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THE CHIROPTICAL PROPERTIES OF SELENOFENCHONE, A SELENOKETONE WITH AN ASYMMETRICALLY PERTURBED C=Se CHROMOPHORE

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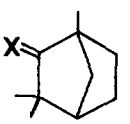
Summary CD, ORD, and UV spectra were obtained for the first time on a selenoketone, the chiroptical properties of the selenoketone and of its analogous thione and ketone were parallel.

Simple selenoketones (selones) were recently synthesized for the first time thus making possible spectroscopic measurements of compounds having a true carbon-selenium double bond.[1] ^{77}Se and ^{13}C NMR spectra have been obtained for a series of selones.[2] We now report the first chiroptical measurements on a selone using selenofenchone (1) as an example and compare our results to those obtained for thiofenchone (2)[3] and fenchone (3), the sulfur and oxygen analogues, respectively Compounds 1 and 2 were both derived from the same sample of (-)-3 All three are therefore of the same configuration and optical purity.



1, X = Se
2, X = S
3, X = O

Selenofenchone, like other selones, is highly colored as a result of its long wavelength absorption This absorption is caused by a transition similar to the $n \rightarrow \pi^*$ transition of ketones, since a change in solvent from ethanol to cyclohexane shifts λ_{max} from 612 to 626 nm.[4] Compounds 2 and 3 behave similarly upon identical solvent changes. The absorption maxima move from 481 to 487 nm for 2 and from 287 to 289 nm for 3

A more intense shorter-wavelength absorption occurs at 275 nm in EtOH for 1. Compound 2 has an analogous absorption at 243 nm whereas for 3, the absorption was below 200 nm and not measured. In ketones such absorptions are generally classified as $\pi \rightarrow \pi^*$ transitions, so, by analogy, the absorptions for 1 and 2 may be classified similarly.[4]

CD, ORD, and UV data for 1, 2, and 3 are given in the table. Long-wavelength negative Cotton effects occur for all three compounds in association with their $n \rightarrow \pi^*$ transitions. Numerous chiroptical studies which continue to the present day have been carried out on ketones The octant rule, based on the $n \rightarrow \pi^*$ transition of the C=O chromophore, often permits absolute configurations to be assigned to ketones[5], this rule is followed by thioketones as well [6,7] However, the applicability of the octant rule to 3 is not at all obvious. Nevertheless, the chiroptical properties of 1, 2, and 3 parallel one another. Perhaps other familial selone, thione, and ketone triads will behave in the same way in view of the similar nature of the $n \rightarrow \pi^*$ transitions of the C=Se, C=S, and C=O chromophores.

CHIROPTICAL PROPERTIES OF 1, 2 AND 3[a]

	CD, nm, $[\theta]$[b]	ORD, nm, $[\phi]$[c]	UV, nm, (log ε)
1 (C_6H_{12})[d]	585(-2300), 271(-13,900), 248(0), 234(+13,300), 226(0) 224(-2280), 220(0), 214(+3800), 210(+2280)	620(-2050), 573(0), 524(+1980), 387(0), 292(-6830) 277(0), 248(+18,700), 228(-6890), 223(0), 210(+2950)	626(1.55), 272.5(4.00), 225(3.65)
1 (EtOH)[e]	572(-3270), 271(-13,900), 249(0), 239(+11,800), 223(0), 218(-1970), 212(0), 210(+2000)	612(-1860), 562(0), 516(+3120), 385(0), 294(-2500), 278(0), 249(+6200) 226(-1240), 218(0), 210(+1650)	612(1.67), 275(4.05), 223(3 63)
2 (C_6H_{12})	485(-2710), 241(-23,900), 225(0), 220(+5950), 210(+4460)	516(-3240), 481(0), 453(+1430), 381(0), 259(-13,200), 243(0), 228(+25,200), 210(+11,630)	487(1.09), 241(3.99), 216(3.57)
2 (EtOH)	478(-3130), 242(-22,900) 225(0), 218(+7700), 210(+4610)	513(-3400), 479(0), 447(+2040), 350(0), 260(-10,200), 248(0), 229(+25,200), 210(+9540)	481(1.09), 243(4.04), 215(3.72)
3 (C_6H_{12})	292(-2230), 210(0)	308(-1690), 292(0), 272(+1300), 210(-260)	289(1.26), < 200
3 (EtOH)	289(-3170), 210(0)	306(-2210), 289(0), 271(+1780), 210(-1630)	287(1 18), < 200

[a]Positive, zero, and minus values given in parenthesis refer to maxima, crossovers, and minima, respectively, for the CD ellipticity values and to peaks, crossovers, and troughs, respectively, for the ORD rotation values, except for the last values listed which refer to the ellipticities and rotations at the lowest wavelengths measured.

[b]$[\theta] = \theta M/1c\ 100$; θ= ellipticity, 1 = cell length in dm, c = g/mL

[c]$[\phi] = \alpha M/1c\ 100$, α = observed rotation. [d]C_6H_{12} = cyclohexane [e]EtOH = absolute EtOH

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