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Natural and Magnetic Circular Dichroism Spectra of Selenofenchone. Evidence for a Singlet–Triplet Component of the n $\rightarrow \pi^*$ Transition of Selenoketones

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Blue (-)-selenofenchone (1) is observed to give a negative long-wavelength Cotton effect (CE), $\Delta \epsilon_{573}^{max} = -0.86$, in addition to a series of CE's down to 190 nm, $\Delta \epsilon_{270}^{\text{max}} = -5.21$, $\Delta \epsilon_{232}^{\text{max}} + 4.90$, in its circular dichroism (CD) spectrum measured in *n*-heptane The long-wavelength CD (573 nm) and UV (625 nm) λ_{max} of 1 are found surprisingly well separated. Support for the singlet-triplet nature of this electronic transition may be found in a sharp positive magnetic CD band centered near 630 nm in (±)-selenofenchone. The CD and UV data are compared with those of thiofenchone (2) and fenchone (3).

Introduction

The preparation of authentic saturated alkyl selenoketones has been reported only recently^{2,3} and then largely in connection with olefin synthesis. During the course of the present work a short communication⁴ appeared reporting (1) same-signed long-wavelength Cotton effects (CE's) for selenofenchone, thiofenchone, and fenchone and (2) characterization of the absorption as $n \rightarrow \pi^*$ based on solvent shifts. The data were not otherwise explained, particularly the large difference between the circular dichroism (CD) and UV λ_{max} . In this work, we report CD and UV data for (-)-selenofenchone ((-)-1(R),3,3-trimethylbicyclo[2.2.1]heptane-2-selone) (1), at present the

1:
$$X = Se$$

2: $X = S$
3: $X = O$
4: $X = N-N=P\phi_3$
5: $X = N-NH_2$

only optically active selone known, and compare them with the corresponding data for thiofenchone (2) and fenchone (3). We report also the first magnetic CD (MCD) spectra of a selone (racemic 1), data which assist in assignment of a triplet component to the long-wavelength transition.

Experimental Section

Circular dichroism (CD) spectra were obtained on a JASCO J-40A automatic recording spectropolarimeter equipped with J-DPY data processor, a photoelastic modulator, and PAR lock-in amplifier. Magnetic circular dichroism (MCD) spectra were measured on a JASCO J-40 instrument equipped with a 15-kG magnet. Ultraviolet

(UV) spectra were collected on a Cary Model 219 spectrophotometer and are presented in Table II along with assignments. All NMR spectra (¹H and ¹³C) were recorded in CD_2Cl_2 , unless otherwise indicated, and are reported in δ (parts per million from an internal standard tetramethylsilane (Me₄Si)). Infrared (IR) spectra were recorded in CCl₄ unless otherwise indicated on a Perkin-Elmer Model 599 instrument. Rotations were run either neat or in CHCl₃, unless otherwise specified, on a Perkin-Elmer Model 141 polarimeter. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. The (-)-fenchone used in this work was from Aldrich and had $[\alpha]^{20}_{589} = -51.25^{\circ}$ (neat). It was >99.9% pure, as were 1 and 2, by gas chromatography $(1/_8 \text{ in.} \times$ 6 ft, 12% QF-1 on Chromosorb W, AW-DMCS).

Selenofenchone (1)^{2,3} The selone was prepared as described previously^{2,3} in 30% yield from (-)-fenchone triphenylphosphoranylidenehydrazone, mp 122-128 °C, $[\alpha]^{21}_{589} = -62.5^{\circ} (c \ 0.66)$, as a blue crystalline solid: mp 44-47 °C (lit.^{2,3} mp 41-47 °C); $[\alpha]^{23}_{546} = +688.5^{\circ}, [\alpha]^{23}_{436}$ = +194.5°, $[\alpha]^{23}_{365}$ = -210.7° (*c* 0.24, *n*-heptane); IR 1045, 1075, 1445, 1465 cm⁻¹; ¹H and ¹³C NMR in Table I; CD and UV in Table II.

Thiofenchone (2). The thione was prepared as described previously⁵ in 45% yield from (-)-fenchone triphenylphosphoranylidenehydrazone above as a yellow-orange liquid: bp 100 °C (6 mm); mp 23–24 °C (lit.^{5a} mp 78–85 °C and lit.^{5b} mp 22–24 °C, bp 105 °C (15 mm), $[\alpha]^{21}_{D} =$ +46.1° (c 1.2, ethyl acetate)); $[\alpha]^{23}_{589} = -513.5^{\circ}$, $[\alpha]^{23}_{578} =$ -573.3°, $[\alpha]^{23}_{546} = -897^{\circ}$, $[\alpha]^{23}_{436} = +1130.8^{\circ}$, $[\alpha]^{23}_{365} =$ +155.4° (c 1.34, ethyl acetate); IR 1090, 1180, 1275, 1450, 1470 cm⁻¹; ¹H and ¹³C NMR in Table I; CD and UV in Table II.

Results and Discussion

Synthesis, Stereochemistry, and ¹³C NMR. Both selenofenchone (1) and thiofenchone (2) were prepared from (-)-fenchone (3) of known absolute configuration⁶ and

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TABLE I: 13 C and 1 H NMR Spectra of Selenofenchone (1), Thiofenchone (2), and Fenchone (3)^a

nosi-	5 e 10 1 Se 1		2		3	
tion	¹³ C	¹ H	¹³ C	¹Н	${}^{13}C^{b}$	${}^{1}\mathrm{H}^{b}$
1	73.20 (s)		66.67 (s)		53.90 (s)	
2	294.16 (s)		280.42 (s)		222.81 (s)	
3	63.94 (s)		58.09 (s)		47.17 (s)	
4	47.85 (d)		47.46 (d)		45.13 (d)	
5	27.87 (t)	1.3-1.9 (br m, 5 H)	29.04 (t)	1.2-1.9 (br m, 5 H)	24.76 (t)	1.1-1.8 (br m, 5 H)
6	33.43 (t)		35.96 (t)		31.68 (t)	
7	42.88 (t)	2.44 (br s)	44.15 (t)	2.33 (br s)	41.52 (t)	2.02 (br s)
8	26.70 (q)	1.23(s)	26.80 (q)	1.23(s)	$23.20 (q)^{c}$	1.01(s)
9	25.44 (q)	1.16(s)	25.53 (q)	1.17(s)	$21.54 (q)^c$	1.01 (s)
10	21.05 (q)	1.44(s)	19.59 (q)	1.31(s)	14.42 (q)	1.09(s)

^{*a*} In CD_2Cl_2 : ¹H NMR at 100 MHz; ¹³C NMR at 25 MHz; values in ppm downfield from tetramethylsilane. Chemical shift values are assigned by using CD_2Cl_2 as an internal standard with the middle line of the CD_2Cl_2 carbon resonance assigned a value of 53.86. ^{*b*} In CDCl₃. ^{*c*} In 3,3-dimethyl-2-norbornanone, the methyl shieldings are reported (exo: 23.4; endo: 21.6 ppm): Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

TABLE II:	Circular	Dichroism	and	Ultraviolet Spectral	
Data for Sel	enofench	one (1), Th	niofe	nchone (2),	
and Fenchor	ne (3)				

	CD			UV		
$\lambda_{\max}, \\ nm$	$\Delta \epsilon$	$[R]^a$	λ_{\max}, nm	e		
		Compd 1				
	n-	Heptane Solu	ition			
573	-0.86	[-3.00]	625	41.5		
270	-5.21	[-14.1]	271	10250		
232	+4.90	[+6.55]	224	3800		
222	-1.30	[-3.24]				
	p-	Dioxane Solu	ition			
565	-0.95	[-3.24]	607	42.9		
275	-5.26	[-16.4]	275	10000		
236	+4.36	[+8.63]	219	4040		
218	-1.79	[-2.25]				
	Br	omoform Sol	ution			
558	-1.08	[-3.85]	576	77.0		
		Compd 2				
	n-	Heptane Solu	ition			
486	-1.05	[-3.23]	486	12.2		
242	-8.57	[-21.3]	240	10000		
220	+3.80	[+2.23]				
	Br	omoform Sol	ution			
484	-1.42	[-4.43]	484	51.2		
		Compd 3				
	n-	Heptane Solu	ition			
292	-0.71	[-2.18]	289	18.4		
193	+0.91	[+1.64]		/-		
a [R] is t	he reduced	l rotational s	trength, [R] =		

 $(R)(1.08 \times 10^{40}).$

essentially 100% enantiomeric excess (ee). Because the precise relationship between fenchone and its ee had not been determined directly, we converted partially racemized fenchone with $[\alpha]^{25}{}_{\rm D} = -13.94^{\circ}$ (c 0.8, *n*-heptane) to α -fenchyl alcohol by reduction with LiAlH₄. Treatment of 99.9% pure α -fenchyl alcohol, so obtained, with the chiral europium shift reagent Eu(facam)₃ showed splitting of the O-C-H into two singlets in a ratio 1.87:1, corresponding



Figure 1. Circular dichroism spectra (-)-selenofenchone (1) determined at room temperature in *n*-heptane (--), *p*-dioxane (---), and bromoform (+++). Visible-ultraviolet spectra of selenofenchone (1) determined at room temperature in *n*-heptane (---), *p*-dioxane (-·-), and bromoform (+++). Scaling factors are indicated on curves and refer to the vertical $\Delta \epsilon$ and ϵ scales.

to a 30.31% ee. Similarly, a sample of fenchone with a higher rotation, $[\alpha]^{25}_{589} = -51.25^{\circ}$ (neat), $[\alpha]^{25}_{589} = -46.52^{\circ}$ (c 1.1, *n*-heptane), when carried through the same analysis, showed the Eu(facam)₃-shifted O-C-H as a single peak, corresponding to 100% ee.

Preparation of the intense blue selone 1 was accomplished according to the procedure of Barton et al.³ by heating the triphenylphosphoranylidenehydrazone (4) of 3 with selenium powder. Similarly,⁵ pink-orange thioketone 2 was prepared in high yield by heating 4 with sulfur. The common intermediate 4 was synthesized by reaction of fenchone hydrazone (5)⁷ with bromotriphenylphosphonium bromide. Similarly, racemic fenchone, $[\alpha]^{20}_{589} = +0.009^{\circ}$ and $[\alpha]^{20}_{365} = -0.007^{\circ}$ (neat) was converted by this method to racemic selenofenchone.

As has been noted previously,⁸ the carbon resonance of C—Se in 1 is strongly deshielded relative to the ketone carbonyl carbon of 3 and more deshielded than the thio-

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Figure 2. Circular dichroism spectra (-)-thiofenchone (2) in n-heptane -) and bromoform $(+\cdot+)$, and (-)-fenchone $(3)(-\cdot)$ in *n*-heptane; all determined at room temperature. Ultraviolet-visible spectra of 2 in *n*-heptane (---) and bromoform (+++) and 3 in *n*-heptane (\cdots) are also recorded at room temperature. Scaling factors are indicated on the curves and refer to the vertical $\Delta \epsilon$ and ϵ scales.

carbonyl carbon of 2. The data suggest increasing polarization of the type C^+-X^- . Sulfur and, even better, selenium act like internal shift reagents in the progression O to S to Se of 3 to 2 to 1. In support of this view, we find that neighboring carbons (C-1 and C-3) of 1 are strongly deshielded relative to 3, and the methyl groups near the C—Se group are also deshielded.

Electronic Excitations. The CD and UV spectra of 1 are shown in Figure 1; those for 2 and 3 are found in Figure 2, and the data may be compared in Table II. The longwavelength transitions are of particular interest in this work. For saturated alkyl ketones and thicketones they have been widely described as $n \rightarrow \pi^*$ transitions.⁹⁻¹⁴ For selenoketone 1, we tentatively assign it to a transition of major $n \rightarrow \pi^*$ character, a description suggested previously⁴ and one consistent with the solvent shift of λ_{max} in going from *n*-heptane to dioxane. The most striking aspect of Figure 1 is the noncoincidence of the long-wavelength CD and electronic transitions. This is not seen with either 2 or 3. Thus, selone 1 in *n*-heptane gives a (-) longwavelength Cotton effect (CE) with λ_{max} at 573 nm, shifted considerably to the short-wavelength side of the visible absorption with λ_{max} at 625 nm. A parallel behavior is found in p-dioxane solvent, but with hypsochromic shifts of the long-wavelength ordinary absorption and CD bands (and bathochromic shifts of the short-wavelength CD and UV bands near 270 nm). The long-wavelength region of the CD spectra in these two solvents almost certainly reveals more than one transition or multiplicities within the same transition. In n-heptane, the less intense component of the electronic transition gives rise to the more intense (-) CD transition centered near 573 nm; whereas, the more intense component of the electronic transition is associated with a weak (+) CD band near 630 nm. In support of this, the broad, nonsymmetric shape of the long-wavelength visible absorption band reflects overlapping transitions.

Noncorrespondence of UV and CD maxima is not especially unusual and has been reported, for example, for camphor.¹⁵ Camphor exhibits $n \rightarrow \pi^*$ CD and UV λ_{max} near 290 and 284 nm, respectively, evidence that the UV band consists of two superimposed (vibronic) components.¹⁵ Thus, the vibronic component built upon the 0-0 line of the campbor $n \rightarrow \pi^*$ UV band carries relatively little electronic intensity compared with the vibronic component built on nontotally symmetric vibrations, but it gives rise to the majority of CD band intensity. A similar, but smaller, $n \rightarrow \pi^* \lambda_{max}$ shift may be found in the CD (λ_{max} = 292 nm) and UV (λ_{max} = 289 nm) maxima of fenchone (3). With selenofenchone (1) the $n \rightarrow \pi^*$ UV and CD maxima are grossly noncoincident. Again, if two vibronic progressions are implicated, as described for ketones by Weigang,¹⁶ then the long-wavelength part of the $n \rightarrow \pi^*$ electronic transition is the totally symmetric vibrational progression built upon the O-O line, and this "allowed" component gives rise to the weak (+) component of the CD band would be derived from the symmetric progression built upon a nontotally symmetric vibration in the upper electronic state, viz., upon a "forbidden" component in the shorter wavelength part of the $n \rightarrow \pi^*$ electronic transition. What is disturbing in this explanation is that, unlike the ketone carbonyl n $\rightarrow \pi^*$ transition, the "forbidden" vibronic component is associated with the majority of the CD intensity. Two other explanations come to mind: (1) the weak (+) part of the long-wavelength CD band is due to a molecular Rydberg transition centered near 623 nm in the electronic spectrum and overlapping with an intense $n \rightarrow \pi^*$ (-) CD transition, or (2) the transition exhibits characteristics of a singlet-singlet and a singlet-triplet excitation.^{11,13} We disfavor explanation 1 because the intensities of the CD transitions are insensitive to solvent, cf. the curves (Figure 1) and data (Table I) from n-heptane and p-dioxane. Explanation 2, which we favor, follows from previously reported studies of the CD¹¹ and MCD¹³ of thiones, in whose absorption spectrum is found a weak $(\epsilon \sim 2)$ band near 550 nm that has been assigned to a singlet-triplet $n \rightarrow \pi^*$ transition. That weak band exhibits the expected relatively more intense MCD signal.¹³ We therefore turn our attention to the question of a singlettriplet component in the $n \rightarrow \pi^*$ transition of 1.

If one could extrapolate from the intensities of the $n \rightarrow$ π^* electronic transitions of 2 ($\epsilon \sim 12$) and 3 ($\epsilon \sim 18$), ϵ for 1 should be much smaller than that ($\epsilon \sim 42$) observed. On the other hand, an emerging long-wavelength singlettriplet component in the $n \rightarrow \pi^*$ transition of 1 might become sufficiently intense so as to dominate the shorter wavelength singlet-singlet component (cf. $\epsilon_{486}^{\text{max}} \sim 12, S_0 \rightarrow S_1; \epsilon_{550}^{\text{sh}} \sim 2, S_0 \rightarrow T_1 \text{ for } 2$). Furthermore, if a singlet-triplet $n \rightarrow \pi^*$ transition is becoming important in 1, it should be detectable by MCD, and it should also exhibit heavy-atom solvent effects similar to those observed for thiones in CHBr₃ solvent.¹³ In accord with this hypothesis, the curves of Figure 1 clearly indicate a pronounced heavy-atom solvent effect on the $n \rightarrow \pi$ transition in going from n-heptane (or p-dioxane) to bromoform. The weak

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Figure 3. Corrected magnetic circular dichroism spectra of racemic selenofenchone in methylcyclohexane–isopentane (4:1 v/v) measured at room temperature (—) and 77 K (---). The curves are corrected for very small signals present in the absence of the magnetic field. The visible part of the electronic spectrum measured at room temperature is shown (···) for comparison. In isooctane or methanol at room temperature, the MCD spectrum is essentially identical with the room-temperature spectrum above.

(+) CE is markedly reduced in intensity and the strong (-) CE is blue shifted and intensity enhanced nearly threefold. The $n \rightarrow \pi^* \lambda_{max}$ is shifted to ~575 nm (vs. ~625 nm in *n*-heptane). The singlet-triplet $n \rightarrow \pi^*$ transition is significantly weakened and the singlet-singlet component is strongly enhanced. Similar wavelength shifts are found for the $n \rightarrow \pi^*$ transitions of thiofenchone 2 (Figure 2, Table II) where CHBr₃ solvent apparently enhances the singlet-singlet $n \rightarrow \pi^*$ transition and weakens the singlet-triplet transition, as has been observed previously with thioadamantanone.¹³

The assignment of an intense, but unresolved, singlettriplet component in the $n \rightarrow \pi^*$ transition of 1 is supported by its MCD spectrum (Figure 3), which exhibits a strong (-) band near 650 nm and a weaker (-) band centered near 600 nm in methylcyclohexane-isopentane. These observations correlate nicely with the results obtained for thiones¹³ in that the stronger MCD bands were associated with the singlet-triplet transition, whereas the weaker MCD bands were found for the singlet-singlet portions of the transition. As might be expected, the intensities of the MCD bands of selenofenchone are approximately 1 order of magnitude more intense than those observed for, e.g., adamantanethione.¹³ Ordinarily, for an electronic transition between a singlet ground state and a spin degenerate excited state one expects to observe A terms¹⁷ such as those which are clearly evident in the vapor-phase spectrum of the prototypical carbonyl compound formaldehyde.¹⁸ In the cases of adamantanethione and bicyclo[2.2.1]heptane-2-thione (which has a structure similar to that of 2) both lobes of the negative A term are evident in their MCD spectra, although a significant con-

tribution from a negative B term¹⁷ results in the positive lobe being much more intense than the negative one for both compounds. In the present case of selenofenchone. the negative lobe of the negative A term anticipated for the singlet-triplet transition is absent in its spectrum (Figure 3). Since the peak-to-peak amplitude of an A term is proportional to the inverse square of the half-width of the absorption band.¹⁹ we had hoped that the negative lobe of the A term would be resolved at low temperature. However, as can be seen from the spectrum obtained in 4:1 methylcyclohexane-isopentane at 77 K (Figure 3), this is not the case, although the positive band does become much sharper and more intense as was observed for adamantanethione.¹³ We attribute this difference in detail between the MCD spectra of 1 and thiones¹³ to significant coincident B-term intensity of the selone and to the effects of band cancellation arising from the closer spacing of the singlet-singlet and singlet-triplet transitions that appears to exist for the selone as compared to the thiones (about 1200 and 2000 cm⁻¹, respectively, as judged from the position of corresponding MCD bands for 1 and adamantanethione). We believe, however, given the security of the assignment of the singlet-triplet transition in thiones.¹³ that the presence of a strong positive MCD band to the red of the main visible absorption band in the spectra of selenofenchone (Figure 3) provides very strong evidence for its presence for this compound and, in extenso, in other selones as well.

Just as the long-wavelength transition of 1 exhibited the wavelength solvent shift characteristic of an $n \rightarrow \pi^*$ type electronic transition, the intense short-wavelength UV transition near 270 nm exhibits (Figure 1) the wavelength solvent shift of a $\pi \rightarrow \pi^*$ type transition.^{4,9,12} The ca. 270-nm UV absorption corresponds nicely with the intensely negative CD transition, also near 270 nm. Interestingly, a close-lying, strongly positive CD band, $\lambda_{max} = 232-236$ nm, appears in a region of weak UV absorption. The assignment of that transition is unclear at present; it may be of an $n \rightarrow \sigma^*$ type.¹² A similar situation seems to emerge, somewhat less clearly, in the short-wavelength region CD of the thione 2.¹²

Conclusions

The long-wavelength $n \rightarrow \pi^*$ electronic transition of selenofenchone (1), and probably other selones, is dominated by a singlet-triplet component. The singlet-triplet component exhibits a pronounced MCD but only a weak CD, whereas the singlet-singlet component exhibits a strong CD and a much weaker MCD. Whether one can actually ascribe unique singlet-singlet or singlet-triplet aspects to the electronic transition, as has been done for thiones, is problematic, especially in view of the increased likelihood for spin-orbit coupling in the higher atomic weight Se.

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