Reversible Photochemistry, Photo-oxidation, and Fluorescence of Dixanthylidene: Temperature and External Spin–Orbit Perturbation Effects

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A detailed experimental study of the photochemistry of dixanthylidene over a wide temperature range indicates the existence of three labile photoisomers, B, C, and P, all of which revert thermally to A. Light-stable B, formed from the excited triplet of the fundamental modification A, is thermally stable below −140°. The structure of B involves torsion of *ca.* 50° about the central double bond. C And its possible precursor P are photolabile isomers formed from excited singlet A. They are photocyclisation products of the 4a,4b-dihydrophenanthrene type; C is photoconvertible into A. The thermal stability of P is much less than that of C. Helixanthen is obtained on thermal dehydrogenation of C with molecular oxygen or iodine. The quantum yield of A $\xrightarrow{h\nu}$ B drops with the temperature and is very small at −140° but can be strongly enhanced (up to 220-fold) by the spin–orbit coupling perturbers molecular oxygen, carbon disulphide, and ethyl iodide.

STUDIES of photochromism in compounds of type (I) have been most extensive with the dianthrones (I; X = CO).[1-4] Dixanthylidene (Ia) and its derivatives have received relatively little attention since Hirshberg's pioneering work.[5] Kortuem and Krieg [6] reported on the thermo-, piezo-, and photo-chromism of (Ia) and some derivatives; Richtol *et al.*[7] described direct and sensitised photocolouration of (Ia) in benzene by means of flash photolysis at room temperature; we briefly reported [8] on the reversible photochemistry of two derivatives of (Ia), applying both stationary and flash methods over a wide temperature range. We now describe in detail the complex reversible photochemistry of (Ia), the way it is affected by triplet sensitisers and by intersystem-crossing promoters, and the mechanism of its oxidation to helixanthen,[9] (III), *via* the dihydro-intermediate (II).

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[1] R. Korenstein, K. A. Muszkat, and E. Fischer, *Helv. Chim. Acta*, 1970, **53**, 2102; T. Bercovici, R. Korenstein, K. A. Muszkat, and E. Fischer, *Pure Appl. Chem.*, 1970, **24**, 531.

[2] T. Bercovici and E. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1114; unpublished results.

[3] G. Kortuem, *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **78**, 391.

[4] (*a*) R. Korenstein, Sh. Sharafi-Ozeri, and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1973, **95**, 6177; (*b*) R. Korenstein, K. A. Muszkat, and E. Fischer, in preparation.

[5] Y. Hirshberg, *Compt. rend.*, 1950, **231**, 903; *J. Amer. Chem. Soc.*, 1956, **78**, 2304; Y. Hirshberg and E. Fischer, *J. Chem. Soc.*, 1953, 629.

[6] G. Kortuem and P. Krieg, *Chem. Ber.*, 1969, **102**, 3033.

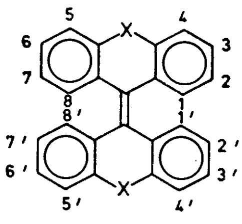
[7] H. H. Richtol, R. L. Strong, and L. J. Dombrowski, *Israel J. Chem.*, 1974, **12**, 791.

[8] R. Korenstein, K. A. Muszkat, and E. Fischer, *Mol. Photochem.*, 1972, **3**, 379.

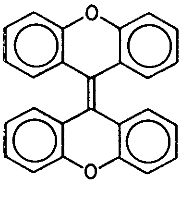
[9] A. Schoenberg and K. Junghans, *Chem. Ber.*, 1965, **98**, 2539.

RESULTS

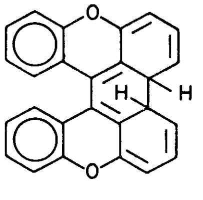
(a) *Photoisomerisation to Isomer B.*—' B ' Denotes the photochromic isomer described before,[4a,5,8] and observed in



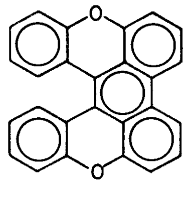
(I)



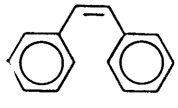
(Ia)



(II)



(III)



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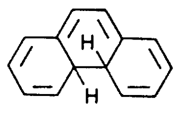

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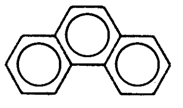

(VI)

practically all derivatives of dianthrone and dixanthylidene.* Because of its thermal reversion to the starting isomer A at higher temperatures it could be observed in (Ia) only below −140°, using static methods. The photostationary state attained is independent of the exciting light wavelength. Irradiation with visible light has no effect, and we conclude that the photoconversion A ⟶ B is not photoreversible and therefore approaches completion on prolonged irradiation (curve B in Figure 1). The quantum yield $\phi_{A\to B}$ of A $\xrightarrow{h\nu}$ B changes greatly with the temperature. By a combination of static and flash experiments we could determine $\phi_{A\to B}$ over a wide temperature range. The results obtained with evacuated or argon-flushed solutions are summarized in Figure 2, curve $\phi^{Ar}_{A\to B}$. $\phi_{A\to B}$ is seen to drop from *ca.* 40% at 20° to 0.02% at −160°. This corresponds to an activation energy of *ca.* 4.5 kcal mol^{-1} for the activated transformation $^1A^*$ ⟶ (intermediates) ⟶ B in the range −40 to −160° [*cf.* section (f) and Discussion section].

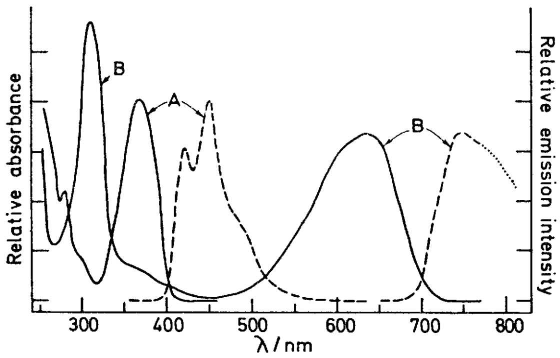

FIGURE 1 Absorption (full lines) and emission (broken lines) spectra of the A and B forms of 4.0 × 10^{-5}M-(I_a) in a mixture of methylcyclohexane (MCH) and 2-methylpentane (2-MP) at −180°

The kinetics of the spontaneous first-order reversal B ⟶ A were measured over the temperature range −20 to −100°, again employing either static or flash methods. The results follow an Arrhenius-type relationship, with an activation energy E_a of 12 ± 0.5 kcal mol^{-1} and a frequency factor A of 10^{13} s^{-1} (Figure 3).

(b) *Photosensitised Isomerisation A ⟶ B.*—Richtol *et al.*[7] reported the existence of this reaction at room temperature in benzene solutions, with biacetyl serving as a triplet sensitiser. We carried out sensitisation experiments in the temperature range −20 to −100°, using solutions of biacetyl and (Ia) in methylcyclohexane (MCH) and employing the photoflash technique with light in the range 430—500 nm. The relative quantum yield of B, as measured by the quantity of B formed per flash, remained constant in the above temperature range while the yield of the *direct* photoconversion falls off 20-fold from −20 to −100°.

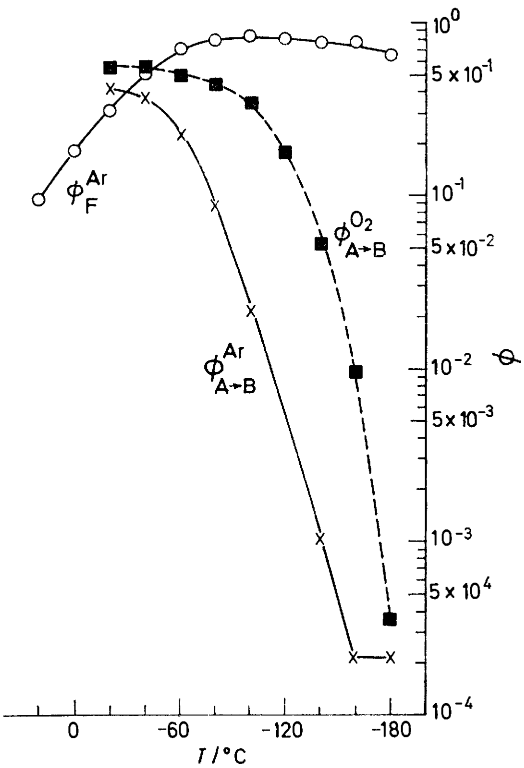

FIGURE 2 Photoisomerisation and fluorescence quantum yields of a 4 × 10^{-5}M solution of (Ia) in a 2 : 1 mixture of MCH and 2-MP as a function of the temperature: ϕ_F fluorescence yields (argon-flushed solutions); $\phi^{Ar}_{A\to B}$ photoisomerisation yields (argon-flushed solutions); $\phi^{O_2}_{A\to B}$ photoisomerisation yields of solutions flushed with O_2 ([O_2] = 1.1 × 10^{-2}M)

(c) *Enhancement of $\phi_{A\to B}$ by External Spin-Orbit Perturbation.*—The rate of photoisomerisation A ⟶ B is strongly enhanced by molecular oxygen,[10] by carbon disulphide, and by ethyl iodide. The results summarised in Figure 4 show oxygen to be *ca.* 50 times more effective (concentration-wise) than CS_2 and 200 times more than C_2H_5I, at −140°. These

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* The nomenclature introduced by Kortuem[3] regarding isomers A—C will be used throughout.

[10] G. Fischer and E. Fischer, *Mol. Photochem.*, 1974, **6**, 463.

results were obtained at $-140°$ because of the thermal instability of B at higher temperatures. The quantum yield in the presence of oxygen was measured with photoflash and with static methods in a wide temperature range (Figure 2, curve $\phi^{O_2}_{A\rightarrow B}$). Comparison with the values in the absence of oxygen, $\phi^{Ar}_{A\rightarrow B}$, shows that the extent of this enhancement as a function of the temperature passes through a maximum at *ca.* $-140°$, where $\phi^{O_2}/\phi^{Ar} = 50$. This is because (i) the potential enhancement increases as $\phi_{A\rightarrow B}$ in the unperturbed solution decreases on cooling and (ii) the perturbation depends on diffusional encounters between excited molecules $^1A^*$ and perturbing molecules within the life-time of the former, and the rate of such encounters decreases on cooling.

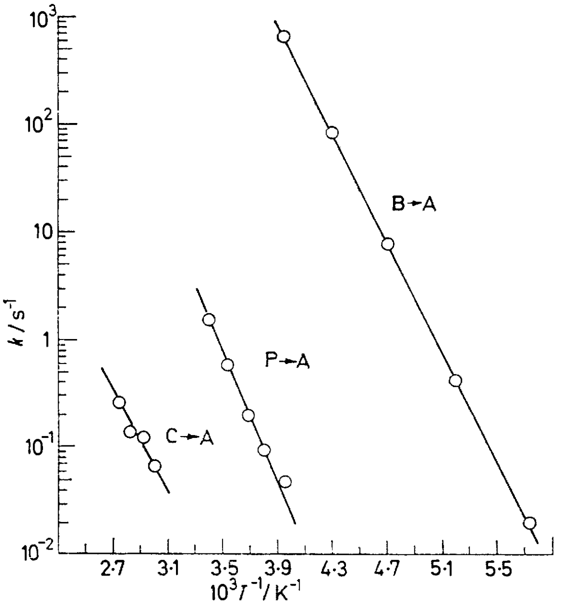

FIGURE 3 Arrhenius plots for the spontaneous processes B ⟶ A, C ⟶ A, and P ⟶ A (see text)

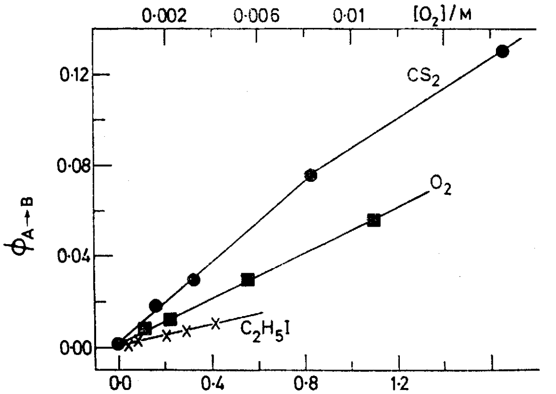

FIGURE 4 $\phi_{A\rightarrow B}$ Measured at $-140°$ with a 4×10^{-5}M solution of (Ia) in MCH-2-MP as a function of the concentrations of CS_2, C_2H_5I, and O_2 (note different concentration scales)

(d) *Photocyclisation of* (Ia) *to the Isomers 'C'.*—U.v. irradiation of evacuated or argon-flushed solutions of (Ia) at 0° causes partial conversion into a new coloured modification C (curve C in Figure 5), which is thermally stable at this temperature, but reverts thermally to the starting material A, at 20° and above. The reaction is photoreversible, irradiation with visible light causing complete reconversion into A. Since B has a life-time of the order of 0.05 ms at 0°, its formation does not interfere with the above observations. The new form reacts quickly with molecular oxygen or atomic iodine to form helixanthen (III), the spectrum of which is known. These observations seem to establish that this isomer is the photocyclisation product (II), by analogy to the dihydrophenanthrene (V) which is formed from *cis*-stilbene (IV) and oxidised to phenanthrene (VI).[11a,c] In this context we note that u.v. irradiation of (Ia) in the presence of oxygen or iodine causes complete oxidation to (III).

Compound (II) is analogous to the isomer C observed in dianthrone [1] and in dixanthylidene methylated in the 1 and 8′ positions.[8] Whenever these positions are not occupied, the C form is the precursor of the corresponding dehydrogenation product, *i.e.* helianthrone,[4b] helixanthen (III), or their derivatives. In all cases the reaction A ⟶ C is photoreversible. The easy oxidation of (II) at 0° by either molecular oxygen or atomic iodine affords an excellent method to estimate its concentration, as employed by us with the unstable dihydrophenanthrenes.[11a] Thus we determined that curve C in Figure 5 corresponds to a conversion A ⟶ C of *ca.* 12%, and therefrom calculated the absorption spectrum of pure (II) by an extrapolation procedure [11a] (curve CC in Figure 5).

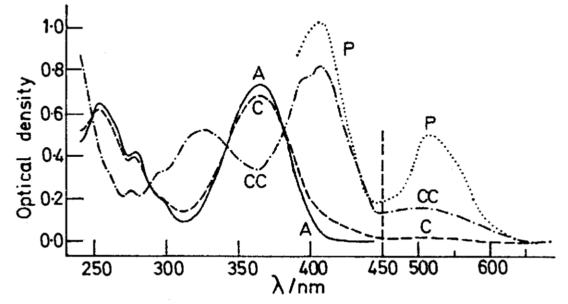

FIGURE 5 Absorption spectra of (Ia) and its photoisomers P and C in MCH-2-MP at 0°: curve A, before irradiation; curve C, following irradiation at 366 nm, causing 12% conversion into C; curve CC, extrapolated spectrum of photoisomer C; curve P, spectrum of photoisomer P (obtained by flash photolysis; the scale of the P spectrum is arbitrary)

The extent of the photoconversion A $\xrightarrow{h\nu}$ C drops sharply on cooling, and no C is observable below $-60°$. The first-order kinetics of the spontaneous reaction C ⟶ A were studied in the temperature range from $+90$ to $-20°$, using flash methods above 10°. The Arrhenius parameters calculated from these results were E_a 11 ± 0.5 kcal mol^{-1}, $\log_{10} A$ 5.8 (line C ⟶ A in Figure 3).

The existence of the photoconversion C ⟶ A could also be demonstrated in flash experiments, by comparing the decay of the absorption due to (II) under conditions of either strong or weak monitoring light (Figures 6d and e). The decay '*y*' is seen to be much faster in the former case.

(e) *Photoformation of the Isomer P.*—In the course of the flash experiments at $+90°$ to $-20°$ described in (d), we observed another coloured isomer, subsequently denoted

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[11] (*a*) K. A. Muskzat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662; (*b*) T. Wismonski-Knittel, T. Bercovici, and E. Fischer, *J.C.S. Chem. Comm.*, 1974, 716; (*c*) A. Bromberg and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1969, **91**, 2860.

tentatively as P. Its absorption spectrum is similar to that of the C isomer (curve P in Figure 5), but its thermal decay is much faster, making it easy to distinguish between the two forms. Typical decay curves are shown in Figures 6b—e. On the time scale of these curves C is practically stable, and all one observes is the decay of the absorption due to P, down to that due to C at the same wavelength. Spectrum P in Figure 5 was constructed from the difference between initial and final values of absorption, *i.e.* '*x*' in curves similar to those in Figures 6b and c. The extent of formation of P drops sharply on cooling, just like that of C, and at −60° neither P nor C are observable flash-photolytically. The first-order decay of P was studied in a wide temperature range, and can be expressed by an Arrhenius equation with the constants E_a 14.6 ± 0.5 kcal mol^{-1}, $\log_{10} A = 11$ (line P ⟶ A in Figure 3).

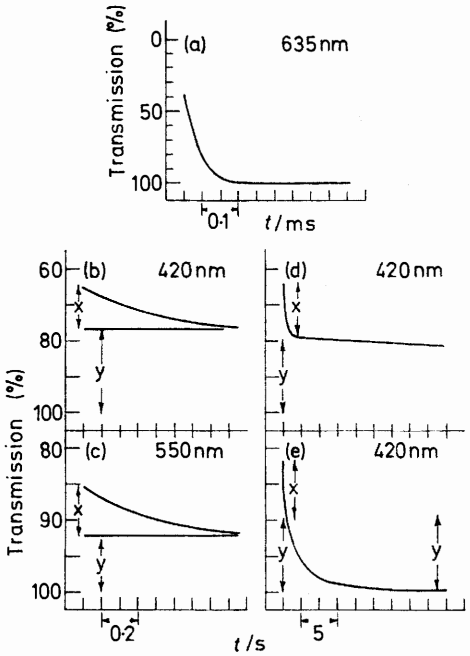

FIGURE 6 Oscilloscope traces obtained in flash-photolytic measurements of solutions of (Ia) in MCH-2-MP at 20°, at the wavelengths indicated: (a) decay of photoisomer B; (b), (c) decay of photoisomer P; (d) decay of P and C using weak-intensity measuring light; (e) ditto, using high-intensity measuring light, which bleaches C [note fast decay along *y*, compared with (d)]. *x* and *y* denote the transmission changes assigned to P and C, respectively

No permanent photochemical change resulted from irradiation under conditions where P is observable as a transient, *i.e.* P reverts eventually to A. No photosensitised formation of either P or C was detected.

The present data suggest that P is a precursor of C: $^1A^* \longrightarrow P \longrightarrow C$. From the pronounced similarity in the absorption spectra we tend to infer that P is a conformational modification of C. In this respect photoisomer P of (Ia) resembles labile precursors observed in other systems, *e.g.*, 'D' in dianthrones,[1,2] and 'Y' in 1,2-di-(2-naphthyl)-ethylene.[11b] However, the possibility that P and C are formed independently: $C \longleftarrow {}^1A^* \longrightarrow P$, cannot be ruled out on the basis of our present results. Spectrum P in Figure 5 was actually constructed on the basis of this assumption, *i.e.* from values similar to '*x*' in Figure 6.

(f) *Fluorescence Spectra and Quantum Yields and their Temperature Dependence*.—The emission and absorption spectra of (Ia) are shown in Figure 1. The fluorescence quantum yields ϕ_F were measured in a wide temperature range, in argon-flushed solutions. The results are shown in curve ϕ_F^{Ar} of Figure 2. ϕ_F Was measured relative to 9,10-diphenylanthracene, assuming its $\phi_F = 1.0$.[12] Below −20° the formation of B is the only process of $^1A^*$ competing with fluorescence (*cf.* Discussion section regarding intersystem crossing to $^3A^*$). It is therefore to be expected that emission and photoisomerisation yields are complementary, as indeed seen qualitatively in Figure 2. Let us assume that the observed temperature dependence of ϕ_F is due to the variations of $k_{A^*\to B} = k_0 \exp(-E_a/RT)$. Denoting the radiative decay rate of $^1A^*$ by k_F and the sum of all non-radiative decay modes besides $k_{A^*\to B}$ by k, we have equations (1) and (2). Introducing $k_{A^*\to B}$ we get (3).

$$\phi_F = k_F/(k_F + k_{A^*\to B} + k) \qquad (1)$$

$$\phi_F^{-1} - 1 = (k_{A^*\to B} + k)/k_F \qquad (2)$$

$$\phi_F^{-1} - 1 = k_F^{-1}\,[k + k_0 \exp\,(-E_a/RT)] \qquad (3)$$

Similarly for $\phi_{A\to B}$ we have equations (4)—(6). Equations

$$\phi_{A\to B} = k_{A^*\to B}/(k_{A^*\to B} + k_F + k \qquad (4)$$

$$\phi_{A\to B}^{-1} - 1 = (k + k_F)/k_{A^*\to B} \qquad (5)$$

$$= (k_F + k)k_0^{-1} \exp\,(E_a/RT) \qquad (6)$$

(6) and (3) should lead to a linear relationship between $\ln(\phi_{A\to B}^{-1} - 1)$ and T^{-1} and, for $k \ll k_{A^*\to B}$, also between $\ln\,(\phi_F^{-1} - 1)$ and T^{-1}. Figure 7 shows that such a relation was indeed observed. The value calculated for E_a from the slope of these lines is 4.5 kcal mol^{-1} for ϕ_F and 4.4 for $\phi_{A\to B}$. At sufficiently low temperatures $\phi_{A\to B}$ reaches a small but temperature-independent value. The above treatment is obviously a rough approximation, valid within a limited temperature range, but gives an indication

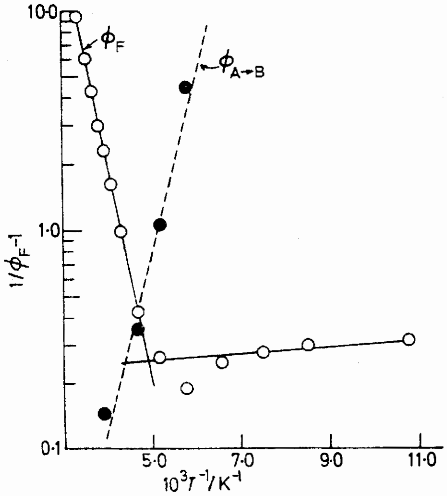

FIGURE 7 Temperature dependence of the quantum yields of fluorescence, ϕ_F, and of the photoconversion A ⟶ B, $\phi_{A\to B}$, plotted as $\log(\phi^{-1} - 1)$ against T^{-1}

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[12] I. B. Berlman, 'Handbook of Fluorescence Spectra,' Academic Press, New York, 1971, 2nd edn.

for the energy barrier of the thermally activated photoisomerisation, or rather the intersystem crossing (*cf.* Discussion section).*

Isomer B is also fluorescent. Its absorption and emission spectra are shown in Figure 1. In the absence of suitable standards in the spectral region 700—800 nm no corrected emission spectrum nor fluorescence quantum yields were estimated in this case. The relative fluorescence quantum yield is almost the same at −140 and −180°.

(g) *Results obtained by the Modulation Excitation Method.*—This method makes it possible to measure absorption spectra of short-lived transients,[13] complementing flash-photolysis methods. The spectra of both the P and B photoisomers were observed in argon-flushed solutions of (Ia) in either MCH or Perspex at room temperature, in good agreement with the relevant photoflash results described above. We adapted this method to observations with polarised light, by introducing polarisers in the path of the measuring and the exciting light beams. Polarisation values of +0.11 at 540 nm (attributed to the P form) and of −0.13 at 630 nm (B form) were measured in Perspex solutions. The latter result indicates that the transition moment of B forms an angle of 55—90° with that of the starting form A. (The lifetime of B under these conditions is *ca.* 10^{-4} s).

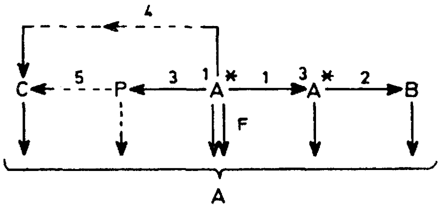
DISCUSSION

All observations regarding the photoformation of isomer B can be rationalised by the assumption that, just as in the dianthrones,[1,2] B is formed from singlet excited A *via* triplet A: $A \xrightarrow{h\nu} {}^1A^* \xrightarrow{1} {}^3A^* \xrightarrow{2} B$, the intersystem crossing (ISC) step 1 being an activated process which is sharply attenuated on cooling and thereby causes the observed attenuation of ϕ (A ⟶ B) on cooling. This activated step is bypassed in the presence of external spin-orbit perturbers, *e.g.* oxygen, carbon disuphide, and ethyl iodide, and of course by triplet sensitisers such as biacetyl. A similar but somewhat less pronounced enhancement by oxygen has been reported for the *trans* ⟶ *cis* photoisomerisation of diarylethylenes,[10] while still larger effects were observed in the related system (I; X = NCH_3).[14] The enhancement by the perturbers is the more pronounced, the smaller the rate of the unperturbed ISC, provided that diffusional interaction between the perturber and excited solute molecules is sufficiently fast. In the dianthrones we observed the reaction ${}^3A^* \longrightarrow B$ directly.[1] With (Ia) this is not possible in the absence of perturbers because at high temperatures the process is too fast, while at low temperatures too little triplet is formed. However, in dibenzdixanthylidene, where ISC is much more efficient and temperature independent, we did indeed observe [8] the formation of B from ${}^3A^*$.

A possible mechanism would be that the activated ISC involves a cross-over from the S_1 state to an energetically somewhat higher triplet state T_2, while the cross-over $S_1 \longrightarrow T_1$ is temperature independent but inefficient. The rate of $S_1 \longrightarrow T_1$, is strongly enhanced by the perturbers. At low temperatures this path remains the only one enabling the formation of B with a low but finite quantum yield. An energy difference of 4—5 kcal mol^{-1} between S_1 and T_2 states could account for the observed temperature dependence of ϕ $(A \xrightarrow{h\nu} B)$, while a large energy gap between S_1 and T_1 could be responsible for the inefficiency of $S_1 \longrightarrow T_1$. So much for the mechanism of formation of B. Concerning the nature of form B we suggest, by analogy with the dianthrones,[4] a conformation consisting essentially of two almost planar halves, twisted against each other so as to avoid overcrowding. Calculations similar to those carried out earlier [4a] indeed predict an energy minimum for an angle of twist of *ca.* 57°, and a long wavelength absorption peak in the 650—700 nm range. B Is separated from A by a potential barrier of 12 kcal mol^{-1}, and its energy content [5] exceeds that of A by 5 kcal mol^{-1}.

The cyclic structure (II) suggested for the photoisomer C is based on its oxidation to the known product (III), and on the similarity with the C forms in the dianthrone series, where ^1H n.m.r. results were found to agree with such a structure.[1,4a] The formation of both C and P probably occurs only from the singlet manifold of the A isomer.[15a] It cannot be sensitised, again in analogy with the modifications C in the dianthrone series,[15b] and with the dihydrophenanthrenes.[11a]

The Scheme summarises the proposed mechanism for the reversible photochemistry of (Ia), starting with singlet excited ${}^1A^*$. All steps are thermally activated to various extents, except 2, which is viscosity controlled.[1,8] Uncertain steps are denoted by broken lines.



SCHEME

EXPERIMENTAL

Spectrophotometry, Photochemistry, and Flash Photolysis in a Wide Temperature Range.—These techniques were

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* The effectiveness of spin–orbit coupling perturbers in the present cases leads us to prefer an $S_1 \longrightarrow T_2$ step as responsible for the temperature dependence over other possibilities such as intersystem crossing from a conformation isomer ${}^1A^*_x$. Some information about this problem could be obtained by examining the effects of high viscosities (*cf.* S. Sharafy and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1971, **93**, 4119; K. A. Muszkat, D. Gegiou, and E. Fischer, *ibid.*, 1967, **89**, 4814).

[13] M. A. Slifkin and R. W. Walmsley, *J. Phys. Eng. Sci. Instr.*, 1970, **3**, 160; M. A. Slifkin, *Phys. Bull.*, 1973, **2**, 4431.

[14] (*a*) R. Korenstein and K. A. Muszkat, 'Environmental Effects on Molecular Structure and Properties,' ed. B. Pullman, D. Reidel, Dordrecht, 1976, p. 561; (*b*) R. Korenstein, K. A. Muszkat, and E. Fischer, *Chem. Phys. Letters*, in the press.

[15] (*a*) For an analysis of the reactivity and mechanism, see K. A. Muszkat and W. Schmidt, *Helv. Chim. Acta*, 1971, **54**, 1195; K. A. Muszkat and S. Sharafi-Ozeri, *Chem. Phys. Letters*, 1973, **20**, 397; K. A. Muszkat, G. Seger, and S. Sharafi-Ozeri, *J.C.S. Faraday II*, 1975, **71**, 1529; (*b*) T. Bercovici, R. Korenstein, G. Fischer, and E. Fischer, *J. Phys. Chem.*, in the press.

applied as described earlier.[16-18] Long-necked spectrophotometric cells were either fused-off after evacuation or left open to allow flushing with either argon, oxygen, air, or nitrogen–oxygen mixtures. Most flash experiments were performed in cells made of rectangular cross-section Pyrex tubing [19] (inner dimensions 3 × 12 mm) with a light path of 20 mm, placed in a thermostatted copper block in a Pyrex Dewar. Quantum yields of the photoformation of the isomers B and C were calculated as usual,[11a, 18] employing ferrioxalate actinometry. The quantum yields of formation of B in the flash experiments over a wide range of temperatures were estimated by comparison with the yield at −140°, at which temperature B is sufficiently stable to make possible static experiments in the Cary 14 spectrophotometer.

Modulation Excitation.—The method used was essentially as described.[13] Briefly, the sample is illuminated by 366 nm light from a 250 W high pressure mercury arc suitably filtered and the intensity decreased by passing through a 15% transmission screen to cut down irreversible photodecomposition. This light is modulated by a rotary chopper at a frequency variable between 5 and 1 000 Hz. The sample is monitored with monochromatic light obtained from a 50 W, 12 V quartz–iodine lamp, powered by a direct current source. This light is detected with a UTC-500-UV solid state detector–amplifier combination. Any modulation on the signal, arising from a light-excited short-lived species, is detected with a phase-sensitive detector. The plastic sample was made as follows: compound (Ia) was added to a freshly distilled quantity of methyl methacrylate (BDH). This solution was polymerised by placing in boiling tubes immersed in a covered water bath maintained at 60° during 3 days. The polymerised sample was cut and polished to give discs 2.5 cm in diameter and *ca.* 3 mm thick, which were mounted in the instrument at 45° to both light beams. For polarisation a Glan–Thomas polarizer was placed in a fixed position in front of the mercury lamp, and a rotatory plastic-in-glass polariser in front of the quartz–iodine lamp. The polarisation R is defined as $(I_{\|}/I_{\perp} - 1)/(I_{\|}/I_{\perp} + 2)$, where $I_{\|}$ and $I_{\perp}$ are the measured absorptions of the excited species with the two polarisers parallel and perpendicular, respectively.

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