2·77 Å in AgCl, which would correspond to 2·65 Å for a coordination number four. The ionic bond distance Ag–S is difficult to estimate but the lowest value (Goldschmidt) calculated after correction for the coordination is 2·71–2·76 Å. These bonds can therefore best be described as ionic bonds Ag^+–SCN^- with a reduced bond length due to polarization. The discussion as to the exact nature of the chemical bond will offer the same problems as arise for AgCl.

The larger values obtained in AgSCN (2·89 and 3·00 Å) are due to the packing of the chains in that structure.

10. Ionic conditions in solution

A very careful study of the ionic conditions in solution has been made by Leden & Nilsson (1955). They have found that in a solution which is saturated with $NaAg(SCN)_2.(H_2O)_2$ the complex ions can be described by the formula $Ag_m(SCN)_{2m+2}^{-(m+2)}$, where small values of m dominate but a series of m values are represented. These results make it easier to understand that no discrete $Ag(SCN)_2^-$ ions are formed in the solid state. On the other hand it is difficult to give a structural interpretation of the formula obtained by Leden. The first two members of the series are evidently related according to the equation

$$2Ag(SCN)_4^{3-} \rightleftharpoons Ag_2(SCN)_6^{4-}+2SCN^-.$$

This suggests that two SCN groups are shared between two silver atoms, forming a double sulphur bridge. $NH_4Ag(SCN)_2$ contains, however, only simple sulphur bridges. Other structural suggestions can be made, but first it would be important to know whether the bonding in the solid state is very similar to that in the concentrated aqueous solution. A study of the infra-red spectra of the solid compound as well as the saturated solution has therefore been started in Uppsala.

Finally we wish to thank Prof. Hägg for all the facilities placed at our disposal.

The work has been supported financially by the Swedish Natural Science Research Council, whose support is gratefully acknowledged.

References

Cernatescu, R. (1921). *Bull. Soc. roum. Sci.* **6**, 53.
Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
Foote, H. W. (1903). *Z. phys. Chem.* **46**, 79.
Gössman, A. (1856). *Liebigs Ann.* **100**, 76.
Hägg, G. & Laurent, T. (1946). *J. Sci. Instrum.* **23**, 155.
Jeffery, J. W. (1947). *Nature, Lond.* **159**, 610.
Leden, I. & Nilsson, R. (1955). *Z. Naturforsch.* **10a**, 67.
Lindqvist, I. (1957). *Acta Cryst.* **10**, 29.
Lu, C.-S. (1943). *Rev. Sci. Instrum.* **14**, 331.
Occleshaw, V. J. (1932). *J. Chem. Soc.* **134:2**, 2404.
Saito, Y., Takeuchi, Y. & Pepinsky, R. (1955). *Z. Kristallogr.* **106**, 476.
Waser, J. (1951). *Rev. Sci. Instrum.* **22**, 567.
Zhdanov, G. S. & Zvonkova, Z. V. (1953). *Communications au XIII Congrès international de chimie pure et appliqué, Stockholm*, p. 175.

Acta Cryst. (1957). **10**, 177

The Fraction of Structure Factors Determined in Sign by a Selected Atom or Group of Atoms in a Molecule

By G. A. Sim*

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 30 *October* 1956)

The number of structure factors whose signs are determined by the presence in a molecule of a selected atom, or group of atoms, is calculated in terms of the ratio of the root-mean-square contribution to the structure factors of the atom or atoms to that of the remainder of the molecule, and is expressed as a fraction of the total number of structure factors.

1. Introduction

Since a crystal-structure analysis depending on the presence in a molecule of an atom or atoms, of higher atomic number than the remaining atoms, can lead to a determination of the molecular structure independently of any chemical information, the heavy-atom technique is of very considerable importance; in the future, with the growing availability of improved computing techniques, it may become for the chemist of even more importance as a rival to conventional chemical methods of determining molecular structure. Among recent examples of the use of this method may be mentioned the analyses of *iso*-cryptopleurine methiodide (Fridrichsons & Mathieson, 1954), and of lanostenyl iodoacetate (Curtis, Fridrichsons &

---

* Present address: Chemistry Department, The University, Glasgow W. 2, Scotland.

Mathieson, 1952), where the complete molecular structures were determined by the X-ray method before conventional chemical techniques were successful.

Unfortunately, when faced with the problem of determining the structure of a molecule containing a certain number of carbon and other light atoms, it is not possible to say that a substituent of a certain minimum atomic number will enable a recognizable picture of the molecule to be obtained. Because of the importance of the technique, however, it is desirable to have some sort of indication of what would be a suitable atomic number for a substituent in any given case, and Lipson & Cochran (1953) have suggested that, as a rough guide, the square of the atomic number of the heavy atom should be equal approximately to the sum of the squares of the atomic numbers of the light atoms.

Luzzati (1953) has investigated the relationship between the true electron density and the electron density calculated from the moduli of the observed structure factors with phase angles corresponding to only some of the atoms in the structure. Woolfson (1956), also, has discussed the heavy-atom method, and has shown that a modified Fourier series gives better resolution of the unknown portion of the molecule than does a series using as coefficients the moduli of the observed structure factors with phase angles corresponding to the heavy-atom contributions.

The present paper examines the simpler problem of estimating how many structure factors in a given case can be expected to be determined in sign by the contributions to the structure factors of a heavy atom, or of a group of atoms, forming part of a molecule of known size. Attention is confined to the space group $P\bar{1}$ and to projections of other space groups possessing this symmetry only.

2. The case of one heavy atom and a large number of light atoms in the asymmetric unit

For a centrosymmetric crystal, space group $P\bar{1}$, containing 2 atoms of scattering factor f_H and $2m$ atoms of scattering factor f_L, let the root-mean-square contribution to the structure factors of the heavy atoms be p and that of the group of light atoms be q. Then the ratio of the root-mean-square contributions of each group is

$$r = p/q = f_H/f_L\sqrt{m}\,.$$

The factor r will in general vary with the Bragg angle θ because of the differing relative variation of scattering factors with θ. Over a small range of θ, however, the factor r may be treated as a constant.

Let the contributions of the heavy atom and the group of light atoms to the structure factors F be F_1 and F_2, respectively. For a particular structure factor let the contribution F_1 of the heavy atom be X. Then the probability that the contribution F_2 exceeds X in magnitude and differs from it in sign is given by

$$P = \frac{1}{q\sqrt{(2\pi)}}\int_X^{\infty}\exp\left(-\frac{X^2}{2q^2}\right)dX = \tfrac{1}{2}-\varphi\left(\frac{X}{q}\right),$$

where $\varphi(z)$ is the well-tabulated statistical integral

$$\frac{1}{\sqrt{(2\pi)}}\int_0^z \exp\left(-\tfrac{1}{2}t^2\right)dt\,.$$

Accordingly, the probability that F_1 determines the sign of this structure factor is $1-P$, i.e. $\frac{1}{2}+\varphi(X/q)$. The number of F_1 values which make a contribution between X and $X+dX$ to the structure factors, when expressed as a fraction of the total number of structure factors, is given by

$$n = dX/\pi\sqrt{(4f_H^2-X^2)}\,.$$

Therefore the number of structure factors which have their signs determined by the contributions of the heavy atom is, expressed as a fraction,

$$N_1 = \frac{2}{\pi}\int_0^{2f_H}\frac{\frac{1}{2}+\varphi(X/q)}{\sqrt{(4f_H^2-X^2)}}dX\,.$$

On making the substitution $y = X/2f_H$ there is obtained

$$N_1 = \frac{1}{2}+\frac{2}{\pi}\int_0^1\frac{\varphi(2f_H y/q)}{\sqrt{(1-y^2)}}dy\,.$$

Since $q = \sqrt{(2m)}\,.\,f_L$ it follows that

$$N_1 = \frac{1}{2}+\frac{2}{\pi}\int_0^1\frac{\varphi(\sqrt{2}\,.\,ry)}{\sqrt{(1-y^2)}}dy$$

$$= \frac{1}{2}+\frac{2}{\pi}\cdot\frac{1}{\sqrt{(2\pi)}}\int_{y=0}^{1}\int_{t=0}^{\sqrt{2}.ry}\frac{\exp\left(-\frac{1}{2}t^2\right)}{\sqrt{(1-y^2)}}dy\,dt\,.$$

By expressing $\exp\left(-\frac{1}{2}t^2\right)$ as an infinite series, integrating with respect to t, substituting $y = \sin\alpha$, and integrating with respect to α, there is obtained

$$N_1 = \frac{1}{2}+\frac{2}{\pi\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-1)^n}{n!\,(2n+1)} \times\frac{2n}{(2n+1)}\cdot\frac{(2n-2)}{(2n-1)}\cdots\frac{2}{3}r^{2n+1}\,.$$

Evaluating the first few coefficients, we obtain

$$N_1 = \tfrac{1}{2}+0{\cdot}3591 \times\left(r-0{\cdot}2222r^3+0{\cdot}0533r^5-0{\cdot}0109r^7+0{\cdot}0019r^9\ldots\right).$$

For $r > 1$ the rate of convergence of this series is not very rapid, and an alternative method of evaluating N_1 in these circumstances is convenient. This is done as follows: in the equation

$$N_1 = \frac{2}{\pi}\int_0^{2f_H}\frac{\frac{1}{2}+\varphi(X/q)}{\sqrt{(4f_H^2-X^2)}}dX$$

substitute $\sin\alpha = X/2f_H$, and obtain

$$N_1 = \frac{2}{\pi}\int_0^{\pi/2}\left\{\tfrac{1}{2}+\varphi(\sqrt{2}\,.\,r\sin\alpha)\right\}d\alpha\,.$$

This expression may be integrated numerically.

Values of N_1 for a range of values of r are listed in Table 1.

Table 1. *Values of N_1 and N_∞ as a function of r*

The fraction of structure factors determined in sign by the presence of a heavy atom (N_1) or of a group of atoms (N_∞), expressed in terms of the ratio of the root-mean-square contribution of the atom or atoms to that of the remainder of the molecule (r)

r	N_1	N_∞	r	N_1	N_∞
0·0	0·500	0·500	1·6	0·877	0·822
0·2	0·571	0·563	1·8	0·893	0·839
0·4	0·639	0·621	2·0	0·905	0·852
0·6	0·700	0·672	2·5	0·926	0·879
0·8	0·752	0·715	3·0	0·939	0·898
1·0	0·795	0·750	3·5	0·948	0·912
1·2	0·830	0·779	4·0	0·955	0·922
1·4	0·856	0·803			

3. The case of two large groups of atoms

Let the atoms in the unit cell be divided into two groups A and B, and let the contributions of these groups to the structure factors be F_1 and F_2, respectively. If the root-mean-square contributions of A and B are p and q, respectively, then the ratio r is

$$r = p/q = (\Sigma f_A^2/\Sigma f_B^2)^{\frac{1}{2}} .$$

The factor r will, as in the previous case, generally vary with θ.

For a particular structure factor let the contribution F_1 be X. Then the probability that F_2 exceeds X in magnitude and differs from it in sign is $\frac{1}{2}-\varphi(X/q)$. The number, expressed as a fraction, of F_1 values which make a contribution between X and $X+dX$ to the structure factors is

$$n = \frac{1}{p\sqrt{(2\pi)}} \exp\,(-X^2/2p^2)\,dX \,,$$

so that the number of structure factors which have their signs determined by the contributions to the structure factors of the atoms in group A, when expressed as a fraction of the total number of structure factors, is given by

$$N_\infty = \frac{1}{p\sqrt{(2\pi)}} \int_{-\infty}^{+\infty} \left\{\frac{1}{2} + \varphi\left(\frac{X}{q}\right)\right\} \exp\left(-\frac{X^2}{2p^2}\right) dX \,.$$

On making the substitution $y = X/p$, the expression becomes

$$N_\infty = \frac{2}{\sqrt{(2\pi)}} \int_0^\infty \{\tfrac{1}{2}+\varphi(ry)\} \exp\,(-\tfrac{1}{2}y^2)\,dy \,.$$

This has been integrated numerically for a range of values of r and the results are listed in Table 1.

4. Discussion

The table of values of N_1 and N_∞ enables the number of structure factors whose signs are determined by a heavy atom or by a group of atoms to be evaluated readily. As the factor r is a function of θ it is necessary either to divide the structure factors into groups, in each of which r may be treated as a constant, and to evaluate N in each of these ranges of θ, or to use some average value of r applicable to the whole range of θ values.

The structure factors of the ($h0l$) zone of 11-amino-undecanoic acid hydrobromide hemihydrate (Sim, 1955) have been examined. As the water molecule occurs in a special position it has been omitted from consideration. An average value of r, the ratio of the root-mean-square contributions of the bromine atom and the 11-amino-undecanoic acid molecule, was derived by assuming that in the range $\sin\theta = 0-0{\cdot}9$, $\bar{f}_{\text{Br}}/\bar{f}_{\text{C}}$ is about 40/6 and that all the light atoms, apart from hydrogen, can be treated as carbon atoms. The value of r in this case is about 1·78, corresponding to a value of N_1 of 0·891. A survey of the 340 calculated values of the ($h0l$) structure factors showed that only in 32 cases do the combined contributions of the atoms in the 11-amino-undecanoic acid molecule exceed and differ in sign from the corresponding contributions of the bromine atom. The bromine atom, therefore, determines the signs of 0·906 of the ($h0l$) structure factors, a value in satisfactory agreement with the value of N_1 deduced above.

One point that emerges from the analysis is that if a choice of several non-isomorphous heavy-atom derivatives of a given molecule is available, it could be argued that the compound containing the substituent of highest atomic number is not necessarily the most suitable for application of the heavy-atom method, for beyond about $r = 1{\cdot}5$ the number of structure factors whose signs are determined by the heavy atom changes only relatively slowly. The advantage of the small increase in the number of sign-determined structure factors obtained by using the substituent of highest atomic number could be more than offset by the increased diffraction effects caused by that substituent, and the decreased accuracy of the F_o values due to absorption.

I would like to express my gratitude to Dr M. M. Woolfson for his advice and considerable aid with the algebra, and to Prof. N. F. Mott and Dr W. H. Taylor for provision of facilities. I am also indebted to the Ramsay Memorial Fellowships Trust for financial support.

References

Curtis, R. G., Fridrichsons, J. & Mathieson, A. McL. (1952). *Nature, Lond.* **170**, 321.

Fridrichsons, J. & Mathieson, A. McL. (1954). *Nature, Lond.* **173**, 732.

Lipson, H. & Cochran, W. (1953). *The Determination of Crystal Structures.* London: Bell.

Luzzati, V. (1953). *Acta Cryst.* **6**, 142.

Sim, G. A. (1955). *Acta Cryst.* **8**, 833.

Woolfson, M. M. (1956). *Acta Cryst.* **9**, 804.