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Chiroptical spectra of bicyclic selenolactams. Optical activity of the singlet–triplet transition

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Abstract

Two selenolactams with rigid 2-azabicyclo[2.2.1]heptane skeletons were prepared by reaction of the corresponding lactams with P_4Se_{10}. A comparison of their UV–vis and CD spectra with those of the carbonyl and thiocarbonyl analogues showed a similar character of the lowest-energy electronic transitions and the same signs of the corresponding Cotton effects. The MCD spectra of selenolactams revealed that their n–π* absorption band is dominated by the singlet–triplet component. A very weak CD corresponding to this component has an opposite sign to its much stronger singlet–singlet counterpart observed at the blue edge of the n–π* band. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Selenocarbonyl compounds are reactive analogues of carbonyl systems and play an increasingly important role in organic synthesis.[1] They have also found application as ligands in organometallic complexes[2] and some of them are used as chiral derivatizing reagents in NMR spectroscopy.[3] Selenoaldehydes and selenoketones are too labile to be isolated unless they are stabilized by resonance effects of aromatic or heteroaromatic rings or are protected by sterically bulky substituents.[4] Usually they are isolated as dimers or trapped as Diels–Alder cycloadducts with dienes.[5] In contrast, selenoamides are stable compounds owing to resonance delocalization of the nitrogen lone-pair electrons onto selenium.[1b,6]

Continuing an interest in the chiroptical properties of amides and thioamides[7,8] we focused our attention on the selenoamide chromophore. Substitution of the carbonyl oxygen with progressively heavier atoms may exert a substantial effect on the spectroscopic properties of the molecules.[9] Particularly, increasing the atomic number is expected to lower the energy of excited states and enhance the singlet–triplet (S–T) transition probability.[10] Whereas the thiocarbonyl chromophore has been the subject of some chiroptical studies[7,8,11] there is, to our best knowledge, only one optically active selenocarbonyl

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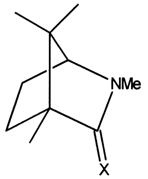
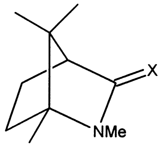
compound, namely (−)-selenofenchone, whose circular dichroism (CD) spectrum has been reported.[12] In this paper we present the synthesis, natural and magnetic circular dichroism (MCD) spectra of the bicyclic selenolactams **1a** and **2a** and compare their spectroscopic properties with those of the structurally related lactams and thiolactams **1b**,**c** and **2b**,**c** recently examined in our laboratory.[8]



1a X = Se
1b X = S
1c X = O



2a X = Se
2b X = S
2c X = O

2. Results and discussion

Tetraphosphorus decaselenide (P_4Se_{10}) is the reagent most frequently used for the conversion of the C═O group into the C═Se moiety.[6,13] However, the reported yields are generally very low. Surprisingly, a simple modification of the procedure of Hallam and Jones,[13c] i.e. a prolonged heating of the lactams **1c** and **2c** with P_4Se_{10}, prepared in situ from grey selenium and red phosphorus, in the presence of barium carbonate in xylene gave the pale yellow selenolactams **1a** and **2a** in nearly quantitative yields. Probably the bicyclic structure and steric overcrowding of **1a** and **2a** enhances their stability. The compounds were characterized by ^{1}H, ^{13}C, ^{77}Se NMR and mass spectrometry. The selenoamide C═Se carbon resonances in **1a** and **2a** are strongly deshielded (about 30 ppm) relative to the amide C═O in **1c** and **2c** and only slightly deshielded compared to the thioamide C═S in **1b** and **2b**.

A comparison of the UV–vis and CD spectra of the selenolactams with those of their thiocarbonyl analogues shows a close correspondence between the absorption maxima and the Cotton effect (CE) signs of both classes of compounds (Fig. 1) that points to a similar character of their lowest-energy electronic transitions. As expected, substitution of selenium for sulphur causes a red shift of all the accessible near UV absorption bands as well as the corresponding CEs (Table 1). The long-wavelength weak absorption of selenolactams occurs near 400 nm in cyclohexane and shifts to ca. 350 nm in methanol. By analogy with thioamides[8,14] it can be attributed to the forbidden $n–\pi^*$ electronic transition. A much stronger absorption band near 300 nm is only slightly influenced by solvent polarity and can be assigned to the allowed $\pi–\pi^*$ excitation. The origin of two moderate intensity bands observed at ca. 245 and 230 nm is less clear. In the case of the parent lactams **1c** and **2c** only two CEs corresponding to the overlapping $n–\pi^*$ and $\pi–\pi^*$ transitions can be observed in the near UV. Obviously, due to similarities in the electronic structure and the nature of electronic transitions, the structurally related lactams and their thiocarbonyl and selenocarbonyl analogues exhibit the same $n–\pi^*$ CE sign which is determined by the chirality of the bicyclic skeleton and therefore the corresponding CD curves of **1a**–**c** and **2a**–**c** are almost mirror images.[8] The magnitude of the $\pi–\pi^*$ CE decreases drastically on going from the oxo **1c** and **2c** to the selenocarbonyl **1a** and **2a** compounds. It has been shown that a strong distortion of the amide bond from planarity, caused by the strain imposed by the bicyclic skeleton, is primarily responsible for the strong CEs in the lactams **1c** and **2c**.[8] On the other hand, the thioamide group in **1b** and **2b** is much less deviated from planarity and the selenoamide moiety in **1a** and **2a** is almost planar,[15] owing to a greater contribution of the bipolar resonance structure in thioamides and selenoamides, that increases double bond character between the neighbouring carbon and nitrogen atoms.[16]

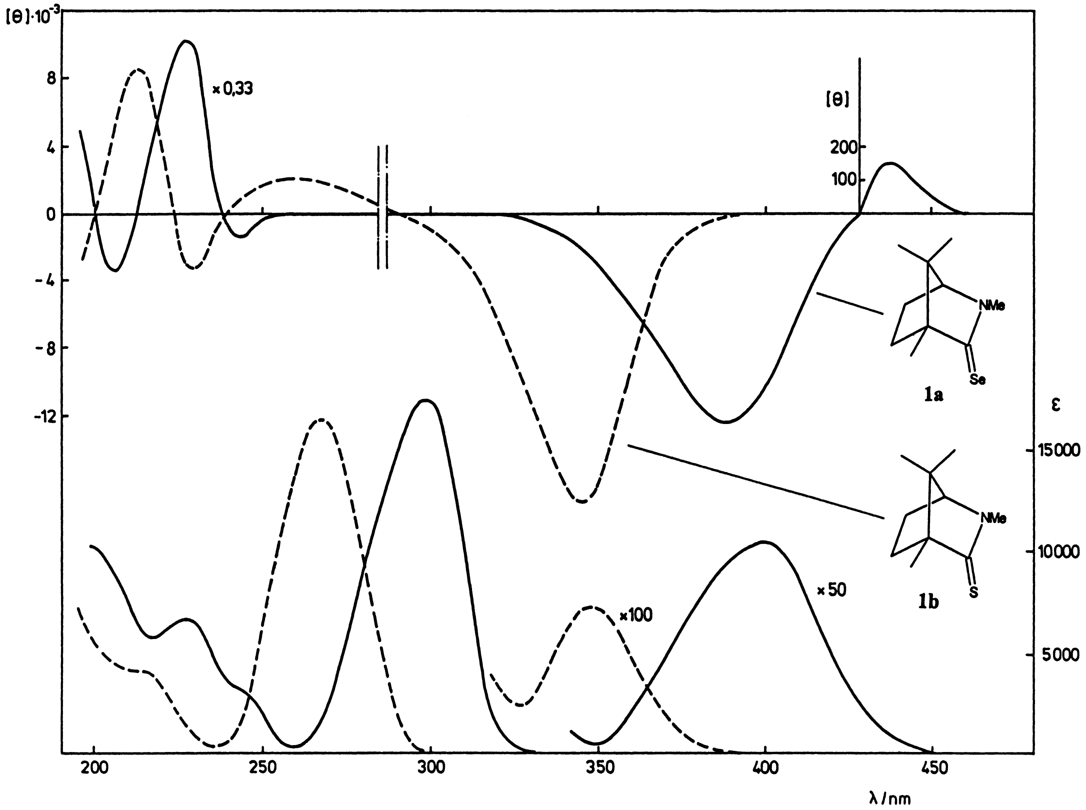


Figure 1. Circular dichroism (CD) and UV–vis spectra of selenolactam **1a** and thiolactam **1b** in cyclohexane

Table 1
Electronic absorption (UV) and circular dichroism (CD) data of compounds **1a**–**c** and **2a**–**c**

Compd.	Solv.^{a}	UV λ, nm (ε)	CD λ, nm (10^{-3}[Θ])^{b}
1a	C^{c}	398 (200), 298 (17600), 242sh (13100), 228 (6100)	440 (0.14), 392 (–12.3), 305 (–0.5), 282 (0.6), 244 (–3.7), 228 (21.6), 205 (–14.7), 189 (47.3)
	M	358 (250), 291 (15200), 218 (5100)	423 (0.06), 358 (–11.8), 278(1.6), 219 (12.1)
1b^{c}	C	346 (71), 269 (16800), 213 (3900)	345 (–17.2), 262 (6.1), 228 (–10.4), 213 (25.6)
1c^{c}	C		225 (–36.5), 203sh (21.5), 191 (35.4)
2a	C	404 (210), 299 (18800), 245 (3100), 228 (5900)	444 (–0.17), 397 (10.4), 298 (0.7), 280 (–0.5), 245 (–9.7), 229 (–15.1), 201 (13.1), 186 (–31.7)
	M	352 (290), 292 (18500), 216 (6800)	423 (–0.05), 354 (9.8), 303 (2.1), 217 (–20.5)
2b^{c}	C	349 (64), 271 (16300), 217 (2300)	350 (14.9), 265 (–4.2), 217 (–14.6)
2c^{c}	C		227 (38.3), 207 (–45.8)

[a] C – cyclohexane; M – methanol. [b] Molecular ellipticity in deg cm^{2} dmol^{-1}. [c] From ref. 8

An important and intriguing feature of the CD spectra of selenolactams is the presence of an additional very weak and oppositely signed CE at the tail of the n–π* band (Fig. 1). Usually a bisignate CD curve may indicate a conformational equilibrium in solution, where two conformers contribute with opposite signs to the CE, or evidence of a contribution from an additional electronic transition within the same absorption band. A conformational equilibrium for molecules with bicyclic rigid skeletons is not possible and the observed lack of sensitivity of the CE magnitudes of **1a** and **2a** to solvent changes remains in line with this supposition. Therefore the second explanation seems to be favoured. The possibility that two electronic transitions are hidden under the envelope of the long-wavelength absorption band can be confirmed by a careful inspection of the selenoamide spectra. They reveal non-Gaussian band shape of the long-wavelength absorption and, furthermore, this band does not coincide with the corresponding CD maximum. In the case of **1a** and **2a** the n–π* CE is shifted by ca. 10 nm to the red with respect to the absorption band. It is known that incorporation of heavier atoms, like sulphur or selenium, into a molecule increases allowedness of the singlet–triplet transition due to a spin-orbit coupling (internal heavy-atom effect).[10b] The predominantly singlet–triplet character of the lowest energy absorption and the corresponding CD band has been detected earlier in (−)-selenofenchone.[12b] If indeed the singlet–triplet transition is a component of the long-wavelength absorption in selenolactams, it should be detectable by MCD. Magnetic CD spectroscopy has already been proven to be very useful in location of the singlet–triplet n–π* transitions in the long-wavelength part of the UV–vis spectra of thioketones,[17] selenoketones[12b] and dithioimides.[18] The MCD spectra of the racemic compounds **1a** and **2a** taken in the region of the n–π* band are shown in Fig. 2. The observed S-shaped curves can be attributed to the A term, which is expected for an electronic transition between a singlet ground state and a spin-degenerate excited state.[19] In the presence of the magnetic field the degeneracy is lifted, which results in two oppositely signed MCD bands of equal magnitude, characteristic for the A term. In the case of low symmetry molecules a spin degeneracy is possible only for triplet excited states. A small contribution from the B term,[19] that usually has a shape similar to that of the absorption band, results in unequal intensity of the positive and the negative branch of the MCD curves. An influence of the heavy-atom solvent (external heavy-atom effect) affords further evidence of the singlet–triplet transition; the extinction co-efficient of the n–π* absorption band in **2a** increases in this order: cyclohexane, CCl_4 and iodobenzene [λ_{max} (ε) of 404 (220), 387 (320) and 377 (430), respectively]. Furthermore, since this band is almost three times stronger than the analogous UV band in thiolactams **1b** and **2b**, the long-wavelength singlet–triplet component probably dominates over the shorter wavelength singlet–singlet component of the selenoamide n–π* transition. The situation is reversed in the corresponding CD spectra, where the CE due to the singlet–singlet component overweights its oppositely signed singlet–triplet counterpart located at the red edge of the n–π* band. As already mentioned, the above observations correlate nicely with the results obtained earlier for (−)-selenofenchone.[12b] Unlike selenocarbonyls, the singlet–triplet components of the n–π* excitation detected in thioketones[11a,b] and dithioimides[7,18] did not lead to any measurable CEs. They are probably cancelled by much stronger overlapping singlet–singlet CEs.

3. Experimental

CD spectra were recorded on a JASCO J-715 dichrograph. MCD curves were taken with a JASCO J-720 instrument equipped with 15 kg electromagnet using 10 mm path length and sample concentration 0.004 mol L^{-1}. UV–vis measurements were performed on a Beckman 3600 spectrophotometer. ^{1}H, ^{13}C and ^{77}Se NMR spectra were obtained with Bruker MSL-300, WP-200 and Varian Unity Plus spectrometers at 300, 50 and 95.4 MHz, respectively. The deuterated solvents were used as an internal lock for ^{1}H and ^{13}C NMR. The ^{77}Se NMR spectra were recorded using diphenyl diselenide as external standard. Chemical shifts are reported relative to dimethyl selenide (δ 0.0 ppm) by assuming that the signal of the standard is at δ 461.0 ppm.[20] FT-IR absorptions were taken with a Bruker IFS66 spectrometer. Specific rotations were measured on a Rudolph Autopol II digital polarimeter. The racemic compounds **1a** (mp 71–72°C) and **2a** (mp 137–138°C) were obtained following the procedures described for optically active selenolactams.

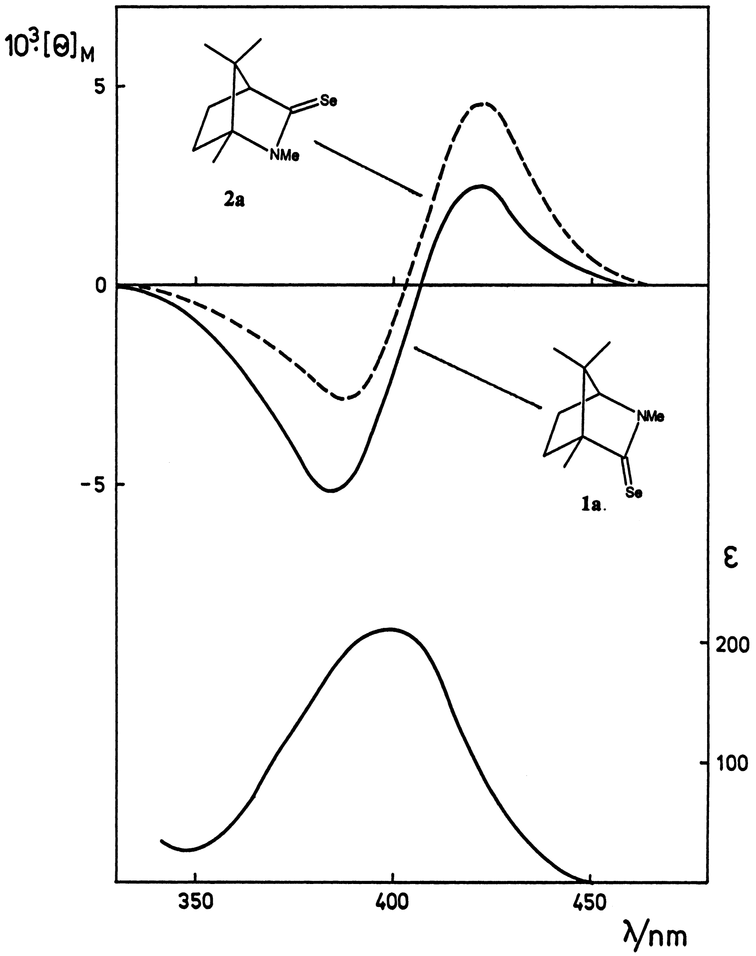


Figure 2. Magnetic circular dichroism (MCD) spectra of the racemic selenolactams **1a** and **2a** in cyclohexane

*3.1. (1*S*)-2,4,7,7-Tetramethyl-2-azabicyclo[2.2.1]heptan-3-selone **1a***

Lactam **1c**[8] (0.84 g, 5 mmol), powdered selenium (1.0 g), red phosphorus (0.4 g) and barium carbonate (1.0 g) were refluxed in xylene (10 mL) for 24 h. After cooling the reaction mixture was filtered and the precipitate was washed with benzene. The solvents were evaporated at reduced pressure and the residue was crystallized from hexane; yield 1.05 g (91%); mp 79°C; $[\alpha]_D^{22}$ −210 (*c* 1, C_6H_6); IR (CCl_4) 1495, 1390, 1290, 995 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.54 (d, *J*=2.2 Hz, 1H), 3.25 (s, 3H), 1.85 (m, 1H), 1.57 (m, 1H), 1.39 (m, 1H), 1.23 (m, 1H), 1.18 (s, 3H), 0.88 (s, 3H), 0.79 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 211.3, 75.4, 65.7, 52.9, 36.5, 31.5, 25.5, 18.2, 17.7, 13.9; ^{77}Se NMR ($CDCl_3$) δ 312.3; *m/z*: 231 (M^+, ^{80}Se). Anal. calcd for $C_{10}H_{17}NSe$ (230): C, 52.17; H, 7.45; N, 6.08. Found: C, 52.07; H, 7.75; N, 6.03.

*3.2. (1*R*)-1,2,7,7-Tetramethyl-2-azabicyclo[2.2.1]heptan-3-selone **2a***

This compound was prepared from lactam **1c**[8] in a similar manner to **1a**; yield 96%; mp 155–156°C (toluene–hexane); $[\alpha]_D^{22}$ +219 (*c* 2, C_6H_6); IR (CCl_4) 1485, 1390, 1260, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.12 (s, 3H), 3.02 (d, *J*=4.0 Hz, 1H), 1.87–1.60 (m, 2H), 1.45–1.25 (m, 2H), 1.23 (s, 3H), 0.85 (s, 3H), 0.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 206.3, 76.1, 68.6, 52.5, 31.9, 31.8, 24.4, 18.3, 17.5, 11.8; ^{77}Se NMR ($CDCl_3$) δ 358.4; *m/z*: 231 (M^+, ^{80}Se). Anal. calcd for $C_{10}H_{17}NSe$ (230): C, 52.17; H, 7.45; N, 6.08. Found: C, 52.07; H, 7.64; N, 5.95.

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