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The Molecular Structure of Gaseous Dibenzene Chromium, $(C_6H_6)_2Cr$

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The molecular structure of gaseous dibenzene chromium has been determined from electron scattering data. Analysis of the radial distribution curve results in a model of symmetry D_{6h} with C_1—C_2 = 1.423 ± 0.002 Å, C_1—H_1 = 1.090 ± 0.005 Å, Cr—C = 2.150 ± 0.002 Å, and a vertical ring to ring distance of 3.226 ± 0.005 Å. No indication for the existence of two different C—C bond distances is found, and if such a difference exists it cannot exceed 0.02 Å.

I. INTRODUCTION

The synthesis of dibenzene chromium, $(C_6H_6)_2Cr$, was reported by Fischer and Hafner[1] nine years ago. Since the compound is diamagnetic and has a zero dipole moment, these workers suggested a ferrocene-like sandwich structure. A preliminary X-ray investigation[2] showed that the molecule occupies a crystal site of symmetry C_{3i}: since free rotation of the ligand rings is unlikely, they must then be parallel and eclipsed. If they have retained the sixfold rotation axis of the free benzene molecule, the molecular symmetry is D_{6h}. But, as the X-ray investigators pointed out, the possibility that the ligands are distorted into a structure with only a threefold rotation axis could not be ruled out. In that case the molecular point group is D_{3d}.

The infrared spectrum of solid $(C_6H_6)_2Cr$ was first interpreted as evidence for[3] and later against[4] such distortion. In 1960, however, Jellinek[5] reported on an X-ray investigation which resulted in a model in which C—C bonds of length 1.439 Å alternated with bonds of length 1.353 Å, bond lengths corresponding very closely to those one would expect in a frozen Kekulé structure. The standard deviation was a mere 0.014 Å. But an attempt to explain this sensational result through a quasi Jahn-Teller effect failed,[6] and the molecular structure was still regarded as not firmly established. Indeed, another X-ray investigation by American workers[7] yielded a model which did not deviate significantly from sixfold symmetry.

These apparently contradictory results might be explained through a rotational disorder of the ligand rings in the crystal used by Cotton *et al.*, so we have, at Dr. Fischer's suggestion, undertaken an investigation of gaseous $(C_6H_6)_2Cr$ by means of electron diffraction.

II. THE ELECTRON DIFFRACTION STUDY

The scattering pattern from gaseous $(C_6H_6)_2Cr$ at 180° was recorded on the Oslo apparatus using two nozzle to plate distances, 19 cm and 48 cm, corresponding to s-ranges from 7 Å^{-1} to 46 Å^{-1} and from 1.5 Å^{-1} to 20 Å^{-1}, respectively. Three apparently perfect plates covering each range were selected for photometering. The intensities were corrected for plate flatness, nonlinearity of plate response, and the intensity reduction by the rotating sector in the usual way.[8] The background was subtracted and the molecular intensity, obtained after multiplication with the normalizing function

$$s\,\varphi(s) = s(Z_C - F_C)^{-2} \tag{1}$$

is shown in Fig. 1 A. The atomic scattering factor of carbon, F_C, was taken from Berghuis and co-workers.[9]

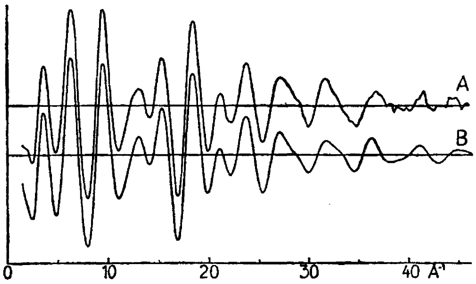

Fig. 1. Molecular intensity curve. (A) experimental and (B) theoretical.

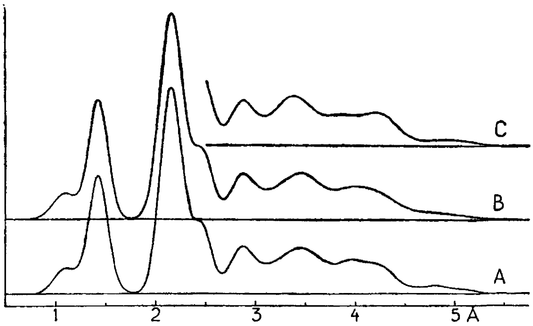

Fig. 2. Radial distribution curves. $k = 0.0036$ Å^2. (A) experimental, (B) theoretical for the model of Table 1, and (C) theoretical for a staggered model.

Fourier inversion, with artificial damping factor $k = 0.0036$ Å^2, yields the radial distribution (RD) curve shown in Fig. 2 A.

Using the results of the X-ray investigations [5,7] the interpretation of the main features of the RD-curve is straightforward: The peak at 1.4 Å must correspond to the C—C bond distance or distances, the unresolved peak at 1.1 Å to the C—H bond distance, the peak at 2.15 Å to the Cr—C distance, and the unresolved peak at 2.4 Å to the C_1—C_3 nonbonded distance. The peak at 2.8 Å contains a C_1—C_4 peak at 2.8 Å and a Cr—H peak at 2.9 Å, and the unresolved peaks at higher r-values arise mainly from distances between atoms in different rings.

If the benzene rings retain their sixfold symmetry in the complex, the peak at 1.423 Å corresponds to 12 identical C_1—C_2 distances. If the rings are distorted, it is the sum of two closely spaced peaks, each corresponding to six identical C_1—C_2 or C_2—C_3 distances. Since the sum of two such Gaussian peaks is itself very nearly Gaussian, our argument as to whether the rings are distorted cannot be based on the shape of the observed peak *per se*, but must be based on the half-width. The latter is determined by the spacing between the two peaks, that is the bond length difference, and the root mean square amplitudes of vibration, the u-values. The u-values can be calculated from the vibrational frequencies, the atomic masses and the temperature: To a first, rough, approximation u^2 is proportional to $T/m\nu$. Two of the C—C stretching frequencies of $(C_6H_6)_2Cr$ are infrared active:[4] $\nu_1 = 971$ (993) cm^{-1} and $\nu_{19} = 1426$ (1482) cm^{-1}. The numbers in parentheses give the corresponding frequencies of free benzene. The root mean square amplitude of the C_1—C_2 bond in $(C_6H_6)_2Cr$ at 180°C should then be equal to — or slightly greater than — the corresponding u-value in benzene at —10°C, that is $u = 0.0454$ Å.[10] According to our experience u-value determination by electron diffraction is not very sensitive to random errors: Two completely independent studies of benzene in this laboratory gave root mean square amplitudes for the C—C bond differing by 0.0002 Å.[10] Ample regard should therefore have been paid to possible experimental errors if we regard $u = 0.0435$ Å as a lower limit for the experimentally determined C_1—C_2 amplitude in $(C_6H_6)_2Cr$.

The radial distribution curve offers no evidence for the existence of two different C—C bond lengths: If the benzene ligands are supposed to have sixfold symmetry, the half width of the experimental peak corresponds to u (C_1—C_2) $= 0.045$ Å. Assuming a bond length difference of 0.02 Å, the half-width can only be reproduced if $u = 0.0435$ Å, a difference of 0.04 Å requires $u = 0.039$ Å. Hence the C—C bond lengths should not differ by more than 0.02 Å.

If there is no split whatsoever, the C—C bond length is 1.423 Å, which is significantly longer (0.026 Å[10]) than in benzene. This elongation is no doubt due to spilling of electrons from the metal atom d-orbitals into the benzene π antibonding orbitals predicted by selfconsistent field molecular orbital calculations.[11]

The C—Cr distance is found to be $R = 2.150$ Å. The corresponding peak is not strictly Gaussian, but is given by the more complicated expression:

$$N(r) = \int_0^\infty \varphi\,(s)\,(Z_C - F_C')\,(Z_{Cr} - F_{Cr}')\cos\,(\eta_{Cr} - \eta_C)\exp\,[(\tfrac{1}{2}u^2 + k)s^2]$$
$$\cos\,[(R - r)s]R^{-1}\,\mathrm{d}s$$

The peak was computed for a series of u-values using the values for F' and η, the phase angles, calculated by Ibers and Hoerni.[12] It was found that the best fit to the experimental RD curve was obtained for $u = 0.070$ Å. This normal curve is shown in Fig. 3 with a Gaussian peak corresponding to $u = 0.074$ Å. The latter was used as an approximation when the RD curve of

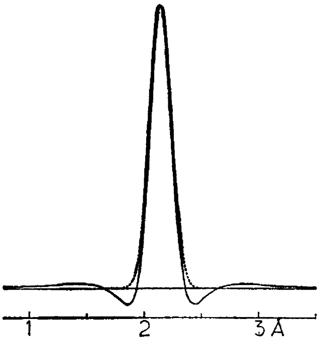

Fig. 3. Cr—C normal curve calculated from eqn. (2) with u = 0.070 Å. A Gaussian peak with u = 0.074 Å is dotted in.

the entire molecule was calculated. It is seen that this will introduce slight errors in the region 1.6 to 2.8 Å.

There are then only two more independent distances to be determined: The C—H bond length was found to be 1.09 Å. If the hydrogen atoms lie in the plane of the carbon ring, this leads to a Cr—H distance of 2.98 Å. It was found, however, that the best agreement between experimental and theoretical RD curves was obtained if the Cr—H distance was 2.935 Å, corresponding to a bending of the C—H bonds 5° out of the plane of the carbon ring towards the chromium atom. This should not be considered significant: The shift may be due to a a shrinkage effect, and the relatively small Cr—H peak may be sensitive to the errors introduced by the non-Gaussian shape of the neighbouring Cr—C peak.

Table 1. The molecular parameters of $(C_6H_6)_2Cr$, D_{6h}.

	$r_g(1)^a$ (Å)	$r_g(0)^b$ (Å)	u (Å)
C_1—C_2	1.423 ± 0.002	1.424 ± 0.002	0.045
$C_1...C_3{}^c$	2.4647		0.055
$C_1...C_4{}^c$	2.8460		0.063
C_1—H_1	1.090 ± 0.005		0.084
$C_1...H_2{}^c$	2.1814		0.100
$C_1...H_3{}^c$	3.4496		0.120
$C_1...H_4{}^c$	3.9332		0.120
Cr—C	2.150 ± 0.002	2.152 ± 0.002	0.070
Cr—H	2.935 ± 0.04		0.140
$C_1...C_1{}^c$	3.226		0.140

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a) The limits indicated are limits of reproducibility.

b) $r_g(0) = r_g(1) + u^2/r_g(1)$. If anharmonicity is disregarded $r_g(0) = r_e$, the equilibrium distance.

c) Calculated from the four bond lengths.

From the four bond lengths mentioned above, all other distances in the molecule could be calculated. These and their u-values are listed in Table 1. A scaled theoretical intensity curve calculated from

$$I_{\text{theor}} = \Sigma_{i>j} Z_i Z_j \exp\left(-\tfrac{1}{2} u_{ij}^2 s^2\right) \sin\left(R_{ij} s\right)/R_{ij} \tag{3}$$

is shown in Fig. 1 B.

Fig. 2 B shows a theoretical RD curve. The agreement is everywhere excellent except in the vicinity of 5 Å. A theoretical RD curve for a staggered, D_{6d}, model is shown in Fig. 2 C. The difference between this curve and the experimental curve should be considered significant.

The independent bond lengths obtained by analysis of the RD curve, $r_g(1)$ in Bartells notation,[13] can be converted into $r_g(0)$, the center of gravity of the radial probability curve, by adding $u^2/r_g(1)$; see Table 1. If anharmonicity is disregarded $r_g(0) = r_e$, the equilibrium distance. It should be emphasized that the limits given are not limits of error, but limits of reproducibility estimated from experience in this laboratory.

Finally we carried out a least square refinement on the intensity curve using a program based on eqn. (3) written by H. M. Seip. All distances except C_1-C_2 were kept constant. The refinement converged to give $C_1-C_2 = 1.4230$ Å with standard deviation 0.0010 Å and $u(C_1-C_2) = 0.0446$ Å with standard deviation 0.0010 Å. $\Sigma(I_{\text{theor}} - I_{\text{obs}})^2 = 2.74$. Next the C_1-C_2 and C_2-C_3 bond lengths were allowed to differ. The calculations converged very slowly to give $C_1-C_2 = 1.3933$ Å, s.d. = 0.0027 Å, $C_2-C_3 = 1.4569$ Å, s.d. = 0.0029 Å, $u_1 = 0.0254$ Å, s.d. = 0.005 Å, $u_2 = 0.0286$ Å, s.d. = 0.005 Å. $\Sigma(I_{\text{theor}} - I_{\text{obs}})^2 = 2.66$. We feel that the low u-values make this result completely unacceptable, and we offer it here only as a comment on the usefulness of least square calculations for electron diffraction studies of this kind.

There are several possible reasons for the present failure: The formula for the theoretical intensity (3) is only an approximation even for the harmonically vibrating molecule.[14] Both this approximation and the advent of anharmonicity would "split" any set of identical distances into one short set with low u-values and a longer set with larger u-values. Errors in the blackness correction applied, in the relative scaling of the data, and in the atomic scattering factor used in the normalizing function, eqn. (1), could easily have the same effect.

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