Table 3. *Hydrogen bonds in hesperetin monohydrate*

| $a-b\cdots c$ | $b-c$ (Å) | $a-c$ (Å) | $abc$ (°) |
|---|---|---|---|
| O(5)–H⋯O(4) | 1·67 (6) | 2·552 (5) | 137 (5) |
| O(7)–H⋯O($W^i$) | 1·68 (5) | 2·713 (7) | 170 (4) |
| O(3')–H⋯O(5$^{ii}$) | 1·64 (7) | 2·731 (4) | 174 (5) |
| O($W$)–H(1)⋯O(3$^{'iii}$) | 2·17 (6) | 2·795 (7) | 170 (7) |
| O($W$) H(2)⋯O(4$^{'iv}$) | 2·47 (10) | 3·159 (7) | 175 (10) |
| O(5)–H⋯O(4$^{''iv}$) | 2·46 (6) | 2·907 (4) | 104 (4) |
| O(3')–H⋯O(4') | 2·36 (6) | 2·678 (5) | 95 (4) |

Symmetry code: none $x, y, z$; (i) $x, y, 1+z$; (ii) $x, 1+y, z$; (iii) $1-x$, $1-y, 1-z$; (iv) $x, -1+y, z$.

only van der Waals interactions between the molecular double layers.

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# Structure of 11,12-Dihydro-6*H*-6,12-methanodibenzo[*b,f*]thiocin-12-carbonitrile

BY J. PODLAHA AND J. PODLAHOVÁ

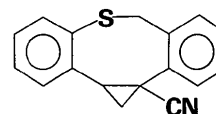*Department of Chemistry, Charles University, 128 40 Prague, Czechoslovakia*

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**Abstract.** $C_{17}H_{13}NS$, $M_r = 263\cdot36$, $P2_1/c$, $a = 8\cdot146$ (3), $b = 18\cdot660$ (8), $c = 8\cdot666$ (2) Å, $\beta = 91\cdot41$ (3)°, $V = 1316\cdot9$ (8) Å$^3$, $Z = 4$, $D_m = 1\cdot296$ (5), $D_x = 1\cdot33$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot213$ mm$^{-1}$, $F(000) = 552$, $T = 295$ K, $R = 0\cdot0425$ for 1836 observed unique reflections. The molecular structure is tetracyclic with a central bicyclo[3.3.1]-2-thianonane-3,7-diene moiety and two phenyl rings *ortho*-condensed to it. Bond lengths and angles are normal.

**Introduction.** The phase-transfer-catalysed reaction of 6,11-dihydrodibenzo[*b,e*]thiepin-11-carbonitrile with excess 1,2-dibromoethane (Šindelář, Holubek, Ryska, Svátek, Urban & Protiva, 1983) afforded three isomeric products of composition $C_{17}H_{13}NS$. On the basis of NMR and mass spectra, the structure below was tentatively assigned to one of the minor products (compound XVI in the original paper). Subsequent detailed ¹H and ¹³C NMR data (Šindelář *et al.*, 1987) indicated, however, that the structure should not involve a cyclopropane ring. The X-ray crystal struc-

ture determination has been undertaken to resolve the ambiguities.



**Experimental.** Single crystals grown from benzene/cyclohexane were kindly provided by K. Šindelář. The density was determined by flotation in aqueous zinc bromide solution. The measurement and refinement data are summarized in Table 1.*

Structure solution and refinement: direct methods; $F$ magnitudes used in full-matrix least-squares refinement; all H atoms found from $\Delta\rho$ synthesis; scale

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44060 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

factor, positions and anisotropic thermal parameters of non-H atoms, positions of aliphatic H atoms, a common isotropic thermal parameter for aliphatic H atoms and another common thermal parameter for aromatic H atoms refined simultaneously; aromatic H atoms fixed in calculated positions; programs used: MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), SHELX76 (Sheldrick, 1976); ICL 4–72 computer. Atomic scattering factors those of SHELX76.

**Discussion.** The atomic coordinates are given in Table 2; Fig. 1 depicts a perspective view of the molecule with

atom numbering. (The numbering is somewhat unusual from the point of view of crystallographic conventions but follows the IUPAC nomenclature rules.) Bond lengths and angles are summarized in Table 3.

The structure consists of discrete molecules packed (Fig. 2) at van der Waals or longer distances. In

### Table 1. Measurement and refinement data

| | |
|---|---|
| Crystal dimensions (mm) | $0.2 \times 0.3 \times 0.15$ |
| No. of reflections for lattice-parameter determination | $20 \ (4 < 2\theta < 25°)$ |
| Diffractometer | Syntex $P2_1$ |
| Scan mode | $\theta$–$2\theta$ |
| Maximum value of $(\sin\theta)/\lambda(\text{Å}^{-1})$ | 0.60 |
| Standard reflections (variation) | Three after every 30 (less than 3%) |
| Absorption correction | None, $\mu = 0.213 \text{ mm}^{-1}$ |
| $h \in$ | $\langle 0,9 \rangle$ |
| $k \in$ | $\langle 0,22 \rangle$ |
| $l \in$ | $\langle -10,10 \rangle$ |
| No. of unique reflections measured | 2512 |
| No. of reflections used $[I > 1.96 \ \sigma_1(I)]$ | 1836 |
| Residual electron density (e Å$^{-3}$) | $0.20, -0.23$ |
| $(\Delta/\sigma)_{\max}$ for non-H atoms | 0.03 |
| for H-atoms | 0.15 |
| Function minimized | $w(|F_o| - |F_c|)^2$ |
| Weight | $\sigma^{-2}(F_o)^*$ |
| $R, wR$ | $0.0425, 0.0501$ |

\* Based on $\sigma_1(I) = $ scan rate $\times$ (total scan counts + left background + right background)$^{1/2}$; $\sigma_2(I) = [\sigma_1^2(I) + (0.06 \ I)^2]^{1/2}$; $\sigma(F_o)/F_o = \frac{1}{2}\sigma_2(I)/I$.

### Table 2. Final coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^4$) with e.s.d.'s in parentheses

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

| | $x$ | $y$ | $z$ | $U_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|
| S | 2535 (1) | 423.3 (4) | 467 (1) | 616 (3) |
| N | −233 (4) | 2868 (1) | 2971 (4) | 938 (12) |
| C(1) | 3953 (3) | 2311 (1) | 2426 (3) | 384 (8) |
| C(2) | 5462 (3) | 2412 (1) | 1776 (3) | 517 (10) |
| C(3) | 6025 (3) | 1933 (2) | 715 (3) | 672 (10) |
| C(4) | 5081 (3) | 1334 (2) | 322 (3) | 598 (9) |
| C(4A) | 3557 (3) | 1222 (1) | 1001 (2) | 449 (7) |
| C(6) | 1036 (3) | 378 (1) | 1995 (3) | 531 (8) |
| C(6A) | 1834 (3) | 147 (1) | 3509 (3) | 457 (7) |
| C(7) | 2307 (3) | −567 (1) | 3721 (3) | 615 (10) |
| C(8) | 3091 (4) | −785 (2) | 5058 (4) | 696 (11) |
| C(9) | 3398 (3) | −292 (2) | 6233 (3) | 697 (11) |
| C(10) | 2922 (3) | 411 (1) | 6049 (3) | 560 (9) |
| C(10A) | 2135 (3) | 639 (1) | 4681 (2) | 425 (7) |
| C(11) | 1604 (3) | 1411 (1) | 4551 (3) | 499 (8) |
| C(12) | 1322 (3) | 1644 (1) | 2860 (3) | 460 (7) |
| C(12A) | 2977 (3) | 1724 (1) | 2044 (2) | 424 (7) |
| C(13) | 169 (3) | 1099 (2) | 2065 (3) | 576 (9) |
| C(14) | 467 (3) | 2348 (2) | 2890 (3) | 642 (10) |

### Table 3. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

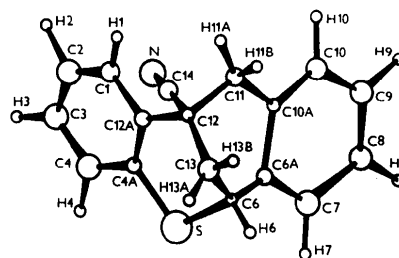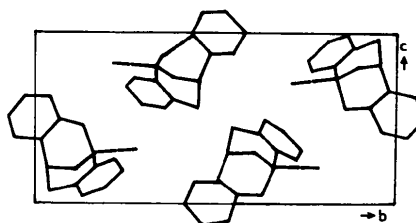| | | | |
|---|---|---|---|
| C(1)–C(2) | 1.378 (4) | C(1)–C(2)–C(3) | 120.1 (3) |
| C(2)–C(3) | 1.369 (4) | C(2)–C(3)–C(4) | 119.7 (2) |
| C(3)–C(4) | 1.394 (4) | C(3)–C(4)–C(4A) | 120.4 (3) |
| C(4)–C(4A) | 1.402 (3) | C(4)–C(4A)–C(12A) | 119.4 (2) |
| C(4A)–C(12A) | 1.392 (3) | C(4A)–C(12A)–C(1) | 118.9 (2) |
| C(12A)–C(1) | 1.390 (3) | C(12A)–C(1)–C(2) | 121.5 (3) |
| | | | |
| C(7)–C(8) | 1.371 (4) | C(7)–C(8)–C(9) | 119.5 (3) |
| C(8)–C(9) | 1.391 (4) | C(8)–C(9)–C(10) | 120.1 (3) |
| C(9)–C(10) | 1.376 (4) | C(9)–C(10)–C(10A) | 120.7 (3) |
| C(10)–C(10A) | 1.400 (3) | C(10)–C(10A)–C(6A) | 119.2 (2) |
| C(10A)–C(6A) | 1.386 (3) | C(10A)–C(6A)–C(7) | 119.4 (2) |
| C(6A)–C(7) | 1.397 (3) | C(6A)–C(7)–C(8) | 121.1 (3) |
| | | | |
| C(4A)–S | 1.764 (2) | C(4)–C(4A)–S | 115.7 (2) |
| S–C(6) | 1.826 (6) | C(12A)–C(4A)–S | 124.9 (2) |
| C(6)–C(6A) | 1.513 (3) | C(4A)–S–C(6) | 99.7 (1) |
| | | S–C(6)–C(6A) | 111.2 (2) |
| | | C(6)–C(6A)–C(7) | 119.8 (2) |
| | | C(6)–C(6A)–C(10A) | 120.8 (2) |
| | | | |
| C(12A)–C(12) | 1.544 (3) | C(4A)–C(12A)–C(12) | 123.2 (2) |
| C(12)–C(11) | 1.541 (3) | C(1)–C(12A)–C(12) | 117.9 (2) |
| C(11)–C(10A) | 1.507 (3) | C(12A)–C(12)–C(11) | 110.6 (2) |
| | | C(12)–C(11)–C(10A) | 112.2 (2) |
| | | C(11)–C(10A)–C(6A) | 122.2 (2) |
| | | C(11)–C(10A)–C(10) | 118.6 (2) |
| | | | |
| C(6)–C(13) | 1.521 (4) | C(6)–C(13)–C(12) | 108.9 (2) |
| C(13)–C(12) | 1.536 (3) | C(6A)–C(6)–C(13) | 114.1 (2) |
| | | S–C(6)–C(13) | 107.9 (2) |
| | | C(12A)–C(12)–C(13) | 112.9 (2) |
| | | C(11)–C(12)–C(13) | 108.3 (2) |
| | | | |
| C(12)–C(14) | 1.488 (4) | C(11)–C(12)–C(14) | 107.0 (2) |
| C(14)–N | 1.128 (3) | C(12A)–C(12)–C(14) | 109.7 (2) |
| | | C(13)–C(12)–C(14) | 108.1 (2) |
| | | C(12)–C(14)–N | 176.4 (3) |



Fig. 1. Perspective view of the molecule (40% probability).



Fig. 2. Unit-cell contents projected onto the bc plane.

Table 4. *Comparison of endocyclic torsion angles* (°, *e.s.d.'s in parentheses*) *of bicyclo*|3.3.1|*nonadiene systems*

*A,B*: the present structure; *C*: Radcliffe *et al.* (1984); *D*: Quast *et al.* (1984) (mean values of four closely related structures); *E*: theoretical values for the ideal half-chair.

| A | | B | C | D | E |
|---|---|---|---|---|---|
| C(4A)–C(12A) | −0·7 (4) | C(6A)–C(10A) | 3·6 (4) | 0·2 (3) | −1 (1) | 0 |
| C(12A)–C(12) | −17·6 (3) | C(10A)–C(11) | −21·3 (4) | −16·1 (4) | −13 (3) | 15 |
| C(12)–C(13) | 57·4 (4) | C(11)–C(12) | 51·5 (3) | 50·5 (3) | 47 (3) | 46 |
| C(13)–C(6) | −76·0 (3) | C(12)–C(13) | −65·5 (4) | −68·7 (3) | −68 (2) | 63 |
| C(6)–S | 50·8 (3) | C(13)–C(6) | 48·1 (3) | 51·0 (3) | 52 (1) | 46 |
| S–C(4A) | −15·0 (3) | C(6)–C(6A) | −17·3 (4) | −16·7 (4) | −18 (2) | −15 |

accordance with recent NMR data (Šindelář *et al.*, 1987), the molecular skeleton is tetracyclic with two phenyl rings *ortho*-condensed to a central bicyclo-[3.3.1]-2-thianonane-3,7-diene system. The bond lengths and angles are all normal, indicating an essentially strain-free conformation. Idealized geometry calculations show that there are two such conformations available which differ in the puckering of the central bicyclononadiene system and, consequently, in the dihedral angle of the aromatic ring planes: (*a*) twin-sofa central rings with dihedral angle *ca* 140°, and (*b*) twin-half-chair central rings with dihedral angle *ca* 90°. In the crystal, the (*b*) conformation is realized: the dihedral angle has the value of 91·2 (3)° and the idealized twofold half-chair axes bisect the C(4A)–C(12A) and C(6A)–C(10A) bonds respectively. This arrangement is closely related (Table 4) to the bicyclo[3.3.1]nonadiene systems whose crystal structures are known (Radcliffe, Gutierrez, Blount & Mislow, 1984; Quast, Gorlach, Stawitz, Peters, Peters & von Schmering, 1984). To our knowledge, no example of such a bicyclic system involving sulfur as a heteroatom has been characterized by crystal structure

determination till now. The asymmetry parameters (Duax, Weeks & Rohrer, 1976) $\Delta C_2(4A-12A) = 5\cdot0°$, $\Delta C_2(6A-10A) = 3\cdot5°$ indicate, however, that the S atom affects the relative conformation of the rings very little.

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# The Structure of the 1:1 Complex of β-1',2',3',4',10,11-Hexahydrocinchonine and β-9-Deoxy-1',2',3',4',10,11-hexahydrocinchonine

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**Abstract.** $C_{19}H_{28}N_2O.C_{19}H_{28}N_2$, $M_r = 584\cdot9$, ortho-rhombic, $P2_12_12_1$, $a = 12\cdot463$ (2), $b = 13\cdot227$ (3), $c = 20\cdot330$ (4) Å, $V = 3351$ (1) Å$^3$, $Z = 4$, $D_m = 1\cdot13$, $D_x = 1\cdot16$ Mg m$^{-3}$, $\lambda(\text{Cu }K\alpha) = 1\cdot54178$ Å, $\mu(\text{Cu }K\alpha) = 0\cdot46$ mm$^{-1}$, $F(000) = 1280$, room temperature, $R = 0\cdot047$ for 2297 observed reflexions. The complex-

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