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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[1] Presented in part before the Division of Inorganic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 31–Sept. 4, 1964.

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

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

[4] E. O. Fischer and K. Öfele, *Chem. Ber.*, **91**, 2395 (1958).

[5] R. A. Bonham and F. A. Momany, *J. Phys. Chem.*, **67**, 2474 (1963).

[6] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectry.*, **7**, 58 (1961).

[7] D. C. Philipps, *Acta Cryst.*, **7**, 746 (1954).

[8] P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC 1604," University of Wisconsin, 1964.

[9] D. L. Smith, "DACOR—A Data Reduction Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix I), University of Wisconsin, 1962.

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 $\sigma(F_o) = F_o/20$.

The lattice lengths were measured from *hk*0 and 0*kl* precession photographs, while the β angle was determined from an *h*0*l* Weissenberg photograph.

Crystal Data

Crystals of $C_4H_4SCr(CO)_3$ are monoclinic with cell parameters $a = 6.06 \pm 0.02$ Å., $b = 10.79 \pm 0.03$ Å., $c = 6.65 \pm 0.02$ Å., $\beta = 102.2 \pm 0.1°$. The experimental density of 1.74 g./cc. agrees well with the density of 1.72 g./cc. calculated for two molecules per unit cell.

The systematic absence of $k = 2n + 1$ for $\{0k0\}$ data indicates the probable space group to be either $P2_1(C_2^2)$ or $P2_1/m(C_{2h}^2)$. With the assumption of no order–disorder phenomenon the acentric space group ($P2_1$) requires the location of one complete formula unit; the centrosymmetric space group ($P2_1/m$) demands that the noncentrosymmetric species possess a crystallographic mirror plane which passes through the chromium, sulfur, and one carbonyl group and which relates in pairs the other atoms to one another (*viz.*, the other two carbonyls and four thiophene ring carbons). The possible space group positions and site symmetry available are given as follows for each of the two probable space groups.[10] $P2_1(C_2^2)$—Twofold set of general positions (2a): $x, y, z;\ \bar{x}, {}^1/_2 + y, \bar{z}$. $P2_1/m$ (C_{2h}^2)—Fourfold set of general positions (4f): $\pm(x, y, z;\ \bar{x}, {}^1/_2 + y, \bar{z})$. Twofold set of special positions (2e) with point symmetry m: $\pm(x, {}^1/_4, z)$.

Solution of Structure

A three-dimensional Patterson function was computed from the corrected intensities, and an interpretation yielded the fractional coordinates of $x = 0.327$ and $z = 0.037$ for the asymmetric chromium atom. The y coordinate of the chromium atom was set equal to ${}^1/_4$ in order to be in agreement with either of the two probable space groups (*i.e.*, arbitrary for $P2_1$ and crystallographically demanded for $P2_1/m$).

For $P2_1/m$ an ordered structure (with the two chromium and two sulfur atoms per unit cell restricted to lie on the crystallographic mirror planes) would give rise to two double-weight Cr–S vectors (*i.e.*, one *intra*- and one *inter*molecular, each as large as the Cr–Cr peak); furthermore, the *intra*molecular Cr–S vector would be expected at a presumed bonding distance of 2.35 Å. from the origin as found for other Cr–S complexes.[11] The Patterson map instead showed at a distance of 2.3 Å. from the origin *two* nonequivalent peaks of similar height but each less than one-half as large as the Cr–Cr peak. One of these presumed Cr–S vectors at fractional coordinates (0.16, 0.01, 0.34) approximately conformed to $P2_1/m$, but the other vector at (−0.16, 0.11, 0.23) then could not be interpreted on the basis of an ordered structure. All of the Patterson peaks except the Cr–Cr peak showed anisotropy in the b direction. An interpretation of all the Patterson vectors including the above peaks was consistent with the determined structure (*vide infra*).

A first approximation to the three-dimensional electron density synthesis based only on the phases of the chromium atoms was computed; this centrosymmetric Fourier map showed one carbonyl group oriented at $y = {}^1/_4$, with a second carbonyl group above the mirror plane. The third carbonyl, obtained by reflection of the second carbonyl across the mirror plane at $b/4$, was so located that the three Cr–CO bonds were nearly orthogonal to one another. Thus, the orientation of the chromium tricarbonyl fragment completely conformed to the symmetry requirements of $P2_1/m$. However, a clear-cut thiophene ring was not resolved on this Fourier map. The large sulfur peak which was expected to appear on the mirror plane approximately opposite the carbonyl group and 2.3 Å. from the chromium atom was not found. Instead, at this position a peak appeared which had a maximum electron density approximately equal to that of an oxygen atom. In addition, the peak was greatly elongated in the y direction, and its maximum did not lie precisely on the mirror plane but was located about 0.4 Å. from it. The two asymmetric peaks expected for the ring carbons also were not clearly defined. Instead, a smeared peak was found which had approximately the same height as the sulfur peak. No other significant peaks appeared on this Fourier map.

Least-squares calculations based on ordered models (which involved (1) the space group $P2_1/m$ with the sulfur of the thiophene ring located on the crystallographic mirror plane and (2) the space group $P2_1$ with the ring sulfur 0.5 Å. off the pseudo-mirror plane) gave completely unsatisfactory results in unrealistic ring distances and in an unusually large temperature factor for the sulfur atom (expected for a disordered structure). However, in both refinements the coordinates and temperature factors obtained for the chromium tricarbonyl fragment were essentially constant, and the resulting distances and angles were reasonable. A three-dimensional difference Fourier map was then obtained by subtracting out the refined chromium tricarbonyl moiety; sections of this map were computed normal to the c axis so as to intersect the unit cell nearly parallel to the ring. The resultant Fourier synthesis indicated a threefold orientational disorder of the thiophene ring wherein one of the three rings is bisected by the mirror plane of $P2_1/m$ and the other two rings are mirror images of each other and are related to the first ring by rotations of ±120° about the principal molecular axis perpendicular to the ring plane (Figures 1 and 2). This disordered model, which also satisfies the centric space group requirements ($P2_1/m$), is assumed to occur at the microscopic level with the thiophene rings randomly distributed at one of the three orientations such that on the average one-third of an atom occupies each atomic position.

A regular centrosymmetric full-matrix least-squares refinement of this disordered model was attempted based on the asymmetric unit being composed of two

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[10] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, pp. 79, 93.

[11] S. Watkins and L. F. Dahl, to be published.

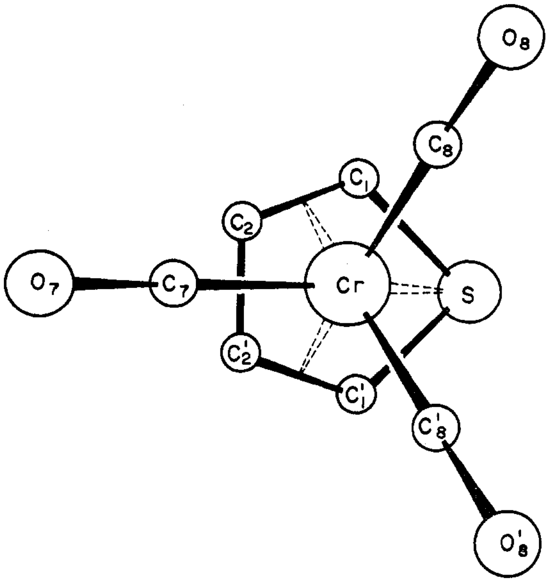


Figure 1.—Molecular configuration of thiophenechromium tricarbonyl.

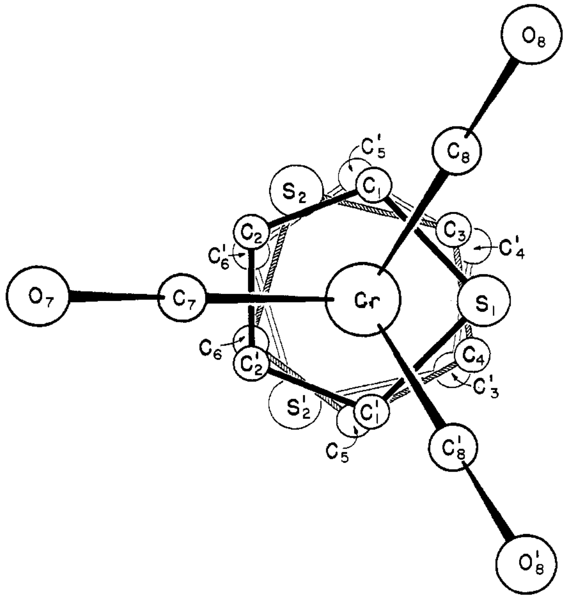


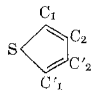
Figure 2.—Configuration of thiophenechromium tricarbonyl showing the threefold molecular disorder in the solid state.

"one-third" sulfur atoms and three "two-thirds" carbon atoms. Each of the latter was used to approximate the pairs of "one-third" carbon atoms whose centers are nearly superimposed (*i.e.*, approximately 0.2 Å. apart) due to the disorder. The refinement indicated that this model was the best yet attempted; however, the expected high interactions of the refined parameters suggested to us that a better solution for this structure (and other disordered ring structures) would be obtained by the use of a rigid-body least-squares refinement.[12] In this refinement the thiophene parameters were constrained to those of free thiophene (Table I), while the orientation and base-point location (defined by the sulfur atom in each case) of the two independent rings were allowed to vary. Ring 1 (bisected by the mirror plane) was constrained to rotate only about an axis parallel to *b;* ring 2 (related to ring 3 by the mirror plane) was not constrained at all by the space group symmetry.

The results of this rigid-body refinement (Tables II and III) were in complete agreement with our assumed model (given above) with a threefold disorder of the thiophene ring. Ring 2 was found to be coplanar with ring 1 and related to it by a rotation of 121° (compared to the theoretical 120°) about the principal molecular axis through the chromium atom.

Table I

Free Thiophene Parameters[5] (Used in the Rigid-Body Refinement of Thiophenechromium Tricarbonyl)



	Distances, Å.		Angles
$S\text{–}C_1$	1.714	$C_1\text{–}S\text{–}C_1'$	92° 10′
$C_1\text{–}C_2$	1.370	$S\text{–}C_1\text{–}C_2$	111° 28′
$C_2\text{–}C_2'$	1.423	$C_1\text{–}C_2\text{–}C_2'$	112° 27′

Final discrepancy factors of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 13.2\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100 = 16.4\%$ were obtained for this least-squares refinement. Table IV gives the comparison of the observed and calculated structure factors. As expected, high correlation among the parameters of the two rings was observed in this rigid-body refinement. During the last four least-squares cycles the parameters of the $Cr(CO)_3$ fragment varied by less than 0.4 standard deviation, whereas the ring parameters varied by two standard deviations (except for θ_2 which changed by as much as $4\ \sigma$). The mean value for each of the ring parameters (based on the results of these last four cycles), however, differed from the corresponding values in each cycle by less than 2.2 standard deviations.

The threefold disorder of the thiophene ring in this chromium complex was checked by a calculation of several three-dimensional difference Fourier sections exactly parallel to the plane of the three sulfur atoms; the equation of this plane was calculated from the sulfur coordinates obtained from the rigid-body refinement. Figure 3 shows the section through the sulfurs obtained by subtracting out the contribution of only the refined $Cr(CO)_3$ moiety, while Figure 4 shows the residual electron density remaining for this $(F_o - F_c)$ section after inclusion of the contribution of the refined thiophene rings in the calculated structure factor equation. The spread of the electron density (Figure 3), attributable both to the superposition of the three possible orientations of the thiophene ring (Figure 2) and to a large thermal motion involving mainly ring libration, makes it impossible to detect any significant differences between the chromium-bonded thiophene ring and the planar structure of free thiophene. The final three-dimensional isotropic $(F_o - F_c)$ synthesis (including the section through the thiophene part (Figure 4)) revealed no residual electron density greater than 1.5 electrons/Å.^{3} or less than −1.6 electrons/Å.^{3}. Although this total difference

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[12] C. Scheringer, *Acta Cryst.*, **16**, 546 (1963).

map indicated some thermal anisotropy of the chromium atom and of the carbonyl groups normal to the bond directions, it was felt that the anisotropy was not sufficiently great to warrant an anisotropic least-squares refinement. The absence of significant positive or negative peaks on this final difference map indicates that the assumed disordered model is a good approximation to the actual crystal structure. The high discrepancy factors (see above) may be in part due to the inadequacy of the assumed geometry of the chromium-complexed thiophene ring.

TABLE II

FINAL PARAMETERS FROM A RIGID BODY ISOTROPIC LEAST-SQUARES REFINEMENT OF THE CENTRIC DISORDERED MODEL[a]

	x	y	z	ϕ, deg.	θ, deg.	ρ, deg.	B, Å.^{2}
Cr	0.3279 (5)	0.2500 (–)	0.0372 (4)				2.1 (1)
C_7	0.5512 (42)	0.2500 (–)	0.2560 (39)				5.4 (5)
O_7	0.6912 (40)	0.2500 (–)	0.4151 (39)				9.1 (6)
C_8	0.1808 (24)	0.3644 (16)	0.1482 (24)				4.6 (3)
O_8	0.0823 (22)	0.4375 (14)	0.2366 (20)				7.1 (3)
Ring 1[b]	0.1564 (38)	0.2500 (–)	−0.3058 (40)	24.3 (17)	0.0 (–)	0.0 (–)	0.2 (5)[c]
Ring 2[b]	0.4898 (27)	0.3573 (16)	−0.1986 (28)	20.0 (12)	2.8 (17)	120.6 (12)	−0.4 (4)[c]

[a] Enclosed in parentheses are the standard deviations of the last significant figures. [b] The internal axial system x', y', z' for each thiophene ring in this rigid-body refinement is as follows: The origin is at the sulfur atom; x' is the twofold axis of the thiophene ring, y' is the vector from C_1 to C_1', and z' is the vector product of y' and x'. The three angles ϕ, θ, and ρ refer to the orientation of the internal axial system with respect to the crystallographic axis by rotations about y', x', and z', respectively. [c] Only an over-all temperature factor, T_0, for each ring was varied in this refinement; the program then adds T_0 for the ring to the temperature factors T_i of each atom in the ring, so that $T_i' = T_i + T_0$. The original T_i were assigned values based on an earlier nonrigid body least-squares refinement of the disordered model. The final temperature factors for the individual ring atoms are given in Table III.

TABLE III

INDIVIDUAL ATOM PARAMETERS OF THE TWO THIOPHENE RINGS (FROM THE RIGID BODY REFINEMENT)

	x	y	z	B, Å.^{2}
S_1	0.1564	0.2500	−0.3058	5.7
C_1	0.3528	0.3645	−0.2304	4.2
C_2	0.5619	0.3160	−0.1502	4.2
S_2	0.4898	0.3573	−0.1986	5.6
C_3	0.5654	0.2045	−0.1625	3.6
C_4	0.3816	0.1280	−0.2142	3.6
C_5	0.1770	0.1948	−0.2840	3.6
C_6	0.2103	0.3203	−0.2836	3.6

TABLE IV

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	FO	FC
0	0	2	39.4	-35.2
0	0	4	24.3	23.8
0	0	5	14.3	12.5
0	1	2	11.4	-10.2
0	1	3	33.6	-33.9
0	1	4	15.2	-17.0
0	1	5	10.3	-10.3
0	1	6	14.9	-13.0
0	1	7	8.1	-7.6
0	1	8	9.6	-7.3
0	2	0	98.6	-84.4
0	2	2	27.9	-25.6
0	2	3	27.1	-24.3
0	2	4	10.3	-10.4
0	3	1	9.3	-7.6
0	3	2	6.1	5.5
0	3	3	24.0	25.2
0	3	4	14.5	12.8
0	3	5	18.7	18.9
0	3	6	16.4	16.8
0	3	7	8.5	8.8
0	4	0	17.4	25.0
0	4	1	16.6	12.8
0	4	2	33.8	36.7
0	4	3	32.1	36.3
0	4	4	13.8	13.2
0	5	1	29.4	-32.4
0	5	2	12.5	-11.8
0	5	4	10.4	-7.0
0	5	5	19.5	-21.2
0	5	6	13.5	-15.9
0	5	7	7.5	-7.3
0	6	0	24.9	-30.3
0	6	1	18.3	-16.9
0	6	2	17.2	-20.4
0	6	3	18.0	-21.9
0	6	4	13.4	-13.0
0	6	5	7.2	-4.1
0	7	1	7.5	9.1
0	7	2	11.1	10.2
0	7	3	13.1	13.5
0	7	4	12.5	10.9
0	7	5	8.5	10.3
0	8	0	18.5	25.3
0	8	1	17.7	18.6
0	8	2	14.6	14.6
0	8	3	7.0	9.1
0	8	5	8.2	6.2
0	9	2	6.8	-7.8
0	9	3	10.6	-12.3
0	9	4	9.8	-9.9
0	10	0	15.4	-20.9
0	10	1	11.3	-13.5
0	10	2	7.2	-7.2
0	11	1	6.0	4.9
0	12	2	8.3	8.8
0	12	3	8.5	8.7
1	0	0	38.9	-33.1
1	0	1	29.4	-25.3
1	0	2	54.2	-54.5
1	0	-2	37.0	31.3
1	0	3	20.5	-19.1
1	0	-3	29.3	25.1
1	0	4	15.1	-14.0
1	0	-4	7.6	6.1
1	0	5	16.7	-17.7
1	0	-5	7.6	-3.2
1	0	6	12.4	-13.6
1	0	-6	14.6	10.2
1	0	7	8.3	-6.8
1	0	-7	13.8	12.5
1	0	-8	8.7	9.4
1	0	-9	8.8	7.1
1	1	0	78.1	-63.7
1	1	1	97.3	-61.2
1	1	2	24.7	-29.0
1	1	-2	24.7	17.4
1	1	3	10.6	-7.2
1	1	-3	33.4	-34.4
1	1	-4	49.1	-41.3
1	1	4	4.7	4.8
1	1	5	11.8	8.5
1	1	-5	15.4	-14.6
1	1	-6	7.4	-5.8
1	1	6	6.8	.0
1	1	8	8.5	5.5
1	2	0	58.0	50.8
1	2	1	8.8	5.4
1	2	-1	39.3	40.5
1	2	2	30.9	26.6
1	2	-2	32.0	-31.0
1	2	3	21.9	22.1
1	2	-3	23.8	-23.6
1	2	4	19.6	21.4
1	2	5	16.2	16.2
1	2	6	11.9	12.1
1	2	-6	15.4	-14.0
1	2	7	8.6	8.0
1	2	-7	11.3	-10.7
1	2	-8	8.1	-6.7
1	2	-9	8.8	-6.5
1	3	0	7.7	7.1
1	3	1	13.6	-10.2
1	3	-1	69.0	70.8
1	3	2	23.7	21.7
1	3	-2	40.1	38.5
1	3	3	30.7	32.7
1	3	-3	20.4	22.6
1	3	4	7.6	5.9
1	3	-4	15.6	17.5
1	3	5	12.8	-10.2
1	3	-5	13.1	13.6
1	3	-6	12.4	10.8
1	4	0	11.9	-10.6
1	4	1	14.0	-8.9
1	4	-1	13.2	-17.0
1	4	2	28.5	-31.6
1	4	-2	10.0	-7.2
1	4	3	17.2	-18.3
1	4	-3	6.4	-3.5
1	4	4	14.5	-14.8
1	4	-4	14.6	12.3
1	4	5	14.4	-14.4
1	4	-5	18.1	17.1
1	4	6	13.4	-13.0
1	4	-6	13.5	14.1
1	4	7	8.4	-8.8
1	5	0	20.3	-15.1
1	5	1	11.9	-8.2
1	5	-1	28.4	-39.4
1	5	2	9.4	-9.1
1	5	-2	28.1	-30.9
1	5	3	13.1	-14.4
1	5	-3	25.3	-27.6
1	5	4	9.1	-8.9
1	5	-4	15.3	-15.2
1	5	-5	8.5	-8.1
1	5	-6	8.4	-8.2
1	5	-7	6.4	-4.0
1	6	1	13.2	12.2
1	6	2	18.3	25.2
1	6	-2	10.6	6.4
1	6	3	15.9	16.3
1	6	-3	7.7	5.0
1	6	4	14.9	15.0
1	6	-4	11.1	-9.4
1	6	5	12.1	12.5
1	6	-5	14.1	-13.3
1	6	6	9.1	8.7
1	6	-6	9.8	-10.4
1	7	0	17.8	18.1
1	7	1	14.8	14.1
1	7	-1	21.9	30.1
1	7	2	11.7	11.0
1	7	-2	19.9	20.1
1	7	-3	11.9	14.0
1	7	-4	9.9	11.2
1	7	-5	11.9	9.9
1	7	-6	9.2	7.1
1	8	0	15.9	-16.1
1	8	1	9.4	-8.2
1	8	2	6.7	-8.9
1	8	-2	10.0	8.8
1	8	3	13.9	-14.6
1	8	-3	7.9	5.8
1	8	4	15.8	-18.2
1	8	5	9.0	-10.3
1	8	-6	7.6	7.5
1	9	0	14.3	-17.2
1	9	1	14.5	-16.3
1	9	-1	10.9	-16.9
1	9	2	8.5	-9.0
1	9	-2	10.0	-10.8
1	9	-3	8.8	-10.7
1	9	-4	9.2	-10.5
1	9	-5	9.5	-8.1
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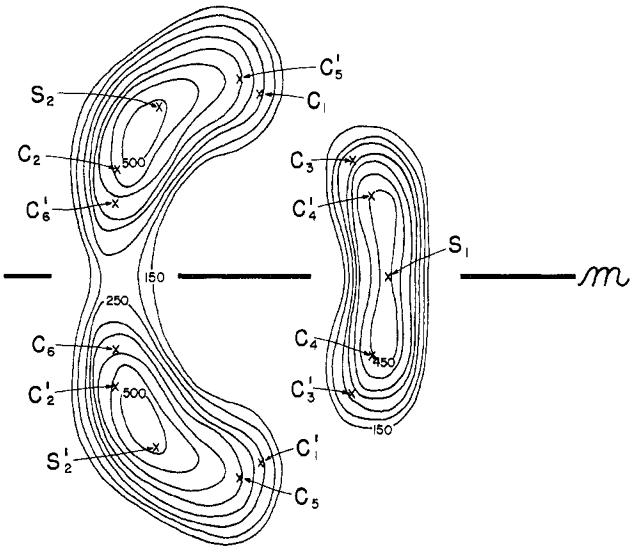

Figure 3.—Three-dimensional difference Fourier sections through a plane of the three sulfur atoms ($0.340X - 0.940Z + 0.248 = 0$). ($F_o - F_c$) with only the refined $Cr(CO)_3$ atoms contributing to F_c.

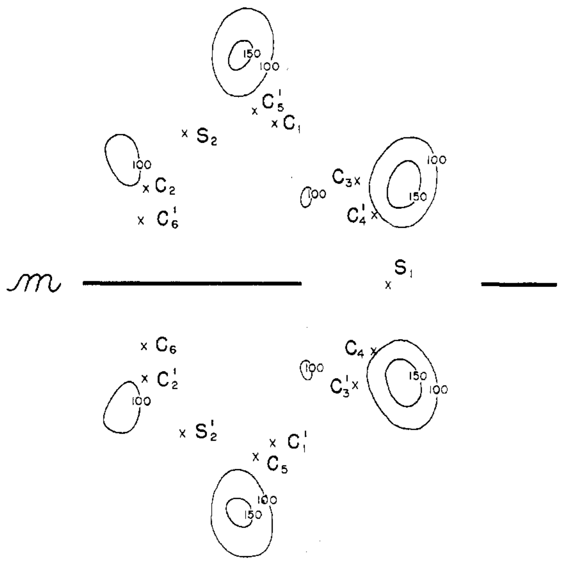

Figure 4.—As Figure 3 but $F_o - F_c$ with all the atoms from the final rigid-body refinement contributing to F_c.

The crystal packing is shown by the [100] and [001] projections given in Figures 5 and 6. Minimum intermolecular distances (oxygen–oxygen, 3.38 Å.; oxygen–carbon(ring), 3.10 Å.; oxygen–sulfur, 3.03 Å.; sulfur–carbon(ring), 3.96 Å.; carbon(ring)–carbon(ring), 3.96 Å.) indicate that the presumed microscopic threefold disorder of the thiophene ring does not result in unusually short contact distances. All of the sulfur–oxygen distances are greater than 3.28 Å., except for the S_1–$O_7{}^{I}$ distance of 3.03 Å. ($O_7{}^{I}$ is at (−0.31, 0.25, −0.58) *vs.* S_1 at (0.16, 0.25, −0.31)). The proximity of these two atoms may account in part for the apparent high thermal motion of the sulfur atom and the carbonyl oxygen in the mirror plane (through $y = {}^1/_4$); a slight displacement of either the carbonyl or the sulfur from this mirror plane would relieve this close contact. The crystal packing does not exclude the possibility of a hindered rotation of the thiophene ring, or even free rotation. The Fourier section through the thiophene ring (Figure 3), however, definitely indicates localization of electron density at the three positions which approximately correspond to the sulfur atoms in our proposed model.

Two further observations give support to this disordered model. First, the height, location, and apparent thermal motion of the Patterson peaks are consistent with the model. All of the Cr–S_1, Cr–S_2, Cr–O_7, and Cr–O_8 vectors (two for each atom pair) can be located on the Patterson map at positions calculated from the final parameters of the rigid-body refinement. These eight peaks are of approximately the same height, as would be expected if each sulfur has an effective scattering power of only five electrons. (Although the oxygen atoms should have greater scattering power than the "one-third sulfur atoms," the high thermal motion of the carbonyls relative to the chromium-bonded sulfur atoms would tend to equalize the Cr–S and Cr–O peak heights.)

Second, the final molecular parameters from the rigid-body refinement (Table V) are in good agreement with our proposed model. The refined Cr–S bond distances are equal within the estimated experimental error and average to 2.31 Å., and the Cr to ring carbon distances range from 2.19 to 2.23 Å. with an average of 2.21 Å. The S–Cr–CO angles for each sulfur and the carbonyl *trans* to it are equal within the estimated error and average to 160°.

TABLE V

INTRAMOLECULAR DISTANCES AND ANGLES

Bond	Distance, Å.	Std. dev., Å.	Angle	Deg.	Std. dev., deg.
Cr–C_7	1.766	0.025	C_7–Cr–C_8	91.3	0.8
Cr–C_8	1.772	0.017	C_8–Cr–C_8'	88.3	1.0
Cr–O_7	2.971	0.024	Cr–C_7–O_7	174.8	2.2
Cr–O_8	2.983	0.016	Cr–C_8–O_8	175.3	1.4
C_7–O_7	1.208	0.027	C_7–Cr–S_1	157.7	0.9
C_8–O_8	1.213	0.019	C_8–Cr–S_2'	161.5	0.6
Cr–S_1	2.298	0.021	S_1–S_2–S_2'	59.9	0.4
Cr–S_2	2.326	0.017	S_2–S_1–S_2'	60.2	0.8
S_1–S_2	2.307	0.020			
S_2–S_2'	2.316	0.032			
Cr–C_1	2.198	0.025			
Cr–C_2	2.195	0.025			
Cr–C_3	2.210	0.021			
Cr–C_4	2.205	0.021			
Cr–C_5	2.220	0.021			
Cr–C_6	2.234	0.021			

The three-dimensional Patterson and electron density maps were calculated on the CDC 1604 computer with the Blount Fourier program[13]; the electron density maps parallel to the plane of the three sulfur atoms (disordered model) were calculated on the IBM 704 with a general plane Fourier program.[14] The full-matrix least-squares refinements for the ordered models

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(13) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

(14) S. C. Abrahams, private communication.

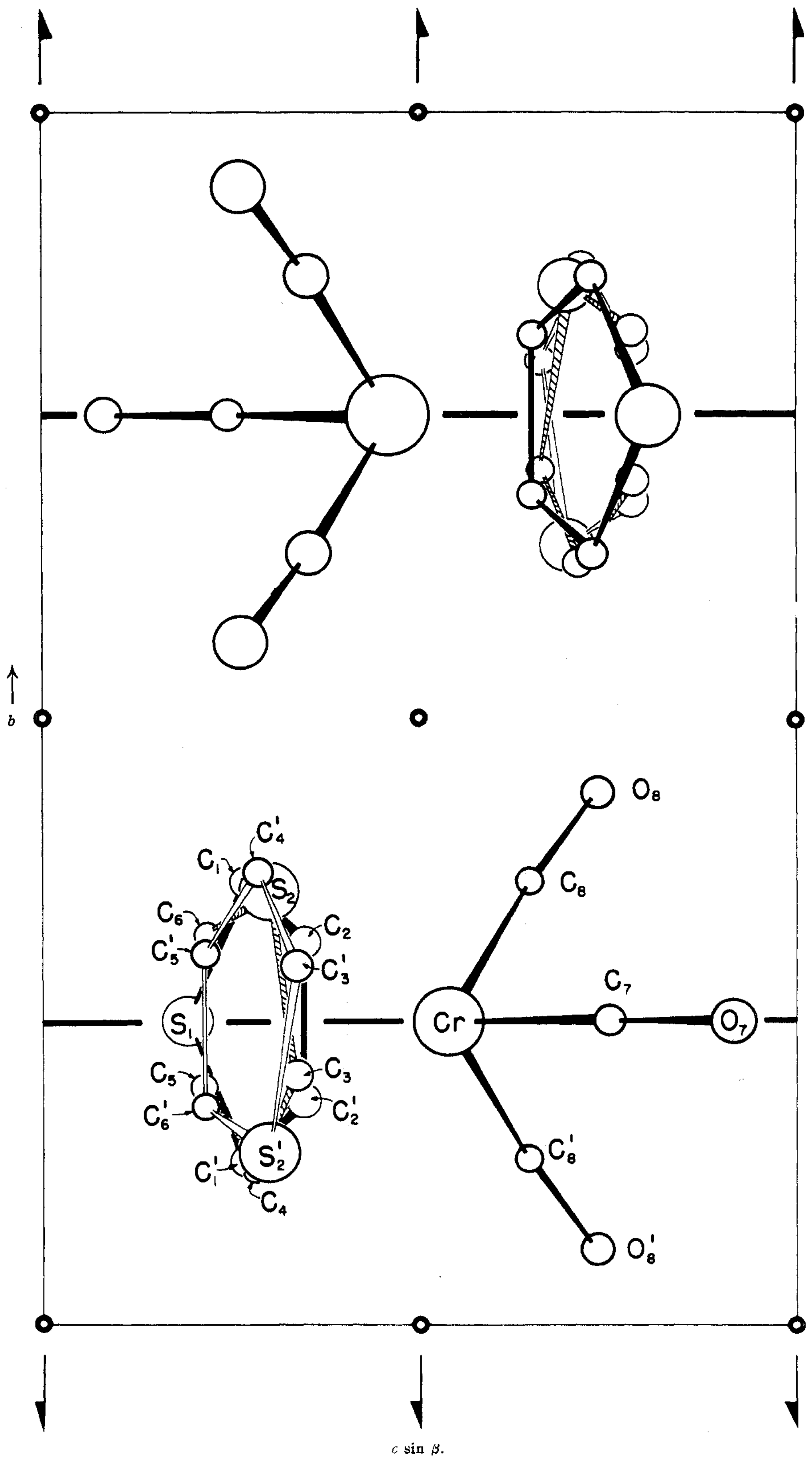

Figure 5.—[100] projection of the unit cell.

were carried out on the IBM 704 with the Busing–Martin–Levy ORFLS program,[15] whereas the refinement of the disordered model was obtained with Scheringer's rigid-body full-matrix least-squares Fortran program for the IBM 704.[12] Bond lengths and angles for all three models were calculated with the Busing–Martin–Levy ORFFE program[16] with errors obtained from the full inverse matrix.

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[15] W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1963.

[16] W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program, ORNL-TM-306, Oak Ridge National Laboratory, 1964.

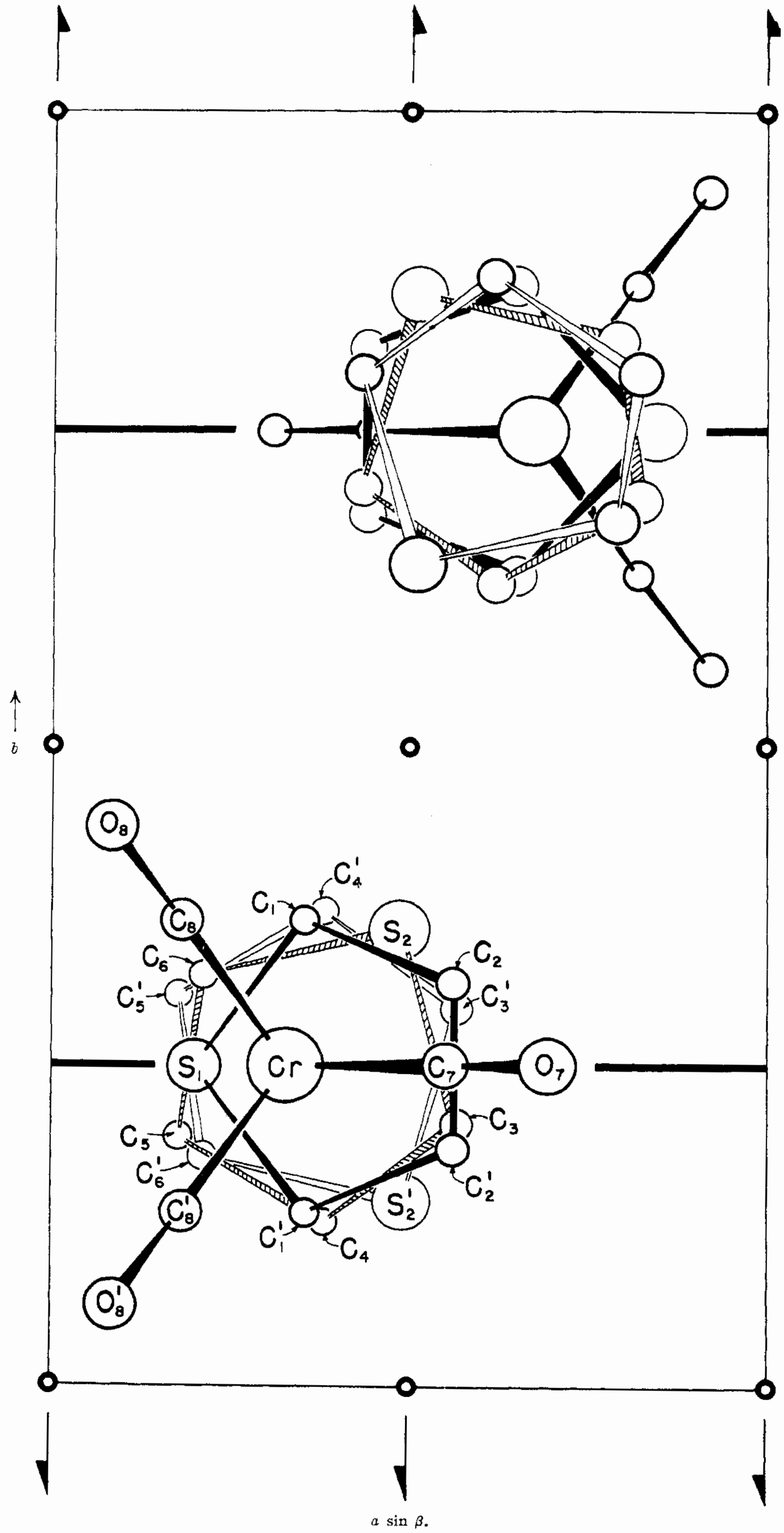

Figure 6.—[001] projection of the unit cell.

Discussion

The results of this three-dimensional X-ray investigation of thiophenechromium tricarbonyl at room temperature conclusively show that a simple ordered crystal structure does not fit the observed data; the threefold disordered rigid-body model which assumes for each molecule one of three equivalent positions of the thiophene ring gives the best refinement. This threefold ring disorder is similar to the twofold disorder found for the cyclopentadienyl ring in C_5H_5-

TABLE VI

COMPARISON OF THE AVERAGE CHROMIUM TRICARBONYL BOND LENGTHS AND ANGLES FOR SEVERAL CHROMIUM CARBONYL COMPLEXES

Compound	Distances, Å.			C–Cr–C angle, deg.
	Cr–O	Cr–C	C–O	
$Cr(CO)_6$[22]	3.08 ± 0.05	1.92 ± 0.04	(1.16 ± 0.05)[a]	(90)[b]
$Cr(CO)_6$[23]	(2.95 ± 0.05)[c]	1.80 ± 0.05	(1.15 ± 0.05)[e]	(90)[b]
$C_6H_6Cr(CO)_3$[24]	3.05 ± 0.06	(1.88)[d]	(1.15)[e]	88 ± 2
$C_{14}H_{10}Cr(CO)_3$[25]	3.01 ± 0.05	1.86 ± 0.05	1.15 ± 0.06	91 ± 2
$(H_3C)_6C_6Cr(CO)_3$[21]	2.98 ± 0.02	1.81 ± 0.02	1.16 ± 0.02	89.3 ± 0.8
$C_4H_4SCr(CO)_3$	2.98 ± 0.03	1.77 ± 0.03	1.21 ± 0.03	89.1 ± 1.0

[a] Obtained by difference of Cr–C and Cr–O distances.[22] [b] *Assumed* octahedral configuration (*i.e.*, all C–Cr–C angles = 90°).[22,23] [c] Obtained by summation of Cr–C and C–O distances.[23] [d] Obtained by difference of Cr–O and C–O distances.[24] [e] Assumed value.[23]

$Rh(C_2H_4)_2$ (*i.e.*, here demanded by the space group symmetry)[17] and each of the three cyclopentadienyl rings in $(C_5H_5)_3Ni_3(CO)_2$.[18] These three examples suggest that any possible n-fold disorder of a metal-bonded ring is determined by the localized n-fold symmetry axis (perpendicular to a given ring) of the other ligands attached to the metal. Although not observed from the X-ray work,[19] a neutron diffraction study[20] of ferrocene, $(C_5H_5)_2Fe$, indicated an orientational molecular disorder involving a twofold rotation with nonequivalent occupancy (*i.e.*, two-thirds of the cyclopentadienyl rings possess one orientation and one-third of the rings the other orientation). Our analysis of thiophenechromium tricarbonyl, however, indicates an *equal* distribution of the thiophene rings among the three possible orientations. Since in each of these three possible thiophene positions the sulfur atom is opposite one of the three carbonyl groups, the molecular configuration (Figure 1) is unaffected by the crystalline disorder.

From a qualitative valence bond view this structure is consistent with a three-point attachment of the thiophene ring (*via* the sulfur and two double bonds) to the chromium which possesses octahedral valency.[4] A qualitative MO description also can be invoked in which for simplification the chromium is assumed to possess trigonal C_{3v}-3m local symmetry (*vide infra*) in the interaction of its orbitals with the three carbonyl groups and C_s-m symmetry in its interaction with the thiophene ring. In this representation the chromium then utilizes for σ bonding with the three carbonyls an a_1 hybrid orbital of form $a_1s + a_2d_{z^2} + a_3p_z$ and one pair of degenerate orbitals of e symmetry, $b_1d_{xz} + b_2p_x$ and $b_1d_{yz} + b_2p_y$ (where the xz plane is the mirror plane of the molecule). The coefficients a_i and b_i stand for the different positive weighting factors, which in principle can be varied to make the bond energies a maximum and the total molecular energy a minimum. The important interactions of the chromium with the thiophene ring involve the overlap of the appropriate orbitals of the thiophene ring with an axially symmetric hybrid orbital of the chromium, $a_4s + a_5d_{z^2} - a_6p_z$, of a_1 symmetry and a pair of chromium orbitals, $b_3d_{xz} - b_4p_x$ and $b_5d_{yz} - b_6p_y$, which under C_s symmetry are nondegenerate. The hybrid orbital $a_7s - a_8d_{z^2}$ of a_1 symmetry and the nondegenerate $d_{x^2-y^2}$ and d_{xy} atomic orbitals, all of which are maximized in the xy plane of the chromium normal to the principal axis of the $Cr(CO)_3$ fragment, overlap with the corresponding ligand orbitals to a much smaller degree. This representation of bonding within the framework of the usual LCAO–MO theory is consistent with a delocalized electron ring distribution. The heterocyclic thiophene ring, however, presumably introduces a certain degree of localized bonding.

Within experimental error the $Cr(CO)_3$ fragment possesses C_{3v} symmetry. The average Cr–O (2.98 Å.), Cr–C (1.77 Å.), and C–O (1.21 Å.) distances are in good agreement with the average distances found for hexamethylbenzenechromium tricarbonyl[21] (Cr–O = 2.98 Å. (av.), Cr–C = 1.81 Å. (av.), and C–O = 1.16 Å. (av.)). These distances based upon three-dimensional X-ray work are considered to be more reliable than those found from a relatively early electron diffraction study of chromium hexacarbonyl[22] and from two-dimensional X-ray studies of chromium hexacarbonyl,[23] benzenechromium tricarbonyl,[24] and phenanthrenechromium tricarbonyl.[25] The average bond lengths and angles for each of these compounds are given in Table VI.

A comparison of the results of this analysis of thiophenechromium tricarbonyl with those of benzenechromium tricarbonyl[24] shows that benzenechromium tricarbonyl is essentially isomorphous with thiophenechromium tricarbonyl insofar as the space group, lattice constants, and atomic positions of the chromium tricarbonyl moiety are concerned. In addition, for the two chromium tricarbonyl complexes the benzene rings (which are parallel to the b axis and are rotated by 20° out of the ab plane) and the disordered thiophene rings (which are oriented parallel to b and are rotated by 22° (av.) out of the ab plane) are similarly oriented in the unit cell. An analogous relationship

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[25] H. Deuschl and W. Hoppe, *Acta Cryst.*, **17**, 800 (1964).

exists between the crystal structures of free benzene and free thiophene.[26]

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(26) On the basis of the lattice constants of benzene initially reported by Cox,[27] as well as their own X-ray structural study of thiophene, Abrahams and Lipscomb[28] suggested that thiophene and benzene may be isomorphous in the solid state. The subsequent determination of the space group and orientation of benzene molecules in crystals at −3°[29] has enabled us to confirm their suggestion and also to determine the degree of structural similarity between the two compounds.

Crystals of thiophene (−55°) contain four molecules in an orthorhombic unit cell of dimensions a = 9.76 Å., b = 7.20 Å., c = 6.67 Å.[28]; the probable space group is either Bmab(D_{2h}^{18}) or the noncentrosymmetric equivalent, B2ab(C_{2v}^{17}). This structure, in which the thiophene molecules lie very nearly in the $(01\bar{1})$ and (011) planes, is complicated by an apparent fourfold positional disorder of the thiophene rings for Bmab, which reduces to a twofold positional disorder of the rings for B2ab. With this disorder the five "$^1/_4$ atoms" (Bmab) or "$^1/_2$ atoms" (B2ab) of one thiophene ring make up the asymmetric unit. For the acentric case (B2ab) the centers of gravity of the two disordered molecules coincide and lie on the 2_a; for the centric case (Bmab) the centers of gravity of the four disordered molecules also coincide and lie on the center of symmetry at the intersection of 2_a and m_a. This fourfold (or twofold) disorder found in free thiophene appears analogous to the threefold disorder found for the thiophene rings in thiophenechromium tricarbonyl.

Solid benzene (−3°) possesses an ordered structure with four molecules in an orthorhombic unit cell of dimensions a = 7.46 Å., b = 9.67 Å., c = 7.03 Å.[29] The unique space group Pbca requires each benzene to lie on a crystallographic center of symmetry; the molecules are so oriented that they lie very nearly in the (101) and $(10\bar{1})$ planes.

By an appropriate transformation of axes one can elucidate the crystallographic similarities of these two compounds. For thiophene, Bmab (B2ab) is equivalent to Cmca(C2ca) by a reversal of the c and b axes, for which the lattice constants transform to a' = 9.76 Å., b' = 6.67 Å., and c' = 7.20 Å.; the thiophene molecules remain nearly in the (011) and $(0\bar{1}\bar{1})$ planes. For benzene one can make the following transformation (to which the space group Pbca is invariant): $a' = b$, $b' = c$, $c' = a$ (*i.e.*, a' = 9.67 Å., b' = 7.03 Å., c' = 7.46 Å.). With this transformation a comparison of the primed lattice constants for the two compounds is in agreement with the proposed isomorphism, and the benzene molecules now are close to the (011) and $(01\bar{1})$ planes. Moreover, if four of the benzene ring carbons were located at $\pm(x_1, y_1, z_1)$ and $\pm(\bar{x}_1, y_1, z_1)$ with the two remaining carbon atoms at $\pm(x_2, 0, 0)$, then the space group symmetry would be Cmca. The actual structure of benzene shows that the carbon atoms are close to these positions with four carbon atoms located at ±(0.05, 0.12, −0.13) and ±(−0.09, 0.13, −0.08) and the other two carbons at ±(0.14, −0.01, −0.05).[29] The observed intensities consequently show a tendency toward C-centering (*i.e.*, on the average, the *hkl* reflections for $h + k$ odd are weaker than those for $h + k$ even).[29]

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Three-Dimensional Crystal Structure of Benzenechromium Tricarbonyl with Further Comments on the Dibenzenechromium Structure[1]

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As part of a systematic investigation of possible threefold distortion of arene rings on π-bonding to chromium, a three-dimensional single crystal X-ray analysis of benzenechromium tricarbonyl, $C_6H_6Cr(CO)_3$, has been carried out. Crystals of benzenechromium tricarbonyl contain two molecules in a monoclinic unit cell of symmetry $P2_1/m$ and dimensions a = 6.17 ± 0.02 Å., b = 11.07 ± 0.04 Å., c = 6.57 ± 0.02 Å., and β = 101.5 ± 0.1°. A final anisotropic least-squares refinement with the hydrogen atoms included in the structure factor calculations has resulted in discrepancy factors of R_1 = 4.2% and R_2 = 4.1% for 518 observed reflections. Benzenechromium tricarbonyl possesses essentially C_{3v} molecular symmetry in agreement with the approximate molecular structure obtained from previous two-dimensional X-ray work. The π-bonded benzene ring, however, shows no significant distortion from the sixfold (D_{6h}) symmetry of "free" benzene, which is indicative of a completely delocalized benzene–chromium interaction. A comparison of the molecular parameters of benzenechromium tricarbonyl, hexamethylbenzenechromium tricarbonyl, and dibenzenechromium is made, and the crystallographic isomorphism of $C_6H_6Cr(CO)_3$ and $C_4H_4SCr(CO)_3$ is discussed.

Introduction

The recent extensive interest concerning possible reduction of the sixfold symmetry of arene rings π-bonded to transition metals has arisen from the conflicting results obtained from several independent three-dimensional X-ray studies of dibenzenechromium.[4–7] This controversy has led to the suggestion that X-ray analyses of arene–chromium tricarbonyl complexes offer a means of clarifying this problem,[8] since the presence of the trigonal field of the chromium tricarbonyl moiety should induce a threefold distortion of the benzene ring if indeed dibenzenechromium exhibits

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(1) Based in part on a dissertation submitted by M. F. Bailey to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) National Science Foundation Predoctoral Fellow, 1962–1964.

(3) Alfred P. Sloan Fellow, 1963–1965.

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