

liberate at least one-half a bromide ion apiece. Such behavior could be observed if the radicals from attack of Fe(III) on bromomalonic acid can disproportionate without further reaction with Fe(III) and if organic oxidation products generate radicals that can further attack bromomalonic acid.¹⁸ Alternatively, slow acid hydrolysis of the organic bromine species may occur rapidly enough to maintain a steady state bromide ion concentration greater than the critical value at which bromous acid formation becomes autocatalytic. Finally, bromous acid may react directly with bromomalonic acid so that autocatalytic generation is made somewhat more difficult.

Although these mechanistic fine points are not yet resolved, the main features of band migration are certainly well accommodated by eq 3 and 4.

Additional Comments. Winfree¹⁹ has clearly recognized two very different mechanisms by which oxidizing bands could propagate through a medium like this. If different regions oscillate at the same frequency but with different phase, or if frequencies are different in different regions because of gradients in concentra-

tion, temperature, etc., regions of oxidation would propagate even if there were no diffusion whatsoever. Winfree calls such propagation a "pseudo-wave," and it is this phenomenon which Kopell and Howard²⁰ have examined recently.

In the system we are studying here, oxidizing bands advance into a uniform medium that is marginally stable to homogeneous oscillation. Diffusion in the region ahead of the band front triggers the reaction that advances the oxidized region. Winfree calls such propagation a "trigger-wave."

Pseudo-waves may propagate at velocities greater than trigger-waves could move. However, a hypothetical system consisting of pseudo-waves moving more slowly than trigger-waves would propagate into the medium in front of each oxidizing region would evolve into one in which band velocities were determined by the trigger-wave mechanism.

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(20) N. Kopell and L. N. Howard, *Science*, **180**, 1171 (1973).

(18) J. J. Jwo, unpublished observations.

(19) A. T. Winfree in "Lecture Notes on Biomathematics," P. van den Driessche, Ed., Springer-Verlag, West Berlin, 1974, in press.

Circularly Polarized Luminescence Spectrum of Camphorquinone¹

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Abstract: The absorption, total luminescence, circular dichroism (CD), and circularly polarized luminescence (CPL) spectra of the α -diketone, *d*-camphorquinone, were measured in solution at room temperature. The CPL and lowest energy CD bands exhibit a near mirror-image relationship as do the total luminescence and lowest energy singlet-singlet absorption bands. The dissymmetry factors measured in the emission experiments are an order of magnitude smaller than those observed in the absorption experiments. These results lead to the conclusions that: (1) the chirality of the dicarbonyl group in the fluorescent state is the same as that in the ground state; (2) except for the dihedral twist angle (ϕ) in the dicarbonyl group, molecular structural parameters are similar in the ground and fluorescent states; (3) the dihedral twist angle (ϕ) is smaller in the fluorescent state than in the ground state; and (4) the fluorescent state and the singlet excited state responsible for CD and absorption in the 480-nm region are identical.

The chiroptical properties, circular dichroism (CD) and optical rotatory dispersion (ORD), have been of great value in obtaining information about the more subtle aspects of molecular stereochemistry and electronic structure. The signs and magnitudes of CD bands and of the Cotton effects observed in ORD spectra exhibit an extraordinary sensitivity to the stereochemical features of chiral systems in their electronic ground states. Furthermore, with the aid of theoretical models, the relative shapes, frequencies, and inten-

sities of CD bands have been used to elicit information about the spectroscopic states responsible for the chiroptical observables. In most cases, this information is qualitative and consists of the orbital nature and symmetries of the electronic, or vibronic, excited states connected to the ground state by direct radiative absorption. In accordance with the Franck-Condon principle, the symmetries of these states are defined with respect to the geometry and point-group symmetry of the molecular ground state. Neither CD nor ORD can provide information concerning the stereochemistry and electronic structure of thermally equilibrated or relaxed electronic excited states, or of excited states inaccessible by direct radiative absorption. Generally,

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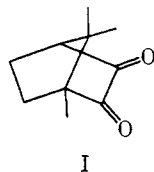
these "relaxed" electronic excited states are the precursors of photochemical processes and are the emitting states in luminescent systems. For this reason, their structural characteristics are of considerable interest in chemistry.

A method analogous to CD is available for studying the stereochemical and electronic structural features of chiral systems which exist in a luminescent electronic excited state. This method is referred to as circularly polarized luminescence (CPL) spectroscopy and involves measuring the differential intensities of left and right circularly polarized radiation in the spontaneous emission spectrum of a luminescent chiral system. Although several CPL measurements had been reported earlier in the literature,² the work of Oosterhoff and coworkers³ must be considered the pioneering effort in developing CPL as a useful spectroscopic technique for obtaining molecular structural information. More recently, Gafni and Steinberg⁴ also have reported construction of CPL instrumentation and have measured the CPL spectra of several chiral molecular systems.

We have constructed a high-sensitivity luminescence spectrophotometer with which it is possible to measure luminescence dissymmetry factors as small as $\sim 10^{-5}$.⁵ The luminescence dissymmetry factor is defined by

$$g(\text{lum}) = (I_L - I_R)/\frac{1}{2}(I_L + I_R) = \Delta I/I \quad (1)$$

where I_L and I_R are respectively the intensities of the left and right circularly polarized components of the luminescence. We report here the CPL spectrum of the chiral α -diketone system, *d*-camphorquinone (I).



Camphorquinone has been studied extensively as a model system for cisoid α -diketones. Perhaps the most thorough spectroscopic examination of this compound and several closely related structures was carried out by Charney and Tsai.⁶ Their objective was to identify and characterize the lower excited states of the molecule and thereby learn something of the interactions between the carbonyl moieties. In this extraordinarily thorough study, Charney and Tsai measured the unpolarized absorption and emission spectra of camphorquinone in solution at room temperature, in solution (solid glass) at liquid nitrogen temperature, and in pure solid form at liquid helium temperature. Additionally, they reported the infrared and Raman spectra of several isotopically substituted derivatives of camphorquinone and measured the CD spectrum of this system down to 180 nm.

(2) (a) B. N. Samojlov, *J. Exp. Theor. Phys.*, **18**, 1030 (1948); (b) M. S. Brodin and V. Ja. Reznichenko, *Ukr. Phys. J.*, **10**, 178 (1965); (c) O. Neunhoeffer and H. Ulrich, *Z. Elektrochem.*, **59**, 122 (1955).

(3) (a) C. A. Emeis and L. J. Oosterhoff, *Chem. Phys. Lett.*, **1**, 129 (1967); (b) H. P. J. M. Dekkers, C. A. Emeis, and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 4589 (1969); (c) C. A. Emeis and L. J. Oosterhoff, *J. Chem. Phys.*, **54**, 4809 (1971).

(4) (a) A. Gafni and I. Z. Steinberg, *Photochem. Photobiol.*, **15**, 93 (1972); (b) I. Z. Steinberg and A. Gafni, *Rev. Sci. Instrum.*, **43**, 409 (1972).

(5) A detailed description of our CPL instrumentation will be given in a later, more complete, report.

(6) E. Charney and L. Tsai, *J. Amer. Chem. Soc.*, **93**, 7123 (1971).

Charney and Tsai adopted a qualitative molecular orbital representation for the electronic excited states of the dicarbonyl moiety, and from this model they deduced selection rules regarding the magnetic dipole and electric dipole nature of transitions connecting dicarbonyl-localized excited states to the ground electronic state. On symmetry grounds, of course, all such transitions are both magnetic dipole and electric dipole allowed for the twisted cisoid (C_2) configuration of the dicarbonyl moiety. However, if the dihedral twist angle between the two C=O bonds is sufficiently small (e.g., $0-10^\circ$, where 0° represents the planar cis configuration), then C_{2v} selection rules might be expected to govern, in large part, the nature of the local dicarbonyl transitions. The absorption spectrum of I in cyclohexane solvent exhibits a relatively weak band with a maximum near 480 nm ($\epsilon_{\text{max}} \sim 40$), and the CD spectrum of a similar solution reveals a negatively signed band near 480 nm ($\Delta\epsilon_{\text{max}} \sim -0.48$).⁶ Charney and Tsai proposed that two different states are responsible for the absorption and CD in the 480-nm region. Both are derived from ${}^1n\pi^*$ dicarbonyl electronic configurations, but one transforms as the B irreducible representation (ir) in the C_2 point group and as the B_1 ir in the C_{2v} point group, and the other transforms as A in C_2 and as A_2 in C_{2v} . Adopting C_{2v} selection rules, transitions to the $A(A_2)$ excited state from the ground state are magnetic-dipole allowed but electric-dipole forbidden, whereas transitions to the $B(B_1)$ excited state are both electric-dipole and magnetic-dipole allowed (with non-parallel components for the electric and magnetic dipole vectors).

Charney and Tsai proposed that the absorption band in the 480-nm region be assigned to a ${}^1G(\text{ground state}) \rightarrow {}^1B(B_1)$ transition and that the negative CD band near 480 nm be assigned to a ${}^1G \rightarrow {}^1A(A_2)$ transition. Additionally, they estimated the splitting between ${}^1A(A_2)$ and ${}^1B(B_1)$ to be $\sim 1500 \text{ cm}^{-1}$ with the ${}^1B(B_1)$ state lying lowest. They also predicted that the ${}^1G \rightarrow {}^1B(B_1)$ transition would yield a positively signed, but weak, CD band in the absence of the stronger and negative CD band due to the ${}^1G \rightarrow {}^1A(A_2)$ transition. This latter prediction rests on the assumption that the two C=O bonds in the dicarbonyl group of I are twisted with a right-handed screw sense (P helix).



ϕ = dihedral twist angle

If the absorption and CD band assignments proposed by Charney and Tsai are correct, then the fluorescence spectrum of I can be assigned to the ${}^1B(B_1) \rightarrow {}^1G$ transition. Furthermore, if their qualitative model is correct in predicting the signs and relative magnitudes of rotatory strengths, then the CPL spectrum of I should exhibit a weak, positive band in the 480–560-nm spectral region, assuming no significant differences in geometry exist between the ground electronic state and the fluorescent state of the system. If the point-group symmetry of the dicarbonyl group differs in the ground and excited states (as would be the case if each $>C=O$ moiety became pyramidal in the excited state), or if the chirality of the dicarbonyl group differs (i.e., the dihedral twist angle has a different sign) in the two states,

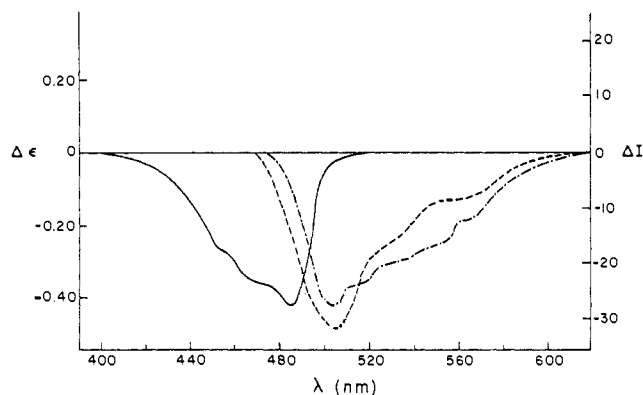
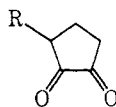


Figure 1. CD (—) and CPL (— · —) of *d*-camphorquinone in cyclohexane; CPL of *d*-camphorquinone in ethanol (---). ΔI is given in relative quanta per unit of frequency interval, and all spectra were taken at room temperature.

then of course the sign of the CPL cannot be predicted directly from the proposals of Charney and Tsai.

Hug and Wagniere⁷⁻⁹ and Richardson and Kreigh¹⁰ have carried out extensive molecular orbital calculations on several dissymmetric model diketone systems and concluded that for twist angles $|\phi| \leq 15^\circ$, the first two $n\pi^*$ singlet excited states are split in energy by an amount at least three times larger than that proposed by Charney and Tsai. The lowest energy $n\pi^*$ state in the cisoid glyoxal structure is calculated to be of B symmetry and the rotatory strength calculated for a transition to this state is >0 for a twist angle giving a right-handed screw sense (P helix). Richardson and Kreigh¹⁰ calculated the chiroptical properties of several structural isomers of II using an INDO-MO model and



II

R = CH₃, H

found the two lowest energy singlet $n \rightarrow \pi^*$ transitions around 440–460 and 275–290 nm. For P chirality of the twisted dicarbonyl group, the rotatory strength of the lowest lying transition was calculated to be negative and that of the higher energy transition was calculated to be positive.

Experimental Section

The CPL spectra were obtained with an instrument similar in design to the one described by Steinberg and Gafni.^{4b,5} The light emitted from the sample was analyzed alternately for left and right circular polarization at a modulation frequency of 50 kHz. The excitation was chopped at a frequency of 13 Hz. The electrical signal at the detector consists, therefore, of a large ac signal, I_t , which is proportional to the total emission intensity (independent of state of polarization) and is modulated at a frequency of 13 Hz, plus a small ac signal, I_c , which is modulated at 50 kHz and whose magnitude and phase carry the CPL intensity and sign variables. This signal is processed by two lock-in amplifiers operating in parallel and tuned at 13 Hz and 50 kHz, respectively. The total luminescence and CPL spectra are recorded simultaneously by a two-pen recorder. The luminescence dissymmetry factor (see eq 1)

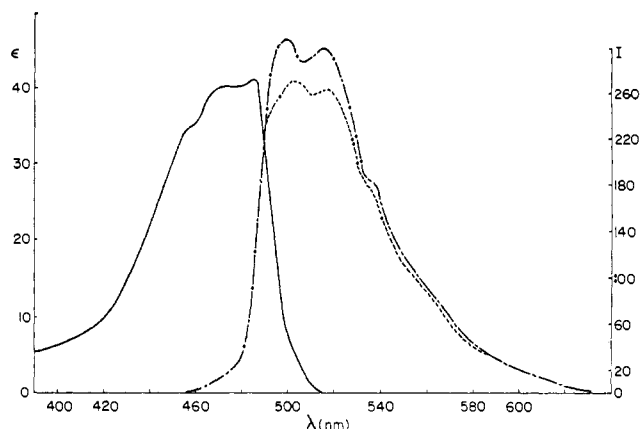


Figure 2. Absorption (—) and total luminescence (— · —) of *d*-camphorquinone in cyclohexane; total luminescence of *d*-camphorquinone in ethanol (---). I is given in relative quanta per unit of frequency interval, and all spectra were taken at room temperature.

was obtained as a function of wavelength by determining (CPL/total luminescence) at various wavelengths.

All CPL experiments were conducted on both *d*-camphorquinone and *dl*-camphorquinone. In all instances the racemic form gave a null CPL. The excitation wavelength was 446 nm, the excitation bandwidth was 100 Å, and the emission bandwidth was 50 Å. Samples of optical density 0.375 (at λ 446 nm) were used. The *d*-camphorquinone and *dl*-camphorquinone were obtained from the Aldrich Chemical Co. and were purified by vacuum sublimation.

The absorption spectra were measured on a Cary 14 spectrophotometer and the CD spectra were obtained with a Durrum-Jasco ORD/UV-5 instrument.

Results and Discussion

The CPL spectra of I in cyclohexane and in ethanol are shown in Figure 1 along with the CD spectrum of I in cyclohexane. The absorption and total luminescence spectra of I are shown in Figure 2. The most prominent features of these spectra are the near mirror-image relationships exhibited by the CPL and lowest energy CD bands and by the absorption and total luminescence spectra. The small, but nonzero, overlap and the similarity in shape between the absorption and luminescence spectra and between the CPL and CD spectra suggest (1) that the electronic state responsible for the CD in the 480-nm region is the emitting state in the observed CPL and (2) that molecular dimensions (bond lengths and bond angles) in the ground state and lowest lying singlet excited state are similar. Furthermore, if the same singlet excited state is responsible for both the CPL and the observed CD, then the spectra of Figure 1 suggest like chiralities for the ground state and fluorescent state of I. If the principal contribution to optical activity derives from a chiral distortion of the dicarbonyl moiety rather than from vicinal influences of the asymmetric centers in the ring system, like signs for the CD and CPL of Figure 1 imply that the dicarbonyl group is twisted with the same handedness (screw sense) in the ground state and lowest lying singlet excited state. That is, the sign of the dihedral twist angle ϕ is the same in the ground and first excited (singlet) states.

Assuming that the observed chiroptical properties arise primarily from inherent dissymmetry in the dicarbonyl moiety, the relative values of the luminescence and absorption dissymmetry factors can possibly provide information about the relative magnitudes of ϕ in

(7) W. Hug and G. Wagniere, *Theor. Chim. Acta*, **18**, 57 (1970).

(8) W. Hug and G. Wagniere, *Helv. Chim. Acta*, **54**, 633 (1971).

(9) W. Hug and G. Wagniere, *Helv. Chim. Acta*, **55**, 634 (1972).

(10) F. S. Richardson and H. Kreigh, unpublished results.

the ground and fluorescent states. The luminescence dissymmetry factor is defined in eq 1 in terms of the experimental observables, ΔI (CPL) and I (total luminescence). The absorption dissymmetry factor can be defined similarly in terms of $\Delta\epsilon$ (CD) and ϵ (total absorption)

$$g(\text{abs}) = (\epsilon_L - \epsilon_R)/\frac{1}{2}(\epsilon_L + \epsilon_R) = \Delta\epsilon/\epsilon \quad (2)$$

where ϵ_L and ϵ_R are respectively the molar extinction coefficients for left and right circularly polarized light. These experimentally defined quantities, $g(\text{lum})$ and $g(\text{abs})$, are, in general, functions of frequency since ΔI , I , $\Delta\epsilon$, and ϵ vary in magnitude over the frequency interval associated with a given electronic transition. For a spontaneous emission process involving an electronic transition $i \leftarrow j$, a total dissymmetry factor may be defined as follows

$$G(i \leftarrow j) = 4R_{ji}/D_{ji} = \int_{i \leftarrow j} \frac{\Delta I(\nu)}{\nu^3} d\nu / \int_{i \leftarrow j} \frac{I(\nu)}{\nu^3} d\nu \quad (3)$$

where R_{ji} and D_{ji} are respectively the rotatory and dipole strengths of the transition, and the integrations are taken over the frequency interval spanned by the vibronic manifold of the electronic transition. Similarly, for an absorption process involving the electronic transition $i \rightarrow j$, we may define a total dissymmetry factor

$$G(i \rightarrow j) = 4R_{ij}/D_{ij} = \int_{i \rightarrow j} \frac{\Delta\epsilon(\nu)}{\nu} d\nu / \int_{i \rightarrow j} \frac{\epsilon(\nu)}{\nu} d\nu \quad (4)$$

The sign and magnitude of $G(i \leftarrow j)$ will depend upon the geometry of the emitting state j , whereas the sign and magnitude of $G(i \rightarrow j)$ will be determined by the geometry of the molecular ground state i . If the molecular geometry is the same in the ground state and emitting state, then $G(i \rightarrow j) = G(i \leftarrow j)$.

For the spectra shown in Figures 1 and 2, the dissymmetry factors (for absorption and emission) are nearly constant over the band envelopes with values of $g(\text{abs}) \sim -9.0 \times 10^{-3}$ and $g(\text{lum}) \sim -1.0 \times 10^{-3}$. If we assume that the emitting state is identical with the terminal state in the transition leading to CD and absorption in the 480-nm region, then the like signs of $g(\text{abs})$ and $g(\text{lum})$ suggest like chiralities in the ground and lowest singlet excited states. Furthermore, assuming inherent dissymmetry in the dicarbonyl group to be the principal source of optical activity, the order of magnitude difference in the absolute values of $g(\text{lum})$ and $g(\text{abs})$ suggests that ϕ differs in the ground and lowest singlet excited states. The observation that $|g(\text{lum})| < |g(\text{abs})|$ suggests that the dicarbonyl moiety is more nearly planar in the excited state than in the ground state (that is, ϕ is smaller in the excited state than in the ground state).

The spectra displayed in Figures 1 and 2 lead us to the

following conclusions regarding the nature and identity of the lower singlet excited states in I: (1) the fluorescent state and the excited singlet state responsible for CD and absorption in the 480-nm region are identical; (2) the chirality of the dicarbonyl moiety in the fluorescent state is the same as in the ground state; (3) the dihedral twist angle ϕ (a measure of inherent dissymmetry in the dicarbonyl group) is smaller in the fluorescent state than in the ground state; and (4) molecular dimensions and stereochemical variables other than ϕ are similar in the fluorescent and ground states (as indicated by the near mirror-image relationships observed in the CPL/CD and total luminescence/absorption spectra).

These conclusions are drawn from what appears to be the most plausible interpretation of the experimental results obtained in this study. These results appear to be at variance with the predictions provided by the Charney and Tsai model of the lower excited states of I. On this model, the CPL and lowest energy CD band can have the same sign only if the screw sense of the twisted dicarbonyl group changes upon excitation (that is, ϕ must have opposite signs in the ground and excited states). Furthermore, even if the energy separation between the two lowest lying ${}^1n\pi^*$ states is as small as 1500 cm^{-1} , the near mirror-image relationship between the CPL and CD bands is difficult to explain on the Charney and Tsai model.

Another possible interpretation of the observation that $|g(\text{lum})| < |g(\text{abs})|$ can be based on the assumption that the two C-C(=O)-C groups of the extended dicarbonyl moiety are individually nonplanar in the $n\pi^*$ emitting state (e.g., pyramidal as in formaldehyde¹¹ and possibly *trans*- β -hydrindanone^{3c}). Molecular orbital calculations¹⁰ on the rotatory strengths of $n\pi^*$ states in α -diketones with pyramidally distorted dicarbonyl moieties would tend to support this interpretation. It should be pointed out, however, that in general a mirror-image relationship between the absorption and fluorescence spectra would not be expected in this case.

Summary

The CPL reported here provides new data on the nature of the lowest lying singlet excited state of I. Additionally, the CPL and CD of I, considered together, provide clues concerning the identities, relative energies, and stereochemical features of the low-lying ${}^1n\pi^*$ states of I. Unfortunately, these results do not yield conclusive evidence concerning the correctness or completeness of the extant theories or hypotheses dealing with the electronic structure of α -diketone systems in their lower excited states, but they are suggestive of certain inadequacies or failures in several of these theories.

(11) (a) G. W. Robinson, *Can. J. Phys.*, **34**, 699 (1956); (b) J. C. D. Brand, *J. Chem. Soc.*, 858 (1956); (c) J. R. Henderson and M. Muramoto, *J. Chem. Phys.*, **43**, 1215 (1965).