

# The Crystal and Molecular Structure of 2-(3-Diethylaminopropylthio)-4,5-dichloropyrimidin-6-one

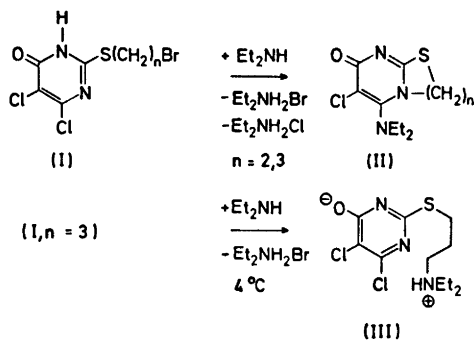
H. J. TALBERG

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystal structure of 2-(3-diethylaminopropylthio)-4,5-dichloropyrimidin-6-one,  $C_{11}H_{17}ON_3SCl_2$ , has been determined from three-dimensional X-ray diffraction data and refined by least-squares methods. The space group is  $P2_1/c$ ,  $a = 9.471 \text{ \AA}$ ,  $b = 17.634 \text{ \AA}$ ,  $c = 9.006 \text{ \AA}$ ,  $\beta = 80.93^\circ$ .

The molecules are forming dimers with hydrogen bonds between the oxygen atom and the aminonitrogen atom. Two nonbonding contacts between atoms in the pyrimidine moiety and atoms in the side chain are rather short ( $N1 \cdots C7$  2.943  $\text{\AA}$ ,  $S2 \cdots C9$  3.205  $\text{\AA}$ ). The C6—O and C2—S bond lengths (1.262  $\text{\AA}$  and 1.764  $\text{\AA}$ , respectively) indicate some double bond character of these bonds.

Berg-Nielsen<sup>1</sup> has shown that 2-(bromoalkylthio)-4,5-dichloropyrimidin-6-ones (I) may cyclize, thus giving compounds (II) which have potential analgetic activity.



At room temperature the 1,3-thiazole, (II,  $n = 2$ ), is more readily formed than the 1,3-thiazine (II,  $n = 3$ ). At  $4^\circ C$  the 1,3-thiazine is not formed at all, and reaction with (I,  $n = 3$ ) gives (III). Studies by Reistad and Undheim<sup>2,3</sup> have shown pyridine[2,1-*b*]-1,3-thiazine derivatives to rearrange to their corresponding thiazole analogs.

These investigations indicate the 1,3-thiazoles to be more stable than their thiazine analogs.

In order to examine the conformation of these thiazine rings, and to shed some light on conformational changes promoted by ring closure, a crystal structure determination of (II,  $n = 3$ ) and (III) was initiated. The structure of (III) is described in this article.

## EXPERIMENTAL

Colourless tabular crystals were obtained by slow evaporation of an acetone solution.

From the systematic absences the space group was determined to  $P2_1/c$ . Unit cell parameters were calculated using measurements of the four equivalents of twelve unique reflections on a manual Picker diffractometer with  $CuK\beta$  radiation ( $\lambda = 1.3922 \text{ \AA}$ ). Three-dimensional data were collected on a punched card controlled four circle Picker diffractometer with  $\omega - 2\theta$  scan technique. The crystal used was approximately  $0.35 \times 0.18 \times 0.07 \text{ mm}^3$ , and was mounted with  $b$  along the  $\phi$  axis. The  $MoK\alpha$  radiation was monochromated with a highly oriented graphite crystal. The  $2\theta$  scan speed was  $2^\circ \text{ min}^{-1}$ . Three test reflections were measured for every 100 reflections and the intensities accordingly adjusted. Estimated standard deviations in the intensities were taken as the square root of the total counts adding 1% to allow for the uncertainty in the adjustments.

2185 unique reflections with  $2\theta$  less than  $50^\circ$  were measured. 1019 of these had intensities larger than  $2\sigma(I)$  and were regarded as observed. The intensity data were corrected for Lorentz, polarization and absorption effects.

Atomic form factors used were those of P. A. Doyle and P. S. Turner<sup>4</sup> for chlorine, sulphur, oxygen, nitrogen, and carbon, and of Stewart *et al.*<sup>5</sup> for hydrogen.

All programs but the *ORTEP* program applied during the structure investigations are described in Ref. 6.

## CRYSTAL DATA

2-(3-Diethylaminopropylthio)-4,5-dichloro-pyrimidin-6-one,  $C_{11}H_{17}ON_3S_2Cl_2$ , monoclinic, space group  $P2_1/c$ .

$a = 9.471(1) \text{ \AA}$ ,  $b = 17.634(4) \text{ \AA}$ ,  $c = 9.006(1) \text{ \AA}$ ,  $\beta = 80.93(1)^\circ$ ,  $V = 1485 \text{ \AA}^3$ ,  $M = 309.27$ ,  $F(000) =$

648,  $\mu = 0.538 \text{ mm}^{-1}$ ,  $Z = 4$ ,  $D_{\text{obs}}$  (flotation) =  $1.37 \text{ g cm}^{-3}$ ,  $D_{\text{calc}} = 1.383 \text{ g cm}^{-3}$ .

## STRUCTURE DETERMINATION

From a sharpened Patterson function the positions of the sulphur and one of the chlorine

Table 1. Observed and calculated structure factors.

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	8	0	0	9.2	6.5	12	0	0	8.1	6.7	16	0	0	10.8	10.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	16	0	0	12.3	9.7	20	0	0	14.8	12.3	24	0	0	16.4	14.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	18	0	0	14.8	11.6	22	0	0	16.4	14.8	26	0	0	18.0	16.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	20	0	0	16.4	13.1	24	0	0	18.0	16.4	28	0	0	19.6	18.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	22	0	0	18.0	14.6	26	0	0	19.6	18.0	28	0	0	21.2	19.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	24	0	0	19.6	16.1	28	0	0	21.2	19.6	30	0	0	22.8	21.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	26	0	0	21.2	17.6	30	0	0	22.8	21.2	32	0	0	24.4	22.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	28	0	0	22.8	19.1	32	0	0	24.4	22.8	34	0	0	26.0	24.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	30	0	0	24.4	20.6	34	0	0	26.0	24.4	36	0	0	27.6	26.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	32	0	0	26.0	22.1	36	0	0	27.6	26.0	38	0	0	29.2	27.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	34	0	0	27.6	23.6	38	0	0	29.2	27.6	40	0	0	30.8	29.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	36	0	0	29.2	25.1	40	0	0	30.8	29.2	42	0	0	32.4	30.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	38	0	0	30.8	26.6	42	0	0	32.4	30.8	44	0	0	34.0	32.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	40	0	0	32.4	28.1	44	0	0	34.0	32.4	46	0	0	35.6	34.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	42	0	0	34.0	29.6	46	0	0	35.6	34.0	48	0	0	37.2	35.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	44	0	0	35.6	31.1	48	0	0	37.2	35.6	50	0	0	38.8	37.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	46	0	0	37.2	32.6	50	0	0	38.8	37.2	52	0	0	40.4	38.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	48	0	0	38.8	34.1	52	0	0	40.4	38.8	54	0	0	42.0	40.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	50	0	0	40.4	35.6	54	0	0	42.0	40.4	56	0	0	43.6	42.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	52	0	0	42.0	37.1	56	0	0	43.6	42.0	58	0	0	45.2	43.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	54	0	0	43.6	38.6	58	0	0	45.2	43.6	60	0	0	46.8	45.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	56	0	0	45.2	40.1	60	0	0	46.8	45.2	62	0	0	48.4	46.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	58	0	0	46.8	41.6	62	0	0	48.4	46.8	64	0	0	50.0	48.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	60	0	0	48.4	43.1	64	0	0	50.0	48.4	66	0	0	51.6	50.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	62	0	0	50.0	44.6	66	0	0	51.6	50.0	68	0	0	53.2	51.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	64	0	0	51.6	46.1	68	0	0	53.2	51.6	70	0	0	54.8	53.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	66	0	0	53.2	47.6	70	0	0	54.8	53.2	72	0	0	56.4	54.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	68	0	0	54.8	49.1	72	0	0	56.4	54.8	74	0	0	58.0	56.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	70	0	0	56.4	50.6	74	0	0	58.0	56.4	76	0	0	59.6	58.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	72	0	0	58.0	52.1	76	0	0	59.6	58.0	78	0	0	61.2	59.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	74	0	0	59.6	53.6	78	0	0	61.2	59.6	80	0	0	62.8	61.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	76	0	0	61.2	55.1	80	0	0	62.8	61.2	82	0	0	64.4	62.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	78	0	0	62.8	56.6	82	0	0	64.4	62.8	84	0	0	66.0	64.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	80	0	0	64.4	58.1	84	0	0	66.0	64.4	86	0	0	67.6	66.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	82	0	0	66.0	59.6	86	0	0	67.6	66.0	88	0	0	69.2	67.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	84	0	0	67.6	61.1	88	0	0	69.2	67.6	90	0	0	70.8	69.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	86	0	0	69.2	62.6	90	0	0	70.8	69.2	92	0	0	72.4	70.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	88	0	0	70.8	64.1	92	0	0	72.4	70.8	94	0	0	74.0	72.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	90	0	0	72.4	65.6	94	0	0	74.0	72.4	96	0	0	75.6	74.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	92	0	0	74.0	67.1	96	0	0	75.6	74.0	98	0	0	77.2	75.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	94	0	0	75.6	68.6	98	0	0	77.2	75.6	100	0	0	78.8	77.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	96	0	0	77.2	70.1	100	0	0	78.8	77.2	102	0	0	80.4	78.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	98	0	0	78.8	71.6	102	0	0	80.4	78.8	104	0	0	82.0	80.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	100	0	0	80.4	73.1	104	0	0	82.0	80.4	106	0	0	83.6	82.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	102	0	0	82.0	74.6	106	0	0	83.6	82.0	108	0	0	85.2	83.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	104	0	0	83.6	76.1	108	0	0	85.2	83.6	110	0	0	86.8	85.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	106	0	0	85.2	77.6	110	0	0	86.8	85.2	112	0	0	88.4	86.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	108	0	0	86.8	79.1	112	0	0	88.4	86.8	114	0	0	90.0	88.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	110	0	0	88.4	80.6	114	0	0	90.0	88.4	116	0	0	91.6	90.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	112	0	0	90.0	82.1	116	0	0	91.6	90.0	118	0	0	93.2	91.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	114	0	0	91.6	83.6	118	0	0	93.2	91.6	120	0	0	94.8	93.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	116	0	0	93.2	85.1	120	0	0	94.8	93.2	122	0	0	96.4	94.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	118	0	0	94.8	86.6	122	0	0	96.4	94.8	124	0	0	98.0	96.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	120	0	0	96.4	88.1	124	0	0	98.0	96.4	126	0	0	99.6	98.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	122	0	0	98.0	89.6	126	0	0	99.6	98.0	128	0	0	101.2	99.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	124	0	0	99.6	91.1	128	0	0	101.2	99.6	130	0	0	102.8	101.2
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	126	0	0	101.2	92.6	130	0	0	102.8	99.6	132	0	0	104.4	102.8
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	128	0	0	102.8	94.1	132	0	0	104.4	101.2	134	0	0	106.0	104.4
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	130	0	0	104.4	95.6	134	0	0	106.0	102.8	136	0	0	107.6	106.0
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	132	0	0	106.0	97.1	136	0	0	107.6	104.4	138	0	0	109.2	107.6
-8	0	0	21.2	17.6	4	0	0	32.4	33.4	134	0	0	107.6	98.6	138	0	0	109.2	106.					



atoms were determined. The corresponding Fourier map revealed the positions of all non hydrogen atoms. Fourier and fullmatrix least squares refinements converged with a conventional  $R$  factor of 0.100 and a weighted  $R_w$  factor ( $R_w = (\sum w\Delta^2 / \sum wF^2)^{1/2}$ ) of 0.062. Least squares refinements using 913 reflections with  $I \geq 2.5\sigma(I)$  yielded an  $R$  of 0.086 and an  $R_w$  of 0.060. There were no significant differences between the two parameter sets. Calculated positional parameters and estimated thermal parameters ( $6-8 \text{ \AA}^2$ ) for hydrogen atoms were included, but not refined, in the last refinements.

Observed and calculated structure factors are given in Table 1. [ $I \geq 2\sigma(I)$ ] and final parameters for non-hydrogen atoms in Table 2. Magnitudes and directions of the principal axes of the vibrational ellipsoids and numbering of atoms are given in Fig. 1. Bond lengths and angles with estimated standard deviations are presented in Table 3. The estimated standard deviations were calculated from the correlation matrix. Short intermolecular contacts and deviations from a least squares plane are given in Table 4. The r.m.s. discrepancy between the atomic vibration tensor components obtained in the structure determination and those calculated from a rigid-body analysis were 0.0087 in the pyrimidine moiety and 0.0227 for the entire molecule. The coordinates were accordingly not adjusted for libration.

## DISCUSSION

Fig. 3. shows the packing of molecules in the crystal, and Fig. 2. shows how molecules related by inversion centres form dimers with hydrogen bonds between the O4 and the N10 atoms.

The hydrogen bond length (2.688 Å) is identical to that ( $\text{NH}^+\cdots\text{O}^-$ ) found in the crystal structure of methoxypromazine malonate.<sup>7</sup> The remaining intermolecular contacts are normal van der Waals contacts.

The conformation in the side chain (with two *gauche* interactions) is probably adapted to the ring system arising when the hydrogen bonds are formed.<sup>8</sup> The contact between S2 and C9 is rather short (3.205 Å), while the N1 $\cdots$ C8 distance (3.755 Å) is somewhat longer than a normal van der Waals contact.

Bond lengths and angles in the side chain are normal. The N10-C bond distances (1.52 Å in average) resemble C-N bond distances found in the  $\text{Et}_3\text{HN}^+$ -groups of isothiazine,<sup>9</sup> procain,<sup>10</sup> and diethazine.<sup>11</sup> The C13-C14 bond length is slightly shorter than the other  $C_{sp^3}-C_{sp^3}$  bond lengths. This is probably a result of high thermal motion in the side chain.

The pyrimidine moiety seems to be nearly planar. The chlorine atoms deviate significantly from this plane, and together with the oxygen atom they form a system similar to that found

Table 3. Bond lengths (Å) and angles (°) with their estimated standard deviations in parenthesis.

N1-C2	1.322(13)	C2-S2	1.764(12)
C2-N3	1.336(13)	S2-C7	1.827(11)
N3-C4	1.334(13)	C7-C8	1.521(15)
C4-C5	1.341(14)	C8-C9	1.516(15)
C5-C6	1.418(15)	C9-N10	1.538(13)
C6-N1	1.388(13)	N10-C11	1.507(13)
C6-O6	1.262(11)	N10-C13	1.537(14)
C5-C15	1.668(13)	C11-C12	1.551(16)
C4-C14	1.743(13)	C13-C14	1.499(16)
N1-C2-N3	127.5(12)	N1-C2-S2	119.1(12)
C2-N3-C4	114.3(12)	N3-C2-S2	113.3(11)
N3-C4-C5	126.5(13)	C2-S2-C7	105.4(7)
C4-C5-C6	115.4(13)	S2-C7-C8	111.9(11)
C5-C6-N1	120.4(11)	C8-C9-N10	112.5(12)
C6-N1-C2	115.9(11)	C7-C8-C9	111.8(12)
N1-C6-O6	118.7(14)	C9-N10-C11	107.2(9)
O6-C6-C5	120.9(14)	C9-N10-C13	116.9(10)
C6-C5-C15	120.6(11)	C11-N10-C13	114.6(10)
C15-C5-C4	124.0(11)	N10-C11-C12	110.8(12)
C5-C4-C14	120.9(12)	N10-C13-C14	112.8(12)
C14-C4-N3	112.6(12)		

Table 4. Deviation (Å) of atoms from a least squares plane through the atoms N1, C2, N3, C4, C5, C6.

N1	-0.002	C7	-0.120
C2	0.008	S2	-0.017
N3	-0.007		
C4	0.004	C14	0.069
C5	0.001	C15	-0.035
C6	-0.001	O6	-0.022
<b>Intramolecular contacts</b>			
N1...C7	2.943	<b>Intermolecular contacts</b>	
S2...C9	3.205	C15...C9(a)	3.487
C8...C13	3.136	C15...C12(b)	3.526
C15...C14	3.170	C15...S2(a)	3.768
C15...O6	2.934	C14...C5(c)	3.592
<b>Hydrogen bond</b>			
O6-N10(d)	2.688	(a) $-1+x,y,z$	
		(b) $-1+x,y,-1+z$	
		(c) $x,\frac{1}{2}-y,-\frac{1}{2}+z$	
		(d) $1-x,-y,1-z$	

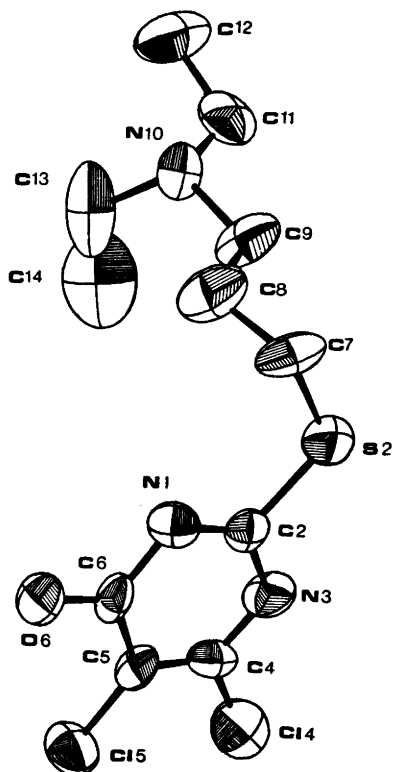
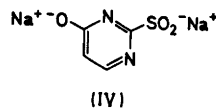


Fig. 1. The molecule viewed along *b*. 50 % probability ellipsoids.

in benzene derivatives possessing molecular overcrowding.<sup>12-14</sup>

It is interesting to compare corresponding bond lengths and angles with those found in disodium 4-oxypyrimidine-2-sulphinal hexahydrate<sup>15</sup> (IV):



Apart from the C-S bonds there is a remarkable similarity between corresponding bond lengths and angles. No significant differences are observed. Thus, the perturbation of the ring system seems to be negligible when chlorine atoms are introduced at position 4 and 5. The observed bond lengths in the pyrimidine moiety are approximately ( $\mp 0.03$  Å) simulated by CNDO/2 calculations<sup>16</sup> and empirical bond length- $\pi$ -bond order relationships.<sup>17</sup> The calculations indicates a  $\pi$ -bond order of 0.73 in the C-O bond. Thus, a zwitterionic state of the molecule seems very probable. The following charge density were found: N1 -0.28; C2 0.26; N3 -0.31; C4 0.31; C5 -0.08; C6 0.25; O6 -0.47; C15 -0.22; C14 -0.26; S2 -0.18.

As to the C2-S2 bond length (1.764 Å) it is very similar to C<sub>sp<sup>3</sup></sub>-S bonds in 1,4-thiazine derivatives.<sup>9,18,19</sup> A calculated  $\pi$ -bond order of 0.20 indicates a barrier against rotation about this bond. This barrier probably forces C7 into the plane through the ring atoms. The N1...C7 contact (2.943 Å), the C2-S and S-C7 bond lengths, the C-S-C angle and the dihedral angle about the C2-S bond are in agreement with those for *S*-methyl-thiourea sulphate<sup>20</sup> (2.99 Å, 1.743(7) Å, 1.790(9) Å, 104.1(4)°, 18°).

The C4-C14 bond length (1.743 Å) is similar to the average value 1.737( $\mp 0.016$ ) Å of 26 C<sub>arom.</sub>-Cl bond lengths reported by Palenik, Donohue and Trueblood(1968).<sup>21</sup> Comparing the C4-C14 bond length with the C4-C14 bond lengths in 6-amino-2,4-dichloropyrimidine<sup>22</sup> [1.76(1) Å] and 2-amino-4,6-dichloropyrimidine<sup>22</sup> [1.77(1) Å] it seems to be somewhat short.

The C5-C15 bond length (1.668 Å) is significantly shorter than both the C4-C14 bond length and the average value.

The observation of two short C-Cl bonds in (III) is not surprising as C-Cl bonds in molecules with chlorine atoms in adjacent positions

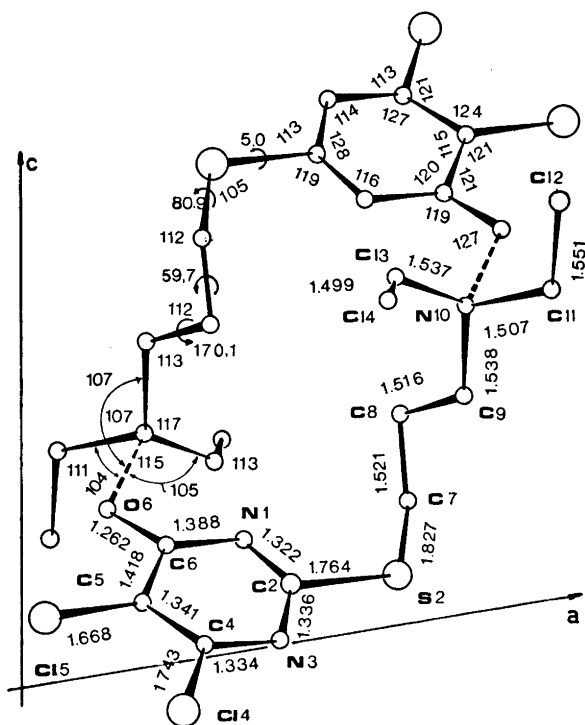


Fig. 2. The dimeric unit. Bond lengths, bond angles, and dihedral angles.

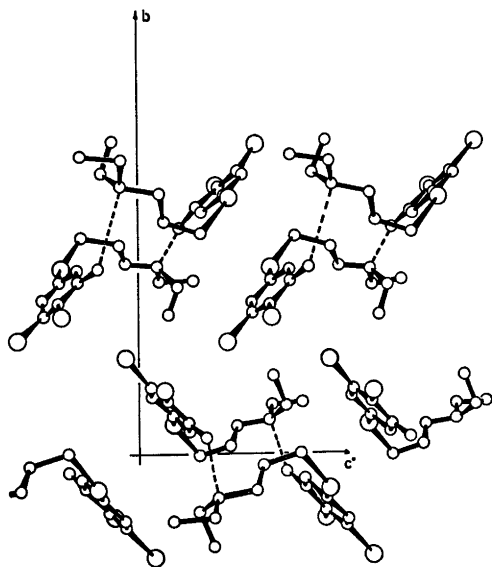


Fig. 3. Packing of molecules. The view is down the *a* axis.

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usually are found to be somewhat short (discussed by Rudman 1971).<sup>12</sup> The difference between the two C–Cl bond lengths may possibly be attributed the overall shape of the pyrimidine ring. Corresponding pyrimidine rings (including IV) have wide internal angles at the C2, C4, and C6 atoms and narrow angles at the N1, N3, and C5 atoms.<sup>22–25</sup> Thus C5–Cl bonds probably get a greater *s*-character than the C4–Cl bonds in pyrimidines.

Morino *et al.* (1967)<sup>26</sup> and Boer and North (1971)<sup>27</sup> attribute the shortening of these C–Cl bonds to an inductive effect from the chlorine atoms lowering the charge densities or increasing the electronegativity (according to Walsh<sup>28</sup> and Dewar<sup>29</sup>) in the adjacent positions.

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