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Stereochemistry and chiroptical spectra of 3-azabicyclo[3.1.0]hexan-2-ones and thiones

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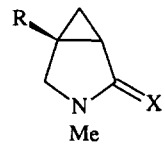
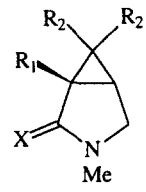
Abstract: Several optically active substituted 3-azabicyclo[3.1.0]hexan-2-ones and their thiocarbonyl analogues have been synthesized, and their circular dichroism spectra studied. The crystal structure of thiolactam **1a** showed that the bicyclic skeleton of the title compounds assumes a sofa-like geometry. It is postulated that the cyclopropyl moiety and amide or thioamide group constitute an inherently chiral chromophore, helicity of which determines the Cotton effect sign corresponding to the n–π* electronic transition. The weak π–π* Cotton effect of thiolactams shows opposite sign to that observed for the lowest energy excitation. © 1997 Elsevier Science Ltd

The chiroptical properties of small amide molecules have been intensively studied in recent years in order to establish general rules relating the CD sign to the absolute configuration and conformation.[1] Conformationally restricted lactam molecules with bicyclic skeletons are particularly well suited model compounds for this purpose. In relation to our previous investigations on the optical activity of cyclopropane-fused heterocyclic systems,[2,3] it seemed of interest to examine the CD of lactams based on the 3-azabicyclo[3.1.0]hexane skeleton.





1a R = H, X = O
1b R = H, X = S
2a R = Ph, X = O
2b R = Ph, X = S

3a R_1 = H, R_2 = Me, X = O
3b R_1 = H, R_2 = Me, X = S
4a R_1 = Ph, R_2 = H, X = O
4b R_1 = Ph, R_2 = H, X = S

These compounds being constrained analogues of δ-lactams attract considerable attention as intermediates in the synthesis of biologically important 2,3-methanoamino acids.[4] In contrast to lactams much less is known on the chiroptical spectra of thiolactams.[5] Two lowest energy transitions of the amide and thioamide chromophores are generally thought to be very similar in nature. However, in the case of thioamides the well separated n–π* and π–π* absorption bands occur at much lower energies than those of the amide chromophore.[6] In this paper we report the synthesis and the CD spectra of lactams **1a–4a** and their thiocarbonyl analogues **1b–4b**.

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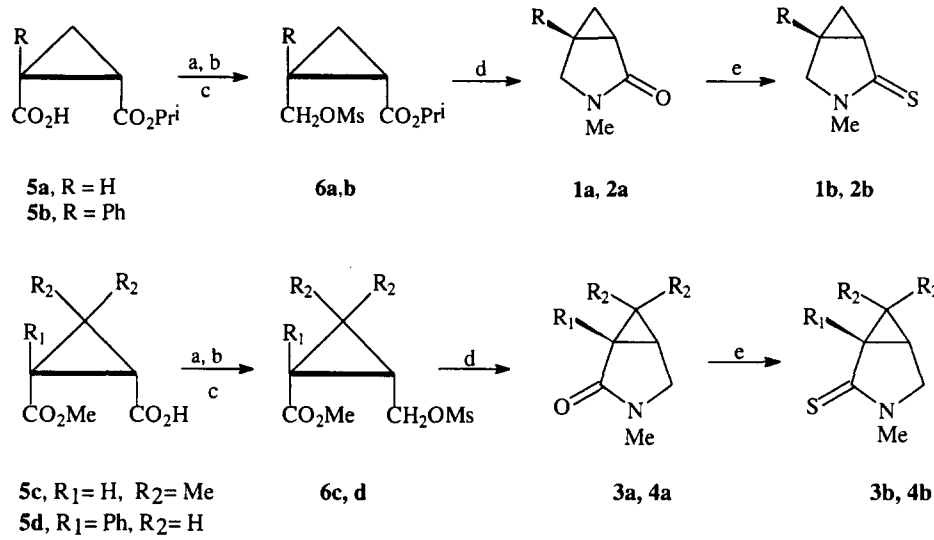
Results and discussion

The synthesis of the lactams **1a–4a** was straightforward and is summarized in Scheme 1. The optically active half-esters **5a–d** of the known absolute configuration, used as substrates, were described previously.[3] Thionation of compounds **1a–4a** with Lawesson's reagent[7] afforded thiolactams **1b–4b**.



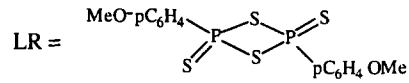
5a, R = H
5b, R = Ph

6a,b **1a, 2a** **1b, 2b**

5c, R_1 = H, R_2 = Me
5d, R_1 = Ph, R_2 = H

6c, d **3a, 4a** **3b, 4b**

a) $(COCl)_2$; b) $NaBH_4$, THF; c) MsCl, NEt_3; d) $MeNH_2$, EtOH, reflux 8h; e) LR, PhMe, reflux 1h



Scheme 1.

The 3-azabicyclo[3.1.0]hexane system favours a boat-like conformation as indicated by *ab initio* calculations and X-ray structural data.[8] However, the sp^2 hybridized atoms introduced into the five-membered ring part of the system are expected to cause its flattening and result in a sofa-like geometry of the bicyclic skeleton.[2a,3] The X-ray crystallographic analysis of a single crystal of thiolactam **1b** (Figure 1) confirmed this supposition and revealed that the dihedral angle between the three- and five-membered ring planes is of 109.1°. A slight deviation of the five-membered ring from planarity[9] is probably due to crystal packing forces.

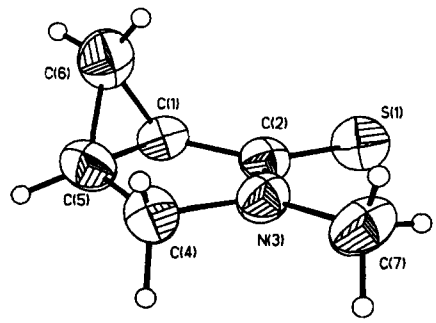


Figure 1. ORTEP draving of the crystal structure of **1b**. Thermal ellipsoids are drawn at the 50% probability level for heavy atoms.

Table 1. CD Data of lactams **1a–4a** and thiolactams **1b–4b**

Compd	Solv.[a]	λ, nm(10^{-3}[Θ])[b]	Compd	Solv.[a]	λ, nm(10^{-3}[Θ])[b]
1a	C	223(-9.3)	**1b**	C	357(-16.6), 270(21.3), 225(-28.4)
	M	210(-12.5)		M	325(-12.5), 267(11.5)
2a	C	231(-44.8), 262(-0.33)	**2b**	C	358(-26.2), 274(11.0), 237(-19.0)
	M	224(-28.2), 262(-0.33)		M	327(-21.3), 270(14.0), 230(61.9)
3a	C	222(11.8)	**3b**	C	358(14.6), 273(-10.2), 208(30.4)
	M	210(39.6)		M	325(11.1), 267(-17.2), 225(42.9)
4a	C	220(16.7), 266(0.38)	**4b**	C	361(9.9), 270(-8.6), 220(-30.2)
	M	216(17.7), 262(0.28)		M	336(5.7), 273(9.1), 225(-48.2)

[a] C - cyclohexane, M - methanol. [b] Molar ellipticity in deg cm^2 $dmol^{-1}$.

The CD spectra of the lactams **1a–4a** (Table 1) show strong Cotton effect (CE) near 220 nm, which is slightly red shifted upon changing the solvent from methanol to cyclohexane. It unequivocally should be assigned to the n–π* electronic transition of the amide chromophore.[10] The compounds **2a** and **4a** exhibit an additional weak and highly structured CD band at 260 nm, which is associated with the ^1L_b excitation of the phenyl group. In the case of the thioamide chromophore there are three low-lying excited states accessible by absorption in the near UV region. A weak absorption occurring near 360 and a strong one centered at 270 nm are well characterized and can be attributed to the forbidden n–π* and the allowed π–π* electronic transition, respectively.[6] A prominent blue-shift (30 nm) of the first band and a weak hypsochromic shift (ca. 3 nm) of the second one observed in going from cyclohexane to methanol are consistent with these assignments. A nature of the third band, centered at 220 nm, is less clear. It is probably associated with the σ_{C-S}-π* excitation.[5] Three well resolved CEs found in the CD spectra of thiolactams **1b–4b** correspond nicely with the above absorption maxima (Figure 2). The long-wavelength CD bands of the lactams **1a–4a** and their thiocarbonyl analogues **1b–4b** are characterized by the same sign and unusually strong magnitude of the CEs, which confirms a close analogy of the corresponding electronic transitions. Moreover, the chiroptical properties of the title compounds are strikingly similar to those of the related cyclopropyl lactones and thionolactones, recently reported by us. They show not only the same sign but also the magnitude of the n–π* CEs. This is apparently due to similarities between molecular geometries of the 3-aza- and 3-oxabicyclo[3.1.0]hexan-2-one systems as well as the nature of their lowest energy transitions. The formation of an inherently chiral chromophore by the carbonyl or thiocarbonyl group 'conjugated' with the cyclopropyl moiety,[11] analogously as it occurs in α,β-cyclopropyl ketones,[12] and the aforementioned lactones and thionolactones,[3] seems to be a reason of the observed extremely strong n–π* CEs. The contribution of this chromophore (chiral first sphere according to Snatzke's theory of spheres[13]) to the CE is much stronger than that made by dissymmetrically placed substituents (chiral third sphere) and determines the n–π* CE sign. It can be predicted using the helicity rule shown on Scheme 2 in agreement with the experimental results.

The π–π* CE sign of thiolactams **1b–4b** is opposite to that observed for the lowest energy transition as required by the sum rule.[10b] It can be also used for stereochemical predictions, however, the strong absorption in this region and the small value of the dissymmetry factor ($g=\Delta\epsilon/\epsilon$ is of 0.001) makes them slightly more difficult. On the contrary, the CD band near 220 nm, though much stronger than the former one, does not show simple correlation with the molecular geometry.

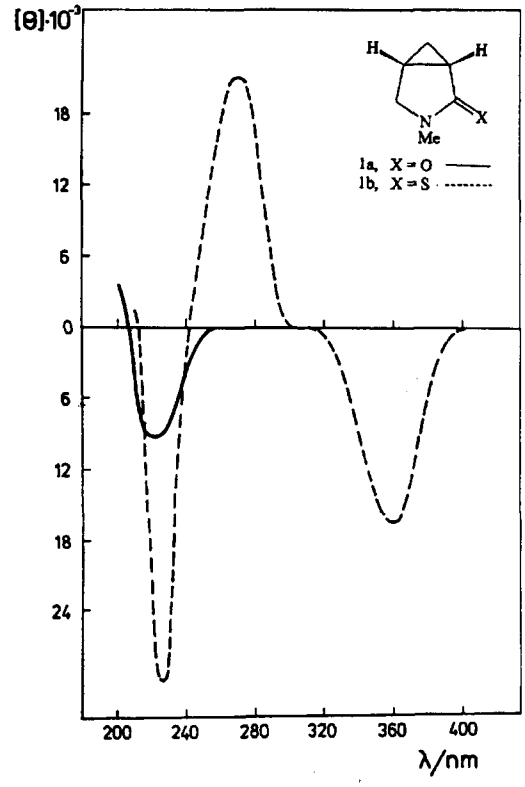
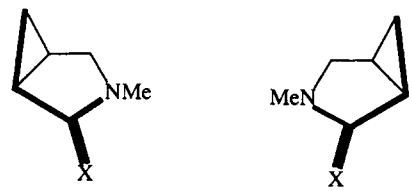


Figure 2. CD spectra of **1a** and **1b**.



(-) (+)

X = O , S

Scheme 2.

Experimental

CD spectra were recorded on a JASCO J-20 spectropolarimeter. 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 operating at 300 and 50 MHz, respectively. IR absorptions were taken with a Bruker IFS66 spectrometer. Specific rotations were measured on a Rudolph Autopol II digital polarimeter.

*(1S,5R)-3-Methyl-3-azabicyclo[3.1.0]hexan-2-one (**1a**)*

Oxalyl chloride (5.0 ml) was added to a solution of (1*R*,2*S*)-2-(1-methylethoxycarbonyl)-1-cyclopropanecarboxylic acid[3] **5a** (4.47 g, 26 mmol) in benzene (5 ml). After vigorous reaction ceased (ca. 1 hr) the solvents were evaporated and the resulted acid chloride was taken into THF (20 ml) and

powdered $NaBH_4$ (2.0 g) was added with stirring. After cooling the reaction mixture to 0°C, 10 ml of water was added dropwise with stirring. The stirring was continued for 0.5 h and the reaction mixture was extracted with three portions of 30 ml AcOEt. The combined extracts were dried (Na_2SO_4) and the solvent was evaporated in vacuo. The resulting syrup (4.2 g) was dissolved in AcOEt (30 ml) and triethylamine (8.0 ml) was added. After cooling the mixture to 0°C methanesulphonyl chloride (3.6 ml) in benzene (20 ml) was dropped in with stirring and cooling. After standing for 3 hr at 0°C the reaction mixture was washed with water, dried ($MgSO_4$) and evaporated to dryness. The residue was dissolved in 30% ethanolic methylamine solution (10 ml) and refluxed for 8 hr. Then the solvents were removed in vacuo and the residue was taken to AcOEt (30 ml), washed with water, dried ($MgSO_4$), and after evaporation of the solvent the residue was chromatographed on silica gel (elution with benzene–AcOEt, 1:1) to obtain 1.51 g (51%) of the product as an oil; $[\alpha]^{21}_D$ −55.6 (*c* 2.75, $CHCl_3$) {lit.[4a] enantiomer $[\alpha]^{25}_D$ +59.9 (*c* 2.95, $CHCl_3$)}; IR (film) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.49 (dd, *J*=5.7 and 10.3 Hz, 1 H), 3.25 (dd, *J*=1.8 and 10.3 Hz, 1 H), 2.71 (s, 3 H), 1.85 (m, 2 H), 1.06 (dt, *J*=3.3 and 8.0 Hz, 1 H), 0.57 (dt, *J*=3.3 and 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 174.7, 51.0, 28.8, 21.4, 19.8, 12.4, 11.4.

*(1S,5S)-3-Methyl-5-phenyl-3-azabicyclo[3.1.0]hexan-2-one (**2a**)*

The lactam **2a** was obtained from (1R,2S)-2-(1-methylethoxycarbonyl)-1-phenyl-1-cyclopropanecarboxylic acid[3] **5b** in a manner similar to that of compound **1a** and had m.p. 51–52°C (Et_2O–hexane); $[\alpha]^{22}_D$ +87 (*c* 2, MeOH); IR (KBr) 1673 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36–7.20 (complex m, 5 H), 3.69 (d, *J*=10.3 Hz, 1 H), 3.62 (dd, J=1.7 and 10.3 Hz, 1 H), 2.82 (s, 3 H), 2.21 (ddd, *J*=1.7, 3.5 and 8.8 Hz, 1 H), 1.50 (dd, *J*=4.5 and 8.8 Hz, 1 H), 1.13 (dd, J=3.5 and 4.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 174.4, 139.5, 128.6, 127.2, 127.0, 56.3, 29.2, 27.7, 20.6.

Anal. Calcd. for $C_{12}H_{13}NO$ (187): C, 76.98; H, 7.00, N, 7.48. Found: C, 76.78; H, 6.94; N, 7.53.

*(1S,5R)-3,6,6-Trimethyl-3-azabicyclo[3.1.0]hexan-2-one (**3a**)*

The lactam **3a** was obtained from (1*R*,2*S*)-2-(methoxycarbonyl)-3,3-dimethyl-1-cyclopropanecarboxylic acid[3] **5c**, in a manner similar to that of compound **1a** as an oil and had $[\alpha]^{21}_D$ +80.2 (*c* 4, C_6H_6); IR (film) 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.50 (dd, *J*=6.6 and 10.9 Hz, 1 H), 4.10 (dq, *J*=0.9 and 10.9 Hz, 1 H), 2.72 (s, 3 H), 1.77(dd, *J*=1.9 and 6.7 Hz, 1 H), 1.57 (td, *J*=0.9 and 6.6 Hz, 1 H), 1.09 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.8, 48.2, 33.1, 28.5, 25.6, 23.9, 21.5, 13.7.

Anal. Calcd for $C_8H_{13}NO$ (139): C, 69.03; H, 9.41; N, 10.06. Found: C, 68.95; H, 9.39; N, 9.82.

*(1R,5S)-3-Methyl-1-phenyl-3-azabicyclo[3.1.0]hexan-2-one (**4a**)*

The lactam **4a** was obtained from (1*S*,2*R*)-2-(methoxycarbonyl)-2-phenyl-1-cyclopropanecarboxylic acid[3] **5d**, in a manner similar to that of compound **1a** as an oil and had $[\alpha]^{22}_D$ +131.7 (*c* 1.7, C_6H_6); IR (film) 1682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.23 (complex m, 5 H), 3.65 (dd, *J*=5.7 and 10.3 Hz, 1 H), 3.32 (d, *J*=10.3 Hz, 1 H), 2.83 (s, 3 H), 2.14 (m, 1 H), 1.50 (dd, *J*=4.6 and 7.8 Hz, 1 H), 1.06 (t, *J*=4.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 174.1, 136.5, 128.3, 128.2, 126.8, 50.1, 33.8, 29.5, 20.1, 20.0.

Anal. Calcd for $C_{12}H_{13}NO$ (187): C, 76.98; H, 7.00, N, 7.48. Found: C, 76.71; H, 7.03; N, 7.31.

*(1S,5R)-3-Methyl-3-azabicyclo[3.1.0]hexan-2-thione (**1b**)*

The lactam **1a** (1.02 g, 9 mmol) and Lawesson's reagent (2.22 g, 5.5 mmol) were refluxed in toluene (6 ml) for 2hr. After removal of toluene the residue was chromatographed on silica-gel (elution with benzene–hexane, 2:1) to obtain 0.65 g (56%) of the product; m.p. 58–59°C (toluene–hexane); $[\alpha]^{20}_D$ −169 (*c* 2, C_6H_6); IR (KBr) 1519, 1306, 1112 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.88 (dd, *J*=6.1 and 12.1 Hz, 1 H), 3.62 (dd, *J*=1.9 and 12.1 Hz, 1 H), 3.13 (s, 3 H), 2.61 (m, 1 H), 1.91 (m, 1 H), 1.25 (dt, *J*=5.0 and 8.1 Hz, 1 H), 0.55 (dt, *J*=3.0 and 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 201.9, 59.2, 34.6, 33.8, 15.7, 14.4; UV (cyclohexane:dioxane, 9:1) λ_{max} 358 (e 60), 270 (14800) and 207 nm (6700); UV (MeOH) λ_{max} 320 (e 90) and 267 nm (15900).

Anal. Calcd. for C_6H_9NS (127): C, 56.68; H, 7.13; N, 11.02; S, 25.17. Found: C, 56.85; H, 7.12; N, 10.95; S, 25.14.

(1S,5S)-3-Methyl-5-phenyl-3-azabicyclo[3.1.0]hexan-2-thione (2b)

The thiolactam **2b** was obtained from **2a** in a manner similar to that of compound **1b** and had m.p. 79–80°C (toluene–hexane); $[\alpha]^{20}_D$ −108 (*c* 2, C_6H_6); IR (KBr) 1520, 1324, 1123 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.20 (complex m, 5 H), 4.08 (d, *J*=12.2 Hz, 1 H), 3.97 (dd, *J*=2.1 and 12.2 Hz, 1 H), 3.22 (s, 3 H), 2.88 (ddd, *J*=2.2, 3.4 and 8.8 Hz, 1 H), 1.70 (dd, *J*=4.8 and 8.8 Hz, 1 H), 1.12 (dd, *J*=3.4 and 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 201.7, 138.6, 128.8, 127.4, 127.3, 63.9, 41.0, 34.8, 30.6, 23.5; UV (cyclohexane:dioxane, 9:1) λ_{max} 355 (e 134) and 271 nm (20000); UV (MeOH) λ_{max} 323 (e 177) and 268 nm (23800).

Anal. Calcd. for $C_{12}H_{13}NS$ (190): C, 70.92; H, 6.45; N, 6.89; S, 15.74. Found: C, 71.20; H, 6.42; N 6.76, S; 16.73.

(1S,5R)-3,6,6-Trimethyl-3-azabicyclo[3.1.0]hexan-2-thione (3b)

The thiolactam **3b** was obtained from **3a** in a manner similar to that of compound **1b** and had m.p. 46–47°C (hexane); $[\alpha]^{20}_D$ +236.9 (*c* 1.6, C_6H_6); IR (KBr) 1516, 1327, 1108 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87 (dd, *J*=6.8 and 12.8 Hz, 1 H), 3.43 (d, *J*=12.8 Hz, 1 H), 3.13 (s, 3 H), 2.50 (dd, *J*=2.4 and 6.3 Hz, 1 H), 1.65 (td, *J*=1.2 and 6.3 Hz, 1 H), 1.15 (s, 3 H), 0.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 199.0, 55.9, 46.2, 34.0, 25.8, 25.3, 23.3, 12.6; UV (cyclohexane:dioxane, 9:1) λ_{max} 351 (e 71) and 271 nm (18600); UV (MeOH) λ_{max} 315 (e 114) and 277 nm (24500).

Anal. Calcd. for $C_8H_{13}NS$ (155): C, 61.39; H, 8.44; N, 9.03; S, 20.62. Found: C, 61.38; H, 8.48; N, 8.89; S, 20.54.

(1R,5S)-3-Methyl-1-phenyl-3-azabicyclo[3.1,0]hexan-2-thione (4b)

The thiolactam **4b** was obtained from **4a** in a manner similar to that of compound **1b** and had m.p. 75°C (toluene–hexane); $[\alpha]^{20}_D$ +133 (*c* 2, C_6H_6); IR (KBr) 1520, 1295, 1132, 1114 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41–7.26 (complex m, 5 H), 4.07 (dd, *J*=5.8 and 12.2 Hz, 1 H), 3.69 (d, *J*=12.2 Hz, 1 H), 3.23 (s, 3 H), 2.17 (m, 1 H), 1.72 (dd, *J*=4.8 and 7.8 Hz, 1 H), 0.96 (t, *J*=4.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 203.1, 137.7, 130.2, 127.9, 127.3, 58.1, 46.5, 35.2 22.0, 20.8; UV (cyclohexane:dioxane, 9:1) λ_{max} 354 (e 42) and 274 nm (15400).

Anal. Calcd. for $C_{12}H_{13}NS$ (190): C, 70.92; H, 6.45; N, 6.89; S, 15.74. Found: C, 71.14; H, 6.43; N, 6.78 S; 15.71.

X-Ray crystal structure analysis[14]

Diffraction data were obtained on a Kuma KM-4 diffractometer with graphite monochromated MoKα radiation for a crystal of **1b** with dimensions 0.7×0.6×0.5 mm. The structure was solved by direct methods with the program SHELXS-86.[15] Full matrix least-squares refinement was carried out with SHELXL-93.[16] Crystal data for C_6H_9NS **1b**: orthorhombic, space group $P2_12_12_1$, *a*=5.357(1) Å, b=5.538(1) Å, *c*=22.159(5) Å, *V*=657.4(2) $Å^3$, Z=4, D_{calcd}=1.285 g cm^{-3}, l(MoKα)=0.71073 Å, *T*=293 K, R_1=0.030, wR_2=0.079 for 1304 independent reflections of which 1178 had $I>2\sigma(I)$.

Acknowledgements

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14. (a) The atomic coordinates are available on request from the Director of the Cambridge Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. b) Supplementary data available: anisotropic displacement parameters, H-atom coordinates, bond lengths and angles, lists of structure factors. See Notice to Authors, *Tetrahedron* **40** (2) ii (1984).
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