2-aminopyridine (Fig. 1). Crystal integrity is maintained through a series of intermolecular (N—H···O) hydrogen bonds with N···O distances in the range 2·699 (4) to 2·914 (5) Å. There is a strong intramolecular hydrogen bond in the salicylate anion with O(hydroxyl)···O(carboxyl) = 2·535 (4) Å. The six-membered rings of pyridine and salicylate are planar within 0·007 and 0·011 Å, respectively. The distance and angles in the complex are normal with N(1)—C(2) and N(1)—C(6) longer and C(2)—N(2) shorter than those observed in the unprotonated parent compound (Hsu & Craven, 1974). The nature of the molecular interaction and the mode of hydrogen bonding in this structure are quite similar to those found in 9-methyladeninium salicylate (Gellert & Hsu, 1983) except that the N(1)···O(carbonyl) separation is longer in the present compound. This suggests that 9-methyladenine is a stronger electron donor than 2-aminopyridine.

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Structure of 7-Chloro-5-(2,6-dichlorophenyl)-1,3-dihydro-2*H*-1,4-benzodiazepin-2-one[*]

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Abstract. $C_{15}H_9Cl_3N_2O$, $M_r = 339·6$, monoclinic, $P2_1/n$ (non-standard setting of $P2_1/c$), $a = 12·311$ (1), $b = 10·082$ (2), $c = 12·360$ (1) Å, $\beta = 104·76$ (7)°, $V = 1483·5$ Å^3, $Z = 4$, $D_x = 1·52$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·55$ mm^{-1}, $F(000) = 688$, $T = 293$ K, $R = 0·036$ for 1868 observed reflections. The seven-membered ring adopts a slightly distorted cycloheptatriene-like boat conformation with bow and stern angles of 59·4 (5) and 31·7 (5)°, respectively. The angle between the 5-phenyl ring and the fused benzo moiety is 78·7 (3)°. The C(5)—C(phenyl) bond length is 1·498 (3) Å.

Introduction. The 5-phenyl-1,4-benzodiazepines have been extensively used in clinical practice as anxiolytics, hypnotics, anticonvulsants and muscle relaxants (*e.g.* Hamor & Martin, 1983). The title compound (Fryer, Leimgruber & Trybulski, 1982) differs from the clinically used benzodiazepines in that the 5-phenyl ring is substituted with chlorine at both *ortho* positions. Its affinity for the benzodiazepine receptor *in vitro* is the same, within the limits of experimental error, as that of the mono-substituted analogue (Squires & Braestrup, 1977; Braestrup & Squires, 1978). As part of a continuing study of structure–activity relationships for this class of compounds, we now report the crystal structure of the title compound.

Experimental. Crystals were grown from ethanol. A crystal of size 0·5 × 0·4 × 0·1 mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Lattice parameters from 25 reflections having $10 < \theta < 19°$. Data collected using ω–2θ scans, $2 < \theta < 25°$; two standard reflections measured every 2 h showed no significant variation over period of data collection; 3231 reflections scanned, 2906 unique, $R_{\rm int} = 0·019$; of these 1868 having $I > 2·5\sigma(I)$ were used in the analysis, index range h −15 to 14, k 0 to 12, l 0 to 15; no absorption corrections applied; structure solved by direct methods; all H atoms located in difference Fourier maps; heavier atoms refined with anisotropic temperature factors, H atoms refined isotropically; full-matrix least-squares refinement on F magnitudes. $R = 0·036$, $wR = 0·049$, $w = 1/[\sigma^2(F) + 0·0008F^2]$, max. Δ/σ 0·06; residual electron density in final Fourier difference map within +0·25 and −0·38 e Å^{-3}; atomic scattering factors were taken from *International Tables*

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for X-ray Crystallography (1974). Computations were carried out with *SHELX* (Sheldrick, 1978) on the University of Birmingham Honeywell computer.

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

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

	x	*y*	*z*	U_{eq}
Cl(7)	482 (1)	−3476 (1)	−5802 (1)	66
Cl(2′)	−3408 (1)	−6257 (1)	−5791 (1)	64
Cl(6′)	−3966 (1)	−1159 (1)	−4627 (1)	55
O(2)	−5922 (2)	−3970 (2)	−9433 (2)	47
N(1)	−4095 (2)	−4358 (3)	−8647 (2)	42
N(4)	−4780 (2)	−2870 (2)	−6835 (2)	39
C(2)	−5046 (2)	−3654 (3)	−8757 (2)	39
C(3)	−4955 (3)	−2458 (3)	−8004 (2)	44
C(5)	−3817 (2)	−3344 (3)	−6351 (2)	33
C(6)	−1772 (2)	−3389 (3)	−6214 (2)	36
C(7)	−874 (2)	−3690 (3)	−6635 (2)	40
C(8)	−1028 (3)	−4204 (3)	−7700 (2)	43
C(9)	−2099 (2)	−4384 (3)	−8347 (2)	42
C(10)	−3027 (2)	−4062 (3)	−7949 (2)	35
C(11)	−2868 (2)	−3568 (3)	−6863 (2)	33
C(1′)	−3632 (2)	−3722 (3)	−5146 (2)	34
C(2′)	−3420 (2)	−5037 (3)	−4812 (2)	44
C(3′)	−3242 (3)	−5417 (5)	−3700 (3)	61
C(4′)	−3267 (3)	−4477 (5)	−2902 (3)	67
C(5′)	−3488 (3)	−3178 (4)	−3203 (3)	55
C(6′)	−3674 (2)	−2813 (3)	−4311 (2)	39

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses, and selected torsion angles* (°), *for which e.s.d.'s are ca* 0·6°

Cl(7)–C(7)	1·737 (3)	C(6)–C(11)	1·394 (3)
Cl(2′)–C(2′)	1·728 (3)	C(7)–C(8)	1·382 (4)
Cl(6′)–C(6′)	1·729 (3)	C(8)–C(9)	1·369 (4)
O–C(2)	1·225 (3)	C(9)–C(10)	1·392 (4)
N(1)–C(2)	1·347 (4)	C(10)–C(11)	1·398 (3)
N(1)–C(10)	1·408 (3)	C(1′)–C(2′)	1·394 (4)
N(4)–C(3)	1·466 (3)	C(1′)–C(6′)	1·392 (4)
N(4)–C(5)	1·277 (3)	C(2′)–C(3′)	1·390 (4)
C(2)–C(3)	1·510 (4)	C(3′)–C(4′)	1·373 (6)
C(5)–C(11)	1·481 (4)	C(4′)–C(5′)	1·370 (6)
C(5)–C(1′)	1·498 (3)	C(5′)–C(6′)	1·380 (4)
C(6)–C(7)	1·370 (4)		

C(2)–N(1)–C(10)	127·1 (2)	C(9)–C(10)–C(11)	119·7 (2)
C(3)–N(4)–C(5)	116·9 (2)	C(5)–C(11)–C(6)	119·2 (2)
O–C(2)–N(1)	121·6 (3)	C(5)–C(11)–C(10)	122·1 (2)
O–C(2)–C(3)	122·8 (3)	C(6)–C(11)–C(10)	118·5 (2)
N(1)–C(2)–C(3)	115·6 (2)	C(5)–C(1′)–C(2′)	120·4 (2)
N(4)–C(3)–C(2)	110·5 (2)	C(5)–C(1′)–C(6′)	123·0 (3)
N(4)–C(5)–C(11)	126·7 (2)	C(2′)–C(1′)–C(6′)	116·5 (2)
N(4)–C(5)–C(1′)	116·6 (2)	Cl(2′)–C(2′)–C(1′)	120·2 (2)
C(11)–C(5)–C(1′)	116·7 (2)	Cl(2′)–C(2′)–C(3′)	118·0 (3)
C(7)–C(6)–C(11)	120·6 (3)	C(1′)–C(2′)–C(3′)	121·7 (3)
Cl(7)–C(7)–C(6)	119·6 (2)	C(2′)–C(3′)–C(4′)	119·6 (4)
Cl(7)–C(7)–C(8)	119·3 (2)	C(3′)–C(4′)–C(5′)	120·2 (3)
C(6)–C(7)–C(8)	121·1 (3)	C(4′)–C(5′)–C(6′)	119·8 (3)
C(7)–C(8)–C(9)	119·0 (3)	Cl(6′)–C(6′)–C(1′)	120·8 (2)
C(8)–C(9)–C(10)	121·2 (3)	Cl(6′)–C(6′)–C(5′)	117·0 (3)
N(1)–C(10)–C(9)	117·2 (2)	C(1′)–C(6′)–C(5′)	122·2 (3)
N(1)–C(10)–C(11)	122·9 (2)		

C(10)–N(1)–C(2)–C(3)	−3·2	C(5)–C(11)–C(10)–N(1)	1·3
N(1)–C(2)–C(3)–N(4)	−68·7	C(11)–C(10)–N(1)–C(2)	40·1
C(2)–C(3)–N(4)–C(5)	72·3	N(4)–C(5)–C(1′)–C(6′)	−62·2
C(3)–N(4)–C(5)–C(11)	−2·5	C(11)–C(5)–C(1′)–C(2′)	−62·6
N(4)–C(5)–C(11)–C(10)	−40·0		

Discussion. Atomic coordinates are listed in Table 1* and bond lengths, bond angles and selected torsion angles are in Table 2. The atomic numbering scheme is illustrated in Fig. 1.

Geometrical parameters generally agree well with those found in other 5-phenyl-1,4-benzodiazepin-2-ones (Hamor & Martin, 1983, and references cited therein). The N(1)–C(2) amide bond is shortened from the single-bond length (1·47 Å) to 1·347 (4) Å, with a near-planar disposition of bonds at N(1) and C(2), so that the geometry of this bond closely resembles that of a double bond, indicative of N→O electron delocalization. The seven-membered ring thus contains three 'double' bonds and adopts a cycloheptatriene-like boat conformation. The angle between the central plane of the boat, atoms N(1), C(2), N(4), C(5), and the 'bow' plane, C(2), C(3), N(4), is 59·4 (5)° and that between the central plane and the 'stern' plane, N(1), C(10), C(11), C(5), is 31·7 (5)°. These values of the stern and bow angles compare with values 32–40 and 58–64° found in a selection of 1,4-benzodiazepin-2-ones (Hamor & Martin, 1983). The deviation of the seven-membered ring from that of an ideal cycloheptatriene with mirror symmetry, in terms of the deviations of the ring torsion angles from mirror symmetry and zero value for those about the three 'double' bonds (see Table 2), expressed as a 'deviation parameter' (Hamor & Martin, 1983), is 2·5°, typical for this class of compounds.

Comparison of geometric parameters with those of the 5-phenyl monochloro-substituted analogue (Chananont, Hamor & Martin, 1981), shows that the additional *ortho*-chloro substituent has little effect. In particular the C(5)–C(1′) bond length and the angle between the 5-phenyl ring and the fused benzo moiety, 1·48 (2) Å and 80 (2)° respectively, do not differ significantly from the corresponding parameters in the title compound [1·498 (3) Å and 78·7 (3)°]. The length of the C(5)–C(1′) bond corresponds to that of a single

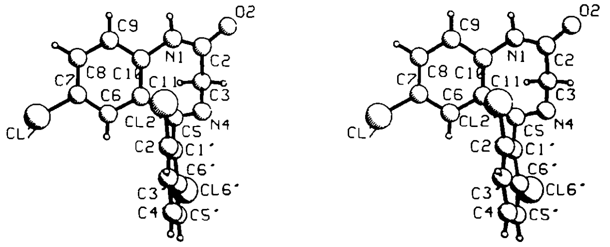

Fig. 1. Stereoscopic view of the molecule in a direction perpendicular to the mean plane through atoms C(6)–C(11), drawn with *PLUTO* (Motherwell & Clegg, 1978).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and the results of mean-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44361 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond between sp^2-hybridized carbon atoms, in agreement with previous results, irrespective of whether the 5-phenyl ring is substituted or not. In this context it may be noted that the value of the N(4)—C(5)—C(1′)—C(6′) torsion angle, −62°, would preclude significant electron delocalization across C(5)—C(1′).

An intermolecular hydrogen bond occurs between the carbonyl O atom and the amide N atom of the centrosymmetrically related molecule at $(-1-x, -1-y, -2-z)$. Pertinent parameters are O(2)···H(1), 2·04 (3), O(2)···N(1) 2·916 (3) Å and angle O(2)···N(1)—H(1), 7 (2)°. Other intermolecular contacts correspond to normal van der Waals interactions.

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4,4′-Thiodi(α-toluenethiol)

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Abstract. $C_{14}H_{14}S_3$, $M_r = 278{\cdot}4$, monoclinic, $C2/c$, $a = 14{\cdot}135\ (5)$, $b = 5{\cdot}949\ (2)$, $c = 17{\cdot}301\ (6)$ Å, $\beta = 114{\cdot}11\ (3)°$, $V = 1327{\cdot}9\ (8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}40\ (1)$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo}\ K\alpha) = 4{\cdot}73$ cm^{-1}, $F(000) = 584$, $T = 292$ K, $R = 0{\cdot}057$ for 529 unique reflections. Atom S(2) lies on a crystallographic twofold axis which relates two toluenethiol moieties of the molecule. The phenyl ring is at 33·4 (5)° to the plane defined by C(4)—S(2)—C(4′) and the valency angle at S(2) is 105·8 (3)°.

Introduction. The X-ray study of 4,4′-thiodi(α-toluenethiol), hereafter referred to as (I), is a continuation of our previous investigation on aryl–sulfuric and alkyl–aryl–sulfuric compounds which are basic structures in the chemistry of polythioesters (Ratajczak-Sitarz, Katrusiak, Kałuski & Garbarczyk, 1987; Garbarczyk, 1984; Andreetti, Garbarczyk & Królikowska, 1981). In the structure of (I) we were mainly interested in the conformation of the molecule – *i.e.* in the torsion of the phenyl ring around bond S(2)—C(4) – and in the geometry of S(2), which bridges the phenyl rings in the molecule.

Experimental. Single crystals of (I) suitable for X-ray investigation were obtained by slow evaporation of its xylene solution at room temperature. They were very small colourless parallelepipeds. The crystal selected for data collection had dimensions of 0·10 × 0·06 × 0·05 mm. The measurement was carried out on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The unit-cell parameters were determined by a least-squares fit to 15 automatically centred reflections ($8{\cdot}39 \leq 2\theta \leq 14{\cdot}14°$). Two control reflections were monitored after each 100 intensity measurements. θ–2θ scan method with a variable scan speed (from 2·1 to 29·3° min^{-1}) was used. 1241 reflections were collected up to $2\theta = 45{\cdot}0°$, with indices: h 0/18, k 0/10, l −20/20. The background and integrated intensity for each reflection were calculated according to the profile-analysis method of Lehmann & Larsen (1974). Of 906 unique reflections ($R_{\text{int}} = 0{\cdot}033$) 529 reflections had $I \geq 1{\cdot}96\sigma(I)$ and were used in the structure refinement. Only Lp corrections were applied. The structure was solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). After the refinement of the non-hydrogen atoms with anisotropic temperature factors all H atoms, except that at S(1) which could not be found, were located from a ΔF map and were included in the refinement with isotropic temperature factors. The function minimized was

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