Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Fair, 1990). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*97.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Chehade, C. C., Dias, R. L. A., Berlinck, R. G. S., Ferreira, A. G., Costa, L. V., Rangel, M., Malpezzi, E. L. A., Freitas, J. C. & Hajdu, E. (1997). *J. Nat. Prod.* **60**, 729–731.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Mitchell, S. S., Whitehill, A. B., Trapido-Rosenthal, H. G. & Ireland, C. M. (1997). *J. Nat. Prod.* **60**, 727–728.
Rasmussen, H. & Sletten, E. (1973). *Acta Chem. Scand.* **27**, 2757–2768.
Rosen, L. S. & Hybl, A. (1971). *Acta Cryst.* B27, 952–960.
Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sletten, J. & Jensen, L. H. (1969). *Acta Cryst.* B25, 1608–1614.

(+)-(2*S*,7*R*,9*R*,10*S*)-2-Ethenyl-4,4,7-trimethyl-3-(toluene-4-sulfonyl)-3,4,4a,5,6,7,8,8a-octahydro-2*H*-1,3-benzoxazine

Fernande D. Rochon and Livain Breau

Département de Chimie, Université du Québec à Montréal, CP 8888, Succ. Centre-Ville, Montréal, Québec, Canada H3C 3P8. E-mail: rochon.fernande@uqam.ca

*(Received 17 December 1998; accepted 17 May 1999)*

Abstract

The title compound, $C_{20}H_{29}NO_3S$, was studied in order to determine its absolute configuration, which could not

be determined unambiguously by NMR techniques. The results have shown a boat conformation for the oxazine moiety, with *S* stereochemistry at the stereocentre bearing the alkene function.

Comment

As part of a study aimed at the development of methods for the asymmetric synthesis of 2-isoxazolines, we have been involved in using conformationally rigid *trans*-decaline systems. To this end, we have prepared the title compound, (2), from the condensation of acrolein diethylacetal and (−)-8-tosylaminomenthol, (1), obtained from pulegone (He & Eliel, 1987).
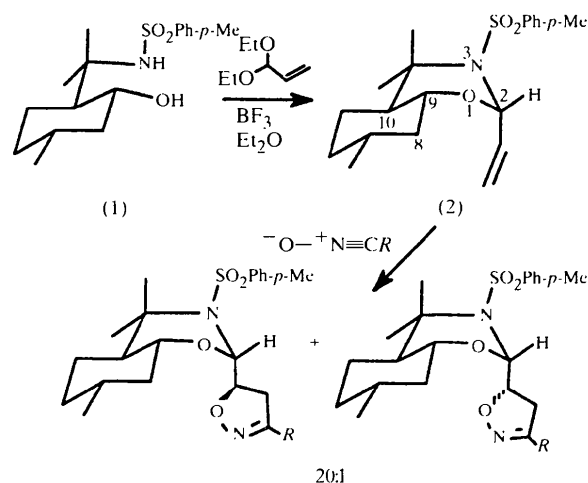
Of some significance was the high level of asymmetric induction observed for the cycloaddition of this compound with nitrile oxides (Lacoste *et al.*, 1998). This finding heightened our interest in understanding the stereochemical bias which leads to olefin facial discrimination. We have carried out extensive NMR experiments but some of the evidence obtained from NOE (nuclear Overhauser effect) experiments was weak. The results were nonetheless inconsistent with the anticipated all-chair *trans* benzoxazine ring system. Also, our NOE results supported a *cis*, but distant, relationship between atoms H9 and H2 and, surprisingly, a possible spatial proximity between the alkene function and protons H10 and $H8_{ax}$. These results point to a half-chair or a boat conformation for the oxazine ring. Since there were striking structural differences between the *N*-benzyl derivative (Soucy *et al.*, 1998), and compound (2), we felt that the absolute configuration required confirmation by X-ray diffraction analysis.

The crystal structure of (2) belongs to the chiral $P2_12_12_1$ space group. A labelled diagram of the molecule is shown in Fig. 1 and selected bond distances and angles are listed in Table 1.

The crystallographic results have shown a boat conformation for the oxazine moiety, with *S* stereochemistry at the C2 stereocentre bearing the alkene function,

while the cyclohexane ring has the normal chair conformation. The boat conformation of the oxazine ring is quite unusual (Boulton, 1996), since many substituents are in eclipsed positions. These crystallographic results are in agreement with the spatial arrangements observed in solution. The strong NOE effect observed in NMR between H10 and the alkene proton (H1') can be related to the boat conformation of the oxazine ring. Due to the free rotation in solution around the C2—C1' bond, H10 and H1' are in close proximity. An S configuration was determined for C10, while R configurations were found for C7 and C9. The environment around atom N3 is close to a trigonal plane. The best plane was calculated
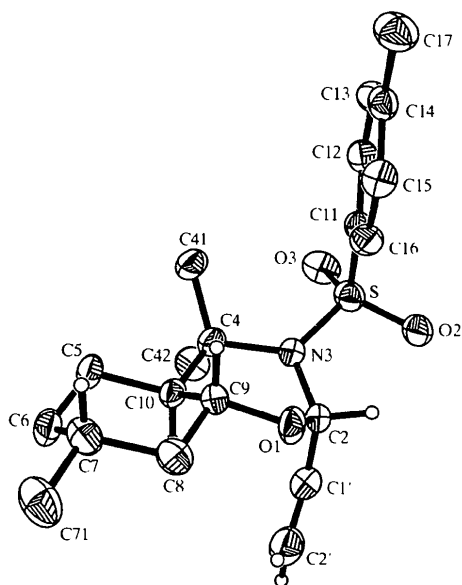

Fig. 1. The structure of (2) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and selected H atoms are shown as spheres of arbitrary radius.

through the three atoms S, C4 and C2, with atom N3 located 0.018 (2) Å from this plane. This geometry is quite surprising, since the N-tosyl group should be located on a pseudopyramidal site (Boulton, 1996). However, in the literature both stereochemistries have been reported, although most authors have not discussed these results (Bernardi et al., 1988; Manzoni et al., 1992). For example, Burgess et al. (1990) have reported two crystal structures of 1,3-oxazines with chair conformations; in one case the N-tosyl group is planar, while in the second it is pseudoaxial. In the present structure, where the oxazine ring has a boat conformation, steric interactions are surely minimized in this stereochemistry. The conformation of (2) observed by NMR in solution correlates well with the results of the crystal structure determination.

The bond distances and angles around the S atom seem normal. The O=S=O angle [119.80 (9)°] is,

as expected, larger than the other angles [average 107.29 (8)°] because of the double bonds. The other bond distances and angles are normal, except for the C1'=C2' double bond, which is shorter than expected [1.239 (3) Å], probably due to unresolved disorder. The internal angles of the C atoms in the oxazine ring vary between 106.2 (1) and 112.7 (1)°, while the internal O and N angles are slightly larger [116.7 (1) for O1 and 117.8 (1)° for N3]. The internal angles of the six-membered ring with the chair conformation are all normal [109.0 (2) to 112.6 (2)°]. The C2—C1'—C2' alkene angle is 126.7 (2)°.

Selected torsion angles, especially those of the oxazine moiety and the alkene substituent, are listed in Table 1, confirming the boat conformation of the oxazine ring. For example, C2—O1—C9—C10 = 18.6 (2) and C2—N3—C4—C10 = 18.3 (2)°. Furthermore, C9—O1—C2—N3 = 36.7 (2), N3—C4—C10—C9 = 36.9 (2), C4—N3—C2—O1 = -58.5 (2) and O1—C9—C10—C4 = -58.4 (2)°. The best plane was calculated through O1, N3, C4 and C9 of the oxazine ring [mean deviation 0.107 (1) Å]. The remaining two atoms are clearly on the same side of this plane, with deviations of C2 = 0.528 (2) and C10 = 0.577 (3) Å. A similar best plane was also calculated through C5, C7, C8 and C10 of the cyclohexyl ring [mean deviation 0.008 (1) Å]. The other two atoms are on opposite sides of the plane, with deviations of C6 = 0.660 (3) and C9 = -0.656 (3) Å. The dihedral angle between the two best planes is 6.7 (1)°.

These results have clearly shown the relative stereochemistry of all the chiral centres. In addition to the present application, this characterization of (2) should render it a useful compound in many other asymmetric processes.

Experimental

Compound (2) was prepared as described previously by Soucy et al. (1998) and single crystals were obtained by recrystallization from pentane.

Crystal data

$C_{20}H_{29}NO_3S$	Mo $K\alpha$ radiation
$M_r = 363.50$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 8.843 (3)$ Å	$\theta = 3.86–9.25°$
$b = 14.085 (5)$ Å	$\mu = 0.184$ mm^{-1}
$c = 15.638 (5)$ Å	$T = 293 (2)$ K
$V = 1947.9 (12)$ Å^3	Plate
$Z = 4$	$0.48 \times 0.31 \times 0.17$ mm
$D_x = 1.240$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Siemens P4 diffractometer	$\theta_{max} = 30°$
$2\theta/\omega$ scans	$h = 0 \rightarrow 12$
Absorption correction: none	$k = 0 \rightarrow 19$
3204 measured reflections	$l = 0 \rightarrow 22$
3204 independent reflections	3 standard reflections
1558 reflections with	every 97 reflections
$I > 2\sigma(I)$	intensity decay: 9.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.099$
$S = 1.046$
3204 reflections
274 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.012P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.04 (13)

Table 1. Selected geometric parameters (Å, °)

S—O3	1.4299 (14)	C4—C10	1.563 (3)
S—O2	1.4353 (14)	C5—C6	1.526 (3)
S—N3	1.6281 (15)	C5—C10	1.531 (2)
S—C11	1.768 (2)	C6—C7	1.525 (3)
O1—C2	1.395 (2)	C7—C8	1.540 (3)
O1—C9	1.446 (2)	C8—C9	1.526 (3)
N3—C2	1.471 (2)	C9—C10	1.514 (2)
N3—C4	1.518 (2)	C1'—C2'	1.239 (3)
C2—C1'	1.537 (3)		
O3—S—O2	119.80 (9)	N3—C4—C10	106.16 (13)
O3—S—N3	108.73 (8)	C6—C5—C10	111.1 (2)
O2—S—N3	107.02 (8)	C7—C6—C5	112.6 (2)
O3—S—C11	107.00 (9)	C6—C7—C8	109.0 (2)
O2—S—C11	106.32 (8)	C9—C8—C7	112.5 (2)
N3—S—C11	107.40 (8)	O1—C9—C10	112.23 (14)
C2—O1—C9	116.71 (13)	O1—C9—C8	106.43 (15)
C2—N3—C4	117.83 (13)	C10—C9—C8	111.97 (14)
C2—N3—S	118.94 (11)	C9—C10—C5	109.75 (15)
C4—N3—S	123.18 (12)	C9—C10—C4	112.73 (14)
O1—C2—N3	111.86 (15)	C5—C10—C4	112.51 (15)
O1—C2—C1'	116.1 (2)	C2'—C1'—C2	126.7 (2)
N3—C2—C1'	111.0 (2)		
C9—O1—C2—N3	36.7 (2)	C7—C8—C9—O1	-178.8 (1)
C9—O1—C2—C1'	-92.1 (2)	C7—C8—C9—C10	-55.8 (2)
C4—N3—C2—O1	-58.5 (2)	O1—C9—C10—C5	175.4 (2)
S—N3—C2—O1	119.2 (1)	C8—C9—C10—C5	55.7 (2)
C4—N3—C2—C1'	72.9 (2)	O1—C9—C10—C4	-58.4 (2)
S—N3—C2—C1'	-109.3 (2)	C8—C9—C10—C4	-178.0 (1)
C2—N3—C4—C10	18.3 (2)	C6—C5—C10—C9	-56.3 (2)
S—N3—C4—C10	-159.3 (1)	C6—C5—C10—C4	177.3 (2)
C10—C5—C6—C7	57.4 (2)	N3—C4—C10—C9	36.9 (2)
C5—C6—C7—C8	-54.8 (2)	N3—C4—C10—C5	161.7 (1)
C6—C7—C8—C9	53.7 (2)	O1—C2—C1'—C2'	-12.1 (3)
C2—O1—C9—C10	18.6 (2)	N3—C2—C1'—C2'	-141.3 (2)
C2—O1—C9—C8	141.4 (2)		

The H atoms of the terminal methyl groups were found in the difference Fourier map and refined normally with isotropic displacement parameters. The remaining H atoms were introduced at calculated positions and treated as riding, with C—H = 0.93–0.95 Å and displacement parameters equal to $1.2U_{eq}$ of the parent atom. An absorption correction based on the equations of the crystal faces did not improve the results (the R factors were higher). Therefore, it was not included in the calculations. The R factors of the other enantiomeric form were also slightly higher (0.054, 0.100).

References

Bernardi, A., Cardani, S., Pilati, T., Poli, G., Scolastico, C. & Villa, R. (1988). *J. Org. Chem.* **53**, 1600–1607.
Boulton, A. J. (1996). Editor. *Comprehensive Heterocyclic Chemistry* II, vol. 6, pp. 306–310. Editors-in-chief: A. R. Katritzky, C. W. Rees & E. F. V. Scriven. Oxford: Pergamon Press.
Burgess, K., Ohlmeyer, M. J. & Whitmire, K. H. (1990). *J. Org. Chem.* **55**, 1359–1361.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
He, X. C. & Eliel, E. L. (1987). *Tetrahedron*, **43**, 4979–4989.
Lacoste, J.-E., Soucy, C., Rochon, F. D. & Breau, L. (1998). *Tetrahedron Lett.* **39**, 9121–9124.
Manzoni, L., Pilati, T., Poli, G. & Scolastico, C. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1027–1029.
Sheldrick, G. M. (1995). *SHELXTL. Structure Determination Programs*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *XSCANS. X-ray Single Crystal Analysis Software*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Soucy, C., Lacoste, J.-E. & Breau, L. (1998). *Tetrahedron Lett.* **39**, 9117–9120.

Propane-1,3-diammonium diperchlorate

SALLY BROOKER* AND DUNCAN J. DE GEEST

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. E-mail: sbrooker@alkali.otago.ac.nz

Abstract

The structure of the title compound, $C_3H_{12}N_2^{2+}\cdot2ClO_4^-$, has been determined at 158 K. The extensive network of hydrogen bonds, including two four-centre bonds, is described.

Comment

In the course of our studies of complexes of *L1*, colourless needles of the title compound, (I), were formed