is probably the result of unfavorable vapor pressure versus decomposition temperature behavior.

The substituent groups, F, $CH_3$, or $C_2H_5$ most likely would not substantially increase the strength of the O–O bond, while they would reduce the volatility of the substituted dioxirane compared with that of dioxirane itself. If this is true, a more sensitive technique is required to observe these species in the gas phase, although spectral studies of these species in the condensed phase might be the best means of characterizing them.

Hull et al.[10] reported a low-temperature infrared study of alkene–ozone reactions with the products in the condensed phase. They assigned a number of new infrared bands by assuming the product was 1,2,3-trioxolane (primary ozonide) and measured the decomposition temperature of the new species for each of the olefins employed. In the case of ethylene they report a decomposition temperature in the range −100 to −80 °C which is strikingly similar to that determined for dioxirane.[13,25] If indeed the infrared bands detected by Hull et al. arose from dioxirane or its derivatives, their measured decomposition temperatures indicate that the derivatives are less stable than dioxirane. Clearly more work is needed to better characterize the products of low-temperature ozone–olefin reactions.

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# Spectroscopic Properties of Cyclic and Bicyclic Azoalkanes

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**Abstract:** The spectroscopy and photochemistry of 19 cyclic azoalkanes have been investigated. The absorption spectra consist of a (usually structured) band in the region of 300–400 nm ($\epsilon$ 100–600 L/(cm mol)) which is assigned to a $(n_-,\pi^*)$ transition. Fluorescence is readily detected from most of the azoalkanes examined, but the fluorescence quantum yields vary from nearly 1.0 to $10^{-4}$ depending upon azoalkane structure as well as the solvent. The absorption maxima show a blue shift and the emission maxima a red shift as solvent polarity increases. For representative examples, the rate constants for photochemical nitrogen extrusion have been determined. These values were found to correlate with the lowest ionization potential of the azoalkane ($n_-$ MO). Finally, the effect of solvent on the fluorescence quantum yields and fluorescence lifetimes were determined. The results are rationalized within the framework of conventional quenching mechanisms.

## Introduction

Although the photochemistry of cyclic azoalkanes has been widely studied[2a,b] only a few systematic investigations have been carried out on their spectroscopic behavior.[2c] Cyclic azoalkanes commonly exhibit fluorescence, in contrast to their acyclic counterparts. The (usually) highly structured absorption and emission spectra and the absence of side reactions which compete with fluorescence and loss of nitrogen (e.g., cis–trans isomerization or tautomerization) make the cyclic azoalkanes (**1–19**) (Scheme I) attractive models for a systematic spectroscopic and photochemical investigation. In this

paper we report a detailed study of the spectroscopic properties of compounds **1–19**.

## Experimental Section

The structures of the azoalkanes investigated in this work are given in Scheme I. Samples of **10, 13, 14,** and **15** were obtained from Professors C. Steel,[3] B. Jacobson,[4] E. L. Allred,[5] and T. J. Katz,[6] respectively. The other azoalkanes were prepared as previously described. For compound **1b** see ref 7; for compounds **2** and **3** see ref 8; for compounds **4–9** and **11** see ref 9, for compounds **16–19** see ref 11, 12, 13a, and 13b, respectively; and for compound **12** see ref 10.

Absorption spectra were measured on a Cary 17 spectrometer. The

**Table I.** Absorption and Emission Data of Cyclic Azoalkanes in Various Solvents at 25 °C[a]

| Compd | Solvent | Absorption | | Fluorescence | | | $E_{S_1}$ | $\phi_D$ |
| | | $\lambda_{max}$ | $\epsilon$ | $\lambda_{max}$ | $\phi_F$ | $\tau_F$ | | |
|---|---|---|---|---|---|---|---|---|
| **1b** | Hexane | 366 | 150 | 390 | *b* | *b* | 78 | |
| | CH$_3$CN | 352 | | 400 | | | | |
| | CH$_3$OH | 352 | | 395 | | | | |
| | Water | 352 | | *b* | | | | |
| **2** | Hexane | 353 | 195 | 375 | 0.002 | ≤1[c] | 80 | |
| | CH$_3$CN | 345 | | 395 | 0.010 | ≤6 | | |
| | CH$_3$OH | 345 | | 395 | 0.002 | ≤1[c] | | |
| | Water | 340 | | 400 | 0.006 | ≤4[c] | | |
| **3** | Hexane | 354 | 195 | 375 | 0.001 | ≤0.7[c] | 80 | 0.36[d,e] |
| | CH$_3$CN | 347 | | 400 | 0.008 | ≤6 | | |
| | CH$_3$OH | 345 | | 405 | 0.002 | ≤1.5 | | |
| | Water | 342 | | 410 | 0.004 | ≤3 | | |
| **4** | Hexane | 327 | 190 | 440 | 0.008 | | 83 | 0.98[g,j] |
| | CH$_3$CN | 327 | | 440 | 0.007 | ≤7 | | |
| | CH$_3$OH | 323 | | 440 | 0.005 | | | |
| | Water | 320 | | 440 | 0.008 | | | |
| **5** | Hexane | 332 | 105 | *b* | *b* | *b* | | 0.12[f,g] |
| | CH$_3$CN | 330 | | | | | | |
| | CH$_3$OH | 328 | | | | | | |
| | Water | 322 | | | | | | |
| **6** | Hexane | 328 | 215 | 440 | 0.003 | 3[c,h] | 83 | 0.44[f,g] |
| | CH$_3$CN | 328 | | 440 | 0.004 | 4[c,h] | | |
| | CH$_3$OH | 327 | | 440 | 0.002 | 2[c,h] | | |
| | Water | 323 | | *b* | *b* | *b* | | |
| **7** | Hexane | 327 | 165 | *b* | *b* | *b* | | 0.86[f,g] |
| | CH$_3$CN | 327 | | | | | | |
| | CH$_3$OH | 325 | | | | | | |
| | Water | 318 | | | | | | |
| **8** | Hexane | 357 | 165 | 510 | 0.001 | 1[c,h] | 74 | 0.012[f,g] |
| | CH$_3$CN | 355 | | 525 | 0.002 | 2[c,h] | | |
| | CH$_3$OH | 350 | | 525 | 0.001 | 1[c,h] | | |
| | Water | 347 | | 525 | 0.0002 | 0.2[c,h] | | |
| **9** | Hexane | 327 | 160 | 450 | 0.07 | 185 | 83 | 0.8[i] |
| | CH$_3$CN | 327 | | 450 | 0.15 | 225 | | 0.7[i] |
| | CH$_3$OH | 322 | | 450 | 0.01 | 13 | | 0.2[i] |
| | Water | 317 | | *b* | *b* | *b* | | <10$^{-3}$[i] |
| **19**[j] | Hexane | 347 | 133 | 386 | 0.01 | 7 | | 0.52[g] |
| | CH$_3$CN | | | | | 25 | | |

[a] The column headings are defined as follows: $\lambda_{max}$, wavelength of highest transition probability in nanometers; $\phi_F$, fluorescence quantum yield of nitrogen saturated solutions $\tau_F$, measured fluorescence lifetime of nitrogen saturated solutions in nanoseconds; $E_{S_1}$, calculated energy of the first excited singlet state in kilocalories/mole; $\phi_D$, reaction quantum yields for *total* disappearance of azoalkanes. [b] Too weak to be determined. [c] Calculated from $\tau_F = \tau_0^F \phi_F$. [d] Reference 16. [e] In pentane. [f] Reference 9. [g] N$_2$ quantum yield in benzene. [h] Assuming $\tau_0^F = 1000$ ns. [i] Reference 17. [j] Reference 13b.

emission spectra were recorded with a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter. The correction for instrument response is relatively small in the range of 380–480 nm so all reported spectra are uncorrected. The relative response at selected wavelengths (nanometers) is as follows: 1.0 (360), 0.94 (380), 0.81 (400), 0.69 (420), 0.56 (440), 0.47 (460), 0.39 (480), 0.38 (500). Fluorescence quantum yields were determined by measurement of corrected emission spectra relative to quinine sulfate as described elsewhere.[14] All solvents were Spectroquality and/or were further purified by standard methods.[15] Lifetimes were determined by the single photon counting technique utilizing a commercial instrument manufactured by Photochemical Research Associates (London, Ontario).

All samples were freed of oxygen by N$_2$ purging. Samples were saturated with N$_2$ at −30 °C, warmed to 30 °C, cooled down to −30 °C, and again purged with N$_2$. This process was repeated until no change in quantum yield or lifetime could be observed. A comparison with the usual vacuum degassing method by repeated thaw–cool cycles showed that the N$_2$-purging technique gave experimentally identical results for the solvents employed.

**Results and Discussion**

The absorption and emission data of the three-, four-, and five-membered-ring azoalkanes (**1–9, 19**) and the polycyclic compounds (**10–18**) are summarized in Tables I and II, re-

spectively.[16–18] To provide a basis for the discussion of the excited-state and ground-state properties, available photoelectron spectroscopic (PES) data are listed in Table III.[19–23]

**Absorption Spectra.** A general feature of the absorption spectra of the azoalkanes is a band in the 320–380-nm range (n,π* transition) and a large optical window of very low transition probability in the range of 220–300 nm. Several of the azoalkanes show an additional absorption band in the 250-nm range whose nature is as yet unclear (see Figures 1a and 1b). The vibrational structure of the n,π* band is resolved in the more rigid bicyclic compounds with the 0-0 band being of highest intensity in many cases. This is especially true in nonpolar solvents. Preliminary results for several azoalkanes indicate that these results also hold true in the gas phase. The magnitude of the extinction coefficients of the n,π* transitions for **1–19** vary between 105 for **5** and 640 cm$^{-1}$ L mol$^{-1}$ for **18**. These $\epsilon$ values are relatively large compared to n,π* transitions in trans acyclic azoalkanes ($\epsilon \simeq 10$–20) and may be explained by the fact that the n,π* transitions in cis-azo compounds are symmetry allowed with polarization perpendicular to the molecular plane.[2] The PES data demonstrate that a large interaction exists between the lone pairs of the adjacent nitro-

**Table II.** Absorption and Emission Data of Bicyclic Azoalkanes in Various Solvents at 25 °C (Column Headings Are Defined in Table I)

| Compd | Solvent | Absorption | | Fluorescence | | | $E_{S_1}$ | $\phi_D$ |
| | | $\lambda_{max}$ | $\epsilon$ | $\lambda_{max}$ | $\phi_F$ | $\tau_F$ | | |
|---|---|---|---|---|---|---|---|---|
| **10** | Hexane | 377 | 193 | 405 | 0.20 | 330[h] | 76 | 0.022[a] |
| | CH₃CN | 376 | | 406 | 0.41 | | | |
| | CH₃OH | 373 | | 406 | 0.02 | | | |
| | Water | 364 | | 416 | 0.5 | 410 | | |
| **11** | Hexane | 383 | 192 | 387 | 0.2 | 420 | 74 | 0.014[b] |
| | CH₃CN | 382 | | 420 | 0.7 | 740 | | 0.15 |
| | CH₃OH | 375 | | 420 | 0.01 | 30 | | 0.25 |
| | Water | 371 | | 425 | 0.3 | 335 | | 0.03 |
| **12** | Hexane | 383 | 205 | 385 | 0.11 | 125 | 74 | 0.20 |
| | CH₃CN | 385 | | 405 | 0.44 | 410 | | |
| | CH₃OH | 382 | | 405 | 0.012 | 20 | | |
| | Water | 373 | | 415 | 0.25 | 275 | | |
| **13** | Hexane | 373 | 250 | 378 | 0.13 | 70 | 77 | 0.01 |
| | CH₃CN | 372 | | 380 | 0.66 | 410 | | |
| | CH₃OH | 367 | | 388 | 0.009 | 15 | | |
| | Water | 358 | | 395 | 0.63 | 275 | | |
| **14** | Hexane | 381 | 442[c] | 382 | 0.17 | 160 | 75 | |
| | CH₃CN | 380 | | 385 | 0.43 | 410 | | |
| | CH₃OH | 375 | | 392 | 0.01 | 20 | | |
| | Water | 367 | | 405 | 0.09 | 120 | | |
| **15** | Hexane | 401 | 150 | 405 | | | 71 | |
| | CH₃CN | 402, 390 | | 420 | *d* | *d* | | |
| | CH₃OH | | | | | | | |
| | Water | 382 | | 445 | | | | |
| **16** | Hexane | 341 | 420 | 358[i] | *e* | *e* | 84 | 1.0[b] |
| | CH₃CN | 340 | | 361[i] | | | | |
| | CH₃OH | 334 | | *e* | | | | |
| | Water | 334 | | 370[i] | | | | |
| **17** | Hexane | 373 | 310 | 397 | 0.05 | 20 | 75 | 0.54[f] |
| | CH₃CN | 369 | | 400 | 0.08 | 30 | | |
| | CH₃OH | 367 | | 410 | 0.002 | *e* | | |
| | Water | 362 | | 415 | 0.0008 | *e* | | |
| **18** | Hexane | 342 | 640 | *e* | *e* | *e*[i] | 84 | 0.44[g] |
| | CH₃CN | 338 | | 350 | 0.0009 | ~2 | | |
| | CH₃OH | 338 | | 355 | 0.0004 | | | |
| | Water | 331 | | 362 | 0.0007 | | | |

[a] Reference 18. [b] Reference 2a. [c] E. L. Allred and B. R. Beck, *Tetrahedron Lett.*, 437 (1974). [d] Decomposed during measurement. [e] Too weak to be determined. [f] N. J. Turro and V. Ramamurthy, unpublished results. [g] Reference 16. [h] In isooctane; ref 18. [i] Emission from impurities cannot be ruled out. [j] See Table I, footnote c.

**Table III.** Photoelectron Spectroscopic Data of Azoalkanes[a]

| Compd | $n_-$ | $n_+$ | $\pi$ | $\sigma$ | $\Delta E$, $n_+$-$n_-$ | $\Delta E$, $n_-$-$\pi$ | Ref |
|---|---|---|---|---|---|---|---|
| **1a** | 9.75 | 13.3 | 12.1 | 11.5 | 3.55 | 2.35 | 19 |
| **2** | 8.9 | 10.45 | 11.3 | 11.5 | 1.55 | 2.4 | 19 |
| **3** | 9.05 | 10.65 | 9.45[b] | 12.2 | 1.6 | 0.4 | 19 |
| | | | 11.8[c] | | | 2.75 | |
| **4** | 8.63 | 11.26 | 10.91 | | 2.63 | 2.28 | 20 |
| **5** | 9.04 | | 11.24 | | | 2.2 | 20 |
| **6** | 8.87 | 10.93 | 10.34 | | | | 22 |
| **7** | 8.94 | 10.9 | 11.18 | | 1.96 | 2.24 | 20 |
| **8** | 8.61 | 11.88 | 11.53 | | 3.27 | 2.92 | 20 |
| **9** | 8.58 | 11.37 | 10.72[d] | | 2.79 | 2.14 | 20 |
| | | | 8.61[e] | | | 0.03 | |
| **10** | 8.32 | 11.3[a] | 10.70 | 11.3[f] | 2.98 | 2.38 | 21 |
| **11** | 8.06 | 10.93 | 10.48 | | 2.87 | 2.42 | 20 |
| **12** | 8.26 | 11.7 | 10.87 | 10.25 | 3.44 | 2.61 | 21 |
| **13** | 8.22 | ≥11.1 | 10.6 | 10.1 | ≥2.9 | ≥2.4 | 22 |
| **15** | 8.15 | 12.0[f] | 11.1 | 9.73 | 3.85 | 2.95 | 21 |
| | | | | 10.16 | | | |
| **16** | 8.82[g] | 11.8 | 11.5 | 12.8 | 2.98 | 2.68 | 23a |
| **17** | 8.54 | 12.1 | 11.59 | 10.41 | 3.56 | 3.05 | 23a |
| | | | | 10.95 | | | |
| **18** | 8.65 | 12.7 | 11.64 | 10.15 | 4.05 | 2.99 | 23a |
| | | | | 11.88 | | | |
| **19** | 8.87 | 10.36 | 11.65 | | 1.49 | 2.78 | 23b |

[a] Energies are given in electronvolts. [b] +. [c] −. [d] N=N. [e] C=C. [f] Broad band; see ref 21. [g] Reference 21 has slightly different values.

Scheme I
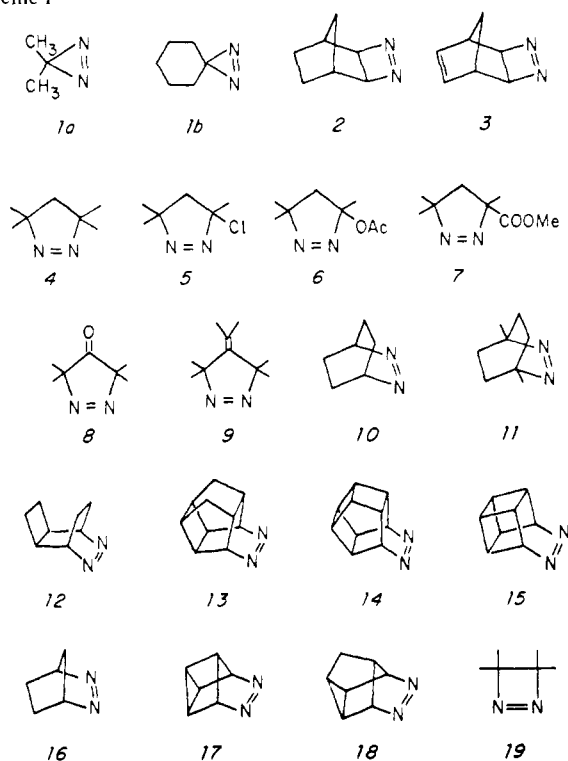




gens.[19-23] As a result the $n_-,\pi^*$ transition is of lower energy than the $n_+,\pi^*$ transition. The blue shift of the absorption maxima with increasing solvent polarity which is typical for $n,\pi^*$ transitions is also observed for the azoalkanes (see Figure 1c).

A more complex problem involves the variation of the absorption maxima with variations in molecular structure. Baird et al.[24] made an attempt to correlate the absorption maximum with the size of the C—N—N angle which should affect the $n_+-n_-$ splitting because of the greater interaction between the nitrogen lone pairs with increasing N=N—C angle. However, our data do not support this correlation because there is no clear relationship of the absorption maxima of three-, four-, and five-membered-ring compounds, e.g., **1, 2, 19,** and **4,** or the bicyclic compounds, e.g., **10** and **16,** with either the bond angle, the $n_+-n_-$ orbital energy splitting, or the lowest ionization potential. As pointed out by Houk, Chang, and Engel,[20] it may generally be concluded that the wavelength of the $n,\pi^*$ absorption maximum is controlled more by factors which influence the energy of the $\pi^*$ orbital rather than the $n_-$ orbital.

**Emission.** Most of the cyclic azoalkanes investigated in this paper exhibit fluorescence but none phosphoresce, even at 77 K. In the more rigid bicyclic compounds, the vibrational fine structure of the fluorescence emission spectrum is well resolved in nonpolar solvents and in some cases the 0-0 band corresponds to the emission maximum (Figure 2a). In the monocyclic five-membered-ring azoalkanes the emission and absorption maxima are separated by more than 100 nm and no fine structure can be observed. This relatively large Stokes shift (Table I) indicates a considerably different structure in the thermally equilibrated $S_0$ and $S_1$ states. This result is in agreement with calculations carried out for cis diimide which predict a widening of the N=N—H angle from 115 to 133° upon transition from the $S_0$ to the $S_1$ state.[25a] In contrast, the N=N bond length is predicted to be similar for both states. For *cis*-azomethane the calculated N=N—CH$_3$ angles of the $S_0$ and $S_1$ states are 119.5 and 130°, respectively.[25b] In the more rigid bicyclic azoalkanes deformation of bond angles is strongly resisted, thus forcing the excited state to maintain a
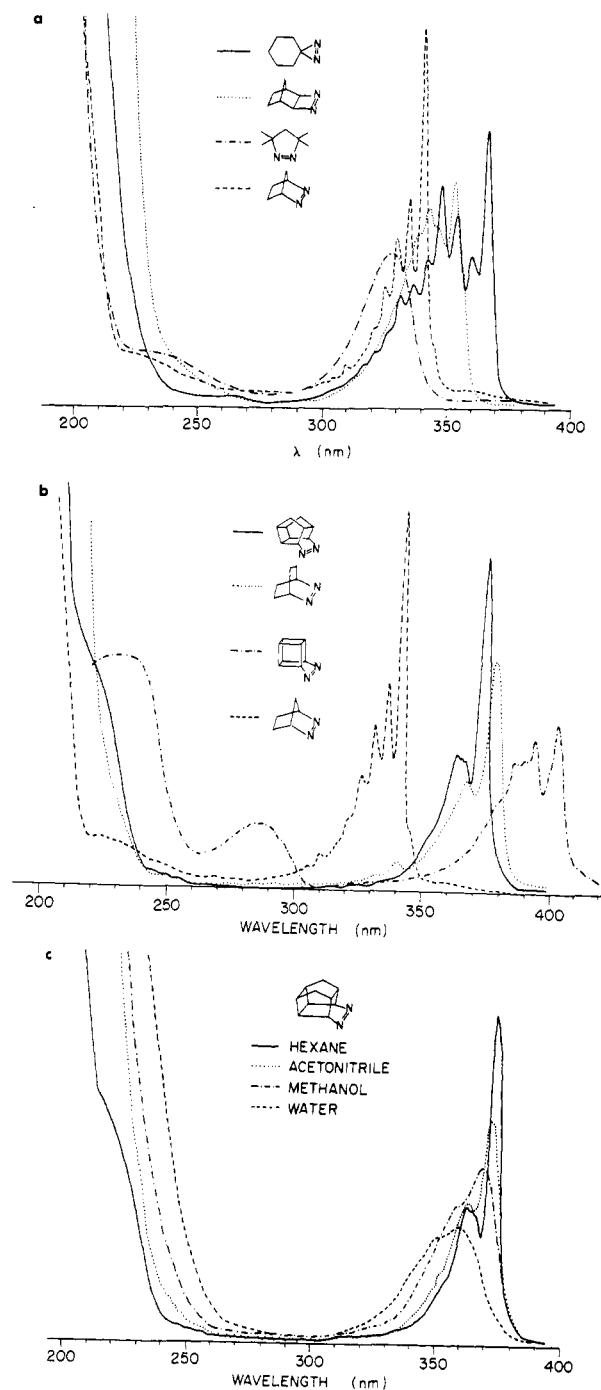
**Figure 1.** (a, b) Absorption spectra of selected azoalkanes in hexane; (c) absorption spectra of azoalkane **13** in various solvents.

geometry very similar to that of the ground state. The similarity of the ground and excited potential energy surfaces is reflected in a well-developed mirror image relationship between the absorption and emission spectra (Figure 3). Furthermore, the fact that the 0-0 band is the most intense in both the absorption and emission spectra of rigid cyclic azoalkanes indicates similar structures for the minima in both the $S_0$ and $S_1$ states.

It is also interesting to note that the emission maxima of the azoalkanes undergo a red shift as the solvent polarity increases. This red shift is not only of opposite direction to the blue shift of the absorption maxima, but it is of greater magnitude. While the maxima change with solvent polarity, the absorption and emission 0-0 bands shift very little (see Figures 2b and 3).

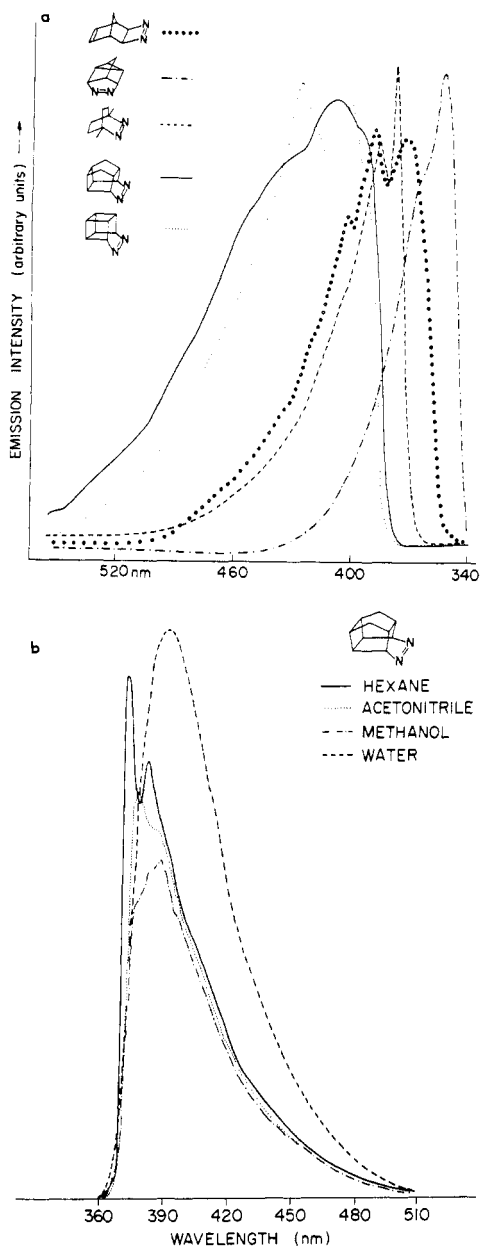Since the energy of the 0-0 band seems not to depend critically on solvent, both the ground and excited states must be

**Figure 2.** (a) Fluorescence spectra of selected azoalkanes in hexane; (b) fluorescence spectra of azoalkane **13** in various solvents.



**Figure 3.** Absorption and fluorescence spectra of azoalkane **3** in various solvents.



**Figure 4.** Schematic diagram of the transition between the ground and first excited singlet state for azoalkanes in (a) nonpolar and (b) polar solvents.

stabilized (or destabilized) to approximately the same extent as the solvent polarity increases. However, the shifts in the absorption and emission maxima indicate that the geometry corresponding to the minimum in the excited and/or ground state must be dependent upon solvent polarity. As illustrated in Figure 4, the minima in $S_0$ and $S_1$ occur at similar geometries in nonpolar solvents. However, as the polarity increases, the similarities between the geometrical structures corresponding to the minima in $S_0$ and $S_1$ decrease, giving rise to the observed spectral shifts.

At least two possible mechanisms responsible for these geometrical changes may be envisioned. Either hydrogen bonding or a dipolar effect (solvent polarity) may cause the observed shifts. However, since neither absorption nor emission maxima display any isotope effect in $CH_3OH/CH_3OD$ or $H_2O/D_2O$, the shifts are apparently due to changes in solvent polarity. Thus, while solvent polarity is responsible for the spectral shifts, we suggest that the mechanism is not a stabilization (or destabilization) of one state more than another but rather geometric changes in the minima of the two states. At this point, it would be premature to speculate on the structural
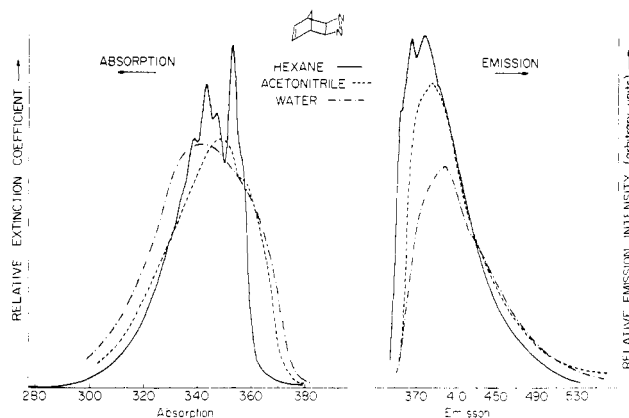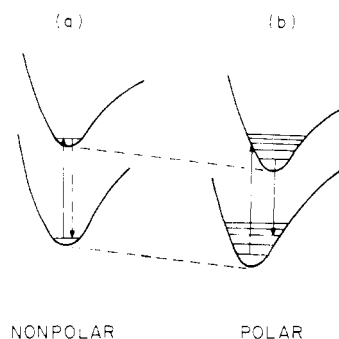
element most affected by solvent polarity. However, the rigidity of many of the compounds examined precludes any large variation in the CNN or dihedral angle of the azo chromophore. Thus, either changes in the C—N or N=N bond lengths are most probably responsible for the solvent effects observed.

**Fluorescence Quantum Yields and Lifetimes.** In the azoalkanes investigated, it was found that the fluorescence quantum yields ($\phi_F$) were roughly proportional to the fluorescence lifetimes ($\tau_F$). The fluorescence rate constant ($k_F$) may be calculated by using the relationship

$$k_F = \phi_F/\tau_F \qquad (1)$$

The values obtained are shown in Table IV. Alternatively, value for $k_F$ may be determined from the integrated absorption spectra[26] and these values are also shown in Table IV. The values of $k_F$ obtained by these two methods agree rather well, deviating by at most a factor of 3 for **9**. This agreement is as good as can be expected owing to the approximation inherent in evaluating $k_F$ from the absorption intensity. In all cases, the value of $k_F$ falls in the range of $4 \times 10^5$ to $7 \times 10^6$ s$^{-1}$. Clark and Steel obtained a value of $6.0 \times 10^5$ s$^{-1}$ for **10** in isooctane,[18] while we obtain a value of $1.2 \times 10^6$ in $H_2O$.

In contrast to $k_F$, the *measured* lifetime ($\tau_F$) and fluorescence quantum yields differ widely for azoalkanes of different structure and range from undetectable fluorescence ($\phi_F <$ $10^{-4}$) in **5** to $\tau_F = 740$ ns and $\phi_F = 0.7$ in **11**. Moreover, the fluorescence intensity of a given compound is strongly dependent on the choice of solvents (vide infra).

Compounds belonging to the diazabicyclo[2.2.2]octene type (**10–15**) exhibit the strongest fluorescence, whereas the three-membered-ring compound **1b** and the bicyclic compound **16** fluoresce only weakly or not at all. Any attempt to ratio-

**Table IV.** Rate Constants for Fluorescence Decay and Decomposition of Azoalkanes

| Azoalkane | $k_F$ (×10^6)[a] | $k_F$ (×10^6)[b] | $k_D$ (×10^8)[c] | $k_D$ (×10^8)[b] |
|---|---|---|---|---|
| 1b | | 0.84 | | |
| 2 | ≥2.0 | | | |
| 3 | ≥1.4 | 2.86 | ≥5.1 | 10 |
| 4 | ≥1.1 | 1.23 | 1.4 | 1.5 |
| 5 | | 7.45[d] | | ≥8.9[e] |
| 6 | ≥1.0 | 1.49 | 1.5 | 2.2 |
| 7 | | 1.26 | | ≥11[e] |
| 8 | ≥1.0 | 1.35 | 0.12 | 0.16 |
| 9 | 3.8 | 1.10 | 0.043 | 0.13 |
| 10 | 0.61 | 0.60 | 0.00067 | 0.00066 |
| 11 | 0.48 | 0.79 | 0.00033 | 0.00055 |
| 12 | 0.88 | | 0.016 | |
| 13 | 1.9 | | 0.0014 | |
| 14 | 1.1 | | | |
| 15 | | 0.69 | | |
| 16 | | 1.79 | | |
| 17 | 2.5 | | 0.27 | |
| 18 | | 0.58 | | |
| 19 | 1.4 | | 0.74 | |

[a] Based on direct measurement of $\tau_F$ and $\phi_F$ in hexane, and eq 1. [b] Based on integration of absorption spectrum for obtaining $k_F$. [c] Based on experimental $\Phi_D$ and $\tau_F$ and eq 2. [d] Only small quantities of this compound were available so the error in this value is larger than the error in the other values. However, $k_F$ is higher than expected. An explanation for this anomaly must await further research. [e] Based on the fact that $\phi_F \leq 0.001$.



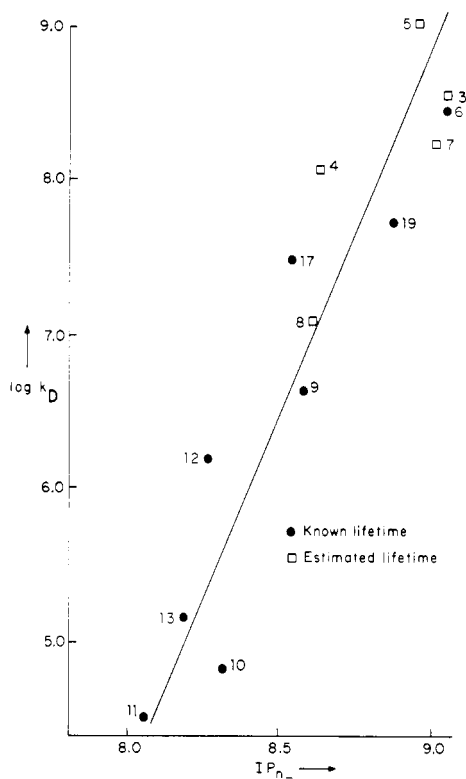**Figure 5.** Plot of log $k_D$ vs. the lowest ionization potential (n₋ MO) for several azoalkanes.

nalize these differences solely on the basis of ring strain seems to be inappropriate. For example, in the series of compounds **16–18**, compound **17** has the highest fluorescence quantum yield ($\phi_F = 0.08$ in $CH_3CN$) although its "ring strain" is certainly higher than that of **16** and **18**. Likewise, the less strained molecules **4–7** fluoresce only weakly. Therefore factors other than, or in addition to, strain must be responsible for the large variation of fluorescence yields of these compounds.

From the assumption that photodecomposition of the cyclic azoalkanes studied occurs only in $S_1$ and with a knowledge of $\tau_F$ and the quantum yield for decomposition ($\phi_D$), the rate constants for decomposition ($k_D$) may be derived via

$$k_D = \Phi_D/\tau_F \qquad (2)$$

and are shown in the last two columns of Table IV. Equation 2 assumes that only fluorescence and loss of nitrogen deactivate $S_1$; i.e., intersystem crossing and decomposition from $T_1$ are ignored. This assumption is not completely general (vide infra), but the values of $k_D$ must be upper limits to the true values. Houk, Chang, and Engel[20] have already postulated that there might be a correlation between the lowest ionization potential (this IP corresponds to the n₋ MO) and the rate of decomposition of azoalkanes but too few data were available at that time to generalize this conclusion. Our values of log $k_D$ for several azoalkanes vs. their lowest $IP_{n_-}$ are plotted in Figure 5. Although there is some scatter in these data, it is apparent that a low $IP_{n_-}$ corresponds to a small value of $k_D$.

At this point we can only speculate about the origin of the relationship between $k_D$ and $IP_{n_-}$. It may be demonstrated theoretically that for cis diimide (HN–NH), both the NH bond strength and $IP_{n_-}$ are critically dependent upon the NNH angle.[27] This is confirmed by ab initio calculation in which the optimum NH bond length decreases by 0.017 Å and the n₋ orbital energy increases by 0.27 eV as the NNH angle decreases from 115 to 110°.[28] We may conclude that, at least for a simple model system, as $IP_{n_-}$ increases the N–H bond be-

**Table V.** Calculated Quenching Constants for the Quenching of Azoalkane Fluorescence by Various Solvents Relative to Acetonitrile[a]

| Compd | Hexane[b] | Methanol[b] | Water |
|---|---|---|---|
| 2 | ≥9 | ≥3 | ≥2 × 10^6 |
| 3 | ≥10 | ≥2 | ≥3 × 10^6 |
| 4 | c | ≥0.3 | c |
| 6 | 1.1 | 1 | ≥2 × 10^9 |
| 8 | ≥5 | ≥2 | ≥8 × 10^7 |
| 9 | 0.06 | 0.3 | ≥1.2 × 10^8 |
| 11 | 0.04 | 0.4 | 3 × 10^4 |
| 12 | 0.1 | 0.4 | 3 × 10^4 |
| 13 | 0.1 | 0.7 | 2 × 10^3 |
| 14 | 0.05 | 0.4 | 2 × 10^5 |
| 17 | 0.3 | 5 | 6 × 10^7 |
| 18 | ≥10 | ~4 | 4 × 10^6 |

[a] $k_q$ values are given in $M^{-1} s^{-1}$ calculated from $\phi_F$ values assuming a linear Stern–Volmer plot up to neat solvent. [b] Values ×10^7. [c] Emission qualitatively more intense than in acetonitrile.

comes weaker. If this is the case for the azoalkanes studied, then removal of an electron from the n₋ MO (as excitation occurs) weakens the C–N bond to an extent dependent upon $IP_{n_-}$. The weakened C–N bonds then lead to a greater rate of $N_2$ extrusion in the excited state.

**Solvent Effects.** An immense solvent effect on fluorescence quantum yields can be noted by a casual perusal of Tables I and II. For example, $\phi_F$ for **11** decreases from 0.7 in acetonitrile to 0.01 in methanol while, for **9**, $\phi_F$ is 0.15 in acetonitrile, but no fluorescence is detectable in water. Hence, hexane, alcohols, and water appear to quench the fluorescence of the azoalkanes. Based upon observed $\phi_F$ and assuming a linear Stern–Volmer plot, the rate constants for quenching of azoalkane fluorescence by hexane, methanol, and water may be determined and are shown in Table V.[29] The rate constants for quenching by methanol and hexane all fall in the range of 4 ×
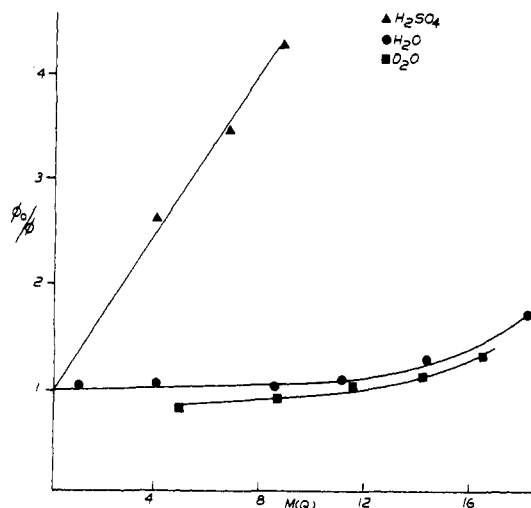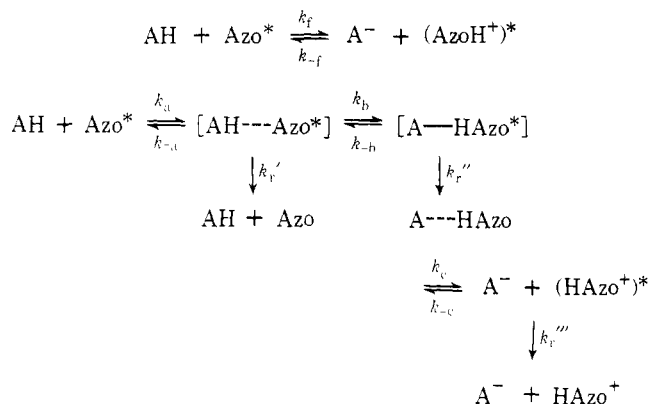
Scheme II

$$AH + Azo^* \underset{k_{-f}}{\overset{k_f}{\rightleftharpoons}} A^- + (AzoH^+)^*$$

$$AH + Azo^* \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [AH\text{---}Azo^*] \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} [A\text{---}HAzo^*]$$

$$\downarrow k_r' \qquad\qquad \downarrow k_r''$$

$$AH + Azo \qquad\qquad A\text{---}HAzo$$

$$\underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} A^- + (HAzo^+)^*$$

$$\downarrow k_r'''$$

$$A^- + HAzo^+$$



Figure 6. Stern-Volmer plot for the quenching of azoalkane 9 by $H_2SO_4$, $H_2O$, and $D_2O$ relative to $CH_3CN$.



$$E(S_1) \sim 71\text{-}84 \text{ kcals/mol}$$
$$\tau_S = (k_F + k_{ic} + k_{st} + k_d)^{-1} \sim 10^{-8} - 10^{-10} \text{ sec}$$
$$\phi_F = k_F \tau_S \sim 10^{-4} - 1.0$$
$$k_F \sim 0.5 - 2.0 \times 10^6 \text{ sec}^{-1}$$
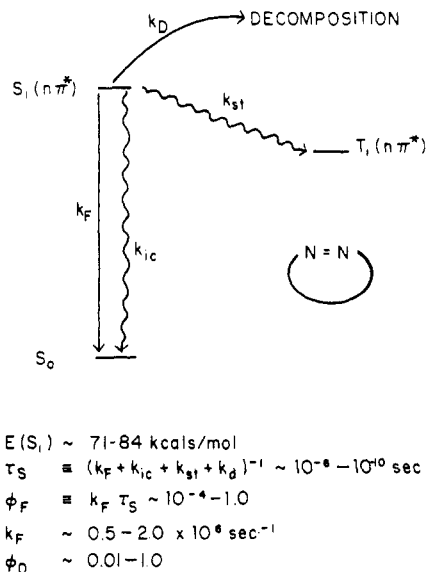$$\phi_D \sim 0.01 - 1.0$$

Figure 7. Energy diagram displaying the range of spectroscopic and photochemical parameters of cyclic azoalkanes, based on data presented in this paper.

$10^5$ to $1.0 \times 10^8$, while those for quenching by water vary from $2 \times 10^9$ for 6 to $2 \times 10^3$ for 13.

This complex solvent dependence can only be explained by a more detailed discussion of the deactivation pathways available to the excited singlet states of the azoalkanes and their dependence on solvents. We shall consider 11 as a typical example.

**A. Acetonitrile.** Unfortunately only a few data for $N_2$ extrusions in acetonitrile are available, but the major pathways for $S_1$ deactivation seem to be fluorescence and reaction. The quantum yields for these processes add up to a value of 0.85 for the compounds studied (9 and 11). Therefore no other radiationless decay can be very important under the present experimental conditions.

**B. Hexane.** In hexane fluorescence quantum yields are lower than in acetonitrile, but quantum yields for azoalkane decomposition are not correspondingly higher. Therefore, a special deactivation pathway must be responsible for the lower fluorescence quantum yields in hexane relative to acetonitrile. Hydrogen abstraction by the $n,\pi^*$ excited azoalkane is one obvious possibility[30] and is supported by the fact that $\phi_F$ of 11 is increased to the acetonitrile value when the solvent is changed from hexane to benzene or Freon.[17,31] Benzene is known to be a poor H donor and rate constants for H abstraction by ketones are usually several orders of magnitude lower in benzene than in hexane.[32] This may be confirmed by the fact that Clark and Steel have noted a discrepancy between the quantum yield of product formation and azoalkane

disappearance.[18] However, one must be careful in interpreting these results since the diradical produced by loss of $N_2$ may also hydrogen abstract, yielding unexpected products. Such is the case in the photolysis of 3 and 18 in pentane.[16] Besides the expected norbornadiene and quadricyclene, a small amount of norbornene is observed.

**C. Methanol, Water.** Since rate constants for H abstraction are usually very low in methanol or water,[33] different processes must be responsible for the rapid deactivation of the excited azoalkanes by these solvents.[17] The fact that fluorescence quantum yields of some azoalkanes (e.g., 10, 11, 9) are decreased by acids and increased by bases and the observation of a large deuterium isotope effect suggest that hydrogen bonding and protonation are responsible for the quenching effect of methanol and water.

The interaction between a proton donor and a base as summarized in Scheme II can be divided into three equilibrium steps, which are (a) complex formation between acid and base, (b) proton transfer, and (c) separation of ions.[34] Since excited states are involved in our particular example, deactivation to the ground state surface may occur from each of the three complexes ($k_r$).

It is difficult to distinguish in which step the actual deactivation occurs because all three possible associations are expected to be less stable in the ground than in the excited state, assuming that the latter is more basic.[35] In methanol, the observed deuterium isotope effect[17] of $\sim 10$ on $\tau_F$ and the magnitude of $\sim 10^7$ for $k_q$ (Table V) indicate the $k_b$ is probably small and most of the deactivation must occur from the hydrogen-bond complex. In water $k_b$ should be faster than for methanol because of the higher acidity. The quenching constants for compounds 6 and 9 are indeed in agreement with this model. For most of the other investigated azoalkanes, however, $k_q$ (water) < $k_q$ (methanol). Furthermore, the Stern-Volmer plot for quenching of fluorescence of compound 9 by both water and methanol in acetonitrile is nonlinear. Low quenching efficiency rises at higher water concentrations (see Figure 6). This nonlinear behavior of water in organic solvents is known for various properties and is usually explained by cluster formation of the water molecules.[36] Transferred to our examples, it means that a water molecule at low water concentrations prefers to form a hydrogen bond with a second water molecule rather than with an azoalkane and $k_a$ now becomes rate de-

termining. The rate constant $k_a$ should be sensitive to two influences, the basicity of the solute molecule (here the excited azoalkane molecule), and the strength of the hydrogen bonds between two solvent molecules. The second point is supported by the observed deuterium isotope effect. The greater degree of cluster formation in $D_2O$ compared with $H_2O$ is explained by the greater strength of -O — D- - -O bonds compared with -O—H- - -O ones. Therefore the same solute molecule is less likely to form a deuterium bond in $D_2O$ than a hydrogen bond in $H_2O$. This could explain the slower increase in the Stern–Volmer slope in Figure 6 for heavy water compared with water.[37]

## Conclusions

Several conclusions may be drawn from Tables I and II. It is apparent that [2.2.2]bicycloazoalkanes have particularly high fluorescence quantum yields. The azoalkanes **10–15** all have this structural feature in common and all show intense fluorescence. This increased fluorescence is matched by a decrease in the quantum yield of decomposition.

For most of the azoalkanes studied, $S_1$ is deactivated (Figure 7) by four pathways: (1) fluorescence; (2) loss of nitrogen; (3) intersystem crossing; (4) a radiationless deactivation which leads eventually back to the ground state. Let $k_F$, $k_D$, $k_{ST}$, and $k_{IC}$ be the rate constants for these four deactivation modes, respectively. The *measured* lifetime $\tau_F$ of $S_1$ will then be given by $\tau_F = (k_F + k_D + k_{ST} + k_{IC})^{-1}$. As mentioned earlier, $k_F$ does not vary by more than a factor of $\sim 3$ for the majority of the azoalkanes studied. Thus, the variation in $\tau_F$ (1000 to <1 ns) cannot be ascribed to variations in $k_F$ and must be controlled instead by changes in the sum $k_D + k_{ST} + k_{IC}$.

While only a few azoalkanes have been thoroughly studied (i.e., **3**, **17**, and **18**), it appears that all three rate constants may vary from structure to structure.[38,39] For example, the values $(s^{-1})$ of $k_D$, $k_{ST}$, and $k_{IC}$ for **17** are $2 \times 10^7$, $8 \times 10^6$, and $7 \times 10^6$, while those for **18** are $5 \times 10^8$, $6 \times 10^8$, and $4 \times 10^8$.[38] Thus, a careful systematic study of the photochemistry of these azoalkanes is required before more general quantitative conclusions may be drawn about the photophysical and photochemical properties of the azo chromophore.

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