

radius for octahedral chromium has been measured, rather than relying on the extrapolation of the covalent radii of the isoelectronic series.

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## Significance Tests on the Crystallographic *R* Factor The Space Group of Chromium Hexacarbonyl

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The Laue symmetry and systematic absences of chromium hexacarbonyl indicated that the space group is either  $Pn2_1a$  or  $Pnma$ . The former had already been reported by other investigators. Structures based on both groups were refined by least squares. The crystallographic evidence of consistency between the results of isotropic and anisotropic refinement – of consistency of equivalent bond lengths, bond angles, parameter standard deviation and isotropic temperature factors – suggests the centrosymmetric structure to be correct. This is reinforced by the morphology, the statistical tests for a centre of symmetry and the relative ease in refining the centrosymmetric structure compared with the non-centrosymmetric one. On the other hand, the weighted residual test strongly suggests a non-centrosymmetric structure. It is thought that this is most likely to originate from an ill-conditioned least-squares matrix which arises from the pseudo-symmetry of the non-centrosymmetric structure. In such cases it would appear unwise to depend on the weighted residual test alone.

### Introduction

Hamilton (1965) has defined a function  $R''$  as

$$R'' = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{\frac{1}{2}}$$

where  $w = 1/\sigma^2$  ( $\sigma^2$  is the variance of  $F_o$ ).  $F_o$  and  $F_c$  are the observed and calculated structure factors.

This function Hamilton (1965) terms the weighted residual. He shows that  $\mathcal{R} = R''_O/R'_O$  (where  $R''_O$  is the weighted residual from an unrestrained least-squares refinement and  $R'_O$  that from a refinement with con-

straints on some parameters) may be statistically significant. Tables are given to obtain the level of significance.

The test was applied during the crystal structure determination of chromium hexacarbonyl.

## CHROMIUM HEXACARBONYL

### 1. Possible space groups

The Laue symmetry and systematic absences of chromium hexacarbonyl indicate that the space group is either  $Pn2_1a$  or  $Pnma$ . The former had already been

reported by previous investigators (Rüdorff & Hofmann, 1935), but this space group became suspect in favour of  $Pnma$ . The latter space group has a mirror plane at  $y=\frac{1}{4}$  and several atoms are near or on this plane depending on the space group.

Structures based on both space groups were refined (Whitaker & Jeffery, 1967), and the refinements were continued until the recommended shifts were less than one-tenth the appropriate standard deviation (Mason, 1964).

The weighting system used was  $w=1/\sigma^2$  where  $\sigma$  was the standard deviation of groups of equivalent reflexions.

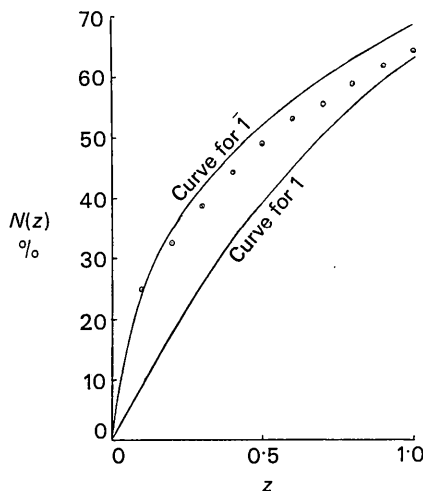


Fig. 1.  $N(z)$  test applied to all data.

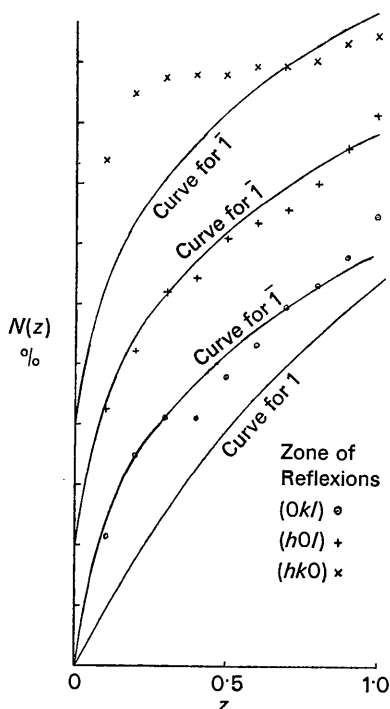


Fig. 2.  $N(z)$  test applied to zones of reflexions.

## 2. Morphological evidence

The crystals were obtained by slowly cooling hot saturated solutions in methylcyclohexane. Most crystals were hexagonal needles. The extinctions were straight in sections both parallel and perpendicular to the needle axis, confirming the crystal system as orthorhombic (Rüdorff & Hofmann, 1935).

Examination of several crystals showed no forms which could not be attributed to point group  $mmm$  and a maximum of four forms per crystal were observed which could differentiate between point groups  $mmm$  and  $m2m$ . This suggested that the crystals were holosymmetric and contradicts the space group given by Rüdorff & Hofmann (1935),  $Pn2_1a$ , in the present orientation.

## 3. Statistical tests of the intensity distribution

### 3a. Wilson ratio

The Wilson ratios (Wilson, 1949a, b) were calculated for the full three-dimensional data and for the crystallographic zones (Table 1).

Table 1. Wilson ratios

Reflexions	Number of reflexions	Wilson ratio
$hkl$	940	0.583
$OkI$	51	0.498
$h0I$	93	0.533
$hk0$	85	0.488

Comparing these values with those for centric and acentric distributions, 0.637 and 0.787 respectively, it can be seen that all groups of reflexions have a centric distribution, thus suggesting the point group  $mmm$ .

### 3b. $N(z)$ test

The  $N(z)$  tests (Howells, Phillips & Rogers, 1949, 1950) for the crystal structure as a whole and its three projections are plotted in Figs. 1 and 2 respectively. In the latter the origins for the  $b$ - and  $c$ -axis projections have been moved along  $N(z)$  by 20% and 40% respectively. All the curves seem to suggest that the structure is centrosymmetric and the curve for the  $c$ -axis projection suggests that this projection may be hypercentrosymmetric (Lipson & Woolfson, 1952). However, these tests for centrosymmetry assume that there is a random distribution of atoms; the presence of pseudosymmetry or of comparatively few atoms dominating the intensity distribution may invalidate them.

## 4. Refinements of the structure

### 4a. Refinements of the non-centrosymmetric structure

The initial coordinates were obtained from a three-dimensional Patterson synthesis; these could fit either the centrosymmetric or the non-centrosymmetric space group, the  $y$  coordinates of the chromium, two oxygen and two carbon atoms being at  $y=\frac{1}{4}$  (the position of

the mirror in the centrosymmetric group), the other atoms being related in pairs by a mirror plane at this position. After five cycles of diagonal-matrix least-squares refinement (Diamand, 1964) it was noticed that the atomic coordinates were oscillating in such a manner that they were still related by a mirror plane at  $y = \frac{1}{2}$ . It was thought that this might be due to a combination of using initial coordinates which could be centrosymmetric and a diagonal least-squares matrix. So the appropriate atoms were moved from this special positions of  $y = \frac{1}{2}$  by varying amounts. The residual and atomic coordinates continued to oscillate, however, and the use of anisotropic temperature factors did not prevent oscillation. Because of this only half the recommended parameter shifts were applied and the structure was independently refined with isotropic temperature factors in one case and anisotropic temperature factors in the other.

At a later stage it was noticed that some parameters were oscillating and others were not. Subsequently half the recommended shift was applied if the parameter was oscillating while the full shift or even twice the recommended shift was applied to the others. The use of full or double shifts was dependent on the number of least-squares refinements undergone since the recommended shift had changed sign.

In spite of the application of differential shifts, the isotropic refinement was very slow; 76 cycles of least-squares analysis were required before the structure was completely refined.

The residual and weighted residual were 9.15% and 8.69% respectively.

In the other case, using anisotropic temperature factors, the refinement was again slow; 84 cycles of refinement were required from the initial data to obtain the final parameters. The residual and weighted residual were 7.23% and 6.45% respectively.

#### 4b. Refinement of centrosymmetric structure

In contrast to the difficulties encountered in the refinement of the non-centrosymmetric structure, refinement of the centrosymmetric structure was straightforward.

Four cycles of refinement using isotropic temperature factors were applied, then refinement with isotropic and anisotropic temperature factors proceeded independently. The numbers of cycles of refinement from the initial data were 13 and 18 respectively.

The final residuals and weighted residuals were 10.15% and 9.39% for the isotropic refinement and 7.79% and 6.83% for the anisotropic refinement.

### 5. Discussion of the space group

#### 5a. Crystallographic evidence

When the position parameters of the isotropic and anisotropic refinements of the non-centrosymmetric space group were compared, appreciable differences were evident. The differences in terms of the larger

standard deviation of each pair are given in Table 2 for both the non-centrosymmetric and centrosymmetric space groups.

Table 2. Differences of the position parameters in terms of the larger standard deviation of each pair when the refinement has been completed twice, with isotropic temperature factors in one case and anisotropic in the other

	Non-centrosymmetric structure			Centrosymmetric* structure		
	$\Delta x$	$\Delta y$	$\Delta z$	$\Delta x$	$\Delta y$	$\Delta z$
Cr	0.6	8.5	0.4	0.0	—	0.3
C(1)	1.0	5.9	1.1	0.2	—	1.7
C(2)	0.0	13.7	2.2	0.6	—	0.9
C(3)	5.5	7.0	5.7	1.3	1.5	0.3
C(4)	5.7	2.6	3.1	0.4	2.2	2.4
C(5)	7.4	4.5	4.5	1.3	1.5	0.3
C(6)	8.7	2.3	7.6	0.4	2.2	2.4
O(1)	0.7	11.2	0.5	0.8	—	0.3
O(2)	1.8	7.7	1.0	0.3	—	1.1
O(3)	7.8	2.0	0.3	0.8	0.9	0.7
O(4)	3.3	7.5	15.4	0.8	0.0	0.2
O(5)	6.7	2.0	0.0	0.8	0.9	0.7
O(6)	2.3	10.2	13.5	0.8	0.0	0.2

\* For the centrosymmetric structure: C(3) and C(5), C(4) and C(6), O(3) and O(5), and O(4) and O(6) are equivalent pairs of atoms.

For the non-centrosymmetric structure, 22 of the 39 position parameters differ by more than  $3\sigma$  (including 5 whose difference is greater than  $10\sigma$ ). Only 9 differences are less than the larger standard deviation. If the non-centrosymmetric structure is correct, it appears surprising that it is possible to refine from the same initial coordinates and get final position parameters so different. This seems unlikely for a correct structure. In addition, refinements using either isotropic or anisotropic temperature factors give position parameters which must be in error by considerably more than the standard deviation calculated by least squares. Thus the accuracy of pseudo-symmetric structures refined with either anisotropic or isotropic temperature factors alone may be suspect. This, if true, would invalidate the accuracy claimed for a number of published structures. It seems much more likely that the structure is actually centrosymmetric, since in that case the differences between the two refinements are much smaller; 16 out of 22 are less than the larger standard deviation and the largest difference is only  $2.4\sigma$ .

Another way of seeing the effect of these differences is to compare intramolecular bond lengths from the various refinements (Table 3). In the case of the non-centrosymmetric structure the differences of bond lengths from the two refinements may be considerable. For example, the bonds Cr–C(4), Cr–C(6) and C(6)–O(6) have differences of  $4.4\sigma$ ,  $8.7\sigma$  and  $3.3\sigma$  respectively, while for the centrosymmetric structure the largest difference is  $2.7\sigma$ , for Cr–C(4).

Further examination of Table 3 indicates that in the case of the non-centrosymmetric structure the range

of Cr–O bond lengths is considerably larger for anisotropic than for isotropic refinement, whereas for the centrosymmetric structure the range of bond lengths is approximately the same (within 10%) for both methods of refinement.

Examination of intramolecular bond angles (Table 4) gives a similar result, the range of the Cr–C–O angles obtained being considerably larger for the non-centrosymmetric structure than for the centrosymmetric one, and the C–Cr–C angles giving a more regular octahedron in the case of the centrosymmetric structure than in the non-centrosymmetric case. In addition, differences of 4° in the angles C–Cr–C were obtained from the isotropic and anisotropic refinements of the non-centrosymmetric space-group. Hence, again it would appear that the centrosymmetric structure is the more likely.

Again, one may examine the standard deviations of the position parameters of the chemically equivalent atoms in similar environments. The ranges of these standard deviations are given in Table 5. It can be seen that the range of standard deviations for chemically equivalent atoms is considerably larger for the non-centrosymmetric structure than the centrosymmetric one, although against this there are six symmetry-independent atoms in the former but only two in the latter. The ranges of values are so much greater in the

non-centrosymmetric case, however, that it is thought that this is further evidence for the centrosymmetric structure. The same effect occurs when comparing the standard deviations of the temperature factors.

One would expect the temperature factors of similar atoms to be similar. In the case of the non-centrosymmetric structure the isotropic temperature factors for carbon are in the range 2.5 to 4.6, while for oxygen the range is 4.5 to 5.6. These ranges are much larger than the same ranges for the centrosymmetric structure, the range for carbon being 3.5 to 3.8, and for oxygen 5.3 to 5.7. In addition in the non-centrosymmetric structure the temperature factor for one carbon atom [C(6)] is less than for the chromium. This appears to be further evidence for the centrosymmetric structure.

It is interesting to note that in the non-centrosymmetric structure three positional parameters [ $x$  and  $z$  coordinates for C(6),  $y$  coordinate for O(2)] have larger standard deviations after refining with anisotropic temperature factors than after refining with isotropic temperature factors. This again is thought to be unusual.

#### *Sb. Computing evidence*

It has been pointed out that considerably greater difficulty was found in the refinement of the non-centrosymmetric structure (§ 4a) than in the refinement of

Table 3. Comparison of intramolecular bond lengths (Å) from the different refinements of the two structures ( $\sigma$  in brackets)

Bond	Non-centrosymmetric		Centrosymmetric*	
	Isotropic refinement	Anisotropic refinement	Isotropic refinement	Anisotropic refinement
Cr–C(1)	1.8793 (85)	1.8846 (66)	1.8782 (88)	1.8907 (66)
Cr–C(2)	1.9281 (88)	1.9458 (69)	1.9181 (92)	1.9277 (67)
Cr–C(3)	1.9462 (105)	1.9604 (94)	1.8983 (58)	1.9099 (44)
Cr–C(4)	1.8988 (137)	1.8380 (92)	1.8930 (60)	1.9093 (46)
Cr–C(5)	1.8530 (120)	1.8716 (89)	1.8983 (58)	1.9099 (44)
Cr–C(6)	1.9064 (99)	1.9929 (94)	1.8930 (60)	1.9093 (46)
C(1)–O(1)	1.1612 (116)	1.1705 (90)	1.1650 (117)	1.1515 (84)
C(2)–O(2)	1.1388 (119)	1.1040 (90)	1.1251 (119)	1.1094 (85)
C(3)–O(3)	1.1331 (138)	1.1049 (110)	1.1464 (77)	1.1368 (57)
C(4)–O(4)	1.1636 (163)	1.1635 (109)	1.1631 (79)	1.1436 (59)
C(5)–O(5)	1.1827 (141)	1.1544 (108)	1.1464 (77)	1.1368 (57)
C(6)–O(6)	1.1678 (130)	1.1255 (111)	1.1631 (79)	1.1436 (59)
Maximum difference				
Cr–C	0.0932	0.1549	0.0399	0.0370
C–O	0.0496	0.0665	0.0380	0.0421

\* See footnote to Table 2.

Table 4. Comparison of intramolecular bond angles from the different refinement of the two structures

Bond angle	Non-centrosymmetric		Centrosymmetric*	
	Isotropic refinement	Anisotropic refinement	Isotropic refinement	Anisotropic refinement
Cr–C(1)–O(1)	174.77 (1.83)	167.93 (1.31)	179.05 (77)	179.56 (58)
Cr–C(2)–O(2)	165.73 (1.45)	170.54 (1.29)	179.18 (80)	178.77 (60)
Cr–C(3)–O(3)	171.03 (87)	178.79 (77)	177.80 (51)	178.26 (39)
Cr–C(4)–O(4)	169.27 (1.13)	175.13 (66)	177.81 (52)	178.53 (40)
Cr–C(5)–O(5)	168.11 (95)	177.49 (68)	177.80 (51)	178.26 (39)
Cr–C(6)–O(6)	168.04 (87)	177.71 (87)	177.81 (52)	178.53 (40)
Maximum difference				
Cr–C–O	9.04	10.86	1.38	1.30

\* See footnote to Table 2.

the centrosymmetric structure (§ 4*b*). It is thought that this would be unlikely if the non-centrosymmetric structure were correct.

### 5*c*. Weighted residual test

The weighted residual test (Hamilton, 1965) was applied to both isotropic and anisotropic refinements of both structures.

For the isotropic refinements, the numbers of parameters were 32 and 53 for the centrosymmetric and non-centrosymmetric structures respectively.

Thus in Hamilton's notation we have  $\mathcal{R}_{53-32,940-53,\alpha}$ , *i.e.*  $\mathcal{R}_{21,887,\alpha}$ , for the significance test. From his tables, for  $\alpha=0.005$ , *i.e.* the  $\frac{1}{2}\%$  significance level (the highest significance level given),  $\mathcal{R}=1.024$ . The experimental ratio is 1.081 which appears to mean that there is considerably less than 1 chance in 200 that the centrosymmetric space group is correct.

For the anisotropic refinements, the number of parameters was 67 and 118 for the centrosymmetric and non-centrosymmetric structures and  $\mathcal{R}_{118-67,940-118,0.005}$ , *i.e.*  $\mathcal{R}_{51,832,0.005}$ , equals 1.047. The experimental value is 1.059 and the same conclusion follows although the significance level, while still more than 200 to 1, is not quite so high. Thus in both cases this test suggests, contrary to all the foregoing, that the non-centrosymmetric structure is correct.

## 6. Summary and conclusions

The crystallographic evidence of consistency between the results of isotropic and anisotropic refinement – of consistency of equivalent bond lengths, bond angles, parameter standard deviations and isotropic temperature factors – suggests the centrosymmetric structure to be correct. This is reinforced by the morphology (§ 2), the statistical tests for a centre of symmetry (§ 3) and the relative ease in refining the centrosymmetric structure compared with the non-centrosymmetric one.

On the other hand, the weighted residual test strongly suggests a non-centrosymmetric structure. However,

this test has only recently been proposed and only once been used as a test for the presence of a centre of symmetry (Hamilton, 1965).

Hence it is believed that the balance of the evidence is that the structure is centrosymmetric and the space group is  $Pnma$  in spite of the results of the weighted residual test.

Cruickshank (1965) agrees that the structure is centrosymmetric. He suggests that the non-centrosymmetric isotropic temperature refinement is significantly better than the centrosymmetric isotropic temperature refinement because the non-centrosymmetric parameters are attempting to correct for the anisotropy of the atoms. This would explain why the significance level of  $\mathcal{R}$  is less for anisotropic refinement than for isotropic refinement. Further, he suggests that even with anisotropic temperature factors the non-centrosymmetric structure is attempting to correct for further real parameters such as non-Gaussian smearing functions. The fact that the vibrations on the outer oxygen atoms must be partly along arcs of circles rather than in straight lines is one possible source of such parameters. The inability of the least-squares program to apply corrections for these factors may, he suggests, be the cause of the failure of the weighted residual test.

Hamilton (1966) also agrees that the structure is probably centrosymmetric although he feels that this deduction must be based almost entirely on the better chemical sense that the centrosymmetric structure makes (better agreement in bond distances and bond angles). He feels that the large differences of positions (many standard deviations) obtained in the isotropic and anisotropic refinements of the non-centrosymmetric structure may be due to severe anisotropy (although, in fact, only the oxygen atoms show appreciable anisotropy) and that the smaller differences in the case of the centrosymmetric structure cannot be used as an argument in its favour. He states that in structures with severe anisotropy the standard deviations obtained for isotropic refinement are too small, that furthermore it is more difficult to refine a non-centro-

Table 5. Range of standard deviations for position parameters of equivalent atoms after isotropic and anisotropic refinement of both structures

The minimum and maximum values are given, separated by an oblique stroke.

Atom	S.D. of parameter	Non-centrosymmetric		Centrosymmetric	
		Isotropic refinement	Anisotropic refinement	Isotropic refinement	Anisotropic refinement
C	$\sigma_x$	66/101	52/72	{ 69/72 45/46	{ 52/55 34/36
	$\sigma_y$	90/198	75/133	54/57	40/43
	$\sigma_z$	137/203	107/159	{ 143/147 90/92	{ 106/106 68/72
O	$\sigma_x$	55/83	47/61	{ 59/64 44/46	{ 45/47 32/32
	$\sigma_y$	75/139	60/145	47/48	33/33
	$\sigma_z$	121/146	83/109	{ 123/125 72/79	{ 81/86 55/62

\* The top entry of each bracketed pair refers to the two independent atoms on the symmetry plane (for which  $\sigma_y$  is zero) and the bottom entry to the two pairs of equivalent atoms above and below the plane.

symmetric structure which is pseudo-centrosymmetric, and that this is the reason for the difficulty in refining the non-centrosymmetric structure.

However, it appears that the weighted residual test can suggest the incorrect non-centrosymmetric structure instead of the correct centrosymmetric one. This may possibly be due to using an incomplete model, but is most likely to originate from an ill-conditioned matrix which arises from the pseudo-symmetry of the non-centrosymmetric structure.

If the matrix is ill-conditioned, it will vitiate the weighted residual test. Because of these difficulties it would appear unwise in such cases to depend on the weighted residual test alone.

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## Structure and Electron Density of 2,5-Dimethyl-*p*-benzoquinone

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The electron distribution in the dimethylquinone molecule has been studied by least-squares refinement of a flexible model chosen to represent the charge redistribution attendant on chemical binding. This model incorporates ellipsoidal pseudo-atoms centred at the mid points of all carbon-carbon and carbon-oxygen bonds and contracted, polarized hydrogen atoms; it assigns individually adjustable occupancy factors and anisotropic 'vibration' parameters to all heavy atoms. Results indicate a build-up of excess charge, amounting to about one-tenth electron, in the C-C bond region, drawn from localized regions on the far sides of the bonded carbon atoms; a further excess charge, of similar magnitude, in the  $\pi$  component of the C=C bond, with its maximum density about 0.5 Å above and below the nodal plane; no appreciable excess density in or near the C=O bond; and a sharp concentration and polarization of charge in hydrogen atoms bonded to carbon. Bond lengths and angles differ from those in the parent benzoquinone principally at the points of methyl substitution. The molecule appears to vibrate essentially as a rigid body except for an appreciable torsional oscillation of the methyl groups.

### Introduction

The X-ray data collected for the crystal-structure determination of 2,5-dimethyl-*p*-benzoquinone (Rabinovich & Schmidt, 1964) have been further analysed for the information they may yield on the distribution of electron density, especially in the regions of the covalent bonds. A preliminary report (Hirshfeld, Rabinovich, Schmidt & Ubell, 1963) concentrated largely on the shape of the hydrogen peaks; the present paper deals more generally with the changes in electron density in the molecule as compared with the separate atoms of which it is composed.

### Experimental data and initial refinement

The unit cell contains two molecules at non-equivalent centres of symmetry in  $P\bar{1}$  and has the cell dimensions, at  $25^\circ \pm 1^\circ\text{C}$ :

$$a = 4.013, b = 9.366, c = 9.738 \text{ \AA}, \\ \alpha = 93.50, \beta = 101.36, \gamma = 98.57^\circ.$$

The X-ray intensities were measured on the General Electric goniostat with nickel-filtered Cu  $K\alpha$  radiation in a convergent beam of  $0.6^\circ$  width, which was considered adequate to permit stationary-crystal-and-counter measurement of the integrated intensities