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(9*S*,9a*R*)-1,3,4,6,7,8,9,9a-Octahydro-2*H*-quinolizine-1-spiro-2′-(1′,3′-dithiane)-9-carbonitrile

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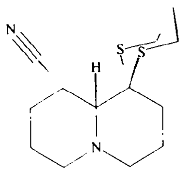
Abstract

The title compound, $C_{13}H_{20}N_2S_2$, was prepared during the intramolecular addition of dithiane anions to unsaturated nitriles. The octahydroquinolizine ring adopts a chair–chair conformation with the dithiane ring in a chair conformation oriented distal to the nitrile moiety.

Comment

The intramolecular cyclization of dithiane anions has been used to assemble rapidly cyclopentyl ketones (Grotjahn & Andersen, 1981) and alcohols (Davey & Taylor, 1987), but is complicated by the competitive reaction of the base with the cyclization precursor. To demonstrate the superiority of the nitrile group for these cyclizations, we prepared the title compound, (I), from 1-[3-(1,3-dithian-2-yl)propyl]-3-cyano-1,4,5,6-tetrahydropyridine by treatment with *n*-butyllithium. A mixture of octahydroquinolizine epimers was obtained, from which the title compound was separated by selective extraction and crystallization.



(I)

The X-ray structure is similar to that of the 1-azabicyclo[4.4.0]decane borine adduct that has been described recently (Tham & White, 1994). In the two cases the octahydroquinolizine rings adopt chair conformations typical of these alkaloids. The metrical parameters of the rings are quite similar, except at the points of substitution (C2, C9 and N2 in the present structure); at these positions the distances are longer in the substituted case. Thus, the average distances for C2—C3 and C8—C9 [1.535 (4) Å] and for C2—C10 and C9—C10 [1.550 (4) Å] in the present structure

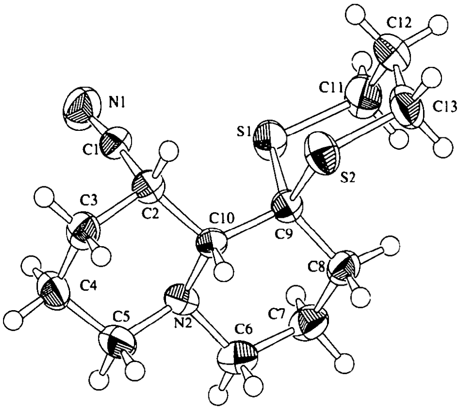


Fig. 1. Perspective drawing of the title compound with displacement ellipsoids drawn at the 50% probability level.

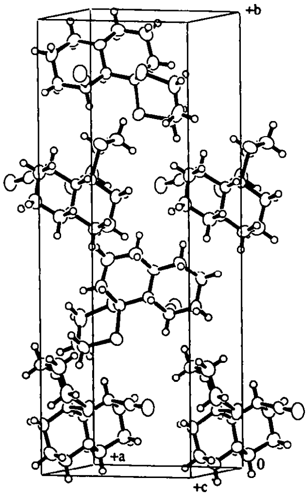


Fig. 2. Packing diagram of the title compound with displacement ellipsoids drawn at the 50% probability level.

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are somewhat longer than the corresponding distances [1.517 (2) and 1.5151 (13) Å, respectively] in the 1-azabicyclo[4.4.0]decane borine adduct (Tham & White, 1994). In contrast, the distances about the N atom are distinctly different: 1.472 (4) Å (the average for N2—C5 and N2—C6) and 1.466 (3) Å for the present structure and 1.5048 (12) and 1.525 (2) Å, respectively, for the 1-azabicyclo[4.4.0]decane borine adduct (Tham & White, 1994). A similar lengthening of the C—N bonds upon forming a borine adduct was observed for the hexamethylenetetramine borine adduct (Hanic & Šubrtová, 1969) relative to hexamethylenetetramine (Becka & Cruickshank, 1963) with C—N distances of 1.527 (5) and 1.478 (1) Å, respectively.

Not surprisingly, the dithiane moiety exists in a regular chair conformation distal to the nitrile group.

Experimental

To a THF solution of 1-[3-(1,3-dithian-2-yl)propyl]-3-cyano-1,4,5,6-tetrahydropyridine at room temperature was added a hexane solution of *n*-butyllithium (1.4 equivalents). After 30 min neat 12-crown-4 was added and the resultant mixture was allowed to react overnight. Saturated aqueous ammonium chloride was added and the aqueous phase was extracted with an ethyl acetate/hexane solvent mixture (3:7). Concentration of the extracts afforded the racemic quinolizine as an oil (47% yield) that slowly crystallized to provide a crystal of the title compound, (I), suitable for X-ray diffraction. A minor isomer was isolated as an oil (21%) and was shown by ^{1}H NMR to be epimeric at the nitrile C atom (C2).

Crystal data

$C_{13}H_{20}N_2S_2$
$M_r = 268.43$
Orthorhombic
$P2_12_12_1$
$a = 8.366\ (1)$ Å
$b = 23.193\ (2)$ Å
$c = 6.854\ (1)$ Å
$V = 1330.0\ (3)$ Å^3
$Z = 4$
$D_x = 1.340$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 15.0$–$20.4°$
$\mu = 0.365$ mm^{-1}
$T = 294.2$ K
Rectangular prism
0.70 × 0.50 × 0.20 mm
Light yellow

Data collection

AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*TEXSAN*: Molecular Structure Corporation, 1985)
$T_{\min} = 0.905$, $T_{\max} = 0.995$
1801 measured reflections
1801 independent reflections

1469 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 30$
$l = 0 \rightarrow 8$
3 standard reflections monitored every 150 reflections
intensity decay: 0.68%

Refinement

Refinement on *F*
$R = 0.0316$
$wR = 0.0278$
$S = 1.646$
1469 reflections
155 parameters
H-atom parameters not refined
$w = 4F^2/\sigma^2(F^2)$
$(\Delta/\sigma)_{\max} = 0.005$

$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: 5.76226
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)*

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

	x	*y*	*z*	$U_{\rm eq}$
S1	−0.02476 (9)	−0.37730 (4)	−0.5302 (1)	0.0452 (2)
S2	−0.11465 (10)	−0.29252 (3)	−0.8465 (1)	0.0472 (2)
N1	0.3801 (3)	−0.3723 (1)	−0.5487 (4)	0.0549 (8)
N2	0.1125 (3)	−0.44508 (9)	−0.9235 (3)	0.0348 (6)
C1	0.3046 (3)	−0.3631 (1)	−0.6839 (4)	0.0376 (8)
C2	0.2303 (3)	−0.3489 (1)	−0.8729 (4)	0.0344 (7)
C3	0.3569 (3)	−0.3608 (1)	−1.0302 (4)	0.0429 (8)
C4	0.3908 (4)	−0.4248 (1)	−1.0397 (5)	0.0466 (9)
C5	0.2366 (4)	−0.4576 (1)	−1.0713 (5)	0.0458 (9)
C6	−0.0271 (4)	−0.4797 (1)	−0.9767 (5)	0.0458 (9)
C7	−0.1671 (4)	−0.4694 (1)	−0.8436 (5)	0.0482 (9)
C8	−0.2133 (3)	−0.4065 (1)	−0.8471 (5)	0.0401 (8)
C9	−0.0713 (3)	−0.3682 (1)	−0.7904 (4)	0.0318 (7)
C10	0.0768 (3)	−0.3832 (1)	−0.9180 (4)	0.0311 (7)
C11	−0.2047 (4)	−0.3484 (2)	−0.4201 (5)	0.055 (1)
C12	−0.2412 (4)	−0.2867 (2)	−0.4690 (6)	0.063 (1)
C13	−0.2799 (4)	−0.2772 (1)	−0.6827 (6)	0.054 (1)

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

S1—C9	1.838 (3)	C2—C10	1.543 (4)
S1—C11	1.813 (3)	C3—C4	1.512 (4)
S2—C9	1.833 (3)	C4—C5	1.513 (4)
S2—C13	1.816 (3)	C6—C7	1.504 (4)
N1—C1	1.142 (4)	C7—C8	1.510 (4)
N2—C5	1.480 (4)	C8—C9	1.534 (4)
N2—C6	1.463 (3)	C9—C10	1.556 (4)
N2—C10	1.466 (3)	C11—C12	1.502 (5)
C1—C2	1.474 (4)	C12—C13	1.517 (5)
C2—C3	1.536 (4)		
C9—S1—C11	100.7 (1)	C7—C8—C9	110.9 (2)
C9—S2—C13	102.0 (1)	S1—C9—S2	110.8 (1)
C5—N2—C6	106.4 (2)	S1—C9—C8	110.1 (2)
C5—N2—C10	110.6 (2)	S1—C9—C10	110.5 (2)
C6—N2—C10	112.3 (2)	S2—C9—C8	110.4 (2)
N1—C1—C2	171.3 (3)	S2—C9—C10	104.7 (2)
C1—C2—C3	106.6 (2)	C8—C9—C10	110.2 (2)
C1—C2—C10	114.3 (2)	N2—C10—C2	109.9 (2)
C3—C2—C10	109.9 (2)	N2—C10—C9	113.3 (2)
C2—C3—C4	109.6 (2)	C2—C10—C9	115.7 (2)
C3—C4—C5	109.9 (2)	S1—C11—C12	115.4 (2)
N2—C5—C4	113.6 (2)	C11—C12—C13	113.4 (3)
N2—C6—C7	112.5 (2)	S2—C13—C12	114.0 (2)
C6—C7—C8	110.1 (3)		

The structure determination was routine. In the weighting scheme, $\sigma^2(F^2) = S^2(C + R^2B) + (0.040F^2)^2/\mathrm{Lp}^2$, where S = scan rate, C = total integrated peak count, R = ratio of scan to background counting times, B = total background count, Lp = Lorentz–polarization factor. The absolute configuration was determined by inversion of the structure and subsequent refinement to convergence. The current structure has a slightly lower R value than the inverted structure ($R = 0.0323$, $wR = 0.0288$).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SIR*93 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Synthesis and Relative Configuration of (±)-(1α,2β,3β,4α)-1,2,3,4-Cyclopentanetetrol 1-Acetate

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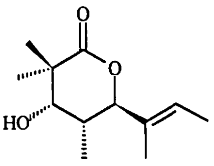
Abstract

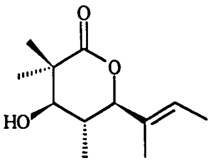
The title compound (alternative IUPAC name: 2,3,4-trihydroxycyclopentyl acetate, $C_7H_{12}O_5$) is a precursor in the reaction pathway of the synthesis of helicascolides. The cyclopentane ring adopts a twist conformation with the two hydroxy groups in β positions. The molecules are linked by a network of hydrogen bonds.

Comment

Helicascolides A, (1), and B, (2), are two isomeric δ-lactones isolated from the Hawaiian mangrove ascomycete *Heliscascus kanaloanus* (Poch & Gloer, 1989), a marine fungus. Metabolites with these kinds of structures have, to the best of our knowledge, never been obtained from terrestrial fungi. Marine microorganisms are therefore a promising source of new potentially bioactive substances (Kobayashi & Ishibashi, 1993).

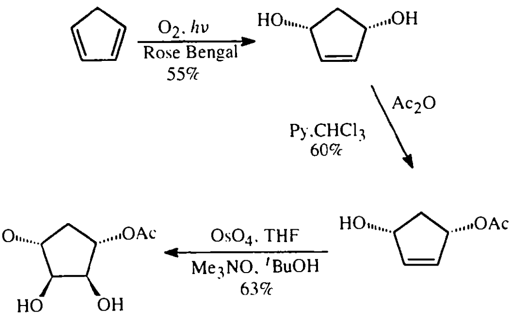


(1)



(2)

The title compound, (3), is a precursor in the reaction pathway to the synthesis of heliscacolides A and B. As shown in the reaction scheme below, (3) was obtained stereoselectively from cyclopentadiene. The enantioselective synthesis of (3), obtained as a clear unstable oil, has been described by Deardorff, Shambayati, Myles & Heerding (1988). In order to determine unambiguously its molecular conformation, which will be of aid in the prediction of the steric course of subsequent reactions, a crystal structure determination was undertaken.



(3)

As shown in Fig. 1, only the compound with two hydroxy groups in β positions was obtained. This result may be ascribed to steric effects due to the voluminous intermediate osmate ester. The cyclopentane ring is in a ^3_4T conformation as shown by the Cremer & Pople (1975) puckering parameters, q_2 = 0.421 (3) Å, Φ_2 = 91.7 (4)°. The molecules are linked by a network of hydrogen bonds: $O1\cdots O3^{i}$ = 2.691 (2), $HO1\cdots O3^{i}$ = 1.83 (4) Å, $O1—HO1\cdots O3^{i}$ = 173 (3)°; $O2\cdots O1^{ii}$ = 2.694 (2), $HO2\cdots O1^{ii}$ = 1.89 (4) Å, $O2—HO2\cdots O1^{ii}$ = 178 (3)°; $O3\cdots O2^{iii}$ = 2.708 (3), $HO3\cdots O2^{iii}$ = 1.88 (4) Å, $O3—HO3\cdots O2^{i}$ = 171 (3)° [symmetry codes: (i) $x - 1, y, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (iii) $\frac{1}{2} + x, y, \frac{1}{2} - z$].

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