

SPECTROSCOPIC AND PHOTOCHEMICAL STUDY OF BIANTHRONE

A Dissertation

Presented to the

Faculty of the Department of Chemistry

College of Arts and Sciences

University of Houston

In partial fulfillment
of the requirements for the Degree
Doctor of Philosophy

by

Charles Earl Earhart, Jr.

August 1967

406676

To Barbara

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Professor Ralph S. Becker for help, encouragement, suggestions and, in many instances, forbearance in his research and personal development; to the other members of his dissertation committee, Professor Eby N. McElrath, Dr. G. G. Meisels, Dr. John Bear, and Professor Martin Wright, for helpful comments and criticisms; to the author's colleagues in the Spectroscopy Laboratory (especially to Dr. Josef Michl) for constant discussions and comments; to Dr. Larry Harrah, formerly with the Air Force Materials Laboratory for helpful discussions and the donation of compounds; to Miss Julie Norris, who smoothed the way as well as typed the dissertation; and to his wife, Barbara, who typed the original manuscript while taking care of the author and their son, Ronald.

The author also acknowledges the support of the National Aeronautics and Space Administration through a NASA Predoctoral Traineeship.

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ABSTRACT

A spectroscopic and photochemical study of 2,7' dimethylbianthrone and 4,5' dimethylbianthrone was carried out. Absorption and emission spectra are reported for 2,7' dimethylbianthrone, 4,5' dimethylbianthrone, 3,6' dimethylhelianthrone, 3,6' dimethylmesonaphthobianthrone, and the photochromic form of 2,7' dimethylbianthrone.

The photochemistry of 2,7' dimethylbianthrone was extensively studied. A free radical mechanism is proposed in which the initial reactive species is an excited state of the photochromic form of bianthrone and a secondary reactive species is the photocyclized helianthrone.

The influence of the viscosity and steric effects of rigid glasses on the spectra and photochemistry is also considered.

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I.

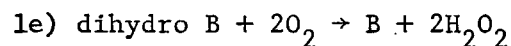
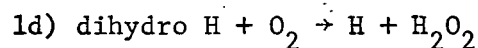
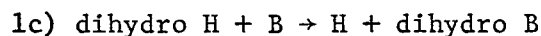
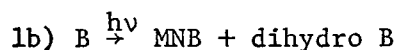
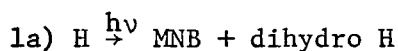
INTRODUCTION

INTRODUCTION

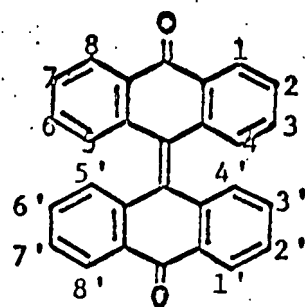
The voluminous literature on bianthrone covers three main areas:

1) the path of the irreversible photochemistry, in particular, the nature of the photo-active species; 2) the nature of the photochromic form; and 3) the nature of the thermochromic form. The structure of the species considered 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 (1) in contrast to that of Kortum et al. (2).

Although the irreversible photochemistry of undeoxygenated solutions of bianthrone has been investigated by others (3), the most recent definitive work is that of Brockmann and Muhlmann (4), 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:

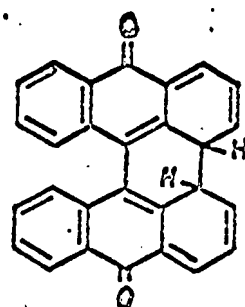


Because of the lack of oxidizing ability of even irradiated bianthrone or helianthrone and the ability of irradiated helianthrone to reduce



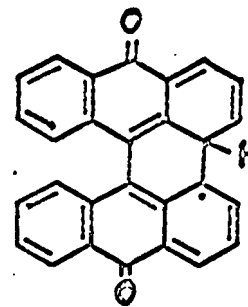
BIANTHRONE

B

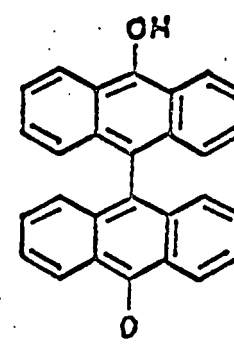


PHOTOCHROMIC FORM
OF BIANTHRONE

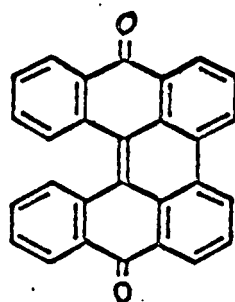
PB



H'H•

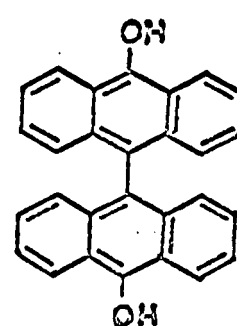


HB•



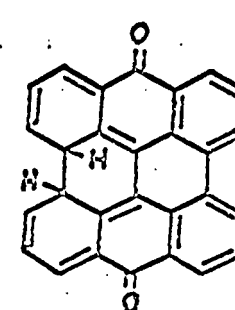
HELIANTHRONE

H



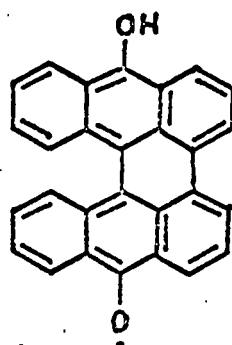
DIHYDROBIANTHRONE

H₂B

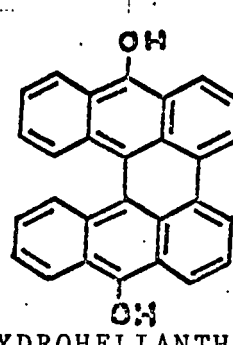


PHOTOCHROMIC FORM OF
HELIANTHRONE

PH

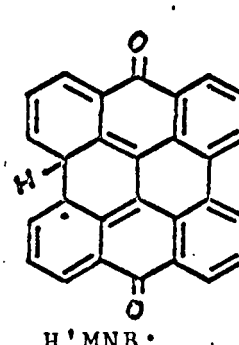


H'H•

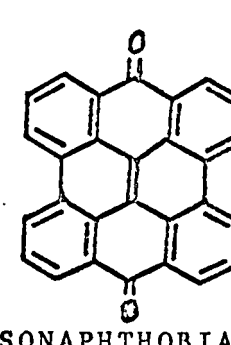


DIHYDROHELIANTHRONE

H₂H



H'MNB•

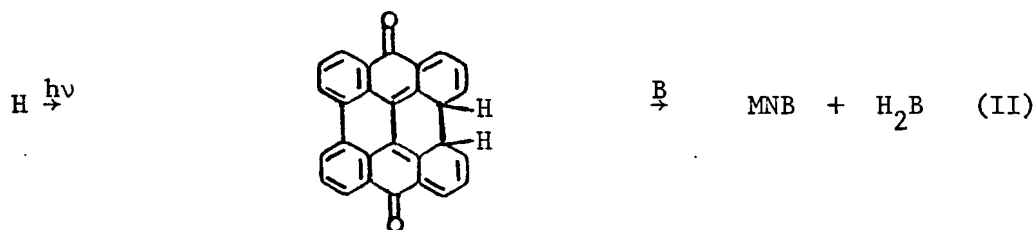
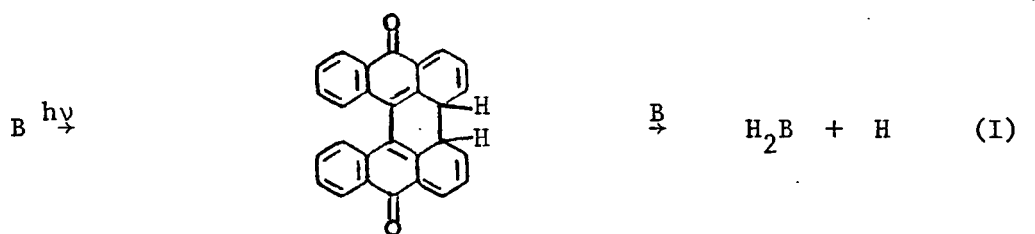


MESONAPHTHOBIANTHRONE

MNB

FIGURE 1. STRUCTURES OF THE COMPOUNDS CONSIDERED

other oxidizing agents such as ferric chloride, they (4) proposed an intermediate with labile protons as the product of the primary photochemical process. The improbability of a tertiary collision indicated that H was an intermediate in the photolysis of bianthrone, hence



In the event any intermediate II reacted with a helianthrone molecule to give mesonaphthobianthrone and dihydrohelianthrone, the latter would immediately react with bianthrone to give helianthrone back and dihydrobianthrone (as in equation 1c), so that the net result is still that of equation 1b (4).

Brockmann and Muhlmann (4) reported the above reactions for helianthrone to occur in acetic acid, dioxane, n-butanol, cyclohexanol,

benzyl alcohol, acetic anhydride, and acetyl chloride, but in benzene, xylene, cynene, 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 (5) reported that the electron spin resonance (EPR) spectra of photolyzed solutions of 2,7' dimethylbianthrone in m-xylene at room temperature or methyltetrahydrofuran (2 MeTHF) at low temperature and at room temperature were identical to that of the negative ion of 2,7' dimethylbianthrone generated in 2 MeTHF by oxidation with potassium tertiary 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 (6) and assigned by him to the thermochromic form of bianthrone in pyridine if Harrah and Becker's spin density assignments are substituted (5).

Dombrowski et al. (7) obtained an absorbance band maximum at 470 mμ by flash photolysis of partially photolyzed benzene solutions of bianthrone which decayed according to second order kinetics.

The thermochromism of bianthrone in melt and solution was first observed by Meyer (8) in 1909 and was subsequently the subject of much study together with other of the "thermochromic ethylenes."

An association-dissociation equilibrium was advanced as the mechanism of the thermochromism of diphenylmethylenanthrone by Padova (9) on the basis of the molecular weight measurements, but this was disproved by Bergmann and Carter (10).

Engel (11) and Bergmann and Carter (10) 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 methyl phenyl-dibenzo-xanthinium perchlorate (12)] and betaines and of bianthrone (13), Schoenberg and co-workers (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 $\epsilon_{T\infty}$ (17) measured by Theilacker et al. (15) for this equilibrium in dimethylphthalate were 3.4 ± 0.2 Kcal and 3.44 ± 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 the coplanar colored form which was only 3.5 Kcal higher than the ground state. However, simple kinetic studies showed a barrier of less than 20 Kcal.

Hirschberg and coworkers (18) pointed out that 4,5' substituted bianthrone 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. (19) upon cooling the solutions to liquid nitrogen temperature ($77^\circ K$). Kortum (2)

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 non-planar ground state and a triplet planar colored configuration (a so-called "bi-radical") with a solvent independent ΔH of 3.4 Kcal.

The reversible photocoloration at low temperature of bianthrone was first observed (19) and identified as a photoprocess (20) by Hirschberg and more thoroughly studied by Hirschberg and Fischer (1) 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 (21) reported spectra for the 4,5' dimethylbianthrone which showed band maxima at 440 and 460 m μ in addition to a band at 660 m μ for the photochromic form. He also noted that the photo-colored form could be photo bleached by irradiation into the 640 m μ band. It was further noted that the 640 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 B respectively indicated to Kortum and co-worker (22) that these

forms actually differed. Some discussions concerning the question of the identity of the two forms ensued (23,24,25,26,27). A more extensive study by Kortum et al. (28) showed that at least two forms of 2,4,5',7' tetramethylbianthrone, A, could be generated by photolysis. One of them, B, which absorbed at 666 m μ , 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 to the thermochromic form for the case of bianthrone itself (28). The other photoproduced form, C, absorbed at 460 and 435 m μ . Its concentration relative to that of form B was found to vary with solvent and to increase with increasing temperature of irradiation.

Magnetic balance measurements by Kortum et al. (29) 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 (30) for solutions of the photochromic form in contrast to the findings of Wasserman (6,31). However, signals reported for the B negative ion by Harrah and Becker (5) are equivalent to those reported by Wasserman (6) and which were assigned to the photochromic form of bianthrone.

Wasserman and Davis (32) also proposed the identity of the colored forms of bianthrone on the basis of identical rate constants for reversion. However, Mills and Nyburg (33) 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 Fisher and coworkers (34) and the flash photolysis study by Huber (35) of 2,4,5',7' tetramethylbianthrone. The former of these (34) indicates that the bridged form, structure II, is correct. The latter study (35) by simultaneous monitoring of the visible absorption band of the photochromic form of bianthrone and the phosphorescence of bianthrone itself showed that the photochromic form is not and does not arise via the triplet state. This conclusion also results from the simultaneous monitoring of the visible absorption band of the photochromic form of bianthrone and the triplet-triplet absorption. Further, Huber obtained photoconversion in rigid media (plexiglass) contrary to Hirschberg (1).

In part, our studies of 2,7' dimethylbianthrone show that a spatial modification of the molecule is required for photoconversion, and photoconversion can be accomplished in rigid glasses where the shape of the absorption is Franck-Condon forbidden, but not in rigid glass where the shape of the absorption is Franck-Condon allowed.

In addition, an excited state of the colored form is the active species for the irreversible step in photocyclization of 2,7' dimethylbianthrone which proceeds via a free radical reaction. Also, previously detected EPR signals ascribed to the photochromic form are very likely due to radicals formed during the irreversible photochemistry rather than from the photochromic form. In accord with the findings of Hirschberg and Fischer (1) and Kortum (28) , our absorption data for the photo- and thermochromic forms of bianthrone indicates 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. This will be discussed in more detail.

II.

EXPERIMENTAL

EXPERIMENTAL

A. The Compounds

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

Thin layer chromatography of the compounds on alumina-5% water plates eluted with either carbon tetrachloride or chloroform gave a single spot.

The 2,7' dimethyldihydrobianthrone was prepared by photolyzing a vacuum degassed sample of 2,7' dimethylbianthrone for two hours through a 466 m μ interference filter with a tungsten lamp after an initial 10 second irradiation through a 300 m μ interference filter. This gave precipitated 2,7' dimethylmesonaphthobianthrone and one other product whose absorption and emission spectra resembled that of 9,10 dichloroanthracene (36). The additional product fluoresced very strongly relative to 2,7' dimethylbianthrone just as dihydro anthraquinone luminesces very strongly relative to anthraquinone (37). The absorption spectrum indicated a relative concentration of 2,7' dimethylmesonaphthobianthrone of less than 3 percent. Because of its low solubility in EPA [ethanol: isopentane:ethyl ether (2:5:5)] [(H₂B):(MNB)>20:1], the 2,7' dimethyl-mesonaphthobianthrone was judged not to interfere with the principal features of the spectra.

The 2,7' dimethylmesonaphthobianthrone was prepared by washing the precipitant from the above photolysis with 95 percent ethanol.

B. Solvents

The solvents for recrystallizations were fractionated after refluxing for 12 hours 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 2MeTHF were used for emission spectra and low temperature absorption spectra. The 2MeTHF was refluxed over sodium for 24 hours, 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 (38) immediately before use.

C. Samples

All 2,7' dimethylbianthrone or 3,6' dimethylhelianthrone samples were prepared under 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 to a calculated oxygen concentration of less than 10^{-7} molar. Appendix I is a sample calculation. All unsealed degassed samples were re-evacuated if utilized for a time period of more than 24 hours.

Some samples were deoxygenated by sweeping the solvent with argon or nitrogen while cycling the solvent from room temperature to the boiling point and back twice, then sweeping the sample after preparation.

Degassing by sweeping was discontinued as it appeared unreasonable to expect an oxygen concentration of less than 10^{-5} molar by this method. This is especially important for photochemical experiments as the concentrations were generally on the order of 10^{-5} molar.

D. Spectra

Absorption spectra were taken on a Beckman DK-1 or Cary 15 recording spectrophotometer. Aminco quartz window cells were used for room temperature spectra of the known compounds with the exception of the 2,7'-dimethylbianthronol. A sealed pyrex emission tube of rectangular cross section was used for the 2,7'-dimethylbianthronol.

Low temperature absorption spectra were taken versus air using pyrex or quartz emission tubes of rectangular cross section with a dewar fitted with Corning 7940 windows. The emission tubes were sealed or closed with a vacuum stopcock. Solvent baselines were run.

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 watt high pressure xenon arcs or Sylvania 150 watt tungsten lamps with dichroic reflectors were used with a Bausch and

Lomb 33-86-40 grating monochromator, a Hilger and Watts D182 prism monochromator, or Optics Technology "Mono pass" interference filters for excitation. An Aminco 4-8401 analyzing monochromator with an EMI 9558 photomultiplier tube was used for monitoring the emissions.

E. Photolysis

A 150 watt tungsten lamp in conjunction with an appropriate filter or an unfiltered 150 watt high pressure mercury arc were used for photolysis of the solutions.

F. Temperature Control

A Wheelco Model 402 Capacitrol was used as the controller for cooling in the 88°K to 223°K range. Vapor from boiling liquid nitrogen was the coolant.

III.

RESULTS

RESULTS

A. Spectral Results

The principal features of the spectra are presented in Table I.

Spectra for compounds of concern are presented in Figures 2 through

9. The results of two typical photolysis experiments are given. Justification for conclusions and products noted is given in the Discussion.

B. Photolysis Results

Irradiation of 2,7' dimethylbianthrone in EPA or 2MeTHF rigid glasses at 77°K for two hours at 400 mμ gave no detectable conversion. However, irradiation of 2,7' dimethylbianthrone in a rigid glass of methylphthalylethylglycolate at 208°K for 20 minutes at 400 mμ gave an estimated 80 percent conversion.

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 mμ for 15 minutes 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.

Because of the nonlinear viscosity of EPA with temperature (39) on slow cooling, the photochemistry of 2,7' dimethylbianthrone was irreversible at 133°K. Irradiation of the initially greenish yellow 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' dimethyl-

TABLE I
SPECTRAL CHARACTERISTICS OF THE COMPOUNDS STUDIED

Compound	Absorption					
	λ_{max}	Room Temperature $\log \epsilon^a$	Franck-Condon Shape ^b	λ_{max}	Low Temperature $\log \epsilon^a$	Franck-Condon Shape ^b
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' dimethylmesonaphthobianthrone	430	---	A	435	---	A
2,7' dimethyldihydrobianthrone	---	---	A	427	4.3	A
2,7' dimethyldihydrohelianthrone	605	---	A	624	---	A
Photochromic form of 2,7' dimethyl- bianthrone	---	---	---	715	≥ 4.2	F
Photochromic form of 4,5' dimethyl- bianthrone	---	---	---	650	≥ 3.7	F

^aextinction coefficients calculated on assumption of 25% volume decrease on cooling from 300°K to 77°K
^bwhere F = forbidden and A = allowed

TABLE I CONTINUED
SPECTRAL CHARACTERISTICS OF THE COMPOUNDS STUDIED

Compound	λ_{max}	Fluorescence		Emission		Phosphorescence		τ (secx10 ⁻³)
		Intensity ^c	Franck-Condon Shape ^b	λ_{max}	Intensity ^c	Franck-Condon Shape ^b		
2,7 dimethylbianthrone	460	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' dimethyldihydro- bianthrone	445	vs	A	---	--	---	---	
2,7' dimethyldihydro- helianthrone	653	m	A	---	--	---	---	
Photochromic form of 2,7' dimethylbianthrone	826	s	A	---	--	---	---	
Photochromic form of 4,5' dimethylbianthrone	---	---	---	---	--	---	---	

^cwhere s = strong; vvs = very, very strong; m = medium; vw = very weak

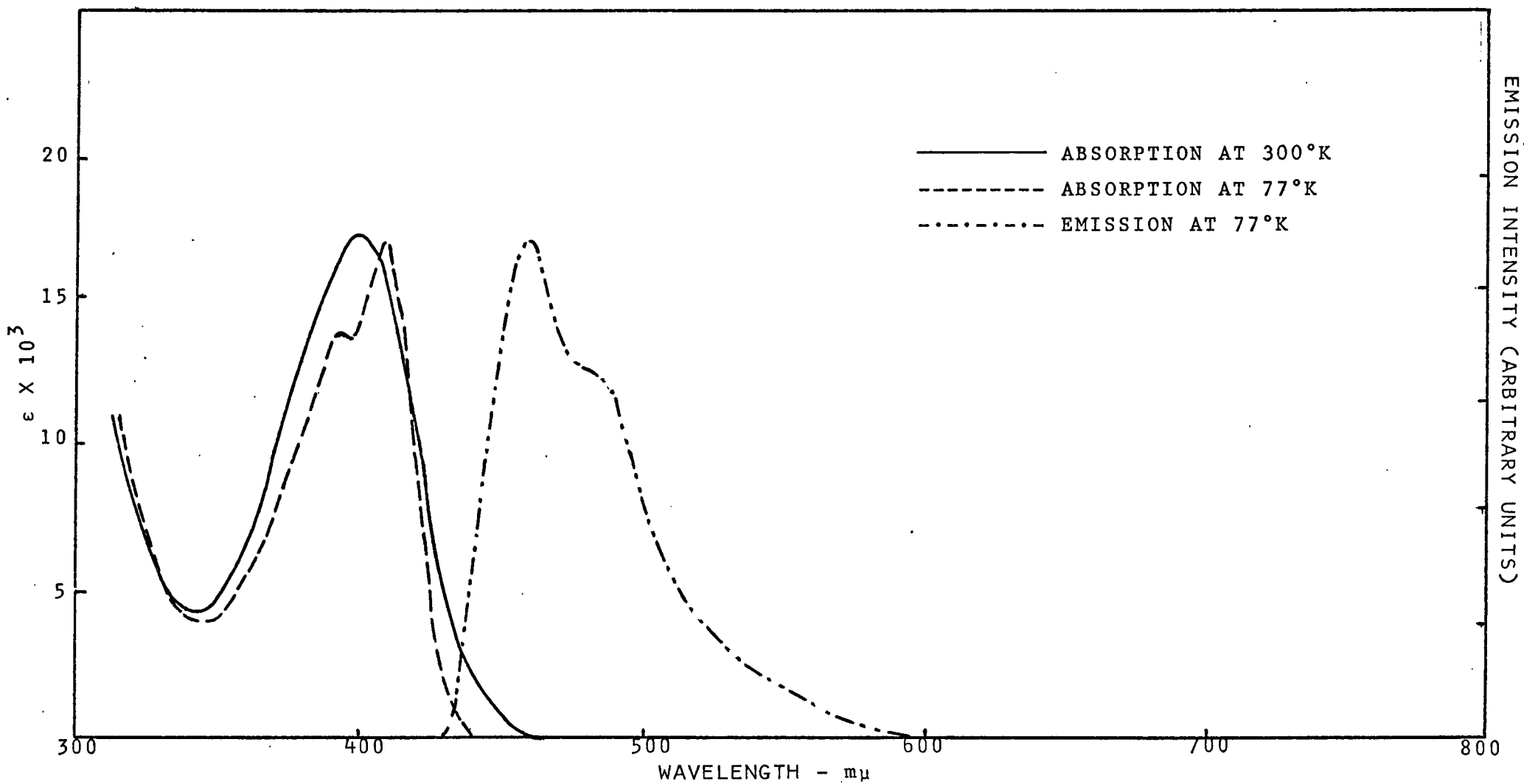


FIGURE 2. ROOM TEMPERATURE ABSORPTION, LOW TEMPERATURE ABSORPTION, AND FLUORESCENCE SPECTRA OF 2,7' DIMETHYLBIANTHRONE IN EPA

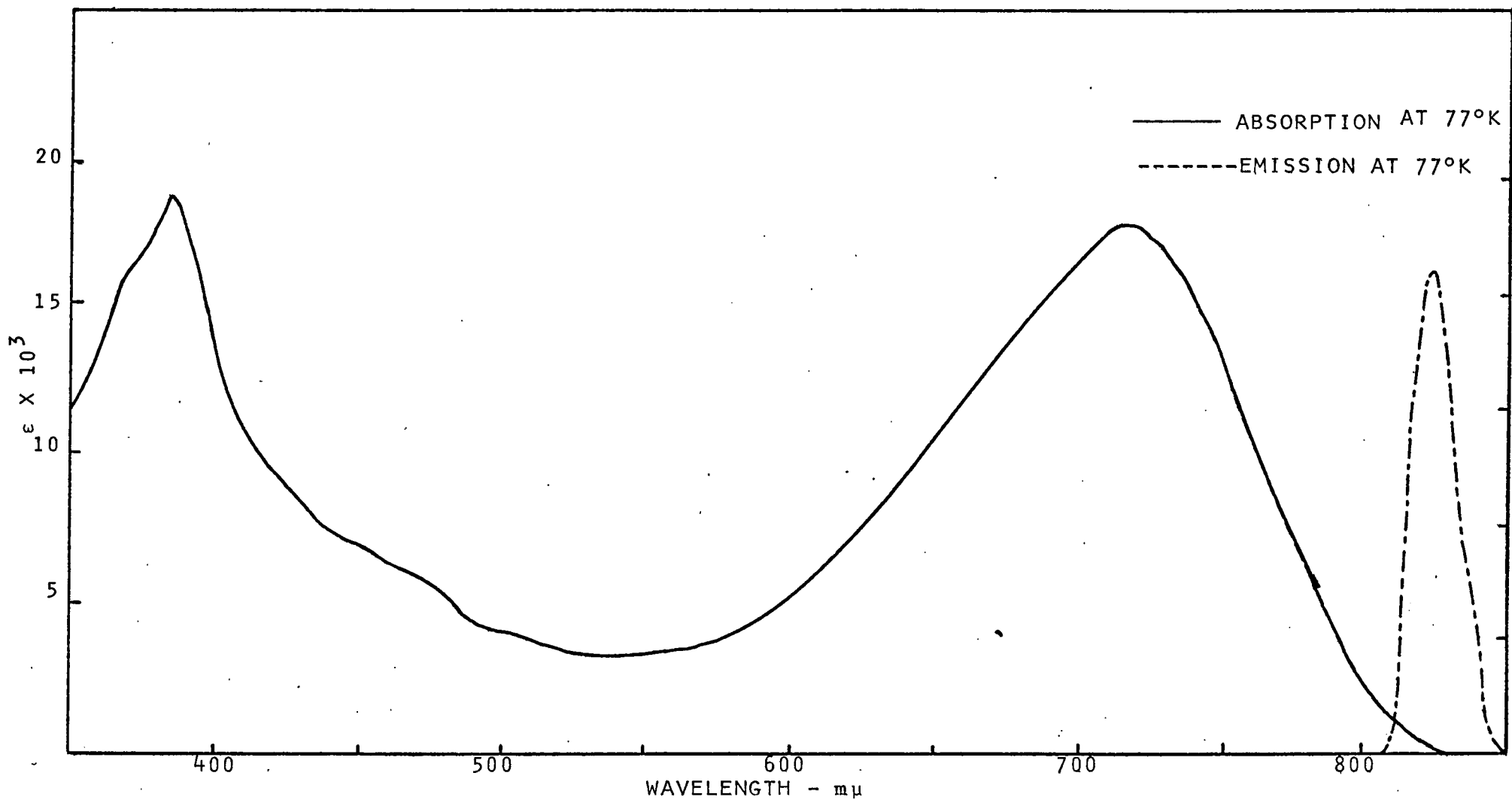


FIGURE 3. ABSORPTION AND FLUORESCENCE SPECTRA OF THE PHOTOCHROMIC FORM OF 2,7' DIMETHYLBANTHRONE IN EPA

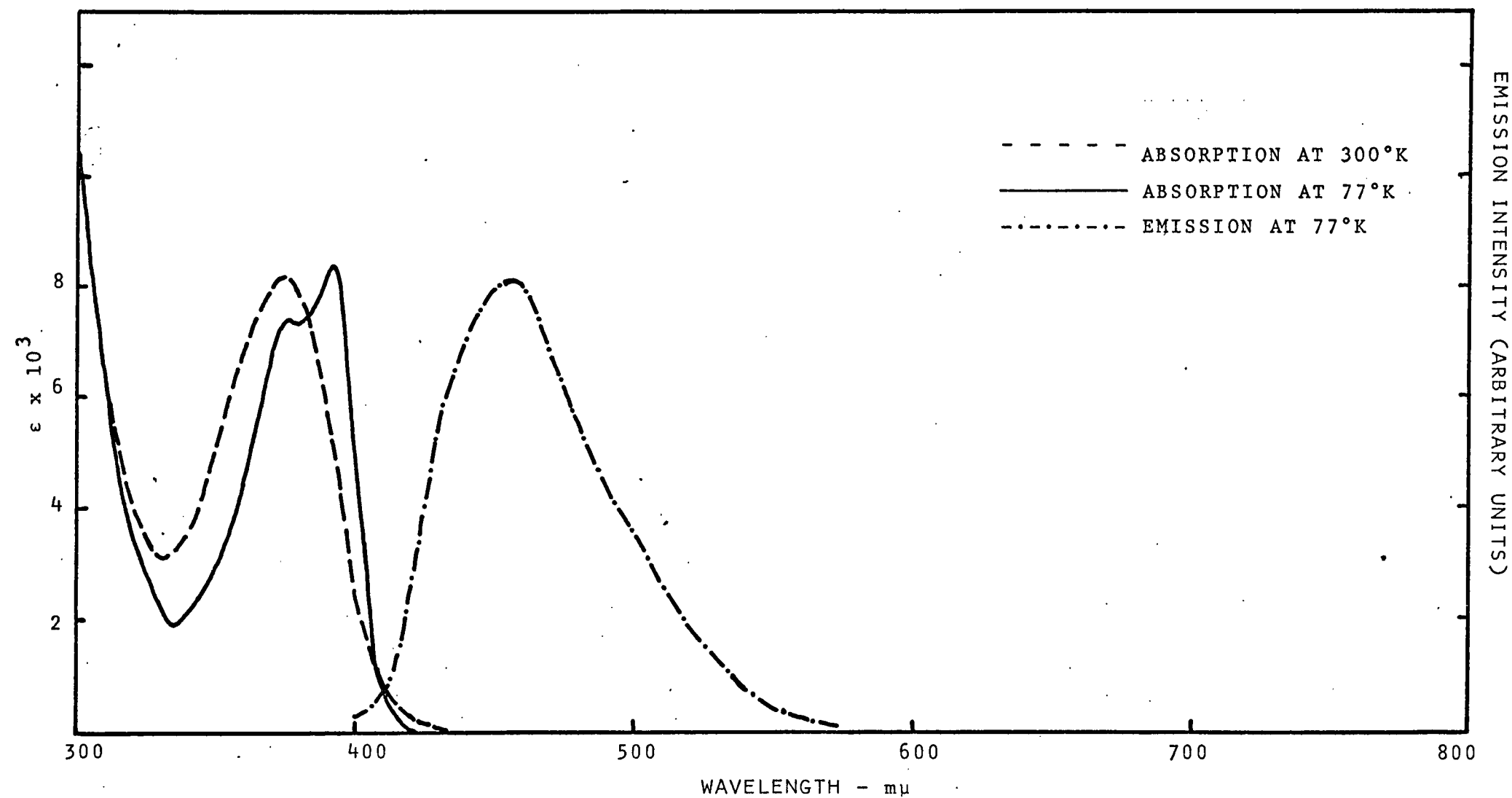


FIGURE 4. ROOM TEMPERATURE ABSORPTION, LOW TEMPERATURE ABSORPTION, AND FLUORESCENCE SPECTRA OF 4,5' DIMETHYLBIANTHRONE IN EPA

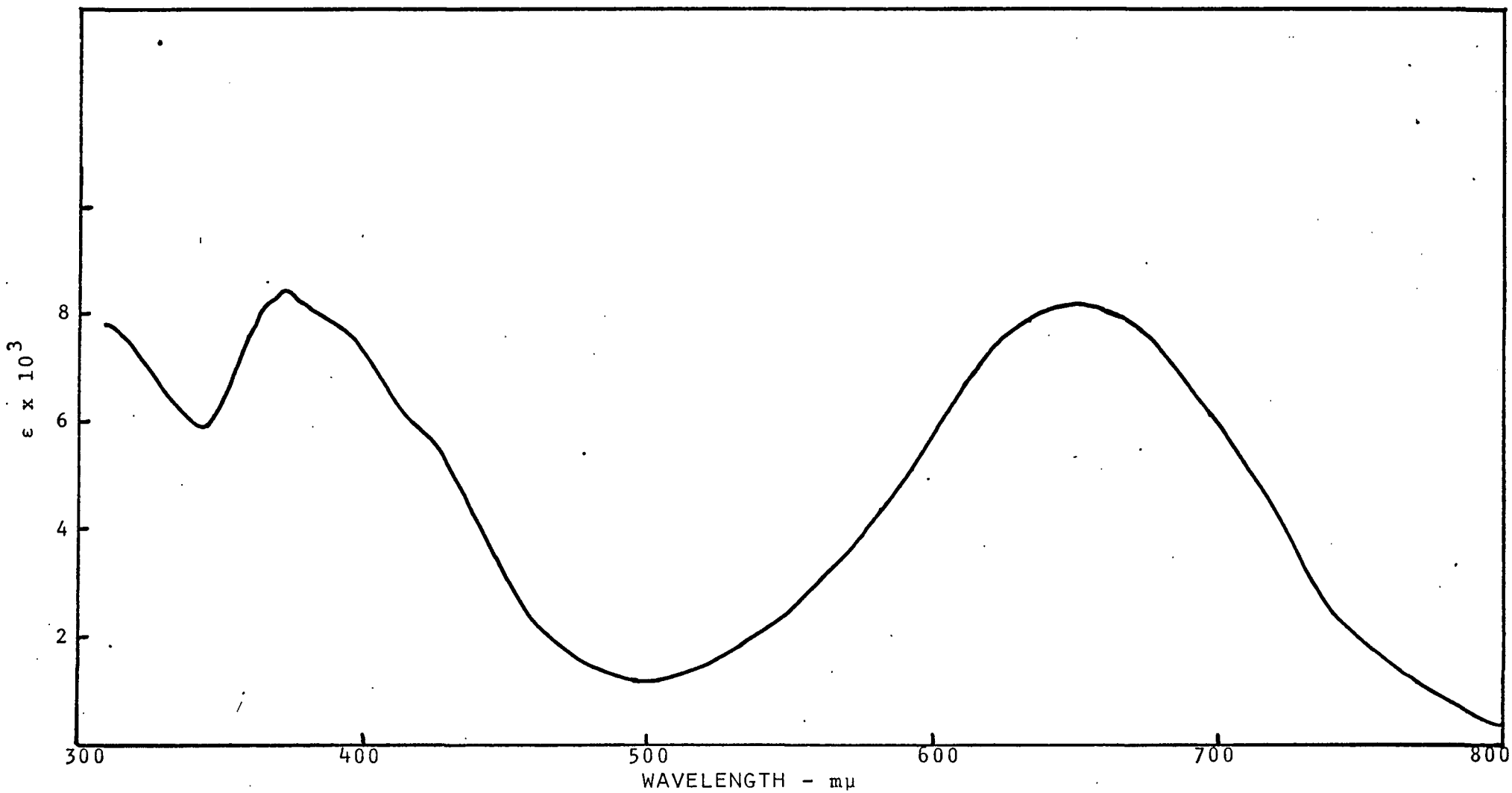


FIGURE 5. ABSORPTION SPECTRUM OF PHOTOCROMIC FORM OF 4,5' DIMETHYLBIANTHRONE AT 77°K

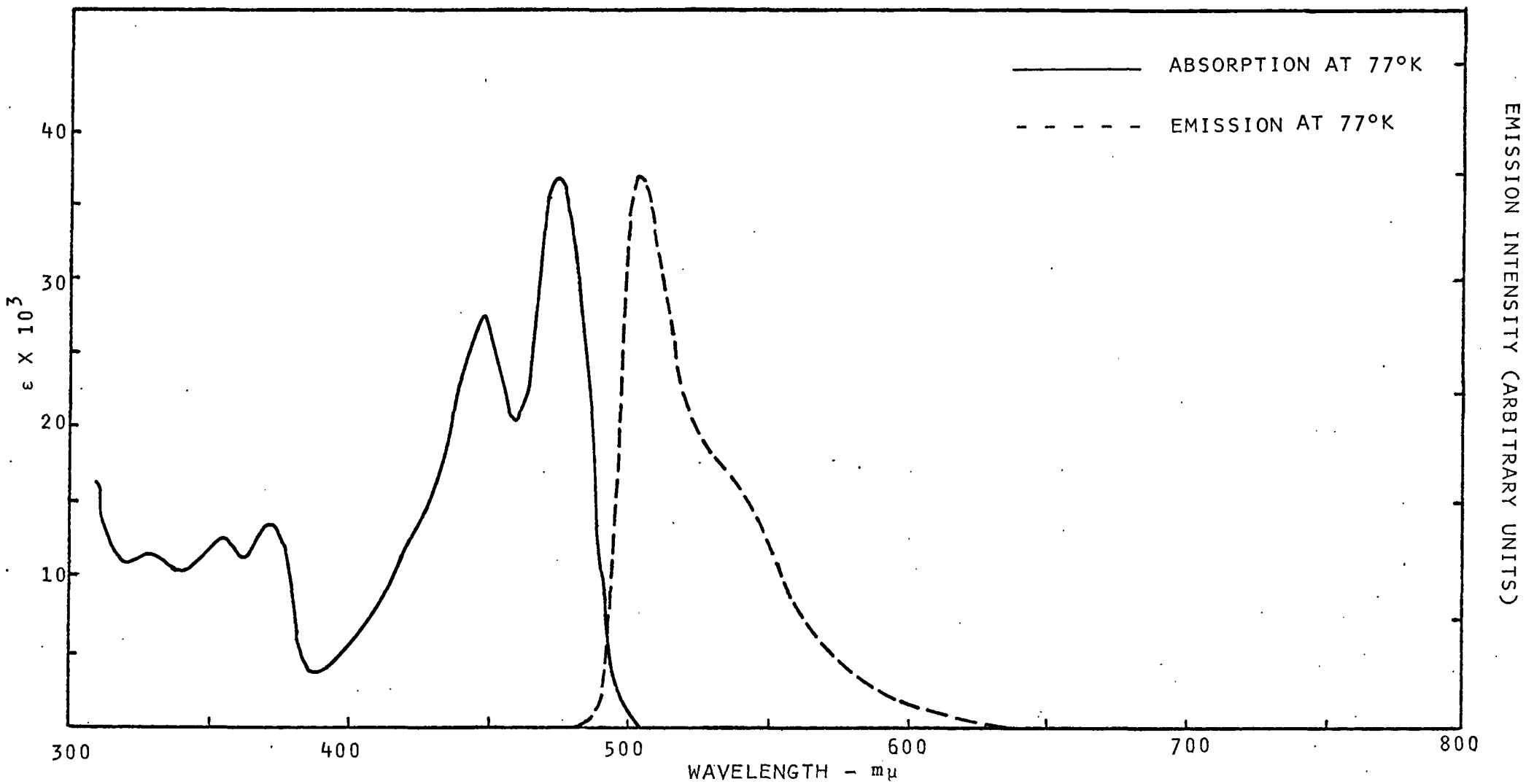


FIGURE 6. LOW TEMPERATURE ABSORPTION AND FLUORESCENCE SPECTRA OF 3,6' DIMETHYLHELIANTHRONE IN EPA.

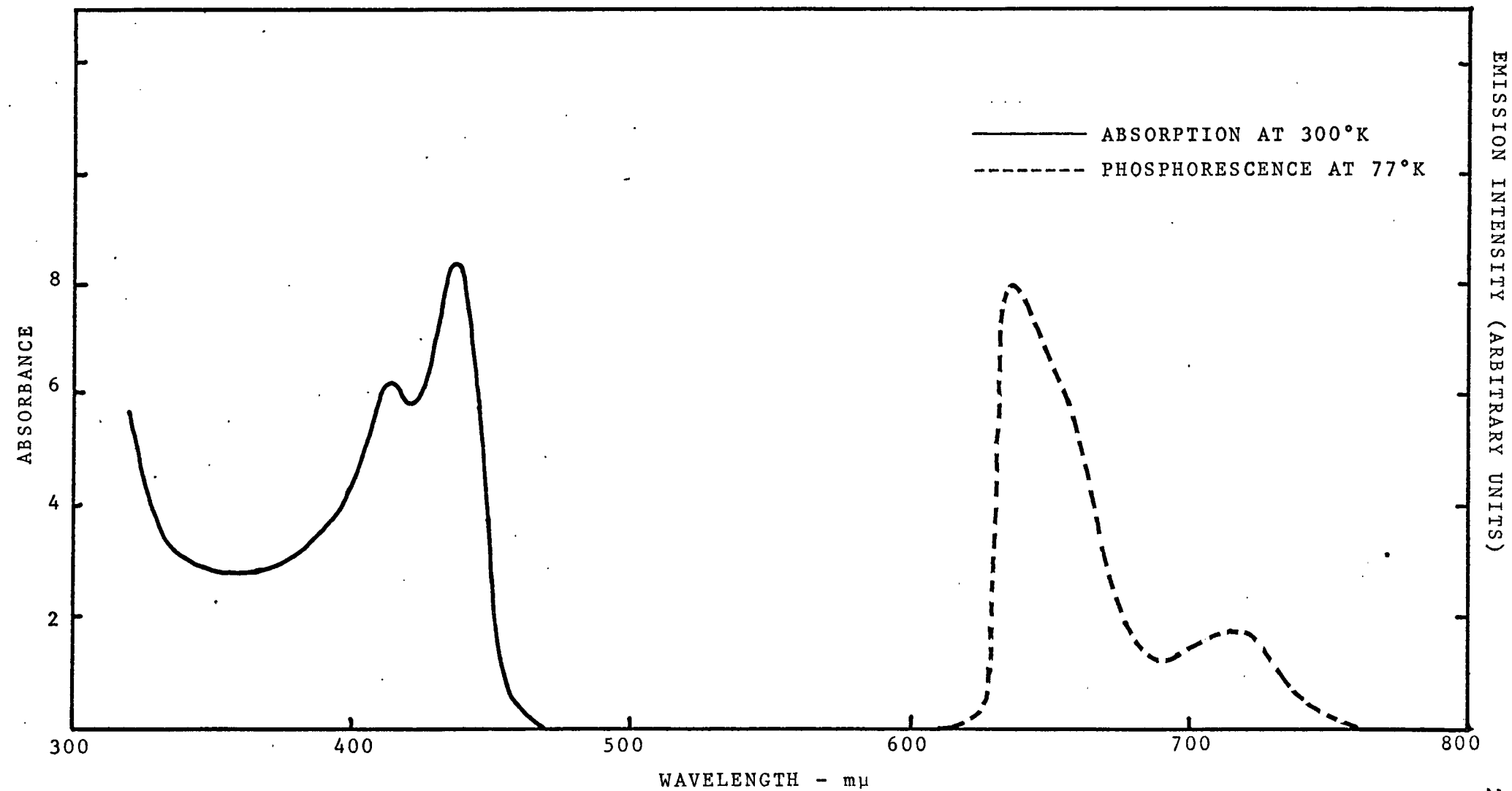


FIGURE 7. ROOM TEMPERATURE ABSORPTION AND LOW PHOSPHORESCENCE SPECTRA OF 3,6' DIMETHYLMESONAPHTHOBIANTHRONE

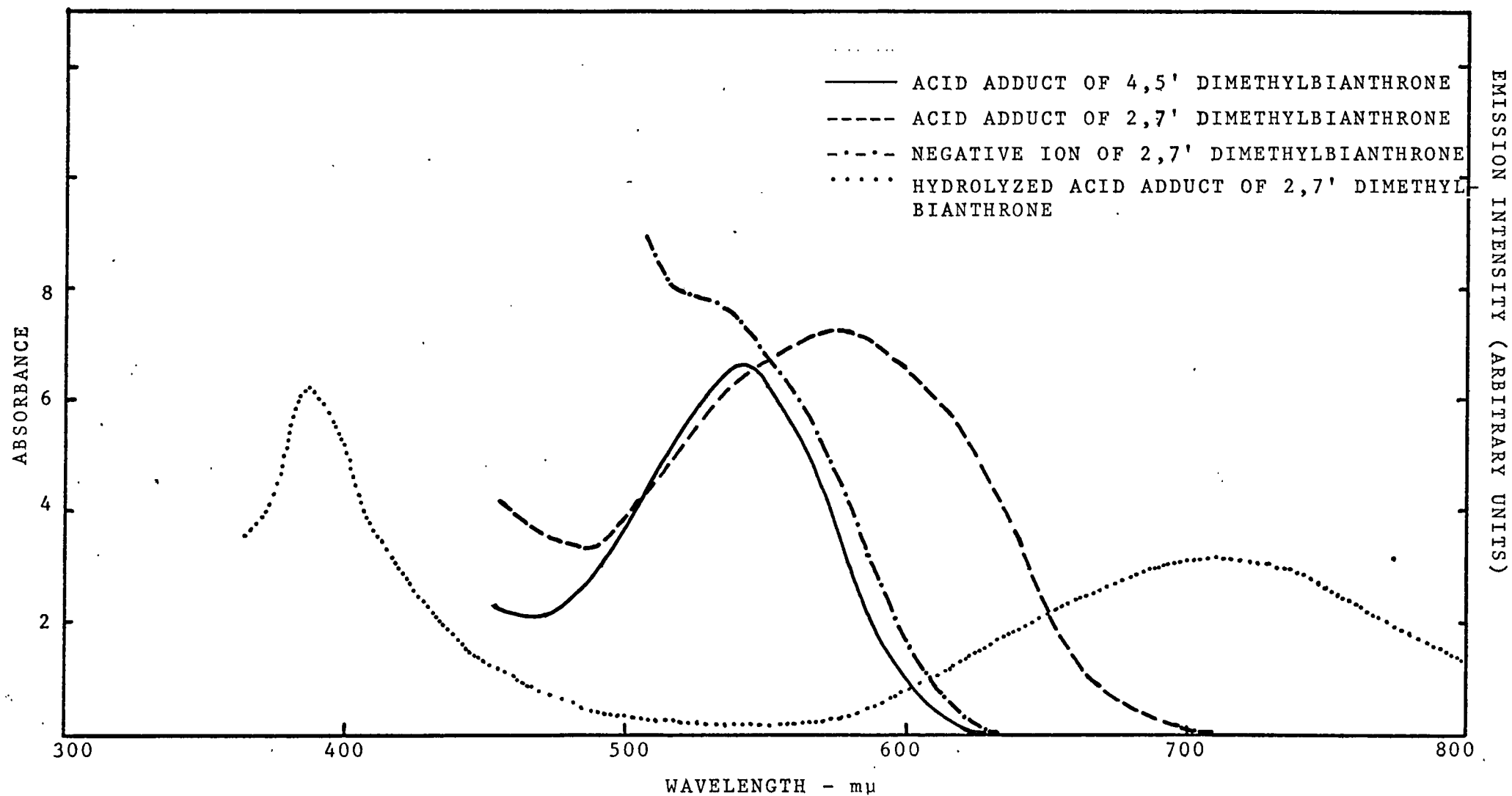


FIGURE 8. ABSORPTION SPECTRA OF ACID ADDUCTS AND NEGATIVE ION OF BIANTHRONE

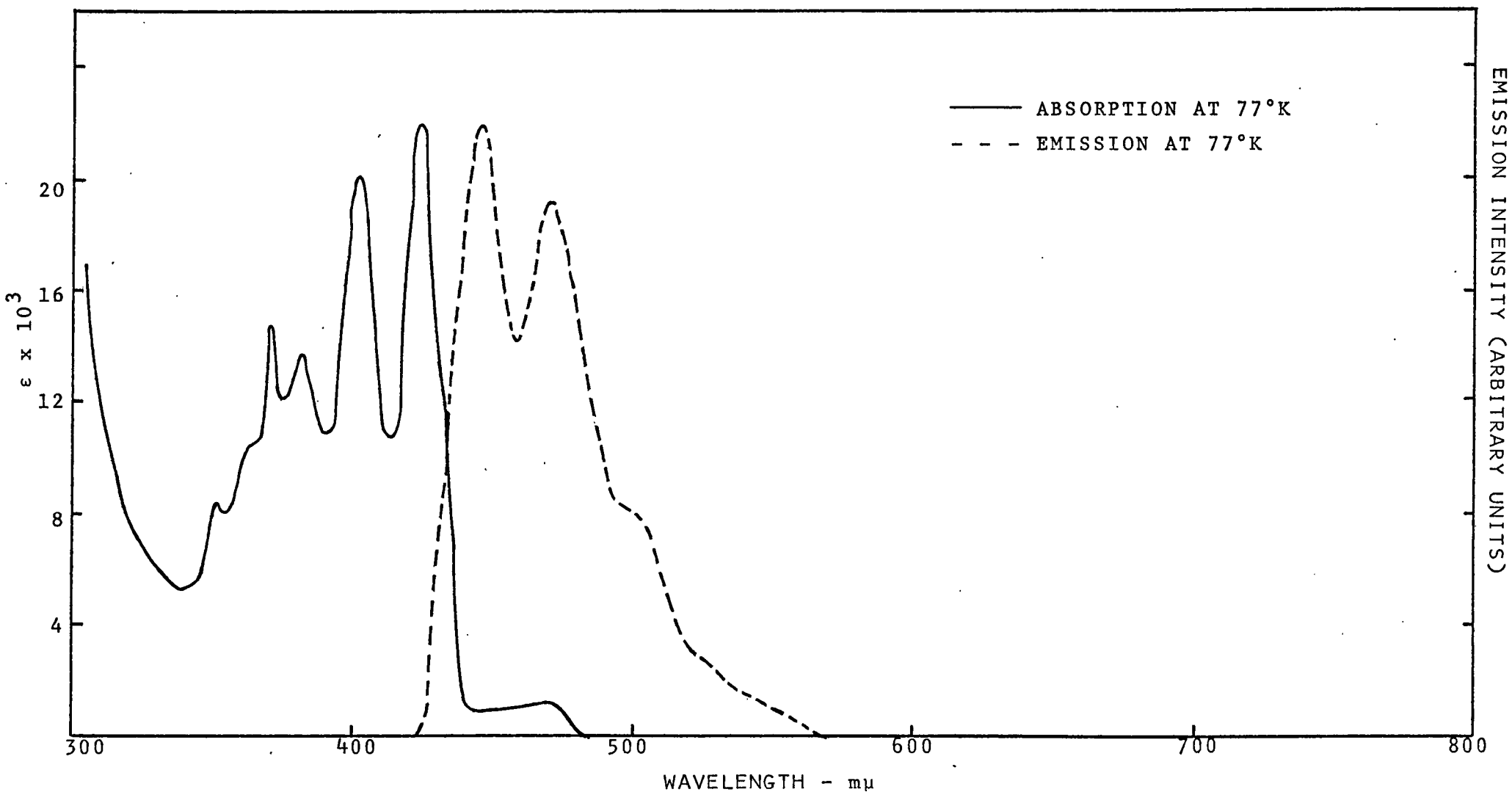


FIGURE 9. LOW TEMPERATURE ABSORPTION AND FLUORESCENCE SPECTRA OF 2,7' DIMETHYLDIHYDROBIANTHRONE

dihydrohelianthrone 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 (approximately 30 mg/liter or saturated if the solubility less than 30 mg/liter) in benzene, m-xylene, chloroform, and 2MeTHF gave dihydrobianthrone, helianthrone, and the semiquinone of bianthrone. Continued photolysis gave helianthrone, dihydrobianthrone, and mesonaphthobianthrone.

IV.
DISCUSSION

DISCUSSION

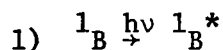
The spectral evidence for equivalence of the photo- and thermo-chromic forms is reviewed. Next, the photochemistry of 2,7' dimethylbianthrone and 4,5' dimethylbianthrone is discussed within the framework of the proposed mechanism. And finally, the spectral evidence for a change in atomic configuration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

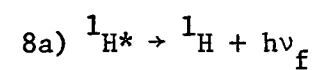
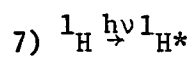
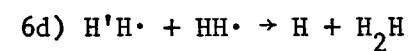
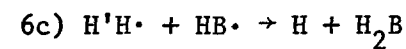
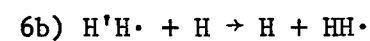
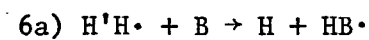
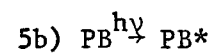
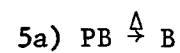
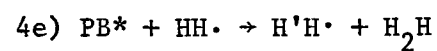
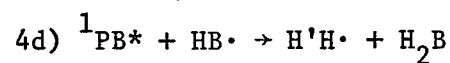
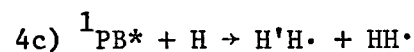
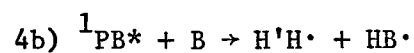
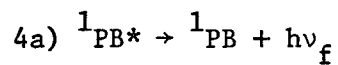
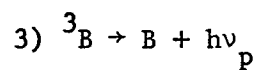
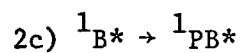
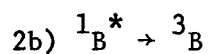
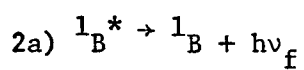
A. The Equivalence of the Photo- and Thermo-chromic Forms

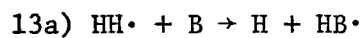
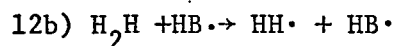
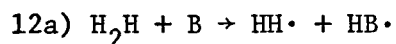
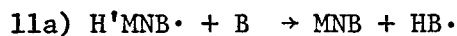
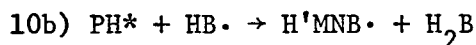
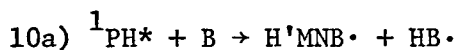
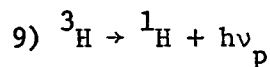
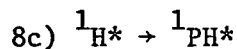
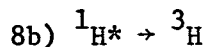
Proof of the identity of the thermo- and photochromic forms of bianthrone was initially based on the identity of the wavelengths of the long wavelength band maxima of the two forms at 680 mμ (1). Then further consideration (28) also revealed the similarity of the spectra of the hydrolyzed sulfuric acid adduct of 4,5' dimethylbianthrone. The present study has shown the absorption spectra of the hydrolyzed acid adduct of 2,7' dimethylbianthrone in ethanol is essentially identical to that of the photochromic form of 2,7' dimethylbianthrone in EPA from 800 mμ to 350 mμ regarding both wavelength and shape (see Figure 8).

B. General Reaction Scheme

The photochemistry of the substituted bianthrone in ethanol is best studied within the framework of the following reactions:







The applicable reactions for 2,7' dimethylbianthrone and 4,5' dimethylbianthrone are discussed for each compound in turn.

C. 2,7' dimethylbianthrone

1, 2a, 2b, 3, 4a, 5b, 7, 8a, 8b, 9. These processes are verified by observation of the absorption, fluorescence, and phosphorescence of the molecules with the known compounds 2,7' dimethylbianthrone, 3,6' dimethylhelianthrone, 3,6' dimethylmesonaphthobianthrone, and 2,7' dimethyldihydrobianthrone.

2c. Using flash photolysis Huber (35) has shown that the photochromic form 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 band and noting that the optical density of the photochromic band remained constant while the occupation of the triplet decreased. It was also verified (35) by simultaneous monitoring of the absorption of the photochromic form and the phosphorescence of 2,4,7',8' tetramethylbianthrone. Reference to Figure 10 indicates that crossing probably occurs from the first excited state of B to an isoenergetic vibrational level of the first excited state of the photochromic form.

4b. The species $\text{HB}\cdot$ cannot be detected by absorption during photolysis of saturated solutions in EPA. However, photolysis of concentrated solutions in m-xylene and 2 MeTHF in which bianthrone is two orders of magnitudes more soluble and the H-bonding is less gives rise to an EPR signal which has been assigned to the negative ion of bianthrone. (5). During photolysis of 2 MeTHF solutions at -100°C ., the EPR signal maximizes before the green coloration of the solution (5).

Absorption studies in this laboratory of the photolysis of concentrated solutions of 2,7' dimethylbianthrone in degassed aromatic hydrocarbons, chloroform, 2 MeTHF, and n-propyl amine gave a 560 m μ shoulder which has been assigned to the protonated bianthrone radical negative (shoulder on 500 m μ helianthrone band shown in Figure 8.)

(A)

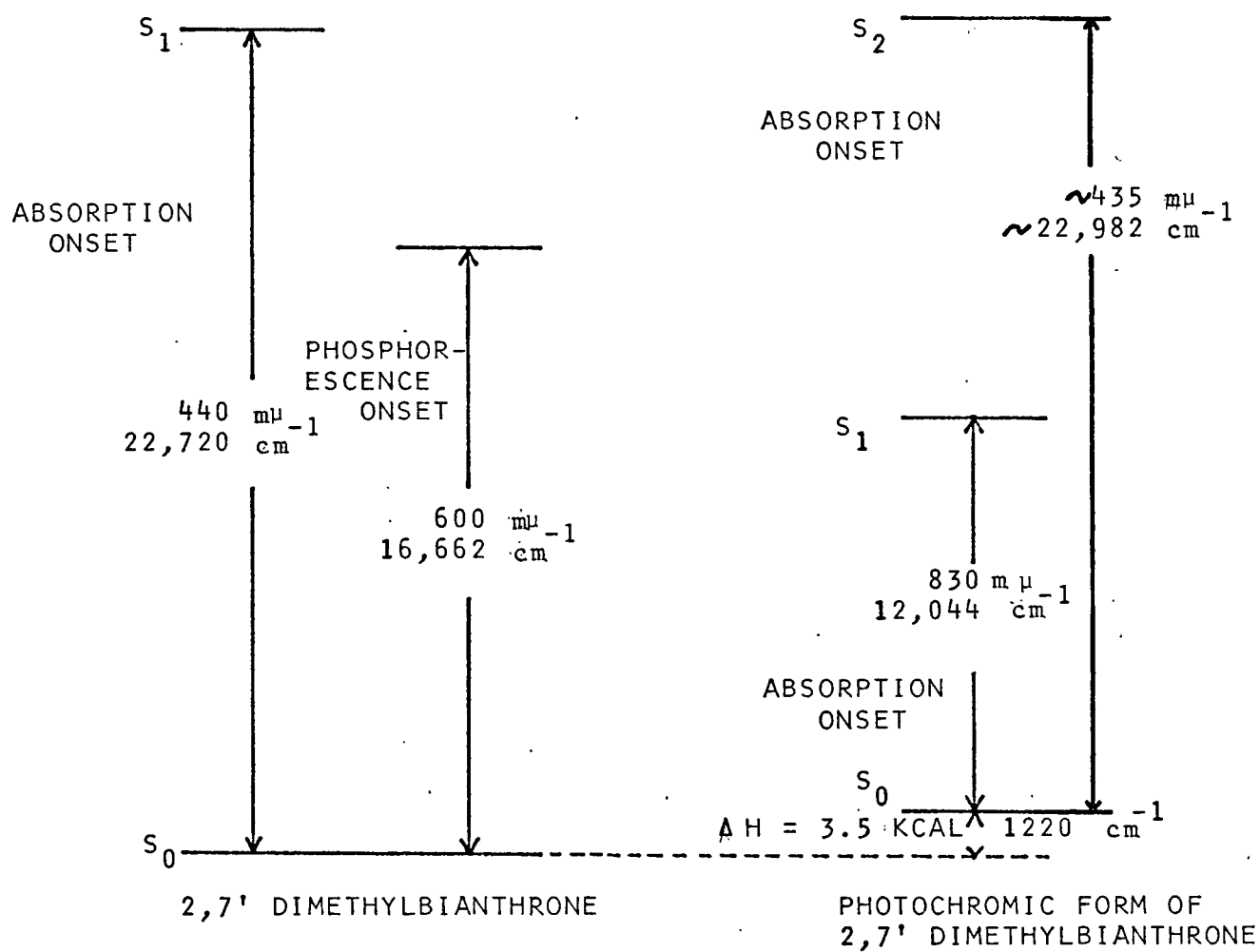


FIGURE 10. PHOTOCHROMIC FORM OF 2,7' DIMETHYLBIANTHRONE
ENERGY LEVEL DIAGRAM

(B)

.....-VISCOSITY BARRIER
——BIANTHRONE
---PHOTOCHROMIC FORM
OF BIANTHRONE

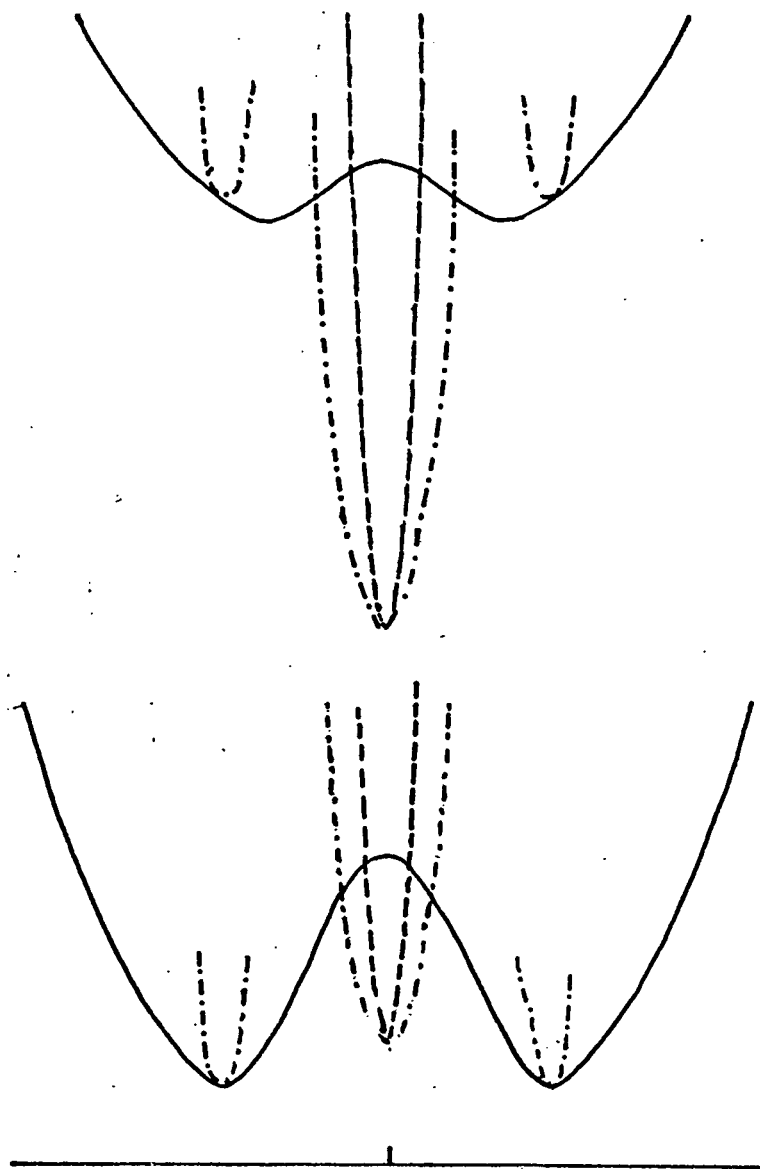


FIGURE 10. PHOTOCHROMIC FORM OF BIANTHRONE
POTENTIAL CURVES

ion, $\text{HB}\cdot$, on the basis of the following evidence: 1) The EPR signal of the negative ion was detected in m-xylene and 2 MeTHF (5); 2) The band is a precursor of the 623 m μ absorption due to 2,7' dimethyldihydrohelianthrone in the photolysis; 3) its concentration in m-xylene solutions is decreased by the removal of 2,7' dimethylbianthrone as photolysis proceeds; 4) it is extremely oxygen sensitive whereas 2,7' dimethylbianthrone, 2,7' dimethyldihydrobianthrone, 2,7' dimethylheliathrone, and 2,7' dimethylmesonaphthobianthrone react not at all or only slowly with oxygen. This is in contrast with dihydrohelianthrone which is easily oxidized by bianthrone or oxygen according to Brockmann and Muhlmann (4) and the present study. An exception is in benzene or m-xylene where it is apparently stabilized by complex formation and reacts only slowly. 5) The spectrum is very similar to that of sulfuric acid adduct of 2,7' dimethylbianthrone, ($\text{H}^+\cdot$ 2,7' dimethylbianthrone), which simple Hueckel theory predicts would absorb at the same wavelength (see Figure 8); and 6) the decay kinetics of the 570 m μ band in the flash photolysis work of Dombrowski et al. (7) are second order.

In the absence of termolecular reactions, the simultaneous generation of the radical, $\text{H}'\text{H}\cdot$, also results. This irreversible photo reaction occurs either via hydrogen atom abstraction or via hydrogen atom donation.

Hydrogen atom abstraction by a photo activated (excited state) bianthrone may be discounted on the following basis. In a study of

substituted anthraquinones, Dearmond and Chan (40) have shown that quinones which fluoresce and hence have the $\pi-\pi^*$ levels lower than the $n-\pi^*$ do not have a photochemically active triplet and are not hydrogen atom abstractors. Conversely, they (40) 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 by hydrogen atom donation by a photocyclized species.

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

4c. The 624 m μ absorption band of H₂H (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 (note no bianthrone present) gave no 3,6' dimethyldihydrohelianthrone even after 2 hours irradiation at 466 m μ at room temperature. Thus, in ethanol only the bridge hydrogen atoms of PB* 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 6c and would also be

formed during the generation of the dihydro compound (note reaction 4c plus reaction 6b or 6d). Thus, the excited state of the photochromic form of bianthrone reduces helianthrone to the dihydro-compound and in the absence of tertiary collisions, the free radicals $H'H\cdot$ and $HH\cdot$ are necessarily intermediates. [Note that the photolysis of helianthrone (reaction 1a of the Introduction) described by Brockmann and Muhlmann (4) does occur in pyridine.]

4d. It is shown in 4b that the excited state of the photochromic form of 2,7' dimethylbianthrone is a reducing agent. The 425 m μ band of 2,7' dihydrobianthrone is detected in photolyzed samples of 2,7' dimethylbianthrone by absorption or excitation spectra. This is a probably reaction for the reduction of the free radical $HB\cdot$ to dihydro-bianthrone.

5a. 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 both from the lack of decrease in the 410 m μ 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 in thermal energy permits this reaction to proceed.

6a and b. The 500 m μ fluorescence and 470 m μ absorption band of helianthrone is detected during the photolysis. These reactions provide

possible paths for the completion of the oxidation of the excited state of the photochromic form of bianthrone to helianthrone. A more definitive statement cannot be made on the basis of the present data.

6c and d. The 460 m μ , 427 m μ , and 624 m μ absorption bands of helianthrone, dihydrobianthrone, and dihydrohelianthrone (4), 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 by the excited state of the photochromic form of bianthrone as well as the completion of the oxidation of the photocyclized bianthrone.

8c. The photocyclization followed by dehydrogenation of helianthrone to mesonaphthobianthrone does occur and this reaction implies 8c as a primary process in the photolytic reaction in analogy with 2c. 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.

10a. In the case of the photocyclization and dehydrogenation of helianthrone to mesonaphthobianthrone, Brockmann and Muhlmann (4) have shown that the process involved is hydrogen atom donation by a photo-excited helianthrone molecule. This can also be argued on the same basis as used for bianthrone in 4b. Then the active species must be an energetic 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 radical $\text{HB}\cdot$ is detected during the photolysis of 2,7' dimethylbianthrone as noted in 4b and in the absence of tertiary collisions $\text{H}'\text{MNB}\cdot$ and $\text{HB}\cdot$ would be the products of this reaction. This is supported by the fact that $\text{H}'\text{MNB}\cdot$ and $\text{HB}\cdot$ are logical precursors of mesonaphthobianthrone and dihydrobianthrone, which are the two principal final products in the photolysis of 2,7' dimethylbianthrone in EPA.

10b. The excited state of the photochromic form of 2,7' dimethylhelianthrone is an active reducing species as noted in 10a and $\text{HB}\cdot$ is produced in 4b, 6a, and 10a. 2,7' dimethylmesonaphthobianthrone and 2,7' dimethyldihydrobianthrone are the primary products of the photolysis. This reaction provides a probable path for the completion of the reduction of $\text{HB}\cdot$ to H_2B . With PH^* as the reducing agent, $\text{H}'\text{MNB}\cdot$ is produced in the absence of tertiary collisions.

11a. Among the final products of the photolysis of bianthrone is 2,7' dimethylmesonaphthobianthrone. The 2,7' dimethylmesonaphthobianthrone is detected as a yellow precipitate which can be dissolved in 2 MeTHF where it absorbs at 440 m μ and phosphoresces at 643 m μ . The 2,7' dimethyldihydrobianthrone is detected as absorption or excitation at 425 m μ and fluorescence at 473 m μ . (The other two of consequence are helianthrone and dihydrohelianthrone with the proportion of each dependent on the wavelength of photolysis.) This reaction provides a reasonable path for the completion of photo-oxidation of bianthrone to 2,7' dimethylmesonaphthobianthrone which is consistent with the total reaction scheme.

11b. 2,7' dimethylmesonaphthobianthrone and 2,7' dimethyldihydrobianthrone 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' dimethylmesonaphthobianthrone and the reduction of bianthrone to 2,7' dimethyldihydrobianthrone.

12a, 12b, 13a, 13b. The total reaction $H_2H + B \rightarrow H + H_2B$ was observed by Brockmann and Muhlmann (4). The present author 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 mμ, 460 mμ, and 624 mμ of 2,7' dimethyldihydrobianthrone, 2,7' dimethylhelianthrone and 2,7' dimethyldihydrohelianthrone, respectively. The 624 mμ band was observed to disappear on warming of the solution to room temperature if residual bianthrone was present. The 624 mμ band did not fade when no bianthrone could be detected from excitation spectra.

The evidence for a free radical is as follows: Wasserman (6) 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 (5) for the negative ion of 2,7' dimethylbianthrone. As noted above and in 6d, photolysis under the conditions described gives irreversible photochemistry rather than simply production of the photochromic form. Thus, the green coloration observed by Wasserman (6) was due to the presence of dihydrohelianthrone. The

EPR signal was due to the radicals generated according to reactions 12a and 12b when the viscosity was decreased and the thermal energy was increased sufficiently that bimolecular reactions occurred rapidly.

D. 4,5' dimethylbianthrone

1, 2a, 2b, 3, and 4a. These reactions are verified by the observation of the absorption and emission of 4,5' dimethylbianthrone and the photochromic form of 4,5' dimethylbianthrone.

4b. This reaction would account for the formation of the species responsible for the bands at 440 and 460 m μ attributed to 'Form C' by Kortum et al. (28) where Form C was the species absorbing at 440 and 460 m μ and Form B the species absorbing at 660 m μ . They noted that as the temperature of photolysis was raised the ratio of [Form C]/[Form B] increased as would be the case for a diffusion controlled bimolecular reaction. It is suggested that the bridged radical is responsible for the 440 m μ band and the semiquinone gives rise to the longer wavelength band since the first would be helianthrone-like and the second would be exactly analogous to the semiquinone of 2,7' dimethylbianthrone.

5a. Warming of EPA solutions of the photochromic forms from 77°K. to 20°C. gave back bianthrone.

5b. The photobleaching of 4,5' disubstituted bianthrone including the methylsubstituted compound was observed by Hirschberg and Fischer (1) on excitation into the long wavelength absorption band.

E. Change in Atomic Configuration during Photoconversion

Two effects of going from fluid to rigid media must be explained. The first is the change in the shape of the absorption spectra of 2,7' dimethylbianthrone and 4,5' dimethylbianthrone from Franck-Condon forbidden to Franck-Condon allowed on cooling of EPA or 2 MeTHF solutions to 77°K. and the second is that samples whose absorption spectra have Franck-Condon allowed shapes do not undergo photochemistry even on extended irradiation while those which have absorption spectra with Franck-Condon forbidden shapes undergo photochemistry quite readily; That is, 1) fluid solutions of 2,7' dimethylbianthrone have absorption spectra with a Franck-Condon forbidden shape and readily undergo irreversible photochemistry on irradiation, via the PB; 2) viscous and rigid glass solutions which have absorption spectra with a Franck-Condon forbidden shape readily undergo photoconversion to the colored form; 3) rigid glasses of bianthrone which have spectra with Franck-Condon allowed shapes do not undergo any photochemistry even on long term irradiation.

These effects can be explained for 2,7' dimethylbianthrone with reference to Figure 9 which is justified on the following basis.

Bianthrone behaves as a hindered ethylene due to the hydrogen-hydrogen repulsion in the case of 2,7' dimethylbianthrone (and the greater methyl-hydrogen repulsion in the case of 4,5' dimethylbianthrone) (see Figure 1). In a simplified scheme considering only the angle of skew (θ) of the anthrone halves the energy minima of the ground state are at a small angle from coplanar for 2,7' dimethylbianthrone (and

a somewhat larger angle for 4,5' dimethylbianthrone) (see Figure 1). In the case of 2,7' dimethylbianthrone the cyclized form has a minimum at θ equal to 0° and 3.5 Kcal above the ground state of bianthrone, and the potentials cross 12-20 Kcal above the ground state of PB. These values are the ΔH for the thermal equilibrium of bianthrone (1,15,16) and the colored form and the barrier to thermal reversion of the photochromic form (1,16).

Excitation to the first excited state decreases the π bond order so that the ethylenic bond lengthens and the steric interaction of the groups at the 4 and 5 positions with those at the 4' and 5' positions is reduced. Thus, the steric hinderance is decreased and the minima of the first excited state lies nearer θ equal to 0° than in the case of the ground state. The potential of the first excited state of the cyclized form crosses the first excited state of bianthrone. The first excited state of the cyclized form of 2,7' dimethylbianthrone lies $12,200 \text{ cm}^{-1}$ above its ground state and the first excited state of 2,7' dimethylbianthrone lies $22,700 \text{ cm}^{-1}$ above its ground state.

The potential of bianthrone rises relatively slowly with increasing θ as it is due solely to the ethylenic bond while that of the cyclized form rises sharply since the anthrone halves are held coplanar by a bond between the 4 and 4' positions.

If the bianthrone is in a rigid medium of high microscopic viscosity, then high barriers which are due primarily to steric effects exist and

the minima of the potential wells lie one above the other (note Figure 10). The two anthrone halves are also constrained from rotating relative to one another. In the case of the cyclized form, the potential barrier due to the viscosity barrier constrains the molecule from rearranging to give back bianthrone.

Any model selected must account for these phenomena: 1) The absorption spectra of fluid solutions of 2,7' dimethylbianthrone at temperatures from 133°K. to 300°K. have a Franck-Condon forbidden shape while the rigid solutions at 77°K. have absorption spectra with a Franck-Condon allowed shape. These same solutions undergo rapid irreversible photochemistry (via the photocyclized form) at temperatures as low as 133°K. But at 88°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., it does not spontaneously fade or erase on irradiation into the long wavelength band. Rigid EPA or 2 MeTHF glasses of 2,7' dimethylbianthrone itself at 77°K. underwent no detectable photochemistry even when irradiated for two hours. The fluorescence spectrum of 2,7' dimethylbianthrone has a Franck-Condon allowed shape while the fluorescence of 4,5' dimethylbianthrone has a Franck-Condon forbidden shape. 2) Solutions of 2,7' dimethylbianthrone in methylphthalylethylglycolate undergo rapid irreversible photochemistry at 300°K., but at 208°K. the primary product (estimated at 80 percent plus) is the photochromic form. The absorption spectrum of the solutions

have a Franck-Condon forbidden shape at 300°K., but at 208°K. the shape of the spectrum is best described as skewed toward Franck-Condon allowed (see Figure 11). 3) J. R. Huber (35) was able to convert 2,4,7',8' tetramethylbianthrone to the photochromic form in a plexiglass matrix at 77°K. The absorption spectrum of the bianthrone sample had a Franck-Condon forbidden shape.

Now the phenomena can be explained in terms of the above model. In fluid solution or microscopically nonviscous glasses, there are no potentials due to viscosity and the excited state geometry of bianthrone is different from that of the ground state so that the absorption spectrum has a Franck-Condon forbidden shape. In addition, the molecule is free to rearrange so that it may cross from a vibrational level of the first excited state of bianthrone to an isoenergetic state of the cyclized form, deactivate, and thermally revert to bianthrone.

Further, if the viscosity and the thermal energy are sufficiently low and high, respectively, then collision with a second bianthrone molecule occurs during the lifetime of the excited state of the photocyclized form and irreversible chemistry occurs.

The Franck-Condon forbidden shape of the absorption of the cyclized form is attributed to shift in the energy minimum with respect to some coordinate other than the skew angle of the anthrone halves. Skewing is not possible because of bridging of the 4 and 4' carbons in the cyclization.

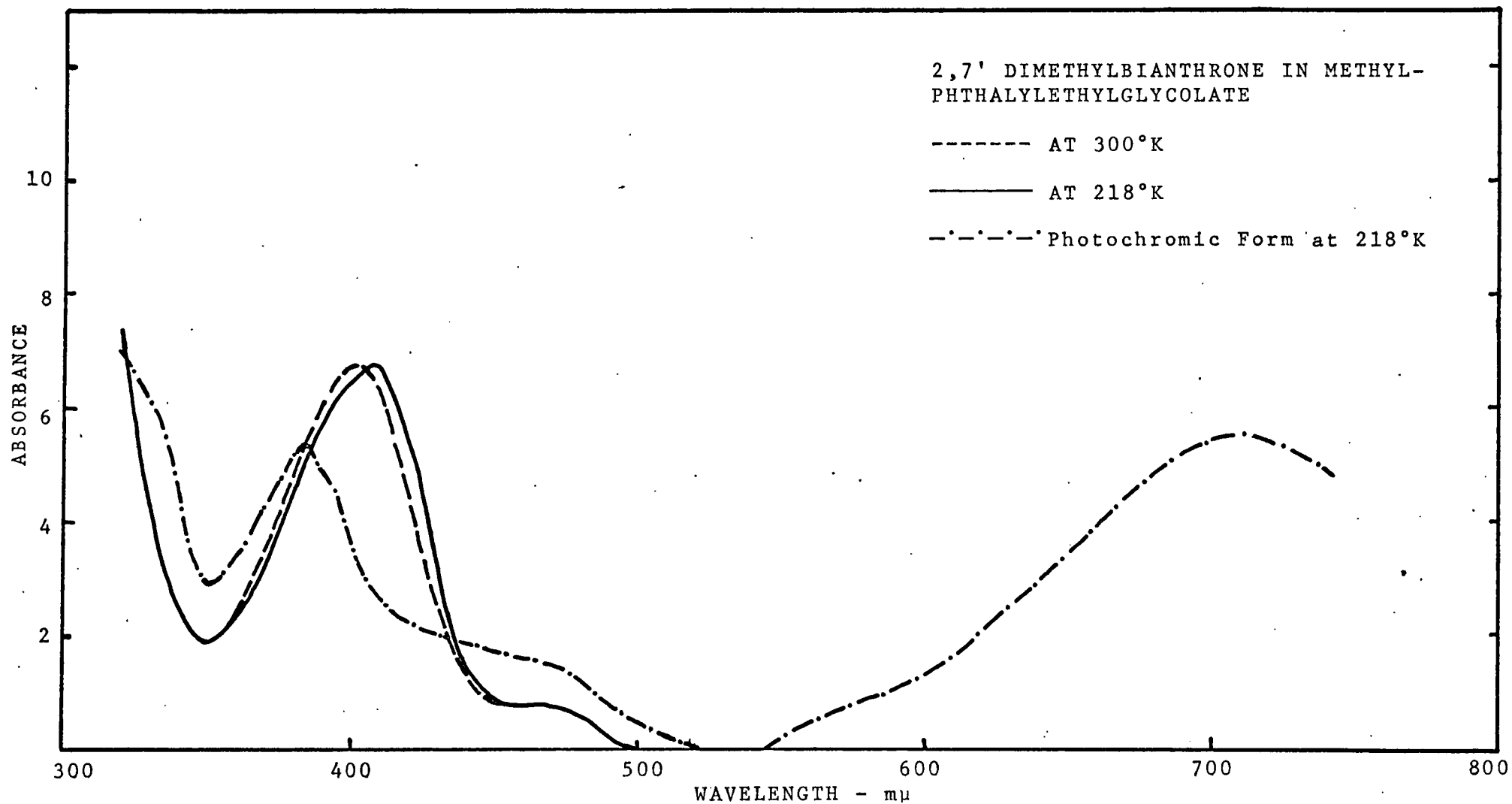


FIGURE 11. ABSORPTION SPECTRA OF 2,7' DIMETHYLBIANTHRONE IN METHYLPHTHALYLETHYLGLYCOLATE AT 300°K AND 218°K AND OF THE PHOTOCROMIC FORM OF 2,7' DIMETHYLBIANTHRONE IN THE SAME SOLVENT

The fluorescence of the 2,7' dimethylbianthrone is Franck-Condon allowed as the model predicts. In the 4,5' dimethylbianthrone, relaxation occurs to some equilibrium state different in geometry from the ground and first excited states during the lifetime of the excited state.

V.

CONCLUSIONS

CONCLUSIONS

The irreversible chemistry of 2,7' dimethylbianthrone in ethanol proceeds via a free radical reaction. The reactive species is an excited state of the cyclized form which acts as a hydrogen atom donor. The observation that irreversible photochemistry occurs readily at temperatures as low as 133°K accounts for the paramagnetism [detected by EPR (6,31) and magnetic balance (29)] detected during the low temperature photolysis and attributed to the photochromic form. Such paramagnetism would be in direct conflict with the findings of Huber et al. (35).

The striking change in the shape of the absorption spectra of 2,7' dimethylbianthrone in EPA or 2 MeTHF from Franck-Condon forbidden to Franck-Condon allowed on cooling from 300°K to 77°K in contrast to the allowed shape of the absorption spectrum of 2,4,5,7' tetramethylbianthrone in plexiglass at both 300°K and 77°K indicates a striking difference in the microscopic properties of the solvents. The fact that photocyclization does not occur for solutions which have spectra with a Franck-Condon allowed shape indicates that the mechanisms of such solutions are constrained from the necessary rearrangement. However, molecules in solutions with absorption spectra which have a Franck-Condon forbidden are not so constrained. The two effects can be accounted for if the steric effects which constrain the molecule from cyclizing are also responsible for potential barriers which give energy minima one above the other (note Figure 10).

APPENDIX I

APPENDIX I

DETERMINATION OF NUMBER OF CYCLES FOR DEGASSING

Assumptions:

1. Concentration of oxygen in sample equals concentration of oxygen above sample (8.9×10^{-3} m/l.).
2. Equilibrium attained during "thaw" part of the freeze, pump, thaw cycle, but not reattained during freeze part. Thus room temperature equilibrium is approximately maintained during freezing. (The initial concentration of oxygen is multiplied by an arbitrary "safety" factor to compensate for the failure of this assumption.)

Since according to assumption (1), a concentration of 10^{-7} molar oxygen corresponds to a pressure of about 40 μ of mercury, all oxygen is considered removed if the system is pumped down to 0.5 μ , or less.

Then

$$C_r = \left(\frac{V_s}{V_c} \right)^n C_o \quad (1)$$

where C_r is the residual oxygen concentration, V_c is the volume above the sample, n is the number of cycles, and C_o is the initial concentration of oxygen in the sample.

Taking the logarithm of both sides of equation (1) and rearranging, we have

$$n = (\log C_r - \log C_o) / \log \left(\frac{V_c}{V_s} \right)$$

or

$$n = \log \left(\frac{C_r}{C_o} \right) / \log \left(\frac{V_c}{V_s} \right)$$

Now if we want a residual oxygen concentration of 10^{-7} molar for a 20 milliliters sample with a volume of 140 milliliters available for expansion:

$$C_o = 8.9 \times 10^{-3} \text{ m/l} \times 5 \text{ ("safety" factor)}$$

$$C_r = 10^{-7} \text{ m/l}$$

$$V_s = 20 \text{ ml}$$

$$V_c = 140 \text{ ml}$$

gives

$$n = \log \left(\frac{10^{-7}}{4.45 \times 10^{-2}} \right) / \log \left(\frac{20}{140} \right)$$

$$n = 6.98 \approx 7$$

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