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Structure of (2R*,8R*)-2-[α-(Thiocarbamoylthio)benzyl]indan-1-one

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Abstract. $C_{17}H_{15}NOS_2$, $M_r = 313.44$, monoclinic, $C2/c$, $a = 20.710(2)$, $b = 9.268(2)$, $c = 17.303(1)$ Å, $\beta = 114.11(1)°$, $V = 3031.5(9)$ Å^3, $Z = 8$, $D_x = 1.37$ Mg m^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1.54184$ Å, $\mu = 3.1$ mm^{-1}, $F(000) = 1312$, $T = 296(1)$ K, $R = 0.041$ for 2289 observed reflections. Only X-ray analysis could reveal the structure of the title compound obtained by the reaction of 2-benzylideneindanone with dithiocarbamic acid. It has been shown to be the diastereomer in which the chiral centres have the stereochemistry: $2R^*,8R^*$ (and/or $2S^*,8S^*$ as indicated by the asterisks).

Introduction. Continuing our earlier studies on the reactions of α,β-unsaturated carbonyl compounds with thiocarbonic acid derivatives (Argay, Kálmán, Perjési & Szabó, 1987; Perjési, Földesi, Szabó, Zschunke & Mák, 1987; Perjési, Szabó, Batta & Földesi, 1987) the reaction of 2-benzylideneindanone (1) with dithiocarbamic acid has been investigated. In this reaction stereohomogeneous 2-[α-(thiocarbamoylthio)benzyl]indan-1-one (2) was formed as depicted in the reaction scheme. However, no spectroscopic answer could be

given as to which of the two possible diastereomers was formed. Consequently, an X-ray analysis of (2) (melted at 407–410 K) has been performed.

(1)   (2)
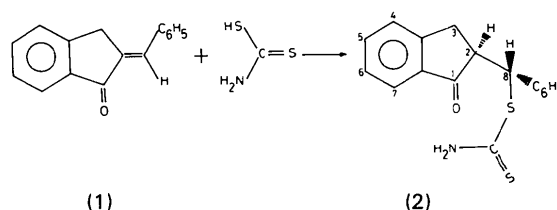
Experimental. Crystal *ca* 0.11 × 0.25 × 0.40 mm was mounted on a CAD-4 diffractometer equipped with graphite monochromator. Cell constants were refined by least-squares fit for 25 centred reflections collected in the range of $25 \le \theta \le 35°$. Systematic absences *hkl*: $h + k = 2n + 1$, *h0l*: $l = 2n + 1$, *0k0*: $k = 2n + 1$ permit space groups *Cc* and *C2/c* of which *C2/c* was substantiated by refinement. Scan range $0.017 \le (\sin\theta)/\lambda \le 0.626$ Å^{-1}, $\omega/2\theta$ scan. A total of 3260 reflections was collected with *h*: 0 to 25, *k*: −11 to 0 and *l*: −21 to 21, of which 2780 were unique, non-zero and not systematically absent. In the refinement,

† Deceased on June 14, 1987.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* B_{eq} (Å²) *for the non-hydrogen atoms with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}$ trace (BG) where G is the direct metric tensor.

	x	y	z	B_{eq}(Å²)
S(9)	0·60695 (3)	0·03423 (8)	0·02529 (3)	2·87 (1)
S(11)	0·74193 (3)	0·19798 (9)	0·13381 (4)	3·62 (1)
O(13)	0·4770 (1)	0·0684 (2)	−0·1611 (1)	3·90 (5)
N(12)	0·6604 (1)	0·0469 (3)	0·1866 (1)	3·52 (6)
C(1)	0·5091 (1)	0·1824 (3)	−0·1401 (1)	2·86 (6)
C(2)	0·5889 (1)	0·2019 (3)	−0·1150 (1)	2·51 (6)
C(3)	0·6041 (1)	0·3562 (3)	−0·0787 (1)	3·16 (7)
C(3a)	0·5329 (1)	0·4234 (3)	−0·1007 (1)	2·90 (6)
C(4)	0·5169 (1)	0·5640 (3)	−0·0872 (1)	3·55 (8)
C(5)	0·4465 (1)	0·5983 (3)	−0·1094 (2)	4·09 (9)
C(6)	0·3934 (1)	0·4984 (4)	−0·1440 (2)	4·7 (1)
C(7)	0·4085 (1)	0·3589 (4)	−0·1574 (1)	4·19 (9)
C(7a)	0·4795 (1)	0·3228 (3)	−0·1352 (1)	3·04 (7)
C(8)	0·6386 (1)	0·0877 (2)	−0·0550 (1)	2·45 (6)
C(10)	0·6732 (1)	0·0946 (2)	0·1221 (1)	2·60 (6)
C(14)	0·6546 (1)	−0·0448 (2)	−0·0951 (1)	2·52 (6)
C(15)	0·7248 (1)	−0·0802 (3)	−0·0744 (1)	3·36 (7)
C(16)	0·7421 (1)	−0·2049 (3)	−0·1053 (1)	3·87 (8)
C(17)	0·6907 (1)	−0·2951 (3)	−0·1571 (1)	3·58 (8)
C(18)	0·6209 (1)	−0·2608 (3)	−0·1793 (1)	3·81 (8)
C(19)	0·6029 (1)	−0·1356 (3)	−0·1488 (1)	3·27 (7)

however, only 2289 with $I > 3\sigma(I)$ were used. 491 were taken as unobserved reflections. Three standard reflections ($26\bar{1}$, $8\bar{4}1$ and $14,0,\bar{6}$) were monitored every hour; no intensity variations were observed. The phase problems were solved by the *MULTAN*82 program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) using 257 $E \geq 1·63$ normalized structure factors. Function $\sum w(\Delta F^2)$ was minimized for 190 variables with $w = 1$. At the end of the isotropic refinement an empirical absorption correction was performed with the *DIFABS* program (Walker & Stuart, 1983); max. and min. transmission coefficients were 1·684 and 0·782. Final $R = 0·041$, $wR = 0·046$, $R_{tot} = 0·055$, $S = 1·97$. $(\Delta/\sigma) = 0·003$. Max. and min. peak heights in the final difference map 0·39 (5) e Å⁻³. Positions of H atoms bound to C atoms were generated from assumed geometries, while those linked to N were located in a difference Fourier map; their positions were taken into account without refinement in structure-factor calculations with isotropic temperature factors ($B_{iH} = B_{iX} + 1$ Å² where $X = $ C or N). Scattering factors were taken from Enraf–Nonius (1983) *SDP-Plus* applied throughout the structure determination adapted to a PDP 11/34 minicomputer (128 Kwords) with local modifications.

Discussion. Atomic coordinates of non-H atoms are in Table 1.* The bond lengths and angles for non-H atoms

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

S(9)—C(8)	1·830 (2)	C(4)—C(5)	1·386 (3)
S(9)—C(10)	1·767 (2)	C(5)—C(6)	1·373 (4)
S(11)—C(10)	1·658 (2)	C(6)—C(7)	1·372 (5)
O(13)—C(1)	1·222 (3)	C(7)—C(7a)	1·399 (3)
N(12)—C(10)	1·325 (3)	C(8)—C(14)	1·512 (4)
C(1)—C(2)	1·539 (2)	C(14)—C(15)	1·389 (3)
C(1)—C(7a)	1·455 (4)	C(14)—C(19)	1·381 (4)
C(2)—C(3)	1·542 (4)	C(15)—C(16)	1·380 (4)
C(2)—C(8)	1·545 (3)	C(16)—C(17)	1·362 (4)
C(3)—C(3a)	1·500 (3)	C(17)—C(18)	1·372 (3)
C(3a)—C(4)	1·387 (4)	C(18)—C(19)	1·388 (4)
C(3a)—C(7a)	1·382 (4)		

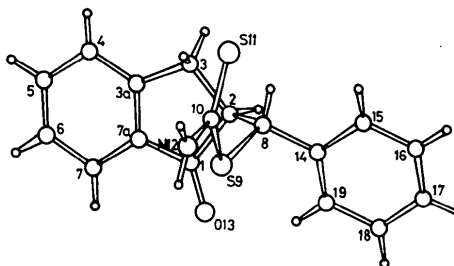|			
C(8)—S(9)—C(10)	104·7 (2)	C(1)—C(7a)—C(7)	128·2 (4)
O(13)—C(1)—C(2)	125·2 (4)	C(3a)—C(7a)—C(7)	121·5 (4)
O(13)—C(1)—C(7a)	126·9 (4)	S(9)—C(8)—C(2)	110·4 (3)
C(2)—C(1)—C(7a)	108·0 (3)	S(9)—C(8)—C(14)	110·0 (3)
C(1)—C(2)—C(3)	103·9 (3)	C(2)—C(8)—C(14)	117·3 (3)
C(1)—C(2)—C(8)	117·0 (3)	S(9)—C(10)—S(11)	126·5 (2)
C(3)—C(2)—C(8)	113·1 (3)	S(9)—C(10)—N(12)	110·3 (3)
C(2)—C(3)—C(3a)	105·4 (3)	S(11)—C(10)—N(12)	123·2 (3)
C(3)—C(3a)—C(4)	128·6 (4)	C(8)—C(14)—C(15)	118·4 (4)
C(3)—C(3a)—C(7a)	111·1 (4)	C(8)—C(14)—C(19)	123·3 (4)
C(4)—C(3a)—C(7a)	120·2 (4)	C(15)—C(14)—C(19)	118·2 (4)
C(3a)—C(4)—C(5)	117·7 (4)	C(14)—C(15)—C(16)	120·5 (4)
C(4)—C(5)—C(6)	122·0 (5)	C(15)—C(16)—C(17)	120·9 (5)
C(5)—C(6)—C(7)	120·8 (5)	C(16)—C(17)—C(18)	119·5 (5)
C(6)—C(7)—C(7a)	117·8 (5)	C(17)—C(18)—C(19)	120·2 (5)
C(1)—C(7a)—C(3a)	110·3 (4)	C(14)—C(19)—C(18)	120·7 (4)

Fig. 1. Perspective view of the molecule with atomic numbering. Bare numbers are for carbon atoms unless indicated otherwise. H atoms are shown but not labelled.

are listed in Table 2. The molecular geometry of the title compound depicted in Fig. 1 reveals a diastereomer in which the chiral centres C(2) and C(8) possess opposite stereochemistry. The enantiomer chosen accidentally in the course of the solution of the phase problems for the space group C2/c exhibits 2R, 8R chirality in accordance with the CIP system (Cahn, Ingold & Prelog, 1956).

The flattened five-membered ring [puckering amplitude, introduced by Cremer & Pople (1975), $Q = 0·115$ (3) Å] retains some envelope character with the chiral C(2) atom on the flap to which the α-(thiocarbamoylthio)benzyl group is bound pseudo-equatorially. Consequently, H(2) is linked pseudo-axially and synclinal with H(8) around the C(2)—C(8) bond. The corresponding torsion angle is about 84°. The planar thiocarbamoylthio moiety bisects sym-

metrically the C(2)–C(8)–C(14) = 117·3 (3)° angle. S(11) is eclipsed with C(8). The short C(10)–N(12) bond length [1·325 (3) Å] indicates that the N lone pair of electrons is delocalized on this group. The S^{II}–$C(sp^3)$ = 1·830 (2) and S^{II}–$C(sp^2)$ = 1·767 (2) Å bond lengths maintained by S(9) – in accordance with the different hybridization of the C atoms – exhibit significant difference (Δ = 0·063 Å), underscoring the observations of Argay, Kálmán, Lazar, Ribár & Tóth (1977, and references therein). The length [1·658 (2) Å] of the polarized S^{II}=C double bond agrees with data found in the literature, cf. for example N-vinyl-2-thiopyrrolidone [1·659 (3) Å] reported by Kálmán, Argay & Cser (1976). The centre-of-symmetry-related enantiomers are bound together by hydrogen-bond pairs having the parameters

	$D\cdots A$ (Å)	$H\cdots A$ (Å)	$DH\cdots A$ (°)
N(12)–H(12)$\cdots$O(13)(1−x, −y, −z)	2·898 (2)	1·99 (2)	160 (1).

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Structure of L-Tyrosyl-L-leucine Monohydrate

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Abstract. $C_{15}H_{22}N_2O_4.H_2O$, M_r = 312·37, monoclinic, $P2_1$, a = 5·577 (2), b = 8·686 (2), c = 16·228 (2) Å, β = 92·63 (2)°, V = 785 (1) Å^3, Z = 2, D_m = 1·34, D_x = 1·32 Mg m^{-3}, Cu $K\alpha$, λ = 1·54184 Å, μ = 0·78 mm^{-1}, $F(000)$ = 320, T = 293 K. The final R value for 1607 observed reflections $[I_o \geq 3\sigma(I_o)]$ is 0·039. The terminal N1 is protonated and the dipeptide exists as a zwitterion. The crystal structure is stabilized by extensive hydrogen-bonding interactions involving N and O atoms, with N$\cdots$O in the range 2·65 (1)–2·95 (1) Å and O$\cdots$O in the range 2·60 (1)–2·78 (1) Å.

Introduction. We report here the structure of the title compound as part of our investigation on peptides which are relevant to the problem of nucleotide–peptide interactions.

Experimental. The dipeptide was purchased from Sigma Chemicals and used without further purification. Platey crystals were obtained by evaporation of an aqueous solution containing 10 mM peptide and 5% Me₂SO at room temperature. The size of the crystal used for

X-ray data collection was 0·10 x 0·2 x 0·5 mm. The cell parameters were initially obtained from Weissenberg photographs and were later refined on a CAD-4 diffractometer using 25 high-angle (10 ≤ θ ≤ 38°) reflections. Three-dimensional intensity X-ray data were collected up to θ = 70° using ω–2θ scans. The crystal was found to be stable to X-rays; standard reflections monitored periodically during data collection showed no significant intensity decrease. The ranges of the indices are h = −6 to 6, k = 0 to 10 and l = 0 to 19. A total of 1607 reflections were considered observed $[I \geq 3\sigma(I)]$ out of 1737 collected. Lorentz and polarization corrections were applied but no absorption correction was made.

The structure was solved using MULTAN11/82 (Germain, Main & Woolfson, 1971). Non-hydrogen atoms were refined anisotropically using full-matrix methods. All hydrogen atoms were located from difference Fourier maps and refined isotropically. The final R = 0·039 and wR = 0·042, where the w is $1/[\sigma(F_o)]^2$. The function minimized was $\sum w(|F_o| - |F_c|)^2$. $(\Delta/\sigma)_{max}$ = 0·13; $\Delta\rho$ variations in a final dif-