molecule, thus it has very similar non-bonding distances to the aromatic C1–C4 atoms. As a consequence, C1···C1 is the shortest intermolecular distance (3.251 Å). The isocyanide C5 atom of another molecule points toward the free side of the aromatic ring and has its shortest contact to C4. This kind of packing differs from that of 4-C_6H_4Br—NC, 4-C_6H_4I—NC and 2,4,6-$C_6H_2Br_3$—NC which have shortest intermolecular distances of 3.25, 3.22 and 3.18 Å, respectively, between the isocyanide C atom and the halogen atom. The shortest intermolecular distance is found between the F1 and F2 atoms.

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Structures of Two Diastereomers of 1-(α-Hydroxy-m-methoxybenzyl)-1-(phenylsulfinyl)cyclopropane

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Abstract. $C_{17}H_{18}O_3S$, S^*R^* diastereomer, $M_r = 302.4$, orthorhombic, *Pbca*, $a = 23.073$ (1), $b = 17.340$ (3), $c = 7.299$ (1) Å, $V = 2920$ Å^3, $Z = 8$, $D_x = 1.375$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.8$ cm^{-1}, $F(000) = 1280$, $T = 295$ K, $R = 0.039$ for 1149 observed [$I \geq 3\sigma(I)$] reflections. R^*R^* diastereomer, triclinic, $P\bar{1}$, $a = 9.873$ (9), $b = 10.009$ (5), $c = 11.024$ (7) Å, $\alpha = 56.67$ (3), $\beta = 55.68$ (5), $\gamma = 69.65$ (5)°, $V = 750$ Å^3, $Z = 2$, $D_x = 1.34$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.8$ cm^{-1}, $F(000) = 320$, $T = 295$ K, $R = 0.041$ for 1231 observed [$I \geq 3\sigma(I)$] reflections. Structure determinations of the two title compounds enable assignment of relative stereochemistries at the chiral centres, inaccessible by other chemical means.

Introduction. Compounds of formula (I) have been shown to be versatile intermediates for the preparation of cyclobutanone derivatives (Hiroi, Nakamura & Anzai, 1987). Recently, compounds of this type

(I)

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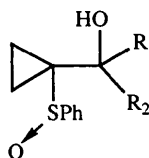
† Author to whom correspondence should be addressed.

Table 1. *Non-H atomic coordinates and equivalent isotropic thermal parameters* (Å²)

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

	x	y	z	U_{eq}
S*R*				
S	0.03622 (5)	0.31307 (7)	0.3818 (2)	0.0341 (7)
O	0.0259 (1)	0.3503 (2)	0.5636 (4)	0.049 (2)
C(11)	0.1006 (2)	0.2563 (2)	0.4022 (6)	0.031 (3)
C(12)	0.1071 (2)	0.1926 (3)	0.2883 (7)	0.040 (3)
C(13)	0.1581 (3)	0.1511 (3)	0.2964 (8)	0.049 (4)
C(14)	0.2003 (3)	0.1704 (3)	0.4193 (8)	0.055 (4)
C(15)	0.1925 (2)	0.2326 (3)	0.5371 (8)	0.047 (4)
C(16)	0.1429 (2)	0.2749 (3)	0.5283 (7)	0.039 (3)
C(1)	0.0665 (2)	0.3879 (2)	0.2361 (6)	0.027 (3)
C(2)	0.1067 (2)	0.4433 (3)	0.3290 (8)	0.040 (3)
C(3)	0.0470 (2)	0.4688 (3)	0.2758 (8)	0.043 (3)
C(4)	0.0740 (2)	0.3623 (3)	0.0401 (6)	0.030 (3)
O(4)	0.0201 (1)	0.3754 (2)	−0.0487 (5)	0.039 (2)
C(41)	0.1245 (2)	0.4015 (3)	−0.0554 (6)	0.029 (3)
C(42)	0.1167 (2)	0.4718 (3)	−0.1440 (6)	0.031 (3)
C(43)	0.1639 (2)	0.5078 (3)	−0.2252 (6)	0.031 (3)
O(43)	0.1614 (1)	0.5765 (2)	−0.3166 (4)	0.049 (2)
C(431)	0.1069 (3)	0.6152 (4)	−0.3176 (9)	0.053 (4)
C(44)	0.2179 (2)	0.4741 (3)	−0.2193 (7)	0.042 (3)
C(45)	0.2252 (2)	0.4048 (3)	−0.1318 (7)	0.047 (4)
C(46)	0.1787 (2)	0.3682 (3)	−0.0506 (7)	0.036 (3)
R*R*				
S	0.0841 (1)	0.2479 (2)	1.0082 (2)	0.047 (2)
O	0.0056 (4)	0.3993 (4)	0.9251 (4)	0.061 (7)
C(11)	0.1834 (5)	0.1514 (5)	0.8794 (5)	0.037 (8)
C(12)	0.2221 (6)	0.2328 (6)	0.7163 (6)	0.05 (1)
C(13)	0.2952 (6)	0.1507 (7)	0.6243 (7)	0.06 (1)
C(14)	0.3254 (6)	−0.0105 (7)	0.6972 (8)	0.06 (1)
C(15)	0.2864 (7)	−0.0929 (7)	0.8601 (8)	0.06 (1)
C(16)	0.2139 (6)	−0.0127 (6)	0.9524 (7)	0.05 (1)
C(1)	0.2607 (5)	0.2975 (5)	0.9789 (5)	0.035 (8)
C(2)	0.3386 (7)	0.1547 (7)	1.0772 (6)	0.05 (1)
C(3)	0.2416 (7)	0.2781 (7)	1.1328 (7)	0.05 (1)
C(4)	0.3556 (5)	0.4370 (5)	0.8131 (6)	0.039 (9)
O(4)	0.3133 (4)	0.5799 (4)	0.8275 (4)	0.058 (7)
C(41)	0.5395 (5)	0.4042 (5)	0.7436 (5)	0.035 (8)
C(42)	0.6180 (6)	0.3123 (5)	0.6594 (5)	0.038 (8)
C(43)	0.7833 (6)	0.2722 (5)	0.6603 (5)	0.042 (8)
O(43)	0.8699 (3)	0.1776 (4)	0.5259 (4)	0.059 (6)
C(431)	0.7864 (8)	0.1259 (8)	0.4892 (8)	0.06 (1)
C(44)	0.8712 (7)	0.3257 (6)	0.6291 (6)	0.048 (9)
C(45)	0.7956 (7)	0.4166 (6)	0.7109 (6)	0.05 (1)
C(46)	0.6288 (6)	0.4574 (6)	0.7671 (6)	0.046 (9)

Table 2. *Selected bond distances* (Å) *and angles* (°)

	S*R*	R*R*
S—O	1.495 (3)	1.481 (3)
S—C(11)	1.788 (4)	1.787 (7)
S—C(1)	1.817 (4)	1.785 (6)
C(1)—C(2)	1.497 (7)	1.513 (7)
C(1)—C(3)	1.502 (7)	1.50 (1)
C(1)—C(4)	1.508 (6)	1.528 (5)
C(2)—C(3)	1.499 (8)	1.47 (1)
C(4)—O(4)	1.421 (6)	1.418 (7)
C(4)—C(41)	1.519 (6)	1.512 (6)
O—S—C(11)	107.2 (2)	106.0 (3)
O—S—C(1)	105.8 (2)	107.6 (2)
C(11)—S—C(1)	97.0 (2)	99.4 (3)
S—C(11)—C(12)	118.6 (3)	117.3 (4)
S—C(11)—C(16)	120.9 (3)	122.3 (4)
S—C(1)—C(2)	115.6 (3)	112.2 (4)
S—C(1)—C(3)	116.0 (3)	113.6 (3)
S—C(1)—C(4)	112.9 (3)	116.3 (4)
C(2)—C(1)—C(3)	59.9 (3)	58.5 (4)
C(2)—C(1)—C(4)	123.2 (4)	124.3 (4)
C(3)—C(1)—C(4)	119.5 (4)	119.2 (6)
C(1)—C(2)—C(3)	60.2 (3)	60.4 (4)
C(1)—C(3)—C(2)	59.9 (3)	61.1 (4)
C(1)—C(4)—O(4)	106.6 (4)	111.1 (4)
C(1)—C(4)—C(41)	113.0 (4)	112.5 (3)
O(4)—C(4)—C(41)	113.1 (4)	108.6 (5)
C(4)—C(41)—C(42)	120.4 (4)	119.0 (6)
C(4)—C(41)—C(46)	119.8 (4)	121.4 (5)

have been obtained as mixtures of diastereomers by fluoride catalyzed condensation of 1-(phenyl-sulfinyl)-1-(trimethylsilyl)cyclopropane with alde-hydes (Pohmakotr & Sithikanchanakul, 1989). All eight adducts obtained from this preparation were characterized by spectroscopic methods [IR, ^{1}H NMR (60 MHz), MS and elemental analysis], but the relative configuration of the two stereogenic atoms (C and S) could not be established. After the investigation of all the crystalline adducts under the polarizing microscope, the two diastereomers of the title compound (R_1 = H, R_2 = PhOMe) were chosen for X-ray structure determination in order to obtain the relative configuration of the stereogenic atoms. The crystals were in two colorless forms: needle and prisms.

Experimental. Preliminary oscillation and Weissenberg photographs were taken on a colourless needle crystal (S^*R^* diastereomer; 0.1 × 0.1 × 0.8 mm) to establish the crystal symmetry and the space group. Accurate determination of cell constants and meas-

urement of data were carried out on an Enraf–Nonius CAD-4 diffractometer. Lattice parameters were determined from the eight equivalent reflections of the form 883 ($2\theta = 29.1°$) for S^*R^*, and six axial reflections ($2\theta = 15–34.6°$) for R^*R^*.

For the S^*R^* diastereomer, a unique data set was measured at 295 K within the limit $2\theta_{max} = 45°$ in a conventional $2\theta/\theta$ scan mode ($h = 0\rightarrow24$, $k = 0\rightarrow18$ and $l = 0\rightarrow7$). Three standard reflections were monitored every hour of X-ray exposure, the variation in the intensities of these reflections being < 2.0%. Of the 1899 reflections measured, 1149 had $I \geq 3\sigma(I)$ and were considered 'observed'.

The structure was solved by direct methods using XTAL2.6 (Hall & Stewart, 1989). The analysis of the E map of the set of phases with the best combined figure of merit revealed the positions of all the non-H atoms. The refinement was performed with a full-matrix least-squares procedure on $|F|$ without absorption correction. Anisotropic thermal parameters were refined for C, O and S atoms. H atoms were found from the difference Fourier map, but were introduced in their theoretical positions with isotropic temperature factors equal to the equivalent U value for the atom to which each of them were linked, and these parameters then refined.

Refinement was ended when the shifts in the atomic coordinates and anisotropic temperature factors for the C, O and S atoms were less than 0.1 of the corresponding standard deviations. Residuals, R, wR and S were 0.039, 0.036 and 1.7, respectively (263 variables). Statistical reflection weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ (I_{diff} = diffractometer intensity), were used. $(\Delta/\sigma)_{max}$ was 0.06 [y(S)]. A Zachariasen isotropic extinction parameter refined to

0.37 (6). No peak exceeding 0.25 e Å^{-3} was observed in the final difference map. Neutral-atom complex scattering factors (Ibers & Hamilton, 1974) were also used.

For the R^*R^* diastereomer, a prismatic colourless crystal of dimensions $0.2 \times 0.2 \times 0.3$ mm was used. The same procedures were repeated for the structure determination. The final residuals R, wR and S were 0.041, 0.042 and 1.3 respectively, for 1231 'observed' out of 1831 independent unique ($h = 0 \rightarrow 8$, $k = -9 \rightarrow 10$, $l = -9 \rightarrow 11$) reflections (263 variables). $(\Delta/\sigma)_{max}$ was 0.03 [y(S)]. The Zachariasen isotropic extinction factor refined to 0.19 (4). The maximum final difference map excursion was 0.28 e Å^{-3}.

The atomic coordinates for the non-H atoms of both diastereomers are given in Table 1 and selected bond distances and angles are listed in Table 2.†

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† Lists of structure factors, anisotropic vibration parameters, H-atom coordinates and complete bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55464 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0338]

Discussion. The molecular structures of the two diastereomers with the atom numbering are illustrated in Fig. 1. Bond lengths and angles are substantially as expected. The orientation of the methoxybenzyl group in the two structures differs in both the torsion angle C(42)—C(41)—C(4)—O(4), which is 33.4 (6) in the S^*R^* and 155.1 (4)° in the R^*R^* diastereomer, and the torsion angle C(42)—C(41)—C(4)—C(1), −87.9 (4) and 81.5 (6)° in S^*R^* and R^*R^*, respectively. Differences in torsion angles also occur at the sulfinyl group O—S—C(1)—C(2) for S^*R^* and R^*R^*, with values of 36.4 (4) and −172.5 (4)° respectively.

The molecular packings are shown in Fig. 2. For the S^*R^* diastereomer there is an intermolecular hydrogen bond: O···H[O(4)] (x, y, 1 + z) 2.10 (4) Å.

S^*R^*

R^*R^*

Fig. 1. Projections of the S^*R^* and R^*R^* isomers. 20% Probability amplitudes are shown for the non-H envelopes; H atoms have arbitrary radii of 0.1 Å.

S^*R^*

R^*R^*

Fig. 2. Unit cells of the S^*R^* and R^*R^* isomers projected down c and a respectively.

The R^*R^* diastereomer shows a shorter hydrogen bond between the O atom of the sulfinyl group and the H atom of the hydroxy group at O(4) ($-x$, $1-y$, $2-z$); the distance is 1.97 (4) Å. These observations are in agreement with the IR spectra of the solids which have OH peaks at 3400 and 3250 cm^{-1} for the S^*R^* and R^*R^* diastereomers respectively. The O···O(4) distances in S^*R^* and R^*R^* are 2.866 (1) and 2.807 (5) Å respectively.

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Structures of Four Tricyclo[3.3.0.0³,⁷]octanes and a 4-Oxatetracyclo[4.2.1.0²,⁵.0³,⁷]nonane Derivative

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Abstract. N,N-Dimethyl-6-methylenetricyclo[3.3.0.0³,⁷]octane-2-carboxamide (1), $C_{12}H_{17}NO$, M_r = 191.27, monoclinic, $P2_1/c$, a = 11.213 (2), b = 6.168 (1), c = 15.268 (3) Å, β = 95.07 (1)°, V = 1051.8 (6) Å^3, Z = 4, D_x = 1.21 Mg m^{-3}, μ = 0.071 mm^{-1}, $F(000)$ = 416, T = 298 K, final R = 0.047 for 1782 observed reflections. 4,6-Diisopropylidenetricyclo[3.3.0.0³,⁷]octan-2-one (2), $C_{14}H_{18}O$, M_r = 202.30, monoclinic, $P2_1/n$, a = 9.532 (1), b = 9.218 (1), c = 13.496 (2) Å, β = 97.57 (1)°, V = 1175.5 (5) Å^3, Z = 4, D_x = 1.14 Mg m^{-3}, μ = 0.065 mm^{-1}, $F(000)$ = 440, T = 208 K, final R = 0.041 for 2244 observed reflections. 4,6,8-Triisopropylidenetricyclo[3.3.0.0³,⁷]octan-2-ol (3), $C_{17}H_{24}O$, M_r = 244.38, monoclinic, $P2_1/c$, a = 8.618 (1), b = 22.054 (5), c = 7.871 (1) Å, β = 93.24 (1)°, V = 1493.6 (7) Å^3, Z = 4, D_x = 1.09 Mg m^{-3}, μ = 0.061 mm^{-1}, $F(000)$ = 536, T = 223 K, final R = 0.049 for 2211 observed reflections. 6,8-Diisopropylidenetricyclo[3.3.0.0³,⁷]octane-2-spiro-1'-cyclopentane-4-one (4), $C_{18}H_{24}O$, M_r = 256.39, monoclinic, $P2_1/c$, a = 11.796 (3), b = 11.483 (2), c = 11.312 (2) Å, β = 96.10 (2)°, V = 1523.6 (7) Å^3, Z = 4, D_x = 1.12 Mg m^{-3}, μ = 0.062 mm^{-1}, $F(000)$ = 560, T = 223 K, final R = 0.047 for 2467 observed reflections. 3-Isopropyl-8,9-diisopropylidene-4-oxatetracyclo[4.2.1.0²,⁵.0³,⁷]nonane (5), $C_{17}H_{24}O$, M_r = 244.38, triclinic, $P\overline{1}$, a = 9.675 (2), b = 12.997 (2), c = 6.454 (1) Å, α = 91.14 (2), β = 100.51 (2), γ = 70.34 (2)°, V = 750.7 (3) Å^3, Z = 2, D_x = 1.08 Mg m^{-3}, μ = 0.060 mm^{-1}, $F(000)$ = 268, T = 295 K, final R = 0.046 for 2486 observed reflections. The radiation used for compounds (1) to (5) was Mo $K\alpha$, λ = 0.7107 Å. The cage-like molecules are highly strained with the consequence that the C—C bridging bonds are distinctly lengthened to 1.606 (2)–1.621 (2) Å.

Introduction. Tricyclo[3.3.0.0³,⁷]octane (bisnoradamantane, stellane) (8) (Vogt, Suter & Hoover, 1968; Gleiter, Sigwart & Kissler, 1989) is the framework structure of compounds (1) to (4). One bridging C atom of (1) and three bridging C atoms in (2) to (4) are sp^2 hybridized. The polycyclic system (8) is also a subgroup of the tetracyclic compound (5). The stellane derivatives (1) to (5) were synthesized in order to understand the observed (Gleiter, Sigwart & Kissler, 1989) Cope-type rearrangement in these systems. Single-crystal X-ray structure determinations were undertaken to confirm the structures

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