

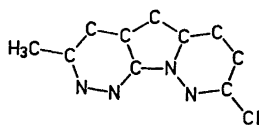
## The Crystal Structure of 8-Chloro-6,7-dihydro-3-methyl-dipyridazino[2,3-a:4,3-d]pyrrole as Determined by the Symbolic Addition Method

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The crystal structure of 8-chloro-6,7-dihydro-3-methyldipyridazino[2,3-a:4,3-d]pyrrole,  $C_{10}H_9N_4Cl$ , was determined using the symbolic addition method. Automatically collected counter data were used but the precision of the determination is low because the crystal was subject to radiation damage. The structure was refined by least squares methods using 1029 reflexions to an  $R$ -value of 13.4 %. The space group is  $P2_1/c$  with  $a = 11.80 \text{ \AA}$ ,  $b = 6.95 \text{ \AA}$ ,  $c = 26.3 \text{ \AA}$ ,  $\beta = 106.4^\circ$ , and eight  $C_{10}H_9N_4Cl$  molecules per unit cell. The two molecules per asymmetric unit appear to be identical. They are nearly planar.

In a paper on quaternisation reactions Lund and Gruhn<sup>1</sup> described a compound  $C_{10}H_9N_4Cl$  to which they ascribed the formula:



The authors kindly supplied us with different preparations of their compound for an X-ray structure determination. One sample was recrystallized from benzene. It gave orthorhombic crystals. Another sample was recrystallized from ethyl alcohol and gave monoclinic crystals. Some of the orthorhombic crystals had a  $c$ -axis of  $6.75 \text{ \AA}$ , others showed a superstructure giving a  $c$ -axis of  $3 \times 6.75 \text{ \AA}$ . The intensities declined rapidly with  $\sin\theta$  and no further work was done on the orthorhombic compound.

A structure determination was carried out on the monoclinic form.

## EXPERIMENTAL

A batch of crystals supplied by Lund and Gruhn was purified by adsorption chromatography on  $Al_2O_3$  using chloroform as eluent. The purified compound was dissolved in ethyl alcohol. Slow evaporation gave prismatic, needle shaped crystals. The needle axis is  $b$ . (Found: C 55.2; H 4.53; N 24.5; Cl 15.5. Calc.: C 54.4; H 4.11; N 25.4; Cl 16.1).

Lattice type and space group extinctions were established from oscillation, Weissenberg, retigraph, and precession photographs. The photographs showed a large amount of diffuse scattering. The high background around many of the Bragg reflexions made it difficult to assess their intensities. An approximately cylindrically shaped crystal of length 1 mm and diameter 0.15 mm was used for collecting intensities on a linear diffractometer of the Arndt-Phillips<sup>2</sup> design. Mo-radiation was used. Balanced filters  $SrO$ ,  $ZrO_2$  in conjunction with a scintillation counter and a pulse-height analyser simulated a practically monochromatic  $MoK\alpha$  beam. The intensities measured were symmetry related in pairs. The crystal was subject to radiation damage. This effect and the high amount of diffuse scattering had an adverse effect on the precision of the data.

The diffractometer data were reduced to relative structure factors using an ALGOL program<sup>3</sup> which evaluated intensities, calculated averages over symmetry related reflexions, Lp-corrections, and standard deviations. 3500 independent reflexions were measured. Only 1031 of these had an intensity greater than twice its standard deviation estimated as the square root of the total number of counts in an intensity measurement.

## STRUCTURE DETERMINATION

Unitary structure factors were calculated using the formula

$$U(hkl) = \varphi \cdot F(hkl)$$

where

$$\varphi^2 = \frac{\sum_{j=1}^N (f_j)^2}{\sum_{j=1}^N f_j^2} \langle F(hkl)^2 \text{ calc} \rangle$$

$\varphi^2$  was evaluated in suitable  $\sin\theta$  intervals (Fig. 1).

Unitary and normalized structure factors were evaluated. The root mean square value of the unitary structure factors is 0.1 and only 2.5 % of the  $U$ -values were greater than 0.4. Harker-Kasper inequalities were therefore not likely to be useful.

Attempts to determine the structure using the  $\Sigma_1$  and  $\Sigma_2$  formulae of Karle and Hauptmann<sup>4</sup> failed. The structure was finally determined using the  $\Sigma_2$  relation with the symbolic addition method of Karle and Karle.<sup>5</sup>

Table 1. Reflexions chosen for initiating sign determination.

$hkl$	$s(hkl)$	$ U(hkl) $
3010	-1	0.60
$\bar{1}25$	-1	0.21
$\bar{5}13$	+1	0.21
$\bar{1}04$	$a$	0.48
1018	$b$	0.60
$\bar{3}08$	$c$	0.30

The initial set of signs and sign symbols are given in Table 1. A program was written by M. S. Lehmann for computer application of the  $\Sigma_2$  formula.

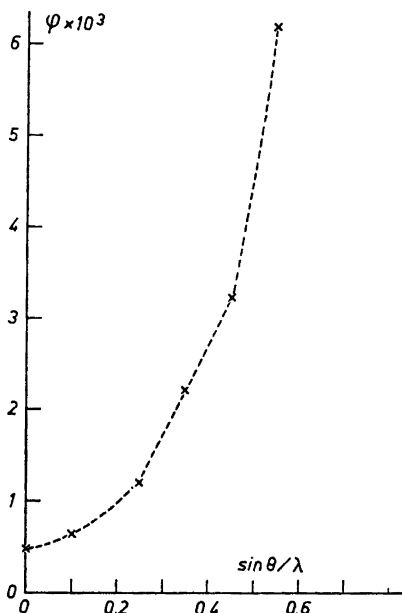


Fig. 1. The coefficient  $\varphi$  as function of  $\sin\theta/\lambda$ .  $\varphi^2$  is defined as

$$\sum_{i=1}^N (f_i / \sum_{j=1}^N f_j)^2 / \langle F(hkl)^2 \text{ calc.} \rangle$$

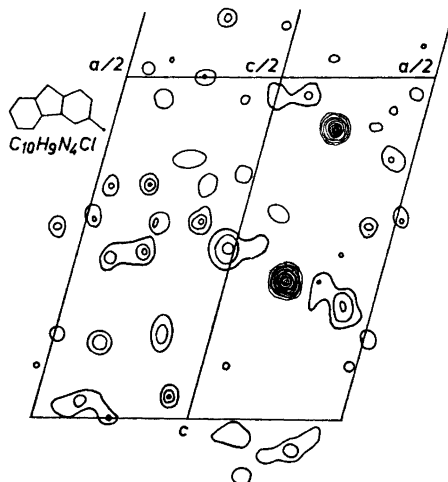


Fig. 2. Bounded projection based upon 320 signs obtained from the symbolic addition method. Electron densities drawn at arbitrary equal intervals.

When 55 signs and sign symbols were established the symbol  $b$  was determined as a negative sign and the rest of the signs were determined as positive or negative or as  $\pm ac$ . Application of further sign determinations with  $ac$  given a negative sign gave 390 sign indications. These signs led to a structure which could not be refined. When  $ac = +$  was tried 320 signs were obtained. A bounded Fourier projection based upon these signs is shown in Fig. 2. The structure determined from this Fourier synthesis was readily refined. The Fourier program used was written by Lauesen.<sup>6</sup>

Table 2.

Index $k$	Number of signs determined	Number of correctly determined signs	
0	114	96	( 84 %)
1	125	120	( 96 %)
2	43	42	( 98 %)
3	32	32	(100 %)
4	6	6	(100 %)
total	320	296	( 92.5 %)

Table 2 shows the agreement between the signs obtained directly with the signs calculated from the refined structure. The Fourier map which was obtained using the 320 signs determined from the direct methods clearly indicated two planar and similar molecules per asymmetric unit. Each molecule showed one atom which was heavier than the rest. These heavier atoms were inserted as chlorine in the structure factor computations and the remaining atoms were inserted as carbon. Structure factors were calculated using Danielsen's D45 program.<sup>7</sup> After two cycles of Fourier and difference Fourier refinement a conventional  $R$ -value of 25.7% was obtained. Refinement continued using a least squares program D28 written by Danielsen.<sup>8</sup> This program employs the diagonal approximation and isotropic temperature factors. Convergence was reached at an  $R$ -value of 21.6%.

According to chemical analysis eight atoms per asymmetric unit must be nitrogen atoms. Seven of the thirty atoms involved in the refinement showed temperature factors between one and two whereas the remaining temperature factors were between three and six. The seven atoms with the lowest temperature factors were inserted as nitrogen atoms in further computations and a new convergence was reached at  $R = 21.4\%$ .

Table 3. Geometric parameters as fractions of cell edges with  $10^4$  times their standard deviations.

Atom	$x$	$\sigma(x)$	$y$	$\sigma(y)$	$z$	$\sigma(z)$
Cl(1a)	0.2201	(5)	0.3514	(12)	0.5803	(2)
N(1a)	0.7608	(16)	0.2258	(42)	0.4974	(7)
N(2a)	0.6397	(16)	0.1972	(51)	0.4800	(9)
C(1a)	0.5881	(18)	0.1594	(40)	0.4306	(9)
C(2a)	0.4514	(18)	0.1234	(58)	0.4159	(9)
C(3a)	0.6541	(19)	0.1196	(45)	0.3926	(8)
C(4a)	0.7705	(21)	0.1387	(65)	0.4075	(8)
C(5a)	0.8696	(22)	0.1337	(56)	0.3864	(9)
C(6a)	0.9722	(18)	0.1934	(39)	0.4255	(7)
C(7a)	0.1024	(18)	0.1798	(47)	0.4287	(8)
C(8a)	0.1733	(19)	0.2970	(53)	0.4711	(9)
C(9a)	0.1239	(19)	0.2856	(59)	0.5182	(8)
N(3a)	0.0200	(15)	0.2507	(33)	0.5211	(6)
N(4a)	0.9426	(14)	0.2161	(36)	0.4720	(6)
C(10a)	0.8189	(19)	0.1905	(64)	0.4616	(7)
Cl(2b)	0.1911	(4)	0.1050	(12)	0.2974	(2)
N(1b)	0.7287	(13)	0.0483	(31)	0.2619	(6)
N(2b)	0.6120	(14)	0.0357	(31)	0.2574	(6)
C(1b)	0.5296	(17)	0.0485	(56)	0.2093	(8)
C(2b)	0.3991	(10)	0.0178	(42)	0.2094	(8)
C(3b)	0.5547	(18)	0.0895	(52)	0.1603	(9)
C(4b)	0.6760	(16)	0.1118	(50)	0.1655	(7)
C(5b)	0.7477	(17)	0.1557	(46)	0.1299	(7)
C(6b)	0.8657	(17)	0.1431	(45)	0.1621	(7)
C(7b)	0.9806	(18)	0.2150	(49)	0.1487	(8)
C(8b)	0.0830	(17)	0.1077	(45)	0.1891	(8)
C(9b)	0.0652	(17)	0.1299	(40)	0.2426	(8)
N(3b)	0.9690	(14)	0.1178	(33)	0.2577	(6)
N(4b)	0.8706	(14)	0.1133	(45)	0.2125	(6)
C(10b)	0.7554	(17)	0.0765	(46)	0.2186	(8)

The computations mentioned so far were carried out on a GIER computer at Aarhus University. Further refinement was carried out on an IBM 7090 computer at NEUCC in Lundtofte. A "full matrix" least squares program written by Gantzel, Sparks, Long and Trueblood<sup>9</sup> was used. Anisotropic temperature factors were used. With 30 atoms in the asymmetric unit it gives 271 parameters. As the program can refine at most 171 parameters those of one molecule were kept constant while those of the other molecule were refined. After four cycles of refinement an *R*-value of 14.5 % was obtained. By examining a Fourier and a difference-Fourier synthesis calculated as bounded projections, the eighth nitrogen atom was located.

After inserting this atom as nitrogen instead of as carbon additional refinement gave an *R*-value of 13.7 %. The reflexion (104) was apparently subject to extinction and (100) was also observed too small. In this case the low setting accuracy close to the axis of the diffractometer might also be the cause of the discrepancy. Both reflexions were left out in the last refinements.

In the least squares computations the weights used were:  $W = 1/\sigma F^2$  where  $\sigma F^2$  was estimated from the counting statistics. The expression  $\sum W \Delta^2/n$  varied but little with the size of *F*.  $\Delta$  is the difference between observed and calculated structure factors and *n* is the number of reflexions in a group of

Table 4. Anisotropic temperature factor parameters in Å<sup>2</sup> × 10<sup>3</sup> with standard deviations.

Atom	<i>U</i> <sub>11</sub>	$\sigma(U_{11})$	<i>U</i> <sub>22</sub>	$\sigma(U_{22})$	<i>U</i> <sub>33</sub>	$\sigma(U_{33})$	<i>U</i> <sub>12</sub>	$\sigma(U_{12})$	<i>U</i> <sub>13</sub>	$\sigma(U_{13})$	<i>U</i> <sub>23</sub>	$\sigma(U_{23})$
Cl(1a)	48	( 3)	76	( 7)	45	( 3)	5	( 4)	- 2	( 3)	- 4	( 5)
N(1a)	53	(12)	128	(26)	37	(10)	9	(16)	3	( 9)	2	(17)
N(2a)	39	(11)	192	(39)	78	(15)	- 3	(18)	- 8	(11)	- 6	(22)
C(1a)	46	(13)	28	(24)	61	(15)	- 4	(15)	- 3	(12)	27	(18)
C(2a)	34	(13)	179	(41)	71	(16)	-34	(21)	- 1	(12)	13	(26)
C(3a)	49	(13)	76	(26)	39	(12)	-33	(18)	-10	(10)	-10	(19)
C(4a)	59	(17)	223	(49)	23	(11)	23	(27)	- 3	(11)	12	(24)
C(5a)	72	(17)	143	(42)	48	(14)	-61	(24)	0	(13)	-36	(23)
C(6a)	55	(13)	52	(24)	27	(10)	32	(15)	19	( 9)	- 1	(15)
C(7a)	47	(13)	109	(33)	43	(12)	-14	(18)	23	(10)	- 6	(20)
C(8a)	47	(14)	150	(39)	55	(14)	-40	(20)	32	(12)	-32	(22)
C(9a)	36	(12)	198	(44)	35	(13)	-12	(22)	- 9	(10)	20	(22)
N(3a)	62	(12)	20	(17)	30	( 9)	13	(12)	4	( 8)	4	(11)
N(4a)	36	(10)	101	(24)	22	( 9)	4	(13)	2	( 7)	-12	(14)
C(10a)	50	(13)	252	(50)	9	( 9)	-36	(25)	4	( 9)	0	(22)
Cl(2b)	27	( 2)	100	( 7)	55	( 3)	9	( 4)	4	( 2)	8	( 5)
N(1b)	25	( 9)	56	(19)	34	( 9)	11	(11)	6	( 7)	- 3	(13)
N(2b)	40	( 9)	50	(20)	41	(10)	-13	(11)	11	( 8)	7	(12)
C(1b)	25	(10)	185	(43)	38	(12)	-10	(19)	0	( 9)	-25	(22)
C(2b)	39	(11)	70	(26)	42	(12)	- 2	(15)	30	(10)	0	(16)
C(3b)	37	(12)	123	(32)	63	(15)	- 1	(18)	31	(11)	- 5	(22)
C(4b)	35	(11)	138	(34)	22	( 9)	-38	(19)	11	( 9)	-25	(19)
C(5b)	44	(11)	98	(29)	22	(10)	13	(17)	10	( 9)	- 5	(17)
C(6b)	41	(11)	88	(27)	25	(10)	13	(16)	15	( 9)	-32	(18)
C(7b)	37	(12)	115	(32)	49	(13)	18	(17)	17	(10)	6	(18)
C(8b)	40	(12)	81	(26)	43	(12)	0	(17)	17	(10)	-12	(18)
C(9b)	31	(11)	45	(25)	48	(13)	-11	(15)	- 8	( 9)	15	(17)
N(3b)	35	(10)	49	(18)	41	(10)	14	(12)	2	( 8)	3	(13)
N(4b)	38	(10)	181	(31)	29	( 9)	33	(17)	10	( 8)	23	(17)
C(10b)	36	(12)	97	(28)	27	(11)	11	(15)	- 8	( 9)	41	(17)

Table 5. Interatomic distances,  $l$ , in Å and angles,  $v$ , in degrees with standard deviations.

Atoms	First molecule		Second molecule	
	$l$	$\sigma(l)$	$l$	$\sigma(l)$
N(1) —N(2)	1.38	(3)	1.35	(2)
N(2) —C(1)	1.30	(3)	1.36	(2)
C(1) —C(2)	1.57	(3)	1.55	(3)
C(1) —C(3)	1.45	(4)	1.43	(4)
C(3) —C(4)	1.32	(3)	1.40	(3)
C(4) —C(10)	1.42	(3)	1.47	(3)
C(4) —C(5)	1.42	(4)	1.45	(3)
C(5) —C(6)	1.41	(3)	1.41	(3)
C(6) —N(4)	1.37	(3)	1.32	(3)
C(6) —C(7)	1.51	(3)	1.57	(3)
C(7) —C(8)	1.44	(4)	1.55	(3)
C(8) —C(9)	1.51	(4)	1.48	(3)
C(9) —Cl	1.76	(2)	1.76	(2)
C(9) —N(3)	1.27	(3)	1.30	(3)
N(3) —N(4)	1.37	(2)	1.41	(2)
N(4) —C(10)	1.41	(3)	1.43	(3)
C(10) —N(1)	1.33	(3)	1.27	(3)

## Angles

Atoms	First molecule		Second molecule	
	$v$	$\sigma(v)$	$v$	$\sigma(v)$
N(1) —N(2) —C(1)	121	(2)	122	(2)
N(2) —C(1) —C(2)	116	(2)	116	(2)
N(2) —C(1) —C(3)	122	(2)	125	(2)
C(2) —C(1) —C(3)	121	(2)	119	(2)
C(1) —C(3) —C(4)	119	(2)	113	(2)
C(3) —C(4) —C(10)	115	(2)	116	(2)
C(3) —C(4) —C(5)	141	(2)	136	(2)
C(10) —C(4) —C(5)	105	(2)	108	(2)
C(4) —C(5) —C(6)	110	(2)	105	(2)
C(5) —C(6) —N(4)	108	(2)	112	(2)
C(5) —C(6) —C(7)	132	(2)	128	(2)
N(4) —C(5) —C(7)	118	(2)	118	(2)
C(5) —C(7) —C(8)	112	(2)	104	(2)
C(7) —C(8) —C(9)	109	(2)	108	(2)
C(8) —C(9) —Cl	117	(2)	117	(2)
C(8) —C(9) —N(3)	131	(2)	130	(2)
Cl —C(9) —N(3)	112	(2)	110	(2)
C(9) —N(3) —N(4)	112	(2)	109	(2)
N(3) —N(4) —C(6)	126	(2)	129	(2)
N(3) —N(4) —C(10)	125	(2)	120	(2)
C(6) —N(4) —C(10)	108	(2)	111	(2)
N(4) —C(10) —C(4)	109	(2)	104	(2)
N(4) —C(10) —N(1)	123	(2)	127	(2)
C(4) —C(10) —N(1)	128	(2)	128	(2)
C(10) —N(1) —N(2)	115	(2)	115	(2)

Table 6. 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>
1	0	22	272	-273	-7	1	12	468	-495
1	0	20	249	-241	-7	1	13	450	-277
1	0	20	207	-149	-7	1	16	286	223
1	0	20	255	98	-7	1	19	195	102
1	0	20	360	-909	-6	1	1	393	304
1	0	20	306	-400	-6	1	4	247	-335
1	0	20	707	692	-6	1	4	264	-240
1	0	20	356	362	-6	1	5	339	-330
1	0	20	396	-400	-6	1	6	100	155
1	0	20	276	-243	-6	1	7	425	427
1	0	20	181	-402	-6	1	8	512	1474
1	0	20	230	197	-6	1	9	600	-540
1	0	20	276	-243	-6	1	10	363	355
1	0	20	175	222	-6	1	11	108	222
1	0	20	130	-245	-6	1	12	226	-152
1	0	20	246	-406	-6	1	13	210	-627
1	0	20	76	406	-6	1	14	182	116
1	0	20	768	606	-5	1	2	101	-151
1	0	20	898	-496	-5	1	2	95	71
1	0	20	572	-359	-5	1	3	100	622
1	0	20	1485	-1437	-5	1	4	624	-603
1	0	20	147	-130	-5	1	5	301	-999
1	0	20	137	-233	-5	1	6	324	104
1	0	20	237	-155	-5	1	7	160	151
1	0	20	237	-155	-5	1	8	211	-67
1	0	20	237	-155	-5	1	9	153	-173
1	0	20	237	-155	-5	1	10	274	407
1	0	20	237	-155	-5	1	11	211	-67
1	0	20	237	-155	-5	1	12	185	-146
1	0	20	237	-155	-5	1	13	222	-626
1	0	20	237	-155	-5	1	14	258	205
1	0	20	237	-155	-5	1	15	263	253
1	0	20	237	-155	-5	1	16	167	-155
1	0	20	237	-155	-5	1	17	185	208
1	0	20	237	-155	-5	1	18	205	208
1	0	20	237	-155	-5	1	19	216	-270
1	0	20	237	-155	-5	1	20	216	-270
1	0	20	237	-155	-5	1	21	216	-270
1	0	20	237	-155	-5	1	22	216	-270
1	0	20	237	-155	-5	1	23	216	-270
1	0	20	237	-155	-5	1	24	216	-270
1	0	20	237	-155	-5	1	25	216	-270
1	0	20	237	-155	-5	1	26	216	-270
1	0	20	237	-155	-5	1	27	216	-270
1	0	20	237	-155	-5	1	28	216	-270
1	0	20	237	-155	-5	1	29	216	-270
1	0	20	237	-155	-5	1	30	216	-270
1	0	20	237	-155	-5	1	31	216	-270
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1	0	20	237	-155	-5	1	33	216	-270
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1	0	20	237	-155	-5	1	35	216	-270
1	0	20	237	-155	-5	1	36	216	-270
1	0	20	237	-155	-5	1	37	216	-270
1	0	20	237	-155	-5	1	38	216	-270
1	0	20	237	-155	-5	1	39	216	-270
1	0	20	237	-155	-5	1	40	216	-270
1	0	20	237	-155	-5	1	41	216	-270
1	0	20	237	-155	-5	1	42	216	-270
1	0	20	237	-155	-5	1	43	216	-270
1	0	20	237	-155	-5	1	44	216	-270
1	0	20	237	-155	-5	1	45	216	-270
1	0	20	237	-155	-5	1	46	216	-270
1	0	20	237	-155	-5	1	47	216	-270
1	0	20	237	-155	-5	1	48	216	-270
1	0	20	237	-155	-5	1	49	216	-270
1	0	20	237	-155	-5	1	50	216	-270
1	0	20	237	-155	-5	1	51	216	-270
1	0	20	237	-155	-5	1	52	216	-270
1	0	20	237	-155	-5	1	53	216	-270
1	0	20	237	-155	-5	1	54	216	-270
1	0	20	237	-155	-5	1	55	216	-270
1	0	20	237	-155	-5	1	56	216	-270
1	0	20	237	-155	-5	1	57	216	-270
1	0	20	237	-155	-5	1	58	216	-270
1	0	20	237	-155	-5	1	59	216	-270
1	0	20	237	-155	-5	1	60	216	-270
1	0	20	237	-155	-5	1	61	216	-270
1	0	20	237	-155	-5	1	62	216	-270
1	0	20	237	-155	-5	1	63	216	-270
1	0	20	237	-155	-5	1	64	216	-270
1	0	20	237	-155	-5	1	65	216	-270
1	0	20	237	-155	-5	1	66	216	-270
1	0	20	237	-155	-5	1	67	216	-270
1	0	20	237	-155	-5	1	68	216	-270
1	0	20	237	-155	-5	1	69	216	-270
1	0	20	237	-155	-5	1	70	216	-270
1	0	20	237	-155	-5	1	71	216	-270
1	0	20	237	-155	-5	1	72	216	-270
1	0	20	237	-155	-5	1	73	216	-270
1	0	20	237	-155	-5	1	74	216	-270
1	0	20	237	-155	-5	1	75	216	-270
1	0	20	237	-155	-5	1	76	216	-270
1	0	20	237	-155	-5	1	77	216	-270
1	0	20	237	-155	-5	1	78	216	-270
1	0	20	237	-155	-5	1	79	216	-270
1	0	20	237	-155	-5	1	80	216	-270
1	0	20	237	-155	-5	1	81	216	-270
1	0	20	237	-155	-5	1	82	216	-270
1	0	20	237	-155	-5	1	83	216	-270
1	0	20	237	-155	-5	1	84	216	-270
1	0	20	237	-155	-5	1	85	216	-270
1	0	20	237	-155	-5	1	86	216	-270
1	0	20	237	-155	-5	1	87	216	-270
1	0	20	237	-155	-5	1	88	216	-270
1	0	20	237	-155	-5	1	89	216	-270
1	0	20	237	-155	-5	1	90	216	-270
1	0	20	237	-155	-5	1	91	216	-270
1	0	20	237	-155	-5	1	92	216	-270
1	0	20	237	-155	-5	1	93	216	-270
1	0	20	237	-155	-5	1	94	216	-270
1	0	20	237	-155	-5	1	95	216	-270
1	0	20	237	-155	-5	1	96	216	-270
1	0	20	237	-155	-5	1	97	216	-270
1	0	20	237	-155	-5	1	98	216	-270
1	0	20	237	-155	-5	1	99	216	-270
1	0	20	237	-155	-5	1	100	216	-270

structure factors in a given range. The weight analysis was computed using a structure factor and least squares program written by R. Grønbaek Hazell.<sup>10</sup>

A final refinement and a computation of bond distances *etc.* was carried out using the programs ORFLS<sup>11</sup> and ORFFE<sup>12</sup> written by Busing, Martin and Levy. The final *R*-value was 13.37 % using 1029 reflexions.

The bond distances were also computed on GIER using a program written by Nyborg and Danielsen.<sup>13</sup> This program computes standard deviations of bond lengths using only a diagonal approximation whereas ORFFE uses the full variance-covariance expression. The two sets of standard deviations are hardly different.

#### CRYSTAL DATA

Crystal system: monoclinic,  $a = 11.80 \text{ \AA}$ ,  $b = 6.95 \text{ \AA}$ ,  $c = 26.3 \text{ \AA}$ ,  $\beta = 106.4^\circ$ , space group  $P2_1/c$  (No. 14). Density measured:  $1.46_4 \text{ g/cm}^3$ , calc.  $1.44 \text{ g/cm}^3$ . 8.16  $\text{C}_{10}\text{H}_9\text{N}_4\text{Cl}$  units per unit cell.

The coordinates and their estimated standard deviations are given in Table 3. Thermal parameters are given in Table 4 and interatomic distances in Table 5. Table 6 gives observed and calculated structure factors. The atomic scattering factors used were taken from *International Tables*, Vol. III.

#### DISCUSSION

From our point of view the main result of this paper is the demonstration that the symbolic addition method was successful in dealing with a structure containing 120 atoms per unit cell even using rather inaccurately measured structure amplitudes. We have looked at the Patterson function of the structure afterwards and found that the Harker sections were obscured by non-Harker peaks to such an extent that it would have been difficult to locate even the chlorine atoms by the usual Patterson approach. The occurrence of two identical molecules per asymmetric unit in an almost parallel arrangement also contributes to making the Patterson approach a difficult one. We believe that we could not have determined the structure from the Patterson function within a reasonable time.

The occurrence of two crystallographically independent molecules per asymmetric unit raises the question: are these molecules identical? A complete statistical analysis of this problem represents a large mathematical problem. We have therefore made the following very simple and not exact analysis: We consider two corresponding bond lengths  $x_1$  and  $x_2$  to differ significantly only if

$$|x_1 - x_2| \geq 1.96 \sigma (x_1 - x_2)$$

A Gaussian error distribution is assumed since the bond lengths are determined from over a 1000 reflexions. Only for C(7)–C(8) is  $|x_1 - x_2| > 1.96\sigma$  ( $2.2\sigma$ ). At this 5 % significance level one might expect one out of seventeen tests to fail.

A multiple comparison test may be based upon the following considerations:



The differences between two corresponding bond lengths  $x_1 - x_2 = \Delta_i$  are supposed to belong to a set of mean values with the common value zero.

We can form a multitude of contrasts based upon the  $\Delta_i$ 's, e.g. the sum  $\theta_m = \sum_{i=1}^{17} a_i \Delta_i$  equals 0.69 Å with  $|a_i| = 1$  and  $\sum a_i = 0$ . Using the standard deviations obtained from the least squares computations the estimated standard deviation of  $\theta_m$  is found as 0.16 Å. We assume that the individual  $\Delta_i$  is based upon a practically infinite number of degrees of freedom and we obtain the 95 % confidence interval for this contrast:

$$\theta_m - S\sigma_{\theta_m} \leq \theta_m \leq \theta_m + S\sigma_{\theta_m}$$

where  $S^2 = \chi_{16,\alpha}^2$  as  $0.69 - 0.80 \leq \theta_m \leq 0.69 + 0.80$ . Any other contrast will also fall within a confidence interval including zero.

We cannot therefore reject the hypothesis that all the bond lengths are equal on the 5 % significance level.

Table 7. Distances  $\delta$  of atoms from least squares planes with standard deviations. The numbers are  $10^2 \times \text{Å}$ .

Atom	First molecule		Second molecule	
	$\delta$	$\sigma(\delta)$	$\delta$	$\sigma(\delta)$
N(1)	1	3	0	2
N(2)	-1	3	-4	2
C(1)	7	3	2	4
C(3)	-2	3	2	3
C(4)	-5	4	-1	3
C(5)	-2	4	-4	3
C(6)	9	3	3	3
N(4)	-2	2	-2	3
C(10)	-5	4	6	3
Cl	7	1	0	1
C(2)	0	4	7	3
C(7)	-10	3	-25	3
C(8)	38	4	40	3
C(9)	6	4	-5	3
N(3)	-13	2	-16	2

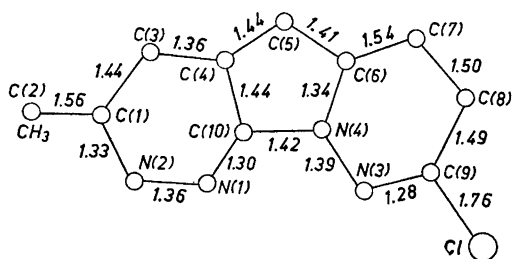


Fig. 3. Projection of molecule giving distances averaged over two independent molecules.

This does not prove that our hypothesis about the equality of the two molecules is correct. Alternative hypotheses are also consistent with this result. The two molecules might be isomers, *e.g.* conformational ones. A multiple comparison test based upon the valency angles is, however, also consistent with the hypothesis that the molecules are equal.

Least squares planes were calculated for the two molecules. The result is shown in Table 7. It is seen that the planarity and deviations from planarity correspond closely for the two molecules.

The combined evidence makes it likely that the two independent molecules are equivalent and a molecule with mean distances is depicted in Fig. 3.

We have confirmed the formula given by Lund and Gruhn. The bond lengths and the planarity indicate that the six-membered ring carrying the methyl group and the five-membered ring are of aromatic character. The bonds from C(7) and C(8) are single bonds. Application of usual valence rules leads to the following assignments of hydrogen atoms: C(2): three H (methyl group), C(3) one H, C(5) one H, C(7) two H, C(8) two H. This corresponds to the assignments made by Lund and Gruhn from chemical considerations and from NMR spectra. Because of the inaccuracy of the X-ray data it was not possible to confirm the location of the hydrogen atoms from Fourier difference maps.

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