C3	0.3192 (2)	0.0400 (5)	0.2710 (6)	0.044 (3)
C4	0.3701 (2)	0.0462 (4)	0.4183 (6)	0.039 (2)
C5	0.3813 (2)	−0.0346 (5)	0.5921 (7)	0.049 (3)
C6	0.4274 (3)	0.0222 (6)	0.7284 (6)	0.051 (3)
C7	0.4682 (3)	0.1633 (5)	0.7039 (6)	0.048 (3)
N7	0.5418 (2)	0.1597 (4)	0.5867 (5)	0.041 (2)
C8	0.6156 (3)	0.0866 (6)	0.6401 (7)	0.051 (3)
C9	0.6822 (3)	0.1389 (7)	0.5077 (8)	0.060 (3)
C10	0.6582 (3)	0.1219 (7)	0.2989 (7)	0.057 (3)
C11	0.5745 (3)	0.1846 (6)	0.2549 (7)	0.049 (3)
C12	0.5148 (2)	0.1231 (4)	0.3948 (6)	0.035 (2)
C13	0.4254 (2)	0.1701 (4)	0.3964 (6)	0.037 (2)
C14	0.4162 (3)	0.2583 (5)	0.5768 (7)	0.047 (3)

Table 2. *Selected geometric parameters* (Å, °)

O1—C2^i	1.381 (5)	C7—C14^i	1.530 (6)
O1—C13^i	1.441 (5)	N7—C8^i	1.451 (6)
C2—O2^i	1.205 (5)	N7—C12^i	1.462 (5)
C2—C3^i	1.452 (6)	C8—C9^i	1.522 (7)
C3—C4^i	1.333 (6)	C9—C10^i	1.528 (7)
C4—C5^i	1.453 (6)	C10—C11^i	1.534 (7)
C4—C13^i	1.495 (5)	C11—C12^i	1.509 (6)
C5—C6^i	1.337 (6)	C12—C13^i	1.541 (5)
C6—C7^i	1.507 (7)	C13—C14^i	1.526 (6)
C7—N7^i	1.467 (5)		
C2^i—O1—C13^i	108.8 (3)	C8^i—N7—C12^i	112.4 (3)
O1^i—C2—O2^i	119.6 (4)	N7^i—C8—C9^i	107.0 (4)
O1^i—C2—C3^i	108.9 (3)	C8^i—C9—C10^i	111.4 (4)
O2^i—C2—C3^i	131.5 (4)	C9^i—C10—C11^i	112.7 (4)
C2^i—C3—C4^i	108.2 (4)	C10^i—C11—C12^i	107.8 (4)
C3^i—C4—C5^i	135.1 (4)	N7^i—C12—C11^i	108.1 (3)
C3^i—C4—C13^i	109.8 (4)	N7^i—C12—C13^i	102.5 (3)
C5^i—C4—C13^i	115.1 (3)	C11^i—C12—C13^i	121.2 (4)
C4^i—C5—C6^i	117.5 (4)	O1^i—C13—C4^i	104.2 (3)
C5^i—C6—C7^i	122.0 (4)	O1^i—C13—C12^i	114.6 (3)
C6^i—C7—N7^i	114.4 (4)	O1^i—C13—C14^i	115.4 (3)
C6^i—C7—C14^i	109.8 (4)	C4^i—C13—C12^i	110.9 (3)
N7^i—C7—C14^i	98.6 (3)	C4^i—C13—C14^i	106.5 (3)
C7^i—N7—C8^i	124.1 (3)	C12^i—C13—C14^i	105.0 (3)
C7^i—N7—C12^i	105.7 (3)	C7^i—C14—C13^i	96.1 (3)

Symmetry code: (i) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$.

Table 3. *Cremer–Pople puckering parameters in the oligocyclic ring system of securinine*

The first line of data represents the free base and the second the hydrobromide dihydrate (Imado, Shiro & Horii, 1965). Ring *A* is the piperidine ring, ring *B* is N7, C7, C14, C13 and C12, and ring *C* is C7, C6, C5, C4, C13 and C14. C = chair, B = boat, H = half-chair, T = twist, E = envelope.

Ring	Size	Q, q_2 (Å)	Φ, ϕ_2 (°)	θ (°)	Type
A	6	0.598 (5)	156 (3)	171.4 (4)	C
		0.770	49	91.6	B
B	5	0.544 (4)	48.9 (4)		T⇌E
		0.513	59.9		T⇌E
C	6	0.675 (4)	105.9 (5)	129.3 (4)	E↔H
		0.600	112.5	132.1	E↔H

Data collection: Stoe software. Cell refinement: Stoe software. Data reduction: *Xtal ADDREF SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *Xtal CRYLSQ* (Hall, Flack & Stewart, 1992). Molecular graphics: *SCHAKAL88* (Keller, 1988). Software used to prepare material for publication: *Xtal BONDLA CIFIO* (Hall, Flack & Stewart, 1992).

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4,5-Dicyclohexyl-1,3,2-dioxathiolane 2-Oxide, C14H24O3S

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Abstract

The title compound, 4,5-dicyclohexyl-1,3,2-dioxathiolane 2-oxide (1), adopts a half-chair (envelope) conformation with the S=O bond taking up a pseudo-axial position. The cyclohexyl groups occupy *trans* positions.

Comment

The conformations of phenyl-1,3,2-dioxathiolane 2-oxides (five-membered cyclic sulfites) have been studied by several physical methods, including X-ray crystallography (Hellier & Motevalli, 1995), from which it is evident that the envelope conformation is adopted with a strong preference for the S=O bond to take up a pseudo-axial position. As a part of our extensive investigation of the structures of a wide variety of cyclic sulfites, we were interested in the

stereochemistry of a 1,3,2-dioxathiolane 2-oxide containing cyclohexyl groups, (1), prepared by an unusual preparative route.* This paper reports the structure of (1) as determined by X-ray crystallography. A *PLUTO* drawing (Spek, 1993) of the two independent molecules is shown in Fig. 1.

(1)
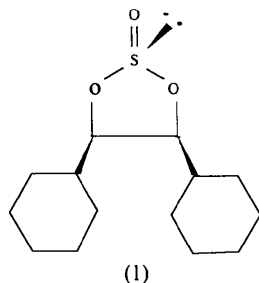
The X-ray structure determination shows that (1) is *trans,trans*-4,5-dicyclohexyl-1,3,2-dioxathiolane 2-oxide in an envelope conformation. The structural parameters of (1) may be compared directly with those of the related compound *trans,trans*-4,5-diphenyl-1,3,2-dioxathiolane 2-oxide (2) (Lowe, Jones & Salamone, 1984). Comparison of the two sets of data reveals very similar values of bond

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* Pinacols are the usual starting materials for the preparation of 1,3,2-dioxathiolane 2-oxides. Methyl- and phenyl-substituted pinacols are readily available or easily prepared (Hellier & Green, 1975). However, preparation of compounds with other substituents often demands unusual procedures. For example, crystals of (1), m.p. 343 K, were obtained through cyclization with thionyl chloride of 1,2-dicyclohexylethane-1,2-diol. The diol was prepared *via* a coupling reaction from cyclohexylcarboxaldehyde and a magnesium/titanium chloride reagent according to a reported procedure (Corey, Danheiser & Chandrasekran, 1976).

Fig. 1. View of the two independent molecules of (1) showing the atom-numbering scheme.

distances and bond angles for (1) and (2), indicating that the geometry of the ring is affected to the same extent by dicyclohexyl or diphenyl substitution. This is also confirmed by very simlar torsion angles around C4 and C5: 34.92° (average) for (1) and 35.46° for (2).

Experimental

Crystal data

$C_{14}H_{24}O_3S$	Mo $K\alpha$ radiation
$M_r = 272.39$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 11.0070\ (10)$ Å	$\theta = 13.5–14.5°$
$b = 19.100\ (3)$ Å	$\mu = 0.218$ mm^{-1}
$c = 14.976\ (2)$ Å	$T = 293\ (2)$ K
$\beta = 110.21\ (2)°$	Rhombic
$V = 2954.6\ (7)$ Å^3	$0.36 \times 0.32 \times 0.2$ mm
$Z = 8$	Transparent colourless
$D_x = 1.225$ Mg m^{-3}	
$D_m = 1.3$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer	$R_{int} = 0.0197$
	$\theta_{max} = 21.97°$
$2\theta/\omega$ scans	$h = -11 \rightarrow 10$
Absorption correction:	$k = -2 \rightarrow 20$
empirical	$l = -5 \rightarrow 15$
$T_{min} = 0.935,\ T_{max} = 0.980$	3 standard reflections
	frequency: 60 min
3857 measured reflections	intensity variation: none
3618 independent reflections	
2248 observed reflections	
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.0489$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.1153$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.242$	$\Delta\rho_{max} = 0.569$ e Å^{-3}
3618 reflections	$\Delta\rho_{min} = -0.506$ e Å^{-3}
335 parameters	Extinction correction: none
H atoms: calculated using *AFIX* in *SHELXL92* (Sheldrick, 1992)	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

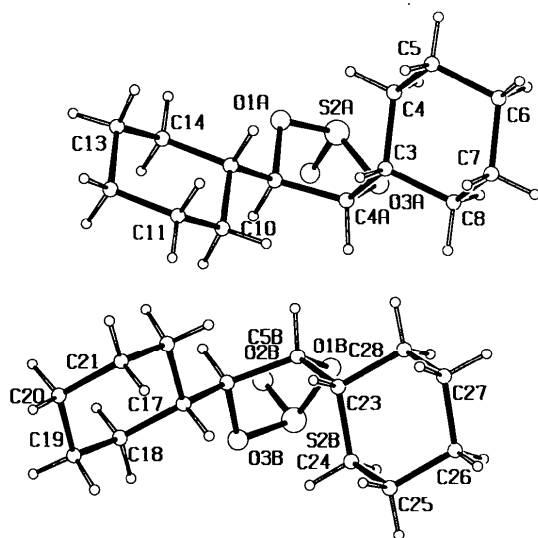Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S2A	0.02104 (9)	0.80353 (5)	0.34462 (7)	0.0711 (3)
O1A	0.0526 (2)	0.73091 (11)	0.40245 (15)	0.0565 (6)
O2A	0.0047 (3)	0.79019 (15)	0.2463 (2)	0.1017 (10)
O3A	0.1657 (2)	0.83337 (11)	0.39211 (15)	0.0643 (7)

C4A	0.2564 (3)	0.7835 (2)	0.4536 (2)	0.0477 (8)
C5A	0.1894 (3)	0.7132 (2)	0.4246 (2)	0.0495 (8)
C3	0.2943 (3)	0.8075 (2)	0.5561 (2)	0.0428 (8)
C4	0.1814 (3)	0.8179 (2)	0.5909 (2)	0.0509 (9)
C5	0.2265 (3)	0.8398 (2)	0.6948 (2)	0.0578 (9)
C6	0.3091 (3)	0.9050 (2)	0.7119 (3)	0.0691 (11)
C7	0.4212 (3)	0.8958 (2)	0.6772 (2)	0.0632 (10)
C8	0.3754 (3)	0.8739 (2)	0.5729 (2)	0.0544 (9)
C9	0.2267 (3)	0.6528 (2)	0.4937 (2)	0.0462 (8)
C10	0.3670 (3)	0.6326 (2)	0.5132 (2)	0.0605 (9)
C11	0.4076 (4)	0.5718 (2)	0.5812 (3)	0.0794 (12)
C12	0.3211 (4)	0.5089 (2)	0.5450 (3)	0.0897 (13)
C13	0.1808 (4)	0.5274 (2)	0.5243 (3)	0.0779 (12)
C14	0.1400 (3)	0.5894 (2)	0.4573 (2)	0.0627 (10)
S2B	0.18490 (11)	0.81074 (5)	0.93464 (7)	0.0729 (3)
O1B	0.1819 (2)	0.83606 (12)	1.03662 (15)	0.0653 (7)
O2B	0.0530 (3)	0.7934 (2)	0.8778 (2)	0.1016 (10)
O3B	0.2621 (2)	0.73947 (11)	0.97614 (14)	0.0580 (6)
C4B	0.2307 (3)	0.7164 (2)	1.0588 (2)	0.0485 (8)
C5B	0.2317 (3)	0.7842 (2)	1.1124 (2)	0.0513 (9)
C17	0.3188 (3)	0.6569 (2)	1.1082 (2)	0.0457 (8)
C18	0.3174 (3)	0.5984 (2)	1.0387 (2)	0.0556 (9)
C19	0.3988 (4)	0.5360 (2)	1.0883 (3)	0.0657 (10)
C20	0.3592 (4)	0.5089 (2)	1.1682 (3)	0.0735 (11)
C21	0.3595 (4)	0.5664 (2)	1.2376 (2)	0.0717 (11)
C22	0.2784 (3)	0.6286 (2)	1.1890 (2)	0.0605 (9)
C23	0.3592 (3)	0.8108 (2)	1.1835 (2)	0.0460 (8)
C24	0.4638 (3)	0.8256 (2)	1.1414 (2)	0.0549 (9)
C25	0.5884 (3)	0.8486 (2)	1.2176 (3)	0.0656 (10)
C26	0.5660 (4)	0.9124 (2)	1.2695 (3)	0.0699 (11)
C27	0.4620 (4)	0.8996 (2)	1.3108 (3)	0.0693 (11)
C28	0.3367 (3)	0.8755 (2)	1.2354 (2)	0.0614 (10)

Table 2. *Selected geometric parameters* (Å, °)

S2A—O2A	1.443 (3)	S2B—O2B	1.445 (3)
S2A—O3A	1.607 (2)	S2B—O3B	1.612 (2)
S2A—O1A	1.608 (2)	S2B—O1B	1.613 (2)
O1A—C5A	1.465 (4)	O1B—C5B	1.462 (4)
O3A—C4A	1.454 (4)	O3B—C4B	1.464 (3)
C4A—C5A	1.522 (4)	C4B—C5B	1.521 (4)
O2A—S2A—O3A	105.6 (2)	O2B—S2B—O3B	108.8 (2)
O2A—S2A—O1A	108.9 (2)	O2B—S2B—O1B	106.3 (2)
O3A—S2A—O1A	94.05 (11)	O3B—S2B—O1B	93.95 (11)
C5A—O1A—S2A	109.6 (2)	C5B—O1B—S2B	114.0 (2)
C4A—O3A—S2A	114.0 (2)	C4B—O3B—S2B	109.5 (2)
O3A—C4A—C5A	103.8 (2)	O3B—C4B—C5B	103.2 (2)
O1A—C5A—C4A	102.7 (2)	O1B—C5B—C4B	103.6 (2)
O2A—S2A—O1A—C5A	79.5 (2)	O2B—S2B—O1B—C5B	104.5 (2)
O3A—S2A—O1A—C5A	−28.6 (2)	O3B—S2B—O1B—C5B	−6.5 (2)
O2A—S2A—O3A—C4A	−105.7 (2)	O2B—S2B—O3B—C4B	−79.6 (2)
O1A—S2A—O3A—C4A	5.3 (2)	O1B—S2B—O3B—C4B	29.1 (2)
S2A—O3A—C4A—C5A	17.9 (3)	S2B—O3B—C4B—C5B	−41.7 (3)
S2A—O1A—C5A—C4A	41.6 (3)	S2B—O1B—C5B—C4B	−16.6 (3)
O3A—C4A—C5A—O1A	−35.3 (3)	O3B—C4B—C5B—O1B	34.6 (3)

Data collection and reduction and cell refinement used *CAD-4/PC* software (Enraf–Nonius, 1989). The structure was solved using *SHELXS*86 (Sheldrick, 1990), refinement was carried out using *SHELXL*92 (Sheldrick, 1992) and the molecular graphics were prepared using *PLUTON* (Spek, 1993). *SHELXL*93 (Sheldrick, 1993) was used to prepare material for publication.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5ar-p-Tolyl-6at,7t,8,9,10t,10at-hexahydro-11H,13H-7,10-methano[1,3]benzoxazino-[2,3-b][1,3]benzoxazin-13-one

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Abstract

The structure of the pentacyclic title compound, $C_{23}H_{23}NO_3$, was established by X-ray diffraction. The *exo* positions of the aryl group, indicated by the NMR data, were confirmed by the relevant torsion angles: C11—O10—C2—C19 = − 79.7 (3), C4—N3—C2—C19 = − 98.5 (3) and C13—N3—C2—C19 = 86.2 (4)°. The position of the aryl group is stabilized by a C24—H24···N3 interaction [H24···N3 2.480 (2), C24···N3 2.855 (4) Å, C24—H24···N3 98.7 (2)°]. The conformations of the benzoxazine rings I and II are twist-boat ($^1T_3$) and screw-boat ($^1S_6$), respectively.

Comment

Partially saturated condensed pentacyclic compounds have been synthesized by 4π cycloaddition, with pharmacological and stereochemical aims (Stájer, Frimpong-Manso, Bernáth & Sohár, 1991). The title compound (1a) was prepared from the