lack of a second H atom on methanol to act as a donor to the acetyl carbonyl oxygen, O7′. Interestingly, this missing interaction is the weakest, by distance criteria, of all the hydrogen bonds in PW and the acetyl oxygen displays a considerable wagging motion in the PM structure, reflecting its lack of constraint by the additional hydrogen bond. As may be seen in the unit-cell drawing, Fig. 2, the acetyl group sits in a cavity formed by the glucose ring and the paucin skeleton. As a result of the crystal packing, and in the absence of the second hydrogen-bonding interaction, the acetyl carbonyl group has a considerable space in which to flex.

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Structure of the *Z* Isomer of 5-(2-Chlorobenzylidene)-2,3-dihydroimidazo[2,1-*b*]-thiazol-6(5*H*)-one

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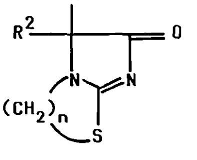
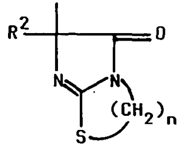
Abstract. $C_{12}H_9ClN_2OS$, $M_r = 264{\cdot}73$, orthorhombic, *Pbca*, $a = 21{\cdot}881\,(3)$, $b = 14{\cdot}619\,(2)$, $c = 7{\cdot}118\,(1)$ Å, $V = 2276{\cdot}8\,(5)$ Å^3, $Z = 8$, $D_x = 1{\cdot}544$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 43{\cdot}77$ cm^{-1}, $F(000) = 1088$, final $R = 0{\cdot}040$ for 887 observed reflections with $F > 6\sigma(F)$ (of 1249 unique data). The molecule is in the *Z* configuration and adopts a non-planar conformation with the two planar rings (benzene and thiohydantoin) forming an angle of 34·2 (2)°. Molecular-mechanics calculations indicate that it is not a minimum-energy conformation.

Introduction. Searching for new compounds influencing the central nervous system we have examined annelated 2-thiohydantoin derivatives of types (1), (2), (3) and (4). The derivatives of 5,5-diphenyl-2-thiohydantoin (DPTH) [(1) and (2)] have shown sedative properties while the derivatives of 5-benzylidene-2-thiohydantoin [of type (4)] possessed analgesic, anxiolytic, antidepressant and anticonvulsive properties (Kolasa, Kleinrok, Pietrusiewiez, Czechowski, Kieć-Kononowicz & Zejc, 1989).





$n = 2, 3, 4$
(1) $R^1 = R^2 = \text{Ph}$ (2)
(3) $R^1 = R^2 =$ (un)substituted benzylidene (4)

In previous investigations on the reactions of DPTH with dibromoalkanes [$Br(CH_2)_nBr$; $n = 2$, 3, 4], depending on the conditions used, different amounts of isomeric bicyclic compounds were formed as a result of intramolecular 1,2- or 2,3-dialkylation [(1) and (2), respectively]. Comparisons of physicochemical properties, stability and X-ray structure analysis were performed (Kieć-Kononowicz, Zatorski & Karolak-Wojciechowska, 1989; Kieć-Kononowicz, Zejc, Mikołajczyk, Zatorski, Karolak-Wojciechowska & Wieczorek, 1980, 1981; Karolak-Wojciechowska, Mikołajczyk, Zatorski, Kieć- Kononowicz & Zejc, 1985).

In the continuation of our studies we have investigated derivatives of type (4) (Karolak-Wojciechowska, Kwiatkowski & Kieć-Kononowicz, 1989; Karolak-Wojciechowska & Kieć-Kononowicz, 1991). The present paper deals with the structure of a 5-benzylidene-2-thiohydantoin derivative of type (3).

Experimental. The title compound recrystallized from benzene in the form of yellow block-like crystals; crystal dimensions 0·1 × 0·1 × 0·2 mm. Unit-cell parameters were obtained on a KM-4 diffractometer (KUMA)* from least-squares refinement of 25 reflections ($50 < 2\theta < 110^\circ$); no absorption corrections were applied; intensities measured on KM-4 diffractometer; $2\theta < 160^\circ$; h 0–24, k 0–15, l 0–7; ω–1·8θ scan technique; intensity of three standard reflections monitored every 50 reflections showed no significant fluctuations; 1249 unique reflections were measured; 892 observed reflections with $F > 6\sigma(F)$ were used in the refinement.

The structure was solved by direct methods (*SHELXS86*; Sheldrick, 1986) with $R(E) = 0·31$ for all 17 non-H atoms. All H atoms were located on the basis of a $\Delta\rho$ map after anisotropic refinement of non-H atoms. Isotropic thermal parameters of H atoms were kept as 1·5 times respective parameter for parent C atoms. The H atoms were refined in the riding model. Refinement by full-matrix least squares (anisotropic temperature factors for all non-H atoms) converged to $R = 0·040$ and $wR = 0·042$ with $w = 0·6935/[\sigma^2(F)^2 + 0·001F^2]$ for 887 reflections (5 reflections affected by secondary extinction omitted in the last cycle); $S = 1·54$; 5·7 reflections per parameter; final $\Delta/\sigma < 0·01$; maximum and minimum peaks in the final $\Delta\rho$ map were 0·27 and $-0·23$ e Å^{-3}. Atomic scattering factor from *SHELX76* (Sheldrick, 1976). All calculations were performed using *SHELX76* on an Amstrad 1512 PC.

Discussion. Fig. 1 shows a molecule of the title compound [type (3)] as found in the crystal and the atom-numbering scheme, and Table 1* gives the final atomic parameters. All bond lengths and angles (Table 2) in the molecule have the expected values. The C6—C11 bond [1·470 (6) Å] may indicate a small π overlap between the aromatic ring and the other conjugated system.

The molecule in the crystal has *Z* configuration. Two rings, benzene and thiohydantoin, are planar while the third one, the five-membered thiazole ring, has an open-envelope conformation with the C7 atom in an open position.

The two planar rings form an angle of 34·3 (2)°. In the molecule of the 2,3-alkylation product with the *Z* configuration [type (4)], the same angle ranged around 0° (Karolak-Wojciechowska *et al.*, 1989; Karolak-Wojciechowska & Kieć-Kononowicz, 1991). Owing to 1,2-substitution in the present structure this dihedral angle was increased. The crystallographic analysis of 5-benzylidene derivatives of hydantoin by Drew and co-workers (Drew, Mok, Ang & Tan, 1987*a*,*b*,*c*) showed that such an angle depends on the substituents in the hydantoin and benzylidene rings and ranges from 5·4 (3)° for unsubstituted to 84·2 (3)° for spatially crowded N1 and 2,4,6-trisubstituted benzylidene derivatives of hydantoin.

To understand better which conformation might be preferred in solution we have calculated the energies of conformations generated by clockwise variation of φ, the C12—C11—C6—C5 torsion angle, using the molecular-mechanics program *MMX* (Burkert & Allinger, 1982). This program takes π overlap into account. The energy was minimized for

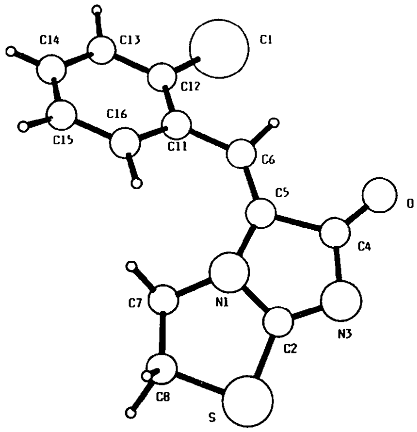


Fig. 1. View of the molecule with atom-numbering system.

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* 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 53622 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Non*-H-*atom fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
Cl	4779 (1)	3419 (1)	1268 (2)	64·0 (5)
S	1424 (1)	3069 (1)	5195 (2)	50·0 (5)
O	3295 (2)	1224 (2)	4091 (6)	56 (1)
N1	2590 (2)	3306 (2)	4732 (5)	33 (1)
C2	2145 (2)	2645 (3)	4926 (6)	37 (1)
N3	2335 (2)	1796 (2)	4804 (6)	44 (1)
C4	2953 (2)	1861 (3)	4357 (7)	42 (1)
C5	3130 (2)	2857 (3)	4284 (7)	33 (1)
C7	2331 (2)	4220 (3)	4292 (8)	42 (1)
C8	1722 (2)	4234 (3)	5285 (8)	50 (1)
C6	3693 (2)	3128 (3)	3892 (7)	39 (1)
C11	3965 (2)	4047 (3)	3864 (7)	36 (1)
C12	4456 (2)	4261 (3)	2691 (7)	41 (1)
C13	4715 (2)	5131 (4)	2619 (7)	48 (1)
C14	4485 (2)	5796 (3)	3796 (9)	53 (1)
C15	4025 (2)	5601 (3)	5064 (8)	50 (1)
C16	3778 (2)	4734 (3)	5117 (7)	42 (1)

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

Cl—C12	1·744 (5)	C5—C6	1·324 (6)
S—C2	1·706 (5)	C7—C8	1·509 (7)
S—C8	1·825 (5)	C6—C11	1·470 (6)
O—C4	1·210 (6)	C11—C12	1·396 (7)
N1—C2	1·379 (6)	C11—C16	1·404 (7)
N1—C5	1·389 (6)	C12—C13	1·393 (7)
N1—C7	1·485 (5)	C13—C14	1·378 (7)
C2—N3	1·312 (5)	C14—C15	1·382 (7)
N3—C4	1·392 (6)	C15—C16	1·378 (6)
C4—C5	1·508 (6)		

C2—S—C8	90·7 (2)	N1—C7—C8	104·5 (4)
C2—N1—C5	107·0 (4)	S—C8—C7	106·7 (3)
C2—N1—C7	112·5 (4)	C5—C6—C11	130·8 (4)
C5—N1—C7	134·6 (4)	C6—C11—C12	121·6 (4)
S—C2—N1	114·2 (3)	C6—C11—C16	121·8 (4)
S—C2—N3	130·1 (4)	C12—C11—C16	116·3 (4)
N1—C2—N3	115·6 (4)	Cl—C12—C11	120·1 (4)
C2—N3—C4	105·0 (4)	Cl—C12—C13	117·3 (4)
O—C4—N3	125·7 (4)	C11—C12—C13	122·7 (4)
O—C4—C5	125·4 (4)	C12—C13—C14	118·2 (5)
N3—C4—C5	108·9 (4)	C13—C14—C15	121·2 (5)
N1—C5—C4	103·3 (4)	C14—C15—C16	119·6 (5)
N1—C5—C6	134·3 (4)	C11—C16—C15	121·7 (4)
C4—C5—C6	122·4 (4)		

each 10° rotation while the torsion angle N1—C5—C6—C11 was kept at the crystallographic value (7°). The results are depicted in Fig. 2.

The calculations indicate unfavorable steric repulsions in two planar forms (20 and 200°). In both energy minima the benzene ring is almost perpendicular to the plane of the thiohydantoin ring. The X-ray conformation [φ = 33·6 (8)°] is calculated to be only about 4·18 kJ mol^{-1} higher than the minimum at 70°. This small energy is presumably provided in the crystal by an increase in packing energy of the molecules in the slightly non-planar form (see Fig. 3).

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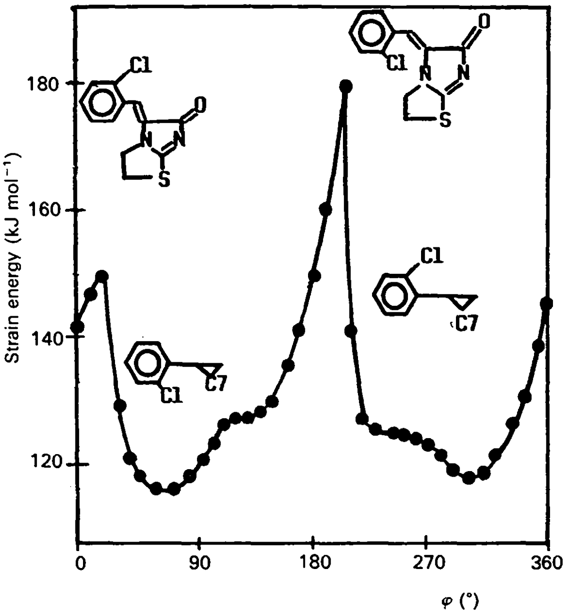

Fig. 2. Molecular-mechanics calculation results; strain energy as a function of φ, the C12—C11—C6—C5 torsion angle.

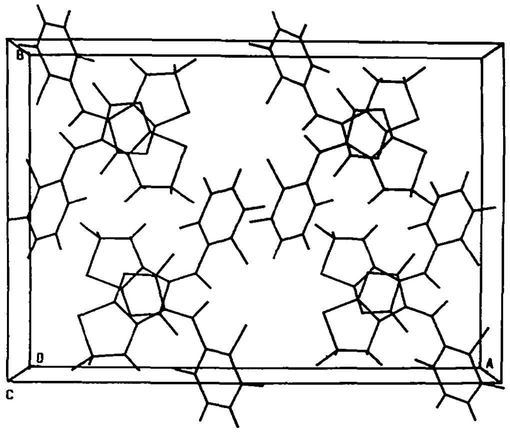

Fig. 3. A view of the crystal packing.

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Structure of (*R*)-*N*,*N*,*N*′,*N*′-Tetramethyl-[1,1′-binaphthalene]-2,2′-diamine

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Abstract. $C_{24}H_{24}N_2$, $M_r = 340{\cdot}5$, tetragonal, $I4_1$, $a = 11{\cdot}872\,(2)$, $c = 13{\cdot}746\,(3)$ Å, $V = 1937{\cdot}5\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}17\ \mathrm{g\,cm^{-3}}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}63\ \mathrm{cm^{-1}}$, $F(000) = 728$, room temperature, $R = 0{\cdot}043$ for 736 reflections with $I > 3\sigma(I)$. The dihedral angle between the planes of the naphthylic rings is $71{\cdot}2(1)^\circ$. The N atoms in the dimethylamino groups are almost sp^2 hybridized.

Introduction. Structural studies on C_2-symmetric 1,1′-binaphthylic compounds have received a great deal of attention in the last few years owing to their relevance in asymmetric synthesis (Noyori & Takaya, 1985; Noyori, 1989). Their conformation has been studied in solution by optical methods like circular-dichroism spectroscopy (Mason, Seal & Roberts, 1974) and liquid-crystal techniques (Gottarelli, Spada, Bartsch, Solladiè & Zimmermann, 1986), and in the solid state by X-ray analysis (Akimoto & Iitaka, 1969; Harata & Tanaka, 1973; Kuroda & Mason, 1981; Pauptit & Trotter, 1981, 1983). We report here the molecular structure of (*R*)-*N*,*N*,*N*′*N*′-tetramethyl-[1,1′-binaphthalene]-2,2′-diamine, a new 1,1′-binaphthylic compound whose potential as a chiral ligand is now being investigated (Salvadori, Rosini & Franzini, in preparation).

Experimental. The title compound was prepared from (*R*)-[1,1′-binaphthalene]-2,2′-diamine according to the method described by Benson, Cai, Colon, Haiza, Tokles & Snyder (1988). Pyramidal (101) yellow crystals were obtained by recrystallization from toluene. A crystal, dimensions *ca* 2 × 1 × 0·5 mm, was chosen for the intensity data collection which was carried out on an Ital Structures four-circle automatic diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Preliminary Weissenberg photographs showed Laue symmetry and systematic absences consistent with space group $I4_1$. The unit-cell parameters were derived through least-squares fitting of 2θ values of 30 reflections ($13 < \theta < 21^\circ$). 1876 reflections measured with $3 \leq \theta \leq 25^\circ$, h 0 to 14, k 0 to 14, l −16 to 16, ω-scan mode, scan width 1·6°, scan speed 2·5° min^{-1}; no significant variation in the intensity of one reflection (226) monitored every 60 measurements; Lorentz and polarization corrections; Friedel opposites merged neglecting the contribution of anomalous scattering, thus obtaining a set of 736 unique reflections with $I > 3\sigma(I)$; absorption correction by *DIFABS* (Walker & Stuart, 1983), correction factors in the range 0·78–1·14. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986) and refined on F with *SHELX76* (Sheldrick, 1976). The atomic scattering factors were those incorporated in *SHELX76*. Final $R = 0{\cdot}043$, $wR = 0{\cdot}033$ [$w = 1/\sigma(F_o)^2$], $S = 4{\cdot}76$. Anisotropic thermal parameters for all non-H atoms, methyl H-atom positions constrained using the AFIX option of *SHELX76*; 147 variables, max. Δ/σ in the final least-squares cycle

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