

tion received validation as central-hypotensive activity was observed for 4-[3-aryl(thio/sulfonyl)propyl] piperazines/piperidines (Rao, Srimal, Audry, Carpy & Saxena, 1991). The title compound is the most promising one of the series. Its molecular structure is comparable with that of 1-(3-methylphenyl)-4-(2- $\beta$ -quinolylethyl)piperazine (centhaquin) (Carpy & Saxena, 1991).

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## Structure and Absolute Configuration of (3*S*)-[(1*S*,2*R*,4*S*)-2-Acetoxy-4-methyl-1-cyclohexyl]-2,2-dichloro-3-methylcyclobutanone

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**Abstract.** C<sub>14</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>3</sub>, *M<sub>r</sub>* = 307.22, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 7.0329 (7), *b* = 9.983 (2), *c* = 22.644 (6) Å, *V* = 1589.8 (9) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.284 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 4.1 \text{ cm}^{-1}$ , *F*(000) = 648, *T* = 298 K, *R* = 0.0412 for 1533 observed reflections. The cyclobutanone ring is puckered with a dihedral angle between C(1)—C(2)—C(4) and C(2)—C(3)—C(4) of 22.0 (8)°. The carbonyl O atom is displaced from the C(1)—C(2)—C(4) plane to the *endo* side by 0.109 (5) Å. The absolute configuration of the molecule was ascertained both by chemical means and by a comparison of the *R<sub>g</sub>* values for the determined structure and its inverse.

**Experimental.** Crystals of the title compound were obtained from ethyl acetate at 277 K. The data collection and refinement parameters are summarized in Table 1.

The structure was solved using standard direct methods and difference Fourier techniques. In the final cycles of full-matrix least-squares refinement all non-H atoms were treated anisotropically. H atoms included, as fixed contributors, at positions found

from a difference synthesis, all with a common isotropic temperature factor that refined to *U* = 0.108 (4) Å<sup>2</sup>. Data were corrected for *L<sub>p</sub>* and absorption, max. and min. transmission factors 1.88, 0.76 (Walker & Stuart, 1983). Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for H atoms scattering factors were taken from Stewart, Davidson & Simpson (1965). Programs used: *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). Most of the calculations were performed on a VAX 6420 computer of the Instituto de Física e Química de São Carlos.

Atomic coordinates are listed in Table 2,\* bond lengths and bond angles are listed in Table 3. Fig. 1 is a projection of the molecule showing the atom labeling.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54419 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystallographic summary*

Data collection	
Unit-cell parameters*	
Number, range (°)	23, 9 < $\theta$ < 21
Diffractometer	Enraf-Nonius CAD-4, graphite monochromator
Mode	$\omega$ -2 $\theta$
Scan rate (° min <sup>-1</sup> )	2.8-10.0
$\theta$ range (°)	0-25
Range of $hkl$	-8 ≤ $h$ ≤ 8, 0 ≤ $k$ ≤ 11, 0 ≤ $l$ ≤ 26
Total reflections measured	2641
Unique reflections	2459
$R_{int}$	0.023
Standard reflection	0,0,18
Variation	None significant
Crystal disk shape	
Diameter (mm)	0.30
Thickness (mm)	0.20
Structure determination	
Reflections used [ $I > 3\sigma(I)$ ]	1533
No. of variables	174
Function minimized	$\sum w( F_o  -  F_c )^2$
$w$	$[\sigma^2(F_o) + 0.0003F_o^2]^{-1}$
$R, wR$	0.0412, 0.0449
Max. shift/e.s.d.	0.002
Max., min. density in final difference map (e Å <sup>-3</sup> )	0.25, -0.23
$S$	1.52
Secondary-extinction correction	$F_{corr} = F_o(1.0 - 10^{-4})\chi F_o^2/\sin\theta$
$\chi$	0.003

\* By least-squares refinement of the setting angles.

Table 2. *Final atomic coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>)*

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	$x$	$y$	$z$	$B_{eq}$
Cl(1)	-0.2772 (2)	-0.0217 (1)	-0.3046 (1)	7.91 (6)
Cl(2)	-0.5136 (3)	-0.2202 (2)	-0.2491 (1)	8.05 (6)
O(1)	-0.0427 (8)	-0.1997 (5)	-0.2099 (2)	11.7 (2)
O(2)	-0.5903 (4)	-0.1986 (3)	-0.3870 (1)	4.31 (9)
O(3)	-0.6046 (5)	-0.1050 (4)	-0.4763 (2)	7.8 (1)
C(1)	-0.135 (1)	-0.2489 (6)	-0.2491 (3)	8.5 (3)
C(2)	-0.2962 (8)	-0.1915 (5)	-0.2866 (2)	6.0 (2)
C(3)	-0.2456 (7)	-0.3004 (4)	-0.3344 (2)	5.0 (2)
C(4)	-0.1274 (8)	-0.3727 (6)	-0.2852 (3)	7.9 (2)
C(5)	-0.1113 (7)	-0.2404 (6)	-0.3801 (3)	7.1 (2)
C(6)	-0.738 (1)	-0.6298 (5)	-0.4824 (3)	9.3 (3)
C(7)	-0.6299 (6)	-0.0999 (5)	-0.4235 (2)	5.1 (2)
C(8)	-0.7149 (7)	0.0186 (5)	-0.3923 (2)	6.8 (2)
C(1')	-0.3993 (5)	-0.3874 (4)	-0.3619 (2)	4.0 (1)
C(2')	-0.5089 (6)	-0.3197 (4)	-0.4114 (2)	4.0 (1)
C(3')	-0.6646 (6)	-0.4094 (4)	-0.4352 (2)	5.0 (2)
C(4')	-0.5849 (7)	-0.5405 (5)	-0.4585 (2)	5.6 (2)
C(5')	-0.4724 (7)	-0.6092 (5)	-0.4103 (2)	5.7 (2)
C(6')	-0.3194 (6)	-0.5195 (5)	-0.3856 (2)	5.3 (2)

**Related literature.** The displacement of O(1) from the C(1)—C(2)—C(4) plane is 0.109 (5) Å and the O atom lies on the same side of the plane as C(3). Such *endo* deviations of O atoms in carbonyl groups have been observed in several cyclobutanones (Martin, Greuter, Rihs, Winkler & Bellus, 1981; Becker, Hohermuth & Rihs, 1982). Bellus & Ernst (1988) suggest that this *endo* deviation enables an optimal

Table 3. *Interatomic bond distances (Å) and angles (°)*

Cl(1)—C(2)	1.749 (5)	Cl(2)—C(2)	1.772 (6)
O(1)—C(1)	1.204 (8)	O(2)—C(7)	1.316 (5)
O(2)—C(2')	1.447 (5)	O(3)—C(7)	1.210 (6)
C(1)—C(2)	1.528 (8)	C(1)—C(4)	1.483 (8)
C(2)—C(3)	1.575 (7)	C(3)—C(4)	1.566 (7)
C(3)—C(5)	1.524 (7)	C(3)—C(1')	1.520 (6)
C(6)—C(4')	1.499 (8)	C(7)—C(8)	1.502 (7)
C(1')—C(2')	1.519 (5)	C(1')—C(6')	1.531 (6)
C(2')—C(3')	1.514 (6)	C(3')—C(4')	1.518 (6)
C(4')—C(5')	1.512 (7)	C(5')—C(6')	1.507 (7)
C(7)—O(2)—C(2')	118.0 (3)	O(1)—C(1)—C(2)	131.0 (6)
O(1)—C(1)—C(4)	136.6 (6)	C(2)—C(1)—C(4)	91.9 (5)
Cl(1)—C(2)—Cl(2)	109.5 (3)	Cl(1)—C(2)—C(1)	115.9 (4)
Cl(1)—C(2)—C(3)	119.5 (3)	Cl(2)—C(2)—C(1)	108.3 (4)
Cl(2)—C(2)—C(3)	114.4 (3)	C(1)—C(2)—C(3)	87.4 (4)
C(2)—C(3)—C(4)	87.1 (4)	C(2)—C(3)—C(5)	109.6 (4)
C(2)—C(3)—C(1')	121.0 (4)	C(4)—C(3)—C(5)	109.6 (4)
C(4)—C(3)—C(1')	113.9 (4)	C(5)—C(3)—C(1')	112.8 (4)
C(1)—C(4)—C(3)	89.4 (4)	O(2)—C(7)—O(3)	123.9 (4)
O(2)—C(7)—C(8)	112.2 (4)	O(3)—C(7)—C(8)	123.8 (4)
C(3)—C(1')—C(2')	114.1 (3)	C(3)—C(1')—C(6')	112.0 (3)
C(2')—C(1')—C(6')	108.1 (3)	O(2)—C(2')—C(1')	106.9 (3)
O(2)—C(2')—C(3')	110.1 (3)	C(1')—C(2')—C(3')	111.5 (3)
C(2')—C(3')—C(4')	111.5 (4)	C(6)—C(4')—C(3')	111.9 (4)
C(6)—C(4')—C(5')	111.5 (4)	C(3')—C(4')—C(5')	109.5 (4)
C(4')—C(5')—C(6')	111.8 (4)	C(1')—C(6')—C(5')	112.3 (4)

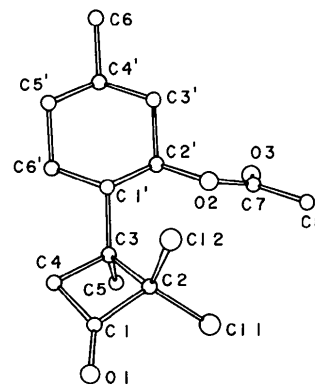


Fig. 1. Perspective view of the molecule showing the atom-numbering scheme.

$sp^2$  hybridization at C(1). A chirality test was performed by reversing all atomic coordinates and refining again to convergence. The  $R_g$  factor  $\{ = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \}$  increased from 0.0498 to 0.0530.

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## Structure of an Enantiomerically Pure Tetrahydropyranyl Ether

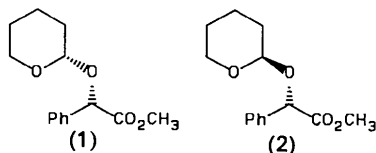
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**Abstract.** (2*S*)-Methyl 2-phenyl-2-[(2*S*)-tetrahydro-2(2*H*)-pyran-2-yl]acetate, C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>, *M<sub>r</sub>* = 250.29, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 7.850 (1), *b* = 8.211 (1), *c* = 21.123 (3) Å, *V* = 1361.5 (3) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.22 g cm<sup>-3</sup>, Mo *Kα*, λ = 0.71073 Å, μ = 0.8 cm<sup>-1</sup>, *F*(000) = 536, *T* = 296 K, *R* = 0.039 for 973 unique reflections with *F<sub>o</sub>*<sup>2</sup> > 3σ(*F<sub>o</sub>*<sup>2</sup>). In this diastereomer the anomeric alkoxy substituent is axially oriented. The absolute stereochemistry at the anomeric carbon is assigned as *S* based upon the known stereochemistry of the mandelate ester.

**Experimental.** The title compound (1) crystallized as white plates by slow evaporation from ether. It was prepared by acid-catalyzed tetrahydropyran-2-yl-ation of (*S*)-(+)-methyl mandelate using 3,4-dihydro-2*H*-pyran, followed by chromatographic separation of the resulting pyranoside diastereomers (1) and (2).



The title compound was the less polar of the two (Mash, Arterburn, Fryling & Mitchell, 1991). Diastereomer (2) could not be induced to crystallize. The data crystal had dimensions 0.50 × 0.50 × 0.30 mm. A Syntex *P2<sub>1</sub>* diffractometer using Mo *Kα* radiation (λ = 0.71073 Å) and equipped with a graphite monochromator was used to collect the data. The lattice parameters were obtained from the least-squares refinement of 25 reflections with 20 < 2θ < 30°. The data were collected from the *hkl* octant using the θ–2θ scan technique to a maximum 2θ of 50.0° (0 < *h* < 10, 0 < *k* < 10, 0 < *l* < 26). The ratio of peak counting time to background counting time was 2:1.

As a check on crystal and electronic stability, two representative reflections were measured after every 98 reflections. The total loss in intensity was 7.8%; a linear decay correction was applied. Lorentz and polarization corrections were also applied to the data, but no absorption correction was made. Of 1442 reflections measured, 1419 were unique and not systematically absent. Reflections having *F<sub>o</sub>*<sup>2</sup> < 3σ(*F<sub>o</sub>*<sup>2</sup>) were considered unobserved (446 reflections). The structure was solved by direct methods and refined by full-matrix least squares where the function minimized was Σ*w*(*F<sub>o</sub>* – |*F<sub>c</sub>*|)<sup>2</sup>. H atoms were added at idealized positions and included in the refinement but restrained to ride on the atom to which they were bonded. All non-H atoms were refined anisotropically. In all, 163 parameters were refined. The refinements converged with *R* = 0.039, *wR* = 0.047, the e.s.d. of an observation of unit weight = 0.44, and a final shift to e.s.d. ratio of 0.00. The weights for each reflection were calculated using the counter weighting scheme *w* = 4(*F<sub>o</sub>*<sup>2</sup>)/σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>). The minimum and maximum peaks in the final Δ*F* map were –0.14 and 0.18 e Å<sup>-3</sup>, respectively, and the maximum |Δ/σ| was 0.03σ. Scattering factors were taken from Cromer & Waber (1974). Anomalous-dispersion effects were included in *F<sub>c</sub>* (Ibers & Hamilton, 1964) and the values for *f*' and *f*'' were those of Cromer (1974). All calculations were performed on a MicroVAX computer using *SDP/VAX* (Frenz, 1978). Atomic coordinates are listed in Table 1, while bond lengths and angles are listed in Table 2.\* The atom-labeling scheme is shown in Fig. 1.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54422 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.