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

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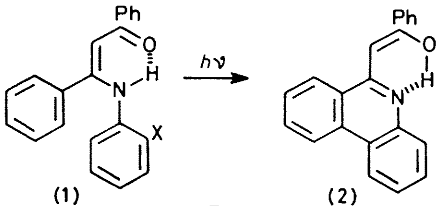
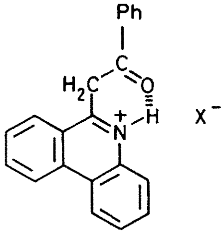
Summary The tautomers (**1**, X=Cl, Br, or I) of anils photocyclise to the phenanthridine derivative (**2**) with varying efficiencies depending on the halogen and the solvent; owing to the low energies of the first excited states the quantum yields vary with irradiation wavelength.

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 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

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

	$10^4\,\phi$		
λ/nm	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), $I_{abs} = (0·3—1·7) \times 10^{-4}$ E l^{-1} h^{-1}

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† 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

[1] A C Pratt, *Chem Soc Rev* , 1977, **6**, 63, A Padwa, *Chem Rev* , 1977, **77**, 37

[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