

Fig. 3. The variation of the energy E (in kJ mol^{-1}) with the torsion angle ϕ ($\text{H}-\text{O}-\text{C}-\text{H}$) ($^\circ$) as calculated by molecular mechanics.

by two independent molecules each connected with a water molecule that substitutes for a cyclohexanol molecule. The H-bond scheme in which the donor H atoms are anticlinal appears to be 5.0 kJ mol^{-1} lower in energy than that with the H atoms in the synclinal conformation. Therefore, also in view of the calculations on the isolated molecule it seems obvious that the failure to detect the hydroxyl-group H-atom positions is due to (dynamic) disorder.

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Stereochemical Studies. 122.* Structures of Two Crystal Modifications of 5,8-Methano-*cis-transoid-cis-tetrahydro-4H-3,1-benzoxazine-2(1H)-thione*

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Abstract. $\text{C}_9\text{H}_{11}\text{NOS}$, $M_r = 181.26$. The title compound has two monoclinic modifications. Modification I: $P2_1/c$, $a = 7.684$ (4), $b = 9.488$ (2), $c = 12.344$ (6) Å, $\beta = 101.93$ (3)°, $V = 880.5$ (7) Å³, $Z = 4$, $D_x = 1.367 \text{ Mg m}^{-3}$, m.p. 424–425 K, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.27 \text{ mm}^{-1}$, $F(000) = 384$, $T = 293 \text{ K}$, final $R = 0.060$ for 931 observed reflections. Modification II: $P2_1/n$, $a = 12.615$ (4), $b = 7.296$ (2), $c = 10.544$ (5) Å, $\beta = 112.89$ (3)°, $V = 894.0$ (6) Å³,

$Z = 4$, $D_x = 1.347 \text{ Mg m}^{-3}$, m.p. 419–421 K, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 2.67 \text{ mm}^{-1}$, $F(000) = 384$, $T = 293 \text{ K}$, final $R = 0.071$ for 1238 observed reflections. The molecules in the two modifications have similar bond lengths and angles and form dimers connected through $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds with lengths $\text{H}\cdots\text{S} = 2.45$, $\text{N}\cdots\text{S} = 3.391$ (5) Å (I), $\text{H}\cdots\text{S} = 2.27$, $\text{N}\cdots\text{S} = 3.317$ (4) Å (II) and angles 145 (4) and 163 (4)°, respectively. The 3,1-benzoxazine ring adopts an E_4 envelope conformation in both modifications.

* Part 121: Richter, Fülöp, Bernáth & Pfügel (1987).

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	(I)				(II)			
	x	y	z	U _{eq}	x	y	z	U _{eq}
S	−1906 (2)	3477 (2)	5570 (1)	54 (1)	4741 (1)	2843 (2)	3401 (1)	50 (1)
N(1)	888 (5)	4886 (5)	6661 (4)	42 (2)	3374 (3)	4197 (4)	4546 (7)	41 (1)
C(2)	−376 (7)	3977 (6)	6694 (5)	40 (2)	3476 (4)	3127 (5)	3586 (4)	39 (1)
O(3)	−511 (4)	3408 (4)	7657 (3)	51 (2)	2571 (2)	2226 (4)	2732 (3)	44 (1)
C(4)	395 (7)	4136 (8)	8656 (5)	62 (3)	1443 (4)	2931 (6)	2530 (4)	45 (1)
C(4a)	2309 (7)	4481 (6)	8635 (4)	45 (2)	1294 (3)	3395 (6)	3852 (4)	45 (1)
C(5)	3707 (7)	3286 (6)	8859 (5)	50 (3)	1030 (4)	1792 (7)	4662 (5)	57 (2)
C(6)	3130 (7)	2175 (7)	7988 (6)	55 (3)	2009 (4)	437 (6)	5017 (5)	58 (2)
C(7)	3355 (7)	2676 (7)	7038 (6)	55 (3)	2926 (5)	1192 (7)	5966 (5)	59 (2)
C(8)	4056 (7)	4161 (7)	7237 (5)	50 (3)	2586 (4)	3088 (7)	6252 (5)	56 (2)
C(8a)	2521 (7)	5047 (6)	7514 (5)	44 (2)	2385 (4)	4257 (6)	4937 (4)	45 (1)
C(9)	5212 (7)	3998 (7)	8406 (5)	53 (3)	1327 (5)	2739 (8)	6055 (6)	70 (2)

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

(I)		(II)	
S—C(2)	1.690 (6)	C(4a)—C(5)	1.547 (7)
N(1)—C(2)	1.305 (6)	C(5)—C(6)	1.506 (8)
N(1)—C(8a)	1.470 (6)	C(5)—C(9)	1.541 (8)
C(2)—O(3)	1.329 (6)	C(6)—C(7)	1.310 (9)
O(3)—C(4)	1.459 (7)	C(7)—C(8)	1.510 (9)
C(4)—C(4a)	1.512 (8)	C(8)—C(8a)	1.544 (8)
C(4a)—C(8a)	1.523 (8)	C(8)—C(9)	1.538 (8)
(I)		(II)	
C(2)—N(1)—C(8a)	125.2 (5)	C(2)—N(1)—C(8a)	125.5 (3)
N(1)—C(2)—O(3)	119.5 (5)	N(1)—C(2)—O(3)	120.1 (4)
N(1)—C(2)—S	123.7 (4)	N(1)—C(2)—S	122.3 (3)
S—C(2)—O(3)	116.8 (4)	S—C(2)—O(3)	117.5 (3)
C(2)—O(3)—C(4)	116.9 (5)	C(2)—O(3)—C(4)	117.4 (3)
O(3)—C(4)—C(4a)	112.5 (4)	O(3)—C(4)—C(4a)	114.2 (3)
C(5)—C(4a)—C(8a)	102.7 (4)	C(5)—C(4a)—C(8a)	102.6 (3)
C(4)—C(4a)—C(8a)	112.3 (5)	C(4)—C(4a)—C(8a)	112.3 (3)
C(4)—C(4a)—C(5)	118.7 (5)	C(4)—C(4a)—C(5)	117.8 (4)
C(4a)—C(5)—C(6)	107.1 (5)	C(4a)—C(5)—C(6)	107.4 (3)
C(4a)—C(5)—C(9)	99.2 (4)	C(4a)—C(5)—C(9)	99.3 (4)
C(6)—C(5)—C(9)	100.3 (5)	C(6)—C(5)—C(9)	100.7 (4)
C(5)—C(6)—C(7)	108.2 (5)	C(5)—C(6)—C(7)	107.8 (4)
C(6)—C(7)—C(8)	107.5 (6)	C(6)—C(7)—C(8)	107.5 (4)
C(7)—C(8)—C(8a)	106.3 (4)	C(7)—C(8)—C(8a)	106.4 (3)
C(7)—C(8)—C(9)	100.2 (5)	C(7)—C(8)—C(9)	100.3 (4)
C(8a)—C(8)—C(9)	99.6 (5)	C(8a)—C(8)—C(9)	99.6 (4)
C(8)—C(8a)—N(1)	111.2 (4)	C(8)—C(8a)—N(1)	111.9 (4)
N(1)—C(8a)—C(4a)	112.2 (5)	N(1)—C(8a)—C(4a)	113.1 (3)
C(8)—C(8a)—C(4a)	103.9 (4)	C(8)—C(8a)—C(4a)	103.1 (3)
C(5)—C(9)—C(8)	93.1 (4)	C(5)—C(9)—C(8)	93.4 (3)

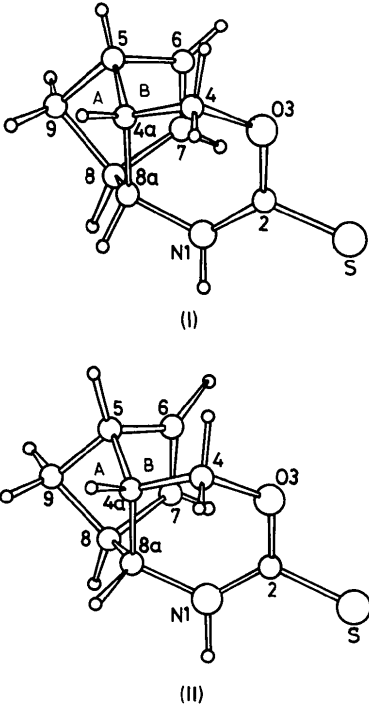


Fig. 1. A perspective view of the molecules showing atomic numbering. The H atoms are shown but not labelled.

Table 3. Bond lengths (Å) and angles (°) in the N(1)—C(2)(=S)—O(3) moieties in different 3,1-benzoxazine-2-thiones

	S=C(2)	N(1)—C(2)	O(3)—C(2)	N(1)—C(2)—O(3)	N(1)—C(2)=S	O(3)—C(2)=S	Reference
C ₉ H ₁₁ NOS-I	1.690 (6)	1.305 (6)	1.329 (6)	119.5 (5)	123.7 (4)	116.8 (4)	(1)
C ₉ H ₁₁ NOS-II	1.696 (4)	1.322 (5)	1.321 (5)	120.1 (4)	122.3 (3)	117.5 (3)	(1)
C ₇ H ₁₁ NOS	1.674 (3)	1.318 (3)	1.329 (4)	119.2 (4)	124.0 (4)	116.8 (4)	(2)
C ₈ H ₁₁ NOS	1.681 (1)	1.321 (2)	1.329 (2)	119.6 (2)	123.5 (2)	116.9 (2)	(3)
C ₈ H ₁₃ NOS-A	1.675 (3)	1.315 (4)	1.332 (3)	119.2 (4)	124.0 (4)	116.8 (4)	(4)
C ₈ H ₁₃ NOS-B	1.679 (3)	1.322 (4)	1.325 (3)	119.3 (4)	123.2 (4)	117.5 (4)	(4)

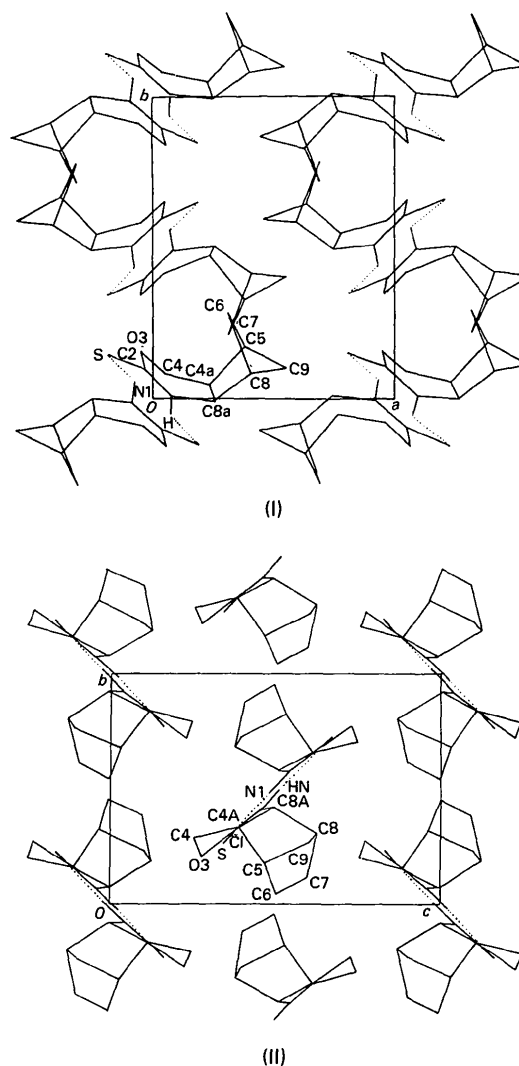
References: (1) present work; (2) *cis*-5,7-trimethylene-5,6-dihydro-4*H*-1,3-oxazine-2(3*H*)-thione (Stanković, Kapor, Ribár, Kálmán, Argay, Karanović, Stájer & Bernáth, 1985); (3) *cis*-4a,5,8,8a-tetrahydro-4*H*-3,1-benzoxazine-2(1*H*)-thione (Argay, Kálmán, Kapor, Stájer & Bernáth, 1985); (4) *cis*-4a,5,6,7,8,8a-hexahydro-4*H*-3,1-benzoxazine-2(1*H*)-thione (Argay, Kálmán, Kapor, Stájer & Bernáth, 1985).

Table 4. Puckering parameters and asymmetry factors for benzoxazine, C(4a)–C(5)–C(9)–C(8)–C(8a) *A* and C(5)–C(6)–C(7)–C(8)–C(9) *B* rings

Ring	$Q(\text{\AA})$	$\theta(^{\circ})$	$\varphi(^{\circ})$	$fC_1(\text{\AA})$	$fC_2(\text{\AA})$	cN_d
Benzoxazine I	0.454 (8)	71.9 (9)	175.0 (10)	0.030 (7) [N(1)]	0.127 (28) [C(2)]	$E_4 > B_{3,1}$
Benzoxazine II	0.400 (6)	68.7 (8)	169.9 (9)	0.054 (3) [N(1)]	0.114 (28) [C(2)]	$E_4 > {}^3S_4$
<i>A</i> five-membered I	0.634 (7)	–	250.0 (6)	0.022 (3) [C(9)]	0.135 (21) [C(8a)]	<i>E</i>
<i>A</i> five-membered II	0.635 (5)	–	250.1 (5)	0.021 (3) [C(9)]	0.137 (21) [C(8a)]	<i>E</i>
<i>B</i> five-membered I	0.551 (7)	–	322.7 (7)	0.012 (2) [C(9)]	0.123 (22) [C(6)]	<i>E</i>
<i>B</i> five-membered II	0.547 (6)	–	323.1 (6)	0.008 (1) [C(9)]	0.125 (22) [C(6)]	<i>E</i>

Introduction. The synthesis of the title compound has been described by Stájer, Szabo, Fülöp, Bernáth & Sohár (1983). The present study reports an X-ray investigation of its modifications, within a study of a series of fused-skeleton 1,3-oxazine and oxazinone derivatives containing the norbornane or norbornene structural unit, synthesized in the Institute of Pharmaceutical Chemistry, University Medical School, Szeged. Pharmacological investigations proved that the related bicyclic compounds, and especially cyclopentane-fused pyrimidinones, possess significant analgesic and anti-inflammatory actions (Bernáth *et al.*, 1977). Through the introduction of a norbornane unit instead of an alicyclic ring, a retarded pharmacological action could be expected.

Experimental. During the synthesis one obtains two crystal modifications in the same preparation, that denoted by (II) being more abundant. Intensity data were collected for both modifications: a colourless needle *ca* 0.41 × 0.11 × 0.05 mm (I) and a plate *ca* 0.56 × 0.29 × 0.02 mm (II). The equipment was a Philips PW 1100 diffractometer with graphite-monochromated Mo *K* α radiation for (I) and Cu *K* α radiation for (II). Systematic absences: $l = 2n + 1$ in $h0l$, $k = 2n + 1$ in $0k0$ (I), and $h + l = 2n + 1$ in $h0l$, $k = 2n + 1$ in $0k0$ (II). Cell parameters were obtained from the least-squares fit of 18 (I) and 16 (II) centred reflections in the θ range 5–10° (I) and 11–16° (II). 1013 (h : –9 to 9, k : 0 to 12, l : 0 to 16, $2\theta_{\max} = 60^\circ$) (I) and 1344 (h : –13 to 13, k : 0 to 8, l : 0 to 12, $2\theta_{\max} = 140^\circ$) (II) independent reflections were measured with the θ – 2θ scanning technique, scan width 1.20 (I) and 1.50° (II), and scan speed 0.04 (I) and 0.05° s^{–1} (II). Three standard reflections every 120 min. Max. and min. correction factors 1.005, 0.983 (I) and 1.027, 1.000 (II). Subsequent calculations involved 931 (I) and 1238 (II) intensity data with $I > 2.5\sigma(I)$. Neither absorption nor extinction corrections were applied. Structures were solved by *SHELX76* (Sheldrick, 1976). Full-matrix refinement, $\sum w(\Delta F)^2$ minimized 12 nonhydrogen atoms (110 parameters). Final $R = 0.060$, $wR = 0.062$ (I), and $R = 0.071$, $wR = 0.080$ (II). $w = 2.386 [\sigma^2(F)]^{-1}$ (I) and $w = [\sigma^2(F) + 29 \times 10^{-4}(F)^2]^{-1}$ (II). The value of the R factor for modification (II) reflects the poor quality of the crystal samples. Difference Fourier maps

Fig. 2. The crystal structures projected along the *c* (I) and *a* (II) axes. Hydrogen bonds are shown by broken lines.

showed no significant peaks [in (I) max. 0.33, min. –0.28 e Å^{–3}; in (II) max. 0.60, min. –0.38 e Å^{–3}]. Positions of H atoms were generated from the assumed geometries and refined in the riding mode with an overall isotropic temperature factor. $\Delta/\sigma = 0.372$ (I)

and 0.958 (II). Scattering factors as in *SHELX76*. All calculations were performed on an IBM 43/41 computer.*

Discussion. The final atomic parameters are listed in Table 1. Fig. 1 shows a perspective view of the molecules of both modifications with the atomic numbering. The relevant bond lengths and bond angles are given in Table 2. There is good agreement between the corresponding values for the majority of bond angles and distances (within experimental error). There are some differences in the bonding around the C(2) atoms, induced by the *exo* S atom, just as in previously solved related structures (Stanković, Kapor, Ribár, Kálmán, Argay, Karanović, Stájer & Bernáth, 1985; Argay, Kálmán, Kapor, Stájer & Bernáth, 1985). Results for structures studied in this and the above papers are given in Table 3.

In accordance with the observations on the structures discussed by Argay *et al.* (1985), the 3,1-benzoxazine ring adopts an *E₄* envelope conformation in both modifications. Puckering parameters (Cremer & Pople, 1975) and asymmetry factors (Kálmán, Czugler & Simon, 1982) for the benzoxazine five-membered rings *A* C(4a)–C(5)–C(9)–C(8)–C(8a) and *B* C(5)–C(6)–C(7)–C(8)–C(9) are given in Table 4.

* 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 43805 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The molecules of the two crystal modifications are connected through hydrogen bonds of N–H...S type, to form dimers. The corresponding bond lengths and angles are: H...S = 2.45, N(1)...S = 3.391 (5) Å, ∠N–H...S = 145 (4)° (I); H...S = 2.27, N(1)...S = 3.317 (4) Å, ∠N–H...S = 163 (4)° (II). These data agree with the theoretical values for this type of bonding: N...S = 3.4, H...S = 3.1 Å (calc.), N...S = 3.4, H...S = 2.4 Å (obs.) (Hamilton & Ibers, 1968). The only substantial differences between the two modifications appear in the molecular packing in the crystal unit cell (Fig. 2).

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(–)-2-Bornyl 3-(9-Anthryl)propionate

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Abstract. C₂₇H₃₀O₂, *M_r* = 386.5, orthorhombic, *P*2₁2₁2₁, *a* = 11.797 (5), *b* = 13.406 (3), *c* = 27.658 (4) Å, *V* = 4374.3 Å³, *Z* = 8, *D_x* =

1.174 Mg m⁻³, λ(Mo Kα) = 0.71073 Å, μ = 0.039 mm⁻¹, *F*(000) = 1664, room temperature, *R* = 0.086 for 2506 observed reflections [*F_o* > 2σ(*F_o*)]. Each asymmetric unit contains two independent molecules, which are related by a pseudo centre of symmetry. The anthracene moieties are paired with their side groups opposed. There is an exceptionally

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