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The crystal symmetry of several diazonium salts.

By CHARLES BUGG, JIMMY LAWSON and RONALD L. SASS, *Department of Chemistry, Rice University, Houston, Texas, U.S.A.*

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The unit-cell dimensions and probable space group of eleven substituted benzenediazonium salts have been determined from X-ray diffraction measurements. The salts used were prepared according to the procedure given in *Organic Syntheses*, Vol. II (Blatt, 1943). Each salt was recrystallized from methanol to a constant ultraviolet absorption.

Suitable single crystals were selected for X-ray analysis. Rotation and Weissenberg photographs were obtained with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The results of the measurements on these photographs are presented in Table 1. In some instances the space group assignment cannot be made unambiguously from the observed absences. In these cases, indicated by an asterisk, the most probable space group, based on the number of molecular units present, is given.

The space group *Pbca* (D_{2h}^{15}) was observed in six of the salts studied; however it is not immediately apparent from the cell constants that they are structurally related. The fluoroborate and fluorosphosphate of the *p*-nitrobenzenediazonium ion both crystallize in the space group *Fdd*2 (C_{2v}^{19}) with similar cell constants and may very well be isostructural.

The calculated molecular volumes of the four fluorophosphate salts are very similar even though they crystallize in three different space groups. The average value of 264 Å^3 has a variance of only ± 2 Å^3. The molecular volumes of the fluoroborate salts appear to be

Table 1. *Unit-cell dimensions and space group information*

Compound	Unit cell constants	Systematic conditions	No. of molecules per unit cell	Probable space group	Molecular volume
p-Methylbenzenediazonium fluorophosphate	$a = 22{\cdot}43$ Å $b = 11{\cdot}98$ $c = 7{\cdot}96$	$0kl$; $k = 2n$ $h0l$; $l = 2n$ $hk0$; $h = 2n$	8	*Pbca* (D_{2h}^{15})	267 Å^3
p-Chlorobenzenediazonium fluorophosphate	$a = 21{\cdot}86$ $b = 9{\cdot}06$ $c = 10{\cdot}68$	$0kl$; $k = 2n$ $h0l$; $l = 2n$ $hk0$; $h = 2n$	8	*Pbca* (D_{2h}^{15})	265
m-Nitrobenzenediazonium fluorophosphate	$a = 34{\cdot}62$ $b = 14{\cdot}56$ $c = 8{\cdot}31$	hkl; $h+k = 2n$ $hk0$; $h = 2n$	16	*Cmma** (D_{2h}^{21})	262
p-Nitrobenzenediazonium fluorophosphate	$a = 29{\cdot}81$ $b = 23{\cdot}63$ $c = 5{\cdot}94$	hkl; $h+k, k+l = 2n$ $0kl$; $k+l = 4n$ $h0l$; $h+l = 4n$	16	*Fdd*2 (C_{2v}^{19})	262
p-Methoxybenzenediazonium fluoroborate	$a = 19{\cdot}98$ $b = 9{\cdot}78$ $c = 10{\cdot}01$	$0kl$; $k = 2n$ $h0l$; $l = 2n$ $hk0$; $h = 2n$	8	*Pbca* (D_{2h}^{15})	244
p-Chlorobenzenediazonium fluoroborate	$a = 22{\cdot}18$ $b = 10{\cdot}92$ $c = 7{\cdot}53$	$0kl$; $k = 2n$ $h0l$; $l = 2n$ $hk0$; $h = 2n$	8	*Pbca* (D_{2h}^{15})	228
m-Chlorobenzenediazonium fluoroborate	$a = 7{\cdot}25$ $b = 16{\cdot}72$ $c = 14{\cdot}90$	$0kl$; $k = 2n$ $h0l$; $l = 2n$ $hk0$; $h = 2n$	8	*Pbca* (D_{2h}^{15})	226
m-Nitrobenzenediazonium fluoroborate	$a = 19{\cdot}82$ $b = 12{\cdot}65$ $c = 7{\cdot}46$	$0kl$; $k = 2n$ $h0l$; $l = 2n$ $hk0$; $h = 2n$	8	*Pbca* (D_{2h}^{15})	234
o-Nitrobenzenediazonium fluoroborate	$a = 7{\cdot}73$ $b = 7{\cdot}53$ $c = 15{\cdot}64$	$h0l$; $l = 2n$	4	$Pmc2_1$* (C_{2v}^2) or *P*2*cm* (C_{2v}^4)	228
p-Nitrobenzenediazonium fluoroborate	$a = 30{\cdot}88$ $b = 22{\cdot}53$ $c = 5{\cdot}40$	hkl; $h+k, k+l = 2n$ $0kl$; $k+l = 4n$ $h0l$; $h+l = 4n$	16	*Fdd*2 (C_{2v}^{19})	235
p-Diazoniobenzenesulfonate	$a = 8{\cdot}10$ $b = 9{\cdot}94$ $c = 13{\cdot}22$ $\beta = 135°\ 14'$	$h0l$; $l = 2n$ $0k0$; $k = 2n$	4	$P2_1/c$ (C_{2h}^5)	187

* See text.

somewhat more sensitive to the substituent on the diazonium ion, ranging from 244 Å^3 in the *p*-methoxy to 226 Å^3 in the *m*-chlorobenzenediazonium salt.

A complete structural analysis of the *p*-methoxybenzenediazonium fluoroborate and *p*-diazoniobenzenesulfonate is now in progress. No additional work is planned on the other salts.

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References

BLATT, A. H. (1943). *Organic Syntheses*, collective Vol. II, p. 295. New York: Wiley.

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The relative orientation of molecules of crystallized human and horse oxyhaemoglobin.

By JOHN W. PROTHERO and MICHAEL G. ROSSMANN, *M.R.C. Laboratory of Molecular Biology, Hills Road, Cambridge, England*

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The horse oxyhaemoglobin molecule consists of four sub-units, namely two α and two β chains, packed in a tetrahedral array (Cullis, Muirhead, Perutz, Rossmann & North, 1962). Human reduced (deoxy) haemoglobin has a similar structure, except that the β chains are translated 7 Å apart (Muirhead & Perutz, 1963). This increased separation of the β chains is probably associated with deoxygenation, but the possibility exists that it merely reflects a difference between human and horse oxyhaemoglobin. The failure of human oxyhaemoglobin crystals to form isomorphous derivatives has hindered X-ray analysis by the isomorphous replacement method. However a method (based on the 'rotation function') of determining the relative orientation of two similar proteins in different crystal lattices was recently described (Rossmann & Blow, 1962). This note reports, as a preliminary step in the structural analysis of human oxyhaemoglobin, the application of the rotation function to a comparison of human and horse oxyhaemoglobin.

Horse oxyhaemoglobin crystals are monoclinic with space group $C2$ and cell dimensions $a=108{\cdot}9$, $b=63{\cdot}5$, $c=54{\cdot}9$ Å, $\beta=110{\cdot}9°$. The molecular twofold axis lies along the crystallographic twofold axis (*i.e.* parallel to *b*). In addition, the molecule possesses an approximate 222 point group symmetry with one of the pseudo twofold axes making an angle of about 5° with the *a* axis. On the other hand human oxyhaemoglobin crystals are tetragonal with space group $P4_12_12$ and with cell dimensions of $a=54{\cdot}3$, $c=196{\cdot}4$ Å. In this case the molecular diad must lie along the [110] and symmetry related directions (Perutz, 1953).

The rotation function program calculates the degree of concurrence arising when the Patterson vectors of one protein are superimposed, in a sphere around the origin, on those of another protein. In order to superimpose the self-Pattersons of human and horse oxyhaemoglobin correctly it is necessary to align the [010] direction of the horse oxyhaemoglobin molecule with the [110] direction of the human oxyhaemoglobin molecule. This result could be obtained by re-indexing the tetragonal unit cell. Maximum agreement between the Pattersons would then be obtained by rotating the tetragonal cell through an unknown angle (say θ) about the common axis. An alternative and more general procedure is to produce alignment of the [010] and [110] directions and rotation through an angle θ in one operation. That is, the tetragonal cell may be rotated through an angle $\varkappa$ about a rotation axis whose position in the monoclinic cell is defined in terms of the polar coordinates ψ and φ (Rossmann & Blow, 1962, Fig. 4).

Assume that initially the *b* and *c* axes of the first crystal are placed on top of the *b* and *c* axes of the second crystal, respectively. If the molecular twofold axes are coincident for a given rotation $\varkappa$, then it can be shown that the position of the rotation axis is given by:

$$y^2=\frac{1-\sqrt{2}\cos\varkappa}{\sqrt{2}(1-\cos\varkappa)}$$

where $\cos\psi=y$

and $$\cos\varphi=(\sqrt{2}-1)y/(1-y^2)^{\frac{1}{2}}$$

It is convenient to define the angle θ, which measures the amount of rotation of one crystal with respect to the other around the twofold axis, as the angle between the monoclinic *a* axis and the tetragonal *c* axis. Both these arbitrary directions are perpendicular to the molecular twofold axes (Fig. 1). The sign of θ is taken so that it is

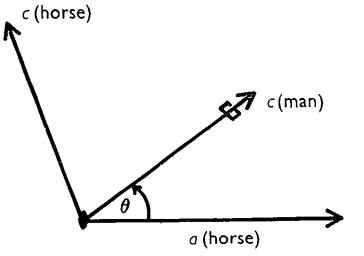

Fig. 1. Relationship between the horse and human oxyhaemoglobin groups viewed down the superimposed molecular twofold axes. θ defines the amount of rotation.

positive when the tetragonal *c* axis lies between the monoclinic *a* and *c* axes. The angle θ is related to $\varkappa$ by

$$\theta=110{\cdot}9°-\cos^{-1}\left[\frac{\sqrt{2}-1+2\sqrt{2}\cos\varkappa}{\sqrt{2}+1}\right].$$

Values of θ from 0° to 180° were explored using 6 Å intensity data and a radius of integration of 35 Å. The 'shaded *G*' function was used. The latter applies a weighting varying exponentially between 1 and 0·1 between the inside and outside of the sphere of integration. Smaller weights near the outside of the sphere emphasize that more cross-vectors between molecules might be found here. A simple sharpening was brought about by omitting