CIRCULAR DICHROISM AND CONFORMATIONAL ANALYSIS OF DIASTEREOMERIC BICAMPHORS

Stefan E. BOIADJIEV[1] and David A. LIGHTNER[2,]*

Chemistry Department, University of Nevada, Reno, Nevada 89557, U.S.A.;
e-mail: [1] *stefcho@scs.unr.edu,* [2] *lightner@scs.unr.edu*

Dedicated to Professor Otakar Červinka on the occasion of his 75th birthday in recognition of his outstanding contributions to the area of organic stereochemistry.

Stereospecific syntheses afforded *endo,endo-* (**1**) and *exo,exo-* (**2**) bicamphors, while the third possible diastereomeric *exo,endo*-bicamphor (**3**) originated from nonselective camphor radical dimerization. The stereochemistry of bicamphor linkage was confirmed by ^{1}H NMR analysis. Chiroptical and ultraviolet spectral data are presented for the three diastereomers **1**–**3** to show interchromophoric interaction. Conformational analysis to evaluate the relative orientation of each pair of carbonyl chromophores was accomplished by ^{1}H NMR spectroscopy and molecular mechanics calculations.
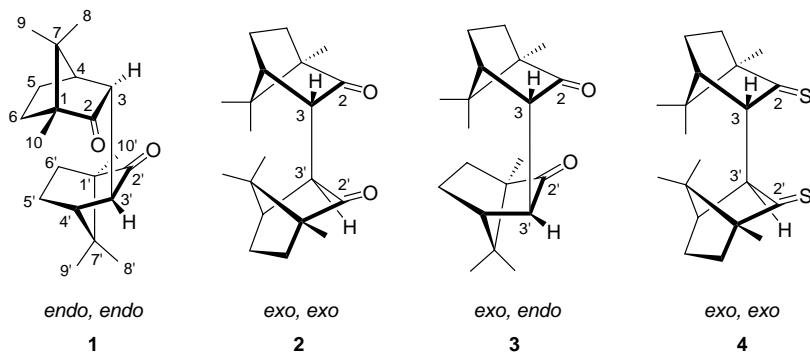
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The ketone carbonyl $n \rightarrow \pi^*$ transition was among the first chromophores studied extensively by modern chiroptical methods: optical rotatory dispersion[1] (ORD) and circular dichroism[2] (CD) spectroscopy. Attractive factors include its accessibility ($\lambda_{max} \approx 300$ nm) and its spectroscopic nature (electric dipole forbidden – magnetic dipole allowed) which leads to a very large Kuhn's dissymmetry factor, $g = \Delta\varepsilon/\varepsilon$. Early investigations led to the first rationalization of optical activity imposed on a symmetric carbonyl group by its chiral environment, the octant rule[3–5]. Over the past fifty years a wealth of experimental data for the carbonyl $n \rightarrow \pi^*$ transition CD and ORD have been accumulated, analyzed and reviewed[1–7]. Although the octant rule has been firmly established and extensively applied in the determination of absolute configuration or conformation of ketones, refinements (such as contributions from front octants[8]) have been made, and reservations have been expressed[6] when new perturbers or cyclic systems were investigated, *e.g.* cyclopropyl-containing tricyclic ketones[9]. The interpretation of CD Cotton

effects in many other cases of rigid bicyclic or polycyclic ketones has also not been straightforward[4].

In 1994 Sotiropoulos and coworkers[10] reported on the X-ray crystallographic analysis of (1*R*,1′*R*,3*R*,3′*R*,4*R*,4′*R*)-3,3′-bibornane-2,2′-dione (**1**) (called bicamphor in this article) and its CD spectrum. The CD spectrum of **1** was unusual in that two n→π* Cotton effects of opposite sign and equal intensity (bisignate shape) were seen near 300 nm and this was interpreted[10] in terms of the exciton theory[11].

Bicamphor **1** is but one of three possible diastereomeric bicamphors formed by linking two (+)-camphor units at C(3): *endo,endo* (**1**), *exo,exo* (**2**) and *exo,endo* (**3**). In the following we report the CD spectral properties of those three isomeric bicamphors and analyze their conformations using molecular mechanics calculations.

endo, endo	*exo, exo*	*exo, endo*	*exo, exo*
1	**2**	**3**	**4**

EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained on a Varian Unity Plus spectrometer operating at a ^{1}H frequency of 500 MHz. *J*-Modulated spin-echo and pulsed field gradient (PFG) versions of HMQC and HMBC experiments were used to obtain ^{1}H and ^{13}C NMR assignments. CDCl$_3$ solvent was used throughout and chemical shifts were reported in δ (ppm) referenced to the residual CHCl$_3$ ^{1}H signal at 7.26 ppm and CDCl$_3$ ^{13}C signal at 77.00 ppm. Optical rotations were measured on a Perkin–Elmer model 141 polarimeter, circular dichroism spectra were recorded on a JASCO J-600 instrument, and UV spectra were recorded on a Perkin–Elmer Lambda 12 spectrophotometer – all in spectral-grade solvents. Gas chromatography/mass spectrometry analyses were carried out on a Hewlett–Packard 5890A capillary gas chromatograph (30 m DB-1 column) equipped with a Hewlett–Packard 5970 mass-selective detector. Analytical thin layer chromatography was carried out on Merck (J. T. Baker) silica gel IB-F plates (125 μm layer) and preparative TLC on Woelm silica gel with added gypsum binder.

(+)-(1*R*)-Camphor was from Aldrich, (+)-(1*R*)-3-*endo*-bromocamphor was synthesized according to Kipping and Pope[12] and (–)-(1*R*)-thiocamphor was prepared according Veenstra and Zwanenburg[13].

(–)-(3R,3′R)-endo,endo-Bicamphor (**1**)

exo,exo-Bicamphor (**2**) (302 mg, 1 mmol) was dissolved in 5 M KOH solution in CH_3OH (8 ml) and stirred for 24 h with occasional heating to maintain homogeneity. Water ($\approx$50 ml) was added dropwise, the product was separated by filtration and recrystallized from EtOH (2.5 ml) to afford 242 mg (80%) of pure *endo,endo* isomer **1**. It had m.p. 162–163 °C (ref.[14] m.p. 161–162 °C); $[\alpha]_D^{20}$ –3.0, $[\alpha]_{365}^{20}$ +24.1 (c 0.6, CH_3OH); $[\alpha]_D^{20}$ –14.7, $[\alpha]_{365}^{20}$ –6.6 (c 0.7, hexane) (ref.[14] $[\alpha]_D^{20}$ –6 (c 0.5, CH_3OH)); gas-chromatography retention time (GC RT) 17.42 min. MS (rel. abundance, %): 302 ([$M^{\bullet+}$], 42), 274 (56), 259 (39), 231 (11), 193 (24), 151 (21), 108 (46), 83 (47), 55 (81), 41 (100).

(+)-(3S,3′S)-exo,exo-Bicamphor (**2**)

This isomer was prepared from 3-*exo*-3′-*exo*-bithiocamphor (**4**) *via* dihydropyridazine[15] intermediate as described by Schroth et al.[16]. It had m.p. 148–150 °C (ref.[13] m.p. 149–150 °C, ref.[16] m.p. 150–151 °C, ref.[17] m.p. 149 °C); $[\alpha]_D^{20}$ +129.2, $[\alpha]_{365}^{20}$ +742.4 (c 0.1, C_2H_5OH); $[\alpha]_D^{20}$ +119.5, $[\alpha]_{365}^{20}$ +702.3 (c 0.1, hexane) (ref.[16] $[\alpha]_D^{20}$ +140 (c 1.0, C_2H_5OH), ref.[14] $[\alpha]_D^{20}$ +137 (c 0.5, CH_3OH), ref.[17] $[\alpha]_D^{20}$ +135 (c 1.0, $CHCl_3$)); GC RT 18.66 min. MS (rel. abundance, %): 302 ([$M^{\bullet+}$], 31), 274 (30), 259 (27), 231 (13), 192 (30), 151 (27), 109 (29), 83 (56), 55 (82), 41 (100).

(+)-(3S,3′R)-exo,endo-Bicamphor (**3**)

This isomer was obtained by preparative TLC separation of a mixture **1**–**3** from nonselective photochemical dimerization of (+)-(1R)-3-*endo*-bromocamphor as described by Orito et al.[14]. It had m.p. 100–101 °C (ref.[14] m.p. 94–95 °C); $[\alpha]_D^{20}$ +118.3, $[\alpha]_{365}^{20}$ +654.0 (c 0.1, CH_3OH); $[\alpha]_D^{20}$ +128.1, $[\alpha]_{365}^{20}$ +715.0 (c 0.1, hexane) (ref.[14] $[\alpha]_D^{20}$ +122 (c 0.5, CH_3OH)); GC RT 17.09 min. MS (rel. abundance, %): 302 ([$M^{\bullet+}$], 100), 274 (41), 259 (30), 231 (14), 193 (16), 151 (40), 108 (42), 83 (53), 55 (84), 41 (100).

(–)-(3S,3′S)-exo,exo-Bi(thiocamphor) (**4**)

The dithione was synthesized stereospecifically from (–)-(1R)-thiocamphor as described by Campbell and Evgenios[18]. It had m.p. 185–187 °C (ref.[18] m.p. 174–175 °C, ref.[19] m.p. 180 °C); $[\alpha]_D^{20}$ –204.1, $[\alpha]_{436}^{20}$ +455.1, $[\alpha]_{365}^{20}$ –495.9 (c 0.1, CH_3OH); $[\alpha]_D^{20}$ –235.0, $[\alpha]_{436}^{20}$ +462.3, $[\alpha]_{365}^{20}$ –448.4 (c 0.2, hexane) (ref.[15] $[\alpha]_D^{20}$ –332.1 (C_6H_6), ref.[17] $[\alpha]_D^{20}$ –333.1 (C_6H_6)).

RESULTS AND DISCUSSION

Synthesis

The (3R,3′R)-*endo,endo* isomeric bicamphor (**1**) was obtained on preparative scale (in 80% yield) by base-catalyzed isomerization of the corresponding *exo,exo* epimer **2**, as suggested by Orito et al.[14], while earlier stereospecific synthesis of **1** was achieved by reduction (Zn/CH_3CO_2H) of (E)-camphorquinone[10]. The stereospecific synthesis of (3S,3′S)-*exo,exo*-bicamphor (**2**)

was carried out as described by Schroth *et al.*[16] starting from *exo,exo*-bi(thiocamphor)[18,19] (**4**) *via* dihydropyridazine derivative[15]. Although longer, this route offered stereochemical homogeneity, which is not readily obtainable, for instance, by camphor enolate oxidative dimerization[20]. Such *exo,exo* dimerization selectivity was only recently observed (LiHMDS/Cu(OTf)$_2$ or LDA/CuCl$_2$/TMEDA) but yet did not allow for preparative isolation of **2**, which was *in situ* reduced to bis-isoborneols[21]. An alternative, higher-yielding route to **2** involves two step oxidation of **4** first to the disulfine (with mCPBA) and then without isolation to diketone **2** (with RuCl$_3$/NaIO$_4$)[17]. Synthetic access to (3*S*,3′*R*)-*exo,endo*-bicamphor (**3**) is limited to a nonselective reaction such as camphor enolate dimerization[20]. Since chromatographic separation of a mixture of **1**–**3** is unavoidable, it was preferable to photolyze (+)-(1*R*)-3-*endo*-bromocamphor to achieve dimerization of the photolytically generated camphor radical[14]. This method afforded a mixture of bicamphors which is statistically enriched in **3**, from which **3** was separated by preparative TLC.

NMR Characteristics and Absolute Configuration

The ^{13}C NMR data of bicamphors **1**–**3** and *exo,exo*-bi(thiocamphor) (**4**) are presented in Table I. The assignments were made on the basis of PFG HMQC and HMBC experiments and closely follow those reported in the literature[14,16,19]. *endo,endo* Isomer **1** and *exo,exo* isomer **2** possess C_2 symmetry axes and consequently showed but one ^{13}C NMR signal for each symmetry-related carbon atom. Only the *exo,endo* isomer **3** exhibited separate signals for all 20 carbons, as if a 1 : 1 mixture of **1** and **2** were being examined. In dithione **4**, the sp^2 carbon was deshielded to 274.68 *vs* 271.52 ppm in the monothione constituent. Compared to diones **1**–**3**, the carbons adjacent to the thiocarbonyl carbons in **4** experience a 10–20 ppm downfield shift.

The ^{1}H NMR data of **1**–**4** are summarized in Table II. They match those reported earlier by other authors[10,14,16]. Crucial for assignment of configuration at the C(3)–C(3′) junction were couplings involving proton at C(3) and C(4). As indicated in Table II, the C(4,4′)-proton in *endo,endo*-**1** is spin coupled with identical *J* = 4.0 Hz to two *exo*-protons at C(5,5′) and C(3,3′), but in *exo,exo*-**2** only the spin coupling to the C(5,5′)-*exo*-proton remains (*J* = 4.2 Hz). The *exo,endo*-bicamphor (**3**) showed its C(4)-proton (d at 2.71 ppm) coupled only to the C(5)-*exo*-proton with *J* = 4.0 Hz, and the C(4′)-proton (t at 2.38 ppm) as apparent triplet (*J* = 4.3 Hz) from coupling to C(5′)- and C(3′)-H-*exo*. Coupling constants within the bornane skeleton from spin simulation were also reported[16].

The absolute configuration (3*R*,3′*R*)-**1** was determined earlier by X-ray crystallographic analyses[10]. The dihedral angles found experimentally in solid state O(21)–C(2)–C(3)–C(3′) +47.35° and O(2′1)–C(2′)–C(3′)–C(3) +47.08° revealed the *endo,endo* junction between the two cyclohexane camphor rings. Assignment of the stereochemistry at the linkage in **2** as (3*S*,3′*S*) is based on its ^{1}H and ^{13}C NMR spectra (degenerate by symmetry), as well as on the zero value of *J* spin-spin coupling constant between C(3)-H and

Position	1	2	3	4
1-C	59.28	57.24	57.50	67.80
1′-C			58.44	
2-CO	218.82	219.36	219.63	274.68
2′-CO			220.67	
3-CH	49.15	54.17	51.75	69.88
3′-CH			51.72	
4-CH	48.98	46.75	46.54	49.23
4′-CH			46.66	
5-CH$_2$	22.25	28.94	29.31	29.21
5′-CH$_2$			21.28	
6-CH$_2$	30.55	28.79	29.00	31.87
6′-CH$_2$			30.66	
7-C	45.72	46.72	45.28	48.85
7′-C			46.40	
8-CH$_3$	19.45	20.02	20.38	20.60
8′-CH$_3$			19.14	
9-CH$_3$	19.98	21.03	19.54	21.18
9′-CH$_3$			21.84	
10-CH$_3$	9.73	9.39	9.56	14.08
10′-CH$_3$			9.60	

^{a} Chemical shifts in ppm downfield from Si(CH$_3$)$_4$; ^{b} for the numbering system, see structure **1**.

C(4)-H (dihedral angle ≈90°). Assignment of linkage stereochemistry in **3** as (3*S*,3′*R*) is supported by more complicated ^{1}H NMR and doubled ^{13}C NMR signals of the compound. An X-ray crystal structure of dithione **4** has been reported[22], confirming the (3*R*,3′*R*) configuration.

TABLE II
^{1}H NMR spectral data of bicamphors **1**–**3** and bi(thiocamphor) **4** in $5\cdot10^{-3}$ M $CDCl_3$ solutions at 25 °C[a]

Position		**1**	**2**	**3**	**4**
3-CH		2.47^b	2.03^c	1.90^d	2.51^c
3′-CH				2.45^e	
4-CH		1.99^f	2.11^g	2.71^h	2.35^j
4′-CH				2.38^i	
5-CH$_2$	*endo*	1.65^k	1.31^l	1.25^m	1.36^k
	exo	1.80^k	1.98^k	2.04^k	2.05^k
5′-CH$_2$	*endo*	1.65^k	1.31^l	1.42^k	1.36^k
	exo	1.80^k	1.98^k	1.79^k	2.05^k
6-CH$_2$	*endo*	1.65^k	1.55^n	1.42^k	1.55^k
	exo	1.80^k	1.64^o	1.64^k	1.75^k
6′-CH$_2$	*endo*	1.65^k	1.55^n	1.64^k	1.55^k
	exo	1.80^k	1.64^o	1.90^k	1.75^k
8-CH$_3$		1.00	0.93	0.95	1.01
8′-CH$_3$				0.99	
9-CH$_3$		0.878	0.75	0.81	0.69
9′-CH$_3$				0.85	
10-CH$_3$		0.883	0.90	0.88	1.09
10′-CH$_3$					

[a] Chemical shifts in ppm downfield from $Si(CH_3)_4$, for the numbering system, see structure **1**; [b] dd, $J = 4.0$, 1.2 Hz; [c] singlet; [d] d, $J = 11.0$ Hz; [e] dd, $J = 11.3$, 4.3 Hz; [f] t, $J = 4.0$ Hz; [g] d, $J = 4.2$ Hz; [h] d, $J = 4.0$ Hz; [i] t, $J = 4.3$ Hz; [j] d, $J = 3.9$ Hz; [k] multiplet; [l] ddd, $^3J = 9.0$, 3.6 Hz, $^2J = 12.5$ Hz; [m] ddd, $^3J = 9.1$, 5.2 Hz, $^2J = 13.7$ Hz; [n] ddd, $^3J = 9.0$, 5.3 Hz, $^2J = 13.9$ Hz; [o] ddd, $^3J = 11.4$, 3.6 Hz, $^2J = 13.9$ Hz.

Conformational Analysis

Molecular mechanics calculations[23] of **1**–**3** may be used to recognize the global energy minimum conformations and explore the relationship between them and other isomers produced by rotation about the C(3)–C(3′) bond. The results are summarized in Fig. 1. In the *exo,endo* isomer **3**, the analysis indicates that the global minimum ($\phi \approx 170°$) lies far below local minima at $\phi \approx 80°$ (7.2 kcal/mol higher) and $\phi \approx -30°$ (9.8 kcal/mol higher), which doubtless do not contribute much to the rotameric population. This conformation places the carbonyl groups *anti* to one another and nearly in line. In the *exo,exo* isomer **2**, the global energy minimum conformation at $\phi \approx 120°$ lies only 1.7 kcal/mol below a broad local minimum at $\phi \approx 40°$. The barrier between these two conformers is very low, suggesting that rotamers between $40° < \phi < 120°$ contribute to the population. Other local minima at $\phi \approx -66$ and $180°$ lie some 6.6 and 7.4 kcal/mol higher than the global minimum and can probably be discounted. The orientation of the two carbonyls in **2** is probably *synclinal*. The *endo,endo* isomer **1** apparently has two nearly isoenergetic global minima, one at $\phi \approx 10°$, the other at $\phi \approx -90°$. Local minima at $\phi \approx 110$ and $-140°$ lie significantly higher (4.4 and 5.4 kcal/mol, respectively). Consequently, **1** might be expected to consist of two rotamers, one with carbonyl groups oriented *syn*, the other with them oriented 90° apart. Just how solvent might perturb the conformational preferences was not assessed, as we were looking for only a qualitative picture. However, the
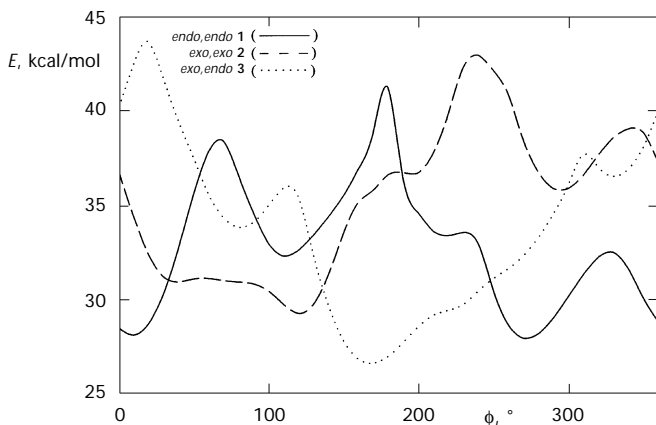

FIG. 1
Plots of steric energy (kcal/mol) *versus* rotation angle in 10° steps about the C(3)–C(3′) bond of bicamphors **1**–**3**. The zero rotation angle ($\phi = 0$) corresponds to the conformation with carbonyl groups eclipsed

^{1}H NMR coupling constants (J(3H,3′H)) may add further insight. In **3**, the value J = 11.3 Hz (Table II) suggests an H(3)–C(3)–C(3′)–H(3′) dihedral angle ≈160°, which translates into a C(3)–C(2)–C(2′)–C(3′) torsion angle of ≈160° consistent with the ϕ ≈ 170° predicted by molecular mechanics calculations. In **1** and **2** (and **4**), the protons at C(3) and C(3′) are isochronous and spin-spin coupling between them is not observable.

Ultraviolet (UV) and Circular Dichroism (CD) Spectroscopy

The UV spectra for the n→π* transitions of bicamphors **1**–**3** are compared to that of camphor in Fig. 2. Interestingly, the UV curves of **1**–**3** are broader (larger band half-widths), more intense (larger ε) and wavelength-shifted relative to that of camphor at twofold concentration. Bicamphors **2** and **3** show an unusual hyperchromicity, with ε values nearly twice that of two camphors; and relative to camphor, **3** is noticeably red-shifted (310 *vs* 290 nm) while **2** is noticeably blue-shifted (280 *vs* 290 nm). The wavelength shift and hyperchromicity behavior in the UV of **2** and **3**, and even **1**, is clear evidence for an electronic interaction between the two bis-homoconjugated chromophores. Such electronic interactions have long been known for β,γ-unsaturated ketones[24], as well as in more remotely con-jugated ketones[4,25]. Such interactions in γ-diketones, of which the bicamphors are but one example, have been shown in the n-orbital splittings observed by photoelectron spectroscopy[4,26], carbonyl
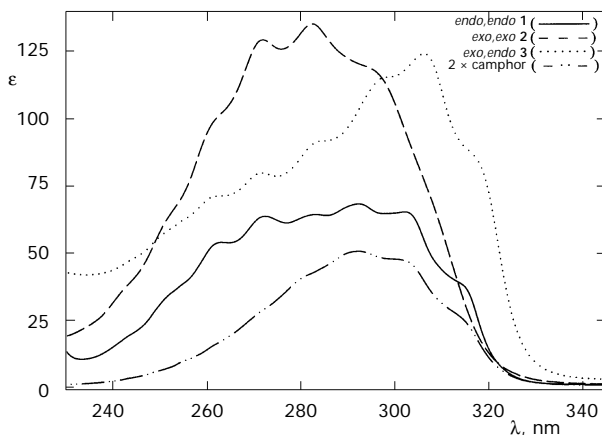

Fig. 2

Ultraviolet spectra of bicamphors **1**–**3** and (+)-(1*R*)-camphor (2 × ε) in 2.9–8.3·10^{-3} M hexane solutions at 23 °C

TABLE III
UV[a] and CD[b] data of bicamphors 1–3, (+)-(1R)-camphor and bi(thiocamphor) 4

Solvent	1		2		3		(+)-Camphor		4	
	UV	CD	UV	CD	UV	CD	UV	CD	UV	CD
Hexane	sh 39(313)	+2.00 (313)	sh 118(295)	+3.77(288)	sh 87(316)	sh +2.51(314)	sh 13(313)	sh +1.11(311)	57 (498)	+0.28(521)
	65(302)	+1.58(306)	135(283)		124(306)	+3.16(304)	sh 24(301)	+1.61(301)	3 240(284)	0(508)
	68(292)	0(298)	129(272)		sh 114(297)	sh +2.61(296)	25(292)	sh +1.44(293)	13 560(242)	-1.91(475)
	64(283)	-1.90(283)	sh 100(262)		sh 91(284)		sh 21(281)			-8.93(302)
	63(272)	sh-1.83(286)			80(272)					-9.10(282)
	54(263)				sh 71(262)					0(260)
	sh 35(253)									+25.0(243)
										0(234)
										-29.5(225)
CH$_3$CN	sh 72(299)	+2.06(310)	152(283)	+4.12(288)	sh 94(313)	sh +2.64(311)			57(482)	+0.45(510)
	82(285)	sh +1.61(304)	152(277)		125(304)	+3.12(303)			3 230(282)	0(495)
	81(271)	0(297)			sh 116(294)				12 810(247)	-1.54(469)
		-2.04(283)								-9.30(300)
										-8.69(279)
										0(268)
										+19.4(249)
										0(239)
										-29.9(229)

TABLE III
(Continued)

Solvent	1		2		3		(+)-Camphor		4	
	UV	CD	UV	CD	UV	CD	UV	CD	UV	CD
CH_3OH	sh 74(302) 95(285) sh 90(278)	+1.86(307) 0(295) –2.12(282)	184(283) 185(277)	+4.55(288)	129(301) sh 105(279)	sh +2.38(312) +3.14(302)	32(288) sh 26(277)	+1.53(294)	57(481) 2 970(281) 12 900(245)	+0.24(515) 0(502) –1.58(470) –8.65(300) –8.50(280) 0(266) +20.8(247) 0(238) –29.9(228)
CF_3CH_2OH	113(285)	+2.17(304) 0(291) –1.84(279)	193(282)	+4.39(285)	157(293)	+3.38(299)	41(283)	+1.58(289)		

[a] ε_{max} (λ_{max}, nm), sh shoulder; [b] $\Delta\varepsilon_{max}$ (λ_{max}, nm); concentration 2.9–$4.2 \cdot 10^{-3}$ mol/l for **1–3**, $6.0 \cdot 10^{-3}$–$6.0 \cdot 10^{-5}$ mol/l for **4**, and 1.1–$1.3 \cdot 10^{-2}$ mol/l for camphor.

deshieldings observed by ^{13}C NMR (refs[4,27]) and by exaltations of $\Delta\varepsilon$ and bathochromic shifts of λ_{max} observed for the n→π* transitions by CD spectroscopy[4]. The blue-shifted and red-shifted UV λ_{max} seen for **2** and **3** (Fig. 2 and Table III) are reminiscent of exciton coupling for parallel and in-line orientations, respectively, of the carbonyl electric transition dipoles of **2** and **3** (refs[4,28]). However, although **3** probably adopts conformations with its carbonyls oriented in-line, and **2** (and **1**) may have them oriented parallel, the nature of the carbonyl n→π* transition (electric dipole forbidden; ε weak, with intensity borrowed from vibronic coupling) would argue against an exciton mechanism for the observations of Fig. 2.

Like the UV spectra, the CD spectra (Fig. 3) for the n→π* transitions of **2** and **3** exhibit a hypsochromic shift in λ_{max} for **2** and a bathochromic shift for **3**. In the CD spectra, however, λ_{max} for **3** is only slightly shifted from that of the parent camphor and there is little change in $\Delta\varepsilon$. In contrast, λ_{max} for **2** is strongly shifted, and $\Delta\varepsilon$ is noticeably increased (Table III). Most remarkable is the bisignate CD curve for **1**. Bisignate curves with strong solvent dependence have previously been shown for camphor analogs[4,29], but whether the CD curve of **1** represents overlapping "solvated" and "unsolvated" species seems unlikely because the shape and intensities remain nearly unchanged when the solvent is changed from hexane to methanol to 2,2,2-trifluoroethanol. Again, although the shape of the CD curve is reminiscent of those seen in examples of exciton coupling CD, it seems more likely that the interaction is that due to a coupling of a locally excited
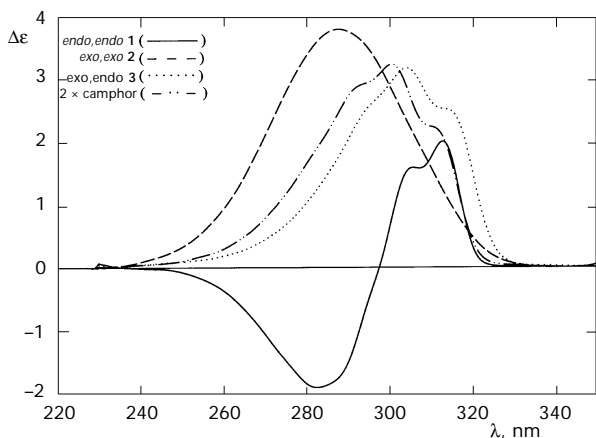

FIG. 3
Circular dichroism spectra of bicamphors **1**–**3** and (+)-(1*R*)-camphor (2 × $\Delta\varepsilon$) in 2.9–8.3·10^{-3} M hexane solutions at 23 °C

carbonyl n→π* state with the locally excited π→π* state of the second carbonyl as described for the β-diketone bicyclo[2.2.1]heptane-2,7-dione by Hansen[4,30].

We had also intended to measure and analyze the UV-VIS and CD spectra of the dithiones corresponding to bicamphors **1**–**3**; however, we were able to prepare only one, *exo,exo*-**4**, whose chiroptical data are given in Table III.

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