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

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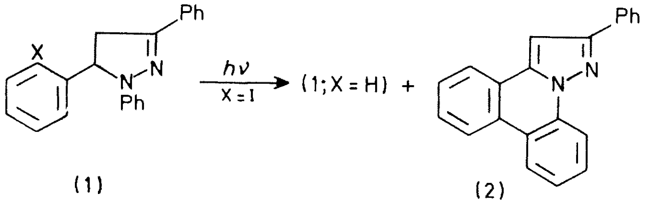
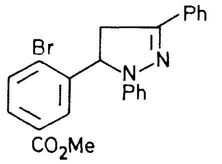
Summary Photoexcited 5-(2-iodophenyl)-1,3-diphenyl-Δ^2-pyrazoline undergoes carbon–iodine bond homolysis *via* energy transfer from the 1,3-diphenylpyrazoline moiety to a dissociative state, whereas photoexcited 5-(5-bromo-3-methoxycarbonylphenyl)-1,3-diphenyl-Δ^2-pyrazoline undergoes electron transfer

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



(1) (2)



(3)

Irradiation (λ > 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 transition[5] 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 Examples[7] 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 viscosity[8] and hydrogen-atom donor-ability[9] 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 workers[10] 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) $\Phi_{-\Delta I}$	$\Phi_{\Delta H}$	$\Phi_{\Delta(2)}$	I_F values [d] (**1**, X = I)	(**1**, X = H)	For decomp (**3**) $\Phi_{-\Delta Br} \times 10^3$
C_6H_{14}	0·31	0·80	—	0·037	0·071	0·20	0·83	4·4
CycloC_6H_{12}	0·98	1·08	0·12	0·034	0·047	0·20	1 00	2·2
CycloC_8H_{16}	2·3	2·9	0 062	0 025	0 020	0 22	1 05	—
C_6H_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, λ = 370 mm, I_{abs} *ca* 1 × 10^{-4} E l^{-1} 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 × 10^{-3}, $\Phi_{\Delta H}$ <3 × 10^{-4}, and $\Phi_{\Delta(2)}$ <1 × 10^{-4} The corresponding *m*- and *p*-iodo-compounds give $\Phi_{-\Delta I}$ <3 × 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 0 °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 × 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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