Crystal Structure of 1,3,4,5,6,8-Hexachlorothieno[2,3-*c*:5,4-*c′*]dipyridine

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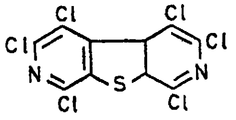
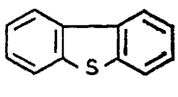
Crystals of the title compound (I) are triclinic, a = 9·07(1), b = 11·37(1), c = 7·10(1) Å, α = 111·1(2)°, β = 90·0(2)°, γ = 105·7(2)°, Z = 2, space group $P\bar{1}$. The structure was determined from precession data by Fourier and least-squares methods, the final R being 5·9% for 1062 non-zero reflections. The analysis revealed the overcrowded nature of the molecule, the two chlorine atoms in the overcrowded region being displaced from the best least-squares plane through the thienodipyridine group by 0·61 and −0·62 Å, respectively.

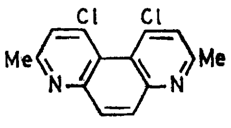
Reaction of heptachloro-5,5′-dilithio-4,4′-bipyridyl with sulphur dichloride yields 1,3,4,5,6,8-hexachlorothieno-[2,3-*c*:5,4-*c′*]dipyridine (I), despite the overcrowded nature of the product.[1] There has been considerable structural interest in overcrowded molecules and recently Wynberg and his co-workers have cited the structures of some of these molecules as evidence for their proposition that ' mononuclear and polynuclear aromatic hydrocarbons are flexible molecules capable of 5—20° deviations from a plane in the ground state.' [2]



(I)



(II)



(III)

The structure analysis of (I) presents the molecular geometry of a molecule whose degree of overcrowding lies between that observed in 1,4,5,8-tetrachloronaphthalene [3] and that in 1,10-dichloro-3,8-dimethyl-4,7-phenanthroline (III).[4] It also provides structural parameters for a class of compounds, the thieno[2,3-*c*:5,4-*c′*]dipyridines, for which none at present are available.

EXPERIMENTAL

Crystal Data.—$C_{10}Cl_6N_2S$, M = 393, Triclinic, a = 9·07(1), b = 11·37(1), c = 7·10(1) Å, α = 111·1(2), β = 90·0(2), γ = 105·7(2)°, U = 654 Å^3, D_c = 1·99 g cm^{-3}, Z = 2, D_m = 1·96 g cm^{-3} (by flotation), $F(000)$ = 384. Mo-K_α radiation, λ = 0·7107 Å; μ (Mo-K_α) = 14·3 cm^{-1}. Space-group $P\bar{1}$. Crystal dimensions *ca.* 0·7 × 0·2 × 0·05 mm; data layers *hk*0—2, 0—2*kl*,

Of 1268 independent reflections recorded by visual estimation from precession photographs, 206 were found to be too weak to be estimated by the technique employed. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

The structure was determined by standard three-dimensional Fourier methods and refined by use of full-matrix least-squares methods. Allowance was made in the final calculations for the anisotropic thermal motion of all the atoms. The weighting scheme used was $w = (4{\cdot}5 + F_0 + 0{\cdot}0022F_0^2)^{-1}$ for the observed reflections. This weighting scheme gave a satisfactory analysis of $w\Delta^2$ in ranges of F_0 and $\sin\theta$. The final value of R over 1062 non-zero reflections was 5·9%. The maximum shift in the final cycle of least squares was $< 0{\cdot}1\sigma$ and a final difference-Fourier map revealed no peak $> \pm 0{\cdot}4$ eÅ^{-3}. Scattering factors from ref. 5*a* were used in the calculations which were carried out on the Salford University KDF 9 computer, with local versions of programs written for the KDF 9 by J. S. Rollett and G. Ford, and at the University of Manchester Regional Computing Centre on the CDC 7600 with the *X*-Ray '70 system.[5b]

RESULTS

Final atomic co-ordinates with their standard deviations are given in Table 1, details of the molecular geometry in Tables 2 and 3; Figure 1 indicates the labelling of the atoms. The measured and calculated structure factors and atomic thermal parameters are listed in Supplementary Publication No. SUP 21115 (18 pp., 1 microfiche).*

DISCUSSION

The main feature of the molecule revealed by the structure analysis is the considerable deviation from coplanarity of Cl(9) and Cl(13) with the thienodipyridine system. The distance between these two atoms in the hypothetical planar molecule (2·05 Å) has increased in the actual molecule to 3·06 Å in an attempt to minimise the repulsion between the two atoms.

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

[1] N. J. Foulger and B. J. Wakefield, *J. Organometallic Chem.*, 1974, **69**, 161.

[2] H. Wynberg, W. C. Nieuwpoort, and H. T. Jonkman, *Tetrahedron Letters*, 1973, 4623.

[3] G. Gafner and F. H. Herbstein, *Acta Cryst.*, 1962, **15**, 1081.

[4] F. H. Herbstein, M. Kapon, and D. Rabinovich, *Israel J. Chem.*, 1972, **10**, 537.

[5] (*a*) ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962; (*b*) ' *X*-Ray '70,' ed. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland Technical Report 67—58.

TABLE 1

Atomic parameters (× 10^4)

Atom	*x*	*y*	*z*
S(1)	2476(2)	7563(2)	2302(4)
C(2)	4291(10)	8707(7)	2478(14)
C(3)	4450(11)	9997(7)	2557(14)
Cl(4)	2790(3)	10,522(2)	2629(4)
N(5)	5831(9)	10,832(6)	2637(13)
C(6)	7088(10)	10,424(7)	2428(16)
Cl(7)	8850(3)	11,572(2)	2493(4)
C(8)	7075(11)	9137(7)	2281(15)
Cl(9)	8748(3)	8690(3)	1654(6)
C(10)	5620(10)	8269(7)	2416(14)
C(11)	5145(10)	6935(7)	2484(14)
C(12)	5973(10)	6087(7)	2701(14)
Cl(13)	7952(3)	6563(2)	3478(5)
C(14)	5091(12)	4807(7)	2530(15)
Cl(15)	6006(4)	3675(2)	2666(4)
N(16)	3507(10)	4363(6)	2288(14)
C(17)	2726(11)	5180(7)	2249(14)
Cl(18)	694(3)	4652(2)	2144(5)
C(19)	3478(9)	6446(6)	2293(13)

TABLE 2

(*a*) Bond lengths (Å), with standard deviations in parentheses

S(1)–C(2)	1·77(1)	C(10)–C(11)	1·48(1)
S(1)–C(19)	1·75(1)	C(11)–C(12)	1·42(1)
C(2)–C(3)	1·42(1)	C(11)–C(19)	1·45(1)
C(2)–C(10)	1·42(1)	C(12)–Cl(13)	1·75(1)
C(3)–Cl(4)	1·76(1)	C(12)–C(14)	1·42(1)
C(3)–N(5)	1·34(1)	C(14)–Cl(15)	1·74(1)
N(5)–C(6)	1·33(1)	C(14)–N(16)	1·38(1)
C(6)–Cl(7)	1·76(1)	N(16)–C(17)	1·32(1)
C(6)–C(8)	1·43(1)	C(17)–Cl(18)	1·77(1)
C(8)–Cl(9)	1·74(1)	C(17)–C(19)	1·41(1)
C(8)–C(10)	1·46(1)		

(*b*) Bond angles (°), with standard deviations in parentheses

C(2)–S(1)–C(19)	87·2(4)	C(10)–C(11)–C(12)	133·4(8)
S(1)–C(2)–C(3)	122·7(7)	C(10)–C(11)–C(19)	110·1(8)
S(1)–C(2)–C(10)	117·8(6)	C(12)–C(11)–C(19)	116·5(7)
C(3)–C(2)–C(10)	119·4(7)	C(11)–C(12)–Cl(13)	125·1(6)
C(2)–C(3)–Cl(4)	118·8(7)	C(11)–C(12)–C(14)	116·8(8)
C(2)–C(3)–N(5)	121·6(9)	Cl(13)–C(12)–C(14)	117·6(8)
Cl(4)–C(3)–N(5)	119·6(7)	C(12)–C(14)–Cl(15)	120·1(8)
C(3)–N(5)–C(6)	120·4(8)	C(12)–C(14)–N(16)	124·9(9)
N(5)–C(6)–Cl(7)	117·6(7)	Cl(15)–C(14)–N(16)	115·0(6)
N(5)–C(6)–C(8)	123·1(8)	C(14)–N(16)–C(17)	118·7(7)
Cl(7)–C(6)–C(8)	119·2(7)	N(16)–C(17)–Cl(18)	118·6(6)
C(6)–C(8)–Cl(9)	116·9(7)	N(16)–C(17)–C(19)	121·2(8)
C(6)–C(8)–C(10)	117·0(9)	Cl(18)–C(17)–C(19)	120·1(7)
Cl(9)–C(8)–C(10)	125·6(7)	S(1)–C(19)–C(11)	116·0(6)
C(2)–C(10)–C(8)	117·9(8)	S(1)–C(19)–C(17)	122·2(7)
C(2)–C(10)–C(11)	108·2(7)	C(11)–C(19)–C(17)	121·6(8)
C(8)–C(10)–C(11)	133·9(9)		

(*c*) Non-bonded intramolecular distances (Å) with standard deviations in parentheses

Cl(7) · · · Cl(9)	3·087(4)	Cl(9) · · · Cl(13)	3·058(5)
Cl(13) · · · Cl(15)	3·119(3)		

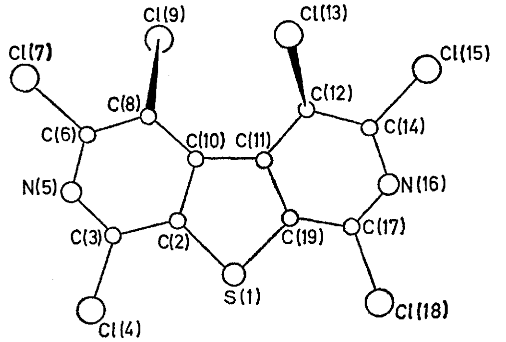

FIGURE 1 View of the molecule, showing the numbering system used in the analysis

TABLE 3

Least-squares planes defined by atomic positions and, in square brackets, distances (Å) of relevant atoms from them. In the equations *X*, *Y*, *Z* are orthogonal coordinates obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a\sin\beta\sin\gamma^* & 0 & 0 \\ -a\sin\beta\cos\gamma^* & b\sin\alpha & 0 \\ a\cos\beta & b\cos\alpha & c \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Plane (1): S(1), C(2), C(3), N(5), C(6), C(8), C(10)—(12), C(14), N(16), C(17), and C(19)

$$0{\cdot}0776X + 0{\cdot}3562Y + 0{\cdot}9312Z - 1{\cdot}4581 = 0$$

[S(1) −0·03, C(6) −0·07, C(11) 0·03, N(16) −0·05, C(2) 0·04, Cl(7) −0·08, C(12) 0·15, C(17) −0·06, C(3) 0·08, C(8) −0·17, Cl(13) 0·61, Cl(18) −0·07, Cl(4) 0·17, Cl(9) −0·62, C(14) 0·06, C(19) −0·05, N(5) 0·10, C(10) −0·03, Cl(15) 0·13]

Plane (2): C(3), N(5), C(6), C(8), and C(10)

$$0{\cdot}1502X + 0{\cdot}3049Y + 0{\cdot}9405Z - 1{\cdot}3516 = 0$$

[C(2) −0·01, C(3) −0·03, N(5) 0·04, C(6) −0·01, C(8) −0·03, C(10) 0·04, Cl(4) −0·10, Cl(7) 0·05, Cl(9) −0·34]

Plane (3): C(11), C(12), C(14), N(16), C(17), and C(19)

$$0{\cdot}0039X + 0{\cdot}3659Y + 0{\cdot}9307Z - 1{\cdot}2433 = 0$$

[C(11) −0·03, C(12) 0·03, C(14) −0·01, N(16) −0·02, C(17) −0·03, C(19) −0·00, Cl(13) 0·37, Cl(15) −0·01, Cl(18) −0·14]

Plane (4): S(1), C(2), C(10), C(11), and C(19)

$$0{\cdot}0662X + 0{\cdot}3431Y + 0{\cdot}9370Z - 1{\cdot}3102 = 0$$

[S(1) −0·00, C(2) 0·03, C(10) −0·05, C(11) 0·04, C(19), −0·02]

TABLE 4

Intermolecular distances (Å) <3·4 Å, with standard deviations in parentheses

N(5) · · · Cl(15^{I})	3·19(1)	C(3) · · · C(2^{II})	3·36(1)
C(2) · · · N(5^{II})	3·32(1)	C(6) · · · Cl(4^{III})	3·37(1)
C(14) · · · C(14^{IV})	3·38(1)	C(14) · · · C(11^{V})	3·37(1

Roman numeral superscripts refer to the positions:

I $x, 1 + y, z$
II $1 - x, 2 - y, 1 - z$
III $1 - x, 2 - y, -z$
IV $1 - x, 1 - y, 1 - z$
V $1 - x, 1 - y, -z$

The C–C and C–N bond distances are all close to their accepted values (1·395 and 1·352 Å).[6] The two C–S bond lengths are 1·77(1) and 1·75(1) Å compared with 1·73 and 1·75 Å in dibenzothiophen (II).[7]

If we compare the bond angles in (I) with those in (II) there is a significant decrease in the value of the C–S–C angle [91·5(4) in (II), 87·2(4)° in (I)]. This decrease, together with the increase in the C(8)–C(10)–C(11) and C(10)–C(11)–C(12) angles [129·3(8) and 129·4(8) in (II), 133·4(8) and 133·9(8)° in (I)], seems to imply a minor in-plane forcing apart of the two halves of the molecule in order to lessen the Cl · · · Cl interaction. Despite this in-plane distortion, the main way in which the ring system accommodates the increased Cl · · · Cl distance is by a number of small out-of-plane displacements.

The deviations of the atoms from a number of specified planes are set out in Table 3. Considering the ring system as a whole, maximum displacements occur for atoms which are closest to the overcrowded region of the molecule. This is in accord with the finding of Herbstein *et al.* in their determination of the overcrowded molecule

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[6] 'Molecular Structures and Dimensions, Interatomic Distances, vol. *A*1, International Union of Crystallography, 1972.

[7] R. M. Schaffrin and J. Trotter, *J. Chem. Soc.* (*A*), 1970, 1561.

(III).[4] A comparison of the out-of-plane displacements of the two molecules is given in Figure 2. The degree of overcrowding in the present molecule is less than that in (III), the two chlorine atoms being displaced from the best least-squares plane through the ring system by 0·61 and –0·62 Å in (I), and by 1·124 and –1·155 Å in (III).

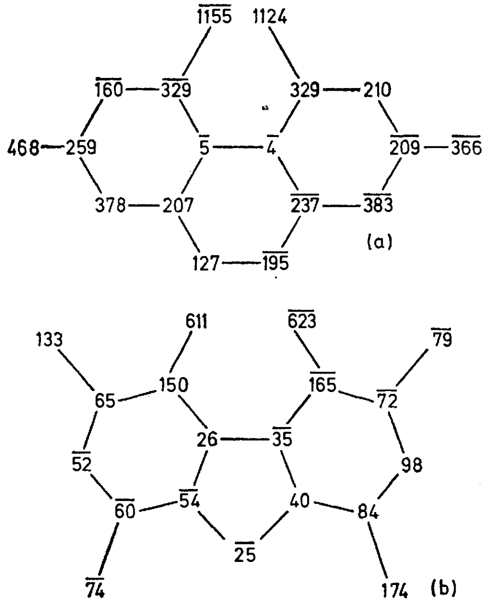

FIGURE 2 Comparison of the out-of-plane displacements in the molecules (a) (III) and (b) (I)

Both the six-membered rings have distorted twist-boat conformations and the five-membered ring has a similar conformation, assuming the sulphur atom to have replaced two carbon atoms. The dihedral angles between the thiophen ring and the six-membered rings are 5·3 and 3·8° compared with 1·2 and 0·4° in (II).

The C–Cl distances range from 1·74 to 1·77(1) Å, which compared well with the range 1·71—1·77 Å for the C(aromatic)–Cl bond length found in 26 different structures.[8] The C–N–C angles [118·7(7) and 120·4(8)°] are considerably larger than the mean (115·7°) obtained from 20 heteroaromatic structures[9] and much closer to those found in (III) which are thought to be caused by intramolecular strain.

The molecules are separated by the usual van der Waals distances (Table 4).

I thank Dr. B. J. Wakefield for suggesting the problem and supplying the crystals.

[4/981 *Received, 20th May*, 1974]

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[8] H. Hope, *Acta Cryst.*, 1969, **B25**, 75.

[9] C. Singh, *Acta Cryst.*, 1965, **19**, 861.