

of Pauling & Corey (1950, 1951) and Bragg, Kendrew & Perutz (1950) was it shown that many previously proposed configurations, formerly believed reasonable, were incompatible with the results of careful X-ray studies on a number of compounds related to proteins. It is likely that more such studies will suggest the formulation of additional protein structures and also might well rule out some of the structures now under consideration.

References

- ALBRECHT, G. A. & COREY, R. B. (1939). *J. Amer. Chem. Soc.* **61**, 1087.
- BINNIE, W. P. & ROBERTSON, J. M. (1949). *Acta Cryst.* **2**, 180.
- BINNIE, W. P. & ROBERTSON, J. M. (1950). *Acta Cryst.* **3**, 424.
- BOOTH, A. D. (1947). *J. Chem. Phys.* **15**, 415.
- BRAGG, W. L., KENDREW, J. C. & PERUTZ, M. (1951). *Proc. Roy. Soc. A*, **203**, 321.
- CARPENTER, G. B. & DONOHUE, J. (1950). *J. Amer. Chem. Soc.* **72**, 2315.
- COREY, R. B. (1938). *J. Amer. Chem. Soc.* **60**, 1598.
- COREY, R. B. & DONOHUE, J. (1950). *J. Amer. Chem. Soc.* **72**, 2899.
- CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
- DONOHUE, J. (1950). *J. Amer. Chem. Soc.* **72**, 949.
- DONOHUE, J. & TRUEBLOOD, K. N. (1952). *Acta Cryst.* **5**, 414.
- FISCHER, E. (1902). *Ber. deutsch. chem. Ges.* **35**, 2662.
- HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
- HUGHES, E. W. & MOORE, W. J. (1949). *J. Amer. Chem. Soc.* **71**, 2618.
- HUNTER, L. (1946). *Rep. Progr. Chem.* **43**, 153.
- KILPATRICK, J. E., PITZER, K. S. & SPITZER, R. S. (1947). *J. Amer. Chem. Soc.* **69**, 2483.
- KLOTZ, I. M. & URQUHART, J. (1949). *J. Amer. Chem. Soc.* **71**, 1597.
- LEVY, H. A. & COREY, R. B. (1941). *J. Amer. Chem. Soc.* **63**, 2095.
- MORRISON, J. D. & ROBERTSON, J. M. (1949a). *J. Chem. Soc.* p. 987.
- MORRISON, J. D. & ROBERTSON, J. M. (1949b). *J. Chem. Soc.* p. 993.
- NEUBERGER, A. (1948). *Advances in Protein Chemistry*, **4**, 321, 325.
- PAULING, L. (1940). *J. Amer. Chem. Soc.* **62**, 2643.
- PAULING, L. & COREY, R. B. (1950). *J. Amer. Chem. Soc.* **72**, 5349.
- PAULING, L. & COREY, R. B. (1951). *Proc. Nat. Acad. Sci. Wash.* **37**, 235, 241, 251, 256, 261, 272, 282.
- PAULING, L., COREY, R. B. & BRANSON, H. R. (1951). *Proc. Nat. Acad. Sci. Wash.* **37**, 205.
- PITZER, K. S. (1945). *Science*, **101**, 672.
- SHOEMAKER, D. P., DONOHUE, J., SCHOMAKER, V. & COREY, R. B. (1950). *J. Amer. Chem. Soc.* **72**, 2328.
- ZUSSMAN, J. (1951a). *Acta Cryst.* **4**, 72.
- ZUSSMAN, J. (1951b). *Acta Cryst.* **4**, 493.

Acta Cryst. (1952). **5**, 431

The Crystal Structure of Solid Chlorine

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The crystal structure of chlorine is based on space group $D_{2h}^{18}-Cmca$ with four molecules in a unit cell of $a = 6.29$, $b = 4.50$ and $c = 8.21$ Å. The bond distance within the molecule is 2.02 Å and the shortest non-bonded distance is 3.34 Å.

Introduction

The crystal structure of chlorine at -185°C . has been investigated by Keesom & Taconis (1936). They used both single-crystal and powder techniques and arrived at a structure based on the space group D_{2h}^{16} which gave a Cl-Cl distance of 1.82 Å. This is considerably shorter than the value of 2.01 Å found for the bond distance in gaseous chlorine by electron diffraction (Brockway, 1936). The close intermolecular approach of 2.52 Å found by Keesom & Taconis is also quite surprising in the light of the many X-ray investigations of organic molecules containing chlorine. In no case is the Cl-Cl approach under 3.0 Å, even in the presence

of strong steric effects that tend to pull the non-bonded atoms together.

Because of these anomalous distances the structure proposed by Keesom & Taconis is open to some question and the present investigation has been carried out to check the early work.

Experimental

The chlorine used in this investigation was obtained from a lecture bottle, dried with P_2O_5 and distilled once under vacuum. While the chlorine was kept liquid in a dry-ice bath, thin-walled glass tubes of about 0.5 mm. diameter were filled with the liquid and then sealed at both ends with a flame. Single crystals were grown in the tubes and precession photographs were taken, at around -160°C ., according to

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Table 1. *A comparison of calculated and observed structure factors*

<i>hkl</i>	F_c	F_o	<i>hkl</i>	F_c	F_o	<i>hkl</i>	F_c	$ F_o $
002	37.1	38.0	111	65.9	79.7	228	- 0.4	< 25.8
004	-68.0	66.4	112	-73.4	74.6	331	-28.1	21.1
006	-43.7	40.7	113	-18.9	20.3	332	-25.4	25.2
008	10.2	12.9	114	-31.7	26.5	333	9.3	< 9.6
0,0,10	19.0	10.4	115	-41.8	39.0	334	-13.1	< 9.6
020	- 5.8	< 7.9	116	21.4	21.0	335	23.1	9.4
021	-51.6	56.6	117	- 8.5	< 9.6	336	9.4	16.9
022	1.5	< 8.5	118	21.5	18.4	337	5.0	6.4
023	-70.8	64.0	119	13.3	15.5	400	63.0	63.1
024	3.1	< 9.7	200	114	106	402	17.9	17.8
025	0	< 10.2	202	30.3	32.1	404	-38.0	42.4
026	2.2	< 10.5	204	-57.4	62.7	406	-26.7	27.2
027	33.2	38.8	206	-38.8	37.9	408	6.8	8.0
028	- 0.5	< 9.7	208	9.3	10.7	440	-24.8	19.2
029	12.3	9.9	220	- 4.7	< 8.0	441	1.8	< 8.5
040	-38.7	31.5	221	-42.8	39.6	442	- 7.3	< 8.0
041	2.9	< 10.5	222	- 1.3	< 8.5	443	2.6	< 7.2
042	-11.3	10.5	223	-57.9	52.5	444	16.0	10.1
043	4.0	< 10.3	224	2.8	< 9.2	600	34.0	31.4
044	24.9	25.4	225	0	< 9.5	602	9.9	< 11.0
045	0	< 9.7	226	1.9	< 9.6	604	-21.8	25.2
046	17.6	19.4	227	29.4	24.6	606	-15.4	11.4

the method described by Abrahams, Collin, Lipscomb & Reed (1950).

Unit cell and space group

Zero- and first-level precession photographs taken about [100], [010], [110] and [1 $\bar{1}$ 0] with Mo *K* radiation show that the symmetry is orthorhombic. The unit cell dimensions are

$$a = 6.29, b = 4.50 \text{ and } c = 8.21 \text{ \AA.}$$

This cell contains four molecules of chlorine to give a calculated density of 2.03 g.cm.⁻³ compared with the observed value of 2.09 g.cm.⁻³. The systematic absences indicate that the space group is probably D_{2h}^{18} -*Cmca* or C_{2v}^{17} -*Cc2a*. The latter has no center of symmetry.

The unit-cell dimensions and space-group possibilities for chlorine are similar to those of iodine (Harris, Mack & Blake, 1928) and bromine (Vonnegut & Warren, 1936) and one is led to suspect that the structures are similar. The centro-symmetrical space group D_{2h}^{18} -*Cmca* was chosen tentatively and a structure postulated with chlorine atoms in the 8(*f*) positions.

The structure factors calculated for this postulated structure were compared with the observed values from the (0*kl*), (*h*0*l*) and (*hkl*) zones. The observed structure factors were derived from the intensities in the usual way. Repeated calculations finally gave the parameters, $y = 0.130$ and $z = 0.100$. A temperature factor $\exp[-3.3 \sin^2 \theta / \lambda^2]$ was found to be necessary to obtain the best agreement between observed and calculated structure factors. A comparison of observed and calculated structure factors for the above parameters is shown in Table 1. The value of $\sum |F_o| - |F_c| \div \sum |F_o|$ for the observed reflections is 0.117.

Since the structure-factor agreement is good the use of the centrosymmetrical space group is justified.

Discussion of the structure

The structure is quite different from that proposed by Keesom & Taconis and the interatomic distances appear to be much more reasonable. The shortest distance between atoms is $2.02 \pm 0.04 \text{ \AA.}$ * This agrees with the intermolecular distance of 2.01 \AA found by electron diffraction and 1.99 \AA found by spectroscopic measurements (Herzberg, 1950). The molecular packing is rather interesting. Each atom is adjacent to two others at a distance of $3.34 \pm 0.04 \text{ \AA}$ in such a way as to form layers of chlorine molecules in the *ac* plane. Chlorine atoms in adjacent layers never approach closer than $3.69 \pm 0.04 \text{ \AA}$.

The structures of bromine and iodine are both quite similar to that of chlorine. In bromine the shortest intermolecular approach is 3.31 \AA and the other intermolecular distances are all equal to or greater than 3.78 \AA . The iodine structure has a closest approach of 3.54 \AA with the other intermolecular distances equal to or greater than 4.06 \AA . In all three elements the packing of the molecules into planar structures means that the intermolecular forces cannot be cylindrically symmetrical about the molecular axis.

References

- ABRAHAMS, S. C., COLLIN, R. L., LIPSCOMB, W. N. & REED, T. B. (1950). *Rev. Sci. Instrum.* **21**, 396.
 BROCKWAY, L. O. (1936). *Rev. Mod. Phys.* **8**, 231.
 HARRIS, P. M., MACK, E. & BLAKE, F. C. (1928). *J. Amer. Chem. Soc.* **50**, 1583.
 HERZBERG, G. (1950). *Molecular Spectra and Molecular Structure*, Vol. 1. New York: Van Nostrand.
 KEESOM, W. H. & TACONIS, K. W. (1936). *Physica* **3**, 237.
 VONNEGUT, B. & WARREN, B. E. (1936). *J. Amer. Chem. Soc.* **58**, 2459.

* The probable errors assigned to the various distances have been derived from simple considerations of how much individual atoms can be moved without introducing serious discrepancies in the structure-factor agreement.