

The Use of Low Temperatures in Accurate Structure Analysis*

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The standard errors in a structure analysis are decreased both by a reduction in the ΔF 's and by an increase in the curvatures of the electron density at peak centers. At low temperatures the peak curvatures are increased as a consequence of reduced thermal vibrations. It is possible that the standard errors in many organic structures could be reduced by a factor of two by recording diffraction data at low temperatures.

Introduction

In an investigation of the crystal structure of chlorine trifluoride (Burbank & Bensey, 1952) the standard errors in the parameters were found to be comparable in magnitude with those in accurately determined organic structures. In the notation of Cruickshank (1949*a*) the errors were evaluated from expressions of the type

$$\sigma(x) = \sigma(A_h)/A_{hh}, \quad (1)$$

where

$$\sigma(A_h) = \frac{2\pi}{aV} \left\{ \sum_3 h^2 (\Delta F)^2 \right\}^{\frac{1}{2}}$$

and

$$A_{hh} = -\partial^2 \rho / \partial x^2,$$

which are appropriate to a centrosymmetric structure based on an orthorhombic lattice. Structure factors were calculated with Hartree scattering factors modified by an isotropic temperature correction of $B = 1.68 \text{ \AA}^2$. Peak maxima were located by the method of Shoemaker, Donohue, Schomaker & Corey (1950) in which the 27 points in a $3 \times 3 \times 3$ grid are fitted by least squares to a 10-parameter Gaussian function. The peak electron densities and curvatures at peak density were obtained directly from the Gaussian function. The following numerical values entered into equation (1) and similar expressions:

$$\sigma(A_h) = 1.362, \quad \sigma(A_k) = 1.097, \quad \sigma(A_l) = 1.425 \text{ e. \AA}^{-4}.$$

	A_{hh}	A_{kk}	A_{ll}	
Cl	828.3	—	803.0	e. \AA^{-5}
F ₁	258.9	—	248.0	e. \AA^{-5}
F ₂	219.4	271.7	179.1	e. \AA^{-5}

The quantities $\sigma(A_h)$, $\sigma(A_k)$ and $\sigma(A_l)$ are more than five times as large as the values quoted by Cruickshank (1949*a*) for dibenzyl. This presumably arises from greater experimental difficulties in the present case, combined with the use of less satis-

factory atomic scattering factors. However, the effect on the standard errors is compensated for by the large values obtained for A_{hh} , A_{kk} and A_{ll} . The curvatures follow from the high densities at peak centers:

Cl	$\rho = 58.44 \text{ e. \AA}^{-3}$
F ₁	$\rho = 20.12 \text{ e. \AA}^{-3}$
F ₂	$\rho = 19.07 \text{ e. \AA}^{-3}$

The high electron densities are attributed to a reduction in thermal vibrations under the experimental conditions at -120°C .

Variation of peak densities and curvatures with temperature

The chlorine trifluoride results were better than anticipated and raised the question of how much variation in peak densities and curvatures is to be expected as a function of temperature. It is instructive to calculate peak densities for a hypothetical crystal using isotropic temperature corrections. We have used a cubic crystal with a single atom at the origin and a cell edge of 3.6 \AA (twice the van der Waals radius of chlorine). We assume that data are recorded out to one reciprocal lattice unit, i.e. $\sin \theta = 0.5$, with $\text{Mo } K\alpha$, $\lambda = 0.7107 \text{ \AA}$. The Fourier series is evaluated only

Table 1. Peak densities for various temperature corrections

	$B=0 \text{ \AA}^2$	$B=2 \text{ \AA}^2$	$B=4 \text{ \AA}^2$	
Cl	80.3	49.0	32.1	e. \AA^{-3}
	49.3	33.4	24.5	e. \AA^{-2}
F	30.8	19.6	13.5	e. \AA^{-3}
	20.4	14.5	11.2	e. \AA^{-2}
O	26.2	16.8	11.5	e. \AA^{-3}
	17.5	12.5	9.7	e. \AA^{-2}
N	22.3	14.0	9.5	e. \AA^{-3}
	14.6	10.3	7.8	e. \AA^{-2}
C	19.3	11.9	7.8	e. \AA^{-3}
	12.2	8.4	6.3	e. \AA^{-2}

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at the origin so that all trigonometric factors are unity and the coefficients are the atomic scattering factors with appropriate multiplicities. Using Hartree scattering factors and successive temperature corrections of $B = 0, 2$ and 4 \AA^2 the peak densities were evaluated for both the three- and two-dimensional cases for chlorine, fluorine, oxygen, nitrogen and carbon. The results are listed in Table 1.

A survey of the peak densities in a number of published structures in which Hartree factors with temperature corrections were used for structure-factor calculation indicates that our crude procedure gives an adequate representation of the peak densities to be expected.

To evaluate the curvatures we assume that a peak shape can be represented by

$$\rho(r) = A \exp[-pr^2],$$

where

$$\begin{aligned} A &= N(p/\pi)^{\frac{3}{2}} \text{ in three dimensions,} \\ A &= N(p/\pi) \text{ in two dimensions,} \\ p &\text{ is a constant and } N \text{ is the atomic number.} \end{aligned}$$

Then at $r = 0$ the curvature is

$$\partial^2 \rho / \partial r^2 = -2pA. \quad (2)$$

Although the above assumption is not generally valid (Cruickshank, 1949a) it will suffice for obtaining an idea of how the curvatures vary as a function of the temperature correction. Applying equation (2) to the data of Table 1 we obtain the values listed in Table 2.

Table 2. Curvatures for various temperature corrections

	$B=0 \text{ \AA}^2$	$B=2 \text{ \AA}^2$	$B=4 \text{ \AA}^2$	
Cl	-1420	-623	-308	$e.\text{\AA}^{-5}$
	-898	-412	-222	$e.\text{\AA}^{-4}$
F	-439	-207	-111	$e.\text{\AA}^{-5}$
	-290	-147	-88	$e.\text{\AA}^{-4}$
O	-363	-173	-92	$e.\text{\AA}^{-5}$
	-240	-123	-74	$e.\text{\AA}^{-4}$
N	-303	-140	-73	$e.\text{\AA}^{-5}$
	-191	-95	-55	$e.\text{\AA}^{-4}$
C	-264	-119	-58	$e.\text{\AA}^{-5}$
	-156	-74	-42	$e.\text{\AA}^{-4}$

Discussion

It can be seen from Table 2 that when the temperature factor is reduced from 4 \AA^2 to 2 \AA^2 the curvatures

increase by about 100% for all atoms in the three-dimensional case. It appears that many organic structures which have been studied at room temperature correspond to a temperature factor of about 4 \AA^2 . It seems likely that the curvatures for carbon, nitrogen and oxygen could be doubled in many structures by recording data at low temperatures. The effect is apparent in the structure of N_2O_5 (Grison, 1950) where at -60°C . the peak densities for nitrogen and oxygen are greater than 17 and $21 e.\text{\AA}^{-3}$ respectively.

Cruickshank (1949b) has stated that 'It would be very desirable to pronounce with confidence on bond-length differences of 0.010 \AA ; for this the coordinate standard deviations would have to be 0.0025 \AA or less.' He estimated that a standard error of 0.0074 \AA in the dibenzyl analysis might be reduced some 25% to 0.0056 \AA by using weighted Fourier syntheses. He concluded that attention would still have to be directed towards further reduction of the ΔF 's.

If an error of 0.0056 \AA could be cut in two by low-temperature experimentation Cruickshank's objective would be within practical reach. Use of the simple low-temperature apparatus described by Post, Schwartz & Fankuchen (1951) would entail a modest effort as compared with the procedures required for further reduction of the ΔF 's. Such an apparatus can be arranged to operate for months on end with a minimum of attention (Burbank & Bensey, 1952). Thus, in the exceptional case where one wishes to reduce the uncertainty caused by random errors to an absolute minimum, it seems reasonable to consider the use of low temperatures. This suggestion is of necessity based on the assumption that other things remain equal; in particular that the atomic scattering factors do not become impossibly anisotropic as the temperature is reduced.

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