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Conformational properties and chiroptical spectra of lactams and thiolactams with 2-azabicyclo[2.2.1]heptane, 2- and 3-azabicyclo[3.2.1]octane skeletons

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Abstract

The CD spectra of several bicyclic lactams and thiolactams were measured in different solvents. The concentration dependence of the spectra observed in hydrocarbon solvents was attributed to shifts in the equilibrium between monomer and hydrogen-bonded dimer forms. The CD of some compounds is characterized by unusually strong Cotton effects resulting from non-planarity of the amide bonds due to internal strain of the bicyclic skeletons. The X-ray crystallographic structures of **2a**,**c**, **3b**,**d** and **4a**,**b** showed different degrees of distortion of the amide or thioamide moieties from planarity, which causes inherent chirality of the chromophores and profoundly affects the Cotton effect sign and magnitude. This distortion also restricts application of the sector rules for prediction of the n–π* CD sign, since they can be used only for compounds with planar chromophores.

1. Introduction

Extensive experimental and theoretical studies have been conducted on the structure–spectra relationships of small amide molecules in recent years.[1,2] The principle objective of many of these efforts was a more complete understanding of polypeptide spectra.[3] The chiroptical spectra are of particular importance for stereochemical considerations due to their extreme sensitivity to molecular geometry changes. However, no satisfactory general rules relating the circular dichroism (CD) to absolute configuration and conformation of amides are yet available.[1,2]

The amide chromophore is characterized by two overlapping absorption bands in the near UV region: a weak one near 220 nm, corresponding to the forbidden n–π* electronic transition, and a strong one

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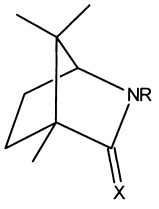
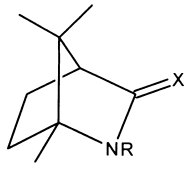
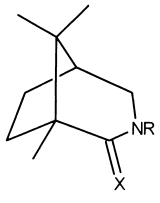
at ca. 190 nm, assigned to the allowed π–π^* transition.[4] The gas phase spectra exhibit an additional transition located between the two above bands, which disappears in condensed phases, and thus can be attributed to the Rydberg excitation.[4,5] On the other hand, a third band, appearing as a shoulder at the short-wavelength tail of the n–π^* band, has also been observed in the CD spectra taken in non-polar solvents. Its origin is not clear, but according to some authors it is probably brought about by the association of amide molecules.[6,7]

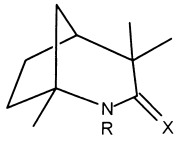
In contrast to amides much less is known on the chiroptical spectra of thioamides.[8,9] Substitution of sulphur for oxygen in the carbonyl results in bathochromic shift of the UV and CD bands and facilitates the measurements.[10] Due to a similiarity of the electronic structures of the amide and thioamide chromophores, there is a close correspondence between their lowest energy electronic transitions.[11] Moreover, because the spectra of thiocarbonyl compounds show very well resolved n–π^* and π–π^* absorption bands, the spectroscopic investigations of thioamides may lead to a better understanding of the amide chromophore.





1a	R = H	X = O	**2a**	R = H	X = O
1b	R = Me	X = O	**2b**	R = Me	X = O
1c	R = H	X = S	**2c**	R = H	X = S
1d	R = Me	X = S	**2d**	R = Me	X = S





3a	R = H	X = O	**4a**	R = H	X = O
3b	R = Me	X = O	**4b**	R = Me	X = O
3c	R = H	X = S	**4c**	R = H	X = S
3d	R = Me	X = S	**4d**	R = Me	X = S

Since compounds with bicyclic structure and restricted conformational mobility are particularly useful as model systems for chiroptical studies, we prepared the lactams **1a**,**b**–**4a**,**b** and their thiocarbonyl analogues **1c**,**d**–**4c**,**d**, and compared the CD spectra of both classes of compounds. Though the chiroptical spectra of the lactams **1a** and **2a** have been already studied by Goodman and co-workers,[7] the origin of their unusually strong Cotton effects (CEs) is not clear and the CD of their thiocarbonyl derivatives may shed more light on this phenomenon. In order to avoid the influence of dimerization of the lactam and thiolactam molecules in solution, which may affect the CD spectra, we prepared and studied the *N*-methyl derivatives **1b**,**d**–**4b**,**d**. Since the analysis of the chiroptical spectra requires careful examination of the molecular conformation, particularly the geometry of the chromophore, we determined the X-ray crystallographic structures of several lactams and thiolactams. In contrast to the compounds **1a**–**d** and **2a**–**d**, with extremely rigid bicyclic skeletons, the derivatives **3a**–**d** and **4a**–**d** possess some degree

of flexibility and therefore conformational equilibria in their solutions are possible. The molecular geometries of some compounds revealed a slight deviation of the amide and thioamide groups from planarity. The non-planar and thus inherently chiral amide and thioamide chromophores generate an additional significant contribution to the CE and thus may strongly influence the spectra.

2. Results and discussion

The lactams **1a** and **2a** were obtained in multistep syntheses from (+)-camphoric acid following the literature methods.[7,12] The compound **3a** (α-camphidone) was prepared from (+)-camphor by insertion of nitrogen with use of hydroxylamine-*O*-sulphonic acid,[13] whereas the Beckmann rearrangement of (−)-fenchone oxime afforded the lactam **4a**.[14] *N*-Methylation of **1a**–**4a** with methyl iodide gave the *N*-methyl derivatives **1b**–**4b**. Thionation of these compounds with Lawesson's reagent[15] afforded the thiolactams **1c**,**d**–**4c**,**d**.

The spectroscopic data of the compounds studied are collected in Tables 1 and 2. The UV spectra of the thiolactams **1c** and **2c** taken in cyclohexane solution show a weak absorption band near 340 nm, which shifts by 15 nm to the blue upon changing the solvent to methanol. It can unequivocally be assigned to the forbidden n–π* electronic transition.[8,11] A much stronger absorption at 270 nm is only slightly dependent on the solvent changes and corresponds to the allowed π–π* excitation. Both above bands in the compounds **3c** and **4c**, with the thioamide moiety being a part of the six-membered ring, are observed at ca. 10 nm longer wavelengths. An introduction of the methyl substituent at the thioamide nitrogen causes a further red shift of the n–π* band. Inspection of the near UV region reveals an additional moderate intensity band near 220 nm of a less clear origin.

Table 1
Circular dichroism data of lactams **1a**,**b**–**4a**,**b**

Compd.	Solvent[a]	CD λ, nm (10^{-3}[Θ])[b]	Compd.	Solvent[a]	CD λ, nm (10^{-3}[Θ])[b]
1a	C[c]	226 (–27.8), 192 (29.5)	**1b**	C	225 (–36.5), 191 (35.4)[d]
	M	217 (–44.9), 197 (32.4)		M	220 (–40.0), 198 (41.0)
2a	C[e]	227 (28.9), 192 (–45.6)	**2b**	C	227 (38.3), 207 (–45.8)
	M	217 (47.5), 197 (–41.0)		M	219 (48.9), 198 (–56.7)
3a	C[e]	228 (11.9), 191 (–38.2)	**3b**	C	229 (15.2), 204 (–48.7)
	M	220 (14.4), 196 (–37.4)		M	225 (12.8), 202 (–48.0)
4a	C[e]	238 (2.1), 194 (–19.4)	**4b**	C	238 (5.6), 213 (–41.7)
	M	238 (0.7), 203 (–14.5)		M	240 (1.6), 212 (–35.8)

[a] C – cyclohexane; M – methanol. [b] Molecular ellipticity in deg cm^2 dmol^{-1}.
[c] c = 0.004 mol dm^{-3}. [d] a shoulder at 203 (21.5). [e] c = 0.003 mol dm^{-3}.

The CD spectra of the lactams **1a** and **2a** are very similar to those reported by Goodman et al.[7] Owing to a close correspondence between the electronic structures and lowest energy transitions of the amide and thioamide chromophores the same rules are expected to govern optical activity of both classes of compounds. Indeed, the n–π* and π–π* CE signs observed for the conformationally rigid thiolactams **1c**,**d** and **2c**,**d** are the same as those measured for the parent lactams **1a**,**b** and **2a**,**b**, respectively. The corresponding CD curves of the compounds **1a**–**d** and **2a**–**d** are essentially mirror images (cf. Figs. 1 and 2). It indicates that the skeleton chirality of the systems is primarily responsible for the CE sign, whereas a contribution from dissymmetrically located substituents is less important. There are several sector and chirality rules proposed for the rationalization of the n–π* CE sign of lactams,[16,17] however their application is usually limited to specific classes of compounds.[1c,2] One of them, a so-called 'lowered symmetry' sector rule, developed by Weigang and co-workers,[17] has been shown to be useful for a wide

Table 2
Electronic absorption (UV) and circular dichroism (CD) data of thiolactams **1c**,**d**–**4c**,**d**

Compd.	Solv.[a]	UV λ, nm (ε)	CD λ, nm (10^{-3}[Θ])[b]
1c	C[c]	338 (80), 270 (14800), 222 (3150)	354 (–13.7), 295 (0.3), 275 (–13.0), 226 (14.0)
	M	323 (90), 268 (14900)	325 (–15.8), 282 (–3.0), 256 (2.9), 211 (14.5)
1d	C	346 (71), 269 (16800), 213 (3900)	345 (–17.2), 262 (6.1), 228 (–10.4), 213 (25.6)
	M	322 (101), 266 (15500), 200 (6000)	322 (–17.1), 263 (7.0), 209 (11.2)
2c	C[d]	340 (78), 270 (15800), 225 (3500)	357 (10.5), 295 (–2.0), 276 (8.0), 225 (–19.0)
	M	319 (94), 268 (16600)	325 (13.7), 279 (3.9), 254 (–1.3), 208 (–26.0)
2d	C	349 (64), 271 (16300), 217 (2250)	350 (14.9), 265 (–4.2), 217 (–14.6)
	M	317 (113), 266 (16600), 205 (3900)	320 (15.5), 265 (–4.7), 208 (–18.0)
3c	C[d]	349 (67), 279 (14000), 224 (3100)	380 (2.4), 332 (–0.3), 279 (–26.7), 223 (14.6)
	M	334 (70), 276 (14900)	367 (0.4), 324 (–1.4), 275 (–20.0), 216 (12.4)
3d	C	366 (38), 273 (15600), 217 (4100)	387 (1.3), 346 (–0.7), 272 (–40.0), 222 (24.6)
	M	340 (52), 271 (15000), 206 (7400)	375 (0.4), 333 (–1.5), 270 (–29.0), 217 (15.6)
4c	C[d]	351 (48), 286 (13300), 225 (2800)	398 (0.6), 357 (–1.5), 285 (–22.6)
	M	330sh (80), 282 (13400)	393 (0.02), 336 (–2.8), 283 (–13.3)
4d	C	368 (34), 281 (13000), 216sh (2800)	407 (0.16), 369 (–5.4), 278 (3.2)
	M	339 (51), 278 (13700), 207 (3600)	400 (0.04), 347 (–3.3), 278 (3.2)

[a] C – cyclohexane; M – methanol. [b]Molecular ellipticity in deg cm^2 dmol^{-1}. [c] c = 0.00013 mol dm^{-3}.
[d] c = 0.0002 mol dm^{-3}.

range of amides.[2,18] It treats the amide group (C_s symmetry) as a perturbed carboxylate ion chromophore (C_{2v} symmetry). The symmetry lowering brought about by the perturbation results in reshaping and reorientation of the nodal planes and leads to the modified octant rule with a curved nodal surface (Fig. 3). On the other hand, the chirality rules[19] emphasize the importance of the lactam ring contribution (chirality second sphere according to Snatzke),[20] which usually overweighs that of the ring substituents (chirality third sphere).[20] It seems reasonable to expect that the Weigang's lactam rule should also work for thiolactams. The amide or thioamide moiety in **1a**–**d** and **2a**–**d** may be considered as a part of the five- or six-membered ring of the bicyclic skeleton. According to the sector projection (Fig. 3) these rings contribute with the opposite signs to the CE. However, by analogy to related bicyclic ketones, the contribution of a smaller or more strained ring should prevail[21] and therefore a negative CE is predicted for **1a**–**d** and a positive one for **2a**–**d**, though the CE magnitude is expected to be rather weak. The measured CE signs are consistent with these predictions but, contrary to expectation, the observed CEs for lactams **1a**,**b** and **2a**,**b** are very strong for both n–π* and π–π* transitions. Moreover, they are much stronger than those mentioned in the literature for the majority of monocyclic five- or six-membered ring lactams.[2,6,22] In contrast, the n–π* CE in the thiolactams **1c**,**d** and **2c**,**d** is about three times weaker, whereas the π–π* CE is ca. 10 times weaker than that in the parent lactams.

A comparison of the X-ray structures of **2a** (Fig. 4) and **2c** may help to explain the above observations. The amide group in **2a** is considerably distorted from planarity as confirmed by the corresponding torsional angles (Table 3), in particular the NH hydrogen and the carbonyl oxygen remain out of the average plane of the C1, N2, C3 and C4 atoms. The amide nitrogen atom shows a significant degree of pyramidalization as evidenced by its displacement of 0.16(2) Å (molecule A) from the plane of three neighbouring atoms. Apparently the observed deformation of the amide moiety can be attributed to the strain imposed by the bicyclic skeleton.[23] In contrast, the thioamide group in **2c** shows much less deviation from planarity and a similar geometry has been found for its *N*-methyl analogue **2d** in the solid state.[24] The non-planar amide group is to be considered as an inherently chiral chromophore, which may exert a strong contribution to the CE.[25] Fortunately, in the case of **1a**–**d** and **2a**–**d**, it is of the same sign as that of the bicyclic skeleton and their CEs obey the sector rule.

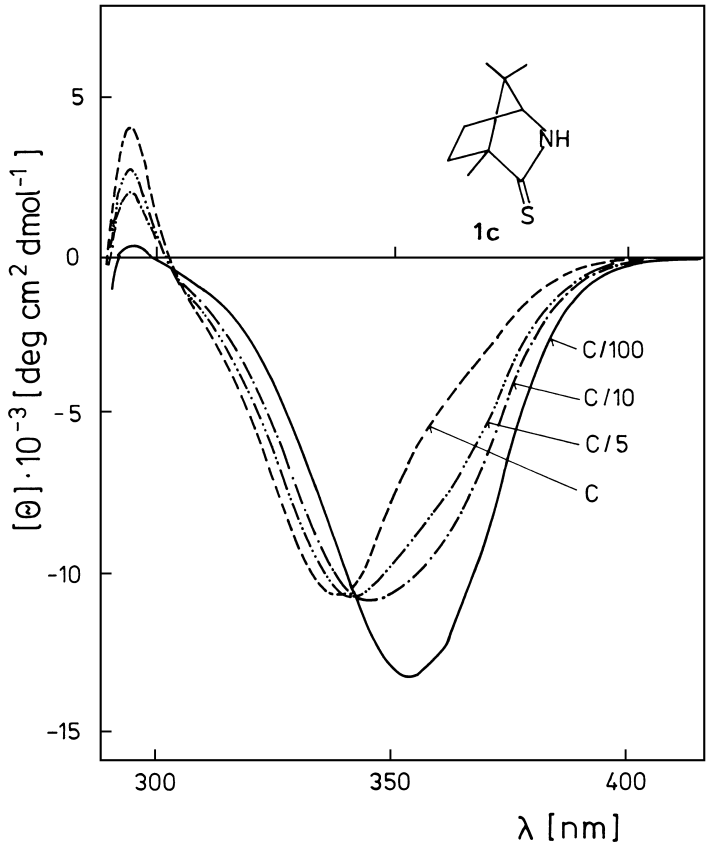


Figure 1. Circular dichroism (CD) spectra of **1c** in cyclohexane at different concentrations (c=0.013 mol dm^{-3})

An important feature of **1c** and **2c** is a strong concentration-dependence of their CD in cyclohexane solution (Figs. 1 and 2). This effect can be attributed to shifts of the equilibrium between monomer and dimer forms of these thiolactams. A formation of the dimer is also reflected by the π–π* CE, which is very weak at low concentrations and splits into a couplet at higher concentrations, due to the exciton coupling between the two allowed π–π* transitions.[26] An analogous behaviour of two monocyclic thiolactams has been described by Kajtar and co-workers.[8] The shape and magnitude of the CD of the *N*-methyl derivatives **1d** and **2d**, that obviously cannot form hydrogen-bonded dimers, is very similar to those of **1c** and **2c** measured in methanolic solution. This solvent inhibits formation of dimeric structures in favour of intramolecular hydrogen bonds.

Many lactams, including **1a** and **2a**, also show concentration-dependence of the CD spectra in hydrocarbon solvents.[6,7] This effect can again be attributed to dimer formation in non-polar media. Usually the CD spectra of amides taken in such solvents exhibit a shoulder between the n–π* and π–π* CD bands but it disappears upon dilution.[7] Though in some earlier reports it has been assigned to a Rydberg excitation,[23,27] it is known that Rydberg transitions can be observed only in the gas phase and cannot be detected upon going to condensed phases.[28] However, recently Clark claimed to identify this band in the single crystal spectrum of propionamide but he was not able to observe it in solution.[5] By analogy with thioamides, the exciton coupling between two amide π–π* transitions in the hydrogen-bonded dimer is very likely to be responsible for the additional CD band. However, a strong overlap of the amide n–π* and π–π* absorptions causes the exciton couplet, due to the dimer form, to be buried

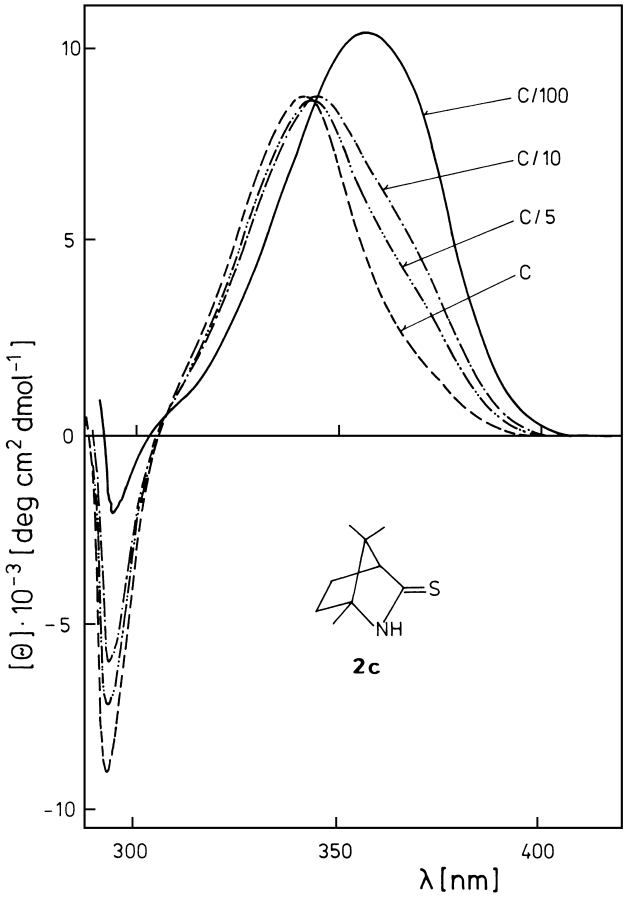


Figure 2. Circular dichroism (CD) spectra of **2c** in cyclohexane at different concentrations (c=0.019 mol dm^{-3})

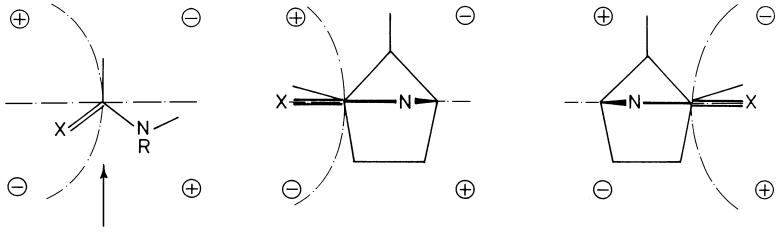


Figure 3. Amide and thioamide sector rule (a) applied to compounds **1a–d** (b) and **2a–d** (c). The arrow shows direction of projection

under these strong bands and manifested only as a shoulder. In contrast, the spectra of non-dimerizing *N*-methyl lactams **1b** and **2b** are only slightly influenced by solvent polarity and do not show the additional band.

The CD spectra of the thiolactams **3c**,**d** and **4c**,**d** are generally more complex than those of the extremely strained compounds discussed above. First of all, they show bisignate CD bands in the region of the lowest energy n–π* transition (Fig. 5). They are also strongly dependent on solvent changes. Such a behaviour is indicative of conformational equilibria in solution. Despite the bicyclic structure of **3a–d** and **4a–d**, their six-membered ring, being a part of the molecular skeleton, possesses some degree of flexibility. It was confirmed by the X-ray structures of **3b**,**d** (Fig. 6) and **4a**,**b** (Fig. 7), which show

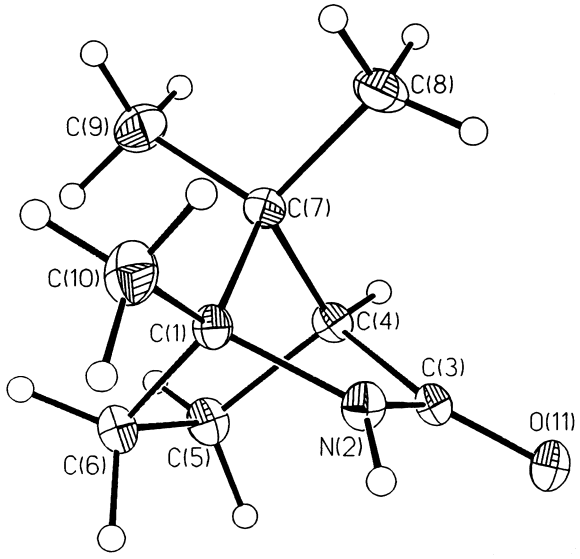
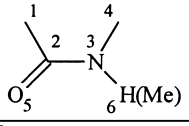
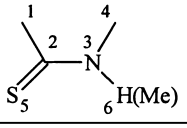


Figure 4. ORTEP drawing of the molecular structure of **2a**. Thermal ellipsoids are drawn at 50% probability level for heavy atoms

Table 3
Selected torsion angles calculated from the X-ray structures





Compd.[a]	1–2–3–4	5–2–3–6	5–2–3–4	1–2–3–6
2a (A)	2.4(3)	–20.8(28)	–175.3(3)	156.9(27)
(B)	2.6(3)	–17.7(27)	–174.3(3)	159.2(26)
2c (A)	–0.2(3)	–7.3(36)	–178.8(3)	171.2(35)
(B)	0.9(4)	–7.5(3)	–174.8(3)	168.3(32)
3b (A)	11.7(3)	–3.9(4)	–170.8(3)	178.7(3)
(B)	13.4(3)	–4.6(4)	–171.1(3)	179.9(3)
3d (A)	9.0(8)	–2.2(8)	–175.0(5)	–178.2(6)
(B)	9.2(8)	–1.8(8)	–175.6(5)	–177.0(6)
4a (A)	2.3(7)	–4.6(38)	–179.5(5)	177.2(37)
(B)	–2.3(7)	–10.8(35)	176.7(5)	170.2(34)
4b	4.8(3)	–9.3(4)	–175.8(3)	171.3(3)

[a] Data for molecule A and B.

significant variations of torsional angles involving the ring atoms as well as the amide and thioamide moieties (Table 3). Therefore conformational changes of the six-membered ring and the chromophore geometry induced by solvents are apparently responsible for the bisignate CEs of the thiolactams. In the case of the lactams **3a**,**b** and **4a**,**b**, a bisignate n–π^* CEs are not observed but in some spectra the measured CD magnitudes are relatively weak owing to a contribution from conformers with opposite signed CEs. Obviously the amide sector rules are not useful for skewed amide or thioamide groups, since the inherent chirality of the chromophore is primarily responsible for the CE sign.[25] The non-planarity of the the amide group in **3b** and **4b** is manifested by the unusually strong magnitude of the π–π^* CEs exhibited by these compounds. Similarly thiolactams **3c**, **3d** and **4c** show quite intense π–π^* CEs in contrast to the rigid thioamides **1c**,**d** and **2c**,**d** with nearly planar chromophores. The amide bond in **4a**

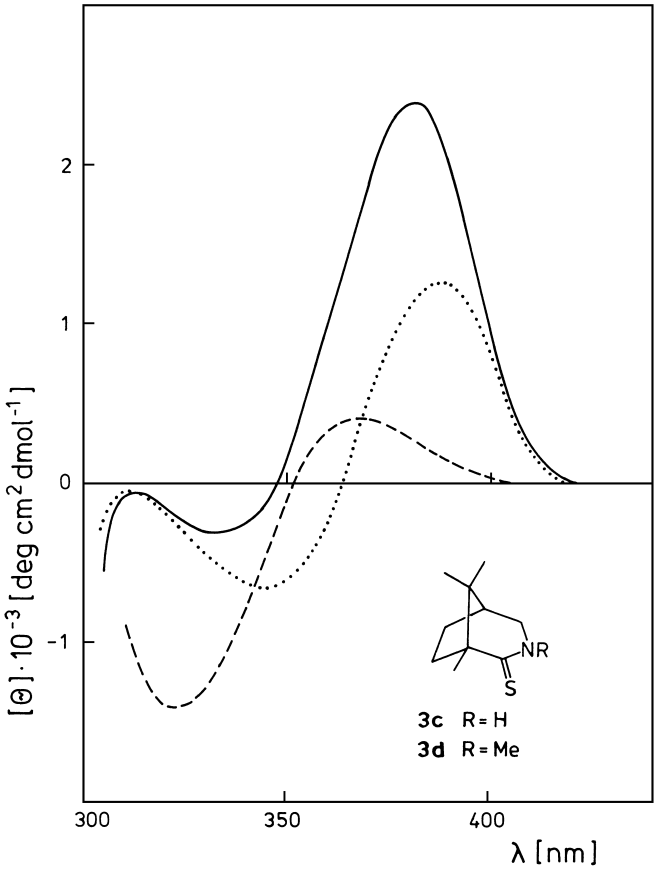


Figure 5. Circular dichroism (CD) spectra of **3c** and **3d** in cyclohexane (solid and broken line, respectively), and **3c** in methanol (dotted line)

is nearly planar, whereas in **4b** it is significantly twisted as a consequence of a steric interaction between the *N*-methyl group and the carbonyl oxygen. It is reflected by the enhanced magnitude of the positive n–π* CE at 238 nm in **4b**. On the other hand, the negative branch of the n–π* CE in the thiolactams **4c**,**d** dominates over the much weaker positive one. It may suggest an opposite sense of the chromophore twisting in **4c**,**d** to that in the parent lactams. In the case of **3a**,**b** strong n–π* CEs point to a severe distortion of the amide group from planarity as confirmed by the X-ray data, whereas much weaker bisignate CEs in the thiocarbonyl analogues **3c**,**d** indicate an equilibrium between two conformers with different chromophore helicites.

In conclusion, the CD spectra of thioamides, owing to a good separation of the n–π* and π–π* bands, may be useful in analysis of the CD curves of the parent amides. The chiroptical spectra of lactams and thiolactams are extremely sensitive to any deviations of the chromophore from planarity. This obviously reduces usefulness of the sector rules for predictions of their CE sign and a careful examination of molecular geometry may be helpful in the interpretation of the spectra. In addition, the CD of amides and thioamides is also influenced by solvent polarity and a solute concentration that reflects conformational changes of the molecules induced by solvents or shifts in association equilibria. Therefore a comparison of the spectra taken in different solvents is always desirable.

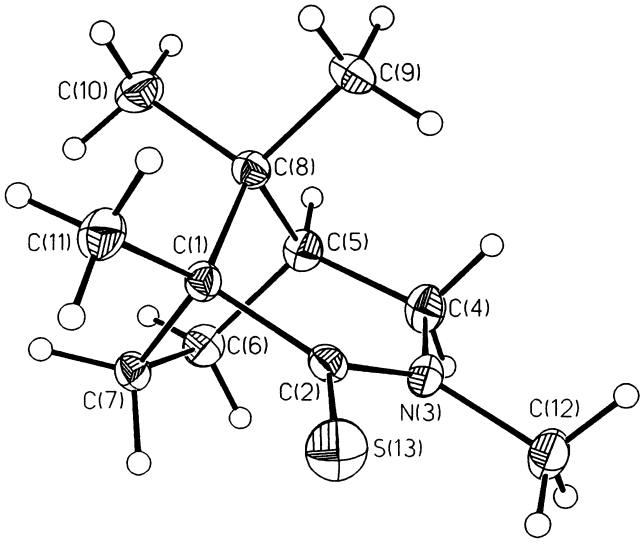


Figure 6. ORTEP drawing of the molecular structure of **3d**. Thermal ellipsoids are drawn at 50% probability level for heavy atoms

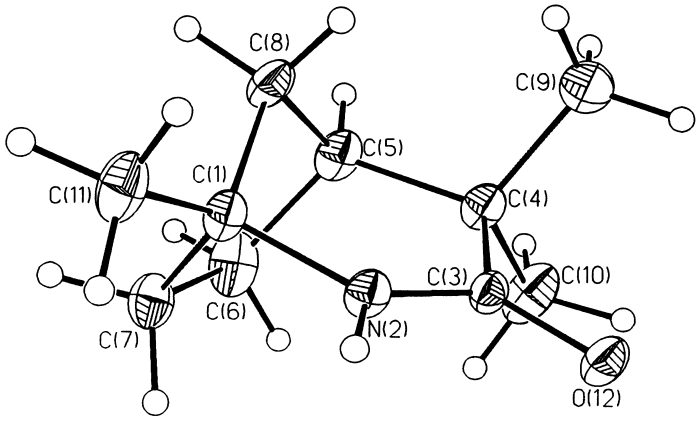


Figure 7. ORTEP drawing of the molecular structure of **4a**. Thermal ellipsoids are drawn at 50% probability level for heavy atoms

3. Experimental

CD spectra were recorded on a Jasco J-20 or J-715 dichrograph. UV–vis measurements were performed on a Beckman 3600 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with Bruker MSL-300 and WP-200 spectrometers at 300 and 50 MHz, respectively. The deuteriated solvents were used as an internal lock for ^{1}H 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)-4,7,7-Trimethyl-2-azabicyclo[2.2.1]heptan-3-one **1a***

This material was prepared from the corresponding amino acid following the procedure of Noyes and Potter;[12] m.p. 208°C (lit.[12] m.p. 203°C, lit.[7] m.p. 202–203°C); $[\alpha]_D^{20}$ −61.5 (*c* 2, EtOH) {lit.[12] $[\alpha]_D^{29}$ −61.5 (*c* 1, EtOH)}; IR (CCl_4) 3446, 3209 (br), 1726, 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.63 (br s, 1H),

3.27 (s, 1H), 1.98–1.82 (m, 1H), 1.65 (m, 1H), 1.53–1.35 (m, 2H), 0.97 (s, 3H), 0.93 (s, 3H), 0.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 182.2, 62.0, 53.8, 50.9, 30.0, 28.9, 18.6, 18.3, 9.0.

3.2. (1S)-2,4,7,7-Tetramethyl-2-azabicyclo[2.2.1]heptan-3-one ***1b***

Sodium hydride (0.29 g, 12 mmol) was added to a stirred solution of **1a** (1.38 g, 9 mmol) in DME (10 mL) and after the reaction ceased (ca. 15 min) methyl iodide (2 mL) was added dropwise. The reaction mixture was stirred for an additional 30 min and poured into water. The product was extracted with Et_2O. After removal of the solvent the residue was distilled at reduced pressure; yield 1.22 g (81%); b.p. 80°C/12 mmHg; m.p. 24°C; $[\alpha]_D^{20}$ −26.6 (neat); IR (CCl_4) 1704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.03 (d, *J*=2.1 Hz, 1H), 2.69 (s, 3H), 1.85–1.70 (m, 1H), 1.65–1.25 (m, 3H), 0.92 (s, 3H), 0.83 (s, 3H), 0.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 178.8, 68.1, 54.1, 49.3, 30.6, 27.5, 25.2, 18.0, 17.6, 9.2. Anal. calcd for $C_{10}H_{17}NO$ (167): C, 71.81; H, 10.25; N, 8.37. Found: C, 71.68; H, 10.28; N, 8.48.

3.3. (1S)-4,7,7-Trimethyl-2-azabicyclo[2.2.1]heptan-3-thione ***1c***

Lactam **1a** (0.77 g, 5 mmol) and Lawesson's reagent (1.21 g, 3 mmol) were refluxed in toluene (10 mL) for 30 min. After removal of toluene the residue was chromatographed on silica gel (elution with toluene) and the product was sublimed; yield 0.52 g (62%); m.p. 186°C; $[\alpha]_D^{20}$ −212 (*c* 2, $CHCl_3$); IR (CCl_4) 3438, 3170 (br), 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$) 8.53 (br s, 1H), 3.49 (s, 1H), 1.97 (m, 1H), 1.71 (m, 1H), 1.50 (m, 1H), 1.29 (m, 1H), 1.13 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 212.3, 66.7, 62.5, 53.6, 31.4, 28.3, 18.6, 18.1, 11.7. Anal. calcd for $C_9H_{15}NS$ (169): C, 63.85; H, 8.93; N, 8.28; S, 18.94. Found: C, 63.87; H, 8.88; N, 8.33; S, 19.14.

3.4. (1S)-2,4,7,7-Tetramethyl-2-azabicyclo[2.2.1]heptan-3-thione ***1d***

Lactam **1c** (1.34 g, 8 mmol) and Lawesson's reagent (2.10 g, 5 mmol) were refluxed in toluene (10 mL) for 6 h. After removal of toluene the residue was chromatographed on silica gel (elution with benzene) and the product was crystallized from pentane; yield 0.85 g (58%); m.p. 70°C; $[\alpha]_D^{20}$ −195 (*c* 2, $CHCl_3$); IR (CCl_4) 1490, 1390, 1304 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.41 (d, *J*=2.1 Hz, 1H), 3.17 (s, 3H), 1.90 (m, 1H), 1.68 (m, 1H), 1.42 (m, 1H), 1.27 (m, 1H), 1.22 (s, 3H), 0.87 (s, 3H), 0.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 207.9, 73.8, 63.1, 52.3, 33.7, 32.3, 26.0, 18.2, 17.9, 12.6. Anal. calcd for $C_{10}H_{17}NS$ (183): C, 65.52; H, 9.34; N, 7.64; S, 17.49. Found: C, 65.64; H, 9.38; N, 7.53; S, 17.64.

3.5. (1R)-1,7,7-Trimethyl-2-azabicyclo[2.2.1]heptan-3-one ***2a***

This material was prepared from the corresponding amino acid following the procedure of Noyes and Potter;[12] m.p. 193°C (lit.[12] m.p. 188–189°C, lit.[7] m.p. 187–188°C); $[\alpha]_D^{20}$ +72.9 (*c* 1.6, EtOH) {lit.[7] $[\alpha]_D^{25}$ +70.1 (*c* 1, EtOH)}; IR (CCl_4) 3437, 3203 (br), 1704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.72 (br s, 1H), 2.16 (d, *J*=3.7 Hz, 1H), 1.95–1.75 (m, 2H), 1.49 (m, 2H), 1.10 (s, 3H), 0.96 (s, 3H), 0.80 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 180.5, 62.0, 55.4, 50.8, 35.4, 22.7, 18.4, 18.0, 13.0.

3.6. (1R)-1,2,7,7-Tetramethyl-2-azabicyclo[2.2.1]heptan-3-one ***2b***

This compound was prepared in a similar manner to **1b**; after sublimation m.p. 125–126°C; $[\alpha]_D^{23}$ +66.4 (*c* 3, C_6H_6); IR (CCl_4) 1702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3H), 2.17 (d, *J*=4.1 Hz, 1H), 1.85

(m, 1H), 1.62 (m, 1H), 1.50–1.25 (m, 2H), 1.05 (s, 3H), 0.84 (s, 3H), 0.79 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 178.1, 69.7, 54.8, 49.2, 31.6, 23.5, 25.2, 18.1, 17.8, 11.7. Anal. calcd for $C_{10}H_{17}NO$: (167) C, 71.81; H, 10.25; N, 8.37. Found: C, 71.56; H, 10.33; N, 8.42.

*3.7. (1*R*)-1,7,7-Trimethyl-2-azabicyclo[2.2.1]heptan-3-thione **2c***

This compound was prepared in a similar manner to **1c**; m.p. 134°C (heptane); $[\alpha]_D^{20}$ +196 (*c* 2, $CHCl_3$); IR (CCl_4) 3428, 3150 (br), 1506, 1395, 1238, 1175, 1097 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.71 (br s, 1H), 2.77 (d, *J*=4.0 Hz, 1H), 2.10–1.85 (m, 2H), 1.62 (m, 1H), 1.44 (m, 1H), 1.22 (s, 3H), 0.96 (s, 3H), 0.88 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 207.7, 72.7, 66.0, 53.9, 34.9, 24.6, 18.3, 18.0, 12.2. Anal. calcd for $C_9H_{15}NS$ (169): C, 63.85; H, 8.93; N, 8.28; S, 18.94. Found: C, 63.71; H, 9.22; N, 8.50; S, 19.06.

*3.8. (1*R*)-1,2,7,7-Tetramethyl-2-azabicyclo[2.2.1]heptan-3-thione **2d***

This compound was prepared in a similar manner to **1d**; m.p. 110°C (hexane); $[\alpha]_D^{20}$ +218 (*c* 1, C_6H_6); IR (CCl_4) 1488, 1390, 1258, 1067 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.02 (s, 3H), 2.78 (d, *J*=4.0 Hz, 1H), 2.00–1.65 (m, 2H), 1.50–1.25 (m, 2H), 1.18 (s, 3H), 0.84 (s, 3H), 0.80 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 204.6, 75.6, 65.7, 51.9, 32.4, 29.2, 25.3, 18.3, 17.8, 12.0. Anal. calcd for $C_{10}H_{17}NS$ (183): C, 65.52; H, 9.34; N, 7.64; S, 17.49. Found: C, 65.50; H, 9.47; N, 7.38; S, 17.56.

*3.9. (1*R*)-1,8,8-Trimethyl-3-azabicyclo[3.2.1]octan-2-one **3a***

This lactam was prepared by reaction of (+)-camphor with hydroxylamine-*O*-sulphonic acid according to the procedure of Krow and Szczepanski;[13] after sublimation m.p. 231–232°C (lit.[29] m.p. 231–232°C); $[\alpha]_D^{20}$ −36.5 (*c* 2, MeOH) {lit.[29] $[\alpha]_D^{25}$ −36.01 (*c* 2, MeOH)}; IR (CCl_4) 3426, 3220 (br), 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.52 (br s, 1H), 3.12 (d, *J*=11.1 Hz, 1H), 2.86 (d, *J*=11.1 Hz, 1H), 2.27 (d, *J*=6.4 Hz, 1H), 2.02 (m, 1H), 1.90–1.70 (m, 3H), 1.02 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 177.7, 55.0, 53.7, 42.1, 42.0, 36.0, 28.0, 22.2, 18.5, 17.5.

*3.10. (1*R*)-1,3,8,8-Tetramethyl-3-azabicyclo[3.2.1]octan-2-one **3b***

This compound was prepared in a similar manner to **1b**; m.p. 43°C (pentane); $[\alpha]_D^{22}$ −65.5 (*c* 2.7, C_6H_6); IR (CCl_4) 1658 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.36 (ddd, *J*=1.5, 2.8, 11.4 Hz, 1H), 2.91 (dd, *J*=1.7, 11.4 Hz, 1H), 2.79 (s, 3H), 2.10–1.85 (m, 3H), 1.69 (m, 1H), 1.47 (m, 1H), 1.07 (s, 3H), 0.89 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 176.3, 55.2, 52.0, 44.0, 42.5, 37.4, 33.7, 27.9, 23.1, 19.1, 13.9. Anal. calcd for $C_{11}H_{19}NO$ (181): C, 72.88; H, 10.56; N, 7.73. Found: C, 72.63; H, 10.79; N, 7.69.

*3.11. (1*R*)-1,8,8-Trimethyl-3-azabicyclo[3.2.1]octan-2-thione **3c***

This compound was prepared in a similar manner to **1c**; m.p. 203–204°C (toluene–hexane); $[\alpha]_D^{23}$ −154.7 (*c* 1.05, C_6H_6); IR (CCl_4) 3390, 3190 (br), 1522, 1347, 1320, 1290, 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.57 (br s, 1H), 3.54 (dm, *J*=13.0 Hz, 1H), 2.91 (ddd, *J*=1.7, 2.1, 13.0 Hz, 1H), 2.10 (m, 2H), 1.93 (m, 1H), 1.82 (m, 1 H), 1.63 (m, 1H), 1.33 (s, 3H), 1.01 (s, 3H), 0.98 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 213.3, 55.9, 51.8, 43.4, 42.1, 40.2, 28.1, 24.3, 18.9, 18.3. Anal. calcd for $C_{10}H_{17}NS$ (183): C, 65.52; H, 9.34; N, 7.64; S, 17.49. Found: C, 65.62; H, 9.10; N, 7.72; S, 17.50.

3.12. (1R)-1,3,8,8-Tetramethyl-3-azabicyclo[3.2.1]octan-2-thione **3d**

This compound was prepared in a similar manner to **1d**; m.p. 126°C (heptane); $[\alpha]_D^{23}$ −189.6 (*c* 1.9, C_6H_6); IR (CCl_4) 1512, 1349, 1320, 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.66 (ddd, *J*=1.7, 4.1, 13.1 Hz, 1H), 3.29 (s, 3H), 3.23 (dd, *J*=1.2, 13.1 Hz, 1H), 2.10–1.95 (m, 2H), 1.93 (m, 1H), 1.75 (m, 1H), 1.52 (m, 1H), 1.36 (s, 3H), 0.94 (s, 3H), 0.88 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.8, 60.7, 56.4, 44.0, 43.2, 42.0, 39.5, 28.2, 24.7, 19.7, 18.8. Anal. calcd for $C_{11}H_{19}NS$ (197): C, 66.95; H, 9.70; N, 7.10; S, 16.25. Found: C, 66.93; H, 9.70; N, 7.30; S, 16.31.

3.13. (1R)-1,4,4-Trimethyl-2-azabicyclo[3.2.1]octan-3-one **4a**

This lactam was prepared by Beckmann rearrangement of (−)-fenchone oxime according to the procedure of Cottingham;[14] after sublimation m.p. 135–136°C (lit.[30] m.p. 140–141°C); $[\alpha]_D^{20}$ −32.4 (*c* 2.2, $CHCl_3$); IR (CCl_4) 3410, 3205 (br), 1663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.96 (br s, 1H), 1.98 (m, 1H), 1.92 (m, 1H), 1.88 (m, 1H), 1.80–1.65 (m, 2H), 1.60–1.45 (m, 2H), 1.27 (s, 3H), 1.19 (s, 3H), 1.13 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.1, 60.1, 45.2, 42.0, 40.1, 28.1, 25.0, 23.9, 23.6.

3.14. (1R)-1,2,4,4-Tetramethyl-2-azabicyclo[3.2.1]octan-3-one **4b**

This compound was prepared in a similar manner to **1b**; m.p. 57–59°C (pentane); $[\alpha]_D^{22}$ −21.6 (*c* 2.2, C_6H_6); IR (CCl_4) 1643 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.83 (s, 3H), 2.05 (m, 1H), 1.93 (m, 1H), 1.92–1.70 (m, 3H), 1.55–1.45 (m, 2H), 1.38 (s, 3H), 1.22 (s, 3H), 1.13 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 176.5, 64.0, 44.5, 42.9, 41.7, 36.6, 28.4, 27.7, 25.5, 25.0, 23.5. Anal. calcd for $C_{11}H_{19}NO$ (181): C, 72.88; H, 10.56; N, 7.73. Found: C, 72.67; H, 10.69; N, 7.78.

3.15. (1R)-1,4,4-Trimethyl-2-azabicyclo[3.2.1]octan-3-thione **4c**

This compound was prepared in a similar manner to **1c**; m.p. 168–169°C (toluene–hexane); $[\alpha]_D^{22}$ −149 (*c* 2.2, C_6H_6); IR (CCl_4) 3375, 3170 (br), 1535, 1490, 1395, 1250, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.68 (br s, 1H), 2.09 (m, 1H), 2.05–1.70 (m, 4H), 1.57 (m, 2H), 1.38 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 211.3, 63.7, 47.2, 45.1, 39.6, 39.4, 31.9, 28.2, 25.1, 22.7. Anal. calcd for $C_{10}H_{17}NS$ (183): C, 65.52; H, 9.34; N, 7.64; S, 17.49. Found: C, 65.58; H, 9.46; N, 7.52; S, 17.35.

3.16. (1R)-1,2,4,4-Tetramethyl-2-azabicyclo[3.2.1]octan-3-thione **4d**

This compound was prepared in a similar manner to **1d**; m.p. 92–93°C (hexane); $[\alpha]_D^{21}$ +50.8 (*c* 2, MeOH); IR (CCl_4) 1465, 1389, 1375, 1269, 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.45 (s, 3H), 2.15–1.95 (m, 2H), 2.0–1.75 (m, 3H), 1.65–1.55 (m, 2H), 1.52 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 209.9, 68.8, 49.5, 44.5, 41.3, 37.9, 37.1, 32.6, 30.4, 25.4, 23.9. Anal. calcd for $C_{11}H_{19}NS$ (197): C, 66.95; H, 9.70; N, 7.10; S, 16.25. Found: C, 67.02; H, 9.92; N, 7.06; S, 16.05.

3.17. X-Ray crystal structure analysis

Diffraction data were collected 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.[31] Full matrix least-squares refinement was carried out with SHELXL-93.[32]

Crystal data for $C_9H_{15}NO$ **2a**: tetragonal, space group $P4_3$, a=10.637(2), c=15.570(3) Å, V=1761.7(6) Å^3, Z=8, D_{calcd}=1.155 g cm^{-3}, T=223(1) K, R_1=0.043, wR_2=0.084 for 1561 reflections with $I \geq 2\sigma(I)$ [R_1=0.112, wR_2=0.109 for all 2673 independent reflections].

Crystal data for $C_9H_{15}NS$ **2c**: monoclinic, space group $P2_1$, a=11.581(2), b=7.2880(10), c=11.717(2) Å, β=97.11(3)°, V=981.3(3) Å^3, Z=4, D_{calcd}=1.146 g cm^{-3}, T=223(2) K, R_1=0.032, wR_2=0.078 for 1619 reflections with $I \geq 2\sigma(I)$ [R_1=0.124, wR_2=0.103 for all 3068 independent reflections].

Crystal data for $C_{11}H_{19}NO$ **3b**: monoclinic, space group $P2_1$, a=11.082(3), b=7.411(4), c=12.871(4) Å, β=93.41(3)°, V=1055.2(7) Å^3, Z=4, D_{calcd}=1.141 g cm^{-3}, T=293(2) K, R_1=0.040, wR_2=0.100 for 1234 reflections with $I \geq 2\sigma(I)$ [R_1=0.110, wR_2=0.123 for all 2028 independent reflections].

Crystal data for $C_{11}H_{19}NS$ **3d**: orthorhombic, space group $P2_12_12_1$, a=7.318(2), b=8.996(2), c=16.160(3) Å, V=1063.9(4) Å^3, Z=4, D_{calcd}=1.232 g cm^{-3}, T=293(2) K, R_1=0.057, wR_2=0.128 for 1755 reflections with $I \geq 2\sigma(I)$ [R_1=0.061, wR_2=0.131 for all 1882 independent reflections].

Crystal data for $C_{10}H_{17}NO$ **4a**: orthorhombic, space group $P2_12_12_1$, a=8.093(13), b=10.447(9), c=21.928(30) Å, V=1854.0(40) Å^3, Z=8, D_{calcd}=1.198 g cm^{-3}, T=293(2) K, R_1=0.062, wR_2=0.130 for 1402 reflections with $I \geq 2\sigma(I)$ [R_1=0.114, wR_2=0.160 for all 2221 independent reflections].

Crystal data for $C_{11}H_{19}NO$ **4b**: tetragonal, space group $P4_1$, a=12.162(2), c=7.235(1) Å, V=1070.2(3) Å^3, Z=4, D_{calcd}=1.125 g cm^{-3}, T=293(2) K, R_1=0.040, wR_2=0.099 for 556 reflections with $I \geq 2\sigma(I)$ [R_1=0.123, wR_2=0.156 for all 922 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.

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