

C(14)	-0.0516 (2)	0.2092 (2)	0.6007 (2)	0.045 (1)
C(15)	0.1159 (2)	0.1696 (2)	0.0940 (2)	0.055 (1)
C(16)	-0.1593 (2)	0.1691 (2)	0.5565 (2)	0.056 (1)
C(17)	0.0452 (2)	0.2111 (2)	-0.0227 (2)	0.060 (1)
C(18)	-0.2709 (2)	0.2110 (2)	0.5099 (2)	0.064 (2)
C(19)	-0.0664 (2)	0.1690 (2)	-0.0690 (2)	0.061 (2)
C(20)	-0.3414 (2)	0.1692 (2)	0.3936 (3)	0.063 (2)
C(21)	-0.1735 (2)	0.2091 (2)	-0.1143 (2)	0.055 (1)
C(22)	-0.4097 (2)	0.2089 (2)	0.2829 (3)	0.059 (1)
C(23)	-0.2837 (2)	0.1836 (2)	-0.0749 (2)	0.050 (1)
C(24)	-0.4129 (2)	0.1835 (2)	0.1423 (2)	0.050 (1)
C(25)	-0.3519 (3)	1/4	-0.0511 (3)	0.046 (2)
C(26)	-0.4152 (3)	1/4	0.0564 (3)	0.047 (2)
C(27)	0.1246 (2)	0.1206 (1)	0.3710 (2)	0.040 (1)
C(28)	0.0579 (2)	0.1204 (1)	0.4835 (2)	0.040 (1)
C(29)	0.0527 (2)	0.0799 (1)	0.2540 (3)	0.050 (1)
C(30)	-0.0546 (2)	0.0797 (1)	0.4344 (3)	0.052 (1)
C(31)	0.0499 (2)	0.1033 (2)	0.1185 (3)	0.056 (2)
C(32)	-0.1600 (2)	0.1031 (2)	0.4725 (3)	0.058 (2)
C(33)	-0.0639 (2)	0.1029 (2)	0.0168 (3)	0.061 (2)
C(34)	-0.2739 (2)	0.1029 (2)	0.3697 (3)	0.061 (2)
C(35)	-0.1684 (2)	0.0787 (2)	0.0555 (3)	0.058 (2)
C(36)	-0.2755 (2)	0.0788 (2)	0.2359 (3)	0.059 (2)
C(37)	-0.2809 (2)	0.1201 (2)	0.0082 (3)	0.053 (1)
C(38)	-0.3469 (2)	0.1200 (2)	0.1198 (3)	0.053 (1)
C(39)	-0.0570 (2)	0.0546 (1)	0.2941 (3)	0.056 (2)
C(40)	-0.1654 (3)	0.0539 (2)	0.1964 (3)	0.060 (2)

Table 2. Selected geometric parameters (Å, °)

C(8)—C(9)	1.514 (4)	C(18)—C(18')	1.374 (5)
C(8)—C(10)	1.516 (4)	C(21)—C(21')	1.440 (5)
C(9)—C(10)	1.635 (4)	C(25)—C(26)	1.396 (5)
C(13)—C(13')	1.438 (4)	C(39)—C(40)	1.395 (4)
C(17)—C(17')	1.370 (5)		
C(5)—C(8)—C(5')	112.1 (2)	C(8)—C(9)—C(10)	57.4 (2)
C(9)—C(8)—C(10)	65.3 (2)	C(8)—C(10)—C(9)	57.3 (2)
C(3)—C(4)—C(5)—C(8)	-173.1 (4)	C(8)—C(5)—C(6)—C(7)	172.5 (4)

Data collection: MAC Science MXC software. Cell refinement: MAC Science MXC software. Data reduction: MAC Science MXC software. Program(s) used to solve structure: *SIR* (Altomare *et al.*, 1994) in *CRYSTAN-GM* (Edwards, Gilmore, Mackay & Stewart, 1995). Program(s) used to refine structure: *LSQ* (Mallinson & Muir, 1985) in *CRYSTAN-GM*. Molecular graphics: *ORTEP* (Johnson, 1965) in *CRYSTAN-GM*. Software used to prepare material for publication: *CRYSTAN-GM*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1208). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1010–1012

3-Cyano-1-[4-(1,3-dithian-2-yl)butyl]-1,4,5,6-tetrahydropyridine

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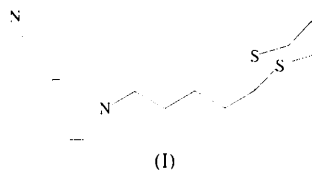
Abstract

The title nitrile {1-[4-(1,3-dithian-2-yl)butyl]-1,4,5,6-tetrahydropyridine-3-carbonitrile, C₁₄H₂₂N₂S₂} was prepared as part of our investigations into the conjugate addition reactions of unsaturated nitriles [Fleming & Pak (1995). *J. Org. Chem.* **60**, 4299–4301]. The tetrahydropyridine ring adopts a half-chair conformation and is appended by a four-carbon chain to the dithiane ring which adopts a chair conformation.

Comment

Conjugate addition to unsaturated nitriles is often problematic with conventional nucleophiles (Lipshutz, Wilhelm & Kozlowski, 1984; House & Umen, 1973). We sought to promote the conjugate addition reaction by tethering a nucleophilic dithiane anion to an unsaturated nitrile and therefore prepared the title compound, (I), as a suitable substrate for this reaction. (I) is readily prepared by coupling 3-cyanotetrahydropyridine (Kikugawa, Kuramoto, Saito & Yamada, 1973) with 2-(4-chlorobutyl)-1,3-dithiane (Seebach, Jones & Corey, 1968). Concentration of the crude reaction mix-

ture followed by recrystallization provided long needle-like crystals from which a single crystal was removed for X-ray analysis and cut down to size.



The structure consists of a dithiane ring linked through a tetramethylene chain to a 3-cyanotetrahydropyridine ring. The tetrahydropyridine ring system is similar to that of a related dithianyl containing dihydroquinolone (Beddoes, Griera, Alvarez & Joule, 1992). In both cases the planar N—C=C unit flattens the six-membered ring so that it exists in a half-chair conformation as is commonly found in cyclohexenes (Guiseppe, Tadini & Bettinetti, 1992). The N1—C2 bond [1.334 (4) Å] is significantly shorter than the N1—C6 bond [1.459 (4) Å], indicative of conjugation between the N atom and the olefin, and correlates well with the bond lengths found in the dihydroquinoline (Beddoes *et al.*, 1992) given the differences due to the benzene ring [1.383 (3) Å and 1.450 (3) Å for the corresponding N—C bond lengths, respectively].

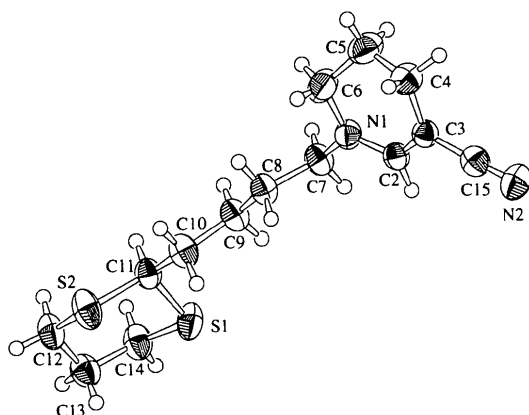


Fig. 1. A perspective drawing of the title compound with displacement ellipsoids drawn at the 50% probability level.

The tether connecting the tetrahydropyridine and the dithiane ring adopts a zigzag conformation found in other alkyl-substituted dithianes (Miyake, Haramoto & Kamogawa, 1994). The dithiane ring exists in the chair conformation with the methylene tether in an equatorial orientation, typical of this functionality (Miyake *et al.*, 1994). The C11—S1 and C11—S2 bonds [1.813 (3) Å and 1.815 (3) Å, respectively] are typical of the range exhibited by the dithianes already mentioned [1.832 (2) and 1.820 (2) Å (Miyake *et al.*, 1994); 1.803 (4) and 1.800 (5) Å (Beddoes *et al.*, 1992)] and a spirocyclic dithianyl quinolizine that we have recently reported

[1.838 (3) and 1.833 (3) Å (Hussain, Fleming, Norman & Chang, 1996)].

Experimental

A dimethylformamide (DMF) solution of 3-cyanotetrahydropyridine (1 equivalent) was added to a room-temperature suspension of potassium hydride (1.2 equivalents) in DMF. The resultant solution was stirred for 0.5 h and then a DMF solution of 2-(4-chlorobutyl)-1,3-dithiane was added. After 2 h, saturated aqueous ammonium chloride was added and the aqueous phase was extracted with ethyl acetate. Concentration of the extracts afforded a white solid that was recrystallized from hexanes to afford the title compound, (I), in 72% yield.

Crystal data

C₁₄H₂₂N₂S₂

M_r = 282.46

Monoclinic

*C*2/*c*

a = 27.253 (3) Å

b = 6.701 (5) Å

c = 19.306 (3) Å

β = 119.782 (9)°

V = 3060 (2) Å³

Z = 8

D_x = 1.226 Mg m⁻³

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 13.73–19.09°

μ = 0.334 mm⁻¹

T = 294.2 K

Plate

0.90 × 0.40 × 0.04 mm

Colorless

Data collection

AFC-7R diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (Molecular

Structure Corporation,

1985)

T_{min} = 0.929, *T_{max}* =

0.999

3896 measured reflections

3813 independent reflections

2083 observed reflections

[*I* > 3σ(*I*)]

R_{int} = 0.098

θ_{\max} = 27.5°

h = 0 → 35

k = 0 → 8

l = -25 → 21

3 standard reflections

monitored every 150

reflections

intensity decay: 2.37%

Refinement

Refinement on *F*

R = 0.0474

wR = 0.0578

S = 1.868

2083 reflections

163 parameters

H-atom parameters not

refined

w = 4*F*²/σ²(*F*²)

(Δ/σ)_{max} = 0.013

$\Delta\rho_{\max}$ = 0.23 e Å⁻³

$\Delta\rho_{\min}$ = -0.40 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
S1	0.08121 (3)	0.1802 (1)	0.72537 (5)	0.0603 (3)
S2	0.14705 (4)	0.2886 (1)	0.64337 (5)	0.0646 (3)
N1	-0.10191 (9)	0.9697 (4)	0.5635 (1)	0.0485 (7)
N2	-0.3006 (1)	0.9199 (5)	0.3867 (2)	0.0650 (9)

C2	-0.1568 (1)	0.9195 (4)	0.5209 (2)	0.0436 (8)
C3	-0.1975 (1)	1.0409 (4)	0.4673 (2)	0.0432 (8)
C4	-0.1845 (1)	1.2508 (5)	0.4538 (2)	0.0577 (9)
C5	-0.1281 (1)	1.3149 (5)	0.5222 (2)	0.070 (1)
C6	-0.0842 (1)	1.1604 (5)	0.5466 (2)	0.068 (1)
C7	-0.0597 (1)	0.8361 (5)	0.6219 (2)	0.0513 (9)
C8	-0.0199 (1)	0.7488 (5)	0.5959 (2)	0.0500 (9)
C9	0.0240 (1)	0.6110 (5)	0.6587 (2)	0.0519 (9)
C10	0.0593 (1)	0.5060 (5)	0.6287 (2)	0.0524 (9)
C11	0.1080 (1)	0.3807 (4)	0.6904 (2)	0.0465 (8)
C12	0.2022 (1)	0.1500 (5)	0.7251 (2)	0.059 (1)
C13	0.1809 (1)	-0.0169 (5)	0.7557 (2)	0.059 (1)
C14	0.1466 (1)	0.0576 (5)	0.7931 (2)	0.0585 (10)
C15	-0.2542 (1)	0.9695 (5)	0.4237 (2)	0.0494 (9)

Miyake, M., Haramoto, Y. & Kamogawa, H. (1994). *Acta Cryst.* **C50**, 805–807.
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Table 2. Selected geometric parameters (Å, °)

S1—C11	1.813 (3)	N1—C2	1.344 (4)
S1—C14	1.802 (3)	N1—C6	1.459 (4)
S2—C11	1.815 (3)	N1—C7	1.452 (4)
S2—C12	1.804 (3)	N2—C15	1.150 (4)
C11—S1—C14	99.9 (1)	N1—C7—C8	113.7 (2)
C11—S2—C12	100.3 (1)	S1—C11—S2	112.3 (2)
C2—N1—C6	118.3 (3)	S1—C11—C10	110.1 (2)
C2—N1—C7	122.2 (3)	S2—C11—C10	107.2 (2)
C6—N1—C7	119.4 (2)	S2—C12—C13	114.1 (2)
N1—C2—C3	124.1 (3)	S1—C14—C13	115.1 (2)
N1—C6—C5	112.4 (3)	N2—C15—C3	176.9 (3)

H atoms were placed in calculated positions. In the weighting scheme, $\sigma^2(F^2) = S^2(C + R^2B) + (0.030F^2)/Lp^2$, where S = scan rate, C = total integrated peak count, R = ratio of scan to background counting times, B = total background count, and Lp = Lorentz-polarization factor.

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: *SAP191* (Fan, 1991). 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: VJ1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Cyanomethyl-6,7,8-trioxabicyclo[3.2.1]-octane

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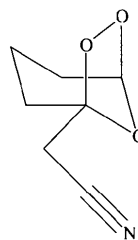
(Received 10 July 1995; accepted 3 October 1995)

Abstract

The title nitrile (6,7,8-trioxabicyclo[3.2.1]octane-1-acetonitrile, C₇H₉NO₃) was prepared by ozonolysis of cyclopentenylacetonitrile. Crystals of the compound display typical metric parameters.

Comment

Ozonolysis of substituted cyclopentenes is known to generate primary ozonides that regioselectively fragment to the corresponding bicyclic ozonides (Bunnelle & Lee, 1992). Most of these bicyclic trioxanes have been analyzed by NMR and only a few have afforded crystals suitable for X-ray crystallography (Bunnelle, Isbell, Barnes & Qualls, 1991). During our studies on the reactivity of unsaturated nitriles (Fleming & Huang, unpublished results), we prepared the title compound, (I), by ozonolysis of cyclopentenylacetonitrile.



(I)