Structure of 1,3-Dichloro-5-phenyl-1λ^4,3λ^4,2,4,6-dithiatriazine

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Abstract. $C_7H_5Cl_2N_3S_2$, $M_r = 266 \cdot 17$, triclinic, $P\bar{1}$, $a = 6 \cdot 028$ (1), $b = 9 \cdot 985$ (2), $c = 10 \cdot 157$ (3) Å, $\alpha = 117 \cdot 33$ (2), $\beta = 106 \cdot 73$ (2), $\gamma = 90 \cdot 31$ (1)°, $V = 513 \cdot 3$ (4) Å³, $Z = 2$, $D_x = 1 \cdot 72$ g cm⁻³, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 9 \cdot 85$ cm⁻¹, $F(000) = 268$, $T = 293$ K, $R = 0 \cdot 032$ for 1547 unique observed reflections. The SNCNS portion of the ring is planar within 0·060 (2) Å and the third N is displaced 0·336 (2) Å from this plane on the side opposite the S-bonded Cl atoms. The S—N distances range from 1·581 (1) to 1·615 (2) Å and the N—C distances are 1·327 (2) and 1·344 (2) Å.

Experimental. Compound prepared by the reaction of chlorine gas with $PhCN_5S_3$ obtained from the reaction of $PhC(NSiMe_3)$ with $S_3N_3Cl_3$. Crystals obtained from a 50:50 mixture of dichloromethane and hexanes. Air-sensitive parallelpiped data crystal $0 \cdot 20 \times 0 \cdot 50 \times 0 \cdot 46$ mm sealed in a glass capillary. Density not measured. Intensities measured with an Enraf–Nonius CAD-4 diffractometer using ω–2θ scans of 4 to 16° min⁻¹ in θ. Unit cell determined from least-squares analysis of angle data for 20 reflections with $22 < 2\theta < 40°$. Analytical absorption correction based on crystal shape varied from 0·67 to 1·00. Data collected to $\sin\theta/\lambda$ of 0·59 Å⁻¹, $-7 \leq h \leq 7$, $-11 \leq k \leq 11$, $0 \leq l \leq 12$. Four standard reflections (244, $\bar{4}4\bar{4}$, $\bar{3}25$, $3\bar{3}5$) varied ±2%; linear-drift correction applied. 1907 reflections measured, 1796 unique ($R_{\text{int}} = 0 \cdot 01$), 247 reflections with $I < 3\sigma(I)$ considered unobserved. Two reflections (101, $1\bar{3}1$) which saturated the counter with their high intensities were omitted. Solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods. Full-matrix least squares minimized $\sum w\Delta F^2$. H atoms refined isotropically, other atoms anisotropically for a total of 147 variables. $R = 0 \cdot 032$, $wR = 0 \cdot 043$, $S = 1 \cdot 64$, where non-Poisson $w^{-2} = \sigma(I) + 0 \cdot 0016F^2$. Final $(\Delta/\sigma)_{\max} < 0 \cdot 03$, $\Delta\rho_{\max} = 0 \cdot 36$ (2) and $\Delta\rho_{\min} = -0 \cdot 35$ (2) e Å⁻³ on final difference map. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974) and programs used those

of Enraf–Nonius (1982) *SDP*.* Table 1 gives the atom parameters and Table 2 bond lengths and angles. Fig. 1 shows the molecule and numbering scheme.

Table 1. *Fractional atomic coordinates, isotropic thermal parameters, and their e.s.d.'s*

$$B_{eq} = \tfrac{4}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + acB_{13}\cos\beta).$$

	x	y	z	$B_{eq}/B(\text{Å}^2)$
Cl(1)	0·0338 (1)	0·60561 (7)	0·38131 (7)	4·47 (2)
Cl(2)	0·3629 (1)	0·61446 (6)	0·15192 (6)	4·54 (1)
S(1)	0·19222 (9)	0·39933 (6)	0·33146 (5)	3·05 (1)
S(2)	0·46456 (8)	0·41377 (5)	0·15988 (5)	2·82 (1)
N(1)	0·0126 (3)	0·2834 (2)	0·1620 (2)	3·18 (4)
N(2)	0·2661 (3)	0·2819 (2)	0·0170 (2)	3·49 (4)
N(3)	0·4451 (3)	0·4384 (2)	0·3246 (2)	3·03 (4)
C(1)	0·0703 (3)	0·2353 (2)	0·0327 (2)	2·64 (4)
C(2)	−0·0977 (4)	0·1129 (2)	−0·1132 (2)	2·83 (5)
C(3)	−0·3030 (4)	0·0491 (2)	−0·1120 (3)	3·36 (5)
C(4)	−0·4602 (2)	−0·0622 (2)	−0·2501 (3)	4·17 (6)
C(5)	−0·4160 (5)	−0·1128 (3)	−0·3895 (3)	4·56 (7)
C(6)	−0·2128 (5)	−0·0513 (3)	−0·3922 (3)	4·51 (7)
C(7)	−0·0537 (4)	0·0612 (2)	−0·2542 (2)	3·67 (6)
H(3)	−0·338 (4)	0·079 (2)	−0·023 (3)	4·5 (6)
H(4)	−0·590 (5)	−0·097 (3)	−0·241 (3)	6·3 (7)
H(5)	−0·531 (5)	−0·177 (3)	−0·477 (3)	6·7 (8)
H(6)	−0·181 (4)	−0·083 (3)	−0·490 (3)	6·2 (7)
H(7)	0·076 (4)	0·105 (3)	−0·255 (3)	5·6 (7)

Table 2. *Selected bond distances* (Å), *bond angles* (°), *and their e.s.d.'s*

|			
S(1)—Cl(1)	2·180 (1)	Cl(1)—S(1)—N(1)	100·49 (6)
S(1)—N(1)	1·600 (1)	Cl(1)—S(1)—N(3)	106·12 (6)
S(1)—N(3)	1·600 (1)	N(1)—S(1)—N(3)	112·16 (8)
S(2)—Cl(2)	2·129 (1)	Cl(2)—S(2)—N(2)	103·36 (6)
S(2)—N(2)	1·581 (1)	Cl(2)—S(2)—N(3)	103·56 (6)
S(2)—N(3)	1·615 (2)	N(2)—S(2)—N(3)	110·84 (8)
N(1)—C(1)	1·327 (2)	S(1)—N(3)—S(2)	118·41 (9)
N(2)—C(1)	1·344 (2)	S(1)—N(1)—C(1)	122·0 (1)
C(1)—C(2)	1·475 (2)	S(2)—N(2)—C(1)	122·1 (1)
C—C(phenyl) range	1·375–1·394	N(1)—C(1)—N(2)	128·4 (2)
C—C(phenyl) mean	1·383	N(1)—C(1)—C(2)	116·8 (2)
C—H range	0·89–0·97	N(2)—C(1)—C(2)	114·8 (2)
C—H mean	0·91	C—C—C range	119·3–120·4
		C—C—H range	115–124
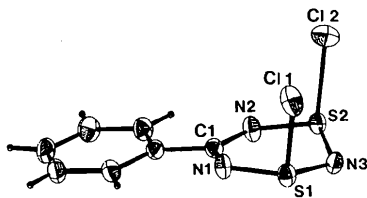
Fig. 1. *ORTEP*II diagram (Johnson, 1976) and atom-numbering scheme. Non-H ellipsoids at 30% probability level, H atoms given arbitrary radius.

Related literature. Structures of three other derivatives of 5-phenyl-1,3,2,4,6-dithiatriazine are in preparation or have been published: $S_3N_5C_7H_5$ (Cordes, Oakley & Boeré, 1985), $PhCS_2N_3.C_7H_8$ (James, Craig, Cordes, Oakley & Boeré, 1985), and $(PhCS_2N_3)_2$ (Boeré, French, Oakley, Cordes, James, Craig & Graham, 1985). The title compound is a member of the series $N_3S_3Cl_3$ (Wiegers & Vos, 1962), $PhCN_3S_2Cl_2$ (this report), $Ph_2C_2N_3SCl$ (Cordes, Hayes, Josephy, Koenig, Oakley & Pennington, 1984), and $Ph_3C_3N_3$ (Damiani, Giglio & Ripamonti, 1965). The heterocyclic ring has also been studied in $Me_2NCN_3S_2Cl_2$ (Hofs. Hartmann, Mews & Sheldrick, 1984) and $CF_3CN_3S_2Cl_2$ (Roesky, Schafer, Noltemeyer & Sheldrick, 1983).

References

BOERÉ, R. T., FRENCH, C. L., OAKLEY, R. T., CORDES, A. W., JAMES, J. A., CRAIG, S. L. & GRAHAM, J. B. (1985). In preparation.
CORDES, A. W., HAYES, P. J., JOSEPHY, P. D., KOENIG, H., OAKLEY, R. T. & PENNINGTON, W. T. (1984). *J. Chem. Soc. Chem. Commun.* pp. 1021–1022.
CORDES, A. W., OAKLEY, R. T. & BOERÉ, R. T. (1985). *Acta Cryst.* C41, 1833–1834.
DAMIANI, A., GIGLIO, E. & RIPAMONTI, A. (1965). *Acta Cryst.* **19**, 161–168.
Enraf–Nonius (1982). *Structure Determination Package.* Enraf–Nonius, Delft.
HOFS, H.-U., HARTMANN, G., MEWS, R. & SHELDRICK, G. M. (1984). *Z. Naturforsch. Teil B*, **39**, 1389–1392.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JAMES, J. A., CRAIG, S. L., CORDES, A. W., OAKLEY, R. T. & BOERÉ, R. T. (1985). In preparation.
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
ROESKY, H. W., SCHAFER, P., NOLTEMEYER, M. & SHELDRICK, G. M. (1983). *Z. Naturforsch. Teil B*, **38**, 347–349.
WIEGERS, G. A. & VOS, A. (1962). *Proc. Chem. Soc. London*, pp. 387–388.