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# Bimanes. 12. Unusual substituent effects on the triplet-state decay of anti-1,5-diazabicyclo[3.3.0]octadienediones (anti-9,10-dioxabimanes)

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continuous decrease occurs at both transitions, confirming the first-order nature of the transitions. These results clearly indicate that dynamic disorder of the alkyl groups sets in at each phase transition.

Associating the reduction at the minor transition in  $C_{12}Cd$  with a 2-fold torsional disorder of the alkyl chain, we calculated  $\Omega \approx 52^\circ$ . This implies a rotation of the head group (the  $C-NH_3$  moiety) by  $\sim 70^\circ$ , in accord with the observations in simpler systems.<sup>12</sup> The reduction factor of ca. 3.4 at the major transition is compatible with chain melting.

For  $C_{12}Mn$ , the order of reductions in second moments is reversed. A reduction by 3.6 at the first transition confirms the onset of chain melting when the alkyl chain becomes normal to the layer. The interpretation at the minor transition is different, however, and must be due to a 2-fold positional disorder of the alkyl chain.

At high temperatures, the second moments are comparable to those in lipids and paraffins, where the narrowing is due to lateral diffusion.<sup>13</sup> To check for this possibility, we performed a spin-labeled EPR experiment<sup>14</sup> on the high-temperature phase of  $C_{12}Cd$  with negative results. This is not surprising, since the  $-NH_3$  moiety is strongly hydrogen bonded to the metal halide layer. Any diffusion of the cations which does occur<sup>8</sup> must occur slowly via

lattice defects. These results are not contradictory to the NMR data, since the 2-fold positional disorder of the alkyl groups will have the same effect on NMR line widths as lateral diffusion.

Finally, a laser Raman study was performed on the  $C_nCd$  salts (including  $C_{10}Cd$ ). In the free amine, a vibration at  $1133\text{ cm}^{-1}$  was observed. This line has been identified as characteristic of the trans conformation in lipid systems, and its intensity has been shown to be sensitive to the number of gauche bonds present.<sup>15</sup> In the  $C_nCd$  systems, this band is split into three bands at 1125, 1142, and  $1175\text{ cm}^{-1}$ , which all show a pronounced drop in intensity at the chain-melting transition. The intensity of the  $1175\text{ cm}^{-1}$  band goes to zero at the chain-melting transition, while that of the  $1125\text{ cm}^{-1}$  band goes to zero at the upper transition. The intensity of the  $1142\text{ cm}^{-1}$  band does not go to zero until several degrees above the upper transition.

In conclusion, the phase transitions in these systems provide an interesting comparison to those occurring in actual lipid bilayers. The rigidity of the metal halide layers imposes constraints which prevent accurate mimicry. The minor transition involves a gauche(+) to gauche(-) conformational change, leading to a 2-fold torsional disorder if it occurs first, or a 2-fold positional disorder if it occurs second. The major transition involves chain melting. The crystallinity of the systems prevents lateral diffusion.

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(14) W. L. Hubbell and H. M. McConnell, *J. Am. Chem. Soc.*, **93**, 314 (1971).

(15) B. P. Gaber, P. Yager, and W. L. Peticolas, *Biophys. J.*, **24**, 677 (1978).

## Bimanes. 12. Unusual Substituent Effects on the Triplet-State Decay of *anti*-1,5-Diazabicyclo[3.3.0]octadienediones (*anti*-9,10-Dioxabimanes)

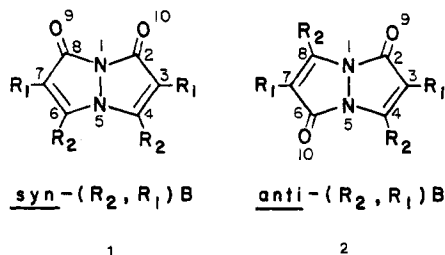
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Triplet-state lifetimes for *anti*-1,5-diazabicyclo[3.3.0]octadienediones (*anti*-9,10-dioxabimanes) decrease substantially on substitution of hydrogen for other substituents at the 3 and 7 positions. The triplet molecules either decay to the original ground state ( $k_{TS}$ ) or rearrange ( $k_I$ ) to an isomeric lactone, viscosity having marked, but not necessarily parallel, effects on the two channels. The maximum value for  $k_L$  ( $10^7\text{ s}^{-1}$ ) suggests that ring inversion and photochemistry are associated. Partial rotation of the three-carbon chain ( $R_1 = \text{H}$  or  $\text{D}$ ) after  $\alpha\text{-N-CO}$  cleavage of the triplet (if faster than twisting) leads to a diradical which can return to the ground state; rotation of the cleaved chain with twisting leads to the photochemical product via a fully rotated diradical. The lack of isotope effect is consistent with a chemical mechanism for fast triplet decay (via reversible bond cleavage to a partially rotated diradical) for *anti*-bimanes with  $R_1 = \text{H}$  or  $\text{D}$ .

### Introduction

*syn*- and *anti*-1,5-diazabicyclo[3.3.0]octadienediones (*syn*- and *anti*-9,10-dioxabimanes) (1 and 2) exhibit in-



(1) (a) Tel-Aviv University. (b) State University of New York, Stony Brook.

teresting chemical and photophysical properties.<sup>2-4</sup> *syn*-Bimanes are strongly fluorescent; *anti*-bimanes are weakly fluorescent and exhibit moderately strong phosphorescence.

Very fast intersystem crossing is the main channel for  $S_1$  loss in *anti*-bimanes, as shown by picosecond pulse techniques.<sup>3</sup> In the course of these studies, triplet absorption was monitored after nanosecond pulses. To our

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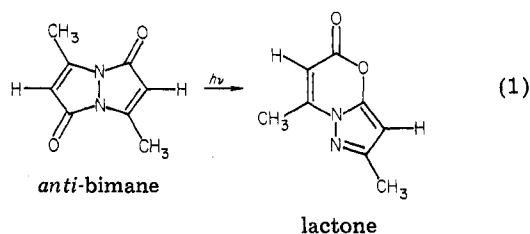
TABLE I: Triplet-State Properties of *anti*-9,10-Dioxabimanes (1,5-Diazabicyclo[3.3.0]octa-3,7-diene-2,6-dione)

substituents <sup>a</sup>	solvent	10 <sup>3</sup> (triplet-state decay rate constant), <sup>b,c</sup> s <sup>-1</sup>	lactone quantum yield	10 <sup>3</sup> k <sub>L</sub> , s <sup>-1</sup>	10 <sup>3</sup> k <sub>TS</sub> , <sup>d</sup> s <sup>-1</sup>
(CH <sub>3</sub> , CH <sub>3</sub> ) <sup>e</sup>	CH <sub>3</sub> CN	450	0.34	306	144
	HOCH <sub>2</sub> CH <sub>2</sub> OH	15	0.20	6	9
	glycerol	1.3	0.18	0.47	0.83
(CH <sub>3</sub> , H)	CH <sub>3</sub> CN	200000 <sup>f</sup>	0.014	5600	190000
	HOCH <sub>2</sub> CH <sub>2</sub> OH	5000 [18.8]			
		5700 [23.5]	0.23 [25]	2600	3100
	glycerol	460, 650 [23]	0.28	360	290
	H <sub>2</sub> O	1750 [18] <sup>g</sup>			
		2100 [26]	0.31	1300	800
		2340 [28]			
		2750 [35]			
		3170 [45]			
	CH <sub>3</sub> OH	30000 [25] <sup>h</sup>	0.22	13000	17000
		8300 [-6]			
		5400 [-17]			
		4100 [-25]			
		2900 [-32]			
		2300 [-35]			
		990 [-49]			
		635 [-52]			
		530 [-61]			
		390 [-72]			
		375 [-76]			
(CH <sub>3</sub> , D)	CH <sub>3</sub> CN	<sup>f</sup>	0.017		
	HOCH <sub>2</sub> CH <sub>2</sub> OH	4000 [18.8]	0.23	1800	2200
	glycerol	720	0.28	400	320
	H <sub>2</sub> O	1540 [18.8]	0.31	960	590
(CH <sub>3</sub> , H)(CH <sub>3</sub> , D)	CH <sub>3</sub> CN	<sup>f</sup>	0.013		
	HOCH <sub>2</sub> CH <sub>2</sub> OH	5600 [16]			
	glycerol	600 [16]	0.36	430	170
(CH <sub>3</sub> , Cl)(CH <sub>3</sub> , H)	CH <sub>3</sub> CN	10000 [16.5]	0.005	100	10000
	HOCH <sub>2</sub> CH <sub>2</sub> OH	160, 50 <sup>i</sup> [19.3]	0.054 [25]	17, 5.4	140, 45
	glycerol	16 [16.5]	0.028 [25]	0.9	15
(CH <sub>3</sub> , Cl)	CH <sub>3</sub> CN	490	0.38	370	120
	HOCH <sub>2</sub> CH <sub>2</sub> OH	20	0.10	4	16
	glycerol	9300 [16.5]	0.004	44	9200
(CH <sub>3</sub> , CH <sub>3</sub> )(CH <sub>3</sub> , H)	CH <sub>3</sub> CN	49 [19.3]	0.065 [25]	6.4	49
	HOCH <sub>2</sub> CH <sub>2</sub> OH	8.6 [16.5]	0.028	0.48	8.1

<sup>a</sup> Substituents are designated in the order (β, α) = (R<sub>2</sub>, R<sub>1</sub>). For unsymmetrical ("mixed") bimanies, the order is (R<sub>2</sub>, R<sub>1</sub>) (R<sub>2</sub>', R<sub>1</sub>'). See: Kosower, E. M.; Pazhenchevsky, B. *J. Am. Chem. Soc.* 1980, 102, 4983-93 for a fuller discussion of nomenclature. <sup>b</sup> ±10%. Each value is the average of at least three measurements. <sup>c</sup> The temperatures (°C) used for the decay measurement are given in square brackets. <sup>d</sup> The quantum yield for intersystem crossing from S<sub>1</sub> to T<sub>1</sub> was taken as 0.5, a lower limit based on phosphorescence quantum yield (up to 0.45) and photochemical quantum yields (up to 0.4). The calculations for k<sub>L</sub> and k<sub>TS</sub> were carried out as described in the text. <sup>e</sup> Values are taken from: Huppert, D.; Kanety, H.; Dodiuk, H.; Kosower, E. M. *Chem. Phys. Lett.* 1979, 65, 164-8. <sup>f</sup> No decay was detectable; the value given for CH<sub>3</sub>CN solution is estimated from the experimental limitations and from the ratios of rate constants at different viscosities. <sup>g</sup> ±2 °C. <sup>h</sup> Value extrapolated from measurements at lower temperatures by using a plot of ln k vs. 1/T. <sup>i</sup> Two decays were observed.

surprise, no signal was observed for *anti*-(CH<sub>3</sub>,H)B in CH<sub>3</sub>CN after a 1-ns pulse. Since glycerol diminishes the *anti*-bimane triplet decay rate by a factor of 500, we examined *anti*-(CH<sub>3</sub>,H)B in glycerol and found a lifetime of ca. 2 μs for the triplet. Thus, substitution of H for CH<sub>3</sub> or Cl at R<sub>1</sub> increased the triplet decay rate by a factor of ~500. We therefore investigated substituent and solvent viscosity effects on the *anti*-bimane triplet-state decay rates, especially for α-hydrogen or deuterium derivatives.

Photoisomerization of the *anti*-bimanies to lactones (eq 1) occurs via the triplet state, with quantum yields as high



as 0.4,<sup>5</sup> with details of an extensive study to be reported

separately.<sup>6</sup> On the basis of both photophysical and photochemical data, we can explain the unusual substituent effects.

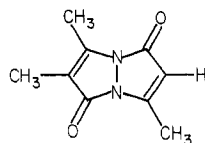
## Results

The triplet-state decay rate of *anti*-(CH<sub>3</sub>,H)B (2, R<sub>1</sub> = H) is ~500 times greater than those of closely related compounds with R<sub>1</sub> ≠ H such as *anti*-(CH<sub>3</sub>,CH<sub>3</sub>)B (2, R<sub>1</sub> = CH<sub>3</sub>) or *anti*-(CH<sub>3</sub>,Cl)B (2, R<sub>1</sub> = Cl). Increased solvent viscosity decreases the rate, that in glycerol being ~500 times lower than in acetonitrile. However, the ratio between the decay rates for *anti*-(CH<sub>3</sub>,H)B and *anti*-(CH<sub>3</sub>,CH<sub>3</sub>)B varies little with viscosity. The decay rate is decreased by lowering the temperature as shown by the data for *anti*-(CH<sub>3</sub>,H)B triplet in water and methanol at various temperatures. Decay rates are summarized in Table I.

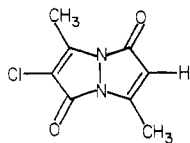
(5) Kanety, H.; Dodiuk, H.; Kosower, E. M. 1979 Abstracts, First European Organic Chemistry Congress, Köln, Germany Aug 20-23, 1979.

(6) Kanety, H.; Dodiuk, H.; Kosower, E. M. (Bimanies. 10) *J. Org. Chem.* in press.

The decay rates of "mixed" *anti*-bimane triplets ( $2, R_1(3) \neq R_1(7)$ ) are intermediate between those for *anti*-(CH<sub>3</sub>,H)B and *anti*-(CH<sub>3</sub>,CH<sub>3</sub>)B, with a factor of 20 between *anti*-(CH<sub>3</sub>,CH<sub>3</sub>)(CH<sub>3</sub>,H)B (3) and *anti*-(CH<sub>3</sub>,CH<sub>3</sub>)B in CH<sub>3</sub>CN.



*anti*-(CH<sub>3</sub>, CH<sub>3</sub>)(CH<sub>3</sub>, H)B  
3



*anti*-(CH<sub>3</sub>, Cl)(CH<sub>3</sub>, H)B  
4

The lactone quantum yield ( $\phi_{ph} = 0.014$ ) from *anti*-(CH<sub>3</sub>,H)B is much lower than that from *anti*-(CH<sub>3</sub>,CH<sub>3</sub>)B in acetonitrile ( $\phi_{ph} = 0.34$ ). Substitution of deuterium for hydrogen at R<sub>1</sub> has very little effect on the decay rates or the photochemical quantum yields.

The lactone yield from *anti*-(CH<sub>3</sub>,H)B rises with viscosity; that from *anti*-(CH<sub>3</sub>,CH<sub>3</sub>)B decreases somewhat from an initial high value in low-viscosity CH<sub>3</sub>CN. The quantum yields of lactone from the mixed *anti*-bimanes are very low, ranging from 0.004 for 3 in CH<sub>3</sub>CN to 0.028 for the same compound in glycerol.

## Discussion

Triplet decay data (as rate constants) and calculated rate constants are assembled in Table I. The rate constants for lactone formation ( $k_L$ ) and intersystem crossing ( $k_{TS}$ ) are derived as follows. (Intersystem crossing (TS) refers to  $T_1 \rightarrow S_0$ ). The triplet lifetime,  $\tau_T$ , is equal to the reciprocal of the sum of these two rates (eq 2). The photochemical quantum yield ( $\phi_{ph}$ ) is the product of the

$$\tau_T = 1/(k_L + k_{TS}) \quad (2)$$

quantum yield for triplet-state formation ( $\phi_{ST}$ ) and the efficiency of lactone formation from the triplet state ( $\phi_L$ ) (eq 3). Since the only important channels for loss of the

$$\phi_{ph} = \phi_{ST}\phi_L \quad (3)$$

triplet state are described by  $k_L$  and  $k_{TS}$ ,  $\phi_{ph}$  may be written as in eq 4. Combination of eq 4 with eq 2 leads

$$\phi_{ph} = \phi_{ST}k_L/(k_L + k_{TS}) \quad (4)$$

to expressions for  $k_L$  and  $k_{TS}$  in eq 5 and 6. The values

$$k_L = \phi_{ph}/\tau_T\phi_{ST} \quad (5)$$

$$k_{TS} = k_L(\phi_{ST}/\phi_{ph} - 1) \quad (6)$$

of the rate constants,  $k_L$  and  $k_{TS}$ , from the expressions in eq 5 and 6 are listed in Table I. Attention should be called to two outstanding points. First, the  $k_{TS}$  values for *anti*-(CH<sub>3</sub>,H)B are higher than those of the mixed bimanes and *anti*-(CH<sub>3</sub>,CH<sub>3</sub>)B in all solvents. Second, the lactone formation rate,  $k_L$ , is higher for *anti*-(CH<sub>3</sub>,H)B than for *anti*-(CH<sub>3</sub>,CH<sub>3</sub>)B and the mixed bimane 3 by a factor of ca. 20. The maximum value for  $k_L$  is  $\sim 10^7$  s<sup>-1</sup>, strikingly close to what might have been expected for ring inversion in *anti*-bimane systems. The probable upper and lower limits are given by ring inversion rates for 1,5-diazabicyclo[3.3.0]octanes ( $> 10^8$  s<sup>-1</sup>)<sup>7</sup> and the corresponding radical cation (ca.  $10^8$  s<sup>-1</sup>)<sup>8</sup>. We conclude that twisting must ac-

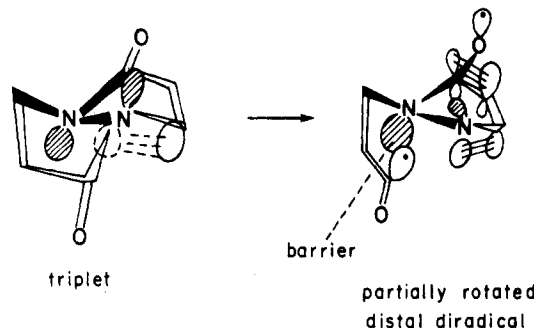


Figure 1. Illustration of the conversion of the triplet state for an *anti*-bimane into a partially rotated distal diradical, with a line marking the nitrogen nonbonding orbital barrier to rotation.

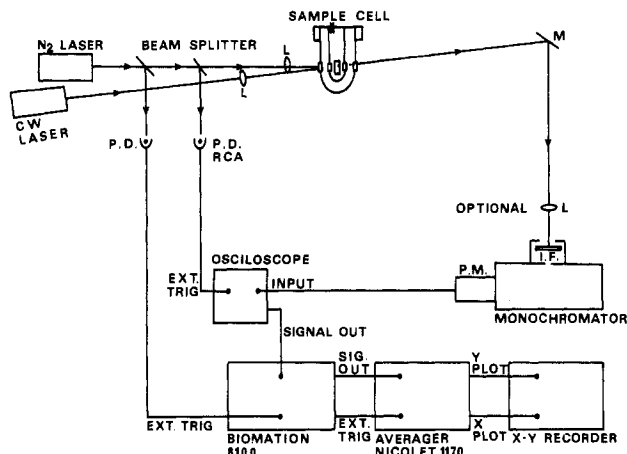


Figure 2. Experimental setup for measurement of triplet decay rates. P.D. = photodiode; P.M. = photomultiplier; I.F. = interference filter.

company ring opening to the diradical for lactone formation.

The twisted form has a geometry suitable for  $\alpha$ -N-CO cleavage (Figure 1). If the cleaved chain is "light" (i.e., if R<sub>1</sub> = H or D), rotation can be faster than the ring inversion in a highly fluid solvent (CH<sub>3</sub>CN,  $\eta = 0.25$  cP). However, if rotation has occurred without flattening or twisting of the ring to which the chain is attached, the nonbonding orbital on the second nitrogen is a barrier to complete rotation (see Figure 1).

The partially rotated diradical would no longer be a triplet (the orbitals are almost orthogonal for each radical). On return to a position of bonding with the nitrogen, a 25% chance of forming a singlet would lead directly to the ground state of the *anti*-bimane. (In one way, this situation is analogous to that of photochemically produced radical pairs trapped within micelles,<sup>9</sup> with trapping by a intramolecular barrier in the case of *anti*-(CH<sub>3</sub>,H)B.) This process would account for high  $k_{TS}$  values.

The high  $k_{TS}$  values and very low photochemical quantum yields for mixed bimanes (3 and 4) are understandable in terms of the model. The lack of isotope effect excludes coupling of the intersystem crossing process to the C-H bond at R<sub>1</sub>. Increased viscosity inhibits the partial rotation in a symmetrical *anti*-bimane more than the twisting motion since the latter is more likely to induce a collective response in the solvent surrounding the molecule. Thus, the photochemical yield for *anti*-(CH<sub>3</sub>,H)B rises rapidly over a narrow viscosity range, reaching reasonably high values in CH<sub>3</sub>OH and even higher values in H<sub>2</sub>O. Solvent

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(8) Nelsen, S. F.; Weisman, G. R.; Hintz, P. J.; Olp, D.; Fahey, M. R. *J. Am. Chem. Soc.* 1974, 96, 2916.

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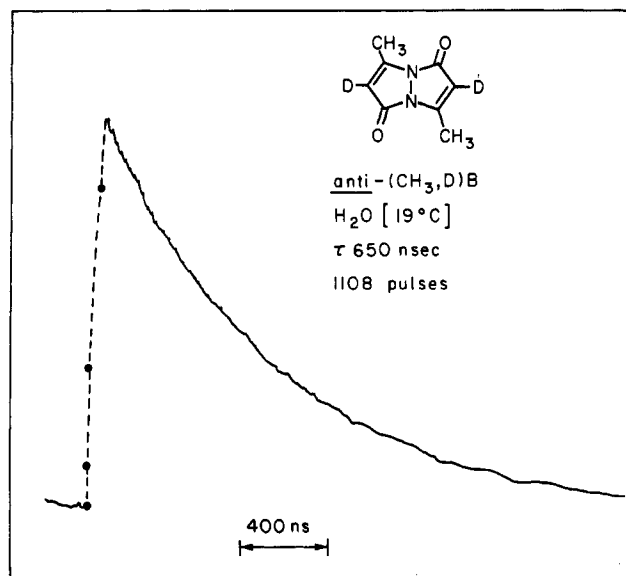


Figure 3. Sample decay curve representing  $T_1 \rightarrow T_n$  absorption for *anti*-(CH<sub>3</sub>,D)B in H<sub>2</sub>O at 19 °C.

polarity and solvent structure also influence the  $k_{TS}$  values appreciably. The low  $\phi_{ph}$  values for mixed bimanes even in glycerol may imply that the dissymmetry in the molecule may disturb the local solvent structure and make the partial rotation more facile than expected.

### Conclusions

The triplet states of *anti*-bimanes decay to the ground state or isomerize to a lactone. Gross changes in decay rates and quantum yields occur in response to rather moderate changes in substitution or extramolecular environment: (a) a large effect of replacing CH<sub>3</sub> (or Cl) by H (or D), (b) no isotope effect on replacing H by D, (c) a substantial effect of solvent viscosity. These points in conjunction with the time scale for lactone formation suggest that the fast decay of *anti*-(CH<sub>3</sub>,H)B is due to  $\alpha$ -N-CO bond cleavage to a diradical, partial rotation of the cleaved chain, and return of the chain to its original position with intersystem crossing.

### Experimental Section

The *anti*-bimanes listed in Table I were synthesized and purified according to variations of established procedures;<sup>4,6</sup> the preparations and physical properties will be reported in detail elsewhere.<sup>6</sup>

Triplet lifetimes were determined by a modification of the techniques previously outlined<sup>3</sup> and described briefly below; photochemical quantum yields were measured by using the Perkin-Elmer-Hitachi MPF-4 spectrofluorimeter as a light source with an actinometrically measured light flux.<sup>10</sup> The chemical details of the photochemical rearrangements will be reported separately.<sup>6</sup> The triplet decay constants and the photochemical quantum yields obtained under a variety of conditions and solvents are reported in Table I. All solutions were prepared on a vacuum line using thoroughly degassed solvents (CH<sub>3</sub>CN, CH<sub>3</sub>OH) or were prepared in a glovebag and then degassed on a high-vacuum line (1,2-ethanediol, glycerol). Aqueous solutions were degassed by a freeze-thaw technique.

A schematic representation of the experimental setup is shown in Figure 2. A nitrogen laser pulse (50-kW peak power, 1-ns full width at half-maximum)<sup>11</sup> was used for exciting the *anti*-bimanes to the  $S_1$  state. A Liconix He-Cd laser, operating at 442 nm, served as the monitoring light source. The He-Cd laser beam was passed through the sample cell and a monochromator (Jarrell-Ash 250 mm) and was detected with an RCA IP-28 photomultiplier. The analog signal derived from the photomultiplier was digitized with a Biomation 8100 transient recorder (time resolution, 10 ns per channel), and the digitized waveform stored in a Nicolet 1170 signal averager. Between 128 and 4098 pulses were averaged, yielding plots of intensity (for  $T_1 \rightarrow T_n$  absorption) vs. time. Kinetic constants were derived through analysis of the latter curves. A sample absorption vs. time plot is given in Figure 3.

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(11) The laser was constructed according to the design of von Bergman, H. M.; Pendris, A. J. *J. Phys. E* **1977**, *10*, 602-8.