The Hydrogen-bond as a Configurational Lock in the Photocyclisation of Dibenzoylmethane o-Halogenoanils: Wavelength Dependence of This Reaction

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Summary The tautomers (1, X=Cl, Br, or I) of anils photocyclise to the phenanthridine derivative (2) with varying efficiencies depending on the halogen and the solvent; owing to the low energies of the first excited states the quantum yields vary with irradiation wavelength.

cis-trans-Photoisomerisations complicate the use of benzylideneanilines in photocyclisation reactions[1] and several means for overcoming this difficulty by incorporating the azomethine link into a ring system have been developed.[2] However, these routes require a rather vigorous degradation step for cleavage of the configuration-holding

ring in order to obtain simple phenanthridines   In contrast, compounds like (1), prepared as described for the aniline derivative,[3] exist as shown with a configuration-holding hydrogen-bond[4] and irradiation directly produces the phenanthridine derivative (2) †

(1)   (2)

(3)
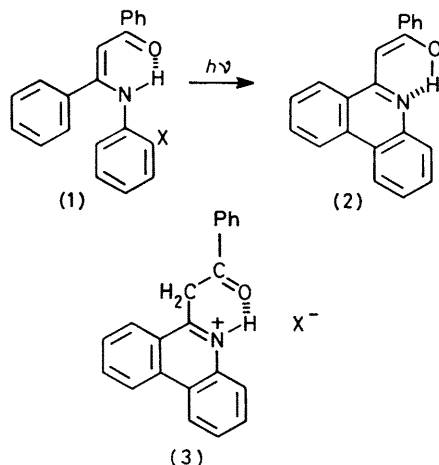
Irradiation of (1, X=Cl, Br, or I)‡ in deoxygenated cyclohexane gives rise to the appearance of a sharp vibrational-banded spectrum due to (2) and with good isosbestic points in the latter two cases   However, a small but significant quantity (*ca* 4% by h p l c) of (1, X=H) is also formed during reactions of (1, X = Br or I) showing that assistance[5] to homolysis is weak owing to the weak π-donor phenyl ring and that reactions proceed *via* phenyl radical intermediates which abstract hydrogen from the solvent in a competing reaction   Preparative photolysis produced a yellow precipitate of (3) with ν_{CO} 1675 cm^{-1}, showing positive tests for halide ion, in up to 60% yield for X = Br or I, from which crystalline (2)‡ can be obtained by basification and chromatography   The slow cyclisation of (1, X=Cl) is not preparatively useful and (1, X=H) is inert under oxidative conditions

Compounds (1, X=Hal) show two absorption bands with λ_{max} 254 and 376 nm which permit selective population of excited states by irradiation into one of the absorption bands, thus allowing a probe into upper excited state reactivity[6] in a relatively simple bond-fission reaction   The quantum yield at 254 nm for the reaction (1, X=Hal)→(2) is moderately dependent on solvent viscosity, suggesting a homolytic step, and proceeds *via* unquenchable excited

Table   Quantum yields (ϕ)[a] for the formation of (2) from (1), 2×10^{-4} M solutions in non-deoxygenated cyclohexane at 20 °C

λ/nm	$10^4\ \phi$		
	X = Cl	X = Br	X = I
254	1·2	110	460
315	<0·2	4	90
335	<0·4	<0 4	9
370	<0·1	<1	<4

[a] Obtained by u v -spectroscopy and ferrioxalate actinometry (±10% error), $I_{abs} = (0\cdot3\text{—}1\cdot7) \times 10^{-4}$ E l^{-1} h^{-1}

states   The Table shows the unprecedented wavelength-dependent photochemistry of an aryl halide in solution which is observable because of the low energy of the first excited states of (1)   The available energy after population of the 360 nm band is not sufficient to overcome the transition state leading to fission of any of the carbon–halogen bonds, thus $E(T_1) < E(S_1) < 268$ kJ mol^{-1} calculated§ from absorption onset at *ca* 440 nm, while currently accepted Ph–X bond dissociation energies[7] are 397, 334, and 268 kJ mol^{-1} for X=Cl, Br, and I respectively   Irradiation of the 250 nm band populates higher excited states $[E(T_2) < E(S_2) < 380$ kJ mol^{-1} calculated from absorbance onset at *ca* 315 nm] which allows a dramatic increase in the fission rate so that crossing into dissociating states must compete effectively with internal conversion to S_1

† If necessary, the Norrish type I photochemistry of salt (3) can be employed for mild degradation.

‡ Correct analytical and spectral data have been obtained

§ Compounds (1) show no fluorescence or phosphorescence in ethanol at 80 K

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[2] S Prabhakar, A M Lobo and M R Tavares, *J Chem Soc , Chem Commun* , 1978, 884, B Mortelmans and G Van Binst, *Tetrahedron*, 1978, **34**, 363, W J Begley, J Grimshaw and J Trocha-Grimshaw, *J Chem Soc Perkin Trans* 1, 1974, 2633

[3] E Roberts and E E Turner, *J Chem Soc* , 1927, 1832, D F Martin, G A Janusonis, and B B Martin, *J Am Chem Soc* , 1961, **83**, 73

[4] For related examples see G O Dudek and E P Dudek, *J Am Chem Soc* , 1964, **86**, 4283, and earlier papers

[5] J Grimshaw and A P de Silva, *J Chem Soc , Chem Commun* , 1979, 93

[6] N J Turro, V Ramamurthy, W Cherry, and W Farneth, *Chem Rev* , 1978, **78**, 125

[7] 'Handbook of Chemistry and Physics,' ed R C Weast, 56th Edn , Chemical Rubber Co , Cleveland, 1975, p F231