Table 3. *Summary of interatomic distances* (Å)

Compound	Octahedral						Tetrahedral
	Metal–oxygen			Oxygen–oxygen			
	Average	Maximum	Minimum	Average	Maximum	Minimum	Average
PNb_9O_{25}	1·98	2·30	1·76	2·79	3·05	2·57	1·65
$WNb_{12}O_{33}$	1·99	2·18	1·80	2·79	3·41	2·15	1·70
$W_3Nb_{14}O_{44}$	1·99	2·18	1·78	2·78	3·19	2·38	1·76
$W_5Nb_{16}O_{55}$	1·97	2·17	1·81	2·78	3·36	2·22	1·76
$W_8Nb_{18}O_{69}$	1·98	2·24	1·74	2·78	3·03	2·50	1·77
Nb_2O_5	1·99	2·26	1·73	2·80	3·25	2·28	1·67
$TiNb_{24}O_{62}$	2·01	2·41	1·72	2·80	3·23	2·31	1·67
$Ti_2Nb_{10}O_{29}$	1·99	2·47	1·72	2·78	3·25	2·37	—
$TiNb_2O_7$	1·99	2·34	1·64	2·77	3·20	2·36	—

Whether a composition corresponds to a discrete phase depends upon whether there is a logical way for blocks of specific sizes to pack together, but it is still a matter for experiment to find out the conditions under which it is formed. Any phase must contain an integral number of metal and oxygen atoms in the unit cell, but its formula need not necessarily be simple, and will almost certainly not be variable to any marked degree. In general the concepts of non-stoichiometric phases in equilibrium systems are all too often deceptive, and have tended to obscure a wealth of subtle detail, now recognizable as multiple phase formation based in the present instance upon building block principles.

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The Structure of 1-(4-Chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)hydrazine Monohydrate

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The monohydrate of 1-(4-chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)hydrazine crystallizes from water as clear, colorless, acicular crystals. The cell dimensions are:

$$a_0=10\cdot434\pm0\cdot004,\ b_0=11\cdot352\pm0\cdot004,\ c_0=11\cdot245\pm0\cdot004\ \text{Å};\ \beta=108\cdot34^\circ\,.$$

The space group is $P2_1/c$ with four molecules per unit cell. The intensities of 1885 reflections with $2\theta\le100\cdot0^\circ$ (copper radiation) were measured with a proportional counter. The 1593 reflections which were 1·1 times the background were considered observed and used in the analysis. The structure was refined by least squares to a final residual R of 9·6% for all the observed reflections.

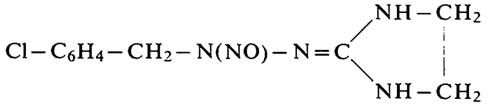
The molecule is a normal *N*-nitroso compound with no unusually short intramolecular distances involving the heavy atoms. The N–O distance of 1·250 Å is comparable to the N–O distance found in similar nitroso compounds. The molecules are joined by five types of hydrogen bond: N–H · · · N, N–H · · · O, O–H · · · O, O–H · · · N and C–H · · · O. The existence of the C–H · · · O hydrogen bond is rather unusual but appears to be real.

Introduction

Certain *N*-nitroso compounds can be cyclized to tetrazoles, sydnones, or oxatriazoles by elimination of a molecule of water or ammonia. Benson (1947) reported that compounds of the type R–N(NO)–NH–C(R′)=NH, where R′ is cyano or 2,4-dibromophenyl, yield substituted tetrazoles by elimination of a water molecule. Boyer & Canter (1955) prepared alkyl ψ-oxatriazoles by deamination of R–N(NO)–NH–C(NH_2)=O.

However, Finnegan & Henry (1965) found that compounds of the type R–N(NO)–NH–C(NH_2) = NH were surprisingly stable, and all attempts to effect ring closure were unsuccessful. They found that in some cases carbamyl azide, $N_3 . CO . NH_2$, was a product of the acid decomposition. Thus, they suggested that the nitroso oxygen might interact with the guanidine group stabilizing the molecule.

It was decided that an X-ray crystal structure determination would aid in explaining the chemistry of the various *N*-nitroso compounds prepared by Finnegan & Henry (1965). Therefore, a determination of the unit cell and space group was made for a number of derivatives. The compound most suitable for an X-ray diffraction study was 1-(4-chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)hydrazine monohydrate (hereafter CBNI):



$$\mathrm{Cl-C_6H_4-CH_2-N(NO)-N=C}\begin{matrix}\diagup \mathrm{NH-CH_2} \\ \qquad\quad | \\ \diagdown \mathrm{NH-CH_2}\end{matrix}$$

Experimental

CBNI forms clear, colorless, acicular crystals on recrystallization from water. The crystals are monoclinic and elongated along the $\bar{c}$ axis. Weissenberg photographs taken about the $\bar{c}$ axis indicated the following extinctions:

hkl no absences
$h0l$ absent if $l = 2n + 1$
$0k0$ absent if $k = 2n + 1$

The space group is uniquely determined to be $P2_1/c$ (C_{2h}^5). A second crystal was cleaved to give a fragment 0·3 mm long with a rhombic cross-section having edges of 0·2 mm. This second crystal, used in all subsequent measurements, was mounted on a glass fiber so that the $\bar{b}$ axis was parallel to the fiber axis.

The unit-cell and intensity measurements were carried out with the General Electric single-crystal orienter and copper radiation ($\alpha_1 = 1{\cdot}54050$, $\alpha_2 = 1{\cdot}54434$ Å). The unit-cell measurements were made with the use of a narrow beam with a narrow slit at the counter window. The average values of these measurements are:

$$a_0 = 10{\cdot}434 \pm 0{\cdot}004,\ b_0 = 11{\cdot}352 \pm 0{\cdot}004,$$
$$c_0 = 11{\cdot}245 \pm 0{\cdot}004\ \text{Å};\ \beta = 108{\cdot}34^\circ .$$

The density measured by flotation in a carbon tetrachloride–pentane solution is 1·41 g.cm^{-3}. The density calculated for four molecules per unit cell is 1·428 g.cm^{-3}.

Intensity measurements were made with a proportional counter using a linear amplifier-pulse height selector combination. The stationary-crystal stationary-counter technique was employed in measuring the intensities of 1885 reflections with $2\theta \le 100{\cdot}0^\circ$. The 1593 reflections which were greater than 1·1 times the background count at that particular value of 2θ were considered to be observed reflections. The reduction of these data to a set of observed structure amplitudes has been described previously by the author (Palenik, 1964).

Determination and refinement of the structure

A sharpened three-dimensional Patterson function with the origin peak removed was calculated. Two possible positions for the chlorine atom were deduced from the Patterson function. A minimum function was computed for each choice using the postulated chlorine–chlorine inversion peak as the superposition point. In one case a benzene ring was located at a distance of 1·8 Å (the Cl–C single bond distance) from the chlorine atom, while in the second case the ring was not discernible. Using the first minimum function, the remaining atoms, with the exception of the oxygen of the water molecule, were easily located.

The first Fourier synthesis was computed with all the observed reflections. The phases were determined by the contribution of all the non-hydrogen atoms with the exception of the nitroso group and water molecule. The nitroso group appeared in the position determined from the minimum function. The remaining large peak (about 4e.Å^{-3}) was assumed to be the water molecule. A new set of coordinates was obtained from the Fourier synthesis by Booth's (1948) method and a new Fourier synthesis was computed. The value of R, the usual residual, at this point was 28·3%. A third set of coordinates was obtained from the Fourier synthesis and was used as the initial parameters for a least-squares refinement.

It should be noted that in all the calculations in this study the following scattering factors were used: chlorine, oxygen, nitrogen and carbon-valence state from *International Tables for X-ray Crystallography* (1962) and hydrogen from McWeeny (1951). For the benzene ring atoms and the trigonal carbon in the dihydroimidazolyl ring, the carbon–graphite curve from McWeeny (1951) was used.

The first stage of the least-squares refinement was carried out with individual isotropic thermal parameters. The full matrix was calculated for each cycle, and the quantity $\Sigma w(\Delta F)^2$ was minimized. The weighting scheme chosen to reflect our prejudice regarding the accuracies of the value of F (observed) was:

if $F_o < 40$ $\quad \sqrt{w} = F_o/40$
if $40 < F_o < 200$ $\quad \sqrt{w} = 1{\cdot}0$
if $F_o > 200$ $\quad \sqrt{w} = 200/F_o$

At this point in the refinement, anisotropic thermal parameters were introduced. The full matrix was approximated by 3 × 3 blocks for the positional and 6 × 6 blocks for the thermal parameters. Partial shifts of 0·75 and 0·50 were used for the positional and thermal parameters respectively. The scale factor G was shifted by 0·25 times the amount calculated by dividing $\Sigma w\Delta F(\delta|F_c|/\delta G)$ by $\Sigma w(\delta|F_c|/\delta G)^2$. A total of six least-squares cycles dropped the residual R to 11·6%.

A difference Fourier synthesis was calculated using the heavy atom parameters from the last least-squares cycle. Hydrogen positions were found by assuming that the C–H and N–H distances were about 1·0 Å. A composite drawing of this difference synthesis is given in Fig. 1. The hydrogen atom positions and peak heights are given in Table 1.

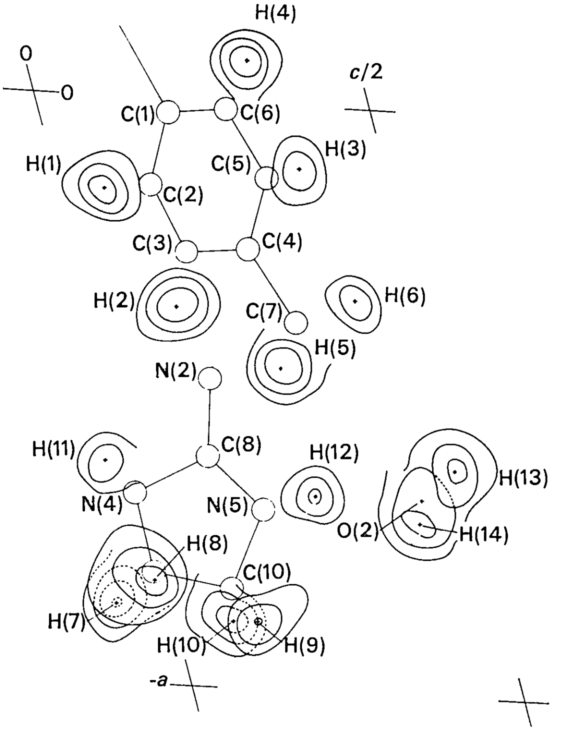


Fig. 1. A composite drawing of the difference Fourier synthesis which illustrates the positions of the hydrogen atoms. Contours are at approximately 0·2 e.Å^{-3} with the lowest contour at 0·2 e.Å^{-3}.

Table 1. *Probable hydrogen positions*

The hydrogen atom is given followed by the position parameters times 10^{+3} and peak height in e.Å^{-3}.

Atom	*X*	*Y*	*Z*	Peak height
H(1)	−156	060	068	0.6
H(2)	−348	114	131	0·6
H(3)	−108	343	370	0·4
H(4)	076	291	333	0·6
H(5)	−445	211	267	0·7
H(6)	−326	269	403	0·4
H(7)	−866	480	−082	0·7
H(8)	−826	579	−013	0·6
H(9)	−888	488	120	0·5
H(10)	−885	376	090	0·6
H(11)	−620	498	−039	0·5
H(12)	−662	386	267	0·5
H(13)	−608	342	484	0·6
H(14)	−700	269	411	0·5

A total of six additional least-squares cycles was calculated using the block approximation. The hydrogen atoms' contribution to the structure factor was computed (assuming $B=5{\cdot}0$) for each cycle but their parameters were not varied. The final residual *R* for the 1593 observed reflections was 9·6%. The final positional and thermal parameters for the non-hydrogen atoms are given in Table 2. The final set of structure factors calculated with the parameters in Tables 1 and 2 is presented in Table 3.

Results and discussion

A number of intramolecular distances and angles were calculated from the parameters given in Tables 1 and

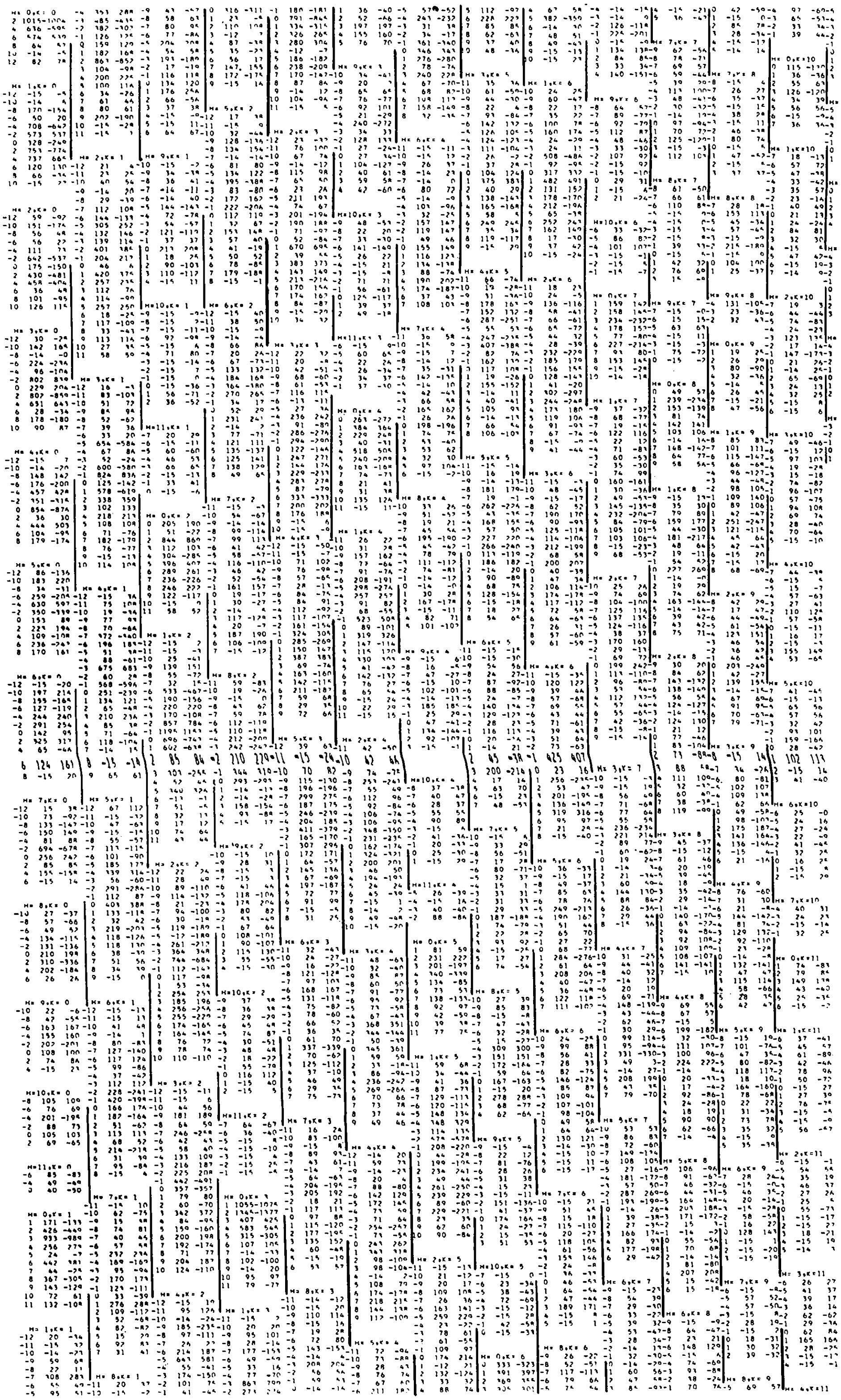
Table 2. *Final atomic parameters for the heavier atoms and their estimated standard deviations*

The temperature factor for each atom is of the form $T_i = \exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$
All values have been multiplied by 10^4.

Atom	*X*	*Y*	*Z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	1161	1292	1559	0128	0114	0149	0042	0087	0009
σ	0002	0002	0002	0002	0002	0002	0004	0004	0004
C(1)	−0242	1745	1945	0073	0065	0087	0028	0014	0029
C(2)	−1475	1230	1370	0121	0073	0081	0016	0015	−0006
C(3)	−2583	1559	1670	0094	0082	0076	−0011	0001	−0005
C(4)	−2474	2386	2598	0075	0057	0070	0016	−0013	0016
C(5)	−1236	2904	3182	0085	0077	0080	−0007	−0012	−0028
C(6)	−0110	2600	2847	0074	0066	0114	−0004	0001	0011
C(7)	−3683	2646	3048	0066	0072	0106	0004	−0002	0023
C(8)	−6041	4318	1140	0058	0067	0082	−0018	0004	−0003
C(9)	−8075	4971	−0152	0067	0089	0080	−0005	−0032	−0001
C(10)	−8282	4388	0960	0071	0110	0094	−0019	0008	0030
σ	0006	0006	0006	0007	0006	0007	0010	0010	0010
N(1)	−4174	3859	2754	0057	0077	0066	0012	−0018	0022
N(2)	−4737	4168	1498	0070	0119	0077	0024	0019	0058
N(3)	−3836	4600	3683	0074	0083	0093	0025	−0008	0024
N(4)	−6724	4586	−0073	0061	0126	0074	−0001	−0012	0050
N(5)	−6900	4207	1786	0058	0091	0083	−0013	0002	0017
σ	0005	0005	0005	0005	0005	0005	0009	0008	0009
O(1)	−4206	5638	3397	0115	0087	0139	0053	−0003	0009
O(2)	−6593	3189	4214	0171	0130	0101	−0093	0010	0042
σ	0005	0005	0005	0007	0005	0006	0010	0009	0009

Table 3. *Observed and calculated structure factors*

The values of *h* and *k* are given above each group with the values of *l*, 10*F* (observed) and 10*F* (calculated) given in that order. A negative *F* (observed) indicates an unobserved reflection.



2. The various distances and angles are tabulated in Table 4 and illustrated in Fig. 2. Least-squares planes were computed for fragments of the molecule and are presented in Table 5.

Table 4. *Intramolecular distances and angles*

Atoms	Distance	Atoms	Distance
Cl–C(1)	1·732 Å	O(1)–C(8)	3·048 Å
C(1)–C(2)	1·375	O(1)–N(5)	3·257
C(2)–C(3)	1·355	O(1)–N(2)	2·629
C(3)–C(4)	1·382	H(1)–C(2)	1·04
C(4)–C(5)	1·383	H(2)–C(3)	1·01
C(5)–C(6)	1·387	H(3)–C(5)	0·81
C(6)–C(1)	1·379	H(4)–C(6)	0·97
C(4)–C(7)	1·531	H(5)–C(7)	0·98
C(7)–N(1)	1·471	H(6)–C(7)	1·05
N(1)–N(2)	1·393	H(7)–C(9)	0·83
N(1)–N(3)	1·300	H(8)–C(9)	0·95
N(3)–O(1)	1·250	H(9)–C(10)	0·94
N(2)–C(8)	1·303	H(10)–C(10)	0·92
C(8)–N(4)	1·360	H(11)–N(4)	0·86
C(8)–N(5)	1·327	H(12)–N(5)	1·03
N(4)–C(9)	1·454	H(13)–O(2)	0·78
N(5)–C(10)	1·463	H(14)–O(2)	0·70
C(9)—C(10)	1.491		

Atoms	Angle	Atoms	Angle
C(1)–C(2)–C(3)	120·7°	H(3)–C(5)–C(4)	126·9°
C(2)–C(3)–C(4)	120·2	H(3)–C(5)–C(6)	112·2
C(3)–C(4)–C(5)	119·3	H(4)–C(6)–C(5)	119·1
C(4)–C(5)–C(6)	120·7	H(4)–C(6)–C(1)	121·7
C(5)–C(6)–C(1)	118·6	H(5)–C(7)–C(4)	112·4
C(6)–C(1)–C(2)	120·5	H(5)–C(7)–N(1)	107·5

Table 4 (*cont.*)

Atoms	Angle	Atoms	Angle
C(5)–C(4)–C(7)	120·3	H(5)–C(7)–H(6)	119·3
C(3)–C(4)–C(7)	120·2	H(6)–C(7)–C(4)	104·0
C(4)–C(7)–N(1)	111·8	H(6)–C(7)–N(1)	101·3
C(7)–N(1)–N(2)	117·9	H(7)–C(9)–N(4)	114·2
C(7)–N(1)–N(3)	116·0	H(7)–C(9)–C(10)	113·5
O(1)–N(3)–N(1)	114·8	H(7)–C(9)–H(8)	98·7
N(3)–N(1)–N(2)	125·0	H(8)–C(9)–N(4)	119·6
N(1)–N(2)–C(8)	114·2	H(8)–C(9)–C(10)	109·1
N(2)–C(8)–N(4)	120·2	H(9)–C(10)–N(5)	120·8
N(2)–C(8)–N(5)	129·7	H(9)–C(10)–C(9)	105·8
C(8)–N(5)–C(10)	109·9	H(9)–C(10)–H(10)	90·3
C(8)–N(4)–C(9)	108·5	H(10)–C(10)–N(5)	114·9
N(4)–C(9)–C(10)	102·2	H(10)–C(10)–C(9)	123·1
N(5)–C(10)–C(9)	102·7	H(11)–N(4)–C(8)	109·2
N(4)–C(8)–N(5)	110·0	H(11)–N(4)–C(9)	123·0
C(2)–C(1)–Cl	119·7	H(12)–N(5)–C(8)	122·6
C(6)–C(1)–Cl	119·8	H(12)–N(5)–C(10)	126·0
H(1)–C(2)–C(1)	119·0	H(13)–O(2)–H(14)	129·7
H(1)–C(2)–C(3)	120·2		
H(2)–C(3)–C(2)	121·9		
H(2)–C(3)–C(4)	117·4		

A review of carbon–chlorine bond distances was recently given by Sakurai, Sundaralingam & Jeffrey (1963) and Gafner & Herbstein (1962). The C(1)–Cl distance of 1·732 ± 0·012 Å is in agreement with the C–Cl distance found in other aromatic compounds.

The average C–C distance in the benzene ring is 1·377 ± 0·016 Å, not significantly different from that in benzene (1·397 Å, Stoicheff (1954); 1·393 Å, Cox

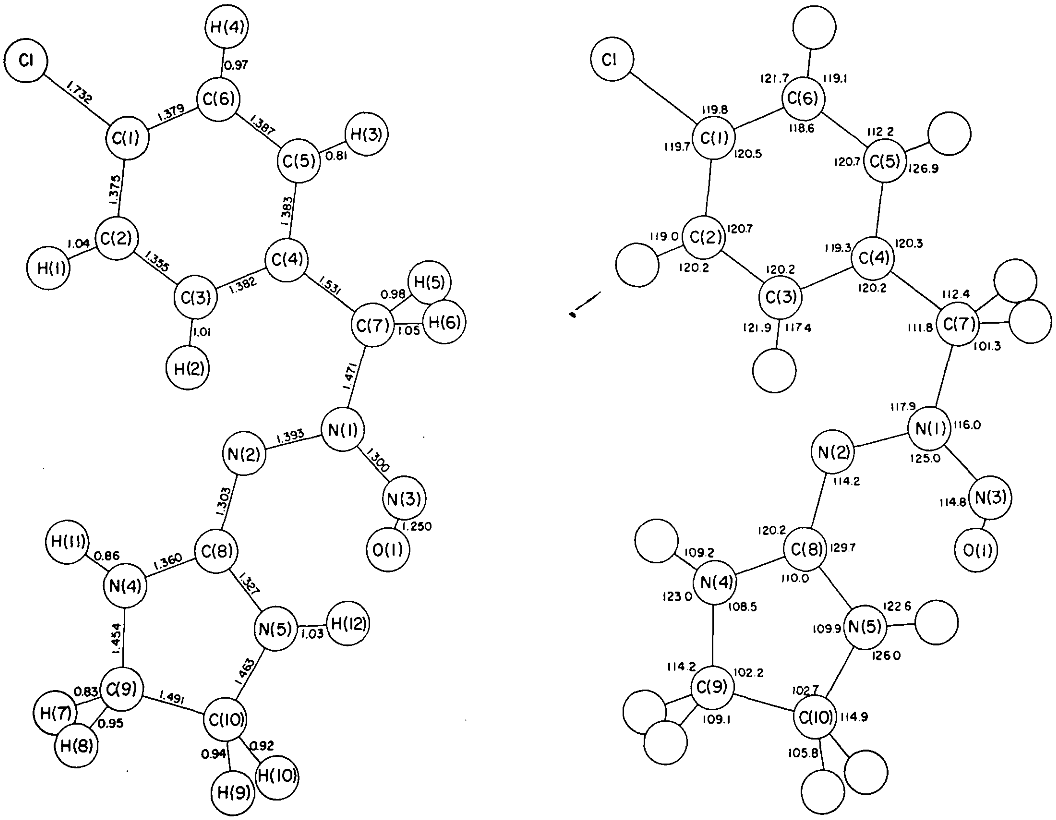
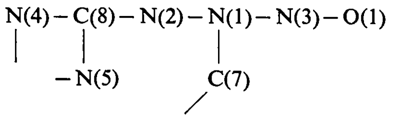


Fig. 2. The numbering of the atoms in the molecule together with the bond distances and angles. The water molecule, H(13)–O(2)–H(14) is not shown.

Cruickshank & Smith (1958)). The C(4)–C(7) distance of 1·531 ± 0·016 Å is longer than the distance of 1·517 Å for the corresponding bond in toluene (Keidel & Bauer, 1956), but the difference is not significant. The average deviation of the six carbon atoms in the benzene ring from the least-squares plane through the ring (Table 5) is 0·010 Å, close to the expected value of 0·011 Å. The value of χ^2 is 8·7 which gives a value of P, for three degrees of freedom, of 0·03. Therefore, the benzene ring can be considered planar. For the least-squares plane through the benzene ring and chlorine atom, the χ^2 test gives $P < 0·001$ and hence, this grouping is nonplanar. The reason for the nonplanarity of the chlorobenzyl group is not understood.

The C(9)–C(10) bond length in the dihydroimidazolyl ring is 1·491 ± 0·016 Å, shorter than the value of 1·533 Å proposed by Bartell (1959) for a normal C–C bond. The smaller value could be a consequence of the strained dihydroimidazolyl ring. Goldish (1959) has tabulated the interatomic distances in small-ring molecules, and the C–C single bond is apparently distorted in these systems. More accurate structural information on small-ring compounds would be desirable in order to resolve the question of bond strain in these cases. The grouping:



$$\begin{array}{ccccccccccc} \mathrm{N(4)} & - & \mathrm{C(8)} & - & \mathrm{N(2)} & - & \mathrm{N(1)} & - & \mathrm{N(3)} & - & \mathrm{O(1)} \\ | & & | & & & & | & & & & \\ & & -\mathrm{N(5)} & & & & \mathrm{C(7)} & & & & \\ & & & & & / & & & & & \end{array}$$

is infrequently encountered, making any direct comparison of bond distances impossible. Some of the possible resonance structures for this group of atoms are illustrated in Fig. 3. No attempt was made to weight the various forms, but they are useful in a qualitative discussion of the various bond orders and lengths.

The C(7)–N(1) bond is expected to be a normal C–N bond since it is not involved in any of the resonance structures. The C(7)–N(1) bond distance of 1·471 ± ± 0·015 Å is in good agreement with the value of 1·472 ± 0·005 Å given by Sutton (1958).

The two bonds C(8)–N(4) and C(8)–N(5) both have an equal amount of double bond character (Fig. 3). The average distance of 1·343 ± 0·015 Å for these two bonds is expected to be longer, though perhaps not significantly, than the corresponding bonds in the imidazolyl ring in histidine. The expected lengthening is

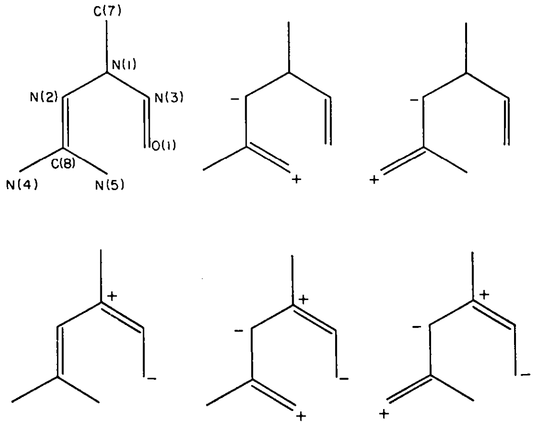


Fig. 3. Some resonance forms for a portion of the molecule·

Table 5. *Least-squares planes*

Plane and deviations (× 10³) from the plane

Atom	I	II	III	IV	V
Cl	063	+022			
C(1)	005	−015			
C(2)	+010	−002			
C(3)	−016	−012			
C(4)	007	+020			
C(5)	008	+012			
C(6)	−014	−026			
C(7)	152	+183		−001	104
C(8)			−013		
C(9)			−336		
C(10)			063		
N(1)				−082	−034
N(2)			005	000	017
N(3)				001	034
N(4)			004		
N(5)			004		
O(1)				−001	−017

	Direction cosines (× 10⁴) with respect to				
Plane	*a*	*b*	*c**	Distance to origin	Description of plane
I	−0138	−7153	6986	0·041	C(1)–C(6) Benzene ring only
II	−0250	−7120	+7018	+0·085	C(1)–C(6), Cl Benzene ring and chlorine
III	−0482	−9717	−2311	−4·707	C(8), N(2), N(4), N(5)
IV	9728	2038	−1103	−4·543	C(7), N(2), N(3), O(1)
V	9810	1686	−0965	−4·749	N(1), N(2), N(3), O(1)

due to the double bond character in the C(8)–N(2) bond which has no analogy in the histidine molecule. Donohue, Lavine & Rollett (1956) reported 1·340 ± 0·012 Å for these C–N bonds in histidine hydrochloride monohydrate, Harding & Cole (1963) reported 1·326 ± 0·020 Å in di(histidino)zinc pentahydrate and Kretsinger, Cotton & Bryan (1963) reported 1·316 ± 0·023 Å in di-(L-histidino)zinc dihydrate.

The distance of 1·303 ± 0·015 Å for the C(8)–N(2) bond corresponds to a bond order of 1·6, suggesting that the three resonance structures with a double bond between C(8)–N(2) contribute substantially to the ground state of the molecule. This observation is in agreement with the favorable charge distribution present in these structures.

The N(2)–N(1) bond distance of 1·393 ± 0·014 Å is shorter than the value of 1·43 to 1·45 Å suggested by Chesnut & Marsh (1958) for a nitrogen–nitrogen single bond. The shortening could be a consequence of the opposite charges on the two atoms in some of the resonance forms, or of a small amount of double-bond character.

The three atoms >N(1)–N(3)–O(1) are somewhat similar to a nitrosoamine grouping. Unfortunately, there is no structural information on nitrosoamines available in the literature for comparison. Both the N(1)–N(2) bond distance of 1·300 ± 0·014 Å and the N(3)–O(1) bond distance of 1·250 ± 0·014 Å correspond to a bond order of about 1·5. A review of the structure of nitroso compounds has been presented recently by Linnett & Rosenberg (1964). The distances found in this study are in agreement with some of the other nitroso compounds. A more complete discussion of this part is being deferred until the completion of our refinement of the crystal structure of the *cis*-nitrosomethane dimer.

The intramolecular distances and angles involving the hydrogen atoms are presented in Table 4 and Fig. 2. The mean C–H distance is 0·95 ± 0·06 Å, not significantly different from the C–H values found in other X-ray diffraction investigations. The H–C–C angles in the benzene ring average 119·9 ± 1·1°, if the angles involving H(3) are excluded. There appears to be a steric repulsion between H(3) and H(6) which increases the H(3)–C(5)–C(4) angle. However, the small H(6)–C(7)–C(4) angle of 104·0° suggests that this apparent repulsion may be an artifact. The two H–C–H angles in the imidazolyl ring are smaller than the usual tetrahedral angle, but there are few X-ray determinations involving small rings to provide a basis for comparison.

The protons on the water molecule are not well resolved in the difference Fourier synthesis. The short O–H distances of 0·78 and 0·70 Å and the large H–O–H angle of 129·7° could be a reflection of the low resolution. While both O–H distances are shorter than the value of 0·96 Å found in neutron diffraction and spectroscopic studies, the O–H distances found in most X-ray diffraction studies are also shorter than the accepted value. Also, since the water molecule does not appear to be strongly hydrogen-bonded in the crystal (see below), the molecule could be undergoing large thermal vibrations. These vibrations would decrease the apparent O–H distances and also reduce the resol-

Table 6. *Mean-square displacements*

Atom	$(r^2)^{\frac{1}{2}}$*	Direction cosines†		
Cl	294	−1173	1127	9867
	286	−5466	−8368	0306
	236	−8292	5357	−1598
C(1)	247	−5215	2464	8169
	219	−5816	−8032	−1290
	165	−6244	5424	−5621
C(2)	274	9028	2036	−3788
	216	1489	−9744	−1685
	205	4034	−0957	9100
C(3)	258	−8367	1268	5328
	232	−0284	−9816	1887
	185	−5470	−1428	−8249
C(4)	250	−7812	0251	6237
	200	−2772	−9093	−3105
	155	−5593	4155	−7173
C(5)	267	7192	2865	−6330
	225	4067	−9123	0491
	170	5634	2928	7726
C(6)	284	−5557	1103	8241
	207	−0533	−9938	0970
	183	−8297	−0100	−5581
C(7)	276	−5296	2170	8200
	215	−2582	−9621	0878
	171	−8080	1652	−5656
C(8)	240	5845	−1742	−7925
	211	1015	−9533	2844
	158	8050	2467	5395
C(9)	269	−7210	0560	6907
	241	−0189	−9980	0611
	151	−6927	−0312	−7206
C(10)	286	−3840	7844	4872
	236	−4237	−6185	6618
	180	−8204	−0477	−5698
N(1)	241	−5817	4653	6672
	221	−4582	−8652	2039
	140	−6721	1871	−7164
N(2)	293	−0589	9113	4076
	219	−7596	−3058	5740
	170	−6477	2758	−7102
N(3)	267	−6293	1401	7644
	238	−3246	−9411	−0947
	167	−7062	3078	−6377
N(4)	300	−2330	8972	3750
	229	−6894	−4244	5870
	152	−6858	1218	−7175
N(5)	259	−4268	7146	5542
	227	−3748	−6975	6108
	161	−8230	−0531	−5655
O(1)	326	−6802	−1684	7134
	256	−3571	−7738	−5231
	197	−6402	6106	−4662
O(2)	362	−7503	6002	2771
	243	−6123	−7890	0512
	228	−2494	1312	−9595

* Values times 10^{+3}, in Å.

† Values times 10^{+4} (cosines are given with respect to *a*, *b*, *c**).

ution of the hydrogen atoms in the difference Fourier synthesis.

The thermal parameters given in Table 2 were used to compute the mean-square displacements and direction cosines given in Table 6. The mean-square displacements are about normal for a covalent-type molecule. The chlorine atom is vibrating almost isotropically, with the slightly larger displacements being perpendicular to the carbon–chlorine bond. The oxygen atom of the water molecule has the largest mean-square displacements, as expected from its relatively unrestrained position.

A projection of the structure on the (010) plane is given in Fig. 4. The intermolecular distances tabulated in Table 7 have the usual values for van der Waals contact except for the O(1) to H(5) distance of 2·270 Å. This contact is definitely shorter than the expected value of 2·6 Å for a non-bonded contact and may represent a C–H · · · O hydrogen bond. The question of the existence of this type of hydrogen bond has been discussed by Sutor (1963). The nitroso oxygen which is the acceptor in this case has a slight overall negative charge as a result of the various resonance structures (Fig. 3). The charge should facilitate the formation of this type of hydrogen bond. The net result of the C–H · · · O hydrogen bond is to produce an infinite spiral of molecules around the twofold screw axis. The pertinent distances and angles for this postulated hydrogen bond are illustrated in Fig. 5.

There are four additional hydrogen bonds possible. Three hydrogen bonds are used to hold together the spirals around the twofold screw axis. The distances and angles for the three hydrogen bonds are given in Fig. 5. An N–H · · · N hydrogen bond is formed between N(4)–H(11) · · · N(2) across the center of symmetry. It is interesting to note that in the resonance structures, N(2) tends to have a net negative charge. In the case of N(3), which tends to have a positive charge, no hydrogen bond is formed.

Another hydrogen bond is formed using N(5)–H(12) · · · O(2), where O(2) is the oxygen in the water molecule. The water molecule apparently acts as a

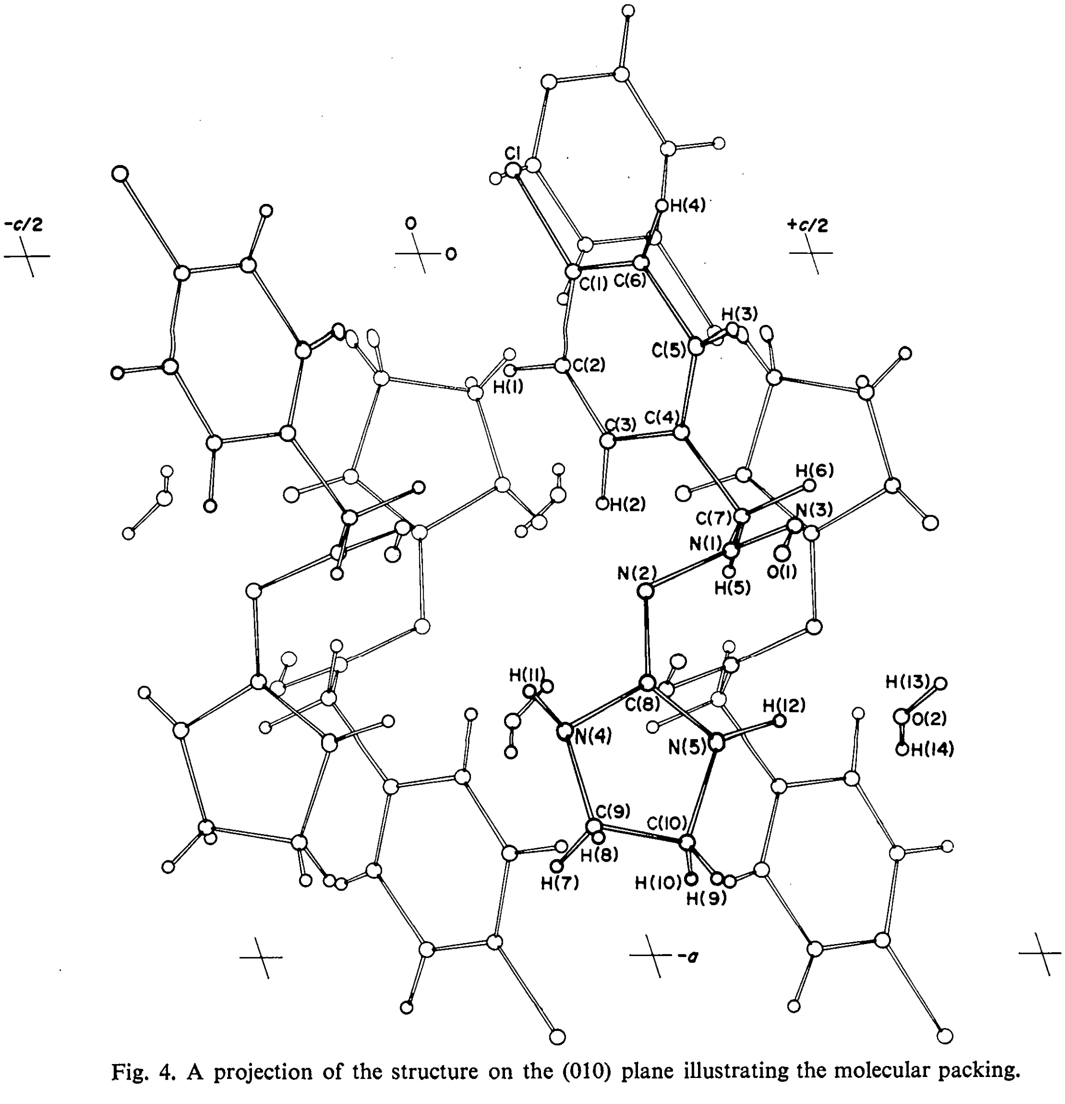


Fig. 4. A projection of the structure on the (010) plane illustrating the molecular packing.

Table 7. *Intermolecular distances*

	Molecule*	Distance
N(3)–Cl	*B*(000)	3·471 Å
O(1)–Cl	*B*(000)	3·250
H(3)–Cl	*B*(000)	3·265
H(8)–H(6)	$B(\bar{1}00)$	2·729
H(8)–C(4)	$B(\bar{1}00)$	3·256
H(9)–C(2)	$B(\bar{1}00)$	3·050
H(9)–C(3)	$B(\bar{1}00)$	3·066
H(9)–C(4)	$B(\bar{1}00)$	3·277
O(1)–C(7)	*B*(100)	3·229
O(1)–H(2)	$B(\bar{1}00)$	2·603
O(1)–H(5)	$B(\bar{1}00)$	2·270
N(5)–C(3)	$B(\bar{1}00)$	3·322
H(12)–H(2)	$B(\bar{1}00)$	2·825
H(11)–C(8)	$C(\bar{1}10)$	2·845
H(11)–N(1)	$C(\bar{1}10)$	3·105
H(11)–N(4)	$C(\bar{1}10)$	2·973
H(11)–H(11)	$C(\bar{1}10)$	2·383
N(4)–N(2)	$C(\bar{1}10)$	2·906
H(4)–O(2)	*A*(100)	2·639
H(4)–H(14)	*A*(100)	2·231
Cl–H(10)	*A*(100)	2·891
C(1)–H(10)	*A*(100)	3·127
C(6)–H(10)	*A*(100)	3·172

* X_i is in the molecule *A* and X_j in the molecule specified after X_j. The molecules are located as follows:

A	*B*	*C*
x, y, z	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	$\bar{x}, \bar{y}, \bar{z}$

The numerals after the molecular designation give the unit-cell translations in the order *a*, *b*, *c*.

link between the two spirals since it forms a hydrogen bond O(2)–H(13) · · · O(1), where O(1) is the nitroso oxygen. The distance from O(2) to N(4), the closest and most logical acceptor for a hydrogen bond involving H(14), is 3·264 Å. While this distance is longer than the average O–H · · · N hydrogen bond, it is shorter than the van der Waals contact. The angle O(1‴)–O(2′)–N(4) of 103·8° is close to the value found in other water molecules. The chlorine atom is the other possible acceptor for a hydrogen bond involving H(14), but the O(2)–Cl distance of 3·824 Å excludes this possibility. Therefore, the water molecule appears to form two hydrogen bonds, one to O(1‴) and the other to N(4), but neither hydrogen bond appears to be very strong.

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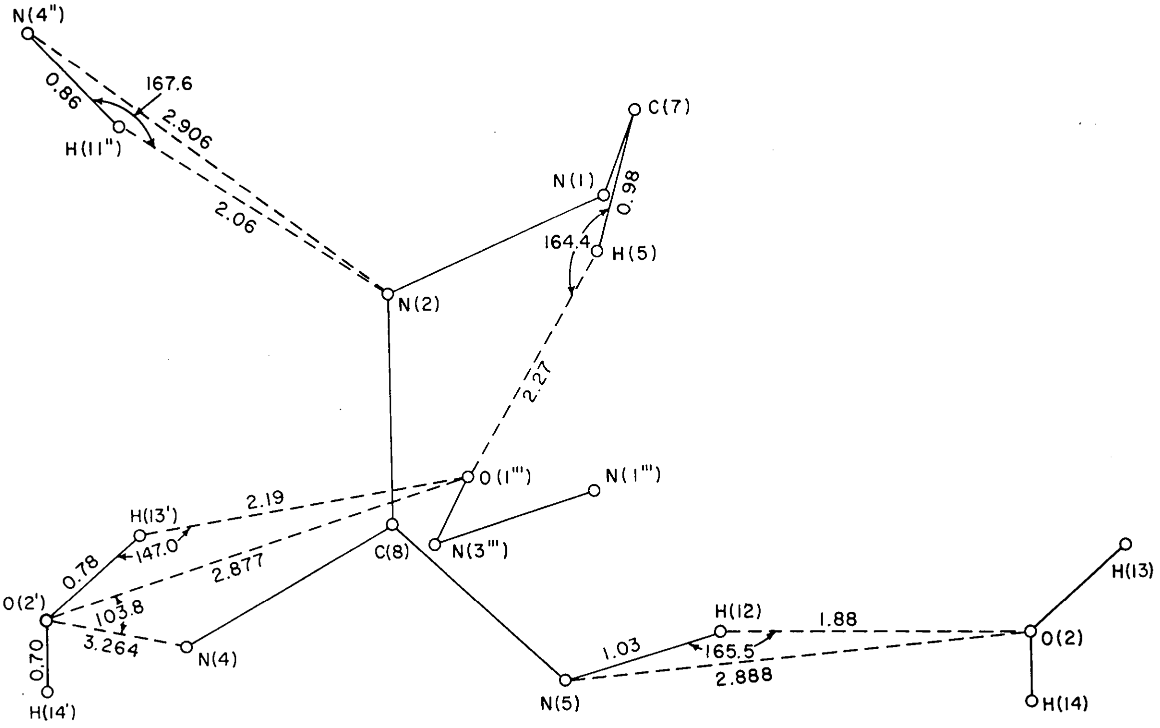

Fig. 5. A view of the part of the molecule which is involved in the formation of hydrogen bonds. The various distances and angles are included.