N(1)—C(7)	1.459 (4)	N(2)—C(6)	1.484 (4)
N(2)—C(12)	1.479 (4)	C(1)—C(2)	1.508 (5)
C(1)—C(6)	1.519 (5)	C(2)—C(3)	1.521 (5)
C(3)—C(4)	1.520 (6)	C(4)—C(5)	1.529 (5)
C(5)—C(6)	1.516 (5)	C(7)—C(8)	1.550 (5)
C(8)—C(9)	1.510 (7)	C(8)—C(10)	1.522 (5)
C(8)—C(11)	1.517 (6)	C(12)—C(13)	1.535 (5)
C(13)—C(14)	1.503 (7)	C(13)—C(15)	1.508 (7)
C(13)—C(16)	1.486 (6)	C(17)—C(20)	1.504 (5)
C(18)—C(19)	1.488 (6)	C(20)—C(21)	1.542 (5)
C(21)—C(22)	1.491 (6)	C(21)—C(23)	1.514 (7)
O(1)—P—N(1)	118.9 (1)	O(1)—P—N(2)	118.3 (1)
N(1)—P—N(2)	95.1 (1)	O(1)—P—C(17)	105.7 (1)
N(1)—P—C(17)	109.0 (1)	N(2)—P—C(17)	109.2 (1)
C(17)—O(2)—C(18)	118.6 (3)	P—N(1)—C(1)	112.0 (2)
P—N(1)—C(7)	123.2 (2)	C(1)—N(1)—C(7)	123.2 (2)
P—N(2)—C(6)	107.8 (2)	P—N(2)—C(12)	120.4 (2)
C(6)—N(2)—C(12)	117.3 (3)	N(1)—C(1)—C(2)	118.0 (3)
N(1)—C(1)—C(6)	104.8 (3)	C(2)—C(1)—C(6)	109.4 (3)
C(1)—C(2)—C(3)	107.9 (3)	C(2)—C(3)—C(4)	112.5 (3)
C(3)—C(4)—C(5)	113.0 (3)	C(4)—C(5)—C(6)	107.9 (3)
N(2)—C(6)—C(1)	104.8 (3)	N(2)—C(6)—C(5)	118.5 (3)
C(1)—C(6)—C(5)	109.6 (3)	N(1)—C(7)—C(8)	120.1 (3)
C(7)—C(8)—C(9)	110.2 (3)	C(7)—C(8)—C(10)	112.8 (3)
C(9)—C(8)—C(10)	109.9 (4)	C(7)—C(8)—C(11)	105.4 (3)
C(9)—C(8)—C(11)	110.8 (4)	C(10)—C(8)—C(11)	107.7 (4)
N(2)—C(12)—C(13)	115.7 (3)	C(12)—C(13)—C(14)	107.2 (4)
C(12)—C(13)—C(15)	111.4 (3)	C(14)—C(13)—C(15)	106.3 (4)
C(12)—C(13)—C(16)	111.7 (3)	C(14)—C(13)—C(16)	110.9 (4)
C(15)—C(13)—C(16)	109.2 (4)	P—C(17)—O(2)	108.6 (2)
P—C(17)—C(20)	113.1 (2)	O(2)—C(17)—C(20)	109.4 (3)
O(2)—C(18)—O(3)	123.0 (4)	O(2)—C(18)—C(19)	109.7 (4)
O(3)—C(18)—C(19)	127.3 (4)	C(17)—C(20)—C(21)	116.2 (3)
C(20)—C(21)—C(22)	113.0 (3)	C(20)—C(21)—C(23)	109.2 (3)
C(22)—C(21)—C(23)	109.1 (4)		

SHELXTL-Plus (Sheldrick, 1991) was used for data reduction, structure solution and refinement. The structure was solved by direct methods. Full-matrix least-squares refinement was carried out minimizing $w(F_o-F_c)^2$. All non-H atoms were refined anisotropically to convergence. H atoms except those on assymmetric C atoms were included in their calculated positions. Atoms H(1), H(6) and H(17) were refined isotropically. Roger's (1981) η test was used [η = 1.2 (3)] for absolute-structure determination.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HU1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,4,6-Trihexyl-1,3,5-trithiane

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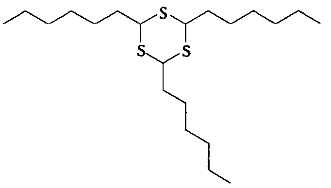
Abstract

The crystal structure of the title compound, $C_{21}H_{42}S_3$, comprises two independent pseudo-enantiomeric molecules, related by an approximate *n*-glide plane operation perpendicular to the *b* axis followed by a rotation of 4.2 (1)° about the *b*-axis direction. This slight but significant deviation from space group $P2_1/n$ to the non-centrosymmetric space group $P2_1$ avoids unrealistically short van der Waals contacts in the chain packing. The trithiane rings have chair conformations.

Comment

Ethylene-bridged cyclic polysulfides are flexible and are often found to possess a *trans* orientation of the S atoms (Cooper & Rawle, 1990). In contrast, methylene-based derivatives exhibit greater rigidity (Edema, Hoogenraad, Kellogg, Kooijman & Spek, 1993) and are often arranged in a crown-type configuration (Edema, Buter, van Bolhuis, Meetsma, Kellogg, Kooijman & Spek, 1993). Trithianes all have three *cis*-oriented S atoms and this rigidity prevents them 'wrapping around' a metal ion and is the cause of their poor solubility in organic solvents (Edema, Hoogenraad, Schoonbeek, Kellogg, Kooijman & Spek, 1993). In order to overcome this problem, we have alkylated 1,3,5-trithiane using various alkyl halides with the aim of increasing the solubility. We report here the crystal structure of the trihexyl derivative (I).



(I)

The monoclinic unit cell contains two crystallographically independent molecules of the title compound (Fig. 1) with enantiomeric conformations. They are related (*i.e.* molecules designated 1555.01 and 1555.02 in Fig. 2) by a combination of a pseudo *n*-glide and a small rotation [quaternion fit: Mackay (1984) as implemented in *PLATON* (Spek, 1990)] of 4.2 (1)° about the *b* axis. The structure probably deviates from exact $P2_1/n$ symmetry for packing reasons (see *Experimental*). The trithiane ring has a chair conformation which is also found for the unsubstituted 1,3,5-trithiane molecule (Edema, Buter, van Bolhuis, Meetsma, Kellogg, Kooijman & Spek, 1993).

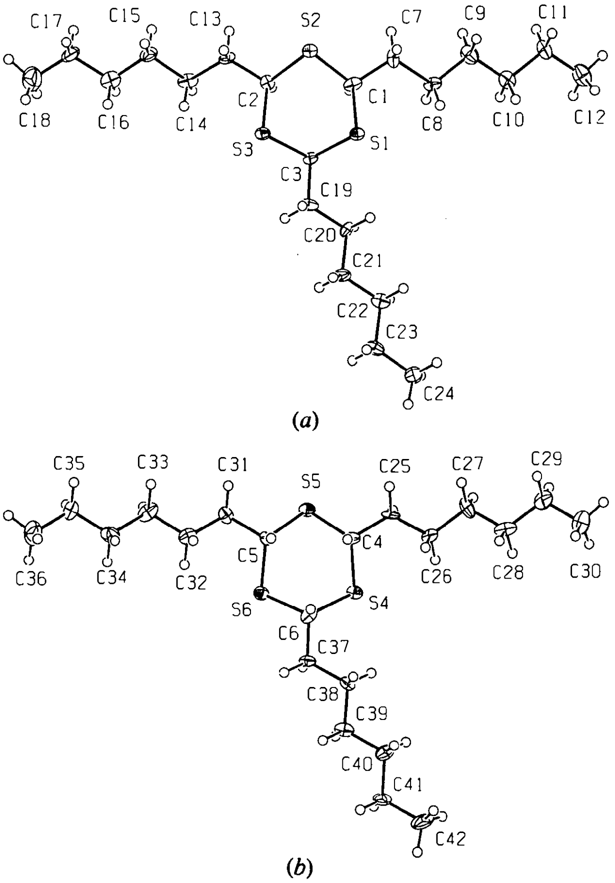


Fig. 1. Displacement ellipsoid plot (50% probability level) of the two independent 2,4,6-trihexyl-1,3,5-trithiane molecules.

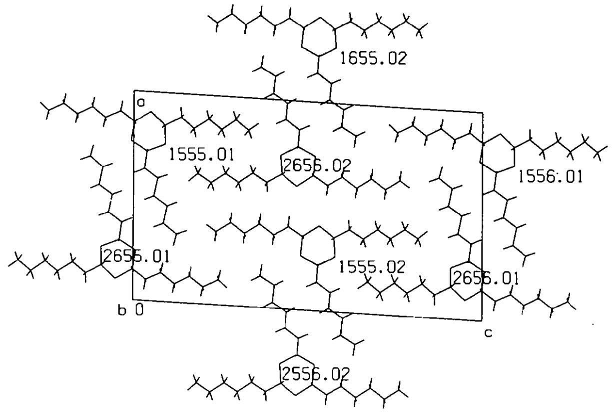


Fig. 2. Projection of the structure down the *b* axis with symmetry codes *sklm.n* (where *s* is the symmetry operation number, *klm* is the translation code and *n* is the number of the residue) illustrating the packing and pseudo symmetry.

Experimental

The title compound was obtained by alkylation of 1,3,5-trithiane. Crystals were obtained by slow evaporation of a solution of the title compound in a mixture of CH_2Cl_2, $CHCl_3$ and CH_3CN.

Crystal data

$C_{21}H_{42}S_3$
$M_r = 390.76$
Monoclinic
$P2_1$
$a = 18.0105\ (12)$ Å
$b = 4.2413\ (3)$ Å
$c = 30.660\ (2)$ Å
$\beta = 93.297\ (5)°$
$V = 2338.2\ (3)$ Å^3
$Z = 4$
$D_x = 1.110$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.1\text{–}15.3°$
$\mu = 0.31$ mm^{-1}
$T = 150$ K
Transparent
0.38 × 0.12 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 Turbo diffractometer
$\omega/2\theta$ scans [$\Delta\omega = (0.82 + 0.35\tan\theta)°$]
Absorption correction: none
9710 measured reflections
4697 independent reflections
2159 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.11$
$\theta_{\rm max} = 25°$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 5$
$l = -35 \rightarrow 35$
3 standard reflections
frequency: 60 min
intensity variation: 3.5%

Refinement

Refinement on F^2
$R(F) = 0.0694$
$wR(F^2) = 0.1768$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.527$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.532$ e Å^{-3}

$S = 0.921$
4684 reflections
438 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

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)

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

	x	y	z	$U_{\rm eq}$
S1	0.75473 (14)	0.5898 (7)	0.09109 (8)	0.0201 (9)
S2	0.90439 (14)	0.5527 (8)	0.05012 (8)	0.0218 (10)
S3	0.76251 (13)	0.5886 (8)	−0.00764 (8)	0.0211 (10)
C1	0.8447 (5)	0.408 (3)	0.0907 (3)	0.023 (4)
C2	0.8540 (5)	0.418 (3)	0.0018 (3)	0.019 (3)
C3	0.7164 (5)	0.443 (3)	0.0395 (3)	0.017 (3)
C7	0.8867 (6)	0.440 (3)	0.1356 (3)	0.027 (4)
C8	0.8402 (5)	0.308 (3)	0.1737 (3)	0.024 (3)
C9	0.8888 (6)	0.252 (3)	0.2151 (3)	0.033 (4)
C10	0.8435 (6)	0.129 (3)	0.2514 (3)	0.026 (3)
C11	0.8937 (6)	0.048 (4)	0.2930 (3)	0.031 (4)
C12	0.8484 (6)	−0.086 (3)	0.3292 (4)	0.040 (4)
C13	0.8992 (5)	0.478 (3)	−0.0377 (3)	0.020 (3)
C14	0.8636 (6)	0.377 (3)	−0.0813 (3)	0.025 (4)
C15	0.9120 (6)	0.412 (3)	−0.1198 (3)	0.028 (4)
C16	0.8717 (6)	0.318 (3)	−0.1623 (3)	0.032 (4)
C17	0.9189 (5)	0.338 (4)	−0.2017 (3)	0.041 (5)
C18	0.8798 (7)	0.252 (5)	−0.2445 (4)	0.061 (6)
C19	0.6328 (5)	0.528 (3)	0.0330 (3)	0.025 (4)
C20	0.5869 (5)	0.445 (3)	0.0700 (3)	0.020 (3)
C21	0.5041 (5)	0.515 (3)	0.0606 (3)	0.029 (4)
C22	0.4570 (5)	0.448 (3)	0.0983 (3)	0.026 (4)
C23	0.3740 (5)	0.525 (3)	0.0882 (3)	0.025 (4)
C24	0.3252 (6)	0.458 (3)	0.1252 (3)	0.030 (4)
S4	0.26409 (14)	−0.2133 (8)	0.57866 (8)	0.0209 (10)
S5	0.40816 (14)	−0.1805 (7)	0.53217 (9)	0.0228 (11)
S6	0.26010 (13)	−0.2222 (8)	0.47960 (8)	0.0214 (11)
C4	0.3545 (5)	−0.021 (3)	0.5753 (3)	0.023 (4)
C5	0.3518 (5)	−0.040 (3)	0.4853 (3)	0.016 (3)
C6	0.2179 (5)	−0.076 (3)	0.5273 (3)	0.023 (4)
C25	0.3977 (5)	−0.043 (3)	0.6188 (3)	0.022 (3)
C26	0.3585 (5)	0.064 (3)	0.6577 (3)	0.019 (3)
C27	0.4071 (6)	0.120 (3)	0.6987 (3)	0.028 (4)
C28	0.3668 (6)	0.245 (3)	0.7365 (4)	0.033 (4)
C29	0.4166 (6)	0.319 (4)	0.7773 (3)	0.037 (4)
C30	0.3746 (7)	0.434 (3)	0.8150 (4)	0.045 (5)
C31	0.3942 (6)	−0.108 (3)	0.4448 (3)	0.025 (4)
C32	0.3522 (6)	−0.006 (3)	0.4021 (3)	0.027 (4)
C33	0.3949 (6)	−0.045 (3)	0.3613 (3)	0.032 (4)
C34	0.3514 (5)	0.040 (3)	0.3192 (3)	0.032 (4)
C35	0.3943 (6)	0.007 (3)	0.2791 (3)	0.034 (4)
C36	0.3498 (6)	0.097 (5)	0.2367 (3)	0.056 (5)
C37	0.1366 (5)	−0.166 (4)	0.5244 (3)	0.024 (4)
C38	0.0941 (5)	−0.058 (3)	0.5644 (3)	0.020 (3)
C39	0.0131 (5)	−0.140 (3)	0.5596 (3)	0.025 (4)
C40	−0.0286 (6)	−0.074 (3)	0.6001 (3)	0.030 (4)
C41	−0.1105 (5)	−0.151 (3)	0.5959 (3)	0.031 (4)
C42	−0.1509 (6)	−0.073 (3)	0.6364 (4)	0.044 (5)

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

S1—C1	1.795 (10)	S4—C4	1.829 (10)
S1—C3	1.800 (10)	S4—C6	1.833 (10)
S2—C1	1.798 (10)	S5—C4	1.813 (10)
S2—C2	1.786 (10)	S5—C5	1.812 (10)
S3—C2	1.808 (10)	S6—C5	1.823 (10)
S3—C3	1.816 (10)	S6—C6	1.797 (10)
C1—S1—C3	98.4 (5)	C4—S4—C6	99.9 (5)
C1—S2—C2	99.7 (5)	C4—S5—C5	99.1 (5)
C2—S3—C3	101.0 (5)	C5—S6—C6	101.5 (5)
S1—C1—S2	115.7 (6)	S4—C4—S5	112.8 (6)
S1—C1—C7	110.7 (7)	S4—C4—C25	109.8 (7)
S2—C1—C7	107.8 (7)	S5—C4—C25	110.6 (7)
S2—C2—S3	114.8 (6)	S5—C5—S6	113.6 (6)
S2—C2—C13	109.7 (7)	S5—C5—C31	107.5 (7)
S3—C2—C13	109.3 (7)	S6—C5—C31	109.6 (7)
S1—C3—S3	114.3 (6)	S4—C6—S6	113.4 (6)
S1—C3—C19	110.7 (7)	S4—C6—C37	111.1 (7)
S3—C3—C19	107.7 (7)	S6—C6—C37	108.6 (7)

X-ray data were collected at 150 K for a crystal glued on top of a Lindemann glass capillary. Observed systematic extinctions ($0k0 = 2n + 1$) are consistent with spacegroups $P2_1$ and $P2_1/m$. The structure refined successfully in the non-centrosymmetric space group $P2_1$. The pseudo symmetry of the structure is clearly illustrated by additional 'exact' ($h00 = 2n + 1$) extinctions and to a much lesser extent by n-glide extinctions [notable exception is the (3,0,12) reflection with $I > 29\sigma(I)$]. The anisotropic displacement parameters, as depicted in Fig. 1, are normal and support a description of the structure in space group $P2_1$. Attempts to solve and refine the structure in space group $P2_1/n$ resulted in 'averaged' structures with many disorder peaks. In addition, the $P2_1/n$ structure can be rejected on the basis of unrealistically short van der Waals contacts involving the sidechain H atoms [*i.e.* H(C5)···H(C15) 1.38 Å]. In the $P2_1$ structure, the two independent molecules avoid such short contacts by a relative rotation of the two molecules by 4.2 (1)°.

All non-H atoms were refined with anisotropic displacement parameters. H atoms were refined with fixed geometry, riding on their carrier atoms, with a fixed isotropic displacement parameter amounting to 1.5 or 1.2 times the value of the equivalent isotropic displacement parameter of their carrier atoms for the methyl and the other H atoms, respectively. The Flack (1983) absolute-configuration parameter refined to zero.

Data collection: locally modified version of *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, and torsion angles have been deposited with the IUCr (Reference: AB1181). 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. (1995). C**51**, 91–93

(3a*S*,3b*R*,6*R*,7a*R*)-2-Benzyl-1,2,3a,3b,4,7a-hexahydro-6-phenyl-3,5-dioxa-2,6a-diazacyclopenta[*a*]pentalen-7-one

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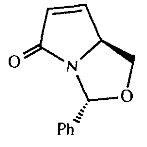
Abstract

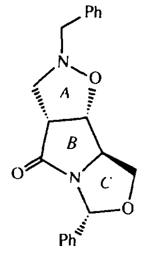
The cycloaddition of *N*-benzylnitrone and the known α,β-unsaturated bicyclic lactam derived from (*S*)-pyroglutaminol and benzaldehyde leads to the tricyclic title compound, $C_{20}H_{20}N_2O_3$. The central ring is nearly planar while the adjacent *cis*-fused rings have envelope conformations.

Comment

Conveniently *N*-protected α,β-unsaturated pyrrolidones can act as good dipolarophiles in the 1,3-dipolar cycloaddition of nitrones. Thus, an adduct was obtained (in 64% isolated yield) through the cycloaddition of *N*-benzylnitrone and the known α,β-unsaturated bicyclic lactam derived from (*S*)-pyroglutaminol and benzaldehyde, (1) (Hanessian & Ratovelomanana, 1990; Hamada, Hara, Kawai, Kohno & Shioiri, 1991; Griffart-Brunet & Langlois, 1994). The regioselectivity generally observed in such cycloadditions (Tufariello, 1984; Carruthers, 1990) and steric considerations support the structure (2). This structure could not be proven easily by ^{1}H NMR owing to the absence of coupling between the adjacent protons H—C3a and H—C3b and the broadening of signals due to relatively slow inversion of the isoxazolidine N atom. Thus, the structure of compound (2) was resolved unambiguously by an X-ray diffraction analysis.



(1)



(2)

The general shape of the molecule is shown in Fig. 1. The ring junction between rings *A* and *B* is *cis*. The oxazolidine ring *A* adopts an envelope conformation with the atom N2 at 0.568 (3) Å from the mean plane of the four other atoms. Ring *B* is nearly planar exhibiting a half-chair conformation. The atom N6a is out of the lactam ring plane [the sum of the three bond angles is 343.5° and the distance of N6a to the plane of the three bonded atoms is 0.336 (2) Å]. The five-membered rings *B* and *C* appear *cis*-fused. Ring *C* exhibits an envelope conformation with atom C3b 0.477 (2) Å out of the mean plane of the four other atoms.

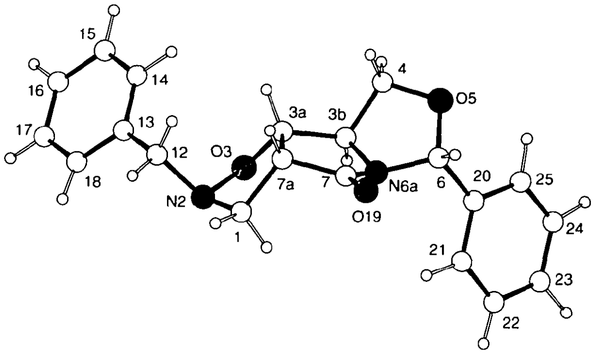


Fig. 1. The structure of compound (2) depicting the general shape of the molecule.

Experimental

Crystal data

$C_{20}H_{20}N_2O_3$
$M_r = 336.39$
Orthorhombic
$P2_12_12_1$
$a = 5.607$ (2) Å
$b = 10.954$ (3) Å
$c = 27.452$ (15) Å
$V = 1686.1$ (11) Å^3
$Z = 4$
$D_x = 1.33$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 11.3$–$24.6°$
$\mu = 0.69$ mm^{-1}
$T = 293$ K
Prism
0.65 × 0.20 × 0.15 mm
Colourless