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The Crystal Structure of Azo-*bis*-N-Chloroformamidine

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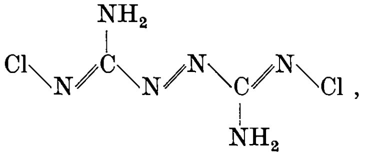
Crystals of azo-*bis*-N-chloroformamidine are monoclinic prismatic, the space group being $P2_1/c$. The unit-cell dimensions are

$$a_0 = 3\cdot70,\quad b_0 = 10\cdot43,\quad c_0 = 9\cdot01\ \text{Å},\quad \beta = 97°\ 50'\ .$$

There are two centrosymmetric molecules per unit cell (calculated density = 1·764 g.cm.$^{-3}$). The crystal structure was determined by generalized Fourier projections, using the $1kl$ data. The molecule is planar to within the accuracy of the atomic coordinates. The Cl–N bond length is 1·73 Å, and the azo N–N bond length is 1·26 Å.

Introduction

Azo-*bis*-N-chloroformamidine,



or azochloramide, was first prepared by the chlorination of azo-*bis*-formamidine with sodium hypochlorite solution (Schmelkes & Marks, 1934). It is very stable when compared with other organic N-chloro compounds. The structures of two other N-chloro compounds, dimethyl chloramine and methyl dichloramine, have been determined by electron diffraction (Stevenson & Schomaker, 1940). Preliminary results for the crystal structure of N-chlorosuccinimide have been reported by Brown (1956), but bond lengths were not given. Thus very little direct structural information is presently available for N-chloro compounds. The crystal structure of azochloramide has been investigated to obtain the lengths of the N–Cl and the azo N–N bonds.

Experimental

The material used was a commercial sample obtained from Wallace and Tiernan Products, Inc. Crystals of azochloramide were grown from absolute alcohol by evaporation at room temperature. They appeared as needles, short prisms and diamond-shaped plates. These different habits were found to be stages of development of the needles, the plates forming prisms and then needles by growth along the axis perpendicular to the plate faces.

X-ray photographs taken about the needle axis showed that the crystals are monoclinic, the space group being $P2_1/c$ ($h0l$ present only with $l = 2n$ and $0k0$ present only with $k = 2n$). The needle axis is the crystallographic a axis. Unit-cell dimensions, obtained from rotation and zero-layer Weissenberg photographs taken about the a and b axes, are

$$a_0 = 3\cdot70\pm0\cdot02,\quad b_0 = 10\cdot43\pm0\cdot05,\quad c_0 = 9\cdot01\pm0\cdot05\ \text{Å}\ ,$$
$$\beta = 97°\ 50'\pm20'\ \ (\lambda \text{ of } \mathrm{Cu}K\alpha = 1\cdot5418\ \text{Å})\ .$$

The calculated density increment per chemical molecule is 0·882 g.cm.$^{-3}$. As the expected density is in the range 1·5–2·0 g.cm.$^{-3}$, there are two chemical molecules per unit cell (calculated density = 1·764 g.cm.$^{-3}$). These molecules must be situated on inversion centers and hence will be in the *trans* configuration.

The intensity data required for the structure determination were measured visually from multiple-film equi-inclination Weissenberg photographs of the $0kl$ and $1kl$ reflections. There were 111 reflections of the $0kl$ type and 214 reflections of the $1kl$ type observed.

Determination of the structure

Determination of the projected structure from the 0*kl data*

The chlorine atom was easily located from an unmodified Patterson projection on (100). An electron-density projection calculated with 53 terms whose phases were determined with some certainty by the chlorine contribution showed an arrangement of peaks which made a reasonable trial structure of the molecule. This arrangement refined rapidly by Fourier methods, the final projection being shown in Fig. 1. The final parameters, corrected for series-termination errors by the method of Booth (1946), are listed in Table 1. The peak heights and curvatures were calculated by a nine-point least-squares Gaussian method. Standard deviations of the y and z coordinates of the atoms were calculated by the method of Cruickshank (1949). These calculations are summarized in Table 1. The observed and calculated structure amplitudes for the $0kl$ reflections are listed in Table 4. The percentage

Table 1. *Results based on 0kl data only*

Atom	y	z	ϱ_0 (e.Å^{-2})	σ (y) (Å)	σ (z) (Å)	$\left\lvert\frac{\partial^2\varrho}{\partial y^2}\right\rvert$ (e.Å^{-4})	$\left\lvert\frac{\partial^2\varrho}{\partial z^2}\right\rvert$ (e.Å^{-4})
Cl	0·1358	0·1377	26·07	0·0018	0·0028	307·2	261·6
N_1	0·4541	−0·0288	9·69	0·006	0·009	94·9	83·7
N_2	0·2608	0·0153	10·03	0·005	0·007	106·5	98·4
N_3	0·3763	0·2224	8·97	0·007	0·010	82·4	73·3
C	0·3551	0·0828	7·87	0·007	0·010	85·8	76·7

$\sigma(A_k) = 0{\cdot}564$ e.Å^{-3}, $\sigma(A_l) = 0{\cdot}734$ e.Å^{-3}, $\sigma(\varrho) = 0{\cdot}263$ e.Å^{-2}.

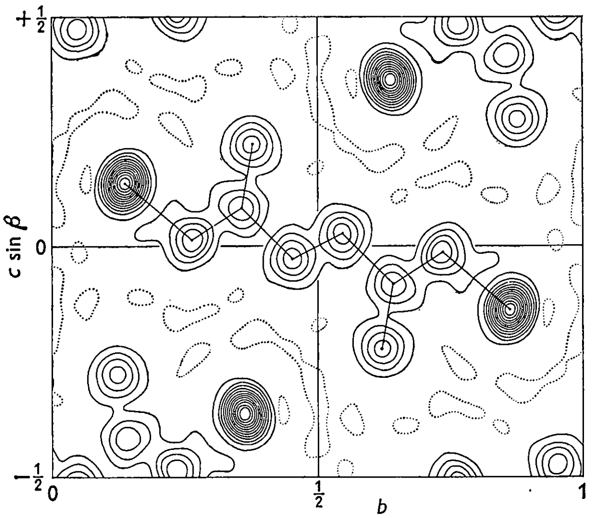


Fig. 1. Projection of azo-*bis*-N-chloroformamidine on (100), calculated from the 0*kl* data. The contour interval is 2 e.Å^{-2}, the zero contour being dotted.

discrepancy for these data is 14·2. The scattering factors of Hoerni & Ibers (1954) were used for the carbon and nitrogen atoms while those given in the *Internationale Tabellen*, vol. 2 (1935), were used for chlorine. An isotropic temperature correction, $\exp[-B(\sin\theta/\lambda)^2]$ with $B = 3{\cdot}073$ Å^2, was used in calculating the final 0*kl* structure amplitudes.

Determination of the complete structure from the 1*kl data*

Electron-density projections along the *b* and *c* axes would give poor values of the *x* parameters of the light atoms because of extensive overlapping. The use of generalized projections (Cochran & Dyer, 1952), however, permits the determination of all atomic coordinates by the use of upper-layer-line data about an axis along which all atoms of a molecule are completely resolved on projection. The method was applied as described by Fridrichsons & Mathieson (1955). The equations for the component projections in the space group $P2_1/c$ are given by White & Clews (1956). Approximate values of the *x* parameters were obtained by trial-and-error calculations, using the 1*k*0 reflections. All parameters were then further refined by making three sets of calculations of the component projections, the final set including F_c as well as F_o projections in order to make backshift corrections. The final component projections are shown in Fig. 2. The final parameters are listed in Table 2. The standard deviations of the *x* parameters were calculated from the standard deviation of the electron density by the

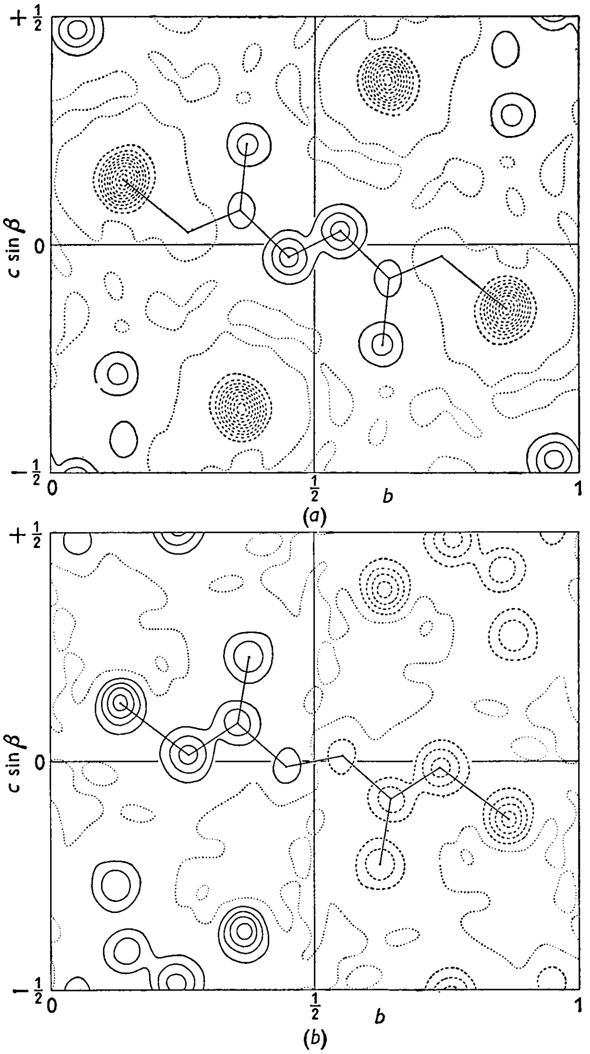


Fig. 2. Component projections of azo-*bis*-N-chloroformamidine on (100), calculated from the 1*kl* data: (*a*) the cosine function, (*b*) the sine function. The positive contours are solid lines, the negative contours are broken lines, and the zero contour is dotted. The contour interval is 2 e.Å^{-2}. The maxima and minima on the projections are indicated rather than the final positions of the atoms.

Table 2. *Final results, based on all data*

Atom	x	y	z	ϱ_0 (e.Å^{-2})	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	$\left\lvert\frac{\partial^2\varrho}{\partial y^2}\right\rvert$ (e.Å^{-4})	$\left\lvert\frac{\partial^2\varrho}{\partial z^2}\right\rvert$ (e.Å^{-4})
Cl	0·429	0·1358	0·1376	20·94	0·0103	0·0038	0·0055	228·5	189·9
N_1	0·069	0·4517	−0·0270	7·67	0·028	0·011	0·015	76·9	68·8
N_2	0·289	0·2590	0·0150	7·44	0·029	0·013	0·016	68·5	66·0
N_3	0·139	0·3738	0·2229	7·58	0·028	0·012	0·017	71·9	62·5
C	0·172	0·3549	0·0822	6·33	0·034	0·013	0·017	69·5	60·2

$\sigma(A_k) = 0{\cdot}876$ e.Å^{-3}, $\sigma(A_l) = 1{\cdot}053$ e.Å^{-3}, $\sigma(\varrho) = 0{\cdot}369$ e.Å^{-2}.

equation given previously (Bryden, 1958). These calculations are summarized in Table 2. The observed and calculated structure amplitudes for the $1kl$ reflections are listed in Table 4. The percentage discrepancy for the $1kl$ data is 15·9. An isotropic temperature correction with $B = 3{\cdot}779$ Å^2 was used in calculating the final $1kl$ structure amplitudes. The use of an isotropic correction in this structure is a rather poor approximation, as shown by the considerable ellipticity of the chlorine peak (see Tables 1 and 2). However, for the purposes of this structure analysis it was considered adequate. The anisotropy of the chlorine atom is undoubtedly the cause of the difference between the values of the constant, B, in the temperature corrections for the $0kl$ and $1kl$ data.

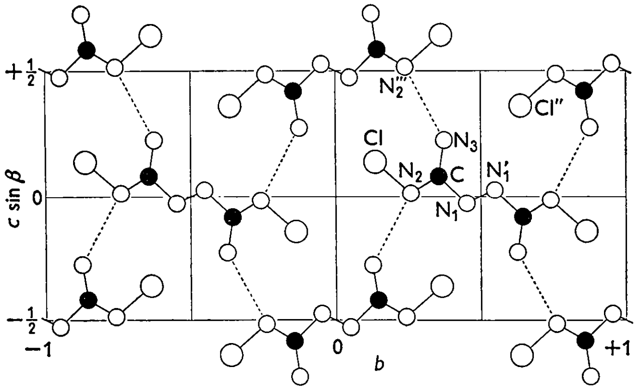


Fig. 3. Schematic drawing of the crystal structure of azo-*bis*-N-chloroformamidine, showing the numbering of the atoms. The broken lines are hydrogen bonds.

Discussion

Dimensions of the molecule

The parameters of Table 2 were transformed from oblique monoclinic coordinates to orthogonal coordinates by the equations

$$X' = X + Z \cos \beta \quad \text{and} \quad Z' = Z \sin \beta\,.$$

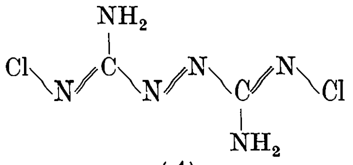
(The unit of measure used in these equations is the Ångström and not the fractional coordinate.) The intramolecular and intermolecular interatomic distances and bond angles calculated from these coordinates are listed in Table 3 (see Fig. 3 for the numbering of the atoms). The Cl–N bond length of 1·73 Å is slightly shorter than the values of 1·77 Å and 1·74 Å found by Stevenson & Schomaker (1940) in dimethyl chloramine and methyl dichloramine. However, it agrees well with the length of 1·73 Å calculated by the equation and bond radii of Schomaker & Stevenson (1941).

Table 3. *Interatomic distances, standard deviations of bond lengths, and bond angles*

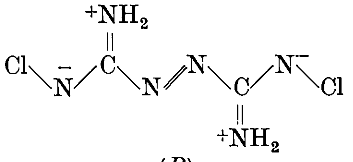
N_1–N_1'	1·26 Å	0·033 Å	C–N_1–N_1'	112·7°
C–N_1	1·42	0·021	N_1–C–N_2	107·7
C–N_2	1·28	0·026	N_1–C–N_3	120,9
C–N_3	1·30	0·025	N_2–C–N_3	131·4
N_2–Cl	1·73	0·016	C–N_2–Cl	111·8
N_3–N_2'''	2·96	0·022	C–N_3–N_2'''	139·8
N_3–Cl	2·85	—		
Cl″–N_1'	3·69	—		
Cl″–N_3	3·32	—		
Cl–Cl	3·85*	—		

* Through inversion center at origin.

The azo bond length of 1·26 Å is definitely longer than 1·20 Å, the length predicted for a N–N double bond from the covalent radii of Pauling (1940), and is somewhat longer, though not significantly longer, than the 1·23 Å found by de Lange, Robertson & Woodward (1939) in *trans* azobenzene and by Hampson & Robertson (1941) in *cis* azobenzene. The carbon–azo nitrogen bond, C–N_1, is slightly shorter than the usual C–N single bond, perhaps indicating some double-bond character in this bond. The other C–N bonds, C–N_2 and C–N_3, are considerably shorter. The following resonance forms probably make the major contributions to the structure of the molecule:



(*A*)

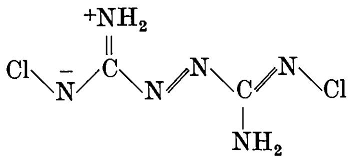


(*B*)

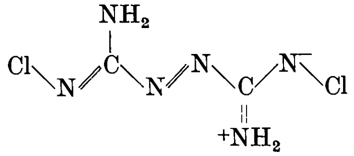
Table 4. *Values of observed and calculated structure amplitudes for the* 0*kl and* 1*kl reflections of azo*-bis-N-*chloroformamidine*

A minus sign attached to a number in the observed structure amplitude column indicates the maximum value of an unobservably weak reflection

0	0	0	-.-	176.0
0	2	0	18.2	16.0-
0	4	0	45.3	44.9-
0	6	0	6.7	5.3
0	8	0	26.7	28.2
0	10	0	20.1	19.1-
0	12	0	12.0	10.0-
0	1	1	12.4	14.7-
0	2	1	10.2	11.1-
0	3	1	23.6	19.3-
0	4	1	4.0	2.6
0	5	1	12.4	12.5-
0	6	1	7.7	5.7
0	7	1	17.4	15.8
0	8	1	7.7	7.5-
0	9	1	5.6	3.9
0	10	1	4.0	4.1-
0	11	1	1.3-	0.1-
0	12	1	4.9	4.4
0	13	1	0.7-	0.3-
0	0	2	16.6	23.3
0	1	2	41.3	58.6-
0	2	2	4.8	5.1-
0	3	2	23.5	24.2-
0	4	2	34.0	33.9
0	5	2	42.5	40.8
0	6	2	12.3	8.7-
0	7	2	12.4	12.1
0	8	2	4.6	5.7-
0	9	2	20.2	20.4-
0	10	2	6.9	6.7-
0	11	2	1.3-	0.5
0	12	2	2.5	2.6
0	13	2	7.6	8.0
0	1	3	30.2	34.3-
0	2	3	28.0	27.1-
0	3	3	17.5	16.4
0	4	3	7.7	7.1-
0	5	3	2.6	2.5
0	6	3	11 5	11.1
0	7	3	10.9	10.0-
0	8	3	3.5	3.7-
0	9	3	2.3	0.1
0	10	3	8.2	7.1-
0	11	3	15.1	12.5
0	12	3	1.0-	0.9
0	0	4	2.5	5.4-
0	1	4	4.4	4.9
0	2	4	2.2	2.0
0	3	4	16.7	18.0
0	4	4	36.0	33.8
0	5	4	3.3	2.6-
0	6	4	17.7	17.4-
0	7	4	2.3	0.4
0	8	4	10.3	9.7-
0	9	4	3.7	3.4
0	10	4	3.0	4.0
0	11	4	1.6	3.1
0	12	4	4.2	3.5
0	1	5	14.8	15.7-
0	2	5	30.4	32.8
0	3	5	2.9	5.6
0	4	5	15.7	14.2-
0	5	5	7.0	4.1
0	6	5	24.7	25.7-
0	7	5	1.5-	1.8-
0	8	5	5.8	5.1
0	9	5	5.3	3.6-
0	10	5	11.4	10.1
0	11	5	5.7	5.7
0	12	5	5.1	5.7-
0	0	6	9.9	11.5
0	1	6	6.7	9.0
0	2	6	4.2	3.4-
0	3	6	13.4	14.9
0	4	6	6.9	4.6
0	5	6	7.8	9.7-
0	6	6	2.3	3.6-
0	7	6	3.5	3.8
0	8	6	1.9	3.1
0	9	6	7.5	8.0
0	10	6	5.6	3.3-
0	11	6	0.7-	0.3-
0	1	7	15.4	17.5
0	2	7	3.4	2.5-
0	3	7	20.5	22.4-
0	4	7	4.1	5.2-
0	5	7	10.3	11.5-
0	6	7	3.8	3.1-
0	7	7	20.6	18.0
0	8	7	5.4	2.7-
0	9	7	2.1	2.2
0	10	7	1.4	0.7
0	0	8	13.5	15.9
0	1	8	2.3	3.5-
0	2	8	2.1	3.9-
0	3	8	8.0	5.2
0	4	8	5.3	7.3-
0	5	8	2.7	3.3
0	6	8	1.8	0.6
0	7	8	3.3	4.2
0	8	8	8.2	7.3
0	9	8	1.1	1.9-
0	1	9	2.3	1.8-
0	2	9	15.1	17.0-
0	3	9	2.2	2.0
0	4	9	1.3-	1.0
0	5	9	1.2-	1.1
0	6	9	7.0	8.6
0	7	9	1.3	0.3-
0	8	9	7.0	7.4-
0	0	10	3.3	5.0-
0	1	10	5.9	7.0-
0	2	10	1.2	1.3-
0	3	10	1.1-	0.8-
0	4	10	5.3	6.0
0	5	10	3.7	5.3
0	6	10	2.5	2.5-
0	1	11	2.1	4.0-
0	2	11	1.3	0.3-
0	3	11	4.5	6.9
1	0	0	-.-	9.1-
1	1	0	61.4	60.0-
1	2	0	22.7	21.8
1	3	0	12.2	12.0-
1	4	0	19.5	18.1
1	5	0	9.3	10.0
1	6	0	7.5	6.4-
1	7	0	11.4	9.1
1	8	0	14.1	13.5-
1	9	0	15.6	15.0-
1	10	0	3.4	3.0
1	11	0	1.1-	1.8
1	12	0	0.9	1.3
1	13	0	3.1	3.3
1	1	1	28.7	35.4-
1	2	1	48.0	47.6
1	3	1	9.3	11.7
1	4	1	9.4	8.0-
1	5	1	7.9	7.0
1	6	1	14.4	14.9-
1	7	1	12.7	11.9-
1	8	1	8.6	6.0
1	9	1	3.0	3.4
1	10	1	8.0	8.1
1	11	1	11.2	8.6
1	12	1	7.1	5.0-
1	13	1	0.5-	0.2
1	0	2	20.0	22.9-
1	1	2	11.5	11.2
1	2	2	18.5	21.5
1	3	2	30.1	29.6
1	4	2	19.5	20.8
1	5	2	28.5	28.5-
1	6	2	1.0-	3.7-
1	7	2	1.8	3.5-
1	8	2	15.5	13.8
1	9	2	7.9	8.2
1	10	2	1.1-	1.5
1	11	2	4.2	3.6
1	12	2	1.8	0.7
1	1	3	1.1	2.1
1	2	3	17.2	20.5
1	3	3	24.0	24.8-
1	4	3	8.7	9.8-
1	5	3	1.5	3.8-
1	6	3	10.8	10.0-
1	7	3	13.7	12.8
1	8	3	4.1	5.7
1	9	3	1.2	3.2
1	10	3	6.8	5.4
1	11	3	5.2	3.6-
1	12	3	4.8	5.0-
1	0	4	29.1	34.9
1	1	4	6.6	6.2-
1	2	4	11.1	11.3
1	3	4	8.8	9.1
1	4	4	23.0	25.6-
1	5	4	2.4	4.9-
1	6	4	4.4	5.8
1	7	4	1.7	4.1
1	8	4	7.4	8.3
1	9	4	1.2	0.8-
1	10	4	5.5	4.7-
1	11	4	3.3	0.9
1	12	4	7.6	6.7-
1	1	5	6.3	8.2
1	2	5	9.3	11.4-
1	3	5	18.5	21.8-
1	4	5	3.3	1.2
1	5	5	5.9	5.4-
1	6	5	3.8	5.7
1	7	5	10.7	12.8
1	8	5	8.1	6.5-
1	9	5	5.7	3.4
1	10	5	0.9-	1.5-
1	11	5	5.0	4.6-
1	0	6	7.4	8.2-
1	1	6	9.5	14.7-
1	2	6	7.6	8.4
1	3	6	1.4	2.8-
1	4	6	4.2	4.8
1	5	6	7.8	10.0
1	6	6	1.2	0.3
1	7	6	7.1	7.1
1	8	6	5.8	6.3-
1	9	6	7.4	7.1-
1	10	6	2.4	0.6-
1	1	7	6.8	9.6-
1	2	7	14.6	17.8-
1	3	7	3.8	5.9
1	4	7	1.2	1.0
1	5	7	1.8	3.8
1	6	7	7.9	9.0
1	7	7	5.7	5.8-
1	8	7	4.4	5.5-
1	9	7	2.4	1.2
1	10	7	4.5	3.8-
1	0	8	4.5	8.4-
1	1	8	3.9	3.7
1	2	8	4.5	5.3
1	3	8	4.9	6.4
1	4	8	1.9	4.6
1	5	8	4.4	3.6-
1	6	8	1.0-	1.1-
1	7	8	3.6	1.3
1	8	8	5.0	5.2-
1	1	9	5.2	6.1-
1	2	9	5.1	7.3
1	3	9	3.7	5.0
1	4	9	3.0	3.3-
1	5	9	3.5	2.9
1	6	9	6.5	6.8-
1	7	9	4.0	4.4-
1	0	10	1.1	1.6
1	1	10	2.1	3.8
1	2	10	0.9	1.3
1	3	10	3.6	4.2
1	4	10	2.9	3.3-
1	5	10	1.0	3.0-
1-	1	1	48.7	44.1-
1-	2	1	44.2	35.6
1-	3	1	24.7	19.4
1-	4	1	12.1	10.4-
1-	5	1	10.6	10.4
1-	6	1	36.9	30.3-
1-	7	1	12.9	11.1-
1-	8	1	7.5	7.1
1-	9	1	2.6	1.4
1-	10	1	8.7	7.8
1-	11	1	8.7	7.1
1-	12	1	3.0	2.5-
1-	13	1	0.5-	0.7
1-	0	2	53.9	45.8
1-	1	2	43.8	37.2
1-	2	2	5.6	4.5
1-	3	2	1.3	1.2
1-	4	2	23.9	19.0-
1-	5	2	1.9	2.0
1-	6	2	9.0	8.3
1-	7	2	2.5	3.1-
1-	8	2	6.3	5.6
1-	9	2	15.3	12.7
1-	10	2	9.3	8.2-
1-	11	2	4.8	3.3-
1-	12	2	4.3	3.3-
1-	13	2	2.0	3.0-
1-	1	3	27.3	20.3
1-	2	3	3.3	2.3-
1-	3	3	40.3	32.3-
1-	4	3	8.9	8.1-
1-	5	3	17.9	15.9-
1-	6	3	12.8	10.3-
1-	7	3	21.3	19.1
1-	8	3	1.4	1.8
1-	9	3	8.3	7.1
1-	10	3	1.1-	1.0-
1-	11	3	8.2	7.0-
1-	12	3	0.7-	0.5
1-	0	4	50.5	36.1
1-	1	4	1.8	0.8
1-	2	4	1.2	1.5-
1-	3	4	9.1	8.9-
1-	4	4	22.8	18.5-
1-	5	4	32.9	26.6
1-	6	4	6.7	6.0
1-	7	4	1.5	0.8-
1-	8	4	9.1	8.8
1-	9	4	3.6	3.8-
1-	10	4	8.5	6.7-
1-	11	4	0.8-	0.0
1-	12	4	3.7	3.3-
1-	1	5	12.4	10.3-
1-	2	5	28.7	25.6-
1-	3	5	6.6	6.0
1-	4	5	2.4	1.5-
1-	5	5	3.5	4.0
1-	6	5	6.8	7.0
1-	7	5	3.2	3.0-
1-	8	5	4.4	4.6-
1-	9	5	1.1-	1.4-
1-	10	5	9.3	7.4-
1-	11	5	2.4	2.4
1-	0	6	15.9	14.7-
1-	1	6	10.6	9.9-
1-	2	6	1.5	1.4
1-	3	6	16.3	13.2-
1-	4	6	16.6	15.6
1-	5	6	28.9	24.6
1-	6	6	7.3	6.8-
1-	7	6	4.9	4.0
1-	8	6	5.4	6.2-
1-	9	6	5.8	5.8-
1-	10	6	4.3	3.5
1-	11	6	2.1	1.7-
1-	1	7	4.3	5.7-
1-	2	7	4.5	4.8
1-	3	7	6.4	7.7
1-	4	7	6.5	4.9-
1-	5	7	1.7	2.6
1-	6	7	10.2	9.0-
1-	7	7	4.4	5.4-
1-	8	7	1.9	1.4
1-	9	7	1.0	1.1-
1-	10	7	0.6-	1.0
1-	0	8	10.5	11.5-
1-	1	8	13.8	15.8
1-	2	8	1.8-	0.8-
1-	3	8	7.1	7.7
1-	4	8	10.8	11.1
1-	5	8	3.1	4.8-
1-	6	8	3.6	4.4-
1-	7	8	2.9	3.3-
1-	8	8	4.0	3.8-
1-	9	8	6.4	7.6
1-	1	9	3.2	3.6
1-	2	9	3.1	5.0
1-	3	9	3.1	2.8-
1-	4	9	3.2	3.5-
1-	5	9	1.5-	0.9-
1-	6	9	6.0	6.7-
1-	7	9	2.9	2.8
1-	8	9	0.7-	1.8
1-	0	10	7.8	8.9
1-	1	10	4.2	4.7
1-	2	10	2.8	3.0-
1-	3	10	1.3-	1.0
1-	4	10	4.7	6.3-
1-	5	10	1.3	0.2
1-	6	10	0.8-	1.0
1-	1	11	4.4	5.0
1-	2	11	2.6	3.7-
1-	3	11	2.1	3.8-



(*C*)



(*D*)

It does not appear possible to write any reasonable resonance form which will give an appreciable amount of single-bond character to the azo group. The azo group in azochloramide is best described as a N–N double bond. When considered with the results reported for azobenzene, a reasonable length for the N–N double bond is 1·24–1·25 Å.

Planarity of the molecule

Using the orthogonal coordinates of the atoms, a least-squares plane was calculated through the ten atoms making up the molecule. The equation of this plane is

$$0{\cdot}9086X+0{\cdot}3896Y+0{\cdot}1504Z = 2{\cdot}032\ .$$

The average deviation of all atoms from this plane is 0·010 Å, the greatest deviation being 0·029 Å for N_1. The molecule is therefore planar to within the accuracy of the atomic coordinates.

Intermolecular distances

There are five interatomic distances which probably represent the minimum approaches of the molecules. The shortest is the N_3–N_2''' distance of 2·96 Å. This is undoubtedly a N–N hydrogen bond since N_2''' lies only 0·04 Å out of the plane of the molecule containing N_3. The geometry of this hydrogen bond is not entirely satisfactory as the angle C–N_3–N_2''' is 139·8°. This appears to be caused by the packing requirements of the surrounding chlorine atoms. The next shortest distance is the N_3–Cl″ distance of 3·32 Å. As this distance is only slightly longer than the usual nitrogen–chloride-ion hydrogen bond (Donohue, 1952), it appears possible that a N–Cl hydrogen bond could exist here. However, the Cl″ is 2·55 Å out of the plane of the molecule containing N_3, making such a hydrogen bond geometrically improbable. The chlorine atom 3·70 Å below Cl″ is only 0·81 Å out of this plane; however, the N_3–Cl″ distance here is 3·77 Å, considerably too large to be a hydrogen bond. Therefore, only one hydrogen bond occurs in this crystal. Other close approaches are Cl″–N_1' of 3·69 Å and the Cl–Cl contact through the inversion center at the origin of 3·85 Å. The perpendicular distance between the planes of molecules separated by one unit cell translation along the *a* axis is 3·37 Å.

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