

Structure of 2-(*p*-Chlorophenyl)thiazolidine

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Abstract. C₉H₁₀ClNS, $M_r = 199.71$, orthorhombic, $P2_12_12_1$, $a = 5.529$ (1), $b = 8.486$ (1), $c = 20.432$ (2) Å, $V = 958.7$ (2) Å³, $Z = 4$, $D_x = 1.38$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 49.19$ cm⁻¹, $F(000) = 416$, $T = 292$ K, final $R = 0.040$ and $wR = 0.045$ for 1086 observed reflections. The thiazolidine ring assumes an envelope conformation. The best plane through the thiazolidine moiety omits the N atom and is approximately perpendicular to the phenyl ring [98.4 (1)°].

Introduction. The discovery of penicillin from the fungi *Penicillium notatum* opened a new era in the field of drugs. The thiazolidine moiety, a five-membered saturated ring containing S and N atoms, is present in the penicillin structure. Thiazolidine and its derivatives have diverse biological importance, such as antiradiation agents (Yakovlev, 1963; Thomson, 1962), antioxidants (Rachinskii, 1964) and flavour-enhancing agents (Dubs, Kuentzel & Heiner, US Patent No. 4011233). The presence of an NCS linkage in the ring enhances the antifungal activity (United States Rubber Co., British Patent No. 1059677). The present study was undertaken to establish the crystal structure of 2-(*p*-chlorophenyl)-thiazolidine and to compare the molecular conformations of 2-phenylthiazolidine (Baert, Muller, Barbry & Couturier, 1987) (hereafter referred as 2PT) and 2-(*p*-chlorophenyl)thiazolidine (hereafter referred as 2CPT).

Experimental. Samples provided by Dr R. Umarani, synthesized as described (Umarani, 1988); crystals grown from ethanol solution by slow evaporation; suitable crystals of size 0.3 × 0.1 × 0.1 mm for data collection; systematic absences characteristic of $P2_12_12_1$; Enraf–Nonius CAD-4 diffractometer,

graphite-monochromated Cu $K\alpha$ radiation, cell parameters from least-squares refinement of 25 reflections with $20 \leq \theta \leq 30^\circ$; ω - 2θ scan; $[(\sin\theta)/\lambda]_{\max} = 0.6092$ Å⁻¹, $h = 0$ to 6, $k = 0$ to 10 and $l = 0$ to 24; intensities of three standard reflections monitored every 2 h showed no radiation decay or significant variation; 1086 unique reflections, 1058 reflections with $I \geq 3\sigma(I)$; Lorentz–polarization corrections applied; structure solved by three-dimensional Patterson synthesis (SHELXS86; Sheldrick, 1986), the position of Cl and S atoms found; successive Fourier and difference Fourier synthesis revealed the positions of all C and N atoms; full-matrix least-squares refinement minimizing $w(F_o - F_c)^2$ with weights $w = 1.0/\sigma^2(F) + 0.00565F^2$ using SHELX76 (Sheldrick, 1976); anisotropic temperature factors for all non-H atoms; all H atoms from difference Fourier synthesis, isotropic temperature factors; minimum and maximum absorption correction of 0.856 and 1.325, using program DIFABS (Walker & Stuart, 1983); R and wR decreased to 0.040 and 0.045; no significant features in the final ΔF synthesis with max. and min. peak heights of +0.20 and -0.39 e Å⁻³; atomic scattering factors, f' and f'' , from *International Tables for X-ray Crystallography* (1974, Vol. IV); all calculations were performed on a MicroVAX II computing system. The positional atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.‡

Discussion. Fig. 1 shows a view of the molecule and the numbering scheme of the atoms. A comparison

‡ Lists of structure factors, anisotropic thermal parameters, positional parameters of H atoms, bond lengths and angles involving H atoms, torsion angles and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52880 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

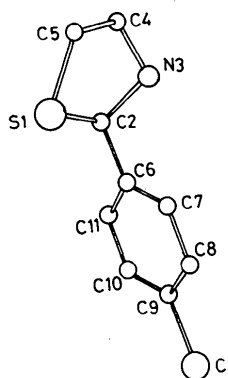
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† Contribution number 754.

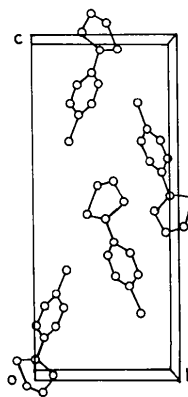
Table 1. Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{\AA}^2 \times 10^3$) with *e.s.d.*'s in parentheses

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cl	8028 (2)	7397 (1)	1885 (1)	70 (1)
S(1)	11745 (1)	3776 (1)	4751 (1)	43 (0)
C(2)	9119 (5)	5143 (3)	4662 (1)	38 (1)
N(3)	9458 (5)	6388 (3)	5143 (1)	44 (1)
C(4)	10281 (7)	5611 (4)	5742 (1)	47 (2)
C(5)	12338 (7)	4459 (4)	5577 (2)	55 (2)
C(6)	8850 (5)	5717 (3)	3968 (1)	37 (1)
C(7)	10570 (5)	6721 (4)	3693 (1)	47 (2)
C(8)	10315 (7)	7245 (4)	3054 (2)	53 (2)
C(9)	8360 (6)	6747 (4)	2692 (2)	48 (1)
C(10)	6649 (6)	5746 (4)	2949 (1)	49 (2)
C(11)	6926 (5)	5243 (3)	3592 (1)	45 (1)

Fig. 1. A perspective view of the 2-(*p*-chlorophenyl)thiazolidine molecule.Table 2. Interatomic distances (\AA), angles ($^\circ$) and some selected torsion angles ($^\circ$) with *e.s.d.*'s in parentheses

S(1)—C(2)	1.868 (3)	C(6)—C(11)	1.372 (4)
S(1)—C(5)	1.814 (3)	C(7)—C(8)	1.387 (4)
C(2)—N(3)	1.455 (3)	C(8)—C(9)	1.377 (5)
C(2)—C(6)	1.507 (4)	C(9)—C(10)	1.376 (5)
N(3)—C(4)	1.463 (4)	C(10)—C(11)	1.389 (4)
C(4)—C(5)	1.537 (5)	C(9)—Cl	1.748 (3)
C(6)—C(7)	1.394 (4)		
C(2)—S(1)—C(5)	91.9 (1)	C(7)—C(6)—C(11)	118.9 (2)
S(1)—C(2)—N(3)	106.5 (2)	C(6)—C(7)—C(8)	120.3 (3)
S(1)—C(2)—C(6)	111.7 (2)	C(7)—C(8)—C(9)	119.2 (3)
N(3)—C(2)—C(6)	114.4 (2)	C(8)—C(9)—C(10)	121.5 (3)
C(2)—N(3)—C(4)	106.1 (2)	C(9)—C(10)—C(11)	118.4 (3)
N(3)—C(4)—C(5)	109.5 (2)	C(6)—C(11)—C(10)	121.6 (3)
S(1)—C(5)—C(4)	105.9 (2)	C(8)—C(9)—Cl	119.5 (3)
C(2)—C(6)—C(7)	120.5 (2)	C(10)—C(9)—Cl	118.9 (3)
C(2)—C(6)—C(11)	120.5 (2)		
S(1)—C(2)—N(3)—C(4)	-42.2 (2)	C(4)—C(5)—S(1)—C(2)	4.7 (2)
C(2)—N(3)—C(4)—C(5)	47.9 (3)	C(5)—S(1)—C(2)—N(3)	21.3 (2)
N(3)—C(4)—C(5)—S(1)	-30.3 (3)		

Fig. 2. The packing of the molecules in the unit cell down *a*.

of 2-phenylthiazolidine (Baert, Muller, Barbry & Couturier, 1987) and 2-(*p*-chlorophenyl)thiazolidine reveals that the two crystals are isostructural. Bond distances, bond angles and some selected torsion angles are given in Table 2. The packing diagram is shown in Fig. 2.

The average C—C bond length of the phenyl ring is 1.383 (7) \AA . Least-squares-plane calculations show that the phenyl ring is planar with a maximum displacement of 0.005 (3) \AA . The Cl and C(2) atoms also lie on the plane of the phenyl ring with deviations of -0.007 (1) and 0.007 (3) \AA , respectively.

The conformations of the 2PT and 2CPT molecules resemble each other closely; the bond distances and angles agree with each other. As can be seen from the torsion angles, the thiazolidine ring of the 2PT and 2CPT molecules adopts an envelope conformation (Wilson & Bazzone, 1974; Baert, Muller, Barbry & Couturier, 1987). The best least-squares plane through four of the five ring atoms of

both molecules omits the N atom (Chacko, 1974; Goodman, Chen, Benedetti, Pedone & Corradini, 1972; Loscalzo, Kallen & Voet, 1973; Parthasarathy, Paul & Korytnyk, 1976). Atom N(3) deviates 0.569 (3) \AA from the thiazolidine plane. The plane of the thiazolidine ring is approximately perpendicular to the phenyl ring and makes an angle with it of 98.4 (1) $^\circ$.

Intermolecular distances correspond to van der Waals interactions; the possible short contacts are $\text{N}(3)\cdots\text{N}(3)(x - \frac{1}{2}, -y + \frac{1}{2} + 1, -z + 1) = 3.398 (4) \text{\AA}$ for 2CPT.

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Structure of *exo* and *endo* Adducts of 1-(*p*-Methoxyphenyl)-2-phenyl-4-trimethylsiloxy-1,2,3,5,6,7,8,8a-octahydroquinoline

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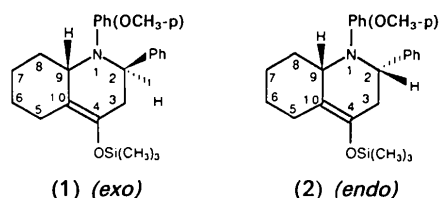
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Abstract. (1) $C_{25}H_{33}NO_2Si$, $M_r = 407.63$, monoclinic, $P2_1$, $a = 6.018$ (2), $b = 8.073$ (3), $c = 24.205$ (4) Å, $\beta = 92.07$ (2)°, $V = 1175$ (1) Å³, $Z = 2$, $D_x = 1.152$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.1143$ mm⁻¹, $F(000) = 440$, $T = 295$ K, final $R = 0.080$ for 608 unique reflections [$I > 2\sigma(I)$]. (2) $C_{25}H_{33}NO_2Si$, $M_r = 407.63$, triclinic, $P\bar{1}$, $a = 9.106$ (3), $b = 10.541$ (4), $c = 13.210$ (3) Å, $\alpha = 79.20$ (2)°, $\beta = 73.04$ (2)°, $\gamma = 88.06$ (3)°, $V = 1191$ (1) Å³, $Z = 2$, $D_x = 1.137$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.1127$ mm⁻¹, $F(000) = 440$, $T = 295$ K, final $R = 0.076$ for 1188 unique reflections [$I > 3\sigma(I)$]. In both diastereoisomers the cyclohexane ring adopts a chair conformation, while the heterocycle prefers a quasi 1,2-diplanar conformation. They essentially differ in the relative configuration of the C(2)—H(2) and C(9)—H(9) bonds. The structural data are in good agreement with previous data obtained by ¹H NMR. There are no unusual bond lengths or angles.

Introduction. The isolation of the two diastereoisomers of the trimethylsilyl ether adduct obtained by imino Diels–Alder reaction has important mechanistic implications. ¹H NMR gave information only on the position of the phenyl group substituent on C(2): this group lies in quasi axial position in (1), and quasi equatorial position in (2); moreover, in both diastereoisomers, the H(9) proton occupies an axial position in the cyclohexane ring which itself adopts a chair conformation. Unambiguous assignment of

their structures has to be obtained from a single-crystal X-ray structure analysis.



We have previously reported (Le Coz, Wartski, Seyden-Penne, Charpin & Nierlich, 1989) isolation and ¹H NMR results on these silanol ethers.

Experimental. Data collected on an Enraf–Nonius CAD-4 diffractometer, graphite monochromator; cell parameters determined by least squares from the setting angles of 25 reflections ($8 \leq \theta \leq 12^\circ$); three standard reflections measured every 60 min [(1) $\bar{1}0\bar{1}$, $\bar{1}\bar{1}\bar{3}$, 020; (2) $\bar{3}\bar{1}1$, 330, $\bar{3}\bar{3}1$], showed no significant deviation from mean intensity; ω – 2θ scan, ω -scan width: $(0.8 + 0.35 \tan \theta)^\circ$; Lorentz–polarization corrections applied; MicroVAXII computer with SDP (Frenz, 1985) and MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) programs; scattering factors and anomalous components f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1), H atoms included using a riding model