variation of the measured bond lengths is well reproduced in both sets of calculated distances. The individual agreements are also remarkably good; for the valence-bond distances, the maximum difference between measured and calculated values is 0·030 Å, and the root-mean-square deviation 0·015 Å, while the corresponding deviations for the molecular orbital method are 0·028 and 0·013 Å. Both sets of calculated distances therefore agree equally well with the measured values.

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*Acta Cryst.* (1961). **14**, 711

# The Crystal Structure of *N*-Chloro-Succinimide

By R. N. Brown*

*Physics Department, University of Adelaide, Adelaide, South Australia*

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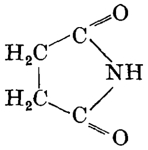
*N*-chloro-succinimide, $C_4H_4ClNO_2$, forms orthorhombic crystals with $a=6·41$, $b=7·11$, $c=11·69$ Å, space group $P2_12_12_1$ and $Z=4$. The structure has been solved by application of the heavy-atom method to the bromine isomorph and refined by two-dimensional projections on the (100) and (010) planes. The molecular bond lengths and angles are bilaterally symmetrical, but the molecule is significantly aplanar. A 'close' intermolecular approach of 2·88 Å has been observed between Cl and O.

## Introduction

Preliminary crystallographic work on the heterocyclic compound succinimide (I) and its *N*-chloro and *N*-bromo derivatives had revealed that the latter two compounds form an isomorphous pair (Brown, 1956).



(1)

## Experimental

*N-chloro-succinimide* (N.C.S.), $C_4H_4ClNO_2$, mol. wt. 133·5, was made from succinimide by the method of Hirst & Macbeth (1922). It is a colourless crystalline solid melting at 148 °C. Crystals were obtained from benzene by slow evaporation as small orthorhombic plates tabular on {001} with the additional forms {111} (always present), {110} (common), {011} (rare) and {101} (very rare). Optic orientation: $X=a$, $Y=b$, $Z=c$; optic sign negative. Refractive indices,

$$n_X=1·492\pm0·002,\quad n_Y=1·625\pm0·002,$$
$$n_Z=1·669\pm0·002\ ,$$

measured by the oil-immersion method. Unit-cell dimensions, assuming the Cu $K\alpha$ wavelengths of Lonsdale (1950):

$$a=6·412\pm0·003, b=7·111\pm0·015, c=11·691\pm0·004\ \text{Å}.$$

Systematic absences: $h00$, $0k0$, $00l$ for odd indices; space group $P2_12_12_1$.

$$V=533\ \text{Å}^3,\ Z=4,\ d(\text{calc.})=1·66,\ d(\text{obs.})=1·65\ \text{g.cm.}^{-3}$$
(Stefl., 1915).

Absorption coeff. for Cu $K\alpha$, $\mu=55$ cm.$^{-1}$.

*N-bromo-succinimide* (N.B.S.), $C_4H_4BrNO_2$, mol.wt. 178·0, was obtained ready-made as crystals melting at 174 °C. Crystals from water were thin {001} plates showing also the faces {111} and {011}. Optic orientation: $X=b$, $Y=a$, $Z=c$; optic sign negative. Refractive indices:

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* Present address: Central Research Laboratories, Imperial Chemical Industries of Australia and New Zealand Limited, Ascot Vale, Victoria, Australia.

$$n_X = 1{\cdot}520 \pm 0{\cdot}002,\ n_Y = 1{\cdot}661 \pm 0{\cdot}002,\ n_Z = 1{\cdot}739 \pm 0{\cdot}002\ .$$

Unit-cell dimensions:

$$a = 6{\cdot}48 \pm 0{\cdot}02,\ b = 7{\cdot}25 \pm 0{\cdot}02,\ c = 11{\cdot}86 \pm 0{\cdot}04\ \text{Å}\ .$$

Systematic absences and space group as for N.C.S.

$$V = 557\ \text{Å}^3,\ Z = 4,\ d(\text{calc.}) = 2{\cdot}12,$$
$$d(\text{obs.}) = 2{\cdot}098\ \text{g.cm.}^{-3}\ (\text{Stefl}).$$
$$\mu\ \text{for Cu}\ K\alpha = 97\ \text{cm.}^{-1}.$$

## Collection of intensity data

Crystals for intensity work were cut in the form of $a$ and $b$ axis needles of roughly square cross-section. Because of their high absorption they were kept as small as possible. For N.C.S. $\mu r$ was kept in the region 0·4–0·5, but for N.B.S. $\mu r$ was 0·8–1·0 and it was necessary to correct the intensities for absorption. The crystals had been found to sublime slowly and were therefore coated with collodion.

Weissenberg intensity photographs were taken by the multiple-film method for the $0kl$ and $h0l$ zones of N.C.S. and N.B.S., using Cu $K\alpha$ radiation. The diffracted intensities were estimated visually, Lorentz and polarization corrections applied and the structure amplitudes $|F_o|$ calculated. Table 1 shows the numbers of observed and observable reflections in each zone.

Table 1. *Reflections in the zones of N.C.S. and N.B.S.*

| | Zone | Observable | Observed |
|---|---|---|---|
| N.C.S. | $0kl$ | 414 | 360 |
| | $h0l$ | 382 | 318 |
| N.B.S. | $0kl$ | 434 | 406 |
| | $h0l$ | 382 | 338 |

## Structure determination

1. *Patterson projections*

Patterson projections were computed in the $0kl$ and $h0l$ zones of both N.C.S. and N.B.S. These allowed placement of the halogen atoms in the cell, but no light-atom positions could be deduced.

2. *Fourier projections*

Changes of origin are necessary in $P2_12_12_1$ when making Fourier projections, and the origins used throughout were

$$(100)\ \text{projections:}\ (x, \tfrac{1}{4}, \tfrac{1}{2})\ ,$$
$$(010)\ \text{projections:}\ (0, y, \tfrac{1}{4})\ .$$

These and all other coordinates quoted are relative to the origin of $P2_12_12_1$ used in the *International Tables*. All references to atoms apply to molecule $A$ of Fig. 4.

An $h0l$ Fourier synthesis was computed using heavy-atom signs with the N.B.S. structure amplitudes, and the postulated trial molecule was placed satisfactorily. This placement was taken to apply to the chlorine isomorph. A $0kl$ synthesis was now made for N.C.S. with heavy-atom signs and the trial molecule was also placed successfully in that zone.

3. *Refinement*

Refinement proceeded in both zones of N.C.S. by the Fourier method. Structure factors were calculated using the light-atom scattering factors of McWeeny (1951) and the chlorine scattering factor of James & Brindley (1932). When first calculated the residual $R$ had the values 23·8 and 25·9% in the $0kl$ and $h0l$ zones respectively. After two $0kl$ cycles and three $h0l$ cycles refinement was changed to the difference synthesis method, and three further cycles in each zone reduced $R$ to 14·4 and 22·5% respectively.

By now the following points were apparent:

(i) Appreciable anisotropic vibration of the chlorine atom was present in both projections.

(ii) The atomic shifts were becoming random.

(iii) The difference maps showed appreciable detail unrelated to the atomic positions.

(iv) The factor $R$ was diminishing only very slowly.

Fresh photographs were taken and the intensities measured. In succeeding computations the contributions of hydrogen were included, using the hydrogen scattering factor of McWeeny (1951). Coordinates were assigned to the four hydrogen atoms assuming a C–H bond length of 1·1 Å and a tetrahedral H–C–H angle, with the atoms disposed symmetrically about the plane of the ring. Further, the more recent chlorine scattering factor of Berghuis *et al.* (1955) was used, and an anisotropic vibration correction was applied in both zones to the chlorine scattering. This was done graphically using an extension of the method of Cochran (1954) to cover the case where the atoms do not all vibrate parallel to each other, but half of them vibrate at a symmetrically related angle.

Use of the new data effected a marked improvement in the difference maps. Where necessary, separate temperature factors $B$ differing from the zone average temperature factor were applied to individual atoms. This related especially to the two oxygen atoms, in both zones. The final temperature factors of the oxygens are shown in Table 2.

Table 2. *Final temperature factors for oxygen B* (Å$^2$)

| Zone | $O_1$ | $O_2$ | Zone av. |
|---|---|---|---|
| $0kl$ | 6·0 | 4·8 | 3·4 |
| $h0l$ | 4·0 | 4·0 | 2·8 |

The direction of the final assumed vibration of the chlorine atom was nearly normal to the N–Cl bond in both projections, indicating its vibration in space in a plane perpendicular to this bond. The magnitude of the vibrations can be indicated in terms of Cochran's (1954) ratios which in the final structure were given the values shown in Table 3.

Table 3. *Final values of Cochran's ratios for chlorine*

| Zone | $u_y/u$ | $u_x/u$ |
|---|---|---|
| 0*kl* | 0·8 | 1·2 |
| *h*0*l* | 0·7 | 1·5 |

After several more difference syntheses in each zone the refinement was stopped, and $R$ then stood at 10·9 and 10·6% in the 0*kl* and *h*0*l* zones respectively.

## Final structure

### 1. *Atomic parameters*

The final atomic parameters for the atoms of N.C.S. are given in Table 4.

Table 4. *Final parameters for N.C.S.*

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cl | 0·386 | $0·780_5$ | 0·580 |
| N | 0·287 | 0·728 | 0·710 |
| $C_1$ | 0·401 | 0·758 | 0·811 |
| $C_2$ | 0·267 | 0·692 | 0·907 |
| $C_3$ | 0·084 | 0·590 | 0·847 |
| $C_4$ | 0·105 | 0·626 | 0·723 |
| $O_1$ | 0·570 | 0·830 | 0·814 |
| $O_2$ | −0·008 | 0·577 | 0·643 |
| $H_1$ | 0·359 | 0·600 | 0·960 |
| $H_2$ | 0·225 | 0·815 | 0·964 |
| $H_3$ | 0·069 | 0·441 | 0·868 |
| $H_4$ | −0·067 | 0·657 | 0·872 |

### 2. *Final projections*

The final electron-density projection on (010) is reproduced in Fig. 1. The thermal vibration of the chlorine atom can be seen plainly. Carbon, nitrogen and oxygen are distinguishable by their peak heights. Fig. 2 shows a final difference synthesis in the 0*kl* zone. The four hydrogen atoms are marked in the positions assumed for them, and a peak of electron density is present near each, confirming its presence in approximately that position.

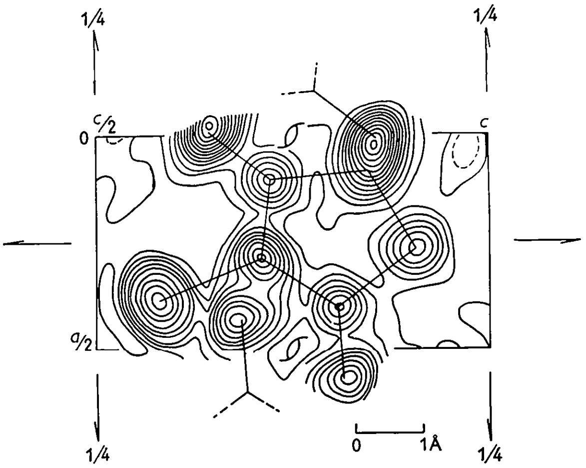

Fig. 1. Fourier projection on (010). Zero contour broken, contour interval 1eÅ$^{-2}$ except for chlorine which has contours at 1, 2, 3, 4, 6, 8, 12. 16, 20, 24 e.Å$^{-2}$.

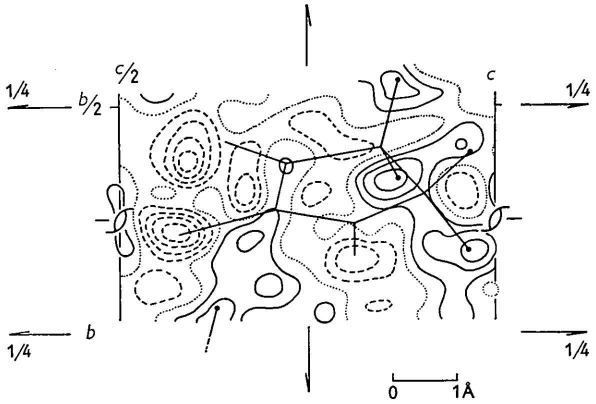

Fig. 2. $(F_o-F_c)$ synthesis on (100). Zero contour dotted, negative contours broken. Contour interval 0·25 e.Å$^{-2}$.

### 3. *Accuracy*

(i) *Coordinates.*—The standard deviation of atomic coordinates was calculated according to Cruickshank (1949, 1954) who shows that

$$\sigma(x) = \sigma\left(\frac{\partial\varrho}{\partial x}\right)\Big/\left|\frac{\partial^2\varrho}{\partial x^2}\right| .$$

Values for $\sigma(\partial\varrho/\partial x)$ were obtained using

$$\sigma(\partial\varrho/\partial x) = (2\pi/aA)\{\Sigma h^2(F_o-F_c)^2\}^{\frac{1}{2}}$$

(Cruickshank, 1949; Jeffrey & Cruickshank, 1953) and for $\partial^2\varrho/\partial x^2$ using the method of Costain (Booth, 1946). Values of $\sigma(x)$ (actually $\sigma(r)$, referring to coordinates independent of crystallographic direction) were calculated for atoms of each type with the results shown in Table 5.

Table 5. *Standard deviations of coordinates*

| | $\sigma(r)$ (Å) | | | |
|---|---|---|---|---|
| Zone | Cl | N | C | O |
| 0*kl* | 0·0035 | 0·016 | 0·017 | 0·014 |
| *h*0*l* | 0·0045 | 0·016 | 0·020 | 0·019 |
| R.M.S. average | 0·0040 | 0·016 | 0·018 | 0·017 |

(ii) *Bond lengths.*—Standard deviations of bond length were calculated from

$$\sigma^2(l) = \sigma^2(A) + \sigma^2(B) ,$$

Table 6. *Standard deviations of bond length*

| Bond | $\sigma(l)$ (Å) | Bond | $\sigma(l)$ (Å) |
|---|---|---|---|
| N–Cl | 0·016 | $C_1$–$C_2$<br>$C_2$–$C_3$<br>$C_3$–$C_4$ | 0·025 |
| N–$C_1$<br>N–$C_4$ | 0·024 | | |
| $C_1$–$O_1$<br>$C_4$–$O_2$ | 0·025 | | |

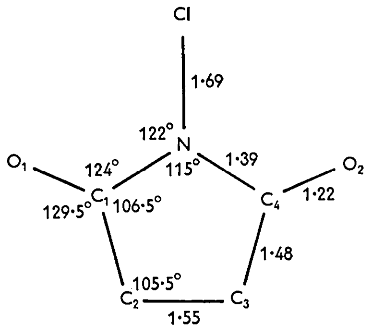

Fig. 3. Final averaged symmetrical dimensions for the N.C.S. molecule.

where *A* and *B* refer to two atoms spaced *l* apart. The results are given in Table 6.

Using the *t* test (Cruickshank & Robertson, 1953) it was found that differences between the three pairs of equivalent bonds in the molecule are not significant, and the average value was taken as the common bond length of each pair.

(iii) *Bond angles*.—Similar calculations for the bond angles (Cruickshank & Robertson, 1953) yielded the values for the standard deviations shown in Table 7.

Table 7. *Standard deviations of bond angles*

| Angle | $\sigma$ | Angle | $\sigma$ |
|---|---|---|---|
| $ClNC_1$, $ClNC_4$ | 1·3° | $NC_1C_2$, $NC_4C_3$ | 1·5° |
| $C_1NC_4$ | 1·5° | $O_1C_1C_2$, $O_2C_4C_3$ | 1·8° |
| $NC_1O_1$, $NC_4O_2$ | 1·8° | $C_1C_2C_3$, $C_4C_3C_2$ | 1·5° |

For chemically equivalent pairs of angles the differences were again not significant and for each pair the average was taken as the final value.

4. *Final dimensions*

The molecular bond lengths and angles are symmetrical and are shown in Fig. 3. Bond lengths are given to the nearest 0·01 Å and angles to the nearest 0·5°.

5. *Planarity*

The method of least squares was used to obtain the equations of the best planes through four chosen groups of atoms. However, in each case the displacements of the atoms from the plane were found by a $\chi^2$ test to represent highly significant aplanarity. A conception of this aplanarity is given by the following: considering molecule *A* of Fig. 4, it lies in the plane

$$-0{\cdot}4732x+0{\cdot}8783y+0{\cdot}0675z=4{\cdot}1588\ ,$$

except that N and $C_2$ are beyond this plane (0·08 and 0·07 Å respectively) and $O_1$ and $C_3$ are in front of it (0·06 Å each). The other four atoms lie in this plane within the limits of significance.

6. *Spatial arrangement*

Fig. 4 shows diagrammatically the projection of the structure on (010). The *b* axis is directed down into the page. The two fully-lined molecules are placed approximately at equal depths just below the $y=0$ plane, and the two dashed ones are at about $\frac{1}{2}b$ with respect

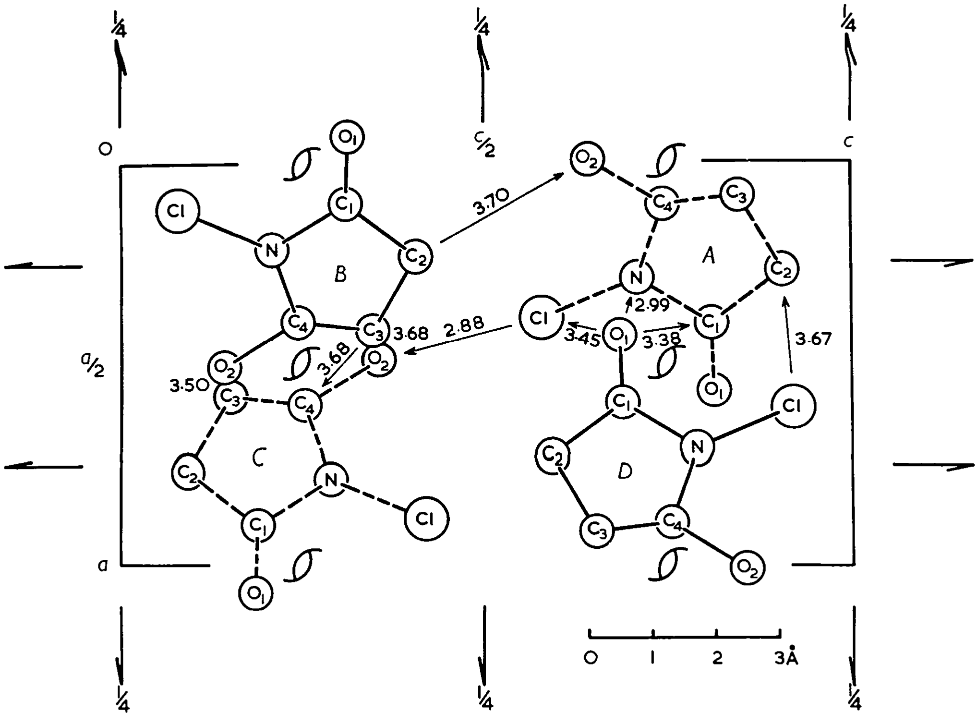

Fig. 4. Diagrammatic projection of the structure on (010). Arrowheads indicate the directions of recession of lines from the observer.

to them. Tilts are suggested with the usual ball and rod representation. All intermolecular approaches of 3·7 Å or less are shown.

## Discussion

When considering the structure described above, it is interesting to compare the results with those of Mason (1956) for succinimide itself.

### 1. *Bond lengths*

The N–Cl bond (1·69 Å) is an acceptable length for a single bond between nitrogen and chlorine. However, the C–N bond (1·39 Å) is considerably shorter than the single-bond value of 1·47 Å suggested by Pauling (1948). More recently suggested values for C–N and C=N are 1·48 and 1·24 Å (Vaughan & Donohue, 1952). These values used with the equation of Pauling (1948, p. 175) indicate a double-bond character of 17%. Such occurrences of $\pi$ bonds in 'single' C–N bonds are found to be common by Cox & Jeffrey (1951) and Brown (1949) lists a large number of short C–N bonds in various compounds. The value found in succinimide by Mason is shorter again (1·27 Å). The $C_1$–$C_2$ bond (1·48 Å) is certainly shorter than the single-bond distance and agrees exactly with the average of Mason's values for this bond in succinimide. Short C–C lengths adjacent to carbonyl groups are commonly observed, e.g., in acetanilide (Brown & Corbridge, 1954) and salicylic acid (Cochran, 1953). Using 1·54 and 1·33 Å for C–C and C=C respectively, one finds that Pauling's equation gives a double-bond character of 12%. Thus we find that the C–O bond should have a double-bond character of 71%, which corresponds to a bond length of 1·23 Å if the bond lengths of C–O and C=O are taken as 1·43 and 1·215 Å (Vaughan & Donohue, 1952; Cochran, 1953). This value agrees well with the observed value of 1·22 Å. The C=O distances found by Mason in succinimide (1·24 and 1·26 Å) are longer than those in N.C.S., in qualitative agreement with his shorter C–N distances. The $C_2$–$C_3$ bond distance of 1·55 Å is close to the accepted single-bond distance and does not require comment. Mason's value for this bond was 1·54 Å.

### 2. *Planarity*

As stated above it is concluded that the N.C.S. molecule in the crystal is significantly aplanar. Wheatley (1953) in discussing the subject of the planarity of molecules in crystals reaches a conclusion which 'suggests that distortions by crystal forces of molecules placed in unsymmetrical surroundings should be quite common'. Thus the observed lack of planarity in N.C.S. is qualitatively to be expected.

### 3. *Intermolecular approaches*

All but two of the intermolecular approaches of Fig. 4 are greater than or equal to the van der Waals' distances of Pauling (1948). These two 'short' approaches are as follows:

(*a*) $(C_2)_A$–$(Cl)_D$ (3·67 Å, predicted 3·8 Å). This is not a great shortening from the expected distance; indeed it is difficult to know what radius to assume for $CH_2$, since it presumably depends on the direction of approach. The methylene value of 2·0 Å was used here.

(*b*) $(Cl)_A$–$(O_2)_C$ (2·88 Å, predicted 3·2 Å). This represents a very close approach for these two atoms, and may mean that electric attraction is present due to charge separation. It is to be expected that both the N–Cl and C=O bonds will display fairly large dipole moments leaving chlorine positive and oxygen negative. This Cl–O 'bond' will link the molecules in zigzag chains parallel to [100] at two different levels above the (010) plane. It can be shown that a (011) cleavage should result and this cleavage, although very indistinct, is the only one observed.

A more detailed description of this work is given by Brown (1957).

I am indebted to Dr S. G. Tomlin and Dr E. H. Medlin for advice and encouragement. Part of this work was done at the University of Western Australia and the facilities and help offered by Prof. C. J. B. Clews are acknowledged. I should like to thank the Commonwealth Scientific and Industrial Research Organization for the award of an Australian Studentship (1955–6) during tenure of which most of the work was done.

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