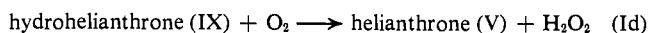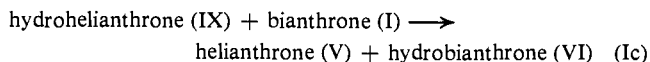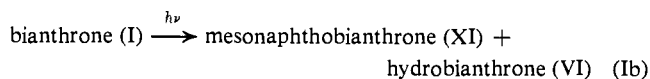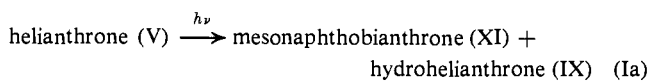# Spectroscopy and Photochemistry of Bianthrones[1]

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Abstract: A spectroscopic and photochemical study of 2,7'-dimethylbianthrone and its reaction products was carried out. The primary photochemical reaction results in a colored cyclized product. Following this, a free-radical mechanism is proposed in which the initial reacting species is an excited state of the photocyclized form. A secondary reactive species in the total reaction sequence is proposed to be a photocyclized helianthrone. The influence of viscosity and steric factors on the spectra and photochemistry is also considered.

The history of the thermo- and photochromism of bianthrone has been a long and quite turbulent one. This results from proposals and counterproposals for the nature and geometry of the species and the relation between the species and the mechanisms involved for both the reversible and irreversible processes. It should be noted that in the discussion of the general reaction scheme, every attempt has been made to relate a complete story. However, because of the large number and complexity of reactions, clear "proof" does not exist for all reactions. Appropriate wording is used to indicate this where necessary. Nonetheless, for the sake of completeness, we believe such a presentation is useful and meaningful. The structures of the species to be considered in the present investigation are shown in Figure 1. The abbreviations used in the equations are also given there. The number system used here is that of Hirschberg and Fischer[3] in contrast to that of Kortum, *et al.*[4] The 2,7-dimethylbiantrone could also be the 2,2'-dimethyl derivative.

Although the irreversible photochemistry of undeoxygenated solutions of bianthrone has been investigated by others,[5] the most recent definitive work is that of Brockmann and Muhlmann,[6] who studied the photochemistry of bianthrone and helianthrone in varied solvents, both in the presence and absence of oxygen. They determined the following reactions to occur (see Figure 1 for structures)

$$\text{helianthrone (V)} \xrightarrow{h\nu} \text{mesonaphthobianthrone (XI)} +$$
$$\text{hydrohelianthrone (IX)} \quad \text{(Ia)}$$

$$\text{bianthrone (I)} \xrightarrow{h\nu} \text{mesonaphthobianthrone (XI)} +$$
$$\text{hydrobianthrone (VI)} \quad \text{(Ib)}$$

$$\text{hydrohelianthrone (IX)} + \text{bianthrone (I)} \longrightarrow$$
$$\text{helianthrone (V)} + \text{hydrobianthrone (VI)} \quad \text{(Ic)}$$

$$\text{hydrohelianthrone (IX)} + O_2 \longrightarrow \text{helianthrone (V)} + H_2O_2 \quad \text{(Id)}$$

$$\text{hydrobianthrone (VI)} + 2O_2 \longrightarrow \text{bianthrone (I)} + 2H_2O_2 \quad \text{(Ie)}$$

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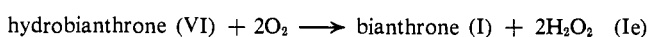
(1) Supported in part by the U. S. Air Force, Wright-Patterson Air Force Base, Ohio, Contract No. AF 33(615)-1733. Reprint requests should be directed to R. S. B.

(2) Taken in part from the Ph.D. dissertation submitted by C. E. E. in partial fulfillment of the requirements for the Ph.D. degree, University of Houston, 1967.
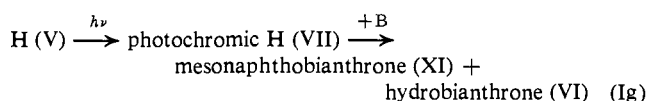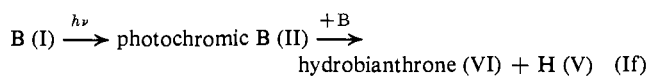
(3) Y. Hirschberg and E. Fischer, *J. Chem. Soc.*, 629 (1953).

(4) G. Kortum, W. Theilacker, H. Zeinizer, and H. Elliehausen, *Chem. Ber.*, **86**, 294 (1953).

(5) H. Meyer, R. Bondy, and A. Eckert, *ibid.*, **45**, 1447 (1912).

(6) H. Brockmann and R. Muhlmann, *ibid.*, **82**, 348 (1949).

Because of the lack of oxidizing ability of even irradiated bianthrone (B) or helianthrone (H) and the ability of irradiated helianthrone to reduce other oxidizing agents such as ferric chloride, they[6] proposed an intermediate with labile H atoms as the product of the primary photochemical process. The improbability of a tertiary collision indicated that helianthrone was an intermediate in the photolysis of bianthrone, hence

$$B\ (I) \xrightarrow{h\nu} \text{photochromic B (II)} \xrightarrow{+B}$$
$$\text{hydrobianthrone (VI)} + H\ (V) \quad \text{(If)}$$

$$H\ (V) \xrightarrow{h\nu} \text{photochromic H (VII)} \xrightarrow{+B}$$
$$\text{mesonaphthobianthrone (XI)} +$$
$$\text{hydrobianthrone (VI)} \quad \text{(Ig)}$$

In the event any intermediate reacted with a helianthrone molecule to give mesonaphthobianthrone and hydrohelianthrone, the latter would immediately react with bianthrone to give helianthrone back and hydrobianthrone (as in eq Ic), so that the net result is still that of eq Ib.[6]

Brockmann and Muhlmann[6] reported the above reactions for helianthrone to occur in acetic acid, dioxane, n-butanyl alcohol, cyclohexanol, benzyl alcohol, acetic anhydride, and acetyl chloride, but in benzene, xylene, chlorobenzene, and carbon disulfide they obtained "red oily" solutions, for which they were unable to account. They reported that bianthrone exhibited no anomalous behavior.

In 1965 Harrah and Becker[7] reported that the electron spin resonance (epr) spectra of photolyzed solutions of 2,7-dimethylbianthrone in m-xylene at room temperature or 2-methyltetrahydrofuran (2-MeTHF) at low temperature and at room temperature were identical with that of the negative ion of 2,7'-dimethylbianthrone generated in 2MeTHF with potassium t-butoxide or stannous chloride. They further noted that the epr signal increased to a maximum prior to the maximizing of the green photoproduct. This signal is equivalent to that observed by Wasserman[8] and assigned by him to the thermochromic form of bianthrone in pyridine if Harrah and Becker's spin density assignments are substituted.[7]

Dombrowski, *et al.*,[9] obtained an absorbance band maximum at 570 mμ by flash photolysis of partially

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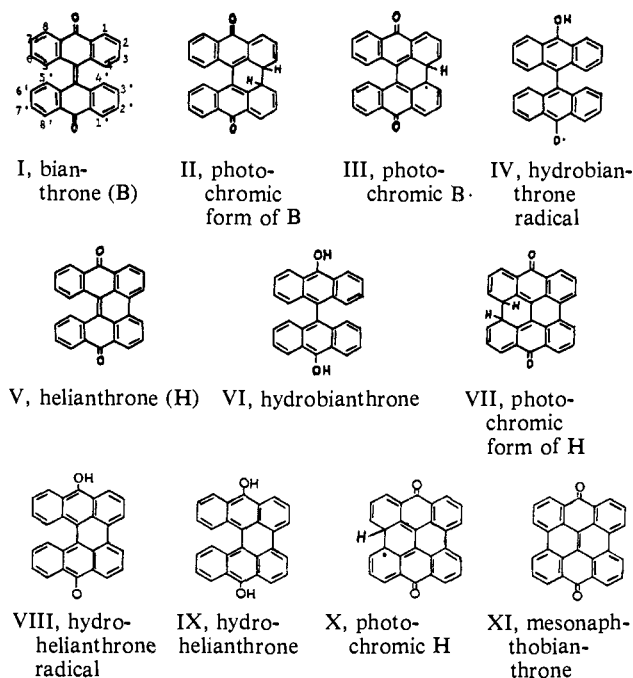
Figure 1. Structures of the compounds.

I, bianthrone (B) II, photochromic form of B III, photochromic B · IV, hydrobianthrone radical

V, helianthrone (H) VI, hydrobianthrone VII, photochromic form of H

VIII, hydrohelianthrone radical IX, hydrohelianthrone X, photochromic H XI, mesonaphthobianthrone

photolyzed benzene solutions of bianthrone which decayed according to second-order kinetics.

Engel[10] and Bergmann and Corte[11] suggested partial dissociation to give a diradical as a mechanism because of the chemical behavior. Drawing a parallel between the ring condensation of salts (such as 18-methylphenyldibenzoxanthynium perchlorate[12]) and betaines and of bianthrone,[13] Schoenberg and coworkers[14] proposed that a betaine form was responsible for the thermochromic band of bianthrone. In 1950 Theilacker and coworkers[15] and Grubb and Kistiakowsky[16] independently published parallel studies of bianthrone as well as other of the thermochromic ethylenes. Both groups showed the solutions to obey Beer's law and suggested that thermochromism was the result of an equilibrium between the ground state of the molecule and a triplet or a diradical.[15,16] The ΔH and ln ϵ_{T_∞} measured by Theilacker, et al.,[15] for this equilibrium in dimethyl phthalate were 3.4 ± 0.2 kcal and 3.55 ± 0.15.

Grubb and Kistiakowsky[16] determined a value of 3.5 kcal for ΔH which was independent of the nature of the solvent within the experimental error. They suggested the thermochromic form was diradical with molecular halves at 90° to one another. Steric considerations indicated a high potential barrier between the ground state of bianthrone and a coplanar colored form which was only 3.5 kcal higher than the ground state. However, similar kinetic studies showed a barrier of less than 20 kcal.

Hirschberg and coworkers[17] pointed out that 4,5'-substituted bianthrones were not thermochromic and argued on this basis that the two halves of the thermochromic form must be coplanar. A green coloration of bianthrone solutions was observed by Hirschberg, et al.,[18] upon cooling the solutions to liquid nitrogen temperature (77°K). Kortum[4] showed that this green coloration was a photochemical, rather than a thermal, phenomenon. Further, Kortum and coworkers concluded that thermochromism was the result of an equilibrium between a nonplanar ground state and a triplet planar colored configuration (a so-called "bi-radiclet") with a solvent-independent ΔH of 3.4 kcal.

The reversible photocoloration at low temperature of bianthrone was first observed[18] and identified as a photoprocess[19] by Hirschberg and more thoroughly studied by Hirschberg and Fischer,[3] although only in the visible region. Furthermore, they found the absorption maxima of the photo- and thermochromic forms of bianthrone and dixanthylene to occur at the same wavelength, and on this basis proposed identical structures for the two colored forms. Because photoconversion occurred in fluids, but not in rigid glasses, they concluded that formation of the colored form involved a change in atomic configuration. The heat of activation for thermal reversion was 12–20 kcal and the calculated frequency factor was felt to preclude the colored form being a triplet.

Later, Hirschberg[20] reported spectra for the 4,5'-dimethylbianthrone which showed band maxima at 440 and 460 nm in addition to a band at 660 nm for the photochromic form. He also noted that the photocolored form could be photobleached by irradiation into the 640-nm band. It was further noted that the 640-nm band was insensitive to variation of pH.

Differences in the near-ultraviolet absorption region of the photo- and thermochromic spectra of 2,4,5',7'-dimethylbianthrone and the unsubstituted bianthrone indicated to Kortum and coworkers[21] that these forms actually differed. Some discussions concerning the question of the identity of the two forms ensued.[22–26] A more extensive study by Kortum, et al.,[27] showed that at least two forms of 2,4,5',7'-tetramethylbianthrone could be generated by photolysis. One of them, which absorbed at 666 mμ, was the same as the form generated by low-temperature hydrolysis of the sulfuric acid adduct of the 2,4,5',7'-tetramethylbianthrone. Form B was taken to be identical with the thermochromic form for the case of the bianthrone itself.[27] The other photoproduced form, C, absorbed at 460 and 435 nm. Its concentration relative to that

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(18) Y. Hirschberg, E. Lowenthal, E. D. Bergmann, and B. Pullmann, Bull. Soc. Chim. Fr., **18**, 88 (1951).
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(23) G. Kortum, W. Theilacker, and V. Braun, ibid., **23**, 1723 (1955).
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(25) Y. Hirschberg and E. Fischer, ibid., **70**, 573 (1958).
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of form B was found to vary with solvent and to increase with increasing temperature of irradiation.

Magnetic balance measurements by Kortum, et al.,[28] showed the thermochromic form of bianthrone to be diamagnetic and the photochromic form of 2,4,5',7'-tetramethylbianthrone to be paramagnetic. No epr signal was found by Hirschberg and Weissman[29] for solutions of the photochromic form, in contrast to the findings of Wasserman.[8,30] However, signals reported for the B negative ion by Harrah and Becker[7] are equivalent to those reported by Wasserman[8] and were assigned to the photochromic form of bianthrone by Wasserman.[8]

Wasserman and Davis[31] also proposed that the piezo-, thermo-, and photocolored forms of bianthrone were identical on the basis of identical rate constants for reversion. However, Mills and Nyburg[32] pointed out that this only indicated that the rate-determining steps might be the same.

The most recent evidence bearing on the nature of the photochromic form comes from the extensive study of the photocyclization of stilbene and 1,1',3,3'-5,5'-hexamethylstilbene by Fischer and coworkers[33] and the flash photolysis study by Huber, et al.,[34] of 2,4,5',7'-tetramethylbianthrone. The former of these[33] indicates that a bridged form intermediate is correct. The latter study,[34] by simultaneous monitoring of the visible absorption bands of the photochromic forms of bianthrone and the phosphorescence of bianthrone itself, surmises that two photochromic forms exist and that these do not arise via a triplet state of bianthrone. It is postulated that these photochromic forms are conformers of the ground state.

In part, our studies of 2,7'-dimethylbianthrone show that a spatial modification of the molecule is required for photoconversion. In addition, an excited state of the bridge colored form is the active species for the irreversible step in photocyclization of 2,7'-dimethylbianthrone which proceeds via a free-radical mechanism. Also, previously detected epr signals ascribed to the photochromic form[8,30] are very likely due to radicals formed during the irreversible photochemistry rather than to the photochromic form. In accord with the findings of Hirschberg and Fischer[3] and Kortum,[27] our absorption data for the photo- and thermochromic forms of bianthrone indicate that these are identical singly bridged isomers, while the photoproducts which absorb at shorter wavelengths might both be the result of photocyclization and partial dehydrogenation. These will be discussed in more detail shortly.

Experimental Section

The 2,7'-dimethylbianthrone and 4,5'-dimethylbianthrone were obtained from the Light Chemical Co. The 3,6'-dimethylhelianthrone and the 3,6'-dimethylmesonaphthobianthrone were supplied by Dr. Larry Harrah. The 3,6'-dimethylmesonaphthobianthrone was recrystallized first from N,N-dimethylformamide, then from pyridine, and finally washed with 95% ethanol. The remaining three compounds were multiply recrystallized from acetic acid and m-xylene.

Thin layer chromatography of the compounds on alumina plates eluted with either carbon tetrachloride or chloroform gave a single spot.

The 2,7'-dimethylhydrobianthrone was prepared by photolyzing a vacuum-degassed sample of 2,7'-dimethylbianthrone for 2 hr through a 466-mμ interference filter with a tungsten lamp after an initial 10-sec irradiation through a 300-mμ interference filter. This gave precipitated 2,7'-dimethylmesonaphthobianthrone and one other product whose absorption and emission spectra resembled that of 9,10-dichloroanthracene.[35] The additional product fluoresced very strongly relative to 2,7'-dimethylbianthrone just as hydroanthraquinone luminesces very strongly relative to anthraquinone.[36] The absorption spectrum indicated a relative concentration of 2,7'-dimethylmesonaphthobianthrone of less than 3%. Because of its low solubility in EPA [ethanol–isopentane–ethyl ether (2:5:5) hydrobianthrone-mesonaphthobianthrone >20:1], the 2,7'-dimethylmesonaphthobianthrone was judged not to interfere with the principal features of the spectrum. The 2,7'-dimethylmesonaphthobianthrone was prepared by washing the precipitant from the above photolysis with 95% ethanol.

Solvents. The solvents for recrystallizations were fractionated after refluxing for 12 hr over anhydrous calcium sulfate or granulated sodium–lead alloy as appropriate. The benzene, toluene, m-xylene, and pyridine for room-temperature spectra were Matheson Coleman and Bell Spectroquality reagent grade. The ethanol was USP–NF reagent quality absolute ethanol. Aminco EPA mixed solvent and 2-methyltetrahydrofuran (2MeTHF) were used for emission spectra and low-temperature absorption spectra. The 2MeTHF was refluxed over sodium for 24 hr, fractionated, and then passed over an alumina column immediately before use. Both solvents for emission were checked for peroxides by use of the luminol reaction[37] immediately before use.

Samples. All 2,7'-dimethylbianthrone or 3,6'-dimethylhelianthrone samples were prepared under a red ruby safe light or a conventional bug light. All other samples were prepared in subdued indirect light. Those samples used for emission, low-temperature absorption, and photochemistry were vacuum degassed by freeze–thaw cycling to a calculated oxygen concentration of less than 10^{-7} M.

Spectra. Absorption spectra were taken on a Beckman DK-1 or Cary 15 recording spectrophotometer. Quartz or Pyrex window cells were used for room-temperature spectra. A sealed Pyrex emission tube of rectangular cross section was used for the 2,7'-dimethylhydrobianthrone. Low-temperature absorption spectra were taken using Pyrex or quartz emission tubes of rectangular cross section in a dewar fitted with quartz windows. The emission tubes were sealed or closed with a vacuum stopcock.

All fluorescence excitation spectra were taken from the front surface, while some fluorescence spectra were taken at 90° to excitation. All phosphorescence spectra and lifetime measurements were taken at 180° to excitation using a modified Becquerel phosphoroscope. A Tektronic 581A oscilloscope with a Type 86 plug-in was utilized for the measurement of phosphorescence lifetimes.

Engelhard-Hanovia 900-W high-pressure xenon arcs or Sylvania 150-W tungsten lamps with dichroic reflectors were used with a Bausch and Lomb grating monochromator, a Hilger and Watts prism monochromator, or Optics Technology "mono pass" interference filters for excitation. An Aminco grating monochromator with an EMI 9558 photomultiplier tube was used for monitoring the emissions.

Photolysis. A 150-W tungsten lamp or a 100-W low-pressure mercury arc with appropriate filters was used for photolysis of the solutions.

Temperature Control. A Wheelco Model 402 Capacitrol was used as the temperature controller in the 88–223°K range. Vapor from boiling liquid nitrogen was the coolant.

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Table I. Absorption Spectral Characteristics of the Compounds Studied

| | Absorption (EPA) | | | | | |
| | Room temperature | | | Low temperature | | |
Compound	λ_{max}, nm	log ϵ	F–C[a] shape[c]	λ_{max}, nm	log ϵ^b	F–C[a] shape[c]
2,7-Dimethylbianthrone	400	4.2	F	410	4.2	A
4,5′-Dimethylbianthrone	375		F	392	3.8	A
3,6′-Dimethylhelianthrone	460	4.3	A	477	4.4	A
3,6′-Dimethylmesonaphtho-bianthrone	430		A	435		A
2,7′-Dimethylhydrobianthrone			A	427		A
2,7′-Dimethylhydrohelianthrone	605		A	624		A
Photochromic form of 2,7′-dimethylbianthrone				715		F
Photochromic form of 4,5′-dimethylbianthrone				650		F

[a] Franck–Condon. [b] Extinction coefficients calculated assuming a 25% volume decrease on cooling from 300 to 77°K. [c] F = forbidden and A = allowed.

Results

Spectral and Photolysis Results. The principal features of the spectra are presented in Tables I and II. Spectra for compounds of concern are presented in Figures 2–5. Based on the sharp onset of the absorp-

Irradiation of 2,7-dimethylbianthrone in EPA or 2MeTHF rigid glasses at 77°K for 2 hr at 400 nm gave no detectable conversion. However, irradiation of 2,7-dimethylbianthrone in a rigid glass of methyl phthalylethyl glycolate at 208°K for 20 min at 400 nm gave an estimated 80% conversion.
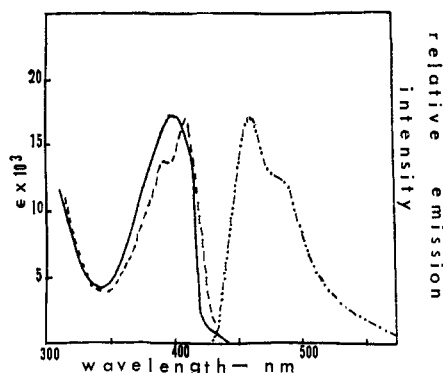

Figure 2. Room-temperature absorption (——), low-temperature absorption (-----), and fluorescence spectra (-·-··-·) of 2,7′-dimethylbianthrone in EPA.
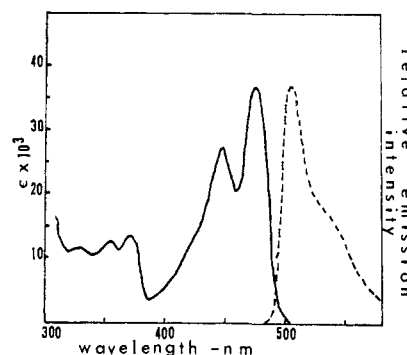

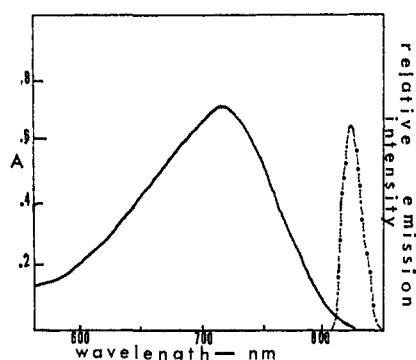Figure 4. Low-temperature absorption (——) and fluorescence spectra (-----) of 3,6′-dimethylhelianthrone in EPA.

Figure 3. Absorption (——) and fluorescence spectra (-·-··-·) of the photochromic form of 2,7′-dimethylbianthrone in EPA.
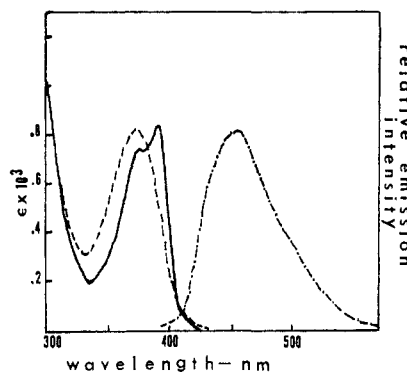

Figure 5. Room-temperature absorption (-----), low-temperature absorption (——), and fluorescence spectra (-·-··-·) of 4,5′-dimethylbianthrone in EPA.

tion (77°K), mirror image relationship of the absorption and fluorescence, and the overlap of the fluorescence with the absorption, all fluorescences are assigned as originating from the lowest π,π^* singlet state. In addition, all phosphorescences are assigned as originating from the lowest π,π^* triplet state.

Samples of 2,6′-dimethylbianthrone in EPA cooled to 77°K by liquid nitrogen, then raised to ~93°K, were converted to the photochromic form by irradiating at 400 nm for 15 min and trapped by recooling to 77°K. On warming, the sample reverted to bianthrone with no net irreversible photochemistry for the total cycle detectable by absorption.

Table II. Emission Spectral Characteristics of the Compounds Studied

Compound	Fluorescence			Phosphorescence			τ, sec $\times 10^{-3}$
	λ_{max}, nm	Intensity[a]	F–C[b] shape[c]	λ_{max}, nm	Intensity[a]	F–C[b] shape[c]	
2,7-Dimethylbianthrone	456	s	A	672	vw	A	1.8
4,5'-Dimethylbianthrone	453	s	A	600	m	A	6.6
3,6'-Dimethylhelianthrone	503	s	A				
3,6'-Dimethylmesonaphtho-bianthrone				640	s	A	4.4
2,7'-Dimethylhydrobianthrone	445	vs	A				
2,7'-Dimethylhydrohelianthrone	653	m	A				
Photochromic form of 2,7'-dimethylbianthrone	826	s	A				
Photochromic form of 4,5'-dimethylbianthrone							

[a] s = strong, vs = very strong, m = medium, vw = very weak. [b] Franck–Condon. [c] F = forbidden and A = allowed.

Because of the nonlinear viscosity of EPA with temperature[38] on slow cooling, the photochemistry of 2,7'-dimethylbianthrone was irreversible at 133°K. Irradiation of the initial solution with an unfiltered high-pressure mercury arc gave a reddish solution containing helianthrone, dihydrobianthrone, and a third substance which was detectable only by its fluorescence in addition to the original bianthrone. Continued irradiation gave a green solution because of the presence of 2,7'-dimethyldihydrohelianthrone, which could be trapped by cooling to 77°K. On warming, the green color faded at a rate apparently dependent upon the concentration of unreacted 2,7'-dimethylbianthrone.
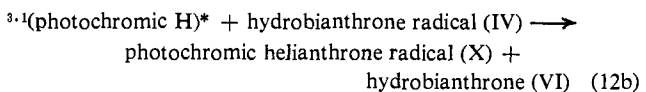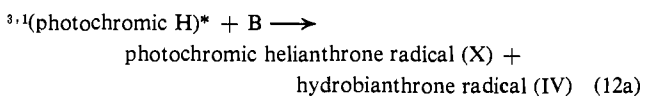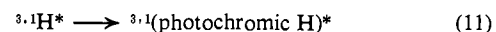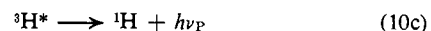
Photolysis of 2,7'-dimethylbianthrone in degassed solutions of high concentration in benzene, m-xylene, and 2MeTHF (approximately 30 mg/l. or saturated if the solubility was less than 30 mg/l.) gave dihydrobianthrone, helianthrone, and the semiquinone of bianthrone. Continued photolysis gave helianthrone, dihydrobianthrone, and mesonaphthobianthrone. Justification for conclusions and products noted is given in the Discussion.

Discussion

The spectral evidence for equivalence of the photo- and thermochromic forms is reviewed. Next, the photochemistry of 2,7'-dimethylbianthrone and 4,5'-dimethylbianthrone is discussed within the framework of the proposed mechanism. Finally, the spectral evidence for a change in atomic configuration during conversion to the photochromic form is discussed.

The basis for considering the thermo- and photochromic forms of bianthrone to be the same is the identity of the wavelengths and shape of the long-wave length band maxima of the two forms at 680 nm as determined in this investigation and in the literature.[3,27]

A. General Reaction Scheme. The photochemistry of 2,7'-dimethylbianthrone, B, in ethanol is best studied within the framework of the following reactions (see Figure 1 for structures), where superscripts 1 and 3 with an asterisk signify the excited singlet and triplet states and subscripts F and P refer to fluorescence and phosphorescence, respectively. Justification for the proposed reactions follows.

(38) H. Greenspan and E. Fischer, *J. Phys. Chem.*, **69**, 2466 (1965).

$$^1\text{B (I)} \xrightarrow{h\nu} {}^1\text{B*} \tag{1}$$

$$^1\text{B*} \longrightarrow {}^1\text{B} + h\nu_\text{F} \tag{2a}$$

$$^1\text{B*} \longrightarrow {}^3\text{B*} \tag{2b}$$

$$^3\text{B*} \longrightarrow \text{B} + h\nu_\text{P} \tag{2c}$$

$$^{3,1}\text{B*} \longrightarrow {}^{3,1}(\text{photochromic B})\text{* (II)} \tag{3}$$

$$^1(\text{photochromic B})\text{*} \longrightarrow {}^1(\text{photochromic B}) + h\nu_\text{F} \tag{4a}$$

$$^{3,1}(\text{photochromic B})\text{*} + \text{B} \longrightarrow$$
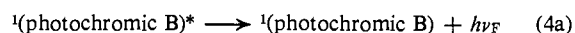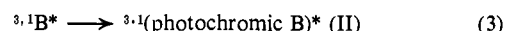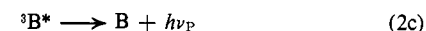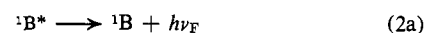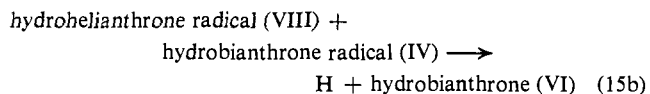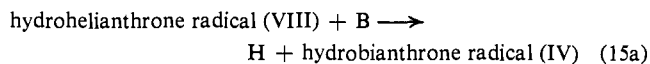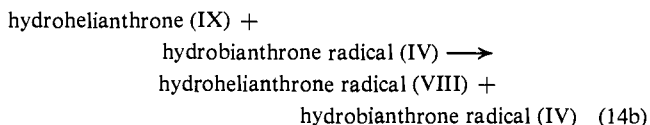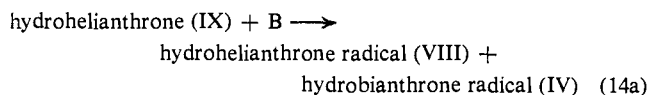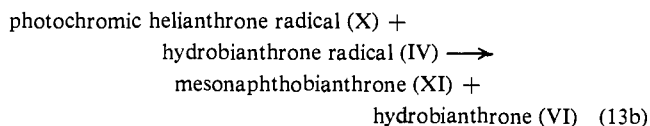$$\text{photochromic bianthrone radical (III)} +$$
$$\text{hydrobianthrone radical (IV)} \tag{4b}$$

$$^{3,1}(\text{photochromic B})\text{*} + \text{hydrobianthrone radical (IV)} \longrightarrow$$
$$\text{photochromic bianthrone radical (III)} +$$
$$\text{hydrobianthrone (VI)} \tag{4c}$$

$$\text{photochromic B} \xrightarrow{\Delta} \text{B} \tag{5}$$

$$\text{photochromic bianthrone radical (III)} + \text{B} \longrightarrow$$
$$\text{H (helianthrone, V)} + \text{hydrobianthrone radical (IV)} \tag{6a}$$

$$\text{photochromic bianthrone radical (III)} + \text{H} \longrightarrow$$
$$\text{H} + \text{hydrohelianthrone radical (VIII)} \tag{6b}$$

$$^{3,1}(\text{photochromic B})\text{*} + \text{H} \longrightarrow$$
$$\text{photochromic bianthrone radical (III)} +$$
$$\text{hydrohelianthrone radical (VIII)} \tag{7a}$$

$$^{3,1}(\text{photochromic B})\text{*} + \text{hydrohelianthrone radical (VIII)} \longrightarrow$$
$$\text{photochromic bianthrone radical (III)} +$$
$$\text{hydrohelianthrone (IX)} \tag{7b}$$

$$\text{photochromic bianthrone radical (III)} +$$
$$\text{hydrobianthrone radical (IV)} \longrightarrow$$
$$\text{H} + \text{hydrobianthrone (VI)} \tag{8a}$$

$$\text{photochromic bianthrone radical (III)} +$$
$$\text{hydrohelianthrone radical (VIII)} \longrightarrow$$
$$\text{H} + \text{hydrohelianthrone (IX)} \tag{8b}$$

$$^1\text{H(V)} \xrightarrow{h\nu} {}^1\text{H*} \tag{9}$$

$$^1\text{H*} \longrightarrow {}^1\text{H} + h\nu_\text{F} \tag{10a}$$

$$^1\text{H*} \longrightarrow {}^3\text{H*} \tag{10b}$$

$$^3\text{H*} \longrightarrow {}^1\text{H} + h\nu_\text{P} \tag{10c}$$

$$^{3,1}\text{H*} \longrightarrow {}^{3,1}(\text{photochromic H})\text{*} \tag{11}$$

$$^{3,1}(\text{photochromic H})\text{*} + \text{B} \longrightarrow$$
$$\text{photochromic helianthrone radical (X)} +$$
$$\text{hydrobianthrone radical (IV)} \tag{12a}$$

$$^{3,1}(\text{photochromic H})\text{*} + \text{hydrobianthrone radical (IV)} \longrightarrow$$
$$\text{photochromic helianthrone radical (X)} +$$
$$\text{hydrobianthrone (VI)} \tag{12b}$$

photochromic helianthrone radical (X) + B ⟶

mesonaphthobianthrone (XI) +

hydrobianthrone radical (IV)　(13a)

photochromic helianthrone radical (X) +

hydrobianthrone radical (IV) ⟶

mesonaphthobianthrone (XI) +

hydrobianthrone (VI)　(13b)

hydrohelianthrone (IX) + B ⟶

hydrohelianthrone radical (VIII) +

hydrobianthrone radical (IV)　(14a)

hydrohelianthrone (IX) +

hydrobianthrone radical (IV) ⟶

hydrohelianthrone radical (VIII) +

hydrobianthrone radical (IV)　(14b)

hydrohelianthrone radical (VIII) + B ⟶

H + hydrobianthrone radical (IV)　(15a)

hydrohelianthrone radical (VIII) +

hydrobianthrone radical (IV) ⟶

H + hydrobianthrone (VI)　(15b)

1, 2a, 2b, 2c, 4a, 9, 10a. These processes are verified by observation of the absorption and emission of 2,7'-dimethylbianthrone, the known 3,6'-dimethylhelianthrone, and the photochromic form of 2,7'-dimethylbianthrone, Figures 2, 3, and 4 and Tables I and II.

3. Using flash photolysis Huber, *et al.*,[34] have shown that two photochromic forms of 2,4,7',8'-tetramethylbianthrone must arise directly from an excited singlet of tetramethylbianthrone rather than *via* a triplet. This was done by simultaneously monitoring the triplet–triplet absorption and the photochromic bands and noting that the optical density of the photochromic bands remained constant while the occupation of the triplet decreased. It was also verified[34] by simultaneous monitoring of the absorption of the photochromic forms and the phosphorescence of 2,4,7',8'-tetramethylbianthrone. However, the authors believe their photochromic forms were conformers of the ground state. Consequently, we are unable to decide in our case whether excited singlets and/or triplet states are involved.[38a]

4b. The species hydrobianthrone radical (IV) cannot be detected by absorption during photolysis of saturated solutions in EPA. However, photolysis of concentrated solutions in *m*-xylene and 2MeTHF in which bianthrone is two orders of magnitude more soluble and the H bonding is less gives rise to an epr signal which has been assigned to hydrobianthrone radical.[5] During photolysis of 2MeTHF solutions at −100°, the epr signal maximizes before the green coloration of the solution.[7]

Absorption studies in this laboratory of the photolysis of concentrated solutions of 2,7'-dimethylbianthrone in degassed aromatic hydrocarbons, chloroform, 2MeTHF, and *n*-propylamine gave a shoulder at approximately 560–570 nm on the 500-nm band of helianthrone which we have assigned to the hydrobianthrone radical (IV). This is based on the following evidence. (1) The epr signal of the hydrobianthrone radical (IV) has been detected in *m*-xylene and 2MeTHF.[7] (2) Its con-

centration in *m*-xylene solutions is decreased by the removal of 2,7'-dimethylbianthrone as photolysis proceeds. (3) It is extremely oxygen sensitive, whereas 2,7'-dimethylbianthrone, 2,7'-dimethylhydrobianthrone, 2,7'-dimethylhelianthrone, and 2,7'-dimethyl-*meso*-naphthobianthrone react not at all or only slowly with oxygen. (These last are in contrast with hydrohelianthrone which is easily oxidized by bianthrone or oxygen according to Brockmann and Muhlmann[6] and the present study.) An exception is in benzene or *m*-xylene where the hydrobianthrone radical (IV) is apparently stabilized by complex formation and reacts only slowly. (4) The decay kinetics of the 570-nm band in the flash photolysis work of Dombrowski, *et al.*,[9] are second order.

In the absence of three-body collisions, the simultaneous generation of the photochromic bianthrone radical (III) also results. This irreversible photoreaction occurs either *via* hydrogen atom abstraction or *via* hydrogen atom donation by a molecule in an excited state.

Hydrogen atom abstraction by a photoactivated (excited state) bianthrone may be discounted on the following basis. In a study of substituted anthraquinones, Dearmond and Chan[39] have shown that the quinones which fluoresce and hence have the π,π^* levels lower than the n,π^* do not have a photochemically active triplet and are not hydrogen atom abstractors. Conversely, they[39] observed that the parent and all derivatives which phosphoresced and did not fluoresce were photochemically active oxidizing agents. This requires that the primary process be hydrogen atom donation by the photocyclized (photochromic) species.

Since the photo- and thermochromic forms are identical, either the thermochromic form must also be a hydrogen atom donor or the active donating species is an excited state of the photochromic form (to which the excited bianthrone initially crosses, assuming a one-photon process; see Figure 6). No similar products of the irreversible reaction were detected by absorption spectroscopy for 2,7'-dimethylbianthrone in 2MeTHF that had been stored at 91° for 28 days. *Thus, the active hydrogen atom donor species involved is an excited state of the photochromic form.* It cannot be stated whether it is *via* the singlet or triplet state.

4c. It is shown in (4b) that the excited state of the photochromic form of 2,7'-dimethylbianthrone is a reducing agent. The 425-nm band of 2,7'-dimethylhydrobianthrone is detected in photolyzed samples of 2,7'-dimethylbianthrone by absorption (Table I) and excitation spectra. This is a probable reaction for the reduction of the hydrobianthrone radical (IV) to dihydrobianthrone.

5. The photochromic form of 2,7'-dimethylbianthrone in EPA which had been converted at 88°K (and trapped at 77°K) disappeared when warmed to room temperature and gave back bianthrone with no irreversible photochemistry, within experimental error. This was determined from the lack of decrease in the 410-nm absorption band of bianthrone, the complete disappearance of the photochromic form, and lack of production of bands of the irreversible products. The removal of the viscosity barrier and the increase

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(38a) NOTE ADDED IN PROOF. Very recently, it has been shown that one of the photochromic forms is produced *via* the triplet state of bianthrone: R. Kornstein *et al.*, *Isr. J. Chem.*, in press. Also see section C and ref 42 and 43.

(39) H. H. Dearmond and A. Chan, *J. Chem. Phys.*, **44**, 416 (1966).

in thermal energy above 77°K permit this reaction to proceed.

6a and 6b. The 500-nm fluorescence and 470-nm absorption band of helianthrone are detected during the photolysis by comparison with similar bands of the known 3,6'-dimethylhelianthrone (Figure 4 and Tables I and II). These reactions provide possible paths for the completion of the oxidation of bianthrone to helianthrone. A more definitive statement cannot be made on the basis of the present data.

7a and 7b. The 624-nm absorption band of hydrohelianthrone (IX)[4] is observed if 2,7'-dimethylbianthrone is photolyzed in ethanol at 153°K then cooled to 77°K. The photolysis of 3,6'-dimethylhelianthrone with *no bianthrone present* gave *no* 3,6'-dimethylhydrohelianthrone (IX) even after 2 hr of irradiation at 466 nm at room temperature. Thus, in ethanol, the bridge hydrogen atoms of (photochromic B)* only are sufficiently labile to reduce the carbonyls of helianthrone. The 2,7'-dimethylhelianthrone is present as a result of reaction 4b plus reaction 6a or 8a and would also be formed during the generation of the hydro compound (note reaction 7a plus reaction 6b or 8b). Thus, the excited state of the photochromic form of bianthrone reduces helianthrone to the hydro compound, and in the absence of three-body collisions, the photochromic bianthrone radical (III) and the hydrohelianthrone radical (VIII) are necessary intermediates. (Note that the photolysis of helianthrone, reaction Ia, described by Brockmann and Muhlmann[6] does occur in pyridine.)

8a and 8b. The 460-, 427-, and 624-nm absorption bands of helianthrone, dihydrobianthrone, and dihydrohelianthrone,[6] respectively, are observed in the low-temperature photolysis of bianthrone. These reactions provide a logical path for the completion of the oxidation of bianthrone to helianthrone.

11. The generation of mesonaphthobianthrone (XI) does occur and necessarily involves the photocyclization of helianthrone followed by dehydrogenation. This implies reaction 11 as a primary process in the photolytic reaction and is analogous to reaction 3. The 2,7' derivative is identified by comparison with 3,6' derivative (Tables I and II). However, no photochromic form of 3,6'-dimethylhelianthrone or helianthrone was detected by absorption spectroscopy when solutions in EPA were photolyzed at 98°K and cooled to 77°K.

12a. In the case of the photocyclization and dehydrogenation of helianthrone to mesonaphthobianthrone (XI), Brockmann and Muhlmann[6] have shown that the process involved is hydrogen atom donation by a photoexcited helianthrone molecule. This mechanism can also be argued on the same basis as that shown by us for the parallel reaction for bianthrone in (4b). Then the active species must be an excited photocyclized one. As noted in (4b), the lack of reaction during the photolysis of 3,6'-dimethylhelianthrone in EPA or ethanol indicates that in ethanol, *only bianthrone may act as an oxidizing agent.* The hydrobianthrone radical (IV) is detected during the photolysis of 2,7'-dimethylbianthrone as noted in (4b), and in the absence of three-body collision, photochromic helianthrone radical (IX) and hydrobianthrone radical (IV) would be the products of this reaction. This is supported by the fact that the latter products are logical precursors of
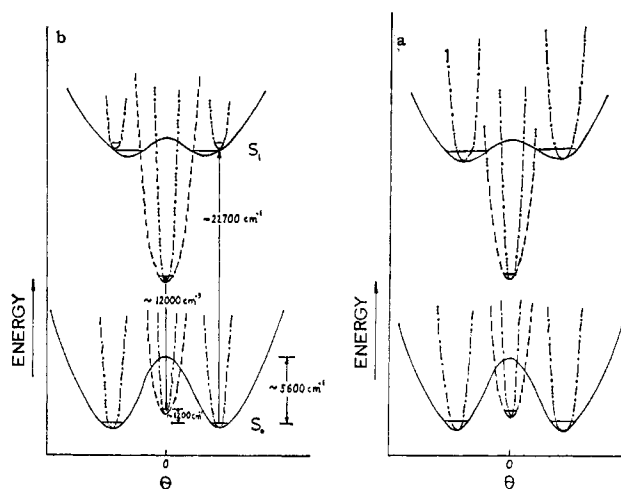

Figure 6. Potential energy curves for 2,7'-dimethylbianthrone (——) and the photochromic form (---) with viscosity barriers (-·-·).

mesonaphthobianthrone and hydrobianthrone, which are the two typical final products in the photolysis of 2,7'-dimethylbianthrone in EPA.

12b. The excited state of the photochromic form of 2,7'-dimethylhelianthrone is an active reducing species, as noted in (12a), and hydrobianthrone radical (IV) is produced in (4b), (6a), and (12a). Both 2,7'-dimethyl-*meso*-naphthobianthrone (XI) and 2,7'-dimethylhydrobianthrone (VI) are the final primary products of the photolysis. This reaction provides a probable path for the completion of the reduction of hydrobianthrone radical (IV) to hydrobianthrone (VI). With (photochromic helianthrone)* as the reducing agent, photochromic helianthrone radical (IX) is produced in the absence of three-body collisions.

13a. Among the final products of the photolysis of bianthrone is 2,7'-dimethyl-*meso*-naphthobianthrone (XI). The 2,7'-dimethyl-*meso*-naphthobianthrone (XI) is detected as a yellow precipitate which can be dissolved in 2MeTHF where it absorbs at 440 nm and phosphoresces at 643 nm (compare with the 3,6'-derivative data in Tables I and II). The 2,7'-dimethylhydrobianthrone (VI) is detected by its absorption or excitation spectral band at 425 nm and fluorescence at 473 nm. This reaction provides a reasonable path for the completion of photooxidation of bianthrone to 2,7'-dimethyl-*meso*-naphthobianthrone (XI), which is consistent with the total reaction scheme.

13b. The 2,7'-dimethyl-*meso*-naphthobianthrone (XI) and 2,7'-dimethylhydrobianthrone (VI) are the two principal final products of the photolysis of bianthrone. This reaction provides a probable path for the completion of the dehydrogenation of the photocyclized form of 2,7'-dimethylhelianthrone to 2,7'-dimethyl-*meso*-naphthobianthrone (XI) and the reduction of bianthrone to 2,7'-dimethylhydrobianthrone (VI).

14a, 14b, 15a, 15b. The total reaction hydrohelianthrone (IX) + bianthrone → helianthrone + hydrobianthrone was observed by Brockmann and Muhlmann.[6] The present investigation verified it in the following manner. Photolysis of 2,7'-dimethylbianthrone in EPA at 133°K gave a green coloration due to the absorptions at 425, 460, and 624 nm of 2,7'-dimethylhy-

drobianthrone (VI), 2,7'-dimethylhelianthrone (V), and 2,7'-dimethylhydrohelianthrone (IX), respectively. The 624-nm band was observed to disappear on warming of the solution to room temperature if residual bianthrone was present. The 624-nm band did not fade when no bianthrone could be detected from the excitation spectrum.

The evidence for a free radical is as follows. Wasserman[8] generated green solutions by photolysis of bianthrone at 173°K. No epr signal was detected in measurements made at 77°K; however, on warming to 227°K a signal was detected which was equivalent to the signal reported by Harrah and Becker[7] for the negative ion of 2,7'-dimethylbianthrone and hydrobianthrone radical (IV). As noted above and in previous discussion, photolysis under the conditions described[8] gives irreversible photochemistry rather than simply production of the photochromic form. Thus, the green coloration observed by Wasserman[8] is interpreted by us to arise from the presence of hydrohelianthrone (IX). The epr signal is considered to be the result of the radicals generated according to reactions 14a and 14b when the viscosity was decreased and the thermal energy increased sufficiently that bimolecular reactions rapidly occurred.

B. 4,5'-Dimethylbianthrone. This compound shows little or no irreversibility, although it is photochromic at low temperatures parallel to the 2,7'-dimethyl derivative. Consequently, we will not be concerned with irreversible reactions for this compound.

C. Potential Energy Curves, Spectra, and Photochemistry. There are two features in particular that require discussion. One of these is the fact that the absorption spectra of the dimethylbianthrones change from Franck–Condon forbidden at room temperature to Franck–Condon allowed at low temperature (77°K) in a rigid matrix. Secondly, irradiated solutions undergo rapid irreversible photochemistry (*via* the photocyclized form) at temperatures as low as 133°K. However, at ∼90°K, where the solution is extremely viscous, though fluid, the only detectable substance formed is the green photochromic species. If the EPA solution of the photochromic form is cooled to 77°K, the color does not spontaneously fade or erase on irradiation into the long-wavelength band. The 2,7'-dimethylbianthrone at 77°K in rigid EPA or 2MeTHF glasses does not undergo any detectable photochemistry even when irradiated for 2 hr.

Figures 6a and 6b show potential energy curves for the 2,7'-dimethylbianthrone and its photochromic form. Bianthrone behaves as a hindered ethylene in the sense that there is hydrogen repulsion in the case of 4,5-dimethylbianthrone. In a simplified scheme considering only the angle of skew (θ) of the anthrone halves, the energy minima of the ground state occur at a small angle from coplanar for 2,7'-dimethylbianthrone (and a somewhat larger angle for 4,5'-dimethylbianthrone). In the case of 2,7'-dimethylbianthrone, the cyclized photochromic form has a minimum at θ equal to 0° and is 3.5 kcal (∼1200 cm^{-1}) above the ground state of bianthrone. The potential energy curves cross approximately 16 kcal (∼5600 cm^{-1}) above the ground state of the photochromic form (Figures 6a and 6b). These values are based on the ΔH for the thermal equilibrium of bianthrone

and the colored form[3,15,16] and the barrier to thermal reversion of the photochromic form.[3] The first excited singlet state of the cyclized photochromic form of 2,7'-dimethylbianthrone lies approximately 12,000 cm^{-1} above its ground state, and the first excited singlet state of 2,7'-dimethylbianthrone lies approximately 22,700 cm^{-1} above its ground state.

The two parts of Figure 6, a and b, represent a slight difference in the relative location of the potential energy minima of the ground and excited states both with and without viscosity barriers. This is necessitated by our lack of knowledge of the overall effect of the $\pi^* \leftarrow \pi$ transition on the geometry of the molecule. That is, in ethylene, the excited state minimum occurs at 90°. However, in our case, π excitation is not from the localized orbital of the ethylene double bond but from one that is delocalized over the whole molecule. It can be argued nonetheless, that the bond will have a lower π-bond order in the excited state and thus be longer. However, because of this, the H–H atom or CH$_3$–H atom repulsion is less and in fact, the rings could be more coplanar. Thus, one case is presented in Figure 6a where essentially no difference exists in the relative location of the ground and excited state minima. In Figure 6b the case where the minima are closer to 0° in the excited state is shown. The case where the minima in the excited state are at larger angles than in the ground state is not shown. However, the general arguments relying on Figure 6b for a basis would not be altered. We will first be concerned with the situation in which the minima lie one above the other, Figure 6a. At room temperature, in the ground state, vibrational levels (from double bond twisting) above the zero level are occupied, giving transitions of 0 ← 1, 1 ← 2 (excited ← ground) type. These will occur at longer wavelengths than the maximum, giving a Franck–Condon-forbidden shape spectrum. At 77°K in a rigid matrix, viscosity barriers exist and furthermore, essentially only the zero level of the ground state is occupied. The spectrum now becomes Franck–Condon allowed (also see later discussion). At low temperature (∼90°K) in a viscous (but not rigid) medium, excitation is followed by vibrational relaxation and crossing with the excited state of the photochromic form. Internal conversion occurs within this state, followed by continued internal conversion to the ground state of the colored form. Alternatively, the ground state of the photochromic form could be created by an emission process. The lack of thermal fading arises because of the high activation energy required which is created by the nature of the crossing of the ground states of the bianthrone and the photochromic form, Figure 6a. In a rigid matrix at 77°K, the potential energy curve of the excited state of bianthrone changes, Figure 6a, and has steep sides which no not cross with the excited state of the photochromic form. Thus, no colored form is created.

In the case where the minima of bianthrone do not lie above one another, Figure 6b, some alternative explanations arise to account for the spectral data. In this case, in fluid solution, the principal source of the Franck–Condon-forbidden character arises because the maximum corresponds to the transition $v' \leftarrow 0$ where v' is not 0. However, when the solution becomes

rigid, the potential energy curve in the excited state is modified, Figure 6b. The maximum corresponds to a vertical excitation which is not to the equilibrium state, but the minimum of the potential energy curve is above that of the ground state, Figure 6b. The presence and abscence of photochemistry in fluid and rigid media, respectively, can be explained in a manner parallel to that described above. That is, in a fluid medium excitation is followed by vibrational relaxation, crossing to the excited state of the photochromic form, and deexcitation to the ground state of the photochromic form. In a rigid medium, vibrational relaxation occurs within the steep-sided potential well of the nonequilibrium state which does not cross with the excited state of the photochromic form so that emission and internal conversion occur from this nonequilibrium bianthrone state.

As stated at the beginning of this discussion, it is difficult to decide which of the two potential energy curve relationships, Figure 6a or 6b, is correct. In either case, the shape of the fluorescence from bianthrone at 77°K in a rigid matrix should be Franck–Condon allowed. This is the case (Figure 2). Also, if the viscosity is sufficiently high and the thermal energy sufficiently low, as at ∼90°K, then the photochromic form can be generated. Further, the photochromic form does not undergo further irreversible photochemistry since bimolecular collisions would be essentially absent. However, under less viscous conditions and higher temperatures, as ∼135°K, the photochromic form can be generated but does undergo irreversible photochemistry. All of these results are in agreement with expectation. In other solvents such as methyl phthalylethyl glycolate, the temperatures at which the foregoing results occur are different. For example, the photochromic form can be produced with little or no irreversible reaction occuring at ∼208°K. For this solvent, the viscosity is 10^8 cp or greater at this temperature.[40] In fact, at ∼208°K, the solution is apparently rigid. However, from other research[41]

it is evident that the viscosity barrier is not as great as might be expected. In other words, the rigidity or viscosity is not as great as for EPA or 2MeTHF at 77°K.

After acceptance of this article, two papers appeared concerning the photochemistry of bianthrone derivatives[42] and the nature of the photochromic form(s) of bianthrone,[42,43] In one,[43] theoretical calculations indicated that the most probable structure for the green photochromic form of bianthrone was structure II of our Figure 1. This is in agreement with our conclusion (vide supra). The other publication[42] considered the photochemistry of different substituted bianthrones at various temperatures. They note that one colored modification is produced at very low temperatures (∼93–108°K) and another at higher temperatures (∼123–155°K). The lower temperature form spontaneously and irreversibly converts to the higher energy form if the temperature is raised 10°. They[42] postulated the structures of the two colored forms to be structures II and IX of our Figure 1. The low-temperature form is postulated to be a high-energy conformer of the high-temperature form. One of the proposed structures (II) is in agreement with our conclusion. The other (IX) appears in our reaction sequence.

Conclusions

We believe the general reaction scheme as given in eq 1–15b is consistent with all previous and present experimental results. Several unique results stemmed from the present investigation. (1) The photochromic form of bianthrone cannot be created in a rigid matrix of high viscosity. The potential energy curves of Figure 6 satisfactorily account for this behavior. (2) The photochromic form is stable providing the viscosity is sufficiently high to prevent bimolecular reactions. (3) In the irreversible photochemistry, the excited state of the photochromic form acts as a hydrogen atom donor in reactions 4b, 7a, and 7b.

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(41) W. F. Richey and R. S. Becker, *ibid.*, **49**, 2092 (1968).

(42) T. Bercovici and E. Fischer, *Isr. J. Chem.*, **7**, 127 (1969).
(43) R. Lorenz, U. Wild, and J. R. Huber, *Photochem. Photobiol.*, **10**, 233 (1969).