

6-Chloro-4-methyl-1,2,3-benzothiadiazole

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Abstract. $C_7H_5ClN_2S$, $M_r = 184.65$, monoclinic, $C2/c$, $a = 32.033$ (11), $b = 3.921$ (1), $c = 26.969$ (7) Å, $\beta = 111.35$ (2)°, $V = 3154.9$ Å³, $D_m = 1.56$ (5) (floatation), $D_x = 1.554$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.665$ mm⁻¹, $Z = 16$, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, at 293 (1) K; final $R = 0.068$ for 1465 reflexions. The two molecules in the asymmetric unit are essentially planar and there are no significant differences in the bond lengths and angles.

Introduction. 6-Chloro-4-methyl-1,2,3-benzothiadiazole was prepared according to Kirby, Soloway, Davies & Webb (1970). Transparent, very thin and fragile needles elongated along **b** were crystallized from methanol. The systematically absent reflexions ($h0l$: $l = 2n + 1$ and hkl : $h + k = 2n + 1$) on Weissenberg and precession photographs and the mean value of $|E^2 - 1| = 1.004$ indicated the space group $C2/c$. Cell dimensions were obtained by least squares from the 2θ values of 30 randomly chosen reflexions measured on a CAD-4 diffractometer [Mo $K\alpha_1$ radiation, $\lambda = 0.70926$ Å, $T = 293$ (1) K].

A single crystal $0.1 \times 0.1 \times 0.6$ mm was used for data collection on an automatic computer-controlled Enraf-Nonius CAD-4 four-circle diffractometer with Mo $K\alpha$ radiation and a graphite monochromator.

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Table 1. Data-collection summary

Temperature (K)	293 (1)
Diffractometer	CAD-4, automatic, four-circle
Radiation (Å)	Mo $K\alpha$ (graphite monochromator) ($\lambda = 0.71069$ Å)
Scan method	ω - 2θ
2θ scan width (°)	$0.8 + 0.2 \tan \theta$
Scan rate (deg min ⁻¹)	Minimum 1.8; maximum 20.1
Background	$\frac{1}{4}$ of the scan time at each of the scan limits
$2\theta_{\max}$ (°)	54
Maximum scan time (s)	40
Aperture (mm)	$2.7 + 0.9 \tan \theta$
Reference reflexions	312, 312
Intensity decrease (%)	None
Measured reflexions	2561 (+ h , + k , + l)
Observed reflexions	1465 [$I > 2\sigma(I)$]
$\sigma(I)$ base	Counting statistics
μ (mm ⁻¹)	0.665 for Mo $K\alpha$

Reflexions were scanned in the ω - 2θ mode (moving crystal-moving counter) with a variable scan rate. A summary of the data collection and reduction is given in Table 1. The data were corrected for variation in reference reflexions and Lorentz-polarization effects. No correction was applied for absorption.

Multisolution \sum_2 sign expansion (Sheldrick, 1976) located all non-hydrogen atoms. Isotropic full-matrix least-squares refinement proceeded to $R = 0.117$, and anisotropic refinement to $R = 0.087$. A subsequent difference synthesis showed all H atoms except H(8A), H(18A) and H(18C) of the methyl groups. Later, these

Table 2. Final fractional coordinates ($\times 10^4$; for H $\times 10^3$) with e.s.d.'s in parentheses

	x	y	z
S(1)	4350 (1)	4315 (6)	1796 (1)
Cl(1)	3237 (1)	-1093 (7)	-108 (1)
N(2)	4066 (3)	5753 (18)	2185 (3)
N(3)	3643 (2)	5252 (17)	1967 (2)
C(3a)	3512 (2)	3650 (17)	1482 (2)
C(4)	3074 (2)	2787 (18)	1174 (3)
C(5)	2996 (2)	1316 (19)	687 (3)
C(6)	3363 (3)	700 (19)	527 (3)
C(7)	3793 (3)	1414 (18)	818 (3)
C(7a)	3867 (2)	2951 (18)	1311 (3)
C(8)	2690 (3)	3529 (24)	1367 (3)
S(11)	298 (1)	3897 (5)	1728 (1)
Cl(11)	2031 (1)	7601 (6)	2052 (1)
N(12)	-75 (2)	4952 (20)	1107 (3)
N(13)	121 (2)	6332 (18)	816 (3)
C(13a)	578 (2)	6676 (17)	1068 (3)
C(14)	865 (3)	8175 (19)	834 (3)
C(15)	1306 (2)	8437 (17)	1153 (3)
C(16)	1467 (2)	7161 (19)	1679 (3)
C(17)	1190 (2)	5589 (17)	1904 (3)
C(17a)	743 (2)	5460 (17)	1592 (2)
C(18)	686 (3)	9534 (24)	274 (3)
H(5)	266	64	43
H(7)	406	85	68
H(8A)	265	626	138
H(8B)	237	247	111
H(8C)	278	251	176
H(15)	154	965	100
H(17)	132	454	230
H(18A)	57	1213	26
H(19B)	97	938	16
H(18C)	42	796	2

atoms were inserted in calculated positions and refined with the other H atoms subject to the constraint that the C—H vectors were constant in magnitude and direction but not position (riding model). A common isotropic temperature factor B for benzene-type H atoms was refined to $4.3(7) \text{ \AA}^2$ whereas the B factors for the methyl H atoms were kept fixed at 5.0 \AA^2 . The final $R = 0.068$, with $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.077$; the weighting scheme was $w = 0.17 / [\sigma^2(F_o) + 0.058F_o^2]$. A final difference map showed no peaks $> 0.3 e \text{ \AA}^{-3}$. The average shift/error in the last cycle was 0.21 with a maximum of 0.9 for x of C(18). Final atomic coordinates are given in Table 2.* The atoms are numbered according to chemical convention. The same numbering scheme is used for each of the two molecules in the asymmetric unit, except that the numbers used for (II) are obtained by adding 10 to those for (I). Because of the limited resolution of the data along b the e.s.d.'s of the y coordinates are several times larger than those in x and z , and this is probably one of the reasons for the rather moderate accuracy of the structure determination.

All calculations were carried out on the CDC CYBER 172 computer at RRC Ljubljana with the SHELX 76 system of computer programs (Sheldrick, 1976).

Discussion. The structure determination was undertaken in order to clarify the NMR spectrum. It was detected that the methyl-group H atoms are coupled to those at positions 5 and 7, which happens very rarely (Dewar & Fahey, 1963; Barfield & Chakrabarti, 1969*a,b*). The bond lengths and angles for the two independent molecules (I) and (II) are summarized in Fig. 1 and in Table 3. In general the bond lengths in the two molecules agree well and are within normal ranges. The differences between comparable bond lengths are not statistically significant, although they may indicate slightly different delocalization around C(7). Consideration of the bond lengths on the whole shows that the compound mainly has the resonance structure with partial double bonds for S(1)—C(7a) and S(1)—N(2) and a nearly completely double bond for N(2)—N(3) in the five-membered thiadiazole rings, while there is considerable π -system conjugation in the benzene parts of the molecules. (I) and (II) are essentially planar, and are described by the equations $-0.1221X + 0.9034Y - 0.4109Z = 0.0577 \text{ \AA}$, and $-0.1185X + 0.9030Y - 0.4129Z = 0.0992 \text{ \AA}$, respectively, where $X = ax \sin \beta$, $Y = by$ and $Z = ax \cos \beta + cz$. The largest deviations from least-squares plane (I) are 0.042 and 0.047 \AA for N(3) and Cl(1); and for plane (II) 0.039 and -0.034 \AA

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34768 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

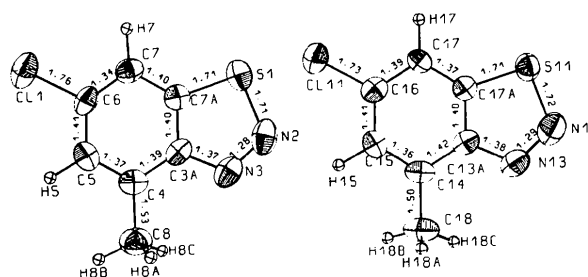


Fig. 1. The molecules of 6-chloro-4-methyl-1,2,3-benzothiadiazole viewed along the normal to the mean plane. The atoms are represented by thermal ellipsoids drawn at the 50% probability level (Johnson, 1965).

Table 3. Bond distances (\AA) and angles ($^\circ$)

Cl(1)—C(6)	1.757 (6)	Cl(11)—C(16)	1.726 (7)
S(1)—N(2)	1.715 (7)	S(11)—N(12)	1.716 (7)
S(1)—C(7a)	1.708 (7)	S(11)—C(17a)	1.710 (7)
N(2)—N(3)	1.284 (9)	N(12)—N(13)	1.291 (10)
N(3)—C(3a)	1.371 (9)	N(13)—C(13a)	1.379 (9)
C(3a)—C(4)	1.389 (9)	C(13a)—C(14)	1.418 (10)
C(4)—C(5)	1.372 (10)	C(14)—C(15)	1.363 (10)
C(5)—C(6)	1.413 (10)	C(15)—C(16)	1.411 (9)
C(6)—C(7)	1.344 (10)	C(16)—C(17)	1.389 (10)
C(7)—C(7a)	1.400 (9)	C(17)—C(17a)	1.372 (9)
C(3a)—C(7a)	1.401 (9)	C(13a)—C(17a)	1.401 (9)
C(4)—C(8)	1.529 (10)	C(14)—C(18)	1.505 (10)
C(7a)—S(1)—N(2)	92.1 (3)	C(17a)—S(11)—N(12)	92.6 (3)
S(1)—N(2)—N(3)	112.1 (5)	S(11)—N(12)—N(13)	111.9 (5)
N(2)—N(3)—C(3a)	114.3 (6)	N(12)—N(13)—C(13a)	114.0 (6)
N(3)—C(3a)—C(4)	125.0 (7)	N(13)—C(13a)—C(14)	124.5 (6)
N(3)—C(3a)—C(7a)	113.7 (6)	N(13)—C(13a)—C(17a)	114.0 (6)
C(4)—C(3a)—C(7a)	121.3 (6)	C(14)—C(13a)—C(17a)	121.5 (6)
C(3a)—C(4)—C(5)	117.8 (7)	C(13a)—C(14)—C(15)	116.1 (6)
C(3a)—C(4)—C(8)	120.8 (7)	C(13a)—C(14)—C(18)	121.4 (7)
C(5)—C(4)—C(8)	121.3 (7)	C(15)—C(14)—C(18)	122.4 (7)
C(4)—C(5)—C(6)	119.0 (7)	C(14)—C(15)—C(16)	121.6 (6)
C(5)—C(6)—C(7)	125.1 (6)	C(15)—C(16)—C(17)	122.5 (6)
C(5)—C(6)—Cl(1)	116.4 (6)	C(15)—C(16)—Cl(1)	118.3 (6)
C(7)—C(6)—Cl(1)	118.5 (6)	C(17)—C(16)—Cl(1)	119.2 (5)
C(6)—C(7)—C(7a)	115.4 (6)	C(16)—C(17)—C(17a)	116.0 (6)
C(7)—C(7a)—S(1)	130.9 (6)	C(17)—C(17a)—S(1)	130.3 (5)
C(7)—C(7a)—C(3a)	121.4 (7)	C(17)—C(17a)—C(13a)	122.2 (6)
S(1)—C(7a)—C(3a)	107.7 (5)	S(11)—C(17a)—C(13a)	107.5 (5)

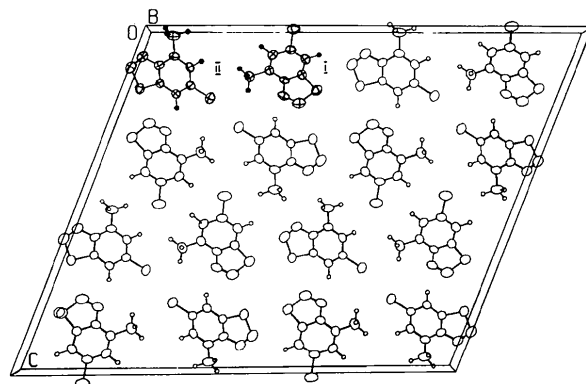


Fig. 2. A view of the unit cell along $[010]$.

for Cl(11) and C(17) respectively. The separate six- and five-membered rings are planar to within 0.015 Å in (I) and to within 0.018 Å in (II). The corresponding dihedral angles between the rings are 1.0 and 1.7° for (I) and (II), and are not significantly different from zero.

A view of the molecular packing along [010] is in Fig. 2. The molecules are packed in layers parallel to the *ac* plane. There are no abnormally short contacts between the molecules.

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Struktur von Phenoxythiophosphoryldihydrazid

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Abstract. C₆H₁₁N₄OPS, triclinic, $P\bar{1}$, $a = 6.349$ (2), $b = 7.457$ (2), $c = 11.339$ (3) Å, $\alpha = 76.99$ (9), $\beta = 77.61$ (9), $\gamma = 79.08$ (9)°, $D_m = 1.42$ (4), $Z = 2$, $D_c = 1.434$ Mg m⁻³. The structure was solved by direct methods and refined to $R = 0.034$. The N atoms in the α positions with respect to the P atom have an almost planar configuration, whereas the β N atoms are pyramidal. The P atom has a distorted tetrahedral environment.

Einleitung. In den von uns aus der Titelverbindung dargestellten konfigurationsisomeren Tetraazadiphosphacyclohexanen besitzen die konstitutionell äquivalenten Ringstickstoffatome zum Teil unterschiedliche sterische Umgebungen im kristallinen Zustand (Engelhardt & Hartl, 1975, 1976). Je zwei im Ring in 1,4-Position gegenüberliegende Stickstoffatome besitzen in beiden Isomeren unabhängig von der unterschiedlichen Ringkonformation eine trigonale ebene Umgebung, die beiden anderen in 2,5-Position dagegen eine abgeflacht pyramidale Anordnung der Substituenten. Bei einem Vergleich mit der Struktur einer in dieser Arbeit untersuchten, analogen offenkettigen Verbindung war interessant, ob und in welchem Mass auch hier unterschiedliche Hybridisierungszustände an den Stickstoffatomen der Hydrazidogruppen zu beobachten sein würden. Darüberhinaus war ein Vergleich der Torsionswinkel

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um die N–N-Bindungen von Interesse, da diese in einer offenkettigen Verbindung nicht wie in den entsprechenden Ringen durch die Ringkonformation weitgehend festgelegt sind. Für viele azyklische Hydrazinderivate wurde als stabilste Konformation diejenige gefunden, bei der die freien Elektronenpaare an den benachbarten Stickstoffatomen ihre Haupttrichtungen in Ebenen einnehmen, die senkrecht aufeinander stehen (man vergleiche z.B.: Nelsen, Hollinsed & Calabrese, 1977, und die dort zitierte Literatur).

Die Verbindung wurde aus Phenoxythiophosphoryldichlorid und Hydrazinhydrat nach bekannten Methoden dargestellt und aus Ethanol umkristallisiert (Smp. 368 K) (Engelhardt & Scherer, 1976). Gitterkonstanten und Kristallsystem wurden aus Drehkristall-, Weissenberg- und Präzessionsaufnahmen ermittelt. Die weiteren röntgenographischen Messungen wurden auf einem DEC PDP 15/40 gesteuerten Stoe-Vierkreisdiffraktometer mit Ni-gelilterter Cu $K\alpha$ -Strahlung ($\lambda = 1.54179$ Å) vorgenommen. Genaue Gitterkonstanten wurden durch Vermessung hochindizierter Achsreflexe bestimmt. In einem Bereich $8,1 < 2\theta < 129,0^\circ$ wurden die integralen Intensitäten von 1707 kristallographisch unabhängigen Reflexen vermessen [θ - 2θ -Abtastung, Abtastbereich $\Delta 2\theta = (1,8 + 0,86 \text{ tg } \theta)^\circ$, Messzeiten zwischen 8 und 30 s pro Grad in Abhängigkeit von der Intensität, Schwächungsfilter bei hohen Intensitäten, Untergrundmessung mit je der