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Fluorescence Spectral Study of Wavelength Shifters for Scintillation Plastics*

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An investigation of the fluorescence spectra of a series of 1,3,5-triaryl-2-pyrazoline indicated that substituents in the 3-phenyl ring shifted the fluorescence emission wavelength linearly with Brown's σ_p^+. On the basis of this evidence the excited state is thought to have a partial positive charge located on carbon-3 of the pyrazoline ring. The shift in the absorption spectral bands of 1,3,5-triphenyl-2-pyrazoline with concentration is presented as evidence of a dimer or an associated complex. The fluorescence quenching at higher concentrations may be due to the energy dissipating effect of the dimers or complexes. The high extinction coefficient of the uv maximum and yet the similarity of the fluorescence intensity of 4,4′-bis-[5-(1,3-diphenyl-2-pyrazolinyl)] benzene to 1,3,5-triphenyl-2-pyrazoline is explained on the basis of an internal quenching mechanism. The efficiency of these two compounds as wavelength shifters in plastic scintillators are approximately equal.

INTRODUCTION

In an effort to achieve a more efficient wavelength shifter for scintillation plastics the effect on the fluorescence light output and fluorescence wavelength was studied as substituents were varied in the 1,3,5-triaryl-2-pyrazolines.[1] An attempt was made to elucidate the mechanism of fluorescence in the compounds.

EXPERIMENTAL[2]

The fluorescence spectra were recorded on an Aminco Bowman spectrophotofluorometer equipped with a xenon light source and an x–y recorder.

All solvents were of spectrograde purity, and a blank was subtracted from the values of the intensity in the final fluorescence spectrum.

The 2-pyrazolines were synthesized as previously described[1] and were purified by repeated recrystallizations before use.

7-Diethylamino-4-methyl coumarin was obtained from Eastman Organic Chemical Company, and was recrystallized from $\frac{1}{3}$ petroleum ether (30°–60°) and $\frac{2}{3}$ heptane by volume.

Preparation of 1,5-diphenyl-3-p-bromophenyl-2-pyrazoline. To a flask containing 10.0 g (0.035M) of benzal-p-bromoacetophenone was added 100 ml of glacial acetic acid and 5.0 g (0.046M) phenylhydrazine. The mixture was heated 3–4 h on a water bath. The product was isolated in 61% yield (8.0 g), mp 149°–153°, $\lambda_{\max}^{\mathrm{CH_3OH}}$ 360 mμ, $\epsilon_{\max}$ 20 500.[3] Analysis calculated for $C_{21}H_{17}BrN_2$: C, 66.7%; H, 4.51%; N, 7.43%. Found: C, 67.02%; H, 4.69%; N, 7.40%.

Preparation of terephthalacetophenone. To a flask containing 179 g (1.49M) of acetophenone was added a solution of 90 g of sodium hydroxide in a mixture of 800 ml water and 400 ml of methanol. Following the sodium hydroxide solution, there was added 100 g terephthalaldehyde (0.746M, Aldrich Chemical Co.) in 100 ml of methanol, and the flask was cooled to 15°–30°. The reaction mixture was stirred for 3–4 h and then the product was isolated in 56% yield, mp 176°–188°. Analysis calculated for $C_{24}H_{18}O_2$: C, 85.1%; H, 5.32%. Found: C, 86.03%; H, 5.57%.

Preparation of 4,4′-bis-[5(1,3-diphenyl-2-pyrazolinyl)]-benzene. To a round-bottom flask containing 5.0 g (0.015M) terephthalacetophenone and 500 ml glacial acetic acid was added 5.0 g phenylhydrazine (0.046M). The mixture was heated for 5–6 h on a water bath. During the initial heating period the contents dissolved and after continued heating the product precipitated as it formed. The product was isolated in 66% yield (5.0 g), mp 263°–267°,

$$\lambda_{\max}^{\mathrm{C_6H_6}} 360\ \mathrm{m}\mu, \qquad \epsilon_{\max} 43\,500.$$

Analysis calculated for $C_{36}H_{30}N_4$: C, 83.4%; H, 5.8%; N, 10.8%. Found: C, 82.96%; H, 5.94%; N, 10.74%.

9-Vinylanthracene.[4] The reduction of 9-anthrylmethylketone (from anthracene, acetyl chloride, and aluminum chloride in 62% yield) with methanolic sodium borohydride containing some sodium hydroxide gave 9-anthrylmethylcarbinol in 96% yield, mp 123°–124°. The dehydration of 9-anthrylmethylcarbinol by means of potassium bisulfate at 200°–230° yielded 9-vinylanthracene in 36% yield (mp 61°–65°).

RESULTS

The fluorescence spectral results of the substituted 2-pyrazolines are presented in Table I. Other wavelength shifters are shown in Table II where the efficiency of 9-vinyl anthracene[5] and 7-diethylamino-4-

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[1] S. R. Sandler, S. Loshaek, E. Broderick, and K. C. Tsou, J. Phys. Chem. **66**, 404 (1962).

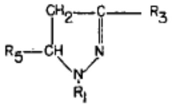
[2] The chemical analyses were performed by S. M. Nagy, Microchemical Laboratory, 78 Oliver Road, Belmont, Massachusetts.

[3] UV spectra determined by J. Kaczaj.

[4] E. G. E. Hawkins, J. Chem. Soc. **1957**, 3858.

[5] While this work was in progress a paper appeared describing the use of 9-vinyl anthracene as a wavelength shifter in liquid scintillators by A. Heller, J. Chem. Phys. **35**, 1980 (1961), and A. Heller and D. Katz, *ibid.*, p. 1987.

TABLE I. Scintillation and spectral[1] characteristics of 2-pyrazolines.



R_1	R_3	R_5	$\lambda_{A\ max}$ mμ	ϵ_{max}[f]	λ_f mμ	I_f[a]	I[b] at 440	I_{max} at λ_f	Conc. at[c] $I_{max}\times10^6$ g/cc	Relative pulse height (RPH) ±2 at 0.05%
C_6H_5	C_6H_5	C_6H_5	355	16 950	440	32	36	100	3.0	51
C_6H_5	CH_3	C_6H_5	276	11 720	390	2	0.16	2	1.0	22
			358	...						
C_6H_5	$—CH{=}CH—C_6H_5$	C_6H_5	380	8 670	460	58	35	100	2.0	41
C_6H_5	$CH_3O—C_6H_4$	C_6H_5	350	18 600	432	36	37	100	4.6	50
C_6H_5	$CH_3—C_6H_4$	C_6H_5	358	11 300	438	31	34	100	8.0	51
C_6H_5	$Cl—C_6H_4$	C_6H_5	360	15 800	448	45	38	100	4.0	52
$C_6H_4NO_2$	C_6H_5	C_6H_5		...	475	3	0.9	100	8.0	0
$C_6H_4CH_3$	C_6H_5	C_6H_5	359	16 700	452		32	100	4.1	51
C_6H_5	$CH_3—C_6H_4$	$(CH_3)_2N—C_6H_4$		...						
			352	15 700	439	46	43	100	4.0	51
C_6H_5	C_6H_5	CH_3	358	20 400	440	45	51	100	2.5	51
C_6H_5	$Br—C_6H_4$	C_6H_5	360	20 500	445	32		100	4.5	51
C_6H_5	C_6H_5	e	360	43 500[g]	443	45		100	1.8	52

[a] 3.36×10^{-6} moles/liter in benzene. The intensity is in arbitrary units.
[b] 3.5×10^{-6} moles/liter in benzene.
[c] Extrapolated from concentration vs intensity data.
[d] R.P.H. for polyvinyl toluene plastic scintillators containing 3% *p*-terphenyl and 0.05% of the 2-pyrazoline.
[e] 1,3-Diphenyl-2-pyrazolinyl group.
[f] In methanol.
[g] In benzene.

methyl coumarin[6] are shown to be almost as good as POPOP. In Fig. 1 the Hammett substituent constant σ_p is plotted against $\Delta\lambda_f(440-\lambda_f)$. A linear correlation is obtained. The results are also plotted against Brown's[7] $\sigma_p{}^+$ and Taft's[8] σ_R and σ_I in Figs. 2, 3, and 4, respectively. Figures 5 and 6 contain a plot of σ_p vs

TABLE II. Scintillation and spectral characteristics of various wavelength shifters.

Compound	λ_{max}[a]	λ_f	I[b] at 440	I_{max} at λ_f	Conc. at[c] $I_{max}\times10^{-6}$ g/cc	RPH±2
9-Vinyl anthracene[d]	360	430	15	100	7.5	50[d]
POPOP or 1,4-di-2-(5-phenyloxazoylyl) benzene	360	415	75	100	1.3	48
Dimethyl POPOP	360	428	85	100	1.0	48
4,4′-Diphenylstilbene	340	410	36	100	2.0	50
7-Diethylamino-4-methyl coumarin	358	408	43	100	3.5	44

[a] Major absorption is listed only. The spectra were taken in chloroform.
[b] The intensity of λ_f at 3.5×10^{-6} moles/liter in benzene. The intensity is measured in arbitrary units.
[c] Extrapolated from concentration vs intensity curves.
[d] Wavelength shifter for scintillation liquids.

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[6] A. Coche, R. Henck and G. Lanstriat, Compt. Rend. **247**, 2123 (1958).
[7] H. C. Brown and Y. Okamoto, J. Am. Chem. Soc. **80**, 4979 (1958).
[8] R. W. Taft in *Steric Effects in Organic Chemistry*, edited by M. Newman (John Wiley & Sons, Inc., New York, 1956), Chap. 13.

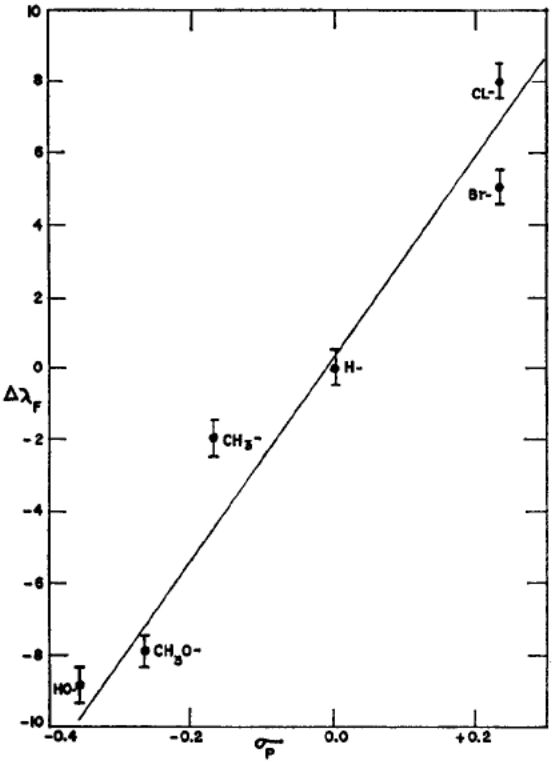

FIG. 1. The change in wavelength of fluorescence of 1,3,5-triphenyl-2-pyrazolines with varying substituents in the *para* position of the 3-phenyl ring vs the Hammett substituent constant σ_p.

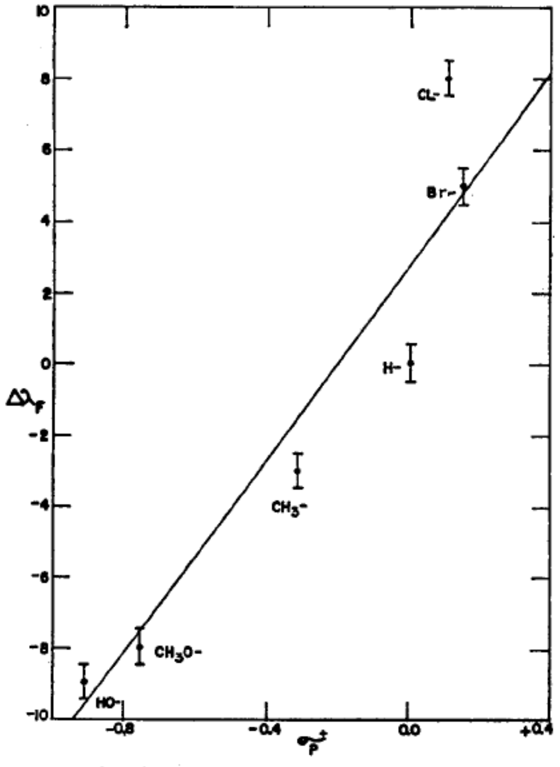

FIG. 2. The change in wavelength of fluorescence of 1,3,5-triphenyl-2-pyrazolines with varying substituents in the *para* position of the 3-phenyl ring vs Brown's substituent constant σ_p^+.

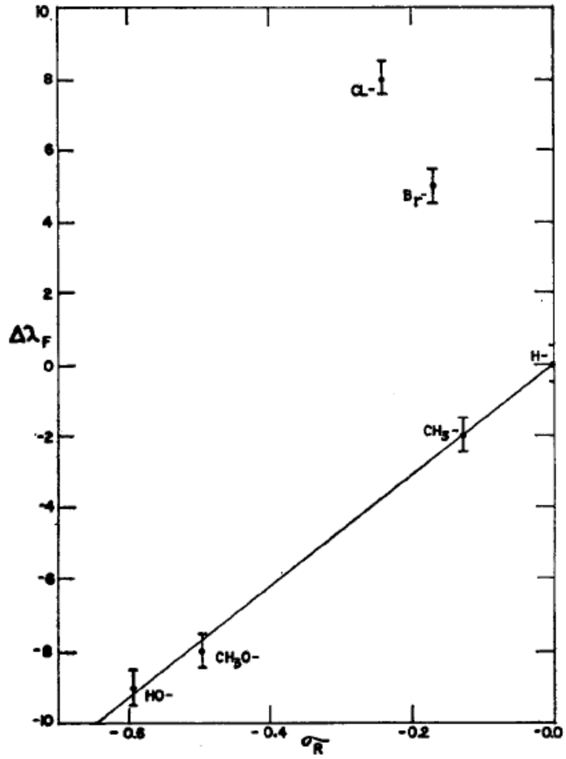

FIG. 3. The change in wavelength of fluorescence of 1,3,5-triphenyl-2-pyrazolines with varying substituents in the *para* position of the 3-phenyl ring vs Taft's substituent resonance constant σ_R.

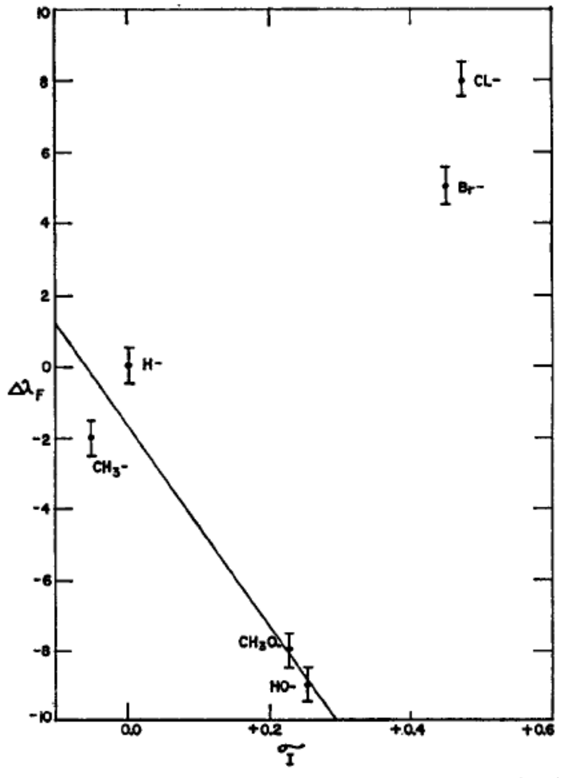

FIG. 4. The change in wavelength of fluorescence of 1,3,5-triphenyl-2-pyrazolines with varying substituents in the *para* position of the 3-phenyl ring vs Taft's substituent inductive constant σ_I.

$\Delta\lambda_f$ for the 5-substituted aryl-2-pyrazolines whose values of λ_f are taken from the literature.[9] This correlation is opposite to that found for the 3-substituted aryl-2-pyrazolines. A suggested explanation of the effect is found in the discussion of the results.

Hyperconjugation of the 3-methyl groups in 1, 5-diphenyl-3-methyl-2-pyrazoline and its absorption at 358 mμ. has been an unsettled question in the literature. Wiley[9] recently reported that 1, 5-diphenyl-3-methyl-2-pyrazoline exhibited fluorescence that was too weak to measure. However, Neunhoeffer[10] mentioned that the 3-methyl-2-pyrazoline showed absorption at 358 mμ and fluorescence probably as a consequence of hyperconjugation. In an attempt to settle this discrepancy the fluorescence characteristics of 1,5-diphenyl-3-methyl-2-pyrazoline was examined in detail.

The scintillation properties of 4,4′-bis[5(1,3-diphenyl-2-pyrazoline)]-benzene and 1,3,5-triphenyl-2-pyrazoline are compared to each other in Table I at 0.05% concentration.

Fluorescence quenching data are presented in Fig. 9 for 1,3,5-triphenyl-2-pyrazoline and the effect of concentration on the position of the absorption bands are shown in Fig. 10.

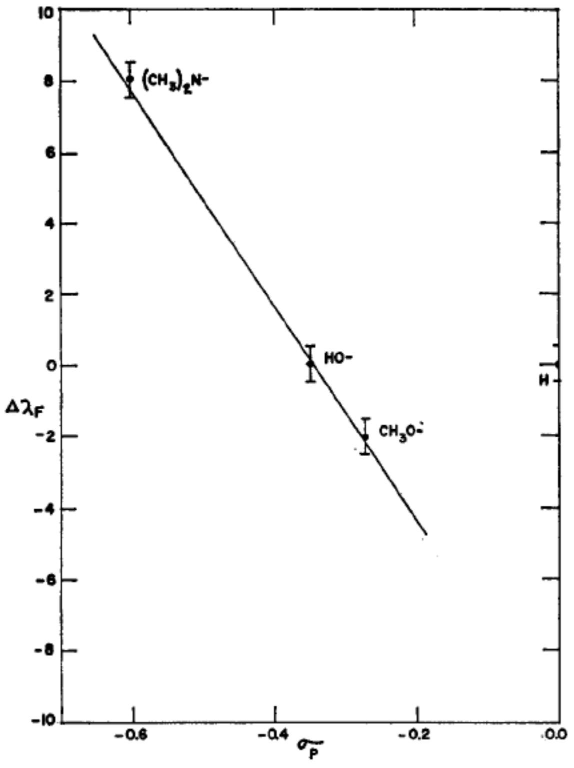

FIG. 5. The change in wavelength of fluorescence of 1,3,5-triphenyl-2-pyrazolines with varying substituents in the *para* position of the 5-phenyl ring vs the Hammett substituent constant σ_p.

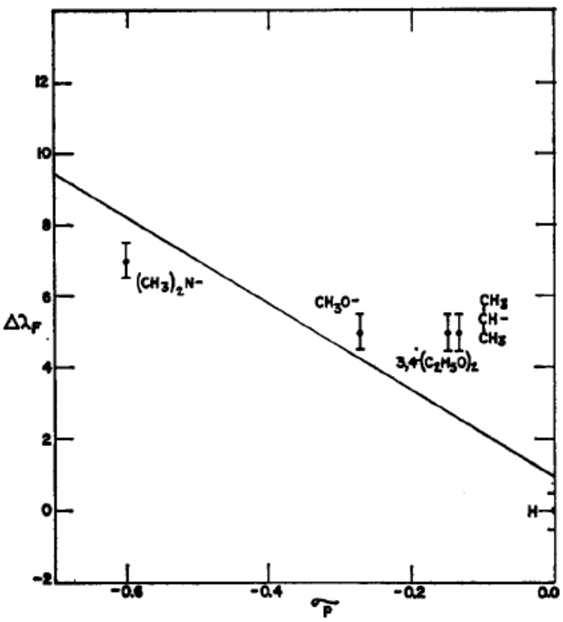

FIG. 6. The change in fluorescence wavelength of 1-phenyl-3-biphenylyl-5-phenyl pyrazoline with varying substituents in the *para* position of the 5-phenyl ring vs the Hammett substituent constant σ_p.

DISCUSSION

The wavelength shifter has the function of absorbing the energy from the excited state of the fluor and re-emitting it at a longer wavelength, usually 430–450 mμ. An increase in the intensity of fluorescence (quantum efficiency) at these wavelengths should lead to an increase in the efficiency of the scintillator.

From the results in Table I it is seen that absorption of energy at 350–360 mμ, and a 3-phenyl group is essential for fluorescence emission at 430–450 mμ. The 5-phenyl group has very little effect on these processes. Duffin and Kendall[11] have shown that the 1-phenyl-2-pyrazolines (without a 3-phenyl group) do not absorb at 350–360 mμ but absorb at 240–280 mμ. The 1-phenyl group is essential to prevent air oxidation for 2-pyrazolines such as 3-phenyl-2-pyrazoline, 3,4,5-triphenyl-2-pyrazoline and 1,5-dimethyl-3-phenyl-2-pyrazoline.[12] Substituents in the 4 and 5 positions have very little effect on the spectral and wavelength-shifting properties of 1,3,5-triphenyl-2-pyrazoline.[2] The 3-styryl and 1-nitro derivatives are not suitable wavelength shifters from the standpoint of λ_A and λ_F. The 1-nitro group is a quencher of fluorescence as is found in other molecules containing a nitro group.[13] On the basis of these results

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[11] G. F. Duffin and J. D. Kendall, J. Chem. Soc. **1954**, 408.

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[13] P. Pringsheim *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949).

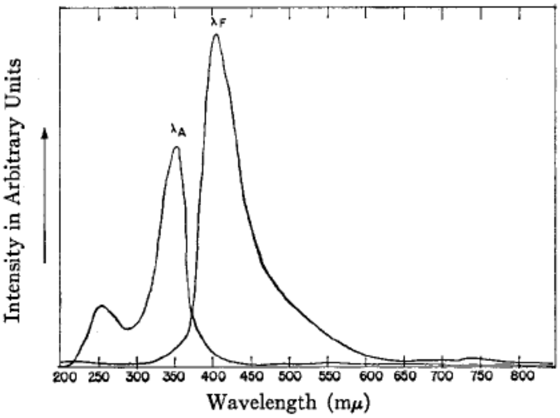
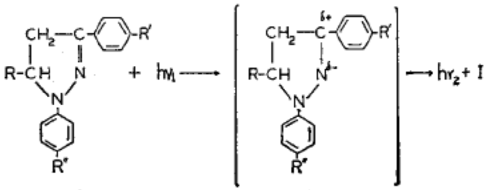


FIG. 7. The fluorescence activation and emission spectrum of 1,5-diphenyl-3-methyl-2-pyrazoline in chloroform at 4.7×10^{-6}g/cc concentration.

the excited state of 1,3,5-triaryl-2-pyrazoline is suggested to be the following:



I

Ia

R is phenyl or methyl, R′ is hydrogen, methyl, methoxy, chlorine or bromine, and R″ is hydrogen, methyl or nitro. According to the proposed excited state I (a) electron withdrawing groups at R′ in the 3 position should enhance the probability of formation of I (a) and have an effect on the $\delta+$ value on the 3-carbon atom. The 3-substituents affect the $\Delta\lambda_f$ value (Fig. 2) in such a way that they correlate well with Brown's σ_p^+ value. These results suggest that the excited state I (a) has some positive character in which the 3-substituents have a direct effect.

From the results of Fig. 1 it is interesting to observe that electron donating groups on the 3-phenyl ring decreases the wavelength of fluorescence whereas electron withdrawing groups increase the wavelength of fluorescence. The latter effect cannot be attributed to the increased resonance or induction since resonance or inductive sigma values alone do not correlate with $\Delta\lambda_f$ (Figs. 3 and 4). However, σ_p which is a composite of inductive, resonance and steric contributions correlates well as seen in Fig. 1. The 5-phenyl group which has no effect on the wavelength shifting efficiency shows the opposite effect as seen in Figs. 5 and 6. The latter result is not unusual for similar substitutions on an isolated aromatic ring. The fact that the 3-position is affected so greatly as to reverse the usual effect indicates its strong effect in the transition state.

Although resonance is not the prodominant factor it is still important in its effect on the absorption characteristics of the 3-substituted 2-pyrazolines. Substituting a 3-methyl group for a phenyl group causes a drastic decrease to weak absorption at 358 mμ which is probably due to hyperconjugation in the case of methyl as suggested by Neunhoeffer. Figure 7 shows the absorption and fluorescence spectra of 1,5-diphenyl-3-methyl-2-pyrazoline.

From the standpoint of achieving a more efficient wavelength shifter by substitution of an appropriate group in the aromatic ring attached to the 3-position we were not successful. This investigation indicates that substituents differing greatly in their ability to donate or withdraw electrons in the 3-position have very little effect on the efficiency as a wavelength shifter in polyvinyl toluene (PVT) scintillators. Figure 8 shows the results of a plot of the Hammett σ_p for the 3-aryl substituent vs the fluorescence intensity at 440 mμ (see Table I) and also the percent RPH of the PVT scintillators.[2] The fact that the range of fluorescent wavelengths vary only from 430–450 mμ may be the explanation for their similar efficiency since the spectral sensitivity curve of the 6199 RCA phototube used for the evaluation of the scintillators is maximum at these wavelengths. The relatively flat portion in the 430–450 mμ range would give equal sensitivity in this wavelength range for compounds with similar quantum yields of fluorescence. However, if the quantum yield of fluorescence of these compounds can be increased in the range of 430–450 by suitable substitution, then the efficiency of the wavelength shifter should be increased. 4,4′bis-[5-(1,3-diphenyl-2-pyrazolinyl)] benzene was therefore prepared and was found to have indeed a much higher extinction coefficient in the ultraviolet absorption spectrum when compared to 1,3,5-triphenyl-2-pyrazoline (Table I). However, there was very little increase in fluorescence in the former compound, and as a result no increase in relative pulse height was observed. This behavior of 4,4′-bis-[5-(1,3-diphenyl-2-pyrazolinyl)] benzene is explained by "internal quench-

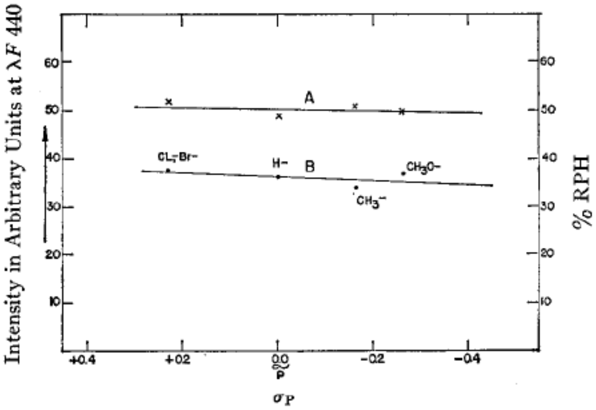
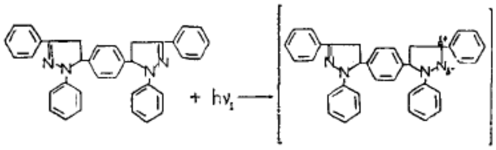


FIG. 8. (a) The relative pulse height of a series of 1,3,5-triphenyl-2-pyrazoline with varying substituents in the *para* position of the 3-phenyl ring vs σ_p, and (b) the fluorescence intensity of the latter series vs σ_p.

ing" which causes the excitation to be degraded to a nonfluorescence state. Such quenching has the same over-all result as concentration quenching in 1,3,5-triaryl-2-pyrazoline which is almost ½ in size of the 4,4′-bis-[5(1,3-diphenyl-2-pyrazolinyl)]-benzene molecule—as is shown in Fig. 9. The excited states that are possible for the latter molecule can be described as follows:



$(W-W)$ $(W-W^*)$ (1)

$$W-W+W-W\rightarrow W^*-W+W^*-W, \quad (2)$$

$$W-W+W-W+h\nu_1\rightarrow W^*-W^*+W-W, \quad (3)$$

$$W^*-W\rightarrow W-W, \quad (4)$$

$$W^*-W\rightarrow h\nu_2+W-W, \quad (5)$$

$$W-W^*+W-W^*\rightarrow W-W+W^*-W^*, \quad (6)$$

$$W^*-W^*\rightarrow W-W, \quad (7)$$

$$W^*-W^*\rightarrow h\nu_3+W-W, \quad (8)$$

$$W-W+W^*-W^*\rightarrow 2W-W. \quad (9)$$

Quenching by internal conversion of the excitation can occur in Steps (4), (7), and (9), whereas transfer occurs in Steps (6), and excitation in Steps (1), (2), and (3). In 1,3,5-triaryl-2-pyrazoline only one excited state as Step (1) (see proposed transition state Ia) is possible, and internal conversion probably occurs to a lesser extent than for $W-W$ shown above.

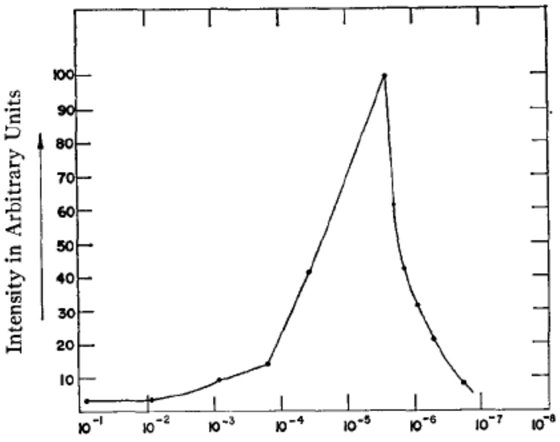


FIG. 9. The intensity of fluorescence vs concentration for 1,3,5-triphenyl-2-pyrazoline in benzene.

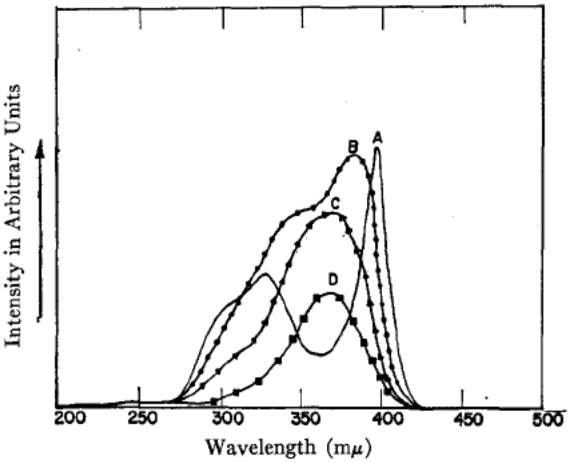
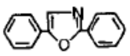


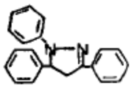
FIG. 10. The fluorescence activation spectra of 1,3,5-triphenyl-2-pyrazoline at varying concentrations in benzene (a) 6.27×10^{-5} g/cc; (b) 2.50×10^{-6} g/cc; (c) 1.00×10^{-6}g/cc; and (d) 4.00×10^{-7} g/cc.

Concentration changes have no effect on the position of the fluorescence wavelength of 1,3,5-triphenyl-2-pyrazoline; however, the absorption spectrum at 6.27×10^{-5} g/cc has two peaks, one at 332 mμ and the other at 402 mμ. The absorption bands disappear at 1.00×10^{-5} g/cc and only one peak appears at 370 mμ. These results are shown in Fig. 10.

This wavelength shift may be due to the formation of dimers at higher concentrations as was found by Berlman[14] and Weinreb[15] for the 2,5-diphenyl-1,3-oxazole (PPO) in cyclohexane and in benzene. The oxazole (PPO) (A) has structural features resembling the 1,3,5-triaryl-2-pyrazolines (B) when pictured as follows:



(A)



(B)

ACKNOWLEDGMENT

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