

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Nakatani, H., Hayashi, H. & Hidaka, T. (1992). *Jpn. J. Appl. Phys.* **31**, 1802–1806.

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2,11-Dithia[3.3]metacyclophane-9-carboxylic Acid *tert*-Butyl Ester

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Abstract

X-ray structure determination of *tert*-butyl 3,11-dithiatricyclo[11.3.1.1^{5,9}]octadeca-1(17),5,7,9(18),13,15-hexaene-17-carboxylate reveals the molecules adopting a *syn* conformation with the sulfur-containing bridging chains in a boat-chair arrangement. The *syn*-orientated arene rings are tilted with respect to each other forming a dihedral angle of 22.9 (2)°.

Comment

The structure determination of the title compound was undertaken within the context of investigations on the synthesis, reactivity and conformation of intra-annular substituted cyclophanes (Vögtle, Grütze, Nätscher, Wieder, Weber & Grün, 1975).

In the solid state, there are four separate molecules per unit cell, each of them adopting a *syn* conformation, as seen in the parent compound 2,11-dithia[3.3]metacyclophane (Anker, Bushnell & Mitchell, 1979).

A dihedral angle of 22.9 (2)° between the arene rings indicates a slightly stronger strain compared with the unsubstituted compound (dihedral angle 20.6°). The methylene C atoms attached to the rings are displaced from the arene-ring planes. The intramolecular S...S distance of 6.37 Å is shorter than

those of the unsubstituted compound (6.97 Å). The other bond lengths and angles are comparable to those of the unsubstituted compound.

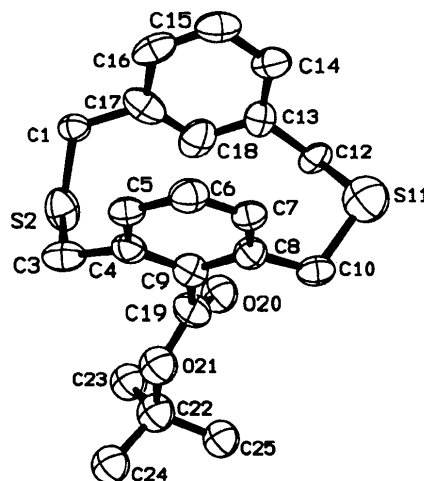


Fig. 1. ORTEP view (Johnson, 1965) of the title compound with thermal ellipsoids shown at the 50% probability level.

Experimental

Crystal data

C₂₁H₂₄O₂S₂

M_r = 372.54

Monoclinic

*P*2₁/*a*

a = 13.317 (5) Å

b = 7.624 (1) Å

c = 19.965 (8) Å

β = 104.15 (2)°

V = 1965.4 (8) Å³

Z = 4

D_x = 1.26 Mg m⁻³

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 15–18°

μ = 0.237 mm⁻¹

T = 293 K

Plate

0.3 × 0.2 × 0.2 mm

Colourless

Data collection

Enraf-Nonius CAD-4

diffractometer

ω scans

Absorption correction:

none

5782 measured reflections

2322 independent reflections

2026 observed reflections

[*F_o* > 3σ(*F_o*)]

R_{int} = 0.0608

θ_{max} = 22°

h = -14 → 14

k = 0 → 8

l = -21 → 21

2 standard reflections

frequency: 60 min

intensity variation: none

Refinement

Refinement on *F*

Final *R* = 0.0558

wR = 0.0510

2026 reflections

229 parameters

w = 1/σ²(*F*)

(Δ/σ)_{max} = 0.003

Δρ_{max} = 0.266 e Å⁻³

Δρ_{min} = 0.259 e Å⁻³

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C1	0.6524 (4)	-0.4681 (7)	0.2318 (3)	0.060 (3)
S2	0.5794 (1)	-0.3438 (2)	0.1592 (1)	0.064 (1)
C3	0.6584 (4)	-0.1493 (7)	0.1610 (2)	0.055 (2)
C4	0.6761 (4)	-0.0487 (6)	0.2283 (2)	0.043 (2)
C5	0.7744 (4)	-0.0530 (7)	0.2716 (3)	0.053 (2)
C6	0.7925 (4)	0.0201 (7)	0.3370 (3)	0.052 (2)
C7	0.7127 (4)	0.0931 (6)	0.3594 (3)	0.046 (2)
C8	0.6126 (4)	0.1019 (6)	0.3177 (2)	0.039 (2)
C9	0.5952 (3)	0.0333 (6)	0.2503 (2)	0.038 (2)
C10	0.5283 (3)	0.1805 (6)	0.3462 (2)	0.044 (2)
S11	0.5085 (1)	0.0654 (2)	0.4219 (1)	0.049 (1)
C12	0.4671 (3)	-0.1552 (6)	0.3898 (2)	0.044 (2)
C13	0.5550 (3)	-0.2727 (6)	0.3811 (2)	0.038 (2)
C14	0.6308 (4)	-0.3319 (7)	0.4371 (3)	0.052 (2)
C15	0.7123 (4)	-0.4343 (7)	0.4261 (3)	0.060 (2)
C16	0.7187 (4)	-0.4761 (6)	0.3607 (3)	0.053 (2)
C17	0.6426 (4)	-0.4186 (6)	0.3042 (3)	0.043 (2)
C18	0.5594 (3)	-0.3207 (6)	0.3146 (2)	0.038 (2)
C19	0.4878 (4)	0.0446 (7)	0.2042 (2)	0.044 (2)
O20	0.4113 (3)	-0.0128 (5)	0.2173 (2)	0.058 (1)
O21	0.4909 (2)	0.1316 (4)	0.1461 (2)	0.049 (1)
C22	0.3945 (4)	0.1717 (8)	0.0926 (2)	0.058 (2)
C23	0.4365 (4)	0.2628 (8)	0.0379 (2)	0.078 (3)
C24	0.3382 (4)	0.0036 (8)	0.0657 (3)	0.085 (3)
C25	0.3276 (4)	0.2938 (8)	0.1235 (3)	0.083 (3)

Table 2. Selected bond distances (\AA) and angles ($^\circ$)

C1—S2	1.805 (5)	C19—O20	1.196 (7)
S2—C3	1.815 (5)	C19—O21	1.345 (6)
C10—S11	1.820 (5)	O21—C22	1.487 (5)
S11—C12	1.836 (5)	C22—C23	1.513 (8)
C1—S2—C3	102.5 (2)	C10—S11—C12	104.2 (2)

The title compound was synthesized by reaction of 2,6-bis-(bromomethyl)benzoic acid *tert*-butyl ester and 1,3-bis(mercaptomethyl)benzene in benzene-ethanol (1:1) with sodium hydroxide as base under high-dilution conditions (Vögtle, Grütze, Nätischer, Wieder, Weber & Grün, 1975). Crystals were grown by recrystallization from acetone and were glued on a glass fibre.

The structure was solved by direct methods (Sheldrick, 1986) and refinement was by full-matrix least-squares techniques (Sheldrick, 1976). H atoms were included at calculated positions (C—H = 1.08 \AA), riding on the carbon skeleton in the final stages of refinement with a common isotropic displacement parameter for the CH, CH₂ and CH₃ groups. Distances and angles were calculated by *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71309 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1046]

References

- Anker, W., Bushnell, G. W. & Mitchell, R. H. (1979). *Can. J. Chem.* **57**, 3080–3087.
 Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

- Sheldrick, G. M. (1986). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
 Vögtle, F., Grütze, J., Nätischer, R., Wieder, W., Weber, E. & Grün, R. (1975). *Chem. Ber.* **108**, 1694–1711.

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Structure of (Z)-L-Pro-D-(α Me)Phe-OH

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Abstract

In this N-protected heterochiral dipeptide (N^α -benzyloxycarbonyl-L-prolyl- C^α -methyl-D-phenylalanine), the tertiary urethane moiety is *cis*. In addition, the L-Pro residue is semi-extended while the D-(α Me)Phe residue is fully extended.

Comment

In connection with our current investigation into analogues at position 3 of morphiceptin, a pentapeptide amide with extreme selectivity for the μ -opiate receptor, the X-ray diffraction analysis of the title compound (N^α -benzyloxycarbonyl-L-prolyl- C^α -methyl-D-phenylalanine) (1) was carried out to determine the structural preference of this conformationally constrained heterochiral dipeptide sequence. Details of the synthetic work will be published elsewhere (Formaggio, Crisma, Toniolo & Kamphuis, 1993).

