Investigation of Singlet → Triplet Transitions by Phosphorescence Excitation Spectroscopy. IX. Conjugated Enones[1a]

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Abstract: The spectroscopic properties of the low-lying excited singlet and triplet states of 19 different steroidal enones have been investigated at both 77 and 4.2°K. The ordering of states was found to be $^1(n,\pi) > {}^3(n,\pi) > {}^3(\pi,\pi)$ in all of the molecules studied, although the $^3(n,\pi)$ and $^3(\pi,\pi)$ states are nearly degenerate in some. Photoselection measurements were used to demonstrate that the S → S (n,π) transition is polarized more or less perpendicular to the S → S (π,π) transition, consistent with the low symmetry of the chromophoric group, and extensive delocalization of the n orbital. The S → T (n,π) transitions are polarized parallel to the S → S (π,π) transition as expected from simple spin–orbit coupling theory. The emission from the $^3(\pi,\pi)$ state is polarized more or less parallel to the S → S (π,π) transition, possibly as a result of vibronic interaction with the $^3(n,\pi)$ state, or, what is more likely, due to a significant change in the geometry (to a distorted nonplanar configuration) upon excitation. This latter interpretation is supported by the high-resolution phosphorescence emission spectrum of testosterone acetate (I), which displays extensive fine structure and generally has the appearance of a highly Franck–Condon-forbidden transition. In general, the S → S (n,π) and S → T (n,π) excitation spectra of crystalline samples remain surprisingly diffuse even at 4.2°K. The one exception to this generalization is XVII, which exhibits a reasonably well-structured S → S (n,π) absorption, but a diffuse S → T (n,π) absorption. This difference in the behavior of the S → S (n,π) and the S → T (n,π) transitions supports our earlier suggestion that the additional broadening of the S → T (n,π) transitions is due to interaction with a nearby lower lying T (π,π) state. Other factors responsible for the broadening of both the S → S (n,π) and the S → T (n,π) transitions in the other compounds remain to be unambiguously identified.

Until rather recently there have been relatively few studies of the spectroscopic properties of α,β-unsaturated enones,[2,3] in spite of the fact that these compounds have been the subject of intensive photochemical investigations.[4] From a theoretical standpoint, the conjugated enones are intermediate in complexity between the simple unsaturated ketones and aldehydes and the more complicated aromatic ketones, and consequently it is important that we have a more complete characterization of the lower lying excited states of this important class of molecules. Such a study appeared to be particularly desirable in view of the fact that any detailed interpretation of the photochemical properties of α,β-unsaturated ketones requires detailed information on both the nature and location of the lower lying excited singlet and triplet states in these molecules. With these factors in mind, we began an investigation of the spectroscopic properties of a series of steroidal enones. These rather complex molecules were chosen for our initial studies, rather than the simpler enones such as cyclopentenone and cyclohexenone, because of the fact that the steroids phosphoresce, whereas the monocyclic enones do not. Consequently, it was possible to utilize phosphorescence excitation spectroscopy for the spectroscopic study of the steroidal enones. As we have discussed before,[5] this powerful technique greatly simplifies a number of experimental problems associated with the investigation of weak singlet–triplet transitions.

In a previous paper we presented the results of our initial study of the spectroscopic properties of different enones (I, III, V, VI, VIII, IX, and X) at 77°K.[2] In the present work we have extended this study to an additional 12 compounds, examined the relative polarizations of the absorption and emission spectra, and carried out high resolution measurements on crystalline samples at 4.2°K.

Experimental Section

(1) **Materials.** 2-Methyltetrahydrofuran (2-MTHF) and ethyl iodide were purchased from Matheson Coleman and Bell and purified by distillation. Spectroquality EPA (diethyl ether, isopentane, ethanol, 5:5:2) was purchased from Matheson Coleman and Bell and required no purification.

The structural formulas of the compounds which we have studied are shown below. The steroidal enones I–XVII and XIX were crystallized to constant melting points, and the methyloctalone (XVIII) was purified by preparative vapor-phase chromatography. All compounds were homogeneous by thin-layer chromatography and ir, nmr, and mass spectroscopy.

(2) **Apparatus and Procedures.** A conventional phosphorimeter was used to obtain the phosphorescence emission spectra of compounds I–XIX.[5b,c] Since these compounds do not phosphoresce in fluid solution at 25°, all solution measurements were performed at 77°K using 2-MTHF as the solvent. For these studies, samples were dissolved in 2-MTHF, placed in 7-ml Pyrex sample tubes, and cooled to liquid nitrogen temperature. Phosphorescence emission and excitation spectra in the singlet–singlet absorption region were then obtained with optically dilute solutions (10^{-2}–10^{-3} *M*), whereas PE spectra in the singlet–triplet absorption region were obtained with more concentrated samples (0.1 *M*).

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[1] (a) This work was supported by grants from the U. S. Public Health Service (No. GM 10449) to D. R. K. and the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung to K. S.; (b) University of California; (c) John Simon Guggenheim Foundation Fellow, 1969–1970; (d) Eidg. Technische Hochschule.

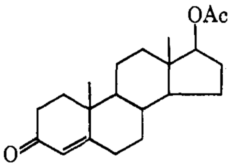
[2] (a) D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968); (b) G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **51**, 1890 (1968).

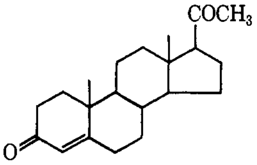
[3] R. L. Cargill, A. C. Miller, D. M. Pond, P. de Mayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, **1**, 301 (1969).

[4] See, for example, K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966).

[5] (a) W. A. Rothman, W. A. Case, and D. R. Kearns, *J. Chem. Phys.*, **43**, 1067 (1965); (b) D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966); (c) A. P. Marchetti and D. R. Kearns, *ibid.*, **89**, 768 (1967); (d) R. F. Borkman and D. R. Kearns, *Chem. Commun.*, 466 (1966).

Absorption spectra of samples in a rigid glass matrix 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. The absorption cell path length was 1 cm and a solvent contraction correction (20% for 2-methyltetrahydrofuran) was used in calculating extinction coefficients.


I, testosterone acetate
(17β-hydroxyandrost-4-en-3-one acetate)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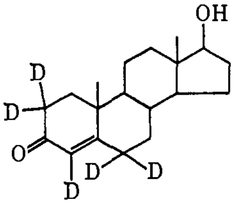
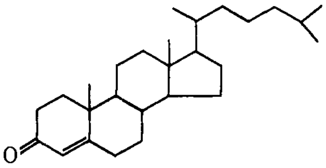
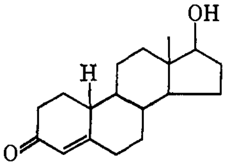
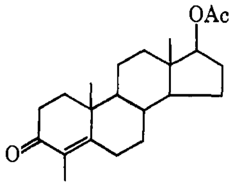
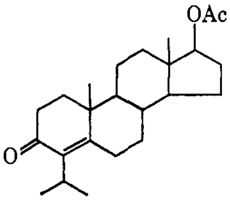
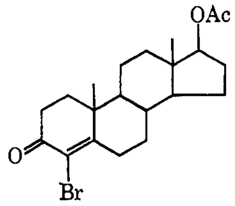

III, 2,2,4,6,6-d_5-testosterone
(2,2,4,6,6-d_5-17β-hydroxyandrost-4-en-3-one)

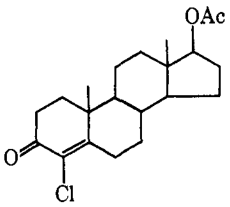

IV, cholestenone
(4-cholesten-3-one)

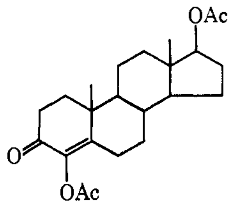

V, 19-nortestosterone
(19-nor-17β-hydroxyandrost-4-en-3-one)

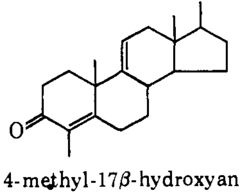

VI, 4-methyltestosterone acetate
(4-methyl-17β-hydroxyandrost-4-en-3-one acetate)

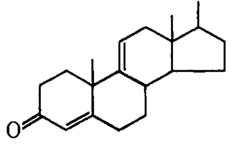

VII, 4-isopropyltestosterone acetate (4-isopropyl-17β-hydroxyandrost-4-en-3-one acetate)


VIII, 4-bromotestosterone acetate
(4-bromo-17β-hydroxyandrost-4-en-3-one acetate)

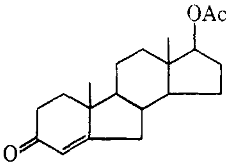

IX, 4-chlorotestosterone acetate
(4-chloro-17β-hydroxyandrost-4-en-3-one acetate)

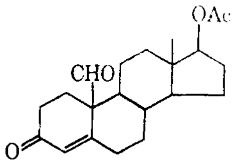

X, 4-acetyltestosterone acetate
(4,17β-dihydroxyandrost-4-en-3-one acetate)

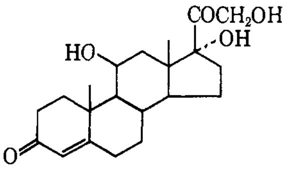

XI, 4-methyl-17β-hydroxyandrosta-4,9(11)-dien-3-one acetate

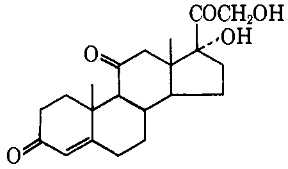

XII, 17β-hydroxyandrosta-4,9(11)-dien-3-one acetate

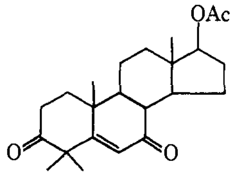
When samples of these compounds in 2-MTHF were excited in the S → S (n,π) absorption region at 77°K, relatively bright phosphorescence was observed. These spectra are presented as curve 4 in Figure 1 for compounds I, IV, V, VII, VIII, and XI–XIX. The phosphorescence spectra of I, III, VI, VIII, IX, and X have been reported elsewhere, but for the purposes of comparison the spectra of I, V, and VIII have been included. In each case the 77°K phosphorescence emission spectrum was characteristically structureless, with an origin located between 3900 and 4200 Å and a broad maximum at between 4400 and 4900 Å, extending past 5500 Å. The spectra have not been corrected for the spectral response of the photomultiplier (RCA 7265) or monochromator (Jarrell-Ash 0.25-m high-intensity monochromator). When this correction is applied, the peaks in the phosphorescence emission are virtually unshifted, but the relative intensity in the long-wavelength portion of the spectrum increases by ~10–20%. For each sample the phosphorescence emission was proven to be authentic by demonstrating that there was a close correspondence between the PE spectrum of the compound obtained using optically dilute solutions (curve 1 in Figure 1) and its S → S (n,π) absorption obtained by direct absorption measurements at 77°K (curve 2 in Figure 1). The relative heights of the bands in the phosphorescence excitation and direct absorption spectra are not exactly comparable because of the wavelength variation in the photon output from the excitation monochromator.[5c] Phosphorescence excitation spectra in the singlet–triplet region were obtained by restricting the wavelength of excitation to the low-energy side of the lowest S → S (n,π) absorption bands and by using solutions that were between 10^{-2} and 10^{-1} *M*. Under these conditions a strong S → T absorption band was observed in each compound on the low-energy side of the first S → S (n,π) band. These spectra are presented as curve 3 in Figure 1. Spectral data for the S → S (n,π) and S → T absorption spectra of compounds I–XIX and phosphorescence emission spectra are summarized in Table I.

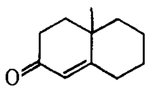

XIII, *B*-nor-testosterone acetate
(*B*-nor-17β-hydroxyandrost-4-en-3-one acetate)

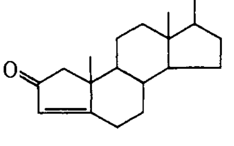

XIV, 19-oxotestosterone acetate
(17β-hydroxyandrost-4-en-3,19-one acetate)


XV, cortisol
(11β,17α,21-trihydroxypregn-4-ene-3,20-dione)


XVI, cortisone
(17α,21-dihydroxypregn-4-ene-3,11,20-trione)


XVII, 4,4-dimethyl-17β-hydroxyandrost-5-ene-3,7-dione acetate


XVIII, 10-methyl-$\Delta^{1(9)}$-octal-2-one


XIX, *A*-nortestosterone acetate
(*A*-nor-17β-hydroxyandrost-4-en-3-one acetate)

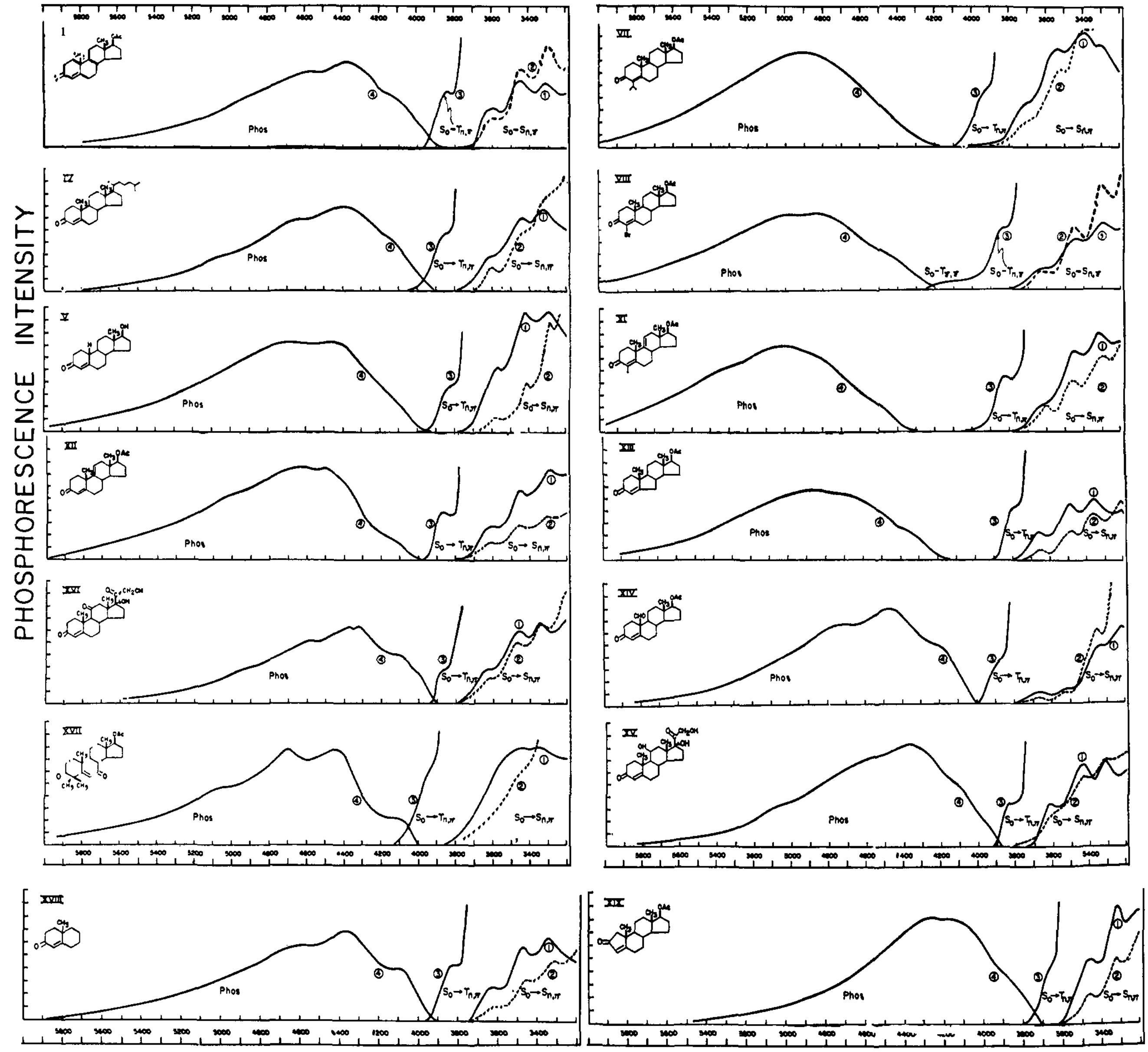


Figure 1. The direct absorption (curve 2), phosphorescence excitation (curve 1 = singlet–singlet region, curve 3 = singlet–triplet region), and phosphorescence emission (curve 4) spectra of 14 selected enones.

Phosphorescence quantum yields (Φ_p) and lifetimes (τ) were measured in 2-MTHF at 77°K for a number of the cyclic enones and these results are reported in Table II. One part ethyl iodide was added to two parts of the 2-MTHF solutions of the enones to examine the external heavy-atom effect on triplet-state lifetimes.

Intersystem crossing quantum yields were obtained by using the method described by Borkman and Kearns,[5d] and application of this technique to testosterone acetate (I) yielded a value of 1.1 ± 0.2.

Polarized phosphorescence excitation spectra for samples in EPA at 77°K were obtained in the $S \to S\ (n,\pi)$, $S \to S\ (\pi,\pi)$, and $S \to T\ (n,\pi)$ absorption regions by inclusion of a Glan–Thompson prism in the exciting light path of the phosphorimeter. A polarizing sheet located in front of the detector was then changed intermittently from parallel to the crossed position while the PE spectrum was continuously recorded. EPA was used exclusively for the polarization measurements at 77°K since it was found to cause less depolarization than did 2-MTHF. The experimental polarization ratio, $P = (I_{\|} - I_{\perp})/(I_{\|} + I_{\perp})$, was obtained for a number of compounds as a function of wavelength of excitation, and these data are presented in Figure 2. Excitation in the wavelength region from 280 to 240 nm corresponds to the $S \to S\ (\pi,\pi)$ absorption.

High-resolution phosphorescence excitation spectra of crystalline samples were obtained at 4.2°K using a McPherson 218 excitation monochromator with slits adjusted to give a resolution of about 1.6 Å (10 cm^{-1}). For these measurements, the samples were immersed in liquid helium and the analyzing monochromator was replaced by a Corning glass filter for maximum sensitivity. Thin crystal films, prepared by melting and crystallizing a small amount of sample between a quartz plate and Pyrex microcover glass slide, were used for examination of the $S \to S\ (n,\pi)$ absorption. Thick (1–3 mm) crystals grown from solution were used to obtain excitation spectra in the $S \to T$ absorption region and to obtain the phosphorescence emission spectra. The 4.2°K excitation spectra of crystalline samples of compounds I, IV, and XVII and VI and IX are presented in Figures 3 and 4, respectively, and the 4.2°K phosphorescence emission spectrum of I is presented in Figure 5.

Discussion

As we have discussed before, acrolein serves as a convenient model for interpreting the spectral properties of the steroidal enones.[2b,6] The lowest energy

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(6) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).

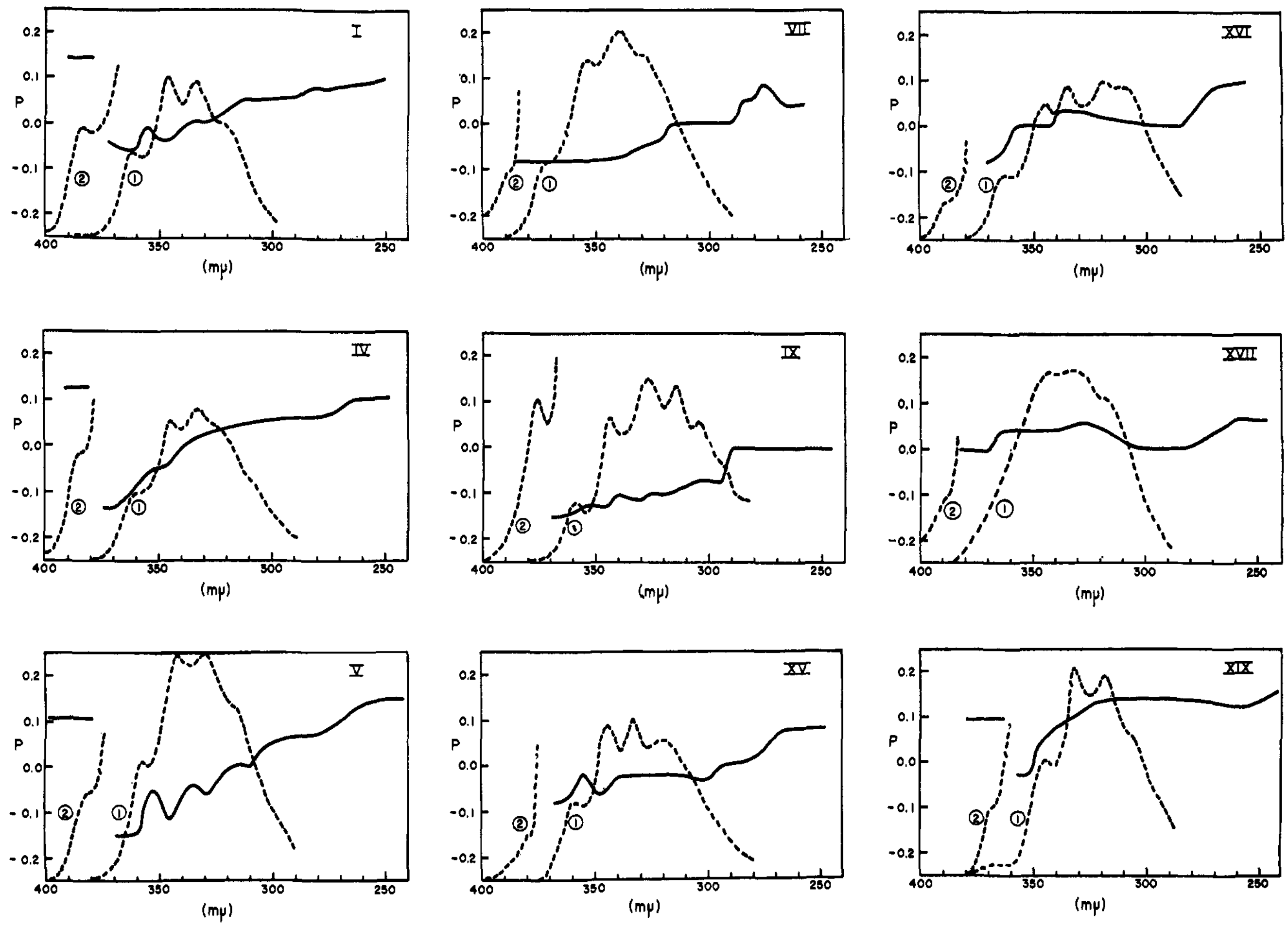

Figure 2. The polarization ratio, P, as a function of wavelength (solid curve) for I, IV, V, VII, IX, XV, XVI, XVII, and XIX. The dashed curves are the PE spectra in the singlet–singlet absorption region (curve 1) and in the singlet–triplet region (curve 2).

Table I. Spectral Data for Compounds I–XIX Abstracted from Figure 1[a]

Compound	Phosphorescence emission, Å	$S_0 \rightarrow T$ absorption, Å	$S \rightarrow S\ (n,\pi^*)$ direct absorption, Å (PE spectra)	$\Delta E_{1,3}$,[b] cm^{-1}	Compound	Phosphorescence emission Å	$S_0 \rightarrow T$ absorption, Å	$S \rightarrow S\ (n,\pi^*)$ direct absorption, Å (PE spectra)	$\Delta E_{1,3}$,[b] cm^{-1}
I[c]	3900 origin	3840	3620, 3470, 3330	1610	XI	4300 origin	3850	3600, 3470, 3312	1800
	4350 maximum		3600, 3450, 3310			5000 maximum	(crystal)	3600, 3450, 3311	
II	3860 origin	3823	3620, 3453, 3326	1400	XII	3950 origin	3900	3630, 3460, 3320	1800
	4340 maximum		3610, 3460, 3340			4600 maximum		3620, 3460, 3300	
III[c]	3900 origin	3840	3600, 3450, 3300	1800	XIII	4150 origin	3810	3650, 3490, 3360	1200
	4400 maximum		3600, 3450, 3310			4850 maximum		3650, 3500, 3350	
IV	3900 origin	3850	3610, 3450, 3330	1580	XIV	4000 origin	3880	3690, 3550, 3350	1400
	4400 maximum		3620, 3460, 3340			4450 maximum	(crystal)	3680, 3550, 3350	
V[c]	3950 origin	3820	3580, 3440, 3300	1700	XV	3880 origin	3826	3600, 3440, 3310	1600
	4650 maximum		3600, 3430, 3300			4350 maximum		3610, 3440, 3320	
VI[c]	4250 origin	3800	3620, 3470, 3310	1300	XVI	3880 origin	3870	3630, 3470, 3340	1700
	4900 maximum		3600, 3450, 3310			4320 maximum		3640, 3460, 3332	
VII	4200 origin	3950	3740, 3530, 3380	1650	XVII	3950 origin	3950	3800 origin;	
	4900 maximum		3750, 3550, 3400			4700 maximum		broad absorption	
VIII[c]	4200 origin	3830	3630, 3450, 3300	1500					
	4900 maximum		3620, 3450, 3300					3480 origin (PE)	
IX[c]	4200 origin	3850	3600, 3420, 3270	1800	XVIII	3930 origin	3850	3610, 3440, 3310	1550
	4900 maximum		3600, 3420, 3290			4400 maximum		3630, 3480, 3350	
X[c]	4100 origin	3750	3550, 3350, 3250	1500	XIX	3600 origin	3680	3450, 3320, 3180	1800
	4900 maximum		3550, 3370, 3250			4100 maximum		3450, 3320, 3190	

[a] All spectra obtained in 2-MTHF at 77°K except $S_0 \rightarrow T$ of XI and XIV, which were observed only in the crystal. [b] Splitting between the 0–0 bands in the observed $S_0 \rightarrow T$ transition and $S \rightarrow S\ (n,\pi^*)$ absorption spectra. [c] Taken from ref 2b.

$S \rightarrow S$ band in acrolein, which is located at 3650 Å, has unambiguously been assigned as the ($^1A' \rightarrow {}^1A''$) $n \rightarrow \pi^*$ transition.[7,8] The oscillator strength for this transition is 6×10^{-4}, and high-resolution studies

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(7) E. Eastwood and C. P. Snow, *Proc. Roy. Soc., Ser. A*, **149**, 446 (1935).

(8) J. C. D. Brand and D. G. Williamson, *Discuss. Faraday Soc.*, **35**, 184 (1963).

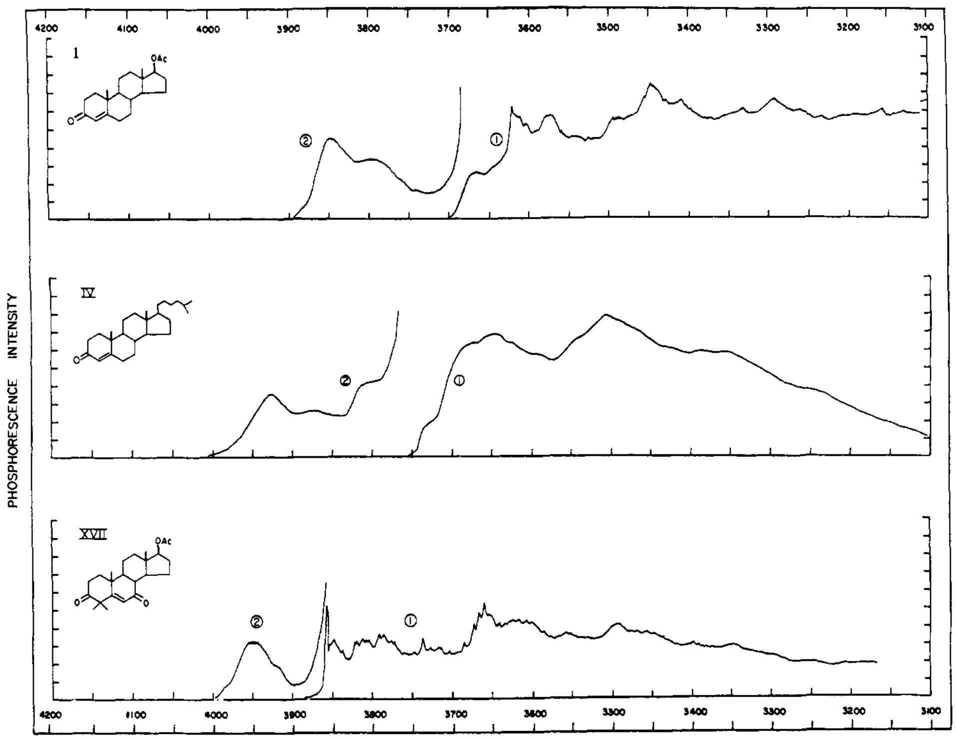

Figure 3. The 4.2°K PE spectra of crystalline samples of I, IV, and XVII: curve 1, PE spectrum in the singlet–singlet absorption region; curve 2, PE spectrum in the singlet–triplet absorption region.

indicate that the true 0–0 band of the S → S (n,π*) transition is allowed polarized perpendicular to the plane of the carbonyl group.[8,9] Allowed character in this transition (~30%) arises from the low symmetry about the C=O group and delocalization of the nonbonding orbital. In addition to the electronically allowed part, there is a significant in-plane polarized contribution to the oscillator strength which is of vibronic origin. Below the origin of the S → S (n,π) absorption, acrolein exhibits a weak system of bands, commencing at 4122 Å, which have been assigned as the S → T (n,π) transition.[8] This transition is expected to be in-plane polarized since it gains intensity by spin–orbit coupling of the ^{3}(n,π) state with the ^{1}(π,π) state. The location of the ^{3}(π,π) state in acrolein is not known, but theoretical calculations by Kato[10] and by Zimmerman[11] suggest that it may lie close to the ^{3}(n,π) state (see Table III).

Table II. Quantum Yields of Phosphorescence, Observed Lifetimes, and Calculated Radiative Lifetimes for Some Cyclic Enones

Compound	Φ_p ± 15%	τ_{obsd},[a] msec	τ_{rad}, msec
Testosterone acetate (I)	0.21[b]	28 (23)[b]	131
Cholestenone (IV)	0.24	26 (20)	110
4-Methyltestosterone acetate (VI)	0.20[b]	58 (33)[b]	286
4-Isopropyltestosterone acetate (VII)	0.27	53 (42)	196
19-Nortestosterone (V)	0.25	23 (20)	19
4-Bromotestosterone acetate (VIII)	0.34[b]	1.5[b]	4.4
XI	0.14	39 (32)	289
XII	0.13	26	196
B-Nortestosterone acetate (XIII)	0.14	7 (7)	50
XIV	0.05	30	578
XVII	0.43	32	76
A-Nortestosterone acetate (XIX)	0.31	22	71

[a] Observed 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). [b] Taken from ref 2b.

Table III. Calculated and Experimental Singlet and Triplet Energies (eV) of *trans*-Acrolein

Transition	E_{calcd}	E_{obsd}
n → π* ^{1}A″	4.24[a]	3.71[b]
	3.85[b]	3.76[c]
	3.33[h]	3.55[d]
n → π* ^{3}A″	3.76[a]	3.05[d]
	2.85[b]	
	3.06[h]	
π → π* ^{1}A′	6.25[a]	5.96[b]
	6.08[b]	6.32[c]
	6.62[e]	6.40[f]
	5.80[f]	
	6.15[h]	
π → π* ^{3}A′	3.85[a]	*g*
	4.17[b]	
	3.50[f]	
	3.29[h]	

[a] Reference 2a. [b] K. Inuzuka, *Bull. Chem. Soc. Jap.*, **34**, 6 (1961). [c] A. D. Walsh, *Trans. Faraday Soc.*, **41**, 498 (1945). [d] Reference 9. [e] M. Klessinger and W. Luttke, *Z. Electrochem.*, **65**, 707 (1961). [f] F. L. Pilar, *J. Chem. Phys.*, **47**, 5375 (1967). [g] Unknown. [h] Reference 11.

(1) Nature of the Lowest Excited Singlet State. Since the π-electronic structure of acrolein and the steroidal enones studied here are similar, their spectral properties should also be similar. In accord with this expectation

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

(10) H. Kato, H. Konishi, H. Yamabe, and T. Yonazawa, *Bull. Chem. Soc. Jap.*, **40**, 2761 (1967).

(11) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

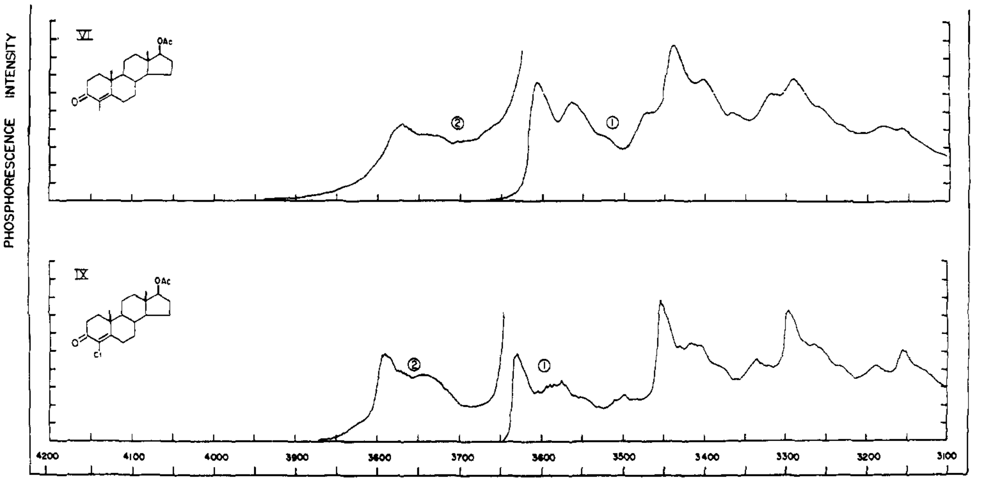

Figure 4. The 4.2°K PE spectra in the crystalline samples of VI and IX: curve 1, PE spectrum in the singlet–singlet absorption region; curve 2, PE spectrum in the singlet–triplet absorption region.

Figure 5. The phosphorescence emission spectrum of single crystals of testosterone acetate (I) at 4.2°K.

we find that, aside from small substituent effects, the solution spectra (see Figure 1) of the steroidal enones are quite similar to that of acrolein with respect to overall intensity, position, and shape.[2b] On this basis the absorption bands observed in the 3800–3100-Å region (ϵ_{max} 30–60 M^{-1} cm^{-1}) are assigned as n → π* ($^1A' \rightarrow {}^1A''$) transitions.

The polarization measurements shown in Figure 2 indicate that the S → S (n,π) transitions in I, II, IV, V, VII, XVI, and XIX are more or less negatively polarized with respect to the S → S (π,π) transition. Since recent studies of the polarized absorption of steroids dissolved in stretched polyethylene films demonstrate that the S → S (π,π) transitions are polarized in the plane of the carbonyl group,[12] our relative polarization data indicate that the S → S (n,π) transitions are primarily polarized perpendicular to the axis of the carbonyl group. As in acrolein, this contribution to the intensity of the S → S (n,π) transition can be attributed to delocalization of the n orbital into the σ framework of the molecule and to the low molecular symmetry about the carbonyl group. Although the spectra start out rather negatively polarized in the region of the 0–0 band, in almost every case they become progressively more positively polarized at shorter wavelengths. This indicates that the spectra also contain significant contributions from positively polarized bands which are vibronically induced through coupling of the S (n,π) and S (π,π) states. Entirely similar effects were also seen in acrolein.[8,9]

The 4.2°K high-resolution spectra of crystalline samples of I, IV, VI, IX, and XVII in the S → S (n,π) region are presented in Figures 3 and 4. The corresponding spectrum for VIII has been published elsewhere.[2a] Within this group of six compounds three distinctly different types of spectra can be distinguished. The S → S (n,π) transitions of compounds I and IV are generally quite diffuse, with little or no fine structure, and the intensity in the region of the "0–0" band is relatively low as compared to other regions of the spectra. The spectra of compounds VI, VIII, and IX are notably different in that the intensity in the region of the 0–0 band is relatively large, and at least three reasonably prominent vibrational progressions, based on 350, 1000, and 1400 cm^{-1} can be discerned. These spectra have the appearance of "allowed" electronic transitions, consistent with the notion that the allowed character in the S → S (n,π) transition depends significantly on the degree to which the n orbital is delocalized and on the nature of this orbital at both the 4 and 2 positions. The apparent simplification of the spectra of the 4-substituted compounds is therefore attributed to the reduced importance of vibronically induced bands in the spectrum relative to the nonvibronically induced bands. As with I and IV, the spectra of the 4-substituted compounds still lack noticeable fine structure.

In view of the fact that the aromatic ketones generally exhibit very sharp spectra with much fine structure at low temperatures, it was somewhat surprising to find that the S → S (n,π) spectra of I, IV, VI, VIII, and IX, as well as of six other enones that we have measured, all appear to be diffuse even at 4.2°K. In principle this diffuseness might be caused by a high degree of vibronic activity involving low-frequency vibrations, significant changes in the molecular geometry upon electronic excitation, significant changes in the *inter*molecular potential upon excitation (similar to excimer forming systems), or simply by randomness in the crystal structure. In attempting to determine the origin of the spectral broadening it is significant that the low-temperature S → S (n,π) spectrum of XVII exhibits well-resolved fine structure. In view of this somewhat unique spectral property it is interesting to note that there are at least two structural features which distinguish this molecule from all of the rest of the compounds which we have studied—the enone chromophore is located in the B ring rather than in the A ring, and there is an opportunity for a transannular interaction

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[12] A. Yogev, L. Margulies, L. Amar, and Y. Mazur, *J. Amer. Chem. Soc.*, 91, 4558, 4559 (1969).

Table IV. Absorption Data for Some Substituted Testosterone Acetates in 2-MTHF at 25° and 77°K[a]

Compound	$\lambda_{S(0-0)}$, Å	ϵ^S_{0-0}, 77°K	$f_S \times 10^3$, 25°	$\lambda_{T(0-0)}$, Å	ϵ^T_{0-0}, 77°K	$f_T \times 10^6$	$\tau_{rad} \times 10^3$, sec
Testosterone acetate (I)	3600	13.6	1.1	3825	0.2	14.9	0.20
4-Methyltestosterone acetate (VI)	3600	9.7	1.1	3850	0.1	12.7	0.19
4-Isopropyltestosterone acetate (VII)	3700	11.5	1.2	3950	0.2	18.3	0.18

[a] Calculated values of the oscillator strength and the radiative lifetime for the S → T (n,π*) transitions are included. An uncertainty of ±15% is present in the ϵ^T_{0-0} values owing to the weak absorptions (OD ± 0.3).

between the 3-keto and Δ^5-7-keto groups. Since molecular models indicate that distortions involving rotations about the C=C bond are much more hindered in the B-ring enone than in the A-ring enones, it may be that geometrical changes about the C=C double bond in the A-ring enones are somehow involved in the broadening phenomenon. This cannot be the complete explanation since the 3β-acetoxy and 3,3-diethylenedioxy analogs of XVII do not exhibit similarly sharp spectra, whereas the spectrum of 9-methyl-$\Delta^{5(10)}$-octalin-1,6-dione is again sharp (unpublished results of C. Jones). This latter observation strongly implies that the transannular interaction between the enone and keto chromophores is playing an important role in the appearance of structure in the spectra of these compounds.

(2) Location and Nature of the n,π Triplet States. With compounds I–XIX we observed a low-intensity band ($\epsilon \simeq 0.2$ M^{-1} cm^{-1}) in the PE spectrum located about 1500 cm^{-1} to the red of the first strong absorption band of the S → S (n,π) transition (curve 3, Figure 1). Because of their location with respect to the first strong S → S (n,π) band (singlet–triplet splitting ~1500 cm^{-1}) and low intensity ($\epsilon \simeq 0.2$ M^{-1} cm^{-1}), these bands are assigned as S → T (n,π) transitions. Table I lists the position of the S → T (n,π) 0–0 band and the singlet–triplet splittings for each compound.

Although the polarization ratios are relatively small (see Figure 2), the data for I, II, IV, V, and XIX demonstrate that the S → T (n,π) transitions in these compounds are in-plane polarized parallel to the lowest S → S (π,π) transition, as expected.

The 4.2°K S → T (n,π) spectra in the steroidal enones were, like the corresponding S → S (n,π) spectra, characterized by a complete lack of fine structure (Figures 3 and 4). Compound XVII is again significant in that the S → T (n,π) transitions remain diffuse in spite of the fact that the S → S (n,π) transition exhibits considerable fine structure. This difference in the behavior of the S → T (n,π) and S → S (n,π) transitions proves that there are additional effects responsible for the broadening of the S → T (n,π) spectrum of XVII which are not effective in perturbing the S → S (n,π) transition. We shall return to this important point later.

(3) Nature of the Emitting State. The assignment of the steroid phosphorescence is complicated by the facts that the emission spectra are all diffuse and devoid of structure at 77°K; the observed lifetimes (30–60 msec) are relatively short for $^3(\pi,\pi)$ states, and yet too long for $^3(n,\pi)$ states; and only small (factors of less than 30%) heavy-atom effects are observed.[2] Because of these difficulties we briefly repeat the arguments which we previously used to assign the emitting states as $^3(\pi,\pi)$ states.[2]

The S → T (n,π) transitions which are observed both in the PE spectra and in the direct absorption spectra are relatively strong transitions (ϵ ~0.1–0.2). Consequently, if the emission occurred from a $^3(n,\pi)$ state the origins of the phosphorescence and the S → T (n,π) absorption should have overlapped. Experimentally, gaps ranging up to 3000 cm^{-1} are observed, and the apparent overlap observed in the low-resolution 77°K spectra of some compounds usually disappears at 4.2°K. This lack of spectral overlap, which is most pronounced with compounds substituted at the 4 position (VIII excepted for reasons discussed in ref 2a), suggests that the $^3(n,\pi)$ state observed in absorption cannot be the emitting state. Consideration of phosphorescence lifetimes and quantum yields provides further confirmation of this conclusion.

The radiative lifetime, τ_{rad}, of the T (n,π) state is related to the oscillator strength, f_T, for the S → T (n,π) transition in the following way[13]

$$f_T = 2.4/(\tau_{rad}\nu^2) \qquad (1)$$

Since we cannot measure the entire S → T (n,π) absorption spectrum, we assume that a reasonable approximation to f_F is given by

$$f_T/f_S \simeq A^T_{0-0}/A^S_{0-0} \simeq \epsilon^T_{0-0}/\epsilon^S_{0-0} \qquad (2)$$

where A^T_{0-0} and A^S_{0-0} are the integrated intensities of the 0–0 bands of the S → T (n,π) and the S → S (n,π) transitions, respectively. The molar extinction coefficients for the first band in the S → T (n,π), ϵ^T_{0-0}, and the S → S (n,π), ϵ^S_{0-0}, spectra were measured directly at 77°K, and the total oscillator strength for the S → S (n,π) transition, f_s, was obtained by integration of the room-temperature absorption spectrum. Values for the oscillator strengths of the S → S (n,π) transition calculated using eq 2 are listed in Table IV for compounds I, VI, and VII, along with f_s and the measured extinction coefficients. Using eq 1 we then estimated that the *radiative* lifetimes for the T (n,π) state in these compounds should be on the order of 0.2 *msec*. If other nonradiative pathways for decay are available, the measured triplet-state lifetimes would be even shorter. If we assume that the intersystem crossing quantum yield, Φ_{isc}, is nearly unity, then the radiative lifetime of the emitting triplet state can be obtained from the experimental lifetime data using the expression

$$\tau_{rad} = \tau_{obsd}/\Phi_P \qquad (3)$$

These values are shown in the last column of Table II.

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(13) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, Chapter 1.

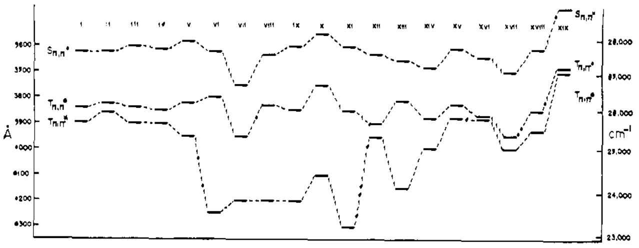

Figure 6. Energies of the lower lying excited singlet and triplet states of compounds I–XIX.

Experimentally we find that $\Phi_{isc} = 1.1 \pm 20\%$ in testosterone acetate, so that the assumption involved in using eq 1 is definitely valid for I, and probably so for related compounds.

The fact that the radiative lifetimes estimated from the emission data are 1000–3000 times *longer* than the $^3(n,\pi)$ radiative lifetimes calculated from absorption data provides the strongest evidence that the emitting triplet states cannot be $^3(n,\pi)$ states. We conclude, therefore, that the emission is from a $^3(\pi,\pi)$ state in each case. A summary of our triplet and singlet assignments is presented schematically in Figure 6.

The location of the $^3(\pi,\pi)$ state below the $^3(n,\pi)$ state now provides an explanation as to why the S → T (n,π) transition in XVII remains broad, in spite of the fact that the S → S (n,π) transition in this compound exhibits considerable fine structure. Hochstrasser[14,15] has previously shown that in azines, transitions to *second* triplet states are considerably broadened by interaction with a continuum of a nearly degenerate set of vibronic states associated with the first triplet state. It appears likely, then, that the interaction of the $^3(n,\pi)$ state with nearly degenerate levels of the lower lying $^3(\pi,\pi)$ state is responsible for the considerable broadening observed in the S → T (n,π) absorption spectrum of the steroidal enones discussed here.

(4) Observation of the S → T (π,π) Transition in PE Spectra. Because of the low oscillator strength for the S → T (π,π) transition (calculated to be 2×10^{-4} from the observed lifetime data) and because of the close proximity to the much stronger S → T (n,π) transition, it is difficult if not impossible to observe the S → T (π,π) transition in the PE spectra of most of the steroidal enones which we studied. 4-Bromotestosterone (VIII) is the only clear exception to this generalization. With this molecule we have been able to observe both the S → T (π,π) as well as the S → T (n,π) transitions in the 77°K PE spectrum, as shown in Figure 1, and even more clearly at 4.2°K.[2b] Our success here is due to the relatively large separation between the S → T (n,π) and the S → T (π,π) transitions, and to the significant enhancement of the S → T (π,π) transition caused by the bromine substituent.

(5) Polarization Measurements. The polarization data presented in Figure 2 indicate that the phosphorescence emission is more or less positively polarized ($P \sim +0.1$) with respect to the S → S (π,π) transition, and therefore in the plane of the molecule. Undoubtedly this in-plane character is derived from interaction with the S (π,π) state. While we cannot experimentally determine the exact route responsible for this mixing, second-order perturbation theory suggests that because of the close proximity of the $^3(n,\pi)$ and $^3(\pi,\pi)$ states, vibronic mixing of the $^3(\pi,\pi)$ state with the $^3(n,\pi)$ state (which is spin–orbitally coupled with the higher energy $^1(\pi,\pi)$ state) is the major route.[16]

The phosphorescence of 4-chlorotestosterone acetate (IX) was anomalous in that it was unpolarized with respect to excitation in the S → S (π,π) band, although it is negatively polarized with respect to the S → S (n,π) transition. It is known that halogen substituents on aromatic molecules significantly enhance S → T (π,π) transitions and that a major portion of this added intensity is derived from mixing with transitions polarized along the carbon–halogen bond.[17] Since the C—Cl bond in IX is oriented roughly perpendicular to the C=O axis, and therefore perpendicular to the polarization of the S → S (π,π) transition, it is not difficult to understand that the emission from the T (π,π) state could be depolarized with respect to the S → S (π,π) and yet remain negatively polarized with respect to the out-of-plane-polarized S → S (n,π) transition.

(6) Geometry of the Emitting Triplet State. One of the objects of the present study was to obtain information about the geometrical as well as the electronic, structure of the emitting triplet state. In this regard, the following observations appear to be relevant.

(i) The 4.2°K phosphorescence emission spectrum of testosterone acetate (I), shown in Figure 5, consists of a large number of closely spaced vibrational bands and generally has the characteristics of a highly Franck–Condon-forbidden transition. The B-ring enones XVII, on the other hand, have phosphorescence emission spectra which are more like that expected for a Franck–Condon-allowed transition.

(ii) The degree of polarization of the emission with respect to either the S → S (n,π) or the S → S (π,π) transitions was surprisingly low in most of the enones which we have studied.

(iii) Monocyclic enones such as cycloheptenone and cyclooctenone undergo a photoinduced cis–trans isomerization about the C=C double bond.[18]

(iv) Theoretical calculations on acrolein indicate that the lowest (π,π) triplet state is stabilized by an out-of-plane distortion involving rotation about the C=C bond.[19]

All these factors taken together indicate that upon excitation to the $^3(\pi,\pi)$ state, an enone adopts a distorted, nonplanar geometry which involves rotation about the C=C bond, unless prevented by structural features, as is the case in XVII. Such a distortion would then explain why the emission spectra are Franck–Condon forbidden in appearance and why the polarization ratios are so small, and at the same time would be consistent with the photochemical observation of the cis–trans isomerization of medium-sized cyclic enones.

(7) Photochemical Implications. Several features which have emerged from our spectral studies of the cyclic enones may be relevant with respect to the inter-

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[14] R. M. Hochstrasser, *Accounts Chem. Res.*, 1, 266 (1968).

[15] R. M. Hochstrasser and C. Marzzaco, *J. Chem. Phys.*, 49, 971 (1968).

[16] G. Marsh, D. R. Kearns, and M. Fisch, *J. Amer. Chem. Soc.*, 92, 2252 (1970).

[17] T. Paulopoulos and M. A. El-Sayed, *J. Chem. Phys.*, 41, 1082 (1964).

[18] P. Eaton, *Accounts Chem. Res.*, 1, 50 (1968).

[19] J. J. McCullough, H. Ohorodryk, and D. P. Santry, *Chem. Commun.*, 570 (1969).

pretation of still other photochemical transformations of cyclic enones.

(i) In many of the compounds which we have studied, the lowest $^3(n,\pi)$ and $^3(\pi,\pi)$ triplet states are nearly degenerate with one another.

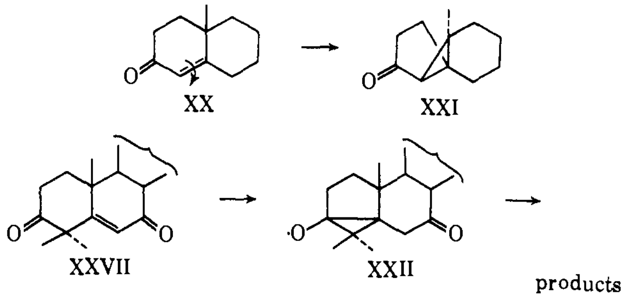
(ii) The relaxed $^3(\pi,\pi)$ state of the ring-A enones has a geometry which is considerably distorted with respect to the ground-state geometry, and it appears that the important distortion involves rotation about the C=C bond. By comparison, the ring-B enone XVII is notably less distorted.

(iii) The emitting $^3(\pi,\pi)$ state lies below the $^3(n,\pi)$ state.

(iv) Within experimental error, the intersystem crossing quantum yield is unity in testosterone acetate (I).

Because of the large intersystem crossing yield, we may anticipate that most of the photochemistry of this molecule, and of similar enones, will proceed from the triplet state. This has been confirmed experimentally for numerous photochemical transformations of cyclic enones, *inter alia* compounds I,[6] XIV,[20] XVII,[21] and XVII.[6] A correlation between spectral and photochemical properties requires that the spectroscopic measurements and the photochemical experiments be carried out under comparable conditions, specifically at the same temperature and in the same matrix (solvent). Such minimal requirements have not yet been satisfied and must await further experimental studies. In spite of this obvious deficiency, a few photochemical observations on some of the enones discussed above merit brief mention in connection with the identification of the reacting excited states. In the photochemistry of both testosterone acetate (I) and the closely related bicyclic compound 10-methyl-$\Delta^{1(9)}$-octalone (XVIII), for example, it appears that there are two different triplets involved, that each triplet state specifically leads to different products, and that the product distribution changes significantly in going from polar solvents such as alcohol to benzene.[6] These two triplet states have been tentatively assigned the $^3(n,\pi)$ and the $^3(\pi,\pi)$ configurations, based on arguments relating to the nature of the photochemical changes involved.[6] These assignments are in accord with the expectations from our spectroscopic observations, and, since the $^3(n,\pi)$ and $^3(\pi,\pi)$ states are known to be nearly degenerate in both of these molecules, the possibility exists that the solvent effect on the photochemistry is due to a solvent effect on the ordering of these two states. The photorearrangement of I and XVIII to bicyclo[3.1.0]hexanone isomers XX → XXI (Chart I) has been ascribed to the (π,π) triplet state.[6] By rotation around the C=C bond, as required for the $^3(\pi,\pi)$ state by the spectroscopic evidence, these molecules may in fact adopt a conformation which approaches a transition-state geometry that is favorable for the conversion to XXI. The photorearrangement of the ring-B enone XVII, on the other hand, is initiated by a bonding process between C-3 and C-5 (XVII → XXII, Chart I) rather than a homocyclic isomerization analogous to XX → XXI.[21] This difference in the reaction pathway appears plausible in view of the spectroscopic evidence indicating that there is a transannular interaction between the 3-keto and Δ^5-7-keto groups and that the geometry of the reacting enone triplet in XVII is considerably less distorted than in I.

Chart I



In view of the near degeneracy between the $^3(n,\pi)$ and $^3(\pi,\pi)$ states, it would be reasonable to expect a thermal equilibrium between these two triplet states. However, the photochemical results of I and XVIII do not indicate the existence of such an equilibration.

Finally, we note that de Mayo[22] finds that the effective triplet energies of cyclic enones determined by energy-transfer experiments involving the sensitized cis–trans isomerization of stilbene are all much lower than the energies determined from the 0–0 band of the phosphorescence emission spectra. In fact, the energies derived from the energy-transfer experiments correspond more nearly to the *maxima* in the phosphorescence emission, as might be expected if the enones have very distorted triplet-state geometries.

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(20) E. Pfenninger, D. E. Poel, C. Berse, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **51**, 772 (1968).

(21) S. Domb, G. Bozzato, J. A. Saboz, and K. Schaffner, *ibid.*, **52**, 2436 (1969); S. Domb and K. Schaffner, *ibid.*, **53**, 677 (1970).

(22) B. S. Kirkiacharian, P. de Mayo, and A. A. Nicholson, in preparation. We thank Professor de Mayo for private communication prior to publication.