

(R)-2,3,4,5-Tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine and rac-5-benzoyl-2,3,4,5-tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine: chains built from N—H···S and C—H···π(arene) hydrogen bonds

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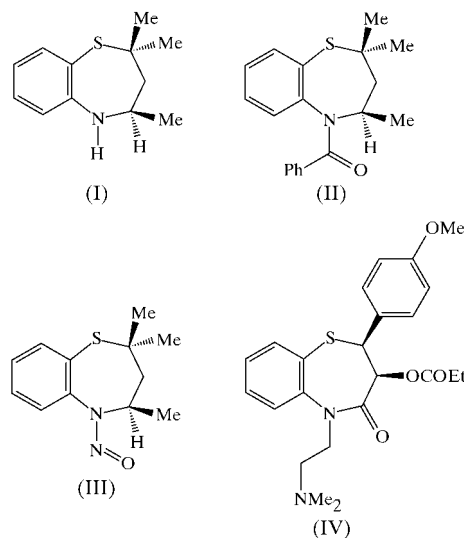
Molecules of (R)-2,3,4,5-tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine, C₁₂H₁₇NS, are linked into spiral C(5) chains by a single N—H···S hydrogen bond, while molecules of rac-5-benzoyl-2,3,4,5-tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine, C₁₉H₂₁NOS, are linked into zigzag chains by a C—H···π(arene) hydrogen bond.

Comment

We report here the molecular and supramolecular structures of two trimethylbenzothiazepines, (I) and (II), and we compare them with the N-nitroso analogue, (III), whose structure has been reported recently (Laavanya *et al.*, 2002). These compounds are of interest because their molecular constitutions have some resemblance to that of the calcium antagonist drug diltiazem [(2S,3S)-3-acetoxy-5-(dimethylaminoethyl)-2-(4-methoxyphenyl)-2,3-dihydro-1,5-benzothiazepin-4(5H)-one, (IV)] and its 2R,3R enantiomer (Kojić-Prodić *et al.*, 1984).

Compounds (I) and (II) (Figs. 1 and 2) both contain a stereogenic centre at atom C4, so giving rise to the possibility of R and S enantiomers. In (I), which crystallizes in the chiral space group P2₁, the crystal examined contained the R enantiomer only. By contrast, (II) crystallizes as a racemic mixture in space group Pna2₁; the reference molecule in (II) was selected as having the R configuration. Compound (III) also crystallizes as a racemate, in space group C2/c (Laavanya

et al., 2002), with the reference molecule again selected as the R enantiomer.



In the thiazepine rings of each of (I)–(III), the C11—C10—S1—C2 and C10—C11—N5—C4 torsion angles (Table 1) have similar magnitudes with opposite signs, as do the S1—C2—C3—C4 and N5—C4—C3—C2 angles, indicative of approximate pseudo-mirror symmetry for these portions of the ring, making due allowance for the differing atom types and bond distances. However, the magnitudes of the final pair of torsion angles, C10—S1—C2—C3 and C1—N5—C4—C3, differ markedly, although they still have opposite signs. Accordingly, it is not possible to describe any of these ring conformations in terms of a single primitive form (Evans & Boeyens, 1989). In (I), the thiazepine conformation is a mixture of boat, chair and twist-chair forms; in (II), the boat form is dominant, with a small contribution from the twist-chair form; and in (III), the conformation is best described as intermediate between boat and twist-boat. The bond lengths and angles in (I) and (II) show no unusual features.

The only direction-specific interaction between the molecules of (I) (Fig. 1) is an N—H···S hydrogen bond (Table 1). Although the N···S distance is greater than the sum (3.3 Å) of the conventional van der Waals radii (Bondi, 1964), an analysis (Allen *et al.*, 1997) of hydrogen bonds having two-

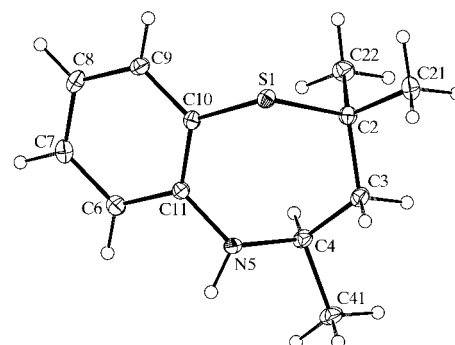


Figure 1
The R enantiomer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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coordinate sulfur as the acceptor, using data retrieved from the Cambridge Structural Database (Allen, 2002), indicated mean $\text{H}\cdots\text{S}$, $\text{N}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{S}$ parameters in such bonds, where S is bonded to two C atoms, of 2.74 (2) Å, 3.58 (3) Å and $145(3)^\circ$, respectively. Accordingly, the $\text{N}-\text{H}\cdots\text{S}$ interaction in (I) appears to be typical of such hydrogen bonds. The status of $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds remains uncertain. While Desiraju & Steiner (1999) regard sulfur as a conventional

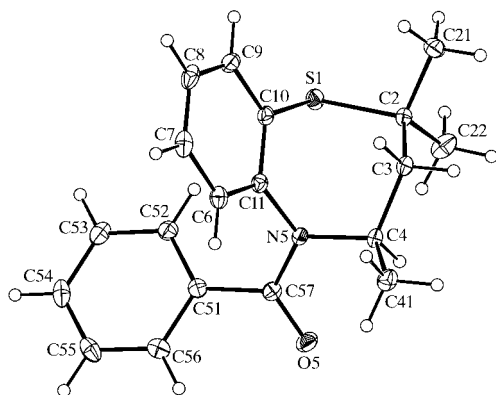


Figure 2
The *R* enantiomer of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

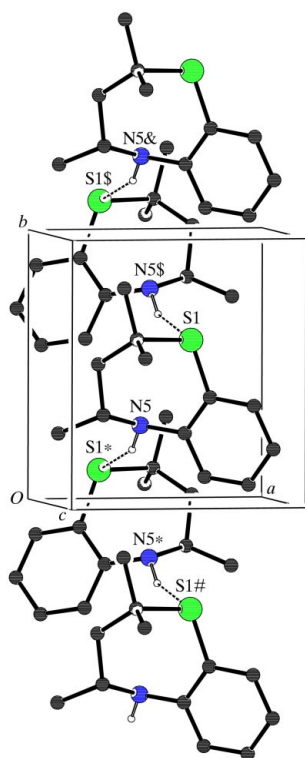


Figure 3
Part of the crystal structure of (I), showing the formation of a $C(5)$ chain along $[010]$. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(1-x, -\frac{1}{2}+y, z)$, $(x, -1+y, z)$, $(1-x, \frac{1}{2}+y, z)$ and $(x, 1+y, z)$, respectively.

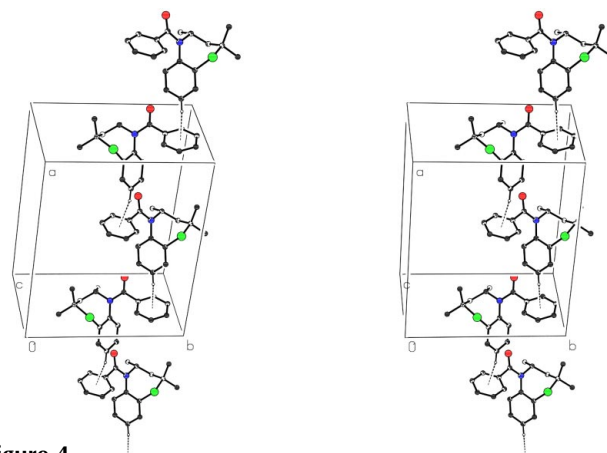


Figure 4
A stereoview of part of the crystal structure of (II), showing the formation of a $\text{C}-\text{H}\cdots\pi(\text{arene})$ chain along $[100]$. For clarity, H atoms that are not involved in the motif shown have been omitted.

hydrogen-bond acceptor, Allen *et al.* (1997) concluded that two-coordinate sulfur is a poor hydrogen-bond acceptor and that only in dialkyl sulfides lacking any other potential acceptors are $\text{X}-\text{H}\cdots\text{S}$ hydrogen bonds ($\text{X} = \text{N}$ or O) likely to be significant contributors to molecular aggregation. Against that view, we note that in triphenylmethanesulfenamide, Ph_3SNH_2 , the molecules are linked into centrosymmetric $R_2^2(6)$ dimers by paired $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds (Glidewell & Ferguson, 1994). The action of the $\text{N}-\text{H}\cdots\text{S}$ hydrogen bond in (I), where atom N5 in the molecule at (x, y, z) acts as a donor to atom S1 in the molecule at $(1-x, -\frac{1}{2}+y, z)$, is to link the molecules into a spiral $C(5)$ (Bernstein *et al.*, 1995) chain running parallel to the $[010]$ direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, 0)$ (Fig. 3).

In (II), the molecules are linked by a single $\text{C}-\text{H}\cdots\pi(\text{arene})$ hydrogen bond (Table 2). Atom C8 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the C51–C56 acyl ring in the molecule at $(-\frac{1}{2}+x, \frac{3}{2}-y, z)$, so forming a zigzag $[100]$ chain generated by the a -glide plane at $y = \frac{3}{4}$ (Fig. 4). Two chains of this type pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

In contrast to the $\text{N}-\text{H}\cdots\text{S}$ and $\text{C}-\text{H}\cdots\pi(\text{arene})$ hydrogen bonds in (I) and (II), respectively, the structure of (III) (Laavanya *et al.*, 2002) contains no hydrogen bonds or direction-specific interactions of any kind between the molecules.

Experimental

Compound (I) was synthesized by reducing 2,3-dihydro-2,2,4-trimethyl-1,5-benzodiazepine with sodium borohydride in methanol at 273 K (Hsing *et al.*, 1966). Compound (II) was prepared by benzylation of (I) with benzoyl chloride and triethylamine in dry benzene under reflux conditions. Analysis for (II) found: C 73.3, H 6.9, N 4.3%; $\text{C}_{19}\text{H}_{21}\text{NOS}$ requires: C 73.3, H 6.8, N 4.5%. Crystals of (I) and (II) suitable for single-crystal X-ray diffraction were grown from solutions in light petroleum [m.p. 358–361 K for (I) and 383–386 K for (II)].

Compound (I)

Crystal data

C₁₂H₁₇NS
M_r = 207.34
 Monoclinic, *P*₂₁
a = 7.2644 (4) Å
b = 7.8657 (3) Å
c = 10.1522 (5) Å
 β = 103.190 (2)°
V = 564.79 (5) Å³
Z = 2
D_x = 1.219 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2550 reflections
 θ = 3.1–27.4°
 μ = 0.25 mm⁻¹
T = 120 (2) K
 Plate, colourless
 0.38 × 0.18 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)
T_{min} = 0.922, *T_{max}* = 0.980
 8535 measured reflections
 2550 independent reflections
 2422 reflections with *I* > 2σ(*I*)
R_{int} = 0.039
 θ_{max} = 27.4°
h = -9 → 9
k = -10 → 10
l = -13 → 12

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.029
wR (*F*²) = 0.070
S = 1.06
 2550 reflections
 130 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.0718P]$
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 $\Delta\rho_{\text{max}}$ = 0.15 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.20 e Å⁻³
 Absolute structure: Flack (1983),
 1163 Friedel pairs
 Flack parameter = -0.03 (6)

Table 1

Selected torsion angles (°) for compounds (I)–(III).

	(I)	(II)	(III)
S1–C10–C11–N5	-6.53 (19)	7.4 (3)	5.7 (5)
C11–C10–S1–C2	62.97 (13)	-69.29 (18)	-60.4 (4)
C10–C11–N5–C4	-69.68 (18)	74.6 (2)	75.1 (4)
S1–C2–C3–C4	63.33 (14)	60.3 (2)	65.2 (5)
N5–C4–C3–C2	-67.82 (17)	-62.3 (2)	-60.2 (5)
C10–S1–C2–C3	-70.33 (13)	24.40 (17)	15.7 (3)
C11–N5–C4–C3	90.42 (16)	-36.1 (2)	-39.6 (5)

Compound (II)

Crystal data

C₁₉H₂₁NOS
M_r = 311.43
 Orthorhombic, *Pna*2₁
a = 16.1757 (2) Å
b = 12.5444 (3) Å
c = 8.2147 (2) Å
V = 1666.88 (6) Å³
Z = 4
D_x = 1.241 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3762 reflections
 θ = 3.0–27.5°
 μ = 0.20 mm⁻¹
T = 120 (2) K
 Block, colourless
 0.30 × 0.08 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)
T_{min} = 0.866, *T_{max}* = 0.983
 19 245 measured reflections
 3762 independent reflections
 3605 reflections with *I* > 2σ(*I*)
R_{int} = 0.064
 θ_{max} = 27.5°
h = -20 → 19
k = -16 → 16
l = -10 → 10

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.045
wR (*F*²) = 0.130
S = 1.26
 3762 reflections
 203 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 0.2569P]$
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 $\Delta\rho_{\text{max}}$ = 0.63 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.84 e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.145 (9)
 Absolute structure: Flack (1983),
 1719 Friedel pairs
 Flack parameter = 0.01 (9)

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N5–H5...S1 ⁱ	0.95	2.75	3.5556 (13)	144

Symmetry code: (i) 1 - *x*, *y* - ½, -*z*.

Table 3

Hydrogen-bonding geometry (Å, °) for (II).

Cg1 is the centroid of the C51–C56 ring.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C8–H8...Cg1 ⁱ	0.95	2.88	3.674 (2)	142

Symmetry code: (i) *x* - ½, ½ - *y*, *z*.

For (I), the systematic absences permitted *P*₂₁ and *P*₂₁/*m* as possible space groups; *P*₂₁ was selected and confirmed by the subsequent structure analysis. For (II), the systematic absences permitted *Pna*2₁ and *Pnam* (= *Pnma*) as possible space groups; *Pna*2₁ was selected and confirmed by the subsequent structure analysis. All H atoms bonded to C atoms were located from difference maps and subsequently treated as riding atoms, with C–H distances of 0.95 (aromatic), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic CH). The H atom bonded to the N atom in (I) was located from a difference map and then allowed to ride at the N–H distance (0.95 Å) deduced from the map. The absolute configuration in (I) and the correct orientation of the structure with respect to the polar axis (Jones, 1986) in (II) were both established from the values [-0.03 (6) and 0.01 (9), respectively] of the Flack (1983) parameter.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants that have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1712). Services for accessing these data are described at the back of the journal.

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supporting information

Acta Cryst. (2004). C60, o346–o349 [doi:10.1107/S0108270104006857]

(R)-2,3,4,5-Tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine and *rac*-5-benzoyl-2,3,4,5-tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine: chains built from N—H \cdots S and C—H \cdots π (arene) hydrogen bonds

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Computing details

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

(I) (R)-2,3,4,5-Tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine

Crystal data

C₁₂H₁₇NS

$M_r = 207.34$

Monoclinic, *P*2₁

Hall symbol: P 2yb

$a = 7.2644$ (4) Å

$b = 7.8657$ (3) Å

$c = 10.1522$ (5) Å

$\beta = 103.190$ (2)°

$V = 564.79$ (5) Å³

$Z = 2$

$F(000) = 224$

$D_x = 1.219$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2550 reflections

$\theta = 3.1$ – 27.4 °

$\mu = 0.25$ mm⁻¹

$T = 120$ K

Plate, colourless

$0.38 \times 0.18 \times 0.08$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: rotating anode

Graphite monochromator

φ scans, and ω scans with κ offsets

Absorption correction: multi-scan
(*SORTAV*; Blessing, 1995, 1997)

$T_{\min} = 0.922$, $T_{\max} = 0.980$

8535 measured reflections

2550 independent reflections

2422 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.4$ °, $\theta_{\min} = 3.1$ °

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -13 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.070$

$S = 1.06$

2550 reflections

130 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.0718P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Absolute structure: Flack (1983), 1163 Friedel
pairs

Absolute structure parameter: -0.03 (6)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.65175 (4)	0.59519 (4)	0.23697 (3)	0.01927 (10)
N5	0.46296 (17)	0.27383 (17)	0.09340 (12)	0.0199 (3)
C2	0.41383 (19)	0.6000 (2)	0.27237 (13)	0.0200 (3)
C3	0.2687 (2)	0.5047 (2)	0.16415 (15)	0.0220 (3)
C4	0.2946 (2)	0.3147 (2)	0.14725 (15)	0.0211 (3)
C6	0.71740 (19)	0.0847 (2)	0.20656 (14)	0.0217 (3)
C7	0.8880 (2)	0.05871 (19)	0.29864 (16)	0.0246 (4)
C8	0.9793 (2)	0.1924 (2)	0.37585 (16)	0.0237 (3)
C9	0.8985 (2)	0.3531 (2)	0.35941 (15)	0.0209 (3)
C10	0.7285 (2)	0.38228 (18)	0.26592 (15)	0.0180 (3)
C11	0.6348 (2)	0.24709 (19)	0.18887 (14)	0.0180 (3)
C21	0.3609 (2)	0.7895 (2)	0.26204 (16)	0.0285 (4)
C22	0.4233 (2)	0.5345 (2)	0.41487 (16)	0.0268 (3)
C41	0.1203 (2)	0.2441 (2)	0.04820 (16)	0.0264 (4)
H3A	0.1427	0.5223	0.1839	0.026*
H3B	0.2660	0.5596	0.0760	0.026*
H4	0.3073	0.2577	0.2369	0.025*
H5	0.4397	0.1812	0.0322	0.024*
H6	0.6557	-0.0083	0.1549	0.026*
H7	0.9428	-0.0515	0.3089	0.030*
H8	1.0958	0.1741	0.4393	0.028*
H9	0.9600	0.4448	0.4128	0.025*
H21A	0.2366	0.8048	0.2828	0.043*
H21B	0.3565	0.8299	0.1701	0.043*
H21C	0.4557	0.8545	0.3267	0.043*
H22A	0.2982	0.5438	0.4353	0.040*
H22B	0.5144	0.6024	0.4799	0.040*
H22C	0.4633	0.4153	0.4211	0.040*
H41A	0.1100	0.2960	-0.0409	0.040*
H41B	0.0068	0.2705	0.0811	0.040*
H41C	0.1326	0.1206	0.0410	0.040*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01718 (17)	0.01833 (16)	0.02206 (17)	-0.00159 (16)	0.00397 (12)	0.00181 (16)
N5	0.0164 (6)	0.0241 (7)	0.0182 (6)	-0.0013 (5)	0.0015 (5)	-0.0052 (5)
C2	0.0178 (6)	0.0225 (7)	0.0206 (6)	-0.0007 (8)	0.0058 (5)	-0.0010 (7)
C3	0.0163 (7)	0.0290 (9)	0.0203 (8)	0.0009 (6)	0.0034 (6)	0.0004 (6)
C4	0.0154 (7)	0.0270 (8)	0.0210 (7)	-0.0036 (6)	0.0040 (6)	-0.0008 (6)
C6	0.0215 (7)	0.0210 (7)	0.0238 (7)	-0.0020 (7)	0.0077 (5)	-0.0010 (7)
C7	0.0245 (8)	0.0242 (10)	0.0273 (8)	0.0054 (6)	0.0104 (6)	0.0038 (6)
C8	0.0168 (7)	0.0319 (9)	0.0220 (8)	0.0035 (7)	0.0038 (6)	0.0065 (6)
C9	0.0172 (7)	0.0269 (8)	0.0182 (7)	-0.0023 (6)	0.0031 (6)	-0.0014 (6)
C10	0.0161 (7)	0.0200 (8)	0.0192 (7)	-0.0005 (6)	0.0066 (6)	0.0011 (6)
C11	0.0167 (7)	0.0224 (8)	0.0155 (7)	0.0001 (6)	0.0048 (5)	-0.0006 (6)
C21	0.0267 (9)	0.0256 (9)	0.0337 (9)	0.0066 (7)	0.0078 (7)	-0.0018 (7)
C22	0.0266 (8)	0.0336 (8)	0.0211 (8)	-0.0016 (7)	0.0076 (6)	-0.0009 (6)
C41	0.0192 (8)	0.0354 (10)	0.0236 (8)	-0.0067 (7)	0.0023 (6)	-0.0041 (7)

Geometric parameters (\AA , $^\circ$)

S1—C10	1.7682 (15)	C4—H4	1.00
S1—C2	1.8443 (13)	C41—H41A	0.98
C2—C22	1.522 (2)	C41—H41B	0.98
C2—C3	1.534 (2)	C41—H41C	0.98
C2—C21	1.537 (3)	N5—C11	1.4107 (18)
C21—H21A	0.98	N5—H5	0.9475
C21—H21B	0.98	C6—C7	1.387 (2)
C21—H21C	0.98	C6—C11	1.406 (2)
C22—H22A	0.98	C6—H6	0.95
C22—H22B	0.98	C7—C8	1.386 (2)
C22—H22C	0.98	C7—H7	0.95
C3—C4	1.521 (2)	C8—C9	1.388 (2)
C3—H3A	0.99	C8—H8	0.95
C3—H3B	0.99	C9—C10	1.394 (2)
C4—N5	1.4842 (19)	C9—H9	0.95
C4—C41	1.530 (2)	C10—C11	1.401 (2)
C10—S1—C2	105.12 (8)	C3—C4—H4	109.0
C22—C2—C3	112.96 (14)	C41—C4—H4	109.0
C22—C2—C21	110.43 (13)	C4—C41—H41A	109.5
C3—C2—C21	107.72 (12)	C4—C41—H41B	109.5
C22—C2—S1	109.71 (10)	H41A—C41—H41B	109.5
C3—C2—S1	111.85 (10)	C4—C41—H41C	109.5
C21—C2—S1	103.76 (11)	H41A—C41—H41C	109.5
C2—C21—H21A	109.5	H41B—C41—H41C	109.5
C2—C21—H21B	109.5	C11—N5—C4	116.98 (11)
H21A—C21—H21B	109.5	C11—N5—H5	109.5
C2—C21—H21C	109.5	C4—N5—H5	111.7

H21A—C21—H21C	109.5	C7—C6—C11	120.64 (15)
H21B—C21—H21C	109.5	C7—C6—H6	119.7
C2—C22—H22A	109.5	C11—C6—H6	119.7
C2—C22—H22B	109.5	C8—C7—C6	120.54 (14)
H22A—C22—H22B	109.5	C8—C7—H7	119.7
C2—C22—H22C	109.5	C6—C7—H7	119.7
H22A—C22—H22C	109.5	C7—C8—C9	119.22 (14)
H22B—C22—H22C	109.5	C7—C8—H8	120.4
C4—C3—C2	118.57 (14)	C9—C8—H8	120.4
C4—C3—H3A	107.7	C8—C9—C10	121.10 (14)
C2—C3—H3A	107.7	C8—C9—H9	119.4
C4—C3—H3B	107.7	C10—C9—H9	119.4
C2—C3—H3B	107.7	C9—C10—C11	119.80 (14)
H3A—C3—H3B	107.1	C9—C10—S1	117.76 (11)
N5—C4—C3	112.83 (13)	C11—C10—S1	122.12 (11)
N5—C4—C41	107.88 (12)	C10—C11—C6	118.68 (13)
C3—C4—C41	108.99 (13)	C10—C11—N5	120.75 (13)
N5—C4—H4	109.0	C6—C11—N5	120.55 (13)
C10—S1—C2—C22	55.83 (14)	C8—C9—C10—C11	1.3 (2)
C10—S1—C2—C3	-70.33 (13)	C8—C9—C10—S1	-172.23 (12)
C10—S1—C2—C21	173.84 (10)	C2—S1—C10—C9	-123.64 (12)
C22—C2—C3—C4	-61.03 (18)	C2—S1—C10—C11	62.97 (13)
C21—C2—C3—C4	176.73 (13)	C9—C10—C11—C6	-1.1 (2)
S1—C2—C3—C4	63.33 (16)	S1—C10—C11—C6	172.19 (11)
C2—C3—C4—N5	-67.82 (17)	C9—C10—C11—N5	-179.79 (13)
C2—C3—C4—C41	172.36 (12)	S1—C10—C11—N5	-6.53 (19)
C3—C4—N5—C11	90.42 (16)	C7—C6—C11—C10	0.1 (2)
C41—C4—N5—C11	-149.12 (13)	C7—C6—C11—N5	178.84 (13)
C11—C6—C7—C8	0.6 (2)	C4—N5—C11—C10	-69.68 (18)
C6—C7—C8—C9	-0.4 (2)	C4—N5—C11—C6	111.62 (15)
C7—C8—C9—C10	-0.6 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N5—H5 \cdots S1 ⁱ	0.95	2.75	3.5556 (13)	144

Symmetry code: (i) $-x+1, y-1/2, -z$.

(II) rac-5-benzoyl-2,3,4,5-tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine

Crystal data

 $C_{19}H_{21}NOS$ $M_r = 311.43$ Orthorhombic, $Pna2_1$ Hall symbol: $P\ 2c\ -2n$ $a = 16.1757$ (2) \AA $b = 12.5444$ (3) \AA $c = 8.2147$ (2) \AA $V = 1666.88$ (6) \AA^3 $Z = 4$ $F(000) = 664$ $D_x = 1.241$ Mg m^{-3} Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 3762 reflections

 $\theta = 3.0\text{--}27.5^\circ$

$\mu = 0.20 \text{ mm}^{-1}$
 $T = 120 \text{ K}$

Block, colourless
 $0.30 \times 0.08 \times 0.08 \text{ mm}$

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: rotating anode
 Graphite monochromator
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995, 1997)
 $T_{\min} = 0.866$, $T_{\max} = 0.983$

19245 measured reflections
 3762 independent reflections
 3605 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$
 $h = -20 \rightarrow 19$
 $k = -16 \rightarrow 16$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.130$
 $S = 1.26$
 3762 reflections
 203 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 0.2569P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.63 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.84 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL97,
 $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.145 (9)
 Absolute structure: Flack (1983), 1719 Friedel
 pairs
 Absolute structure parameter: 0.01 (9)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.35861 (3)	1.00783 (4)	0.65275 (8)	0.02546 (17)
O5	0.46969 (10)	0.75387 (13)	1.0173 (2)	0.0321 (4)
N5	0.36028 (10)	0.84474 (14)	0.9163 (2)	0.0194 (4)
C2	0.36814 (13)	1.09036 (17)	0.8392 (3)	0.0224 (4)
C3	0.33323 (12)	1.03476 (16)	0.9894 (3)	0.0216 (4)
C4	0.37080 (13)	0.92861 (16)	1.0427 (2)	0.0202 (4)
C6	0.22101 (13)	0.77625 (18)	0.8617 (3)	0.0251 (4)
C7	0.14577 (13)	0.7840 (2)	0.7786 (3)	0.0310 (5)
C8	0.13534 (13)	0.86172 (19)	0.6599 (4)	0.0326 (5)
C9	0.19989 (14)	0.93082 (18)	0.6213 (3)	0.0295 (5)
C10	0.27479 (13)	0.92396 (16)	0.7038 (3)	0.0232 (4)
C11	0.28502 (12)	0.84576 (16)	0.8245 (3)	0.0208 (4)
C21	0.31840 (18)	1.19232 (19)	0.8090 (3)	0.0367 (5)
C22	0.45944 (15)	1.1166 (2)	0.8593 (3)	0.0367 (6)
C41	0.33211 (15)	0.89267 (19)	1.2033 (3)	0.0285 (5)
C51	0.40869 (12)	0.68026 (16)	0.7812 (3)	0.0219 (4)
C52	0.39837 (12)	0.70733 (18)	0.6177 (3)	0.0252 (4)
C53	0.39977 (13)	0.6278 (2)	0.4995 (3)	0.0311 (5)
C54	0.41053 (14)	0.5217 (2)	0.5445 (3)	0.0330 (6)

C55	0.42120 (15)	0.49529 (18)	0.7042 (4)	0.0323 (6)
C56	0.42168 (13)	0.57368 (17)	0.8238 (3)	0.0270 (5)
C57	0.41511 (12)	0.76167 (17)	0.9146 (3)	0.0222 (4)
H21A	0.3182	1.2359	0.9079	0.055*
H21B	0.2615	1.1736	0.7799	0.055*
H21C	0.3437	1.2326	0.7197	0.055*
H22A	0.4911	1.0504	0.8700	0.055*
H22B	0.4672	1.1602	0.9571	0.055*
H22C	0.4788	1.1561	0.7638	0.055*
H3A	0.2735	1.0229	0.9704	0.026*
H3B	0.3380	1.0849	1.0821	0.026*
H4	0.4313	0.9395	1.0609	0.024*
H41A	0.3551	0.8234	1.2346	0.043*
H41B	0.2721	0.8863	1.1900	0.043*
H41C	0.3443	0.9452	1.2882	0.043*
H52	0.3904	0.7797	0.5871	0.030*
H53	0.3934	0.6460	0.3879	0.037*
H54	0.4104	0.4676	0.4637	0.040*
H55	0.4284	0.4227	0.7339	0.039*
H56	0.4308	0.5548	0.9344	0.032*
H6	0.2283	0.7235	0.9435	0.030*
H7	0.1019	0.7363	0.8033	0.037*
H8	0.0839	0.8678	0.6047	0.039*
H9	0.1927	0.9828	0.5384	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0344 (3)	0.0239 (3)	0.0181 (3)	-0.00135 (18)	0.0035 (2)	-0.0022 (2)
C2	0.0268 (10)	0.0204 (9)	0.0198 (10)	-0.0012 (7)	-0.0027 (7)	-0.0023 (8)
C21	0.0580 (15)	0.0251 (11)	0.0271 (11)	0.0094 (10)	-0.0062 (11)	-0.0014 (9)
C22	0.0277 (12)	0.0530 (16)	0.0294 (12)	-0.0157 (10)	-0.0022 (9)	0.0086 (11)
C3	0.0221 (9)	0.0242 (10)	0.0185 (9)	-0.0011 (8)	0.0001 (8)	-0.0036 (8)
C4	0.0215 (9)	0.0218 (10)	0.0173 (9)	-0.0021 (7)	-0.0010 (7)	-0.0040 (8)
C41	0.0334 (12)	0.0332 (12)	0.0189 (9)	-0.0050 (9)	0.0022 (8)	0.0007 (9)
N5	0.0204 (9)	0.0202 (9)	0.0175 (8)	-0.0005 (6)	-0.0019 (6)	-0.0019 (7)
C57	0.0216 (9)	0.0253 (10)	0.0198 (9)	0.0004 (7)	0.0014 (8)	-0.0002 (8)
O5	0.0296 (8)	0.0369 (9)	0.0297 (9)	0.0088 (6)	-0.0107 (7)	-0.0051 (7)
C51	0.0150 (9)	0.0235 (10)	0.0274 (11)	0.0011 (7)	0.0002 (7)	-0.0018 (8)
C52	0.0228 (10)	0.0276 (10)	0.0251 (11)	0.0041 (8)	-0.0012 (8)	-0.0024 (8)
C53	0.0260 (10)	0.0410 (13)	0.0263 (11)	0.0049 (9)	-0.0034 (9)	-0.0077 (10)
C54	0.0233 (10)	0.0325 (12)	0.0432 (15)	-0.0025 (9)	0.0016 (9)	-0.0182 (11)
C55	0.0246 (11)	0.0205 (10)	0.0518 (17)	-0.0021 (7)	0.0048 (10)	-0.0030 (10)
C56	0.0209 (10)	0.0276 (11)	0.0323 (11)	0.0011 (8)	0.0042 (8)	0.0041 (9)
C6	0.0230 (10)	0.0265 (10)	0.0259 (10)	-0.0012 (8)	0.0040 (8)	-0.0067 (8)
C7	0.0216 (11)	0.0340 (12)	0.0374 (13)	-0.0022 (8)	0.0020 (8)	-0.0150 (10)
C8	0.0216 (10)	0.0403 (12)	0.0359 (12)	0.0078 (8)	-0.0084 (9)	-0.0180 (12)
C9	0.0323 (11)	0.0309 (11)	0.0253 (11)	0.0094 (8)	-0.0090 (8)	-0.0076 (9)

C10	0.0256 (10)	0.0228 (10)	0.0211 (9)	0.0034 (7)	-0.0026 (8)	-0.0065 (8)
C11	0.0187 (9)	0.0221 (9)	0.0215 (9)	0.0019 (7)	-0.0007 (7)	-0.0050 (8)

Geometric parameters (Å, °)

S1—C10	1.767 (2)	C57—C51	1.501 (3)
S1—C2	1.855 (2)	C51—C52	1.396 (3)
C2—C22	1.522 (3)	C51—C56	1.398 (3)
C2—C3	1.526 (3)	C52—C53	1.392 (3)
C2—C21	1.531 (3)	C52—H52	0.95
C21—H21A	0.98	C53—C54	1.392 (4)
C21—H21B	0.98	C53—H53	0.95
C21—H21C	0.98	C54—C55	1.364 (4)
C22—H22A	0.98	C54—H54	0.95
C22—H22B	0.98	C55—C56	1.390 (4)
C22—H22C	0.98	C55—H55	0.95
C3—C4	1.528 (3)	C56—H56	0.95
C3—H3A	0.99	C6—C11	1.388 (3)
C3—H3B	0.99	C6—C7	1.399 (3)
C4—N5	1.488 (3)	C6—H6	0.95
C4—C41	1.528 (3)	C7—C8	1.390 (4)
C4—H4	1.00	C7—H7	0.95
C41—H41A	0.98	C8—C9	1.393 (4)
C41—H41B	0.98	C8—H8	0.95
C41—H41C	0.98	C9—C10	1.391 (3)
N5—C57	1.369 (3)	C9—H9	0.95
N5—C11	1.432 (2)	C10—C11	1.404 (3)
C57—O5	1.225 (3)		
C10—S1—C2	101.53 (10)	O5—C57—N5	121.39 (19)
C22—C2—C3	111.73 (17)	O5—C57—C51	119.87 (18)
C22—C2—C21	110.3 (2)	N5—C57—C51	118.72 (18)
C3—C2—C21	108.58 (18)	C52—C51—C56	119.5 (2)
C22—C2—S1	106.91 (16)	C52—C51—C57	123.04 (19)
C3—C2—S1	112.46 (14)	C56—C51—C57	117.2 (2)
C21—C2—S1	106.76 (15)	C53—C52—C51	119.7 (2)
C2—C21—H21A	109.5	C53—C52—H52	120.2
C2—C21—H21B	109.5	C51—C52—H52	120.2
H21A—C21—H21B	109.5	C52—C53—C54	120.1 (2)
C2—C21—H21C	109.5	C52—C53—H53	119.9
H21A—C21—H21C	109.5	C54—C53—H53	119.9
H21B—C21—H21C	109.5	C55—C54—C53	120.3 (2)
C2—C22—H22A	109.5	C55—C54—H54	119.9
C2—C22—H22B	109.5	C53—C54—H54	119.9
H22A—C22—H22B	109.5	C54—C55—C56	120.6 (2)
C2—C22—H22C	109.5	C54—C55—H55	119.7
H22A—C22—H22C	109.5	C56—C55—H55	119.7
H22B—C22—H22C	109.5	C55—C56—C51	119.9 (2)

C2—C3—C4	118.88 (17)	C55—C56—H56	120.1
C2—C3—H3A	107.6	C51—C56—H56	120.1
C4—C3—H3A	107.6	C11—C6—C7	119.9 (2)
C2—C3—H3B	107.6	C11—C6—H6	120.1
C4—C3—H3B	107.6	C7—C6—H6	120.1
H3A—C3—H3B	107.0	C8—C7—C6	119.8 (2)
N5—C4—C41	110.31 (17)	C8—C7—H7	120.1
N5—C4—C3	111.75 (16)	C6—C7—H7	120.1
C41—C4—C3	109.98 (18)	C7—C8—C9	120.3 (2)
N5—C4—H4	108.2	C7—C8—H8	119.8
C41—C4—H4	108.2	C9—C8—H8	119.8
C3—C4—H4	108.2	C10—C9—C8	120.2 (2)
C4—C41—H41A	109.5	C10—C9—H9	119.9
C4—C41—H41B	109.5	C8—C9—H9	119.9
H41A—C41—H41B	109.5	C9—C10—C11	119.3 (2)
C4—C41—H41C	109.5	C9—C10—S1	121.06 (18)
H41A—C41—H41C	109.5	C11—C10—S1	119.55 (15)
H41B—C41—H41C	109.5	C6—C11—C10	120.43 (18)
C57—N5—C11	123.53 (17)	C6—C11—N5	120.84 (19)
C57—N5—C4	118.12 (17)	C10—C11—N5	118.56 (18)
C11—N5—C4	117.28 (16)		
C10—S1—C2—C22	147.38 (16)	C52—C53—C54—C55	-1.2 (4)
C10—S1—C2—C3	24.40 (17)	C53—C54—C55—C56	-0.2 (4)
C10—S1—C2—C21	-94.59 (17)	C54—C55—C56—C51	1.9 (3)
C22—C2—C3—C4	-60.0 (3)	C52—C51—C56—C55	-2.3 (3)
C21—C2—C3—C4	178.19 (18)	C57—C51—C56—C55	-176.37 (19)
S1—C2—C3—C4	60.3 (2)	C11—C6—C7—C8	-0.4 (3)
C2—C3—C4—N5	-62.3 (2)	C6—C7—C8—C9	1.0 (3)
C2—C3—C4—C41	174.84 (17)	C7—C8—C9—C10	-1.3 (3)
C41—C4—N5—C57	-82.1 (2)	C8—C9—C10—C11	0.9 (3)
C3—C4—N5—C57	155.24 (18)	C8—C9—C10—S1	177.97 (17)
C41—C4—N5—C11	86.5 (2)	C2—S1—C10—C9	113.68 (18)
C3—C4—N5—C11	-36.1 (2)	C2—S1—C10—C11	-69.29 (18)
C11—N5—C57—O5	-165.3 (2)	C7—C6—C11—C10	0.0 (3)
C4—N5—C57—O5	2.6 (3)	C7—C6—C11—N5	175.18 (19)
C11—N5—C57—C51	16.1 (3)	C9—C10—C11—C6	-0.3 (3)
C4—N5—C57—C51	-176.06 (17)	S1—C10—C11—C6	-177.36 (16)
O5—C57—C51—C52	-133.1 (2)	C9—C10—C11—N5	-175.56 (18)
N5—C57—C51—C52	45.5 (3)	S1—C10—C11—N5	7.4 (3)
O5—C57—C51—C56	40.7 (3)	C57—N5—C11—C6	67.3 (3)
N5—C57—C51—C56	-140.68 (19)	C4—N5—C11—C6	-100.6 (2)
C56—C51—C52—C53	1.1 (3)	C57—N5—C11—C10	-117.4 (2)
C57—C51—C52—C53	174.71 (19)	C4—N5—C11—C10	74.6 (2)
C51—C52—C53—C54	0.7 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C8—H8···Cg1 ⁱ	0.95	2.88	3.674 (2)	142

Symmetry code: (i) $x-1/2, -y+3/2, z$.