On the basis of the model for relative diffusion phenomena presented in this paper, the experimental quantum yield data can be interpreted in terms of transient processes dependent upon the iodine–solvent interaction described by $\psi(r)$ and longer lived processes dependent upon $D_{rr}(r)$. Immediately after dissociation, the separating iodine atoms encounter the barrier in $\psi(r)$ between first and second nearest-neighbor positions. If the excess energy provided by the exciting photon is small, the atoms are reflected from the barrier and recombine quickly; but if the excess energy is sufficient to permit the separating atoms to reach second nearest-neighbor positions, the barrier will tend to keep them apart and thus prevent recombination. Furthermore, if $D_{rr}(r)$ increases with increasing r, pairs of atoms that initially achieve a large separation will diffuse away from each other more quickly, and thus be even less likely to recombine. In reality of course, the successive maxima in $\psi(r)$ and the r-dependence of $D_{rr}(r)$ are the result of interactions between the solute iodine atoms and surrounding solvent molecules, and are truly descriptive only of an equilibrium situation. Monchick[28] has however presented a theoretical treatment of photodissociation processes that includes an "effective" potential much like $\psi(r)$, although no theory incorporating both $\psi(r)$ and an r-dependent relative diffusion coefficient has previously been treated.

Acknowledgments. We wish to thank Professor G. Wilse Robinson for his helpful discussions and his critical reading of this paper. One of the authors (C. A. E.) gratefully acknowledges the support of The Netherlands Organization for the Advancement of Pure Research (ZWO).

(28) L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

Investigation of Singlet → Triplet and Singlet → Singlet Transitions by Phosphorescence Excitation Spectroscopy. VIII. Santonins

Grace Marsh,[1a] David R. Kearns,[1b] and Michael Fisch[1c]

Contribution from the Department of Chemistry, University of California, Riverside, California 92502, and the Department of Chemistry, University of California, Irvine, California 92664. Received September 15, 1969

Abstract: The singlet → singlet and singlet → triplet transitions in α-santonin (I), 6-episantonin (II), and 2-bromosantonin (III) have been investigated at both 77 and 4.2°K. The results may be summarized as follows. (i) Polarization measurements demonstrate that vibronic coupling between the $S(n,\pi)$ and $S(\pi,\pi)$ states is the principal source of intensity for the $S_0 \rightarrow S(n,\pi)$ transition. The magnitude of the electronically allowed contribution to the intensity appears to depend upon the molecular structure. (ii) The lowest excited triplet state in each case is identified as a $^3(\pi,\pi)$ state. (iii) The $^3(n,\pi)$ state has been observed in each compound just above (1200–1600 cm^{-1}) the $^3(\pi,\pi)$ state. The intensity in the $S_0 \rightarrow T(n,\pi)$ transition of α-santonin ($\epsilon_{\max} \simeq 0.3$) is attributed to strong spin–orbit coupling with the $^1(\pi,\pi)$ state. (iv) Diffuseness observed in the $S_0 \rightarrow T(n,\pi)$ absorption spectra at 4.2°K is attributed to vibronic interaction between the $^3(n,\pi)$ state and nearly degenerate vibronic levels of the lower lying $^3(\pi,\pi)$ state. These spectroscopic observations appear to have an important bearing on the interpretation of the α-santonin photochemistry and the possible role of the $^3(n,\pi)$ and $^3(\pi,\pi)$ states in the excited state transformations.

Since they were first identified in 1944,[2] interest in triplet state molecules has grown, and this growth has been particularly rapid during the last few years. Of the many types of molecules which have been studied considerable attention has been given to organic ketones and aldehydes.[3-10] Surprisingly enough most of these studies have been concerned with aromatic carbonyl compounds and there have been relatively few studies of "simple" carbonyl-containing molecules such as enones and dienones.[8-10] Because of this, and because of the current interest in their photochemical properties, we have started a comprehensive investigation of the spectroscopic properties of a wide variety of enones and dienones. Some of our earlier studies of enones have already been published,[11,12] and more detailed results will be forthcoming.[13] In the present paper we discuss results obtained with the following three cross-conjugated dienones: α-santonin (I), 6-epi-

---

(1) (a) Riverside; (b) to whom correspondence should be addressed at Riverside; (c) Irvine.

(2) (a) G. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944); (b) A. Terenin, *Acta Physicochim. URSS*, **18**, 210 (1943); *Zh. Fiz. Khim.*, **18**, 1 (1944).

(3) R. Shimada and L. Goodman, *J. Chem. Phys.*, **43**, 2027 (1965).

(4) J. M. Hollas, E. Gegorek, and L. Goodman, *ibid.*, **49**, 1745 (1968).

(5) Y. Kanda, H. Kasada, and T. Matamura, *Spectrochim. Acta*, **20**, 1387 (1964).

(6) D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966).

(7) S. Dym, R. M. Hochstrasser, and M. Schafer *J. Chem. Phys.*, **48**, 646 (1968).

(8) E. Eastwood and C. P. Snow, *Proc. Roy. Soc., Ser. A*, **149**, 434 (1935).

(9) J. M. Hollas, *Spectrochim. Acta*, **19**, 1425 (1963).

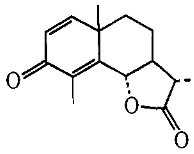
(10) G. Herzberg, "Electronic Spectra and Structure of Polyatomic Molecules," D. Van Nostrand Co., Inc., Toronto, 1966.

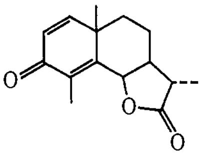
(11) D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968).

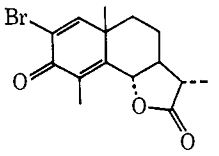
(12) G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **51**, 1890 (1968).

(13) G. Marsh, Ph.D. Thesis, University of California, Riverside, Cal., 1969.

santonin (II), and 2-bromosantonin (III). Our first goal was to locate and assign the lower lying excited states of these molecules and to obtain quantum yields for phosphorescence and intersystem crossing. Secondly, we wanted to examine in detail the various mechanisms responsible for bringing intensity into $S_0 \rightarrow S(n,\pi)$, $S_0 \rightarrow T(n,\pi)$, and $S_0 \rightarrow T(\pi,\pi)$ transitions in these molecules. Finally, we were interested in determining whether or not certain other unusual spectral features previously observed in a study of steroidal enones were also present in the santonins.[11-13]


I


II


III

While our principal interests in this study were spectroscopic in nature, we were also interested in the possibility that our spectroscopic findings might be useful in the interpretation of the photochemical properties of dienones. α-Santonin and the two related compounds were therefore logical choices for this study since α-santonin has played an important role in mechanistic organic photochemistry.[14]

Experimental Section

Materials. α-Santonin (I) was obtained from Aldrich Chemical Co. and recrystallized from ethanol. 6-Episantonin (II) and 2-bromosantonin (III) were prepared using literature procedures[15,16] and purified by recrystallization. 2-Methyltetrahydrofuran (2-MTHF) and ethyl iodide (EtI) purchased from Matheson Coleman and Bell were distilled in a 5-ft vacuum-jacketed column filled with glass helices to remove interfering impurity absorption or emission. The purified solvents were then stored at 0° under nitrogen until used.

Apparatus and Experimental Procedure. The absorption spectra of compounds I, II, and III in a rigid glass (2-MTHF) were measured with a Cary Model 14 recording spectrophotometer using a dewar and sample holder which maintained the sample at 77°K and allowed the sample to be reproducibly positioned in the light beam. For solution measurements the cell path length was 1 cm and a solvent contraction correction factor (20% for 2-MTHF) was used in calculating molar extinction coefficients.

Low-temperature absorption spectra on crystals of 2-bromosantonin were also obtained on this spectrophotometer; however, because of the small size of the crystals it was necessary to replace the 125-W tungsten lamp Cary source with a 500-W tungsten lamp. Single crystals (~2 mm thick) of 2-bromosantonin were grown from acetone, and then stacked in 7- or 9-mm Pyrex tubing to produce a sample of desired thickness (7–12 mm).

Phosphorescence emission spectra, excitation spectra, and lifetimes for α-santonin and 6-episantonin in 2-MTHF at 77°K were obtained using instruments described previously.[6,17]

Phosphorescence emission and excitation spectra of crystalline samples of I and II were also obtained at 4.2°K. For these experiments, a helium dewar was used in conjunction with a phosphorimeter with excitation and monitor systems placed in a 180° configuration. Thick crystals (~1 mm) were used to examine the $S_0 \rightarrow T$ absorption region and thin crystal films were used to measure $S_0 \rightarrow S$ absorption spectra.

The photoselection method[3,18,19] was used to investigate the polarization of the phosphorescence emission relative to various bands in the absorption spectrum. The polarization of the emission with respect to absorption is given by P, where

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

and $I_{\parallel}$ represents the intensity of the phosphorescence emission with the polarizers parallel to each other and $I_{\perp}$ represents the polarizers in the crossed position. In the polarization studies, a Glan–Thompson prism was used in the phosphorimeter as the excitation polarizer and a polaroid sheet (Polacoat, Inc., GS-10) in the monitoring light path served as an analyzer.

Phosphorescence quantum yields (φ_p) were obtained by comparing the intensity of phosphorescence emission from optically dilute solutions of compounds I and II with that from benzophenone ($\varphi_p = 0.72$)[20] when excited under comparable conditions (equal number of photons absorbed, identical excitation wavelength and detection geometry).

Intersystem crossing quantum yields, φ_{isc}, at 77°K were obtained using the Borkman–Kearns procedure.[21] In this method the sample is excited in either the triplet (λ_t) or singlet (λ_s) absorption regions. The relative phosphorescence intensities are related as follows

$$\frac{I(\lambda_s)}{I(\lambda_t)} = \frac{\epsilon_{ss}(\lambda_s)C_s\varphi_{isc}L(\lambda_s)}{\epsilon_{st}(\lambda_t)C_tL(\lambda_t)} \qquad (1)$$

where C_s, C_t = molar concentration of sample used for singlet or triplet excitation, $L(\lambda)$ = intensity of exciting light at wavelength λ, and $I(\lambda)$ = intensity of phosphorescence resulting from excitation at wavelength λ.

Direct measurement of the triplet extinction coefficient, ϵ_{st}, and the singlet extinction coefficient, ϵ_{ss}, allowed us to compare the phosphorescence intensity resulting from excitation in the triplet absorption region, $I(\lambda_t)$, and in the singlet absorption region, $I(\lambda_s)$. Since all other quantities could be experimentally obtained, eq 1 could be used to calculate intersystem crossing yields. When this method was applied to α-santonin, a value of $\varphi_{isc} = 1.1 \pm 20\%$ was obtained.

Results

77°K Measurements. α-Santonin (I), 6-episantonin (II), and 2-bromosantonin (III) all exhibited a set of weak ($\epsilon_{max} \simeq 30\ M^{-1}\ \text{cm}^{-1}$) absorption bands in the region between 3900 and 3200 Å which can be confidently identified as $S_0 \rightarrow S(n,\pi)$ transitions. (See Figures 1 and 2.) When samples of I and II in 2-methyltetrahydrofuran were excited in the $S_0 \rightarrow S(n,\pi)$ region at 77°K, relatively bright phosphorescence was observed, and these emission spectra are presented in Figure 1. As expected, the emission spectra of I and II are generally quite similar, except that the phosphorescence from II is red-shifted about 250 Å from I. Since the phosphorescence emission spectra of I and II had not previously been reported and since the spectra we obtained were quite different from those obtained by Zimmerman with other cross-conjugated dienones,[22] it was important to prove that the emission was authentic and not from impurities. This was accomplished by demonstrating that there is a close correspondence between the position of peaks in the dilute solution PE spectrum of the compound and in the $S_0 \rightarrow S(n,\pi)$ absorption spectrum obtained by direct measurements at 77°K[23] (see Figure 1). (The relative heights of the bands in the PE and the direct absorption spectra

---

(14) P. J. Kropp in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967.

(15) H. Ishikawa, *Bull. Pharm. Soc. Jap.*, **76**, 504, 507 (1956).

(16) E. Wedekind and A. Koch, *Chem. Ber.*, **38**, 429 (1905).

(17) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(18) P. P. Feofilov, "The Physical Basis of Polarized Emission," Consultants Bureau, New York, N. Y., 1961, Chapter IV.

(19) A. Albrecht, *J. Mol. Spectrosc.*, **6**, 84 (1961).

(20) E. H. Gilmore, G. Gibson, and D. S. McClure, *J. Chem. Phys.*, **20**, 829 (1952); **23**, 399 (1955).

(21) R. F. Borkman and D. R. Kearns, *Chem. Commun.*, **14**, 446 (1966).

(22) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **86**, 1436 (1964); **89**, 906 (1967).

(23) (a) W. Rothman, A. Case, and D. R. Kearns, *J. Chem. Phys.*, **43**, 1067 (1965); (b) A. Marchetti and D. R. Kearns, *J. Amer. Chem. Soc.*, **89**, 768 (1967).

Table I. Spectral Data,[a] Observed Lifetimes, Phosphorescence Quantum Yields, and Intersystem Crossing Quantum Yields for Compounds **I**, II, and III

Compound	S(n,π),[b] Å	T(n,π),[b] Å	T(π,π),[c] Å	$\Delta^{1,3}$,[d] cm^{-1}	τ_{obsd},[e] msec	φ_p[f]	φ_{isc}
α-Santonin (I)	3730	3930	4100	1600	79 (44)	0.3_0	$1._1$
6-Episantonin (II)	3830	4050	4250	1600	33 (32)	0.5_2	
2-Bromosantonin (III)	3690	3850	4100[g]	1400		0.0_0	

[a] All spectra obtained in 2-MTHF at 77°K. [b] First peak in excitation spectra. [c] Phosphorescence emission origin. [d] Splitting between the 0–0 bands in the $S_0 \rightarrow T(n,\pi)$ and the $S_0 \rightarrow S(n,\pi)$ absorption spectra. [e] Phosphorescence lifetime measured in 2-MTHF at 77°K. The numbers in parentheses are the lifetimes measured in a 2-MTHF:EtI solution (1.7:1). [f] Phosphorescence quantum yield determined by comparison with benzophenone in 2-MTHF. [g] Obtained by direct absorption.

are not comparable because of the wavelength variation in the photon output from the excitation monochromator). The phosphorescence lifetimes and quantum yields of I and II are presented in Table I.

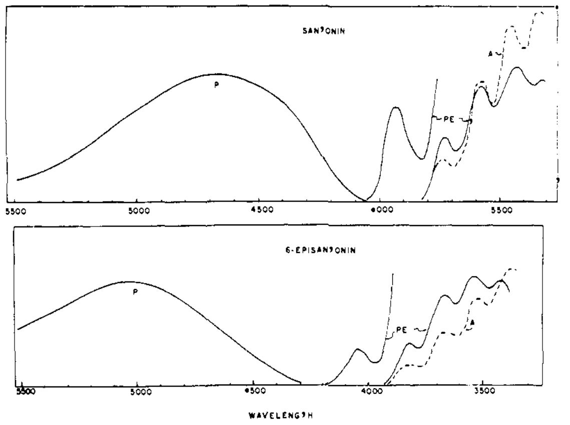


Figure 1. Direct absorption (A), phosphorescence excitation (PE), and phosphorescence (P) of santonin and 6-episantonin. All spectra were obtained in 2-methyltetrahydrofuran at 77°K. More concentrated samples were used to obtain the PE spectra in the triplet region.

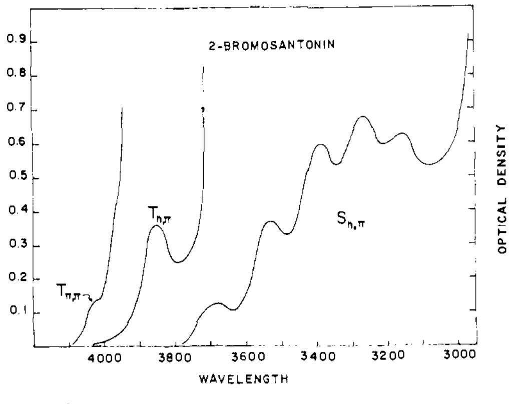


Figure 2. Direct absorption spectra of 2-bromosantonin at 77°K. The $S_0 \rightarrow S(n,\pi)$ absorption spectrum was obtained using a 2.2×10^{-2} *M* solution in 2-MTHF with a 1-cm cell. The $S_0 \rightarrow T(n,\pi)$ absorption spectrum was obtained with a 0.7-cm thick crystal and the $S_0 \rightarrow T(\pi,\pi)$ absorption spectrum was obtained with a 1.2-cm thick crystal.

With the high sensitivity of the PE method, it was relatively easy to observe $S_0 \rightarrow T$ transitions in both I and II using solutions ranging from 10^{-2} to 10^{-1} *M*. Under these conditions a strong $S_0 \rightarrow T$ absorption band was observed at 3930 Å in I and at 4050 Å with II, and these spectra are also presented in Figure 1.

The photoselection method was used to determine the polarization of the phosphorescence of each compound relative to excitation in the $S_0 \rightarrow T(n,\pi)$, $S_0 \rightarrow S(n,\pi)$, and $S_0 \rightarrow S(\pi,\pi)$ regions, and these data are presented in Figure 3 for I and II. The phosphorescence is polarized parallel ($P = +0.2\text{–}0.3$) to all of these transitions, indicating that it is polarized more or less parallel to the $S_0 \rightarrow S(\pi,\pi)$ transition.

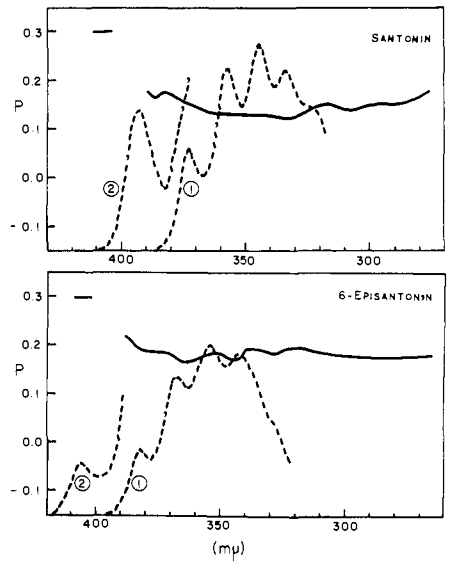


Figure 3. Polarization ratio, *P*, *vs.* wavelength of excitation for santonin and 6-episantonin. Curve 1 is the PE spectrum in the singlet–singlet region and curve 2 is the PE spectrum in the singlet–triplet absorption region. The polarization ratio was measured in EPA at 77°K.

2-Bromosantonin does not phosphoresce and it was therefore necessary to measure the singlet–triplet absorption of this compound by direct absorption techniques using thick crystals. With a 7-mm thick sample of 2-bromosantonin a strong singlet–triplet absorption band was observed at 3850 Å. With a 12-mm thick sample a low intensity band (25 times weaker than the 3850-Å $S_0 \rightarrow T$ band) was observed at 4025 Å as indicated in Figure 2.

4.2°K Measurements. The spectra obtained at 77°K in glasses were relatively diffuse, so to improve the resolution PE spectra of crystalline samples of I and II were also measured at 4.2°K, and these results are presented in Figure 4. The relatively weak origin band of the $S_0 \rightarrow S(n,\pi)$ transition in α-santonin is located at 3755 Å and, with the exception of this band and additional broad bands at 3631 and 3614 Å, the rest of the spectrum is almost devoid of noticeable vibrational structure. The $S_0 \rightarrow S(n,\pi)$ spectrum of 6-episantonin differs from α-santonin in that the 0–0 band at 3850 Å is relatively strong, and some (diffuse) vibrational structure can be discerned throughout the spectrum. The absorption spectra of I and II are also quite diffuse in the $S_0 \rightarrow T$ region, and significantly, both appear to lack well-defined 0–0 bands under conditions where 0–0 bands were resolved in the $S_0 \rightarrow S(n,\pi)$ spectra.

Discussion

1. The $S_0 \rightarrow S(n,\pi)$ Transition

(i) **Nature of the Lowest Excited Singlet States.** On the basis of the 77°K spectra, the assignment of the lowest excited singlet states of I, II, and III as $^1(n,\pi)$ states appears to be straightforward. All three compounds exhibit weak absorption bands ($\epsilon_{max} \simeq 30\ M^{-1}\ cm^{-1}$), in the spectral region 3000–3800 Å, which displayed expected blue shifts when the solvent was changed from benzene to ethanol. These observations, coupled with the fact that no other electronic transitions are expected in this region, make any other assignment unreasonable.

(ii) Polarization and Intensity of the $S_0 \rightarrow S(n,\pi)$ Transitions. Because of the intrinsic weakness of $S_0 \rightarrow S(n,\pi)$ transitions, even in ketones where they are symmetry-allowed, a significant amount of the intensity in the $S_0 \rightarrow S(n,\pi)$ transitions can be derived from vibronic mixing of the $S(n,\pi)$ state with higher energy $^1(\pi,\pi)$ states.[3,4] As the polarization data shown in Figure 3 clearly indicate, the $S_0 \rightarrow S(n,\pi)$ and $S_0 \rightarrow S(\pi,\pi)$ transitions are indeed polarized roughly parallel to one another, and therefore in-plane. This indicates that mixing with the $^1(\pi,\pi)$ state could be the major source of intensity in the $S_0 \rightarrow S(n,\pi)$ transition. Allowed character in the $S_0 \rightarrow S(n,\pi)$ transition, due to departure from C_{2v} symmetry, would have been introduced out-of-plane polarization, but the polarization measurements indicate that this contribution must be relatively small. The polarization of the 0–0 bands of the $S_0 \rightarrow S(n,\pi)$ transition is not known since this weak band is not resolved in the 77°K spectra.

The 4.2°K spectra shown in Figure 4 provided some additional information regarding the intensity of the 0–0 band, and diffuseness in the spectra.

(iii) 0–0 Bands. Insofar as their π-electron systems are concerned, α-santonin and 6-episantonin have approximately C_{2v} symmetry, and to the extent that this is valid, the lowest $^1(n,\pi)$ state is an A_2 state, and the $S_0 \rightarrow S(n,\pi)$ transition is symmetry-forbidden. However, because neither of these molecules has perfect C_{2v} symmetry, some allowed character is expected to appear in the 0–0 band. How much intensity appears in the 0–0 band will, of course, depend upon the extent to which the π systems depart from C_{2v} symmetry. The 0–0 band observed in the α-santonin spectrum is quite weak, whereas the 0–0 band in the spectrum of 6-episantonin is quite strong. We believe that high intensity of the 0–0 band in 6-episantonin is due to the perturbing interaction of the *cis*-fused lactone ring with the π system of the dienone which destroys the C_{2v} symmetry in 6-episantonin. Such an interaction would also account for the ~1,000-cm^{-1} red shift of the 6-episantonin spectrum relative to α-santonin. No such interaction is possible in α-santonin where the lactone ring is *trans*-fused.

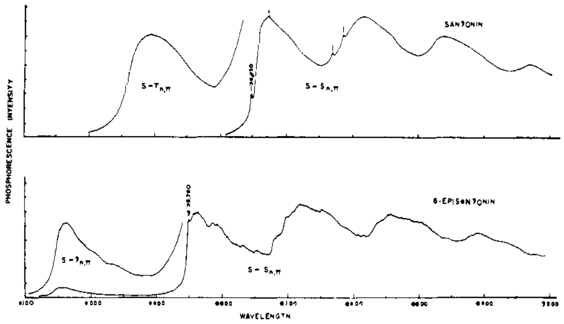


Figure 4. The 4.2°K phosphorescence excitation spectra of santonin and 6-episantonin in the $S_0 \rightarrow S(n,\pi)$ and the $S_0 \rightarrow T(n,\pi)$ absorption regions. The resolution in these spectra is about 1 Å (~10 cm^{-1}).

(iv) Vibronic Structure. In view of our experience with aromatic ketones, we were initially surprised that the 4.2°K $S_0 \rightarrow S(n,\pi)$ spectra of the santonins were so diffuse. In compounds such as 1-indanone,[24] for example, line widths in the $S_0 \rightarrow S(n,\pi)$ spectrum were less than 5 cm^{-1}, whereas the bands in the 6-episantonin spectra appear to be broader than about 100 cm^{-1} and the α-santonin spectrum is almost without vibrational structure except for a progression of very broad bands (1100 cm^{-1}). While we have not been able to identify the source of this broadness it could be due to (i) large changes in the interaction with neighboring molecules upon excitation; (ii) randomness in the crystal structure caused, for example, by methyl group rotations; (iii) significant changes in molecular geometry upon excitation; or (iv) the presence of a considerable vibronic activity. Preliminary studies of a number of steroidal enones clearly indicate that changes in molecular geometry may be involved,[13] but more examples will be required before we can sort out the relative importance of the various sources of spectral broadening.

2. The $T(n,\pi)$ States

(i) Nature and Location of $T(n,\pi)$ State. Compounds I and II exhibited a low intensity band ($\epsilon_{max} \simeq 0.3\ M^{-1}\ cm^{-1}$), at 3930 and 4050 Å, respectively, located about 1600 cm^{-1} to the red of the first strong absorption band of the $S_0 \rightarrow S(n,\pi)$ transition. A similar band located 1,400 cm^{-1} to the red of the first strong singlet band was observed in 2-bromosantonin at 3850 Å using direct absorption techniques. These low intensity, long wavelength bands cannot be assigned as weak origins of $S_0 \rightarrow S(n,\pi)$ transition for several reasons. First of all, they are too far to the red ($\simeq$1600 cm^{-1}) from the first strong $S_0 \rightarrow S(n,\pi)$ band to be seriously considered as origin bands. Numerous low frequency vibrational bands of good intensity should have appeared in between the weak band and the first strong $S_0 \rightarrow S(n,\pi)$ band if this were the case. Secondly, if we accepted these weak bands as $S(n,\pi)$ origins, then the position of the phosphorescence origins in I and II would lead to unreasonably small $S \rightarrow T$ splittings (<500 cm^{-1}). Rather, on the basis of their location with respect to the first strong $S_0 \rightarrow S$

---

[24] W. A. Case and D. R. Kearns, *J. Chem. Phys.*, in press.

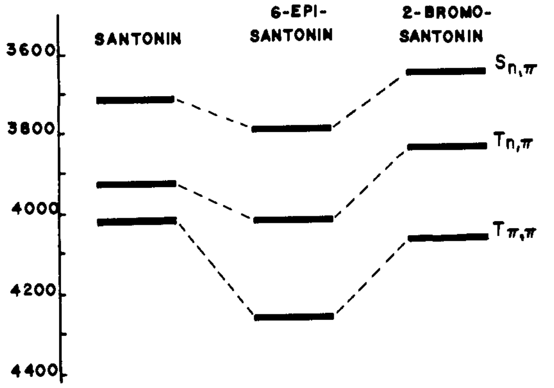


Figure 5. Location and assignments of the lower lying excited singlet and triplet states of santonin, 6-episantonin, and 2-bromosantonin.

(n,π) band (singlet-triplet splitting ±1600 cm^{-1}) and low intensity ($\epsilon \simeq 0.3\ M^{-1}$ cm^{-1}), these bands are assigned as $S_0 \rightarrow T(n,\pi)$ transitions. The observed intensity of these bands is in accord with our expectation that the $S_0 \rightarrow T(n,\pi)$ transition should be relatively strong as a result of direct spin-orbit coupling between the $T(n,\pi)(^3A_2)$ state and a higher energy singlet $^1(\pi,\pi)$ state of $^1A_1$ symmetry (assuming a C_{2v} molecular symmetry).[25,26] The polarization data shown in Figure 3 confirm that the $S_0 \rightarrow T(n,\pi)$ transition is in-plane polarized parallel to the lowest $S_0 \rightarrow S(\pi,\pi)$ transition as required by theory.[26,27]

(ii) 4.2°K $S_0 \rightarrow T(n,\pi)$ Spectra. The low temperature $S_0 \rightarrow T(n,\pi)$ spectra of both α-santonin and 6-episantonin were characterized by a complete lack of fine structure, and in particular well-defined 0–0 bands were absent in the $S_0 \rightarrow T$ spectra of both I and II. This was surprising since spin-orbit coupling between the $^3A_2(n,\pi)$ state and the $^1A_1(\pi,\pi)$ state makes the 0–0 transition allowed, and since the 0–0 bands were evident in $S_0 \rightarrow S(n,\pi)$ spectra of both of these compounds. (See Figure 4.) These observations suggest that in addition to those mechanisms mentioned in our discussion of the singlet spectra there is another one which is responsible for the additional broadening observed in the $S_0 \rightarrow T(n,\pi)$ spectra. As we shall demonstrate below, the lowest triplet states of I, II, and III are $^3(\pi,\pi)$ states, rather than $^3(n,\pi)$ states. Because of this ordering of states there may be a breakdown of the Born-Oppenheimer approximation, with substantial mixing between what might have been discrete $^3(n,\pi)$ states and a near continuum of vibronic levels associated with the lower lying $^3(\pi,\pi)$ state and consequent broadening of the $S_0 \rightarrow T(n,\pi)$ transitions.[28,29] While it might be tempting to attribute all of the broadening of the $S_0 \rightarrow T(n,\pi)$ transitions to this effect, the similar broadening of the $S_0 \rightarrow S(n,\pi)$ spectra clearly shows that other effects are operative as well.

3. The T(π,π) States

(i) Nature of the Emitting Triplet State. As we indicated above, we do not believe that phosphorescence originates from T(n,π) states for several reasons. If the T(n,π) state were the emitting state, the origins of the phosphorescence emission and the $S_0 \rightarrow T(n,\pi)$ absorption should have overlapped. Experimentally we observed a gap of ~400 cm^{-1} between the origin of emission and the origin of the $S_0 \rightarrow T(n,\pi)$ PE spectrum for 6-episantonin, and the apparent overlap in the low resolution 77°K spectra of α-santonin disappears at 4.2°K. This lack of spectral overlap obviously suggests that the $^3(n,\pi)$ states observed in absorption are not the emitting states in these compounds and consideration of the triplet lifetime data confirm this. The extinction coefficient for the first broad band in the $S_0 \rightarrow T(n,\pi)$ spectrum of I was found by direct absorption measurements to be 0.3 M^{-1} cm^{-1}, and making reasonable assumptions about the shape of the complete $S_0 \rightarrow T(n,\pi)$ absorption spectrum we estimate a value of 1.0 msec for the radiative lifetime of the $^3(n,\pi)$ state in this molecule.[30] Since the observed triplet state lifetime ($\tau_{\text{obsd}} = 80$ msec, $\tau_{\text{rad}} = \tau_{\text{obsd}}/\varphi_{\text{p}} = 260$ msec) is longer than the expected radiative lifetime by a factor of 80, it is clear that the emitting triplet state cannot be a $^3(n,\pi)$ state. This assignment is further supported by the observation that the splitting between the $^3(n,\pi)$ and $^1(n,\pi)$ states is the same for I, II, and III, whereas the origin of the emission relative to the $S_0 \rightarrow S(n,\pi)$ 0–0 band changes from I to II. This is graphically shown in Figure 5. Finally, we should note that there is a significant heavy atom solvent effect on the triplet lifetime of α-santonin. No heavy atom effect on the triplet lifetime of 6-episantonin was observed, probably because the natural lifetime is already quite short (33 msec). On the basis of the above considerations, we assign the emitting triplet states of I and II as a $^3(\pi,\pi)$ state.

To eliminate the possibility of an interchange in the ordering of the $^3(n,\pi)$ and $^3(\pi,\pi)$ states between absorption and emission we wanted to observe the $^3(\pi,\pi)$ state in absorption. This was expected to be difficult with I and II because of the weakness of the $S_0 \rightarrow T(\pi,\pi)$ transition ($\epsilon_{\max} \simeq 3 \times 10^{-4}$) relative to the nearby strong $S_0 \rightarrow T(n,\pi)$ transition, and because the $S_0 \rightarrow T(\pi,\pi)$ absorption was expected to be diffuse like the phosphorescence emission spectra. We, therefore, examined the $S_0 \rightarrow T$ absorption spectrum of 2-bromsantonin since the heavy atom substituent was expected to make detection of the $S_0 \rightarrow T(\pi,\pi)$ transition possible. Using a thick sample of 2-bromosantonin (single crystals stacked in 9-mm Pyrex tubing to a length of 12 mm), a low intensity band at 4025 Å was observed by direct absorption measurements (see Figure 2). On the basis of position with respect to the $^3(n,\pi)$ state and intensity we have assigned this as the transition to the $^3(\pi,\pi)$ state.

(ii) Polarization of the Phosphorescence. In planar dienones, there are various mechanisms whereby $S_0 \rightarrow T(\pi,\pi)$ radiative transitions may gain intensity, including (i) direct spin-orbit coupling with the allowed component of the $^1(n,\pi)$ state leading to out-of-plane polarization;[6,31,32] (ii) direct spin-orbit coupling with high energy $^1(\sigma,\pi)$ states, again leading to out-of-plane polarization;[25,26] and (iii) indirect coupling with a

---

(25) J. W. Sidman, *Chem. Rev.*, 58, 689 (1958).
(26) J. W. Sidman, *J. Chem. Phys.*, 29, 644 (1958).
(27) M. A. El-Sayed, *ibid.*, 41, 2462 (1964).
(28) R. M. Hochstrasser, *Accounts Chem. Res.*, 1, 266 (1968).
(29) R. M. Hochstrasser and C. Marzzacco, *J. Chem. Phys.*, 49, 971 (1968).
(30) R. F. Borkman and D. R. Kearns, *ibid.*, 46, 2333 (1967).
(31) M. A. El-Sayed, *ibid.*, 38, 2834 (1963).
(32) D. S. McClure, *ibid.*, 17, 905 (1949).

$^{1}(\pi,\pi)$ state by vibronic interaction with the low-lying $^{3}(n,\pi)$ state, which in turn is spin-orbitally coupled with the $^{1}(\pi,\pi)$ state (route A), or alternatively, through spin-orbit coupling of the $^{3}(\pi,\pi)$ state with certain vibronic levels of the $^{1}(n,\pi)$ state, which in turn are vibronically coupled with the $^{1}(\pi,\pi)$ state (route B). Either of these coupling route would lead to in-plane polarization.

The observation that the phosphorescence emission from both I and II is polarized parallel to the $S_0 \rightarrow S(\pi,\pi)$ transition indicates that the $^{1}(\pi,\pi)$ state is the principal source of intensity in the $S_0 \rightarrow T(\pi,\pi)$ transition. While the polarization experiments do not distinguish between routes A and B, the following theoretical argument suggests that indirect coupling involving the $^{3}(n,\pi)$ state is the principal route. If we assume that the singlet and triplet (n,π) states have similar spatial wave functions and likewise for the $^{1,3}(\pi,\pi)$ states, then

$$\langle T(n,\pi)|H_{so}|S(\pi,\pi)\rangle \simeq \langle T(\pi,\pi)|H_{so}|S(n,\pi)\rangle$$

$$\langle T(\pi,\pi)|H_{vib}|T(n,\pi)\rangle \simeq \langle S(\pi,\pi)|H_{vib}|S(n,\pi)\rangle$$

Now, according to second-order perturbation theory, the extent of mixing, $\lambda^{(2)}$, of the $T(\pi,\pi)$ state with $S(\pi,\pi)$ state will be

Route A

$$\lambda_A^{(2)} = \frac{\langle T(\pi,\pi)|H_{vib}|T(n,\pi)\rangle}{E_{T(\pi,\pi)} - E_{T(n,\pi)}} \frac{\langle T(n,\pi)|H_{so}|S(\pi,\pi)\rangle}{E_{T(\pi,\pi)} - E_{S(\pi,\pi)}}$$

Route B

$$\lambda_B^{(2)} = \frac{\langle T(\pi,\pi)|H_{so}|S(n,\pi)\rangle}{E_{T(\pi,\pi)} - E_{S(n,\pi)}} \frac{\langle S(n,\pi)|H_{vib}|S(\pi,\pi)\rangle}{E_{T(\pi,\pi)} - E_{S(\pi,\pi)}}$$

and

$$(\lambda_A^{(2)}/\lambda_B^{(2)}) = \frac{E_{T(\pi,\pi)} - E_{S(n,\pi)}}{E_{T(\pi,\pi)} - E_{T(n,\pi)}}$$

Because of the near degeneracy of the $^{3}(\pi,\pi)$ and the $^{3}(n,\pi)$ states

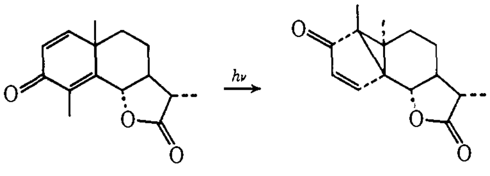
$$[E_{T(\pi,\pi)} - E_{S(n,\pi)}] > [E_{T(\pi,\pi)} - E_{T(n,\pi)}]$$

and in the present case we expect $\lambda_A \simeq 3\lambda_B$. This is probably an underestimate since the spacing between the $T(n,\pi)$ and $T(\pi,\pi)$ states determined experimentally includes a shift due to their vibronic interaction with one another. Route A is therefore expected to be more important than route B by about a factor of 10. If the $^{3}(\pi,\pi)$ state is shifted away from the $^{3}(n,\pi)$ state, then the two routes will become more nearly comparable in importance, but at the same time the overall mixing of the $^{3}(\pi,\pi)$ with the $^{1}(\pi,\pi)$ state will be decreased.

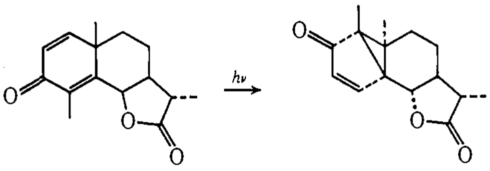
While we can readily account for some spectral features there is still the problem of accounting for the almost complete lack of vibrational structure in the phosphorescence emission spectra of I and II. We suggest that this diffuseness in the phosphorescence emission which we observed both at 77°K in glasses and at 4.2°K in single crystals is due, at least partly, to the fact that the molecules in their lowest $T(\pi,\pi)$ state have a geometry which is considerably different from that in the ground state. Although the nature of this distortion remains to be elucidated it would not be surprising to find that it is related to the excited state valence isomerization which these molecules undergo.[14,33]

Relation between Spectroscopic and Photochemical Observations

In neutral media both α-santonin and 6-episantonin undergo similar photoisomerizations to the corresponding lumisantonins as depicted below.[14,33]



I



II

The question of which states are involved in the photoisomerization reactions has been the subject of a recent investigation by Fisch[34] and Schuster.[35] Through a combination of quenching and sensitization experiments Fisch has shown that the reaction proceeds exclusively from triplet state intermediates and that two different triplet states are involved.[34] Our spectroscopic studies combined with Fisch's chemical studies immediately allow us to identify these two reactive triplet states as the $^{3}(\pi,\pi)$ and the $^{3}(n,\pi)$ states.

In order for both the $^{3}(n,\pi)$ and $^{3}(\pi,\pi)$ states of α-santonin to be involved in the photoisomerization to lumisantonin, however, the following conditions must be satisfied: (i) intersystem crossing from the $S(n,\pi)$ state must proceed largely *via* the $^{3}(n,\pi)$ state, (ii) the reaction from the $^{3}(n,\pi)$ state must be exceedingly fast in order to compete with internal conversion to the lower lying $^{3}(\pi,\pi)$ state, and (iii) the $^{3}(n,\pi)$ and $^{3}(\pi,\pi)$ states must rearrange to the same intermediate.

The first condition appears to contradict an earlier suggestion by El-Sayed that, in the neglect of vibronic interactions, intersystem crossing from an $^{1}(n,\pi)$ state to a lower lying $^{3}(\pi,\pi)$ state should always be faster than to the $^{3}(n,\pi)$ state.[31] Our spectroscopic observations demonstrate, however, that vibronic interactions are very important in these molecules, so that perhaps the El-Sayed selection rules on intersystem crossing are somewhat relaxed in these molecules.

In view of the near degeneracy of the $^{2}(n,\pi)$ and $^{3}(\pi,\pi)$ states which we found in the santonins we should expect that the interpretation of the room temperature photochemical properties of related cross-conjugated dienones could be complicated by the existence of a thermal equilibrium between the lowest triplet state and the nearly degenerate second triplet state. Thus, we might find cases where the lowest triplet of a dienone is unreactive, but because of a favorable Boltzmann factor, reactions could occur from the second triplet state. In this case the photochemical reaction should exhibit a significant temperature dependence.

Acknowledgment. The support of the U. S. Public Health Service (GM10449) is most gratefully acknowledged.

---

(33) M. Fisch and J. H. Richards, *J. Amer. Chem. Soc.*, **85**, 3026 (1963).

(34) M. Fisch and R. Nonnenmacher, unpublished results.

(35) D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 1301 (1968).