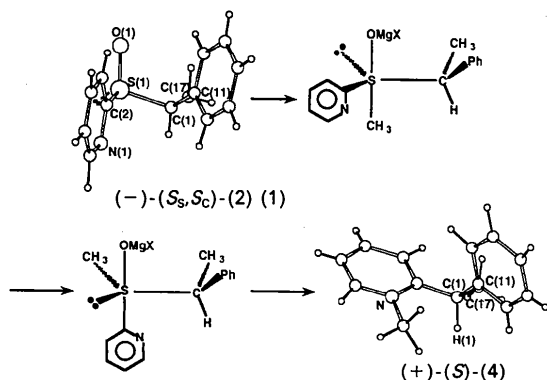ligands within the hypervalent σ-sulfurane formed by nucleophilic attack of the Grignard reagent on the sulfinyl S atom, has been proved (Oae *et al.*, 1987).

$(-)-(S_S,S_C)-(2)$ (1)

$(+)-(S)-(4)$

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Absolute Structures of (+)-(R_S,R_C)-1-Phenylethyl 2-Quinolyl Sulfoxide and (−)-(R_C,R_C)-Bis[2-(1-phenylethyl)quinolato]silver Perchlorate

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Abstract. (I) $C_{17}H_{15}NOS$, $M_r = 281.38$, orthorhombic, $P2_12_12_1$, $a = 10.429$ (2), $b = 16.894$ (2), $c = 8.105$ (2) Å, $V = 1428.2$ (5) Å^3, $Z = 4$, $D_x = 1.309$ Mg m^{-3}, λ(Cu Kα) = 1.54184 Å, $\mu = 1.912$ mm^{-1}, $F(000) = 592$, $T = 295$ K, $R = 0.046$ for 1992 observed reflections. (II) $C_{34}H_{30}AgN_2^+.ClO_4^-$, $M_r = 673.94$, orthorhombic, $P2_12_12_1$, $a = 11.686$ (2), $b = 22.938$ (1), $c = 11.364$ (1) Å, $V = 3046.3$ (5) Å^3, $Z = 4$, $D_x = 1.470$, $D_m = 1.470$ (5) Mg m^{-3}, λ(Cu Kα) = 1.54184 Å, $\mu = 6.550$ mm^{-1}, $F(000) = 1376$, $T = 295$ K, $R = 0.052$ for 4811 observed reflections. The conformations of (I) are similar to those of the corresponding pyridyl compound. In (II) two quinolyl groups are coordinated at Ag with Ag$\cdots$N distances of 2.195 (4) and 2.192 (5) Å. The N(1A)$\cdots$Ag$\cdots$N(1B) angle is 151.6 (2)°. There are weak interactions between the cation and the anion with Ag$\cdots$O distances of 2.98 (1) and 2.97 (1) Å. The absolute configurations of these compounds were determined to be R_S,R_C and R_C,R_C for (I) and (II), respectively. The absolute configurations of the phenylethyl groups are retained completely and the reaction mechanism of the ligand coupling *via* hypervalent σ-sulfurane is concluded.

Introduction. When the reaction of (+)-(1) (I) with ethylmagnesium bromide was carried out (−)-2-(1-phenylethyl)quinoline, (−)-(2), was obtained. (−)-(2) was converted to (−)-2-(1-phenylethyl)quinolinium perchlorate, (−)-(3) (Oae, Takeda & Wakabayashi, 1989), in order to introduce a heavy atom to determine the absolute configuration by an X-ray method. The X-ray structure determination of (+)-(1) (I) and (−)-(3) was carried out to explain a reaction mechanism. During the structure analysis, the crystals of the latter compound were revealed not

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to be (−)-(3) but an Ag-complex salt of (−)-(4) (II). In this paper the structures and absolute configurations of (+)-(1) (I) and (−)-(4) (II) are reported.
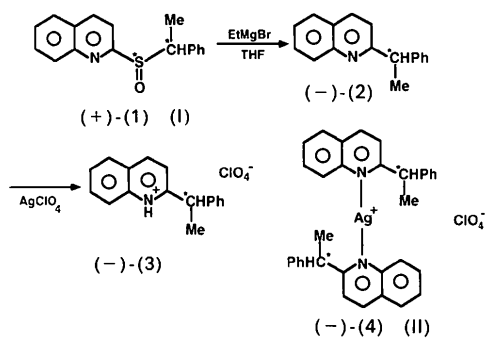
Experimental. Details of data collection and structure refinement are listed in Table 1. D_m for (II) was measured by flotation in a benzene–CCl_4 mixture. Intensity data were collected using Rigaku diffractometers with graphite monochromators. For these compounds intensities of Bijvoet pairs were measured and treated as independent reflections. Absorption corrections were applied experimentally to (I) and numerically to (II). The structure of (I) was solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms were found from the D maps. Block-diagonal least-squares refinement with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. Further cycles of refinement were carried out on two enantiomorphic structures taking the anomalous-dispersion effect into consideration. $\sum w(|F_c| - k^{-1}|F_o|)^2$ was minimized. $w = 1/[\sigma(F)^2 + 0.000115|F_o| + 0.00200|F_o|^2]$. The final R values for two enantiomers were 0.046 ($wR = 0.061$) and 0.055 ($wR = 0.079$), the former corresponding to the R_S,R_C configuration. For 81 Bijvoet-paired reflections under the conditions of $|F_o| \geq 5.0$, $0.1 \leq (\sin\theta/\lambda) \leq 0.5 \text{ Å}^{-1}$ and $\Delta F/\langle F\rangle = 2||F(hkl)| - |F(h\bar{k}l)||/\{|F(hkl)| + |F[h\bar{k}l)|\} \geq 0.1$, R values were 0.052 for R_S,R_C and 0.099 for S_S,S_C.

The first stage of the structure analysis of (3) was started assuming that $Z = 8$. After failure to solve the stucture of (3) by direct methods, a preliminary structure was obtained by the Patterson method using *SHELXS*86 (Sheldrick, 1986). However, Fourier maps showed a peak higher than the Cl atom between N atoms of two quinoline rings, where the distances N···peak were about 2·2 Å. When the peak was assigned to be Ag, assuming that the crystals were not those of the compound (3) but a complex salt of (4) (II) with $Z = 4$, the calculated density coincided with the observed value and the refinement converged successfully. H atoms of phenyl groups were found from the D maps and the

Table 1. *Details of data collection and structure refinement*

	(I)	(II)
Colour	Pale yellow	Colourless
Crystal shape	Plates	Prisms
Crystal size (mm)	0·25 × 0·23 × 0·21	0·30 × 0·28 × 0·21
Diffractometer	AFC-5R (50 kV, 150 mA)	AFC-4 (40 kV, 25 mA)
2θ range for cell parameters (°)	78–80	69–71
Number of reflections	24	25
Scan range 2θ (°)	2–120	2–130
Scan width $\Delta\omega$ (°)	1·05 + 0·3tanθ	1·3 + 0·4tanθ
Scan speed 2θ (° min^{-1})	16	4
Scan mode	2θ–ω	2θ–ω
Monitored reflections	340, 230, 04$\bar{1}$ (every 150 reflections)	023, 410, 080 (every 50 reflections)
Variation of intensities	0·984–1·029	0·960–1·015
Range of h, k, l	0–11, −18–18, 0–9	0–13, −26–26, 0–13
Time for background (s)	10	10
Transmission factor A_{max}–A_{min}	0·990–0·971	0·417–0·175
Number of reflections		
Measured	2465	6060
Unique, R_{int}	2121, 0·027	5134, 0·024
Observed [$|F_o| > 3\sigma(F)$]	1992	4811
R	0·046	0·052
wR	0·061	0·069
$\Delta\rho_{max}$ (e Å^{-3})	0·448	0·936
$(\Delta/\sigma)_{max}$	0·065	0·098
S	1·128	0·996

others were obtained from the calculations. Block-diagonal least-squares refinement with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. Further cycles of refinement were carried out on two enantimorphic structures taking the anomalous-dispersion effect into consideration. $\sum w(|F_c| - k^{-1}|F_o|)^2$ was minimized. $w = 1/[\sigma^2(F) + 0.00342|F_o|^2]$. The final R values were 0.052 ($wR = 0.069$) for the R_C,R_C configuration and 0.076 ($wR = 0.111$) for S_C,S_C. For 430 Bijvoet-paired reflections under the conditions of $|F_o| \geq 10.0$, $0.1 \leq (\sin\theta/\lambda) \leq 0.5 \text{ Å}^{-1}$ and $\Delta F/\langle F\rangle \geq 0.1$, R values were 0.057 for R_C,R_C and 0.124 for S_C,S_C.

The final atomic parameters are given in Table 2.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were performed on HITAC M260D and IBM3090-180S computers at the Information Processing Center, University of Electro-Communications, with the programs *UNICS*III (Sakurai & Kobayashi, 1979), *MULTAN*78 (Main *et al.*, 1978) and *SHELXS*86 (Sheldrick, 1986).

Discussion. The molecular structures with the atom numbering are shown in Fig. 1. Bond distances and angles are listed in Table 3.

Structure of (I). The absolute configuration of (+)-(1) is R_S,R_C. Geometry of the sulfinyl group is

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* Lists of structure factors, anisotropic thermal parameters of non-H atoms, H-atom parameters, and bond lengths and angles for benzene rings of (II) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54282 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters* ($\times 10^5$ *for* S *and* Ag, $\times 10^4$ *for others*) *and equivalent isotropic temperature factors* ($\mathring{A}^2$) *for non-*H *atoms*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(I)				
S(1)	24746 (7)	−36940 (4)	15390 (8)	4·48 (2)
O(1)	1389 (2)	−4234 (1)	1911 (3)	6·21 (6)
N(1)	2632 (2)	−2168 (1)	957 (2)	3·64 (5)
C(1)	3435 (2)	−3578 (2)	3456 (3)	4·19 (7)
C(2)	1839 (2)	−2704 (2)	1495 (3)	3·73 (6)
C(3)	541 (2)	−2577 (2)	1933 (3)	4·12 (6)
C(4)	90 (2)	−1836 (2)	1824 (3)	4·33 (7)
C(5)	471 (3)	−431 (2)	1086 (4)	5·01 (8)
C(6)	1253 (3)	129 (2)	469 (5)	5·94 (9)
C(7)	2526 (3)	−64 (2)	−13 (4)	5·59 (8)
C(8)	2974 (3)	−810 (2)	173 (4)	4·56 (7)
C(9)	2171 (2)	−1409 (2)	816 (3)	3·54 (6)
C(10)	880 (2)	−1219 (2)	1258 (3)	3·89 (6)
C(11)	2637 (2)	−3283 (1)	4856 (3)	3·73 (6)
C(12)	1851 (3)	−3786 (2)	5744 (4)	4·71 (7)
C(13)	1103 (3)	−3496 (2)	7018 (4)	5·59 (9)
C(14)	1152 (3)	−2702 (2)	7434 (4)	5·70 (9)
C(15)	1935 (3)	−2203 (2)	6558 (4)	5·76 (9)
C(16)	2667 (3)	−2490 (2)	5291 (4)	4·60 (7)
C(17)	4118 (4)	−4356 (2)	3736 (5)	6·62 (10)
(II)				
Ag(1)	32496 (4)	32673 (2)	21783 (4)	5·09 (1)
N(1A)	2324 (4)	3919 (2)	1132 (4)	3·93 (10)
C(1A)	3823 (6)	3843 (3)	−329 (6)	5·24 (15)
C(2A)	2639 (5)	4047 (2)	55 (5)	4·45 (13)
C(3A)	1909 (7)	4371 (3)	−696 (6)	6·20 (19)
C(4A)	857 (7)	4551 (3)	−321 (6)	6·39 (19)
C(5A)	−537 (6)	4627 (3)	1322 (8)	6·63 (21)
C(6A)	−788 (6)	4507 (3)	2479 (8)	6·86 (22)
C(7A)	−13 (6)	4207 (3)	3180 (7)	6·61 (21)
C(8A)	996 (5)	4010 (3)	2745 (6)	5·27 (14)
C(9A)	1292 (4)	4118 (2)	1566 (5)	3·99 (11)
C(10A)	522 (5)	4439 (2)	844 (6)	5·24 (15)
C(11A)	3833 (5)	3198 (3)	−582 (5)	4·92 (14)
C(12A)	2945 (6)	2922 (3)	−1129 (6)	5·64 (17)
C(13A)	3027 (7)	2335 (3)	−1444 (6)	6·50 (21)
C(14A)	4001 (9)	2036 (4)	−1245 (9)	8·56 (29)
C(15A)	4899 (8)	2312 (4)	−663 (11)	9·01 (32)
C(16A)	4809 (7)	2881 (3)	−333 (8)	7·09 (23)
C(17A)	4276 (9)	4184 (3)	−1394 (9)	8·23 (28)
N(1B)	3291 (4)	2492 (2)	3306 (4)	4·22 (9)
C(1B)	3805 (6)	3119 (3)	4920 (5)	5·36 (16)
C(2B)	3491 (4)	2532 (3)	4457 (5)	4·85 (14)
C(3B)	3370 (7)	2042 (3)	5187 (6)	6·26 (19)
C(4B)	3057 (5)	1519 (3)	4741 (7)	6·07 (18)
C(5B)	2665 (6)	910 (3)	2972 (9)	7·12 (22)
C(6B)	2563 (8)	877 (3)	1791 (9)	7·47 (24)
C(7B)	2620 (8)	1372 (3)	1115 (8)	7·17 (23)
C(8B)	2875 (6)	1897 (3)	1579 (6)	5·84 (17)
C(9B)	3017 (4)	1959 (2)	2822 (6)	4·59 (13)
C(10B)	2895 (6)	1445 (3)	3538 (6)	5·23 (15)
C(11B)	2789 (6)	3459 (3)	5438 (5)	5·44 (16)
C(12B)	1856 (5)	3178 (3)	5947 (6)	5·93 (17)
C(13B)	968 (6)	3514 (4)	6425 (7)	6·98 (22)
C(14B)	990 (7)	4106 (4)	6400 (7)	7·31 (23)
C(15B)	1907 (8)	4383 (4)	5886 (8)	7·70 (25)
C(16B)	2794 (8)	4063 (4)	5407 (8)	7·16 (22)
C(17B)	4783 (6)	3084 (4)	5846 (8)	7·35 (23)
Cl(1)	5770 (1)	4165 (1)	2597 (1)	5·90 (4)
O(1)	4616 (6)	4341 (4)	2621 (8)	12·90 (33)
O(2)	6327 (8)	4355 (5)	1560 (7)	14·16 (37)
O(3)	6315 (6)	4397 (3)	3594 (6)	9·33 (21)
O(4)	5691 (9)	3572 (3)	2553 (11)	13·85 (39)

Table 3. *Bond lengths* ($\mathring{A}$) *and angles* (°) *of non-*H *atoms*

(I)

S(1)—O(1)	1·485 (3)	C(5)—C(10)	1·405 (4)
S(1)—C(1)	1·859 (3)	C(6)—C(7)	1·422 (5)
S(1)—C(2)	1·799 (3)	C(7)—C(8)	1·353 (5)
N(1)—C(2)	1·302 (3)	C(8)—C(9)	1·413 (4)
N(1)—C(9)	1·374 (3)	C(9)—C(10)	1·430 (4)
C(1)—C(11)	1·493 (4)	C(11)—C(12)	1·382 (4)
C(1)—C(17)	1·512 (5)	C(11)—C(16)	1·385 (4)
C(2)—C(3)	1·416 (4)	C(12)—C(13)	1·384 (5)
C(3)—C(4)	1·340 (4)	C(13)—C(14)	1·383 (5)
C(4)—C(10)	1·406 (4)	C(14)—C(15)	1·372 (5)
C(5)—C(6)	1·345 (5)	C(15)—C(16)	1·369 (5)

O(1)—S(1)—C(1)	107·8 (1)	C(7)—C(8)—C(9)	120·2 (3)
O(1)—S(1)—C(2)	107·1 (1)	N(1)—C(9)—C(8)	119·4 (2)
C(1)—S(1)—C(2)	96·7 (1)	N(1)—C(9)—C(10)	121·2 (2)
C(2)—N(1)—C(9)	117·1 (2)	C(8)—C(9)—C(10)	119·4 (2)
S(1)—C(1)—C(11)	111·7 (2)	C(4)—C(10)—C(5)	123·9 (3)
S(1)—C(1)—C(17)	106·7 (2)	C(4)—C(10)—C(9)	117·8 (2)
C(11)—C(1)—C(17)	116·0 (2)	C(5)—C(10)—C(9)	118·3 (2)
S(1)—C(2)—N(1)	114·8 (2)	C(1)—C(11)—C(12)	121·4 (2)
S(1)—C(2)—C(3)	119·2 (2)	C(1)—C(11)—C(16)	120·2 (2)
N(1)—C(2)—C(3)	125·8 (2)	C(12)—C(11)—C(16)	118·4 (2)
C(2)—C(3)—C(4)	117·4 (3)	C(11)—C(12)—C(13)	120·3 (3)
C(3)—C(4)—C(10)	120·6 (3)	C(12)—C(13)—C(14)	120·3 (3)
C(6)—C(5)—C(10)	121·3 (3)	C(13)—C(14)—C(15)	119·5 (3)
C(5)—C(6)—C(7)	120·4 (3)	C(14)—C(15)—C(16)	120·1 (3)
C(6)—C(7)—C(8)	120·4 (3)	C(11)—C(16)—C(15)	121·4 (3)

(II)

	A	B
Ag(1)—N(1)	2·195 (4)	2·192 (5)
N(1)—C(2)	1·312 (7)	1·332 (8)
N(1)—C(9)	1·380 (7)	1·378 (8)
C(1)—C(2)	1·524 (9)	1·492 (9)
C(1)—C(11)	1·508 (9)	1·538 (10)
C(1)—C(17)	1·536 (12)	1·556 (11)
C(2)—C(3)	1·417 (10)	1·405 (10)
C(3)—C(4)	1·365 (12)	1·354 (11)
C(4)—C(10)	1·404 (11)	1·390 (10)
C(5)—C(6)	1·376 (13)	1·350 (14)
C(5)—C(10)	1·419 (11)	1·412 (11)
C(6)—C(7)	1·388 (12)	1·372 (13)
C(7)—C(8)	1·357 (10)	1·348 (12)
C(8)—C(9)	1·406 (9)	1·430 (10)
C(9)—C(10)	1·423 (9)	1·439 (10)
Cl(1)—O(1)	1·409 (10)	
Cl(1)—O(2)	1·415 (11)	
Cl(1)—O(3)	1·403 (8)	
Cl(1)—O(4)	1·366 (12)	

N(1A)—Ag(1)—N(1B)	151·6 (2)		
Ag(1)—N(1)—C(2)	121·3 (4)	121·4 (4)
Ag(1)—N(1)—C(9)	117·5 (3)	118·8 (4)
C(2)—N(1)—C(9)	120·3 (5)	119·6 (5)
C(2)—C(1)—C(11)	111·3 (5)	113·7 (6)
C(2)—C(1)—C(17)	112·5 (6)	111·9 (6)
C(11)—C(1)—C(17)	110·3 (6)	109·6 (6)
N(1)—C(2)—C(1)	117·0 (5)	116·9 (6)
N(1)—C(2)—C(3)	120·7 (6)	120·5 (6)
C(1)—C(2)—C(3)	122·4 (6)	122·6 (6)
C(2)—C(3)—C(4)	120·8 (7)	121·0 (7)
C(3)—C(4)—C(10)	119·4 (7)	120·9 (7)
C(6)—C(5)—C(10)	119·3 (8)	121·3 (9)
C(5)—C(6)—C(7)	120·6 (8)	120·4 (9)
C(6)—C(7)—C(8)	121·5 (7)	122·1 (8)
C(7)—C(8)—C(9)	120·2 (6)	120·1 (7)
N(1)—C(9)—C(8)	119·8 (5)	120·6 (6)
N(1)—C(9)—C(10)	121·2 (5)	121·6 (6)
C(8)—C(9)—C(10)	119·0 (5)	117·7 (6)
C(4)—C(10)—C(5)	123·2 (7)	125·5 (7)
C(4)—C(10)—C(9)	117·5 (5)	116·3 (6)
C(5)—C(10)—C(9)	119·3 (6)	118·2 (7)
C(1)—C(11)—C(12)	122·3 (6)	122·0 (6)
C(1)—C(11)—C(16)	119·0 (6)	119·6 (6)
O(1)—Cl(1)—O(2)	111·6 (6)	
O(1)—Cl(1)—O(3)	108·1 (5)	
O(1)—Cl(1)—O(4)	102·8 (7)	
O(2)—Cl(1)—O(3)	110·3 (6)	
O(2)—Cl(1)—O(4)	107·9 (7)	
O(3)—Cl(1)—O(4)	115·9 (6)	

similar to that of the corresponding pyridyl sulfoxide (Iwasaki & Yamazaki, 1991). Selected torsion angles are listed in that paper with those of pyridyl sulfoxide. The conformations are also similar to each other except those about the phenyl groups. O(1) is *gauche* to the methyl and phenyl groups across the S(1)—C(1) bond and *trans* to N(1) across the S(1)—C(2) bond. The dihedral angle between the quinolyl and

the phenyl planes is 38·46 (9)°. The maximum deviation from the plane defined by ten atoms of the quinoline ring is 0·047 (3) Å for C(7). The dihedral angle between the two six-membered rings in the quinoline group is 2·3 (1)°. In this group, bond alteration is observed clearly with N(1)—C(2), C(3)—C(4), C(5)—C(6) and C(7)—C(8) bonds short and other bonds long. The crystal structure is shown in Fig. 2. There are no intermolecular distances shorter than the van der Waals distances.

Structure of (II). Two quinolyl groups are coordinated to Ag with Ag···N distances of 2·195 (4) and 2·192 (5) Å. The N(1A)···Ag···N(1B) angle is 151·6 (2)°. The complex has very distorted twofold symmetry. In the case of nine divalent N-coordinated Ag complexes obtained from the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) Ag···N distances and N···Ag···N angles are 2·087–2·268 Å and 163·6–180·0°, respectively. The dihedral angles between the plane defined by N(1A)···Ag(1)···N(1B) and the quinolyl planes are

133·9 (3) and 73·2 (3)° for *A* and *B* ligands, respectively. In the reaction for the pyridyl derivative, methylation at the N atom with CH₃I was carried out before obtaining the perchlorate salt in order to protect the N atom, while in the present case the salt was obtained without methylation. This is the reason why the Ag complex was obtained only in the quinolyl derivative. The bond alternation in the quinolyl ring is slightly less than that in (I). The C(2)—N(1)—C(9) bond angles are larger than those in (I), which is the same as that in pyridine derivatives. Some torsion angles are listed in Table 4 with those of 2-(1-phenylethyl)pyridinium cations (Iwasaki & Yamazuki, 1991). The difference of the torsion angles across the C(2)—C(1) bond between the ligands *A* and *B* and that across the C(1)—C(11) bond are about 21 and 10°, respectively. The torsion angles in the pyridinium cations are similar to those in the *A* ligand. The dihedral angles between quinolyl and phenyl planes are 97·7 (2) and 110·7 (2)° for the *A* and *B* ligands, respectively. The crystal structure is shown in Fig. 3. There is a weak interaction between the cation and the anion as shown in Fig. 1(b). The Ag···O(1) and Ag···O(4) distances are 2·98 (1) and
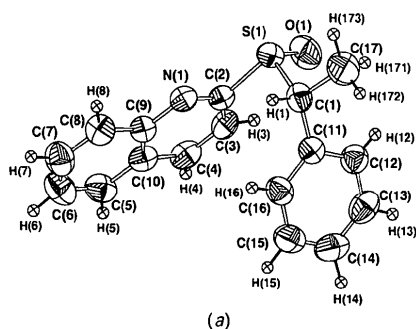
(a)
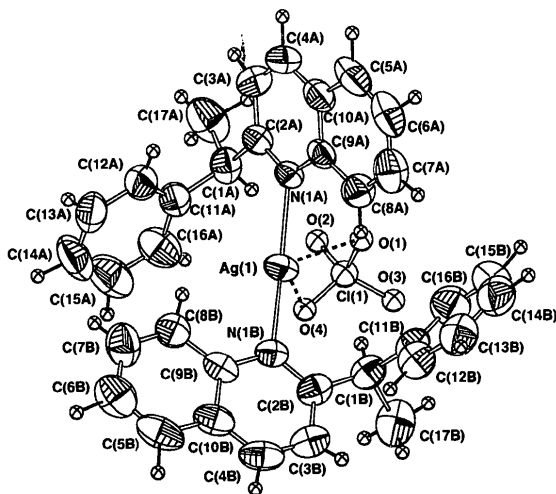
(b)

Fig. 1. *ORTEP*II (Johnson, 1976) drawings of (a) (I) and (b) (II), with atom numbering. Thermal ellipsoids for non-H atoms are drawn at 50% probability. The Cl and O atoms are represented by spheres of arbitrary scale for clarity. Dotted lines show Ag···O interactions.
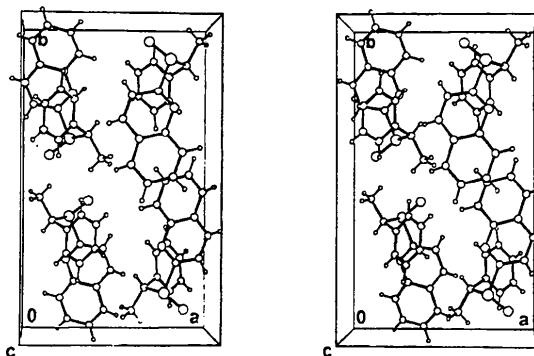

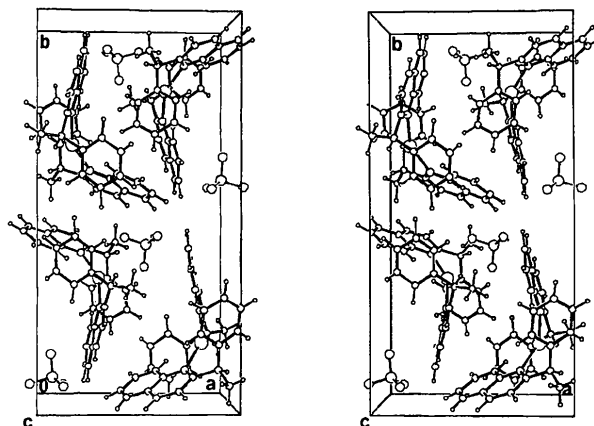Fig. 2. Stereoscopic drawing of (I) viewed along the *c* axis.

Fig. 3. Stereoscopic drawing of (II) viewed along the *c* axis.

Table 4. *Selected torsion angles* (°)

	(IIA)	(IIB)	Pyridinium ClO₄⁻* (A)	(B)
N(1')—Ag(1)—N(1)—C(2)	−130·5 (3)	−106·1 (4)		
N(1')—Ag(1)—N(1)—C(9)	39·0 (4)	68·9 (4)		
Ag(1)—N(1)—C(2)—C(1)	−14·6 (6)	−6·2 (6)		
C(11)—C(1)—C(2)—N(1)	75·7 (6)	96·5 (6)	67·4 (4)	74·0 (4)
C(17)—C(1)—C(2)—N(1)	−159·9 (5)	−138·6 (5)	−167·1 (3)	−161·1 (3)
C(2)—C(1)—C(11)—C(12)	39·0 (7)	29·4 (7)	34·7 (4)	41·6 (4)
C(2)—C(1)—C(11)—C(16)	−146·1 (5)	−150·9 (5)	−148·9 (3)	−142·7 (3)
C(17)—C(1)—C(11)—C(12)	−86·6 (7)	−96·7 (6)	−91·9 (4)	−84·3 (4)
C(17)—C(1)—C(11)—C(16)	88·3 (7)	83·0 (7)	84·6 (4)	91·4 (4)

* Iwasaki & Yamazaki (1991).

2·97 (1) Å, respectively, which are shorter than the sum of the van der Waals radii (3·24 Å). This interaction is probably related to the unusually small N⋯Ag⋯N angle. The O(1)⋯Ag(1)⋯O(4), N(1A)—Ag(1)⋯O(1), N(1A)—Ag(1)⋯O(4), N(1B)—Ag(1)⋯O(1) and N(1B)—Ag(1)⋯O(4) coordination angles are 42·8 (3), 78·0 (2), 113·0 (3), 124·1 (2) and 94·9 (3)°, respectively.

For both ligands the configurations are R_C. In the reaction shown in the scheme the absolute configurations of the phenylethyl groups are also retained completely and the reaction mechanism of the ligand coupling *via* hypervalent σ-sulfurane is concluded (Oae, Takeda, Wakabayashi, Iwasaki, Yamazaki & Katsube, 1990).

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Structure of a Dihydrooxazole Oxa-Bridged Octalin*

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Abstract. $C_{26}H_{41}NO_7$, $M_r = 479·61$, triclinic, $P\overline{1}$, $a = 11·894$ (4), $b = 12·360$ (2), $c = 9·969$ (2) Å, $\alpha = 106·11$ (2), $\beta = 100·68$ (2), $\gamma = 99·02$ (2)°, $V = 1349·5$ (6) Å³, $Z = 2$, $D_x = 1·180$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·079$ mm⁻¹, $F(000) = 520$, $T = 296$ K, $R = 0·041$, $wR = 0·047$ for 3196 observed unique reflections. A new approach to the total synthesis of the nargenicin macrolide system employing a [2,3] Wittig rearrangement to control the remote C16—C17 stereochemistry required characterization of a pivotal intermediate by X-ray single-

crystal methods. The structure is characterized by the formation of strong intermolecular alcohol to dihydrooxazole-N hydrogen bonds, an essentially strain-free tricyclic oxa-bridged octalin nucleus, and low-energy conformations of the methoxymethyl ether side chains.

Introduction. The nargenicins [(1a), (1b)] comprise a new class of macrolide antibiotics which have attracted attention owing to their novel structure and activity against drug-resistant microorganisms (Celmer, Chmurny, Moppett, Ware, Watts & Whipple, 1980; Whaley, Chidester, Mizsak & Wnuk, 1980; Whaley & Coates, 1981). In 1988, we described the first synthesis of the naturally occurring 18-deoxynargenicin A₁ (1b), in which the nargenicin

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* IUPAC name: (E)-4-{(1S*,2S*,3R*,3'R*,4R*,4'R*,5R*,6R*,-7R*)-3,5-bis(methoxymethoxy)-4-methyl-11-oxatricyclo[4.4.1.0²·⁷]-undec-9-en-1-yl}-1-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-2,4-dimethyl-3-buten-1-ol.

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