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The Structure of Hexamethylbenzenechromium Tricarbonyl with Comments on the Dibenzenechromium Structure[1]

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The controversy concerning the molecular symmetry of dibenzenechromium has prompted a three-dimensional X-ray investigation of the molecular configuration of hexamethylbenzenechromium tricarbonyl, $(H_3C)_6C_6Cr(CO)_3$, which has produced results pertinent to the nature of *arene complexes.* Hexamethylbenzenechromium tricarbonyl crystallizes with eight molecules in an orthorhombic unit cell of symmetry Pbca and dimensions $a = 13.67 \pm 0.03$ Å., $b = 13.53 \pm 0.03$ Å., and $c = 15.27 \pm 0.03$ Å. The structural determination including rigid-body analysis and anisotropic least-squares refinement has resulted in final discrepancy factors of $R_1 = 10.5\%$ and $R_2 = 10.0\%$ for 1447 observed reflections. In each molecule the carbonyl groups occupy three trigonal coordination sites of the chromium atom; the hexamethylbenzene ring lies on the opposite side of the chromium atom, parallel both to the plane of the three carbonyl carbon atoms and to the plane of the three oxygen atoms. The $Cr(CO)_3$ fragment is oriented such that (for a valence bond model with localized octahedral-type chromium orbitals) three assumed chromium orbitals (which can be delocalized in an MO formulation) point toward the midpoints of the alternate C–C bonds of the hexamethylbenzene ring. The methyl carbon atoms of the hexamethylbenzene ring are essentially coplanar with the benzene carbon atoms. The trigonal field of the $Cr(CO)_3$ moiety produces no evidence of a threefold distortion of the ring. Instead, a twofold deformation of both the benzene carbon and methyl carbon atoms is indicated which is attributable to asymmetric crystal forces and to a possible absence of the sixfold symmetry of the carbon skeletal structure in "free" hexamethylbenzene due to intramolecular steric interactions of the methyl groups.

Introduction

This X-ray study of hexamethylbenzechromium tricarbonyl was prompted by a controversy concerning the structure of the sandwich-bonded dibenzenechromium complex. Independent three-dimensional X-ray analyses of dibenzenechromium[4-6] have given conflicting answers with respect to the symmetry of the π-bonded benzene ring. Jellinek[4] found a significant difference in adjacent bond lengths which was interpreted to result from a partial threefold localization of the π-electrons of each ring as a result of bonding to a chromium of octahedral valency, whereas the work by Cotton, Dollase, and Wood[5] indicated the equivalence of all the C–C bonds of both rings within estimated error with the resulting retention of the sixfold symmetry axis for benzene. In addition, Ibers[6] carried out refinements of the X-ray data collected by Cotton, *et al.*,[5] wherein the resultant R values were compared for models of both D_{3d} and D_{6h} molecular symmetry. Ibers concluded that the X-ray data of Cotton, *et al.*, are completely consistent with D_{6h} symmetry for the dibenzenechromium molecule. Consequently, the studies both by Cotton and co-workers[5] and by Ibers[6] yielded no evidence for any π-electron localization in the benzene ring when bonded to the chromium. Theoretical arguments have been put forward by several groups in support of both points of view.[7-11]

The structural analysis of dibenzenechromium is made difficult by the high crystallographic point group symmetry of C_{3i} imposed on the molecule; this means that only two of the six C–C bond lengths of benzene are crystallographically independent. Furthermore, Jellinek[4] suggested that the X-ray data of Cotton, *et al.*,[5] may be based on a crystal with has a twofold orientational disorder about the molecular threefold axis (*i.e.*, through the chromium atom and the center of the benzene ring). Such a disorder then would give two equal C–C bond lengths which essentially are the average of the two distinct C–C distances observed by Jellinek.[4] Also, the large uncertainty in the hydrogen positions due to the relatively low scattering power of the hydrogen atoms made it virtually impossible in the X-ray studies at room temperature[4-6] to ascertain the degree of coplanarity of the hydrogen atoms in the molecule.

In light of the above difficulties, it was felt that an X-ray investigation of hexamethylbenzenechromium tricarbonyl would possibly clarify the chromium–benzene problem. The chromium tricarbonyl fragment would serve to locate the assumed localized octahedral (or trigonal) type orbitals (which of course for the D_{6h} model are delocalized) of the chromium atom; these chromium orbitals involved in the benzene ring bonding would be directed either (1) toward the midpoints of the alternate C–C bonds or (2) toward alternate ring carbon atoms. In the former case (1) the presence of the six methyl groups on the benzene

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ring would provide an added check on ring distortion, since an X-ray structural determination of "free" hexamethylbenzene[12] indicated a sixfold coplanar system for the carbon framework. Thus, if a threefold distortion of the metal-complexed ring exists, it presumably could result (in the absence of significant distortions from packing effects) in alternating C–C distances both in the inner hexagon of ring atoms and in the outer hexagon of methyl carbons. In the latter case (2), where the assumed chromium orbitals would be directed toward the alternate carbon atoms, it would be expected from other organometallic structural studies that the attached alternate methyl carbons might be deformed from the benzene plane to a different degree than the other three methyl carbons.

Structural investigations of benzenechromium tricarbonyl,[13] biphenyl bis(chromium tricarbonyl),[14] and phenanthrenechromium tricarbonyl[15] have shown the $Cr(CO)_3$ fragment to be oriented such that the three orbitals point toward the midpoints of the ring bonds. Since these X-ray analyses were based only on two-dimensional data, the results were not sufficiently precise to allow any conclusions to be made concerning possible distortion of the rings when π-bonded to the chromium. In contrast, our three-dimensional single crystal X-ray study of hexamethylbenzenechromium tricarbonyl, which included anisotropic least-squares refinement, has revealed the detailed molecular configuration with structural information of significance to the dibenzenechromium structural problem.

Experimental

Well-formed yellow crystals of hexamethylbenzenechromium tricarbonyl were generously supplied to us by Professor E. O. Fischer of München. The density was obtained by the flotation method. A crystal cut down to a cube approximately 0.03 cm. on a side was used for obtaining intensity data. Due to possible air sensitivity, the crystal was mounted in a capillary which then was evacuated and filled with argon. No surface or internal decomposition was observed during the 2 months of exposure to the X-ray beam.

Lattice constants were measured from precession photographs of the three principal zones, and the resulting agreement was well within the indicated experimental error. The precession camera settings were calibrated with a NaCl crystal. Multiple-film equi-inclination Weissenberg data about both the b and c rotation axes (*viz.*, ***hkl*** reciprocal levels with l = 0–10, 12, 14, 16; ***hkl*** levels with k = 0–10) were obtained with zirconium-filtered Mo Kα radiation. The intensities were visually estimated by comparison with a calibrated standard strip. After Lorentz-ploarization and spot extension corrections,[16] the 1147 and 1119 Weissenberg reflections collected about the b and c rotation axes, respectively, were correlated *via* least squares[17] to give a final total of 1447 independent reflections on a common scale. The weighted reliability index R_2 for this merging was 2.7%.

The structure was solved with the corrected, unscaled data taken about the c axis. The final least-squares refinements (both isotropic and anisotropic) were carried out on the merged data. Absorption was neglected due to the low absorption coefficient ($\mu R_{\max} < 0.4$). The standard deviations of the structure amplitudes were estimated as follows[18]: If $I_0(hkl) < \sqrt{10}I_{\min}$, then $\sigma(F_o) = (F_o/20)[\sqrt{10}I_{\min}/I_0(hkl)]^2$; if $I_0(hkl) \geqslant \sqrt{10}I_{\min}$, then $\sigma(F_o) = (F_o/20)$.

Crystal Data

The unit cell of $C_6(CH_3)_6Cr(CO)_3$ is orthorhombic with lattice parameters $a = 13.67 \pm 0.03$ Å., $b = 13.53 \pm 0.03$ Å., and $c = 15.27 \pm 0.03$ Å. The calculated density of 1.40 g./cc. for eight molecules per unit cell agrees well with the measured density of 1.39 g./cc. Systematic absences of $h = 2n + 1$ for $\{hk0\}$, $k = 2n + 1$ for $\{0kl\}$, and $l = 2n + 1$ for $\{h0l\}$ indicate the probable space group Pbca($D_{2h}{}^{15}$), later confirmed by the structural refinement.

All atoms were found to be in the eightfold set of general positions (8c): $\pm(x,\ y,\ z;\ ^1/_2 + x,\ ^1/_2 - y,\ \bar{z};\ \bar{x},\ ^1/_2 + y,\ ^1/_2 - z;\ ^1/_2 - x,\ \bar{y},\ ^1/_2 + z)$.[19] The asymmetric unit consists of one hexamethylbenzenechromium tricarbonyl molecule, which required the location of one chromium, fifteen carbon, and three oxygen atoms (and ideally eighteen hydrogen atoms). Since the intensities of the ***hkl*** reflections with $l = 2n + 1$ were observed to be weak relative to those with l even, it was concluded that the chromium atoms were spaced in pairs at half-cell intervals along the c direction (which occurs when the asymmetric chromium possesses a y coordinate of $^1/_4$).

Solution of Structure

A three-dimensional Patterson function was calculated from the corrected Weissenberg data taken about the c axis. An interpretation of the Cr–Cr vectors yielded initial coordinates of $x = 0.193$, $y = 0.250$, $z = 0.077$ for the asymmetric chromium atom. When only the eight symmetry-related chromium atoms are considered, the y coordinate of $^1/_4$ results in four chromium atoms being related to the other four by a translation of $c/2$. Hence, the unit cell is halved in the c direction, and the space group transforms to Pbma ($D_{2h}{}^{11}$) with the four chromium atoms in the reduced unit cell located in the following set of fourfold special positions (4d) of point symmetry C_s-m: $\pm(x,\ ^1/_4,\ z;\ ^1/_2 + x,\ ^1/_4,\ \bar{z})$. The consequence of the chromium atoms possessing higher symmetry than the actual crystallographic symmetry of Pbca imposed on the eight molecules in the unit cell is that the chromium atoms have no effect on the phases for the ***hkl*** reflections with l odd (*i.e.*, for these reflections the calculated structure factors based on the positions of the chromium atoms alone would be zero). With the use of only the even l reflections a first approximation to a three-dimensional electron density synthesis was computed phased on the chromium atoms. Although the two halves of the asymmetric molecule were superimposed

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to give mirror images of the approximately correct peaks, none of the peaks overlapped. An interpretation of this map produced initial coordinates for the eighteen carbon and oxygen atoms. The hexamethylbenzene ring was found to be oriented nearly perpendicular to the *b* axis.

A three-dimensional isotropic least-squares refinement of the nineteen nonhydrogen atoms resulted in discrepancy factors of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 12.3\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100 = 13.3\%$. A three-dimensional difference map based on the parameters from the isotropic refinement showed evidence for thermal anisotropy only for the $Cr(CO)_3$ fragment; an attempt was made to locate the methyl hydrogen positions, but no peaks were observed in the regions where expected. In order to provide a better calculated model and thereby to obtain more reliable positional parameters, an anisotropic least-squares refinement then was undertaken. After three cycles all coordinate shifts were less than 12% of their individual standard deviations. This anisotropic refinement of all atoms (based on the merged data with one scale factor) resulted in final discrepancy factors of $R_1 = 10.5\%$ and $R_2 = 10.0\%$ for the 1447 nonzero reflections. All positional parameters obtained from the anisotropic least-squares refinement were within 2.0 standard deviations of the corresponding final parameters from the isotropic refinement. A three-dimensional difference map based on the anisotropic refinement revealed no residual electron density greater than 0.7 electron/Å.^{3} or less than −1.6 electrons/Å.^{3}; in the regions where the hydrogens might be expected, no peaks were observed, and the positive electron density of all points was less than 0.4 electron/Å.^{3}.

The full-matrix least-squares refinements (isotropic and anisotropic) were carried out on the IBM 704 computer with the Busing–Martin–Levy ORFLS program[20]; bond lengths and angles were calculated with the Busing–Martin–Levy ORFFE program[21] with errors obtained from the full inverse matrix. The Patterson and electron density maps were calculated on the CDC 1604 computer with the Blount program.[22]

The final positional parameters and anisotropic thermal coefficients, with standard deviations, are given in Tables I and II. A comparison of the observed and calculated structure factors based on the final anisotropic refinement is given in Table III. Table IV shows the intramolecular distances and angles calculated from the positional parameters of the last cycle of the anisotropic refinement. In Table V are listed the intermolecular distances, which are within 0.4 Å. of the estimated minimum packing distances, as calculated from the van der Waals radii[23] of the atoms involved. The "best" molecular planes formed by sets of atoms and the perpendicular distances of these and other atoms from the planes were calculated by a least-squares method with the Smith program.[24]

TABLE I

FINAL POSITIONAL PARAMETERS WITH STANDARD DEVIATIONS FROM ANISOTROPIC REFINEMENT

Atom	x	10^3 $\sigma(x)$	y	10^3 $\sigma(y)$	z	10^3 $\sigma(z)$
Cr	0.1927	0.09	0.2431	0.11	0.0770	0.07
C(7)	0.1994	1.0	0.3381	0.8	−0.0074	0.7
O(7)	0.2070	0.8	0.3953	0.7	−0.0615	0.5
C(8)	0.2888	0.7	0.3062	1.0	0.1391	0.7
O(8)	0.3477	0.6	0.3474	0.7	0.1790	0.6
C(9)	0.1042	0.8	0.3163	0.9	0.1340	0.7
O(9)	0.0421	0.6	0.3645	0.7	0.1696	0.6
C(1)	0.1358	0.7	0.1057	0.7	0.1366	0.6
C(2)	0.0816	0.8	0.1223	0.7	0.0564	0.7
C(3)	0.1384	0.8	0.1366	0.8	−0.0238	0.6
C(4)	0.2390	1.0	0.1300	0.8	−0.0204	0.7
C(5)	0.2908	0.6	0.1120	0.7	0.0586	0.7
C(6)	0.2358	0.8	0.0989	0.7	0.1370	0.6
$H_3C(1)$	0.0745	0.8	0.0908	0.9	0.2220	0.8
$H_3C(2)$	−0.0275	0.8	0.1286	0.9	0.0567	0.9
$H_3C(3)$	0.0796	1.0	0.1540	0.9	−0.1062	0.7
$H_3C(4)$	0.3014	0.9	0.1389	0.9	−0.1039	0.7
$H_3C(5)$	0.3987	0.9	0.0991	0.9	0.0599	0.7
$H_3C(6)$	0.2918	0.8	0.0795	1.0	0.2218	0.8

TABLE II

FINAL ANISOTROPIC TEMPERATURE COEFFICIENTS (×10^4)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	32 ± 1	25 ± 1	18 ± 1	−3 ± 1	0 ± 1	−2 ± 1
C(7)	72 ± 9	40 ± 8	25 ± 5	0 ± 8	−6 ± 6	−6 ± 5
O(7)	174 ± 11	62 ± 6	28 ± 4	−21 ± 7	17 ± 6	19 ± 4
C(8)	40 ± 8	73 ± 9	29 ± 5	5 ± 7	12 ± 4	−19 ± 6
O(8)	42 ± 5	105 ± 8	65 ± 6	−28 ± 5	−4 ± 4	−36 ± 5
C(9)	43 ± 8	49 ± 8	34 ± 5	−12 ± 6	−4 ± 5	4 ± 6
O(9)	66 ± 6	74 ± 7	59 ± 5	14 ± 5	5 ± 5	−17 ± 5
C(1)	26 ± 6	33 ± 7	24 ± 5	−7 ± 5	3 ± 4	7 ± 5
C(2)	43 ± 7	26 ± 7	48 ± 7	−1 ± 5	−8 ± 5	−6 ± 5
C(3)	46 ± 8	42 ± 8	18 ± 5	3 ± 6	−8 ± 5	−7 ± 5
C(4)	74 ± 10	36 ± 8	23 ± 6	12 ± 7	21 ± 6	−7 ± 5
C(5)	23 ± 6	28 ± 6	34 ± 5	1 ± 4	0 ± 4	−1 ± 4
C(6)	52 ± 7	28 ± 7	26 ± 5	−8 ± 6	6 ± 5	9 ± 5
$H_3C(1)$	82 ± 9	67 ± 10	41 ± 6	−1 ± 8	33 ± 7	23 ± 6
$H_3C(2)$	24 ± 6	73 ± 9	73 ± 9	−3 ± 6	2 ± 5	4 ± 7
$H_3C(3)$	122 ± 11	54 ± 9	35 ± 6	−16 ± 9	−37 ± 7	−3 ± 5
$H_3C(4)$	80 ± 9	75 ± 9	30 ± 5	−32 ± 9	18 ± 7	−2 ± 5
$H_3C(5)$	56 ± 8	65 ± 9	51 ± 7	2 ± 7	4 ± 6	−3 ± 6
$H_3C(6)$	48 ± 9	96 ± 11	49 ± 6	8 ± 8	−19 ± 6	2 ± 7

In an attempt to assess the significance of the deviation of the aromatic carbon–carbon distances in this compound (*vide infra*) from the carbon–carbon distances in free benzene, an isotropic least-squares rigid-body refinement was carried out with a modified version of the Scheringer program,[25] in which the inner six carbon atoms were constrained to the well-known benzene geometry (1.392 Å.) with D_{6h} symmetry.[6] For this rigid-body refinement the 24 parameters of the six ring carbons reduce to seven parameters, which consist of three positional parameters defining the center of the ring, three angular parameters defining the ring's orientation, and an over-all group thermal parameter for the six carbon atoms. The resultant R values for this rigid-body refinement were $R_1 = 12.31\%$ and $R_2 = 13.42\%$ which can be compared with $R_1 = 12.27\%$ and

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TABLE III

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	FO	FC
0	4	0	283.4	-313.4
0	6	0	112.6	-118.7
0	8	0	165.1	190.4
0	10	0	48.3	-47.0
0	12	0	43.5	39.5
0	14	0	52.3	-55.1
0	16	0	32.2	29.6
2	3	0	52.0	45.1
2	4	0	54.2	-46.8
2	5	0	36.9	-36.1
2	6	0	107.1	116.7
2	7	0	90.8	91.7
2	8	0	65.0	-71.9
2	9	0	57.3	-62.9
2	10	0	28.2	28.5
2	11	0	34.0	32.6
2	12	0	44.6	-42.3
2	13	0	33.6	-33.4
2	14	0	34.3	40.1
2	15	0	29.6	27.0
4	0	0	29.5	25.6
4	1	0	45.9	43.7
4	3	0	148.0	-174.5
4	5	0	138.4	166.3
4	6	0	34.6	-34.0
4	7	0	95.5	-105.1
4	8	0	23.7	25.3
4	9	0	60.6	64.2
4	11	0	53.9	-58.3
4	13	0	51.6	54.8
4	15	0	26.0	-26.2
6	0	0	51.6	15.7
6	1	0	69.8	-80.8
6	2	0	77.7	-79.2
6	3	0	99.1	96.8
6	4	0	95.0	86.4
6	5	0	74.6	-76.7
6	6	0	25.2	-25.1
6	7	0	61.9	66.1
6	8	0	36.2	40.1
6	9	0	59.5	-62.3
6	10	0	50.8	-55.2
6	11	0	54.7	59.9
6	12	0	25.1	27.0
6	13	0	37.6	-40.7
8	0	0	102.3	-111.6
8	1	0	46.8	41.1
8	2	0	85.3	92.1
8	3	0	25.4	-24.6
8	4	0	78.4	-76.6
8	6	0	61.5	69.6
8	8	0	52.4	-59.5
8	9	0	25.2	25.6
8	10	0	51.9	56.2
8	11	0	21.9	-14.8
8	12	0	37.8	-40.0
8	14	0	23.2	25.0
8	16	0	25.0	-21.5
10	0	0	77.9	83.8
10	1	0	42.0	42.0
10	2	0	66.4	-69.7
10	3	0	32.8	-31.2
10	4	0	62.5	67.2
10	5	0	33.8	31.4
10	6	0	54.3	-58.9
10	7	0	21.3	-18.5
10	8	0	26.7	27.2
10	9	0	18.0	16.3
10	10	0	28.3	-21.9
10	12	0	34.7	31.3
10	14	0	24.3	-30.7
12	0	0	42.5	-54.4
12	1	0	44.5	-42.6
12	2	0	29.4	26.6
12	3	0	73.7	86.5
12	4	0	16.5	-5.2
12	5	0	44.0	-49.1
12	8	0	17.7	-15.6
12	9	0	30.6	-27.2
12	11	0	36.4	42.3
12	13	0	24.8	-23.7
14	1	0	34.7	42.3
14	3	0	38.7	-39.8
14	4	0	19.3	-24.5
14	5	0	31.2	29.6
14	7	0	32.2	-28.6
14	9	0	34.1	32.0
16	2	0	20.4	-23.3
16	4	0	33.3	36.9
16	5	0	20.6	-16.1
16	6	0	26.7	-27.4
16	8	0	23.8	18.3
18	0	0	29.2	-37.0
18	2	0	20.0	21.2
18	6	0	23.6	19.5
18	8	0	27.6	-26.5
20	1	0	27.0	23.9
0	4	1	173.1	-186.3
0	8	1	96.8	114.2
0	12	1	19.9	-16.4
0	14	1	26.9	-22.6
1	3	1	55.0	-48.1
1	4	1	46.0	-45.5
1	5	1	16.3	-10.2
1	6	1	61.6	57.9
1	7	1	20.8	24.0
1	8	1	43.7	47.4
1	9	1	22.1	17.6
1	10	1	64.7	-67.7
1	11	1	28.9	-30.4
1	12	1	27.8	25.8
2	3	1	19.6	22.0
2	4	1	41.6	32.7
2	5	1	27.5	20.8
2	6	1	15.2	-12.5
2	7	1	16.4	10.6
2	8	1	30.3	-25.3
2	9	1	26.3	-25.8
3	1	1	49.9	33.3
3	2	1	30.0	-20.6
3	4	1	19.8	-16.1
3	5	1	48.0	-46.0
3	6	1	15.7	16.1
3	7	1	20.7	20.9
3	9	1	22.7	-21.0
3	10	1	20.6	19.2
3	11	1	32.9	33.7
3	12	1	22.3	-14.2
3	13	1	24.9	-22.6
4	1	1	47.4	43.3
4	2	1	29.8	-30.4
4	3	1	108.3	-106.6
4	4	1	18.1	15.9
4	5	1	33.3	34.2
4	7	1	30.5	29.6
4	11	1	23.9	-22.3
5	1	1	52.0	-48.5
5	3	1	35.4	27.9
5	5	1	64.2	65.0
5	7	1	55.3	-62.2
5	9	1	19.4	18.6
6	1	1	32.3	27.1
6	2	1	38.6	36.2
6	4	1	34.3	25.3
6	5	1	43.9	-42.0
6	6	1	26.2	-27.0
6	7	1	28.5	28.3
7	1	1	48.2	43.3
7	2	1	88.0	72.9
7	3	1	32.5	-28.1
7	4	1	23.5	21.5
7	5	1	46.5	-44.6
7	6	1	69.6	-64.5
7	7	1	34.8	35.0
7	8	1	16.8	14.5
8	6	1	26.6	24.0
8	9	1	19.0	14.0
9	1	1	14.6	-14.8
9	2	1	21.6	19.3
9	8	1	18.8	-17.0
9	10	1	29.7	32.0
9	12	1	23.0	-20.4
10	2	1	21.5	-19.3
11	1	1	17.3	-17.7
11	2	1	16.0	12.9
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11	8	1	20.7	18.3
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12	3	1	17.7	-16.1
13	1	1	18.0	19.2
13	5	1	18.1	-18.6
13	7	1	21.1	18.5
0	4	2	50.1	-41.0
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0	8	2	108.9	121.1
0	10	2	44.1	-44.4
0	14	2	30.5	-26.7
0	16	2	24.0	24.9
1	3	2	14.4	10.9
1	4	2	77.2	-77.4
1	5	2	20.4	-17.9
1	6	2	99.3	119.2
1	7	2	47.5	53.6
1	8	2	57.9	-56.9
1	9	2	29.0	-29.9
1	10	2	20.5	14.2
1	12	2	43.0	-42.9
1	14	2	47.5	50.4
1	15	2	23.0	20.5
1	16	2	26.6	-20.6
2	3	2	68.4	59.4
2	6	2	39.1	38.4
2	7	2	22.7	17.8
2	8	2	60.4	-63.2
2	9	2	54.8	-52.9
2	10	2	31.4	31.1
2	11	2	35.9	34.1
2	12	2	26.5	-20.4
2	14	2	22.1	19.5
3	1	2	42.3	38.6
3	2	2	65.6	-61.1
3	3	2	137.5	-146.9
3	4	2	98.5	103.7
3	5	2	117.5	130.8
3	6	2	47.5	-46.0
3	7	2	62.5	-65.6
3	8	2	14.2	15.6
3	9	2	41.7	43.1
3	10	2	26.6	-27.5
3	11	2	45.5	-42.9
3	12	2	25.4	27.4
3	13	2	37.1	40.0
3	15	2	23.3	-24.4
4	0	2	41.4	39.3
4	1	2	172.3	172.9
4	2	2	29.1	-24.8
4	3	2	19.6	-10.8
4	4	2	14.4	-12.0
4	5	2	42.9	42.1
4	7	2	54.3	-57.3
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4	9	2	35.2	34.0
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5	7	2	67.8	70.5
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5	9	2	78.6	-83.3
5	10	2	24.2	-22.1
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6	0	2	12.7	19.1
6	1	2	43.1	-47.3
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6	13	2	32.0	-29.1
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7	3	2	53.3	-53.4
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9	12	2	22.9	19.5
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11	0	2	37.1	-37.8
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12	0	2	13.8	-17.0
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13	1	2	46.3	51.7
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13	11	2	29.8	-25.9
14	1	2	23.8	22.6
14	3	2	24.7	-22.5
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15	1	2	19.9	-15.1
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17	2	2	20.6	16.6
17	6	2	24.5	24.8
17	8	2	23.3	-18.1
18	0	2	18.2	-21.0
18	2	2	20.1	13.8
19	0	2	18.9	18.3
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11	11	3	22.4	14.4
12	11	3	23.1	19.1
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15	3	3	20.7	10.5
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1	2	4	100.1	116.2
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1	12	4	39.0	-39.8
1	14	4	39.9	42.0
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2	7	4	27.4	-24.1
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2	13	4	27.0	23.0
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6	1	6	56.0	56.3
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6	6	6	50.1	48.9
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6	8	6	33.1	-32.9
6	9	6	31.9	29.0
6	10	6	23.2	22.2
6	11	6	28.8	-25.0
6	13	6	29.1	28.5
6	15	6	26.1	-22.1
7	0	6	37.6	-36.7
7	1	6	27.5	26.0
7	2	6	26.6	23.9
7	3	6	28.1	-26.3
7	4	6	13.9	-10.1
8	0	6	91.2	108.7
8	1	6	24.7	-19.1
8	2	6	67.2	-71.5
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8	4	6	45.6	41.7
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8	7	6	23.4	21.3
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8	9	6	20.2	-17.3
8	10	6	38.2	-36.0
8	12	6	24.2	24.8
8	14	6	28.5	-27.4
9	0	6	68.9	77.1
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9	3	6	35.5	30.9
9	4	6	40.0	-37.7
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9	8	6	45.3	44.9
10	0	6	86.0	-98.1
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10	6	6	51.6	56.0
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10	9	6	30.6	-26.1
10	10	6	31.1	28.8
11	1	6	24.4	-23.2
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12	1	6	35.5	34.5
12	3	6	40.7	-40.9
12	4	6	24.3	16.6
12	5	6	46.2	50.0
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12	7	6	41.4	-42.3
12	9	6	30.0	25.1
14	1	6	28.1	-28.0
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14	5	6	37.6	-38.7
14	7	6	27.6	24.3
16	0	6	17.3	-19.3
16	1	6	21.2	15.4
16	2	6	27.9	27.5
16	3	6	20.7	-16.0
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18	2	6	22.8	-19.9
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1	5	7	26.7	-24.1
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1	12	7	27.3	-27.2
1	14	7	27.1	19.9
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5	13	7	36.7	-37.4
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6	1	7	18.6	17.1
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7	10	7	25.4	22.0
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8	12	12	26.8	-21.6
9	0	12	39.6	-38.9
9	2	12	29.0	27.7
9	10	12	22.0	15.3
10	0	12	22.9	25.6
10	2	12	30.7	-31.2
10	3	12	21.4	-14.4
10	4	12	37.8	36.7
10	5	12	21.5	16.8
10	6	12	33.3	-33.1
10	8	12	28.4	22.5
10	10	12	22.6	-18.5
11	0	12	23.2	20.2
11	1	12	17.6	8.3
11	3	12	26.0	-21.2
12	0	12	24.2	-6.8
12	1	12	29.9	-32.9
12	2	12	18.5	13.5
12	3	12	24.6	14.5
12	5	12	26.0	-24.2
12	7	12	33.6	31.6
12	9	12	22.0	-20.1
13	3	12	26.0	25.7
13	5	12	26.1	-20.8
14	1	12	27.6	27.8
14	3	12	21.3	-17.4
14	9	12	23.3	18.8
0	2	13	79.1	91.8
0	4	13	36.3	36.4
0	6	13	65.2	-74.5
0	8	13	21.4	-17.0
0	10	13	31.9	27.8
1	6	13	23.4	-19.8
1	8	13	30.4	29.3
2	2	13	21.6	-18.0
2	4	13	23.7	-21.3
2	5	13	23.0	-19.2
2	6	13	20.6	21.0
2	8	13	19.4	14.1
2	9	13	20.3	11.2
3	7	13	20.1	20.6
3	9	13	25.4	-21.5
5	5	13	21.8	20.2
7	6	13	17.9	-10.5
12	1	13	18.7	-20.1
0	0	14	75.4	82.4
0	2	14	46.6	-46.0
0	4	14	39.3	42.0
0	6	14	63.1	-71.6
0	8	14	29.1	28.9
0	12	14	29.6	28.5
0	14	14	34.9	-40.0
1	2	14	22.4	18.0
1	4	14	47.9	-48.3
1	5	14	21.4	-17.1
1	6	14	32.4	33.6
2	0	14	55.4	-60.9
2	1	14	42.9	-42.3
2	2	14	43.3	42.1
2	3	14	28.1	25.0
2	4	14	31.6	-27.7
2	5	14	28.0	-27.6
2	6	14	36.3	34.7
2	7	14	33.5	31.6
2	8	14	24.6	-26.4
2	9	14	21.6	-17.1
2	11	14	24.8	14.8
2	12	14	25.9	-19.6
3	0	14	15.8	12.1
3	1	14	21.6	20.4
3	2	14	16.0	-11.5
3	3	14	27.8	-23.5
3	4	14	21.2	16.4
3	5	14	28.1	25.6
3	6	14	19.9	-14.4
3	7	14	24.7	-17.8
4	1	14	53.1	58.1
4	3	14	43.0	-39.5
4	4	14	18.7	.3
4	5	14	24.8	23.7
4	7	14	40.8	-39.2
4	9	14	45.8	45.7
4	11	14	31.9	-31.1
5	1	14	28.6	-31.4
5	3	14	24.5	21.9
5	7	14	24.9	19.9
5	9	14	22.4	-17.1
6	0	14	16.6	15.5
6	1	14	29.2	-30.9
6	2	14	27.5	-25.9
6	3	14	35.3	31.2
6	4	14	28.2	27.6
6	5	14	32.1	-29.2
6	6	14	21.9	-15.0
6	7	14	34.8	32.5
6	8	14	25.2	17.2
6	9	14	35.5	-30.9
6	10	14	26.6	-20.4
7	0	14	33.4	-33.8
7	2	14	17.1	18.5
7	6	14	22.6	17.7
7	7	14	26.2	-19.4
7	8	14	24.8	-19.0
8	0	14	35.7	-37.7
8	2	14	37.4	37.0
8	4	14	36.2	-37.7
8	6	14	32.0	29.4
8	8	14	25.0	-20.1
8	10	14	30.2	25.4
9	4	14	19.3	17.3
9	6	14	24.2	-22.3
9	8	14	20.5	11.2
10	0	14	35.7	40.2
10	2	14	34.1	-35.5
10	4	14	26.5	25.7
10	5	14	24.8	13.8
10	6	14	22.8	-14.1
10	8	14	21.0	13.8
10	10	14	23.8	-21.7
12	1	14	22.1	-24.5
12	2	14	19.5	12.7
12	3	14	30.6	31.4
12	5	14	23.0	-22.2
13	5	14	22.4	9.3
14	1	14	22.3	20.7
1	4	15	17.7	-19.6
1	8	15	23.1	23.3
3	7	15	20.1	13.7
0	0	16	25.9	21.3
1	0	16	44.8	-50.2
1	1	16	18.5	-16.2
1	2	16	44.2	47.0
1	3	16	20.6	17.8
1	4	16	44.1	-48.0
1	5	16	22.3	-18.9
1	6	16	37.1	43.2
1	8	16	23.7	-20.3
1	12	16	27.2	-28.6
3	0	16	23.1	23.5
3	1	16	35.9	38.2
3	2	16	21.1	-19.5
3	3	16	34.9	-33.5
3	4	16	22.5	19.9
3	5	16	41.8	40.3
3	6	16	27.5	-26.3
3	7	16	39.7	-39.7
3	8	16	21.9	17.3
3	9	16	25.4	24.5
5	1	16	25.6	-27.1
5	3	16	35.9	34.9
5	5	16	43.6	-49.5
5	7	16	44.3	45.3
5	9	16	31.8	-26.5
5	11	16	25.5	-20.0
7	0	16	27.0	-29.2
7	1	16	20.6	15.0
7	2	16	27.3	28.0
7	3	16	24.3	-20.7
7	4	16	30.7	-28.8
7	5	16	28.3	24.8
7	6	16	30.1	28.7
7	7	16	23.3	-17.4
7	8	16	28.3	-25.7
7	10	16	28.0	21.8
9	0	16	31.4	36.9
9	2	16	36.3	-39.2
9	4	16	30.9	30.4
9	6	16	24.2	-14.6
9	8	16	25.3	22.8
9	10	16	30.4	-31.9
11	0	16	23.4	-23.7
11	1	16	23.0	-20.8
11	2	16	23.4	23.1
11	3	16	28.0	28.2
11	4	16	25.1	-16.2
13	1	16	26.4	19.2
13	3	16	28.7	-25.5
13	5	16	23.4	23.2
2	6	17	19.3	2.6
4	7	17	21.9	-16.4
5	3	17	23.0	17.0
0	0	18	24.1	-26.0
0	2	18	34.8	36.3
0	4	18	36.7	-34.4
0	6	18	23.6	19.4
1	0	18	18.5	-21.3
1	2	18	26.4	22.5
1	4	18	24.8	-25.7
1	6	18	22.9	21.9
2	0	18	28.0	29.0
2	1	18	22.8	25.0
2	2	18	25.1	-24.5
2	4	18	20.0	16.5
2	6	18	20.0	-17.6
2	7	18	25.7	-23.1
3	3	18	30.1	-27.1
3	4	18	20.1	17.6
3	5	18	34.5	32.5
3	6	18	20.1	-13.5
3	7	18	21.1	-16.8
4	1	18	33.6	-33.5
4	5	18	21.1	-18.5
4	7	18	34.6	35.2
4	9	18	30.6	-27.1
5	1	18	16.8	-14.3
5	3	18	28.0	26.7
5	5	18	32.1	-28.5
6	1	18	19.0	12.6
6	3	18	21.0	-19.0
6	5	18	21.6	22.9
6	7	18	25.0	-20.2
7	0	18	17.8	-16.6
7	1	18	19.4	11.5
7	2	18	19.7	17.9
7	8	18	23.7	-21.0
8	2	18	20.0	-22.5
8	4	18	32.2	36.0
9	0	18	18.5	21.6
9	8	18	23.0	22.2
10	2	18	20.8	21.3
10	3	18	22.5	21.9
10	4	18	29.3	-29.0
3	3	19	21.0	-18.3
0	0	20	31.4	-35.7
0	2	20	25.0	28.5
0	4	20	27.4	-23.3
0	6	20	27.4	27.0
0	8	20	27.5	-26.5
1	0	20	24.6	29.7
2	0	20	22.2	23.1
2	1	20	24.5	26.8
2	2	20	23.0	-21.3
2	3	20	21.7	-14.0
2	4	20	21.5	19.0
2	6	20	21.4	-18.0
2	7	20	22.4	-21.3
4	1	20	28.9	-32.4
4	3	20	26.0	26.3
4	5	20	22.6	-20.5
4	7	20	26.1	25.9
4	9	20	26.5	-26.3
6	1	20	22.4	20.6
6	2	20	20.7	14.4
6	3	20	22.4	-21.9
6	5	20	25.0	19.6
8	0	20	19.3	11.8
8	2	20	21.3	-18.3
8	4	20	25.2	27.5
10	4	20	27.0	-22.6
1	0	22	22.2	29.0
1	2	22	22.8	-21.3
1	4	22	22.9	15.9
5	3	22	25.3	-20.7

TABLE IV

MOLECULAR BOND LENGTHS AND ANGLES FROM ANISOTROPIC LEAST-SQUARES REFINEMENT

Bond lengths			Angles		
Atoms	Distance, Å.	σ, Å.	Atoms	Angle, deg.	σ, deg.
C(1)–C(2)	1.448	0.013	C(1)–C(2)–C(3)	117.2	0.9
C(2)–C(3)	1.461	0.014	C(2)–C(3)–C(4)	119.3	1.0
C(3)–C(4)	1.379	0.014	C(3)–C(4)–C(5)	122.7	1.0
C(4)–C(5)	1.419	0.014	C(4)–C(5)–C(6)	118.1	0.9
C(5)–C(6)	1.424	0.013	C(5)–C(6)–C(1)	121.0	1.0
C(6)–C(1)	1.370	0.013	C(6)–C(1)–C(2)	121.6	1.0
H_3C(1)–H_3C(2)	2.928	0.018	H_3C(1)–H_3C(2)–H_3C(3)	121.2	0.5
H_3C(2)–H_3C(3)	2.905	0.019	H_3C(2)–H_3C(3)–H_3C(4)	119.0	0.5
H_3C(3)–H_3C(4)	3.038	0.019	H_3C(3)–H_3C(4)–H_3C(5)	118.9	0.5
H_3C(4)–H_3C(5)	2.883	0.017	H_3C(4)–H_3C(5)–H_3C(6)	121.8	0.5
H_3C(5)–H_3C(6)	2.882	0.018	H_3C(5)–H_3C(6)–H_3C(1)	120.2	0.5
H_3C(6)–H_3C(1)	2.975	0.017	H_3C(6)–H_3C(1)–H_3C(2)	118.9	0.5
C(1)–H_3C(1)	1.564	0.013	H_3C(1)–C(1)–C(2)	116.8	0.9
C(2)–H_3C(2)	1.495	0.015	H_3C(1)–C(1)–C(6)	121.5	1.0
C(3)–H_3C(3)	1.511	0.014	H_3C(2)–C(2)–C(3)	121.7	1.0
C(4)–H_3C(4)	1.538	0.014	H_3C(2)–C(2)–C(1)	121.1	1.0
C(5)–H_3C(5)	1.486	0.014	H_3C(3)–C(3)–C(4)	124.9	1.1
C(6)–H_3C(6)	1.527	0.015	H_3C(3)–C(3)–C(2)	115.8	1.0
Cr–C(1)	2.211	0.009	H_3C(4)–C(4)–C(5)	116.1	1.0
Cr–C(2)	2.253	0.010	H_3C(4)–C(4)–C(3)	121.1	1.2
Cr–C(3)	2.235	0.010	H_3C(5)–C(5)–C(6)	119.9	1.0
Cr–C(4)	2.226	0.011	H_3C(5)–C(5)–C(4)	121.8	1.0
Cr–C(5)	2.241	0.009	H_3C(6)–C(6)–C(1)	121.1	0.9
Cr–C(6)	2.233	0.011	H_3C(6)–C(6)–C(5)	117.9	0.9
Cr–C(7)	1.823	0.012	C(7)–Cr–C(8)	90.1	0.6
Cr–C(8)	1.831	0.012	C(7)–Cr–C(9)	89.2	0.5
Cr–C(9)	1.789	0.013	C(8)–Cr–C(9)	88.6	0.4
C(7)–O(7)	1.137	0.012	Cr–C(7)–O(7)	177.0	1.2
C(8)–O(8)	1.153	0.012	Cr–C(8)–O(8)	178.4	0.9
C(9)–O(9)	1.200	0.012	Cr–C(9)–O(9)	177.3	0.9
Cr–O(7)	2.959	0.009	O(7)–Cr–O(8)	89.8	0.3
Cr–O(8)	2.984	0.008	O(7)–Cr–O(9)	90.0	0.3
Cr–O(9)	2.988	0.009	O(8)–Cr–O(9)	89.0	0.3

TABLE V

INTERMOLECULAR DISTANCES[a]

Atoms	Distance, Å	Atoms	Distance, Å.
O(8)–H_3C(4)^{I}	3.38	O(7)–H_3C(4)^{IV}	3.36
O(9)–H_3C(3)^{I}	3.47	O(7)–H_3C(5)^{IV}	3.62
H_3C(6)–O(7)^{I}	3.52	O(9)–H_3C(5)^{IV}	3.68
H_3C(1)–O(7)^{I}	3.77	O(9)–H_3C(6)^{IV}	3.77
O(8)–H_3C(3)^{II}	3.36	O(8)–H_3C(6)^{IV}	3.73
O(7)–H_3C(2)^{II}	3.64	O(8)–H_3C(1)^{IV}	3.52
C(7)–H_3C(2)^{II}	3.83	O(8)–C(1)^{IV}	3.56
H_3C(4)–O(9)^{II}	3.44	O(8)–C(6)^{IV}	3.65
H_3C(6)–H_3C(1)^{III}	3.96	H_3C(2)–H_3C(3)^{V}	3.96
H_3C(5)–H_3C(1)^{III}	4.11	H_3C(2)–H_3C(2)^{V}	3.96
O(7)–C(5)^{IV}	3.46	H_3C(1)–O(9)^{VI}	3.83
O(7)–C(4)^{IV}	3.32		

[a] Superscripts refer to the following positions: I $x, {}^1/_2 - y, {}^1/_2 + z$; II ${}^1/_2 + x, {}^1/_2 - y, -z$; III ${}^1/_2 + x, y, {}^1/_2 - z$; IV ${}^1/_2 - x, {}^1/_2 + y, z$; V $-x, -y, -z$; VI $-x, -{}^1/_2 + y, {}^1/_2 - z$.

R_2 = 13.05% for the original isotropic refinement (no ring constraints). By application of the Hamilton statistical R factor ratio test,[6,26] the significance of the improvement in agreement between $|F_o|$ and $|F_c|$ in going from a model with D_{6h} symmetry and with one thermal parameter for the six ring carbons to a model with no constraints and with individual isotropic thermal parameters can be obtained. With an increase of 17 parameters for the 1446 diffraction data, the weighted R factor ratio of 1.028 ($R_2(D_{6h})/R_2$(no constraints)) implies an improvement (based on the assumed absence of systematic error in the data) which is significant at the 0.5% level. This means that the D_{6h} rigid-body constraint with equal temperature factors for the six benzene ring carbons is not a good assumption in this case.

Discussion

Hexamethylbenzenechromium tricarbonyl exists in the solid state as discrete monomeric molecules with the hexamethylbenzene ring sandwich-bonded to the chromium tricarbonyl moiety (Figure 1). The $Cr(CO)_3$ fragment is oriented such that (with the assumption of octahedral valency for the chromium atom) three octahedral bonding orbitals are directed toward the centers of the alternate carbon–carbon bonds of the hexamethylbenzene ring. The six carbon atoms of the ring then are equivalent and hence this organometallic interaction could give rise to the following deviations from "free" hexamethylbenzene: (a) alternate carbon–carbon bond lengths due to partial localization of the π-electron system in the ring; and (b) bending of the six methyl carbons out of the plane of the ring carbons and away from the chromium atom.

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(26) W. C. Hamilton, "Statistics in Physical Science," Ronald Press Co., New York, N. Y., 1964, p. 159.

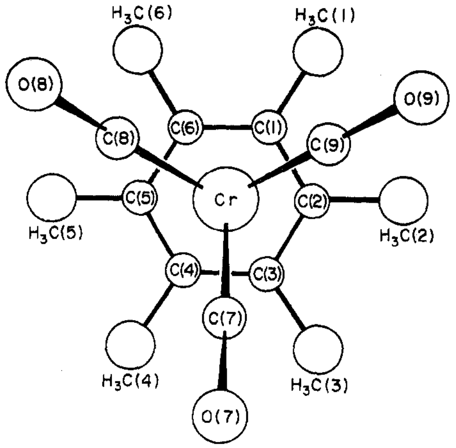

Figure 1.—Molecular configuration of hexamethylbenzenechromium tricarbonyl.

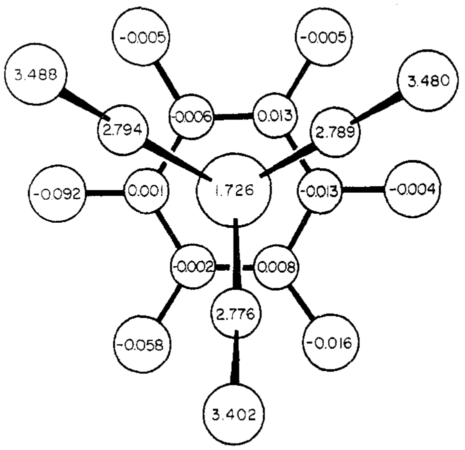

Figure 2.—Deviations (Å.) of all atoms from the mean plane of the six ring carbons.

Noteworthy is that this configuration presumably eliminates any possibility of a twofold molecular disorder similar to that suggested by Jellinek[4] for dibenzenechromium, since for any ring–chromium tricarbonyl complex a twofold molecular disorder would involve disorder of the three carbonyl groups. A threefold orientational disorder has been observed in another ring–chromium tricarbonyl compound, thiophenechromium tricarbonyl.[27] In this compound the thiophene rings are randomly distributed in one of three positions in the crystal, such that for a given molecule the thiophene sulfur is always *trans* to a carbonyl. A similar threefold ring disorder in hexamethylbenzenechromium tricarbonyl, however, would have no effect on a possible threefold distortion of the ring.

Figure 2 shows the deviations of all twelve carbon atoms of the hexamethylbenzene ring from the "best" molecular plane passing through the six ring carbons. Although the six methyl carbons are very close to the plane of the ring carbons, all deviations from the mean plane are in the direction away from the chromium atom. These results indicate that to a first approximation the planarity of the ring is invariant to the metal interaction, and an arene ring π-orbital system remains intact for chromium tricarbonyl complexes as contrasted to the nonplanarity (dihedral angle of 132°) of the benzene ring in π-cyclopentadienylhexakis(trifluoromethyl)benzenerhodium; in this latter complex only four atoms of the benzene nucleus are involved in bonding to the Rh(I).[28]

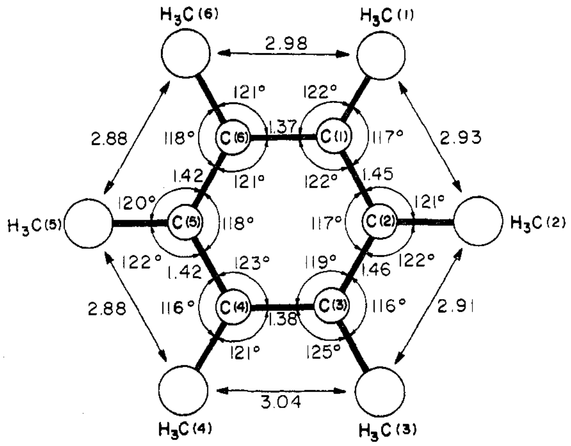

Figure 3.—Hexamethylbenzene parameters as found in $(H_3C)_6C_6Cr(CO)_3$.

The perpendicular distance of the chromium atom from the mean plane of the ring carbons is 1.73 Å., which is in close agreement with the corresponding chromium–ring distance of 1.70 Å. found for benzenechromium tricarbonyl,[13] but is significantly longer by 0.11 Å. than the value of 1.60 Å. (av.) found for dibenzenechromium.[6] Each of the three presumed localized octahedral chromium orbitals, determined by the direction of the *trans* carbonyl line passing through the chromium atom, intersects the normal to the plane of the benzene ring carbons through the midpoint of the C–C bond opposite each carbonyl at an average distance of 1.52 Å. from the chromium and at an average distance of 0.85 Å. from the C–C midpoint being considered.

Figure 3 shows the molecular parameters found in the hexamethylbenzene ring. The six C–C bond lengths range in value from 1.370 ± 0.014 to 1.461 ± 0.014 Å. with an average distance of 1.42 Å. The averages of each of the two sets of alternate bond lengths are 1.41_7 and 1.41_6 Å.; thus our analysis does not exhibit even a tendency toward a threefold distortion of the hexamethylbenzene ring in this chromium tricarbonyl complex. There is an indicated twofold distortion of the ring with two short bonds (C(1)–C(6), C(3)–C(4)) of 1.37 Å. (av.) and four longer bonds which average to 1.44 Å. The nonbonding carbon–carbon distances of the outer hexagon of methyl carbons also suggest a twofold distortion from a regular hexagon, but in the opposite direction with two long distances ($H_3C(1)$–$H_3C(6)$, $H_3C(3)$–$H_3C(4)$) of 3.01 Å. (av.) and four shorter distances of 2.90 Å. (av.). The deviations from the idealized 120° bond angles about each ring carbon atom also reflect this twofold distortion.[29]

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[27] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1306 (1965).

[28] M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 365 (1963).

[29] Although the standard deviations of the individual bond lengths and angles derived from the least-squares analysis are reliable only insofar as the data are not subject to systematic errors, the low value of 2.7% for the least-squares merging of the two sets of intensity data (see Experimental section) indicates that the suggested twofold distortion is not attributable to the noncorrection for absorption and extinction effects.

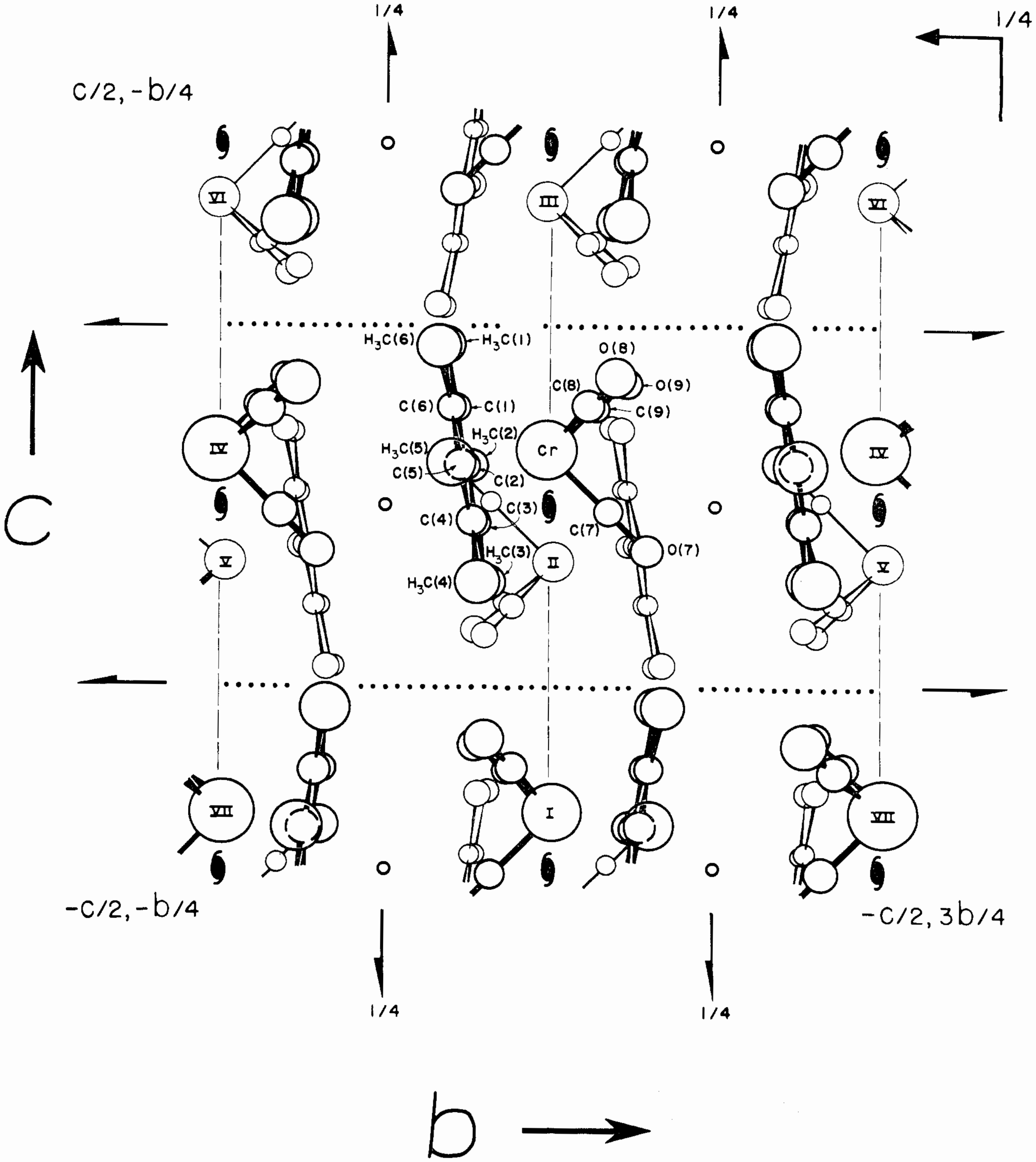

Figure 4.—[100] projection of the unit cell.

Although the nearest intermolecular $H_3C\cdots OC$ distances of 3.3 Å. indicate no interaction other than that expected for the usual van der Waals forces, the molecules directly above and below the asymmetric molecule along the c axis (*i.e.*, each related to the asymmetric molecule by the symmetry operation c_b located at $b/4$) may account in part for this indicated distortion. The [010] and [100] projections (Figures 4 and 5) show that the carbonyl groups of these two neighboring molecules are quite symmetrically placed with respect to the nearest methyl carbon atoms (O(7) *vs.* $H_3C(6)^I$ and $H_3C(1)^I$; O(8) and O(9) *vs.* $H_3C(3)^I$ and $H_3C(4)^I$). The closest approaches of other molecules to this basic hexamethylbenzene ring, including intermolecular methyl–methyl, methyl–oxygen, and methyl–carbon (both ring and carbonyl) interactions, are not nearly so symmetrical.

Apart from the electronic interaction of the chromium tricarbonyl group and intermolecular packing effects, a possible explanation of the indicated distortion of

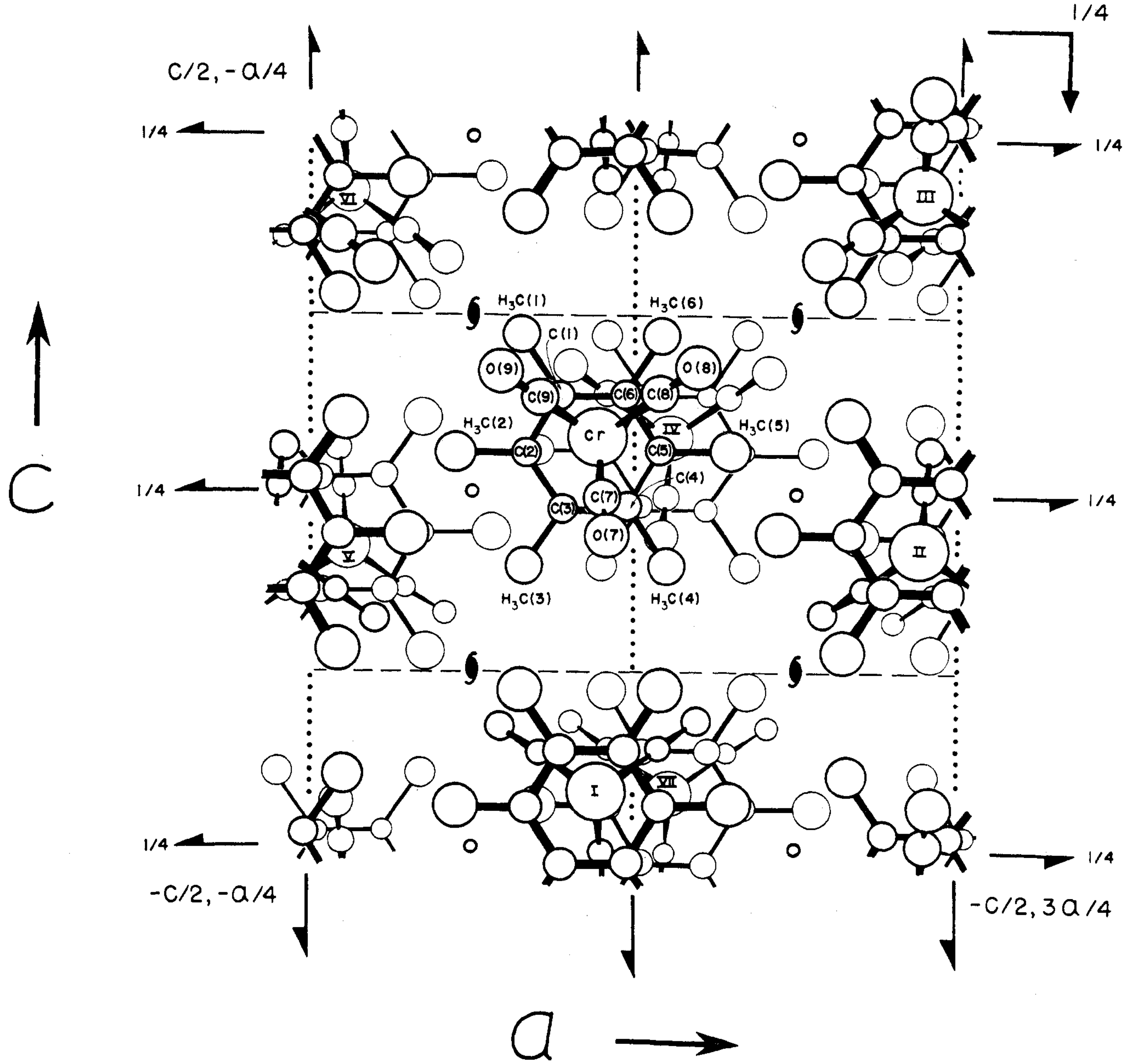

Figure 5.—[010] projection of the unit cell.

the metal-complexed hexamethylbenzene ring is that the "free" molecule itself does not possess sixfold symmetry due to intramolecular steric interactions of the methyl groups. Although the two-dimensional X-ray studies of "free" hexamethylbenzene[12] did not reveal any ring distortion, the combination of an implicit assumption of D_{6h} symmetry for the carbon framework and the inherent imprecision of two-dimensional X-ray work would prevent the detection of any distortion in the hexamethylbenzene ring of the order of 0.07 Å. as found in our study of hexamethylbenzenechromium tricarbonyl. Furthermore, a twofold distortion of the hexamethylbenzene ring in crystals of "free" hexamethylbenzene at temperatures above −163° was postulated by Schnepp[30] on the basis of a discontinuous change in the near-ultraviolet absorption spectra of oriented single crystals. Heat capacity measurements[31] also indicated a phase transition at this temperature. Schnepp[30] suggested that the molecular ring distortion might be caused by asymmetric crystal forces acting on the methyl substituents as the methyl groups begin to rotate freely at the transition temperature. (Either fixed methyl groups or geared rotation were assumed to occur at temperatures below −163°[30]; n.m.r. studies of "free" hexamethylbenzene,[32] however, do not support this postulated onset of free rotation at −163°.) In any event, the above results certainly indicate that a three-dimensional X-ray refinement is needed to clarify the status of the symmetry of "free" hexamethylbenzene.

Of significance is that no evidence of a threefold dis-

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[30] O. Schnepp, *J. Chem. Phys.*, **29**, 56 (1958).

[31] H. M. Huffman, G. S. Parks, and A. C. Daniels, *J. Am. Chem. Soc.*, **52**, 1547 (1930).

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tortion appears in the hexamethylbenzene ring of the chromium tricarbonyl complex, not even as a superposition upon the twofold distortion of the ring. In the absence of a threefold distortion of an arene ring complexed to a chromium tricarbonyl group possessing trigonal symmetry, it is concluded that dibenzenechromium should not be expected to show threefold distortion of the benzene rings.

Our results show that three-dimensional investigations of other arenechromium tricarbonyl systems will further verify the presence or absence of sixfold symmetry for the arene ring. Toward this end three-dimensional X-ray work is being carried out in this laboratory on several other chromium tricarbonyl complexes.

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Structure of Thiophenechromium Tricarbonyl, $C_4H_4SCr(CO)_3$[1]

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A three-dimensional X-ray analysis of $C_4H_4SCr(CO)_3$ has revealed a threefold orientational disorder of the thiophene ring. The crystals contain two molecules in a monoclinic unit cell of symmetry $P2_1/m$ and dimensions $a = 6.06 \pm 0.02$ Å., $b = 10.79 \pm 0.03$ Å., $c = 6.65 \pm 0.02$ Å., and $\beta = 102.2 \pm 0.1°$. Fourier syntheses and an isotropic rigid-body least-squares refinement based on a disordered model, in which the thiophene rings are randomly distributed in one of three orientations, have yielded an unweighted discrepancy factor of 13.2% for 653 observed reflections. The molecular configuration with the thiophene sulfur atom always *trans* to one of the three carbonyl groups is invariant to the crystalline disorder. However, the disordered structure has made impossible a detailed comparison of the molecular parameters of the metal-complexed thiophene with those of "free" thiophene. A comparison of the crystal structures of $C_4H_4SCr(CO)_3$ and $C_6H_6Cr(CO)_3$ is given.

Introduction

An X-ray study of thiophenechromium tricarbonyl has been performed in order to determine the effect of the chromium–thiophene interaction on the thiophene ring parameters. Fischer and Öfele,[4] who first prepared this complex by the reaction of thiophene with chromium hexacarbonyl, proposed an octahedral valency model involving a three-point attachment of the chromium to the sulfur and to the double bonds of the thiophene ring. Since the intramolecular parameters of free thiophene have been determined with high precision by means of both electron diffraction[5] and microwave spectroscopy,[6] this investigation offered the opportunity for a detailed comparison of the structural features of the free and chromium-bonded thiophene ring.

Experimental

Large red crystals of thiophenechromium tricarbonyl were kindly supplied to us by Professor Dr. E. O. Fischer. Two crystals, each approximately cubic in shape and about 0.025 cm. on a side, were used for obtaining intensity data. Since the compound is moderately air-sensitive, the crystals were loaded into thin-walled glass capillaries which were subsequently evacuated, filled with argon, and then hermetically sealed. Although surface decomposition (as evidenced by the formation of a thin green coating on both crystals) was observed toward the end of the five weeks of exposure to the X-ray beam, no internal decomposition manifested by weakened intensities for given reflections was detected. Since the crystals are not transparent, the polarizing microscope could not be used to detect twinning; however, no evidence of disorder, diffuse scattering, or split spots characteristic of twinning was observed on the Weissenberg and precession photographs.

Multiple-film equi-inclination Weissenberg photographs were obtained with Zr-filtered Mo Kα radiation about the b rotation axis for seven reciprocal levels ($h0l$–$h6l$) and about the c rotation axis for seven levels ($hk0$–$hk6$). The intensities of the reflections thus obtained were visually estimated, and spot extension[7] as well as Lorentz-polarization corrections were applied. The resultant data were then merged to one scale factor *via* least squares[8] to give 653 independent reflections. The weighted reliability index R_2 for the merging of the 403 duplicate reflections was 3.4%. Absorption corrections were neglected due to the low absorption coefficient ($\mu R_{\max} < 0.4$). The standard deviations of the observed structure amplitudes were estimated as follows[9]:

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[2] National Science Foundation Predoctoral Fellow, 1962–1964.

[3] Alfred P. Sloan Fellow, 1963–present.

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