

In methanol there was additional exchange broadening of the OH resonance due to incomplete averaging of that resonance by hydrogen ion catalyzed OH-proton exchange. This additional exchange broadening is the sum of two terms,  $B_Q + B_{O-17}$ , owing to ( $B_Q$ ) transfers between the individual components of the OH spin-spin quadruplet, and ( $B_{O-17}$ ) transfers between  $\text{CH}_3^{16}\text{OH}$  and  $\text{CH}_3^{17}\text{OH}$  at natural isotopic abundance. The theory has been stated by Grunwald, Jumper, and Meiboom.<sup>21</sup>  $B_{O-17}$  was calculated according to eq 4 of that paper, using  $\tau_1 = 2.80 \times 10^{-10}/[\text{H}^+]$  at 30° and  $J'$  and  $T^1$  of  $^{17}\text{O}$  as given in that paper.<sup>21</sup>  $B_Q$  at 30° was calculated from (12), which can be obtained from eq 2 of that paper.<sup>21</sup>

$$B_Q = (2.19 \times 10^{-7}[\text{H}^+])(2 + 2.50 \times 10^{-14}[\text{H}^+]^2)/(1 + 2.50 \times 10^{-14}[\text{H}^+]^2) \quad (12)$$

The exchange broadening,  $B_{\text{NH-OH}}$ , due to NH-OH proton exchange was taken as the difference (13).

$$B_{\text{NH-OH}} = (1/T_2) - (1.07/T_1) - B_Q - B_{O-17} \quad (13)$$

In methanol also, some solutions that exhibited a large amount of exchange broadening were examined in slow passage (rather than by spin-echo) and gave kinetic results in agreement with those obtained by direct measurement of  $T_2$  and  $T_1$ .

(21) E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 522 (1963).

**Acidity Function for Tertiary Anilines in *t*-BuOH-HOH-HCl.** In order to interpret kinetic data at high HCl concentrations, we measured the Hammett acidity function  $H_0$ ,<sup>22</sup> using *N,N*-dimethyl-*p*-nitroaniline (I) as indicator.  $\text{p}K_A^0$  for  $\text{IH}^+$  was found to be  $-0.84$  at 26.7° in 11.47 mole % *t*-BuOH-88.53 mole % water. In preparing the concentrated solutions, the alcohol/water mole ratio was kept constant as HCl was added. By definition,  $H_0 = \text{p}K_A^0 + \log (\text{I})/(\text{IH}^+)$ . (I) was measured spectrophotometrically at 26.7° and 390  $\text{m}\mu$ . Between 0.20 and 3.25 *M* HCl,  $H_0$  was an accurately linear function of pH and [HCl], according to

$$H_0 = \text{p}_c\text{H} - (0.493 \pm 0.005)[\text{HCl}] \quad (14)$$

By using  $H_0$  rather than pH for the measure of acidity, we were able to extend our kinetic analysis to rather high HCl concentrations.<sup>2,9</sup> It was found that the viscosity of these solutions increases by no more than a few per cent in the experimental range, and changes in viscosity were therefore neglected. The theoretical curve in Figure 2 is calculated using  $h_0$  instead of  $[\text{H}^+]$ , where  $-\log h_0 = H_0$ . The fit of the data is good up to the highest HCl concentration, 2.6 *M*.

In treating the data in methanol, it was not considered necessary to use an acidity function rather than  $\text{p}_c\text{H}$  because the rate became too slow to be measurable accurately at about 0.6 *M* HCl.

(22) See, for example, E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964), and references cited therein.

## Conversion of Electronic Excitation into Thermal Energy. Effect of Solvent and Substituents in the 4 and 5 Positions on Absorption and Fluorescence Spectra of 1,3-Diphenyl- $\Delta^2$ -pyrazolines

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**Abstract:** Investigated were 1,3-diphenyl- $\Delta^2$ -pyrazoline (4), compounds obtained by fusion of 4 to the cyclopentane (5) and the norbornane (6) rings, and derivatives of 5 and 6 with substituents in the 5-pyrazoline position. From the absorption and fluorescence spectra recorded in cyclohexane and isopropyl alcohol, and the photostability tests, were calculated the quantum yields of fluorescence ( $\Phi_f$ ) and of photodegradation ( $\Phi_d$ ), the ratio of quanta converted into thermal energy to quanta emitted as light ( $\Theta$ ), and the lifetimes of the excited states: actual ( $\tau$ ), radiative ( $\tau_0$ ), and nonradiative ( $\tau_{nr}$ ). Isopropyl alcohol produced a *blue* shift in the absorption spectra (except for the hydroxy derivative of 6) and a *red* shift in the fluorescence spectra indicating stabilization, relative to cyclohexane, of the ground state and, after relaxation of the solvent cage had occurred, of the excited state. Fusion of 4 to the cyclopentane or norbornane resulted in *red* shifts in the absorption spectra, but the shifts were obliterated by the second substituent in the 5 position. The  $\Phi_d$  figures did not exceed 0.00025 and the  $\Phi_f$ 's ranged from 0.52 to 0.94. Efficiency in the conversion of electronic excitation into thermal energy, measured by  $\Theta$ , was governed by the rigidity of the molecule and the solvent; least efficient was 6. Isopropyl alcohol markedly increased this efficiency in 4 but had no effect on 6. Substitution of 6 increased the  $\Theta$ ; the hydroxyl and the dimethylpiperazinium groups were most effective. Rates of fluorescence,  $1/\tau_0$ , were slightly retarded by isopropyl alcohol and little affected by structural modifications, except for the hydroxy derivative of 6 in cyclohexane. Consequently, differences in the efficiency in the conversion of electronic excitation into thermal energy were principally manifested in changes in the nonradiative lifetimes,  $\tau_{nr}$ .

Fluorescence of 1,3-diphenyl- $\Delta^2$ -pyrazolines has been attributed to planarity of the molecule and the presence of two substituents, capable of interaction by way of the mesomeric forms **1b** and **1c**.<sup>1-6</sup> The non-

planar compounds **2** and **3** do not fluoresce,<sup>1,4</sup> and marked changes in the emission of light are induced by

(4) A. Wagner, C. W. Schellhammer, and S. Petersen, *Angew. Chem., Intern. Ed. Engl.*, **5**, 699 (1966).

(5) A structure alternative to **1b** and **1c**, with the partial positive charge localized on the C-3 of the pyrazoline ring, has been suggested in ref 6.

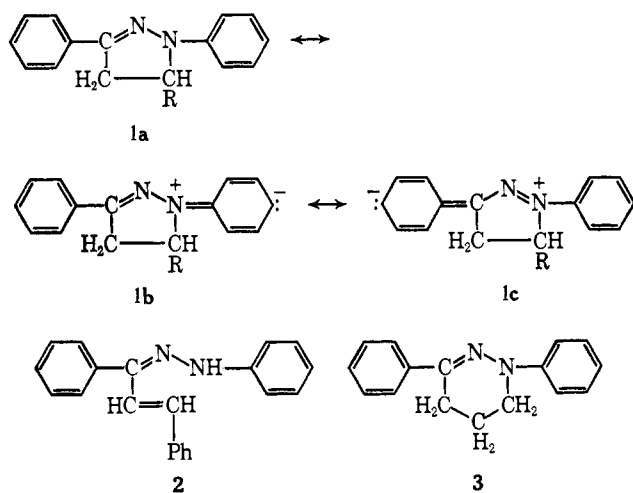
(6) S. R. Sandler and K. C. Tsou, *J. Chem. Phys.*, **39**, 1062 (1963).

(1) O. Neunhoeffer and D. Rosahl, *Z. Elektrochem.*, **57**, 81 (1953).

(2) O. Neunhoeffer and H. Ulrich, *Ber.*, **88**, 1123 (1955).

(3) O. Neunhoeffer, G. Alsdorf, and H. Ulrich, *ibid.*, **92**, 252 (1959).

substitution of the phenyls in **1**,<sup>1,2,4,6-8</sup> extension of the conjugated system,<sup>1,2,6,8,9</sup> or replacement of the phenyl at the 3 position in **1** with the CH<sub>3</sub> or the CF<sub>3</sub> group.<sup>3,6</sup> In contrast, the presence and the nature of the substituent in the 5 or the 4 position has little influence demonstrating its isolation from the conjugated system.<sup>1,6,7,10-13</sup>



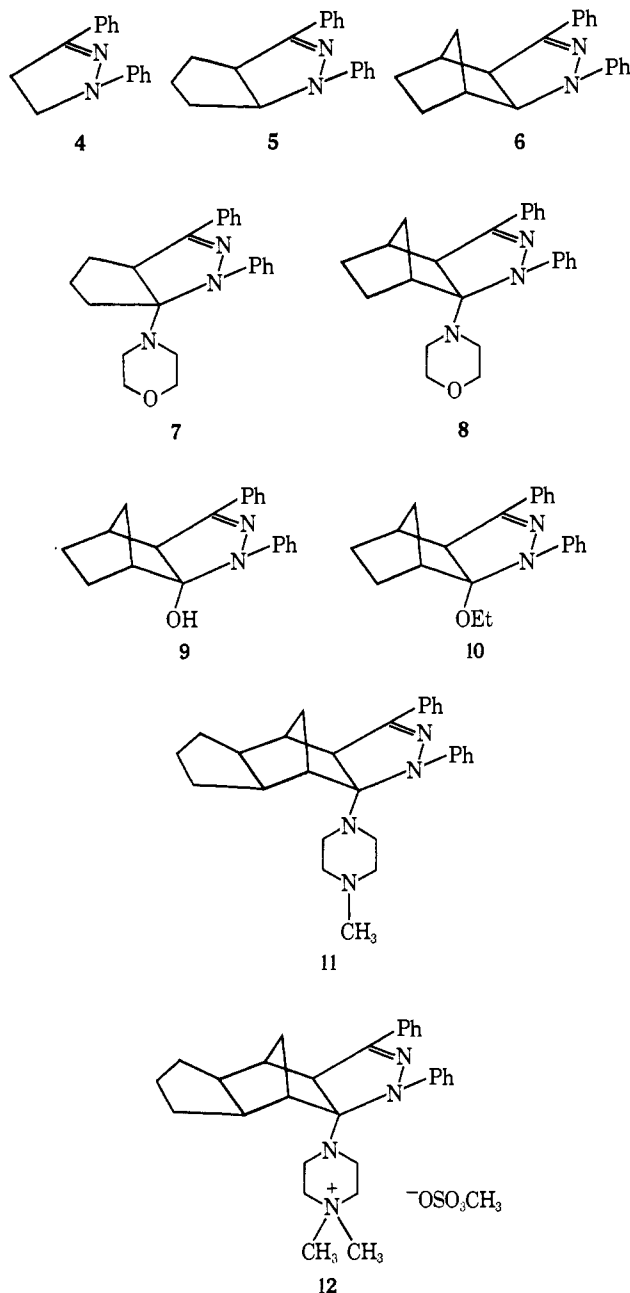
We have investigated the ultraviolet and fluorescence spectra of a series of pyrazolines, **4-12**, in order to elucidate the effects of rigidity of the molecule and planarity of the pyrazoline ring, and of the presence of a second substituent in the 5 position. The spectra were recorded in cyclohexane and isopropyl alcohol. From these data, the quantum yields of fluorescence and the lifetimes of the excited state were calculated. Stability of the representative samples on irradiation with ultraviolet light also was tested.

### Experimental Section

**Reagents.** Compounds **4**, **5**, and **6** were prepared according to Madinaveita<sup>14</sup> and Huisgen, *et al.*<sup>15</sup> The preparation of **7-12** will be reported separately.<sup>16</sup> Purification was accomplished by repeated crystallizations and, in some cases, by additional chromatography on silica. Spectral grade solvents were used.

**Spectra.** The absorption and the fluorescence spectra were recorded with a Cary 14 spectrophotometer and an Aminco 4-8202 spectrophotofluorometer equipped with a R136 photomultiplier tube (response near S-13). Molar absorptivities,  $\epsilon$ , were calculated after establishing that the compounds follow the Beer-Lambert law. The true emission spectra were obtained by calibrating the spectrophotofluorometer with rhodamine B according to Melhuish.<sup>17</sup> All samples were excited with light of 363 nm. The mirror-image symmetry between the absorption and the emission spectra was observed.

For the measurement of fluorescence the dilute solutions ( $\epsilon_{363}C$  range: 0.0094-0.0108 cm<sup>-1</sup>) were degassed by the usual freezing-



refreezing technique.<sup>18</sup> Rectangular sealed cells of 0.80-cm path length were used and the results were corrected for small differences (1-2%) in the reflection of light by solvents of different refractive indices.<sup>19</sup>

**Quantum Yields of Fluorescence.** Quantum yields of fluorescence,  $\Phi_f$ , were obtained from the areas under the true emission spectra.<sup>21</sup> Quinine sulfate in 0.1 N H<sub>2</sub>SO<sub>4</sub>, with  $\Phi_f = 0.46$ ,<sup>22</sup> was used as a

(7) M. Pestemer, A. Berger, and A. Wagner, *Schweiz. Ver. Faerbereifachleut., Fachorgan Textilveredlung*, **14**, 420 (1964).

(8) E. A. Andreeshchev, E. E. Baroni, K. A. Koyrzina, I. E. Pani, I. M. Rozman, and V. M. Shonyia, *Priboiy i Tekhn. Ekspierim.*, **1**, 32 (1956).

(9) F. Strauss, *Ber.*, **51**, 1458 (1918).

(10) I. M. Rozman and S. F. Kilin, *Usp. Fiz. Nauk*, **69**, 459 (1959).

(11) E. A. Andreeshchev and I. M. Rozman, *Opt. i Spektroskopiya*, **8**, 828 (1960).

(12) E. A. Andreeshchev, S. F. Kilin, I. M. Rozman, and V. I. Shilov, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **27**, 533 (1963).

(13) I. M. Rozman, *Opt. i Spektroskopiya*, **2**, 480 (1957).

(14) J. Madinaveita, *J. Chem. Soc.*, 1929 (1937).

(15) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knapfer, *Tetrahedron*, **17**, 3 (1962).

(16) J. F. Stephen and E. Marcus, to be submitted for publication.

(17) W. H. Melhuish, *J. Opt. Soc. Am.*, **52**, 1256 (1962).

(18) Quantum yields of fluorescence obtained with solutions deoxygenated by passing in nitrogen were, on average, 24% lower than the yields of solutions degassed by freezing-refreezing. The calculations (*vide infra*) indicated that the lifetimes of the investigated compounds were of the order of 5 nsec. Under these circumstances, the referee pointed out, little care should be needed in treatment of the samples to prevent oxygen quenching. Thus, either the lifetimes were longer than calculated or there was a specific interaction with oxygen in the ground state. At present, this question remains unresolved.

(19) The corrections were calculated from the refractive indices of the pure solvents<sup>20</sup> at about the excitation wavelengths and the mean wavelengths of the fluorescence bands.

(20) (a) "International Critical Tables," Vol. 7, McGraw-Hill Book Co., New York, N. Y., 1926, pp 30, 35, 40; (b) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1950, pp 196, 318.

(21) C. A. Parker and W. T. Rees, *Analyst*, **85**, 587 (1960).

(22) R. Rusakowicz and A. C. Testa, *J. Phys. Chem.*, **72**, 793 (1968).

standard for calculation of the absolute figures. Its absorption and emission maxima, at 347 and 465 nm, respectively, approximate the corresponding maxima of the investigated compounds. The  $\Phi_f$  figures were calculated from duplicate area determinations except for compounds **7**, **8**, and **11**, and for quinine sulfate, where five determinations were made to give a more reliable estimate of the standard deviation. In no case did the standard deviation exceed 10% of the reported  $\Phi_f$  figures. (The average standard deviation was 5% of the  $\Phi_f$ .)

**Lifetimes of Excited States in Solution.** The radiative lifetimes,  $\tau_0$ , were calculated from the equation of Strickler and Berg<sup>23</sup>

$$(\tau_0)^{-1} = 2.880 \times 10^{-9} n^2 (\bar{\nu}_f^{-3})_{av}^{-1} \int \epsilon(\bar{\nu}) d \ln \bar{\nu}$$

where

$$(\bar{\nu}_f^{-3})_{av}^{-1} = \int F(\bar{\nu}) d\bar{\nu} / \int F(\bar{\nu}) \bar{\nu}^{-3} d\bar{\nu}$$

$F(\bar{\nu})$  is the intensity of fluorescence in relative quanta at each wave number. For the refractive index,  $n$ , the values for the pure solvents at about the mean wavelengths of the fluorescence bands were used.<sup>20</sup>

The actual lifetimes,  $\tau$ , were obtained from the relation

$$\tau = \tau_0 \Phi_f$$

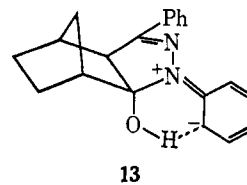
and the nonradiative lifetimes,  $\tau_{nr}$ , from

$$(\tau_{nr})^{-1} = (\tau)^{-1} - (\tau_0)^{-1}$$

**Photostability.** Degassed, by freezing-refreezing, solutions of the representative samples (**4**, **5**, **6**, **8**, and **9**) were irradiated at 25° with light of 365 nm in an apparatus consisting of a General Electric H100A38-4 lamp, a collimating lens, a Corning CS 7-83 narrow-band-pass filter, and a Bausch and Lomb 45-9 beam divider. The solutions were contained in sealed cylindrical cells of 10-cm path length, and their concentration was sufficiently high to absorb no less than 99.9% of the incident light. The light flux, determined by the potassium ferrioxalate actinometry,<sup>24</sup> was  $3.83 \times 10^{-6}$  and  $1.51 \times 10^{-6}$  einstein hr<sup>-1</sup> in the main and in the reflected (by the beam divider) beam, respectively. Irradiation times ranged from 34 to 92 hr. Changes in the concentration of the irradiated compounds were followed by ultraviolet spectroscopy in the range 300–450 nm, and the results were expressed as quantum yields of photodegradation,  $\Phi_d$ . No changes in the shape of the absorption curves were observed. Absorbance at the maximum was used for calculation of the  $\Phi_d$ . The estimated uncertainty of the latter was not greater than  $\pm 55 \times 10^{-6}$  unit.

## Results and Discussion

Positions of the long-wavelength maxima of absorption and emission in cyclohexane and isopropyl alcohol are reported in Table I. A small *blue* shift in the absorption spectra, characteristic of all compounds except for **9** and perhaps **4** and **5**, and the *red* shift in the emission spectra on passing from cyclohexane to isopropyl alcohol are consistent with the different charge distribution and greater polarity of the excited state relative to the ground state. It appears that the ground state was slightly more stabilized by isopropyl alcohol than cyclohexane, but the relaxation of the solvent cage was slower than changes in the electronic structure on excitation. This relaxation did occur during the lifetime of the excited state and consequently the energy level from which fluorescence originated was lower in isopropyl alcohol than in cyclohexane. The presence of the hydroxy substituent in **9** stabilized the ground state more effectively than isopropyl alcohol, probably by intramolecular hydrogen bonding, as in **13**, or by intermolecular association. Isopropyl alcohol interfered with this stabilization and as the fluo-



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resence data (see below) appear to indicate, no internal stabilization occurred in the excited state.

**Table I.** Wavelengths of Maximum Absorption and Emission of Pyrazolines in Cyclohexane and Isopropyl Alcohol

Compd	Absorption			Emission		
	C <sub>6</sub> H <sub>12</sub> , nm <sup>a</sup>	<i>i</i> -PrOH, nm <sup>c</sup>	$\Delta$ , <sup>b</sup> kcal/mole	C <sub>6</sub> H <sub>12</sub> , nm <sup>c</sup>	<i>i</i> -PrOH, nm <sup>d</sup>	$\Delta$ , <sup>e</sup> kcal/mole
<b>4</b>	356	355	0.2	431	478	-6.6
<b>5</b>	363	361	0.4	433	472	-5.4
<b>6</b>	368	365	0.6	435	472	-5.1
<b>7</b>	357	354	0.7	420	450	-4.6
<b>8</b>	358	355	0.7	425	458	-4.9
<b>9</b>	353	357	-0.9	425	458	-4.9
<b>10</b>	358	354	0.9	420	450	-4.6
<b>11</b>	359	356	0.7	431	455	-3.4
<b>12</b>	...	346	...	...	458	...

<sup>a</sup> Estimated uncertainty:  $\pm 1$  nm. <sup>b</sup> Shift in  $\lambda_{max}$  on passing from cyclohexane to isopropyl alcohol. Estimated uncertainty:  $\pm 0.45$  kcal/mole. <sup>c</sup> Estimated uncertainty:  $\pm 2$  nm. <sup>d</sup> Estimated uncertainty:  $\pm 4$  nm. <sup>e</sup> Shift in  $\lambda_{max}$  on passing from cyclohexane to isopropyl alcohol. Estimated uncertainty:  $\pm 0.85$  kcal/mole.

Fusion of the pyrazoline **4** to the cyclopentane and norbornane rings (**5** and **6**) produced *red* shifts in the absorption spectra that amounted to about 1.5 and 2.5 kcal mole<sup>-1</sup>, respectively, in both solvents. This effect was virtually obliterated by the second substituent in the 5 position. The nature of the substituent was of little consequence except for the case of **9** in cyclohexane and particularly when, in **12**, it carried a positive charge (inductive effect?).

Very broad fluorescence bands, especially in isopropyl alcohol, were unsuited for the detection of small shifts in the position of the maxima caused by structural modifications. The major shifts confirmed the hypsochromic effect of the second substituent in the 5 position of the pyrazoline.

Quantum yields of fluorescence and the related quantities are reported in Table II. The  $\Phi_f$  figures range

**Table II.** Quantum Yields of Fluorescence ( $\Phi_f$ ), Ratio of Quanta Converted into Thermal Energy to Quanta Emitted as Light ( $\Theta$ ), and Quantum Yields of Photodegradation ( $\Phi_d$ ) of Pyrazolines in Cyclohexane and Isopropyl Alcohol<sup>a</sup>

Compd	$\Phi_f$		$\Theta^b$		$10^6 \Phi_d$	
	C <sub>6</sub> H <sub>12</sub>	<i>i</i> -PrOH	C <sub>6</sub> H <sub>12</sub>	<i>i</i> -PrOH	C <sub>6</sub> H <sub>12</sub>	<i>i</i> -PrOH
<b>4</b>	0.77	0.52	0.32	0.92	35	30
<b>5</b>	0.78	0.69	0.28	0.44	0	110
<b>6</b>	0.93	0.94	0.08	0.07	65	-55
<b>7</b>	0.73	0.69	0.36	0.44	...	...
<b>8</b>	0.79	0.87	0.27	0.15	225	0
<b>9</b>	0.71	0.74	0.41	0.35	120	.
<b>10</b>	0.81	0.85	0.24	0.18	...	...
<b>11</b>	0.82	0.83	0.21	0.20	...	...
<b>12</b>	...	0.76	...	0.32	...	...

<sup>a</sup> Excitation wavelength 363 nm. <sup>b</sup>  $\Theta = (1 - \Phi_f)/\Phi_f$ .

from 0.52 to 0.94. The  $\Phi_f$  figures in all the investigated cases, and presumably also in cases that had not been

(23) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

(24) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

tested, are much smaller ( $\Phi_d < 0.00025$ ). Consequently, the quantity

$$\Theta = (1 - \Phi_f)/\Phi_f = \tau_0/\tau_{nr}$$

is a good measure of the absorbed quanta that are converted by a given compound in a given solvent into thermal energy *per* one quantum emitted as light.<sup>25</sup> It is more convenient to use  $\Theta$ , rather than  $\Phi_f$ , for demonstration of the effects of structure and of the solvent. However, experimental uncertainty in quantum yields of fluorescence indicates that only large changes in  $\Phi_f$ , or the corresponding changes in  $\Theta$ , are significant.

Efficiency in the conversion of electronic excitation into thermal energy depends on the rigidity of the molecule. Compound **5** is probably not much more rigid than **4**, but a very substantial increase in the rigidity is achieved in **6** by fusion of the pyrazoline to the norbornane ring and holding it firmly in a planar conformation. These changes are reflected in the decrease of the  $\Theta$  figures in cyclohexane, from 0.32 for **4** to 0.08 for **6**, that apparently exceed the limits of experimental uncertainty. The difference in isopropyl alcohol is even larger, 0.92–0.07, clearly indicating the participation of the alcohol in the conversion process. This participation is most pronounced in the case of **4**. It is smaller in **5** and absent in **6**. Thus, the interaction between the pyrazoline moiety and isopropyl alcohol is dependent on steric requirements of the molecule or/and its rigidity.

Introduction of a second substituent in the 5 position of the pyrazoline appears to facilitate, with one exception, the conversion of electronic excitation into thermal energy. The increase in  $\Theta$  on passing from **5** to **7** is very small in cyclohexane and does not occur in isopropyl alcohol. In contrast, there is a consistent increase when the rigid compound **6** is used as the parent structure. It is particularly large with the hydroxy and the dimethylpiperazinium substituents. It is conceivable that the substituents facilitate the conversion by providing the rigid molecule with new vibrational modes and increasing the probability of coupling between the vibrational and the electronic transitions.<sup>26</sup> Isopropyl alcohol appears to be involved in this process<sup>27</sup> (*vide infra*).

In Table III are summarized the calculated lifetimes of excited states and molar absorptivities of the long-wavelength absorption peaks. The actual lifetimes,  $\tau$ , can be determined experimentally, and if the  $\Phi_f$ 's are

(25) The conversion of electronic excitation into thermal energy could proceed by a direct crossover from a higher electronic state to the isoenergetic level of a lower lying electronic state, or it could involve the intermediacy of a thermodynamically unstable isomer. Alternatively, other molecules (solvent, impurities, or the irradiated species) could participate in the primary step of the conversion. In order to avoid at this stage any mechanistic implications, we prefer to use the most general terminology rather than refer to processes of a more limited scope, such as nonradiative transition, internal conversion, etc.

(26) In light of these observations no great differences in  $\Phi_f$  are expected in nonpolar, or nonhydrogen-bonding, solvents between **4** and **5** and compounds derived from **4** by substitution with a phenyl in the 4 or 5 position. In agreement with our results are the literature data for the following ( $\lambda_{exc} = 313$  nm): 1,3,4-triphenyl- $\Delta^2$ -pyrazoline in polystyrene,  $\Phi_f = 0.76$ ,  $\lambda_f = 436$  nm;<sup>10,11</sup> 1,3,5-triphenyl- $\Delta^2$ -pyrazoline in polystyrene,  $\Phi_f = 0.74$ ,  $\lambda_f = 436$  nm; and in dioxane,  $\Phi_f = 0.76$ ,  $\lambda_f = 436$  nm.<sup>12,13</sup> Higher figures are reported for 1,5-diphenyl-3-(*p*-methoxyphenyl)- $\Delta^2$ -pyrazoline,  $\Phi_f = 0.84$  in polystyrene.<sup>5</sup>

(27) It has been observed by other authors<sup>28</sup> that formation of a hydrogen bond from the solvent to the fluorescent  $\pi$  system quenches the fluorescence. However, fluorescence is enhanced when the hydrogen bond outside the  $\pi$  system is formed.

(28) N. Mataga and S. Tsuno, *Bull. Chem. Soc. Japan*, **30**, 711 (1957); G. Tomita, *Z. Naturforsch.*, **23b**, 922 (1968).

**Table III.** Calculated Lifetimes, Actual ( $\tau$ ), Radiative ( $\tau_0$ ), Nonradiative ( $\tau_{nr}$ ), and Molar Absorptivities ( $\epsilon_{max}$ ) of Pyrazolines in Cyclohexane and Isopropyl Alcohol

Compound	$\tau$ , nsec		$\tau_0$ , nsec		$\tau_{nr}$ , nsec		$10^{-3}\epsilon_{max}^a$	
	C <sub>6</sub> -H <sub>12</sub>	<i>i</i> -Pr-OH	C <sub>6</sub> -H <sub>12</sub>	<i>i</i> -Pr-OH	C <sub>6</sub> -H <sub>12</sub>	<i>i</i> -Pr-OH	C <sub>6</sub> -H <sub>12</sub>	<i>i</i> -Pr-OH
<b>4</b>	3.4	3.2	4.3	6.1	15	6.6	20.5	19.7
<b>5</b>	3.4	4.6	4.4	6.6	15	15	22.3	21.6
<b>6</b>	4.4	5.9	4.8	6.3	61	95	20.2	19.3
<b>7</b>	3.0	3.8	4.1	5.5	11	12	23.8	22.8
<b>8</b>	3.4	5.3	4.4	6.1	16	40	22.5	21.3
<b>9</b>	4.3	4.4	6.1	6.0	15	17	15.5	21.4
<b>10</b>	3.4	4.7	4.2	5.6	18	32	22.8	22.3
<b>11</b>	4.0	5.1	4.9	6.1	23	31	21.1	20.65
<b>12</b>	...	4.6	...	6.1	...	19	...	20.55

<sup>a</sup> The wavelengths of  $\epsilon_{max}$  are reported in the second and third columns of Table I.

known the experimental  $\tau$  or  $\tau_0$  can be compared with the calculated figures. Such a comparison has been done on eight compounds by Ware and Baldwin.<sup>29</sup> They found that the figures calculated from the Strickler and Berg equation<sup>23</sup> are usually lower than the experimental data and that the difference may be as high as 29%. Our data are probably reliable within similar limits (see, however, footnote 18).<sup>30</sup>

In essence, the calculated lifetimes  $\tau_0$  and  $\tau_{nr}$  reflect our experimental observation that, in a given solvent, the substitution of **4** has relatively little effect on the molar absorptivity, except for **9** in cyclohexane, but significantly influences the intensity of fluorescence. Consequently, except for **9** in cyclohexane, the  $\tau_0$  figures do not change appreciably and the gross changes in  $\tau_{nr}$  follow a similar pattern to changes in  $\Theta$ , indicating that fusion of **4** to the norbornane ring hinders principally the nonradiative deactivation and that the introduction of a second substituent in **6** has the opposite effect. Isopropyl alcohol somewhat reduces the rate of fluorescence,  $1/\tau_0$ . In the case of **4**, it facilitates the nonradiative transition, but in **8**, **10**, and **11** it tempers the accelerating influence of the second substituent on the latter. The hydroxy substituent in **9** also reduces the rate of fluorescence.

In summary, polarity and/or hydrogen-bonding ability of the solvent, rigidity of the molecule, and the presence of the second substituent in the 5 position of the pyrazoline affect the wavelengths of the absorption maxima, but only the influence of the solvent and of the second substituent can be recognized in changes in the position of the very broad fluorescence bands. These three factors have little effect on the molar absorptivity (compound **9** in cyclohexane is an exception) in contrast to their effect on the intensity of fluorescence. Consequently, the influence of these factors is correspondingly manifested in the changes in quantum yields of fluorescence, in calculated radiative and nonradiative lifetimes and, since the compounds are photochemically stable, in the ratio of quanta converted into thermal energy to quanta emitted as light.

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(29) H. R. Ware and B. A. Baldwin, *J. Chem. Phys.*, **40**, 1703 (1964).

(30) We have not detected in the emission spectra any additional peaks indicative of a contribution of phosphorescence to the fluorescence.