Table 3. *Bond distances* (Å), *bond angles* (°) *and their standard deviations for the heavy atoms*

C(1)–N(6)	1·126 (4)	N(6)–C(1)–C(2)	178·8 (4)	C(8)–C(9)	1·397 (6)	C(7)–C(8)–C(9)	119·4 (3)
C(1)–C(2)	1·486 (4)			C(9)–C(10)	1·358 (6)	C(8)–C(9)–C(10)	121·2 (3)
C(2)–C(3)	1·557 (5)	C(1)–C(2)–C(3)	106·2 (3)	C(10)–C(11)	1·382 (6)	C(9)–C(10)–C(11)	119·8 (4)
C(2)–C(7)	1·537 (4)	C(7)–C(2)–C(13)	109·4 (3)	C(11)–C(12)	1·385 (6)	C(10)–C(11)–C(12)	120·0 (4)
C(2)–C(13)	1·533 (3)	C(1)–C(2)–C(7)	107·8 (2)			C(11)–C(12)–C(7)	120·8 (3)
		C(1)–C(2)–C(13)	110·5 (2)	C(13)–C(14)	1·387 (4)	C(2)–C(13)–C(14)	122·4 (2)
		C(3)–C(2)–C(7)	112·7 (2)	C(13)–C(18)	1·388 (4)	C(2)–C(13)–C(18)	118·9 (2)
		C(3)–C(2)–C(13)	110·3 (2)			C(14)–C(13)–C(18)	118·7 (3)
C(3)–C(4)	1·450 (4)	C(2)–C(3)–C(4)	111·9 (2)	C(14)–C(15)	1·387 (5)	C(13)–C(14)–C(15)	119·9 (3)
C(4)–C(5)	1·180 (5)	C(3)–C(4)–C(5)	117·9 (3)	C(15)–C(16)	1·360 (6)	C(14)–C(15)–C(16)	121·0 (3)
C(7)–C(8)	1·393 (4)	C(2)–C(7)–C(8)	122·4 (3)	C(16)–C(17)	1·378 (5)	C(15)–C(16)–C(17)	119·9 (3)
C(7)–C(12)	1·386 (5)	C(2)–C(7)–C(12)	118·7 (2)	C(17)–C(18)	1·385 (4)	C(16)–C(17)–C(18)	119·8 (3)
		C(8)–C(7)–C(12)	118·9 (3)			C(17)–C(18)–C(14)	120·7 (3)

Å); and H(5,I)···C(17,I′) = 2·892 Å, H(5,I)···C(18,I′) = 2·886 Å (the distance to the centre of the ring is 2·947 Å). Thus, H(5) is almost facing a ring in the (I′) molecule [which is a distance of *b* away from (I)]. H(9,I)···C(18,IV) = 2·979 Å, but this interaction has poorer geometry. The angle between the phenyl rings is 82·3°.

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References

Barral, M. C., Moreno, V. & Santos, A. (1975). *An. Real. Soc. Esp. Fís. Quím. Ser. B*, **71**, 770–774.

Chiaroni, A., Riche, C. & Pascard-Billy, C. (1975). *Acta Cryst.* B**31**, 2122–2123.

Goldberg, I. (1975). *Acta Cryst.* B**31**, 754–761.

Gopalakrishna, E. N. & Cartz, L. (1972). *Acta Cryst.* B**28**, 2917–2924.

Ikemoto, I., Chikaishi, K., Yakushi, K. & Kuroda, H. (1972). *Acta Cryst.* B**28**, 3502–3506.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Kokkou, S. C. & Rentzeperis, P. I. (1975). *Acta Cryst.* B**31**, 2793–2799.

Main, P., Woolfson, M. M., Lessinger, L., Germain, G. & Declercq, J. P. (1974). *MULTAN 74, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York/Louvain.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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cis-2-Phenyl-4-thiolanone 1-Oxide

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Abstract. $C_{10}H_{10}O_2S$, monoclinic, $P2_1/c$, a = 10·858 (7), b = 9·546 (7), c = 21·118 (14) Å, β = 122·66 (2)° at 25 °C, M_r = 194·3, Z = 8, D_m = 1·37, D_x = 1·400 g cm^{-1}. The structure was solved by direct methods and refined to a final R of 0·047 for 1762 observed intensities. The configuration of the phenyl group with respect to the sulfoxide oxygen is *cis*.

Introduction. White, prismatic crystals of the high-melting racemic modification of 2-phenyl-4-thiolanone 1-oxide [m.p. 149–152 °C (dec.)] were obtained by slow recrystallization from ethyl acetate. A single crystal, 0·2 × 0·04 × 0·08 mm, was used for data collection. Preliminary precession photographs showing systematic absences of $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ identified the space group as $P2_1/c$. Unit-cell parameters were refined by the least-squares method with the diffractometer angles of 12 reflections measured at $\pm 2\theta$ by the automatic centering routine (λ = 0·71069 Å). Intensity data were collected with Mo $K\alpha$ radiation on a Picker FACS-1 diffractometer equipped with a graphite monochromator. All reflec-

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* Contribution No. 2983.

tions ($hk \pm l$, $\bar{h}\bar{k} \pm l$) in the range $1 \le 2\theta \le 55°$ were scanned with the θ–2θ scan mode, a scan rate of 1° min^{-1}, and 20 s background counts at both ends of the scan range of 2° + dispersion. The intensities of three standard reflections were measured every 50 reflections. No significant trends were observed. Intensities, I, were assigned standard deviations, $\sigma(I)$, according to counting statistics plus a term $(0{\cdot}05I)^2$ to allow for unaccountable errors. The intensities were corrected for Lorentz and polarization effects but not for absorption. Of 3324 independent reflections, 1762 were considered observed by the criterion $(F_o)^2 \ge \sigma[(F_o)^2]$.

The structure was solved by direct methods (Long, 1965). Initially a false solution was obtained, which seemed to indicate disorder in one of the molecules in the asymmetric unit. The omission of two-dimensional E_{hkl}'s led to the correct solution. All H atoms were located in a difference Fourier map. Least-squares refinements were carried out with the full-matrix program of Busing, Martin & Levy (1962). The function minimized was $\Sigma\, w(|F_o|^2 - |F_c|^2)^2$ with $w = 1/\sigma^2(F_o)^2$. Atomic scattering factors for S, O, and C were taken from *International Tables for X-ray Crystallography* (1962), whereas those for H were taken from Stewart, Davidson & Simpson (1965). No anomalous-dispersion corrections were made. Because of program limitations the refinement was completed as follows: two cycles of refinement of all non-hydrogen atom parameters, two further cycles in which all hydrogen atom parameters were varied isotropically, and finally two cycles varying only the non-hydrogen atoms. The final R was 0·047 for 1762 reflections for which $(F_o)^2 \ge \sigma[(F_o)^2]$ and $R_{wF^2} = (\Sigma\, w||F_o|^2 - |F_c|^2|^2/\Sigma\, w|F_o|^4)^{1/2}$ was 0·068. For the complete data set of 3324 reflections $R = 0{\cdot}124$; in no case was the difference between $(F_o)^2$ and $(F_c)^2$ greater than $\sigma[(F_o)^2]$. A final difference Fourier map revealed no maxima greater than 0·39 e Å^{-3}. The final positional parameters are given in Table 1.[*]

Discussion. Interest in the stereochemistry of ionization of sulfoxides led to the synthesis of the racemic *cis* and *trans* sulfoxide isomers of 2-phenyl-4-thiolanone (Carson & Leonard, 1972). The necessity for reliable assignment of configuration to these isomers prompted the present investigation in which the crystal structure of the *cis* isomer has been determined.

Table 1. *Final positional* ($\times 10^4$, *for* H $\times 10^3$) *parameters with standard deviations in parentheses*

	x	y	z
Molecule *A*			
S(1)	7350 (1)	3788 (1)	1834 (1)
C(2)	8236 (4)	2141 (4)	1811 (2)
C(3)	6979 (4)	1132 (5)	1372 (2)
C(4)	5642 (5)	1948 (5)	791 (2)
C(5)	5916 (4)	3504 (5)	866 (2)
C(6)	9454 (4)	1776 (4)	2596 (2)
C(7)	9270 (4)	870 (4)	3044 (2)
C(8)	10412 (5)	618 (4)	3776 (2)
C(9)	11728 (5)	1290 (5)	4068 (2)
C(10)	11911 (5)	2190 (5)	3619 (3)
C(11)	10793 (4)	2428 (4)	2888 (2)
O(1)	6667 (3)	3478 (3)	2270 (1)
O(2)	4504 (3)	1430 (4)	333 (2)
H(1)	861 (3)	247 (3)	152 (1)
H(2)	720 (3)	43 (3)	111 (2)
H(3)	670 (3)	71 (3)	167 (2)
H(4)	633 (3)	380 (3)	58 (1)
H(5)	505 (3)	404 (4)	77 (2)
H(6)	838 (3)	45 (3)	285 (1)
H(7)	1026 (3)	−3 (3)	408 (2)
H(8)	1247 (3)	109 (4)	458 (2)
H(9)	1276 (3)	264 (3)	382 (2)
H(10)	1089 (3)	302 (3)	258 (2)
Molecule *B*			
S(1)	7002 (1)	1211 (1)	3997 (1)
C(2)	7645 (4)	3037 (4)	4098 (2)
C(3)	6255 (4)	3896 (5)	3753 (2)
C(4)	5030 (5)	3103 (5)	3100 (2)
C(5)	5476 (4)	1623 (5)	3071 (2)
C(6)	8849 (4)	3323 (4)	4901 (2)
C(7)	8785 (4)	4408 (4)	5314 (2)
C(8)	9917 (5)	4661 (5)	6043 (2)
C(9)	11138 (4)	3827 (5)	6377 (2)
C(10)	11229 (4)	2752 (5)	5972 (2)
C(11)	10094 (4)	2502 (5)	5240 (2)
O(1)	6381 (3)	1075 (3)	4475 (1)
O(2)	3840 (3)	3571 (4)	2658 (2)
H(1)	804 (3)	310 (3)	376 (2)
H(2)	598 (3)	403 (3)	413 (2)
H(3)	636 (3)	481 (3)	359 (2)
H(4)	466 (3)	92 (3)	292 (2)
H(5)	582 (3)	158 (3)	277 (2)
H(6)	797 (3)	502 (3)	510 (2)
H(7)	986 (3)	550 (3)	636 (2)
H(8)	1192 (3)	396 (3)	693 (2)
H(9)	1201 (3)	216 (3)	619 (2)
H(10)	1022 (3)	179 (3)	497 (2)

A perspective view of the two molecules in the asymmetric unit is given in Fig. 1. Fig. 2 shows the averaged values of the molecular parameters for molecules *A* and *B*. The agreement between the two molecules is very good; the largest deviations are 0·010 Å for the S(1)–C(2) bond length and 1·2° for the angles C(2)–C(6)–C(11) and C(11)–C(6)–C(7). The points on a normal probability plot (Abrahams &

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[*] Lists of structure factors and thermal parameters and tables of bond lengths, bond angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32545 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England. Supplementary data are also available, in microfiche form only, for $2.00 from the Chemistry Department Library, Indiana University, Bloomington, Indiana 47401, USA. Request Molecular Structure Center Report No. 7508.

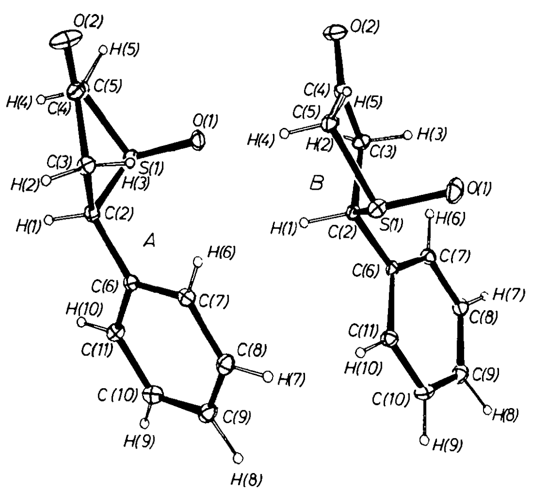

Fig. 1. Perspective view of the two molecules (*A* and *B*) in the asymmetric unit. The numbering system is indicated.

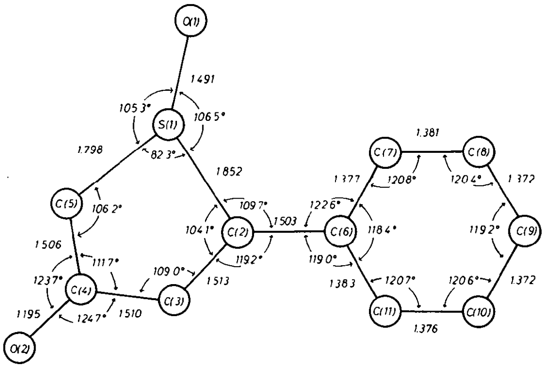

Fig. 2. Molecular dimensions for the title compound. The parameters are averaged over the two molecules in the asymmetric unit. The average e.s.d. for bond lengths is 0·005 Å, for bond angles 0·3°. The range of C–H distances is 0·89 (3)–1·07 (3) Å. The full list of distances and angles has been deposited (see footnote on p. 2279).

Keve, 1971) comparing 14 bond lengths and 19 bond angles (not involving H) fall close to a line with 0·0 intercept and a slope of 1·25. The only significant difference between the two molecules appears to be the orientation of the phenyl ring with respect to the five-membered ring, as evidenced in the torsion angles around C(2)–C(6) (Table 2). A few close intramolecular contacts between the H atoms of the phenyl group and the H atoms on the heterocyclic ring also indicate the difference in twist: H(3)–H(6) 2·17 in molecule *A* and 2·69 Å in molecule *B*; H(2)–H(6) 3·17 in *A* and 2·23 Å in *B*; H(1)–H(10) 2·33 in *A* and 2·68 Å in *B*.

The thiolanone ring is envelope shaped with the S atom at the tip of the flap. The angle of flap is about 140° in both molecules. The S atom is 0·84 Å out of the plane defined by the four C atoms, while C(6), the adjoining atom of the benzene ring, is 0·56 Å out of the plane. This results in an axial orientation of the sulfoxide oxygen and a pseudo-equatorial orientation of the phenyl group. A similar ring system is found in the tetrahydrothiophene ring in biotin (De Titta, Edmonds, Stallings & Donohue, 1976), where the S atom is 0·87 Å out of the C plane and the C–S–C angle is 89·4°. The C–S bond lengths of 1·798 and 1·852 Å are

Table 2. *Torsion angles*

The signs of corresponding angles differ because the molecules being compared are those related by the pseudo glide.

	Molecule *A*	Molecule *B*
S(1)–C(2)–C(3)–C(4)	32·16°	−35·08°
C(2)–C(3)–C(4)–C(5)	−4·97	9·95
C(3)–C(4)–C(5)–S(1)	−25·65	20·88
C(4)–C(5)–S(1)–C(2)	38·11	−35·71
C(5)–S(1)–C(2)–C(3)	−41·10	40·93
O(1)–S(1)–C(2)–C(3)	64·24	−65·06
O(1)–S(1)–C(5)–C(4)	−68·84	71·28
O(1)–S(1)–C(2)–C(6)	−64·74	62·88
O(2)–C(4)–C(3)–C(2)	175·68	−170·66
O(2)–C(4)–C(5)–S(1)	153·71	−158·52
S(1)–C(2)–C(6)–C(7)	94·95	−124·74
S(1)–C(2)–C(6)–C(11)	−82·13	57·18
C(3)–C(2)–C(6)–C(7)	−24·92	−5·38
C(3)–C(2)–C(6)–C(11)	157·99	176·53
C(2)–C(6)–C(7)–C(8)	−177·08	−178·68
C(6)–C(7)–C(8)–C(9)	1·40	−0·34
C(7)–C(8)–C(9)–C(10)	−1·62	1·08
C(8)–C(9)–C(10)–C(11)	0·47	0·91
C(9)–C(10)–C(11)–C(6)	0·92	−0·01
C(10)–C(11)–C(6)–C(2)	176·02	178·92

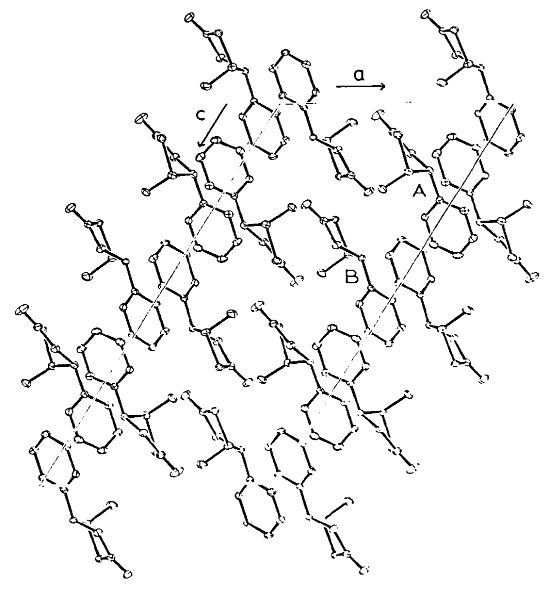

Fig. 3. Packing of the molecules viewed along **b**. Hydrogen atoms are omitted for clarity. The two molecules labeled *A* and *B* are related by an approximate glide-plane operation (*x*, 0·50 − *y*, 0·23 + *z*).

within the range observed in heterocyclic molecules (Abrahams, 1956). The S—O bond length of 1·491 Å agrees well with the values observed in other sulfoxides such as cycloalliin (Palmer & Lee, 1966).

The molecular packing is illustrated in Fig. 3. In retrospect we attribute our initial difficulty in solving the structure to the presence of an approximate glide along **c**, having a translation of 0·23*c* and relating molecule *A* to molecule *B*. All contacts to 4 Å were computed; the closest non-hydrogen contacts are O(1)*A*–C(4)*B*, 3·12 Å and O(1)*A*–C(5)*B*, 3·17 Å.

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References

Abrahams, S. C. (1956). *Quart. Rev.* **10**, 407–436.

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* A**27**, 157–165.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Carson, F. W. & Leonard, T. A. (1972). Private communication.

De Titta, G. T., Edmonds, J. W., Stallings, W. & Donohue, J. (1976). *J. Amer. Chem. Soc.* **98**, 1920–1926.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–246. Birmingham: Kynoch Press.

Long, R. E. (1965). PhD Thesis, Univ. of California, Los Angeles.

Palmer, K. J. & Lee, K. S. (1966). *Acta Cryst.* **20**, 790–796.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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1,4,7,10-Tetraoxacyclododecane–Uranyl Nitrate Dihydrate

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Abstract. $C_8H_{16}O_4UO_2(NO_3)_2.2H_2O$, monoclinic, $P2_1/c$, $a = 9{\cdot}048$ (5), $b = 14{\cdot}366$ (8), $c = 6{\cdot}720$ (26) Å, $\beta = 99{\cdot}38$ (15)°, $M_r = 606{\cdot}26$, $Z = 2$, $D_o = 2{\cdot}327$, $D_x = 2{\cdot}236$ g cm^{-3}. The molecule has a crystallographic centre of symmetry which is occupied by the U atom. The uranyl group is surrounded equatorially by a near-planar hexagon comprised of four O atoms from the ether ring and two water O atoms. Intermolecular binding is a result of the hydrogen bonds between nitrate O atoms and the water molecules.

Introduction. This work is one of the first structural studies of 12-crown-4 ether and its complexes. The crystals used were supplied by the Chemistry Department of the University of Ankara.

The crystals were transparent, prismatic and determined to be twins with (100) composition plane. They were cut into single crystals having (010) as prominent faces. It was observed that the crystals decompose on exposure to X-rays. Thus three-dimensional data were collected with various crystals whose details are given in Table 1.

Systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ confirmed the space group as $P2_1/c$. 46 high-angle reflexions of $hk0$ and $h0l$, including 18 α_1,α_2 separated reflexions measured from the equi-inclination Weissenberg films, were used for the refinement of the lattice parameters with the least-squares computer program *CELCIUS* (Tegenfeldt, 1967). Ambiguity in the molecular formula was clarified by determining the number of water molecules. Intensity data were recorded with Cu $K\alpha$ radiation and the multiple-film technique. Intensities were measured with a Joyce–Loebl microdensitometer. Owing to the high linear absorption coefficient, $\mu = 374{\cdot}17$ cm^{-1} for Cu $K\alpha$ radiation, absorption corrections were made by the computer program *ABSOT* (Coppens, Leiserowitz & Rabinovich, 1967). 850 unique reflexions were obtained from the 2681 measured reflexions with $0 \le l \le 5$ and $0 \le k \le 1$. The *c* axis data were then brought to the same scale by means of the *b* axis data. Lorentz–polarization corrections were applied to the data in the usual way (Zalkin, 1967).

In the solution of the structure the heavy-atom method was employed. The distribution of the molecules among the equi-points showed that the asymmetric unit consists of one-half of the molecule, and that the U atoms occupy the special positions 2(*a*).