C20—C21—O36	110.1 (4)	C11—C12—O34	109.3 (3)
C20—C22—C23	109.1 (5)	C11—C12—C13	105.8 (2)
C22—C23—O36	110.1 (5)	C13—C12—O34	111.5 (2)
C24—C25—O34	110.9 (3)	C12—C13—C18	112.0 (2)
C24—C25—O33	125.6 (3)	C12—C13—C17	115.0 (2)
O33—C25—O34	123.5 (3)	C12—C13—C14	99.0 (2)
C1—O30—C14	117.3 (2)	C17—C13—C18	111.8 (2)
C7—O32—C26	115.3 (3)	C14—C13—C18	111.9 (2)
C12—O34—C25	117.9 (2)	C14—C13—C17	106.5 (2)
C21—O36—C23	105.5 (5)	C8—C14—C13	102.0 (2)
C16—O37—C17	124.2 (3)	C13—C14—O30	104.3 (2)
C6—O39—C9	113.5 (2)	C13—C14—C15	112.8 (2)
C10—C1—O30	112.7 (1)	C8—C14—O30	108.4 (2)
C2—C1—O30	104.2 (2)	C8—C14—C15	119.8 (3)
C2—C1—C10	109.5 (2)	C15—C14—O30	108.4 (2)
C1—C2—C3	115.8 (2)	C14—C15—C16	112.1 (3)
C2—C3—O40	119.8 (3)	C15—C16—O38	123.1 (3)
C2—C3—C4	119.2 (3)	C15—C16—O37	119.0 (3)
C4—C3—O40	121.0 (3)	O37—C16—O38	117.7 (4)
C3—C4—C28	109.1 (3)	C13—C17—O37	110.3 (2)
C3—C4—C27	107.2 (2)	C13—C17—C20	117.5 (3)
C3—C4—C5	105.6 (2)	C20—C17—O37	103.8 (2)
C27—C4—C28	108.3 (2)	C17—C20—C22	128.3 (3)
C5—C4—C28	108.4 (2)	C17—C20—C21	126.8 (4)
C5—C4—C27	118.0 (3)	C21—C20—C22	104.9 (4)
C4—C5—C10	117.8 (2)		

Ring *A*			
C1—C2—C3—C4	−43.6 (3)	C4—C5—C10—C1	63.0 (3)
C2—C3—C4—C5	40.4 (3)	C5—C10—C1—C2	−56.6 (2)
C3—C4—C5—C10	−52.0 (3)	C10—C1—C2—C3	50.0 (3)
Ring *B*			
C5—C6—O39—C9	−17.6 (3)	C9—C10—C5—C6	−34.3 (2)
C6—O39—C9—C10	−4.5 (3)	C10—C5—C6—O39	32.9 (3)
O39—C9—C10—C5	24.3 (3)		
Ring *C*			
C8—C11—C12—C13	−7.5 (3)	C13—C14—C8—C11	45.4 (3)
C11—C12—C13—C14	33.7 (3)	C14—C8—C11—C12	−23.2 (3)
C12—C13—C14—C8	−48.5 (3)		
Ring *D*			
C13—C14—C15—C16	−46.9 (4)	C16—O37—C17—C13	37.3 (4)
C14—C15—C16—O37	25.1 (4)	O37—C17—C13—C14	−54.0 (3)
C15—C16—O37—C17	−21.7 (5)	C17—C13—C14—C15	62.3 (3)
Ring *E*			
C20—C21—O36—C23	3.6 (6)	C23—C22—C20—C21	−2.4 (6)
C21—O36—C23—C22	−5.1 (7)	C22—C20—C21—O36	−0.8 (6)
O36—C23—C22—C20	4.8 (7)		

The space group was determined using *STATCW* (Sekar, 1991). The structure was solved with *SHELXS*90 (Sheldrick, 1990) and refined with *SHELX*76 (Sheldrick, 1976). *PARST* (Nardelli, 1983) was used to calculate the molecular parameters. The figure was drawn using *PLUTO* (Motherwell & Clegg, 1978). Refinement was by full-matrix least squares and all calculations were performed on a MicroVAX II.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and geometry, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71569 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1044]

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trans-2-Phenyltetrahydropyran-3-ylmethyl *p*-Toluenesulfonate

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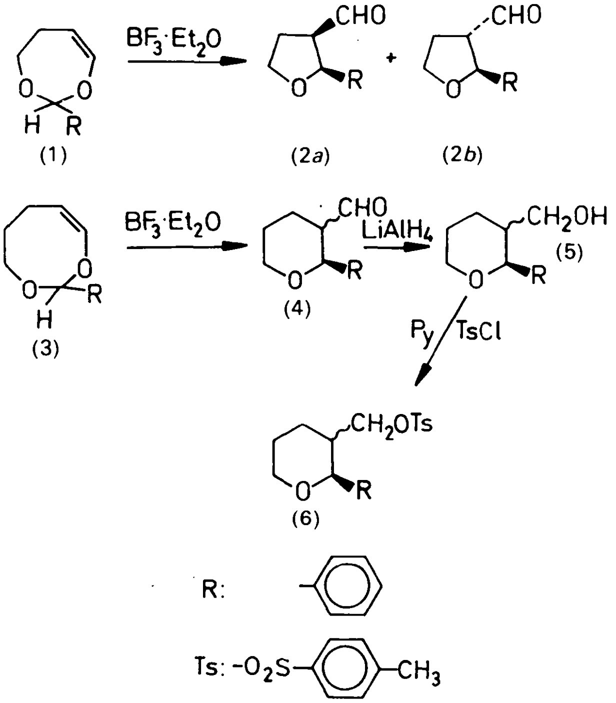
Abstract

trans-2-Phenyltetrahydropyran-3-ylmethyl *p*-toluenesulfonate, $C_{19}H_{22}O_4S$, (6), crystallizes with two molecules (*A*, *B*) in the asymmetric unit. The shortest intermolecular distance between the independent species involving non-H atoms only (C···O) is 3.138 (4) Å. The bulky substituents in (6) are oriented *trans* to each other and, as expected, occupy equatorial positions (*ee*). However, semi-empirical calculations on one precursor of (6), 2-phenyltetrahydropyran-3-carbaldehyde (4), indicate that at least in the case of isolated molecules the energy difference between an *ee* species and its isomer with both substituents in axial positions (*aa*) might be quite low (< 13 kJ mol^{-1}).

Comment

Compounds of general structure (1) undergo Lewis acid-catalyzed rearrangement resulting in five-membered ring structures (2) which are formed in a *cis*:*trans* ratio of 9–10:1 (Frauenrath, Runsink & Scharf, 1982). 2-Phenyl-5,6-dihydro-4*H*-1,3-dioxocine, (3), undergoes a similar rearrangement when treated with $BF_3.Et_2O$ ($Et = C_2H_5$), yielding aldehydes (4) as a *cis–trans* mixture with one isomer in high excess (Frauenrath & Sawicki, 1990). The major component is further enriched upon distillation (333 K, 4 Pa) of the mixture resulting in an essentially pure product. Since analysis of ^{1}H NMR coupling constants, used to identify the major component, met with failure, we reduced aldehyde (4) with $LiAlH_4$. Subsequent tosylation of the resulting alcohol (5) in pyridine (Py) yielded a racemic mixture of the *trans* diastereomer of (6) in the form of colourless crystals (f.p. 351 K).



The results of the X-ray structure analysis are compiled in Tables 1 and 2. Fig. 1 shows one of the two independent molecules of the asymmetric unit and Fig. 2 the relative orientation of the subunits linked by the C(2)—C(3) bond. The packing of the molecules in the cell is plotted in Fig. 3.

X-ray structure determination based on a single crystal of the title compound shows that this substance crystallizes with two molecules (*A* and *B*) in the asymmetric unit which both have the same absolute configuration at C(2) and C(3). *A* and *B* approach as close as 2.484 (3) Å [O(3*B*)···H(18*A*); H(18*A*)···O(3*B*)—S(2) = 155.27°]. This intermolecular distance is somewhat less than the sum of the isotropic van der Waals radii of H (1.17 Å) and O (1.52 Å)† (Kitaigorodskii, 1973). Taking into

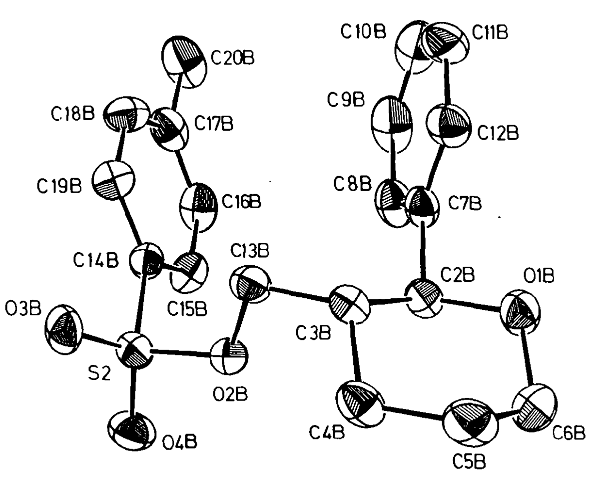


Fig. 1. *ORTEP* (Johnson, 1965) plot of (6), molecule *B*, in the solid state. Ellipsoids are plotted at the 30% probability level.

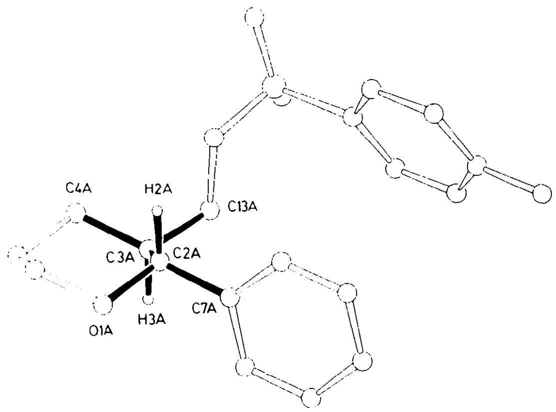


Fig. 2. Conformation about the C(2)—C(3) bond in (6), molecule *A* (*SCHAKAL*; Keller, 1986).

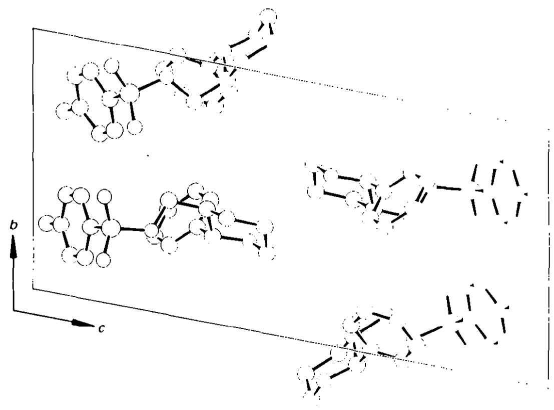


Fig. 3. Packing of (6) in the cell. View along *a* (*SCHAKAL*; Keller, 1986).

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† The value of 1.36 Å suggested by the author in an earlier book (Kitaigorodskii, 1961) was subsequently corrected (Kitaigorodskii, 1967).

account the uncertainty of the H-atom position and the well known tendency of C bonded H to form short intermolecular contacts to O, this value, although worth mentioning, is not unusual (Taylor & Kennard, 1982). The shortest intermolecular distance between *A* and *B* involving only non-H atoms is 3.138 (4) Å [O(4*B*)···C(16*A*)]; this value is close to the sum of the van der Waals radii of O and aromatic C atoms (~ 1.70 Å). The lengths of corresponding bonds are virtually identical in both molecules and the differences between equivalent bond angles do not exceed 2°. Both molecules, however, differ as far as the relative orientation of the tolyl substituents [C(14*A*,*B*)–C(20*A*,*B*)] and the SO_3 groups are concerned. Comparison of the relevant dihedral angles in Table 2 results in differences between 7 and 8.5°. The dihedral angles defining the relative orientation of the phenyl substituents [C(7*A*,*B*)–C(12*A*,*B*)] and the pyranyl system are almost identical in both molecules. The substituents at C(2) and C(3) are oriented *trans* to each other. Both bulky groups occupy equatorial positions thus avoiding unfavourable 1,3-diaxial repulsive interactions. Since the relative orientation of the substituents will not be changed during the reactions linking (4) and (6), the major component of (4) is also a *trans* species.

To estimate the possible role of diaxial repulsive interactions in the aldehyde we performed quantum-chemical calculations for isolated free molecules of (4) with the semi-empirical MNDO method (Dewar & Thiel, 1977), where the structures of the molecules under consideration were completely optimized with respect to their total valence-shell energy. These calculations show that in the case of free isolated molecules, the *ee–trans* aldehyde is only about 13 kJ mol^{-1} lower in energy than the *aa–trans* species. Although this energy gap might increase when bulky substituents are present in position 3, it is doubtful whether it plays a decisive role in determining the structure of a molecule in the solid state when such substituents are absent.

Experimental

Crystal data

$C_{19}H_{22}O_4S$
M_r = 346.45
Triclinic
$P\bar{1}$
a = 9.225 (2) Å
b = 10.141 (3) Å
c = 20.198 (4) Å
α = 98.65 (1)°
β = 98.34 (1)°
γ = 101.70 (1)°
V = 1798.8 Å^3
Z = 4
D_x = 1.279 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 7.91–17.49°
μ = 0.2 mm^{-1}
T = 295 K
Irregular
0.4 × 0.4 × 0.4 mm
Colourless
Crystal source: cyclohexane/diethyl ether/ethanol 7:2:1

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
8884 measured reflections
6495 independent reflections
4657 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.011
$\theta_{\rm max}$ = 25.3°
$h = -12 \rightarrow 11$
$k = -13 \rightarrow 12$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity variation: 1%

Refinement

Refinement on F
R = 0.053
wR = 0.056
S = 2.738
4657 reflections
434 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} < 0.0005$

$\Delta\rho_{\rm max}$ = 0.3 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.5 e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 4925
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
S(1)	0.01090 (9)	0.82374 (8)	0.18880 (4)	0.0541 (4)
O(1*A*)	0.4137 (2)	1.1387 (2)	0.4335 (1)	0.062 (1)
O(2*A*)	0.0870 (2)	0.9126 (2)	0.2606 (1)	0.053 (1)
O(3*A*)	−0.0789 (2)	0.6985 (2)	0.1981 (1)	0.070 (1)
O(4*A*)	−0.0575 (2)	0.9143 (2)	0.1543 (1)	0.069 (1)
C(2*A*)	0.3476 (3)	1.0511 (3)	0.3691 (2)	0.051 (1)
C(3*A*)	0.2085 (3)	0.9463 (3)	0.3774 (2)	0.054 (1)
C(4*A*)	0.0956 (3)	1.0222 (4)	0.4047 (2)	0.068 (2)
C(5*A*)	0.1704 (4)	1.1244 (4)	0.4681 (2)	0.077 (2)
C(6*A*)	0.3104 (4)	1.2152 (4)	0.4574 (2)	0.073 (2)
C(7*A*)	0.4664 (3)	0.9856 (3)	0.3436 (2)	0.050 (1)
C(8*A*)	0.5029 (4)	1.0016 (4)	0.2808 (2)	0.066 (2)
C(9*A*)	0.6070 (4)	0.9365 (5)	0.2557 (2)	0.082 (2)
C(10*A*)	0.6737 (4)	0.8555 (5)	0.2921 (2)	0.084 (2)
C(11*A*)	0.6396 (4)	0.8394 (4)	0.3547 (2)	0.077 (2)
C(12*A*)	0.5372 (4)	0.9050 (4)	0.3810 (2)	0.063 (2)
C(13*A*)	0.1410 (3)	0.8421 (3)	0.3140 (2)	0.058 (2)
C(14*A*)	0.1619 (3)	0.7889 (3)	0.1510 (2)	0.051 (1)
C(15*A*)	0.2289 (4)	0.8787 (3)	0.1133 (2)	0.059 (2)
C(16*A*)	0.3481 (4)	0.8503 (4)	0.0837 (2)	0.065 (2)
C(17*A*)	0.4018 (4)	0.7352 (4)	0.0924 (2)	0.064 (2)
C(18*A*)	0.3338 (4)	0.6482 (3)	0.1307 (2)	0.069 (2)
C(19*A*)	0.2133 (4)	0.6731 (3)	0.1596 (2)	0.062 (2)
C(20*A*)	0.5343 (5)	0.7074 (5)	0.0619 (2)	0.099 (2)
S(2)	0.40513 (9)	0.70720 (9)	−0.15213 (4)	0.0570 (4)
O(1*B*)	0.0530 (2)	0.6594 (2)	−0.4208 (1)	0.065 (1)
O(2*B*)	0.3397 (2)	0.6888 (2)	−0.2302 (1)	0.054 (1)
O(3*B*)	0.4547 (3)	0.5877 (2)	−0.1399 (1)	0.073 (1)
O(4*B*)	0.5094 (3)	0.8364 (3)	−0.1370 (1)	0.080 (1)
C(2*B*)	0.1007 (3)	0.6655 (3)	−0.3495 (2)	0.052 (1)
C(3*B*)	0.1972 (3)	0.5611 (3)	−0.3385 (2)	0.052 (1)
C(4*B*)	0.3290 (3)	0.5844 (4)	−0.3766 (2)	0.065 (2)
C(5*B*)	0.2743 (4)	0.5892 (4)	−0.4504 (2)	0.079 (2)
C(6*B*)	0.1784 (4)	0.6913 (4)	−0.4545 (2)	0.078 (2)
C(7*B*)	−0.0397 (3)	0.6400 (3)	−0.3192 (2)	0.053 (2)
C(8*B*)	−0.0575 (4)	0.7326 (4)	−0.2649 (2)	0.068 (2)
C(9*B*)	−0.1873 (5)	0.7081 (5)	−0.2365 (2)	0.090 (3)
C(10*B*)	−0.2975 (5)	0.5928 (6)	−0.2628 (3)	0.097 (3)
C(11*B*)	−0.2820 (4)	0.4995 (4)	−0.3170 (2)	0.082 (2)
C(12*B*)	−0.1533 (4)	0.5245 (4)	−0.3454 (2)	0.066 (2)
C(13*B*)	0.2433 (3)	0.5557 (3)	−0.2646 (2)	0.055 (2)
C(14*B*)	0.2502 (3)	0.7172 (3)	−0.1124 (2)	0.051 (1)
C(15*B*)	0.2047 (4)	0.8389 (3)	−0.1012 (2)	0.065 (2)

C(16*B*)	0.0793 (5)	0.8434 (4)	−0.0726 (2)	0.075 (2)
C(17*B*)	−0.0026 (4)	0.7296 (5)	−0.0545 (2)	0.071 (2)
C(18*B*)	0.0457 (4)	0.6095 (4)	−0.0655 (2)	0.072 (2)
C(19*B*)	0.1716 (4)	0.6021 (3)	−0.0941 (2)	0.061 (2)
C(20*B*)	−0.1432 (5)	0.7357 (5)	−0.0262 (2)	0.103 (3)

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

S(1)—O(3*A*)	1.423 (2)	S(2)—O(3*B*)	1.421 (3)
S(1)—O(4*A*)	1.423 (3)	S(2)—O(4*B*)	1.421 (2)
S(1)—O(2*A*)	1.569 (2)	S(2)—O(2*B*)	1.572 (2)
S(1)—C(14*A*)	1.754 (3)	S(2)—C(14*B*)	1.751 (3)
O(1*A*)—C(2*A*)	1.433 (3)	O(1*B*)—C(6*B*)	1.431 (5)
O(1*A*)—C(6*A*)	1.436 (5)	O(1*B*)—C(2*B*)	1.433 (4)
O(2*A*)—C(13*A*)	1.465 (4)	O(2*B*)—C(13*B*)	1.466 (3)
C(2*A*)—C(7*A*)	1.504 (5)	C(2*B*)—C(7*B*)	1.503 (5)
C(2*A*)—C(3*A*)	1.538 (4)	C(2*B*)—C(3*B*)	1.535 (5)
C(3*A*)—C(13*A*)	1.496 (4)	C(3*B*)—C(13*B*)	1.505 (5)
C(3*A*)—C(4*A*)	1.531 (5)	C(3*B*)—C(4*B*)	1.528 (5)
C(4*A*)—C(5*A*)	1.498 (5)	C(4*B*)—C(5*B*)	1.514 (5)
C(5*A*)—C(6*A*)	1.491 (5)	C(5*B*)—C(6*B*)	1.495 (6)
C(7*A*)—C(8*A*)	1.383 (5)	C(7*B*)—C(12*B*)	1.380 (4)
C(7*A*)—C(12*A*)	1.386 (5)	C(7*B*)—C(8*B*)	1.385 (5)
C(8*A*)—C(9*A*)	1.382 (6)	C(8*B*)—C(9*B*)	1.395 (6)
C(9*A*)—C(10*A*)	1.360 (7)	C(9*B*)—C(10*B*)	1.363 (6)
C(10*A*)—C(11*A*)	1.372 (6)	C(10*B*)—C(11*B*)	1.380 (7)
C(11*A*)—C(12*A*)	1.382 (6)	C(11*B*)—C(12*B*)	1.386 (5)
C(14*A*)—C(19*A*)	1.377 (5)	C(14*B*)—C(19*B*)	1.374 (5)
C(14*A*)—C(15*A*)	1.381 (5)	C(14*B*)—C(15*B*)	1.380 (5)
C(15*A*)—C(16*A*)	1.384 (5)	C(15*B*)—C(16*B*)	1.372 (6)
C(16*A*)—C(17*A*)	1.382 (6)	C(16*B*)—C(17*B*)	1.374 (6)
C(17*A*)—C(18*A*)	1.375 (5)	C(17*B*)—C(18*B*)	1.378 (6)
C(17*A*)—C(20*A*)	1.503 (6)	C(17*B*)—C(20*B*)	1.500 (6)
C(18*A*)—C(19*A*)	1.378 (5)	C(18*B*)—C(19*B*)	1.380 (5)
O(3*A*)—S(1)—O(4*A*)	119.9 (1)	O(3*B*)—S(2)—O(4*B*)	119.9 (1)
O(3*A*)—S(1)—O(2*A*)	108.7 (1)	O(3*B*)—S(2)—O(2*B*)	108.9 (1)
O(3*A*)—S(1)—C(14*A*)	109.1 (1)	O(3*B*)—S(2)—C(14*B*)	108.7 (2)
O(4*A*)—S(1)—O(2*A*)	104.1 (1)	O(4*B*)—S(2)—O(2*B*)	104.1 (1)
O(4*A*)—S(1)—C(14*A*)	109.6 (2)	O(4*B*)—S(2)—C(14*B*)	110.0 (1)
O(2*A*)—S(1)—C(14*A*)	104.4 (1)	O(2*B*)—S(2)—C(14*B*)	104.2 (1)
C(2*A*)—O(1*A*)—C(6*A*)	110.9 (2)	C(6*B*)—O(1*B*)—C(2*B*)	111.6 (2)
C(13*A*)—O(2*A*)—S(1)	117.9 (2)	C(13*B*)—O(2*B*)—S(2)	118.0 (2)
O(1*A*)—C(2*A*)—C(7*A*)	108.1 (2)	O(1*B*)—C(2*B*)—C(7*B*)	106.6 (2)
O(1*A*)—C(2*A*)—C(3*A*)	109.4 (2)	O(1*B*)—C(2*B*)—C(3*B*)	110.1 (2)
C(7*A*)—C(2*A*)—C(3*A*)	113.2 (3)	C(7*B*)—C(2*B*)—C(3*B*)	113.2 (3)
C(13*A*)—C(3*A*)—C(4*A*)	113.2 (2)	C(13*B*)—C(3*B*)—C(4*B*)	113.7 (2)
C(13*A*)—C(3*A*)—C(2*A*)	113.0 (3)	C(13*B*)—C(3*B*)—C(2*B*)	113.0 (3)
C(4*A*)—C(3*A*)—C(2*A*)	109.5 (3)	C(4*B*)—C(3*B*)—C(2*B*)	110.2 (3)
C(5*A*)—C(4*A*)—C(3*A*)	110.4 (3)	C(5*B*)—C(4*B*)—C(3*B*)	110.8 (3)
C(6*A*)—C(5*A*)—C(4*A*)	111.2 (3)	C(6*B*)—C(5*B*)—C(4*B*)	109.9 (3)
O(1*A*)—C(6*A*)—C(5*A*)	112.1 (3)	O(1*B*)—C(6*B*)—C(5*B*)	111.4 (3)
C(8*A*)—C(7*A*)—C(12*A*)	118.9 (3)	C(12*B*)—C(7*B*)—C(8*B*)	118.9 (3)
C(8*A*)—C(7*A*)—C(2*A*)	119.9 (3)	C(12*B*)—C(7*B*)—C(2*B*)	120.6 (3)
C(12*A*)—C(7*A*)—C(2*A*)	121.2 (3)	C(8*B*)—C(7*B*)—C(2*B*)	120.5 (3)
C(9*A*)—C(8*A*)—C(7*A*)	120.2 (4)	C(7*B*)—C(8*B*)—C(9*B*)	120.3 (3)
C(10*A*)—C(9*A*)—C(8*A*)	120.5 (4)	C(10*B*)—C(9*B*)—C(8*B*)	119.7 (4)
C(9*A*)—C(10*A*)—C(11*A*)	120.0 (4)	C(9*B*)—C(10*B*)—C(11*B*)	120.8 (4)
C(10*A*)—C(11*A*)—C(12*A*)	120.2 (4)	C(10*B*)—C(11*B*)—C(12*B*)	119.4 (3)
C(11*A*)—C(12*A*)—C(7*A*)	120.2 (3)	C(7*B*)—C(12*B*)—C(11*B*)	120.8 (3)
O(2*A*)—C(13*A*)—C(3*A*)	108.5 (3)	O(2*B*)—C(13*B*)—C(3*B*)	108.6 (2)
C(19*A*)—C(14*A*)—C(15*A*)	120.6 (3)	C(19*B*)—C(14*B*)—C(15*B*)	120.2 (3)
C(19*A*)—C(14*A*)—S(1)	119.8 (3)	C(19*B*)—C(14*B*)—S(2)	119.6 (3)
C(15*A*)—C(14*A*)—S(1)	119.5 (3)	C(15*B*)—C(14*B*)—S(2)	120.2 (3)
C(14*A*)—C(15*A*)—C(16*A*)	119.1 (3)	C(16*B*)—C(15*B*)—C(14*B*)	119.4 (3)
C(17*A*)—C(16*A*)—C(15*A*)	120.9 (3)	C(15*B*)—C(16*B*)—C(17*B*)	121.7 (4)
C(18*A*)—C(17*A*)—C(16*A*)	118.7 (3)	C(16*B*)—C(17*B*)—C(18*B*)	117.9 (4)
C(18*A*)—C(17*A*)—C(20*A*)	120.7 (4)	C(16*B*)—C(17*B*)—C(20*B*)	120.6 (4)
C(16*A*)—C(17*A*)—C(20*A*)	120.6 (4)	C(18*B*)—C(17*B*)—C(20*B*)	121.4 (4)
C(17*A*)—C(18*A*)—C(19*A*)	121.4 (4)	C(17*B*)—C(18*B*)—C(19*B*)	121.7 (3)
C(14*A*)—C(19*A*)—C(18*A*)	119.2 (3)	C(14*B*)—C(19*B*)—C(18*B*)	119.1 (3)

O(3*A*)—S(1)—O(2*A*)—C(13*A*)	38.6 (2)
O(4*A*)—S(1)—O(2*A*)—C(13*A*)	167.4 (2)
O(2*A*)—S(1)—C(14*A*)—C(15*A*)	−89.2 (2)
O(2*A*)—S(1)—C(14*A*)—C(19*A*)	90.4 (2)
O(3*A*)—S(1)—C(14*A*)—C(15*A*)	154.8 (2)
O(3*A*)—S(1)—C(14*A*)—C(19*A*)	−25.6 (3)
O(4*A*)—S(1)—C(14*A*)—C(15*A*)	21.8 (3)
O(4*A*)—S(1)—C(14*A*)—C(19*A*)	−158.7 (2)
O(3*B*)—S(2)—O(2*B*)—C(13*B*)	42.5 (2)
O(4*B*)—S(2)—O(2*B*)—C(13*B*)	171.4 (2)
O(2*B*)—S(2)—C(14*B*)—C(15*B*)	−80.7 (3)
O(2*B*)—S(2)—C(14*B*)—C(19*B*)	97.4 (3)
O(3*B*)—S(2)—C(14*B*)—C(15*B*)	163.3 (2)
O(3*B*)—S(2)—C(14*B*)—C(19*B*)	−18.6 (3)
O(4*B*)—S(2)—C(14*B*)—C(15*B*)	30.3 (3)
O(4*B*)—S(2)—C(14*B*)—C(19*B*)	−151.6 (2)

The time to measure the background was half that spent measuring the peak. The intensity of a reflection and its e.s.d. were calculated from $I = INT - 2(BGL + BGR)$ and $\sigma(I) = [INT + 4(BGL + BGR)]^{1/2}$, where *INT*, *BGL* and *BGR* are the peak intensity and left and right background, respectively. The horizontal detector aperture and the ω scan range varied as $(1.9 + 1.05\tan\theta)$ mm and $(0.8 + 0.35\tan\theta)^\circ$, respectively. Data were corrected for Lorentz and polarization effects. The structure was solved by means of direct methods employing *GENSIN* (Hall, 1989) to generate structure invariant relationships and *SIMPEL* (Schenk & Hall, 1989) for the symbolic addition phase procedure. Displacement parameters for C, O and S were refined anisotropically. The positions of the H atoms were located in a difference electron density map and were subjected to five cycles of isotropic refinement [$U(\mathrm{H}) = 0.038$ Å^2] but excluded from the final full-matrix refinement. The *Xtal*2.6 program package (Hall & Stewart, 1989) was used for the refinement and crystallographic calculations. Molecular drawings and cell plots were generated using *ORTEP* (Johnson, 1965) and *SCHAKAL* (Keller, 1986), respectively. The semi-empirical calculations were performed employing the *MOPAC* set of quantum chemical routines (Stewart, 1989).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71562 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1064]

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Two Substituted Pyrazolo[1′,2′:1,2]pyrazolo[4,3-*d*]tetrazolo[1,5-*b*]pyridazines

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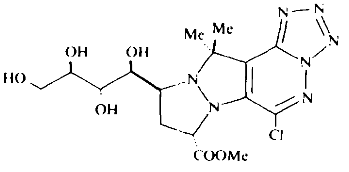
Abstract

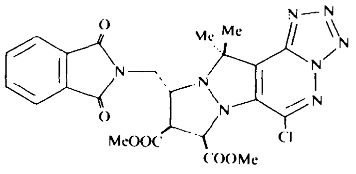
The compound methyl (1′*S*,8*S*,10*S*)-6-chloro-9,10-dihydro-12,12-dimethyl-10-(D-erythritol-1-yl)-8*H*,12*H*-pyrazolo[1′,2′:1,2]pyrazolo[4,3-*d*]tetrazolo-[1,5-*b*]pyridazine-8-carboxylate, $C_{16}H_{22}ClN_7O_6$ (I), is an example of a new C-nucleoside. Both (I) and dimethyl (6-chloro-9,10-dihydro-12,12-dimethyl-10-phthalimidomethyl-8*H*,12*H*-pyrazolo[1′,2′:1,2]pyrazolo[4,3-*d*]tetrazolo[1,5-*b*]pyridazine-8,9-dicarboxylate, $C_{23}H_{21}ClN_8O_6$, (II), contain heterocyclic systems consisting of four condensed fused rings. In each compound, the tetrazole ring is planar to within experimental error; the pyridazine ring and the pyrazole ring, which is fused to the pyridazine ring, deviate slightly from planarity, as does the phthalimido group of (II).

Comment

(I) was obtained by 1,3-dipolar cycloaddition of 2-diazopropane to 6-chorotetrazolo[1,5-*b*]pyridazine. This is highly regiospecific and proceeds as a cycloaddition across the partially localized C(7)=C(8) double bond of the pyridazine ring. Rearrangement of two H atoms produced NH—NH dihydro intermediates, which were then used for the regioselective synthesis of a C-nucleoside, employing D-ribose as a carbonyl reagent. The product was then converted with methyl acrylate into (I) (Žličar, Stanovnik & Tišler, 1992). The synthesis of (II) was analogous, with two exceptions: phthalimidoacetaldehyde was used as the carbonyl reagent and, instead of methyl acrylate, dimethyl maleate was employed. Views of the molecules with atomic numbering and of the molecular packing are presented in Figs. 1, 2, 3 and 4.



(I)



(II)

Although azolopyridazines with bridgehead N atoms are generally considered to be fully aromatic ten-π-electron systems, some reactions have indicated that these compounds have two localized double bonds (Golič, Leban, Stanovnik & Tišler, 1978). The double-bond character of these two bonds is also indicated by the bond lengths N(5)—C(1) [1.301 (3) in (I) and 1.303 (2) Å in (II)] and C(2)—C(7) [1.358 (2) Å in (II)]; the C(2)—C(7) bond in (I) [1.372 (3) Å] is slightly larger. The tetrazole unit is planar to within 0.004 (3) Å in (I) and 0.006 (4) Å in (II). The pyridazine unit deviates from planarity. The largest deviation is 0.020 (3) Å for C(8) in (I) and −0.013 (2) Å for C(2) in (II). The dihedral angles between tetrazole and pyridazine planes are 2.13 (8) in (I) and 1.2 (1)° in (II). The pyrazole ring that is fused to the pyridazine ring also deviates from planarity. The largest deviation in (I) is −0.050 (2) Å for C(7) and in (II) −0.075 (2) Å for C(6). The fact that Hückel's rule cannot be fulfilled indicates that this ring does not have aromatic character. The dihedral angles between the pyrazole and pyridazine ring planes are 4.87 (8) in (I) and 2.97 (7)° in (II). The dihedral angles between the best planes for both pyrazole rings are 34.29 (8) in (I) and 33.35 (6)° in (II). The remaining bond lengths and angles are within the normal ranges for such heterocyclic systems (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987; Golič *et al.*, 1978; Leban, Golič, Stanovnik & Tišler, 1987). The phenyl C atoms of the phthalimido group of (II) are coplanar to within 0.003 (3) Å. The whole phthalimido group deviates from planarity. The largest deviation is 0.031 (2) Å for O(5). The bond lengths and angles of groups bonded to the rings are within the normal ranges (Allen *et al.*, 1987). Methoxycarbonyl groups are bonded to the ring system on the side opposite to the phthalimidomethyl or erythritol group. This cor-

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