On the Crystal and Molecular Structure of $PyCrO_5$

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Stomberg [1] has recently published a short note on the crystal structure of $CrO_5 \cdot C_5H_5N$, based on three-dimensional X-ray diffraction data.

We have been working on the same problem for some time, using two-dimensional data. The work is not completed, but as there seems to be some discrepancy between Stomberg's results and ours, we want to publish a short account of our results now.

The compound was prepared as given by Wiede [2]. The single crystals were grown from the mother liquor, containing more than the stoichiometric amount of pyridine, and cooled by a dry ice/acetone mixture. They were not recrystallized. The crystals were inevitably diamond shaped with the *b*-axis perpendicular to the plate and the *a*-axis parallel to one of the plate edges. Stomberg [1] recrystallized the compound and got needle shaped crystals. Work by Schwartz and Giese [3] indicates that the two crystalline forms obtained might differ in chemical properties.

Oscillation and zero-, first-, and second-layer Weissenberg diagrams were taken rotating about the *a*-axis, and oscillation and zero-layer Weissenberg diagrams were taken rotating about the *b*-axis. Our intensity data consisted of multiple film Weissenberg diagrams taken rotating about the *a*- and *c*-axes, and using Cu$K\alpha$ radiation. The intensities were estimated visually, corrected for Lorentz- and polarization effects, but not for absorption and extinction. The compound crystallizes in the monoclinic system. Systematic absences were:

in $h0l$: $l = 2n + 1$
in $0k0$: $k = 2n + 1$

Further, only a few weak reflextions were observed in $0kl$ when $k = 2n + 1$. This uniquely determines the space group to be $P2_1/c$. The density determined by the floatation method is 1.9 g/cm³, and the unit cell dimensions were determined to:

$a = 5.13$ Å, $b = 16.39$ Å, $c = 8.98$ Å,
$\beta = 101.6°$, $c \sin \beta = 8.80$ Å

This gives four molecules in the unit cell, and hence only one molecule in the asymmetric unit.

Stomberg [1] gives the space group $P2_1$ with two molecules in the asymmetric unit, and the following cell parameters:

$a = 5.107$ Å, $b = 16.31$ Å, $c = 11.29$ Å,
$\beta = 128.35°$, $c \sin \beta = 8.85$ Å

It is evident that his *a*- and *b*-axes are the same as ours, but his *c*-axis is our longest diagonal in the *xz* plane. Consequently this

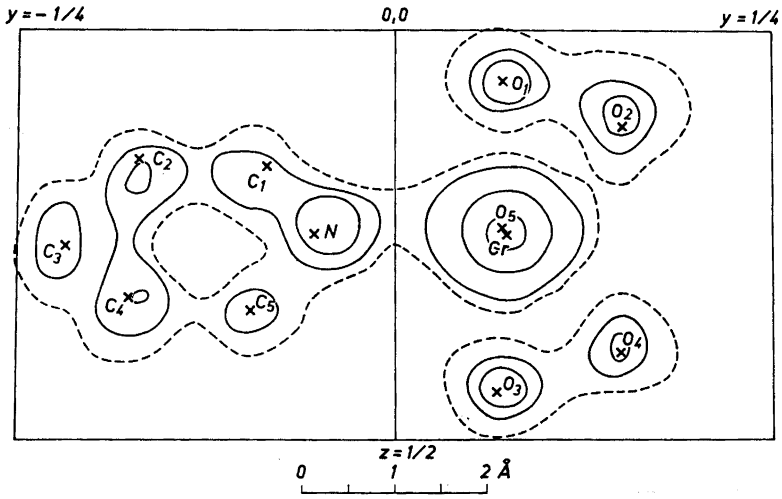

Fig. 1. Final Fourier map in the 100 projection.

Table 1. Positional parameters as fractions of the cell edges.

Atom	Stomberg's parameter values						Our parameter values		
	x_1	y_1	z_1	x_2	y_2	z_2	x	y	z
Cr	0.146	0.077	0.245	0.150	0.074	0.243	0.1554	0.0743	0.2500
O_1	0.210	0.071	0.058	0.225	0.070	0.060	0.216	0.071	0.063
O_2	0.184	0.150	0.097	0.217	0.150	0.098	0.197	0.153	0.120
O_3	0.343	0.071	0.435	0.352	0.072	0.433	0.337	0.068	0.439
O_4	0.278	0.150	0.386	0.305	0.153	0.390	0.272	0.150	0.393
O_5	−0.182	0.076	0.264	−0.181	0.069	0.264	−0.162	0.073	0.247
N	0.211	−0.053	0.253	0.209	−0.051	0.253	0.171	−0.054	0.250
C_1	0.361	−0.085	0.172	0.371	−0.085	0.170	0.350	−0.087	0.070
C_2	0.409	−0.172	0.186	0.427	−0.171	0.181	0.408	−0.170	0.160
C_3	0.284	−0.217	0.275	0.314	−0.214	0.266	0.308	−0.218	0.265
C_4	0.116	−0.180	0.352	0.138	−0.175	0.345	0.124	−0.177	0.330
C_5	0.069	−0.092	0.340	0.094	−0.093	0.341	0.025	−0.097	0.342

should lead to the space group $P2_1/n$ where the absent reflextions in $h0l$ should be for $h + l = 2n + 1$.

The structure was solved starting from the Patterson projections, and using the heavy atom technique. Several Fourier syntheses were calculated. The structure was refined by the use of difference-syntheses where the chromium atom had been subtracted, and by the method of least squares. The final Fourier map in the 100 projection is shown in Fig. 1.

The parameters are given in Table 1 together with the two symmetry unrelated sets of Stomberg's parameters, transferred to the same origin ($\bar{1}$) as we have used. As can be seen from the table, our parameter values are close to the mean of Stomberg's parameter values.

Our parameters are not as accurate as we would like them to be, but our intensity data are not extensive enough to carry out a further refinement.

The reliability indexes for the two projections are: for $hk0$ $R = 0.12$ and for $0kl$ $R = 0.13$. We have also calculated R from Stomberg's parameters and our $hk0$ data, and found 0.20. Stomberg gives the reliability index for his $hk0$ data as $R = 0.15$. Hence, the R-value is higher when Stomberg's parameters are used even with his own data. One might expect the contrary because Stomberg's parameter set contains twice as many parameters and no center of symmetry.

Our 100 projection has a quasi symmetry: a mirror plane normal to the c-axis and the b-axis halved, as there are only a few weak reflexions in $0kl$ when $k = 2n + 1$. This is caused by the fact that the molecule is almost symmetrically arranged along $z = 1/4$, see Fig. 1. This, however, made the refinement of the 100 projection difficult and slow. In the 001 projection there is some overlap of atoms and consequently the refinement is rather difficult there too. The y-parameters given are the medium values found from the two projections except for $y(O_5)$, which is the value obtained from the 001 projection, as there is

Table 2.

Cr−O_1	1.80 Å	O_5−O_3	2.78 Å	O_1−O_4	3.23 Å
Cr−O_2	1.80 »	O_5−O_1	2.84 »	O_2−O_3	3.16 »
Cr−O_3	1.78 »	O_5−O_4	2.67 »	O_1−O_3	3.55 »
Cr−O_4	1.81 »	O_5−O_2	2.73 »	N−C_1	1.41 »
Cr−O_5	1.64 »	N−O_5	2.70 »	C_1−C_2	1.40 »
Cr−N	2.10 »	N−O_1	2.71 »	C_2−C_3	1.42 »
O_1−O_2	1.45 »	N−O_3	2.66 »	C_3−C_4	1.39 »
O_3−O_4	1.42 »	N−O_2	3.59 »	C_4−C_5	1.41 »
O_2−O_4	2.44 »	N−O_4	3.59 »	C_5−N_1	1.39 »
N−Cr−O_5	92°	N−O_3−O_4	120°	O_3−O_4−O_2	107°
O_3−N−O_1	77°	N−O_1−O_2	116°	O_4−O_2−O_1	110°

heavy overlap of chromium and this oxygen atom in the 100 projection.

The structure is built up of discrete molecules where the chromium atom is surrounded by a somewhat distorted pentagonal pyramid with the oxygen O_5 at the apex. This is the same configuration as described by Stomberg.

Calculation shows that $Cr-O_1-O_3$ are situated in a plane approximately perpendicular to the b-axis, and O_5 is only 0.14 Å out of this plane. Further, the Cr—N bond is almost perpendicular to the plane, and O_2 and O_4 are situated on the opposite side of the plane, 1.16 Å and 1.07 Å away from it.

Calculated interatomic distances and angles are given in Table 2.

The interatomic distances found, seem reasonable and indicate that the molecule is built up of two peroxide groups and one oxide oxygen.

1 Stomberg, R *Nature* **196** (1962) 570.
2. Wiede, O. F. *Ber.* **30** (1897) 2178.
3. Schwartz, R. and Giese, H. *Ber.* **65** (1932) 871.

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X-Ray Crystal Data on Some *p*-Bromophenylhydrazones and *p*-Bromophenylosazones

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The hydrazones and osazones are of considerable importance in carbohydrate chemistry, but in spite of this the structure of most of these substances are still incompletely known. As for the hydrazones, both ring and open-chain forms of the sugar have been shown to exist [1]. The solid state structure of individual hydrazones is, however, known only in a few cases. For the osazones the evidence is in favour of an open-chain structure stabilized by different types of chelate bonds [2-4], but a direct determination of the structure in the solid state would appear desirable. We have therefore started an investigation of a number of hydrazones and osazones, using the methods of X-ray crystallography. In order to facilitate the structure determinations the *p*-bromoderivatives of the compounds were used.

The hydrazones were prepared by mixing equivalent amounts of sugar and *p*-bromophenylhydrazine in dilute alcohol at room temperature. In order to obtain the osazones, an aqueous solution of the sugar and NaAc was treated with *p*-bromophenylhydrazine hydrochloride at 80° — 100° [5].

Unit cell dimensions and space groups were derived from X-ray oscillation and Weissenberg diagrams, using copper radiation (λ = 1.542 Å). The measurements are believed to be accurate to within about 1 %. The densities were measured in carbon tetrachloride-bromoform mixtures, but only approximate values were obtained for the osazones due to the poor quality of the crystals and their solubility in the liquid.

Hydrazones

Ribose-p-*Br-phenylhydrazone.* Orthorhombic, flat needles, elongated along the c axis, with unit cell dimensions a = 9.46 Å, b = 23.71 Å, and c = 5.78 Å. Space group $P2_12_12_1$. Density 1.63 g/cm³, corresponding to four (calc. 3.98) molecules in the unit cell.

An electron density projection has been calculated (Fig. 1), showing that the ribose probably occurs in its openchain form in this compound. Further work on the structure is in progress.

Arabinose-p-*Br-phenylhydrazone.* Unit cell dimensions a = 7.12 Å, b = 6.15 Å, c = 14.09 Å, and β = 96°. Space group $P2_1$.

The crystal structure of this compound has been determined and a full account of the work published [6]. The arabinose occurs in the pyranose chair form, with conformation 1e2e3e4a.

Mannose-p-*Br-phenylhydrazone.* Small, well-developed triclinic crystals, elongated along a, with (001) as the dominating face. Unit cell dimensions a = 4.73 Å, b = 5.67 Å, c = 19.02 Å, α = 135°, β = 106° and γ = 73°. Density 1.70 g/cm³, corresponding to one (calc. 1.00) molecule in the unit cell. Space group $P1$.

The a and b axes are both relatively short. This may indicate that the sugar has an extended, open-chain conformation. A study of models shows that the likely length of such a molecule is in the order of 19 Å, in agreement with the observed length of the c axis.

Glucose-p-*Br-phenylhydrazone.* Big prisms were obtained, with m.p. 165°C and density 1.67 g/cm³. They are orthorhombic, with a = 6.82 Å, b = 32.52 Å and c = 6.19 Å. Space group $P2_12_12_1$. Four (calc. 3.97) molecules in the unit cell.