

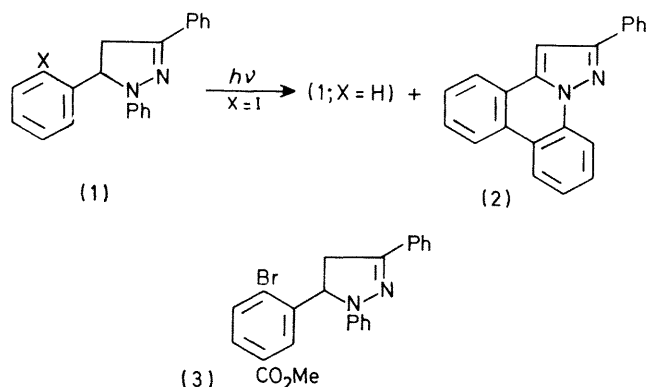
Example of Predissociation between Separate Chromophores in 5-(2-Halogenoaryl)-1,3-diphenyl- Δ^2 -pyrazolines

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Summary Photoexcited 5-(2-iodophenyl)-1,3-diphenyl- Δ^2 -pyrazoline undergoes carbon-iodine bond homolysis *via* energy transfer from the 1,3-diphenylpyrazoline moiety to a dissociative state, whereas photoexcited 5-(5-bromo-3-methoxycarbonylphenyl)-1,3-diphenyl- Δ^2 -pyrazoline undergoes electron transfer

iodo-compounds are unique among the aryl halides in possessing energetically accessible $n\sigma^*$ states. Therefore the photoreactivity of iodoarenes usually involves the predissociation of a $\pi\pi^*$ state into an $n\sigma^*$ state of the carbon-iodine bond.¹ Physicochemical studies of aryl iodide photochemistry have been confined to examples where the two excited states share a carbon atom. Here we provide the first example, apparently, of a system with separated chromophores,² where the excitation energy of the principle chromophore, the 1,3-diphenylpyrazoline moiety (E_S 293 and E_T 184 kJ mol⁻¹),³ is transferred to the iodobenzene moiety (for benzene E_S = 418 and E_T = 347 kJ mol⁻¹, both $\pi\pi^*$ states)⁴ leading to an efficient carbon-iodine bond homolysis.



Irradiation ($\lambda > 355$ nm) of (**1**, X = I) in de-aerated cyclohexane gave 49% of the pyrazole (**2**) and 24% of (**1**, X = H), whereas (**1**, X = Cl, Br, or OMe) showed no reaction. Related compounds with *m*- and *p*-iodo-substitution on the 5-phenyl ring also showed no reaction. Easy dehydrogenation of a first-formed pyrazoline to give (**2**), which possesses an extended aromatic system, is to be expected. Formation of (**1**, X = H) gives rise to radical species which can effect the dehydrogenation. The structural feature necessary for carbon-iodine bond fission is the proximity of the fissioning bond to the pyrazoline moiety which implies a necessity for orbital overlap. Fluorescence quantum yields for the above reactions vary in a manner complementary to the reaction quantum yields in that (**1**, X = I) alone shows a low quantum yield for fluorescence at 293 K which is temperature dependent and no longer anomalously low at 80 K. The 1,3-diphenylpyrazoline chromophore is known to be excited by an internal charge-transfer transition⁵ and this type of transition appears to be immune to internal heavy-atom effects.⁶ Thus, it is understandable that (**1**, X = I) suffers no heavy-atom perturbation. Examples⁷ can be cited of $\pi\pi^*$ transitions which suffer heavy-atom perturbation where the perturber is intramolecular and extrachromophoric as our example here.

The sensitivity of the Φ values (see Table) of product formation from (**1**, X = I), to solvent viscosity⁸ and hydrogen-atom donor-ability⁹ suggest phenyl σ -radical intermediates *via* carbon-iodine bond homolysis as the simplest explanation. The lower Φ value in a polar solvent is attributable to a lower E_S value relative to hydrocarbon solvents. A further examination of the temperature dependence of the fluorescence emission and photoreactivity gave the activation energy for interchromophore energy-transfer (which leads to fluorescence quenching) and for the subsequent overall chemical reaction as 16 kJ mol⁻¹. Other workers¹⁰ have found a temperature dependence in the photoreactivity of simple iodoarenes which can be

TABLE Photochemical reactions of (**1**, X = I) and (**3**)^a

Solvent	η (20 °C) ^b	k_H/k_C ^c	For decomp (1 , X = I)			I_F values ^d		For decomp (3)
			$\Phi_{-\Delta I}$	$\Phi_{\Delta H}$	$\Phi_{\Delta(2)}$	(1 , X = I)	(1 , X = H)	$\Phi_{-\Delta Br} \times 10^3$
C ₆ H ₁₄	0.31	0.80	—	0.037	0.071	0.20	0.83	4.4
CycloC ₆ H ₁₂	0.98	1.08	0.12	0.034	0.047	0.20	1.00	2.2
CycloC ₈ H ₁₆	2.3	2.9	0.062	0.025	0.020	0.22	1.05	—
C ₆ H ₆	0.6	0.00	0.10	<0.001	0.049	0.14	0.77	0.2
MeOH	0.55	0.13	0.042	0.003	0.010 ^e	0.14	0.29	0.7

^a 5×10^4 M Aerated solutions, $\lambda = 370$ nm, $I_{\text{abs}} \text{ ca } 1 \times 10^{-4} \text{ E l}^{-1} \text{ h}^{-1}$. Air quenching of fluorescence and photoreactivity is small. Φ Determined by u v for (**3**), otherwise by h p l c. (**1**, X = Br and Cl) give $\Phi_{-\Delta X} < 2 \times 10^{-3}$, $\Phi_{\Delta H} < 3 \times 10^{-4}$, and $\Phi_{\Delta(2)} < 1 \times 10^{-4}$. The corresponding *m*- and *p*-iodo-compounds give $\Phi_{-\Delta I} < 3 \times 10^{-3}$. ^b Viscosity taken from J. A. Riddick and W. B. Bunger, 'Organic Solvents', 3rd Edn., Wiley, New York (1970) except for cyclo-octane which was determined at 20 °C. ^c A measure of hydrogen-atom donor-ability (k_H) relative to chlorine-atom donor-ability of carbon tetrachloride (k_C), see ref. 9. ^d Fluorescence intensity at λ_{max} , relative to (**1**, X = H), which has Φ_F 0.8 (I. H. Leaver and D. E. Rivett, *Mol. Photochem.*, 1974, **6**, 113) in aerated solution at 293 K excited at 350 nm. In all solvents λ_{max} 425 nm except benzene (435 nm) and methanol (465 nm). In cyclohexane, (**1**, X = OMe, Cl, or Br) all had I_F 1.00 (λ_{max} 425 nm), the corresponding *m*- and *p*-iodo-compounds had I_F 0.95 and 0.90 respectively, (**3**) had I_F 0.005 (λ_{max} 425 nm). At 80 K in ethanol (**1**, X = H, OMe, Cl, Br, or I) all had I_F 1.0 (λ_{max} 414 and 426 nm) with no detectable phosphorescence. ^e In this solvent (**1**, X = Br or Cl) give $\Phi_{\Delta(2)} < 2 \times 10^{-4}$.

accounted for by assuming thermally activated predissociation of the same order of magnitude as described here.

The $n\sigma^*$ states for the carbon-bromine bond are of a prohibitively high energy to allow predissociation as a relaxation pathway from the π^* state and so (**1**; X = Br) fluoresces strongly. In contrast, (**3**) has a low fluorescence quantum-yield (Φ_F). The likely alternative relaxation pathway which operates is electron transfer from the excited 1,3-diphenylpyrazoline moiety to the aryl halide moiety which is now considerably more electron deficient

than a simple benzene ring. Intermolecular, photoinduced electron transfer is well established.¹¹ The quantum yield ($\Phi_{-\Delta Br}$) for decomposition of (**3**) is small. Rapid, thermal back-electron transfer in the excited-state, radical-ion pair, is implied by the inequality $1 - \Phi_F \gg \Phi_{-\Delta Br}$ and also by the absence of an increase in $\Phi_{-\Delta Br}$ in a more polar solvent, implying that the mean lifetime of the radical-ion pair is less than the mean time for solvent-dipole relaxation.

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