

REVERSIBLE PHOTOISOMERIZATION AND FLUORESCENCE OF BITHIOXANTHENE: TEMPERATURE AND SPIN-ORBIT PERTURBATION EFFECTS

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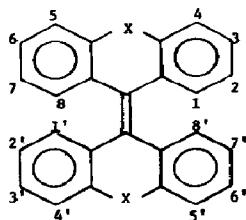
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Summary

A detailed experimental study of the reversible photochemistry of bithioxanthene over a wide temperature range indicates the photoformation of two unstable isomers: E, absorbing at shorter wavelength, and P, absorbing at longer wavelengths. Both isomers revert thermally to the parent compound, A. E is formed through the triplet manifold while P is formed directly from the excited singlet state. The quantum yield for the A → E process is temperature dependent and is enhanced by molecular oxygen and by xenon. A low temperature proton n.m.r. analysis of the E and A forms indicates a structure for E which involves *cis-trans* isomerization about the 9–9' central double bond and additional torsion about the four single bonds attached to it.

Introduction

The nature of photochromism [1] and thermochromism of bianthrone (Ia) has been recently established by applying low temperature n.m.r. techniques in conjunction with a computational approach based on the evaluation of minimum energy geometries of the unstable modifications [2].



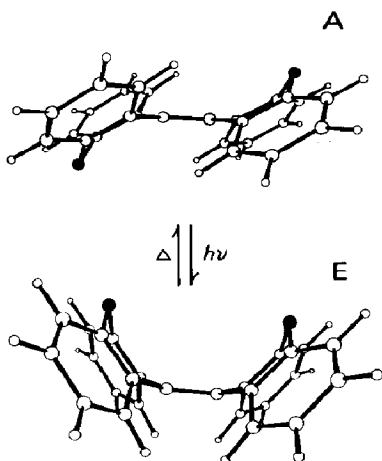
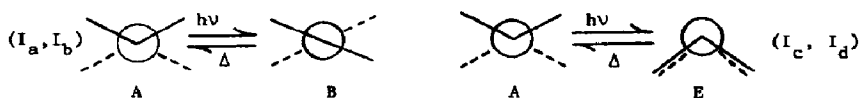


Fig. 1. Suggested molecular conformation of the A and E forms of bithioxanthene.

The structure of the labile B photoisomer responsible for both the thermo and photochromic properties of Ia and Ib, involves a torsion of $\sim 57^\circ$ about the 9-9' double bond [2]. Appearance of a different type of isomer, denoted as E isomer, was observed in the non-photochromic derivatives Ic and Id [3]. The structure of this photoisomer involves torsion about the four single bonds attached to the 9-9' double bond [4] (Fig. 1). These two types of isomerization in Ia, Ib, Ic and Id are shown in the following scheme:



[A denotes the parent compound; B and E are the labile photoisomers.]

Kortüm [5] found that both the photochromic and the thermochromic properties were absent when $X = S$, *i.e.* in compound I.

In this publication we wish to describe the results of an extensive investigation of the photochemistry of dithioxanthene (I) undertaken within the framework of our studies of the relationship between photochromic properties and type of bridging group.

Experimental

Chemicals

Bithioxanthene was synthesized according to a procedure described by Schönberg [12]. MCH (spectrograde) and 2-MP were freed from traces of water and aromatic impurities by passage through a Woelm basic alumina column. Solutions were flushed continuously with either argon containing <5 p.p.m. oxygen, or with the desired nitrogen-oxygen mixture. Such mixtures were prepared by introducing the two gases into an empty gas cylinder at the required pressures

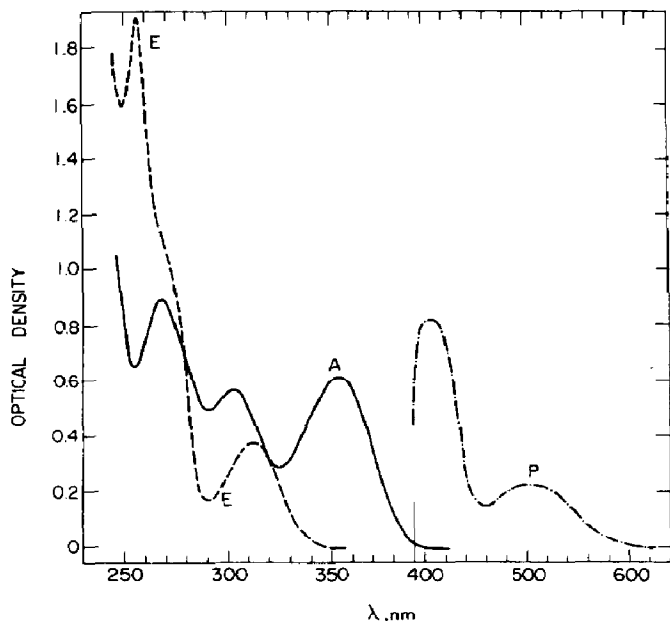


Fig. 2. Absorption spectra of bithioxanthene and its photoisomers E and P. A, absorption spectrum of the A form; E, absorption spectrum of the E form; P, spectrum of photoisomer P (obtained by flash photolysis; the scale of the P spectrum is arbitrary), 4×10^{-5} M in MCH/2-MP mixture.

Spectrophotometry, photochemistry and flash photolysis in a wide temperature range

These techniques were applied as described earlier [13]. The flash experiments were performed in cells made of rectangular quartz tubing (inner dimensions 16×4 mm) with a light path of 70 mm, placed in a thermostated copper block maintained inside a quartz Dewar. Quantum yields were calculated employing ferrioxalate actinometry. The quantum yields for the formation of E in the flash experiments were estimated by comparison with the yield at -60 °C, at which temperature E is sufficiently stable so that its formation yield could be determined by a stationary spectrophotometric method.

Results

Photoisomerization to the E isomer

At sufficiently low temperatures bithioxanthene [A form; Fig. 2 (A)] undergoes complete photoisomerization in polar(2-methyltetrahydrofuran MTHF) and non-polar(methylcyclohexane/2-methyl pentane mixture MCH-MCP) solvents yielding a short wavelength photoisomer [E form; Fig. 2 (E)]. The E isomer is light stable and reverts thermally to the parent compound at temperatures higher than -20 °C. The $E \xrightarrow{\Delta} A$ spontaneous

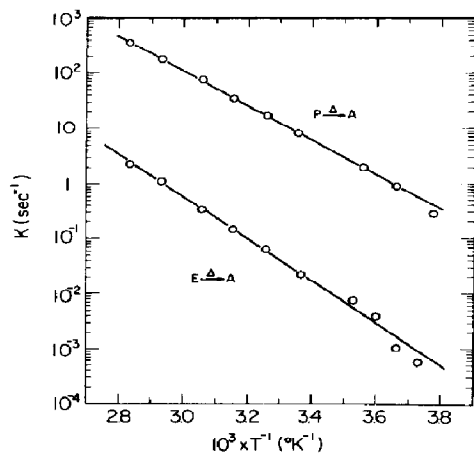


Fig. 3. Arrhenius plots for the spontaneous processes $E \rightarrow A$ and $P \rightarrow A$ (see text).

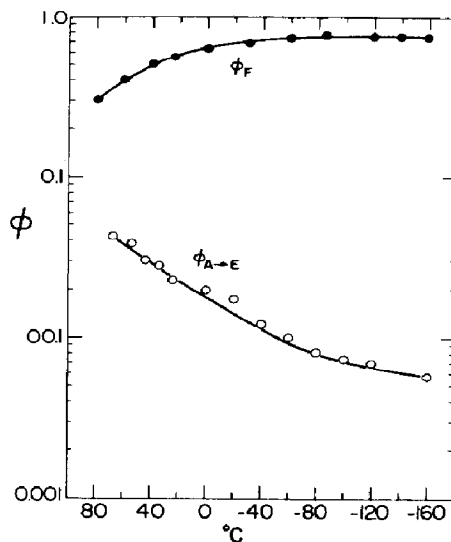


Fig. 4. Temperature dependence of $\Phi_{A \rightarrow E}$ and Φ_F in bithioxanthene, in MCH/2MP.

process was measured over the temperature range from -5° to $+80^\circ \text{C}$ employing a flash photolysis method and was found to follow first order kinetics with an activation energy E_a of $18 \pm 0.5 \text{ kcal/mol}$ and a frequency factor A of 10^{12} s^{-1} (Fig. 3). The temperature dependence of the photoisomerization quantum yield $\Phi_{A \rightarrow E}$ was measured over a wide temperature range, from $+60^\circ$ to -180°C (Fig. 4). $\Phi_{A \rightarrow E}$ decreases gradually on cooling, from 0.04 at $+60^\circ$ to 0.006 at -160°C . Further cooling to -180°C causes a sharp drop in the yield, to 0.0002. $\Phi_{A \rightarrow E}$ is independent of the concentration of the parent compound.

Photosensitized isomerization

Argon-flushed solutions (MCH/2-MP) of bithioxanthene ($5 \times 10^{-5} \text{ M}$) as acceptor with biacetyl as donor ($1.3 \times 10^{-2} \text{ M}$, triplet energy 56 kcal/mol) [6] were irradiated at -60°C with 436 nm light so as to limit excitation only to the biacetyl molecules. The same spectral changes and the same rate constants for the $E \rightarrow A$ process were measured as in direct excitation. These results show that (a) formation of E is possible through the triplet manifold and (b) that the triplet energy of bithioxanthene is lower than 56 kcal/mol. The quantum yield of the photosensitized isomerization shows no temperature dependence down to -100°C .

Enhancement of $\Phi_{A \rightarrow E}$ by external spin-orbit perturbation

The rate of the photoisomerization $A \rightarrow E$ is enhanced by both molecular oxygen and by xenon. The results are summarized in Table 1.

TABLE 1

Enhancement of $\Phi_{A \rightarrow E}$
by O_2 and Xe (I, 5×10^{-5}
 M solutions in MCH at $-80^\circ C$).

Dissolved gas*	$\Phi_{A \rightarrow B}$
Argon	0.008
Oxygen	0.024
Xenon	0.034

*For solubility data, see ref. 7.

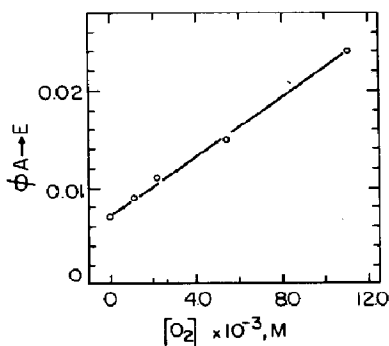


Fig. 5. Effect of oxygen concentration on the quantum yield $\Phi_{A \rightarrow E}$ of bithioxanthene, MCH/2-MP solution, $4 \times 10^{-5} M$, at $-140^\circ C$.

The enhancement as function of perturber concentration was measured by changing partial oxygen pressures (Fig. 5). The linear dependence of $\Phi_{A \rightarrow E}$ on the oxygen concentration indicates that even at the highest concentration of oxygen ($1.1 \times 10^{-2} M$) the observed enhancement is still far from its maximum value. Thus it seems possible, in this case, to enhance farther the photoisomerization quantum yields $\Phi_{A \rightarrow E}$ by working at oxygen pressures higher than 1 atm.

Low temperature proton n.m.r. measurements of A and E forms

The low temperature 90 megacycles proton n.m.r. spectrum of the E photoisomer (Fig. 6) was recorded in the FT mode at $-60^\circ C$. The solution of bithioxanthene in CD_2Cl_2 was irradiated with 365 nm light inside the n.m.r. probe. In the spectrum of the A form (parent compound; full curve) the 4,5,4',5' hydrogens appear in the lowest field (7.7 - 8.0 p.p.m.), the 1,8,1',8' hydrogens appear at the highest field (7.18 - 6.65 p.p.m.) and the 2,3,6,7,2',3',6',7' hydrogens appear at 7.18 - 7.7 ppm. Comparison of the spectra of forms A (full curve) and E (broken curve) indicates that no valence isomerism is involved in the process $A \rightarrow E$ as no new signals are observed at higher fields than 6.6 p.p.m. In the process $A \rightarrow E$ both the 1,8,1',8' protons and the 2,7,2',7' protons are shifted downfield as a result of a

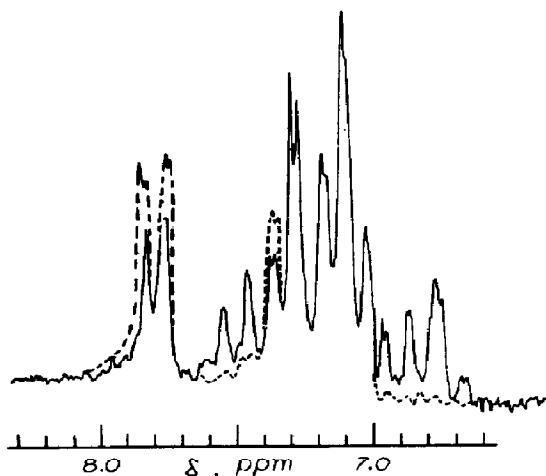


Fig. 6. Proton n.m.r. spectra of the A form (—) and the E form (· · · · ·) of bithioxanthene, in CD_2Cl_2 at -70°C .

deshielding effect, and the 3,6,3',6' hydrogens are shifted upfield as a result of a shielding effect.

The semiclassical ring current method of Johnson and Bovey [8a] was used in order to interpret the changes of the proton chemical shifts for the $A \rightarrow E$ process in a more quantitative manner. Although many quantum mechanical treatments [8b] of ring current have been described, the above method within its classical limitations is quite adequate and gives surprisingly good results. The diamagnetic shielding is a function of two geometric parameters: ρ , the distance of the proton from the sixfold axis of the ring and z , the distance between the proton and the plane of the ring. The diamagnetic shielding of the 1,2,3,4 protons by the opposite benzene ring both in the A and E conformations (Fig. 1) was calculated. The atomic coordinates of the two conformations were obtained from a minimum energy calculation on Id, serving as a model compound [4]. The calculated proton shifts are listed in Table 2. The calculated difference $\Delta_E - \Delta_A$ is in good agreement (within 0.1 p.p.m.) with the observed shielding changes for the 1,8,1',8' and the 2,7,2',7' hydrogens, thus indicating a conformation similar to that deduced [4] for the E isomer of Id.

Photoformation of the P photoisomer

Flash photolysis experiments at temperatures from 80° to -20°C indicate the formation of another photoisomer denoted as P, absorbing at longer wavelengths (Fig. 2). This photoisomer, like the E photoisomer, is light stable. P reverts quantitatively to the parent compound, the activation energy being 15 kcal/mol ($A = 10^{12}$). The rates are much faster than the comparable rates for the $E \xrightarrow{\Delta} A$ transition at similar temperatures (Fig. 3). Flushing the solutions with oxygen reduces the quantum yield by a factor of 3 (at 25°C). The absorption spectrum, the Arrhenius parameters and the light stability of this isomer are very similar to those found for the P photo-

TABLE 2

Proton type	Δ_A	Δ_E	$\Delta_E - \Delta_A$	$\Delta_E - \Delta_A$ (exp.)
1,8	1.07	-0.067	-1.1	-1.0
2,7	+0.14	0	-0.14	-0.25
3,6	-0.09	+0.096	+0.15	+0.20
4,5	0	+0.12	+0.12	0

isomer in Ib [9]. No photosensitized formation of P was detected using biacetyl as the donor. The extent of photoconversion $A \rightarrow P$ drops sharply on cooling ($\Phi_{A \rightarrow P}^{70^\circ} / \Phi_{A \rightarrow P}^{-20^\circ} = 40$), and P is not observed below -40°C . The amount of conversion $A \rightarrow P$ as inferred from the decrease in the first maximum absorbance of A at 350 nm is very low ($\sim 2\%$).

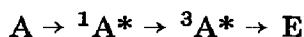
Fluorescence spectra and quantum yields and their temperature dependence

The emission and absorption spectra of bithioxanthene are shown in Fig. 7. The fluorescence quantum yields were measured between $+80$ and -160°C , in argon-flushed solutions (Fig. 4). Φ_F was measured relative to the Φ_F of 9,10-diphenyl anthracene (1.0) [10]. As seen from Fig. 3, emission quantum yields decrease on increase of the temperature, from 0.75 at -160°C to 0.3 at $+80^\circ\text{C}$. Since $\Phi_{A \rightarrow E} = 0.05$ at 80°C , most of the deactivation of $^1A^*$ at higher temperatures takes place by non-radiative paths not involving formation of E. Possible modes are internal conversion into the ground state, or intersystem crossing and efficient quenching of the resulting $^3A^*$. The attenuation of the fluorescence quantum yield by air [9] at 25°C , suggests a value of ~ 5 ns for the excited singlet lifetime of bithioxanthene.

The E photoisomer is non-fluorescent. The absence of fluorescence and the light stability indicate that radiationless transition to the ground state of the E form is the main route of decay of the excited state of this form.

Discussion

The photoisomerization process $A \rightarrow E$ probably proceeds through the triplet manifold of the parent compound:



This assumption is based on two indirect observations: (a) sensitization of the $A \xrightarrow{h\nu} E$ process by biacetyl, (b) enhancement of photoisomerization quantum yield, $\Phi_{A \rightarrow E}$, by xenon and by molecular oxygen. Both xenon and molecular oxygen serve as external spin-orbit perturbers. As seen from Table 1 molecular oxygen is more efficient concentrationwise than Xe, probably owing to their different mechanism of action. The mode of action of

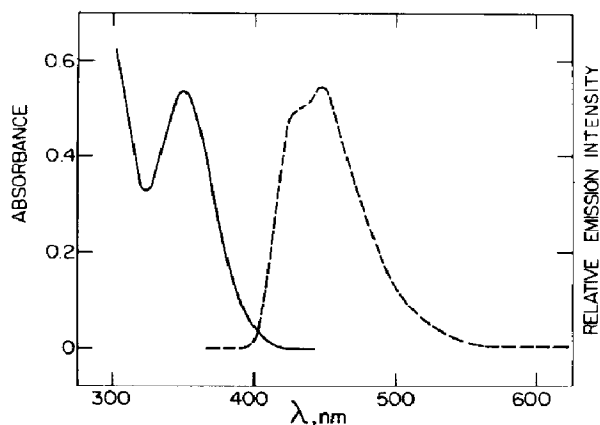
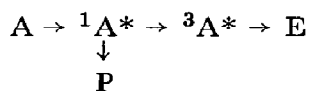


Fig. 7. Absorption and emission spectra of bithioxanthene in MCH/2-MP at -180°C .

oxygen has been a subject of considerable debate [11]. Thus it has been suggested that the spin-orbit perturbation by oxygen proceeds both by exchange and charge-transfer mechanisms with the second mechanism predominating [11].

The temperature dependence of $\Phi_{A \rightarrow E}$ (Fig. 4) indicates the existence of a thermally activated process in the sequence $^1A^* \rightarrow ^3A^* \rightarrow E$. The temperature-independent sensitized photoisomerization indicates that it is the ISC (intersystem crossing) process which requires activation. It is a common approach [9] to interpret an activated ISC in terms of crossover from the S_1 state to an energetically somewhat higher triplet state T_2 , while the crossover $S_1 - T_1$ is temperature independent, but very slow. At low temperatures the $S_1 - T_1$ path is the only route for the $A \rightarrow E$ process, and therefore $\Phi_{A \rightarrow E}$ diminishes as the temperature decreases. In the presence of external spin-orbit perturbors the rate of the $S_1 - T_1$ process is strongly enhanced.

The decrease in the photoformation yields of the P isomer brought about by oxygen, and the absence of sensitization by biacetyl indicate that P is formed directly from the excited singlet state. The reversible photochemistry of bithioxanthene can thus be summarized in the following scheme:



The lack of fluorescence from the E photoisomer and its light stability, contrary to the case of the parent compound A, indicate that the structural changes due to the $A \rightarrow E$ process introduce a very efficient path of radiationless transitions.

The low temperature proton n.m.r. analysis of the change in chemical shifts in the $A \rightarrow E$ process is in agreement with the structures A and E given in Fig. 1. Like in the cases of bianthrylidene (Id) and of 10,10'-dimethyl biacridan (Ic), the process $A \rightarrow E$ involves *cis-trans* isomerization, in addition to torsion about the four single bonds attached to the 9,9' double bond. The

similarity of the absorption spectra of the P isomer to that of the photo-cyclic C isomer in bianthrone derivatives and their common formation through the excited singlet suggest similarity of the structures of P and of C.

The reversible photochemistry of bithioxanthene is an example of a general pattern observed in bianthrylidene, Id, and in 10,10'-dimethyl biacridan (Ic) that whenever the C-X-C bond angle approaches the tetrahedral value, the isomer formed is of the E type and not of the B type, and for this reason bithioxanthene just like Ic and Id is devoid of photochromic properties.

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