

at a carbonyl could be the predominate factor here. This seems rather more likely than a postulate of a gross difference in charge distribution in these molecules to explain the position of attack.

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Molecular symmetry and crystal structure of dibenzene chromium

There has been considerable discussion concerning the symmetry of the $\text{Cr}(\text{C}_6\text{H}_6)_2$ molecule in solid dibenzene chromium. A room-temperature X-ray diffraction study by one of the present authors^{1,2} indicated a distortion from D_{6h} molecular symmetry; in the ligand rings carbon-carbon bonds of 1.436 ± 0.012 Å were found to alternate with bonds of 1.366 ± 0.012 Å. Another determination of the crystal structure of dibenzene chromium at room temperature was undertaken by Cotton *et al.*³ In this investigation no significant deviation from D_{6h} symmetry was observed; the length of both independent sets of carbon-carbon bonds was given as 1.387 ± 0.017 Å. Cotton's experimental data were also refined and analyzed by Ibers⁴, who found these data to provide no evidence for significant deviations from D_{6h} symmetry of the dibenzene chromium molecule.

A critical comparison and analysis of Cotton's³ and Jellinek's² data and results was undertaken by Wheatley⁵. His independent refinement of the structure, based on Jellinek's experimental data, confirmed the apparent distortion of the benzene ligands and led to essentially the same interatomic distances and standard deviations as those published previously². Wheatley's results confirmed our view² that more and better experimental data were needed to solve the problem. We had, therefore, started a study of the crystal structure of dibenzene chromium at low temperatures, in order to suppress thermal motion which puts a serious limitation on the accuracies with which the atomic positions can be determined at room temperature.

It has been suggested² that the discrepancy between Cotton's³ and Jellinek's² experimental data might be caused by orientational disorder in the crystals studied by Cotton *et al.* Since mesitylene is frequently used as a catalyst in the synthesis of

dibenzene chromium, a possible disorder in the crystals could be due to the substitution of a (very small) part of the benzene rings by mesitylene. Therefore, dibenzene chromium prepared in the absence of mesitylene was used in our study; good crystals were obtained by vacuum sublimation.

Single-crystal data were collected at a temperature of 100°K by means of a manually operated three-circle counter diffractometer⁶; Mo K α radiation was employed which was monochromatized by balanced filters. The intensities of all 771 independent reflexions up to $\Theta = 37.5^\circ$ were measured; the usual corrections were applied, including corrections for absorption, for attenuation filters and for the non-linearity and drift of the counting system. The reflexions include 543 independent reflexions with mixed (even and odd) indices hkl , to which reflexions the Cr atom does not contribute (apart from a very small contribution due to the thermal anisotropy); the intensities of 83 of these reflexions were not significantly different from zero, while 197 other reflexions were too weak to be measured with high accuracy. The remaining 263 independent reflexions with mixed indices were used in the refinement of the structure, as were 223 independent reflexions with hkl all even or all odd; the strongest five reflexions with unmixed indices were excluded from the refinement, since their intensities may be affected by extinction.

The positional and (anisotropic) thermal parameters of Cr, of the two independent sets of carbon atoms and of the two independent sets of hydrogens were refined by least squares, using various schemes of weighting of the intensities. The scattering factors for Cr, as given in the International Tables⁷, were corrected for the real part of the anomalous scattering; scattering factors for C were taken from the International Tables⁷, for H from Stewart *et al.*⁸

TABLE 1

ATOMIC PARAMETERS IN DIBENZENE CHROMIUM AT 100°K

	<i>x</i>	<i>y</i>	<i>z</i>
Cr	0	0	0
C 1	0.1471	0.1677	-0.0233
C 2	0.0471	0.0264	0.2174
H 1	0.174	0.210	-0.109
H 2	0.007	-0.023	0.290

The final positional parameters in space group $Pa\bar{3}$ are given in Table 1. The standard deviation in the parameters of the carbon atoms are calculated as 0.0002, those of the hydrogen atoms as 0.003; the dependence of the parameters on the weighting scheme employed was somewhat less than these standard deviations. The final value of R was 3.1% for the 486 independent reflexions used in the refinement and about 4.5% for all 771 independent reflexions within the reflexion sphere investigated.

The interatomic distances derived from the parameters in Table 1 and the dimensions of the cubic unit cell ($a = 9.553 \text{ \AA}$ at 100°K) are listed in Table 2. Also included in the Table are the distances after correction for the observed thermal motion. The major axes of the thermal ellipsoids of the carbon atoms correspond to a libration of the rings about the molecular axis with a r.m.s. amplitude of 3° or 0.07 \AA . This

TABLE 2

INTERATOMIC DISTANCES IN DIBENZENE CHROMIUM AT 100°K (IN Å).

	Distance	s.d.	Distance corrected for effect of thermal motion
C 1-C 2'	1.417	0.003	1.420
C 1-C 2''	1.416	0.003	1.419
Cr-C 1	2.143	0.002	2.147
Cr-C 2	2.140	0.002	2.144
C 1-H 1	0.95	0.03	
C 2-H 2	0.92	0.03	
<i>Distances from mean carbon plane</i>			
Cr	±1.606	0.001	±1.609
C 1	-0.002	0.001	-0.002
C 2	±0.002	0.001	±0.002
H 1	±0.09	0.03	
H 2	±0.09	0.03	

torsional motion causes an apparent shortening of the C-C bonds by 0.003 Å (and of the C-H bonds by 0.002 Å); the total libration of the molecule reduces the apparent Cr-C distances by 0.004 Å.

It is seen that our present results do not indicate any significant deviation from D_{6h} molecular symmetry and that the two independent sets of carbon-carbon distances are found to be of equal length. Unfortunately, the results of our present study are not sufficient for disproving the hypothesis² of orientational disorder in the crystal being the cause of the (apparent) D_{6h} symmetry: if the two C-C distances differ by 0.07 Å, such a disorder would appear as a libration of the rings with a r.m.s. amplitude of only 0.8° or 0.02 Å, which would be swamped by the real libration, even at 100°K. It is felt, however, that the basis of the hypothesis of orientational disorder has been considerably weakened by the present investigation, the more so since our results are in good agreement (except for the C-H distances) with those of an electron-diffraction study of gaseous dibenzene chromium³.

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