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(3a*S**,9b*S**)-(±)-3a,9b-Dihydro-2,9b-dimethylthiazolo[5,4-*c*]quinolin-4(5*H*)-one

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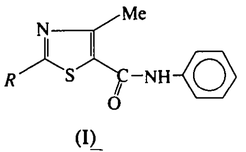
Abstract

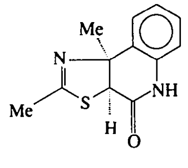
The stereochemistry of the title compound, $C_{12}H_{12}N_2OS$, is established as *cis*. There are two very similar independent molecules in the asymmetric unit. The five-membered rings have envelope conformations and the six-membered hetero-rings are in skew-boat conformations. The molecules are linked by N—H···O hydrogen bonds with N···O distances in the range 2.996 (2)–3.114 (2) Å.

Comment

Certain carboxanilidothiazoles, (I), are known to have powerful fungicidal activity (Harrison & Kulka, 1973), and as part of our ongoing research aimed at the development of new fungicides we studied the photolysis of 2,4-dimethyl-5-carboxanilidothiazole (Metsulfovax), (I*a*), in the aqueous phase. We report here the structure of the main photolysis product, (II).



(I)
(I*a*) *R* = Me



(II)

There are two chiral centres in each molecule of (II) and the compound crystallizes with two independent molecules (labelled *A* and *B*) in the asymmetric unit. Molecules *A* and *B* have identical relative stereochemistries. The centrosymmetric space group *C*2/*c* requires that both enantiomers be present in equal amounts and the asymmetric unit was chosen so as to contain one of each enantiomer. The two molecules have very similar dimensions and conformations; an *ORTEP*II (Johnson, 1976) plot of molecule *A* with the crystallographic numbering scheme is shown in Fig. 1, while a similar plot of molecule *B* has been deposited with the Supplementary Material.

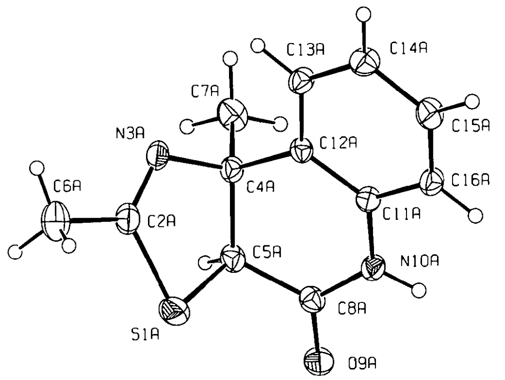


Fig. 1. A view of molecule *A* with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The analysis establishes the structure and relative stereochemistry as shown in Fig. 1, with the methyl group at C4 and H atom at C5 *cis*. The molecular dimensions (Table 2) are entirely in accord with anticipated values (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1994). The six-membered hetero-ring (C4, C5, C8, N10, C11, C12) in each molecule has a skew-boat conformation with C5 and C8 displaced by 0.502 (3) and 0.228 (3) Å, respectively, in molecule *A*, and 0.482 (3) and 0.267 (3) Å, respectively, in molecule *B* from the relevant C4–C12–C11–N10 planes. In each molecule, the five-membered ring (S1, C2, N3, C4, C5) has an envelope conformation with C5 at the flap [C5 0.454 (2) and 0.421 (2) Å from the S1–C2–N3–C4 plane in *A* and *B*, respectively]. 5-Dimethylaminocarbonyl-4-ethoxycarbonyl-2-phenyl-Δ^2-thiazoline (Chehna, Pradere, Vicens, Toupet & Quiniou, 1988) contains the same five-membered heterocyclic ring as (II), with similar geometry and C5-envelope conformation.

The molecules are linked by N—H···O hydrogen bonds (Table 3) to form infinite chains in the *b*-axis direction, with molecules in the sequence *A*···*B*···*A*···*B*···. These chains are cross-linked as a result of the N—H group of the *B* molecules forming additional (bifurcated) N—H···O hydrogen bonds to adjacent carbonyl O atoms of *A* molecules; in this way pairs of *A* and *B* molecules are linked about inversion centres. Views of the hydrogen-bonding patterns have been deposited with the Supplementary Material.

Experimental

1.00 g of Metsulfovax (I*a*) was dissolved in 10 ml of acetonitrile. To this was added 1 l of a buffer solution prepared from 1 l of deionized distilled water, 1.40 g of NaH_2PO_4 and 0.30 g of 85% H_3PO_4. This solution, in a water-cooled quartz flask, was irradiated with a 450 W medium pressure Hg lamp for 3 days. The solution was then extracted with CH_2Cl_2 (3 × 100 ml). Evaporation of the combined CH_2Cl_2 extracts yielded 0.80 g of a greenish yellow solid. Recrystallization from methanol gave pale-green crystals of (II), m.p. 463–464 K.

Crystal data

$C_{12}H_{12}N_2OS$
$M_r = 232.30$
Monoclinic
$C2/c$
$a = 24.032$ (4) Å
$b = 8.109$ (2) Å
$c = 24.014$ (3) Å
$\beta = 98.470$ (10)°
$V = 4628.7$ (15) Å^3
$Z = 16$
$D_x = 1.333$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9.55$–$12.75°$
$\mu = 0.259$ mm^{-1}
$T = 294$ (1) K
Plate
0.42 × 0.32 × 0.13 mm
Pale green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5135 measured reflections
5024 independent reflections
3543 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 26.9°$
$h = -30 \rightarrow 30$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 30$
3 standard reflections
frequency: 120 min
intensity decay: none, variation 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0367$
$wR(F^2) = 0.1134$
$S = 1.065$
5024 reflections
293 parameters
H atoms treated using a riding model (C—H 0.93–0.98, N—H 0.86 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 1.6815P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.004$
$\Delta\rho_{\rm max} = 0.278$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.237$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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	$U_{\rm eq}$
S1*A*	0.04344 (2)	0.55570 (8)	0.18013 (2)	0.0555 (2)
C2*A*	0.10768 (8)	0.6322 (2)	0.21646 (8)	0.0407 (4)
N3*A*	0.15174 (6)	0.6091 (2)	0.19471 (6)	0.0363 (3)
C4*A*	0.14197 (7)	0.5108 (2)	0.14217 (7)	0.0307 (3)
C5*A*	0.07837 (7)	0.5215 (2)	0.11890 (7)	0.0343 (4)
C6*A*	0.10634 (11)	0.7193 (3)	0.27109 (10)	0.0657 (6)
C7*A*	0.17684 (8)	0.5828 (2)	0.09971 (8)	0.0454 (4)
C8*A*	0.05155 (7)	0.3753 (2)	0.08682 (7)	0.0327 (3)
O9*A*	0.00733 (5)	0.3920 (2)	0.05418 (5)	0.0421 (3)
N10*A*	0.07729 (5)	0.2291 (2)	0.09606 (6)	0.0339 (3)
C11*A*	0.12710 (6)	0.2020 (2)	0.13396 (6)	0.0297 (3)
C12*A*	0.15981 (6)	0.3345 (2)	0.15657 (6)	0.0288 (3)
C13*A*	0.21001 (7)	0.3008 (2)	0.19144 (7)	0.0338 (4)
C14*A*	0.22680 (7)	0.1408 (2)	0.20449 (8)	0.0394 (4)
C15*A*	0.19322 (8)	0.0108 (2)	0.18294 (8)	0.0415 (4)
C16*A*	0.14352 (7)	0.0410 (2)	0.14775 (7)	0.0361 (4)
S1*B*	−0.03866 (3)	0.07003 (7)	0.15232 (2)	0.0563 (2)
C2*B*	−0.10897 (10)	0.1368 (2)	0.15247 (9)	0.0536 (5)
N3*B*	−0.14471 (8)	0.1055 (2)	0.11010 (8)	0.0502 (4)
C4*B*	−0.12115 (7)	0.0087 (2)	0.06659 (7)	0.0358 (4)
C5*B*	−0.05633 (7)	0.0254 (2)	0.07770 (7)	0.0348 (4)
C6*B*	−0.12181 (14)	0.2277 (3)	0.20339 (12)	0.0870 (9)
C7*B*	−0.14401 (9)	0.0777 (3)	0.00830 (9)	0.0511 (5)
C8*B*	−0.02166 (7)	−0.1186 (2)	0.06303 (7)	0.0339 (4)
O9*B*	0.02836 (5)	−0.0995 (2)	0.05874 (6)	0.0447 (3)
N10*B*	−0.04723 (6)	−0.2651 (2)	0.05577 (6)	0.0376 (3)
C11*B*	−0.10329 (7)	−0.2978 (2)	0.06373 (7)	0.0340 (4)
C12*B*	−0.13990 (7)	−0.1694 (2)	0.07039 (7)	0.0348 (4)
C13*B*	−0.19465 (8)	−0.2080 (2)	0.07726 (9)	0.0487 (5)
C14*B*	−0.21321 (9)	−0.3685 (3)	0.07738 (10)	0.0538 (5)
C15*B*	−0.17622 (9)	−0.4948 (3)	0.07135 (10)	0.0551 (5)
C16*B*	−0.12152 (8)	−0.4601 (2)	0.06449 (9)	0.0481 (5)

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

S1*A*—C2*A*	1.770 (2)	S1*B*—C2*B*	1.775 (2)
S1*A*—C5*A*	1.818 (2)	S1*B*—C5*B*	1.816 (2)
C2*A*—N3*A*	1.262 (2)	C2*B*—N3*B*	1.257 (3)
C2*A*—C6*A*	1.494 (3)	C2*B*—C6*B*	1.498 (3)
N3*A*—C4*A*	1.482 (2)	N3*B*—C4*B*	1.484 (2)
C4*A*—C5*A*	1.551 (2)	C4*B*—C5*B*	1.547 (2)
C4*A*—C12*A*	1.517 (2)	C4*B*—C12*B*	1.520 (2)
C4*A*—C7*A*	1.528 (2)	C4*B*—C7*B*	1.532 (3)
C5*A*—C8*A*	1.506 (2)	C5*B*—C8*B*	1.506 (2)
C8*A*—O9*A*	1.231 (2)	C8*B*—O9*B*	1.231 (2)
C8*A*—N10*A*	1.340 (2)	C8*B*—N10*B*	1.337 (2)
N10*A*—C11*A*	1.410 (2)	N10*B*—C11*B*	1.413 (2)
C2*A*—S1*A*—C5*A*	88.80 (8)	C2*B*—S1*B*—C5*B*	88.76 (9)
N3*A*—C2*A*—S1*A*	117.91 (13)	N3*B*—C2*B*—S1*B*	118.29 (15)
C2*A*—N3*A*—C4*A*	113.27 (14)	C2*B*—N3*B*—C4*B*	113.0 (2)
N3*A*—C4*A*—C5*A*	107.51 (13)	N3*B*—C4*B*—C5*B*	108.13 (15)
C4*A*—C5*A*—S1*A*	105.37 (11)	C4*B*—C5*B*—S1*B*	105.72 (11)
S1*A*—C2*A*—N3*A*—C4*A*	−3.1 (2)	S1*B*—C2*B*—N3*B*—C4*B*	2.2 (2)
N10*A*—C11*A*—C12*A*—C4*A*	1.5 (2)	N10*B*—C11*B*—C12*B*—C4*B*	2.8 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10*A*—H10*A*···O9*B*	0.86	2.17	2.996 (2)	161
N10*B*—H10*B*···O9*A*$^{\rm i}$	0.86	2.29	3.077 (2)	153
N10*B*—H10*B*···O9*A*$^{\rm ii}$	0.86	2.54	3.114 (2)	125

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, -y, -z$.

The title compound crystallized in the monoclinic system. The space groups *C*2/*c* or *Cc* were consistent with the systematic absences; *C*2/*c* was assumed and confirmed by the analysis. Fig. 1 was prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1994*a*). Examination of the structure with the *SOLV* option in *PLATON* showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: Enraf–Nonius *SET*4 and *CELDIM*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *PLATON* (Spek, 1994*a*) and *PLUTON* (Spek, 1994*b*). Software used to prepare material for publication: *NRCVAX*94 and *SHELXL*93.

GF thanks NSERC (Canada) for Grants in Aid of Research.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and torsion angles, a plot of the structure of molecule *B* and plots showing the patterns of hydrogen bonding have been deposited with the IUCr (Reference: NA1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Four Isomeric Dioxolane Derivatives of D-Camphorquinone

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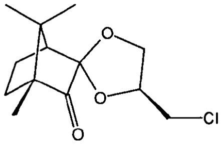
Abstract

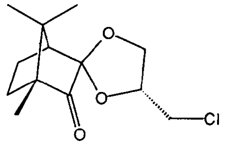
The bicyclo[2.2.1]heptane unit is essentially invariant in all four structures, reflecting its rigid nature. The four isomers (1*S*,2*S*,4*R*,4′*S*)-, (1*S*,2*S*,4*R*,4′*R*)-, (1*S*,2*R*,4*R*,4′*R*)- and (1*S*,2*R*,4*R*,4′*S*)-4,7,7-trimethylbicyclo[2.2.1]heptan-3-one-2-spiro-2′-(4′-chloromethyl-1′,3′-dioxolane), $C_{13}H_{19}ClO_3$, have different positions of substitution by the CH_2Cl group in the ethylene segment of the dioxolane ring. In each case, this ring has an envelope conformation but the identity of the flap atom varies. All four molecules have a similar overall shape and hence give similar packing patterns, resulting in close correspondence or simple relationships for the four sets of unit-cell parameters and the space groups of the structures.

Comment

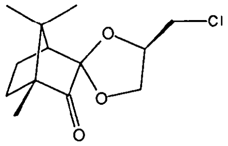
The four isomers, (1)–(4), whose structures are reported here are the major products of the reaction of 3-chloropropane-1,2-diol [$HOCH_2CH(OH)CH_2Cl$] with D-camphorquinone. They are produced by dioxolane formation involving the less sterically hindered of the two carbonyl groups of the quinone, with respective yields for (1)–(4) of 23, 14, 24 and 14%. The corresponding four products obtained in the same reaction from attack on the more hindered carbonyl had yields of 3–10%. All the products were separated by HPLC (Ellis, Golding, Maude & Watson, 1991). The crystal structures of the four major products have been determined to confirm the assignments made on the basis of high-field proton NMR spectroscopy.



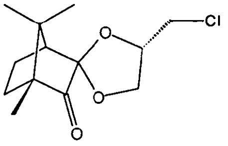
(1)



(2)



(3)



(4)

The structure of the bicyclo[2.2.1]heptane unit is essentially invariant in all four structures, as it is in several hundred other structures in the Cambridge Structural Database (CSD; Allen, Davies, Galloy, Johnson, Kennard, Macrae, Mitchell, Mitchell, Smith & Watson, 1991), reflecting its rigid nature. The four structures differ in the conformation and substitution of their dioxolane rings. All are envelopes, but the identity of the flap atom varies, as is shown by the torsion angles and mean-plane parameters in Table 9; the two disorder components of compound (2) also have different conformations. The dioxolane ring displays a variety of conformations in over 800 structures in the CSD (Allen *et al.*, 1991). In each of the structures (1)–(4), the conformation adopted extends the CH_2Cl substituent away from the bicyclic core. This, despite the different substitution and stereochemistry of the four molecules, makes