anormales correspondent à des effets physiques réels ou à un manque de précision dans les coordonnées atomiques. Nous étudions simultanément la structure du dérivé bromé de l'acétamide, isomorphe du dérivé chloré, afin de préciser l'influence du halogène sur le comportement de la molécule.

Nous remercions Monsieur le Professeur Brasseur pour l'intérêt qu'il a porté à ces recherches, Monsieur Toussaint pour les précieux conseils qu'il nous a donnés.

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Further least-squares refinement of the crystal structure of sodium nitrite.* By G. B. Carpenter,

Metcalf Research Laboratory, Brown University, Providence 12, *R.I., U.S.A.*

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Recently Carpenter (1952; hereafter referred to as C) and Truter (1954; hereafter referred to as T) independently have re-examined the crystal structure of $NaNO_2$, and have obtained results in good agreement with one another (except for the calculated errors) and similar to the early results of Ziegler (1931). The present note reports the continuation of the least-squares refinement of C, wherein (*a*) more data are included, (*b*) the scale and temperature-factor parameters are allowed to vary simultaneously with the atomic coordinates, and (*c*) an improved weighting scheme is employed. In addition, the effects of several factors on the standard deviations of atomic positions are examined.

New multiple-film Weissenberg photographs were prepared by Mr Lincoln Ekstrom from a crystal rotating about the *c* axis (notation of C). The structure-factor magnitudes of C were combined with those from the new films and were supplemented by 17 values used in T (Truter, private communication) to give values for a total of 83 reflections.†

The combined structure factors were used in two further cycles of least squares refinement of atomic coordinates and scale and temperature-factor parameters. The temperature factor was taken to be $\exp(-\alpha h^2-\beta k^2-\gamma l^2)$, as in C. The weight w of a structure factor was calculated from the formula (Lee, unpublished) $\sqrt{(p/w)} = 0{\cdot}00883 + 0{\cdot}0102|U|_o + 0{\cdot}00430 \sin\theta + 0{\cdot}0350|U|_o \sin\theta$, where $|U|_o$ is the observed unitary structure-factor magnitude and p is the number of independent measurements. This formula resulted from empirical examination of the errors in other non-centrosymmetric structures determined from visual intensity values. These weights do not differ radically from those used in C, but they are believed to be better.

Coordinates, dimensions, standard deviations and discrepancy factors from several sources are summarized in Table 1. The final coordinates and dimensions (C′) lie between those of C and those of T, but are believed to be better than either. The standard deviations σ from the least-squares calculations were calculated from the usual expression (Shoemaker, Donohue, Schomaker & Corey, 1950). In the calculation C′, the covariance between Z_N and Y_O is negligible, unlike that in the 'modified Fourier method' of T.

Table 1. *Atomic coordinates, dimensions, standard deviations and discrepancy factors for* $NaNO_2$

Quantity	Z*	T*	C*	C′*
Z_{Na}/c	0·583	0·5852	0·5870	0·5862
Z_N/c	0·083	0·1217	0·1180	0·1188
Y_O/b	0·194	0·1946	0·1941	0·1944
N–O (Å)	1·13	1·247	1·233	1·236
O–N–O (°)	132	114·2	115·7	115·4
$\sigma(Z_{Na})$ (Å)	—	0·01	0·0068	0·0106
$\sigma(Z_N)$ (Å)	—	0·03	0·0147	0·0212
$\sigma(Y_O)$ (Å)	—	0·018	0·0084	0·0100
σ(N–O) (Å)	—	0·035	(0·017)	0·014
σ(O–N–O) (°)	—	4	—	1·73
R	—	0·154	0·110	0·123

* Z: Ziegler (1931).

T: Truter (1954 and private communication) from the 'modified Fourier method'.

C: Carpenter (1952) but with errors in standard deviations corrected. The value in parentheses for σ(N–O) was calculated by Truter from the coordinate standard deviations above it in column C.

C′: The present least-squares refinement.

Detailed examination of these calculations shows that the increases in the standard deviations on going from C to C′ result chiefly from the larger errors present in the extra reflections included in C′. The corresponding increase of the discrepancy factor indicates this also. This means that the weighting system failed properly to de-emphasize these reflections. Since, however, most of the values taken from T occur in this group, and the weighting system need not apply as well to values determined in another laboratory by different techniques, this is not unreasonable. The lesser standard deviations in C′ compared to T appear to result from the smaller errors in the former.

The effect on atomic coordinates of ignoring changes in scale and temperature-factor parameters was large in the first cycle of the present refinement (coordinate changes respectively −0·0023, −0·0022 and 0·0055 Å instead of −0·0029, 0·0040 and 0·0000 Å), where these

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† Copies of the final list of structure factors may be obtained on request to the author.

parameters changed appreciably from those used in C because of the inclusion of more data and the different weighting system. The effect was much smaller in the second cycle (changes −0·0015, −0·0000 and 0·0021 Å instead of −0·0016, 0·0008 and 0·0015 Å). Allowing the scale and temperature-factor parameters to change simultaneously with the atomic coordinates here accelerates the refinement while these parameters change appreciably, but the coupling between these parameters and the coordinates would presumably be smaller in another structure composed of more atoms in more general positions.

The standard deviations at the end of the first cycle of this refinement would differ only slightly from those under C′. Neglect of scale and temperature-factor-parameter changes has a smaller effect on the standard deviations than on the atomic positions; in fact, neglecting all off-diagonal elements in the normal equations yields standard deviations differing by less than 10% from the correct values.

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Calculated form factors for the 18-residue 5-turn α-helix.*

By LINUS PAULING, ROBERT B. COREY, HARRY L. YAKEL, JR.† and RICHARD E. MARSH, *Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.*

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Cochran, Crick & Vand (1952) have derived expressions for the evaluation of the Fourier transform of atoms on a helix. With the help of these expressions we have calculated form factors for the equator and first 28 layer lines of the 18-residue 5-turn α-helix.

For atoms arranged in a helical structure, the form factor expression, as derived by Cochran *et al.*, is

$$F_h(R,\psi,l/c) = \sum_n \sum_j f_j J_n(2\pi R r_j) \exp\{i[n(\psi-\varphi_j+\tfrac{1}{2}\pi)+2\pi l z_j/c]\}\,,$$

where R, ψ and l/c are cylindrical coordinates in reciprocal space, r_j, φ_j and z_j are the cylindrical coordinates of atom j in real space, f_j is the atomic form factor, and J_n is the nth-order Bessel function. The summation extends over all values n that satisfy the condition

$$n/P+m/p = l/c\,,$$

where P is the pitch of the helix and p is the vertical spacing between equivalent atoms; m and n are integers.

Table 1. *Atomic coordinates for the* 18-*residue* 5-*turn helix* (*left-handed configuration*)

Atom	r (Å)	φ (°)	z (Å)
C	2·28	0·0	1·48
N	1·57	29·1	0·62
C′	1·61	74·6	1·09
O	1·76	83·5	2·29
βC(1)	3·20	−19·3	0·65
βC(2)	3·44	16·1	2·12

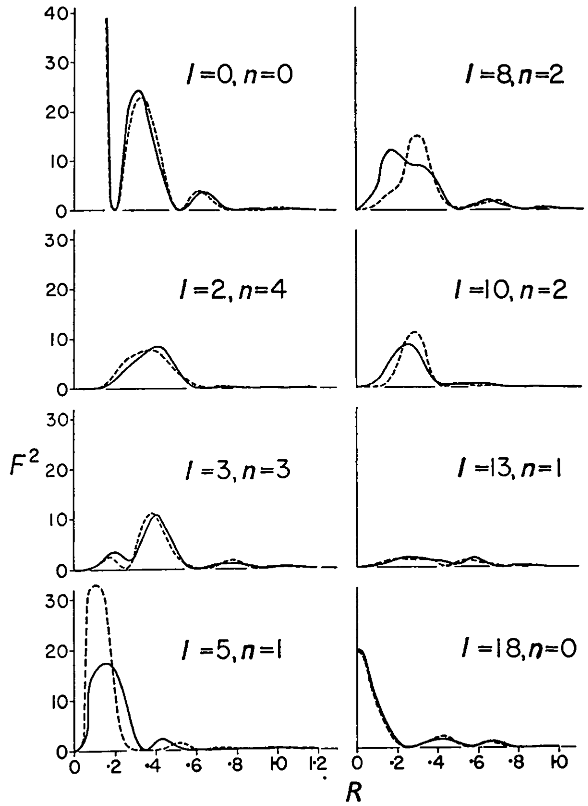

Fig. 1. Plots of F^2 for the most prominent layer lines of the 18-residue 5-turn α-helix. The solid curves are for the β-carbon atom in position 1 (*d* configuration for the left-handed helix) and the dashed curves are for the β-carbon atom in position 2 (*l* configuration for the left-handed helix).

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† Present address: Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.