Identification of a Remarkably Long-Lived Azoalkane Triplet State

Waldemar Adam,* Werner M. Nau, and Jürgen Sendelbach

Institut für Organische Chemie der Universität Würzburg
Am Hubland, D-97074 Würzburg, FRG

Jakob Wirz*

Institut für Physikalische Chemie der Universität Basel
Klingelbergstrasse 80, CH-4056 Basel, Switzerland

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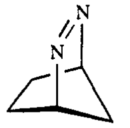
"Of the mysteries surrounding the deceptively simple azo chromophore, the one that has received the least attention is the nature of its lowest triplet state" (Engel et al.).[1] An extensive study by these authors led to the conclusion that "the triplet lifetime of cyclic azoalkanes is much shorter than their singlet lifetime".[1] We report herein chemical and spectroscopic evidence for efficient intersystem crossing (ISC) of azoalkane **1**[2] (Scheme I), a derivative of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), to its triplet state, ^{3}**1**, that has a lifetime of ca. 0.63 μs in degassed benzene at ambient temperature. The involvement of this triplet in the photoreactions of azoalkane **1** is established by studies of product distributions, quantum yields, and transient kinetics including triplet energy transfer.



DBH

Near-UV irradiation of azoalkane **1** in benzene solution produced not only the expected housane **2** but also diazine **3** (Table I, entry 1), the product of an unprecedented photorearrangement for DBH derivatives. These photoproducts are presumably derived from α C–N and β C–C cleavage of the excited azoalkane **1** to give the hydrazonyl and diazenyl diradicals **1**(α) and **1**(β), respectively, as primary intermediates (Scheme I). Related dichotomies have been observed in the photoreactions of other rigid polycyclic azoalkanes;[3] in two cases[3a,c] the triplet state was considered to be the immediate precursor for β C–C cleavage.

Scheme I

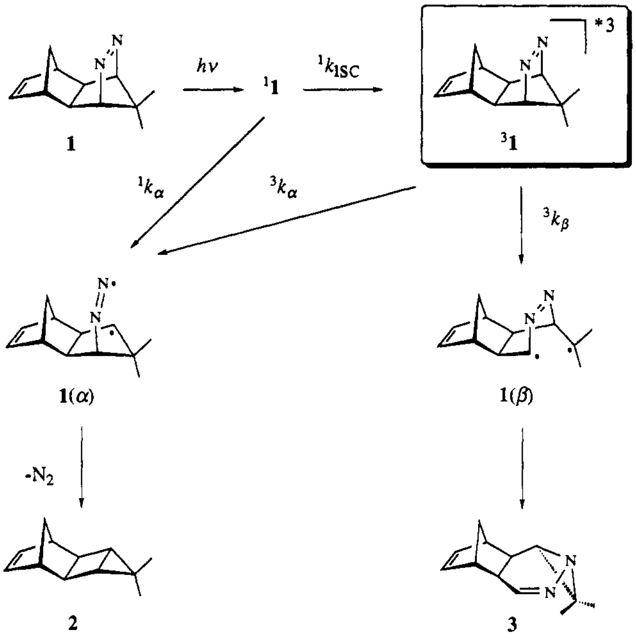


Table I. Photoproducts and Quantum Yields of Azoalkane **1**[a]

entry no.	[*trans*-piperylene],[b] 10^{-3} M	product composition[c] % **2**	% **3**	ϕ_r[d]
1	0	67.8	32.2	0.59 ± 0.03
2	0.60	69.3	30.7	0.46 ± 0.02
3	1.2	70.8	29.2	0.41 ± 0.02
4	2.4	71.6	28.4	0.32 ± 0.02
5	4.2	74.7	25.3	0.26 ± 0.01
6	6.0	76.5	23.5	0.21 ± 0.01
7	9.0	80.0	20.0	
8	1000	>99.5	<0.5[e]	0.044 ± 0.010
9[f]	0	51.5	48.5	

[a] Photolyses (λ_{exc} = 351 nm) were run at 27 °C with 8 mg of **1** in 0.7 mL of degassed benzene-d_6; azoalkane **1** consumptions and mass balances were >90%, except for entry 8 (70 ± 5%). [b] Freshly recondensed. [c] Relative yields (normalized to 100%) are based on base-line-corrected ^{1}H NMR integrals of methyl singlets (δ = 0.95 ppm for **2** and 0.70 ppm for **3**); the reproducibility of the integral ratios in independent experiments was ±0.5%. [d] See footnote 4 for details. [e] Trace detected. [f] Sensitization with benzophenone in degassed benzene; Rayonet photoreactor (λ_{max} = 300 nm); for comparison with the other entries, the values quoted for 27 °C were obtained by linear interpolation from values determined at 17.5, 23.0, and 46.0 °C.

The results given in Table I show that the quantum yield[4] for photoreaction of **1**, ϕ_r, decreases from 0.59 in degassed benzene solution to about 0.044 at 1 M concentration of *trans*-piperylene. The product composition ratio **2**/**3** increases with increasing concentration of quencher; at a quencher concentration of 1 M the formation of diazine **3** is almost completely suppressed. Azo compound **1** exhibits a weak fluorescence emission spectrum which is a near mirror image of the absorption spectrum with a small Stokes shift characteristic for such a rigid structure, λ_{max}(abs) = 361 nm and λ_{max}(em) = 367 nm in benzene solution; the fluorescence quantum yield for excitation at 340 nm was estimated as ϕ_f = 0.02 ± 0.01 relative to quinine bisulfate as a reference (ϕ_f = 0.546).[5] Quenching of the singlet excited state[6] ^{1}**1** cannot be responsible for the changes in product yield and distribution, since the fluorescence intensity is hardly quenched by the addition of 1 M *trans*-piperylene. This indicates that the quencher intercepts a relatively long-lived triplet state of the azo compound, ^{3}**1**.

Thus, the quantum yield measured in the presence of *trans*-piperylene (1 M) is assigned to α cleavage from the singlet excited

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[1] Engel, P. S.; Horsey, D. W.; Scholz, J. N.; Karatsu, T.; Kitamura, A. *J. Phys. Chem.* **1992**, *96*, 7524.

[2] IUPAC name of **1**: (*c*-4a,*c*-8a)-1,4,4a,5,8,8a-hexahydro-10,10-dimethyl-*r*-1,*c*-4:*t*-5,*t*-8-dimethanophthalazine. For the synthesis of **1**, see: Beck, K.; Höhn, A.; Hünig, S.; Prokschy, F. *Chem. Ber.* **1984**, *117*, 517. The sample was purified by chromatography and subsequent sublimation; purity was established to be better than 99.8% by ^{1}H NMR and capillary GC.

[3] (a) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 4320. (b) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7388. (c) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333.

[4] The measured quantum yields refer to consumption of **1** relative to DBH as an actinometer (ϕ(DBH) = 1.0; see: Clark, W. D. K.; Steel, C. *J. Am. Chem. Soc.* **1971**, *93*, 6347). Excellent mass balance (Table I) ensured that the quantum yield for consumption of **1** equaled that for product formation, ϕ_r. Aliquots of degassed solutions of DBH and azoalkane **1** were evenly irradiated with the widened beam of a CW argon ion laser. Only the 333-nm line was selected, and the light intensity was kept within ±0.05% by using the laser light regulation of the instrument. The decrease of absorbance (A) with irradiation time was monitored by UV spectroscopy. Plots of $\log([10^{A_0}-1]/[10^{A}-1])$ vs t were linear and gave slopes of $S = \epsilon I \phi$, where t = irradiation time, I = light intensity, A = absorbance at 333 nm, $A_0 = A(t{=}0)$, and ϵ = extinction coefficient of **1** at 333 nm. For identical I, the ratio $S(\mathbf{1})/S(\mathrm{DBH})$ gave $\epsilon(\mathbf{1})\phi_r/\epsilon(\mathrm{DBH})\phi(\mathrm{DBH})$ from which ϕ_r was calculated using ϕ(DBH) = 1.0, ϵ(**1**) = 35, and ϵ(DBH) = 216 M^{-1} cm^{-1}.

[5] Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251.

[6] Quenching of a singlet excited azoalkane by *trans*-piperylene was found to occur with a rate constant of ca. 10^7 M^{-1} s^{-1}; see: Day, A. C.; Wright, T. R. *Tetrahedron Lett.* **1969**, 1067.

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azoalkane ^{1}**1**, $^1\phi_\alpha = 0.044 \pm 0.010$ (see, however, below for a possible systematic error of this value); β cleavage of ^{1}**1** is negligible (entry 8, Table I). The remainder of the quantum yield of product formation which is measured in the absence of quencher, $\phi_r - {}^1\phi_\alpha = 0.55$, is attributed to reaction through the triplet state and partitions into the quantum yields for formation of housane **2**, $^3\phi_\alpha = 0.36 \pm 0.02$, and of diazine **3**, $^3\phi_\beta = 0.19 \pm 0.01$. A substantial deficit of the total quantum yield remains for radiationless deactivation processes, $\phi_d = 0.39 \pm 0.04$.

The product distribution obtained upon triplet sensitization of **1** with benzophenone is given as entry 9 in Table I. The relative yield of **2** is somewhat less than that obtained by direct irradiation (entry 1). Correction of entry 1 to account for the formation of **2** by the singlet pathway does not fully eliminate the difference; this indicates that $^1\phi_\alpha$ may be somewhat higher than $\phi_r = 0.044$ determined in the presence of 1 M *trans*-piperylene (entry 8). Some light absorption by the side products formed under these conditions or some quenching of ^{1}**1** by *trans*-piperylene would tend to make this value systematically too low.

Flash photolysis of **1** in degassed benzene with a 25-ns pulse from an excimer laser operated with XeF (351 nm, ca. 100 mJ) gave a transient absorption, $\lambda_{max} = 315$ nm, which decayed by first-order kinetics with a lifetime of $\tau = 0.63 \pm 0.02$ μs at ambient temperature. No transient absorption was found in the visible region. The transient was quenched by *trans*-piperylene, $k_q = (1.0 \pm 0.1) \times 10^9$ M^{-1} s^{-1} (six data points, [q] = 0–0.019 M). This transient was unambiguously identified as an excited triplet state by energy transfer to tetracene; flash photolysis of **1** at 351 nm in the presence of tetracene (1×10^{-5} M) gave a step-and-rise growth of transient absorption at 460 and 480 nm, the characteristic absorption maxima of triplet-excited tetracene.[7] The step is attributed to direct excitation of tetracene (absorbance at the excitation wavelength of 351 nm: ca. 0.006); the time-resolved growth rate was equal, within experimental error, to the decay rate of the transient observed at 315 nm. This energy-transfer experiment negates the possibility that the transient arises from some adventitious impurity,[2] since a simple calculation shows that the impurity would have to absorb at least 10% of the exciting light in order to account for the extent of the observed energy transfer to tetracene. The rate of quenching k_q suggests that energy transfer from ^{3}**1** to *trans*-piperylene is slightly endothermic, i.e., $E_T(\mathbf{1}) \cong 58$ kcal mol^{-1}. The triplet energy of DBH is 62 kcal mol^{-1}.[1] Thus the above value for **1** is reasonable in view of a similar bathochromic shift in the singlet absorption.

The value of $^3k_q(^3\tau) = 630 \pm 70$ M^{-1} thus determined by flash photolysis may be compared to that obtained independently from the dependence of the quantum yield for diazine formation, $^3\phi_\beta$, on the concentration of *trans*-piperylene, [q]. The values for $^3\phi_\beta$ are obtained from the measured quantum yields ϕ_r (Table I) by multiplication with the fraction of diazine formation for the various quencher concentrations. Since diazine **3** is (almost) exclusively formed from the triplet state ^{3}**1**, the quantum yield $^3\phi_\beta$ should depend linearly on [q], eq 1. Linear regression gives a slope of $^3k_q(^3\tau) = 460 \pm 20$ M^{-1}. The difference between the two values is sigificant on purely statistical grounds, but considering likely systematic errors of either of the two entirely independent measurements (e.g., different samples of *trans*-piperylene were used in the two laboratories), the agreement is quite satisfactory.

$$^3\phi_\beta^0/{}^3\phi_\beta^q = 1 + {}^3k_q(^3\tau)[q] \qquad (1)$$

A third, independent if less accurate value for $^3k_q(^3\tau)$ is obtained from the data for the product distribution as a function of quencher concentration. Steady-state analysis of the reaction in Scheme I leads to the prediction that the product ratio **2**/**3** should increase linearly with [q], eq 2. This dependence is obeyed accurately by

$$\frac{[\mathbf{2}]}{[\mathbf{3}]} = \frac{^3k_\alpha}{^3k_\beta} + \frac{^1k_\alpha}{^1k_{ISC}(^3k_\beta)(^3\tau)}\{1 + {}^3k_q(^3\tau)[q]\} \qquad (2)$$

entries 1–7 of Table I, i.e., [**2**]/[**3**] = (2.11 ± 0.04) + (203 ± 8)[q]. Making use of the relation $^3\phi_\alpha = {}^1\phi_{ISC}(^3k_\alpha)(^3\tau)$, the ratio of intercept and slope is converted to $(^3\phi_\alpha/{}^1\phi_\alpha + 1)/(^3k_q(^3\tau))$, from which $^3k_q(^3\tau) = 880 \pm 100$ M^{-1} is calculated. This estimate depends strongly on the rather uncertain value of $^1\phi_\alpha$. A somewhat higher value, $^1\phi_\alpha = 0.06$, would give $^3k_q(^3\tau) = 670$ M^{-1}. Thus, the Stern–Volmer analyses are in satisfactory agreement with the result obtained by flash photolysis; i.e., transient kinetics and the analysis of the quantum yields and product distributions provide consistent evidence for the intervention of the triplet state of azoalkane **1** with a lifetime of ca. 0.63 μs.

In conclusion, azoalkane **1** has offered the unique opportunity to perform a joint analysis of spin-selective product studies and transient kinetic measurements. This led to the first direct characterization of a triplet-excited azoalkane by means of transient absorption spectroscopy and its interception as a reactive intermediate by external quenchers. Structural rigidity appears to be a common denominator of azoalkanes that undergo intersystem crossing.[3] Further work will be required to explore the structural features responsible for the unusually long lifetime of triplet azoalkane **1**.

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(7) Porter, G.; Windsor, M. W. *Proc. R. Soc. London, A* **1958**, *245*, 238.