12578 J. Am. Chem. Soc. 1995, 117, 12578−12592

Phosphorescence and Transient Absorption of Azoalkane Triplet States

Waldemar Adam,[†] Gianfranco Fragale,[‡] Dieter Klapstein,[§] Werner M. Nau,*[,†] and Jakob Wirz[‡]

Contribution from the Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany, Department of Chemistry, St. Francis Xavier University, Antigonish, Nova Scotia B2G 2W5, Canada, and Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Received June 2, 1995[⊗]

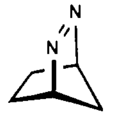
Abstract: Fused derivatives of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) were studied by transient absorption, optical emission, and photoelectron spectroscopy, and their reaction quantum yields were measured. For the first time, long-lived azoalkane triplet states were observed by phosphorescence and transient absorption spectroscopy. The assignment of the transient absorptions to the triplet states of the azoalkanes was proven by quenching and energy transfer experiments in solution. Quantitative agreement was found between the real-time kinetic data of triplet quenching determined by flash photolysis and Stern−Volmer analyses of the effect of quenchers on the product distributions and quantum yields. Triplet energies of 62.5 ± 1 kcal mol^{-1} were determined from the 0−0 bands of the phosphorescence spectra. The triplet energies of azoalkanes that have been previously evaluated by techniques other than phosphorescence are critically evaluated. The radiative rate constant of azoalkane phosphorescence was determined as ca. 3 s^{-1}. The transient absorption spectra had maxima at ca. 315 and 500 nm, and the triplet lifetimes were as long as 0.63 μs. Intersystem crossing (ISC) was found to be an efficient process for most of the azoalkanes examined; for azoalkane **1a**, the triplet quantum yield was estimated to be 0.5 ± 0.2 at ambient temperature. No internal or external heavy-atom effects were observed on phosphorescence and ISC. In some cases, formation of 1,3-cyclopentanediyl biradicals from the azoalkane triplet states was observed by transient absorption spectroscopy. The yield of triplet biradicals, generated by direct photolysis of azoalkanes in solution, served as a qualitative probe for the involvement of ISC and azoalkane triplet states. Possible factors which govern the triplet lifetimes and ISC of azoalkanes are discussed; molecular rigidity appears to favor both high triplet yields and long triplet lifetimes. Assignments of the two T−T absorption bands are proposed. All experimental results are consistent with the expected n,π^* configuration for the lowest excited singlet and triplet states of aliphatic azoalkanes.

Introduction

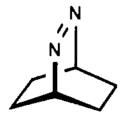
The photochemistry of the azo functionality $-$N=N$-$ has long been under intensive investigation.[1] Studies of the photophysical properties of the azo chromophore,[2,3] which are essential for an in-depth mechanistic understanding of its photoreactions, have revealed poor intersystem crossing (ISC) and exceedingly short triplet lifetimes. These peculiarities have impeded the spectroscopic characterization of the azoalkane triplet state since phosphorescence and transient triplet absorption could not be observed.[3,4]

Nevertheless, from product studies, a distinct chemical reactivity of the azoalkane triplet state has been inferred,[1,5] and from triplet energy transfer experiments,[3,4,6] the energies of the triplet states have been estimated. Additional techniques, namely electron energy loss spectroscopy[7] and measurement of the S_0-T_1 absorptions,[8] have provided vertical triplet energies which may be significantly higher than the energies of the relaxed triplet states.[7b,8b]

The bicyclic derivatives 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) serve as instructive probes for the photochemical and photophysical properties of azoalkanes. These rigid azoalkanes were also expected to be excellent candidates for the direct detection and characterization of their triplet states, as attested by Engel's spectroscopic studies.[3]



DBH



DBO

DBH and DBO exhibit quite contrasting behaviors. Derivatives of DBH extrude molecular nitrogen from their excited

---

[†] Universität Würzburg.

[‡] Universität Basel.

[§] St. Francis Xavier University.

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1995.

(1) (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (b) Engel, P. S.; Nalepa, C. J. *Pure Appl. Chem.* **1980**, *52*, 2621.

(2) (a) Rau, H. *Angew. Chem.* **1973**, *85*, 248; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 224. (b) Bisle, H.; Rau, H. *Chem. Phys. Lett.* **1975**, *31*, 264.

(3) (a) Engel, P. S.; Horsey, D. W.; Scholz, J. N.; Karatsu, T.; Kitamura, A. *J. Phys. Chem.* **1992**, *96*, 7524. (b) Engel, P. S.; Steel, C. *Acc. Chem. Res.* **1973**, *6*, 275. (c) Engel, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 6903. (d) Engel, P. S. *J. Am. Chem. Soc.* **1967**, *89*, 5731.

(4) Dürr, H.; Ruge, B. *Top. Curr. Chem.* **1976**, *66*, 53.

(5) Note that in the majority of cases the spin multiplicity dependence of the product distribution is related to the spin multiplicity of the nitrogen-free biradical intermediates: (a) Bartlett, P. D.; Porter, N. A. *J. Am. Chem. Soc.* **1968**, *90*, 5317. (b) Allred, E. L.; Smith, R. L. *Ibid.* **1969**, *91*, 6766. (c) Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *Ibid.* **1982**, *104*, 6533. (d) Samuel, C. J. *J. Chem. Soc., Perkin Trans. 2* **1993**, 405. (e) Anderson, M. A.; Grissom, C. B. *J. Am. Chem. Soc.* **1995**, *117*, 5041. (f) References 1 and 3b.

(6) (a) Andrews, S. D.; Day, A. C. *J. Chem. Soc. B* **1968**, 1271. (b) Wamser, C. C.; Medary, R. T.; Kochevar, I. E.; Turro, N. J.; Chang, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 4864. (c) Turro, N. J.; Ramamurthy, V. *J. Photochem.* **1979**, 173. (d) Turro, N. J.; Cherry, W. R.; Mirbach, M. J.; Mirbach, M. F.; Ramamurthy, V. *Mol. Photochem.* **1978**, *9*, 111.

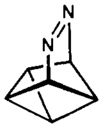
0002-7863/95/1517-12578$09.00/0

singlet and triplet states with quantum yields close to unity.[2,9] The lifetimes of singlet- and triplet-excited DBH in solution have been estimated to be shorter than 0.1 and 1 ns.[9] ISC from the excited singlet to the triplet state of DBH is too slow ($<10^6$ s^{-1}) to compete with extrusion of molecular nitrogen (ca. 10^{10} s^{-1}).[9,10] Furthermore, while fluorescence of several DBH derivatives has been observed,[11] earlier claims[6d,12a] of their S−T absorptions have been attributed to sample impurities.[13]

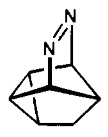
In sharp contrast, DBO and most derivatives are "photoreluctant", i.e., they exhibit very low decomposition quantum yields.[2,9] Instead, strong fluorescence with lifetimes of 1.0 μs in the gas phase and 0.7 μs in acetonitrile solution has been reported.[11,14,15] In more recent experiments,[3a] rapid population of the triplet state of a DBO derivative was achieved through *intra*molecular triplet sensitization and quenching experiments have led to an estimate of ca. 7 ns for the triplet lifetime of DBO.[16] Although the latter value constitutes a lower limit due to the assumption of a diffusion-controlled quenching rate constant, the triplet lifetime is clearly much shorter than that of the singlet. Again, product studies implied[2,15b,17] that ISC from singlet-excited DBO is too slow to compete with fluorescence and radiationless deactivation.

Substituents on the bicyclic azoalkane skeletons, except for a few DBH[12b,18,19] and DBO[15,20] derivatives, do not markedly alter the photochemical properties of the parent molecules. This happenstance has led to several empirical generalizations in regard to the dichotomy of DBH and DBO derivatives,[2,15] which is still not fully understood. Despite the contrasting photochemistry of DBH and DBO, the photophysical traits common to both, namely inefficient ISC, very short triplet lifetimes, and the absence of phosphorescence,[3,15a] have been stipulated to be general for azoalkanes.[2,9,10,17,21]

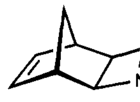
It is interesting to observe, however, that on the basis of spin-selective reactivity and temperature dependence of product distributions, ISC from the excited singlet state to the triplet state has been claimed for the cyclic azoalkanes **I**−**VI**,[18−23]



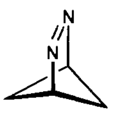
I



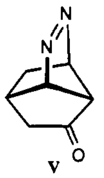
II



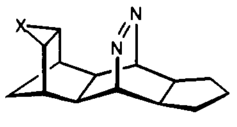
III



IV

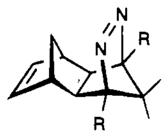


V

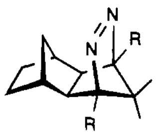


VI

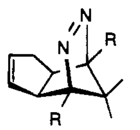
Moreover, a closer inspection of the literature reveals at least two cases (azoalkanes **V** and **VI**)[18b,20c] for which triplet quenchers affected the product distribution obtained on direct irradiation. The latter results imply that spontaneous ISC leads to relatively long-lived (since quenchable) triplet states. Yet, for none of the azoalkanes **I**−**VI** has this knowledge gained from product studies been used to investigate the photophysical properties spectroscopically, e.g., by transient absorption spectroscopy to acquire direct evidence on their triplet states.



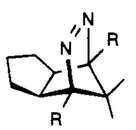
1a (R = H)
1b (R = Me)
1c (R = Ph)



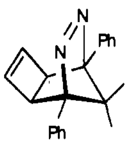
2a (R = H)
2b (R = Me)
2c (R = Ph)



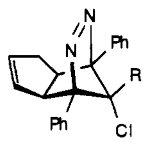
3a (R = H)
3b (R = Me)
3c (R = Ph)



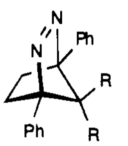
4a (R = H)
4b (R = Me)
4c (R = Ph)



5



6a (R = Me)
6b (R = Cl)



7a (R = H)
7b (R = Me)

Recently we have reported the first direct spectroscopic characterization of the long-lived triplet state of the DBH derivative **1a**,[24a] and the mechanistic implications on its photoreactivity (Scheme 1).[24b] The photophysical and photochemical properties of azoalkane **1a** are exceptional: **1a** shows efficient ISC ($\Phi_{ISC} \gtrsim 0.5$), a remarkably long triplet lifetime in solution (0.63 μs), and β C−C cleavage. The involvement of a long-lived triplet state is borne out by linear Stern−Volmer quenching plots of the quantum yields for product formation and of the product ratio of the α C−N and β C−C cleavages, namely housane and azirane (Scheme 1).[24]

---

(7) (a) Kuppermann, A.; Flicker, W. M.; Mosher, O. A. *Chem. Rev.* **1979**, *79*, 77. (b) Allan, M. *J. Electr. Spectr.* **1989**, *48*, 219.

(8) (a) Metcalfe, J.; Chervinsky, S.; Oref, I. *Chem. Phys. Lett.* **1976**, *42*, 190. (b) Turro, N. J.; Cha, Y.; Gould, I. R.; Moss, R. A. *J. Photochem.* **1987**, *37*, 81. (c) Robertson, L. C.; Merritt, J. A. *J. Chem. Phys.* **1972**, *56*, 2919.

(9) Clark, W. D. K.; Steel. C. *J. Am. Chem. Soc.* **1971**, *93*, 6347.

(10) Engel, P. S.; Culotta, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 2686.

(11) (a) Solomon, B. S.; Thomas, T. F.; Steel, C. *J. Am. Chem. Soc.* **1968**, *90*, 2249. (b) Mirbach, M. J.; Liu, K.-C.; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *Ibid.* **1978**, *100*, 5122. (c) Mirbach, M. F.; Mirbach, M. J.; Liu, K.-C.; Turro, N. J. *J. Photochem.* **1978**, *8*, 299.

(12) Turro, N. J. In *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991. (a) p 122. (b) pp 187−188. (c) pp 31, 107, 189. (d) pp 153−187. (e) pp 128−129. (f) pp 191−193. (g) pp 362−377. (h) p 436.

(13) Adam, W.; Dörr, M.; Hössel, P. *Angew. Chem.* **1986**, *98*, 820; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 818.

(14) Steel, C.; Thomas, T. F. *Chem. Commun.* **1966**, 900.

(15) (a) Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 7108. (b) Engel, P. S.; Keys, D. E.; Kitamura, A. *Ibid.* **1985**, *107*, 4964. (c) Engel, P. S.; Kitamura, A.; Keys, D. E. *J. Org. Chem.* **1987**, *52*, 5015.

(16) The triplet lifetime of unsubstituted DBO has recently been determined by time-resolved photoacoustic calorimetry to be 25 ns in cyclohexane: Caldwell, R. A. Personal communication.

(17) Engel, P. S.; Keys, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 6860.

(18) (a) Padwa, A.; Kumagai, T.; Tohidi, M. *J. Org. Chem.* **1983**, *48*, 1834. (b) Adam, W.; Hill, K. *J. Am. Chem. Soc.* **1985**, *107*, 3686. (c) Adam, W.; De Lucchi, O.; Hill, K.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1985**, *118*, 3070. (d) Albert, B.; Berning, W.; Burschka, C.; Hünig, S.; Prokschy, F. *Ibid.* **1984**, *117*, 1465.

(19) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 4320.

(20) (a) Turro, N. J.; Liu, K.-C.; Cherry, W.; Liu, J.-M.; Jacobson, B.; *Tetrahedron Lett.* **1978**, *19*, 555. (b) Engel, P. S.; Nalepa, C. J.; Leckonby, R. A.; Chae, W.-K. *J. Am. Chem. Soc.* **1979**, *101*, 6435. (c) Hünig, S.; Schmitt, M. *Tetrahedron Lett.* **1987**, *28*, 4521. (d) Adam, W.; Grabowski, S.; Platsch, H.; Hannemann, K.; Wirz, J.; Wilson, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 751.

(21) Engel, P. S.; Soltero, L. R.; Baughman, S. A.; Nalepa, C. J.; Cahill, P. A.; Weisman, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 1698.

(22) Dougherty, D. A.; Chang, M. H. *J. Am. Chem. Soc.* **1982**, *104*, 2333.

(23) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7388.

(24) (a) Adam, W.; Nau, W. M.; Sendelbach, J.; Wirz, J. *J. Am. Chem. Soc.* **1993**, *115*, 12571. (b) Adam, W.; Nau, W. M.; Sendelbach, J. *Ibid.* **1994**, *116*, 7049.

Herein, we report in detail on the photophysical properties of azoalkanes **1a–c**, which include the first phosphorescence spectra of azoalkanes. These studies were extended to the related azoalkanes **2–7** in an effort to define the essential structural requirements for the exceptional photophysical features of azoalkanes **1**, which are compared in Table 1 with those of DBH and DBO.

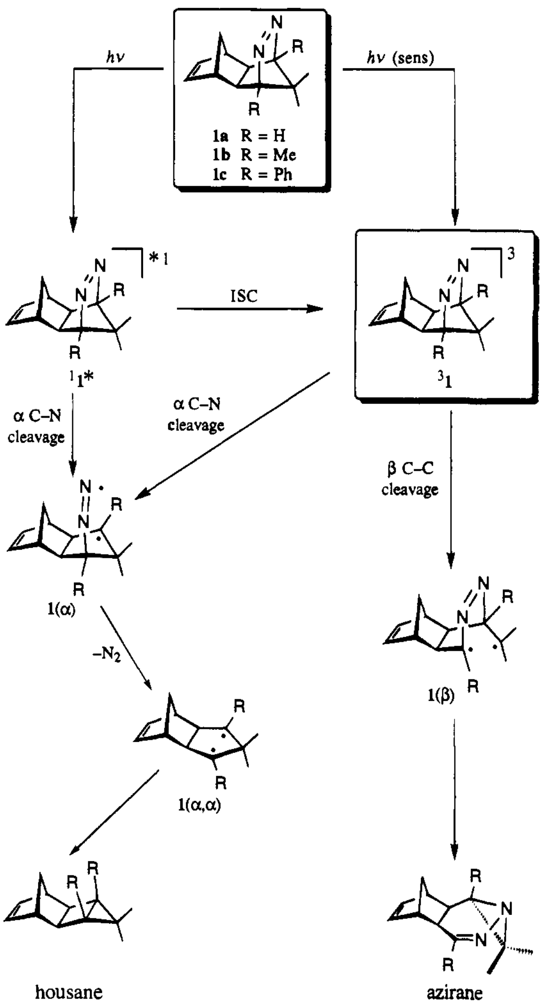
Results

Photoproducts. The DBH derivatives **1–7** were prepared according to literature procedures.[25–29] Direct irradiation of azoalkanes **1** afforded the previously reported housanes and aziranes (Scheme 1).[24] The product distribution was strongly affected by triplet quenchers like *trans*-piperylene (reduced azirane formation), by triplet sensitizers like benzophenone (enhanced azirane formation), and by elevated temperatures (reduced azirane formation). These findings suggested that α cleavage from the singlet-excited state competes with ISC to the triplet state (*cf.* Scheme 1) and that β cleavage and rearrangement to the aziranes occur exclusively from the triplet states of **1**. For the parent DBH, neither ISC nor azirane formation were observed.[9] Scheme 1 also holds for the C=C saturated azoalkane **2a**; the corresponding housane (ca. 90%) and a small amount of the azirane (ca. 10%) were obtained on direct irradiation, and the fraction of the azirane increased to 34% when benzophenone was added as a sensitizer.[29d]

The photochemistry of the related azoalkanes **3c**, **4c**, **5**, and **7** differed from Scheme 1 in that both direct and triplet-sensitized irradiations gave exclusively the corresponding housanes (>90%), i.e., β cleavage was not observed.[24b,26–29] Irradiation of **3b** and **4b** produced the housanes (ca. 25% and 50%) along with significant amounts of cyclopentenes from rearrangement.[29d] The chlorine-substituted azoalkanes **6** proved to be rather photoreluctant, and complex product mixtures were obtained on prolonged direct irradiation.[29b] Notwithstanding the variable photoreactivity of the DBH derivatives **1–7**, spontaneous ISC from the singlet- to the triplet-excited state (Scheme 1) was found to be a competitive process in all these azoalkanes except **7**.

Photoreaction Quantum Yields. The quantum yields for the consumption of azoalkanes **1–4** were determined by irradiation with selected UV lines of a CW argon ion laser (Table 2). Excellent mass balances (>95%) ensured that the quantum yields of azo consumption equaled those for product formation (Φ_r). Absolute quantum yields in the absence of external quenchers were determined by irradiation with the 333-nm laser line; DBH was used as the actinometer ($\Phi_{DBH} = 1.0$).[9] The azoalkane conversion was monitored spectrophotometrically by their absorbance A. The function $\log([10^{A_0} - 1]/[10^{A} - 1])$ increased linearly with irradiation time (Figure 1), as expected[30] for a light source of constant intensity and a simple photoreaction in which only the starting material absorbs at the irradiation wavelength. The photoreaction quantum yields (Φ_r) for **1–4** were calculated from the ratio of the slopes $S(\mathbf{1})/S(\mathrm{DBH}) = \epsilon_{azo}\Phi_r/(\epsilon_{DBH}\Phi_{DBH})$, where ϵ_{azo} and ϵ_{DBH} are the extinction coefficients of **1–4** and DBH at the irradiation wavelength of 333 nm.

Scheme 1



Relative quantum yields for azoalkanes **1** and **2** at various quencher concentrations were determined similarly by using a solution without quencher as a reference. In these experiments, the full UV output of the laser (at 333, 351, and 364 nm) was employed.

Detection of Azoalkane T–T Absorption by Flash Photolysis. We deal first with the azoalkanes that do not carry phenyl groups on the bridgehead, derivatives **1a–4a** and **1b–4b**; 1,3-cyclopentanediyl biradicals formed therefrom [*cf.* **1**(α,α) in Scheme 1] are invisible to transient absorption spectroscopy. The more complex transient absorptions observed with the phenyl-substituted derivatives **1c–4c** and **5–7** will be discussed below. Direct excitation of **1a,b** and **2a** in degassed benzene solution at 25 °C with a 351-nm laser pulse of 25-ns duration gave rise to a transient absorption in the near-UV (λ_{max} ca. 315 nm) and a broad band with lower intensity in the visible region (λ_{max} ca. 500 nm). The latter was not detected in our preliminary experiments.[24a]

The transients were best monitored at 315 nm. They reached their maximum intensity at the end of the laser pulse and

---

[25] (a) Beck, K.; Höhn, A.; Hünig, S.; Prokschy, F. *Chem. Ber.* **1984**, *117*, 517. (b) Beck, K.; Hünig, S. *Ibid.* **1987**, *120*, 477. (c) Hünig, S.; Kraft, P. *J. Prakt. Chem.* **1990**, *332*, 133. (d) Hünig, S.; Prokschy, F. *Chem. Ber.* **1984**, *117*, 534.

[26] Paquette, L. A.; Leichter, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 5128.

[27] (a) Coms, F. D.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 3753. (b) Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 6894.

[28] (a) Adam, W.; Fröhlich, L.; Nau, W. M.; Korth, H.-G.; Sustmann, R. *Angew. Chem.* **1993**, *105*, 1383; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1339. (b) Adam, W.; Fröhlich, L.; Nau, W. M.; Wirz, J. *J. Am. Chem. Soc.* **1993**, *115*, 9824. (c) Adam, W.; Platsch, H.; Wirz, J. *Ibid.* **1989**, *111*, 6896. (d) Adam, W.; Reinhard, G.; Platsch, H.; Wirz, J. *Ibid.* **1990**, *112*, 4570. (e) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165. (f) Adam, W.; Harrer, H. M.; Nau, W. M. Unpublished results.

[29] (a) Adam, W.; Harrer, H. M.; Nau, W. M.; Peters, K. *J. Org. Chem.* **1994**, *59*, 3786. (b) Adam, W.; Ammon, H.; Nau, W. M.; Peters, K. *Ibid.* **1994**, *59*, 7067. (c) Nau, W. M.; Harrer, H. M.; Adam., W. *J. Am. Chem. Soc.* **1994**, *116*, 10972. (d) Adam, W.; Nau, W. M.; Sahin, C.; Sendelbach, J. Unpublished results.

[30] (a) Gauglitz, G.; Hubig, S. *Z. Phys. Chem. (München)* **1984**, *139*, 237. (b) Persy, G.; Wirz, J. *EPA Newsl.* **1987**, *29*, 45.

Table 1. Photophysical Properties[a] of Bicyclic Azoalkanes

	DBH	DBO	**1a**	**2a**
$^1\tau$	0.15[b]	682[c]	2.4[b]	2.9[b]
$^3\tau$	<1[d]	≥7[e]	630	580
Φ_{ISC}	≈0[d]	≈0[f]	≈0.5	0.59[b]
Φ_{fl}	<0.001[b]	≈0.5[g]	0.02	0.02
Φ_{ph}	0.00	0.00	0.052	0.035
Φ_r	1.0[d]	0.02[c]	0.59	0.75
E_S[h]	84.5	76[i]	78.1	78.8
E_T	≈62[i]	≈53[i]	62.4	63.1
ΔE_{ST}	≈22.5	≈23	15.7	15.7
k_{ISC}	$<10^6$[d]	$<10^5$	2×10^8	2×10^8
k_{fl}	$\leq 10^7$	$\approx 10^6$[j]	$\approx 10^7$	$\approx 10^7$
k_{ph}			2.1−4.4[k]	1.4−2.3[k]
IP	8.83	8.19[l]	8.41	8.35

[a] The meaning of the parameters in the left column from top to bottom is as follows: lifetimes (τ) of singlet- and triplet-excited states in solution (in ns), quantum yields (Φ) for intersystem crossing, fluorescence, phosphorescence (at 77 K) and chemical reaction, energies (E) of singlet- and triplet-excited states (in kcal mol^{-1}) and S_1−T_1 energy gaps (ΔE_{ST}), rate constants (k) for intersystem crossing, fluorescence, and phosphorescence (in s^{-1}) calculated as $k_{ISC} = \Phi_{ISC}/{}^1\tau$ and $k_{fl} = \Phi_{fl}/{}^1\tau$, and lowest vertical ionization potentials (IP in eV); data are taken from the text or from Tables 2−5. [b] Reference 39. The singlet lifetime for DBH is based on the fluorescence decay observed in CCl_4 solution; this assignment is tentative. [c] Reference 15. [d] References 9 and 10. [e] References 3a and 16. [f] References 2, 15, and 17. [g] Reference 11. [h] Reference 57. [i] Reference 3a. [j] Using an upper limit of 0.1 for Φ_{ISC}, ref 15. [k] Calculated as $k_{ph} = \Phi_{ph}/(\Phi_{ISC}\tau_{ph})$; τ_{ph} were the phosphorescence lifetimes at 77 K from Table 5; the value of Φ_{ISC} in solution was assumed as a lower limit for Φ_{ISC} at 77 K, *cf.* text. [l] Reference 40 g.

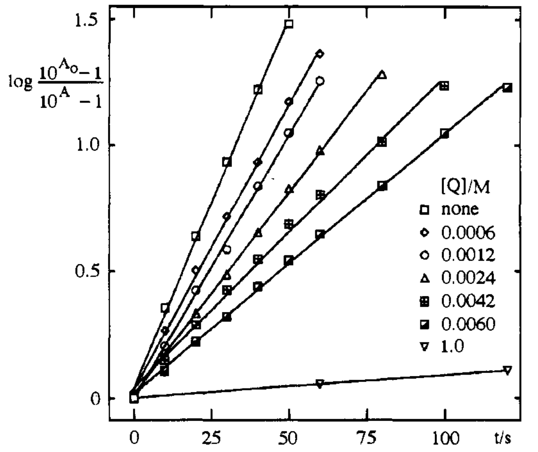


Figure 1. Plots of $\log([10^{A_0} - 1]/[10^A - 1])$ *versus* irradiation time (t) for azoalkane **1a** at various *trans*-piperylene concentrations [Q]. The ratio of the slopes with and without quencher yields the relative quantum yield for **1a** at the particular *trans*-piperylene concentration (see Table 2 and ref 24a).

decayed by clean first-order kinetics with lifetimes of ca. 0.5 μs (Table 2). Control experiments were carried out at various azoalkane concentrations and laser pulse intensities, but the kinetics of the transient decays remained unchanged, which establishes that self-quenching and triplet−triplet annihilation are inefficient processes. The transient absorption spectrum for **1a** and a typical decay trace for **1b** are shown in Figure 2 and in the inset of Figure 3. The identification of the transients as azoalkane triplets was firmly established (*cf.* the Discussion). For example, the lifetimes were shortened on addition of the triplet quencher *trans*-piperylene. The same amount of quenching was observed at 315 and 500 nm, which establishes that the two absorption bands belong to the same transient. The second-order quenching rate constants (k_q) were determined by linear regression of the observed decay rates against the quencher concentration and were found to be (1.0 ± 0.1) × 10^9 M^{-1} s^{-1} for **1a**, (8 ± 1) × 10^8 M^{-1} s^{-1} for **1b**, and (2.5 ± 0.5) × 10^9 M^{-1} s^{-1} for **2a**. The related azoalkanes **3a,b** and **4a,b** and the parent compounds DBH and DBO did not show any transient absorptions under these conditions.

Table 2. Quantum Yields and Transient Spectroscopic Data

			transient lifetimes[b]	
azoalkane	[*trans*-piperylene] (M)	Φ_r[a]	^{3}azoalkane (ns)	^{3}biradical (μs)
1a		0.59	630 ± 20	
	0.006	0.21	132[c]	
	1.0	0.04[d]	<20[e]	
1b		0.60	440 ± 10	
	0.006	0.28	141[c]	
	1.0	0.07[d]	<20[e]	
1c		0.88	200 ± 10	10 ± 2
	1.4	0.73[d]	140 ± 10	10 ± 2
2a		0.75	580 ± 20	
	0.006		59[c]	
	1.0	0.23[d]	<20[e]	
3a,b			*e*	
3c		1.0	27 ± 2[f]	1.75 ± 0.02[f,g,h]
4a,b			*e*	
4c		1.0	95 ± 10[f]	2.56 ± 0.07[f,g,h]
5			*i*	2.20 ± 0.15
6a,b			*e*	*e*
7a			*j*	17 ± 4[h,j]
7b			*j*	1.09 ± 0.03[j]

[a] Error ca. 10%, except for **1a** (5%). [b] Measured in degassed benzene at 25 °C; direct photolysis at λ_{exc} = 351 nm and λ_{obsd} = 315 nm; for assignments see text; the triplet biradical lifetimes could only be determined for substrates with a benzylic chromophore. [c] Linear Stern−Volmer quenching was observed up to 0.02 M. [d] A systematic error (ca. 10−20% too low) applies to these values, *cf.* ref 45. [e] Not detected on the nanosecond time scale. [f] Same value in 1.0 M *trans*-piperylene solution. [g] Same transient lifetime observed on triplet sensitization with benzophenone. [h] Taken from ref 28. [i] Short-lived transient may have escaped detection due to low signal intensity. [j] No signal without triplet sensitizer; values refer to transient produced by benzophenone sensitization; short-lived transients were not detected due to sensitizer T−T absorption on short time scales.

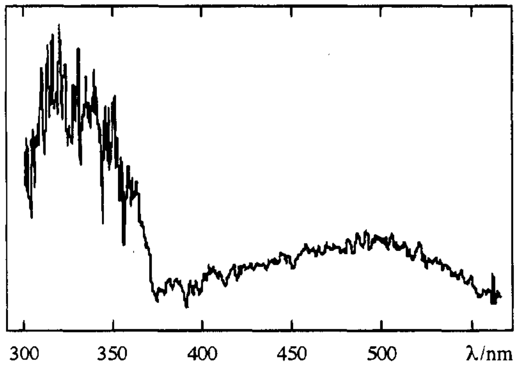


Figure 2. T−T absorption spectrum of the triplet-excited azoalkane ^{3}**1a** recorded with an optical multichannel analyzer (OMA) in degassed benzene solution.

The lifetimes of the triplet azoalkanes vary strongly with temperature. The triplet lifetime of **1a** in degassed benzene obeys the Arrhenius temperature dependence $\ln(1/{}^3\tau) = (32.1 \pm 0.3) - (5300 \pm 80)\text{K}/T$ (r^2 = 0.992 for six temperatures between 8 and 38 °C). From the intercept the preexponential factor $A = (9 \pm 3) \times 10^{13}$ s^{-1} and from the slope the activation energy E_a = 10.5 ± 0.2 kcal mol^{-1} were obtained.

Triplet Energy Transfer. Laser flash photolysis of azoalkane **1a** at 351 nm in the presence of ca. 1 × 10^{-5} M tetracene gave a step-and-rise growth of transient absorption at λ_{max} = 460 and 480 nm, the absorption maxima of triplet tetracene in benzene.[31a] The step portion is attributed to the visible absorption of the azoalkane triplet (Figure 2) and to the direct

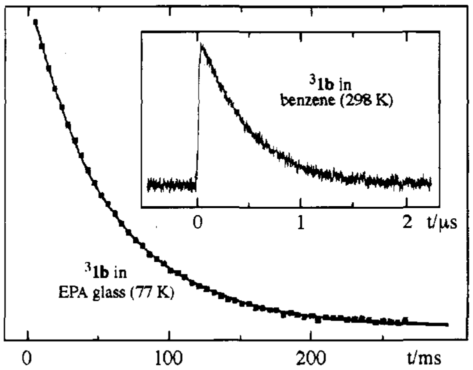


Figure 3. Phosphorescence decay of the triplet-excited azoalkane $^3\mathbf{1b}$ in EPA matrix at 77 K monitored at 500 nm and decay of the transient T−T absorption of $^3\mathbf{1b}$ in benzene at 298 K monitored at 315 nm (inset).

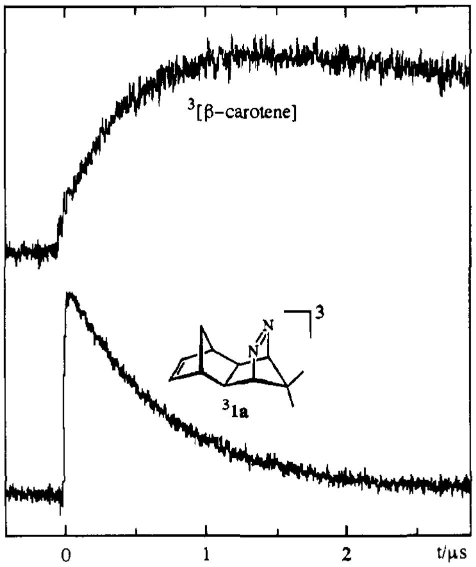


Figure 4. Decay of the triplet-excited azoalkane $^3\mathbf{1a}$ observed at 315 nm (lower trace) in the presence ca. 10^{-5} M β-carotene in benzene at 298 K and concomitant growth observed at 520 nm (upper trace) of β-carotene T−T absorption. Different absorbance scales apply for the upper and lower traces.

excitation and subsequent ISC of tetracene (absorbance of 0.006 at $\lambda_{exc} = 351$ nm). The time-resolved growth, $k_{obsd} = (1.77 \pm 0.14) \times 10^6$ s^{-1}, was equal within experimental error to the decay rate of the transient observed at 315 nm, $k_{obsd} = (1.68 \pm 0.09) \times 10^6$ s^{-1}. This implies triplet energy transfer from $^3\mathbf{1a}$ to tetracene, which is strongly exothermic in view of the low triplet energy of tetracene (29 kcal mol^{-1})[31b] and the much higher triplet energy of **1a** (62.4 kcal mol^{-1}, see below). The triplet absorption of tetracene eventually disappeared at much longer times (100 μs).

Experimental conditions for the direct observation of energy transfer from the azoalkane triplets $^3\mathbf{1a}$ and $^3\mathbf{1b}$ were improved when β-carotene was used as a triplet energy acceptor. A representative pair of traces for the triplet energy transfer from $^3\mathbf{1a}$ to β-carotene is shown in Figure 4. Although part of the 351-nm excitation pulse is unavoidably absorbed by β-carotene, spontaneous ISC of β-carotene is inefficient on direct excitation.[31c] Hence, the small immediate rise in transient absorption at 530 nm during the laser pulse must be entirely due to the azoalkane T−T absorption (Figure 2). Only a small fraction of the azoalkane triplets is intercepted at the low concentration of β-carotene used in this experiment (ca. 1×10^{-5} M). Nevertheless, a pronounced time-resolved growth at 530 nm is observed due to the high extinction coefficient of the β-carotene triplet (ϵ = 187 000 M^{-1} cm^{-1} at $\lambda_{max} = 515$ nm in hexane).[31d]

Table 3. Energy Transfer from the Triplet Azoalkane $^3\mathbf{1a}$ to β-Carotene (**C**) in Benzene

[C]/10^{-5} M	[^{3}C]$_{max}$/10^{-6} M expt[a]	calcd[b]	$\Phi(^3\mathbf{C})$[a] (%)
7.23	2.26 ± 0.42	29.6	7.6 ± 1.5
3.61	1.60 ± 0.30	45.8	3.5 ± 0.8
1.45	1.17 ± 0.22	73.6	1.6 ± 0.3
0.723	0.60 ± 0.11	85.0	0.7 ± 0.1

[a] The experimental yield of triplet β-carotene formed by energy transfer from $^3\mathbf{1a}$ was calculated from the observed amplitude A of the rising absorbance at $\lambda_{max} = 535$ nm, *cf.* Figure 4, $[^3\mathrm{C}] = A/[\epsilon(^3\mathrm{C})d]$, where $d = 4.25$ cm (cell pathlength) and $\epsilon(^3\mathrm{C}) = 1.87 \times 10^5$ M^{-1} cm^{-1} (ref 33); errors are standard errors of the mean for at least five measurements (reproducibilities). [b] The calculated maximum yield of triplet β-carotene was determined by assuming an energy transfer quantum yield of unity, i.e., $\Phi(^3\mathrm{C}) = 1$; laser pulse intensities I_0 were determined for each shot with a calibrated thermopile, and the amount of light absorbed by **1a** was calculated from $I_{abs} = I_0A(\mathbf{1a})/A_{tot}$, where $A(\mathbf{1a})$ is the absorbance of **1a** and A_{tot} is the total absorbance of the solution at $\lambda_{exc} = 351$ nm.

ISC Quantum Yield. The quantum yield of triplet β-carotene formation by energy transfer [$\Phi(^3\mathbf{C})$] is equal to the product of the quantum yield for spontaneous ISC (Φ_{ISC}) of **1a** and the efficiency of energy transfer (ϕ_{et}) from $^3\mathbf{1a}$ to carotene: $\Phi(^3\mathbf{C}) = \Phi_{ISC}(\mathbf{1a})\phi_{et}$. The value for $\Phi(^3\mathbf{C})$ can be determined directly from the amplitude of the rising absorbance due to triplet β-carotene, since its extinction coefficient is known.[31d] The efficiency ϕ_{et} depends on the concentration of β-carotene and is given by $\phi_{et} = k_{et}[\mathrm{C}]/(k_{et}[\mathrm{C}] + k_d)$, where k_d is the decay rate constant of $^3\mathbf{1a}$ in the absence of β-carotene. The inverse of $\Phi(^3\mathbf{C})$ is linear in β-carotene concentration (eq 1).

$$\Phi(^3\mathbf{C})^{-1} = \{1 + k_d/(k_{et}[\mathbf{C}])\}/\Phi_{ISC}(\mathbf{1a}) \qquad (1)$$

The results of a series of experiments are summarized in Table 3. Linear regression analysis[32] of the data gave a slope of $(9.8 \pm 0.7) \times 10^{-4}$ M and an intercept of 0.03 ± 1.55. The concentrations of β-carotene were limited to below 10^{-4} M due to the strong absorbance of β-carotene at the excitation wavelength of 351 nm. At these concentrations, energy transfer is quite inefficient, $\phi_{et} \ll 1$ and the lifetime of $^3\mathbf{1a}$ is not significantly affected by the presence of β-carotene. Unfortunately, the intercept of eq 1 is not sufficiently well defined to allow a direct determination of $\Phi_{ISC}(\mathbf{1a})$. Notwithstanding these limitations, an estimate of $\Phi_{ISC}(\mathbf{1a})$ could be obtained from the well-defined slope of eq 1, i.e., $k_d/(k_{et}\Phi_{ISC}) = (9.8 \pm 0.7) \times 10^{-4}$ M, by employing the known lifetime of the azoalkane triplet state, $^3\tau(\mathbf{1a}) \equiv 1/k_d = 0.63$ μs, and by assuming a reasonable value[33] for the rate constant of energy transfer from $^3\mathbf{1a}$ to β-carotene, i.e., $k_{et} = (4 \pm 1) \times 10^9$ M^{-1} s^{-1}. This procedure afforded the ISC quantum yield $\Phi_{ISC} = 0.5 \pm 0.2$ for **1a**, which is unexpectedly large for an azoalkane.

---

(31) (a) Porter, G.; Windsor, M. W. *Proc. R. Soc. A* **1958**, *245*, 238. (b) Birks, J. B. In *Photophysics of Aromatic Molecules*; Wiley: London, 1970. (c) Bensasson, R. V.; Land, E. J.; Truscott, T. G. *Flash Photolysis and Pulse Radiolysis*; Wheaton: Exeter, U.K., 1983; p 70. (d) Bonneau, R.; Carmichael, I.; Hug, G. L. *Pure Appl. Chem.* **1991**, *63*, 289.

(32) A weighted least-squares regression was done by using the inverse square of the standard errors.

(33) Lissi, E. A.; Encinas, M. V. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, Chapter 7, p 111.

Cyclopentanediyl Triplet Biradicals Derived from Nitrogen Extrusion. Azoalkane **1c** carries two phenyl substituents at the bridgehead positions, and therefore, the benzylic biradicals formed by α C−N or β C−C scission possess absorptions in the near UV. The generally observed short lifetimes of known open-chain biradicals (<20 ns)[34] suggest that the primary triplet biradicals **1c**(α) and **1c**(β), which are formed by initial one-bond cleavage (Scheme 1), would be too short-lived to allow detection by flash photolysis with a laser pulse of 25-ns half-width. On the other hand, from previous studies of structurally related systems,[28] we expected that the 1,3-cyclopentanediyl triplet biradical **1c**(α,α) in Scheme 1 should have a lifetime in the microsecond range and an absorption near 315 nm. The decay of the transient absorption generated by 351-nm laser excitation of **1c** in benzene solution was clearly nonexponential, which indicated the presence of two transient intermediates. A good fit to the experimental decay traces was obtained by a dual exponential decay function with lifetimes of 200 ± 10 ns and 10 ± 2 μs (Table 2). Addition of *trans*-piperylene to a solution of **1c** had no effect on the decay rate of the long-lived intermediate ($k_q < 10^4$ M^{-1} s^{-1})[35] but increased the fast decay rate at high concentrations (1.4 M; $k_q \cong 2 \times 10^6$ M^{-1} s^{-1}; Table 2). This implies the involvement of an electronically excited state as the shorter-lived species. Thus, the long-lived transient is assigned to the 1,3-cyclopentanediyl triplet biradical **1c**(α,α) (*cf.* Scheme 1). The shorter lifetime is again attributed to T−T absorption of the triplet azoalkane as in the case of **1a** and **1b**, which also display triplet lifetimes in the same range.

Azoalkanes **3c** and **4c** also showed biexponential transient absorptions at 315 nm, similar to that of **1c** (Table 2). A typical decay trace for **3c** is shown in Figure 5. Triplet-sensitized flash photolysis of **3c** and **4c** with benzophenone at 308 nm also gave transient absorptions at 315 nm, whose lifetimes coincided with those of the long-lived triplet biradicals observed on direct irradiation. The short-lived transient (triplet azoalkane) was not observed upon sensitization since its decay rate is faster than that of its formation. This experimental limitation is related to the low solubility of the phenyl-substituted azoalkanes **1c**−**4c** (ca. 15 mmol in benzene) and to the rate constant of energy transfer from triplet benzophenone to these azoalkanes, which is less than diffusion control, e.g., $k_{et} = 1.6 \pm 0.5 \times 10^9$ M^{-1} s^{-1} for **1c**. As expected, the lifetimes of the triplet biradicals derived from **3c** and **4c** remained the same on addition of *trans*-piperylene.

Azoalkane **5** gave a very weak transient with a lifetime in the microsecond range, which is tentatively attributed to the triplet biradical derived from nitrogen extrusion (Table 2). The closely related azoalkanes **7** did not produce any transient absorption on direct photolysis. Thus, the lifetimes of the corresponding triplet biradicals given in Table 2 had to be assessed through triplet-sensitized photolysis.[28c,d]

The two amplitudes determined by fitting dual exponential functions to each of the decay traces observed for **1c**, **3c**, and **4c** provided an estimate for the extinction coefficients of the triplet azoalkanes. The extinction coefficients of the triplet biradicals (two benzyl chromophores) were assumed to be about twice that of the benzyl radical ($\lambda_{max} = 317$ nm and $\epsilon_{benzyl} = 8800$ M^{-1} cm^{-1} in cyclohexane at 295 K).[36] It was also assumed that the triplet biradicals are formed quantitatively from the triplet azoalkanes. As can be seen from Figure 5, a fraction of the triplet azoalkane absorbance decays within the laser pulse. The maximum absorbance A_0 of the azoalkane triplet was thus estimated by extrapolation of the fitted decay curve to the center of the laser pulse. On the average, this amplitude A_0 was about three times larger than the amplitude of the slow decay due to the biradicals (Figure 5). The T−T extinction coefficient of the azoalkane triplets (ϵ_{T-T}) at the observation wavelength of 315 nm is then given by $2 \times 3 \times \epsilon_{benzyl}$, from which $\epsilon_{T-T} \approx 5 \times 10^4$ M^{-1} cm^{-1} was obtained for **1c**, **3c**, and **4c**. Although this estimate is only accurate within 1 order of magnitude, it demonstrates that an allowed T−T transition is observed.

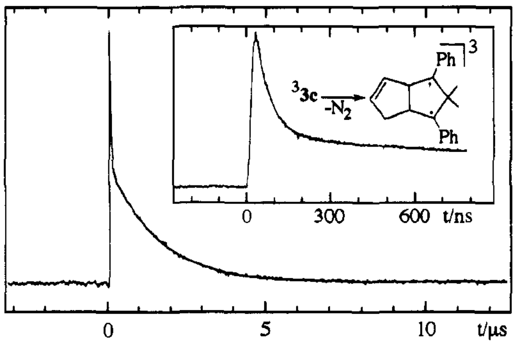


Figure 5. Transient decay trace obtained on photolysis of azoalkane **3c** in benzene at 298 K (observed at 315 nm) and blowup for the short time scale.

Absorption and Fluorescence Spectra. The UV spectra of the azoalkanes in benzene exhibit absorption maxima at 360 nm ($\epsilon = 237$ M^{-1} cm^{-1}) for **1a**, 366 nm (231) for **1b**, 365 nm (104) for **1c**, and 357 nm (285) for **2a**. Vibrational structure is most pronounced for derivative **1a** ($\Delta\tilde{\nu} \approx 880$ cm^{-1}) but also discernible for **1b** (1350 cm^{-1}), **1c** (1000 cm^{-1}), and **2a** (900 cm^{-1}). For comparison, the ground state IR spectra of **1**−**7** exhibit a band at 1440−1470 cm^{-1} attributable to the ν(N=N) stretching vibration[25,37] and two characteristic bands at ca. 1020 and 1080 cm^{-1}. Thus, the vibrational progressions in the absorption spectra may correspond to the ν(C−N) or ν(N=N) stretching frequencies in the excited singlet state, of which the latter is expected to be lower than in the ground state. The excitation spectrum for azoalkane **1a**, which matches the absorption spectrum, is displayed in Figure 6.

Azoalkanes **1a,b** and **2a** show weak fluorescence in degassed benzene solution. The fluorescence quantum yields (Φ_{fl}) for excitation at 345 nm were determined as 0.02 ± 0.01 for **1a** and **2a** and as 0.04 ± 0.02 for **1b** relative to quinine bisulfate as a reference ($\Phi_{fl} = 0.546$).[38] Addition of *trans*-piperylene (up to 1.0 M) did not significantly decrease Φ_{fl}. The quantum yields of fluorescence were of comparable magnitude in solution and in low-temperature glasses. The fluorescence spectra have their maxima located at 366, 372, and 363 nm for azoalkanes **1a,b** and **2a**. The first band of a vibrational progression (850 ± 150 cm^{-1}) was indicated as a shoulder at 376, 386, and 373 nm for **1a,b** and **2a**. Since the fluorescence spectrum of DBO exhibits an unusual intensity pattern,[2,11] it is noteworthy that a near mirror image relationship of fluorescence and absorption spectra is observed for azoalkanes **1**. The small Stokes shift (ca. 450 cm^{-1}, Figure 6) is considered to be diagnostic for the rigid structures of **1**. The fluorescence excitation spectra of **1** and **2a** in benzene solution matched the absorption spectra.

---

[34] Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521.

[35] The results obtained when the transient absorptions of **1c** solutions were monitored in the presence of benzophenone as a triplet sensitizer or high concentrations of 1,3-cyclohexadiene as a triplet quencher are not understood at present since long-lived species (τ > 20 μs) were generated. The observed signals might arise from chemical reactions of the excited **1c** with 1,3-cyclohexadiene.[15b,c] Attempts to detect energy transfer from ^{3}**1c** to β-carotene met with failure due to the short lifetime of ^{3}**1c**.

[36] Claridge, R. F. C.; Fischer, H. *J. Phys. Chem.* **1983**, *87*, 1960.

[37] A recent Raman analysis for parent DBH places the ν(N=N) mode at 1497 cm^{-1}: Gernet, D.; Kiefer, W.; Kammel, T.; Nau, W. M.; Adam, W. *J. Mol. Struct.* **1995**, *348*, 333.

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

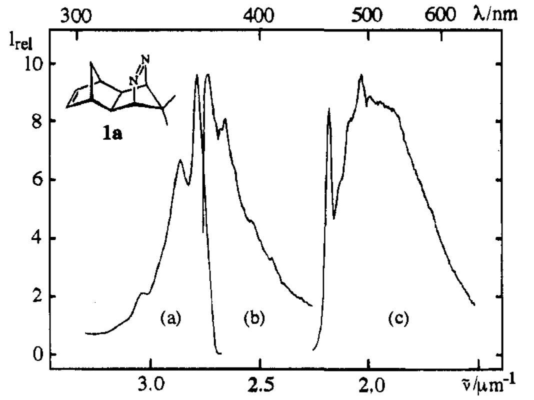


Figure 6. Corrected excitation (*a*), fluorescence (*b*), and phosphorescence (*c*) spectra of azoalkane **1a** in EPA glass at 77 K (arbitrary intensity scales in units of quanta per wavenumber); the intensity of the phosphorescence emission, curve *c*, was reduced by a factor of 0.23 relative to the fluorescence emission, curve *b*. The phosphorescence excitation spectrum is in good agreement with the absorption spectrum of **1a** in EPA at 77 K.

The fluorescence emission of azoalkanes **1** and **2** followed the time profile of the nanosecond laser excitation pulse, which indicated singlet lifetimes ($^1\tau$) of less than 10 ns. Indeed, picosecond time-resolved fluorescence detection (streak camera) afforded singlet lifetimes of 2.4 and 2.9 ns for **1a** and **2a** in benzene (Table 1).[39]

Phosphorescence Spectra. Phosphorescence was not detected for the azoalkanes **1** in benzene solution at ambient temperature. In the glassy EPA matrices at 77 K, however, **1** and **2a** showed remarkably strong phosphorescence, which was about five times more intense than the fluorescence (τ_{ph} = 25−60 ms, Φ_{ph} = 0.03−0.10, Figure 6 and Table 4). The phosphorescence excitation spectra of **1** (Figure 6) agreed well with their absorption spectra.

Sharp 0−0 bands at 458 (**1a**), 463 (**1b**), 462 (**1c**), and 453 nm (**2a**) define the corresponding triplet energies accurately (Table 4). The vibrational progressions with $\Delta\tilde{\nu}$ = 460 ± 50 cm^{-1} are at lower frequency than the C−N or N=N stretching modes of the ground state but may be associated with a twisting mode of the C−N=N−C bridge (*cf.* the Discussion).

Phosphorescence spectra were also recorded for the azoalkanes **4a**, **6**, and the *para*-disubstituted derivatives of **3c** (X = *p*-F, *p*-Br). Their phosphorescence intensity was 1 order of magnitude weaker ($\Phi_{ph} \cong 1\%$), and the phosphorescence lifetimes (τ_{ph}) were substantially shorter (3−10 ms). Thus, the 0−0 bands could not be resolved on the conventional spectrophotometer used. The onsets of the broad phosphorescence bands and the (vertical) band maxima of these compounds ($\lambda_{max} \approx$ 490−500 nm) were, however, not significantly displaced relative to those of **1** and **2** (Table 4). Hence, all triplet energies were found to lie within the same range of 62.5 ± 1 kcal mol^{-1}.

An effort to improve the conditions for the detection of phosphorescence emission was made by isolating the azoalkanes in a xenon matrix at 15 K. The effect on the phosphorescence lifetime and on the phosphorescence quantum yield of **2a** was, however, moderate (Table 4). Finally, both DBH and DBO failed to show any phosphorescence emission under the same conditions.

Photoelectron Spectra. The He(I) photoelectron (PE) spectra of **1a**,**b** and **2a** were recorded and are compared with that of the parent DBH in Figure 7. Vertical ionization energies and their assignments are given in Table 5, along with some particularly relevant energy separations. The PE spectra of DBH[11b,40a−d] and of the *endo* isomers of **1**[40e,f] have been reported earlier. The spectra of the latter are dominated by π−π interactions and, thus, are quite different from those of the *exo*-azoalkanes **1** determined presently.

Table 4. Phosphorescence Emission Parameters of Azoalkanes

azoalkane	τ_{ph} (ms)	Φ_{ph}[a] (%)	E_T[b] (kcal mol^{-1})	E_{vert}[c] (kcal mol^{-1})
1a	24.3 ± 0.2	5.2 ± 0.7	62.4	58.4
1b	58.7 ± 0.4	10.1 ± 1.5	61.8	58.4
1c	43.4 ± 1.2[d]	3.6 ± 0.5	61.9	58.4
2a	25,6 ± 0,7[e]	3.5 ± 0.5	63.1	59.0
3c(*p*-F)[f]	10.6 ± 0.6	0.9 ± 0.2	*i*	57.8
3c(*p*-Br)[g]	8.0 ± 0.1	*h*	*i*	57.8
4a	4.5 ± 0.3	*h*	*i*	58.4
6a	10.1 ± 0.5	*h*	*i*	57.8
6b	2.9 ± 0.2	*h*	*i*	57.8

[a] Determined with reference to the fluorescence intensity of 9,10-diphenylanthracene (Φ_{fl} = 1.0). [b] Determined from 0−0 transition, ±0.1 kcal mol^{-1}. [c] Vertical T−S energy derived from phosphorescence emission maximum, ±0.5 kcal mol^{-1}. [d] Excimer laser excitation gave a value of 41 ± 5 ms. [e] Lifetime in xenon matrix at 15 K was 17.6 ± 0.3 ms. [f] *para*-Difluoro-substituted derivative. [g] *para*-Dibromo-substituted derivative. [h] Not measured, estimated to be ca. 1%, i.e., an intensity similar to that of **3c**(*p*-F). [i] 0−0 band not resolved.

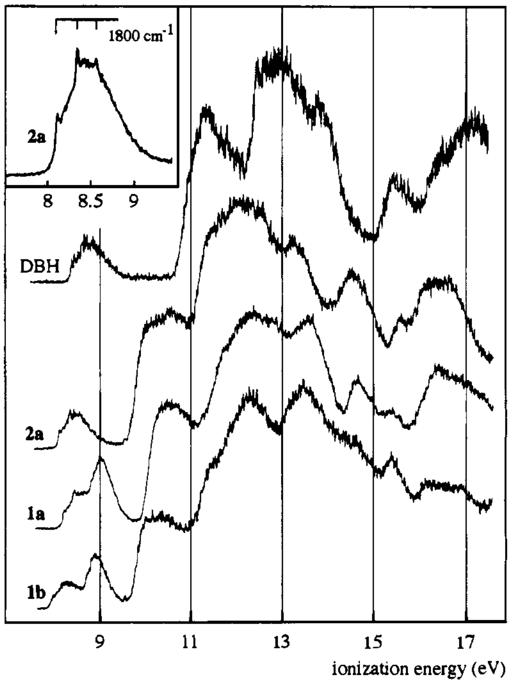
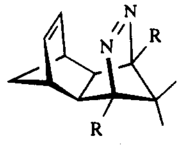


Figure 7. He(I) photoelectron spectra of the azoalkanes **1a**, **1b**, **2a**, and DBH. The fine-structure of the low-ionization energy band of **2a** is shown in the inset.



endo-**1**

The bands at low ionization energies (8.0−9.5 eV) were resolved and their assignment to ionization from the n_ HOMO (antisymmetric combination of the nitrogen lone pairs) and from the π(C=C) orbital was made by analogy to DBH and related azoalkanes.[40] For **1a**,**b** and **2a**, two overlapping bands were

---

(39) Nau, W. M.; Scaiano, J. C. Unpublished results.

Table 5. Photoelectron Spectroscopic Data (in eV)[a]

azoalkane	n_-	π(N=N)	n_+	π(C=C)	σ	$\Delta E_{n_-,\pi}$	$\Delta E_{n_-,n_+}$
1a	8.41	10.7	11.8	9.00	10.7	2.3	3.39
1b	8.25	10.6	11.56	8.89	10.2	2.35	3.31
2a[b]	8.35[c]	10.7	11.5		10.2	2.35	3.15
DBH	8.83[d,e]	11.5[d,f]	12.0[d]		12.6[d]	2.67	3.17

[a] The vertical ionization energies are given; for assignments see text. [b] AM1 calculated (ref 41) eigenvalues are 10.23 eV (n_-), 11.04 (σ), 11.11 (π), and 11.37 (n_+). [c] $\Delta\bar{\nu} = 1800 \pm 150$ cm^{-1}. [d] In good agreement with ref 40d. [e] The values in ref 40a−c are slightly higher. [f] $\Delta\bar{\nu} = 1300 \pm 150$ cm^{-1} (ref 40a,b).

found in the 10−11 eV region, of which the band at the lower ionization energy was attributed to a σ and the following band to the π(N=N) orbital. These assignments are supported by the orbital energies calculated with the AM1 model[41] and by the general observation[40a] that the energy difference between the π(N=N) and n_- orbitals ($\Delta E_{n_-,\pi}$) is ca. 2.5 ± 0.2 eV for bicyclic azoalkanes. For **1a,b** and **2a** the location of the n_- and $\pi_{N=N}$ bands is virtually unchanged (Table 5) and gives no indication for the existence of a remote π−π interaction between the C=C and N=N double bonds in *exo*-azoalkanes **1**.

Vibrational fine-structure was resolved for the n_- band of azoalkane **2a** with a progression of 1800 ± 150 cm^{-1} (inset of Figure 7). This is the first report on vibrational structure for the n_- band of a DBH derivative.[40] Engel *et al.* have reinvestigated the PE spectra of some DBO derivatives[40g] and, in contrast to earlier studies,[40a−d] were able to resolve vibrational structure for the n_- bands ($\Delta\bar{\nu} \approx 1880 \pm 40$ cm^{-1}). The high frequency of the progression found for **2a** indicates that the N=N double bond is strengthened on ionization from the antibonding combination of the lone pairs [*cf.* $\Delta\bar{\nu}$(N=N) ≈ 1450 cm^{-1} in ground state azoalkanes]. On the other hand, the vibrational progressions for the $\pi_{N=N}$ bands have a spacing of ca. 1250 cm^{-1} in the PE spectra of DBH and DBO and reflect a weakening of the N=N bond in the resulting radical cations.[40a,b]

A correlation between the lowest ionization potentials and the absorption maxima of azoalkanes has been suggested.[40a,d] Such correlation is expected to be most satisfactory for a closely related series of azoalkanes.[1a] Indeed, the lowest ionization potentials for the DBH derivatives in Table 5 and their absorption maxima follow a similar trend in both energies, i.e., DBH > **1a** ≈ **2a** > **1b**, but the relationship is only approximate.

PE-spectral data of azoalkanes have also been employed in correlations with their chemical reactivity. Thus, the decomposition quantum yield is expected to decrease with ionization potential.[11b,40d] The quantum yields and ionization potentials for **1** and **2** are, indeed, lower than the corresponding values for DBH, but no reliable relationship is found. This is not surprising in view of the distinct photochemistry observed for these azoalkanes (Scheme 1) and in view of recent work[40g] which has questioned the proposed correlation between the electronic structure and photoreactivity of azoalkanes.

Discussion

Previous product studies and preliminary spectroscopic evidence have demonstrated that the photochemistry of azoalkanes **1** involves spontaneous ISC to form long-lived triplet states.[24] The intention of the present work is to corroborate these unprecedented findings and extend the investigations to azoalkanes **2**−**7**. The first phosphorescence emission of azoalkanes is reported.

Intersystem Crossing. The photoreactions of **1a** and **1b** proceed with high efficiency, but the quantum yields are considerably less than unity ($\Phi_r \approx 0.6$, Table 2), unlike that of the parent DBH ($\Phi_r = 1.0$).[9] *trans*-Piperylene as a triplet quencher affects the product distribution obtained on direct irradiation and diminishes the total quantum yield of the photoreaction. For example, at high concentrations (1.0 M) of this diene, the photoreactivity of **1a** and **1b** is reduced by 10-fold ($\Phi_r \approx 0.05$, *cf.* Table 2 and Figure 1). Such drastic effects of a triplet quencher are unique in the photochemistry of azoalkanes.[42] Since *trans*-piperylene is known to quench efficiently triplet-excited states with energies higher than its own triplet energy of 59.2 kcal mol^{-1},[43] and since the triplet energies of azoalkanes **1** are indeed higher than this value (62.5 ± 1 kcal mol^{-1}), both effects are attributed to quenching of the azoalkane triplet states. The fact that high concentrations (1.0 M) of *trans*-piperylene do not significantly reduce the fluorescence intensity of **1a** and **1b** strictly negates that the interception of the singlet-excited azoalkanes ^{1}**1*** is responsible for the drastic reduction of the quantum yield.[44] Furthermore, a singlet quenching mechanism cannot account for the observed effect on the product distribution.

The large effect of piperylene on both the product distributions and the quantum yields leaves no doubt that spontaneous ISC in azoalkanes **1** is an efficient process. As a consequence, the quantum yields Φ_r given in Table 2 must be considered as composites of the quantum yields for singlet and triplet reactions ($^1\Phi_r$ and $^3\Phi_r$). However, since the characteristic triplet product of azoalkanes **1** (azirane, *cf.* Scheme 1) is not formed at high *trans*-piperylene concentrations (1.0 M),[24] it would be expected that the triplet states of **1** are quantitatively quenched under these conditions and that the measured quantum yields Φ_r (0.04 for **1a** and 0.07 for **1b**) correspond to photoreactions from the excited singlet states ^{1}**1*** ($^1\Phi_r$).[45]

The total quantum yield of the photoreaction in the absence of a quencher equals $\Phi_r = {}^1\Phi_r + {}^3\Phi_r$. By setting the quantum

---

[40] (a) Boyd, R. J.; Bünzli, J. C.; Snyder, J. P.; Heyman, M. L. *J. Am. Chem. Soc.* **1973**, *95*, 6478. (b) Boyd, R. J.; Bünzli, J.-C. G.; Snyder, J. P. *Ibid.* **1976**, *98*, 2398. (c) Schmidt, H.; Schweig, A.; Trost, B. M.; Neubold, H. B.; Scudder, P. H. *Ibid.* **1974**, *96*, 622. (d) Houk, K. N.; Chang, Y.-M.; Engel, P. S. *Ibid.* **1975**, *97*, 1824. (e) Beck, K.; Hünig, S.; Kleefeld, G.; Martin, H.-D.; Peters, K.; Prokschy, F.; von Schnering, H. G. *Chem. Ber.* **1986**, *119*, 543 (we thank Prof. H.-D. Martin for additional data). (f) Albert, B.; Berning, W.; Burschka, C.; Hünig, S.; Martin, H.-D.; Prokschy, F. *Ibid.* **1981**, *114*, 423. (g) Engel, P. S.; Gerth, D. B.; Keys, D. E.; Scholz, J. N.; Houk, K. N.; Rozeboom, M. D.; Eaton, T. A.; Glass, R. S.; Broeker, J. L. *Tetrahedron* **1988**, *44*, 6811.

[41] (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) The program used was *VAMP* 5.0 by Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T. Universität Erlangen-Nürnberg, Germany, 1993.

[42] In earlier studies, no[9] or very little[3a] quenching was reported, although the efficient generation of azoalkane triplets was ensured through triplet sensitization.

[43] Kellogg, R. E.; Simpson, W. T. *J. Am. Chem. Soc.* **1965**, *87*, 4230.

[44] The singlet-excited state of DBO is quenched by piperylene with a rate constant of ca. 10^7 M^{-1} s^{-1}: (a) Day, A. C.; Wright, T. R. *Tetrahedron Lett.* **1969**, *10*, 1067. (b) Andrews, S. D.; Day, A. C. *Chem. Commun.* **1967**, 477. (c) Reference 15c. A rate constant of this order of magnitude does not allow for significant (>5%) singlet quenching of azoalkanes **1** due to their short lifetimes ($^1\tau$ = 2.4 ns for **1a**).

[45] The values determined at high quencher concentrations (1.0 M) are expected to be somewhat too low since some light absorption by impurities or photoproducts of the diene may occur.[24a] In a control experiment we have determined the quantum yield for DBH in the presence of 1.0 M *trans*-piperylene with reference to a neat solution; for the 1.0 M solution, a 14% lower quantum yield was calculated although the quantum yield for DBH decomposition should remain unaffected by external quenchers.[9] Thus, the deviation between these values provides an estimate on the systematic error for the quantum yields at the 1.0 M quencher concentration given in Table 2 (10−20% too low). It should be noted that at the lower concentration of 0.006 M (this applies to several entries in Table 2) no change of the quantum yield for DBH decomposition was found.

yield at high quencher concentration equal to $^1\Phi_r$, the difference $\Phi_r - {}^1\Phi_r$ provides the quantum yield for the photoreactions which proceed through the azoalkane triplet state ($^3\Phi_r$). Within an error of ca. 10%, the values $^3\Phi_r = 0.55$ for **1a** and $^3\Phi_r = 0.53$ for **1b** are obtained. For the related azoalkane **2a** a similar treatment gives $^3\Phi_r = 0.52$. These values are lower limits for the quantum yield of ISC (Φ_{ISC}) because some of the azoalkane triplets may deactivate by radiationless decay. An estimate of Φ_{ISC} has been obtained by flash photolysis (energy transfer from the triplet-excited azoalkane **1a** to β-carotene, Table 3). The resulting value of $\Phi_{ISC}(\mathbf{1a}) = 0.5 \pm 0.2$ compares well with the lower limit (0.55 ± 0.05) derived above. Although ISC in azoalkanes has been invoked previously,[18,19,22,23] the present results for azoalkanes **1** have made possible a quantification of Φ_{ISC} with values of at least 50%.

Triplet Lifetimes of Azoalkanes. The effect of triplet quenchers on the product distribution and quantum yields suggests that ISC in **1a** and **1b** generates long-lived triplet states, which we sought to detect by flash photolysis. Indeed, we have detected and characterized their T–T absorptions and decays (Figures 2 and 3), which constitute the first transient spectroscopic data of azoalkane triplets. The lifetimes are 1 or 2 orders of magnitude longer than previously stipulated for DBH and DBO.[9,10,15,16] The transients were unambiguously identified by monitoring the triplet energy transfer to tetracene and β-carotene. Quantitative agreement of the observed quenching rates by *trans*-piperylene with the spin-dependent product distributions[24] and the direct observation of phosphorescence at low temperatures (Figure 6) provide further strong evidence for this assignment.

The triplet state ^{3}**1a** decayed by first-order kinetics with a lifetime ($^3\tau$) of 630 ns in degassed benzene solution (Table 2). Hydrogenation of the C=C double bond of the norbornene moiety in azoalkanes **1** hardly affected the triplet lifetime in solution ($^3\tau$ = 580 ns for **2a**), but bridgehead alkylation shortened the triplet lifetime slightly ($^3\tau$ = 440 ns for **1b**). Rate constants for triplet quenching (k_q) of azoalkanes **1** by *trans*-piperylene were determined by measuring triplet lifetimes as a function of quencher concentration: $k_q = 1 \times 10^9$ M^{-1} s^{-1} for **1a**, $k_q = 8 \times 10^8$ for **1b**, and $k_q = 2.5 \times 10^9$ for **2a**. These rate constants are lower than those found for the quenching of ketone triplets by piperylene (ca. 5×10^9 M^{-1} s^{-1} for acetone and benzophenone).[12h,33] Turro has proposed[46] that the rate constants for quenching of ketone triplets by dienes are sensitive to steric restrictions and stereoelectronic requirements, and the same argument may apply to the bicyclic azoalkanes investigated here. In addition, the relatively small energy gap between the triplet azoalkanes (62.5 ± 1 kcal mol^{-1}) and piperylene (59 kcal mol^{-1})[43] may be relevant. Incidentally, the relative order of the quenching rate constants, i.e., **1b** < **1a** < **2a**, follows the order of increasing triplet energies (61.8 < 62.4 < 63.1 kcal mol^{-1}, *cf.* Table 3) and, thus, supports the energy gap argument.

Conversely, from the quenching rate constants k_q, the triplet lifetimes may be calculated from (i) the quantum yields ($^3\Phi_r$) for reaction through the triplet state, (ii) the quantum yields for azirane formation (Scheme 1), and (iii) the ratio of the photoproducts housane and azirane. Each procedure requires measurements as a function of diene concentration, and the latter two have been demonstrated for **1a** in the preliminary report.[24a] Both procedures also give good results for **1b**, although only two data points of *trans*-piperylene concentration are available (Table 2 and ref 24b). The various Stern–Volmer analyses, which all provide consistent evidence for the long triplet lifetimes of **1a** and **1b**, will not be discussed here in detail because the values obtained by laser flash spectroscopy (Table 2) are more direct and undoubtedly more accurate. The consistency of all photophysical data is, however, crucial to support the mechanistic information in Scheme 1 and the assignments of the long-lived transients as azoalkane triplets.

Why have azoalkane triplets *hitherto* been so elusive? Do other azoalkanes have much lower quantum yields of ISC or much shorter lifetimes? The lifetimes of the azoalkane triplet states **1** in solution are essentially controlled by their rates of competitive chemical reactions[24b] (α C–N and β C–C cleavage, Scheme 1), which in turn should also depend on structural characteristics and substituent effects of the azoalkanes. Since it is known that the photochemical denitrogenation of azoalkanes shows an appreciable temperature dependence,[6d,11c,20b,21,23] it was expected and confirmed for azoalkanes **1** that the triplet lifetimes vary strongly with temperature. From this temperature dependence, the activation energies for the chemical reactions of the intermediary triplet azoalkanes may be determined.[24b] For example, the triplet lifetime of **1a** at 7 °C is three times longer than at 25 °C and an Arrhenius plot provides an activation energy of 10.5 ± 0.2 kcal mol^{-1}. This rather pronounced temperature effect suggests that the spectral observation of DBH-type triplets depends primarily on the activation energies for their chemical reactions. Accordingly, the α-phenyl-substituted azoalkanes **1c**, **3c**, and **4c** display relatively short triplet lifetimes (Table 2). The shorter lifetime of **1c** (200 ns) compared to **1a,b** can be rationalized in terms of a reduction of the activation energy for C–N bond cleavage by benzylic radical stabilization.

The same explanation does not apply, however, to the series of azoalkanes **3** and **4**. No transient absorption of **3a,b** or **4a,b** was observed in solution, and their triplet states were detected only through their phosphorescence at low temperature. The available experimental data suggest that the absence of the triplet transients on direct excitation of **3a,b** and **4a,b** is related to less efficient ISC rather than to a lower persistence of their triplet states. Similarly, inefficient ISC might also be responsible for the absence of the triplet signals of azoalkanes **6** and **7** at ambient temperature in solution, albeit the phosphorescence emission of derivatives **6** was observed at 77 K. The solution data for the azoalkanes examined in Table 2 show that the transient triplet absorption disappears either (i) on replacement of the norbornene and norbornane annelation as in azoalkanes **1** and **2** by cyclopentene and cyclopentane as in **3** and **4**, (ii) on removal of the annelated ring as in **7**, or (iii) on substitution of the methyl groups at C-7 by chlorines as in **6**. Only for some phenyl-substituted cases, e.g., the derivatives **3c**, **4c**, and **5**, weaker and more short-lived signals are still observed. At present we cannot offer definitive evidence to show whether inefficient ISC or short triplet lifetimes are responsible for our failure to observe triplet azoalkanes for some derivatives.

There is little doubt that increasing molecular rigidity enhances the persistence of the excited states of bicyclic azoalkanes as manifested by longer singlet and triplet lifetimes. Molecular rigidity may impede intramolecular dissipation of electronic into vibrational energy and impose higher activation energies for unimolecular chemical reactions. Thus, for the *least rigid* parent DBH, the singlet- and triplet-excited states are too short lived to allow detection of fluorescence or observation of its triplet state.[9,10] Enhanced rigidity, as imposed by the annelation in azoalkanes **1**–**6** or by the bridging in azoalkanes **I**, **II**, and **V**, results in measurable fluorescence,[11] i.e., longer singlet lifetimes, and in a higher persistence of their triplet states; the latter effect is attested either by the long triplet lifetimes

---

[46] Turro, N. J.; Tanimoto, Y. *J. Photochem.* **1980**, *14*, 199 (for steric effects on triplet quenching by azoalkanes as acceptors, see ref 6b).

for **1−4** (Table 2) or by the interception of azoalkane **V** triplets by external quenchers.[18b] For a given set of azoalkanes **1−4** with identical bridgehead substituents, the trend in the triplet lifetimes ($^3\tau$) in solution and in EPA glass (Table 2 and 4), i.e., **3c**, **4c** < **1c** and **3a**, **4a** < **1a**, **2a**, follows the intuitive notion of decreasing molecular flexibility, i.e., cyclopentene or cyclopentane annelation should allow for more flexibility than that of norbornene or norbornane. This trend, however, is only approximate and not displayed by all cases in Tables 2 and 4.

Be this as it may, on the basis of rigidity alone, the extraordinarily long singlet[11,14,15] but much shorter triplet[3,16] lifetime of the parent DBO cannot be rationalized (Table 1).[47] Similarly, the fluorescence lifetimes of the DBH derivatives **I** and **II** are long (30 and 2 ns) compared to those of the parent compound, but phosphorescence could not be detected[11] despite spontaneous intersystem crossing;[18,19,23] this finding suggests much shorter lived triplets in these two cases as well. In conclusion, the dependence of azoalkane triplet lifetimes on structural rigidity does not universally apply, but it may help to understand the trend in lifetimes within a series of closely related molecules, e.g., for differently substituted DBH derivatives. It also provides a rationale for the surprising persistence of the triplet states of azoalkanes **1**.

Electronic Configuration of the Azoalkane Triplet State. The empirical criteria for an n,π* configuration of an excited state refer traditionally to ketones[12c,d] and must be applied with caution to azoalkanes. With respect to these criteria, the n,π* configuration of the lowest *singlet-excited state* of azoalkanes is supported by the low extinction coefficient of their near-UV absorption band,[1,2,3b] the typical hypsochromic shift of the absorption maximum with increasing solvent polarity,[11b] the fluorescence emission rate constants,[11,15] and the chemical reactivity (hydrogen abstraction),[15b,c] Evidence for the n,π* nature of the *triplet state* is reported herein; it comprises the relatively high emission rate constants, the absence of heavy-atom effects on phosphorescence, and the relatively small singlet−triplet energy gap. The relatively large S−T extinction coefficients observed for diazirines,[8b] and the general observation[2,3] of poor ISC in azoalkanes ("forbidden" $^1n,\pi^* \rightarrow {}^3n,\pi^*$ transition) also support the n,π* assignment of the lowest triplet state. Moreover, the chemical reactivity of the azoalkane triplet state is also characteristic for an n,π* state, e.g., hydrogen abstraction is observed.[39]

T−T Absorption Spectra. The T−T absorption spectrum of azoalkane **1a** is shown in Figure 2. The near-UV transition centered around 315 nm and the broad band in the visible region supposedly correspond to two distinct electronic transitions. Figure 8 shows the three lowest single-electron excitations that are to be considered for the lowest electronic transitions of an azoalkane in the lowest $\pi^* \leftarrow n_-$ triplet state. The energy ordering of the MO's is taken to be the same as that derived from PE-spectral assignments (Table 5). Whereas the $n_- \leftarrow \pi$ transition *c* belongs to the representation A_2 under C_{2v} symmetry and is forbidden, the excitations *a* and *b* both belong to representation B_1 and are symmetry allowed.

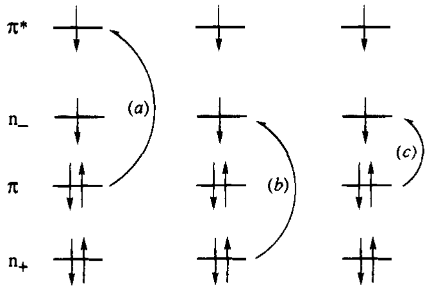
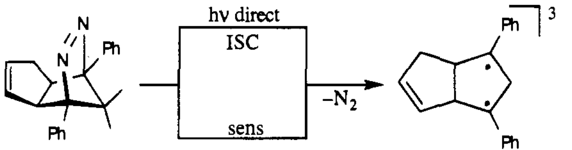


Figure 8. Possible T−T transitions in the n,π* azoalkane triplet state. The qualitative MO ordering is based on the assignments of the PE spectra of azoalkanes (*cf.* Table 5). The excitations *a*, *b*, and *c* represent the symmetry allowed $\pi^* \leftarrow \pi$ and $n_- \leftarrow n_+$ and the symmetry forbidden $n_- \leftarrow \pi$ transitions.

The extinction coefficient of the strong, near-UV band (ca. 5×10^4 M^{-1} cm^{-1} for **1c**, **3c**, and **4c**) is within the range characteristic for allowed transitions, while the weaker transition in the visible region is characteristically about 1 order of magnitude less (Figure 2). The T−T absorption in the UV region is tentatively assigned to the π,π* transition (*a*) of the triplet and signifies that its energy is significantly lower than that of the singlet ground state, which is typically located below 220 nm.[11b] The PE spectrum of DBH indicates an energy difference of ca. 3.2 eV for ionization from the n_+ and n_- lone pairs (Table 5). This energy difference would correspond to an $n_- \leftarrow n_+$ transition (*b*) around 400 nm, if changes in the electronic interaction terms are neglected, and may account for the observed visible band (λ_{max} ca. 500 nm). It must be noted, however, that the forbidden $n_- \leftarrow \pi$ excitation (*c*), which alters the triplet configuration from n,π* to π,π*, should also occur in the visible spectrum. The expected wavelength for the latter excitation can be estimated from the electron energy loss spectrum of the parent DBH,[7b] which indicates an energy difference between the $^3n,\pi^*$ and $^3\pi,\pi^*$ configurations of ca. 1.8 eV or an excitation wavelength of ca. 700 nm. More detailed theoretical and experimental work will be required to substantiate the tentative assignments of the novel T−T absorption of azoalkanes.

Scheme 2



3c

3c(α,α)

Cyclopentanediyl Triplet Biradicals Generated by Direct Photolysis of Azoalkanes. While previously the generation of triplet hydrocarbon biradicals from azoalkanes required triplet sensitization,[28c−e] the spontaneous ISC in azoalkanes **1−5** provides now the novel opportunity to generate and observe them by direct photolysis (Scheme 2). Indeed, the coincidental observation of triplet biradicals in the direct laser flash photolysis of **3c** has provided the first evidence for ISC in this class of azoalkanes (Figure 5).[28b] The triplet lifetimes of the 1,3-cyclopentanediyl biradicals[28,48] generated upon direct photolysis of **1c**, **3c**, **4c**, and **5** were obtained by monitoring the transient absorption of the benzylic chromophore at 315 nm (Table 2).[36] In some cases, the biradicals were independently generated by sensitized photolysis. Note that azoalkanes **7** do not form triplet biradicals on direct excitation, i.e., ISC in **7** is not an efficient process. Since azoalkanes **6** do not produce housanes on direct irradiation, competitive photochemical behavior other than

---

(47) The short triplet lifetime of DBO can be accounted for by large spin−orbit coupling (SOC), which is expected to result in fast deactivation by T_1-S_0 ISC: Caldwell, R. A. Personal communication . If one assumes that SOC is approximately constant for DBH and DBO derivatives, the longer triplet lifetime of azoalkanes **1** could be explained by means of their higher triplet energies (by ca. 10 kcal mol^{-1}), since the rate for ISC is expected to decrease with the inverse square of the T_1-S_0 energy gap: (a) Caldwell, R. A.; Carlacci, L.; Doubleday, C. E., Jr.; Furlani, T. R.; King, H. F.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 6901. (b) Reference 31b.

(48) The detected biradicals cannot be the ones derived from β C−C cleavage, i.e. **1**(β) in Scheme 1, since **1c**, **3c**, **4c**, and **5** do not produce β-cleavage products in solution at ambient temperature.[24,28,29]

denitrogenation[29b] may account for the failure to observe triplet biradicals in these cases. Alternatively, the 2-chloro-substituted 1,3-cyclopentanediyl biradicals **6**(α,α) may be too short lived to allow detection on the nanosecond time scale.[28d]

The transient absorptions of the phenyl-substituted azoalkanes **1c**, **3c**, **4c**, and **5** deserve more detailed discussion. In addition to the formation of the triplet biradicals with lifetimes of a few microseconds, short-lived transients were observed in many cases (Figure 5 and Table 2). Possible precursors of the triplet biradicals, which would all be expected to absorb at the monitored wavelength (315 nm), are (i) singlet biradicals, (ii) singlet or triplet diazenyl biradicals, and (iii) triplet-excited azoalkanes. Evidence for the stepwise photocleavage of azoalkanes to proceed through singlet diazenyl biradicals is available,[49] but these are expected to be far too short-lived for detection on the nanosecond time scale.

Any singlet or triplet biradicals derived from α or β cleavage of **1a,b** (Scheme 1) will be transparent for optical absorption spectroscopy in the near-UV region; this simplifies the assignment of their transient absorptions to the triplet states, which is strongly supported by energy transfer experiments and by the observation of phosphorescence at low temperature. By analogy, we propose that the short-lived transient absorptions formed upon excitation of **1c**, **3c**, and **4c** are also due to the triplet azoalkanes. This is again supported by the observation of phosphorescence for the triplet-excited azoalkane **1c** and *para*-substituted derivatives of **3c** in the matrix at 77 K.[50] In view of the phosphorescence lifetimes and phosphorescence quantum yields for **1c**, which are similar to those of **1a,b** (Table 4), the relatively long-lived triplet state of **1c** in solution (200 ns, Table 2) is quite reasonable. We conclude that the decay shown in Figure 5 represents the nitrogen extrusion from the triplet-excited azoalkane ^{3}**3c** to form the triplet biradical **3c**(α,α). The direct observation of the denitrogenation of photochemically excited azoalkanes by time-resolved transient absorption spectroscopy has not been reported previously.

The low efficiency of *trans*-piperylene as a triplet quencher of ^{3}**1c** is surprising (Table 2).[35] Quenching is barely observable even at high quencher concentrations, *cf.* $k_q \cong 2 \times 10^6$ M^{-1} s^{-1} for **1c** and $k_q \cong 10^9$ M^{-1} s^{-1} for **1a,b**. Since the triplet energy of **1c** falls in the same range as that of **1a,b** (62.5 ± 1 kcal mol^{-1}, Table 4), energy transfer to *trans*-piperylene should still be exothermic.[41] We propose tentatively that stereoelectronic requirements for triplet quenching of azoalkanes are quite stringent and that the approach of the quencher is sterically hindered in the phenyl-substituted derivatives **1c**, **3c**, and **4c**.

Phosphorescence from Azoalkanes. The absence of phosphorescence from azoalkanes has been a subject of continuing debate in the literature.[1-17] The first quest was made nearly 50 years ago by Kasha in his epoch-making review on phosphorescence:[52] "... the two simple aliphatic azo compounds (azomethane and diazomethane) are also of interest for the present discussion, but luminescence studies of these have not yet been made". An experimental study on the absence of phosphorescence from azomethane dates back to 1965.[53] Attempts to observe phosphorescence of the parent DBH and DBO molecules, which are in the focal point of the present discussion, were made by Engel shortly thereafter.[3c] In addition, Mirbach *et al.*[11b] have examined a set of 20 cyclic and bicyclic azoalkanes, among them several DBH and DBO derivatives, but could not detect any phosphorescence. The lack of phosphorescence has been attributed to the high photochemical reactivity of the parent DBH (biradicals are produced even at 4 K)[51] and to efficient radiationless T_1-S_0 deactivation for triplet DBO.[3,15] These circumstances, combined with the poor ISC, obstruct a significant population of the DBH and DBO triplet states that would allow phosphorescence to be observed.

From the Arrhenius dependence for the triplet lifetime of **1a** (see above), it was extrapolated that its triplet state should persist at temperatures below 130 K. Since radiative rate constants for phosphorescence are typically in the range $k_{ph} = 10^{-1}-10^2$ s^{-1} for organic compounds,[12c,52,54] T_1-S_0 emission was expected to become competitive with radiationless deactivation and chemical processes in a low-temperature glass. Indeed, strong phosphorescence emission was observed for **1a,b** in an EPA glass at 77 K with lifetimes of 25–60 ms and quantum yields of 5–10%.

On the basis of the observed quantum yields and lifetimes of phosphorescence given in Table 4, the radiative phosphorescence rate constants (k_{ph}) can be determined from the relation[12e,54] $k_{ph} = \Phi_{ph}/(\Phi_{ISC}\tau_{ph})$. One may assume that the quantum yield for ISC (Φ_{ISC}), which is estimated to be ca. 0.5 at room temperature, should increase further under the low-temperature phosphorescence conditions, i.e., $0.5 \leq \Phi_{ISC} \leq 1$. This follows from the fact that among the three established processes of the singlet-excited azoalkanes **1**, i.e., fluorescence, ISC, and α C–N cleavage (Scheme 1), only the chemical reaction is expected to possess an appreciable activation barrier. Indeed, this has been confirmed for azoalkanes **1** by means of product studies[24b] and by the temperature dependence of the triplet lifetimes. Thus, one obtains $k_{ph} = 3.2 \pm 1.2$ s^{-1} for azoalkane **1a** and $k_{ph} = 2.6 \pm 1.0$ s^{-1} for **1b**. It is important to recognize that the k_{ph} values for azoalkanes (ca. 10^0-10^1 s^{-1}) appear to fall between the typical values found for n,π* ketones (ca. 10^2 s^{-1}) and those characteristic for π,π* states without heavy atoms (ca. 10^{-1} s^{-1}).[12c,52,54]

Our experimental data (Table 4) on the phosphorescence of azoalkanes **1–6** confirm the viability of ISC in azoalkanes and reveal the expected relationship between the phosphorescence lifetimes and the phosphorescence quantum yields.[12f,54] A qualitative correspondence also exists between the phosphorescence lifetimes of azoalkanes in the low-temperature glass matrix and their triplet lifetimes in solution. For example, the azoalkanes **1a** and **2a** with no bridgehead substituents show similar triplet lifetimes in solution (ca. 0.6 μs) and similar phosphorescence lifetimes in the EPA glass (ca. 25 ms). Thus, long triplet lifetimes of azoalkanes in solution are a good empirical indicator for strong phosphorescence in low-temperature matrices (*cf.* **1** and **2** in Tables 2 and 4). Nevertheless, the failure to observe T–T absorption at ambient temperature does not preclude the observation of (weak) phosphorescence at lower temperatures as for **4a** and **6**. At present, we have no explanation for the absence of phosphorescence in azoalkanes **I–III**,[11b] which resemble azoalkanes **1–5** in their ability to undergo significant ISC.[19,23]

Despite the above trend, the dependence of the low-temperature phosphorescence lifetimes on the R substituents (H,

---

(49) (a) Adam, W.; Dörr, M. *J. Am. Chem. Soc.* **1987**, *109*, 1240. (b) Reedich, D. E.; Sheridan, R. S. *Ibid.* **1988**, *110*, 3697. (c) Adams, J. S.; Weisman, R. B.; Engel, P. S. *Ibid.* **1990**, *112*, 9115. (d) Andrews, B. K.; Burton, K. A.; Weisman, R. B. *J. Chem. Phys.* **1992**, *96*, 1111.

(50) Direct evidence for the intermediacy of the 1,3-cyclopentanediyl biradical **1c**(α,α) under low-temperature matrix conditions was obtained by observation of its triplet EPR spectrum on irradiation of **1c** in a glassy MTHF matrix.[28f] Biradical **1c**(α,α) persists at 77 K and possesses the zero-field splitting parameters $|D/hc| = 0.0491 \pm 0.0001$ cm^{-1} and $|E/hc| < 0.0023 \pm 0.0004$ cm^{-1}, which are in the expected range for benzylic 1,3-biradicals.[28a] However, no triplet EPR spectra could be observed on irradiation of **1a,b** in MTHF glass at 77 K; presumably, lower temperatures (< 10 K) will be required to detect these triplet biradicals.[51]

(51) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

(52) Kasha, M. *Chem. Rev.* **1947**, *47*, 401.

(53) Rebbert, R. E.; Ausloos, P. *J. Am. Chem. Soc.* **1965**, *87*, 1847.

(54) Lower, S. K.; El-Sayed, M. A. *Chem. Rev.* **1966**, *66*, 199.

Me, Ph) in azoalkanes **1** (Me > Ph > H) differs from the ordering found for the triplet lifetimes in solution (H > Me > Ph). This implies that different molecular mechanisms determine the triplet lifetimes in the solid and the liquid phases. These are chemical reactions in solution (*cf.* Φ_r in Table 2) and supposedly radiationless processes in the low-temperature glass. Since the activation energies for phosphorescence[12b] are expected to be much lower than for chemical reactions, the former can only compete at low temperatures when the chemical reactions are sufficiently slow. It is noteworthy, however, that chemical reactions of azoalkanes **1** are not entirely suppressed under the conditions of the phosphorescence experiment. Thus, as evidenced by EPR spectroscopy of **1c** in 2-methyltetrahydrofuran glass at 77 K,[50] α cleavage to the triplet biradical **1c**(α,α) occurs to some extent even at low temperatures.

In view of the observed phosphorescence for the DBH-type azoalkanes **1**−**7**, the lack of phosphorescence from DBO-type molecules is even more surprising (Table 1).[3,15] DBO is photoreluctant, and once generated in its triplet state (e.g., by sensitization[3c]), emission should actually be more likely than for DBH, since only the latter possesses efficient reaction channels. We have confirmed the absence of phosphorescence for DBH and DBO even in a xenon matrix at 15 K, which corroborates Engel's previous observations[3c,15a] on the absence of phosphorescence (at 77 K in EPA glass) for these molecules. A simple calculation, based on the phosphorescence rate constants determined for **1a**,**b** ($\approx 3\ s^{-1}$) and the triplet lifetime of DBO ($\approx$10 ns),[3,16] demonstrates that the expected emission from triplet DBO is far too weak to be detected at ambient temperature (estimated Φ_{ph} for DBO $\leq 3 \times 10^{-8}$). Moreover, since the quantum yield for triplet-sensitized decomposition of DBO is very low (0.014),[15] the triplet lifetime must be limited by radiationless deactivation.[15] Thus, the triplet lifetime of DBO should be quite independent of temperature and the same should apply for Φ_{ph}, which precludes detection of phosphorescence at 77 K and even 15 K.

Triplet Energies of Azoalkanes. The phosphorescence spectra of azoalkanes **1** and **2** show clearly resolved 0−0 bands (Figure 6) that serve to define their triplet energies accurately (Table 4) and provide a range of 61.8−63.1 kcal mol^{-1}. For the derivatives **3**−**6** no 0−0 band could be resolved because larger slit widths were required to detect their weaker emission. While these spectra were broadened, their maxima appeared at the same wavelengths, which suggests that the range of 62.5 ± 1 kcal mol^{-1} applies to all the azoalkanes **1**−**7**. Since phosphorescence spectra of azoalkanes were previously not accessible, efforts have been made to estimate their triplet energies by alternative, indirect methods.[1−8] Clearly, the present phosphorescence experiments provide the most direct and accurate triplet energies for azoalkanes, but any comparison with previous results is limited to DBH derivatives, since the triplet energies of other azoalkanes, e.g., the next higher homologue DBO, vary quite significantly.[3]

For the parent DBH a triplet energy of 62 kcal mol^{-1} has been determined by Sandros' method,[55] which requires the determination of energy transfer rates for a series of triplet sensitizers with properly tuned triplet energies.[3a,56] The agreement with our spectroscopic triplet energy of 62.5 ± 1 kcal mol^{-1} for the DBH-type azoalkanes **1**−**7** may be fortuitous (Table 1).[57] Although the "energy titration" method is expected to provide the *adiabatic* (0−0) triplet energy as well, caution must be exercised when employing this method which implicitly assumes that the distribution of excitation energy between the donor and the acceptor reaches thermodynamic equilibrium in the encounter complex.[55] For example, apparent triplet energies may be obtained which are too low when the triplet lifetime of the acceptor is very short;[58] the latter situation applies for DBH and DBO. Thus, the value determined for DBH (62 kcal mol^{-1}) should be considered as a lower limit, and since several Sandros' plots provided values between 59−65.5 kcal mol^{-1} for DBH[3a,c,d] and 53−56.5 kcal mol^{-1} for DBO,[3a,9,15a] the accuracy cannot be better than ±3 kcal mol^{-1}.

A significantly higher triplet energy of 68 kcal mol^{-1} has been derived by electron energy loss spectroscopy (EELS) for gaseous DBH.[7b] The discrepancy with the value from the energy titration method (62 kcal mol^{-1}),[3a] however, does not necessarily invalidate the latter since the spectroscopic method provides the vertical rather than the adiabatic triplet energy. Fortunately, the present spectral data allow us to analyze the expected variances between the actual triplet energies of azoalkanes and the vertical S_0-T_1 energies. By assuming a perfect mirror image relationship between the S_0-T_1 absorption and T_1-S_0 emission and the absence of a Stokes shift, one expects the spacing between the adiabatic and vertical transitions to be the same in the S_0-T_1 absorption and phosphorescence spectrum. For the phosphorescence spectra of azoalkanes **1** and **2** the adiabatic and vertical transitions correspond to the sharp 0−0 band and to the band maximum (Figure 6), which differ by ca. 4 kcal mol^{-1} (Table 4). Thus, since EELS[7b] and S_0-T_1 absorption spectra[8b] yield the vertical S_0-T_1 energies, the actual triplet energies of azoalkanes should be at least 4 kcal mol^{-1} lower than the values determined by these spectroscopic techniques. This correction does not only apply for the EELS triplet energy of DBH[7b] (68 kcal mol^{-1}) *versus* that of the energy transfer method[3] (62 kcal mol^{-1}) and our values in Table 4 (62.5 ± 1 kcal mol^{-1}), it applies as well to the vertical energy derived from the S_0-T_1 absorption for the most strained cyclic azoalkane diazirine[8b] (77 kcal mol^{-1}) *versus* its energy transfer value (73 kcal mol^{-1}).[8b]

From the fluorescence and phosphorescence emission spectra of azoalkanes **1** and **2**, one can accurately determine the S_1-T_1 energy gaps (ΔE_{ST}) as 15.7 kcal mol^{-1} for **1a** and **2a** and 15.1 kcal mol^{-1} for **1b**. Since the absorption and phosphorescence spectra of **3**−**6** virtually coincide with those of **1** and **2**, an S_1-T_1 energy gap of 15−16 kcal mol^{-1} seems to be characteristic for all azoalkanes **1**−**6**. Earlier studies which included DBH and DBO have placed ΔE_{ST} of various azoalkanes in the range 18 ± 5 kcal mol^{-1} (Table 1).[3a] The magnitude of ΔE_{ST} is associated with the electronic configuration of the excited states. Small energy gaps are expected for transitions with charge transfer character and, hence, for small values of the exchange

---

[55] Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355.

[56] Much lower triplet energies of 54−56 kcal mol^{-1} have been derived from the claimed S_0-T_1 absorption spectra of the DBH derivatives **I** and **II**.[6d,12a] These values appear to be too low for DBH-type molecules, especially it is recalled that such spectra provide the vertical triplet energies, which are higher than the adiabatic ones. Indeed, the assignment of the observed absorption bands as S_0-T_1 absorptions has been disputed.[13]

[57] From the 0−0 fluorescence band of the parent DBH,[11a] a singlet energy of 84.5 kcal mol^{-1} may be determined, whereas the fluorescence maxima for **1a**,**b**, which are assumed to correspond to the 0−0 transitions, suggest a singlet energy of only 77.8 ± 1.0 kcal mol^{-1}. It is intriguing that the triplet energies of azoalkanes **1**−**7** and DBH appear to be very similar, while their singlet energies are substantially different (by ca. 7 kcal mol^{-1}). On the other hand, the drastically different shifts in the singlet and triplet energies may provide a reasonable explanation for the efficient ISC of azoalkanes **1** (see below).

[58] (a) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769. (b) Orlandi, G.; Monti, S.; Barigelletti, F.; Balzani, V. *Chem. Phys.* **1980**, *52*, 313. (c) The problem is similar for the determination of redox potentials when the oxidation or reduction of the substrate is irreversible, *cf.*: Andrieux, C. P.; Hapiot, P.; Saveant, J.-M. *Chem. Rev.* **1990**, *90*, 723. See also: (d) Porter, G. B. *Theor. Chim. Acta* **1972**, *24*, 265. (e) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.

integral between the orbitals involved in the transition. Values of 8–10 kcal mol^{-1} are considered to be typical for n,π^* excited ketones, whereas gaps of 30–40 kcal mol^{-1} are found for the π,π^* states of small benzenoid hydrocarbons.[12c] As observed for the radiative phosphorescence rate constants, the value for ΔE_{ST} in azoalkanes falls in between these typical limits.

Heavy-Atom Effects. The effect of heavy atoms[12g,54,59] on the phosphorescence of azoalkanes was also examined. For the *para*-dibromo-substituted azoalkane **3c**, the phosphorescence lifetime is 8.0 ms, whereas for the *para*-difluoro-substituted derivative, it is 10.6 ms (Table 4). This difference in phosphorescence lifetimes is too small to be interpreted in terms of an *internal* heavy-atom effect. Similarly, we have found virtually no *external* heavy-atom effect when the phosphorescence spectrum of **2a** was recorded in a xenon matrix at 15 K since the measured lifetime (17.6 ± 0.3 ms) was only slightly lower than in an EPA matrix at 77 K (25.6 ± 0.7 ms). Perhaps even more convincing is the observation that the ratio between the fluorescence and phosphorescence intensities of **2a** remained constant on going from the EPA glass at 77 K to the Xe matrix[60] at 15 K ($\Phi_{ph}/\Phi_{fl} = 5.0 \pm 0.2$ for both experiments). This indicates that neither phosphorescence from nor ISC to the triplet state is accelerated by xenon atoms, since both effects should have enhanced the intensity of phosphorescence relative to that of fluorescence. Thus, both internal and external heavy atom effects on the phosphorescence of azoalkanes are very small.

Our results are in line with the general postulate, based on theoretical considerations and experimental studies for ketones, that heavy-atom effects should be small for the T_1-S_0 emission of n,π^* states: the inherent spin–orbit coupling is already high ("allowed" $^3n,\pi^* \rightarrow {}^1\pi,\pi$ transition), such that additional contributions by heavy atoms become negligible.[12g,54,59a] The absence of heavy-atom effects on radiationless ISC (S_1-T_1 transition) of azoalkanes is less straightforward to understand since an additional enhancement of spin–orbit coupling should become sizable due to the forbidden nature of this $^1n,\pi^* \rightarrow {}^3n,\pi^*$ transition.[54] However, as outlined below, spin–orbit coupling for this transition may be larger than expected due to mixing of states. Moreover, a practical problem for the observation of heavy-atom effects on ISC arises when the lifetime of the singlet-excited state is very short (*cf.* 2.4 ns for **1a**),[39] since the rate enhancement due to the additional spin–orbit coupling is limited, e.g., to 10^8-10^9 s^{-1} for bromine perturbation.[12g] The same conflict between theory and experiment arises for aliphatic ketones, for which heavy atoms do not accelerate the S_1-T_1 ISC process;[61] again, the singlet-excited ketones may be too short lived to allow a measurable enhancement of ISC.

Molecular oxygen perturbation in various azoalkanes has been studied previously by means of product studies, which indicated an enhancement of S_1-T_1 ISC.[6d,19] Moreover, oxygen-enhanced ISC in singlet-excited DBO takes place with unit efficiency.[39] Of course, the mechanisms of enhanced ISC induced by molecular oxygen and heavy atoms are different in that heavy atoms operate exclusively by enhancement of spin–orbit coupling, whereas an electron exchange mechanism is involved for $^3O_2$, which leaves the total spin in the encounter complex intact. To be noted also is the observation that molecular oxygen enhances the S_0-T_1 absorptions of several azoalkanes[8] except DBH derivatives.[6d]

Factors Governing ISC in Azoalkanes. To determine the structural features responsible for the efficient ISC in azoalkanes **1** the studies were extended to azoalkanes **2–7**. The following observations allow one to assess whether ISC occurs in a particular azoalkane: (i) T–T absorption in solution, (ii) phosphorescence emission, (iii) quenching effects upon the quantum yield or product distribution, (iv) products derived from β cleavage (Scheme 1), and (v) transient absorption of triplet biradicals in solution (Scheme 2). The former three methods all require the triplet state of the examined azoalkane to be relatively long-lived to allow (i) detection under nanosecond time resolution, (ii) measurable phosphorescence with $k_{ph} \approx 3$ s^{-1}, and (iii) interception by an external quencher with $k_q \approx 10^9$ M^{-1} s^{-1}. The latter two methods are indirect probes for the involvement of ISC in azoalkanes and their triplet states. Nevertheless, the observation of triplet biradicals like **3c(α,α)**, *cf.* Scheme 2, is an appealing alternative to substantiate ISC in azoalkanes due to the strong benzylic absorption and the relatively long lifetimes of such biradicals (Table 2).[28,34,36]

The direct observation of an azoalkane triplet state was first accomplished for azoalkane **1a**. The following questions were raised as to why ISC in this azoalkane is so efficient, and these served to guide our choice of the other test cases **1–7**: Is the C=C double bond in the norbornene moiety responsible for the efficient ISC due to bichromophoric interaction? Is the norbornene moiety prerequisite for ISC? Must the bridgehead of the DBH skeleton be unsubstituted? Is the geminal dimethyl group at the C-7 position required to promote ISC? The answer to all these questions is no. Hydrogenation of the C=C double bond in azoalkane **2a** leaves the transient triplet absorption (Table 2), the phosphorescence (Table 4), and the photochemistry (β cleavage, Scheme 1) virtually unchanged; in fact, our photoelectron spectra reveal no measurable interaction between the remote C=C and N=N double bonds. Similarly, if the whole norbornene moiety is replaced by cyclopentene, cyclopentane, or cyclobutene as in **3–5**, the observed phosphorescence and transient absorption due to triplet azoalkanes or triplet biradicals unambiguously speak for ISC (Tables 2 and 4). Finally, ISC in DBH-type azoalkanes cannot be conditional on *gem*-dimethyl substitution at the C-7 position since substitution by a *gem*-dichloro group still results in phosphorescence for **6** (Table 4). Furthermore, the presence of the *gem*-dimethyl group alone does not ensure ISC as evidenced by the absence of transient triplet absorption for **7b** (Table 2). Consequently, the present results for azoalkanes **1–6** suggest that the annelation (or alkylation) of the ethano bridge in DBH (5,6-position)—an apparently subtle change in molecular structure—is crucial to facilitate ISC. Anellation does not, however, guarantee that ISC is always as efficient as in the norbornene-substituted azoalkanes **1** and **2**. This follows from the absence of measurable transient absorption signals for **3a,b** and **4a,b**.

The efficient ISC in azoalkanes **1** might be partly due to the fact that other singlet deactivation processes, e.g., α cleavage,[24b] are slower than in the parent DBH. This is implied by the longer singlet lifetimes for azoalkanes **1** (*cf.* $^1\tau = 2.4$ ns for **1a** *versus* ca. 0.15 ns for DBH, Table 1).[9] However, if merely a higher persistence of the azoalkane singlet-excited state were responsible for ISC, the fact that the long-lived singlet state of DBO is reluctant to undergo ISC could not be explained.[2,11–17] Instead, from the short singlet lifetimes of azoalkanes **1a** and **2a** and their relatively high ISC quantum yields (Table 1), ISC rate constants (k_{ISC}) of 2×10^8 s^{-1} can be calculated according to $k_{ISC} = \Phi_{ISC}/{}^1\tau$. These k_{ISC} values are at least 1 order of magnitude larger than those for the parent DBH and DBO ($<10^6$ s^{-1}, Table 1)[9–17] and approach those for ketones.[12d] Thus, there

---

(59) (a) El-Sayed, M. A. *J. Chem. Phys.* **1964**, *41*, 2462. (b) El-Sayed, M. A. *Ibid.* **1965**, *43*, 2864.

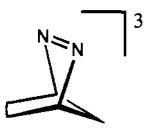
(60) For heavy-atom effects of rare gas matrices on the fluorescence/phosphorescence intensity ratio, see: Medinger, T.; Wilkinson, F. *Trans. Faraday Soc.* **1965**, *61*, 620.

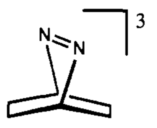
(61) (a) Wagner, P. J. *J. Chem. Phys.* **1966**, *45*, 2335. (b) Wagner, P. J.; Hammond, G. S. *Adv. Photochem.* **1968**, *5*, 21.

is no doubt that the annelation in the DBH-type azoalkanes **1** causes a significant *enhancement* of the ISC rate which we shall now attempt to account for.

ISC in organic molecules has been found to be predominantly dependent on the magnitude of spin−orbit coupling[54,62] and the S_1-T_1 energy gap (ΔE_{ST}).[12e,31b] With regard to the latter, Turro and Engel have attributed the differences in ISC rates between azoalkanes and ketones (which often undergo quantitative ISC) to the smaller S_1-T_1 energy gap in ketones.[3c,12c,d] In a similar manner, the enhanced ISC in **1−6** can be rationalized in terms of their energy gaps ($\Delta E_{ST} = 15-16$ kcal mol^{-1}) which appear to be significantly smaller than for DBH and DBO (ca. 23 kcal mol^{-1}, Table 1).[3a] Of course, this interpretation relies on the estimated triplet energies for DBH and DBO,[3a] which in contrast to azoalkanes **1−6** cannot be assessed through their phosphorescence spectra (see above).

Whether enhanced spin−orbit coupling is also responsible for the ISC in azoalkanes **1−6** is less straightforward to evaluate. The El-Sayed rule[54,62] predicts spin−orbit coupling between n,π^* states to be inherently small, and thus, ISC from the singlet-excited state of an azoalkane to its lowest triplet state should be inefficient. This situation can be remedied when either a $^3\pi,\pi^*$ state lies at intermediate energies ($^1n,\pi^* \rightarrow {}^3\pi,\pi^* \rightarrow {}^3n,\pi^*$ mechanism)[62] or if an admixture of π,π^* character applies.[12e] Experimental data are available on the vertical energy of the $^3\pi,\pi^*$ state of DBH (110 kcal mol^{-1}), which should not be accessible for ISC from the lowest n,π^* singlet state of DBH. The energies of the $^3\pi,\pi^*$ states of **1−6** might well lie at lower energies than for the parent DBH. Such a trend in state energies is suggested by comparison of their PE spectra (Table 5), which reveal a significantly lower (by ca. 0.35 eV) energy splitting of the n_- and π MO's in **1** and **2** relative to DBH, but it is unlikely that the energy of the $^3\pi,\pi^*$ state drops below $^1n,\pi^*$.


^{3}DBH


^{3}DBO

Alternatively, even a very small admixture of π,π^* character to the n,π^* state of azoalkanes could result in a significant enhancement of spin−orbit coupling and could be important to facilitate ISC in azoalkanes. In this context, it has apparently not been recognized[3,11,49c] that even the excited states of such rigid azoalkanes as DBH and DBO may be significantly twisted around the C—N=N—C bridge (see structures above). Such twisting, which is suggested by semiempirical and *ab initio* MO calculations,[63] should promote mixing of the π,π^* and n,π^* states of excited azoalkanes. The dependence of mixing between the two states might resemble the situation for formaldehyde and aliphatic ketones, for which the (experimentally observed)[64] pyramidalization in the excited states is expected to have the same net effect.[12e] As a consequence, the ISC rates of azoalkanes will become strongly dependent on the absolute magnitude of the C—N=N—C dihedral angle in the excited states and also on the normal modes associated with the corresponding twisting vibrations. An experimental hint for twisting of the triplet-excited state of azoalkanes comes from the vibrational progression ($\Delta\tilde{\nu} = 460 \pm 50$ cm^{-1}) in the phosphorescence spectra of azoalkanes **1** and **2**. The value falls in the expected range for the associated fundamental twisting vibration in the ground state (experimental value for DBH[37] is 518 cm^{-1}; calculated value by the UHF/6-31G* method is 568 cm^{-1}), which suggests that the ground state molecules are born in a twisted conformation. The vibrational progression in the gas-phase fluorescence spectrum of the parent DBH ($\Delta\tilde{\nu} = 410$ cm^{-1}) indicates a similar situation for the excited singlet state.[11a,14] Significant structural variations between the ground and excited states of azoalkanes, which have been postulated on the basis of their solvent-dependent electronic spectra and attributed to changes in C—N and N=N bond lengths,[11] are also in line with variations of the azo dihedral angle.

We suggest tentatively that the expected twisting in the excited azo chromophore is strongly dependent on molecular structure and that the substitution patterns in azoalkanes **1−6** result in an enhanced twisting about the C—N=N—C bridge, which accelerates **ISC** through an increased admixture of π,π^* character to the excited azoalkane; such admixture may be further favored by a lower energy of the π,π^* state in **1−6** (*vide supra*). Rau's previous comment that the $^1n,\pi^* \rightarrow {}^3n,\pi^*$ transition is forbidden in planar *cis*-azoalkanes[2b] is fully in line with the proposed argument. How a particular substitution pattern affects the degree of twisting in the excited states of azoalkanes is not entirely understood at present. In view of the rigid azoalkane structures **I−VI**, which all show intersystem crossing as well, one is tempted to argue that increased rigidity, which is also imposed by the annelation in **1−6**, inhibits other pathways for energy relaxation through molecular distortions; consequently, enhanced twisting about the azo group may serve as predominant alternative for energy relief in their excited states.

Conclusions

Azoalkanes **1−7** have offered the unique opportunity of performing a joint analysis of spin-selective product studies and photophysical measurements. A detailed mechanistic description of the fate of electronically excited DBH derivatives was acquired, the involvement of long-lived triplet states has been unambiguously established, and the long-sought phosphorescence of azoalkanes has been observed. The long triplet lifetimes for these DBH-type azoalkanes provide an exception to the general assessment (based on studies of DBO and pyrazoline derivatives) that the lifetime of azoalkane triplets is much shorter than that of their excited singlet states.[3a] Molecular rigidity of azoalkanes appears to be an important denominator for both long triplet lifetimes and efficient intersystem crossing.

The properties of the azoalkane triplet state could previously be assessed only by indirect means. Despite this severe limitation, it is impressive how much useful data have been accumulated over the years. At least eight detailed discussions[1,3,6b,d,9] and even a review article[4] have been devoted to the elusive triplet state. The present spectroscopic characterization of the azoalkane triplet state for **1−6** complements the indirect information gained by the earlier studies. Clearly, further spectroscopic investigations of these azoalkane triplet states are warranted, which should include EELS, time-resolved EPR, IR, and Raman spectroscopy. The latter two techniques

---

(62) El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834.

(63) Calculated C—N=N—C dihedral angles for the triplet-excited azoalkanes are 22° for DBH and 36° for DBO if the semiempirical UHF/AM1 method is used and 30° for DBH and 46° for DBO if an *ab initio* method (UHF/6-31G*) is employed. Note that the singlet-excited state of DBH is also predicted to be twisted by *ab initio* calculations (Olivucci, M. Personal communication) and that the C—N=N—C dihedral angle in singlet- and triplet-excited azomethane is ca. 100° according to *ab initio* methods, which reveals the inherent tendency for twisting in the excited azo chromophore: Hu, C.-H.; Schaefer, H. F., III. *J. Phys. Chem.* **1995**, *99*, 7507.

(64) In *Energy Transfer and Organic Photochemistry*; Turro, N. J., Leermakers, P. A., Weissberger, A., Eds.; Interscience: New York, 1970; Vol. XIV; pp 133−295.

could help to evaluate the possibility of a twisted excited state conformation for such "rigid" azoalkanes. The postulated twisted geometry and its consequences for state mixing and enhanced spin–orbit coupling warrant a more detailed quantitative exploration. For example, it would be instructive to calculate the spin–orbit coupling as a function of the azo dihedral angle by employing diimine and azomethane as model compounds. Similar calculations have been performed previously for the excited (biradicaloid) states of ethylene.[47a]

The design and the investigation of additional azoalkanes with the desirable photophysical characteristics (ISC, long-lived triplets, phosphorescence) present another challenge. In this respect, the present study of the azoalkanes **1**–**7** offers useful guidelines for the design of tailor-made azoalkanes that will help to understand and to explore further the structural constraints that govern triplet lifetimes and ISC in azoalkanes. For example, it should be of interest to examine whether the annelation in DBH-type azoalkanes, which we believe to be responsible for efficient ISC and long-lived triplet states, has the same effect on the next higher homologue DBO. Since DBO-type azoalkanes are photoreluctant, such substituted DBO derivatives[25d] should show extremely long triplet lifetimes. Consequently, the formerly elusive azoalkane triplet state might be exploited as a novel triplet-sensitizing moiety with potentially useful photophysical properties.

Experimental Section

Instrumentation and General Aspects. Quantum yields for azoalkane consumption were determined by irradiation with the near-UV lines (333, 351, and 364 nm) of a CW argon ion laser (INNOVA 100, Coherent Co.). Transient absorption spectra were recorded with a nanosecond flash photolysis setup by using the 25-ns pulses from an excimer laser (Lambda Physik EMG 101 MSC). UV absorption spectra were recorded on a Hitachi U 3200 or a Hewlett-Packard 8452A diode array spectrophotometer. Optical emission and excitation spectroscopy were carried out with a Perkin-Elmer LS 50 luminescence spectrometer or a Spex Fluorolog 111 spectrometer equipped with an EMI R928 phototube operated in the single photon counting mode. Lamp intensity fluctuations and the wavelength dependence of the excitation source in the excitation spectra were corrected with the reference signal from a rhodamine 6G quantum counter. Emission spectra were corrected with a reference file containing the sensitivity curve of the instrument (in quanta per unit wavenumber) which was measured with the light from a calibrated tungsten quartz lamp whose spectrum was well represented by Planck's formula for black body radiation, $T = 2550$ K at a current of 1.40 A. The Rayonet photochemical reactor of the Southern New England UV/Co., fitted with 350- and 300-nm lamps, was used as an irradiation source. Spectral grade benzene (>99.8%) was used as the solvent.

Determination of Photolysis Quantum Yields. Aliquots (2.1 mL) of degassed benzene solutions (with and without *trans*-piperylene as an additive) of DBH and azoalkanes **1**–**4** (absorbance ca. 1.0) were placed into the UV cuvettes (1 × 1 cm) and evenly irradiated with the 333-nm widened beam (ca. 5 cm^2) of a CW argon ion laser. The laser light intensity was adjusted by using the instrumental intensity regulation (± 0.05%). The decreasing absorbance (A) *versus* irradiation time was monitored by UV spectrophotometry. The plots were linear with correlation coefficients (r) greater than 0.98. The irradiation was conducted up to a maximum absorbance of 0.2 units with 8–20 data points per experiment. The extinction coefficients at the excitation wavelength of 333 nm are $\epsilon(\mathbf{1a}) = 35$ M^{-1} cm^{-1}, $\epsilon(\mathbf{1b}) = 32$, $\epsilon(\mathbf{1c}) = 23$, $\epsilon(\mathbf{2a}) = 58$, $\epsilon(\mathbf{3c}) = 28$, $\epsilon(\mathbf{4c}) = 24$, and ϵ(DBH) = 216 M^{-1} cm^{-1} [λ_{max}(DBH) = 342 nm]. The quantum yields in the presence of *trans*-piperylene were determined with reference to a solution without quencher and by using all UV lines of the CW laser (at 333, 351, and 364 nm). In these cases, the errors were assumed to depend linearly on the error of the quantum yield Φ_r without quencher.

Transient Absorption Spectroscopy. Samples were prepared by dissolving the particular azoalkane (ca. 0.02 mmol) in 5 mL of benzene, and the absorbance at the irradiation wavelength was adjusted between 0.3 and 0.6. The samples were carefully degassed by at least three freeze–pump–thaw cycles, and the transient triplet absorptions (λ_{exc} = 351 nm) were monitored at 315 ± 5 and 430–500 nm for azoalkanes, at 315 ± 5 nm for biradicals, at 470 ± 10 nm for the energy transfer experiment with tetracene, and at 535 ± 5 nm for β-carotene.

Fluorescence Spectroscopy. The fluorescence spectra and intensities of fluorescence emission for the azoalkanes were determined for deaerated benzene solutions with and without *trans*-piperylene (1.0 M). Oxygen was removed either by purging the solutions with argon gas (for **1** and **2a**) or by three freeze–pump–thaw cycles (for **1b**). The fluorescence intensities (I_{fl}) were calibrated relative to that of quinine bisulfate (QBS) in a 1 N H_2SO_4 solution at the same excitation wavelength. From the relation $\Phi_{fl}(\mathbf{1})\epsilon(\mathbf{1})/I_{fl}(\mathbf{1}) = \Phi_{fl}(\mathrm{QBS})\epsilon(\mathrm{QBS})/I_{fl}(\mathrm{QBS})$, where ϵ is the extinction coefficient at the excitation wavelength (345 nm), the fluorescence quantum yields Φ_{fl} were determined using $\Phi_{fl}(\mathrm{QBS}) = 0.546$.[38]

Phosphorescence Spectroscopy. Samples were dissolved in an EPA solvent mixture (ether/isopentane/alcohol, 5:5:2 by volume) and immersed in liquid N_2 with a 1-mm quartz tube that was held in a quartz dewar. A stroboscopic light source and gating of the photomultiplyer were used to separate the fluorescence and phosphorescence spectra. In most cases the phosphorescence was sufficiently strong and spectrally well separated from the fluorescence emission, such that the phosphorescence emission was easily observed with continuous excitation and detection. This mode allowed for a direct comparison of the fluorescence and phosphorescence intensities after correcting for the wavelength-dependent instrument sensitivity (*vide supra*). Phosphorescence lifetimes were determined by variation of the active time window of the gated photomultiplyer, Δt. The decay rate constant k was calculated by nonlinear least-squares fitting of the phosphorescence intensities (I) to the integrated rate law $I_{obsd} = I_{max}(1 - \exp[-k\Delta t])$. Phosphorescence quantum yields were determined from the integrated, corrected emission spectra using the fluorescence emission of 9,10-diphenylanthracene in EPA at 77 K as a reference ($\Phi_{fl} = 1.00 \pm 0.05$).[65]

Photoelectron Spectroscopy. The spectrometer incorporated a helium high-voltage dc discharge lamp and a 127° cylindrical electron energy analyzer (32 mm mean radius), operated with a constant bandpass (resolution 30 meV). The ionization energy scale was calibrated with argon, nitrogen, and iodomethane gases. The band positions possess an uncertainty of ±0.02 eV when well resolved, otherwise ±0.1 eV. The sample of DBH showed sufficiently high vapor pressure at ambient temperature to be volatilized into the ionization chamber from an external container, while samples of **1a,b** and **2a** were introduced into the ionization chamber at temperatures up to 70 °C by using a direct probe.

Acknowledgment. The authors are most grateful for financial support by the Deutsche Forschungsgemeinschaft, the Swiss National Science Foundation, and the Natural Sciences and Engineering Research Council of Canada. W.M.N. thanks the Fonds der Chemischen Industrie for a Kekulé fellowship (1992–94). We would also like to thank Prof. R. A. Caldwell and Prof. J. C. Scaiano for helpful discussions and for allowing us to cite unpublished results from their laboratories.

JA951790T

---

(65) Mantulin, W. W.; Huber, J. R. *Photochem. Photobiol.* **1973**, *17*, 139.