

Measurement of the Optical Activity of Triplet-Singlet Transitions. The Circular Polarization of Phosphorescence of Camphorquinone and Benzophenone

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Abstract: The optical activity of chiral molecules in their triplet states is reflected in the circular polarization of the phosphorescence emitted by these molecules. Molecular conformations in the triplet state can thus be studied in much the same way as the conformations in the ground state and in the first excited singlet state, S_1 , are studied by circular dichroism and circular polarization of fluorescence, respectively. The instrument for the measurement of circular polarization of phosphorescence is a modified version of the one used for the measurements of circular polarization of fluorescence. It allows cooling of samples to the low temperatures required for phosphorescence measurements and avoids artifacts which originate in linear polarization of emission from the rigid samples. Two phosphorescent carbonyl compounds have been studied under a variety of experimental conditions. The inherently chiral D-camphorquinone showed very large differences between the optical activities of its $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transitions. Effects of solute concentration and of the composition of the solvent glass on the circular polarization of phosphorescence of camphorquinone are presented. The optical activity induced in the triplet-singlet transition of benzophenone and acetophenone by the presence of L-menthol was measured and found to be markedly larger in the former ketone. The optical activity induced in the phosphorescence of benzophenone increased monotonously with the menthol concentration. The data are compatible with the formation of a 1:1 complex between the two molecules with an association constant of 1.69 M^{-1} . The optical activity induced in benzophenone by L-menthol was found to be very sensitive to the solvent used. This may be due to differences in the conformations assumed by benzophenone in the various solvents. The marked differences observed between the optical activity in the phosphorescence and in the fluorescence spectra of camphorquinone may originate in differences between the conformations of the molecule in the T_1 and S_1 states and in inherent differences between the optical activity of triplet-singlet and singlet-singlet transitions.

Introduction

The optical activity of a compound is customarily measured by the circular dichroism exhibited by its various absorption bands, i.e., by the difference in the absorption intensity of left-handed and right-handed circularly polarized light. From the practical point of view such measurements are not feasible if the absorption intensity is extremely weak. Furthermore, for characterization of the optical activity of a given transition, it is desirable, and sometimes essential if the transition is weak, that the transition be spectrally isolated from other transitions. Both of these requirements make it practically impossible to routinely study the optical activity of singlet-triplet transitions by CD,¹ since they are extremely weak as a rule and are often masked by much more intense overlapping singlet-singlet transitions. This is especially so in the case of organic molecules. It may be noted that measurements of optical rotatory dispersion, ORD, practically miss completely the weak singlet-triplet transitions, since ORD at any given wavelength has contributions from all absorption bands weighted among other factors by their intensity.

In contrast to the inherent limitations of CD in the study of the optical activity of singlet-triplet transitions, the study of the circular polarization of the luminescence, CPL, involving such transitions, i.e., circular polarization of phosphorescence, CPP, seems to offer some obvious advantages. CPL is the emission analogue of CD in so far as both characterize the optical activity of the electronic transition under discussion, except that CPL relates to the molecular conformation in the electronically excited state, whereas CD relates to the molecular conformation in the ground state.¹⁻⁴ As long as the phosphorescence is observed, it is in principle as amenable to study by CPL as is fluorescence of comparable intensity. Moreover, it is by far easier to isolate the phosphorescence from other emissive transitions than to separate

the corresponding absorption processes, because there are fewer transitions observed in emission than in absorption, they are usually better resolved spectrally, and moreover one can utilize the differences in lifetime to resolve phosphorescence from prompt fluorescence, an option which is not available in absorption processes.

A few studies were carried out in the past on the CPL of forbidden transitions, most of them on optically active chelated metal ions. Thus, the CPL of Tb^{3+} was used to study the binding of this ion to a few proteins and to low molecular weight ligands.⁵⁻⁸ The CPL of $\text{Ru}(\text{bpy})_3^{2+}$ (bpy = bipyridyl) was used to demonstrate both singlet-singlet and triplet-singlet transitions in the emission of this compound.⁹ The spin-forbidden transition of the type doublet \rightarrow quartet was studied by CPL in the compound $\text{Cr}(\text{ethylenediamine})_3^{3+}$.¹⁰ To our knowledge the only CPL measurement on the phosphorescence of an organic molecule has been done on thiocamphor by Dekkers.¹¹ Besides their intrinsic interest, such measurements may be of importance in the study of photochemical reactions since many of these proceed via the triplet excited state, and, as explained above, the circular polarization of the phosphorescence is related to the molecular conformation in this state.

In the following we present studies of the CPP of the intrinsically chiral camphorquinone and of benzophenone in which chirality was induced by the presence of L-menthol in the solution. To obtain good phosphorescence yields, we carried out the measurements in frozen glasses at low temperatures. These conditions presented some experimental difficulties which had to be solved. Since most CPP measurements are likely to require the above

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experimental conditions, the experimental and instrumental procedures we have used will be presented in some detail.

Experimental Section

Materials. DL-Camphorquinone was purchased from Aldrich and purified by recrystallization from petroleum ether. D-camphorquinone, a product of Eastman Organic Chemicals, was repeatedly recrystallized from petroleum ether, and was finally purified by sublimation under vacuum. Acetophenone was purified by repeated vacuum distillation while benzophenone was zone refined. L-menthol (BDH, >99%) and DL-menthol (Aldrich, 99%) were used without further purification. 1-propanol was of analytic quality while all other solvents were of spectrograde.

Methods. Absorption spectra at room temperature were studied by using a Zeiss Model PMQ II spectrophotometer. Measurements of absorption spectra at low temperatures were done by using a Cary 14M-50 spectrophotometer modified to allow the controlled cooling of the sample cell. This cooling technique was also used in measurements of low-temperature luminescence, CD, and CPP spectra and will be described in detail below.

Corrected emission spectra were recorded both at room temperature and at low temperature by using a Perkin-Elmer MPF-44A fluorimeter. CD spectra at room temperature as well as that of cooled samples were recorded on a Cary 60 spectropolarimeter equipped with a 6002 CD accessory.

Instrument for the Measurement of CPP. The instrument used for CPP measurements is essentially like that used for the measurement of circularly polarized fluorescence,¹² except for some additions and modifications which were introduced in order to tackle specific problems which are associated with the phosphorescence measurement.

(a) **Cooling of Sample.** We followed the technique described by Fischer.¹³ The sample cell is placed in a hollow copper block through which liquid nitrogen can be pumped. This copper block has openings to allow the passage of excitation and emission light and is inserted into a silica Dewar flask which has strainless optical grade windows. The windows are opposite to one another so that the emitted light is collected at 0° to the excitation beam. This geometry permits the elimination of linear polarization of the emitted light if the excitation light is unpolarized. This is especially important in CPP measurements since depolarization by rotatory diffusion of the emitting molecules is not possible in the frozen glasses used as solvents in these measurements.

As mentioned above the cooling of the sample is by liquid nitrogen which is pumped through the hollow copper block. The flow of nitrogen is controlled by a magnetic valve regulated by a Wheelock Capacitrol (Model 472) thermoregulator using an iron constantan thermocouple for temperature sensing. Vapor condensation on the external optical windows was avoided by warming the windows by a heating coil. It takes about 10 min for the sample to reach thermal equilibrium with the cooling system. The temperature stability is better than 1 °C.

(b) **Depolarization of the Incident Light.** This was found to be essential in order to obtain accurate measurements of the circularly polarized component in the emitted light. The reason for this is twofold. First, any strain in the frozen glass used as solvent in the studies of phosphorescence may render linearly polarized light into elliptically polarized light, which will give a signal at the fundamental frequency of the elastooptic modulator (about 50 KHz in our case). Second, although linearly polarized light should theoretically be modulated at double the frequency of the vibration of the elastooptic modulator, it was found that in all four of the modulators available to us linear polarization yielded an appreciable signal (a few percent as large as that at the first overtone) at the fundamental frequency. This had been noted before¹⁴ and was attributed to artifacts in the phase-sensitive amplifier, which supposedly yielded an artificial signal at the fundamental frequency when a signal was fed in at the overtone. We have found, however, this not to be the case, since upon rotation of the modulator around its optical axis, orientations could be found at which the signal at the overtone frequency vanished (supposedly due to the coincidence of the plane of polarization with one of the principal axes of the modulator); still the signal at the fundamental did not vanish. Static strain in the optical element of the modulator was found to be negligible and thus cannot be the cause of the above artifact. This artifact was observed when either optical or dichroic polarizers were used in conjunction with the elastooptic modulator. The reason for the above behavior of the modulator is far from being clear. In any case, to avoid such artifacts, we very carefully depolarized the excitation light by using a Lyot double-plate calcite polarization scrambler (a product of Karl Lambrecht). The thicknesses of the plates were

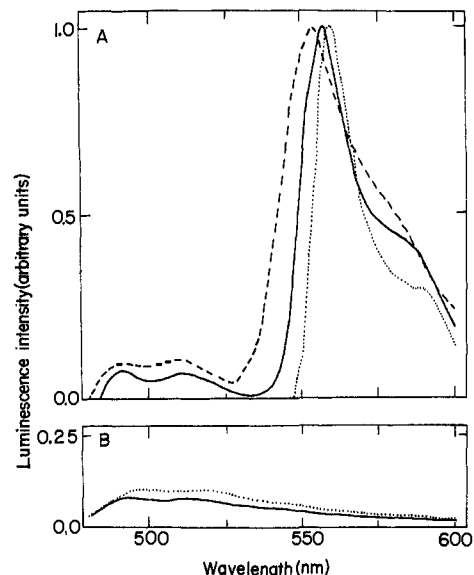


Figure 1. Emission spectra of D-camphorquinone under various conditions. (A) Low-temperature luminescence: (—), emission of a 10^{-2} M solution in TFE-MeOH (1:1) at -150 °C; (---), luminescence of a 3×10^{-2} M solution in TFE-MeOH (1:1) at -150 °C; (···), 10^{-2} M D-camphorquinone in 1-propanol-2-propanol (1:1) at -160 °C. The spectra were all brought to the same peak height. (B) Room-temperature luminescence of D-camphorquinone: (—), 10^{-2} M solution in TFE-MeOH (1:1); (···), 10^{-2} M solution in 1-propanol-2-propanol (1:1). The luminescence intensity of each solution at room temperature is drawn to the same scale as the corresponding spectrum at low temperature to allow direct comparison of the spectra. The excitation wavelength in all cases was 440 nm.

2 and 4 mm. This depolarizer was found to be adequate with the quasi-monochromatic excitation light of 30–40 nm used in the CPP instrument. To ascertain that artifacts of the above kind were negligible, racemic mixtures of the substance tested were run under conditions identical with those used for the active compound. The racemic mixtures yielded zero readings for the circularly polarized component of the phosphorescence. It should be noted that if the sample can be excited at such a wavelength at which the resultant phosphorescence has no linear polarization, artifacts due to linear polarization are completely circumvented.

(c) **Separation of Phosphorescence from the Fluorescence.** In the studies to be described fluorescence did not interfere with the studies on the phosphorescence either because the fluorescence intensity was negligibly small or because it was spectrally resolved from the phosphorescence. In cases where the fluorescence and phosphorescence do overlap spectrally, it should be possible to separate them in principle by proper chopping techniques utilizing their vastly different lifetimes. In practice one should be careful to avoid interference between this chopping procedure and the modulation technique inherent in the measurement of CPP.

(d) **Preparation of Frozen Glasses for CPP Measurements.** Solvent mixtures for the preparation of glasses were chosen to yield matrices which are free of strain and completely clear. To minimize effects of strain, we used optical sample cells of relatively short optical path (1–2 mm). Care was taken to cool the samples in different experiments at the same rate to avoid the possibility that in different experiments the solute molecules were trapped in different distribution ratios of possible conformers. The cooling rate was kept at 40 °C/min until a temperature about 20 °C above the desired one was reached and was then reduced to about 7 °C/min.

The concentrations quoted are those measured at room temperature. The concentrations at low temperature are probably higher due to increase in density; these changes were, however, difficult to estimate quantitatively.

Results and Discussion

The circular polarization of phosphorescence was measured for two compounds: D-camphorquinone and benzophenone in which chirality was induced by adding L-menthol to the solvent mixture. The phosphorescence intensity is quite significant for these compounds when dissolved in glasses at low temperatures, and it is free from interference by fluorescence under these conditions.

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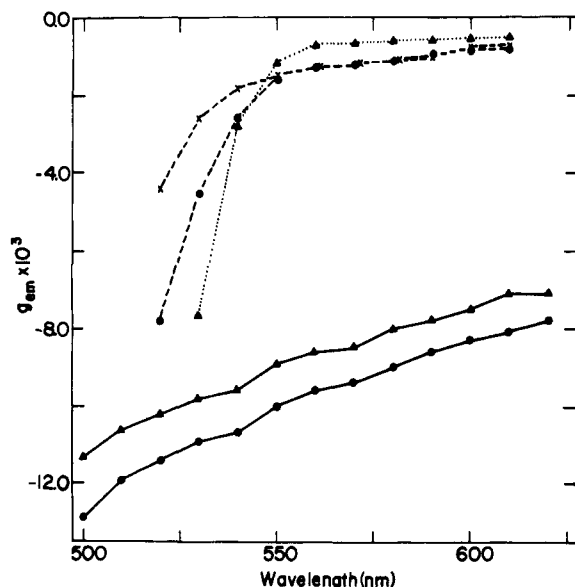


Figure 2. CPL spectra of D-camphorquinone at room temperature (—), at $-150\text{ }^{\circ}\text{C}$ (---), and at $-160\text{ }^{\circ}\text{C}$ (···): (●), $4.5 \times 10^{-3}\text{ M}$ or 10^{-2} M in TFE-MeOH (1:1); (▲), $4.5 \times 10^{-3}\text{ M}$ or 10^{-2} M in 1-propanol-2-propanol (1:1); (×), $3 \times 10^{-2}\text{ M}$ in TFE-MeOH (1:1). The luminescence was excited at 440 nm and the CPL recorded by using a spectral resolution of 16 nm. The experimental error in the g_{em} values is $\pm 10^{-4}$ for the spectra at room temperature and $\pm 2 \times 10^{-4}$ for the low temperature data.

D-Camphorquinone. The emission spectrum of D-camphorquinone in a trifluoroethanol-methanol (TFE-MeOH) (1:1, v/v) mixture is shown in Figure 1. At room temperature the emission is predominantly fluorescence. Some phosphorescence emission which showed up as a shoulder at the red part of the emission band, when glycerol served as solvent.¹⁵ Such a shoulder is not evident in TFE-MeOH as solvent, but the presence of small amounts of phosphorescence at the red part of the spectrum at room temperature cannot be excluded. At $-150\text{ }^{\circ}\text{C}$ the picture is entirely different. Two distinct regions of emission are evident, the dividing wavelength being 530–540 nm. Below 530 nm there is a relatively weak double-peaked band (maxima at 492 and 513 nm) due to fluorescence; above 540 nm there is a much stronger band with a peak at 556 nm, due to phosphorescence.

The circular polarization of the luminescence light is presented in Figure 2. The degree of circular polarization is expressed by the emission anisotropy factor, g_{em} , defined as $\Delta I/(I/2)$, where ΔI is the intensity of the circularly polarized component in the emitted light (ΔI is defined as positive when the light contains an excess of left-handed circular polarization), and I is the total intensity of the emitted light.³ g_{em} is analogous to the absorption anisotropy factor $g_{ab} = \Delta\epsilon/\epsilon$, and should equal g_{ab} for transitions involving the same quantum levels if the molecular geometry is the same in the ground and emitting states.³ The absorption spectrum of D-camphorquinone and the spectrum of g_{ab} obtained under a variety of conditions are presented in Figure 3, for the spectral range of 400–500 nm.

A few features of the spectra presented in Figures 2 and 3 are worth noticing. The absolute values of g_{ab} and g_{em} at room temperature are quite large, being more than 0.01, which is most probably due to the fact that the transitions involved are not strong; such transitions may indeed assume large values for their anisotropy factors.³ At room temperature g_{ab} at the red edge of the absorption spectrum is quite close in value to g_{em} at the blue edge of the emission band. Given that both of these spectral ranges relate to the same singlet-singlet transition, the above result is understandable if one assumes that there is not a marked change in the molecular geometry upon excitation to the first singlet

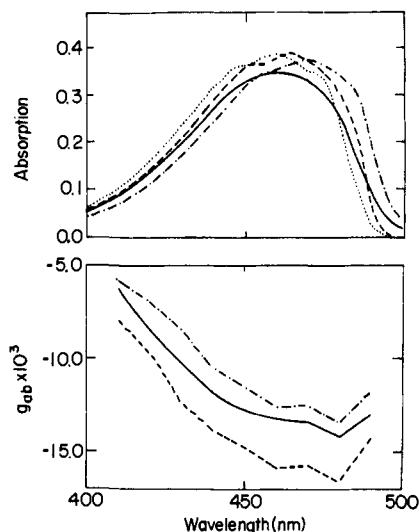


Figure 3. Absorption (upper part) and CD spectra (lower part) of D-camphorquinone under various conditions: (—), $9.3 \times 10^{-3}\text{ M}$ in TFE-MeOH (1:1) at room temperature; (---), $9.3 \times 10^{-3}\text{ M}$ in TFE-MeOH (1:1) at $-150\text{ }^{\circ}\text{C}$; (···), $3 \times 10^{-2}\text{ M}$ in TFE-MeOH (1:1) at $-150\text{ }^{\circ}\text{C}$, normalized at the peak to the same height as the $9.3 \times 10^{-3}\text{ M}$ solution; (-·-·), $1.1 \times 10^{-2}\text{ M}$ in 1-propanol-2-propanol (1:1) at room temperature. The experimental error in the g_{ab} values is $\pm 5 \times 10^{-4}$ and is due mainly to the low optical densities of the samples.

excited state. Arnett et al.¹⁶ studied the excited electronic states of several α -dicarbonyls and concluded that in cases where the ground state is twisted there is a tendency to assume a planar configuration in the S_1 or T_1 state. As mentioned above our results indicate that this is not the case for the S_1 excited state of camphorquinone.

The most conspicuous feature in Figure 2 is the very large difference in the values of g_{em} of camphorquinone measured at room temperature and at $-150\text{ }^{\circ}\text{C}$ in the spectral range above 540 nm. The value of g_{em} at the low temperature is by about 1 order of magnitude smaller than its value at room temperature. In contrast, the change in g_{ab} upon going from room temperature to $-150\text{ }^{\circ}\text{C}$ is relatively small, showing an increase of about 10–15% (see Figure 3). Thus, the ground-state conformation does not seem to be highly sensitive to the above temperature change. The very large difference in g_{em} between room temperature and $-150\text{ }^{\circ}\text{C}$ is of course due to the fact that different electronic states participate in the emission process at the two temperatures, i.e., singlet-singlet and triplet-singlet states, respectively. The triplet-singlet transition assumes its intensity and rotatory strength by spin-orbit coupling of the triplet state to a variety of excited singlet states and by coupling of the ground-singlet state to a variety of excited triplet states. The low overall value obtained for g_{em} of the phosphorescence is thus the consequence of the particular coupling scheme which involves strong coupling to intense transitions, favoring on the whole low values for g_{em} . There is also the possibility of partial cancelling of contributions of opposite signs resulting from different coupling terms. In addition to the above the molecular conformations in the excited singlet and triplet states are not expected to be the same,¹⁶ which may be an additional cause for the marked differences between the values of g_{em} in the fluorescence and phosphorescence. The resolution of the various contributions will require extensive theoretical studies of the optical activity of the camphorquinone system.

The steep change in g_{em} at the low temperatures at wavelengths below 540–550 nm is probably due to increasing contributions of fluorescence to the emitted light. At the spectral resolution of our measurements, some contribution of fluorescence is possible already at 540 nm.

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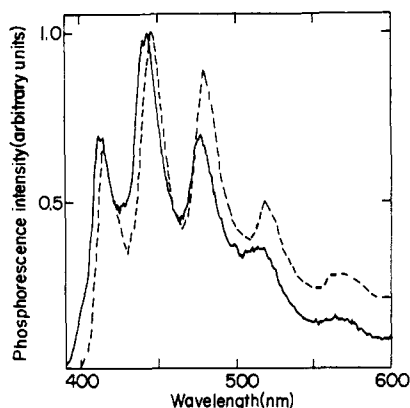


Figure 4. Phosphorescence spectra of benzophenone in TFE-MeOH (1:1) glass at $-150\text{ }^{\circ}\text{C}$: (---), 1.84×10^{-2} M benzophenone; (—), 1.05×10^{-2} M benzophenone in the presence of 1.95 M L-menthol. The spectra are normalized at the peak. Excitation wavelength was 280 nm.

The variation of g_{em} with wavelength in TFE-MeOH glass at $-150\text{ }^{\circ}\text{C}$ was investigated for three concentrations of camphorquinone (4.5×10^{-3} , 10^{-2} , and 3×10^{-2} M). While the same CPL spectrum was obtained for 4.5×10^{-3} and 10^{-2} M, a smaller change in g_{em} with decreasing wavelength was observed for the solute at the high concentration. Further investigation of the high concentration revealed a blue shift in the absorption spectrum and marked changes in the emission spectrum, the most conspicuous of which is the enhancement of the phosphorescence at the expense of the fluorescence. In particular the smaller relative contribution of the fluorescence to the emission in the 520–540-nm region readily explains the behavior of the anisotropy factor in this case. The results obtained for 3×10^{-2} M camphorquinone can be accounted for by aggregate formation at this concentration. Such aggregate formation is known to enhance the phosphorescence at the expense of the fluorescence.¹⁷ Similar results were obtained in 1-propanol-2-propanol glass at $-160\text{ }^{\circ}\text{C}$.

The effects of the solvent on the g_{em} spectra of camphorquinone, which are shown in Figure 2, are worth noting. At room temperature the differences between the anisotropy factors in 1-propanol-2-propanol mixture and in TFE-MeOH are about 10–15%. At low temperature the spectral behavior is more complex. Across the phosphorescence band the values of g_{em} in TFE-MeOH are larger than those in the propanol glass by a factor of 1.5–2, while at the short wavelengths region where the emission is predominantly due to fluorescence the anisotropy factor in the propanol glass assumes the larger values. The two spectra cross at 543 nm. It should be noted that while at room temperature the g_{em} of camphorquinone fluorescence in TFE-MeOH is larger than in the propanol mixture, the scheme is reversed at low temperature. This change, as well as the differences that exist between the g_{em} values (both in the fluorescence and phosphorescence) of samples in the two glasses, indicates that the conformation of the rigid camphorquinone molecule may be influenced both by the solvent and by the temperature.

Benzophenone in Solutions Containing L-Menthol. The induction of optical activity in the $n-\pi^*$ transition of achiral carbonyl-containing molecules in the presence of chiral molecules in the solution has been investigated by CD.¹⁸ Two possible mechanisms have been proposed for this kind of induction of optical activity:¹⁹ (a) the formation of a chiral network by the chiral molecules, which exerts a time-averaged dissymmetric potential on the carbonyl

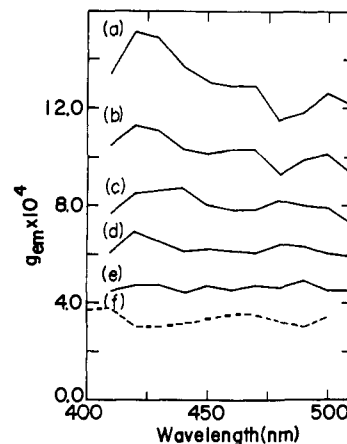


Figure 5. Circular polarization of phosphorescence spectra of acetophenone and of benzophenone in a TFE-MeOH (1:1) glass at $-150\text{ }^{\circ}\text{C}$ in the presence of various concentrations of L-menthol: (a) 6.7×10^{-2} M benzophenone-1.98 M L-menthol; (b) 8.0×10^{-2} M benzophenone-1.18 M L-menthol; (c) 8.9×10^{-2} M benzophenone-0.66 M L-menthol; (d) 9.2×10^{-2} M benzophenone-0.46 M L-menthol; (e) 9.6×10^{-2} M benzophenone-0.26 M L-menthol; (f) 1.4×10^{-2} M acetophenone-1.98 M L-menthol. The luminescence of benzophenone was excited at 280 nm while that of acetophenone was excited at 300 nm. The experimental error in g_{em} is $\pm 1 \times 10^{-4}$, and the spectra were recorded with a bandwidth of 16 nm.

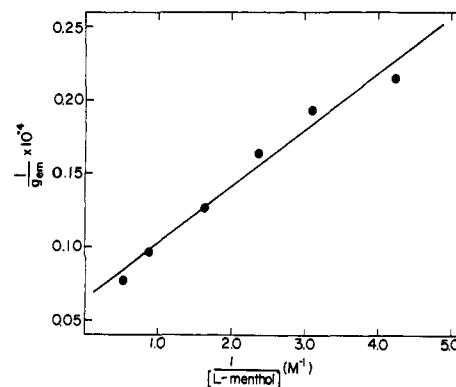


Figure 6. A plot of the reciprocal of the emission anisotropy factor of benzophenone at 460 nm (data taken from Figure 5) vs. the reciprocal of menthol concentration. The linear dependence indicates the formation of a 1:1 complex between the two species. The association constant, evaluated by means of eq 1, was found to be 1.69 M^{-1} .

chromophore, either by hydrogen bonding or by dipole-dipole interactions; (b) preferential solvation of some chiral configurations of the carbonyl-containing molecule, which renders it optically active. In the following we describe measurements on the optical activity of benzophenone and acetophenone induced by L-menthol as revealed in their phosphorescence.

The phosphorescence spectrum of benzophenone in a TFE-MeOH (1:1, v/v) glass at $-150\text{ }^{\circ}\text{C}$ is presented in Figure 4. The emission is highly structured exhibiting five peaks. In the presence of 1.95 M of L-menthol a similar spectrum is obtained; there is, however, a small shift of about 2 nm to the blue, and the intensity in the blue part of the spectrum is enhanced relative to that in the red part.

The CPP spectrum of benzophenone in the presence of L-menthol at various concentrations is presented in Figure 5. The solvent was TFE-MeOH (1:1, v/v) at $-150\text{ }^{\circ}\text{C}$. It is evident that the optical activity increases monotonously with the menthol concentration at the range studied (0.26–1.98 M). Acetophenone also exhibits optical activity in its phosphorescence in the presence of L-menthol; under equal conditions the induced activity is, however, appreciably smaller (by about fivefold) in acetophenone than in benzophenone. It may be noted that g_{em} is not strictly constant across the emission band. This may be rationalized as due to spin-orbit coupling of the triplet state to some singlet states

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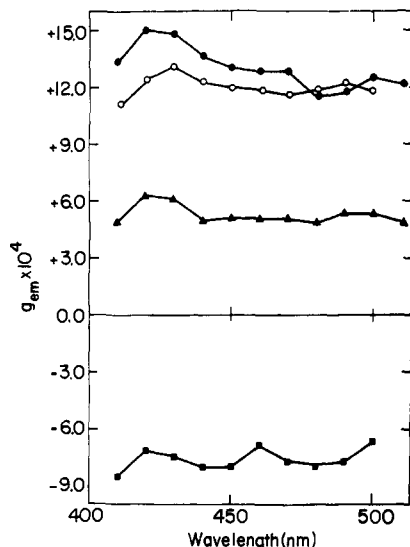


Figure 7. Solvent and temperature effects on the circular polarization of phosphorescence of benzophenone induced by L-menthol. CPP spectra at $-150\text{ }^{\circ}\text{C}$ were measured under the following conditions: (●), 6.7×10^{-2} M benzophenone–1.98 M L-menthol in TFE–MeOH (1:1) glass; (▲), 6.5×10^{-2} M benzophenone–1.96 M L-menthol in EtOH–MeOH (1:1) glass; (■), 6.6×10^{-2} M benzophenone–1.98 M L-menthol in ether–2-propanol (3:1) glass. CPP at $-130\text{ }^{\circ}\text{C}$ was measured for 6.7×10^{-2} M benzophenone–1.98 M L-menthol in TFE–MeOH (1:1) glass (○). The excitation wavelength in all cases was 280 nm. The experimental error in g_{em} is $\pm 1 \times 10^{-4}$ and the spectral resolution 16 nm.

of weak radiative coupling to the ground state. Such transitions show vibronic details in their anisotropy spectra.³

While the exact mechanism of the induction of optical activity in benzophenone by menthol is not easy to determine unequivocally, it seemed of interest to check whether the data presented in Figure 5 are compatible with the formation of stoichiometric complexes between the molecules of these compounds. If a one-to-one complex is formed, eq 1 holds, where α is a constant and K is the association constant.

$$1/g_{em} = \frac{1}{\alpha K} \frac{1}{[\text{menthol}]} + 1/\alpha \quad (1)$$

Thus, a plot of $1/g_{em}$ vs. $1/[\text{menthol}]$ should yield a linear relationship. This was indeed found to be the case (see Figure 6). From this plot an association constant of 1.69 M^{-1} (at $-150\text{ }^{\circ}\text{C}$) was calculated. It may be noted that a similar value for the association constant between cyclohexanone and menthol (in

methanol solutions) was found by Noack at room temperature by CD measurements.^{18c} It is quite probable that in our measurements at $-150\text{ }^{\circ}\text{C}$ the value derived for the association constant does not apply to this temperature but rather to some higher temperature, since the rate of reaching equilibrium in the glass at low temperature may be rather slow. In any case, while the above results are compatible with the idea of formation of a one-to-one complex between the benzophenone and menthol molecules, they do not prove it.

The effect of the solvent on the optical activity induced in benzophenone by L-menthol is illustrated in Figure 7. As is seen in this figure, the induced optical activity is appreciably smaller (by 2.5-fold) in an ethanol–methanol (1:1, v/v) solvent than in the TFE–MeOH (1:1, v/v) solvent. In ether–2-propanol (3:1, v/v) the g_{em} even changes sign. It is conceivable that the mutual orientation of the two phenyl rings which is a dominant factor in determining the optical activity of this molecule is quite sensitive to the solvent used. The temperature in the range of -130 to $-150\text{ }^{\circ}\text{C}$ was found to have relatively little effect on the optical activity (see Figure 7). Unfortunately a wider range of temperatures could not be studied due to technical difficulties with the glasses used.

Optical activity of singlet–singlet transitions, as revealed by CD and by circular polarization of fluorescence, has been extensively studied and applied to a large number of chiral systems. The theoretical basis of these two spectroscopic phenomena has been developed, making it possible to correlate the experimental results with molecular conformations and with the details of the electronic transitions involved. The results discussed in the present study relate to triplet–singlet transitions of carbonyl compounds. The marked changes found between the CPP and the circular polarization of fluorescence (or CD) spectra may originate in differences of molecular conformation between S_1 and T_1 states or be due to inherent properties of optical activity of triplet–singlet transitions. Also the origin for the changes in g_{em} across the phosphorescence band is not clear. In symmetry-forbidden electronic transitions (like the singlet–singlet $n\pi^*$ transition of the carbonyl chromophore) which gain their small intensity by vibronic coupling such changes in g_{em} are expected from theoretical considerations.³ Triplet–singlet transitions, however, are forbidden by spin selection rules, and the effects of the latter on the anisotropy factor have yet to be evaluated. Obviously advancement in the theory of optical activity of triplet–singlet transitions is needed to enable a more thorough interpretation of the experimental results.

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