Crystal and Molecular Structure of 2,3,5,6-Tetrachloro-4-(methylthio)-benzonitrile

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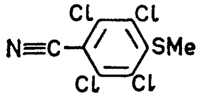
The molecular and crystal structures of the title compound have been determined by three-dimensional *X*-ray diffraction methods from diffractometer data. Crystals are triclinic, space group $P\bar{1}$, with a = 7·559, b = 8·332, c = 8·912 (Å), α = 78·63°, β = 80·95°, and γ = 80·60°, and Z = 2. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to R 3·6% for 2172 reflections. All atoms but those of the methyl group lie in the (2,1,0) planes of the crystal. The methylthio-group forms a dihedral angle of 87·1° with respect to the ring plane. The four C–Cl bond distances range between 1·717 and 1·725, C(sp^2)–S is 1·763, S–CH_3 1·826 Å, and C–S–C 102·0°.

THE benzonitrile derivative (I) belongs to a series of substituted benzenes, pyridines, and pyrazines which have potentially useful biological properties. The solution of its crystal structure by single-crystal *X*-ray diffraction was undertaken to identify the isomer (m.p. 135—137 °C) and establish its geometry for structure-property comparisons with other compounds in the series.



(I)

Description of the Structure.—The results demonstrated that the methylthio-group was *para* to the nitrile substituent and thus identified (I) as 2,3,5,6-tetrachloro-4-(methylthio)benzonitrile. The molecular structure and atom numbering system are shown in Figure 1.[1] Bond distances and angles (Table 1) are generally as expected. Carbon–carbon bonds in the aromatic ring range from 1·382—1·409 Å and the internal ring angles, 118·4—121·3°, are close to the nominal value of 120°. Carbon–chlorine bonds, 1·717—1·725 Å, are very similar to those found (1·711—1·735 Å) in a closely related compound, 2,4,5-trichloro-6-(methylthio)benzene-1,3-dicarbonitrile.[2] The S(1)–C(8) bond (1·826 Å) and the C(4)–S(1)–C(8) angle (102·0°) agree well with values found in the literature for paraffinic sulphides and sulphoxides.[3,4] The analogous S–CH_3 distances in the dinitrile are 1·818 and 1·827 Å and the C–S–C angles are 102·1 and 102·2° respectively for the two unique molecules in that structure.[2] The literature contains fewer examples of structures where sulphur is bonded to

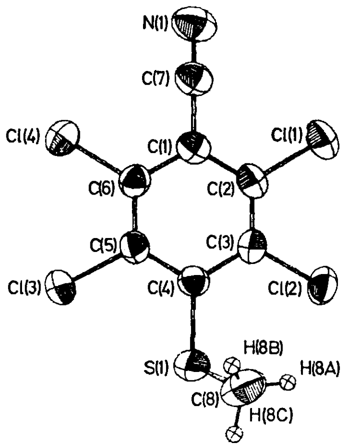


FIGURE 1 The molecular structure. Atoms are represented by 0·50 probability ellipsoids, with hydrogens as 0·10 Å spheres

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[1] Drawings by ORTEP, a FORTRAN thermal ellipsoid plot program, by C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee, modified for an IBM 1130 Computer by T. P. Blumer.

[2] D. R. Carter, J. W. Turley, and F. P. Boer, *Acta Cryst.*, in the press.

[3] Chem. Soc. Special Publ., No. 11, 1958, p. 22*s*.

[4] (*a*) J. V. Silverton, D. T. Gibson, and S. C. Abrahams, *Acta Cryst.*, 1965, **19**, 651; (*b*) D. R. McGregor and J. C. Speakman, *ibid.*, 1969, *B*, **25**, 540; (*c*) J. Karle, I. L. Karle, and D. Mitchell, *ibid.*, p. 866; (*d*) D. Mitchell, *ibid.*, p. 998.

aromatic rings, but our C(4)–S(1) bond length (1·763 Å) is reasonable in comparison[4d] with 1·800 Å for *m*-carboxyphenyl benzyl disulphide, and agrees closely with the aromatic C–S distances 1·757 and 1·775 Å in the dinitrile.[2]

TABLE 1

Bond distances (Å) and angles (deg), with errors in parentheses; corrected bond distances are in square brackets

(*a*) Bonds

C(1)–C(2)	1·409(3)[1·413]	C(3)–Cl(2)	1·725(2)[1·728]
C(2)–C(3)	1·382(3)[1·385]	C(4)–S(1)	1·763(2)[1·766]
C(3)–C(4)	1·401(3)[1·405]	S(1)–C(8)	1·826(3)[1·831]
C(4)–C(5)	1·399(3)[1·404]	C(5)–Cl(3)	1·718(2)[1·722]
C(5)–C(6)	1·390(3)[1·393]	C(6)–Cl(4)	1·718(2)[1·722]
C(6)–C(1)	1·385(3)[1·389]	C(8)–H(8A)	0·92(3)
C(1)–C(7)	1·442(3)[1·444]	C(8)–H(8B)	0·92(4)
C(7)–N(1)	1·137(3)[1·138]	C(8)–H(8C)	0·90(3)
C(2)–Cl(1)	1·717(2)[1·720]		

(*b*) Angles

C(1)–C(2)–C(3)	119·5(2)	Cl(3)–C(5)–C(6)	119·0(1)
C(2)–C(3)–C(4)	121·3(2)	C(5)–C(6)–Cl(4)	121·4(2)
C(3)–C(4)–C(5)	118·3(2)	Cl(4)–C(6)–C(1)	118·4(1)
C(4)–C(5)–C(6)	120·8(2)	C(6)–C(1)–C(7)	120·9(2)
C(5)–C(6)–C(1)	120·2(2)	C(1)–C(7)–N(1)	177·9(3)
C(6)–C(1)–C(2)	119·7(2)	C(7)–C(1)–C(2)	119·4(2)
C(1)–C(2)–Cl(1)	118·4(2)		
Cl(1)–C(2)–C(3)	122·1(2)	S(1)–C(8)–H(8A)	105(2)
C(2)–C(3)–Cl(2)	118·3(2)	S(1)–C(8)–H(8B)	114(2)
Cl(2)–C(3)–C(4)	120·4(2)	S(1)–C(8)–H(8C)	104(2)
C(3)–C(4)–S(1)	122·2(2)	H(8A)–C(8)–H(8B)	116(3)
C(4)–S(1)–C(8)	102·0(1)	H(8A)–C(8)–H(8C)	109(3)
S(1)–C(4)–C(5)	119·5(1)	H(8B)–C(8)–H(8C)	107(3)
C(4)–C(5)–Cl(3)	120·2(1)		

Thermal least-squares analysis was performed to determine to what extent the molecule vibrates as a rigid body and to estimate the bond-length corrections resulting from thermal motion.[5] The 12 atoms excluding N(1) and the methyl group appear to approximate to a rigid body fairly well, as indicated by a root-mean-square ΔU_{ij} 0·0021 Å^2 and a maximum ΔU_{ij} of 0·0062 Å^2 for ΔU_{13} of S(1). The inclusion of all non-hydrogen atoms in the calculation raises these values to 0·0035 and 0·0108 Å^2, and supports the view that only the ring and its directly bonded atoms should be considered part of the rigid body. Bond lengths corrected for the effects of rigid-body thermal motion are included in Table 1 for comparison. The average correction is 0·003—0·004 Å with extremes of 0·001 Å for C(7)–N(1) and 0·005 Å for S(1)–C(8) and C(4)–C(5).

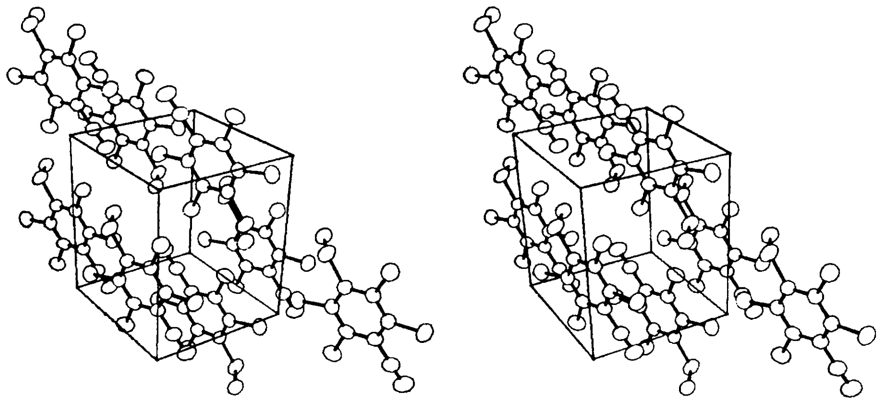

FIGURE 2 Unit-cell molecules with selected neighbours to illustrate packing details. Origin is at the bottom rear corner with positive *x* forward to the left, *y* to the right, and *z* vertical. Co-ordinates in Table 4 refer to the lower front molecule in the cell

Molecular distortion from the expected planar structure is seen in Table 2, which lists the magnitudes of atomic deviation from the least-squares plane[6] through the ring atoms. The ring atoms themselves exhibit significant nonplanarity and this effect is accentuated in the substituents. The pattern of distortion of the ring resembles a shallow boat. The methylthio-plane, defined C(4),S(1),C(8), forms an angle of 87·1° with the ring plane and is inclined toward Cl(2).

TABLE 2

Deviations (Å) from least-squares plane

Plane: C(1)—(6) $7{\cdot}125x + 3{\cdot}467y - 0{\cdot}024z = 7{\cdot}073$

C(1) −0·020, C(2) 0·000, C(3) 0·023, C(4) −0·026, C(5) 0·006, C(6) 0·018, C(7) −0·086, N(1) −0·177, Cl(1) −0·003, Cl(2) 0·156, S(1) −0·099, C(8) 1·647, Cl(3) 0·057, Cl(4) 0·066

The arrangement of the molecules in and adjacent to a unit cell is drawn as a stereoscopic pair in Figure 2, where packing can be seen to occur in sheets [corresponding to the (2,1,0) crystal planes] 3·55 Å apart. Table 3 lists close intermolecular contacts[1] in order of increasing differences from the sum of the appropriate van der Waals radii.[7] The distances which are less than or nearly equal to van der Waals contacts [Cl(2) · · · Cl(2), N(1) · · · Cl(3), S(1) · · · Cl(1), and N(1) · · · Cl(4)] are all contacts between coplanar molecules, indicating the efficiency of the packing within the (2,1,0) crystal planes. Although the repulsion forces between non-bonded

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[5] V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, *B*, **24**, 63.

[6] J. Gvildys, 'Least-Squares Plane and Line Fitter,' see V. Schomaker, J. Waser, R. E. March, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600, Program Library B 125, Argonne National Laboratory.

[7] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1969, p. 260.

atoms may be assumed to be approximately minimized for the entire system, the crowding which does occur [note especially Cl(2) ··· Cl(2)] may contribute to the observed distortions from planarity. Finally, the methyl groups occupy space between the (2,1,0) planes and are arranged to point away from one another where adjacent molecules are coplanar (right-hand side of Figure 2). Thus, methyl groups from every second plane approach each other with a separation of 3·85 Å. This arrangement can be seen in the left-hand side of Figure 2 near the centre of symmetry at ½, 0, ½.

TABLE 3

Intermolecular contacts (Å) near the sums of van der Waals radii

Cl(2) ··· Cl(2$^{\mathrm{I}}$)	3·431	N(1) ··· H(2$^{\mathrm{VI}}$)	2·899
N(1) ··· Cl(3$^{\mathrm{II}}$)	3·287	C(5) ··· Cl(1$^{\mathrm{V}}$)	3·624
S(1) ··· Cl(1$^{\mathrm{II}}$)	3·639	Cl(4) ··· H(3$^{\mathrm{VII}}$)	3·229
N(1) ··· H(3$^{\mathrm{III}}$)	2·754	H(2) ··· H(2$^{\mathrm{VIII}}$)	2·646
N(1) ··· Cl(4$^{\mathrm{IV}}$)	3·385	C(2) ··· C(7$^{\mathrm{VI}}$)	3·472
C(7) ··· Cl(2$^{\mathrm{V}}$)	3·577	S(1) ··· C(8$^{\mathrm{IX}}$)	3·713

Roman numerals as superscripts refer to the following transformations relative to the reference molecule at x, y, z:

I $1 - x, -1 - y, -1 - z$
II $x, y, -1 + z$
III $x, 1 + y, -1 + z$
IV $-x, 1 - y, -1 - z$
V $1 - x, -y, -1 - z$
VI $-x, -y, -1 - z$
VII $-x, -y, -z$
VIII $-x, -1 - y, -z$
IX $1 - x, 1 - y, -z$

TABLE 4

Final structure parameters with standard deviations in parentheses

(*a*) Anisotropic heavy atoms *

	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
C(1)	0·7069(2)	0·5814(2)	0·0305(2)	171(4)	145(3)	110(3)	−52(3)	−13(2)	−10(2)
C(2)	0·7892(2)	0·4189(2)	0·0229(2)	173(4)	161(3)	105(3)	−57(3)	2(2)	−37(2)
C(3)	0·8424(2)	0·3159(2)	0·1546(2)	168(4)	123(3)	133(3)	−26(2)	−7(2)	−39(2)
C(4)	0·8097(2)	0·3697(2)	0·2977(2)	170(4)	130(3)	113(3)	−31(2)	−25(2)	−19(2)
C(5)	0·7341(2)	0·5344(2)	0·3017(2)	179(4)	132(3)	110(2)	−33(2)	−14(2)	−37(2)
C(6)	0·6844(2)	0·6391(2)	0·1689(2)	178(4)	120(3)	130(3)	−29(2)	−17(2)	−21(2)
C(7)	0·6459(3)	0·6861(2)	−0·1055(2)	209(5)	172(4)	126(3)	−58(3)	−21(3)	−70(2)
N(1)	0·5930(3)	0·7684(2)	−0·2108(2)	321(6)	227(4)	142(3)	−57(4)	−56(3)	15(2)
Cl(1)	0·8200(9)	0·3530(8)	−0·1514(1)	273(1)	226(1)	113(1)	−58(1)	1(8)	−66(7)
Cl(2)	0·9559(8)	0·1220(7)	0·1395(1)	254(1)	142(1)	174(1)	4(8)	−2(9)	−63(7)
S(1)	0·8644(9)	0·2381(7)	0·4699(1)	295(2)	156(1)	140(1)	−9(1)	−82(9)	−17(7)
C(8)	0·7288(40)	0·0751(32)	0·4839(3)	262(6)	161(4)	183(4)	−16(4)	−17(42)	−19(31)
Cl(3)	0·7055(9)	0·6097(7)	0·4712(1)	308(2)	155(1)	124(1)	−10(9)	−46(8)	−58(6)
Cl(4)	0·5939(9)	0·8415(7)	0·1717(1)	294(1)	115(1)	169(1)	−33(8)	−40(9)	−26(6)

(*b*) Isotropic hydrogen atoms

	x	y	z	B/Å^2
H(8A)	0·791(4)	0·008(3)	0·418(3)	8·2(8)
H(8B)	0·610(4)	0·117(40)	0·470(3)	9·0(9)
H(8C)	0·730(4)	0·021(3)	0·582(4)	9·7(9)

* The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k_2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

EXPERIMENTAL

Crystal Data.—$C_8H_3Cl_4NS$, $M = 287{\cdot}0$., Triclinic, $a = 7{\cdot}559 \pm 0{\cdot}003$, $b = 8{\cdot}332 \pm 0{\cdot}004$, $c = 8{\cdot}912 \pm 0{\cdot}004$ Å, $\alpha = 78{\cdot}63 \pm 0{\cdot}01$, $\beta = 80{\cdot}95 \pm 0{\cdot}02$, $\gamma = 80{\cdot}60 \pm 0{\cdot}02°$, $U = 538{\cdot}3$ Å^3, $D_m = 1{\cdot}77$, $Z = 2$, $D_c = 1{\cdot}773$, $F(000) = 284$. Space group, $P\bar{1}$ (C_i^1 No. 2). Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 12·35 cm^{-1}).

A single crystal of dimensions 0·46 × 0·46 × 0·36 mm (along *a*, *c*, and *b*) was sealed in a thin-walled glass capillary. Preliminary Weissenberg photographs indicated space group $P1$ or $P\bar{1}$, shown to be the latter by the subsequent successful refinement. A Picker four-circle diffractometer was then used to locate the reciprocal axes which were labelled according to the convention $a < b < c$, and shown to be consistent with a Dirichlet reduced cell. After the crystal was oriented to set the *a* axis collinear with ϕ, a least-squares analysis on the setting angles of 22 reflections gave the cell constants and errors.

Intensity data were collected using Mo-K_α radiation selected by reflection from the (0,0,2) planes of a highly oriented graphite crystal and a 3° take-off angle. 2642 Reflections, covering the hemisphere $0 \leq \sin\theta \leq 0{\cdot}461$, were collected by use of the θ—2θ scan mode at 2 deg min^{-1} with attenuators set to prevent count rates exceeding 12,000 s^{-1}. The scan range over a given peak was $2° + \Delta$, where Δ is the separation of the K_α doublet. Background counts were taken at each end of the scan for 10 s by the stationary-crystal–stationary-counter method. A test reflection (2,3,4) was monitored every 50 measurements and showed fair stability. An error $\sigma(I) = [(0{\cdot}025I)^2 + N_0 + k^2N_b]^{\frac{1}{2}}$ was assigned to the net intensity, $I = N_0 - kN_b$, of each reflection to calculate its relative weight, $w(F) = 4F^2/\sigma^2(F^2)$, for subsequent least-squares refinement where the quantity $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2$ was to be minimized. Here N_0 is the scan count, N_b is the background, k is the ratio of scan time to background time, and the F^2 are the net intensities after Lorentz and polarization corrections.

Subsequently a second unique data set was gathered similarly from the other hemisphere of the reciprocal lattice. The redundant sets (*hkl* and $\bar{h}kl$) agreed within 2·2% (based on F) and were merged into a single set. 470 reflections having $I < 0$ or $I/\sigma(I) < 2$ were denoted absent and omitted from the refinement. Absorption corrections were not made.

Structure Determination and Refinement.—A structure-factor calculation based on the heavy-atom positions derived from a Patterson analysis and an overall temperature factor (3·79 Å^2) from a Wilson plot gave R 0·26 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$ 0·35. An electron-density difference-Fourier map revealed the positions of the remaining non-hydrogen atoms and three cycles of full-matrix least-squares refinement [scattering factors for carbon, nitrogen, chlorine, and sulphur were taken from ref. 8(*a*) and hydrogen from ref. 8(*b*)] on atomic positions and isotropic temperature factors produced[9] R 0·144 and R' 0·189. After location of the hydrogen atoms from another difference-Fourier map, refinement was continued. Isotropic hydrogens were assumed while anisotropic thermal parameters were used for all other atoms. Convergence under these assumptions was attained at R 0·036 and R' 0·043. A secondary extinction correction,[10] $F_o{}^{\text{corr}} = F_o{}^{\text{obs}}\ (1 + c\beta I_o)$, was then applied to a group of intense low-order reflections which had shown fairly large negative values of $F_o - F_c$. The constant c, referred to the scaled intensities, was found to be $2{\cdot}04 \times 10^{-6}$, and the maximum correction in any F was 23% for the very strong (2,1,0) reflection. Three addition cycles of refinement, by use of the corrected data, reduced R and R' to final values of 0·034 and 0·042. In the last cycle no parameter shift was $>0{\cdot}13\sigma$, and a difference-Fourier map calculated from these parameters revealed no deviations $>0{\cdot}3$ eÅ^{-3}. Table 4 lists the final co-ordinates and thermal parameters with standard deviations computed[11] from the least-squares analysis. The final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20513 (2 pp., 1 microfiche).*

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full sized copies).

[8] (*a*) 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 201—209; (*b*) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] J. Gvildys, 'A Fortran Crystallographic Least-Squares Refinement Program,' Program Library 14E7043, Argonne National Laboratory.

[10] W. H. Zachariasen, *Acta Cryst.*, 1963, **16**, 1139.

[11] J. Gvildys, 'A FORTRAN Crystallographic Function and Error Program,' based on ORFFE, Program Library B 115, Argonne National Laboratory.