

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

The substituent groups, F, CH₃, or C₂H₅ 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 (ϵ 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 ($n-\text{MO}$). 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}	ϕ_D
		λ_{max}	ϵ	λ_{max}	ϕ_F	τ_F		
1b	Hexane	366	150	390	<i>b</i>	<i>b</i>	78	
	CH ₃ CN	352		400				
	CH ₃ OH	352		395				
	Water	352		<i>b</i>				
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	≤7	83	0.98 ^{g,j}
	CH ₃ CN	327		440	0.007			
	CH ₃ OH	323		440	0.005			
	Water	320		440	0.008			
5	Hexane	332	105	<i>b</i>	<i>b</i>	<i>b</i>		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		<i>b</i>	<i>b</i>	<i>b</i>		
7	Hexane	327	165	<i>b</i>	<i>b</i>	<i>b</i>		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		
	CH ₃ OH	322		450	0.01	13		
	Water	317		<i>b</i>	<i>b</i>	<i>b</i>		
19^j	Hexane	347	133	386	0.01	7		0.52 ^g
	CH ₃ CN							

^a The column headings are defined as follows: λ_{max} , wavelength of highest transition probability in nanometers; ϕ_F , fluorescence quantum yield of nitrogen saturated solutions; τ_F , measured fluorescence lifetime of nitrogen saturated solutions in nanoseconds; E_{S_1} , calculated energy of the first excited singlet state in kilocalories/mole; ϕ_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 N₂ 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 N₂ purging. Samples were saturated with N₂ at –30 °C, warmed to 30 °C, cooled down to –30 °C, and again purged with N₂. 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 N₂-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 ϵ values are relatively large compared to n, π^* transitions in trans acyclic azoalkanes ($\epsilon \approx 10$ –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}	ϕ_D	
		λ_{max}	ϵ	λ_{max}	ϕ_F	τ_F			
10	Hexane	377	193	405	0.20	330 ^h	76	0.022 ^a	
	CH ₃ CN	376		406	0.41				
	CH ₃ OH	373		406	0.02				
	Water	364		416	0.5				
11	Hexane	383	192	387	0.2	420	74	0.014 ^b	
	CH ₃ CN	382		420	0.7				
	CH ₃ OH	375		420	0.01				
	Water	371		425	0.3				
12	Hexane	383	205	385	0.11	125	74	0.20	
	CH ₃ CN	385		405	0.44				
	CH ₃ OH	382		405	0.012				
	Water	373		415	0.25				
13	Hexane	373	250	378	0.13	70	77	0.01	
	CH ₃ CN	372		380	0.66				
	CH ₃ OH	367		388	0.009				
	Water	358		395	0.63				
14	Hexane	381	442 ^c	382	0.17	160	75		
	CH ₃ CN	380		385	0.43				
	CH ₃ OH	375		392	0.01				
	Water	367		405	0.09				
15	Hexane	401	150	405	<i>d</i>	<i>d</i>	71		
	CH ₃ CN	402, 390		420					
	CH ₃ OH								
	Water	382		445					
16	Hexane	341	420	358 ⁱ	<i>e</i>	<i>e</i>	84	1.0 ^b	
	CH ₃ CN	340		361 ⁱ					
	CH ₃ OH	334		<i>e</i>					
	Water	334		370 ⁱ					
17	Hexane	373	310	397	0.05	20	75	0.54 ^f	
	CH ₃ CN	369		400	0.08				
	CH ₃ OH	367		410	0.002				
	Water	362		415	0.0008				
18	Hexane	342	640	<i>e</i>	<i>e</i>	<i>e</i> ⁱ	84	0.44 ^g	
	CH ₃ CN	338		350					0.0009
	CH ₃ OH	338		355					0.0004
	Water	331		362					0.0007

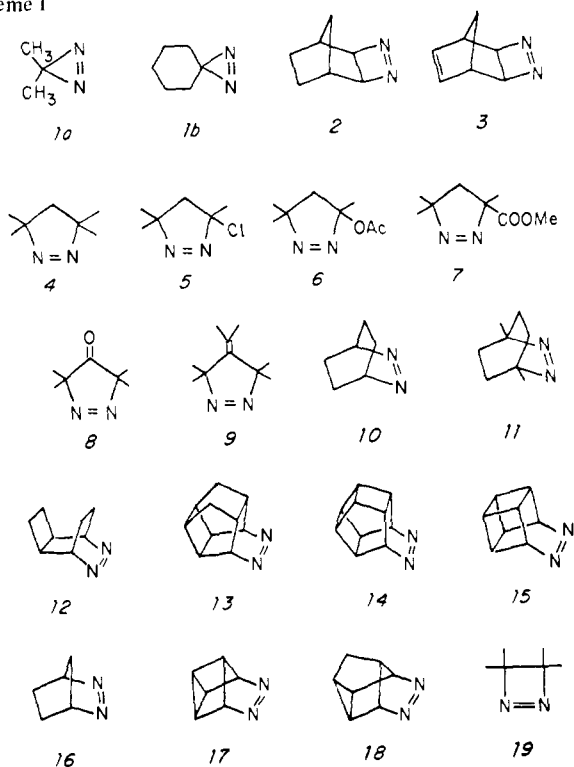
^a Reference 18. ^b Reference 2a. ^c E. L. Allred and B. R. Beck, *Tetrahedron Lett.*, 437 (1974). ^d Decomposed during measurement. ^e Too weak to be determined. ^f N. J. Turro and V. Ramamurthy, unpublished results. ^g Reference 16. ^h In isoctane; ref 18. ⁱ Emission from impurities cannot be ruled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

Table III. Photoelectron Spectroscopic Data of Azoalkanes^a

Compd	n-	n+	π	σ	$\Delta E, n_+-n_-$	$\Delta E, n_--\pi$	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 1



gens.¹⁹⁻²³ As a result the n_{-},π^{*} transition is of lower energy than the n_{+},π^{*} transition. The blue shift of the absorption maxima with increasing solvent polarity which is typical for n,π^{*} 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,π^{*} absorption maximum is controlled more by factors which influence the energy of the π^{*} 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—CH₃ 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

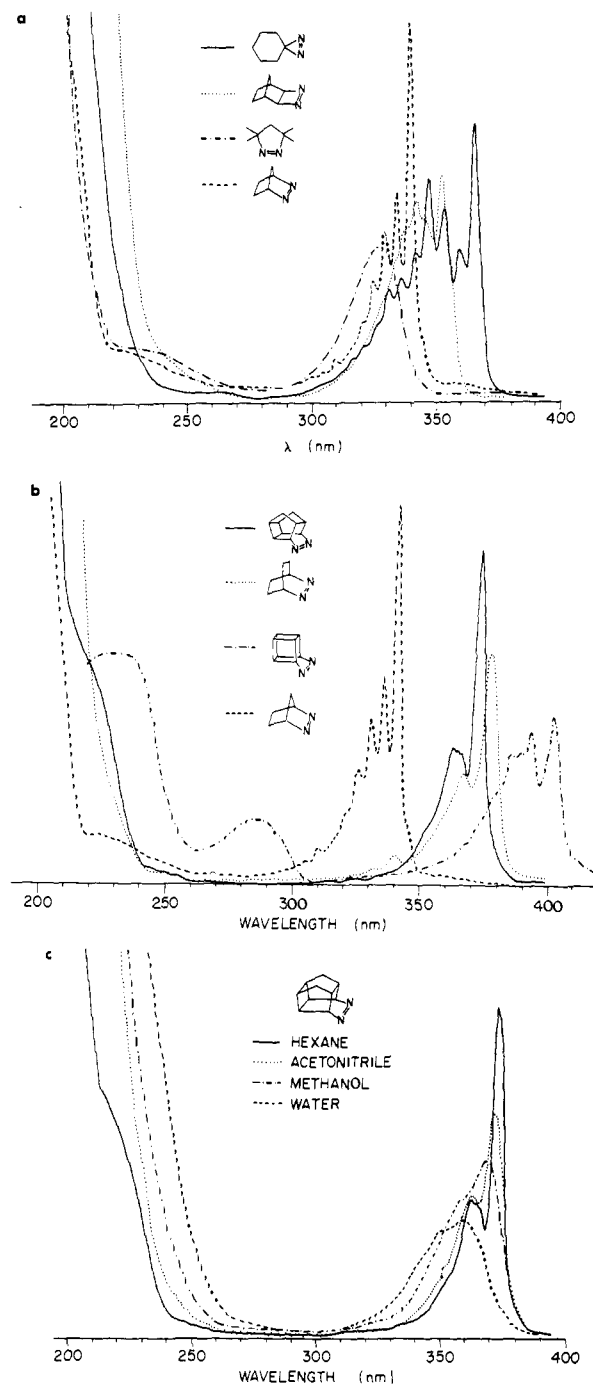


Figure 1. (a, b) Absorption spectra of selected azoalkanes in hexane; (c) absorption spectra of azoalkane **13** in various solvents.

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

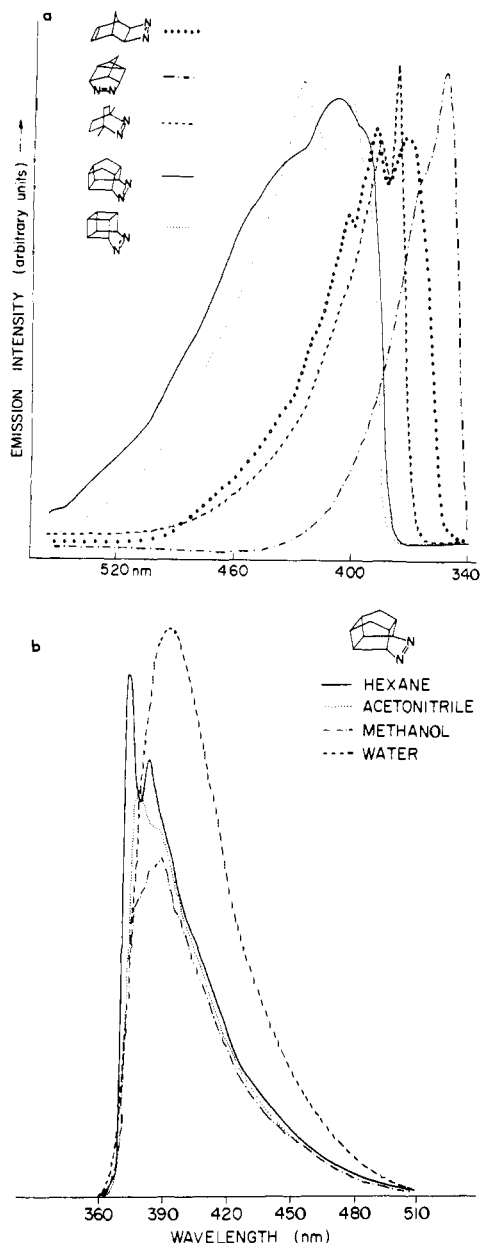


Figure 2. (a) Fluorescence spectra of selected azoalkanes in hexane; (b) fluorescence spectra of azoalkane **13** in various solvents.

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 $\text{CH}_3\text{OH}/\text{CH}_3\text{OD}$ or $\text{H}_2\text{O}/\text{D}_2\text{O}$, 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

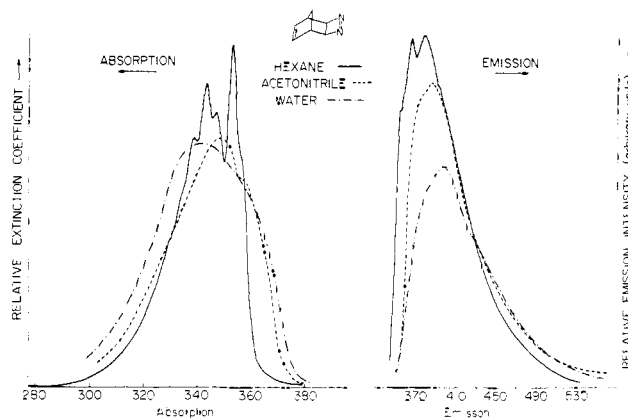


Figure 3. Absorption and fluorescence spectra of azoalkane **3** in various solvents.

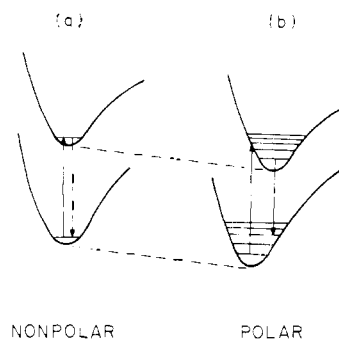


Figure 4. Schematic diagram of the transition between the ground and first excited singlet state for azoalkanes in (a) nonpolar and (b) polar solvents.

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 (ϕ_F) were roughly proportional to the fluorescence lifetimes (τ_F). The fluorescence rate constant (k_F) may be calculated by using the relationship

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

The values obtained are shown in Table IV. Alternatively, value for k_F may be determined from the integrated absorption spectra²⁶ 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 4×10^5 to $7 \times 10^6 \text{ s}^{-1}$. Clark and Steel obtained a value of $6.0 \times 10^5 \text{ s}^{-1}$ for **10** in isooctane,¹⁸ while we obtain a value of 1.2×10^6 in H_2O .

In contrast to k_F , the measured lifetime (τ_F) and fluorescence quantum yields differ widely for azoalkanes of different structure and range from undetectable fluorescence ($\phi_F < 10^{-4}$) in **5** to $\tau_F = 740 \text{ ns}$ 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 ($\times 10^6$) ^a	k_F ($\times 10^6$) ^b	k_D ($\times 10^8$) ^c	k_D ($\times 10^8$) ^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 τ_F and ϕ_F in hexane, and eq 1.

^b Based on integration of absorption spectrum for obtaining k_F .

^c Based on experimental Φ_D and τ_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 $\phi_F \leq 0.001$.

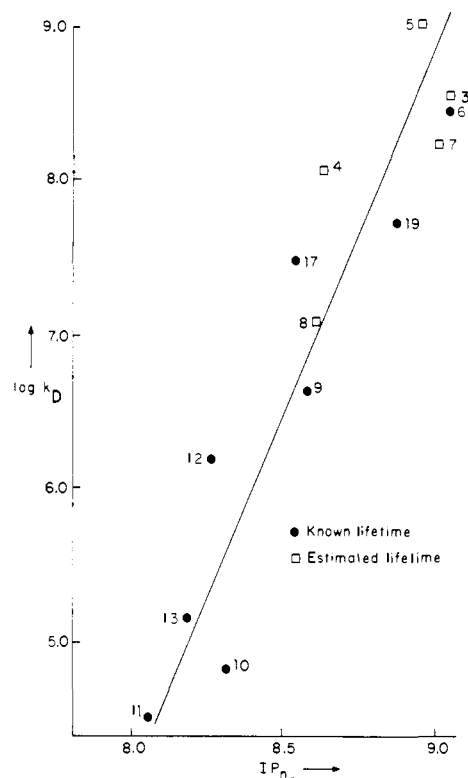
nalize these differences solely on the basis of ring strain seems to be inappropriate. For example, in the series of compounds **16–18**, compound **17** has the highest fluorescence quantum yield ($\phi_F = 0.08$ in CH_3CN) although its “ring strain” is certainly higher than that of **16** and **18**. 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 τ_F and the quantum yield for decomposition (ϕ_D), the rate constants for decomposition (k_D) may be derived via

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

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 Engel²⁰ 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-

**Figure 5.** Plot of $\log k_D$ vs. the lowest ionization potential (n_- MO) for several azoalkanes.**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	$\geq 2 \times 10^6$
3	≥ 10	≥ 2	$\geq 3 \times 10^6$
4	^c	≥ 0.3	^c
6	1.1	1	$\geq 2 \times 10^9$
8	≥ 5	≥ 2	$\geq 8 \times 10^7$
9	0.06	0.3	$\geq 1.2 \times 10^8$
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 $\text{M}^{-1} \text{s}^{-1}$ calculated from ϕ_F values assuming a linear Stern-Volmer plot up to neat solvent. ^b Values $\times 10^7$. ^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, ϕ_F for **11** decreases from 0.7 in acetonitrile to 0.01 in methanol while, for **9**, ϕ_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 ϕ_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 $4 \times$

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 τ_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 ~ 3 for the majority of the azoalkanes studied. Thus, the variation in τ_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 2×10^7 , 8×10^6 , and 7×10^6 , while those for **18** are 5×10^8 , 6×10^8 , and 4×10^8 .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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