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(*Z*)-7-Chloro-3-[(3-chlorophenyl)-methylidene]-4-*p*-tosyl-3,4-dihydro-2*H*-1,4-benzoxazine

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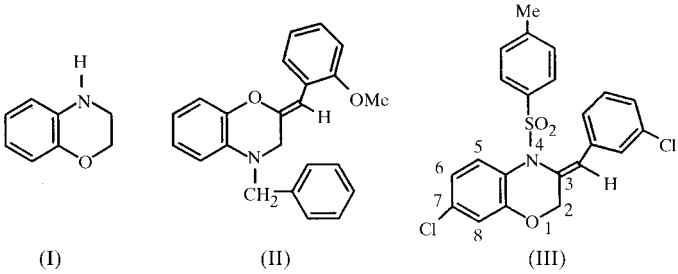
In the title compound, $C_{22}H_{17}Cl_2NO_3S$, the molecule is a substituted 3,4-dihydro-2*H*-1,4-benzoxazine compound which has three phenyl rings which are essentially planar. The 3,4-dihydro-2*H*-oxazine part of the molecule is fused to the benzo ring and has a half-boat conformation; the dihedral angle between the planar part of the oxazine ring and the benzo ring is 10.2 (2)°. The (3-chlorophenyl)methylidene substituent has a *Z* configuration in relation to the ring N atom of the oxazine moiety. Interestingly, the *p*-toluenesulfonyl (*p*-tosyl) substituent on the ring N atom protrudes away from the 3-chlorophenyl substituent thus avoiding any steric interaction.

Comment

The 3,4-dihydro-2*H*-1,4-benzoxazine structure, (I), has been the integral part of many naturally occurring substances (Sainsbury, 1984). Also, various benzoxazine derivatives have shown interesting pharmacological activities, *e.g.* anticancer (Sugimoto *et al.*, 1990; Zhen *et al.*, 1989), antiemetic (Fukuda *et al.*, 1991), antitubercular (Hirata *et al.*, 1995) and antirheumatic properties (Matsuoka *et al.*, 1997).



(I) (II) (III)

As a continuation of our studies on the synthesis of heterocyclic structures of biological importance (Nandi & Kundu, 2000; Chaudhuri & Kundu, 2000), we have recently reported the synthesis and X-ray structure determination of (*Z*)-*N*-benzyl-2,3-dihydro-2-(2-methoxybenzylidene)-4*H*-1,4-benzoxazine, (II) (Maiti *et al.*, 1999). In the present paper, we describe the synthesis and X-ray structure determination of a 3-alkylidene benzoxazine, namely (*Z*)-7-chloro-3-[(3-chlorophenyl)methylidene]-4-*p*-tosyl-3,4-dihydro-2*H*-1,4-benzoxazine, (III).

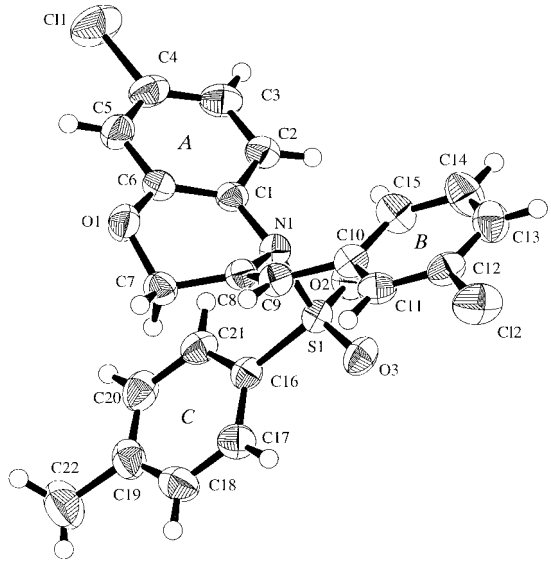


Figure 1
ORTEP (Johnson, 1965) plot of (III) shown with 50% probability ellipsoids.

The geometric parameters determined for (III) show some similarities to those found in (II) (Maiti *et al.*, 1999); the heterocyclic ring adopts a half-boat conformation and the planar part of the heterocyclic ring (atoms O1, N1, C6 and C8) forms a dihedral angle with the fused phenyl ring *A* (Fig. 1) of 10.2 (2)°, with C1 and C7 on opposite sides of the best plane by 0.085 (3) and 0.611 (4) Å, respectively. This dihedral angle is, however, somewhat larger than that in (II), which is 4.70 (6)°. A shortening of bond lengths involving atoms adjacent to phenyl rings *A* and *B* (the 3-chlorophenyl ring), due to conjugation, is seen which is particularly marked for the bond length O1—C6 of 1.361 (3) Å [compared with 1.434 (3) Å for O1—C7]. The effect of conjugation is less evident for the bond lengths to N1, which are 1.439 (3) and 1.443 (3) Å for N1—C1 and N1—C8, respectively, although these values are still significantly shorter than the N—C single-bond length of 1.48 Å (Allen *et al.*, 1987). The dihedral angles *A*/*B*, *A*/*C* and *B*/*C* (ring *C* is the phenyl ring of the *p*-tosyl substitutent) are 42.18 (9), 52.49 (8) and 26.9 (1)°, respectively. The geometric parameters of the *p*-tosyl group and of the chlorophenyl group are within normal ranges, with the *p*-tosyl group angled away from the 3-chlorophenyl derivative reducing steric hindrance.

Experimental

4-Chloro-2-(prop-2-ynyloxy)aniline was arylated with 3-chloroiodobenzene under palladium–copper catalysis in triethylamine (Kundu *et al.*, 2001). This was converted to the corresponding tosylate with tosyl chloride in the presence of pyridine in dichloromethane. The tosylate was then cyclized with CuI in the presence of K_2CO_3 and tetra-

butylammonium bromide in acetonitrile by refluxing at 353 K to yield the title compound, (III) (m.p. 428 K). Single crystals suitable for X-ray analysis were obtained from $CHCl_3$/petroleum ether (b.p. 333–353 K) (1:3) by slow crystallization.

Crystal data

$C_{22}H_{17}Cl_2NO_3S$	$Z = 2$
$M_r = 446.33$	$D_x = 1.479$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 10.899$ (5) Å	Cell parameters from 20 reflections
$b = 12.211$ (4) Å	$\theta = 6.8$–$8.2°$
$c = 7.775$ (3) Å	$\mu = 0.45$ mm^{-1}
$\alpha = 102.23$ (2)°	$T = 296.2$ K
$\beta = 92.21$ (3)°	Block, colourless
$\gamma = 96.64$ (3)°	0.40 × 0.37 × 0.37 mm
$V = 1002.4$ (6) Å^3	

Data collection

Rigaku AFC-5*R* diffractometer	$R_{int} = 0.018$
ω–2θ scans	$\theta_{max} = 27.6°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 14$
$T_{min} = 0.800$, $T_{max} = 0.846$	$k = -15 \rightarrow 15$
4862 measured reflections	$l = -10 \rightarrow 10$
4619 independent reflections	3 standard reflections
3158 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: 0.3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.3626P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R(F) = 0.049$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.118$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
$S = 1.09$	$\Delta\rho_{min} = -0.22$ e Å^{-3}
4619 reflections	
262 parameters	
H-atom parameters constrained	

H atoms were included in calculated positions, with C—H distances in the range 0.93–0.97 Å. The H atoms bonded to C22 (the *p*-methyl group) were disordered over two sets of sites, rotated with respect to one another by 60°. They were modelled using the *AFIX* 123 command of *SHELXL*97 (Sheldrick, 1997) and assigned occupancies of 0.5 each.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995*b*); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1131). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans*. 2, pp. S1–19.

Chaudhuri, G. & Kundu, N. G. (2000). *J. Chem. Soc. Perkin Trans.* 1, pp. 775–779.

Fukuda, T., Setoguchi, M., Inaba, K., Shoji, H. & Tahara, T. (1991). *Eur. J. Pharmacol.* **196**, 299–305.

Hirata, T., Saito, H., Tomioka, H., Sato, K., Jidoi, J., Hosoe, K. & Hidaka, T. (1995). *Antimicrob. Agents Chemother.* **39**, 2295–2303.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kundu, N. G., Chaudhuri, G. & Upadhyay, A. (2001). *J. Org. Chem.* **66**, 20–29.

Maiti, S., Mukherjee, M., Chaudhuri, G., Helliwell, M. & Kundu, N. G. (1999). *Acta Cryst.* C**55**, 1154–1156.

Matsuoka, H., Ohi, N., Mihara, M., Suzuki, H., Miyamoto, K., Maruyama, N., Tsuji, K., Kato, N., Akimoto, T., Takeda, Y., Yano, K. & Kuroti, T. (1997). *J. Med. Chem.* **40**, 105–111.

Molecular Structure Corporation (1995*a*). *MSC/AFC Diffractometer Control Software*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995*b*). *TEXSAN*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nandi, B. & Kundu, N. G. (2000). *Org. Lett.* **2**, 235–238.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sainsbury, M. (1984). *Oxazines, Thiazines and their Benzoderivatives* in *Comprehensive Heterocyclic Chemistry*, Vol. 3, edited by A. R. Katritzky & C. W. Rees, pp. 995–1035. Oxford: Pergamon Press.

Sheldrick, G. M. (1985). *SHELXS*86. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sugimoto, Y., Otani, T., Oie, S., Wierzba, K. & Yamada, Y. (1990). *J. Antibiot.* **43**, 417–421.

Zhen, Y., Ming, X., Yu, B., Otani, T., Saito, H. & Yamada, Y. (1989). *J. Antibiot.* **42**, 1294–1298.