ nm. Fluorescence and intersystem crossing do not compete measurably, and photodenitrogenation is a minor side reaction (<1%). The rate constant for recyclization in the ground state, $\mathbf{2} \rightarrow \mathbf{1}$, is on the order of $2 \times 10^9$ s$^{-1}$ in aprotic solvents, and $3.2 \times 10^7$ s$^{-1}$ in aqueous solution. DFT calculations gave $\Delta_{\mathbf{2}\rightarrow\mathbf{1}}G^{\ddagger} = 3.7$ and $\Delta_{\mathbf{2}\rightarrow\mathbf{1}}G^{\circ} = -28.0$ kcal mol$^{-1}$ for the activation and reaction free energies, respectively. Imine **2** is a moderately strong base, p$K_a$ = 12.7, that is protonated by water yielding 2-aminophenyl diazonium ion ($\mathbf{2}^+$), $\lambda_{max} = 405$ nm. The rate constant for cyclization of the cation, $\mathbf{2}^+ \rightarrow \mathbf{1} + H^+$, is $k = 3$ s$^{-1}$. The reversible photoreaction of **1** may be used to induce an upward pH jump in unbuffered water, or as a kinetic pH-indicator for the range of 6−12 in buffered solutions. An erroneous value for the acidity constant of protonated **1** is corrected to p$K_a(\mathbf{1}^+) = 0.42 \pm 0.02$ ($I = 1.0$ M). Several derivatives of **1** were also investigated.

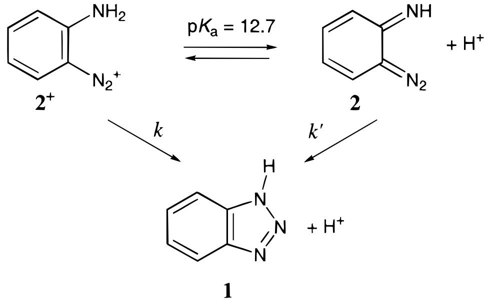
1*H*-Benzotriazole (**1**) is surprisingly stable to irradiation in solution. Prolonged irradiation of **1** and its derivatives gives poor yields of isolable products formed by nitrogen elimination.[1−4] Nevertheless, derivatives of **1** have been propagated as a new family of light-activated DNA cleaving agents (triazole photonucleases).[5] Rich and interesting chemistry has been observed by irradiation of **1** in rigid glassy solutions at low temperature, namely formation of 6-diazo-2,4-cyclohexadien-1-imine (**2**),[6] iminocarbene (**3**),[7] and 6-iminofulvene (**4**)[8] (Scheme 1).

The apparent photostability of **1** in solution is deceptive. Using picosecond and nanosecond laser flash photolysis we discovered that N−N bond fission of **1** yielding imine **2** is fast (<2 ps) and efficient at room temperature in solution. Recyclization to **1** is complete within a few nanoseconds in aprotic solvents. The imine **2** is a fairly strong nitrogen base that is intercepted by protonation in the presence of water (Scheme 2). The conjugate acid $\mathbf{2}^+$ is the intermediate formed in the synthesis of **1** by diazotization of *o*-phenylene diamine and is characterized here for the first time.

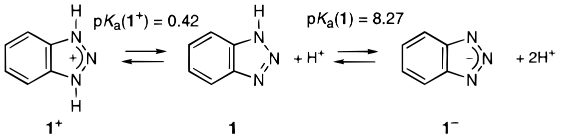
**Scheme 1**



**Scheme 2**



**Scheme 3**



## Results

**Protonation Equilibria in the Ground State.** The two NH dissociation constants of protonated benzotriazole ($\mathbf{1}^+$) were determined by spectrophotometric titration of $1 \times 10^{-4}$ M solutions of **1** at 25.0 ± 0.1 °C (Scheme 3). A calibrated glass

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10.1021/ja994464c CCC: $19.00

electrode[9] was used to determine proton concentrations [H$^+$]. The first acidity constant was measured by titrating a solution of **1**$^+$ in 1 N HCl with 1 N NaOH, the second by addition of 0.1 N NaOH to an aqueous solution of **1** containing 0.01 N tris(hydroxymethyl)methyl amine, 0.01 N HCl and 0.09 N NaCl. About 15 absorption spectra were digitized at intermediate stages of the titrations and the data matrices were subjected to factor analysis using the program SPECFIT.[10] Two significant spectral components were obtained in each case, and the concentration quotients $K_a$ of the indicator were then determined by nonlinear least-squares fitting of a titration function to the linear weighting coefficients of the eigenspectra. Three independent titrations for each of the two dissociation quotients gave average values of p$K_a$(**1**$^+$) = 0.42 ± 0.02 (ionic strength $I$ = 1.0 M) and p$K_a$(**1**) = 8.27 ± 0.02 ($I$ = 0.1 M). The former value should be a close to the thermodynamic dissociation constant, p$K_a°$(**1**$^+$), because dissociation of **1**$^+$ involves only a charge shift, not an ionization. Extrapolation of the second ionization quotient to zero ionic strength, using activity coefficients recommended by Bates,[11] gives the thermodynamic ionization constant of **1**, p$K_a°$(**1**) = 8.42 ± 0.05, which is in good agreement with the values of p$K_a°$(**1**) = 8.38 ± 0.03 (calorimetric)[12] and p$K_a°$(**1**) = 8.44 (potentiometric)[13] reported in the literature. Our value for the first dissociation quotient, p$K_a$(**1**$^+$), is in accord with some earlier qualitative data,[14,15] but the value of 1.6 that is quoted without reference to an original source in various compilations[16] should be ignored.

**Luminescence of Benzotriazole.** Schütt and Zimmermann[17] and later Shizuka and co-workers[6] have reported fluorescence and phosphorescence spectra of benzotriazole in rigid glassy solvents at low temperature. The 0−0 transition of phosphorescence was reported to lie at 24 700[17] or 24 300 cm$^{-1}$ (3.02 eV)[6] corresponding to a triplet energy of 70.0 ± 0.5 kcal mol$^{-1}$. Shizuka et al.[6] also reported lifetimes and quantum yields of fluorescence, $\tau_F = 5$ ns and $\phi_F = 0.1$, and of phosphorescence, $\tau_P = 4.45$ s and $\phi_P = 0.024$, for **1** in an EPA glass (ether, isopentane, alcohol 5:5:2) at 77 K. We could not detect genuine fluorescence emission of **1** in solution at room temperature using either a conventional fluorescence spectrometer or picosecond laser excitation and a streak camera for detection. Nevertheless, a relatively high value of $\phi_f \leq 10^{-3}$ must be given as an upper limit for the fluorescence quantum yield of **1**, because more strongly fluorescent impurities—possibly trace amounts of the 2*H*-tautomer of **1** or photoproducts—interfered with the measurements.

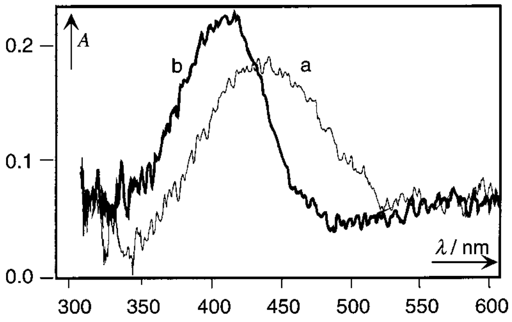

**Figure 1.** Absorption spectra of the transient generated by flash photolysis of **1** using an excitation pulse from a KrF-excimer-laser ($\lambda_{exc}$ = 248 nm, 100 mJ per pulse, pulse width ~25 ns, delay after the pulse maximum ~30 ns). Spectrum a: 1.0 N aqueous NaOH. Spectrum b: 0.001 N aqueous NaOH.

**Flash Photolysis of Benzotriazole in Aqueous Solution.** Flash photolysis of a solution of **1** in 1 N aqueous NaOH with a 248-nm laser pulse of 20 ns duration produced strong transient absorption in the range of 350−550 nm, $\lambda_{max}$ = 430 nm, $\tau \approx$ 30 ns. The broad absorption band of the transient (Figure 1, curve a) was very similar to that of the "yellow intermediate" ($\lambda_{max}$ = 423 nm) that was observed by Shizuka et al.[6] after irradiation of **1** in EPA glass at 77 K, and was identified as 6-diazo-2,4-cyclohexadien-1-imine (**2**). All results of the present work confirm that assignment.

In more dilute base, pH < 13, the absorption band of the transient was blue-shifted, $\lambda_{max}$ = 405 nm (Figure 1, curve b), and the lifetime increased. The transient absorbances were formed within the duration of the laser pulse at all pH, and their subsequent decay, monitored at 410 nm, obeyed the first-order rate law accurately. The observed rate constant, $k_{obs}$, depended strongly on pH (Table 1), but not on buffer concentration.[18] It decreased from a maximum of 3.2 × 10$^7$ s$^{-1}$, observed above pH 13, to 3.0 s$^{-1}$ in acidic solutions at pH < 5 (Table 1). Both the change in the absorption spectrum of the transient and the downward bend of the pH profile around pH 13 (Figure 2) are indications of a rapid protonation equilibrium, $\mathbf{2} + H^+ \rightleftarrows \mathbf{2}^+$. On the other hand, the upward bend of the pH profile at pH 5 marks a change in the reaction mechanism. At pH > 5 the decay of **2**$^+$ proceeds via **2**; hence, the rate increases with base concentration. Below pH 5 the equilibrium concentration of **2** is so small that the slow, direct cyclization of **2**$^+$ becomes competitive.

The rate law for the decay of imine **2** that is defined by this mechanism (Scheme 2), is given by eq 1

$$-d[\mathbf{2}]_t/dt = k_{obs}[\mathbf{2}]_t = k[\mathbf{2}^+] + k'[\mathbf{2}] \qquad (1)$$

where $[\mathbf{2}]_t \equiv [\mathbf{2}] + [\mathbf{2}^+]$ is the total concentration of **2**, $k$ is the rate coefficient for cyclization of **2**$^+$, and $k'$ that of **2**. The variables [**2**$^+$] and [**2**] can be replaced using the definition of the dissociation quotient of **2**$^+$, $K_a = [H^+][\mathbf{2}]/[\mathbf{2}^+]$, to express the dependence of $k_{obs}$ on acidity in terms of three parameters, the rate constants $k$ and $k'$, and $K_a$, eq 2.

$$k_{obs} = \{k[H^+] + k'K_a\}/\{[H^+] + K_a\} \qquad (2)$$

Nonlinear least-squares fitting of eq 2 to the data given in Table 1 provided the best-fit values for these parameters (Table 2). Only data measured in the range 1 ≤ p[H$^+$] ≤ 13 ($I$ = 0.1 M) were included for fitting, but Figure 2 shows that the extrapolated fit function follows the experimental data determined outside that range at ionic strengths exceeding 0.1 M.

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**Table 1.** Rate Profile of the Cyclization **2** → **1**[a]

| $-\log[H^+]$ | $k_{obs}/s^{-1}$ | no. of experiments |
|---|---|---|
| −0.54 | $3.06 \pm 0.03$ | 6 |
| −0.48 | $2.54 \pm 0.02$ | 6 |
| −0.40 | $2.58 \pm 0.03$ | 8 |
| −0.30 | $2.53 \pm 0.01$ | 8 |
| −0.18 | $2.28 \pm 0.01$ | 6 |
| −0.10 | $2.48 \pm 0.01$ | 6 |
| 0.00 | $2.54 \pm 0.01$ | 10 |
| 0.25 | $2.64 \pm 0.02$ | 8 |
| 0.50 | $2.69 \pm 0.01$ | 10 |
| 1.00 | $2.76 \pm 0.01$ | 20 |
| 1.50 | $2.86 \pm 0.03$ | 12 |
| 2.00 | $2.92 \pm 0.02$ | 15 |
| 2.50 | $3.05 \pm 0.03$ | 15 |
| 3.00 | $3.03 \pm 0.02$ | 12 |
| 3.50 | $3.00 \pm 0.01$ | 12 |
| 4.57[b] | $3.64 \pm 0.05$ | 10 |
| 6.78[c] | $58.40 \pm 1.20$ | 10 |
| 9.80 | $(3.89 \pm 0.04) \times 10^4$ | 8 |
| 10.80 | $(3.87 \pm 0.02) \times 10^5$ | 10 |
| 11.30 | $(1.15 \pm 0.01) \times 10^6$ | 8 |
| 11.80 | $(3.84 \pm 0.02) \times 10^6$ | 10 |
| 12.30 | $(9.99 \pm 0.08) \times 10^6$ | 8 |
| 12.80 | $(1.90 \pm 0.01) \times 10^7$ | 15 |
| 13.68[e] | $(2.79 \pm 0.02) \times 10^7$ | 15 |
| 14.08[e] | $(3.28 \pm 0.02) \times 10^7$ | 8 |
| 14.48[e] | $(3.39 \pm 0.02) \times 10^7$ | 8 |

[a] Solutions with hydrogen ion concentrations in the range $10^{-1}$ M $\geq [H^+] \geq 10^{-13}$ M were adjusted to an ionic strength of $I = 0.1$ M by addition of $NaClO_4$. Decay rates in aqueous NaOH were determined by laser flash photolysis (excitation at 248 nm), those in buffered or acidic solutions on a setup with conventional flash lamp excitation (1000 J, 20 μs). All decay rate constants were measured at room temperature, 20 ± 1 °C. [b] $p[H^+] \leq 3.5$: nominal $HClO_4$ concentrations. $9.8 \leq p[H^+] \leq 12.80$: calculated from nominal NaOH concentrations, $p[H^+] = pK_w - p[OH^-]$ with $K_w$ ($I = 0.1$ M, 20 °C) $= 1.08 \times 10^{-14}$ $M^2$.[11] $p[H^+] \geq 14$: $p[H^+] = H_-$ acidity function (Yagil, G. *J. Phys. Chem.* **1967**, *71*, 1034−1044). [c] Acetic acid buffer up to 0.2 M, $[AcOH]/[AcO^-] = 1.0$, $I = 0.10$ M. [d] Proton concentrations were calculated using thermodynamic dissociation constants from the literature[18] and activity coefficients ($I = 0.1$ M) recommended by Bates.[11] [e] Potassium phosphate buffer, $[H_2PO_4^-]/[HPO_4^{2-}] = 1.0$, $I = 0.10$ M.

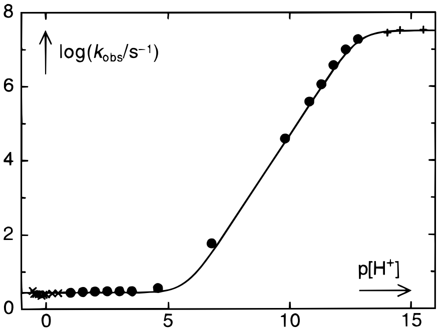


**Figure 2.** pH-rate profile for the decay of **2** in aqueous solution. The solid line represents the best fit of eq 2 to the data points within pH 1−13 (●, Table 1), which defines the fit parameters given in Table 2.

The thermodynamic acidity constant of $\mathbf{2}^+$ may be estimated using the activity coefficients recommended by Bates,[11] $pK_a° = 12.9 \pm 0.1$.

**Table 2.** Decay Rate Constants of the *o*-Amino Diazonium Salts, *k*, and of the Neutral Diazo Imines, *k*′, Generated by Flash Photolysis of Benzotriazoles **1**, **5**, and **7**, and NH Dissociation Quotients $K_a$ of the Resulting Transient *o*-Amino Diazonium Ions[a]

| benzotriazole | $k/s^{-1}$ | $k'/(10^5\ s^{-1})$ | $pK_a$ |
|---|---|---|---|
| **1** | $3.0 \pm 0.1$ | $345 \pm 68$ | $12.71 \pm 0.09$ |
| **5** | $26.3 \pm 5.0$ | $570 \pm 230$[b] | $12.3 \pm 0.2$[b] |
| **7**[c] | $0.83 \pm 0.10$ | $7.2 \pm 1.0$ | $10.4 \pm 0.2$ |

[a] The parameters were determined by nonlinear least-squares fitting of eq 2 to the observed rate constants. Error ranges are 90% confidence limits. [b] The decays at pH > 13 were close to the time resolution of the ns laser flash photolysis apparatus. [c] The kinetic Scheme 2 is probably too simple for this case, see text.

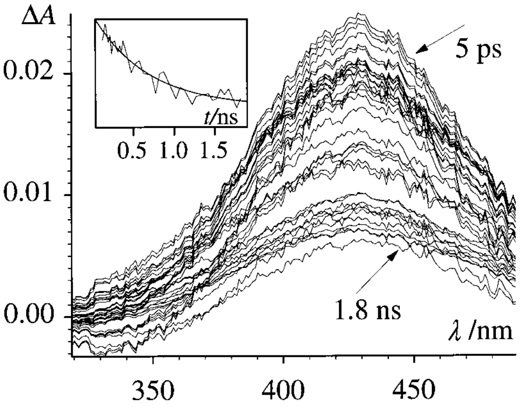
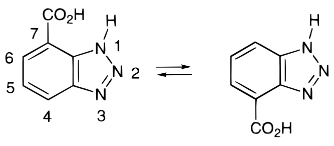


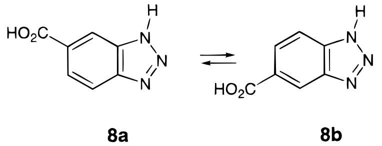
**Figure 3.** Pump−probe absorption spectra observed at several delay times from 5 ps to 1.8 ns after 248-nm subpicosecond excitation of **1** in acetonitrile. The inset shows the global kinetic fit to a single-exponential function, $k = (1.5 \pm 0.2) \times 10^9$ $s^{-1}$.

**Derivatives of Benzotriazole.** To confirm the assignment of the transient imine **2** and its conjugate acid $\mathbf{2}^+$ proposed above, 1-methyl-1*H*-benzotriazole (**5**) was chosen as a reference compound that lacks an ionizable NH group. If the observed preequilibrium is protonation of **2**, then the transient formed by flash photolysis of **5** should behave similarly. This was found to be the case. Laser flash photolysis of **5** in 1 N aqueous NaOH yields a single transient intermediate, $\lambda_{max} = 460$ nm, which is attributed to 6-diazo-2,4-cyclohexadiene-1-(*N*-methyl)imine (**6**). The absorption maximum of the transient shifts to $\lambda_{max} = 430$ nm at pH < 12 due to protonation forming the conjugate acid, 2-(*N*-methylamino)phenyldiazonium ion ($\mathbf{6}^+$). The pH-rate profile was similar in shape to that generated upon flash photolysis of **1** and was again analyzed on the basis of eq 2. The resulting parameters are given in Table 2.

The carboxylic acid derivatives **7** and **8** were chosen to determine the effect of an intramolecular acid function in aprotic media (vide infra). In water, a single first-order decay was observed with 1*H*-benzotriazole-4(7)-carboxylic acid (**7**) and the



**7a** **7b**



**8a** **8b**

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(18) Buffer dilution series gave no evidence for general acid or general base catalysis, i.e., decay rates were independent of buffer concentration for acetic acid buffer ([HAc] + [Ac$^-$] = 0.04−0.2 M, [HAc]/[Ac$^-$] = 1, 36 measurements) and phosphate buffer ($[H_2KPO_4] + [HK_2PO_4] = 0.008-0.04$ M, $[H_2KPO_4]/[HK_2PO_4] = 1$, 50 measurements). The following acidity constants were used for calculation of the proton concentration in the buffer solutions. $pK_a°$(HAc, 20 °C) = 4.76: Harned, H. S.; Ehlers, R. W. *J. Am. Chem. Soc.* **1933**, *55*, 652−656. $pK_a°$ $H_2KPO_4$, 20 °C) = 7.21: Grzybowski, A. K. *J. Phys. Chem.* **1958**, *62*, 555−559.

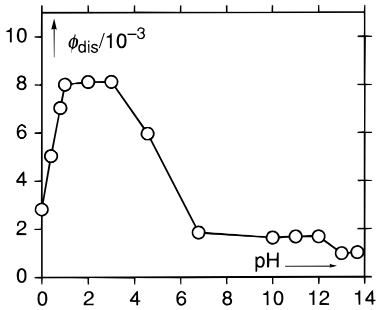
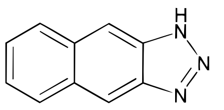


**Figure 4.** pH dependence of the quantum yields of photodecomposition of **1** ($10^{-4}$ M). Acetic acid and phosphate buffer solutions were used for the points at pH = 4.7 and 6.7. For pH 1−13 all solutions were adjusted to an ionic strength of $I = 0.10$ M by the addition of $NaClO_4$.

pH rate profile of the decay rates resembled those described above for benzotriazole **1** and its *N*-methyl derivative **5**.

The two NH prototropic tautomers **7a** and **7b** cannot be separated. The rate law given by eq 2 is, therefore, too simple for compound **7**, first, because photolysis of a mixture of isomers **7** may produce the corresponding mixture of isomeric diazo imines, and second, because ionization of the carboxyl group may affect the decay rate of the diazonium ion as pH is changed. Dual exponential decays that would have indicated the presence of two isomers in comparable amounts were not observed. Minor deviations of the observed rate constants from the rate profile predicted by eq 2 suggested some influence of carbonic acid ionization. However, the deviations were too small to allow for a reliable determination of the two additional parameters involved. The parameters given in Table 2 were obtained by fitting of eq 2 to the observed first-order rate constants. On the other hand, the transient decay traces generated by flash photolysis of 1*H*-benzotriazole-5(6)-carboxylic acid (**8**) did require biexponential functions for fitting, which indicates that the prototropic mixture **8a** and **8b** gives two isomeric diazo imines in comparable yield. The pH rate profile of this compound was not studied in detail.

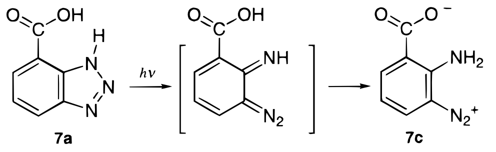
Solutions of 1*H*-naphtho[2,3-*d*]triazole (**9**) in water or 0.1 N aqueous HCl containing 20% acetonitrile as a cosolvent exhibited strong fluorescence ($\lambda_{max} = 430$ nm, shoulder at 470 nm). No transient absorption was detected in the visible region by nanosecond flash photolysis at 351 nm. The fluorescence excitation spectrum ($\lambda_{emission} = 430$ nm) matched the absorption spectrum of **9**.



**9**

**Flash Photolysis of Benzotriazoles in Aprotic Solvents.** Only very weak transient absorptions (≪1%) were detected following nanosecond flash photolysis of benzotriazole (**1**) in aprotic solvents, because the cyclization of **2** was beyond the time resolution of our system. Subpicosecond excitation of **1** at 248 nm in acetonitrile solution gave a strong transient absorption, $\lambda_{max} = 430$ nm, that was fully developed within a few picoseconds of excitation and decayed by a first-order rate law with a rate constant of $(1.5 \pm 0.2) \times 10^9$ $s^{-1}$ (Figure 3). The short-lived intermediate **2** was intercepted when acetic acid or water was added to the acetonitrile solution. Long-lived transient absorptions that are attributed to *o*-aminophenyldiazonium ion **2**$^+$, $\lambda_{max} = 405$ nm, now appeared with decay rate constants $k_{obs} = 0.35$ $s^{-1}$ in $CH_3CN/CH_3COOH$ 4:1 and $k_{obs} = 0.69$ $s^{-1}$ in $CH_3CN/H_2O$ ~10:1.

**Scheme 4**



When the carboxylic acid derivative **7** was excited in dry acetonitrile with a flash from a conventional electric discharge flashlamp, a long-lived transient absorption, $\lambda_{max} = 420$ nm, with a first-order decay, $k = 0.15 \pm 0.01$ $s^{-1}$, was observed. This indicates that some of the 7-carboxylic acid isomer **7a** is present in dry acetonitrile, and that intramolecular proton transfer to form the zwitterion 2-aminophenyldiazonium-3-carboxylate (**7c**) takes place after photolytic ring cleavage (Scheme 4). In accord with this proposal, no long-lived transient absorption was observed by flash photolysis of 1*H*-benzotriazole-5(6)-carboxylic acid (**8**) in dry acetonitrile.

**Triplet Sensitization.** The triplet energy of benzotriazole (**1**) is known from phosphorescence, $E_T = 70.0 \pm 0.5$ kcal $mol^{-1}$.[6,17] That of benzophenone, $E_T = 69.1$ kcal $mol^{-1}$,[19] is slightly lower, but by so little that triplet energy transfer should nevertheless be observable. Excitation of a solution of benzophenone ($5 \times 10^{-3}$ M) in acetonitrile with a 20-ns pulse from an excimer laser operated on XeF (351 nm) gave the well-known triplet−triplet absorption of benzophenone, $\lambda_{max} = 530$ nm, with a half-life of ~20 $\mu$s in degassed solution. As usual, the decay was largely second order due to triplet−triplet annihilation.

In the presence of **1** ($8.4 \times 10^{-3}$ M), the transient absorbance at 530 nm decayed in two phases: the faster decay with about 75% of the total amplitude was first order with a rate constant of about $1.4 \times 10^7$ $s^{-1}$, and the rest decayed by a slower process that was predominantly second order. The fast process is attributed to equilibration of the triplet excitation energy between benzophenone (the only compound excited by the laser pulse) and **1**, and the slow process, to the decay of the two triplets in equilibrium. With a 10-fold higher concentration of **1**, equilibration between the triplets was reached largely within the laser pulse duration of 20 ns, and only about 10% of the benzophenone triplet remained after the pulse. The transient absorption spectrum exhibited a broad band, $\lambda_{max} = 380$ nm, with weak tailing into the visible beyond 530 nm due to the benzophenone triplet. These findings are consistent with the small energy gap between the triplet excitation energies of benzophenone and **1** determined by phosphorescence. The triplet state of **1**, $^3$**1**, has a strong absorption band at 380 nm, and is intrinsically long-lived (>20 $\mu$s).

Unambiguous identification of the 380-nm transient as $^3$**1** was obtained by dual energy transfer. Flash photolysis of benzophenone in degassed acetonitrile containing 0.08 M of **1** and $3.0 \times 10^{-4}$ M of naphthalene gave the expected kinetic and spectrographic traces. Following rapid formation of $^3$**1** within the first 100 ns after excitation, triplet energy transfer from $^3$**1** to naphthalene was manifested by a decay of the transient absorbance at 380 nm and a concomitant growth at 412 nm due to triplet naphthalene. The first-order rate constant of this process was $3.6 \times 10^6$ $s^{-1}$, from which a second-order rate constant of energy transfer from $^3$**1** to naphthalene of $1.2 \times 10^{10}$ $M^{-1}$ $s^{-1}$ is calculated. Energy transfer to naphthalene, $E_T = 60.9$ kcal $mol^{-1}$, was irreversible and gave the characteristic spectrum of triplet naphthalene, $\lambda_{max} = 412$ and 390 nm. Direct excitation of **1** in acetonitrile solution at 248 nm gave no

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**Table 3.** Results of DFT Calculations of **1** and **2** and of the Free Energies of Reaction and Activation for the Cyclization Reaction $\mathbf{2} \rightarrow \mathbf{1}$

| structure | HF (6-21G*) $\mathbf{E}_\mathrm{h}$ | B3LYP (6-31G*) $\mathbf{E}_\mathrm{h}$ | $\Delta G^\circ$ [a] kcal mol$^{-1}$ |
|---|---|---|---|
| **2** | −391.141101 | −395.817656 | 0 |
| **1** | −391.197773 | −395.867179 | −28.0 |
| transition state $\mathbf{2} \rightarrow \mathbf{1}$ | | −395.812361 | 3.7 |

[a] Including zero-point energies and thermal contributions to the free energies at 298 K.

detectable transient absorption at 380 nm. This observation shows that the quantum yield of intersystem crossing of **1** is very small (<1%) at room temperature.

**Quantum Yields of Photodecomposition.** Material balance is notoriously poor in preparative photolyses of benzotriazole.[1−4] Irradiation of **1** in aqueous acid is reported to give a single photoproduct, 2-aminophenol, in 16% yield.[2a] The same product is formed in neutral solution but is photooxidized upon continued irradiation. Aniline is the major product formed in 6% yield by irradiation of **1** in acetonitrile.[3a] Accurate determination of quantum yields is difficult under these circumstances. Order-of-magnitude estimates were obtained by 254-nm irradiation of **1** ($\sim 2 \times 10^{-4}$ M) in aqueous and aprotic solutions and spectrophotometric monitoring of the photoreaction. The quantum yields depended on the pH of the solution (Figure 4), but were less than 1% throughout. The quantum yield of photodecomposition was below 0.1% upon triplet sensitization of **1** by irradiation of benzophenone in acetonitrile at 365 nm. The UV-spectral changes induced by irradiation of the *N*-methyl derivative **5** in 0.1 N aqueous $HClO_4$ were similar to those of **1**, and the quantum yield of disappearance was about the same for both compounds, 0.8%.

**Calculations.** Density functional theory (DFT) was used to calculate the energies of the valence isomers **1** and **2** and of the transition state for the cyclization reaction, $\mathbf{2} \rightarrow \mathbf{1}$. Geometries determined at the Hartree−Fock level with the 6-21G(d) basis set were used as input for B3LYP(6-31G(d)) full geometry optimization. B3LYP is a combination of Becke's three-parameter exchange functional[20] with a slightly modified Lee−Yang−Parr (LYP)[21,22] correlation functional as implemented in GAUSSIAN 98.[23] The transition structure was located on the potential energy surface using the STQN method.[24] Wave function stability was tested, and harmonic vibrational frequencies were calculated by using analytical second derivatives. The results are summarized in Table 3.

## Discussion

The relative stability of the prototropic tautomers of benzotriazole (1*H* vs 2*H*) has been studied extensively. The solid contains exclusively the 1*H*-tautomer **1**.[25] Electronic absorption spectra indicate that **1** also predominates in various solvents,[26] but that the 2*H*-tautomer is the most stable form in the gas phase.[27,28] Evidence for a thermal equilibrium between 1*H*-benzotriazole (**1**) and the quinonoid valence isomer **2** has not been obtained. However, replacement of the NH group of **1** by an O atom in benzo[1,2,3]oxadiazole shifts the equilibrium to the *o*-quinonoid structure 6-diazo-2,4-cyclohexadien-1-one (1,2-benzoquinone diazide).[29]

Irradiation of **1** in solution generates the quinonoid imine **2** within a few picoseconds by N−N bond fission. The triplet state of **1** has been generated and identified as a long-lived intermediate by sensitization with benzophenone. It is not formed by intersystem crossing following direct excitation of **1**, and it is not involved in the formation of **2**. The observation of saturable, specific[18] base catalysis in the decay of **2** (Figure 2) provides conclusive evidence for a rapid and reversible proton-transfer reaction that is established prior to the rate-determining cyclization step (Scheme 2). The maximum rate of cyclization, $k' = 3.2 \times 10^7\ \mathrm{s}^{-1}$, is reached when pH exceeds $\mathrm{p}K_\mathrm{a}(\mathbf{2}^+) = 12.7$, where the equilibrium shifts to the neutral diazo compound **2**. At the same time, the absorption maximum shifts from 405 nm ($\mathbf{2}^+$) to 430 nm (**2**). The spectral shift is similar to that observed upon deprotonation of phenol-2-diazonium ion to 1,2-benzoquinone diazide (353 to 395 nm).[30] In less basic solutions, pH $< \mathrm{p}K_\mathrm{a}(\mathbf{2}^+)$, the observed rate constant decreases linearly with increasing proton concentration, until a constant value of $k = 3\ \mathrm{s}^{-1}$ is reached around pH = 5. This reaction is 7 orders of magnitude slower than that in aqueous base and corresponds to cyclization of the diazonium ion $\mathbf{2}^+$. The barrier for cyclization of **2** determined by the DFT calculations (Table 3) is only 3.7 kcal mol$^{-1}$. We could not locate a minimum for the primary product that would be formed by cyclization of $\mathbf{2}^+$, namely a protonated form of **1** carrying two protons at N1. This suggests that the observed, slow cyclization of $\mathbf{2}^+$ occurs in concert with proton transfer to water, $\mathbf{2}^+ \rightarrow \mathbf{1} + \mathrm{H}^+$.

Imine **2** is quite sensitive to light when generated in rigid glasses.[6−8] Due to its short lifetime in solution, secondary irradiation of **2** does not occur with continuous light sources. Although the lifetime of diazonium ion $\mathbf{2}^+$ is much longer, we could not detect any photosensitivity of $\mathbf{2}^+$ in solution. The decay rate of $\mathbf{2}^+$ in aqueous acid (0.1 N $HClO_4$) was insensitive to 100-fold changes in the intensity of the monitoring light, and the quantum yield of nitrogen elimination determined for 254-nm irradiation was independent of the light intensity (varied up to 10-fold using neutral density filters).

Benzotriazole (**1**) is an amphoteric molecule. It absorbs at

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$\lambda_{max}$ = 258 nm with a shoulder at 275 nm in weakly acidic and neutral aqueous solutions. In strong acid it is protonated and its conjugate acid, $\mathbf{1}^+$, exhibits a single absorption band, $\lambda_{max}$ = 270 nm. Ionization of **1** in aqueous base gives the conjugate base $\mathbf{1}^-$, $\lambda_{max}$ = 274 nm (Scheme 3). The dissociation quotients of $\mathbf{1}^+$ and **1**, $pK_a(\mathbf{1}^+) = 0.42 \pm 0.02$ ($I = 1.0$ M) and $pK_a(\mathbf{1}) = 8.27 \pm 0.02$ ($I = 0.1$ M), were determined in this work because conflicting data were encountered in the literature. The corresponding thermodynamic constants are estimated as $pK_a°(\mathbf{1}^+) = 0.4 \pm 0.1$ and $pK_a°(\mathbf{1}) = 8.42 \pm 0.05$. Due to these ionization equilibria, three different species are irradiated as the pH of aqueous solutions is raised from 0 to 14. Both neutral **1** and its conjugate anion $\mathbf{1}^-$ undergo light-induced ring cleavage, but the conjugate acid $\mathbf{1}^+$ does not. The initial absorbance of transient $\mathbf{2}^+$ decreases below pH 2 and follows a titration curve, from which a $pK_a$ of $0.40 \pm 0.02$ was determined in excellent agreement with the $pK_a$ of $\mathbf{1}^+$. Cleavage of the N−N bond in protonated benzotriazole $\mathbf{1}^+$ would produce a highly energetic protonated diazonium function $[-NH{=}N]^{2+}$.

The transient that was observed by flash photolysis of *N*-methylbenzotriazole (**5**) exhibited very similar behavior to that formed from **1**. This confirms that the photoreaction of **1** does not involve ionization of the NH proton. The rate of cyclization of the diazonium ion $\mathbf{6}^+$ is about 9 times faster than that of $\mathbf{2}^+$, presumably due to the increased nucleophilicity of the NHMe group in $\mathbf{6}^+$.

Photodecomposition of **1** and **5** is a minor side reaction of the reversible fission-recyclization reaction described above. The quantum yield of nitrogen elimination is strongly pH-dependent, but always below 1% (Figure 4. Qualitatively similar results have been reported recently[4] and may be relevant to the photochemical treatment of benzotriazole-containing wastewaters). The major features of the pH-dependence are readily understood in view of the present results. Nitrogen loss occurs in competition to recyclization of the quinonoid photoproduct. The drop below pH 2 is due to protonation of **1** to the cation $\mathbf{1}^+$, which is stable to irradiation. The drop above pH 4 is attributed to acceleration of the cyclization of $\mathbf{2}^+$ by base catalysis. (In previous work[4] the drop was attributed to ionization of **1**.) The residual quantum yield of 0.2% at high pH may be due to nitrogen elimination that occurs either directly from the excited state of **1** or during vibrational relaxation of the primary photoproduct **2**.

The standard synthesis of 1*H*-benzotriazole (**1**) by diazotization of *o*-phenylenediamine in aqueous acid is generally assumed to proceed via the diazonium ion $\mathbf{2}^+$.[31] The synthetic procedures recommend that a reaction temperature of 0−5 °C be maintained, where nitrogen elimination from $\mathbf{2}^+$ is negligible compared with ring closure to **1**. We detected formation of 2-aminophenol by GC/MS, when we conducted the diazotization in a hot water bath. The same reaction presumably accounts for the formation of 2-aminophenol upon irradiation of **1** in aqueous acid at room temperature.

Aniline does not ionize measurably as an acid in water, but its NH acidity in DMSO was determined as $pK_a = 30.7$ at 25 °C.[32] The $pK_a$ values of phenol and benzoic acid in this medium are about 7 units higher than those determined in aqueous solution.[33] A $pK_a$ of about 24 may, therefore, be estimated for the ionization constant of aniline in aqueous solution. Thus, the acidity of the *o*-diazonium substituted aniline $\mathbf{2}^+$, $pK_a(\mathbf{2}^+) = 12.7$, exceeds that of aniline by 11 p*K* units. Such a strong substituent effect seems reasonable, since the diazonium group $[-N{\equiv}N]^+$ is the most electron-withdrawing substituent known.[34] Similarly, the acidifying effect of the diazonium group makes *o*-hydroxyphenyldiazonium cation about 9 p*K* units more acidic than phenol.[30,32]

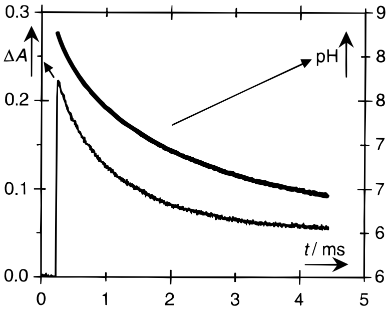

**Figure 5.** Nonexponential decay trace of $\mathbf{2}^+$ generated by laser flash photolysis of **1** in degassed, unbuffered water. The upper trace (right-hand scale) shows the change of pH during the reaction that was calculated from the slope of the absorbance decay trace (lower curve, left-hand scale) using eq 2.

In contrast to **1**, 1*H*-naphtho[2,3-*d*]triazole (**9**) is strongly fluorescent and does not undergo N−N bond fission upon excitation. A plausible explanation is that the reactive singlet state of **1** is of n,$\pi$* character, whereas the lowest excited singlet state of **9** is clearly of $\pi$,$\pi$* character. The fluorescence spectrum of **9** mirrors the first $\pi$,$\pi$* absorption band.

The subnanosecond lifetime of **2** in aprotic solvents is probably too short to make it useful as a photolatent base in such media. It is, however, intercepted efficiently in wet acetonitrile and by the adjacent carboxylic acid in the derivative **7**.

The decay of the 405-nm transient generated by flash photolysis of **1** in unbuffered, degassed water is distinctly nonexponential (Figure 5). This is due to the upward pH-jump generated by the fast formation and protonation of base **2**. The pre-flash pH is then gradually restored as $\mathbf{2}^+$ recyclizes to **1**. The varying slope of the decay trace may be analyzed to determine the current pH during the decay of $\mathbf{2}^+$, which is defined by eq 2. The resulting pH-time profile covering a range of about two units is also shown in Figure 5. Conversely, the first-order decay rates observed in buffered solutions may be used as an accurate kinetic pH indicator in the range of 6−12, where the decay rate is very sensitive to pH.

## Experimental Section

**Materials.** 1-Methyl-1*H*-benzotriazole (**5**),[35] 1*H*-benzotriazole-4(7)-carboxylic acid (**7**),[36] and 1*H*-naphtho[2,3-*d*]triazole (**9**)[37] were prepared according to the procedures described in the literature. 1*H*-benzotriazole-5(6)-carboxylic acid (**8**) was purchased from Aldrich and 2,3-diaminonaphthalene for the synthesis of **9** from Fluka. $^1$H NMR (**7**, DMSO-$d_6$): 8.35 (*d*, $J$ = 8.3, 1H), 8.12 (*d*, $J$ = 7.3, 1H), 7.53 ppm (*dd*, $J_1$ = 8.3, $J_2$ = 7.4 Hz, 1H). (**7**, $CD_3OD$): 8.25 (*d*, $J$ = 8.1, 1H), 8.19 (*d*, $J$

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= 7.3, 1H), 7.52 ppm (*dd*, $J_1$ = 8.3, $J_2$ = 7.4 Hz, 1H). (**8**, $CD_3OD$): 8.61 (*d*, *J* = 1.8, 1H), 8.12 (*dd*, $J_1$ = 7.8, $J_2$ = 1.0, 1H), 7.88 ppm (*d*, *J* = 7.7 Hz, 1H). (**9**, $CDCl_3$): 8.0−8.1 (*m*, 3H), 7.46−7.54 (*m*, 3H). UV (**7**, $H_2O$): $\lambda_{max}$/nm (log $\epsilon$/[$M^{-1}$ $cm^{-1}$]): 267.6 (3.87), 292.2 (3.82).

**Kinetic and Spectrographic Flash Photolysis.** Transient absorption measurements were done by excitation with a conventional electrical discharge (1000 J, 20 $\mu$s) for long-lived transients ($\tau > 50$ $\mu$s), and with pulses from an excimer laser operated on KrF (248 nm) or XeCl (351 nm) for transients on time scales from 30 ns to 100 $\mu$s. Transients with lifetimes below 20 ns were observed on a pump−probe system with subpicosecond excitation pulses at 248 nm.[38]

**Irradiation of 1 in Aqueous Solution.** Benzotriazole ($4.20 \times 10^{-2}$ M) was irradiated in aerated, 0.1 M aqueous $HClO_4$ by 254-nm light. After neutralization of the solution with $Na_2CO_3$ and extraction with *tert*-butyl methyl ether, the products were separated by thin-layer chromatography on silica gel with 9:6 $CH_2Cl_2/CH_3CN$ as an eluent. *o*-Aminophenol was identified as the major product by comparison with authentic material $R_f = 0.60$; the starting compound **1** had $R_f = 0.53$. Analysis by GC showed that *o*-aminophenol was produced with a yield of about 10%. In neutral and basic solutions, *o*-aminophenol is easily photooxidized upon irradiation, and an absorption band in the visible, $\lambda_{max}$ = 430 nm, is formed.

**Quantum Yield Determinations.** Solutions were irradiated with 254-nm light that was isolated from a stabilized medium-pressure mercury arc (Hanau St. 41) with an interference filter. Actinometry of the light source using either azobenzene[39] or ferrioxalate[40] gave consistent results. The light-induced spectral changes differed considerably in the different media, but appeared to be largely uniform throughout the conversions. The amount of converted starting material was estimated from the absorbance changes relative to the total change after extensive irradiation. The value of the extinction coefficient of **1** in aqueous solution at $\lambda_{max}$ = 258 nm is $\epsilon$ = 5623 $M^{-1}$ $cm^{-1}$.[41] Controls by GC−MS analysis gave similar results at conversions below 20%.

**Acknowledgment.** This work was supported by the Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung.

JA994464C

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