

ließ. Die Wichtung erfolgte mit $w = 1/\sigma^2(F_o)$. Die Restelektronendichte in einer abschließenden ΔF -Synthese betrug max. +0,93 und min. -0,79 e Å⁻³. Die max. Parameterverschiebung/Standardabweichung in den letzten Zyklen betrug 0,029. $\sum w(\Delta F)^2$ minimalisiert. Atomformfaktoren aus *International Tables for X-ray Crystallography* (1974).

Die Struktur mußte zum Schluß komplett invertiert werden, um die vorgegebene Konfiguration 'S' am optisch aktiven C-Atom im Pyrrolidinring zu erhalten. Damit ergab sich für das silylierte α -C-Atom die Konfiguration 'R', was bei dieser enantioselektiv synthetisierten Verbindung auch der Erwartung entsprach. Der R-Wert verbesserte sich dabei nach der Verfeinerung insignifikant.

Tabelle 1 zeigt die erhaltenen Atomparameter, einige ausgewählte Bindungslängen und -winkel sind in Tabelle 2 aufgeführt.* Fig. 1 zeigt die räumliche Darstellung eines Moleküls des α -silylierten SAMP-Hydrazons.

Relevante Literatur. Wie oben erwähnt, können die C-silylierten SAMP (bzw. RAMP)-Hydrazone durch

* Die Liste der Strukturparameter, der anisotropen Temperaturfaktoren, die Parameter der H-Atome und der Bindungslängen und -winkel sind bei dem British Library Document Supply Centre (Supplementary Publication No. SUP 52913: 30 pp.) hinterlegt. Kopien sind erhältlich durch: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

oxidative Spaltung mit Ozon in die entsprechenden α -Silylketone überführt werden. Diese eignen sich für diastereo- und enantioselektive Aldolreaktionen. So gelang Enders & Lohray (1988) die asymmetrische Synthese des Aggregationspheromons Sitophilur über ein α -Silylketon, welches aus dem hier untersuchten SAMP-Hydrazon gewonnen wurde. Aufgrund der hier erfolgten eindeutigen Bestimmung der absoluten Konfiguration ist nun eine Aussage über die Konfiguration der Produkte aus diastereo-selektiven Reaktionen mit diesen α -Silylketonen möglich.

Wir danken Herrn Professor Enders, RWTH Aachen, für die Überlassung von Kristallen und für die Anregung zu dieser Untersuchung.

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Structure of 2-(5-Methyl-3-thienyl)-2*H*,5*H*-pyrazolo[4,3-*c*]quinolin-3-one

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Abstract. C₁₅H₁₁N₃OS, $M_r = 281.33$, monoclinic, $P2_1/c$, $a = 11.245$ (2), $b = 8.562$ (1), $c = 13.852$ (2) Å, $\beta = 102.22$ (1)°, $V = 1303.5$ (3) Å³, $Z = 4$, $D_x = 1.433$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 2.13$ mm⁻¹, $F(000) = 584$, $T = 295$ K, $R = 0.072$ for 2280 observed reflections [$F_o > 3\sigma(F_o)$]. The rather high R value may be due to the absorption effect, owing to the laminar shape of the crystal. The molecule is almost planar except for H atoms of the methyl group, but torsion angles N(11)—N(12)—C(15)—C(16) = -5.4 (2) and C(13)—N(12)—C(15)—C(19) = -3.5 (3)° show about 4.5° rotation of the thiophene ring around the N(12)—C(15) bond. The molecules form an intermolecular hydro-

gen bond between NH and O(- x , $\frac{1}{2} + y$, $\frac{1}{2} - z$), N...O = 2.722 (2) Å [1.91 (2) Å for H...O].

Experimental. Yellow plate crystals obtained from dimethyl sulfoxide. Crystal of dimensions 0.8 × 0.6 × 0.1 mm. Rigaku AFC-5R diffractometer, graphite-monochromatized Cu $K\alpha$. Cell dimensions determined from 2θ angles for 25 reflections in the range $31 < 2\theta < 40^\circ$. Intensities measured up to $\theta = 70^\circ$ in h 0/13, $k - 10/0$ and $l - 16/16$, $\omega - 2\theta$ scans, ω -scan width $(1.2 + 0.2 \tan \theta)^\circ$, three standard reflections monitored every 100 measurements showed no significant change. 2401 unique reflections measured, 2280 intensities observed [110 with $F_o \leq 3\sigma(F_o)$] and

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Å²) with e.s.d.'s in parentheses
$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B _{eq}
C(1)	-0.1646 (1)	-0.3924 (2)	0.5500 (1)	3.82 (4)
C(2)	-0.2594 (1)	-0.4949 (2)	0.5365 (1)	4.30 (4)
C(3)	-0.3035 (2)	-0.5640 (2)	0.4444 (1)	4.53 (4)
C(4)	-0.2506 (1)	-0.5292 (2)	0.3664 (1)	4.21 (4)
N(5)	-0.1002 (1)	-0.3927 (2)	0.2986 (1)	3.86 (3)
C(6)	-0.0093 (1)	-0.2932 (2)	0.3034 (1)	3.71 (3)
C(7)	0.0389 (1)	-0.2201 (2)	0.3910 (1)	3.39 (3)
C(8)	-0.0053 (1)	-0.2518 (2)	0.4784 (1)	3.10 (3)
C(9)	-0.1069 (1)	-0.3557 (2)	0.4721 (1)	3.17 (3)
C(10)	-0.1533 (1)	-0.4251 (2)	0.3793 (1)	3.45 (3)
N(11)	0.0591 (1)	-0.1796 (1)	0.5568 (1)	3.23 (3)
N(12)	0.1482 (1)	-0.0981 (1)	0.5196 (1)	3.28 (3)
C(13)	0.1385 (1)	-0.1150 (2)	0.4191 (1)	3.38 (3)
O(14)	0.2049 (1)	-0.0498 (1)	0.3687 (1)	4.42 (3)
C(15)	0.2372 (1)	-0.0124 (2)	0.5856 (1)	3.39 (3)
C(16)	0.2362 (1)	0.0062 (2)	0.6824 (1)	4.32 (4)
S(17)	0.35630 (4)	0.12013 (6)	0.73946 (3)	4.85 (1)
C(18)	0.4099 (1)	0.1418 (2)	0.6326 (1)	4.33 (4)
C(19)	0.3365 (1)	0.0644 (2)	0.5566 (1)	4.10 (4)
C(20)	0.5192 (2)	0.2383 (3)	0.6304 (2)	5.97 (6)

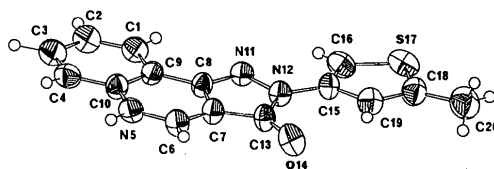


Fig. 1. ORTEP drawing (Hall & Stewart, 1987). Non-H atoms are represented by thermal ellipsoids with 50% probability.

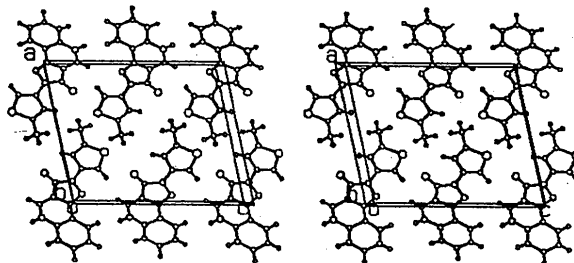


Fig. 2. A stereoview of the unit-cell packing drawn by PLUTO (Motherwell & Clegg, 1978)

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

C(1)—C(2)	1.363 (2)	C(9)—C(10)	1.412 (2)
C(1)—C(9)	1.407 (2)	N(11)—N(12)	1.405 (2)
C(2)—C(3)	1.398 (3)	N(12)—C(13)	1.381 (2)
C(3)—C(4)	1.372 (3)	N(12)—C(15)	1.410 (2)
C(4)—C(10)	1.393 (2)	C(13)—O(14)	1.256 (2)
N(5)—C(6)	1.321 (2)	C(15)—C(16)	1.353 (2)
N(5)—C(10)	1.402 (2)	C(15)—C(19)	1.425 (2)
C(6)—C(7)	1.371 (2)	C(16)—S(17)	1.717 (2)
C(7)—C(8)	1.429 (2)	S(17)—C(18)	1.722 (2)
C(7)—C(13)	1.425 (2)	C(18)—C(19)	1.364 (2)
C(8)—C(9)	1.436 (2)	C(18)—C(20)	1.487 (3)
C(8)—N(11)	1.324 (2)		
C(2)—C(1)—C(9)	120.8 (2)	N(5)—C(10)—C(9)	120.3 (2)
C(1)—C(2)—C(3)	120.9 (2)	C(8)—N(11)—N(12)	103.9 (1)
C(2)—C(3)—C(4)	119.8 (2)	N(11)—N(12)—C(13)	114.0 (1)
C(3)—C(4)—C(10)	119.8 (2)	N(11)—N(12)—C(15)	118.9 (1)
C(6)—N(5)—C(10)	122.9 (2)	C(13)—N(12)—C(15)	127.0 (1)
N(5)—C(6)—C(7)	119.7 (2)	C(7)—C(13)—N(12)	103.4 (1)
C(6)—C(7)—C(8)	121.3 (2)	C(7)—C(13)—O(14)	130.9 (2)
C(6)—C(7)—C(13)	132.1 (2)	N(12)—C(13)—O(14)	125.8 (2)
C(8)—C(7)—C(13)	106.4 (1)	N(12)—C(15)—C(16)	123.4 (2)
C(7)—C(8)—C(9)	118.8 (2)	N(12)—C(15)—C(19)	123.3 (2)
C(7)—C(8)—N(11)	112.2 (1)	C(16)—C(15)—C(19)	113.4 (2)
C(9)—C(8)—N(11)	129.0 (2)	C(15)—C(16)—S(17)	110.6 (1)
C(1)—C(9)—C(8)	125.6 (2)	C(16)—S(17)—C(18)	92.9 (1)
C(1)—C(9)—C(10)	117.6 (2)	S(17)—C(18)—C(19)	110.3 (1)
C(8)—C(9)—C(10)	116.9 (2)	S(17)—C(18)—C(20)	121.3 (2)
C(4)—C(10)—N(5)	118.7 (2)	C(19)—C(18)—C(20)	128.5 (2)
C(4)—C(10)—C(9)	121.0 (2)	C(15)—C(19)—C(18)	112.9 (2)

11 very strong reflections rejected], no absorption corrections. Structures solved by *MULTAN84* (Main, Germain & Woolfson, 1984). H atoms located on a difference density map. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined by block-diagonal least squares. Temperature factor of each H atom equal to B_{eq} of the bonded atom. $\sum(w|\Delta F|^2)$ minimized, $w = 1/[\sigma^2(F_o) + 0.00576|F_o|^2]$, $w = 0$ for nine reflections with $w^{1/2}|\Delta F| \geq 3$. Final $R = 0.072$,

$wR = 0.089$, $S = 1.17678$. The highest and lowest peaks in the final difference map are 0.8 and $-0.4 e \text{ \AA}^{-3}$. Max. Δ/σ in the final cycle 0.2. Atomic scattering factors calculated by $\sum[a_i \exp(-b_i \lambda^{-2} \times \sin^2 \theta)] + c$ ($i = 1, \dots, 4$) (*International Tables for X-ray Crystallography*, 1974). Calculations performed on FACOM M730 computer at Shionogi Research Laboratories. The final atomic coordinates and equivalent isotropic temperature factors are given in Table 1. Bond distances and angles are listed in Table 2.* A perspective view of the molecule with the atom-numbering system and a stereoview of the crystal packing are presented in Figs. 1 and 2, respectively.

Related literature. The structure of the title compound reported here has been referred to in structure-activity relationships (Shindo, Takada, Murata, Eigyo & Matsushita, 1989). The structures of similar compounds have been reported by Nakai (1990) and Shiro (1990).

The author thanks Dr Takada for the supply of the crystals.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52919 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Nematogenic Oxathiane Derivative

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(Received 11 January 1990; accepted 3 April 1990)

Abstract. 4-Cyanophenyl *trans*-4-(*trans*-5-*n*-hexyl-1,3-oxathian-2-yl)cyclohexanoate, $C_{24}H_{33}NO_3S$, $M_r = 415.6$, triclinic, $P\bar{1}$, $a = 5.619$ (1), $b = 14.201$ (2), $c = 16.591$ (2) Å, $\alpha = 112.99$ (1), $\beta = 92.67$ (1), $\gamma = 104.08$ (1)°, $V = 1167.1$ (3) Å³, $Z = 2$, $D_x = 1.183$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 13.7$ cm⁻¹, $F(000) = 448$, $T = 291$ K, final $R = 0.054$ for 2647 observed reflections. The molecules adopt a rod-like shape, only very slightly 'banana' bent. The oxathiane ring has a distorted chair conformation and is most puckered in the vicinity of the O atom. The orientation of the oxathiane ring and the cyclohexane ring in the molecule is almost the same. Centrosymmetric pairs of molecules form a parallel imbricated packing within the crystal.

Experimental. Colourless, clear crystals were recrystallized from a methanol/benzene mixture. Phase behaviour: nematic range from 376 K (melting point) to 478 K (clearing point), appearance of a monotropic smectic A phase at 343 K by strong undercooling of the nematic phase. Synthesized by Tschierske, Joachimi, Vorbrod, Zschke, Wiegeleben, Hauser & Demus (1989). A crystal of dimensions 0.37 × 0.34 × 0.15 mm was mounted on a Syntex $P2_1$ diffractometer with graphite monochromator (angle 26.57°). Unit-cell parameters were determined by least-squares treatment of the setting angles for 13 counter reflections within $20 \leq 2\theta \leq 30^\circ$. Intensity data were collected to $2\theta = 115^\circ$, $-6 \leq h \leq 6$, $-15 \leq k \leq 15$, $0 \leq l \leq 18$, in $\theta/2\theta$ scan (bisecting mode). Intensity variation of two check reflections: $\pm 1.8\%$ for $04\bar{1}$ and $\pm 2.2\%$ for 025 . 3037 unique reflections, 2647 with $I \geq$

$1.96\sigma(I)$ were considered observed. Only L_p correction applied during data reduction. Structure solved by direct methods in *SHELXS86* (Sheldrick, 1986) and refined by full-matrix least-squares techniques on F in *SHELX76* (Sheldrick, 1976). The non-H atoms were refined with anisotropic displacement parameters, H atoms located in a difference Fourier map were refined isotropically in a separate block, resulting in a total of 6.7 reflections per parameter and a final R of 0.054. Unit weights were used throughout the refinement. $(\Delta/\sigma)_{\max} = 0.06$ in the last cycle, $\Delta\rho_{\max} = 0.30$ and $\Delta\rho_{\min} = -0.31$ e Å⁻³ in the final difference map. Atomic scattering factors were from *SHELX76*. All calculations were on an IBM XT computer. Final non-H-atom parameters are given in Table 1, selected bond lengths, angles and torsion angles in Table 2. The molecular structure with atom labels is shown in Fig. 1; Fig. 2 gives an impression of the packing arrangement in the crystalline phase of the mesogene.†

Related literature. To our knowledge only one crystal structure analysis of a 1,3-oxathiane derivative has been reported (2-*p*-nitrophenyl-1,3-oxathiane; de Wolf, Verschoor & Romers, 1972). The geometric parameters for the heterocycle agree well with those of the compound presented in this article. The mutual orientation of the two saturated rings is almost the same as that of the two cyclohexane moieties in other mesogenic bicyclohexyl derivatives

† Lists of structure factors, anisotropic displacement parameters for non-H atoms and H-atom parameters, as well as a fuller list of bond lengths and angles, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52937 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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