background effect as measured by the CD of the corresponding hydrogenated structure ($\Delta\epsilon = -1.3$), for this works in the opposite direction. We suspect that the difference is, at least in part, due to a larger amplitude of the rotation around the vinyl bond in solution. Inspection of Dreiding models shows that rotation of the vinyl moiety out of the position, as determined by the X-ray analysis, almost invariably results in a decrease of the angle ξ. Hence, the X-ray structure having the maximum $|R|/D^{1/2}$ value, all contributions of other rotamers will result in a lower $|R|/D^{1/2}$ value. Although the rather low $|\cos\theta|$ value in solution suggests a large amplitude of rotation, contributions of rotamers with positive $\cos\xi$ values, which would arise when the double bond is under the steroid skeleton, seem unlikely.

Acknowledgment. It is a pleasure to acknowledge Dr. H. J. C. Jacobs for stimulating discussion and helpful suggestions.

Registry No. 1, 73586-29-5; **1a**, 30979-67-0; **1b**, 83780-96-5; **2**, 694-98-4; **2a**, 22516-10-5; **2b**, 66088-27-5; **3**, 61207-62-3; **4**, 74183-81-6; **5a**, 2220-40-8; **5b**, 83731-99-1; **6a**, 50585-71-2; **6b**, 473-06-3; **7**, 57226-88-7; **8a**, 57969-20-7; **8b**, 57969-21-8; 9, 61765-61-5.

Circular Polarization in the Fluorescence of β,γ-Enones: Distortion in the $^1n\pi^*$ State

P. H. Schippers, J. P. M. van der Ploeg, and H. P. J. M. Dekkers*

Contribution from the Department of Theoretical Organic Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands. *Received March 15, 1982*

Abstract: The circular dichroism (CD) and the circular polarization of the luminescence (CPL) in the $n-\pi^*$ transition were measured for a series of five rigid β,γ-unsaturated ketones: (1*S*,3*R*)-4-methyleneadamantan-2-one (**1**), (1*S*,3*R*)-4-adamantylideneadamantan-2-one (**1a**), (1*R*,4*R*)-bicyclo[2.2.1]hept-5-en-2-one (**2**), (1*R*)-7-methylenebicyclo[2.2.1]heptan-2-one (**3**), and (1*S*)-2-methylenebicyclo[2.2.1]heptan-7-one (**4**). All compounds exhibit marked differences between the degree of circular polarization in absorption and in fluorescence, giving evidence of important changes in molecular geometry upon excitation. The nature of these distortions is tentatively analyzed by using the previously found quantitative chirality rule for β,γ-enones (preceding paper in this issue). In the $^1n\pi^*$ state of β,γ-enones, the carbonyl group no longer is planar but is pyramidal due to an out-of-plane displacement of the oxygen atom (local symmetry C_s instead of C_{2v}). The out-of-plane angle is large, and its direction is such that the oxygen approaches the double bond, pointing to a bonding interaction in the excited state, which is briefly discussed.

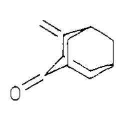
Chiral molecules exhibit circular dichroism (CD): they absorb left and right circularly polarized light to a different extent. Analogously, in the spontaneous emission of such molecules, the left and right circularly polarized photons are unequal in number: circular polarization of the luminescence (CPL).[1,2] Whereas circular dichroism provides information on the chirality of the molecule in its ground state, CPL probes the molecular structure of the excited species.

We were inspired by the interesting photophysics[3,4] and photochemistry[3,5] of the $^1n\pi^*$ state of β,γ-enones to study the circular polarization in the $n-\pi^*$ absorption and fluorescence of some of these compounds. From the results (next section), it appears that frequently the optical activity in emission differs drastically from that in absorption, pointing to severe distortions in the $^1n\pi^*$ state. These are analyzed and discussed in the last part of this paper.

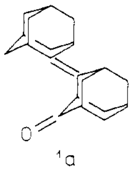
Discussion of the Spectra

We have studied the CD and CPL of five β,γ-unsaturated ketones: (1*S*,3*R*)-4-methyleneadamantan-2-one (**1**), (1*S*,3*R*)-4-adamantylideneadamantan-2-one (**1a**), (1*R*,4*R*)-bicyclo[2.2.1]hept-5-en-2-one (**2**), (1*R*)-7-methylenebicyclo[2.2.1]heptan-2-one (**3**), and (1*S*)-2-methylenebicyclo[2.2.1]heptan-7-one (**4**).

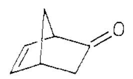
In the absorption spectra of the β,γ-enones, two main regions can be distinguished. First, the usually well-structured absorption around 33 000 cm^{-1} (Figures 1–5), which is due to the carbonyl $n \rightarrow \pi^*$ transition. Compared with saturated ketones ($\epsilon_{max} \sim$ 20–40), its intensity is strongly enhanced, a common phenomenon with many β,γ-enones.[6-9] The circular dichroism shows a fine structure coinciding with that in the unpolarized absorption. For the adamantanone derivatives **1** and **1a**, shape and magnitude of the CD are almost identical (Figures 1 and 2). Whereas the intensity of the Cotton effect of these compounds ($\Delta\epsilon_{max} \simeq 2, 5$) is not much larger than that found for saturated ketones, the intensity of the CD of **2** ($\Delta\epsilon_{max} = 18.8$) is greatly enhanced (Figure 3) relative to its saturated counterpart, and a similar observation is made for **3** ($\Delta\epsilon_{max} = 7.6$) and **4** ($\Delta\epsilon_{max} = -5.7$) (Figures 4 and 5). The opposite and roughly equal CD values in the $n \rightarrow \pi^*$ transitions of **3** and **4**, compounds that differ only by interchanged carbonyl and methylene groupings, suggest an approximately enantiomeric relationship of the chromophoric systems involved.



1



1a



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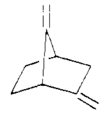

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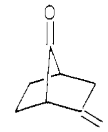

4

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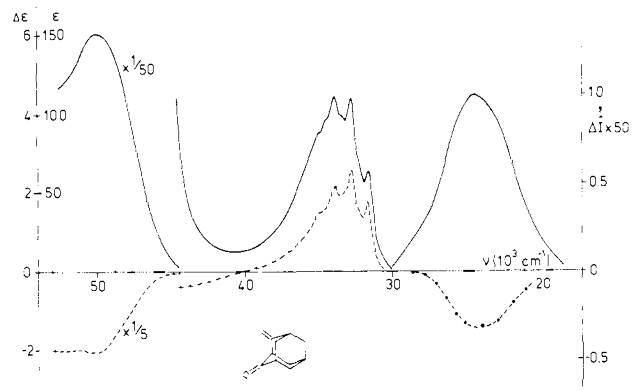

Figure 1. Spectra of enone **1** in *n*-heptane at room temperature: (—) unpolarized absorption (ϵ) and fluorescence (I); (---) circular dichroism ($\Delta\epsilon$) and circular polarization of the fluorescence (ΔI). The standard error in the ΔI values, when not negligible, is given by the height of the vertical bars.

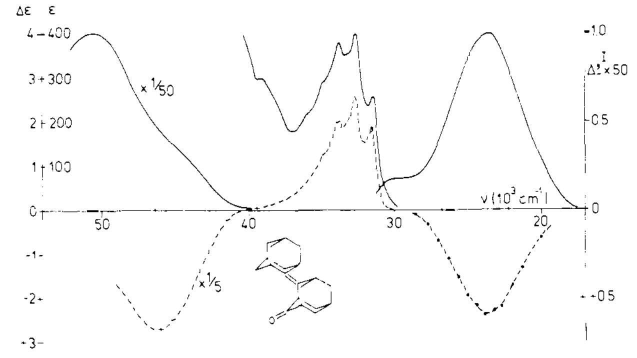

Figure 2. Spectra of enone **1a**; see Figure 1 for explanation.

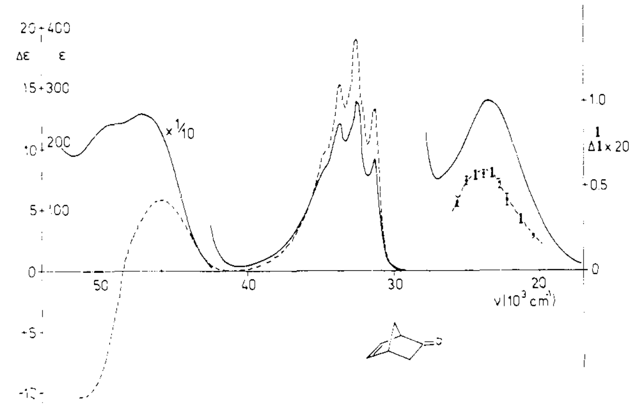

Figure 3. Spectra of enone **2**; see Figure 1 for explanation.

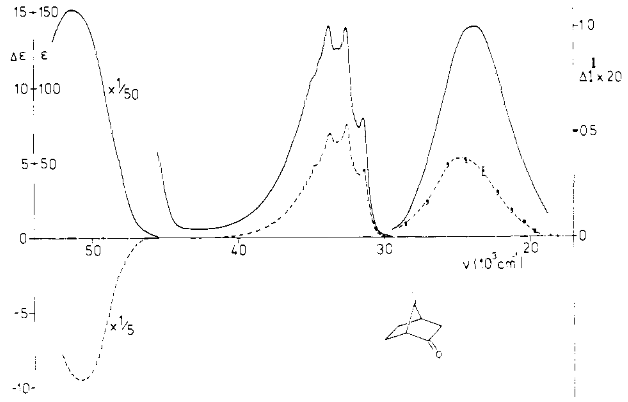

Figure 4. Spectra of enone **3**; see Figure 1 for explanation.

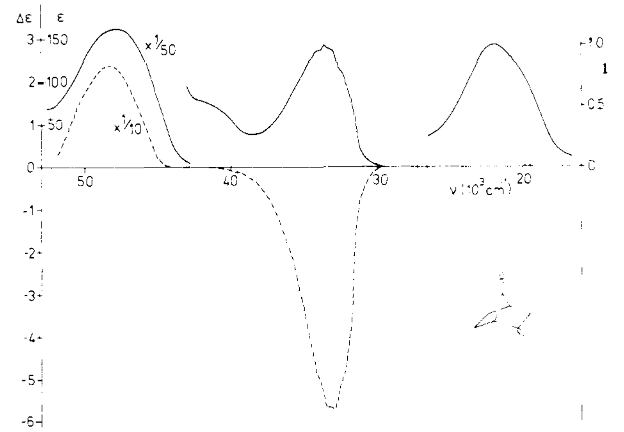

Figure 5. Spectra of **4**. Left: (—) unpolarized absorption (ϵ); (---) circular dichroism ($\Delta\epsilon$) in *n*-heptane at room temperature. Right: emission (I) of **4** in methylcyclohexane/isopentane (1:3) at 90 K. Fluorescence efficiency and circular polarization of the fluorescence at room temperature are low, see text.

Table I. Chiroptical Properties and Quantum Yields of Fluorescence of the β,γ-Enones

	n → π^* absorption			n ← π^* fluorescence	
	D_a, 10^{-40} cgs	R_a, 10^{-40} cgs	g_a, 10^{-3}	ϕ_F	g_e, 10^{-3}
1	1400	6.22	17.8	1.7×10^{-3}	−6.3
1a	5090	6.29	5.0	2.0×10^{-3}	−12.0
2	3600	51.1	56.8	$\sim 5 \times 10^{-5}$	29.4
3	1790	20.5	45.8	6×10^{-4}	15.7
4	1870	−15.2	−32.5	$<2 \times 10^{-5}$	<3

By contrast with the other enones, the CD in the n → π^* transition of **4** virtually lacks fine structure. Secondly, the spectra show a strong absorption in the 50 000–40 000-cm^{-1} region, containing the typical charge-transfer band of β,γ-enones,[8-10] which we shall not consider further here.

From the absorption and circular dichroism of the 33 000-cm^{-1} band, we find the dipole strength D_a, the rotational strength R_a, and the dissymmetry factor g_a of the n → π^* transition by using the well-known relations[1bc,2]

$$D_a = 4c\int(\epsilon/\nu)\,d\nu \qquad (1a)$$

$$R_a = c\int(\Delta\epsilon/\nu)\,d\nu \qquad (1b)$$

$$g_a = 4R_a/D_a \qquad (1c)$$

Here the integration is over the entire electronic absorption band, the constant c equals 23.0×10^{-40} if $\Delta\epsilon$ (ϵ) is expressed in units L.mol^{-1}.cm^{-1} and R_a (D_a) in cgs units. The results are collected in Table I.

Upon excitation in the n → π^* absorption band, the compounds yield with low efficiency a broad structureless emission. Excitation spectra showed that the emission belongs to the enone chromophore. Because of the short lifetimes (see Experimental Section) the emission is assigned as fluorescence. Its shape and position are very similar to the typical n ← π^* fluorescence of saturated ketones. Several data are available on the weak n ← π^* fluorescence of β,γ-unsaturated ketones,[4,11] which seems to be quite general.[11h]

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With **1**, the circular polarization of the fluorescence, ΔI, surprisingly proves to be negative (Figure 1), i.e., opposite in sign to the circular polarization in the n → π^* absorption. The fluorescence band of the related compound **1a** (Figure 2) closely resembles that of **1** (the shoulder at 30 000 cm^{-1} in **1a** is due to an impurity, see Experimental Section). Again the optical activity in emission is opposite to that in absorption. For ketone **2** (Figure 3) the fluorescence yield ($\phi_F = 5 \times 10^{-5}$) is nearly two orders of magnitude smaller than that of the adamantanone derivatives, resulting in a severe overlap of fluorescence and Rayleigh and Raman scattered excitation light under the conditions of the CPL experiment; laser excitation yields the uncontaminated, ketone-like, fluorescence band shape.[12] Although the poor fluorescence yield and the rather low photostability of **2** made the CPL measurements very laborious and the scattered light prevented measurements in the short wavelength tail of the fluorescence band, the result is rewarding. Already from a qualitative inspection of the spectra (Figure 3), it appears that, contrary to the case of the adamantanones, CPL and CD are identical in sign. A similar situation occurs with enone **3** (Figure 4), although here the degree of circular polarization in emission has decreased significantly as compared with that in absorption.

Due to its extremely low fluorescence yield ($<2 \times 10^{-5}$), **4** was the most difficult enone to study. Its CPL could only be detected in the long-wavelength tail of the emission, and the circular anisotropy appeared to be zero. From the limits of noise, this implies 3×10^{-3} as an upper limit of the degree of circular polarization. The fluorescence spectrum,[13] in Figure 5 was measured at 90 K, for it appeared with all enones that lowering of the temperature resulted in a 10–30-fold increase of the quantum yield of luminescence. This interesting phenomenon will be discussed elsewhere.

The elaboration of the I and ΔI data is very similar to that of the ϵ and $\Delta\epsilon$ data, with one exception. Generally in emission experiments the circular polarization $\Delta I = I_L - I_R$ and the average fluorescence intensity $I = {}^1/_2(I_L + I_R)$—where L_L (I_R) is the left (right) circularly polarized intensity—are obtained as relative quantities. This implies that in the relations 2a and 2b, connecting

$$D_e = 4c'\int (I/\nu^4)\,d\nu \tag{2a}$$

$$R_e = c'\int (\Delta I/\nu^4)\,d\nu \tag{2b}$$

$$g_e = 4R_e/D_e \tag{2c}$$

ΔI and I with the rotational and dipole strength in emission,[2] the constant c' is unknown. The dissymetry factor g_e, however, is an absolute quantity. Thus from a CPL experiment, the value of R_e can be obtained if the dipole strength in emission were known, e.g., from the measurement of the radiative lifetime of the emitting state. In our case the experimental determination of D_e proved impossible (cf. Experimental Section), and later on we shall introduce an estimated value. For the present, the discussion will be in terms of g_e only. These values and those of the fluorescence yield ϕ_F are also collected in Table I.

From an inspection of the data in the table, several points may be noted. The close analogy of the CD spectra of **1** and **1a** is reflected in the almost identical R_a values. The analogy does not extend, however, to the dipole strengths D_a. The replacement of the methylene group in **1** by an adamantylidene fragment causes a nearly 4-fold increase in intensity. With **2**, both dipole strength and, more important, rotational strength are strongly enhanced, giving rise to the large dissymmetry factor in absorption. The approximately enantiomeric relationship of the enones **3** and **4** is further specified by their D_a and R_a values. With respect to the optical activity in the fluorescence vs. that in absorption, for all enones studied, a rather drastic change of the dissymmetry factor upon excitation is observed and for enones **1** and **1a** a change of sign is observed.

In the Born–Oppenheimer approximation, the theoretical expression for the rotational and dipole strength in absorption is given by eq 3a and 3b.[2] Here o is the vibrational wave function of the

$$R_a = \langle o|\mathrm{Im}\ \vec{r}_{0,n\pi^*}\cdot\vec{\mu}_{n\pi^*,0}|o\rangle \tag{3a}$$

$$D_a = \langle o|\vec{r}_{0,n\pi^*}\cdot\vec{r}_{n\pi^*,0}|o\rangle \tag{3b}$$

electronic ground state 0, and the electronic matrix elements $\vec{\mu}_{n\pi^*,0}$ and $\vec{r}_{0,n\pi^*}$ are the magnetic and electric moments in the 0 → $^1n\pi^*$ transition. Equation 3a expresses the fact that R_a is obtained by weighting the electronic quantity Im $\vec{r}_{0,n\pi^*}\cdot\vec{\mu}_{n\pi^*,0}$, which is a function of the nuclear coordinates Q, with the nuclear density distribution $0(Q)^2$. This has the important implication that R_a is completely determined by the geometry of the molecule in its vibronic ground state, or even by the equilibrium geometry, when we neglect vibronic coupling effects. Since a similar result holds for the dipole strength D_a, we have

$$R_a = \mathrm{Im}\ \vec{r}_{0,n\pi^*}\cdot\vec{\mu}_{n\pi^*,0} \tag{4a}$$

$$D_a = |\vec{r}_{0,n\pi^*}|^2 \tag{4b}$$

where the electronic transition moments are those in the equilibrium geometry in the ground state (Q_e). Analogous arguments show that the relevant quantities for the $^1n\pi^*$ → 0 emission, R_e and D_e, are also governed by the expression 4, when it is understood that now the values of $\vec{\mu}_{n\pi^*,0}$ and $\vec{r}_{0,n\pi^*}$ refer to the equilibrium geometry in the excited state ($\bar{Q}_e$). Accordingly, the value of the quantities R, D, and g in emission can differ from that in absorption only if $\bar{Q}_e \neq Q_e$. Therefore the data in Table I lead to the conclusion that with the β,γ-enones important distortions must have occurred upon excitation, and it is the nature of these distortions we want to evaluate.

Experimental Section

Methods. The absorption spectra were taken with a Cary 15 or a Cary 219 spectrophotometer and the CD spectra with a Jouan Dichrograph (M III). The emission measurements were done on a home-built spectrometer. The excitation light is obtained from a 900-W xenon arc (for the measurement of the unpolarized fluorescence of **2** we also used a 200-W mercury arc) and a Bausch and Lomb "High intensity" monochromator, followed by a cutoff filter when necessary. The emission channel, which is perpendicular to the excitation line, contains a Spex monochromator (Minimate) and an S-11 photomultiplier (EMI 6256 S). Before passing through the emission optics, the circular polarization of the fluorescence ΔI is modulated at a frequency of 50 kHz by an acoustooptic modulator (Morvue/Hinds) followed by a linear polarizer (Polacoat 105 UV WRMR). For one of the compounds, **1**, the CPL was detected as ac photocurrent and the total fluorescence I as dc photocurrent. The other compounds were studied with the recently modified spectrometer, which measures I and ΔI digitally by using a photon counting technique.[14] The $\Delta I/I$ values were corrected for the chromatic polarization characteristics of the sheet polarizer.[14] Calibration of the spectrometer was done by measuring the (known) CD of samples, placed between the fluorescence cell, now containing an achiral luminescent compound, and the emission optics. The calibration is estimated to be correct within 5%.

For all compounds absorbance, CD in the long-wavelength band, fluorescence I and the circular polarization in the fluorescence ΔI were measured on the same sample solution (solvent *n*-heptane, Merck spectrophotometric grade). Concentrations were $\sim 5 \times 10^{-3}$ M (**1**, **2**, **3**), 2×10^{-3} M (**1a**), and 1×10^{-2} M (**4**). During the CPL measurements, the quality of the sample was checked regularly from its absorbance, CD, and unpolarized fluorescence. When necessary, the experiments were continued with a fresh solution. Excitation was effected as 290 (**1**, **1a**), 310 (**2**), or 300 nm (**3**, **4**) with a bandwidth of 10 (**1**, **1a**) or 20 nm (**2**, **3**, **4**). Emission bandwidths were 10 (**1**, **1a**) or 20 nm (**2**, **3**, **4**). All CPL measurements were performed at room temperature.

The CPL spectrometer was adapted for the measurement of linear polarization by placing a quarter-wave plate (400 nm) in front of the

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(12) We are indebted to Dr. P. H. M. van Zeyl for performing the laser excitation experiment.

(13) Although the luminescence is perceptible only at lower temperatures, it is assigned to fluorescence and not to phosphorescence, since its yield does not depend on solvent viscosity. The unusually large Stokes shift of **4** is also found in the room-temperature fluorescence of the related saturated ketone *exo*-2-acetoxy-7-norbornanone (Schippers, P. H., unpublished result).

(14) Schippers, P. H.; van den Beukel, A.; Dekkers, H. P. J. M. *J. Phys. E* **1982**, *15*, 945–950.

modulator. The instrument was calibrated by measuring fluorescence light that had been rendered linearly polarized. The measurements were performed at 90 K on solutions of **2**, **3**, and **4** in methylcyclohexane/isopentane (1:3). Excitation occurred at 300 nm with a bandwidth of 10 (**2**, **3**) or 20 nm (**4**). The polarization was measured at several points in the fluorescence band with a bandwidth of 10 (**2**, **3**) or 20 nm (**4**).

The fluorescence spectra have not been corrected for the transmission characteristics of the emission channel. Fluorescence yields were measured relative to adamantanone ($\phi_F = 5.2 \times 10^{-3}$).[15] Measurement of the excited-state lifetimes of the available enones turned out to be impossible due to the very low fluorescence efficiency (**2**, **4**) or a lifetime too short (<5 ns for the enones **1a** and **3**) to be studied with the available single-photon counting technique.

Materials. (1*S*,3*R*)-4-Methyleneadamantan-2-one (1) and (1*S*,3*R*)-4-Adamantylideneadamantan-2-one (1a). The adamantanone derivatives (**1**, **1a**) were prepared by Numan.[16] The optical purity, estimated from chemical correlation,[16] was better than 80%. Compound **1a** and to a lesser extent **1** contained a small amount of a persistent contamination resulting—as evidenced by excitation spectra—in a spurious emission at the short-wavelength side of the ketone fluorescence band. Repeated purification of **1** by GLC, having no perceptible effect on either absorption, CD, or CPL caused the spurious emission to diminish but not to disappear [**1** ($[\alpha]_{578}$ +38.6° (*c* 0.21, isooctane)),[16] **1a** $[\alpha]_{578}$ −4.4° (*c* 1.0, *n*-hexane)).[16]].

(1*R*,4*R*)-Bicyclo[2.2.1]hept-5-en-2-one (2). Dehydronorcamphor (**2**) was prepared via a hydroboration reaction[17] starting from norbornadiene and (+)-α-pinene.[18] The reaction product was directly hydrolyzed with $LiAlH_4$ to yield *exo*-bicyclo[2.2.1]hept-5-en-2-ol, which was oxidized with pyridinium chlorochromate in CH_2Cl_2.[19] Purification of the final product proceeded chromatographically. From GLC, it appeared that the sample contained 2% isopinocampheone. We have checked whether this might influence the spectra by studying a solution of isopinocampheone in *n*-heptane. Because its extinction coefficient and fluorescence yield proved to be $^1/_{10}$ and 10 times, respectively, that of dehydronorcamphor, the isopinocampheone can at the most account for 2% of the emission. Since its g_e value proved very small, we may safely conclude that it cannot have influenced the CPL spectrum. Due to the limited optical purity of the starting material (+)-α-pinene (α^{25}_D +19.9, neat liquid, 1-dm cell), **2** was not optically pure either (30% by comparison with the CD data given by Lightner[20]). The spectra have been corrected accordingly.

(1*R*)-7-Methylenebicyclo[2.2.1]heptan-2-one (3) and (1*S*)-2-Methylenebicyclo[2.2.1]heptan-7-one (4). The compounds **3** and **4** were also prepared via a hydroboration reaction[17] with (+)-α-pinene (α^{25}_D +40.3, neat liquid, 1-dm cell) and 7,7-dimethoxybicyclo[2.2.1]heptene.[21] The obtained (−)-*exo*-7,7-dimethoxybicyclo[2.2.1]heptan-2-ol was oxidized to the (+)-7,7-dimethoxybicyclo[2.2.1]heptan-2-one, which was further converted to **4** by a Wittig reaction and deketalization. Enone **3** was prepared from the same exo alcohol via subsequent acetylation, deketalization, Wittig reaction, and finally oxidation. The complete synthesis of both **3** and **4** will be described elsewhere.[22] The optical purity of the dimethoxy ketone was determined directly as 38.3 ± 1.5% by a method, suggested before,[23] that makes use of the CPL technique. The results of a systematic investigation into the applicability and accuracy of this method will be given elsewhere.[24] Since care was taken to ensure that enantiomeric excess was conserved[25] in the sequence of reactions following the preparation of the exo alcohol, the enones **3** and **4** both have an optical purity of 38.3%. The spectra have been corrected for this. The CD of **4** appeared to be similar in shape but almost three times larger than that reported before.[26] GLC showed that **3** was ca. 99% chemically pure (ca. 1% of the precursor (+)-*exo*-7-methylenebicyclo[2.2.1]heptan-2-ol was still present) and that **4** was contaminated with 2% of an unknown compound. Probably this contamination is responsible for the spurious shoulder (at 250 nm) in the absorption spectrum of **4** [$[\alpha]^{25}_D$ (*c* ~1.8, *n*-pentane): **3** (+95.4°), **4** (−63.7°), ^{13}C NMR ($CDCl_3$, 26 °C, δ relative to Me_4Si), **3** (212.68 (s), 153.01 (s), 101.41 (t), 54.45 (d), 48.17 (t), 40.59 (d), 26.94, 23.93 (multiplets), **4** (213.11 (s), 144.73 (s), 106.90 (t), 48.88 (d), 40.86 (d), 35.58 (t), 24.60, 23.45 (multiplets))].

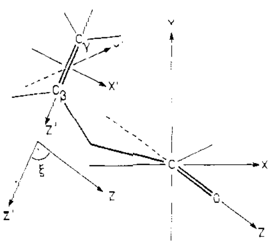

Figure 6. Reference frame for carbonyl group (*x*, *y*, *z*) and ethylenic group (*x'*, *y'*, *z'*) in β,γ-enones. The C_α atom connecting the moieties lies in the *xz* plane. The *y'* axis is perpendicular to the plane of the ethylenic group; ξ denotes the angle between *z* and *z'* axes.

Interpretation of the CPL Data

Apart from its radiative properties, the $^1n\pi^*$ state of β,γ-enones is overwhelmingly of local $n_{CO}\pi^*_{CO}$ type. For the discussion of its geometrical features, a comparison with the $^1n\pi^*$ state of saturated ketones is therefore quite relevant. Upon excitation of formaldehyde to its $^1n\pi^*$ state, two main geometry changes occur:[27] the C=O bond is stretched and the molecule becomes bent; i.e., the nuclear configuration around the carbon atom is no longer planar but pyramidal. If a reference frame as in Figure 6 is adopted, the C=O bond is no longer directed along the *z* axis but, while still being in the *yz* plane, it makes an angle ϕ or $-\phi$ with it (out-of-plane angle, ϕ_{oop}): in the $^1n\pi^*$ state the electronic energy as a function of ϕ_{oop} is a symmetric double-minimum well[27] (Figure 7). Similar phenomena have been found with other ketones of C_{2v} or C_2 symmetry.[1,28,29] The analogy with saturated ketones suggests that the predominant geometry changes in the $^1n\pi^*$ state of β,γ-enones are also in the carbonyl stretch and out-of-plane direction. One expects that it is particularly the latter motion, no longer governed by a symmetric potential because of loss of local carbonyl symmetry by the interaction with the β,γ-olefinic bond, that offers the opportunity to explain the occasionally large changes in rotational strength upon excitation.

To analyze the CPL data, we first assume that nonplanar $^1n\pi^*$ states of β,γ-enones are still adequately described by the wave function 5 that was found for the planar situation.[30] That is, we

$$^1n\pi^* = n_{CO}\pi^*_{CO} + \lambda\pi_{CC}\pi^*_{CC} \qquad (5)$$

take it that nonplanarity of the carbonyl moiety affects only the coefficient λ in the wave function. Second, we assume that also in the nonplanar situation, the magnetic-dipole transition moment derives from the $n_{CO}\pi^*_{CO}$ part of eq 5 and amounts to 1.1×10^{-20} cgs along the C=O bond, whereas the electric-dipole transition moment derives only from the $\pi_{CC}\pi^*_{CC}$ contamination. Then the previously found chirality rule[30] is also adequate to interpret the optical activity in emission:

$$\frac{R_e}{D_e^{1/2}\cdot|\vec{\mu}|} = \cos\theta_e = -(\text{sign } xy)\cdot(\cos\xi) \qquad (6)$$

where *xy* denotes the product of coordinates of the olefinic C_β atom and ξ the angle between the carbonyl bond and the C=C

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direction (Figure 6), where both structural parameters, of course, refer to the excited state.

In the analysis of the CPL data, we proceed as follows. With the experimental value of D_e not being available, we assume for a start $D_e \simeq D_a$. Further, we take the change of $\cos\theta$ upon excitation as a measure for the change of the structural parameter (sign xy)·($\cos\xi$). This procedure accounts best for the discrepancy in Figure 2 of ref 30 between the position of an enone and the theoretical line, provided it does not change very much upon excitation. The quantity (sign xy)·($\cos\xi$) is then readily available and can be translated into an out-of-plane angle ϕ with the help of Dreiding models. We note that a given $\cos\theta_e$ value in principle yields two solutions ($\mp\cos\xi$, depending on the sign of xy). However, with the enones studied, one of them can easily be ruled out, since it would require extremely large out-of-plane angles. The significant solutions are given in Table II.

The inequality signs in the table result when the assumption that $D_e \simeq D_a$ is abandoned. For a discussion of this point, it is useful to differentiate among the enones.

(i) The fact that g_e of **4** is zero (or almost zero) implies that $R_e/D_e^{1/2} \simeq 0$ (only a huge change in dipole strength upon excitation would affect this conclusion), fixing ξ at $\sim 90°$ and therefore the out-of-plane angle ϕ at $\sim +35°$ (a plus sign always denotes the oop displacement toward the double bond).

(ii) For **1** and **1a**, the negative sign of R_e implies an obtuse angle ξ, whatever the value of D_e. It appears from Dreiding models that in these molecules an obtuse angle ξ is always associated with a positive angle ϕ_{oop}; i.e., upon excitation the oxygen atom approaches the C=C bond. We now assume that in a given enone the dipole strength D increases with decreasing C=O—C=C distance, which for all five enones amounts to $D(\phi \text{ pos}) > D(\phi = 0) > D(\phi \text{ neg})$. This assumption seems quite reasonable since it is from ${}^1n_{CO}\pi^*_{CO}$–C=C interaction that the dipole strength results. The positive oop angles of **1** and **1a** therefore imply $D_e > D_a$. As compared with the situation $D_e = D_a$, this implies, the value of g_e being fixed from experiment, also an increase of $|R_e|$ and thus of $|\cos\xi| = |R_e|/D_e^{1/2}\cdot|\vec{\mu}|$, which leads to the inequality signs given in the table.

(iii) With **2** and **3**, the supposition $D_e < D_a$ would give rise to a decrease of $\cos\xi$ and hence to oop angles exceeding +50° and +20°, respectively. These values are incompatible however with the assumption mentioned in (ii), and therefore we must have $D_e > D_a$, which gives rise to the oop angles stated in the table.

Table II bears out that, provided the discrepancies between the optical activities in absorption and fluorescence are due to an out-of-plane distortion, this distortion is always in the direction of the double bond. A specific value for the oop angle is obtained only for **4** (~35°). For the other enones, the analysis specifies the oop angle only within a certain range. However, excluding **3**, the data are compatible with an oop angle of ~35°. (In the next section it appears that our analysis is not adequate for **3**.) This would substantiate our expectation that ϕ does not vary appreciably among individual enones. As we will discuss, however, the presuppositions in our analysis imply that the oop angles given in Table II should not be considered as quantitatively correct. Nevertheless we are convinced that qualitatively our conclusion holds; that is, in their ${}^1n\pi^*$ state, β,γ-enones show large carbonyl out-of-plane distortions in the direction of the olefinic bond.

Discussion

In analyzing the optical activity in the fluorescence, we have used a procedure identical with that in absorption.[30] A first assumption then is that in a nonpolar carbonyl group the magnetic-dipole transition moment $\vec{\mu}_{n\pi^*,0}$ retains the magnitude it has in the planar situation and remains directed along the C=O axis. An indication about the quality of this assumption may be gathered from quantum chemical calculations on formaldehyde, which show that upon an out-of-plane displacement of the oxygen atom, the magnitude of $\vec{\mu}_{n\pi^*,0}$ virtually does not change but that its direction does not quite follow the C=O axis: the angle ϕ' between $\vec{\mu}_{n\pi^*,0}$ and the z axis appears to be smaller than the oop angle ϕ.[31] In our analysis, correction for such an effect would be straightforward: the values of ϕ given in Table II, which are basically obtained as angles between $\vec{\mu}_{n\pi^*,0}$ and the z axis, are in fact those of ϕ'. The actual oop angles ϕ then would come out larger. The uncertainty about the magnitude of $\phi-\phi'$[31] adds an extra uncertainty to the numerical values of the oop angles in Table II.

Another assumption is that the enone's n–π^* transition retains in fluorescence the predominant z' polarization it has in absorption. Whereas in absorption it is ensured by local carbonyl symmetry that no dipole strength derives from the $n_{CO}\pi^*_{CO}$ part of eq 5, in fluorescence—at least if it occurs from a nonplanar excited state—it is not. Here the $n_{CO}\pi^*_{CO}$ charge density may provide a nonvanishing electric-dipole transition moment, which, being in the x direction, does contribute to the dipole but not to the rotational strength. It has the effect of rotating the transition moment away from the z' direction in absorption. Since such a rotation may directly be probed by the linear polarization of the fluorescence,[35] we have applied this technique to **2**, **3**, and **4**, the enones still available. With **3**, we observed a low degree of polarization ($p \sim 0$), which, since it implies a large rotation of electric-dipole transition moment upon excitation, is in contradiction with the adopted model. Therefore we conclude that the analysis for this enone is inadequate. On the other hand, we observed high polarizations ($p \sim +0.3$) for both **2** and **4**. This indicates that with these enones the transition moment approximately retains the original direction upon excitation, which provides support for the neglect of n_{CO}–π^*_{CO} intensity and for the adequacy of eq 5 in describing the excited state.

The starting point in our analysis is that the geometry of the ${}^1n\pi^*$ state of β,γ-enones bears a close analogy with that of saturated ketones. As evidenced by the prominent 1150-cm^{-1} progression in the absorption and CD spectra of most enones (Figures 1–4), the excited state is distorted in the C=O-stretch direction. From a tentative analysis of the Franck–Condon factors, we find that upon excitation the C=O bond in **1** is lengthened by ~0.12 Å, which is practically identical with the value obtained for adamantanone.[29]

Detailed data on the shape of the out-of-plane potential-energy curves in the ${}^1n\pi^*$ state of ketones are scanty. Notorious exceptions are the symmetrical double-minimum potentials (Figure 7) in formaldehyde ($\phi \sim \pm 35°$, height of the energy barrier at planar configuration: 350 cm^{-1})[36] and cyclopentanone ($\phi \sim \pm 35°$, barrier 700 cm^{-1}).[28] Recently we have found that the ${}^1n\pi^*$ state of adamantanone has a double-minimum potential with a rather high barrier (~1100 cm^{-1}).[29] Unfortunately, the value of ϕ is not available. One might argue, however, that—if differing at all from that in formaldehyde—it is somewhat larger. In adamantanone derivatives containing an sp^2-hybridized carbon atom, considerable ring strain is present, as indicated by an X-ray study on adamantylideneadamantane:[37] the C_α—C(=C)—$C_{\alpha'}$ angle

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(31) From semiempirical SCF–MO calculations according to the scheme of Jungen et al.,[32] Emeis found[1c] $\phi' \sim +14°$ for $\phi = +20°$. CNDO/2 calculations by Linder et al.[33] yield $\phi' \sim +6.7°$ for $\phi \sim +10.5°$; inclusion of CI results in a decrease of the difference between both angles: $\phi' \sim +8.6°$ for $\phi \sim +10.5°$. No results are available on formaldehyde with larger oop angles, but CNDO/S calculations[41] on cyclohexanone yield[34] $\phi' \sim +29°$ for $\phi = +40°$. In all calculations it was found that the magnitude of the magnetic-dipole transition moment virtually did not change upon the oop distortion.

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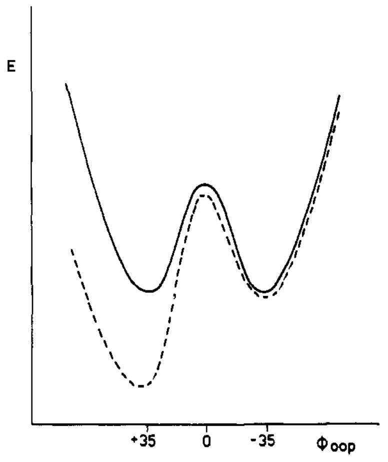

Figure 7. Sketch of the symmetrical double-minimum potential-energy curve in the $^1n\pi^*$ state of formaldehyde (—) and qualitative shape of the corresponding curve in β,γ-enones (---).

Table II. Angle ξ between Ethylenic and Carbonyl Bond and Out-of-Plane Angle ϕ in the $^1n\pi^*$ State of the β,γ-Enones 1–4

	ξ, deg	ϕ, deg
1	>100	>+15
1a	>105	>+20
2	<70	<+50
3	<85	<+20
4	~90	~+35

is found to be 110°, considerably less than the ideal sp^2-hybridization angle. When the oop distortion is viewed as the result from an increase of sp^3 character in the electronic configuration around the carbonyl C atom, the higher barrier in adamantanone—resulting from a certain relief of ring strain as a consequence of the oop distortion—prevents ϕ from becoming smaller than that in formaldehyde. On the other hand, the oop angle will be well below 55°, the angle expected with a purely sp^3-hybridized carbon atom. Similar arguments may hold for other ketones where the carbonyl is part of a five- or six-membered ring.

We have examined whether the electrostatic admixture of ethylenic $\pi_{CC}\pi^*_{CC}$ character into the carbonyl $n_{CO}\pi^*_{CO}$ configuration, which can explain the n → π* optical properties of β,-γ-enones,[30] can also account for the out-of-plane distortions in the $^1n\pi^*$ state of these compounds. Taking **1** as an example, we have, for various oop angles, evaluated λ (given by eq 7 of ref 30) using London's method. As mentioned (cf. footnote 27 of ref 30), the λ values from this procedure are only qualitatively correct; they rather underrate the observed rotational and dipole strengths. To prevent this shortcoming from entering the interaction energy, we have scaled λ such that at $\phi_{oop} = 0$, the experimental dipole strength of **1** is reproduced, i.e., equals $\lambda^2 D_{C=C}$, where $D_{C=C}$ is the dipole strength of the ethylenic $\pi \rightarrow \pi^*$ transition, taken as 2.5×10^{-35} cgs.[35] On the assumption that this scaling factor is not a function of ϕ_{oop}, the interaction energy $E_{int} = \lambda \langle n_{CO}\pi^*_{CO}|V|\pi_{CC}\pi^*_{CC}\rangle = \lambda^2\,\Delta E$ is calculated for various out-of-plane angles. The results are (ϕ_{oop}, E_{int}) = +40°, −900 cm^{-1}; +20°, −400 cm^{-1}; 0°, −100 cm^{-1}; −20°, 0 cm^{-1}; −40°, −50 cm^{-1}. The potential energy curve of **1** is then obtained by superposing these interaction energies upon the double-minimum curve of adamantanone (cf. Figure 7). Although the resultant energy curve can at most be expected to be qualitatively correct, it appears that an electrostatic coupling mechanism can account for a considerable lowering of the well at positive ϕ relative to that at negative out-of-plane angles.[40]

The out-of-plane distortion may have consequences for the photophysical and photochemical processes in the lowest excited-singlet state of β,γ-enones. For instance, the out-of-plane distortion may be a first step along the reaction coordinate of the intramolecular oxetane formation observed with flexible β,γ-enones[42] and also with γ,δ-enones.[43] Further, we remark that the interaction we have studied might have an intermolecular analogue. The fluorescence of ketones is known to be quenched by olefins.[44] As a mechanism for this energy transfer, the formation of an exciplex has been proposed.[45] Exciplexes between $^1n\pi^*$ excited ketones and olefins are also suggested[46] as intermediates in intermolecular oxetane formation[47] (Paterno–Büchi reaction). Without the severe geometrical restraints in β,γ-enones, the bonding in such exciplexes could be quite strong.

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Registry No. **1**, 83829-09-8; **1a**, 83829-10-1; **2**, 16346-63-7; **3**, 83829-11-2; **4**, 83829-12-3; *exo*-bicyclo[2.2.1]hept-5-en-2-ol, 71030-15-4; (−)-*exo*-7,7-dimethoxybicyclo[2.2.1]heptan-2-ol, 70981-37-2; (+)-7,7-dimethoxybicyclo[2.2.1]heptan-2-one, 83829-13-4.

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(39) This value corresponds to an electric-dipole transition moment of about 1 Å·e = 4.8 × 10^{-18} cgs, as is found from simple MO theory.

(40) (a) We also have performed some explorative CNDO/S–CI calculations[41] (CI between the lowest 60 singly excited states) on 3-methylenecyclohexanone and cyclohexanone. It is found that the shape of the ground-state potential curve is virtually unaffected by the introduction of the double bond. In the $^1n\pi^*$ state, the curve for the saturated ketone has a local maximum at $\phi = 0$ and falls off in both oop directions, although at $\phi = +40°$, no minima are achieved actually. The introduction of the double bond affects the shape of the ketone $^1n\pi^*$ potential at positive and negative ϕ differently: +40°, −130 cm^{-1}; +20°, −60 cm^{-1}; 0°, 0 cm^{-1} (zero of relative energy scale); −20°, +90 cm^{-1}; −40°, +10 cm^{-1}. Although the double bond works out in favor of a positive oop angle, one may question the significance of this result because (i) the parametrization in CNDO/S is not chosen for total energy calculations and (ii) the result depends critically on the CI: at the SCF stage the interactions are much larger and they are in the opposite direction, i.e., negative oop angles are favored. Incidentally, in contrast to the situation with saturated ketones,[40b] the CNDO/S scheme does not well reproduce the radiative properties of the enone n → π* transition either, dipole strength being overestimated by more than an order of magnitude. (b) Bouman, T. D.; Lightner, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3145–3154.

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