Pergamon

Tetrahedron: *Asymmetry* 9 (1998) 3011–3023

TETRAHEDRON: *ASYMMETRY*

Chiroptical spectra and molecular geometry of bicyclic dithioimides

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Received 24 June 1998; accepted 24 July 1998

Abstract

Several chiral bicyclic dithioimides were prepared by thionation of the parent imides with Lawesson's reagent. Due to a flexibility of the dithioimide chromophore, their CD spectra show significant solvent dependence. A substantial deviation of the chromophore from planarity was confirmed by the MNDO calculations and crystallographic structures of **4**, **5b**, **6** and **7**. The observed CE sign corresponding to the lowest energy n–π* transition can be predicted, upon careful examination of the molecular geometry, by the antioctant rule with sector signs opposite to those known for ketones.

1. Introduction

While spectroscopic properties of simple thiocarbonyl compounds have been studied and their excited states identified,[1] fewer dithiocarbonyl systems have been investigated.[2] The interaction of two thiocarbonyl groups causes splitting of the n, π and π* levels and leads to several absorption bands in the low energy part of the spectrum, similar to the spectra of related dicarbonyl compounds.[3] Examples of such systems are dithio analogues of β-diketones,[4] oxalates,[2] oxamides,[2,5] and imides.[6,7] In relation to our previous investigations on the structure, absorption and circular dichroism (CD) spectra of imides,[8] it seemed interesting to examine the chiroptical properties of the dithioimide chromophore. The electronic absorption spectra of simple imides are characterized by two weak n–π* transitions followed by a moderately intense π–π* band in the near UV region.[8a,9] It has been shown that their chiroptical spectra are extremely sensitive to the molecular geometry and even slight deviation of the chromophore from planarity strongly affects the magnitude and sign of the Cotton effects (CEs) associated with the n–π* transitions.[8] The substitution of sulfur for carbonyl oxygen shifts absorption maxima to considerably

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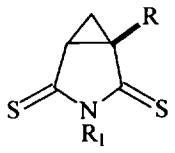
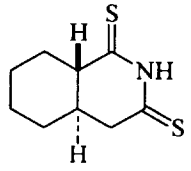
0957-4166/98/$ - see front matter
PII: S0957-4166(98)00293-6

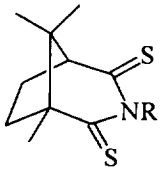
longer wavelengths and therefore the lowest energy excited states of thiocarbonyls can be observed at the visible and near UV region.[1] In contrast to the related imides, dithioimides show better separation of the long-wavelength absorption bands, which may facilitate interpretation of their CD spectra.[7]

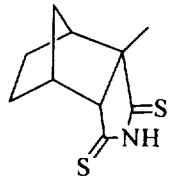


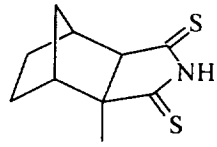


1 R = Me, R_1 = H
2 R = Pr^i, R_1 = H
3 R = Ph, R_1 = Me

4







5a R = H
5b R = Me

6

7

In this paper we report the synthesis and chiroptical spectra of dithioimides **1–7**. We have chosen compounds with bicyclic skeletons to diminish the effect of conformational equilibria on the spectra. However, our earlier CD studies on the parent imides revealed that despite a relative rigidity of their skeletons, the imide chromophore itself posesses some degree of flexibility. Therefore we carefully examined molecular geometries of several dithioimides by molecular modeling and X-ray crystallography.

2. Results and discussion

Dithioimides **1–5a** were prepared by thionation of the corresponding enantiomerically pure imides of known absolute configuration with Lawesson's reagent[10] in boiling toluene. In the case of the sterically hindered compounds **5b**, **6** and **7**, the reaction was very slow and therefore dithionation was accomplished by heating the parent imides with P_4S_{10} in xylene. Due to their bright orange color, dithioimides can be readily separated from the reaction mixture and purified by column chromatography.

A typical UV–vis spectrum of dithioimide, as that observed for **5a** in cyclohexane (Fig. 1), is characterized by two weak absorption bands at 470 and 419 nm (ε 67 and 190, respectively). They can be attributed to two forbidden n–π^* electronic transitions as confirmed by their blue shift upon changing the solvent to methanol. Two 'non-bonding' n orbitals (Scheme 1) involved in these transitions are symmetric and antisymmetric combinations of two sulphur 3p orbitals.[2,7] The strong band near 326 nm (ε 30 000) can be identified as the allowed π–π^* excitation, whereas the origin of two higher energy bands of moderate intensity at 240 and 197 nm is unclear. There is an additional extremely weak absorption appearing as a shoulder at 495 nm, which has proved to be due to the singlet–triplet (S–T) transition responsible for a strong phosphorescence of these compounds.[7b] In the case of the five-membered ring

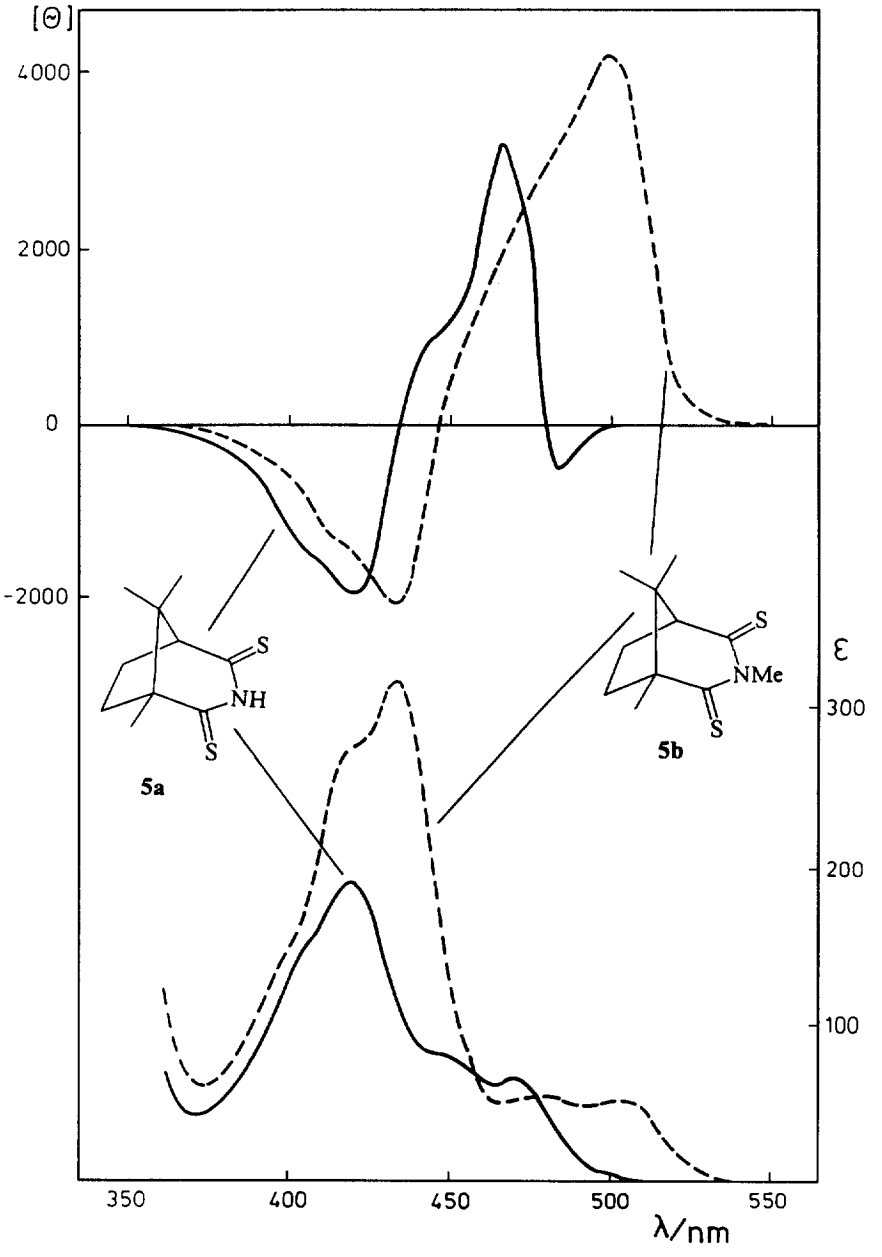
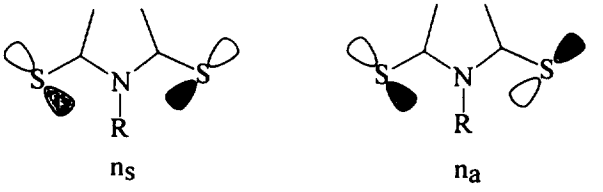


Fig. 1. CD and UV–vis spectra of dithioimides **5a** and **5b** in cyclohexane



n_S n_a

Scheme 1.

Table 1
CD data of dithioimides **1–7**

compd	solvent[a]	λ, nm (10^{-3} [θ])[b]
1	C	470(9.39), 418(-4.32)
	A	458(9.05), 412(-4.58)
	M	467(2.68), 417(-1.49)
	HFP	453(-2.85), 373(3.96)
2	C	468(7.77), 414(-1.39)
	M	463(5.42), 395(0.61)
	HFP	465(-3.04), 414sh(2.22), 374(5.94)
3	C	473(10.21), 433sh (2.23)
	M	466(7.86), 400(1.10)
	HFP	439(4.47), 385(3.45)
4	C	489(3.53), 416(-0.38)
	M	474(3.14), 400(0.14)
5a	C	484(-0.52), 467(3.07), 421(-1.89)
	M	497(-0.10), 467(3.04), 413(-1.40)
	HFP	436(3.27), 378(-1.60)
5b	C	498(4.24), 432(-2.10)
	M	493(4.54), 425(-1.96)
6	C	485(-0.03), 457(3.08), 413(-0.68)
	M	454(2.99), 408(-0.02), 383(0.28)
	HFP	424(3.75), 368(1.81)
7	C	472(-0.13), 445(1.57), 409(0.35)
	M	477(-0.02), 449(2.21), 388(0.32)
	HFP	423(3.75), 365(0.71)

[a] C - cyclohexane, A - acetonitrile, M - methanol, HFP - 1,1,1,3,3,3-hexafluoro-2-propanol. [b]Molecular ellipticity in deg cm^2 $dmol^{-1}$.

dithioimides, all the above bands are shifted to slightly shorter wavelengths (e.g., **6** and **7**), whereas *N*-methylation causes a red shift of these absorptions (e.g., **5b**).

The CD data of compounds **1–7** are collected in Table 1. Due to several overlapping CEs and a pronounced vibronic fine structure of the bands, the shape of the CD curves is rather complex (Figs 1–3). Because of the opposite symmetry of the excited states involved in the n–π* transitions, two CEs of opposite signs can be expected in the spectra, similar to the spectra of the parent imides.[8a] Indeed, in many cases the bisignate curves are observed in the long-wavelength part of the spectra. On the other hand, several spectra show two CEs of the same sign (e.g., **3** and **4** in methanol) or there are three or more CD bands with alternating signs in this region (e.g., **5a**). Another important feature of the dithioimide spectra is their strong dependence on solvent polarity (Fig. 2). In particular,

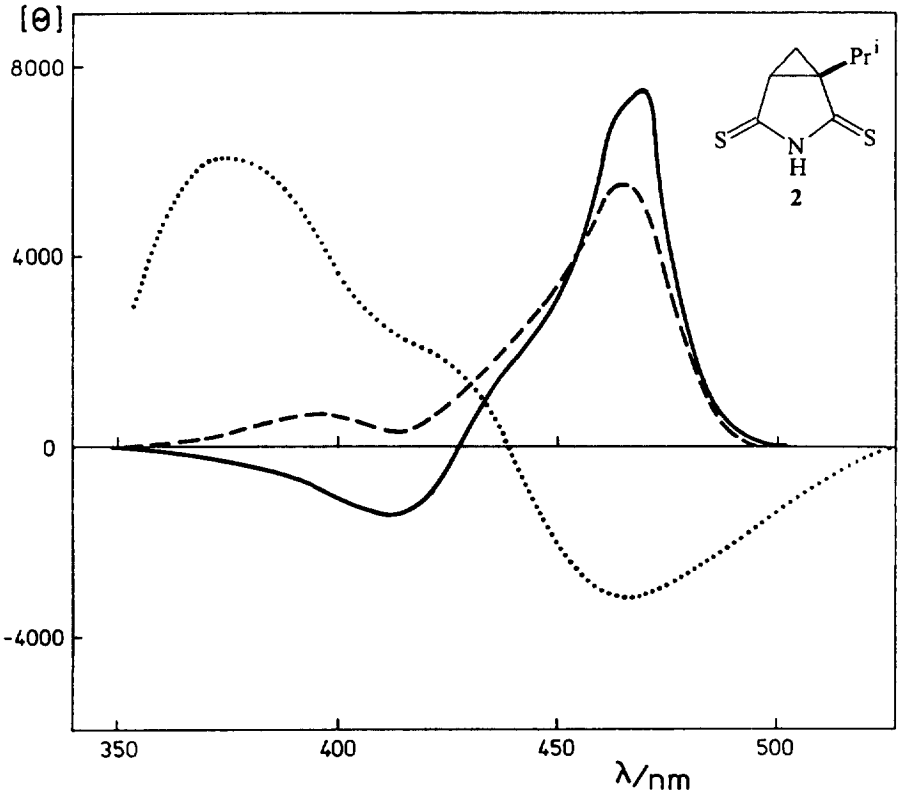


Fig. 2. CD spectra of dithioimide **2** in cyclohexane, methanol and HFP (solid, broken and dotted line, respectively)

cyclopropanedicarboxylic dithioimides **1–3** are extremely sensitive to solvent changes. Such a behavior usually reflects a contribution of two or more forms, differing slightly in energy and characterized by the opposite CE signs, to conformational equilibrium. The recently reported significant temperature dependence of the CD of **5a** remains in line with this supposition.[7b] A contribution of two forms differing in the CE signs in both n–π* regions may lead to double-humped CD curves [e.g., **2** in methanol (Fig. 2)] or to the curves with three CEs in this part of the spectrum. Although conformational changes of the bicyclic skeletons are rather unlikely, it has been shown that small distortions of the imide group from planarity do not increase the steric energy of a molecule considerably.[8c] Dithioimides are expected to behave in a similar manner, and small deviations of the chromophore from the ideal C_{2v} symmetry can be induced by solvation or temperature effects.

The X-ray crystallographic structures of **4**, **5b**, **6** and **7** (Fig. 4) show that in the solid state, the dithioimide group is more or less deviated from planarity. Also the dithioimide five-membered rings in **6** and **7** are slightly distorted from a planar geometry. Moreover, two types of molecules with slightly different geometries are present in asymmetric units of the **4** and **6** crystals. This result, as well as strong thermal vibrations of the sulfur atoms displayed by **6**, reflects a significant flexibility of the dithioimide chromophore.

The molecular geometries of the compounds studied were optimized by the MNDO calculations.[11] It has been shown that the above method gives more reliable results for thiocarbonyl compounds than the other semiempirical techniques.[12] The calculated torsional angles are compared with the experimental values in Table 2. Obviously the calculations refer to isolated molecules (in the gas phase) and therefore some discrepancies observed between the calculated and experimental values may be due to packing

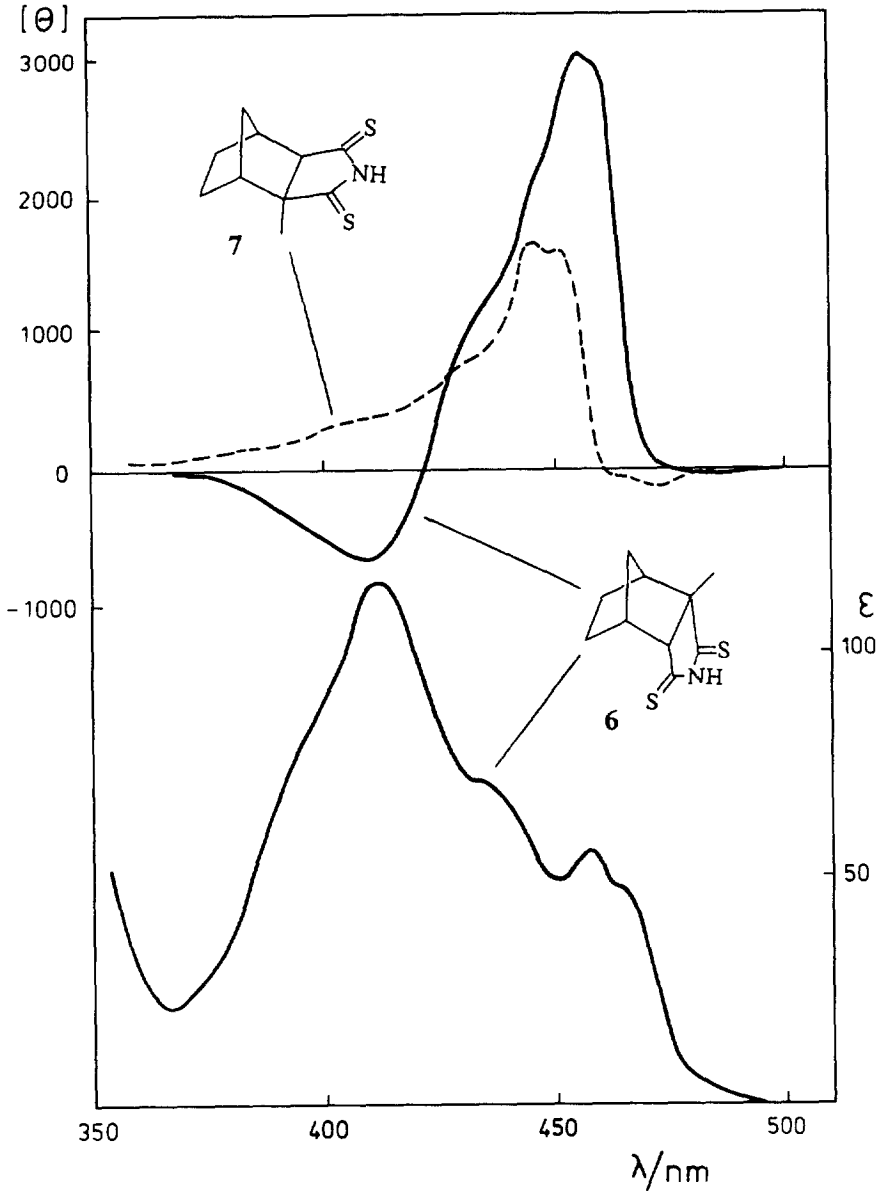
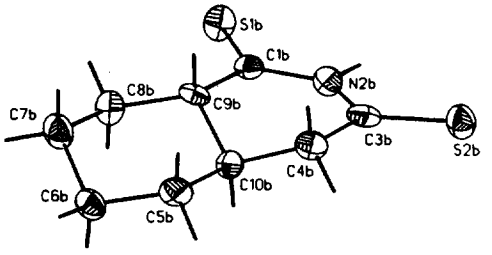


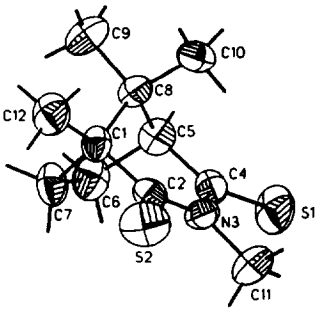
Fig. 3. CD of dithioimides **6** and **7** and UV–vis spectrum of **6** in cyclohexane (the UV–vis curve of **7** is nearly identical with that of **6**)

forces in the crystal state. Nevertheless, the results obtained with the aid of semiempirical calculations confirm that the chromophore can be easily distorted from the C_{2v} symmetry.

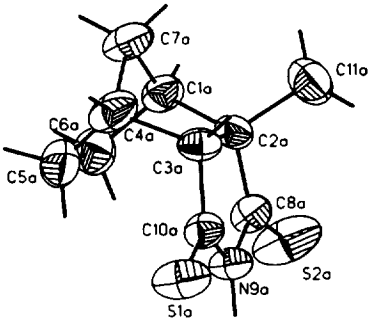
By analogy with the parent imides showing the same symmetry of the excited states,[7b] the CE sign corresponding to the lowest energy n–π* transition could be tentatively predicted by the antioctant rule with sector signs opposite to those known for ketones (Fig. 5), whereas the octant rule should operate for the next n–π* excitation.[8] The above rules are valid provided the imide or dithioimide chromophores are



4 (mol. B)



5b



6 (mol. A)

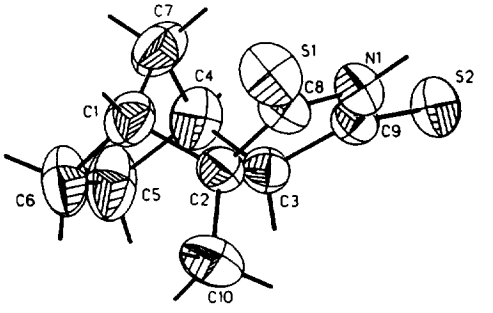


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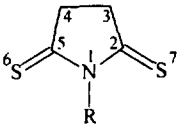
Fig. 4. ORTEP drawings of the molecules in the crystal structures of **4**, **5b**, **6** and **7**. Displacement ellipsoids are drawn at the 50% probability level

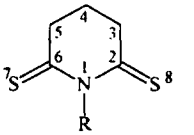
planar (C_{2v} symmetry) and then only dissymmetrically located substituents exert chiral perturbation and contribute to the CE. However, any twisting of the dithioimide group results in the inherent chirality of the chromophore and generates an additional strong contribution to the CE.[13] Its sign is governed by the helicity of the dithioimide system.

Assuming a planar geometry of the imide ring, the only source of chirality in **6** and **7** is the methyl substituent at C-2 and according to the rule (Fig. 5c), it should lead to a sequence of positive and negative CEs. The observed CD of **6** in cyclohexane is fairly consistent with this pattern. However, in more polar solvents an increased contribution of a twisted form, which differs in the CE signs, results in a more complex shape of the curve, i.e. three bands can be seen in methanol or a double-humped curve appears in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP). In the case of the isomeric compound **7**, an equilibrium between the undistorted and twisted forms affects the spectrum even in hydrocarbon solvent; the CD is much weaker than that displayed by **6** (Fig. 3), a stronger positive band at 440 nm, exhibited by a form with the planar chromophore, is consistent with the sector rule and a weak negative one near 470 nm is likely to be due to a twisted form. The behavior of **4** and **5a,b** is analogous to their parent imides and points to a domination of distorted conformers in solution.[8b] Owing to a steric interaction between the methyl group at C-8 and the chromophore in **5a,b**, the nitrogen atom is located below the plane formed by the thiocarbonyl groups. This type of distortion was predicted by the MNDO calculations

Table 2
Selected torsional angles calculated by MNDO and resulting from X-ray crystallography



compd	2-3-4-5	1-2-3-4	1-5-4-3	2-1-5-6	5-1-2-7
1	-2.3	3.6	0.2	-178.3	176.0
2	-4.3	5.7	1.3	-178.0	173.2
3	-2.6	4.5	-0.1	-177.4	174.6
6	5.1	-3.1	5.1	177.7	178.7
6[a]	[3.2(3)]	[-0.7(3)]	[-4.6(3)]	[178.0(2)	[-176.5(2)]
6[b]	[2.7(3)]	[-3.2(3)]	[-1.4(3)]	[179.3(2)]	[-178.7(2)]
7	6.3	-7.0	-3.6	-179.9	-175.4
7[c]	6.4(4)	-6.4(4)	-4.3(4)	-179.3(3)	-176.7(3)



compd	1-2-3-4	1-6-5-4	2-1-6-7	6-1-2-8
4	24.4	-25.6	179.4	-177.0
4[a]	[27.8(10)]	[-27.4(10)]	[-175.9(6)]	[180.0(6)]
4[b]	[32.7(10)]	[-25.2(10)]	[-176.6(7)]	[171.5(7)]
5a	41.3	-44.0	-171.5	172.8
5b	43.0	-44.8	-169.0	169.6
5b[c]	[38.8(3)]	[-41.3(3)]	[-175.8(2)]	[177.7(2)]

[a]X-ray data for molecule A. [b]X-ray data for molecule B. [c]X-ray data.

and confirmed by the X-ray structure. It is noteworthy that the crystallographic structures of camphoric anhydride and *N*-substituted imide also showed this kind of geometry.[14] In consequence, the methyl substituent at C-1 is located in the lower left octant and contributes with the positive sign to the lowest energy CE (Fig. 5d). A weak positive CD band near 480 nm, exhibited by **5a**, probably corresponding to the form with the planar chromophore,[15] disappears in polar solvents. It is absent in the spectrum of the *N*-methyl derivative **5b**, since *N*-methylation increases the above steric interaction and diminishes a contribution of the undistorted form.

The CD of compounds **1–3** illustrate an important role of the three-membered ring in the generation of optical activity. In hydrocarbon solvent they exhibit a positive CE near 470 nm, due to a contribution of the substituent at C-1, as predicted by the antioctant rule (Fig. 5b). Surprisingly the CE magnitude decreases in more polar solvents and in the case of **1** and **2** dissolved in the strongly hydrogen bonding HFP, both CEs change sign. It is likely that a solvation may cause a distortion of

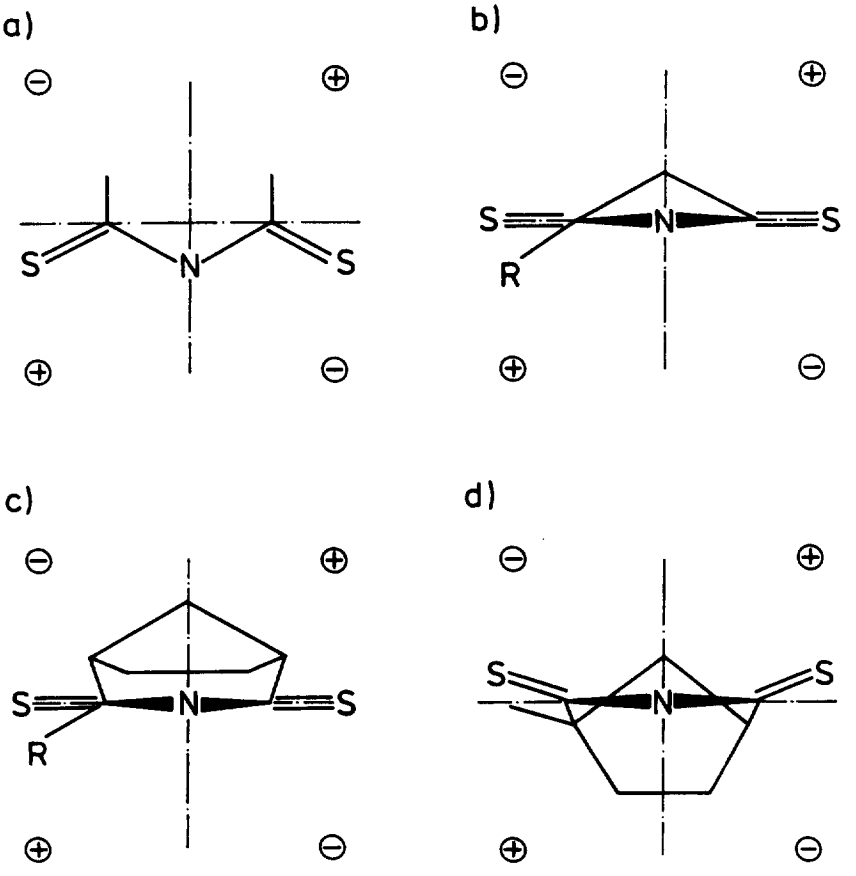


Fig. 5. Sector projections of **6**, **1–3** and **5a,b**

the 3-azabicyclo[3.1.0]hexane skeleton from the C_s symmetry and the cyclopropane ring is no longer symmetrically disposed with respect to the nodal plane and therefore strongly contributes to the CE. Analogously to the parent cyclopropanedicarboxylic imides[8d] and other cyclopropyl carbonyl[13a,16] and thiocarbonyl derivatives[17] a 'conjugation' of the three-membered ring with the neighbouring thiocarbonyl groups[18] leads to the formation of an inherently chiral chromophore. Apparently its contribution in symmetry distorted systems outweighs the vicinal effect of the substituent at C-1.

In conclusion, the presented results demonstrate extreme sensitivity of the chiroptical spectra of dithioimides to even small distortions of the chromophore from planarity. The CE sign can be predicted upon thorough examination of the molecular geometry and careful analysis of the CD in several solvents.

3. Experimental

CD spectra were recorded on a JASCO J-20 dichrograph using a 10 mm path length and sample concentrations 3.0–5.5 mol L^{-1}. UV–vis measurements were performed on a Beckman 3600 spectrophotometer and reported as λ_{max} (nm), ε_{max} (L mol^{-1} cm^{-1}). ^1H and ^{13}C NMR spectra were obtained with Bruker MSL-300 and WP-200 spectrometers at 300 and 50 MHz, respectively. The deuterated solvents were used as an internal lock for ^1H and ^{13}C NMR. FT-IR absorptions were taken with a Bruker IFS66 spectrometer. Specific rotations were measured on a Rudolph Autopol II digital polarimeter.

3.1. (1S,5R)-1-Methyl-3-azabicyclo[3.1.0]hexane-2,4-dithione 1

A mixture of (1*S*,2*R*)-1-methyl-1,2-cyclopropanedicarboximide[8d] (0.50 g, 4 mmol) and Lawesson's reagent (2.43 g, 6 mmol) in toluene (10 mL) was refluxed for 2 h. The toluene was evaporated at reduced pressure. The residue was chromatographed on silica gel using hexane:AcOEt (10:1) as the eluent. After collection of the orange fraction and evaporation of the solvent, the product was crystallized from hexane; yield 0.39 g (62%); m.p. 43–44°C; $[\alpha]_D^{20}$ +191 (*c* 1, benzene); IR (CCl_4) 3408 (br), 1435, 1142 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.59 (br s, 1H, NH), 2.96 (ddd, *J*=1.7, 4.3 and 7.3 Hz, 1H), 1.72 (m, 2H), 1.62 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 212.9 (C=S), 209.9 (C=S), 41.5, 33.0, 16.4; UV (cyclohexane) λ_{max} 440sh (ε 290), 420 (595), 322 (30 000), 260 (6100) and 237 nm (4100). Anal. calcd for $C_6H_7NS_2$ (157): C, 45.87; H, 4.49; N, 8.91; S, 40.73. Found: C, 45.68; H, 4.51; N, 8.72; S, 40.81.

3.2. (1R,5R)-1-Isopropyl-3-azabicyclo[3.1.0]hexane-2,4-dithione 2

Compound **2** was obtained from (1*R*,2*R*)-1-isopropyl-1,2-cyclopropanedicarboximide[8d] in a similar manner to **1**; m.p. 85–86°C (hexane); $[\alpha]_D^{22}$ +66 (*c* 2, benzene); IR (KBr) 3164 (br), 1467, 1446, 1129 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.09 (br s, 1H, NH), 2.92 (ddd, *J*=1.6, 3.5 and 8.4 Hz, 1H), 2.63 (sep, *J*=6.9 Hz, 1H), 1.81 (dd, *J*=4.8 and 8.4 Hz, 1H), 1.56 (dd, *J*=3.5 and 4.8 Hz, 1H), 1.01 (d, J=6.9 Hz, 3H), 0.95 (d, J=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 213.0 (C=S), 210.8 (C=S), 51.6, 38.5, 30.8, 27.6, 20.7, 19.3; UV (cyclohexane) λ_{max} 450sh (ε 170), 420 (510), 322 (32 000), 263 (6700) and 234 nm (5000). Anal. calcd for $C_8H_{11}NS_2$ (185): C, 51.89; H, 5.99; N, 7.56; S, 34.56. Found: C, 51.80; H, 6.11; N, 7.49; S, 34.55.

3.3. (1S,5R)-3-Methyl-1-phenyl-3-azabicyclo[3.1.0]hexane-2,4-dithione 3

Compound **3** was obtained from (1*S*,2*R*)-3-methyl-1-phenyl-1,2-cyclopropanedicarboximide[8d] in a similar manner to **1**; m.p. 83°C (hexane); $[\alpha]_D^{22}$ +421 (*c* 1, benzene); IR (KBr) 1320, 1301, 1093 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (s, 5H), 3.60 (s, 3H), 3.35 (dd, *J*=3.6, and 8.3 Hz, 1H), 2.17 (dd, *J*=4.4 and 8.3 Hz, 1H), 1.82 (dd, *J*=3.6 and 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 210.9 (C=S), 209.3 (C=S), 134.7, 130.4, 128.5, 48.2, 40.7, 33.0, 32.2; UV (cyclohexane) λ_{max} 460sh (ε 95), 425 (350), 333 (27 500) and 256 (4000). Anal. calcd for $C_{12}H_{11}NS_2$ (233): C, 61.76; H, 4.75; N, 6.00; S, 27.48. Found: C, 61.88; H, 4.71; N, 5.89; S, 27.45.

3.4. (4aR)-trans-1,3(2H,4H)-Hexahydroisoquinolinedithione 4

Dithioimide **4** was prepared from the corresponding imide[8b] in a similar manner to **1**; m.p. 131°C (heptane); $[\alpha]_D^{20}$ −46 (*c* 1.1, $CHCl_3$); IR (CCl_4) 3335 (br), 1466, 1285, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.73 (br s, 1H, NH), 3.32 (dd, *J*=3.5, and 18.3 Hz, 1H), 2.67 (m, 1H), 2.57 (dd, *J*=12.5 and 18.3 Hz, 1H), 2.03 (m, 1H), 2.0–1.7 (complex m, 4H), 1.45–1.05 (complex m, 4H); ^{13}C NMR ($CDCl_3$) δ 208.0 (C=S), 203.1 (C=S), 51.5, 48.6, 36.6, 32.6, 30.8, 26.0, 25.1; UV (cyclohexane) λ_{max} 505sh (ε 6), 480 (34), 428 (181), 333 (33 000), 239 (8400) and 202 nm (6400). Anal. calcd for $C_9H_{13}NS_2$ (199): C, 54.26; H, 6.58; N, 7.03; S, 32.13. Found: C, 54.01; H, 6.67; N, 6.89; S, 32.25.

3.5. (1R,5S)-1,8,8-Trimethyl-3-azabicyclo[3.2.1]octane-2,4-dithione **5a**

Dithioimide **5a** was prepared from camphorimide[19] in a similar manner to **1**; m.p. 136.5°C (hexane) (lit.[20] m.p. 135°C); $[\alpha]_D^{22}$ +63.5 (*c* 0.5, MeOH) [lit.[20] $[\alpha]_D^{22}$ +63.3 (*c* 0.8, MeOH)]; IR (KBr) 3156 (br), 3121, 1499, 1111, 1051 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.51 (br s, 1H, NH), 3.27 (m, 1H), 2.29 (m, 1H), 2.02 (m, 2H), 1.89 (m, 1H), 1.34 (s, 3H), 1.01 (s, 3H), 0.97 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 215.0 (C=S), 210.1 (C=S), 65.5, 60.0, 46.4, 38.2, 29.3, 23.4, 18.7, 18.4; UV (cyclohexane) λ_{max} 494sh (ε 11), 470 (67), 419 (190), 326 (30 000), 240 (10 000) and 197 nm (9000); UV (MeOH) λ_{max} 457 (ε 67), 417 (156), 330 (31 000) and 241 (8700).

3.6. (1R,5S)-1,3,8,8-Tetramethyl-3-azabicyclo[3.2.1]octane-2,4-dithione **5b**

A mixture of *N*-methylcamphorimide[19] (2.50 g, 12.8 mmol) and phosphorus pentasulfide (3.50 g, 28.5 mmol) in xylene (5 mL) was refluxed for 12 h. After filtering, the solid was washed with hexane. The filtrate was concentrated at reduced pressure and chromatographed on silica gel using benzene as the eluent. The product was recrystallized from pentane; yield 2.71 g (93%); m.p. 62°C; $[\alpha]_D^{20}$ +213 (*c* 1.6, CCl_4); IR (CCl_4) 1320, 1260, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.09 (s, 3H), 3.63 (d, *J*=6.9 Hz, 1H), 2.32 (m, 1H), 2.02 (m, 2H), 1.88 (m, 1H), 1.44 (s, 3H), 1.03 (s, 3H), 0.93 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 217.4 (C=S), 213.3 (C=S), 68.2, 62.6, 45.5, 41.8, 37.6, 28.8, 23.6, 21.1, 18.8; UV (cyclohexane) λ_{max} 503 (ε 51), 433 (310), 330 (37 000), 239 (6000) and 199 nm (8300); UV (MeOH) λ_{max} 488 (ε 43), 427 (230), 329 (33 000), 252 (4800) and 240 (4800). Anal. calcd for $C_{11}H_{17}NS_2$ (227): C, 58.14; H, 7.54; N, 6.16; S, 28.16. Found: C, 58.28; H, 7.74; N, 5.90; S, 28.35.

3.7. (1S)-2-Methyl-endo,endo-bicyclo[2.2.1]heptane-2,3-dicarboxdithioimide **6**

Compound **6** was obtained from the corresponding imide[8c] in a similar manner to **5b**; m.p. 93–94°C (hexane); $[\alpha]_D^{22}$ +58.4 (*c* 5, benzene); IR (KBr) 3147 (br), 1460, 1203, 1138, 1125, 1072 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.34 (br s, 1H, NH), 3.07 (d, *J*=5.5 Hz, 1H), 2.83 (m, 1H), 2.37 (m, 1H), 1.90 (m, 1H), 1.51 (m, 5H), 1.42 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 220.4 (C=S), 214.1 (C=S), 67.9, 64.8, 47.8, 42.4, 39.3, 26.6, 24.8, 22.7; UV (cyclohexane) λ_{max} 457 (ε 56), 434sh (71), 412 (116), 320 (35 000) and 241 (6400). Anal. calcd for $C_{10}H_{13}NS_2$ (211): C, 56.87; H, 6.20; N, 6.63; S, 30.30. Found: C, 56.93; H, 6.28; N, 6.63; S, 30.49.

3.8. (1R)-2-Methyl-exo,exo-bicyclo[2.2.1]heptane-2,3-dicarboxdithioimide **7**

Compound **7** was obtained from the corresponding imide[8c] in a similar manner to **5b**; m.p. 120–122°C (hexane); $[\alpha]_D^{22}$ +63.6 (*c* 1.4, benzene); IR (KBr) 3175 (br) 1468, 1440, 1195, 1136, 1066 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.28 (br s, 1H, NH), 2.67 (m, 1H), 2.56 (m, 1H), 2.47 (m, 1H), 1.72 (m, 2H), 1.55–1.20 (complex m, 4H), 1.36 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 221.8 (C=S), 215.2 (C=S), 68.8, 62.8, 47.3, 45.9, 35.1, 27.7, 23.2, 21.9; UV (cyclohexane) λ_{max} 453 (ε 59), 428sh (66), 405 (126), 315 (36 000) and 238 (9400). Anal. calcd for $C_{10}H_{13}NS_2$ (211): C, 56.87; H, 6.20; N, 6.63; S, 30.30. Found: C, 56.77; H, 6.22; N, 6.49; S, 30.27.

3.9. X-Ray crystal structure analysis

Diffraction data were obtained on a Kuma KM-4 diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073 Å). The structures were solved by direct methods with the program SHELXS-86.[21] Full matrix least-squares refinement was carried out with SHELXL-93.[22]

Crystal data for $C_9H_{13}NS_2$ (**4**): monoclinic, space group $P2_1$, a=8.880(2) Å, b=7.941(2) Å, c=14.109(3) Å, β=102.12(3)°, V=972.7(4) Å^3, Z=4, D_{calcd}=1.361 g cm^{-3}, T=130 K, R_1=0.054, wR_2=0.150 for 1322 reflections with $I>2\sigma(I)$. [R_1=0.076, wR_2=0.176 for all 1631 independent reflections.]

Crystal data for $C_{11}H_{17}NS_2$ (**5b**): orthorhombic, space group $P2_12_12_1$, a=7.471(1) Å, b=9.520(2) Å, c=16.745(3) Å, V=1191.0(4) Å^3, Z=4, D_{calcd}=1.268 g cm^{-3}, T=293 K, R_1=0.043, wR_2=0.118 for 1792 reflections with $I>2\sigma(I)$. [R_1=0.058, wR_2=0.122 for all 2106 independent reflections.]

Crystal data for $C_{10}H_{13}NS_2$ (**6**): monoclinic, space group $P2_1$, a=10.279(2) Å, b=9.233(2) Å, c=11.444(2) Å, β=96.57(3)°, V=1079.0(4) Å^3, Z=4, D_{calcd}=1.301 g cm^{-3}, T=293 K, R_1=0.033, wR_2=0.089 for 2915 reflections with $I>2\sigma(I)$. [R_1=0.046, wR_2=0.095 for all 3318 independent reflections.]

Crystal data for $C_{10}H_{13}NS_2$ (**7**): orthorhombic, space group $P2_12_12_1$, a=9.524(1) Å, b=9.631(1) Å, c=11.517(2) Å, V=1056.4(2) Å^3, Z=4, D_{calcd}=1.329 g cm^{-3}, T=293 K, R_1=0.057, wR_2=0.166 for 1654 reflections with $I>2\sigma(I)$. [R_1=0.060, wR_2=0.174 for all 1705 independent reflections.]

The atomic coordinates for the reported crystal structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by a full literature citation.

Acknowledgements

The financial support by the Committee of Scientific Research is gratefully acknowledged.

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