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Circular Polarization of the Phosphorescence of α,β-Enones: Effect of Triplet–Triplet Coupling. Evidence for Nondistorted $^3\pi\pi^*$ States

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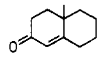
Abstract: For a series of α,β-enones, mostly of steroidal type, the circular polarizations of the phosphorescence (CPP) data are reported along with the phosphorescence spectra, quantum yields and lifetimes, and the $S_0 \rightarrow {}^1n\pi^*$ circular dichroism (CD) and absorption spectra. The data were obtained in organic glasses (77–92 K). From the large values of the degree of CPP (g_{lum}) and of the phosphorescence lifetime it is concluded that in all compounds the phosphorescent state is of the $^3\pi\pi^*$ type and acquires its radiative properties predominantly from spin–orbit coupling with the $^1n\pi^*$ state. Whereas for many enones the order of magnitude of g_{lum} equals the degree of circular polarization of the $S_0 \rightarrow {}^1n\pi^*$ transition (g_{abs}), the sign does not. According to the magnitude of the CD, the enones are divided in two groups: the molecules in group I ($|g_{abs}| < 15 \times 10^{-3}$) are assumed to have approximately planar enone chromophores, those in group II ($|g_{abs}| \geq 15 \times 10^{-3}$) essentially nonplanar ones. In contrast to group I, in group II g_{lum} and g_{abs} are systematically opposite in sign. It is argued that in the nonplanar enones $^1n\pi^*$–$^1\pi\pi^*$ coupling is an important mechanism for the generation of optical activity, leading to oppositely signed CD in the $S_0 \rightarrow {}^1n\pi^*$ and $S_0 \rightarrow {}^1\pi\pi^*$ bands—as experimentally observed. Since the $n\pi^*$–$\pi\pi^*$ separation is much smaller in the triplet than in the singlet manifold, the coupling of the triplet states is enhanced. For the level ordering $E(^3\pi\pi^*) < E(^3n\pi^*) < E(^1n\pi^*) < E(^1\pi\pi^*)$ it necessarily leads to opposite signs of g_{lum} and g_{abs}—without the necessity of invoking geometry changes in the $^3\pi\pi^*$ state. Together with the fact that group II consists of a structurally heterogeneous collection of enones, this implies that, at least in glassy matrices at low temperatures, the spectroscopic $^3\pi\pi^*$ state of α,β-enones does not exhibit appreciable distortion relative to the ground state.

Introduction

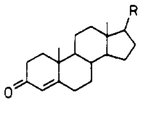
In the last two decades, circular polarization of the luminescence (CPL), the emission analogue of circular dichroism (CD), has been shown to be a valuable technique to study molecules in their excited states. Most of the measurements reported so far[1] pertain to fluorescent samples at ambient temperature, and we thought it of interest to try to extend the scope of the CPL technique to the phosphorescence of organic molecules (circular polarization of the phosphorescence, CPP). In this paper, we report and discuss the CPP data of a series of α,β-enones, mostly steroidal ones, that emit from a $^3\pi\pi^*$-type state. For various reasons, α,β-enones appear to be an interesting class to study. One reason is that in many instances the $^3\pi\pi^*$ and $^3n\pi^*$ states are nearly degenerate so that they may interact. Another reason is that on the basis of photochemical[2] and theoretical[3] evidence the enone chromophore has a tendency to distortion in the $^3\pi\pi^*$ state (rotation around the $C_\alpha{=}C_\beta$ bond). There is evidence that in cyclic enones at low temperatures the distortion occurs in actual fact, but there is also evidence to the contrary. In view of the sensitivity of optical activity toward molecular conformation, we thought it of interest to investigate whether CPP data can be of help.

Experimental Section

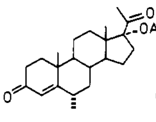
Materials. Samples of $9\beta,10\alpha$-testosterone (17β-hydroxy-$9\beta,10\alpha$-androst-4-en-3-one, **9a**), $9\beta,10\alpha$-ergosta-4,22-dien-3-one (**9b**), 4-methyl-$9\beta,10\alpha$-androst-4-ene-3,17-dione (**10**), and 9β-testosterone (17β-hydroxy-9β-androst-4-en-3-one, **11**) were obtained as gifts from Duphar B. V. (Weesp, The Netherlands) through the courtesy of Dr. M. P. Rappoldt. (*R*)-(−)-10-Methyl-1(9)-octal-2-one ((*R*)-(−)-4,4a,5,6,7,8-hexahydro-4a-methyl-2(3*H*)-naphthalenone, **1a**), its enantiomer **1b**, and 3β-acetoxy-16-methylpregna-5,16-dien-20-one (**16**) were purchased from Aldrich Chemical Co., Inc. Medroxyprogesterone acetate (17α-acetoxy-6α-methylpregn-4-ene-3,20-dione, **3**) and norethisterone acetate (17-acetoxy-19-nor-17α-pregn-4-en-20-yn-3-one, **8**) were available from Sigma Chemical Co. and 17β-hydroxy-1α-methylandrost-4-en-3-one (**4**) and β-glycyrrhetinic acid (**13**) from Janssen Chimica. 3α-Acetoxy-12-oxo-5β-chol-9(11)-en-24-oic acid (**14**) and 3β-acetoxypregna-5,16-dien-20-one (**15**) were purchased from Steraloids, Inc. Testosterone (17β-hydroxyandrost-4-en-3-one, **2a**), testosterone acetate (17β-acetoxyandrost-4-en-3-one, **2b**), progesterone (pregn-4-ene-3,20-dione, **2c**), cholest-4-en-3-one (**2d**), 17β-acetoxy-4-methylandrost-4-en-3-one (**5**), 19-nortestosterone (17β-acetoxyestr-4-en-3-one, **7a**), 19-nortestosterone acetate (17β-acetoxyestr-4-en-3-one, **7b**), and 3β-acetoxy-5α-cholest-7-en-6-one (**12**) were available from the steroid collection of the Gorlaeus Laboratories.



1a, b (R, S)



R	
2a	OH
b	OAc
c	$COCH_3$
d	C_8H_{17}



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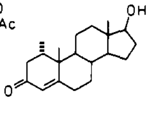

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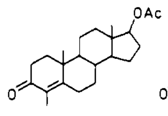

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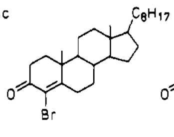

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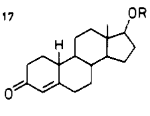
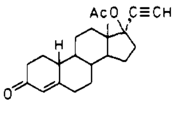


R	
7a	H
b	Ac



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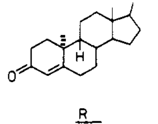
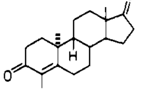


R	
9a	OH
b	C_9H_{17}



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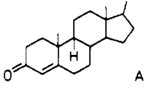

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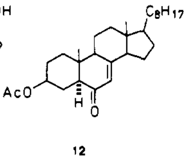

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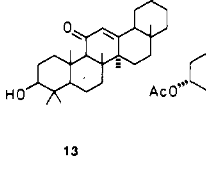

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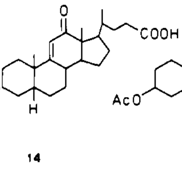

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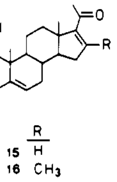

R	
15	H
16	CH_3

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[1] (a) Richardson, F. S.; Riehl, J. P. *Chem. Rev.* **1977**, *77*, 773–792. (b) Riehl, J. P.; Richardson, F. S. *Ibid.* **1986**, *86*, 1–16.

[2] Schuster, D. I. In *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Essay 17.

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Table I. Chiroptical Data, Phosphorescence Lifetime (τ), Quantum Yield (ϕ_P), and T–T Energy Gap of α,β-Enones at Low Temperatures[a]

compd	$10^3 g_{abs}$[b]	FC contour	$10^3 g_{lum}$ (fine str)	τ[c] (ms)	ϕ_P	T–T gap (cm^{-1})	*R*/*I*
9a	10	–	11 (+)	70	0.31	500	*R*
9b	11	–	16 (+)	>50	0.26		*R*
10	8	–	–15 (+)	71	0.2		*I*
13	–1	–	–16 (+)	39	0.06	<500	*R*
6	–6	–	11 (±)	2.0	0.4	2500	*I*
1a	–7	–	9 (±)	65	0.1	600	*I*
11	19	+	–40 (+)	>50	0.09	900	*I*
5	–17	+	32 (±)	59	0.20	2700	*I*
4	–63	+	54 (±)	27	0.07	1100	*I*
2b	–22	+	31 (±)	65	0.21	700	*I*
14	–30	+	42 (±)	20	0.47		*I*
3	–27	+	51 (±)	36	0.17		*I*
16	38	+	–65 (–)	26	0.04	2500	*I*
8	–20	+	54 (–)	>30	0.17		*I*
7b	–23	+	50 (–)	36	0.17	1100	*I*
12	70	+	–68 (–)	25	0.12	1900	*I*

[a] The results for testosterone (**2a**), progesterone (**2c**), and cholest-4-en-3-one (**2d**) were similar to those found for **2b**; this also holds for the pairs **7a**/**7b** and **15**/**16**, and for the pair of enantiomers **1a**/**1b** (apart, of course, from the sign of the chiroptical properties). Values of g_{abs} and g_{lum} were measured at 80–90 K (see Experimental Section), except for g_{abs} of **10** and **11** (room temperature, dioxane); phosphorescence quantum yields, lifetimes, and T–T gaps were obtained at 77 K. [b] Because occasionally there is a considerable uncertainty in the low-temperature $S_0 \rightarrow {}^1n\pi^*$ absorption spectra due to a nonflat base line and/or overlap with the $S_0 \rightarrow {}^1\pi\pi^*$ transition, we have obtained g_{abs} (cf. (1)) using the integrated value of ϵ/ν at room temperature. For the case of **2b** we have found that the value of the integral changes less than 10% when the temperature is lowered from 300 to 80 K. For the enones having an additional nonconjugated carbonyl group (**3** and **10**), we hvae estimated g_{abs} using the long-wavelength part ($\lambda >$ ~330 nm) of the CD and absorption spectra. [c] Since the observed phosphorescence decays appear to be nonexponential, lifetime is expressed as mean lifetime (statistical average lifetime) as defined by Demas; see: Demas, J. N. *Excited State Lifetime Measurements*; Academic Press: New York, 1983; p 32.

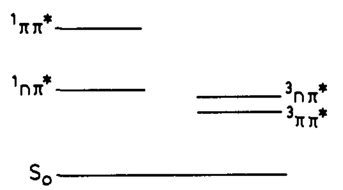
4-Bromocholest-4-en-3-one (**6**) was prepared following the procedure reported by Shaw and Stevenson,[4] mp 115 °C (lit.[4] mp 114–5 °C).

Purification. The enones were recrystallized once or twice from methanol (**3**, **9a**, **9b**, **12**, and **13**) or acetone (**2a,b**, **4**, **7a,b**, **8**, **14**, **15**, and **16**), subjected to column chromatography (silica gel) (**1a** and **1b**), or used as received (**5**, **10**, and **11**). The purity of the compounds was checked by GC (SE 30 column, 220 °C). Ethanol and isopentane were purified by distillation, and diethyl ether and 2-methyltetrahydrofuran (MTHF) were distilled from $LiAlH_4$.[5]

Apparatus. CPL and linear polarization data were acquired with a home-built instrument[6] equipped with a chopper, circular dichroism spectra with a Jobin-Yvon MIII dichrograph, and UV–vis absorption spectra with a Cary 14 spectrometer. Emission and excitation spectra were recorded on a Spex Fluorolog-II spectrometer or on the CPL apparatus and phosphorescence decay curves on the Spex instrument. For measurements at low temperatures, we used either a simple suprasil Dewar (77 K) or a variable-temperature cryostat (Oxford Instruments, DN704, modified). Square suprasil cells (1 cm × 1 cm, Hellma) or cylindrical suprasil tubes (diameter, 5 mm) were used.

Methods. The differential photon-counting technique used in the CPL measurement ensures that the polarization data—obtained with liquid solutions at room temperature—are absolute, provided the dark-current signal is negligible and correction is made for the polarization characteristics of the linear polarizer in the emission channel.[6,7] To minimize birefringence artifacts in the CPP measurements,[8] we normally used the CPL spectrometer in the 90° excitation–emission geometry employing horizontally polarized excitation light, and we only used relatively soft glassy solvents such as EPA (ethanol/isopentane/diethyl ether (2:5:5)) or MIP/MTHF (methylcyclohexane/isopentane/2-methyltetrahydrofuran (3:9:8)). Down to liquid nitrogen temperature, these glasses do not depolarize the light; the CD signal of an auxiliary sample of (1*S*)-(–)-1-bromo-α-fenchocamphoronequinone in dioxane (300 K) was not affected when the cryostat was put in front of this sample in the light beam of the CD spectrometer. All CPP measurements were repeated at least once with a fresh sample; g_{lum} data prove to be reproducible within 2×10^{-3}. Orientational dependence of the CPP was studied[8] by varying the plane of polarization of the incident light from horizontal to vertical in the 90° setup or by using depolarized excitation light in the 180° setup. Precision of the CPP data is determined by photon noise; in this work, measurement was generally continued until a standard error of 1×10^{-3} in g_{lum} was reached.

Chart I



Phosphorescence quantum yields (ϕ_p) were determined in 2-MTHF at 77 K relative to testosterone (**2a**) ($\phi_p = 0.21$).[9] Phosphorescence spectra were not corrected for the transmission characteristics of the emission channel of the phosphorimeter. Concentrations were (1–2) × 10^{-2} M. Solvents and temperatures in absorption (A), CD, phosphorescence (P), and CPP experiments were as follows: **1a** EPA 80 K (A, CD), EPA 77 K (P, CPP); **2b** MIP/MTHF 91 K (A, CD), EPA 77 K (P, CPP); **3** EPA 87 K; **4** EPA 91 K (A, CD), 77 K (P, CPP); **5** MIP/MTHF 91 K (A, CD), EPA 77 K (P, CPP); **6** EPA 82 K (A, CD), 77 K (P, CPP); **7b** EPA 86 K (A, CD), 88 K (P, CPP); **8** EPA 88 K (A, CD), 84 K (P, CPP); **9a** EPA 80 K (A, CD), 77 K (P, CPP); **9b** EPA 86 K; **10** EPA 82 K; **11** EPA 82 K; **12** EPA 90 K (A, CD), 84 K (P, CPP); **13** EPA 90 K (A, CD), 87 K (P, CPP); **14** EPA 82 K; **16** MIP/MTHF 89 K (A, CD), MTHF 77 K (P), EPA 80 K (CPP). Phosphorescence decay curves were obtained in EPA at 77 K.

When the phosphorescence spectra, decay curves, and CPP data were acquired, the excitation wavelength was set at ~330 nm with a bandwidth of ~32 nm. The phosphorescence spectra were obtained with an emission bandwidth <4 nm and the CPP data and decay curves with <8 nm (wavelength for the latter was set at the emission maximum).

Results

The compounds investigated are shown above. Representative results, including absorption and emission data, are depicted in Figure 1 and summarized in Table I. It is convenient to present them in the context of a qualitative spectroscopic level scheme of α,β-enones (Chart I).

$S_0 \rightarrow {}^1n\pi^*$ and $S_0 \rightarrow {}^1\pi\pi^*$. The singlet–singlet (S–S) transition of lowest energy is of $S_0 \rightarrow {}^1n\pi^*$ type. In the absorption spectra it manifests itself as a broad band in the region 270–370 nm with low extinction coefficient ($\epsilon_{max} \approx 40$ dm^3 mol^{-1} cm^{-1}). In chiral α,β-enones, the magnetic dipole allowedness of the transition can

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(5) Pestemer, M. *Anleitung zum Messen von Absorptions-spektren im Ultraviolett und Sichtbaren*; Thieme Verlag: Stuttgart, 1964.

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give rise to circular dichroism of considerable magnitude (e.g., in the case of testosterone (**2a**) $\Delta\epsilon_{\max} = -1.82$ dm^3 mol^{-1} cm^{-1} at 330 nm, EPA, 123 K).[10] A convenient measure for the optical activity is the dissymmetry factor $g_{\mathrm{abs}}(\lambda)$, i.e., the ratio $\Delta A/A$ at a specific wavelength. Whereas these $g_{\mathrm{abs}}(\lambda)$ values, which can be inferred from the figures, refer to the circular anisotropy in vibronic transitions, that of the electronic transition is measured by the dissymmetry factor of the entire band:

$$g_{\mathrm{abs}} = \int \Delta\epsilon/\nu \, d\nu \Big/ \int \epsilon/\nu \, d\nu \qquad (1)$$

The two dissymmetry factors are equal if absorption and CD have identical band shapes. In the enones studied this is not the case, with fine structure being more developed in CD than in unpolarized absorption. It appears that with **1**, **6**, **9**, **10**, and **13** the CD within the $S_0 \rightarrow {}^1n\pi^*$ band is bisignate; i.e., it crosses zero (Figure 1). For these enones, the bisignate character goes along with a strong deviation of the CD band shape from a simple Franck–Condon contour. Such behavior has been ascribed[11] to vibronic coupling effects. For the various enones, the values of g_{abs} are collected in Table I.

The next S–S transition is the electric dipole allowed transition $S_0 \rightarrow {}^1\pi\pi^*$ ($\lambda_{\max}$ 240–260 nm; $\epsilon_{\max} \approx 16 \times 10^3$ dm^3 mol^{-1} cm^{-1}), which is characterized by small absolute values of g_{abs} ($<10^{-3}$). Qualitative measurements show that in all enones described here the CD crosses zero upon passing from the $S_0 \rightarrow {}^1n\pi^*$ to the $S_0 \rightarrow {}^1\pi\pi^*$ spectral region. The fact that in transoid α,β-enones the signs of the CD in the two lowest S–S transitions nearly always are opposite has been recognized before.[12a]

$S_0 \rightarrow {}^3n\pi^*$. The lowest part of the triplet manifold of α,β-enones is characterized by proximate ${}^3\pi\pi^*$ and ${}^3n\pi^*$ states. In most steroidal α,β-enones, the ${}^3\pi\pi^*$ state is lowest in energy and responsible for the phosphorescence. As shown by Kearns and Schaffner and co-workers[9,13] the presence of the ${}^3n\pi^*$ level is unveiled by a weak band or a shoulder in the phosphorescence excitation (PE) spectrum. For all enones we have observed this feature; for **4** it is included in Figure 1. The extinction coefficient of this band can be calculated by comparing its intensity in the PE spectrum with that of the $S_0 \rightarrow {}^1n\pi^*$ band using the fact[9,14] that in α,β-enones the efficiency for the ${}^1n\pi^* \rightarrow$ triplet intersystem crossing is about unity. In the case of **2a** we find $\epsilon \approx 0.2$ dm^3 mol^{-1} cm^{-1}.

At the highest sensitivity of the CD instrument a very weak, oppositely signed, CD lobe outside the $S_0 \rightarrow {}^1n\pi^*$ band shows up in the spectra of **2**–**5**; with **7**, **8**, **12**, **14**, and **16** the feature is not detectable. Following Beecham et al.,[15] we assign it to the $S_0 \rightarrow {}^3n\pi^*$ transition.

${}^3n\pi^*$–${}^3\pi\pi^*$ Energy Gap. The magnitude of the ${}^3n\pi^*$–${}^3\pi\pi^*$ energy gap of the various enones is given in Table I. The gaps were estimated as follows: the energy of the ${}^3n\pi^*$ level was found from the position of the peak/shoulder in the PE spectrum while the onset of the phosphorescence band (taken rather arbitrarily at 5% of the maximum amplitude) was used as a measure of the energy of the ${}^3\pi\pi^*$ level. This approach gives results similar to triplet–triplet (T–T) gaps reported by Marsh et al.[9] for some identical compounds.

${}^3\pi\pi^* \rightarrow S_0$. Figure 1 also shows the phosphorescence spectra of the enones (with all enones studied we failed to observe fluorescence). The emissions appear to be rather structureless: fine structure is limited to the occurrence of shoulders. The phosphorescence lifetimes, which generally are in the range 20–70 ms, and quantum yields (ϕ_P) are given in Table I.

Like in the case of absorption, two dissymmetry factors can be defined: the degree of circular polarization at each wavelength, $g_{\mathrm{lum}}(\lambda) = \Delta I(\lambda)/I(\lambda)$, which is directly obtained from experiment, and the dissymmetry factor as defined in (2) pertaining to the

$$g_{\mathrm{lum}} = \int \Delta I/\nu^4 \, d\nu \Big/ \int I/\nu^4 \, d\nu \qquad (2)$$

entire electronic band. Figure 1 shows $g_{\mathrm{lum}}(\lambda)$ data, Table I gives g_{lum}. With some enones, for instance **7**, **8**, **12**, and **16**, $g_{\mathrm{lum}}(\lambda)$ appears to be nearly structureless; others, notably **9a** and **9b**, exhibit pronounced fine structure. In column 4 of Table I this is indicated by a minus or plus sign, respectively. In the remaining enones, the amount of fine structure in g_{lum} is in between (± in Table I). In these cases the largest change in $g_{\mathrm{lum}}(\lambda)$ is found near the onset of the phosphorescence band. With **5**, this change even includes sign.

From our data, it appears that for some enones g_{lum} and g_{abs} have equal sign and for others there is sign inversion (indicated by *R* and *I*, respectively, in the table).

At variance with reports in the literature,[13a] we find that the phosphorescence decay curve of all enones studied is not a single exponential at all concentrations (1×10^{-4}–2×10^{-2} M) and in all solvents used (2-MTHF, EPA, methanol/ethanol (1:1), methylcyclohexane/methylcyclopentane (1:1)). This prompted us to measure g_{lum} as a function of chopper frequency. Within experimental error there appears to be no time dependence. Moreover, the g_{lum} values equal those obtained without chopper. For **2a** (EPA, 77 K), the experiment was repeated with improved time resolution by use of a time-resolved CPL setup.[16] Detection of CPP in the time interval 0.1–1.1 ms after the excitation flash yields g_{lum} $(29 \pm 2) \times 10^{-3}$; the same value is obtained in the intervals 0.5–0.55, 0.1–10, 10–20, 20–30, 30–40, 40–50, and 0.1–400 ms. With the time-viewing windows 50–100, 100–200, and 100–400 ms we observe $g_{\mathrm{lum}} = (23 \pm 2) \times 10^{-3}$. With several of the enones, we also measured the phosphorescence spectrum as a function of delay and found that its band shape does not change.

Some further observations include the following: (1) On samples where orientational relaxation of the excited species is slow on the time scale of the emission,[1a] the anisotropy of g_{lum} is potentially observable. With our enones this anisotropy proves to be undetectable. A possible explanation is offered elsewhere.[8b] (2) When the temperature is increased from 77 K, ϕ_P decreases. The phosphorescence intensity of **2a** at ~95 K has dropped to ~5% of its maximum value both in 2-MTHF and in glycerol as a solvent. (3) For most enones g_{lum} appears to be independent of temperature. Exceptions are the unsubstituted 4-en-3-ones **2**: with both **2b** and **2d** the value of g_{lum} decreases by a factor of 2 upon increasing the temperature from ~80 to ~95 K. (4) In line with the results of Kearns et al.,[13] the degree of linear polarization of the phosphorescence relative to the $S_0 \rightarrow {}^1n\pi^*$ band appears to be small and positive and virtually independent of wavelength.

Arrangement of Table I. The enones can be divided in two groups: at the top of the table are the enones with relatively small CD (**1a**, **6**, **9a**,**b**, **10**, and **13**), $|g_{\mathrm{abs}}| < 15 \times 10^{-3}$, group I; the other enones, group II, have larger values of $|g_{\mathrm{abs}}|$. The enones in group II are characterized by CD spectra having the appearance of an almost perfect Franck–Condon contour[15] in a single progression; with the enones in group I the CD spectra evidence clear vibronic coupling effects. In the table this is indicated by a + or − in the column FC contour.

As a (rough) ordering criterion within the groups, the degree of fine structure of g_{lum} was used. At the top of the table are the enones **9** with structured $g_{\mathrm{lum}}(\lambda)$, and at the bottom are **7**, **8**, **12**, **15**, and **16** where $g_{\mathrm{lum}}(\lambda)$ is essentially flat.

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Discussion

The optical activity of S–T transitions in organic molecules is a nearly unexplored phenomenon.[17,18] In principle, its theoretical description is similar to that of S–S transitions since an intrinsic contribution of spin—that is, an effect due to the operator $2S$ in eq 7, vide infra—is not expected[19] to contribute appreciably to the rotational strength R. In practice, the description is essentially more complex since spin–orbit coupling must be invoked as an extra perturbation. In the following text we shall provide a qualitative explanation of the observed CPP data. After a short discussion of the relations between experimental and molecular quantities and of the relevant wave functions of α,β-enones, we argue that the observed phosphorescence is of $^3\pi\pi^*$ type in all cases and that the nonexponential character of the emission does not hamper a molecular interpretation of the CPP results. Next, we present a simple model to describe the optical activity in the $^{1,3}\pi\pi^* \rightarrow S_0$ and $^{1,3}n\pi^* \rightarrow S_0$ transitions of α,β-enones. After a discussion of the relevance of the model, its predictions are confronted with experimental results.

General Considerations. The rotational strength (R), the dipole strength (D), and the dissymmetry factor (g) in an electronic transition $i \leftrightarrow j$ are defined by (3)–(5), respectively. In these

$$R = \mathrm{Im}\ \mu_{ij}\cdot\mathbf{m}_{ji} \tag{3}$$

$$D = |\mu_{ij}|^2 \tag{4}$$

$$g = 4R/D \tag{5}$$

equations, μ_{ij} ($\mathbf{m}_{ji}$) represents the electronic matrix element of the electric (magnetic) dipole operator μ ($\mathbf{m}$) of the electronic transition $i \leftrightarrow j$. $\mathbf{L}$ and $\mathbf{S}$ are the operators for orbital and spin angular

$$\mu_{ij} = \langle i|\mu|j\rangle \tag{6}$$

$$\mathbf{m}_{ji} = \langle j|\mathbf{m}|i\rangle = \langle j|e/(2mc)(\mathbf{L} + 2\mathbf{S})|i\rangle \tag{7}$$

momentum, respectively. Equations 3-5 hold for both absorption and emission (fluorescence or phosphorescence) provided it is understood that i always pertains to the state of lower energy.[21]

In absorption, R (D) can be found from experiment by integrating the CD (absorption) over all vibrational fine structure

$$R = 23 \times 10^{-40} \int \Delta\epsilon/\nu\ \mathrm{d}\nu \tag{8}$$

$$D = 92 \times 10^{-40} \int \epsilon/\nu\ \mathrm{d}\nu \tag{9}$$

where R and D are in cgs units and $\Delta\epsilon$ and ϵ in dm^3 mol^{-1} cm^{-1}. In luminescence the rotational and dipole strengths are equal to

$$R_{\mathrm{lum}} = c \int \Delta I/\nu^4\ \mathrm{d}\nu \tag{10}$$

$$D_{\mathrm{lum}} = 4c \int I/\nu^4\ \mathrm{d}\nu \tag{11}$$

in which integration is over the entire emission band. Generally, only the value of g_{lum} is obtained, not those of R_{lum} and D_{lum} separately, since in a standard emission experiment the value of c is not easily determined.

With pure spin states, the phosphorescent transition is rigorously spin-forbidden and the intensity entirely derives from spin–orbit coupling of the initial triplet state and the final singlet state to other states:

$$^1\phi(Qq) \rightarrow {}^1\phi(Qq) + \sum_i \lambda_i(Q)^3\phi_i(Qq) \tag{12}$$

$$^3\phi(Qq) \rightarrow {}^3\phi(Qq) + \sum_j \lambda_j(Q)^1\phi_j(Qq) \tag{13}$$

The degree of mixing is governed by the magnitude of the coefficients λ_i that contain energy denominators such as $E(^3\phi_i) - E(^1\phi)$ and matrix elements $\langle ^3\phi_i|\mathbf{L}\cdot\mathbf{S}|^1\phi\rangle$. The variables Q and q in (12) and (13) denote the coordinates of nuclei and electrons, respectively.

Generally, the admixing of triplet character to the singlet ground state will be small because of the large energy difference involved. Phosphorescence therefore mostly occurs predominantly via the mechanism implied in (13): its intensity originates from S → S transitions. It can be argued[20] that in (approximately) planar α,β-unsaturated ketones the intensity of $^3\pi\pi^*$ phosphorescence predominantly derives from $^1n\pi^*$ admixture and that of $^3n\pi^*$ phosphorescence from $^1\pi\pi^*$ admixture:

$$^3\pi\pi^* + \lambda_1{}^1n\pi^* \tag{14a}$$

$$^3n\pi^* + \lambda_2{}^1\pi\pi^* \tag{14b}$$

In this approximation, the radiative properties of the $^3\pi\pi^*$ state are determined by the nature and the amount of the singlet admixture: $R(\mathrm{T} \rightarrow \mathrm{S})$ and $D(\mathrm{T} \rightarrow \mathrm{S})$ are equal to $|\lambda_1|^2$ times the corresponding quantities in the $S_0 \rightarrow {}^1n\pi^*$ transition. Being an intensive quantity, the dissymmetry factor in the phosphorescence depends on the nature of the singlet blend.

So the simple description (14) predicts identical values of g_{lum} and g_{abs}—provided no geometry changes occur upon excitation. Although the order of magnitude of the assessed dissymmetry factors is the same, the sign inversions observed demonstrate that the description is inadequate. In the next sections we investigate whether the reversal of sign is primarily due to a more complex spin–orbit coupling than assumed in (14) or to the alleged drastic geometry change in the $^3\pi\pi^*$ states of α,β-enones.

Nothwithstanding the obvious inadequacy of (14), a conclusion can already be drawn from the order of magnitude of the effects[20] alone. A high value of g_{lum} implies that in the phosphorescent transition the ratio of $\mathbf{m}$ to μ is high, which cannot be so in the case of a $^3n\pi^* \rightarrow S_0$ transition. It can be derived that in the absence of T–T coupling a value of $|g_{\mathrm{lum}}|$ larger than 8×10^{-3} is incompatible with $^3n\pi^*$ emission of α,β-enones.[20] Although, of course, this value has to be adapted when allowance is made for T–T interaction, it does not change largely. Even in the case of 1:1 mixing of $^3n\pi^*$ and $^3\pi\pi^*$, i.e., a state described by the wave function $2^{-1/2}(^3n\pi^* + {}^3\pi\pi^*)$, the dipole strength is reduced by only a factor of 2 compared to the pure $^3n\pi^*$ situation. This leads to a slightly higher limiting value of $|g_{\mathrm{lum}}|$: 12×10^{-3}. We note that the limiting value is a theoretical one[20] and that in actual fact—depending on the degree of dissymmetry of the molecule—g_{lum} can be considerably lower. So we can conclude that all emissions from the enones of group II are predominantly of $^3\pi\pi^* \rightarrow S_0$ type. This conclusion also holds for **9b**, **10**, and **13**, whereas for **1a**, **6**, and **9a** the $^3\pi\pi^* \rightarrow S_0$ assignment is supported by the fact that here the magnitude of $|g_{\mathrm{lum}}|$ is of the same order as (or larger than) that of $|g_{\mathrm{abs}}|$.

Other properties to distinguish $^3\pi\pi^*$ from $^3n\pi^*$ emission are the radiative lifetime and the phosphorescence band shape. In α,β-enones, the radiative lifetime of a $^3n\pi^*$ state is typically on the order of 1 ms, that of a $^3\pi\pi^*$ state is 2 orders of magnitude larger.[9,13,22] $^3n\pi^* \rightarrow S_0$ phosphorescence characteristically has a rather structured band shape; $^3\pi\pi^* \rightarrow S_0$ emission is devoid of appreciable vibrational fine structure.[9,13,22] Application of these criteria similarly leads to the conclusion that the emission of the enones of Table I occurs from a $^3\pi\pi^*$-type excited state. For an analogue of **6** and for **2a–d**, **5**, and **7a**, this assignment agrees with earlier work.[9,13a,23]

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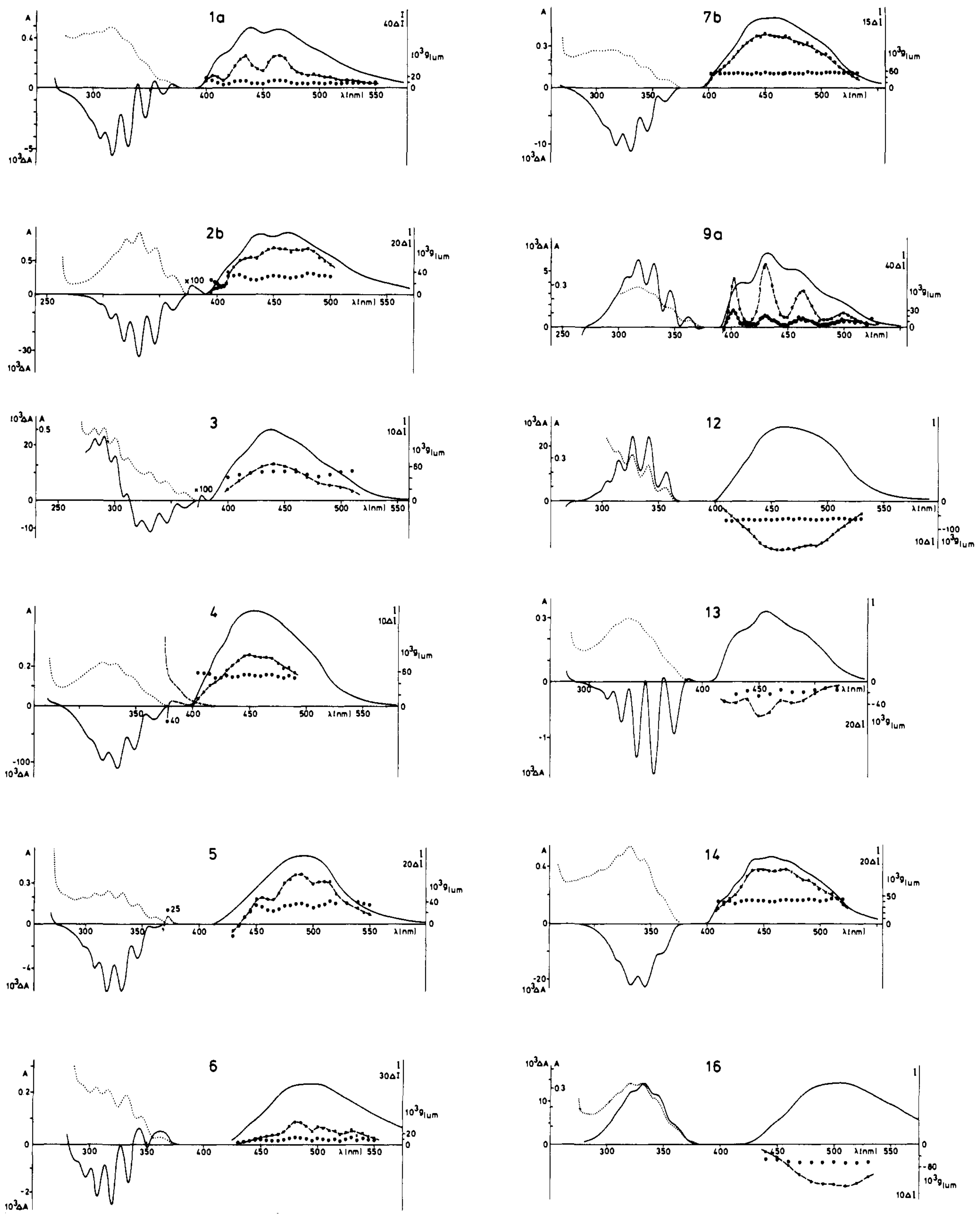

Figure 1. Low-temperature spectra of the α,β-enones **1a**, **2b**, **3–6**, **7b**, **9a**, **12–14**, and **16**. To the right: phosphorescence *I* (—, arbitrary units), g_{lum} values (-o-o, scale $10^3 g_{lum}$), and ΔI (-■-■-). To the left: absorbance *A* (···) and circular dichroism ΔA (—, scale $10^3\Delta A$). In the spectra of some of the enones the long-wavelength CD lobe is enlarged (-·-); for enone **4** is also depicted the part of the phosphorescence excitation spectrum pertaining to the $S_0 \rightarrow {}^3n\pi^*$ transition (———), see text. Standard error in g_{lum} is 1×10^{-3}. For further instrumental and for sample conditions (solvent, concentration, and temperature), see Experimental Section.

The nonexponential character of the phosphorescence decay suggests the presence of more than one emitting species, which might prohibit a molecular interpretation of the g_{lum} data. We believe that this is not the case here: (a) The fact that emission band shape is virtually independent and g_{lum} only weakly dependent on time delay indicates that the optical and chiroptical properties of the various species are not essentially different (except, of course, phosphorescence lifetime). (b) In a different context we have shown[25] that the multiple character of the phosphorescence of α,β-enones has to be attributed to inhomogeneous solvation in the ground state. With several enones from the present work we have studied the effect of replacement of solvent EPA by the non-hydroxylic MIP/MTHF on $g_{abs}(S_0 \rightarrow {}^1n\pi^*)$ and on the CPP; we observed modest changes only.

Model for the Optical Activity in Twisted α,β-Enones. We consider an α,β-enone chromophore with four excited states: singlet and triplet $n\pi^*$ and $\pi\pi^*$ states. In the planar conformation the $S_0 \rightarrow {}^1n\pi^*$ transition is **m**-allowed ($|\mathbf{m}| \approx 1\ \mu_B$, direction approximately parallel to the C=O axis[26]), and the $S_0 \rightarrow {}^1\pi\pi^*$ transition μ-allowed (direction of μ parallel to a line through the O- and the C_β-atom[27]). We assume that spin–orbit coupling of ${}^3n\pi^*$ only occurs with ${}^1\pi\pi^*$ and that of ${}^3\pi\pi^*$ only with ${}^1n\pi^*$. That is, the triplet wave functions are given by (14a) and (14b). The coefficients λ_1 and λ_2, which are purely imaginary, are given by

$$\lambda_1 = \langle {}^1n\pi^* | H_{so} | {}^3\pi\pi^* \rangle / [E({}^3\pi\pi^*) - E({}^1n\pi^*)] \qquad (15a)$$

$$\lambda_2 = \langle {}^1\pi\pi^* | H_{so} | {}^3n\pi^* \rangle / [E({}^3n\pi^*) - E({}^1\pi\pi^*)] \qquad (15b)$$

Subsequently, the transitions of the chromophore are rendered optically active by introducing a small twist ($\phi(C-C_\alpha)$ and/or $\phi(C_\alpha-C_\beta)$ and/or pyramidalization of the carbon atoms) in the chromophore. We assume that this chiral perturbation H_{chir} does not affect the spin–orbit coupling (more precisely, the ratio of λ_1 to λ_2).

From perturbation theory the wave functions of the excited singlet and triplet states are obtained as follows:

$$|{}^1n\pi^*\rangle = {}^1n\pi^* + b\,{}^1\pi\pi^* \qquad (16a)$$

$$|{}^1\pi\pi^*\rangle = {}^1\pi\pi^* - b\,{}^1n\pi^* \qquad (16b)$$

$$b = \langle {}^1n\pi^* | H_{chir} | {}^1\pi\pi^* \rangle / [E({}^1n\pi^*) - E({}^1\pi\pi^*)] \qquad (16c)$$

$$|{}^3n\pi^*\rangle = {}^3n\pi^* + a\,{}^3\pi\pi^* \qquad (17a)$$

$$|{}^3\pi\pi^*\rangle = {}^3\pi\pi^* - a\,{}^3n\pi^* \qquad (17b)$$

$$a = \langle {}^3n\pi^* | H_{chir} | {}^3\pi\pi^* \rangle / [E({}^3n\pi^*) - E({}^3\pi\pi^*)] \qquad (17c)$$

The matrix elements in (16a) and (17a) are real and have the same sign provided the spatial parts of the ${}^1n\pi^*$ and ${}^3n\pi^*$ and of the ${}^1\pi\pi^*$ and ${}^3\pi\pi^*$ wave functions are similar and the interaction is dominated by one-electron terms.

The rotational strength of the $S_0 \rightarrow {}^1n\pi^*$ transition is given by

$$R(S_0 \rightarrow {}^1n\pi^*) = \mathrm{Im}\ \langle S_0|\mu|{}^1n\pi^* + b\,{}^1\pi\pi^*\rangle \cdot \langle {}^1n\pi^* + b\,{}^1\pi\pi^*|\mathbf{m}|S_0\rangle = b\ \mathrm{Im}\ \langle S_0|\mu|{}^1\pi\pi^*\rangle \cdot \langle {}^1n\pi^*|\mathbf{m}|S_0\rangle \qquad (18)$$

In deriving the right-hand side of (18) we have used the assumption that the $S_0 \rightarrow {}^1n\pi^*$ transition is only **m**-allowed and the $S_0 \rightarrow {}^1\pi\pi^*$ transition only μ-allowed. If allowance had been made for a nonvanishing rotational strength of the enone in the planar conformation (e.g., due to chirally disposed extrachromophoric groups), the right-hand side of (18) would have contained extra terms such as $\mathrm{Im}\ \langle S_0|\mu|{}^1n\pi^*\rangle \cdot \langle {}^1n\pi^*|\mathbf{m}|S_0\rangle$. We further mention that in our model the CD is conservative: $R(S_0 \rightarrow {}^1\pi\pi^*) = -R(S_0 \rightarrow {}^1n\pi^*)$.

With the inclusion of the singlet admixtures the wavefunction for a ${}^3\pi\pi^*$ state reads

$$|{}^3\pi\pi^*\rangle = {}^3\pi\pi^* + \lambda_1\,{}^1n\pi^* - a({}^3n\pi^* + \lambda_2\,{}^1\pi\pi^*) \qquad (19)$$

Therefore, the rotational strength of the ${}^3\pi\pi^* \rightarrow S_0$ phosphorescence is given by

$$R({}^3\pi\pi^* \rightarrow S_0) = \mathrm{Im}\ \langle S_0|\mu|\lambda_1\,{}^1n\pi^* - a\lambda_2\,{}^1\pi\pi^*\rangle \cdot \langle \lambda_1\,{}^1n\pi^* - a^*\lambda_2\,{}^1\pi\pi^*|\mathbf{m}|S_0\rangle = -a\lambda_2\lambda_1^*\mathrm{Im}\ \langle S_0|\mu|{}^1\pi\pi^*\rangle \cdot \langle {}^1n\pi^*|\mathbf{m}|S_0\rangle \qquad (20)$$

Again, optical activity is conservative: $R({}^3n\pi^* \rightarrow S_0) = -R({}^3\pi\pi^* \rightarrow S_0)$.

Upon comparison of the rotational strength in the $S_0 \rightarrow {}^1n\pi^*$ and ${}^3\pi\pi^* \rightarrow S_0$ transitions we get

$$R(S_0 \rightarrow {}^1n\pi^*):R({}^3\pi\pi^* \rightarrow S_0) = +b/(-a\lambda_2\lambda_1^*) \qquad (21)$$

The matrix elements in the expression for λ_1 and λ_2 can be easily evaluated:[28] they are purely imaginary and opposite in sign. With the level ordering of Chart I, i.e., $E({}^3\pi\pi^*) < E({}^3n\pi^*) < E({}^1n\pi^*) < E({}^1\pi\pi^*)$, the energy denominators in the expressions for λ_1 and λ_2 are negative, so $\lambda_2\lambda_1^*$ is positive. Since for this level ordering a and b have been chosen to have the same sign, the model predicts sign inversion between the CD in the $S_0 \rightarrow {}^1n\pi^*$ transition and the CPP from a (predominantly) ${}^3\pi\pi^*$ level. Note that, whereas in the model $R({}^3n\pi^* \rightarrow S_0) = -R({}^3\pi\pi^* \rightarrow S_0)$, the corresponding dipole strengths—and thus the absolute values of g_{lum}—differ widely. Equation 20 predicts zero rotational strength for vanishing T–T coupling. This arises because in deriving (20) we have assumed that optical activity is created by twist only, but the model can easily be extended to incorporate zero-order rotational strength in the transitions of the planar chromophore.

The above concept can also cover situations with different ordering of the energy levels. For example, when the order of the triplet levels (both still lower than the ${}^1n\pi^*$ state) is reversed, the dissymmetry factor in the transition from the upper triplet (${}^3\pi\pi^*$) to the ground state has the same sign as that in the $S_0 \rightarrow {}^1n\pi^*$ transition. Consequently, g_{lum} in the ${}^3n\pi^* \rightarrow S_0$ phosphorescence is predicted to have the opposite sign (but considerably lower magnitude because of the larger dipole strength) as $g(S_0 \rightarrow {}^1n\pi^*)$. As compared with this situation, the sign of $g_{lum}({}^3n\pi^* \rightarrow S_0)$ again equals that of $g(S_0 \rightarrow {}^1n\pi^*)$ if the energy of the ${}^3\pi\pi^*$ state happens to be higher than that of the ${}^1n\pi^*$ state.

Relevance of the Model. Already, in an early stage Whalley[29] and Djerassi et al.[30] correlated the sign of the $S_0 \rightarrow {}^1n\pi^*$ and $S_0 \rightarrow {}^1\pi\pi^*$ Cotton effects of *s-trans*-enones with the sense of helicity in the enone chromophore, and Snatzke[31] showed that more skewed *s-trans*-enones characteristically have larger $\Delta\epsilon$ values in the $S_0 \rightarrow {}^1n\pi^*$ transition. From later studies it appeared that allylic axial substituents also affect the CD, both in the $S_0 \rightarrow {}^1\pi\pi^*$ region[32,33] and in the $S_0 \rightarrow {}^1n\pi^*$ region,[12b,33,34] particularly when the substituents are heteroatoms. From an empirical analysis of the CD data of a large number of α,β-enones of the cyclohexenone type, Burnett and Kirk[35] have confirmed the view[31d] that enone helicity controls the CD of the $S_0 \rightarrow {}^1n\pi^*$ band in the absence of strongly electron-donating or -withdrawing γ-axial substituents. Small $|\Delta\epsilon|$ values and bisignate Cotton effects in the $S_0 \rightarrow {}^1n\pi^*$ band of some cholest-4-en-3-one derivatives were attributed[35] to flattening of ring A. We therefore conclude that the two groups in Table I, distinguished on the basis of the absolute magnitude of g_{abs}, i.e., CD, correspond with enones with small twist (group I) and significant twist (group II), respectively.

The relationship between $S_0 \rightarrow {}^1n\pi^*$ CD and twist of transoid α,β-enones has been qualitatively described by Snatzke[26] as due to mixing of the oxygen nonbonding n-orbital with the 4-center π-HOMO in the nonplanar enone chromophore. This, exactly, amounts to our model of ${}^1n\pi^*$–${}^1\pi\pi^*$ coupling. Further support for the viability of our model, which predicts that $R(S_0 \rightarrow {}^1\pi\pi^*) = -R(S_0 \rightarrow {}^1n\pi^*)$, is the fact that in α,β-enones the sign of the

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CD in the $S_0 \rightarrow {}^1n\pi^*$ CD is almost universally[12a] found to be opposite to that in the $S_0 \rightarrow {}^1\pi\pi^*$ transition and that the degree of linear polarization in the two bands is similar.[9,13] At the same time, the observation that the CD in the two transitions is not conservative illustrates that our model is too simple—as expected. Firstly, a description of optical activity in terms of one ${}^1n\pi^*$ and one ${}^1\pi\pi^*$ state can only be qualitative: for a better description more extensive configuration interaction is imperative, certainly for the ${}^1\pi\pi^*$ state, since at wavelengths slightly lower than that of the $S_0 \rightarrow {}^1\pi\pi^*$ transition other bands are present.[35] Secondly, R is not determined by the C=C—C=O moiety alone; there must be contributions from the ring system in which it is contained[35] and from chirally disposed substituents.

Essentially, the g_{lum}/g_{abs} sign inversion may be thought to result from the $n\pi^*,\pi\pi^*$ level inversion in the triplet manifold as compared to the singlet manifold. An underlying assumption is that the matrix elements in a and b (cf. (16c) and (17c)) have similar values, which in turn presupposes that the spatial part of the wave functions of the singlet and triplet $\pi\pi^*$ state (and $n\pi^*$ state) are similar. This is nicely supported by the results of MRD–CI calculations on the parent enone acrolein.[36]

Comparison with Experiment. As argued previously, the enone phosphorescence studied here occurs, to a first approximation, from a ${}^3\pi\pi^*$ state and derives its intensity from ${}^1n\pi^*$ admixture. In enones that are nonplanar in the phosphorescent state, electronic T–T coupling ensures that this state acquires ${}^3n\pi^*$ admixture. To the extent that our four-level model for the description of the optical activity is adequate, such T–T coupling necessarily implies inversion of sign of g_{lum} as compared to g_{abs}. This situation is met with the enones of group II.

In the enones of group I, the generation of optical activity cannot be attributed to inherent twist of the chromophore. This implies that $R({}^3\pi\pi^* \rightarrow S_0)$ cannot in a simple way be related to $R(S_0 \rightarrow {}^1n\pi^*)$. Since in these enones the chromophore's planarity is retained in the ${}^3\pi\pi^*$ state (vide infra), electronic T–T coupling is essentially absent. However, vibronic coupling is not—as evidenced by the considerable amount of vibrational fine structure observed in g_{lum}. In fact, with, e.g., **9a** the "mirror-image" relationship between the $g_{abs}(\lambda)$ ($=\Delta A(\lambda)/A(\lambda)$) and $g_{lum}(\lambda)$ spectra suggests similar vibronic coupling effects in the phosphorescence and in the $S_0 \rightarrow {}^1n\pi^*$ absorption. The dips in the g_{lum} spectrum might well correspond to positions on the wavelength scale where vibronically induced $S_0 \rightarrow {}^1\pi\pi^*$ intensity is prominently present. This suggests a close analogy with the linear polarization spectra of planar aromatic ketones and heterocyclic nitrogen compounds.[37] The amount of fine structure in g_{lum} may tentatively be taken as a measure for the relative weight of vibronic vs electronic T–T coupling. For **7**, **8**, **12**, **15**, and **16**, where g_{lum} is practically devoid of structure, electronic coupling prevails, and for **9a** and **9b** the coupling is of the Herzberg–Teller type, while for the other enones both types of coupling may occur.

Obviously, T–T coupling not only affects the rotational strength of the phosphorescence transition but also affects dipole strength. Except for **6** and **14**, the triplet's radiative lifetime (τ/ϕ_P; cf. Table I) is considerably larger than 100 ms. The lifetime of **6** is short not because of T–T coupling but because the value of the matrix element $\langle {}^1n\pi^*|\mathbf{L}\cdot\mathbf{S}|{}^3\pi\pi^*\rangle$ is enlarged owing to the heavy bromine substituent at the enone chromophore. In **14** the smaller radiative lifetime (42 ms) might arise from more substantial T–T coupling than with the other enones. On an absolute scale, however, the coupling is small because in α,β-enones the radiative lifetime of a pure ${}^3n\pi^*$ state (about 1 ms) is at least 100 times smaller than that of a ${}^3\pi\pi^*$ state. This warrants that the emission of **14**—and a fortiori that of the other enones—is still of predominant ${}^3\pi\pi^*$ type.

The coefficient a (eq 17c), which plays a crucial role in our description of the optical activity associated with the phosphorescence, is a function of the helicity of the chromophore and of the T–T energy gap. A demanding confrontation of model and experiment would involve the comparison of two cases with the same conformation and different T–T gap. Such a situation might be experimentally realized if the gap can be significantly modified by the solvent. Unfortunately, our choice of solvents is severely restricted due to solubility and/or birefringence problems. Replacing EPA by MIP/MTHF as a solvent hardly affects the position of the $S_0 \rightarrow {}^1n\pi^*$ absorption and of the phosphorescence band. So, one must expect only a minor effect of solvent on the magnitude of the T–T gap as well. We can tentatively compare testosterone acetate (**2b**) and its 4-methyl derivative **5**: judged from the CD, the compounds may have similar conformations whereas the methyl substitution at the chromophore substantially enlarges the T–T gap. The drop of g_{lum} near the onset of the phosphorescence of **5** (no sign inversion of $g_{lum}(\lambda)$ near the 0–0 transition) is compatible with an important part of the T–T coupling being vibrationally induced. In this view, **5** constitutes a case where both types of T–T coupling are present. It is interesting that **5** is also on the borderline between group I and group II (cf. Table I) when using CD band shape as a criterion—the relative intensity of the first CD band being too small for a simple one-dimensional Franck–Condon contour.

Geometry in the ${}^3\pi\pi^*$ State. The above μ–$\mathbf{m}$ mechanism explains the sign pattern in the CD of twisted enones and is a fortiori relevant in the triplet manifold. It requires sign inversion of g_{lum} relative to $g(S_0 \rightarrow {}^1n\pi^*)$ while the chromophore's helicity is retained upon excitation. Thus, there is no need to invoke torsional distortion in the ${}^3\pi\pi^*$ state in order to explain the sign inversion. Moreover, distortion is unlikely also. First, in the enones of group II, the sign inversion occurs systematically. This would imply that there is a one to one relation between the sense of twist $\phi(C-C_\alpha)$ in the ground state (prevailing the CD) and that of the distortion $\phi(C_\alpha-C_\beta)$ in the ${}^3\pi\pi^*$ state (expected to dominate the CPP). Such a relation might be conceivable within one structural class of enones (e.g., the 4-en-3-ones with natural configuration), but not in the heterogeneous collection studied here. Second, the smallness of g_{lum} in the enones of group I indicates that planarity persists in the ${}^3\pi\pi^*$ state. Yet, we see no stereochemical reasons why these species should oppose more effectively a tendency toward $C_\alpha=C_\beta$ distortion than those of group II. We conclude that, at least in glassy matrices at low temperatures, the spectroscopic ${}^3\pi\pi^*$ state of the α,β-enones does not exhibit appreciable distortion relative to the ground state.

This conclusion is in line with the latest spectroscopic work of Kearns c.s.[13c] where from the relatively high intensity of the 0–0 band in the ${}^3\pi\pi^* \rightarrow S_0$ phosphorescence of some steroidal enones (single crystals, 4.2 K) it is concluded that excited-state distortion must be small; their earlier conclusion[9,13a,b] that at low temperatures steroidal ${}^3\pi\pi^*$ enones are distorted is withdrawn.

From time-resolved EPR studies it was found recently[38] that monocyclic α,β-enones at 77 K in glasses exhibit largely twisted ${}^3\pi\pi^*$ states, the rotation about the $C_\alpha=C_\beta$ bond decreasing in the order 1-acetylcyclohexene, 2-cyclohexenone, 2-cyclopentenone. A correlation was established[38] between the magnitude of the distortion and the lifetime of the (nonphosphorescent) triplet species. Extrapolation—if allowed—to the steroidal enones with triplet lifetimes that are larger by a factor of 10^4 or more predicts very small distortions in the chromophore.

Upon excitation of monocyclic α,β-enones at room temperature, triplet intermediates are formed,[2] which are identified[39] with twisted ${}^3\pi\pi^*$ states in which the angle of torsion around the $C_\alpha=C_\beta$ bond and the triplet excitation energy vary as a function of the structural constraints of the system. For a series of 2-cyclohexenones, the lifetime of the transients correlates with the enone's ability to twist about the $C_\alpha=C_\beta$ bond,[40] a result that is completely in line with the findings of Yamauchi et al.[38] The transient species not only were found for monocyclic but also for

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polycyclic enones such as testosterone.

Torsional distortions in the ${}^3\pi\pi^*$ state of α,β-enones have been claimed to be a major deactivation pathway leading to disappearance of phosphorescence.[41] Tentatively, we suggest that the spectroscopic triplet state is separated from the relaxed one(s) observed at room temperature by an energy barrier. In the monocyclic enones studied by Yamauchi et al.,[38] the barrier then should be very low. In two bicyclic α,β-enones (in which the double bond is common to both rings) the study of the temperature and viscosity dependence of ϕ_P has led[22] to the conclusion that the barrier is predominantly viscosity-induced. Our experiments on the temperature dependence of ϕ_P of the enones also indicate the existence of a barrier. Interestingly, the fact that $\phi_P(T)$ of **2a** in EPA and in the much more viscous glycerol are about equal shows the absence of a viscosity effect and suggests that the barrier is of intrinsic nature.

Concluding Remarks

CPP turns out to be a useful technique to distinguish ${}^3\pi\pi^*$ from ${}^3n\pi^*$ states, and it supplements the arsenal of already existing techniques. It is gratifying that the inherent sensitivity of optical activity toward molecular structure—long exploited to probe ground-state conformation and, more recently, the geometry of the lowest excited singlet state[42]—can also be used to study the phosphorescent triplet state.

In view of the many approximations used, our explanation of the CPP data of α,β-enones is tentative and further investigations should be made. An essential feature of our model is the strong dependence of g_{lum} on the magnitude of the T–T gap and on the twist in the chromophore. It would be interesting to study the relationship quantitatively with enones that are more rigid and have larger angles of twist than the compounds described here.

The enhancement of optical activity by T–T coupling opens other interesting possibilities. For instance, the mere fact that g_{lum} values of ${}^3\pi\pi^*$ phosphorescences can be very high can be exploited in the study of racemization rates[43] and energy-transfer processes[44] in the triplet state.

Further, in the ${}^3\pi\pi^*$ state a planar α,β-unsaturated ketone with a very small T–T gap might adopt a twisted conformation due to the pseudo-Jahn–Teller effect. One of the enantiomeric twisted conformers might be stabilized in a chiral solvent.

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Registry No. 1a, 63975-59-7; **1b**, 4087-39-2; **2a**, 58-22-0; **2b**, 1045-69-8; **2c**, 57-83-0; **2d**, 601-57-0; **3**, 71-58-9; **4**, 604-26-2; **5**, 1923-21-3; **6**, 3702-37-2; **7a**, 434-22-0; **7b**, 1425-10-1; **8**, 51-98-9; **9a**, 571-41-5; **9b**, 3986-85-4; **10**, 571-45-9; **11**, 897-03-0; **12**, 988-19-2; **13**, 1449-05-4; **14**, 130798-68-4; **15**, 979-02-2; **16**, 982-06-9.

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Examination of Allyl Radical Excited-State Dynamics and Ground-State Vibrational Frequencies by Ultraviolet Resonance Raman Spectroscopy

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Abstract: The first Raman spectra of the allyl radical have been obtained. The intensities of the observed Raman spectra indicate excited-state dynamics consistent with a disrotatory photoisomerization of the allyl radical to form a cyclopropyl radical. Prior to this work, direct examination of the photoisomerization pathway was not possible due to limitations of the techniques applied. The ground-state vibrational frequencies observed are found to be in excellent agreement with recent theoretical calculations suggesting a reassignment of the literature infrared frequencies. This work demonstrates that resonance Raman spectroscopy is a powerful method for examination of gas-phase free radicals.

Introduction

The allyl radical is the simplest conjugated hydrocarbon radical. It is an important intermediate in many photochemical reactions and a proposed intermediate for soot formation in hydrocarbon combustion.[1] Though numerous theoretical[2-4] and experimental investigations[5-11] have been performed on the allyl radical, there remain several discrepancies between the experimental and theoretical ground-state frequencies for this system. The ground-state vibrational frequencies of the allyl radical have been experimentally examined by Oakes and Ellison,[5] Maier et al.,[6] Sappey and Weishaar,[7] and Hudgens and Dulcey.[8] Maier and co-workers utilized matrix isolation techniques to obtain the infrared spectra of the allyl radical. However, Maier et al. had difficulties assigning their matrix spectra due to spectral congestion and overlapping bands from secondary photoproducts. Sappey and Weishaar[7]

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