THE CRYSTAL STRUCTURE OF DIBENZENE CHROMIUM AT ROOM TEMPERATURE

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INTRODUCTION

The first approximate determination of the crystal structure of dibenzene chromium was performed by Weiss and Fischer[1]. These authors found the compound to be cubic with a cell edge of 9.67 Å and four molecules of $Cr(C_6H_6)_2$ per unit cell. The space group was found to be $Pa3$ which requires the molecule to have at least C_{3i} symmetry. Assuming D_{6h} as the molecular symmetry Weiss and Fischer derived the distances C–C in the ligands to be 1.38 ± 0.05 Å and Cr–C as 2.19 ± 0.10 Å.

ISOTROPIC REFINEMENT BY DIFFERENCE SYNTHESES

A refinement of the crystal structure of dibenzene chromium at room temperature was undertaken by us several years ago[2]. This refinement was based on three-dimensional X-ray diffraction data obtained by Professor I. Lindqvist and Dr. R. D. Rosenstein, then at the University of Uppsala, Sweden. The data comprise the visually estimated intensities of 177 independent reflexions, covering 3,560 points of the reciprocal lattice. The reflexions had been recorded on Weissenberg photographs taken with Mo$K\alpha$ radiation around [110] as the rotation axis; for the zero and first layer lines exposures with Cr$K\alpha$ radiation had also been made. The observed reflexions include 29 independent reflexions (corresponding to 636 reciprocal-lattice points) with mixed (even and odd) indices hkl, to which reflexions the Cr atom does not contribute. The space group $Pa3$ derived by Weiss and Fischer[1] was confirmed and the cube edge was determined to be 9.667 Å.

Because of the high multiplicity most reflexions were recorded several times on different layer lines. Scaling of the various layer lines was, therefore, straightforward; in addition, it was possible to determine the accuracy of a single estimation of the intensity as a function of the intensity. The standard deviation of a single estimation was found to be of the order of 10% in F for strong and moderate reflexions and gradually increasing to almost 20% for the weakest observed reflexions. The standard deviations of the experimental structure factors used in the refinement depend on the number of individual intensity estimations of the reflexions concerned. On the average the s.d. is 6% but it is somewhat better for the reflexions with mixed indices where the intensities were estimated from films taken with both Mo and Cr radiations.

Therefore, for a completely refined structure a disagreement factor R of slightly less than 5 % may be expected due to experimental inaccuracies only.

Starting from a model with D_{6h} symmetry the structure was refined by successive difference syntheses. The calculations were performed on the electronic computer Zebra of our University, with programmes written by Dr. D. W. Smits. Scattering factors for C were taken from Berghuis *et al.*[3] and for H from McWeeny[4]. The values for Cr were calculated from the scattering factors of Cr^{2+} given by Berghuis *et al.*[3], which were corrected for the non-ionization of the metal—as in reference 5—and for the real part of the anomalous scattering[6]. In all stages of the refinement the hydrogen atoms were placed in calculated positions; their positions were not refined independently. The hydrogen atoms were assigned the same isotropic temperature factor as was found for both independent sets of carbon atoms; for chromium another–smaller–thermal correction was applied. Refinement was straightforward and no difficulties due to extinction were encountered.

When the refinement had converged, R had a value of 6.3%. The final atomic positions are given in Table 1; the hydrogen positions given in the table are not calculated ones, but they were derived from low-angle difference syntheses[7] in which both sets of hydrogen atoms showed up quite clearly. The corresponding interatomic distances etc. and their estimated standard deviations are listed in Table 2; these values differ slightly from those given in our preliminary communication[2], where they were discussed at some length. The most remarkable result is the deviation of the benzene ligands from sixfold symmetry; C–C bonds of 1.44 Å are found to alternate with bonds of 1.36 Å. These distances (and all other distances in Table 2) are uncorrected for the libration of the rings about the molecular axis which was visible in high-angle difference syntheses. This torsional motion causes an apparent shortening of about 0.01 Å of all C–C bond distances; the corrections that should be applied

TABLE 1

ATOMIC PARAMETERS IN DIBENZENE CHROMIUM AT ROOM TEMPERATURE

		Isotropic refinement		*Anisotropic refinement*	
		value	*s.d.*	*value*	*s.d.*
Cr	$x=y=z$	0		0	
C1	x	0.1461	0.0010	0.1462	0.0009
	y	0.1643	0.0010	0.1654	0.0008
	z	−0.0198	0.0010	−0.0200	0.0009
C2	x	0.0494	0.0010	0.0493	0.0009
	y	0.0241	0.0010	0.0240	0.0008
	z	0.2137	0.0010	0.2136	0.0008
H1	x	0.163		0.169	
	y	0.222		0.230	
	z	−0.113		−0.114	
H2	x	0.015		0.014	
	y	−0.030		−0.038	
	z	0.298		0.302	

TABLE 2

INTERATOMIC DISTANCES AND ANGLES IN DIBENZENE CHROMIUM AT ROOM TEMPERATURE

	Isotropic refinement		*Anisotropic refinement*		*Cotton et al.*[a]	
	value	*s.d.*	*value*	*s.d.*	*value*	*s.d.*
Distances in Å						
C1–C2	1.438	0.014	1.436	0.012	1.407	0.017
C1–C2′	1.357	0.014	1.366	0.012	1.386	0.017
difference	0.081	0.024	0.070	0.020	0.021	0.030
Cr–C1	2.134	0.010	2.143	0.008	2.138	0.012
Cr–C2	2.132	0.010	2.132	0.008	2.132	0.012
difference	0.002	0.014	0.011	0.012	0.006	0.017
C1–H1	1.06		1.12			
C2–H2	1.03		1.10			
Distances from mean carbon plane in Å						
Cr	+1.612	0.007	+1.614	0.006	1.616	0.010
C1	−0.010	0.007	−0.013	0.006	0.004	0.010
C2	+0.009	0.007	+0.013	0.006	0.004	0.010
difference	0.019	0.014	0.026	0.012	0.008	0.020
H1	+0.10		+0.03			
H2	+0.04		+0.06			
Angles in degrees						
C2–C1–C2′	121.4	1.0	120.9	0.8		
C1–C2–C1′	118.5	1.0	119.0	0.8		

to the Cr–C and C–H distances are even smaller, while the bond angles and the planarity of the rings are not affected by the libration. For further refinement the anisotropy in the thermal motion had to be taken into account, but no Zebra programme for anisotropic refinement was available at the time.

ANISOTROPIC REFINEMENT BY LEAST SQUARES

I was most happy, therefore, when Mr. O. S. Mills of the Chemistry Department of the University of Manchester invited me to Manchester, to do a least-squares refinement of the structure with anisotropic temperature factors on the Mercury computer of the University.

A version of Rollett's structure-factor and least-squares programme[8] was available; Dr. J. S. Rollett had adapted the programme for the case that some atoms are in special positions of space group *Pa*3. The calculations on the Mercury computer were performed in November 1960. After some trials a weighting scheme was derived which approximately took into account the standard deviations of the experimental structure factors, depending on the s.d. of the intensity estimation as a function of the intensity and also on the number of independent estimations of the reflexions concerned. The same set of experimental data and the same atomic scattering factors were used as in the isotropic refinement by difference syntheses.

To avoid biasing the result, refinement was again started from a model with D_{6h} symmetry. However, it soon became evident that this symmetry is not compatible with the experimental data. After some cycles of refinement the hydrogen atoms were also included and their positions (but not their temperature factors) were refined simultaneously with those of the other atoms. The atomic positions, found after the refinement had converged, are included in Table 1, together with their standard deviations. Thermal parameters are listed in Table 3 and the observed and calculated structure factors in Table 4. The final value of the disagreement factor *R* for the observed reflexions is 5.3%.

TABLE 3

THERMAL PARAMETERS OF DIBENZENE CHROMIUM AT ROOM TEMPERATURE

The temperature factors are: exp. $(-\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j)$

	Cr		*C₁*		*C₂*	
	value	*s.d.*	*value*	*s.d.*	*value*	*s.d.*
$10^4\ \beta_{11}$	61.6	0.4	120	6	128	6
$10^4\ \beta_{22}$	61.6	0.4	89	5	109	10
$10^4\ \beta_{33}$	61.6	0.4	120	9	92	5
$10^4\ \beta_{12}=\beta_{21}$	—1.9	1.6	—37	5	—5	5
$10^4\ \beta_{13}=\beta_{31}$	—1.9	1.6	+2	6	—15	5
$10^4\ \beta_{23}=\beta_{32}$	—1.9	1.6	—16	5	—5	5

Interatomic distances, etc., were calculated by means of programmes written by R. A. Sparks; they are given in Table 2. The results do not differ significantly from those of the isotropic refinement, except that the accuracy has been improved. The difference between the alternating long and short C–C bonds in the rings is found as 0.07 Å with a standard deviation of 0.02 Å and is to be regarded as significant. This distortion from sixfold symmetry is too large to be ascribed to intermolecular interaction and should, therefore, be inherent in the $Cr(C_6H_6)_2$ molecule. Furthermore, the ligand rings are found to be slightly puckered, but the deviation of the carbon atoms from their mean plane (0.013 Å with a standard deviation of 0.006 Å) is barely significant. Such a puckering would lower the molecular symmetry from D_{3d} to C_{2h}.

It was felt that the fundamental problem of the symmetry of dibenzene chromium can only be solved unambiguously by further improvement of the experimental accuracy and by suppressing thermal motion which puts a serious limitation on the accuracy with which the carbon (and hydrogen) atoms can be placed. A low-temperature X-ray study by counter methods was accordingly started in our laboratory some time ago. A detailed discussion of the structure is postponed until the results of our low-temperature investigation are available.

COMPARISON WITH THE STUDY OF COTTON *et al.*

Recently, however, Cotton and coworkers[9] published preliminary results of an independent refinement of the crystal structure of dibenzene chromium at room temperature by isotropic least-square methods. Their results, before inclusion of the hydrogen atoms into the refinement, are also given in Table 2. It is seen that Cotton *et al.* find that the carbon atoms of the benzene rings form a regular hexagon within

Table IV. Observed and calculated structure factors.

h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c
1	1	1	142.4	146.6	5	5	4	10.3	-10.9	9	7	3	15.1	13.4
2	0	0	121.2	125.6	7	3	3	22.1	21.9	7	9	3	14.2	15.0
2	1	0	33.6	-34.7	8	2	0	13.9	15.7	10	6	2	11.5	13.0
2	1	1	39.3	-40.4	2	8	0	35.4	36.0	6	10	2	16.6	14.9
2	2	0	29.0	28.1	6	4	4	24.8	23.5	12	0	0	16.3	12.7
2	2	1	41.7	-40.6	2	8	1	7.3	-9.1	8	8	4	13.0	13.4
3	1	1	39.3	40.3	8	2	2	28.7	28.6	11	5	1	10.0	12.4
2	2	2	14.8	13.1	6	6	0	37.2	40.1	5	11	1	9.1	8.9
2	3	1	40.2	-41.5	7	5	1	35.4	35.9	7	7	7	20.9	19.6
4	0	0	99.7	97.7	5	7	1	25.1	24.3	12	2	0	12.7	14.0
4	1	0	10.3	10.3	5	5	5	24.9	23.9	2	12	0	9.7	11.5
3	3	1	47.8	47.1	6	6	2	30.0	30.3	12	2	2	10.0	12.7
4	2	0	63.5	59.5	8	4	0	19.0	19.0	10	6	4	10.6	10.6
2	4	0	52.9	60.1	4	8	0	29.0	27.4	6	10	4	12.4	12.6
4	2	1	18.1	-18.5	9	1	1	26.0	26.0	11	5	3	10.0	11.8
4	2	2	59.2	59.1	7	5	3	30.2	28.0	5	11	3	10.0	11.2
4	3	0	6.6	7.9	5	7	3	17.2	16.1	9	7	5	10.9	11.0
3	4	1	23.6	21.9	8	4	2	30.2	30.3	7	9	5	11.8	12.4
5	1	1	77.4	78.0	4	8	2	23.6	24.1	12	4	0	11.8	12.4
3	3	3	78.3	83.1	6	6	4	21.5	21.5	4	12	0	11.8	6.6
4	3	2	21.2	21.1	9	3	1	22.1	22.9	9	9	1	10.3	11.3
3	4	2	13.0	-12.2	3	9	1	34.2	34.3	12	4	2	9.7	11.2
2	5	1	14.2	-14.3	8	4	4	26.0	24.4	4	12	2	8.8	8.1
4	4	0	55.3	52.9	9	3	3	32.6	34.5	8	10	0	11.8	12.5
5	2	2	11.2	11.2	7	7	1	27.8	27.0	8	8	6	11.2	12.7
4	3	3	25.1	25.8	7	5	5	21.5	21.6	10	8	2	11.9	12.3
5	3	1	47.2	47.7	10	0	0	15.4	16.1	8	10	2	11.8	13.2
3	5	1	42.9	46.8	8	6	0	23.3	23.0	13	1	1	12.1	13.2
6	0	0	84.0	82.9	6	8	0	23.6	24.1	11	7	1	11.2	12.0
4	4	2	61.4	64.6	10	2	0	19.6	18.6	7	11	1	11.3	13.6
6	1	1	11.5	-10.5	2	10	0	23.9	24.7	9	9	3	12.7	12.4
6	2	0	33.2	38.8	8	6	2	23.6	24.4	10	6	6	6.6	9.2
2	6	0	52.0	51.8	6	8	2	19.0	19.5	13	3	1	11.5	11.1
4	5	0	18.7	-13.0	9	5	1	17.5	18.7	3	13	1	10.3	10.7
4	4	3	9.7	10.2	5	9	1	19.3	20.2	11	7	3	12.4	11.0
5	4	1	13.0	-12.9	7	7	3	19.9	19.9	7	11	3	9.7	12.9
5	3	3	51.1	50.9	10	2	2	26.4	28.3	9	7	7	9.1	10.2
6	2	2	31.4	31.1	6	6	6	28.7	26.4	12	6	0	13.0	12.3
4	5	2	11.2	10.3	9	5	3	26.3	24.6	6	12	0	11.5	11.7
4	4	4	59.5	58.0	5	9	3	19.3	19.3	10	8	4	10.3	10.7
7	1	1	36.6	37.5	10	4	0	13.6	15.8	8	10	4	10.0	11.5
5	5	1	44.1	42.9	4	10	0	16.3	17.1	12	6	2	12.7	11.3
6	4	0	35.7	38.1	8	6	4	20.9	19.8	9	9	5	9.4	9.8
4	6	0	31.7	28.8	6	8	4	17.2	16.4	5	13	1	10.0	10.2
6	3	3	7.9	8.2	10	4	2	24.5	23.9	7	11	5	11.5	10.5
6	4	2	37.2	35.2	4	10	2	21.5	20.9	14	2	0	9.7	9.8
4	6	2	25.7	23.9	11	1	1	12.1	14.9	2	14	0	8.5	11.6
7	2	2	7.6	-7.8	7	7	5	21.2	20.7	10	10	0	10.9	8.5
7	3	1	18.7	17.9	8	8	0	12.7	14.9	11	9	1	10.9	10.7
3	7	1	25.7	26.4	11	3	1	15.4	17.3	14	2	2	8.8	10.3
5	5	3	37.2	34.1	3	11	1	14.2	13.4	10	10	2	9.4	9.6
6	5	0	24.5	-24.0	9	7	1	9.1	11.4	12	8	0	9.4	11.2
4	6	3	6.6	-7.4	7	9	1	17.8	15.9	8	12	0	12.4	9.7
3	7	2	8.8	-9.3	9	5	5	14.2	15.0	11	9	3	10.0	10.3
6	5	1	5.5	-7.5	10	4	4	18.4	18.5	4	14	0	11.8	10.7
5	6	1	16.0	-14.9	8	8	2	14.5	15.3	12	8	2	13.9	10.3
8	0	0	31.4	31.2	6	10	0	12.7	13.7	13	7	1	10.3	9.7
6	5	2	6.0	-6.3	8	6	6	19.0	18.1	3	15	1	9.4	8.6
8	1	1	7.6	-5.9	11	3	3	15.7	16.4	15	3	3	10.0	7.4

the limits of accuracy. After the inclusion of hydrogen the two independent C–C distances are even found to be exactly equal, namely 1.387 Å with a standard deviation of 0.017 Å.

This discrepancy of the results of Cotton *et al.* with ours obviously calls for some comment and we shall try to offer a possible explanation. At first sight it may be thought that the discrepancy is due to an underestimation of the standard deviations in either or both of the investigations. However, it is believed that this is not the case. The fact that the standard deviations we derived are slightly lower than those obtained by Cotton *et al.*[9] is probably due to our taking into account of the anisotropy of the thermal motion. The difference in standard deviations is in keeping with that of the final values of R, which are 6.1% in the study by Cotton *et al.* compared to 5.3% in ours. Furthermore, we find the thermal motions of the two independent sets of carbon atoms in good agreement with each other; it is hard to assume that this agreement is coincidental, as it would be if the accuracy attained was less than calculated.

Another possible explanation might seem that our experimental data are affected by a systematic error. Let us assume for the moment that the true symmetry of the molecule is D_{6h} and that, therefore, the ligand rings are regular hexagons. What distortions would be needed to convert this model into one with rings containing alternating long and short carbon bonds? Analysis shows that the x parameters of both C1 and C2 should increase and the y parameters of both C1 and C2 decrease in order to pass from the D_{6h} model to the "distorted" one. (The distortion is not sensitive to a change in the z parameters). Just these parameter changes were found in our structure refinement (which started from a D_{6h} model) and it would seem too much of a coincidence if a systematic error in the experimental data would cause exactly these four mutually independent effects (and leave the thermal motion almost unaffected). We conclude, therefore, that the possibility of the distortion of the rings found by us being an artifact should also be discarded.

The opposite effect, that is the enhancement of the symmetry of a C_{3i} or D_{3d} molecule to D_{6h} symmetry, however, needs only the addition of a twofold rotation axis which passes through the metal atom and is perpendicular to the planes of the rings. Such an apparent twofold axis may very well be due to orientational disorder of the molecules. Disorder of this type is not unlikely, since the two orientations would be nearly equivalent. Indeed, orientational disorder of this kind has been observed in a three-dimensional neutron-diffraction study of ferrocene[10], even though the two orientations of the ferrocene molecules are not equivalent in the crystal. A similar effect was also observed in an X-ray study of ferrocene[11], but there it was ascribed to extinction. In the case of odd-membered rings, such as in ferrocene, an additional twofold molecular axis can easily be recognized as an artifact, since it doubles the apparent number of ring members. In the case of even-membered rings, such as in dibenzene chromium, the additional axis only enhances the apparent symmetry of the rings and such an effect—if it is not large—can hardly, if at all, be discovered by diffraction methods.

Addition of an apparent twofold axis, caused by orientational disorder, to the dibenzene chromium molecule with the geometry found in our study would have the same (within a fraction of a percent) effect on the diffraction intensities as a libration of the rings with a r.m.s. amplitude of only 0.8° or 0.02 Å, which would be almost undetectable as such. Furthermore, an additional twofold axis would make both sets of C–C distances equal to 1.401 Å and both sets of Cr–C distances 2.138 Å; the carbon rings would become exactly planar, while the distance of the metal atom from this plane would remain 1.614 Å. In other words: addition of a twofold axis to the dibenzene chromium molecule as we found it, leads to a model which is exactly that found by Cotton *et al.*[9]. These authors did indeed observe a libration of the rings about the molecular axis; very probably the small artificial libration caused by the orientational disorder is, however, swamped by a considerably larger real libration, which was also found in our study.

It appears, therefore, that the discrepancies between Cotton's results and ours on the room-temperature structure of dibenzene chromium can be completely explained by the presence of orientational disorder in the crystals investigated by Cotton *et al.* It should be emphasized, however, that the evidence for orientational disorder in dibenzene chromium is indirect only. While orientational disorder of odd-membered rings can be discovered directly by diffraction methods (and has been found in ferrocene), no direct proof or disproof by such methods is possible for even-membered rings. Nevertheless it is hoped that our low-temperature study of dibenzene chromium will shed some light on this problem too.

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SUMMARY

The crystal structure of dibenzene chromium at room temperature has been refined from three-dimensional X-ray diffraction intensities. The results of the least-squares refinement, which takes account of the anisotropy of the thermal atomic motions, confirm our earlier preliminary results[2] which were obtained from difference syntheses. In the ligand rings C–C bonds of 1.436 ± 0.012 Å alternate with bonds of 1.366 ± 0.012 Å. The different results of Cotton *et al.*[9], who found no significant distortion from D_{6h} molecular symmetry, are probably due to orientational disorder in their crystals, such as has also been observed in ferrocene. In even-membered rings this disorder causes an enhancement of the apparent symmetry.

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