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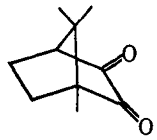
Spectroscopic Examination of the Lower Excited States of α-Diketones. Camphorquinone

E. Charney[1a] **and L. Tsai**[1b]

Contribution from the National Institute of Arthritis and Metabolic Diseases and the National Heart and Lung Institute, National Institutes of Health, Bethesda, Maryland 20014. *Received January 25, 1971*

Abstract: Camphorquinone is chosen as a model compound for studying the lower excited state of nonenolizable systems. The chiral nature of the molecule permitted the use of the circular dichroism as an added spectroscopic tool. Theoretical treatment of the diketone system as a dissymmetric chromophore leads to the analysis of the bands in the CD spectrum at 4780 and 2900 Å as arising from magnetically allowed transitions from an antisymmetric LCAO–MO of the carbonyl nonbonding orbitals. The upper states are respectively ^1A and ^1B and thus give rise to optical activity of different polarizations whose signs are predicted to be respectively negative and positive for a right-handed skew sense of the diketone system. However, the optical transition which gives rise to most of the ordinary *absorption* intensity in the 4700-Å band is due to a ^1B state; this band is thus a composite band containing the transitions to ^1B and ^1A states which are respectively electric dipole allowed and forbidden in the corresponding planar cis diketone. The 7 quanta of a 1540-cm^{-1} sharp vibrational progression which are observed in the 2900-Å CD and absorption bands are interpreted as due to a symmetric stretching mode of the excited diketone system. The polarized Raman spectra show the corresponding ground-state mode to be at 1759 cm^{-1}. Finally, the CD spectrum of camphorquinone reveals three optically active transitions at 2220, 2041, and 1923 Å buried in the apparent single absorption band which peaks at about 1755 Å.

While the lowest excited electronic states of nonconjugated carbonyl compounds are well characterized by the extensive studies[2] of formaldehyde, the situation is quite different with α-diketones. Glyoxal, the simplest conjugated dicarbonyl, which is predominantly *s*-trans in its ground state, has been carefully studied,[3] but not even the lowest two spectroscopically accessible singlet states of this molecule are unambiguously understood. In the present work we have investigated the *s*-cis α-diketone system in camphorquinone (I). The rationale for this choice involves the facts of its rigid structure, lack of an element of rotation–reflection symmetry, chemical stability, relative ease with which it may be prepared in high chemical and optical purity, and the fact that several of its lower excited states are in wavelength regions suitable for accurate measurements.



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[1] (a) National Institute of Arthritis and Metabolic Diseases; (b) National Heart and Lung Institute.

[2] (a) C. W. Robinson and V. E. DiGiorgia, *Can. J. Chem.*, **36**, 31 (1958); (b) J. C. D. Brand, J. H. Callomon, and J. K. G. Watson, *Discuss. Faraday Soc.*, No. 40, 175 (1963); (c) J. H. Callomon and K. K. Innes, *J. Mol. Spectrosc.*, **10**, 166 (1963); (d) R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935); (e) H. L. McMurray, *ibid.*, **9**, 231 (1941); (f) A. D. Walsh, *J. Chem. Soc.*, 2306 (1953); (g) J. C. D. Brand, *ibid.*, 858 (1956); (h) C. W. Robinson, *Can. J. Phys.*, **34**, 699 (1956); (i) S. F. Mason, *Mol. Phys.*, **5**, 343 (1962); (j) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957); (k) J. M. Parks and R. G. Parr, *ibid.*, **32**, 1657 (1960); (l) J. M. Forster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 303 (1960); (m) P. L. Goodfriend, F. W. Birss, and A. B. F. Duncan, *ibid.*, **32**, 307 (1960); (n) T. G. Edwards and R. Grinter, *Mol. Phys.*, **15**, 357 (1968).

[3] (a) W. H. E. Eberhardt and H. Rennes, *J. Mol. Spectrosc.*, **6**, 483 (1961); (b) G. W. King, *J. Chem. Soc.*, 5054 (1957); (c) J. Paldus and D. A. Ramsey, *Can. J. Phys.*, **45**, 1389 (1967).

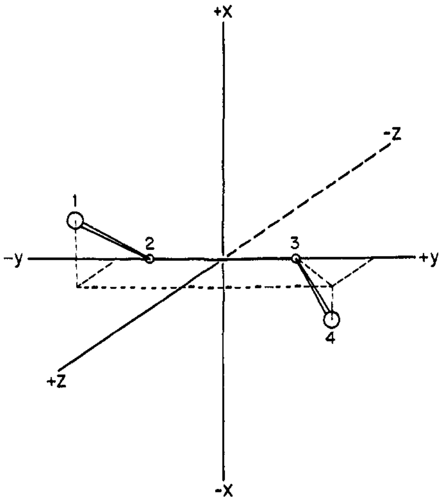

Figure 1. The configurational relationship of the diketone system in (−)-camphorquinone prepared from *d*-(+)-camphor. Atoms 1 and 4 are oxygen and 2 and 3 are carbon.

Molecular Orbitals and the States of Conjugated Diketones

In this report we will have little to say about states more than 4.3 eV above the ground state, although some observations of optically active electronic transitions to these states will be reported. The lower excited states, characterized by molecular orbitals of the α-diketone system which largely ignore the σ core, will be approximated by single configurations arising from one-electron promotions from the fully occupied molecular orbitals in the ground state, as discussed by McMurray.[4] We will depart from his description only slightly by calling attention to the vibronically induced states and to calculations[5] which indicate that the ordering of the nonbonding molecular orbitals of the oxygen atoms may be different from that usually assumed.[6]

The molecular orbitals are formed by an LCAO procedure from the oxygen p_x and p_y and the carbon p_x orbitals only. If we fix the geometry as illustrated in Figure 1, then these orbitals are designated in order of the descending energy predicted by Hoffmann[5]

$$\pi_-{}^* = a\phi_{1x} - b\phi_{2x} + b\phi_{3x} - a\phi_{4x}$$

$$\pi_+{}^* = b\phi_{1x} - a\phi_{2x} - a\phi_{3x} + b\phi_{4x}$$

$$n_+{}^* = (1/2)(\phi_{1y} + \phi_{4y})$$

$$n_- = (1/2)(\phi_{1y} - \phi_{4y})$$

$$\pi_- = b\phi_{1x} + a\phi_{2x} - a\phi_{3x} - b\phi_{4x}$$

$$\pi_+ = a\phi_{1x} + b\phi_{2x} + b\phi_{3x} + a\phi_{4x}$$

where ϕ_{ix} and ϕ_{iy} are pure 2p orbitals. The carbon orbitals are represented by the subscripts 2, 3 and the oxygen by subscripts 1, 4. In this treatment, we assume that the radial parts of all $2p_x$ and $2p_y$ orbitals are identical, since we are not concerned with absolute magnitudes; the fact that the carbon and oxygen radial parts are better represented by different Slater exponents is of no importance. Also, by including some ϕ_{iy} AO's in the π MO's we find from symmetry considerations that all the nonbonding interactions eventually cancel out.

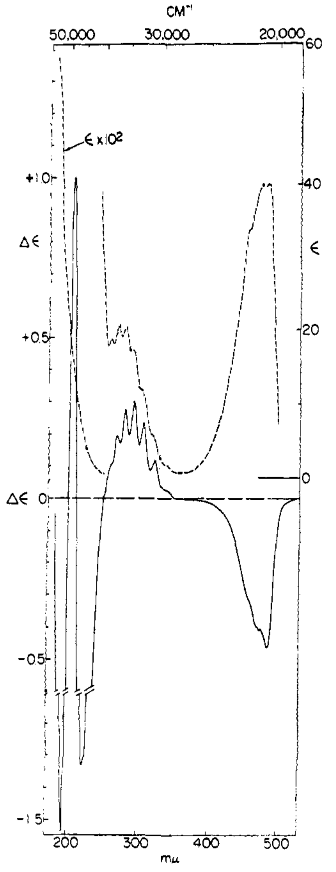

Figure 2. The circular dichroism (——) and the absorption (- - - -) spectra of (−)-camphorquinone in cyclohexane at room temperature.

From these molecular orbitals, the closed- and open-shell configurations of the ground and excited states are formed by one-electron promotion. These configurations, state designations, and symmetry for a planar cis conformation and a twisted cisoid configuration are listed in Table I.

Table I

		Symmetry	
Configuration	State	Planar cis C_{2v}	Twisted cisoid C_2
(σ core)$(\pi_+)^2(\pi_-)^2(n_+)^2(n_-)^2$	N	$^1A_1$	^1A
(σ core)$(\pi_+)^2(\pi_-)^2(n_+)(n_-)^2(\pi_+{}^*)$	$n_+\pi_+{}^*$	$^1B_1$, $^3B_1$	^1B, ^3B
(σ core)$(\pi_+)^2(\pi_-)^2(n_+)^2(n_-)(\pi_+{}^*)$	$n_-\pi_+{}^*$	$^1A_2$, $^3A_2$	^1A, ^3A
(σ core)$(\pi_+)^2(\pi_-)^2(n_+)(n_-)^2(\pi_-{}^*)$	$n_+\pi_-{}^*$	$^1A_2$, $^3A_2$	^1A, ^3A
(σ core)$(\pi_+)^2(\pi_-)^2(n_+)^2(n_-)(\pi_-{}^*)$	$n_-\pi_-{}^*$	$^1B_1$, $^3B_1$	^1B, ^3B
(σ core)$(\pi_+)^2(\pi_-)(n_+)^2(n_-)^2(\pi_+{}^*)$	$\pi_-\pi_+{}^*$	$^1B_2$, $^3B_2$	^1B, ^3B

Absorption Spectra

(1) Room-Temperature Solution Spectra. The solution spectra to 2380 Å have been presented and discussed by previous authors.[7] Several new considerations arise from our spectra. In cyclohexane (Figure 2),

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[4] H. L. McMurray, *J. Chem. Phys.*, **9**, 241 (1941).

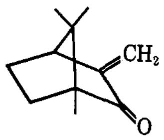
[5] J. R. Swenson and R. Hoffmann, *Helv. Chim. Acta*, **53**, 2331 (1970).

[6] (a) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967; (b) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962; (c) S. F. Mason, *Quart. Rev., Chem. Soc.*, **15**, 287 (1961).

[7] R. A. Ford and F. Parry, *Spectrochim. Acta*, **12**, 78 (1958).

there are two areas of relatively weak absorption with maxima near 4780 Å (ϵ_{max} 40) and 2900 Å, the latter actually being somewhat weaker than indicated by its peak extinction (ϵ_{max} 21), because of underlying intensity from the strong band which follows at shorter wavelengths. The lowest energy band has some structure but no clearly analyzable vibrational intervals. The remarkable feature is the very regular relatively sharp vibrational progression with an interval of 1540 cm^{-1} exhibited by the second band. The strong band at 1755 Å is relatively featureless.

Solution spectra of precursors and related compounds help clarify the spectroscopic states in α-diketones. For formaldehyde the C_{2v} symmetry forbids an electric dipole transition to the $n\pi^*$ state so that the observed weak band at about 2700 Å arises almost entirely from vibronic interaction with higher states.[2a–i] The transition is, however, allowed in magnetic dipole radiation, and, while this contributes negligibly to the ordinary absorption,[2c] it is of the utmost importance with regard to the origin of the optical activity of carbonyl-containing compounds. The most pertinent precursor is camphor, whose absorption spectrum is given in Figure 3 along with those of 3-methylenecamphor (II) (which is the closest α,β-unsaturated precursor), camphorquinone, and 3,4-di-*tert*-butylcyclobutanedione.[8] Several relationships are apparent among these spectra. (1) The longest wavelength bands are weak, as expected of transitions to $n\pi^*$ states. (2) Conjugation of the carbonyl as in 3-methylenecamphor lowers the relative energy of the $n\pi^*$ state. (3) Conjugation produced by two carbonyls as in camphorquinone and 3,4-di-*tert*-butylcyclobutanedione results in two weak bands separated by about 9000 cm^{-1} in the former and 11,000 cm^{-1} in the latter. This strongly suggests that two $n\pi^*$ states are involved, each produced by one-electron transitions from the ground state to the π_+^* and π_-^* orbitals. (4) The greater separation of the two bands in the cyclobutanedione compound as compared to camphorquinone indicates that there is a higher interaction energy between these orbitals in the cyclobutanedione, possibly because the four-atom system is closer to planarity than it is in camphorquinone.[6,9] (5) Comparison of the shape of the longest wavelength band reveals a highly significant difference, that of the cyclobutanedione having a predominant maximum on its long-wavelength edge, while that of camphorquinone is somewhat broader and exhibits two fairly prominent maxima. If the diketone system in cyclobutanedione is less skewed than in camphorquinone, this is precisely what would be expected (see Discussion), since in the C_{2v} symmetry of a planar diketone system only one transition is allowed, while in the C_2 symmetry of the skewed system two transitions are symmetry allowed to low-lying $n\pi^*$ states split by n-orbital interaction. The single prominent maximum at the leading edge of the absorption band is very likely the allowed 0–0 vibrationless transition in the cyclobutanedione. In the low-temperature spectrum of camphorquinone (*vide infra*), the change in intensity distribution reveals the prominence of this band in this compound as well.



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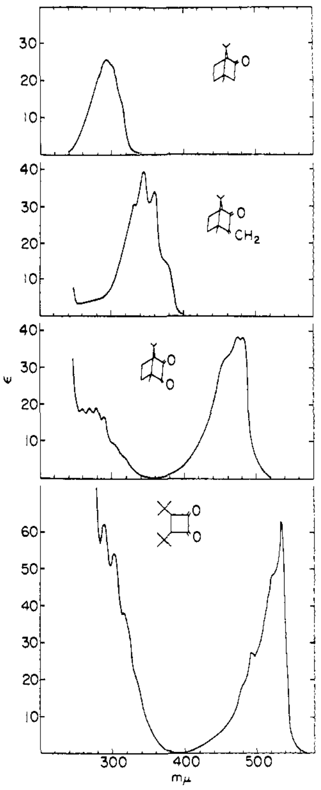

Figure 3. The solution spectra of camphor, 3-methylenecamphor, camphorquinone, and 3,4-di-*tert*-butylcyclobutanedione. We wish to thank Professor H. Wynberg for providing the latter spectrum and for his kind permission to publish it.

The counterpart of the sharp vibrationally resolved second band of camphorquinone has been observed in the transoid α-dicarbonyls, glyoxal[10] and biacetyl,[11] but only as diffuse bands without discrete vibrational structure in the vapor, although there is some evidence of such structure in the spectrum of biacetyl in cyclohexane solution.[12] This discrete vibrational structure appears also in other cisoid α-dicarbonyl compounds[13] as well as in 3,4-di-*tert*-butylcyclobutanedione (Figure 3) and 3,3,5,5-tetramethylcyclopentanedione.[9b] This phenomenon may be related to the rigidity of the molecular framework, which is a common feature among this group of α-diketones. However, other factors, the separation between the first and second singlets, the separation between the second singlet and still higher energy transitions, and the geometry of the excited states, cannot be disregarded.

A common criterion of $n\pi^*$ character of an electronic absorption band is a shift to higher frequencies in polar solvents relative to nonpolar solvents. The long-wavelength band of camphorquinone is typical in this respect, with a shift of the maximum from 4780 Å (mean

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[8] Ae. de Groot, D. Oudman, and H. Wynberg, *Tetrahedron Lett.*, 1529 (1969).

[9] (a) N. J. Leonard and P. M. Mader, *J. Amer. Chem. Soc.*, **72**, 5388 (1950); (b) C. Sandris and G. Ourrison, *Bull. Soc. Chim. Fr.*, 350 (1958); (c) K. Alder, H. K. Schaffer, H. Esser, H. Frieger, and R. Reuttse, *Justus Liebigs Ann. Chem.*, **593**, 23 (1955).

[10] H. W. Thompson, *Trans. Faraday Soc.*, **36**, 988 (1940).

[11] J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, **77**, 6461 (1955).

[12] L. W. Forster, *ibid.*, **77**, 1417 (1955).

[13] H. Gervais and A. Rassat, *Bull. Soc. Chim. Fr.*, 743 (1961).

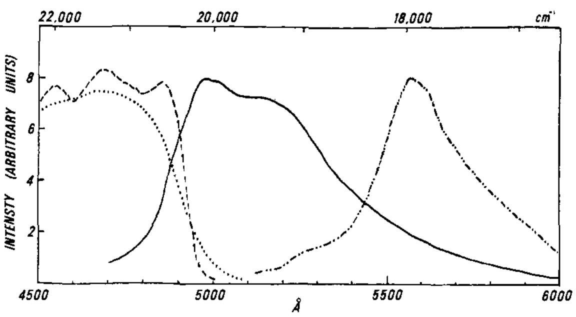

Figure 4. The absorption (·····), fluorescence (——), and phosphorescence (–·–·–) of camphorquinone at room temperature; the absorption (– – – – –) at 77°K. The phosphorescence emission is from a finely powdered crystalline solid; the absorption and fluorescence in ethanol.

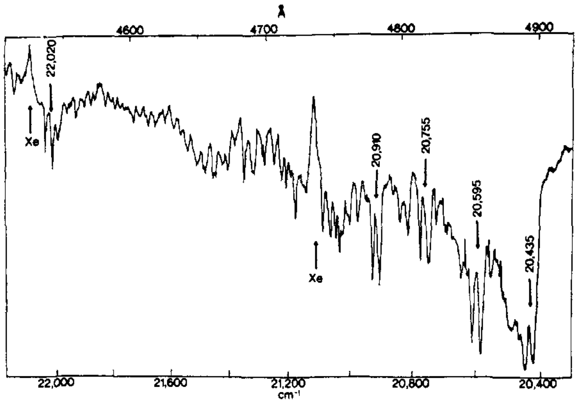

Figure 5. The crystal spectrum of camphorquinone at 4.2°K showing the origin band at 20,435 cm^{-1}, four members of a 165-cm^{-1} progression each in turn split by 27 cm^{-1}, and the onset of a second transition at 22,020 cm^{-1}. Only the wavelength scale is linear. The lines marked Xe are xenon emission lines from the source.

of the two prominent maxima) in cyclohexane to 4660 Å in acetonitrile and 4560 Å in methanol. The solvent dependence of the second transition is not quite so apparent, the shift in acetonitrile and methanol being only about 20 Å from the 2800-Å peak in cyclohexane. However, in circular dichroism the measurements reveal that this apparent insensitivity to solvent results from the overlap with the nearby strong bands which move to lower frequency in polar solvents. The maxima of the CD peaks, which appear at 4780 and 2790 Å in cyclohexane, move respectively about 300 and 200 cm^{-1} to higher frequencies in acetonitrile. The solvent behavior and low intensities are thus indicative of the nπ^* character of the transitions which give rise to these absorption bands.

Although we have confirmed the existence of a low-lying triplet transition at 19,500 cm^{-1} (Figure 4), there is no evidence of this triplet in the solution absorption spectrum or in the optical rotation and circular dichroism spectra. The transition found by Ford and Parry[7] at about 18,000 cm^{-1} did not appear in the CD and absorption spectra of our highly purified samples with or without heavy atom solvents.

(2) Low-Temperature Spectra. To help fix the origin of the 4780-Å band, the spectrum of camphorquinone was taken at liquid N_2 temperature in solution[14] (solid glass, Figure 4) and at liquid He temperature[15] (pure solid, Figure 5). The large overlap of the fluorescence (Figure 4) and absorption bands which persists even at low temperature demonstrates that the 4780-Å band contains at least one electronic transition which is symmetry allowed. There is considerable uncertainty in trying to locate the origin of the 4780-Å band from this overlap because of the difficulty of relating the relative intensities. The clearly defined origin in the 4°K spectrum (Figure 5) at 20,435 cm^{-1} can, however, be correlated with the maximum at 4860 Å (20,580 ± 25 cm^{-1}) in the liquid N_2 spectrum to locate the 0–0 band. It is in fact clear that some of the width of the room-temperature solution spectrum arises from hot-band intensity, as witness the disappearance of the intensity below the sharp absorption edge at 4950 Å in the liquid N_2 spectrum. We have not yet attempted an analysis of the fine structure in the crystal spectrum at 4°K, but two features are quite distinct (Figure 5). There is an apparent splitting of many of the vibrational bands, for example, the origin band at 20,435 cm^{-1} and those at 20,595, 20,755, and 20,910 cm^{-1}. This splitting is a constant 27 ± 2 cm^{-1} and almost certainly arises from the existence of an asymmetric site in the unit cell.[16] The alternative possibility that this represents the n-orbital splitting in the ground state is tentatively rejected on the grounds that a larger n-orbital splitting is expected and that the relative intensities of the two components should then be substantially different because of the relative symmetry allowedness of the transitions. The observed intensities are identical within experimental error. The second feature is the appearance of a distinctly new band of lower intensity at 22,020 cm^{-1}, which is 1580 cm^{-1} to the high-frequency side of the origin of the first band. The implication of this feature is discussed later.

(3) Infrared and Raman Spectra. It is unusual for a molecule with more than a very few atoms to exhibit well-defined vibrational structure in the spectrum of upper excited electronic states in solution. The existence of a distinct vibrational progression in the triplet–triplet absorption spectra,[17] the singlet absorption, and the CD spectra of camphorquinone near 2900 Å (Figure 2) and the possibility that symmetry considerations would be an aid in helping to define the nature of the electronic state involved led us to examine the Raman polarization of the more likely candidates for the pertinent vibrational mode and to attempt to identify it by means of isotopic frequency shifts.

The vibrational interval observed in the singlet absorption and CD spectra is 1540 ± 20 cm^{-1}. Since the electronic transitions are identified with the α-diketone moiety, a most likely candidate for this mode is an excited-state vibration of the carbonyl groups. It is easy to identify the ground-state carbonyl stretching frequencies in the infrared and Raman spectra as one or both of the bands at 1776 and 1759 cm^{-1} in $CHCl_3$

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[14] While this manuscript was in preparation, a camphorquinone spectrum at liquid N_2 temperature was published by A. Kuboyama, R. Yamazaki, S. Yabe, and Y. Uehara, *Bull. Chem Soc. Jap.*, **42**, 10 (1969), without comment on the features discussed here.

[15] We wish to thank Dr. Charles Marzacco and Dr. Robin Hochstrasser for this spectrum.

[16] X-Ray crystallographic examination shows that there are eight molecules per unit cell with two molecules in an assymmetric site in the crystal: J. Silverton, personal communication.

[17] A. Singh, A. R. Scott, and R. Sopchyshyn, *J. Phys. Chem.*, **73**, 2633 (1969).

Table II. Infrared and Raman Spectral Data^a

Ir, cm^{-1}	Raman, cm^{-1}	Raman polarization^b
1776	1776	0.75 ± 0.05
1760	1759	0.13 ± 0.02
908	908	*c*
894	894	0.09 ± 0.02
	562	0.82 ± 0.07
	167	0.75 ± 0.01

^{a} Only bands significant to the discussion are included. The weak Raman bands at 562 and 167 cm^{-1} are included to demonstrate the reliability of data for the bands in the 1750- and 900-cm^{-1} regions. Except for the 894-cm^{-1} band in the infrared spectrum, which was taken in CCl_4, all data are taken from solutions in $CHCl_3$. ^{b} Values of ρ, the Raman depolarization ratio. Values are the average of four scans for each polarization. The calibration was checked with the 1224-cm^{-1} band of $CHCl_3$, which gives a value of 0.78 ± 0.02, *i.e.*, less than 4% from the predicted value of 0.75 or within 1% when the precision of the measurement is taken into account. ^{c} This Raman band was too weak to measure with any accuracy. Note that in accord with the difference in polarization, the 894-cm^{-1} band is more intense than the 908-cm^{-1} band in the Raman spectra, while the reverse is true for these bands in the infrared spectra.

solution. Identification of the 1540-cm^{-1} band as a corresponding excited-state vibration could be made on the basis of correspondence in isotopic shifts between ground and excited states and on the determination of the symmetry species of the ground-state modes from Raman polarization.

The infrared and Raman bands of intrinsic interest for this investigation are given in Table II. In Table III, we list the ground- and excited-state frequencies associated with the carbonyl stretching frequencies of pertinent monocarbonyls. The infrared spectra of samples substituted with varying amounts of ^{18}O were analyzed for bands in the 1600–1800-cm^{-1} region. The eight distinct bands observed are listed in Table IV.

Table III^a

Compound	ν'', cm^{-1}	ν', cm^{-1}	Source
Formaldehyde	1744	1180	*b*
Propenal	1723	1266	*c*
Camphor	1748	1200	*d*
3-Methylenecamphor	1738^e	1250	*d*

^{a} ν' is the mean vibrational interval based on the observation of at least 4 excited-state quanta; ν'' is the ground-state vibrational interval. ^{b} G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, Van Nostrand, Princeton, N. J., 1966, p 518 ff. ^{c} J. C. D. Brand and D. G. Williamson, *Discuss. Faraday Soc.*, **35**, 184 (1963). ^{d} Our measurements. ^{e} This band is not positively identified. It is the strongest band in the infrared spectrum in this region.

Table IV.^{a} Infrared Carbonyl Bands of Camphorquinone Species

Species	Antisymmetric, cm^{-1}	Symmetric, cm^{-1}
Di-^{16}O	1776 ± 1	1759 ± 1
$^{16}O_1$–$^{18}O_4$	1769 ± 2	1735 ± 2
$^{18}O_1$–$^{16}O_4$	1744 ± 2	1731 ± 2
Di-^{18}O	1742 ± 2	1724 ± 1

^{a} Assignments to the mono-^{18}O species are based on the relation of the relative intensities of the spectral features to estimates of the ease with which the substitution occurs at each carbonyl group, and are thus tentative. The assignments of the di-^{16}O and di-^{18}O species are definitive.

The attempt to identify the 1540-cm^{-1} progression in the 2900-Å band of camphorquinone from isotopic frequency shifts in the electronic spectrum was unsuccessful because of the difficulty of preparing the di-^{18}O species in sufficiently high concentration to permit observation of the shift. However, some important and interesting conclusions can be drawn from the results.

From Table III, the observed decrease of ~500 cm^{-1} in the carbonyl frequencies on electronic excitation of a monocarbonyl to an $n\pi^*$ state is seen to be at least twice as large as the decrease of about 200–225 cm^{-1} from the 1776- or 1759-cm^{-1} ground-state carbonyl stretching frequency of camphorquinone. This and the existence of eight distinct bands (Table IV) in the spectra of ^{18}O-substituted compounds, corresponding to two per species,[18] indicate that strong coupling exists between the two frequencies in each species. The frequency shifts are of the order expected for the changes in mass on ^{18}O substitution, considering the diketone as an isolated system. The Raman polarization data of Table II further show that one of these is antisymmetric ($\rho = 0.75$) and one symmetric ($\rho < 0.75$) with respect to a twofold rotation axis; since the molecule has C_1 symmetry, for which no twofold axis exists, it is apparent that to a large extent the twofold axis of the diketone system itself controls the infrared and Raman activity. The two bands are thus strongly coupled symmetric and antisymmetric carbonyl frequencies. Their appearances in the electronic spectrum is governed by different selection rules. Depending on the electronic symmetry of the transition to any given state, one might expect a progression in one or the other to appear strongly while the other appears weakly or not at all.

Optical Activity

Camphorquinone is one of the earliest compounds to have its optical rotatory power studied through an absorption band,[19] but these earliest measurements were insufficient to reveal much in the way of theoretical interest. We have made extensive ORD measurements to ascertain whether the band attributed to the triplet[7] at 5555 Å contributes to the optical activity,[20] but no such contribution could be detected. The circular dichroism measurements are plotted in Figure 2, where the observable band systems are seen to be the two bands, respectively negative and positive in sign, at approximately 4780 and 2900 Å corresponding to the weak absorption bands at these wavelengths, plus three strong optically active bands at 2220, 2041, and 1923 Å which are not separately observable in the absorption spectrum. The circular dichroism of the two longest wavelength bands, like the absorption, is attributable to the α-diketone system. We summarize below the considerations which lead us to treat this dichroism as re-

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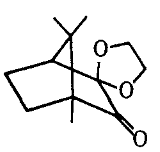
(18) The presence of two peaks for each isotopic species eliminates the possibility of these two bands arising from Fermi resonance with an overtone of the 894- or 908-cm^{-1} bands.

(19) T. M. Lowry, *J. Chem. Soc.*, 1156 (1936).

(20) No contribution from electron spin is expected between states of the same multiplicity because the magnetic moment operator does not contain a contribution from spin–orbit coupling. However, between states of different multiplicity, for example in a nominal singlet-to-triplet transition, the excited-state wave function is a mixture of singlet and triplet parts and both the magnetic and electric dipole transition moments are allowed through spin–orbit interaction. It would be of considerable interest to observe this phenomenon by means of optical activity measurements.

sulting largely from a coupled dissymmetric chromophore.

Crabbe[21] has summarized the experimental work[22] on the optical activity associated with the $n\pi^*$ bands of α,β-unsaturated carbonyls and α-diketones. Theoretically, the octant rule[23] has provided the basis for the analysis of the optical activity of carbonyls.[24] Boys, *et al.*,[25] and Klyne[26] have shown that the octant rule can explain the optical activity of the camphor series. Since this rule does not account for either the n-orbital or π^* splitting of the optical transitions, noncritical application to camphorquinone would lead to the conclusion that the $n\pi^*$ transitions are optically inactive because of substantial cancellation of the activity induced in the separate carbonyl groups. The fact that the carbonyl groups in camphorquinone are located in two different asymmetric environments is also not sufficient to explain the results, since the $n\pi^*$ bands of 3-ethylenedioxycamphor (III) and 2-ethylenedioxyepicamphor (IV), which have almost precisely mirror image ORD curves, occur at the *same* wavelength.[27] The two long-wavelength CD bands of camphorquinone are thus not the sum of the bands expected for individually perturbed carbonyl groups, as is the case for nonconjugated diketones.[21]



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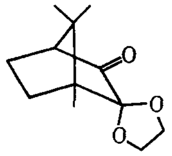

IV

We have therefore treated the α-diketone system as a dissymmetric chromophore, using arguments previously developed[28-30] for the dissymmetric skewed dienes. Experimentally this is justified by the following observations: (1) the optical activity of the $\pi\pi^*$ bands of 3-methylenecamphor and camphorquinone is of the magnitude expected for the nonplanar π system in this approximation and (2) the n-orbital splitting, as determined from the polarized single crystal spectra, is of the order of 1500 cm^{-1} or more[31] and thus indicates significant coupling between the individual carbonyl groups. The second band system at 1580 cm^{-1} to higher frequency than the first band in the 4.2°K spectrum of camphorquinone is thus attributed to a second electronic transition arising from n-orbital splitting. While progressive decoupling of the π system in the series diene → α,β-unsaturated carbonyl → dicarbonyl is indicated by the lengthening of the central C–C bond,[32] the known effect of conjugation on the $\pi^* \leftarrow \pi$ transitions of carbonyls demonstrates that substantial coupling exists. Walsh,[33] for example, has pointed out that the weak long-wavelength band is shifted to about 3300 Å in acrolein and crotonaldehyde compared to its location at about 2900 Å in simple aldehydes, and that in biacetyl, which contains two such bands, the lowest energy one shifts to about 4300 Å. Correspondingly, we have seen above the progressive shift to lower energies of the longest wavelength band in going successively from camphor to 3-methylenecamphor to camphorquinone.

Molecular orbital theory cannot be applied to the optical activity of α-dicarbonyls with the same degree of approximation as to skewed dienes. One reason for this is that the two-center integrals, $(\phi_{iy}|\nabla|\phi_{jx})$, where ϕ_{iy} and ϕ_{jx} are respectively $2p_y$ and $2p_x$ atomic orbitals, are identically zero.[34] In the zero-order treatment, these integrals which appear in the electronic transition moments would not yield finite absorption or optical activity even for the skewed C_2 system. Since we nevertheless wished, for simplicity, to retain the formalism of that treatment and are primarily interested in the sign rather than the magnitude of the optical activity, we have simply assumed that ϕ_{iy} and ϕ_{jx} represent perturbed wave functions such that the absolute magnitudes of these two-center integrals are not identically zero. In addition to this approximation, the following assumptions are made. (1) The interactions between nonbonded atoms are ignored as in the diene treatment, because at the distances involved both the dipole matrix elements and the overlap integrals are at least an order of magnitude smaller than those for the bonded atoms. (2) In the magnetic transition moment connecting upper and lower states, *e.g.*, $[(n_-\pi_+{}^*/r)(\nabla/N)]$, the only significant matrix elements are those containing orbitals with nodes in orthogonal planes, and these reduce to the magnitude of overlap integrals. These are of two types: one-center, in which both orbitals are on the same atom ($2p_x$ and $2p_y$ on the oxygen atoms) and two-center ($2p_y$ on oxygen and $2p_x$ on the adjacent carbon atom). Of these we have considered only the contribution of the two-center integrals. By symmetry, the one-center integrals vanish for promotions from the n_+ orbitals. They do not vanish for the promotions from the n_- orbitals, but do contribute to the optical activity with the same sign as the contributions from the two-center integrals. From these considerations and approximations, the sign of the rotational strengths of the four possible $n \rightarrow \pi^*$ transitions is determined by the sign of the appropriate coefficients of the atomic orbitals in the various MO's and the product of the signs of the coordinates $x_1y_2z_1$, where x_i, y_i, and z_i are the coordinates of atom i in the

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[21] P. Crabbe, "Optical Rotary Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, San Francisco, Calif., 1965.

[22] (a) G. Jacob, G. Ourrisson, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1374 (1959); (b) C. Velluz and M. Legrand, *Angew. Chem.*, 73, 603 (1961); (c) P. Witz, Ph.D. Thesis, University of Strasbourg, 1964.

[23] W. Moffit, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, **83**, 4013 (1961).

[24] Some work has been done in which the $n\pi^*$ states of carbonyls have been treated as dissymmetric chromophores; see, *e.g.*, Y. H. Pao and D. P. Santry, *ibid.*, **88**, 4157 (1966), or as vibronically coupled chromphores symmetric in their ground state: O. E. Weigang, Jr., *J. Chem. Phys.*, 43, 3609 (1965); G. M. Robinson and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, **91**, 3709 (1969).

[25] D. E. Boys, G. W. Common, and R. C. Cookson, *J. Chem. Soc.*, 885 (1966).

[26] W. Klyne, *Tetrahedron*, 13, 29 (1961).

[27] K. M. Baker and B. R. Davis, *ibid.*, **24**, 1655 (1968).

[28] A. Moscowitz, E. Charney, U. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.*, **83**, 4661 (1961).

[29] E. Charney, *Tetrahedron*, 21, 3127 (1965).

[30] A. Moscowitz, Ph.D. Thesis, Harvard University, March 1957.

[31] A preliminary measurement of the spectra of a crystal of camphorquinone in light polarized along two different optic axes yields a polarization ratio spectrum with an inflection point in the first band. An estimate of the two subbands of different polarization which results in this inflection places them at about 480 and 450 mμ, corresponding to a 1500-cm^{-1} separation. We would like to thank Dr. W. A. Eaton for his help with this measurement.

[32] (a) K. Kuchitsu, T. Fukuijama, and Y. Marino, *J. Mol. Struct.*, 1, 463 (1967–1968); (b) see also E. A. Cherinik and C. C. Costain, *J. Chem. Phys*, 45, 104 (1966).

[33] A. D. Walsh, *Trans. Faraday Soc.*, 41, 498 (1945).

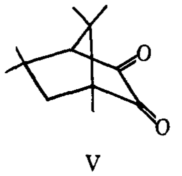
[34] In the dienes, the only two-center integrals which appear are the finite integrals of the type $(\phi_{iy}|\nabla|\phi_{jy})$.

coordinate system of Figure 1. To determine the sign of the coordinates to be used for comparison with the experimental results, we observe that the positive sign and large magnitude of the intense CD band in 3-methylenecamphor at 2250 Å (Figure 6), which is assigned to the lowest energy $\pi\pi^*$ state, indicate that the four-atom unsaturated system in this compound is nonplanar, with a right-handed skew sense.[35] In this treatment, we assume that camphorquinone prepared from *d*-(+)-camphor has the same absolute configuration as 3-methylenecamphor also prepared from *d*-(+)-camphor. Then the absolute configuration determined from the positive sense of the $\pi^* \leftarrow \pi$ CD of 3-methylenecamphor is such that for camphorquinone x_1 is negative, y_2 is negative, and z_1 is positive, leading to a positive product for the three coordinates. Combining this with appropriate signs of the MO coefficients, the predicted signs of the optical activity are given in Table V. The observed optical activity for the lower energy band is negative, which thus implicates $n_-\pi_+^* \leftarrow N$ ($^1A \leftarrow {}^1A$), and positive for the higher energy band, implicating $n_-\pi_-^* \leftarrow N$ ($^1B \leftarrow {}^1A$). As a test of this result, we can apply the foregoing considerations to other α-diketones of known absolute configurations, (+)-isofenchoquinone (V) and (+)-longidione (VI).[36]

Table V

Transition	Symmetry selection rules: C_{2v}: Electric dipole	C_{2v}: Magnetic dipole	C_2: Electric dipole	C_2: Magnetic dipole	Sign of the rotational strength[a]
$n_+\pi_+^* \leftarrow N$	x	y	x, y	x, y	+
$n_-\pi_+^* \leftarrow N$		z	z	z	−
$n_+\pi_-^* \leftarrow N$		z	z	z	−
$n_-\pi_-^* \leftarrow N$	x	y	x, y	x, y	+
$\pi_-\pi_+^* \leftarrow N$	y	x	x, y	x, y	+

[a] Sign of rotational strength predicted for configuration of Figure 1.


V


VI

The stereochemistry of these compounds imposes a skew sense opposite to that of camphorquinone upon the α-diketone system. The first two CD bands of these compounds should therefore be opposite in sign to those of camphorquinone. This is in perfect agreement with experimental observations.[13,22]

Two other aspects of the optical activity require comment. We have already noted that the vibrational substructure of the 2900-Å absorption band consists of a regular progression with a frequency separation of about 1540 cm^{-1}. The separation in the CD spectrum is identical and, within experimental error, also the same as the interval obtained in the excited triplet absorption spectrum.[17] As a consequence, the same excited configuration (not including spin) is involved in all three observations. On the basis of the sign of the CD, this appears to be the $n_-\pi_-^*$ state which is electronically allowed in C_2 and C_{2v} symmetry, so that the vibrational interval is most likely the excited-state symmetric stretching frequency corresponding to the ground-state 1759-cm^{-1} vibration. The discrete vibrational interval implies that any other transitions in this vicinity must be extremely weak.

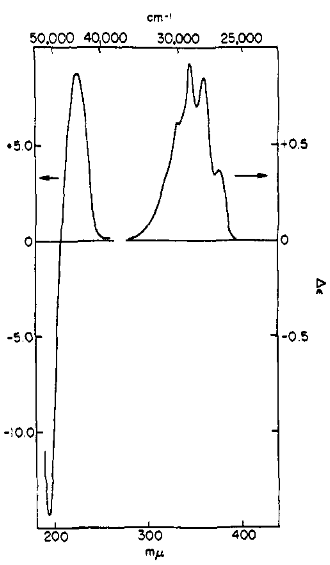


Figure 6. The circular dichroism of (+)-3-methylenecamphor in cyclohexane at room temperature.

The three CD bands observed at higher frequencies cannot be definitely assigned at this time. The rotational strengths of these bands is large, much larger perhaps than the CD amplitudes would indicate, since the lack of inflection points at the intersections of the positive and negative bands indicates that overlapping and consequently considerable mutual cancellation occurs. The estimated rotational strengths of each of the three bands is between 5×10^{-39} and 15×10^{-39} cgs unit, values which are characteristic of skewed p_π orbital systems and magnetically allowed σ^* transitions, and rather larger than has been observed in transitions originating on oxygen nonbonding orbitals. Very likely the strong positive peak at 2041 Å is the $\pi \rightarrow \pi^*$ promotion $\pi_-\pi_+^* \leftarrow N$. The number of possibilities for the origin of other bands is too large to permit assignment with confidence. Transitions to or from σ states undoubtedly appear in this region,[7,37] and some of these can have large rotational strengths. In addition, of course, configuration mixing will make these descriptions overly simplistic.

Emission Spectra. In addition to the singlet states, each of the excited configurations gives rise to a triplet. The separation of the triplets from the corresponding singlets is important in the photochemistry of these compounds[38] and in theoretical considerations of intra-

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[35] C. Djerassi, R. Records, E. Bunenberg, K. Mislow, and A. Moscowitz, *J. Amer. Chem. Soc.*, **84**, 870 (1962), established the applicability of simple dissymmetric chromphore rules to the $\pi\pi^*$ bands, but H. Ziffer and C. W. Robinson, *Tetrahedron*, **24**, 5803 (1968), have demonstrated that this statement is an oversimplification because of interaction of the $\pi\pi^*$ states with nearby higher energy states. The situation in 3-methylenecamphor, however, seems to be quite straightforward and will be discussed in more detail in the summary.

[36] G. Ourrison, *Bull. Soc. Chim. Fr.*, 895 (1955).

[37] (a) R. S. Holdsworth and A. B. F. Duncan, *Chem. Rev.*, **41**, 311 (1947); (b) E. E. Barnes and W. T. Simpson, *J. Chem. Phys.*, **39**, 670 (1963); (c) A. Udvarhazi and M. A. El-Sayed, *ibid.*, **9**, 3335 (1965).

[38] (a) B. M. Monroe and S. A. Weiner, *J. Amer. Chem. Soc.*, **91**,

molecular energy transfer. The emission of α-diketones has, in fact, recently received considerable study.[39] We have measured the emission of camphorquinone from solution at room temperature, from a glass at 77 °K, and from powdered crystals at room temperature. In addition, the excitation spectrum for the phosphorescent emission has been previously reported.[40] We have already alluded to the fact that the emission and absorption spectra overlap so strongly that the emission must come from an electronically allowed transition. The origin of this transition is at 20,580 cm^{-1} in EPA or ethanol. Since in the C_2 symmetry, which we believe controls the α-diketone optical transitions, both of the lower $\pi^* \leftarrow n$ transitions are permitted, this overlap by itself is insufficient to distinguish whether this promotion is to the lowest ^1A or ^1B state. In the summary and discussion, we will attempt to further clarify this problem.

The excitation spectrum of the long-lived emission at 5580 Å was interpreted to demonstrate intersystem crossing into the second $^3n\pi^*$ system.[40] Such intersystem crossing would have important consequences for photochemistry of α-diketones. The photoenolization of biacetyl, for example, has indeed recently been reported[41] to involve the second triplet state. The origin of this highly efficient intersystem crossing from an upper singlet to upper triplet is not immediately obvious. It is generally accepted that intersystem crossing between excited $^1\pi\pi^*$ and $^3n\pi^*$ states by vibronic coupling is relatively efficient. It may be that the enhanced efficiency in our experiments is in part due to excitation into the $\pi_-\pi_+^*$ manifold. In solution at room temperature, the 2900-Å $n\pi^*$ system is overlapped by the higher frequency strong absorption, at least part of which must be to the $\pi_-\pi_+^*$ manifold. However, the facts that the excitation spectrum shows no excitation in this region and that samples excited at wavelengths shorter than about 2900 Å lose their emission ability may be evidence that excitation into the $\pi_-\pi_+^*$ manifold leads to decomposition and thus would not provide a good mechanism for enhanced intersystem crossing from upper states. An alternative explanation is that in the upper levels a larger spin–orbit coupling results from a redistribution of charge closer to the oxygen nuclei. McGlynn, Azumi, and Kinoshita[42] have pointed out that the increase in the attractive Coulombic forces as the local charge density is increased results in a larger apparent nuclear angular momentum and thus enhanced spin–orbit coupling. Still a third enhancement mechanism arises out of the relative density of vibrational states in the triplet manifolds at or near the vibrationless singlet level from which most of the intersystem crossing occurs.

Discussion and Summary

In Table V, transitions to the lower states of the cisoid α-diketone system, based on molecular orbitals constructed primarily from the 2p orbitals of carbon and oxygen, are summarized together with selection rules for electronic and magnetic dipole transitions moments for both planar (C_{2v}) and skewed (C_2) systems, and the signs of the predicted optical activity associated with the skewed system having the absolute configuration of Figure 1. In C_{2v} the *electric dipole* transition ($^1A_2$) $n_-\pi_+^* \leftarrow N$ is forbidden. In C_2, transitions to both (^1A) $n_-\pi_+^*$ and (^1B) $n_+\pi_+^*$ are allowed with different polarizations; *magnetic dipole* transition moments have allowed components in these same directions. One might therefore expect five optically active transitions arising from valence transitions involving only 2p atomic orbitals. Additional transitions would of course be expected at still higher energies, but configurational mixing with other states, already apparent in the near-vacuum uv (*vide infra*), would certainly invalidate any description in terms of these single configurational states. Because n-orbital splitting is expected to be rather small,[43] transitions to $n_-\pi_+^*$ and $n_+\pi_+^*$ as well as to $n_-\pi_-^*$ and $n_+\pi_-^*$, respectively, should be almost degenerate. Transitions of the type $\pi^* \leftarrow n$ are generally rather weak, with molar extinctions rarely greater than about 100. Consequently, the spectrum at low energies may be expected to consist of two regions of weak absorption, each of which can include two electronically allowed transitions and, in addition, weak vibronically induced transitions, followed by a strong ($\pi^* \leftarrow \pi$) transition to the $^1B_2$ state. We have already noted that the singlet absorption spectrum (Figure 2) fits this description very well. The longest wavelength region near 480 nm is more diffuse even in nonpolar solvents than that of the corresponding monocarbonyls (Table III), suggesting the possibility that this band consists of more than one electronic transition. The polarized single-crystal spectra do show two differently polarized contributions to the first band at 478 nm. The observed negative CD in this region suggests that the optical activity arises primarily from the $n_-\pi_+^* \leftarrow N$ transition. According to the extended Hückel calculation by Hoffmann,[5] the antisymmetric orbital, n_-, is lower in energy than n_+; therefore, $n_-\pi_+^* \leftarrow N$ should be at shorter wavelengths than $n_+\pi_+^* \leftarrow N$. The latter is predicted to give a positive CD band. There is no evidence in the CD measurement (Figure 2), however, of a positive contribution in this band system. One possible explanation for this is that overlap of the larger negative contribution of the $n_-\pi_+^* \leftarrow N$ swamps the small positive contribution. It is also possible that vibronic contributions[24] of opposite sign to that determined by the electronic symmetry of $n_+\pi_+^*$ could result in a negative contribution from weakly allowed $n_+\pi_+^* \leftarrow N$ transition. The CD of one α-diketone sesquiterpene (VII) has been reported[22c] to show both positive and negative contributions in this band, sepa-

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450 (1969); (b) J. Meinwald and H. O. Klingle, *J. Amer. Chem. Soc.*, **88**, 2071 (1966); (c) M. B. Rubin, *Tetrahedron Lett.*, 3931 (1969).

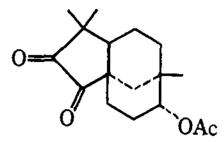
(39) (a) A. Kuboyama and S. Yabe, *Bull. Chem. Soc. Jap.*, **40**, 2475 (1967); (b) T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, **89**, 4380 (1967).

(40) L. Tsai and E. Charney, *J. Phys. Chem.*, **73**, 2462 (1969).

(41) J. Lemaire, M. Niclause, X. Deglise, J. C. André, G. Persson, and M. Bonchy, *C. R. Acad. Sci., Ser. C*, **267**, 33 (1968).

(42) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

(43) Until very recently, this assumption, based on ref 4, has gone unchallenged. However, R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968), have predicted that the n-orbital splitting in some nitrogen heterocyclics should be quite large, and this has been confirmed experimentally by M. Bischof, J. A. Hashmall, E. Heilbronner, and J. L. Hornung, *Tetrahedron Lett.*, 4025 (1969). Hoffmann[5] has called our attention to new calculations that indicate that the energy gap between the antisymmetric orbital n_- and the symmetric orbital n_+ may be as large as 0.68 eV in norbornane-2,3-dione, a model rigid α-diketone related to camphorquinone, and the energy ordering may be reversed from that predicted by McMurray and by simple Hückel theory. Our experiments discussed below throw some light on both these predictions. We wish to thank Professor Hoffmann for this and subsequent communications.



VII

rated by about 2200 cm^{-1}. This rather large splitting, if correct, would be a positive indication that the two transitions identified from our polarized-crystal spectra arise from n-orbital splitting. The n-orbital splitting predicted by Hoffmann[5] for norbornane-2,3-dione is about 5500 cm^{-1}, clearly much larger than the 2200 cm^{-1} in the CD of VII or the approximately 1500-cm^{-1} splitting obtained from the polarized-crystal spectrum and the 4.2°K spectrum of solid camphorquinone, which are nevertheless much larger than previously assumed. Our results are consistent with the prediction that the antisymmetric n-orbital combination in this configuration is more stable than the symmetric one rather than the reverse, as originally predicted by McMurray.[2e] Also in accord with this assignment is the spectrum of the cyclobutanedione discussed above, where it was noted that in this apparently less skewed dione the long-wavelength band has a prominent maximum on its low-frequency edge, indicative of the greater relative allowedness of the $n_{+}\pi_{+}^{*} \leftarrow N$ compared to that of the $n_{-}\pi_{+}^{*} \leftarrow N$ transition in absorption. In camphorquinone, both transitions contribute to the observed absorption band at 4780 Å, but the magnitude of their relative contributions apparently reverse between absorption and circular dichroism.[44]

This reversal must come from the relative magnitudes of the electric and magnetic dipole transition moments. Because of the approximations discussed in the section on optical activity, any attempt to calculate these magnitudes would be gratuitous.[45] However, some idea of the relative intensities predicted by this treatment can be obtained from the relationship of the geometric factors for the components of the contributing electric and magnetic moment matrix elements. The ratio of the *electric* transition moments for the (^{1}A) $n_{-}\pi_{+}^{*} \leftarrow N$ to the (^{1}B) $n_{+}\pi_{+}^{*} \leftarrow N$ transition is *0.4* for a dihedral angle between the OCC planes of 15°.[46] The ratio of the *magnetic* transition moments for the same transition is *7.5*. Since this does not include the effect produced by the one-center integrals, which would tend to increase the ratio of the magnetic transition moments without contributing anything to the isotropic absorption, it is apparent that *this treatment predicts that the CD and absorption of the first band of camphorquinone have their primary origins in two different electronic transitions. The treatment, however, does not preclude the possibility that vibronic contributions are also important.*

Completely consistent with this assignment of the long-wavelength CD band to the $n_{-}\pi_{+}^{*} \leftarrow N$ transition is the appearance of the positive CD band at 2900 Å attributable to the $n_{-}\pi_{-}^{*}$ transition[47] by this simple molecular orbital treatment. This transition is electric dipole allowed in C_{2v} as well as in C_2 symmetry and is the predominant contributor to *both* the absorption and the circular dichroism. With this assignment the 1540-cm^{-1} vibrational interval corresponds to a totally symmetric vibration (1759 cm^{-1} in the ground state). The question then arises as to where the $n_{+}\pi_{-}^{*} \leftarrow N$ transition appears, if at all, and if it does not, why not.[48] One possibility is the assignment of the negative CD band at 2220 Å (45,050 cm^{-1}) to a nominal (^{1}A) $n_{+}\pi_{-}^{*} \leftarrow N$ transition as predicted for a band of this symmetry. This assignment is, however, inconsistent with Hoffmann's prediction of a higher orbital energy for the symmetric, n_{+}, than for the antisymmetric, n_{-}, orbital, and is moreover about 10,500 cm^{-1} from the 2900-Å band. Another possibility is that it appears in the order predicted by the CNDO calculation[10] some 3700 cm^{-1} below the 2900-Å band; the basis for this suggestion is the observation of an inflection point in the broad band centered around 3800–3900 Å in the phosphorescence excitation spectrum which we have previously attributed[40] to excitation from the ground singlet to $^{3}n_{-}\pi^{*}_{-}$ *or* $^{3}n_{+}\pi_{-}^{*}$. Decomposition of this band into two components[49] gives a band at about 3650 Å which is about 3700 ± 500 cm^{-1} from the origin of the 2900-Å band at 29,590 cm^{-1}. This would in fact shift the triplet excitation peak corresponding to the $^{1}n_{-}\pi_{-}^{*}$ down by about 500 cm^{-1} and bring the triplet–triplet separation[40] to within 60 cm^{-1} of the predicted separation based on the comparison of our CD, absorption and emission data with the triplet–triplet absorption spectrum.[17] The triplet–triplet absorption spectra do not, unfortunately, distinguish between the possibilities for the symmetry of the lower excited states since the selection rules permit transitions from either the $^{3}n_{-}\pi_{-}^{*}$ (B) or $^{3}n_{+}\pi_{-}^{*}$ (A) states to the upper triplets. Indeed even in the planar C_{2v} symmetry, these transitions are symmetry and parity allowed. The polarization directions are, of course, different, but no polarization data for these transitions exist.

On the foregoing basis, we assign the vibrationally structured band which starts at 29,580 cm^{-1} (2900-Å band) to the $n_{-}\pi_{-}^{*} \leftarrow N$ transition and tentatively as-

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(44) A comparison of the experimental CD and absorption curves in the 4780-Å region does not reveal the 1500-cm^{-1} blue shift of the CD compared to the absorption which might be predicted from this difference in their optical origins. The longest wavelength peaks in the CD and absorption spectra are within 2 or 3 mμ (less than 100 cm^{-1}) of each other in cyclohexane solvent. However, this is precisely the type of transition which W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959), predicted could give rise to the appearance of the CD band at slightly longer wavelengths than the absorption band. The difference, according to these authors, would be of the order of an antisymmetric vibrational mode of the molecule. A very likely candidate is the mode corresponding to the antisymmetric stretching vibration of the O=C—C=O system, which is 1776 cm^{-1} in the ground state and probably close to 1550 cm^{-1} in the excited state. With this mode active, the leading edge of the CD would be expected very close and perhaps even a little to the red of the long-wavelength peak of the absorption curve where it is indeed observed.

(45) For example, camphorquinone would have some optical activity even if the four-atom system is planar because of the assymmetric centers at carbons 1 and 4.

(46) While only limited significance can be attached to the exact magnitudes, the square root of the measured ratio of the integrated intensities reasonably attributed to the origin bands of these transitions in the 4.2°K spectrum is 0.4 ± 0.05, in excellent agreement with the calculated value of the ratio of the transition moment. Since the absorption in the planar C_{2v} conformation originates from allowed transitions to only the $^{1}B_1$ and $^{1}B_2$ states, it may be expected that intensity arising from transitions to the ^{1}A states will be small if the dihedral twist angle, δ, is fairly small (see Figure 1).

(47) The assignment of the corresponding band in the spectrum of glyoxal as an $\pi^{*} \leftarrow n$ transition has been questioned (ref 21).

(48) The role of configuration interaction among higher configurations, which could mix and split the upper excited states differently from the lower excited states, is not explored here.

(49) The possibility that there are more than two components in this band envelope, including, *e.g.*, $^{3}\pi_{-}\pi_{+}^{*}$ states, cannot be completely ignored. This will make large uncertainties in the numbers discussed here, but does not affect the argument.

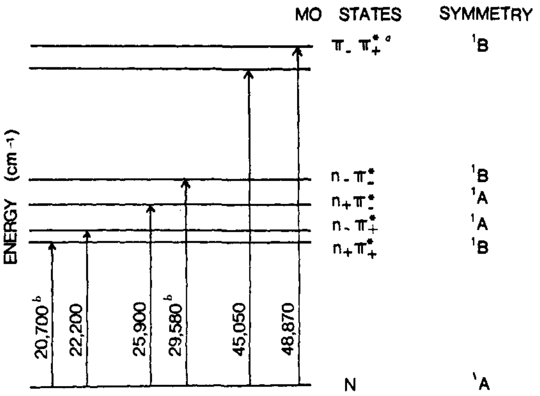

Figure 7. Spectroscopic states of camphorquinone. (a) The assignment of this band is tentative; see text. (b) These values are spectroscopic origins, not peak positions.

sign the $n_+\pi_-^* \leftarrow N$ transition energy as 25,900 ± 500 cm^{-1} (3860 Å). This latter assignment is, however, unable to account for the absence of a CD band in this region. The only reasonable explanation for this, which, however, must remain speculative at this point, is that virtually all the magnetic dipole intensity attributable to the $n_+\pi_-^* \leftarrow N$ transition appears in the $n_-\pi_-^*$ transition because of a large change in geometry in the $n_-\pi_-^*$ state. Strong support for a change in geometry comes from the fact that at least 7 quanta of the 1540-cm^{-1} vibration are observed in the excited state of this transition before overlapping with the next state obscures or broadens additional vibrational sub-bands.

A summary of the assignments based on the work reported here is given in Figure 7.[50]

Experimental Section

Except for the liquid helium crystal spectrum, uv absorption measurements were made at a spectral bandwidth of about 2 Å, CD measurements at a spectral bandwidth of about 10 Å. Emission excitation spectra were measured with about a 40-Å bandwidth in the emission and excitation monochromator respectively and emission measurements generally at higher resolution. The infrared spectra for Tables III and IV were obtained at a spectral bandwidth of about 0.6 cm^{-1}, and the Raman spectra (for which we wish to acknowledge the aid of Drs. Thomas Lewis and Ira Levin) at a bandwidth of about 1–2 cm^{-1} using a helium–neon laser. In the case of the solid emission experiments, it is worth noting that it was necessary to powder the solid in order to produce reproducible emission and excitation spectra, and considerable care was exercised to prevent direct reflection of any but a very small amount of scattered radiation into the detecting system when these measurements were made. The temperature at which the sample was held in the liquid nitrogen dewar during the uv absorption measurements is unknown, but experience indicates that it was within 5° of 77°K.

Nmr spectra were measured on a Varian A60 or Varian HA-100 spectrometer. Mass spectra were determined on a LKB-9000 mass spectrometer using a direct inlet probe. Glc was carried out on a 3% OV-17 on Gas Chrom P 6-ft column at 90° using argon as the carrier gas.

(−)-Camphorquinone was prepared by SeO_2 oxidation of (+)-camphor.[51] Purification was achieved by repeated recrystallizations from hydrocarbon solvents, and by vacuum sublimation. The degree of purity was tested by glc and mass spectrometry.

(+)-3-Methylenecamphor was prepared from (+)-camphor by a modification of the method reported by Rupe, Akermann, and Takagi.[52] 3-Hydroxymethylenecamphor (2 g), obtained from condensation of (+)-camphor and ethyl formate,[53] in 40 ml of chloroform was added under vigorous stirring to a solution of 0.6 g of KBH_4 in 40 ml of 10% Na_2CO_3 at room temperature. After stirring for 2.5 hr, the mixture was allowed to settle, and the organic aqueous layers were separated. The aqueous layer was extracted three times with chloroform. The extracts were combined with the organic layer and dried over anhydrous $MgSO_4$. Upon removal of the solvent under reduced pressure, 3-hydroxymethylcamphor was obtained as a colorless oil, 1.95 g. Dehydration of this β-hydroxy ketone was carried out as described.[52] The crude product was chromatographed over a silica gel column. 3-Methylenecamphor was found in fractions eluted by a cyclohexane–benzene (8:2) mixture. The fractions were combined and distilled *in vacuo*. The colorless distillate solidified upon cooling: mp 40°; glc single peak, mass spectrum $M^+ = 164$; nmr ($CDCl_3$, internal reference Me_4Si) δ 5.13, 5.78 ppm (two olefinic protons).

^{18}*O*-Camphorquinone. A solution of camphorquinone in $CHCl_3$ was stirred at room temperature with a small amount of activated Al_2O_3 (Woelm, acidic) and $^2H_2{}^{18}O$ under dry N_2 atmosphere for 7 days; the solution was filtered under N_2 atmosphere, dried over $MgSO_4$, and evaporated under reduced pressure. The sample was analyzed for ^{18}O content in a mass spectrometer. This process was repeated two times, and the highest incorporation of ^{18}O achieved was estimated to be about 90%.

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(50) The treatment of diketone systems by extended Hückel and SCF–CNDO methods by W. Hug and G. Wagnière, *Theor. Chim. Acta*, **18**, 57 (1970), appeared just before this manuscript was submitted for publication. These authors attribute both the absorption and the optical activity of the first band to the same ^1B transition, in contrast to our interpretation that the absorption is derived from the ^1B, whereas the rotation is predominantly from a ^1A. Moreover, the SCF–CNDO calculation predicts an order of magnitude difference between the rotational strengths of the ^1B and ^1A transitions corresponding to the absorption bands at 4780 and 2900 Å, but the experimental rotational strengths are almost identical (Figure 2). Professor Wagnière, in a private communication for which we wish to thank him, pointed out, however, that the magnitudes of the rotational strengths are much more sensitive to chosen parameters than are the energies. Nevertheless, in view of the difference between the SCF–CNDO calculation and the observed rotational strength, and the considerations discussed in the text, we prefer at this time to retain the present interpretation subject to confirmation of the absolute configuration of the diketone by X-ray analysis and/or the positive determination of the vibronic or electronic origin of the band at 22,020 cm^{-1} in the 4.2°K spectrum.

(51) H. Rupe and A. T. diVignano, *Helv. Chim. Acta*, 20, 1078 (1937).

(52) H. Rupe, A. Akermann, and H. Takagi, *ibid.*, 1, 452 (1918).

(53) R. Adams, *Org. React.*, 8, 120 (1964).