

Photocyclization of Aryl Halides. Part 4.¹ 5-(2-Halogenophenyl)-1,3-diphenyl- Δ^2 -pyrazolines. Predissociation and Electron Transfer between Intramolecular but Separate Chromophores

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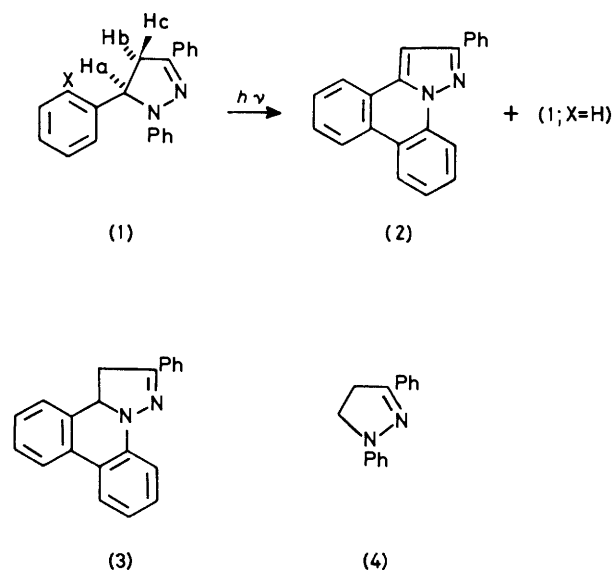
Photoreaction of 5-(2-iodophenyl)-1,3-diphenyl- Δ^2 -pyrazoline proceeds by simple bond homolysis from the S_1^0 state to give 1,3,5-triphenylpyrazoline and 2-phenylpyrazolo[1,5-*f*]phenanthridine in a ratio which depends on the hydrogen atom donor ability of the hydrocarbon solvent. The quantum yield for decomposition of the iodo-compound depends on the viscosity of the hydrocarbon solvent and on the temperature. The corresponding chloro- and bromo-compounds as well as the 3-iodo- and 4-iodo-phenyl compounds are photostable. Consideration of these facts and the complementary fluorescence data suggests a mechanism of interchromophoric predissociation to an $n\sigma^*$ state. However, examples are given where there is a smaller electron donor-acceptor energy gap between the two chromophores so that photoreaction occurs by an electron transfer pathway.

In Part 1² we considered the photochemical behaviour of 5-(2-halogenophenyl)-1,3-diphenylpyrazoles. Now we examine their precursor Δ^2 -pyrazolines (1). The halogenobenzene moiety in these substrates is insulated from the long wavelength pyrazoline chromophore which makes them interesting examples of a bichromophoric system.³ Also, the 1,3-diphenylpyrazoline system shows a strong fluorescence which has been exploited in optical brighteners.⁴ This fluorescence presents an additional probe to aid study of photoreactivity while new means for influencing and controlling the fluorescence emission would be of some commercial importance.

Spectroscopy.—Conjugation in the 1,3-diphenyl- Δ^2 -pyrazoline system raises the energy barrier to torsion about the nitrogen-phenyl bond so that any steric strain introduced upon *ortho*-substitution by the X group will be taken up by rotation of the halogenobenzene ring about the connecting single bond rather than by distorting the components of the pyrazoline chromophore. This reorientation of the halogenobenzene ring would influence the deshielding effect at the pyrazoline ring proton in the 5-position.⁵ The n.m.r. data for compounds (1) (Table 1) bears out this suggestion that the halogenobenzene ring is made more orthogonal to the plane of the heterocycle upon *ortho*-substitution. The principal u.v. chromophore is hardly affected by such substitution.

The series of halogen derivatives (1; X = Cl, Br or I) provides fundamental information on the heavy atom perturbation effect where the heavy atom is with the same molecule but not attached to the chromophore. Previous studies in this area⁶ examined the significant heavy atom effect on $\pi\pi^*$ states. In complete contrast, for our system at 80 K the effect is negligible. The 1,3-diphenylpyrazoline chromophore is known to be excited by an internal charge-transfer transition⁷ and this class appears to be immune to the heavy atom effect when the perturbing atom is attached to the chromophore.⁸ For the present examples also no perturbation of the fluorescence is detectable as a result of extra chromophoric substitution by halogen. Therefore it appears that internal charge-transfer states behave differently to $\pi\pi^*$ states with regard to the heavy atom effect.

Preparative Photochemistry.—Only (1; X = I) reacted at a rate significant from a preparative point of view. When irradiated in deaerated cyclohexane at its longest wavelength absorption band the iodo-compound gave a mixture of the cyclised pyrazole (2), 39% yield, and the parent pyrazoline (1; X = H), 24% yield. The bromo-compound (1; X = Br)



reacted slowly to give (2) identified by t.l.c. and a second unidentified product with M^+ 392 and containing bromine. The chloro-compound gave pyrazoles only upon prolonged irradiation. Photochemical dehydrogenation of 1,3,5-triphenylpyrazoline is known to proceed both in the presence of⁹ and without oxidants.¹⁰ Thus formation of the pyrazole (2) during the above photochemical reactions is to be expected. Other workers¹¹ have noted dehydrogenation following photocyclization reactions. No photoproducts arising from pyrazoline ring fission⁹ were found during any of the present experiments.

Photochemical Kinetics.—A systematic examination was made of the effect of photochemical variables on the fluorescence properties of pyrazolines and on the reaction quantum yield. Quantum yield measurements were made under conditions of low conversion when all the light is absorbed by the starting material in order to avoid interference from any subsequent photochemical dehydrogenation. Dehydrogenation of (3) to (2) occurs on work-up after exposure to air.

Effect of Additives.—Quantum yield data are summarized in Table 2. Quantitative confirmation was obtained of the nearly

Table 1. Spectroscopic data

		(4)	Pyrazoline (1) X =				
			H	OMe	Cl	Br	I
U.v. absorption (cyclohexane)	$\lambda_{\max.}/\text{nm}$	239	238	237	236	236	243
	$\epsilon_{\max.}/10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$	1.10	1.34	1.30	1.44	1.48	1.46
	$\lambda_{\max.}/\text{nm}$	357	360	360	357	358	358
N.m.r. (CDCl_3) ^a	$\epsilon_{\max.}/10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$	1.94	1.97	2.01	2.03	2.05	1.84
	δ_a		5.23	5.63	5.66	5.63	5.50
	δ_b		3.82	3.93	3.97	3.98	4.02
	δ_c		3.07	3.02	3.02	3.03	2.98
Fluorescence ^b (EtOH, 80 K)	$\lambda_{\max.}/\text{nm}$	{ 416 428	414	414	412	412	412
	Rel. intensity (1; X = H) is 1.0	1.0	1.0	1.2	1.0	0.9	1.2

^a In all cases J_{ab} 12, J_{ac} 8, J_{bc} 18 Hz. ^b Excitation at 350 nm. Leaver¹² gives for (4), $\lambda_{\max.}$ 415 and 437 nm. For (1; X = I), E_s 290 kJ mol⁻¹.

Table 2. Compound (1; X = I) irradiated at 370 nm in cyclohexane deoxygenated by freeze-pump-thaw cycles. $I_{\text{abs}} 1.3 \times 10^{-4} \text{ E l}^{-1} \text{ h}^{-1}$

Additive	Quantum yield ^a for		
	loss of (1; X = I)	formation of (1; X = H)	(2)
None	0.13	0.042	0.051
0.17M-Cyclohexadiene	0.15	0.037 ^b	0.024 ^b
0.20M-Piperylene	0.17	0.031	0.044
Oxygen (atmospheric)	0.12	0.034	0.046
0.04M-Michler's ketone ^c		6×10^{-4}	0.003

^a Under identical conditions (1; X = Br or Cl) gave no detectable reaction. ^b Another unidentified product was detected by h.p.l.c. ^c The solvent was benzene with irradiation at 405 nm. Some direct absorption by (1; X = I) was evidenced by a weak blue fluorescence.

specific photoconversion of (1; X = I) into a mixture of (2) and (1; X = H). The chloro- and bromo-compounds gave no detectable reaction.

A search for possible triplet quenching by cyclohexadiene or piperylene was undertaken although it was realised that the pyrazoline T_1 state (for 1,3-diphenylpyrazoline E_T 184 kJ mol⁻¹)¹² is of such low energy that no quenching can be expected. In fact a small enhancement of the quantum yield for disappearance of (1; X = I) in the presence of the additive was observed. This appears to be another example of quencher-enhanced fission rate.¹³ Fission is enhanced and further products are found, probably from reaction between radicals and the additive. Quenchers of the diene type have polarizable π -clouds and we have suggested before that such rate enhancements can be the result of the assisted homolysis model with complexation between the diene and the developing radical centres of the excited aryl halide.²

Michler's ketone, which has a strong absorption in the u.v. region, has a low triplet energy (E_T 260 kJ mol⁻¹)¹⁴ but is still capable of transferring triplet energy to the pyrazoline T_1 state and so can act as a triplet sensitizer. However, it failed to induce any significant reaction probably due to the very low E_T relative to the carbon-iodine bond dissociation energy¹⁵ of 267 kJ mol⁻¹. We conclude that the reactive state for the pyrazoline is its S_1 state. Atmospheric oxygen exerts a small quenching effect consistent with previous observations that the S_1 state of 1,3-diphenylpyrazolines is sufficiently long lived to be quenched noticeably by air.¹⁶

The quantum yields (see Table 3) show no effect of varying concentration of (1; X = I), implying a totally intramolecular

Table 3. Compound (1; X = I) irradiated at 370 nm in cyclohexane under air. $I_{\text{abs}} 1.3 \times 10^{-4} \text{ E l}^{-1} \text{ h}^{-1}$

10 ⁴ Concentration (M)	Quantum yield for formation of	
	(1; X = H)	(2)
2.4	0.033	0.050
4.7	0.034	0.047
14.1	0.034	0.048
47.0	0.039	0.049

reaction, although Leaver¹² noted association phenomena for pyrazolines in aliphatic hydrocarbon solution at 80 K.

The observed photochemical reaction involves absorption of energy by the pyrazoline chromophore and then its transfer to the 2-iodophenyl substituent. It was therefore of interest to examine the influence of halogen-containing additives in particular on the fluorescence of pyrazolines and the results are given in Table 4.

The reduced efficiency of fluorescence quenching by ethanol and by halogen-containing additives upon 1,3,5-triphenylpyrazolines (1) compared to (4) can be attributed to steric influences which interfere with solvation of the chromophore. *ortho*-Substitution of the 5-aryl ring causes a further decrease in the fluorescence quenching effect of tetrachloromethane. Quenching of 1,3-diphenylpyrazoline fluorescence by tetrachloromethane appears to be diffusion controlled since, taking the fluorescence lifetime of 1,3-diphenylpyrazoline¹² as 4.2 ns and using the data from Table 4 in a Stern-Volmer relationship, the rate constant for the quenching process is calculated as $0.5 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. This compares favourably with the rate constant¹⁴ for a diffusion-controlled process in cyclohexane of $1.0 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

The effectiveness of a given halide quencher parallels its reduction potential, suggesting that the act of quenching involves electron transfer to the halide. The appropriate irreversible polarographic half-wave reduction potentials,¹⁷ each determined under the same conditions, are tetrachloromethane -0.78 V, iodobenzene -1.62 V (as a model for 2-iodotoluene), and iodoethane -1.67 V.

Russian workers¹⁸ have reported on the irradiation in tetrachloromethane solution of 1,3,5-triphenyl- Δ^2 -pyrazoline to give the pyrazole. However, in our hands similar irradiation of (1; X = I) under carefully degassed conditions gave only intractable mixtures with no detectable pyrazole formation. In what may be regarded as related reactions involving simple electron transfer, pyrazoles can be obtained by oxidation of

Table 4. Relative fluorescence intensity for some pyrazolines in aerated cyclohexane at 20 °C, without (I_0) and in the presence (I_A) of additives

	Fluorescence parameter ^a	(4)	Substance under examination (1) where X =				
			H	OMe	Cl	Br	I
None	I_0^b	1.0	0.9	0.9	0.9	0.9	0.17
3M-Ethanol	$\lambda_{max.}/nm$	442	440	438	434	434	434
	I_0/I_A	2.5	1.6	1.5	1.4	1.4	1.0
0.07M-Tetrachloromethane	I_0/I_A	2.3	1.9	1.7	1.5	1.5	1.5
0.3M-2-Iodotoluene	I_0/I_A	1.3	1.2				1.3
0.4M-Iodoethane	I_0/I_A	1.07	1.06				1.02

^a Fluorescence $\lambda_{max.}$ 425 nm unless otherwise stated. For (4) and (1) (X = H), fluorescence ϕ 0.8 rising to 1.0 upon deoxygenation, see ref. 12. ^b Relative to I_0 for (4) 1.0.

pyrazolines with some metal ions¹⁹ but anodic and iron(III) chloride oxidation of pyrazolines yields pyrazoline dimers in neutral solution and pyrazoles only in the presence of pyridine acting as a base.^{19,20}

The photochemistry underlying the weak quenching action of 2-iodotoluene (Table 4) was probed further since this may shed light on the intramolecular interaction found in the photochemistry of (1; X = I). Iodine is released upon excitation at 370 nm of a solution of (1; X = H) in aerated 2-iodotoluene with an efficiency which *decreases* with increasing concentration of (1; X = H). The relative rates at concentrations of 0.00, 0.47, 1.41 and $3.76 \times 10^{-3}M$ are 100, 37, 31, and 23 respectively while a $0.47 \times 10^{-3}M$ solution of (1; X = I) forms iodine with a relative rate of 55 under the same conditions. This evidence indicates that the principal origin of iodine formation is not an intermolecular photo-assisted charge-transfer phenomenon but rather is due to the direct absorption of a fraction of the incident light into the $S_0 \rightarrow T_1$ band of 2-iodotoluene solvent,²¹ the remaining light being passively absorbed into the $S_0 \rightarrow S_1$ band of (1; X = H). The high concentration of 2-iodotoluene compensates for the low molar absorptivity of the intercombination band.

The direct photochemical reaction of (1; X = I) cannot have a related origin because the iodobenzene chromophore and the pyrazoline chromophore are now present in equal molar concentrations and practically all the light will be absorbed by the pyrazoline chromophore. In one experiment where an aerated cyclohexane solution of 2-iodotoluene and (1; X = H), both $0.47 \times 10^{-3}M$, was irradiated under identical conditions to those used in the previous paragraph, no iodine was produced.

Irradiation Wavelength.—At least three bands are discernible in the electronic spectrum of (1; X = I), one of these appearing as a shoulder on the short wavelength side of the long wavelength absorption maximum. Selective population of these states does not lead to any outstanding reactivity differences (see Table 5), which suggests that relaxation to S_1^0 precedes any step leading to reaction. A quantum yield of 0.007 was found for the cyclization of (1; X = Br) on irradiation at 254 nm with no reaction detected at longer wavelengths. This is an indication of reactions proceeding from upper excited states,²² most likely those located in the bromobenzene moiety. A similar, small component of reaction may be present in the iodo-case but it would not be detectable within the limits of experimental error, as an addition to the efficient reaction from the S_1^0 state. Unless the carbon-halogen bond fission is rapid any excitation energy localised in the halogenobenzene moiety will be transferred exothermically to the pyrazoline moiety. For the corresponding chloro-

Table 5. Influence of irradiation wavelength on quantum yields for the reaction of $5 \times 10^{-4}M$ solutions of (1; X = I) in cyclohexane under air

Irradiation wavelength (nm)	$I_{abs}/10^{-4} E^{-1} h^{-1}$	Quantum yield for		
		loss of (1; X = I)	formation of (1; X = H)	(2)
370	1.3	0.12	0.034	0.047
335	0.3	0.11	0.031	0.043
315	0.5	0.14	0.025	0.039
254	0.7	0.12	0.044	0.053

compound (1; X = Cl), cyclization was negligible at all wavelengths studied. Robinson and Vernon²³ have described closely related examples where reactivity depends critically on the nature of the halogen.

Solvent and Temperature.—Data on the influence of solvents on the photoreactivity of (1; X = I) are summarized in Table 6. In hydrocarbon solvents the fluorescence intensity is virtually constant but the quantum yield for decomposition of the iodo-compound is related to the solvent viscosity,²⁴ being highest in solvents of low viscosity. The ratio of reductive dehalogenation to cyclization parallels the availability toward phenyl σ -radicals of hydrogen atoms in the solvent. Hydrogen donor ability has been measured by other workers relative to the chlorine donor ability of tetrachloromethane.²⁵ These facts can be accommodated by a mechanism involving simple homolysis of the carbon-iodine bond to give a caged radical pair which may either recombine or one radical may escape from the cage resulting in detectable reactions. The probability of a detectable reaction is governed by solvent viscosity.

Out of line with these observations is the low photoreactivity in methanol solution. This low reactivity is attributable to solvent-polarity-induced lowering of E_S evidenced by a red shift of the fluorescence band.²⁶ The data in Table 4 show the red shift in fluorescence induced on addition of ethanol to cyclohexane solutions.

These photocyclizations show all the characteristics expected for a reaction which involves phenyl σ -radical intermediates. The radical complexation effects discussed for reactions of the corresponding pyrazoles appear to be unimportant.² Complexation of the forming phenyl radical is unlikely for the pyrazolines because the potential π -donor *N*-phenyl ring is held in an unfavourable conformation by overlap between the ring and the pyrazoline chromophore. Further the relatively low electron affinity of iodine atoms will further reduce any degree of π -complexation.

At room temperature the fluorescence intensity for the iodo-compound (1; X = I) is considerably less than that of 1,3,5-

Table 6. Influence of solvent on the photochemical reactions of 5×10^{-4} M aerated solutions of (1; X = I). For ϕ determinations, λ 370 nm, I_{abs} ca. 1×10^{-4} E l $^{-1}$ h $^{-1}$. Air quenching of fluorescence and photoreactivity is small

	η (20 °C) ^a / cP	$k_{\text{H}}/k_{\text{C}}$ ^b	For decomposition of (1; X = I)			I_{F} values ^c (arbitrary units)	
			$\phi - \Delta_{\text{I}}$	$\phi_{\Delta\text{H}}$	$\phi_{\Delta(\text{Z})}$	(1; X = I)	(1; X = H)
Hexane	0.31					20	83
Cyclohexane	0.98	1.08	0.12	0.034	0.047	20	100
Cyclo-octane	2.3	2.9	0.062	0.025	0.020	22	105
Benzene	0.6	0.00	0.10	0.001	0.049	14	77
Methanol	0.55	0.13	0.042	0.003	0.010	14	29

^a Viscosity taken from J. A. Riddick and W. B. Bunger, 'Organic Solvents,' Wiley, New York, 1970, 3rd. edn., except for cyclo-octane which was determined at 20.0 °C relative to cyclohexane. ^b A measure of hydrogen atom donor ability (k_{H}) relative to chlorine atom donor ability (k_{C}) of tetrachloromethane (see ref. 25). ^c Fluorescence intensity at λ_{max} , normalized relative to (1; X = H) in cyclohexane in aerated solutions at 20 °C, excitation at λ 350 nm. In all solvents λ_{max} , 425 nm except benzene (435 nm) and methanol (465 nm).

triphenylpyrazoline and the internal fluorescence quenching process appears to be genuinely thermally activated, rather than controlled by temperature-induced viscosity changes of the solvent. There are examples in the literature²⁷ of viscosity-controlled intramolecular photophysical processes.

Of the pyrazolines (1), only the iodo-compound exhibited fluorescence quenching. Pyrazolines (1; X = OMe, Cl, or Br) all had I_{F} 100 (λ_{max} , 425 nm) in cyclohexane and on the same scale as used in Table 6. The bromo-compound has been studied by other workers who obtained a similar result.²⁸ For the iodo-compound no fluorescence quenching was found at 80 K in an ethanol glass (Table 1). A 50% decrease in fluorescence intensity occurred on warming an aerated cyclohexane solution from 20 to 60 °C while a control experiment with 1,3,5-triphenylpyrazole showed a 3% increase attributable to air quenching effects.

A detailed temperature variation study on both the fluorescence intensity and the photoreactivity of the iodo-compound revealed the complementary nature of the two quantum yields (Table 7). This again points to the fluorescing S_1 state as the origin of the photochemical reactions leading to cyclization and to reductive dehalogenation. However, the transfer of excitation from the 1,3-diphenylpyrazoline chromophore (E_{S} 293, E_{T} 184 kJ mol $^{-1}$)¹² to the iodobenzene moiety (for benzene E_{S} 418, E_{T} 347 kJ mol $^{-1}$)¹⁴ cannot involve simple energy transfer between relatively stable states as this is energetically impossible.

Mechanism.—So far we have shown that photochemical reactions of (1; X = I) proceed by homolytic fission of the carbon-iodine bond to give non-complexed phenyl σ -radicals. The reactive excited state is the pyrazoline S_1 state and the question arises, how is this energy transferred to the iodobenzene chromophore?

Iodoaromatic compounds are unique among aryl halides in possessing accessible $n\sigma^*$ -states which can intervene in their photoprocesses. Early spectroscopic work²⁹ showed that the singlet $\pi\pi^*$ -state of iodobenzene is overlapped by a singlet $n\sigma^*$ -state of the carbon-iodine bond and this favourable energy overlap allows depopulation of the S_1 -state by predissociation into the $n\sigma^*$ -state, even though spacial overlap is unfavourable. The efficiency of predissociation depends on the degree of energy overlap and this can be altered by substitution in the iodobenzene ring of appropriate groups.³⁰ Direct triplet excitation of iodoarenes can also cause efficient carbon-iodine bond rupture by predissociation via $n\sigma^*$ -states.³¹ Further insight into predissociation can be gained by considering the results of Levy *et al.*,²¹ who demonstrated that population of the T_1 -state of iodobenzene leads to a slower reaction than by population of the S_1 -state at room tem-

Table 7. Temperature effect on the fluorescence and total product quantum yields from irradiation of (1; X = I) in undeoxygenated cyclohexane

T/K	ϕ_{F} ^a	ϕ_{tot} ^b	log- $\left(\frac{1}{\phi_{\text{F}}} - 1\right)$	log- $\left(\frac{1}{\phi_{\text{tot}}} - 1\right)$
284	0.20	0.070	0.60	1.02
293	0.17	0.082	0.69	0.96
308	0.13	0.120	0.83	0.80
322	0.103	0.158	0.94	0.67

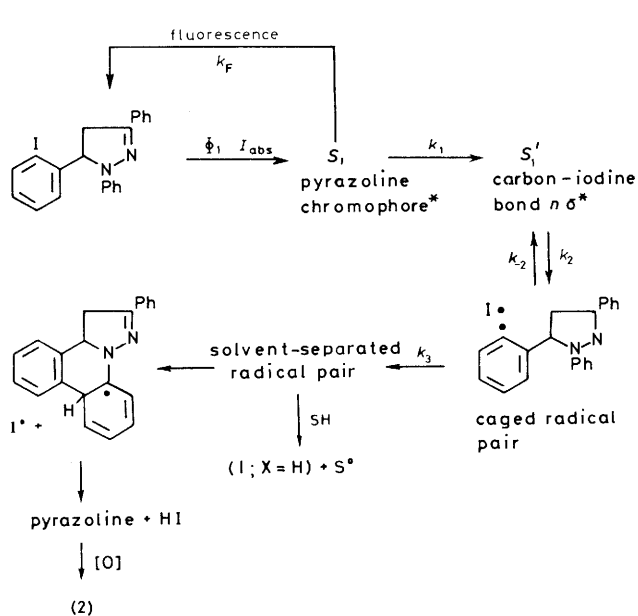
^a (1; X = H) was used as a standard ($\phi_{\text{F}} = 0.8$ in undeoxygenated cyclohexane) and as a check for stability of the excitation source (313 nm). There are no appreciable wavelength effects in either the photochemistry or photophysics over the range 313–370 nm. ^b $\phi_{\text{tot}} = \phi_{\Delta\text{H}} + \phi_{\Delta\text{phen}}$, determined at 370 nm in undeoxygenated cyclohexane.

perature, though both states show equal reactivity at higher temperatures. Thus we may infer that over and above the rate increase due to reduction in solvent viscosity,²⁴ these examples of predissociation show thermal activation implying an energy barrier to the process.

Efficient $n\sigma^*$ state participation, sometimes with thermal assistance, is therefore common in the photochemistry of simple iodobenzenes. For other iodoarenes with lower lying excited states such participation is less prominent except in processes involving upper excited states. In 1-iodonaphthalene, for example, the state closest in energy to $^1n\sigma^*$ is S_2 , a $\pi\pi^*$ state,³⁰ and the wavelength-dependent phosphorescence quantum yield reflects the efficiency of predissociation from S_2 compared with the internal conversion $S_2 \rightarrow S_1$.³²

When we view (1; X = I) as an iodobenzene with a proximate reservoir of energy in the singlet energy of the pyrazoline moiety, the information summarized in the previous paragraphs becomes relevant. The S_1 state may cross into an $n\sigma^*$ state in the iodobenzene manifold leading to the observed reaction. Thus the observed photochemistry becomes a probable example of predissociation between separated chromophores. In simple iodobenzenes, the corresponding states $^1\pi\pi^*$ and the carbon-iodine $n\sigma^*$ share a carbon atom which is also a nodal point.

The temperature effects can be analysed according to the mechanistic Scheme which is consistent with the results so far obtained. For normal pyrazoline chromophores $\phi_{\text{F}} = 1.0$ in deaerated cyclohexane so that S_1 can only undergo fluorescence or energy transfer followed by further reaction. Reverse energy transfer from S_1^1 to S_1 is assumed to be insignificant. Writing equation (1) and applying steady-state kinetics, expressions (2)–(5) can be derived. We assume $\phi_1 = 1$ and



Scheme. Photolysis of the carbon-iodine bond in 5-(2-iodophenyl)-1,3-diphenyl- Δ^2 -pyrazoline

$$\varphi_{\text{tot}} \cdot I_{\text{abs}} = \frac{d}{dt} (\text{Products}) = \frac{k_3 k_2}{k_3 + k_2} [S_1'] \quad (1)$$

use the symbols k , E , and A for the rate constant, energy of activation, and pre-exponential factor of a process defined by the subscript.

$$\frac{1 - \varphi_F}{\varphi_{\text{tot}}} = 1 + \frac{k_{-2}}{k_3} \quad (2)$$

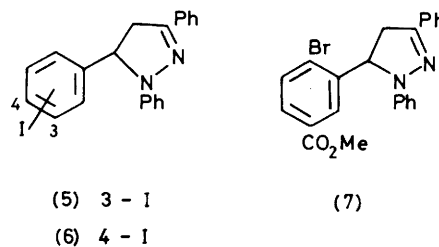
$$\therefore \log_{10} \left(\frac{1 - \varphi_F}{\varphi_{\text{tot}}} - 1 \right) = \log_{10} \left(\frac{A_{-2}}{A_{-3}} \right) + \frac{(E_3 - E_{-2})}{2.3R} \cdot \frac{1}{T} \quad (3)$$

$$\frac{1}{\varphi_F} - 1 = \frac{k_1}{k_F} \quad (4)$$

$$\therefore \log_{10} \left(\frac{1}{\varphi_F} - 1 \right) = \log_{10} \left(\frac{A_1}{A_F} \right) - \frac{(E_1 - E_F)}{2.3R} \cdot \frac{1}{T} \quad (5)$$

Because of the nature of the processes, E_{-2} and E_F are almost zero. Plotting the data in Table 7 according to equations (3) and (5) gives E_1 , the activation energy for interchromophoric predissociation and E_3 , the energy barrier to radical separation as 16 kJ mol⁻¹ each. E_3 is expected to be the barrier to viscous flow in cyclohexane. The latter has been measured³³ as 12 kJ mol⁻¹ which is in satisfactory agreement with the value obtained for E_3 .

An alternative mechanism which accounts for the present observations is electron transfer from the excited pyrazoline moiety to the halogenobenzene moiety. In this case the specific reaction of the iodo-compound may be due to the lower reduction potential of iodobenzene compared with chloro- and bromo-benzene,³⁴ coupled with the low singlet energy of the pyrazoline moiety. Electron donors with higher singlet energies are known to cause carbon-halogen bond fission with chloro-, bromo- and iodo-benzene, although for iodo-benzene reaction is fastest.³⁵ Further studies on related compounds, detailed below, have eliminated the electron transfer mechanism for photochemical reaction of (1; X = I).



Related Compounds.—Compounds (5) and (6) proved to be photostable under irradiation at 370 nm, almost all the absorbed energy being re-emitted as fluorescence. At room temperature the relative quantum yields for fluorescence of (1; X = H), (1; X = I), (5), and (6) are 1.0, 0.20, 0.95, and 0.90 respectively, and the quantum yields for disappearance of (5) and (6) are both 3×10^{-3} in cyclohexane. Other workers²⁸ have obtained a similar result for the fluorescence of (6). This critical dependence of reactivity on the proximity of the carbon-iodine bond to the pyrazoline moiety is to be expected on the predissociation mechanistic model since energy transfer efficiency is inversely proportional to a high power of the interspecies separation. In contrast, if the electron-transfer mechanistic model were operative, the aromatic π -system would provide a conducting channel to the carbon-iodine bond irrespective of the position of this bond. Negligible quenching of the room temperature fluorescence is also shown by the bromo-compound (1; X = Br) which also shows negligible photoreactivity.

Electron-withdrawing substituents in the 5-phenyl ring of (1; X = H) give rise to a dramatic quenching of the room temperature pyrazoline fluorescence.²⁸ This must be due to intramolecular photoelectron transfer which provides a route for relaxation of the excited state, although the authors make no comment on their observation. Compound (7) was prepared because this possesses an electron-deficient aryl halide moiety which should encourage the electron transfer process. The carbon-bromine bond does not possess any accessible $n\sigma^*$ states to allow predissociation. Thus any photobehaviour of (7) may be understood in terms of electron transfer only.

Compound (7) is almost non-fluorescent, φ_F 0.005, but only a small part of the radiationless decay is represented by net chemical decomposition. In cyclohexane, the quantum yield for decomposition is 2.2×10^{-3} . This is most probably due to rapid thermal back-electron-transfer following the initial photoinduced electron transfer.

In summary, we have shown that energy transfer to a dissociative state controls the photobehaviour of (1; X = I). When the 5-phenyl substituent carries an electron-withdrawing group then the photobehaviour of 1,3,5-triphenylpyrazolines is controlled by electron transfer from the pyrazoline excited state to the 5-phenyl group.

Experimental

Quantum Yield Determinations.—Optically dense samples were irradiated on a merry-go-round apparatus using the combination of a medium pressure mercury arc lamp (Thorn; 250 W) and a high radiance grating monochromator described in Part 2.³⁶ The reactions were monitored by h.p.l.c. The photolyte was washed with sodium carbonate and water then chromatographed on a column of Spherisorb silica 55W (25 cm \times 0.36 mm diameter) eluting with cyclohexane-dichloromethane (2:1 v/v) at a flow rate of 1.2 ml min⁻¹ while monitoring the optical density at 260 nm.

Fluorescence Measurements.—A Baird Atomic SFR-100

instrument was available but this was not readily adaptable for variable temperature work. For the latter purpose the sample was held in a copper block through which water circulated from a thermostat. It was irradiated by a medium pressure mercury lamp running from a constant voltage transformer, the 313 nm line being isolated using an interference filter. The generated fluorescence fell on the slit of a Beckman prism monochromator fitted with a detector system.

Pyrazolines.—These were prepared by the usual route from the corresponding chalcone and phenylhydrazine.³⁷ The intermediate chalcone was not purified. The following pyrazolines are new and were recrystallized from ethanol: 5-(2-iodophenyl)-1,3-diphenyl- Δ^2 -pyrazoline, m.p. 148—149 °C (Found: C, 59.5; H, 4.2; N, 6.7. C₂₁H₁₇IN₂ requires C, 59.4; H, 4.0; N, 6.6%); 5-(3-iodophenyl)-1,3-diphenyl- Δ^2 -pyrazoline, m.p. 107—108 °C (Found: C, 59.4; H, 4.0; N, 6.5%); δ (CDCl₃) with pyrazoline ring protons H_a 5.10, H_b 3.75, H_c 3.00 and J_{ab} 12, J_{ac} 7, J_{bc} 17 Hz.

5-(2-Bromo-5-methoxycarbonylphenyl)-1,3-diphenyl- Δ^2 -pyrazoline.—4-Bromo-3-methylbenzonitrile³⁸ (14 g) was dissolved in acetic anhydride (80 ml) and sulphuric acid (16 ml) added at 0 °C, followed by a solution of chromium trioxide (20 g) in acetic anhydride (90 ml) keeping the temperature below 10 °C. After a further 2 h, the mixture was poured into water and the precipitated diacetoxymethyl compound collected as a yellow solid. This was dissolved in ethanol (15 ml) and water (15 ml) containing sulphuric acid (2 ml) and refluxed for 30 min. On cooling the solution in ice, 2-bromo-5-cyanobenzaldehyde (2.7 g) separated as a brown solid.

The crude aldehyde (2.7 g) and acetophenone (1.6 g) in methanol (100 ml) were cooled in ice and a solution of sodium hydroxide (0.8 g) in methanol (30 ml) added. After 10 h, the solution was neutralized with hydrochloric acid, most of the solvent evaporated under reduced pressure, and water added to the residue. Extraction with ether afforded a brown oil (2.4 g) which showed ν_{CO} 1 725 and 1 680 cm⁻¹ as well as ν_{CN} 2 240 cm⁻¹. Partial alcoholysis of the nitrile group had occurred.

The crude chalcone (2.4 g), phenylhydrazine (1.6 g), and acetic acid (10 ml) were heated on a water-bath for 2 h and the solution diluted with ethanol and cooled. A yellow solid (0.5 g), m.p. 170—175 °C, with the characteristic n.m.r. spectrum of a pyrazoline separated. Recrystallization from methanol afforded 5-(2-bromo-5-methoxycarbonylphenyl)-1,3-diphenyl- Δ^2 -pyrazoline as yellow needles, m.p. 183—185 °C (Found: C, 63.5; H, 4.4; N, 6.4. C₂₃H₁₉BrN₂O₂ requires C, 63.1; H, 4.4; N, 6.4%), M^+ 426 and 434, ν_{CO} 1722 cm⁻¹, δ (CDCl₃) with CO₂CH₂ protons 3.75 (s), pyrazoline protons H_a 5.58, H_b 3.98, H_c 3.40 with J_{ab} 10, J_{ac} 7, J_{bc} 15 Hz.

Preparative Photochemistry.—A solution of the iodo-compound (1; X = I) (0.280 g) in cyclohexane (100 ml) was purged with nitrogen and irradiated with a medium pressure lamp (Hanau 150 W, TQ-150P) fitted into a Pyrex immersion well (0.2 cm path length of Pyrex glass) until no further wall deposits formed. The purple photolysis mixture and the wall deposits were combined, washed with aqueous sodium thiosulphate, then sodium hydrogencarbonate, and water, dried (Na₂SO₄), and evaporated under reduced pressure to leave an oil. Preparative t.l.c. on silica, elution with cyclohexane-dichloromethane (2 : 1 v/v), and crystallization from ethanol afforded 2-phenylpyrazolo[1,5-f]phenanthridine (2), m.p. 153—154 °C (lit.,² 153 °C) (77 mg, 39%), and 1,3,5-triphenylpyrazoline, m.p. 133—135 °C (lit.,³⁹ 138 °C) (48 mg, 24%), both identified by comparison with authentic specimens.

The corresponding bromo- and chloro-compounds showed

negligible reaction under similar conditions. Upon more prolonged irradiation the bromo-compound afforded two products in very small amounts. One had t.l.c. properties identical with (2) and the other showed a mass spectrum indicating the presence of bromine with M^+ 394 (8%) and 392 (8).

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