

The Location of Light-Atom Positions in Crystal Structures

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(Received 31 January 1975; accepted 17 March 1975)

A procedure is described for the location of light atoms, particularly hydrogen, by means of a weighted difference synthesis, in which the weight is taken to be the scattering factor of the light atom which is sought. This convolution technique is illustrated in applications to the structures of an amine hydrochloride, $C_{20}H_{27}N.HCl$, and a complex borohydride, $Mg(B_6H_9)_2 \cdot 2C_4H_8O$.

Introduction

In many crystal structure determinations, the location of light atoms, particularly hydrogen atoms, has been a difficult problem. Difference Fourier syntheses which are employed for this purpose often show such high backgrounds that the light-atom peaks are obscured by 'noise'. This work reports the location of hydrogen atoms in the structures of *N*-*n*-butyl-2,3-dimethyl-1,4-indo-(3',4'-pyrrolidino)-1,4-dihydronaphthalene hydrochloride, $C_{20}H_{27}N.HCl$ (Argos & Clayton, 1973) and magnesium bis(nonahydrohexaborate)-bis(tetrahydrofuran), $Mg(B_6H_9)_2 \cdot (C_4H_8O)_2$ (Denton, Clayton & Shore, 1974) by means of a weighted difference synthesis first described by Smith, Zingaro & Meyers (1971).

Theory

The problem of the separation of a signal from the 'noise' which accompanies it is one that has been described in its application to radar (Woodward, 1953). In general terms, a signal $y(t)$ is observed (as a function of time) which is composed of noise, $n(t)$, and a true signal, $u(t)$:

$$y(t) = n(t) + u(t).$$

If it is assumed that the transmitted signal is known, it is possible to improve the signal-to-noise ratio by means of the following convolution integral where N_0 is the mean noise per unit bandwidth,

$$q(\tau) = \frac{2}{N_0} \int_T y(t)u(t-\tau)dt,$$

which is assumed to be Gaussian, and T is the time of observation, long compared to the time in which $u(\tau)$

is appreciable. This integration may be carried out provided that the functional form of $u(t)$ is known.

The *a posteriori* probability that the signal occurs in the interval of time $d\tau$ is given by

$$P_y(\tau)d\tau = kp(\tau) \exp \left[-\frac{1}{N_0} \int_T u^2(t-\tau)dt \right] \\ \times \exp \left[\frac{2}{N_0} \int_T y(t)u(t-\tau)dt \right] d\tau$$

where k is a normalization constant and $p(\tau)d\tau$ is the *a priori* probability that the true signal will occur in $(\tau, \tau+d\tau)$.

The translation of the above problem for its use in the location of light atoms is as follows. The unweighted difference synthesis corresponds to $y(t)$; the electron density of the light atom, with scattering factor, f_j , to $u(t-\tau)$. The function $u(t-\tau)$ may be replaced by

$$\varrho_j = \frac{1}{V} \sum_h \sum_k \sum_l f_j \exp [-2\pi i \{h(x-x_j) \\ + k(y-y_j) + l(z-z_j)\}]$$

and the function $y(t)$ by

$$\Delta q = \frac{1}{V} \sum_h \sum_k \sum_l (F_o - F_c) \exp [-2\pi i (hx + ky + lz)]$$

and the convolution integral over the unit cell (which is large compared to the dimensions of ϱ_j) by

$$\Delta \varrho_j = \frac{1}{V} \sum_h \sum_k \sum_l f_j(hkl) (F_o - F_c) \\ \times \exp [-2\pi i (hx_j + ky_j + lz_j)].$$

This function, $\Delta\rho_j$, is simply a weighted difference synthesis.

The synthesis suggested above seems intuitively appealing since it weights the various terms in the difference synthesis in accordance with the maximum contribution that can be made by the light atom which is sought. The central limit theorem makes it seem likely that the 'noise' in the usual difference synthesis is close to Gaussian. The enhancement of spurious peaks may be overcome in the usual way, *i.e.* by a judicious prejudice represented by the replacement of $p(\tau)$ in the expression for $P_y(\tau)$ by the *a priori* knowledge of the approximate expected positions of the light atoms in order to have a reasonable structure. It might be expected that non-Gaussian errors, such as systematic errors in $|F_o|$, might be emphasized in the weighted sum.

Results

The framework of $C_{20}H_{27}N.HCl$ is shown in Fig. 1. Heavy atoms were located in the usual manner from *E*-map constructs and difference syntheses. Location of hydrogen-atom positions posed a problem. An unweighted difference synthesis showed positive electron densities over broad areas in which hydrogen atoms might be expected to be located. However, no reasonable positions could be assigned with confidence. In particular, nine hydrogens associated with the three terminal methyl groups in the structure were particularly diffuse. Several of the most intense peaks could be identified as residual 'ripple' from the chlorine position. A difference synthesis was constructed in which $f_H(\bar{h}\bar{k}\bar{l})$ was used as the weighting function. The diffuse regions of positive electron density became reasonably sharp peaks at 19 of the predicted hydrogen positions. Residual 'ripple' in the vicinity of the chlorine position was noticeably reduced. Three clearly defined toroids of electron density appeared at the three terminal methyl positions. This was interpreted as free rotation of the methyl groups about their C-C axes.

The framework structures of $B_6H_5^-$ and tetrahydrofuran (THF) are shown in Fig. 2. THF is coordinated to Mg through oxygen while $B_6H_5^-$ is bonded to Mg through a three-center bond.

An unweighted difference synthesis was constructed once all heavy atoms had been found. This map was examined by computer-search procedures using the program *PEKPIK* (*X-RAY System*, 1972). The 95 largest unique peaks within a sphere of resolution 0.75 Å radius were examined. The majority of these peaks were identifiable as heavy-atom 'ripple'. Few were in chemically reasonable positions; none could be assigned with confidence.

A weighted difference synthesis was constructed and examined by means of program *PEKPIK*. The 15 most intense peaks were at chemically reasonable positions. Two of the four next most intense peaks were at reasonable positions while the other two were

at bridging positions between B(2)–B(3) and B(5)–B(6). The former bridging position was not expected to be occupied owing to Mg–B bonding while the latter had a short B–B bond distance characteristic of non-hydrogen bridged B–B bonds. Nonetheless, the possibility of fractional occupancy in one or both positions was not immediately discounted owing to the observed fluxional nature of this anion in solution. It is conceivable that tautomeric $B_6H_5^-$ structures might be 'frozen' into the crystalline solid.

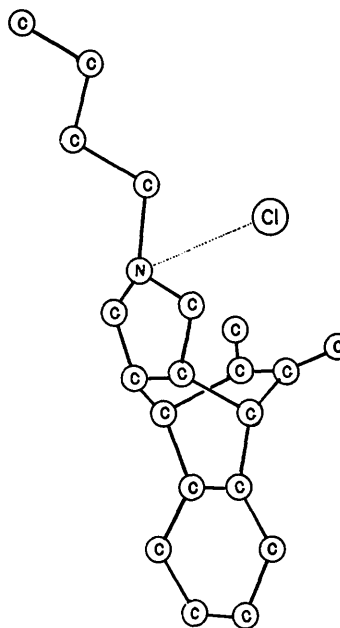


Fig. 1. The structure of $C_{20}H_{27}N.HCl$.

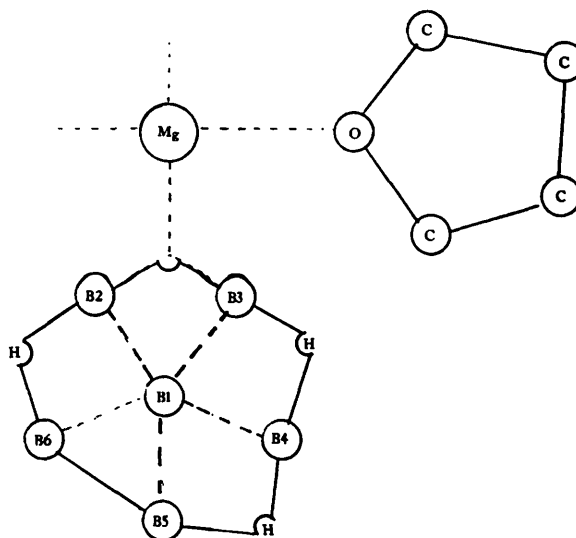


Fig. 2. Representation of $Mg(B_6H_5)_2(THF)_2$ topography. The diagram does not imply bonding or structural details.

Therefore, a second series of difference syntheses were prepared in which the eight THF hydrogens and five terminal $B_6H_5^-$ hydrogens were included in the sums. The omitted terminal hydrogen [H(4)] had shown a tendency to diverge from its assigned position. Again, program *PEKPIK* failed to locate any reasonable hydrogen positions from the unweighted synthesis. The most intense peak on the weighted synthesis map coincided with the B(5) location. Three of the four next most intense peaks were identical to three previously found bridging hydrogen positions.* Careful examination of the weighted difference map showed no evidence of bridging hydrogen at positions 23 or 56. A final weighted difference synthesis was examined. The largest remaining residuals could be identified as heavy-atom 'ripple' or 'ripple' at points midway between heavy atoms.

* A peak was found for the H(4) terminal hydrogen position which moved but little during subsequent refinements.

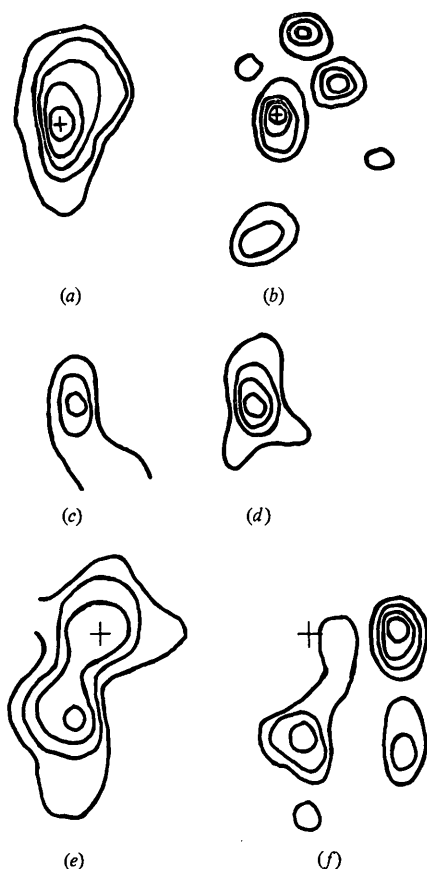


Fig. 3. Comparison of weighted and unweighted difference syntheses for $Mg(B_6H_5)_2(THF)_2$. (a) Weighted, (b) unweighted sections through H(26) position. (c) Weighted, (d) unweighted sections of heavy-atom 'ripple'. (e) Weighted, (f) unweighted sections through H(45) and B(5) positions. (Contour divisions are arbitrary.)

Discussion

Fig. 3 consists of representative electron-density contour sections from the second series of difference syntheses for $Mg(B_6H_5)_2(THF)_2$ as described above. The scale factor of the weighted difference synthesis has been adjusted by the factor $\langle f_H^{-1} \rangle$. The mean was calculated over all reflections in the octant used for Fourier synthesis including 'unobserved' reflections, but excluding systematic absences. Thus, the arbitrary contour divisions used for comparison should be approximately on the same scale.

Figs. 3(a) and 3(b) are, respectively, weighted and unweighted sections through the H(26) bridging position. The correct position is visible on the unweighted map, but is obscured by a three-dimensional cluster of peaks of similar size and magnitude. This peak-clustering effect is responsible for the failure of computer-search procedures. Sufficient resolution between peaks is necessary to enable the search procedures to converge to a single peak. The weighted synthesis shows one peak with shoulders retaining the general contours of the unweighted cluster. This is in accord with the predicted enhancement of the signal to noise.

Figs. 3(c) and 3(d) represent a 'ripple' associated with the magnesium position. The peak shown in Fig. 3(d) was, in fact, the largest single peak found on the unweighted difference synthesis. It remained prominent on the weighted synthesis, but had only half the peak height of the four hydrogens found on the map. A reduction of heavy-atom 'ripple' was a general feature of all weighted synthesis maps examined for the two structures.

The final two figures, 3(e) and 3(f), were the most interesting pair examined. The H(45) bridging hydrogen was resolved in a fashion identical to that described for H(26) in Figs. 3(a) and 3(b). However, the residual peak at the B(5) position was also enhanced in comparison to the background and became the most intense peak on the weighted map. A possible interpretation might be that the net effect of previous least-squares refinement was to alter the anisotropic temperature coefficients sufficiently to average the scattering power of the boron atom over both the boron and hydrogen positions. The disappearance of this residual peak from subsequent difference syntheses supports this hypothesis.

A cautionary note should be sounded concerning the application of this weighting scheme. *Ex post facto* examination of unweighted difference syntheses showed positive electron densities at, or close to, positions found on weighted difference syntheses. There is undoubtedly a limit beyond which no convolution can recover a poor signal. It should be emphasized that non-Gaussian errors, especially for low-angle data, may not be reduced in comparison to the desired signal. On a positive note, the first structure discussed had a known problem involving proper estimation of background values and a moderately large absorption

correction. Reasonable estimations of systematic effects seem to be adequate for the successful application of this method of locating light atoms. In its original application to *n*-propylarsonic acid, (Smith, Zingaro & Meyers, 1971) a computer program was modified to allow the calculation of weighted difference syntheses, but a mistake was made in the programming. This may be responsible for the lack of success of the method in that case.

We wish to thank the Robert A. Welch Foundation, Houston, Texas, for financial support during the development of the method.

References

- ARGOS, P. & CLAYTON, R. (1973). *Acta Cryst.* B29, 910–913.
 DENTON, D. L., CLAYTON, W. R. & SHORE, S. G. (1974). Submitted for publication.
 SMITH, M. R., ZINGARO, R. A. & MEYERS, E. A. (1971). *J. Organometal. Chem.* 27, 341–347.
 WOODWARD, P. M. (1953). *Probability and Information Theory with Applications to Radar*. New York: McGraw-Hill.
 X-RAY System (1972). Technical Report TR-192 of the Computer Science Center, Univ. of Maryland. Version of June 1972.

Acta Cryst. (1975). A31, 746

Calculated Images of Crystal Lattices by Axial Illumination with 1 MeV Electrons

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(Received 11 February 1975; accepted 28 March 1975)

Multibeam (001) electron-microscope lattice-image ($N=3,5$) properties are studied when axial illumination is used. Numerical calculations were particularly applied to (001)-oriented gold foils observed with 1 MeV electrons. Conditions for obtaining images showing no artificial periodicity are determined. It is shown that in a particular range of thickness (40–60 Å for three-beam interference or 70–120 Å for five-beam interference) and with the proper defocusing distance high-contrast images would be obtained: the exact projected atomic positions are directly visible on these images. The influence of departure from exact symmetry conditions, and of large variation of the lattice parameter, are also studied. These calculations suggest that it would be possible to observe direct lattice images of metals and to study their defects with actual 1 MeV electron microscopes.

1. Introduction

Lattice fringe images are commonly produced by interference of two beams either with axial illumination or with a tilted illumination. As demonstrated by several authors (Dowell, 1963; Cockayne, Parsons & Hoelke, 1971), these procedures give a displacement of the fringes relative to the atomic position, which is a function of several parameters (spatial frequency, specimen thickness of Bragg deviation). Therefore this procedure is not suitable to obtain an image which reproduces the projected potential, and direct correlation between the object and the image intensity is not valid.

On the other hand for weak phase objects, observed with axial illumination and symmetrical diffraction conditions the transfer between phase changes in the object and intensity in the image is linear and there is no lateral shift apart from contrast inversion (Hanszen, 1971). In contrast, in a strong phase object (such as a crystal) the transfer is no longer linear. Nevertheless,

the lateral shift is still zero when symmetrical diffraction conditions are concerned (Laue position) and the image can be interpreted in terms of the crystal structure as shown by Cowley & Iijima (1972). These properties were applied extensively to study large unit cells of complex oxide structure with 100 keV electrons (Allpress & Sanders, 1973). But because of the spherical aberration of the objective lens, the maximum scattering angle is limited. The desirable cut-off angle and optimum defocus appear to be given by Scherzer's (1949) conditions. With the available 100 keV electron microscope the optimum resolution determined by these conditions is limited to approximately 3 Å: in complex oxides where distances between metal atom columns larger than 3.8 Å are clearly resolved this limit is nearly attained.

The use of 1 MeV electrons seems to be a powerful means to increase the resolution: the optimum resolution given by Scherzer's conditions is of the order of 1.2 Å with actual objective lenses so that imaging of atomic columns closer than 3 Å is possible. In partic-