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

(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 (01$\bar{1}$) 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 $\pm(0.05, 0.12, -0.13)$ and $\pm(-0.09, 0.13, -0.08)$ and the other two carbons at $\pm(0.14, -0.01, -0.05)$.[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).[28]

(27) E. G. Cox, *Proc. Roy. Soc.* (London), **A135**, 491 (1932).

(28) S. C. Abrahams and W. N. Lipscomb, *Acta Cryst.*, **5**, 93 (1952).

(29) E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. Roy. Soc.* (London), **A247**, 1 (1958); E. G. Cox and J. A. S. Smith, *Nature*, **173**, 75 (1954).

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

By MARCIA F. BAILEY[2] and LAWRENCE F. DAHL[3]

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 $a = 6.17 \pm 0.02$ Å., $b = 11.07 \pm 0.04$ Å., $c = 6.57 \pm 0.02$ Å., and $\beta = 101.5 \pm 0.1°$. 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

(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.

(4) F. Jellinek, *Nature*, **187**, 871 (1960); F. Jellinek, *J. Organometal. Chem.* (Amsterdam), **1**, 43 (1963).

(5) F. A. Cotton, W. A. Dollase, and J. S. Wood, *J. Am. Chem. Soc.*, **85**, 1543 (1963).

(6) J. A. Ibers, *J. Chem. Phys.*, **40**, 3129 (1964).

(7) For a discussion of this problem, including extensive comments on the dibenzenechromium structural analyses, see P. J. Wheatley's review on "Structure Determinations of Benzenoid–Transition Metal Complexes," to be published.

(8) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1298 (1965).

only threefold symmetry. The absence of any three-fold symmetry in the $Cr(CO)_3$-complexed benzene ring thereby would cast serious doubt on the possibility of observing for dibenzene metal complexes threefold symmetry which could be ascribed to intramolecular bonding effects. The above ideas prompted a three-dimensional anisotropic X-ray investigation of hexamethylbenzenechromium tricarbonyl which produced no evidence of a threefold distortion of the ring.[8] However, an indicated twofold deformation of the benzene and methyl carbon atoms was found which was attributed both to asymmetric crystal forces and to a possible absence of the sixfold symmetry of the carbon skeletal structure in "free" hexamethylbenzene due to the intramolecular steric interactions of the methyl groups. The presence of the methyl groups established that the twelve carbon atoms of the hexamethylbenzene ring were essentially coplanar in this π-bonded ring–chromium tricarbonyl complex and that, to a first-order approximation, the arene ring π-orbital system remains intact for chromium tricarbonyl complexes. Hence, from these results it was concluded that the hydrogen atoms (or other substituents) of the π-bonded benzene rings in dibenzenechromium, benzenechromium tricarbonyl, and similar chromium–arene complexes also remain approximately coplanar with the ring carbon atoms.

In order to investigate further possible arene ring distortion on π bonding to chromium, a three-dimensional X-ray analysis of benzenechromium tricarbonyl was undertaken. Although a two-dimensional study of this complex has been reported by Corradini and Allegra,[9–11] the large standard deviations of their final parameters prevented detection of any possible threefold distortion of the six carbon atoms of the benzene ring in this complex.[11] Our three-dimensional single crystal X-ray study of benzenechromium tricarbonyl, which included anisotropic least-squares refinement of the nonhydrogen atoms, has provided additional stereochemical information of importance to the dibenzenechromium dispute.

Experimental

Yellow crystals of benzenechromium tricarbonyl were prepared by the method of Nicholls and Whiting,[12] with sublimation *in vacuo* at 70° to give crystals suitable for X-ray study. Two uniformly-shaped crystals of 0.02 cm. maximum diameter were used for gathering intensity data. Lattice constants were measured from precession photographs of the three principal zones, and the resulting internal agreement was well within the indicated error. The settings of the precession camera were calibrated with a sodium chloride crystal.

Multiple-film equi-inclination Weissenberg photographs were obtained with Zr-filtered Mo Kα radiation about the a rotation axis for six reciprocal levels ($0kl–5kl$) and about the c rotation axis for seven levels ($hk0–hk6$). The intensities of the reflections were visually estimated and spot extension[13] as well as Lorentz-polarization corrections were applied; no correction was made for

extinction effects. The linear absorption coefficient, μ, of $C_6H_6Cr(CO)_3$ for Mo Kα radiation is 13.4 cm.$^{-1}$; due to this small absorption coefficient ($\mu R_{max} < 0.2$), absorption corrections were neglected. The data were subsequently merged to one scale factor *via* least squares[14] to give 518 independent reflections; for the merging of 349 duplicate reflections the weighted reliability index R_2 was 3.3%. The standard deviations of the observed structure amplitudes were estimated as follows[15]: If $I_0(hkl) < \sqrt{10 I_{min}}$, $\sigma(F_0(hkl)) = (|F_0(hkl)|/20)[\sqrt{10 I_{min}}/I_0(hkl)]^2$; if $I_0(hkl) \geqslant \sqrt{10 I_{min}}$, $\sigma(F_0(hkl)) = |F_0(hkl)|/20$.

Crystal Data

Crystals of benzenechromium tricarbonyl are monoclinic with cell parameters $a = 6.17 \pm 0.02$ Å., $b = 11.07 \pm 0.04$ Å., $c = 6.57 \pm 0.02$ Å., and $\beta = 101.5 \pm 0.1°$. For two molecules per unit cell, our calculated density of 1.62 g./cc. agrees well with the experimental (1.64 g./cc.) and calculated (1.65 g./cc.) densities obtained by Corradini and Allegra.[10] The corresponding values for the lattice constants of benzenechromium tricarbonyl obtained by Corradini and Allegra[10] are $a = 6.09 \pm 0.04$ Å., $b = 10.99 \pm 0.07$ Å., $c = 6.58 \pm 0.04$ Å., and $\beta = 101.5°$.

The systematic absence of $k = 2n + 1$ for $\{0k0\}$ data indicates the probable space group to be either $P2_1(C_2{}^2)$ or $P2_1/m(C_{2h}{}^2)$. The acentric space group ($P2_1$) requires the location of one complete formula unit, whereas the centrosymmetric space group demands that the noncentrosymmetric molecule possess a crystallographic mirror plane which passes through the chromium atom and one carbonyl group (and possibly two ring carbon atoms) and relates in pairs the other atoms (*viz.*, the remaining two carbonyls and six (or possibly four) ring carbon atoms).

Solution of Structure

A three-dimensional Patterson function calculated from the merged data revealed the single-weight Cr–Cr vector and the ten double-weight Cr–C and four double-weight Cr–O vectors at positions very close to those predicted on the basis of the atomic coordinates obtained two-dimensionally by Corradini and Allegra.[10,11] On this three-dimensional vector map it was verified that two atoms which correspond to one carbonyl group possess exactly the same y coordinate as the chromium atom and that none of the ring carbon atoms lies in this plane; rather, three ring carbon atoms are located above the plane, and the other three are related by reflection through this plane (Figure 1). The remaining two carbonyls are similarly related to each other. Since the Patterson function involves no assumptions concerning the atomic positions of any of the atoms, the relative weights and positions of the observed vectors strongly indicate that crystals of this compound indeed are centric and of space group $P2_1/m$.

A three-dimensional isotropic least-squares refinement carried out on the independent nonhydrogen atoms resulted in discrepancy factors of $R_1 = [\Sigma||F_0| - |F_c||/\Sigma|F_0|] \times 100 = 9.0\%$ and $R_2 = [\Sigma w||F_0| -$

(9) P. Corradini and G. Allegra, *J. Am. Chem. Soc.*, **81**, 2271 (1959).

(10) P. Corradini and G. Allegra, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **26**, 511 (1959).

(11) G. Allegra, *ibid.*, **31**, 241 (1961).

(12) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

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

(14) P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC 1604," University of Wisconsin, 1963.

(15) D. L. Smith, "DACOR—A Data Reduction Program for the 1604 Computer," Ph.D. Thesis (Appendix I), University of Wisconsin, 1962.
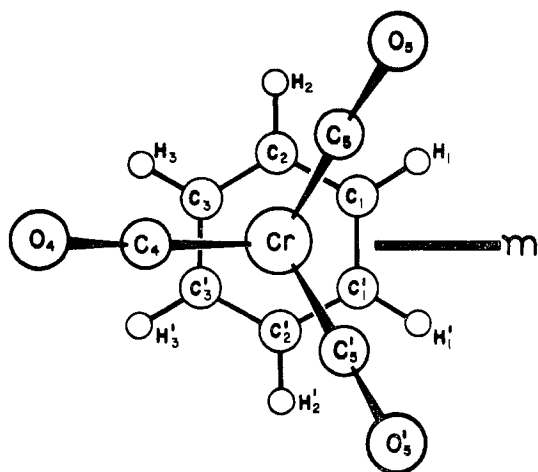
Figure 1.—Molecular configuration of benzenechromium tricarbonyl.

$|F_c||^2 / \Sigma w' F_o|^2]^{1/2} \times 100 = 10.2\%$. A three-dimensional difference synthesis based on the final parameters of this refinement showed the hydrogen atom peaks of 0.5–0.6 electron/Å.^{3} in height and at positions consistent with the structure of "free" benzene. In addition, this map revealed for all the atoms anisotropic thermal motion which was especially noticeable for the two independent carbonyl oxygen atoms. At this point the average carbon–carbon bond distance in the ring was 1.41$_2$ Å. with three of the four independent distances less than 1 standard deviation (0.015 to 0.021 Å.) from this average, and the other length (bisected by the mirror plane) at 2.5 standard deviations below the average bond length.

A further isotropic least-squares refinement of the eight nonhydrogen atoms was made in which the contribution of the hydrogen atoms was included in the structure factor calculations. Each of the hydrogen atoms was constrained to lie at a distance of 1.08 Å. from the carbon atom to which it is bonded and to sit on the vector determined by that carbon atom and the carbon atom in the *para* position. The hydrogen atoms were assigned isotropic temperature coefficients of 4.5 Å.^{2}. This isotropic refinement yielded discrepancy factors of $R_1 = 8.7\%$ and $R_2 = 9.8\%$; for the resultant positional parameters the carbon–carbon distances of the ring averaged to 1.394 Å.; three of the distances were within 1 σ (0.014–0.020 Å.), two were within 2 σ, and the sixth bond length was just within 3 σ of the average value. The two sets of three alternate bond lengths averaged to 1.39$_5$ and 1.39$_3$ Å. Noteworthy is the average decrease of 0.018 Å. in the bond distances of the ring when the contribution of the hydrogen atoms is also included in the calculated structure factors of the least-squares refinement.

A rigid-body least-squares refinement[16] then was undertaken in which the benzene ring was constrained to D_{6h} symmetry with carbon–carbon distances of 1.392 Å. and carbon–hydrogen distances of 1.08 Å. In addition, the carbon and hydrogen atoms of the ring were required to have equal isotropic temperature

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

coefficients. Refinement of this model yielded discrepancy factors of $R_1 = 8.6\%$ and $R_2 = 10.0\%$. For 518 reflections and a reduction of the number of variables from 30 to 22, Hamilton's R factor ratio test[6,17] on the two R_2 values $(R_2(D_{6h})/R_2(C_s) = 1.021)$ indicates that the model requiring D_{6h} symmetry and one thermal parameter for the ring is not statistically equivalent to the model obtained when only the crystallographically required C_s symmetry is forced on the ring; the significance of the difference in models is at the 1% level. This test is consistent with the spread in ring distances observed in the C_s model, where one bond distance was 3 standard deviations below the average. However, it was felt that this irregular deviation of the benzene ring from D_{6h} symmetry no doubt partly stemmed from the use of isotropic thermal motion which from an examination of the previously calculated difference Fourier map was not a good assumption. Our subsequent anisotropic least-squares refinement supported this conclusion. Three-dimensional anisotropic least-squares refinement of the eight independent nonhydrogen atoms resulted in considerable decreases of the discrepancy factors to give $R_1 = 4.2\%$ and $R_2 = 4.1\%$. The hydrogen atoms were included in the structure factor calculations, and their positions and temperature coefficients (4.5 Å.^{2}) were constrained as outlined above for the second isotropic refinement. It is of interest that the drop in R_2 in going from the isotropic model with hydrogen atoms and C_s symmetry to the anisotropic model with similar hydrogen positions and ring symmetry results in an R factor ratio (R_{iso}/R_{aniso}) of 2.41. For 518 reflections and an increase of 34 (from 30 to 64) variables, this ratio is highly significant (*i.e.*, far below the 0.5% level),[17] and thus in this crystal structure the model which allows individual atomic anisotropic thermal motion is indeed far superior to that which assumes individual atomic isotropic motion.

A difference Fourier based on the parameters of this

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^a	0.3319	0.15	0.2500	...	0.0225	0.13
C$_1$	0.1804	0.8	0.3119	0.4	−0.2973	0.6
C$_2$	0.3761	1.0	0.3769	0.4	−0.2273	0.6
C$_3$	0.5753	0.8	0.3142	0.4	−0.1598	0.7
C$_4{}^a$	0.5538	1.2	0.2500	...	0.2557	1.0
O$_4{}^a$	0.6899	0.9	0.2500	...	0.4002	0.8
C$_5$	0.1827	0.8	0.3642	0.4	0.1453	0.7
O$_5$	0.0894	0.7	0.4341	0.3	0.2248	0.5
H$_1{}^b$	0.0280	...	0.3606	...	−0.3505	...
H$_2{}^b$	0.3761	...	0.4745	...	−0.2273	...
H$_3{}^b$	0.7278	...	0.3629	...	−0.1066	...

^{a} The y coordinates of Cr, C$_4$, and O$_4$ were constrained by the crystal symmetry to be $^1/_4$. ^{b} The three hydrogen positions were not varied, but each hydrogen atom was constrained to be 1.08 Å. from the corresponding carbon atom and collinear with that carbon atom and the *para* carbon atom.

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

TABLE II

FINAL ANISOTROPIC TEMPERATURE COEFFICIENTS ($\times 10^4$) WITH STANDARD DEVIATIONS[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	151 ± 3	67 ± 1	165 ± 3	0	41 ± 2	0
C_1	306 ± 15	101 ± 4	174 ± 9	14 ± 8	46 ± 10	13 ± 6
C_2	471 ± 23	83 ± 5	213 ± 13	-6 ± 10	123 ± 14	11 ± 6
C_3	250 ± 14	150 ± 6	234 ± 11	-62 ± 8	108 ± 10	-12 ± 6
C_4	252 ± 22	116 ± 8	275 ± 21	0	113 ± 20	0
O_4	250 ± 17	335 ± 11	216 ± 13	0	-47 ± 13	0
C_5	253 ± 15	75 ± 5	236 ± 12	8 ± 8	46 ± 12	34 ± 6
O_5	527 ± 15	95 ± 4	387 ± 11	100 ± 7	215 ± 11	2 ± 5

[a] Individual atom temperature factors of the form exp $\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$ were used.[19]

TABLE III

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS FROM THE ANISOTROPIC REFINEMENT

[Table III consists of an extensive multi-column listing of H, K, L, FO, and FC values for the structure factor comparison.]

final refinement revealed no positive electron density greater than 0.50 electron/Å.³ or less than −0.35 electron/Å.³; the absolute value of the electron density within 0.2 Å. of the hydrogen positions was less than 0.1 electron/Å.³. The final positional parameters and temperature coefficients from the anisotropic refinement are given in Tables I and II. In Table III observed and calculated structure factors are compared for these final parameters. Table IV includes the molecular bond distances and angles calculated from

the final positional parameters obtained in the anisotropic refinement. Table V indicates the perpendicular deviations (Å.) of all atoms from the plane of the ring.

TABLE IV
MOLECULAR BOND LENGTHS AND ANGLES
FROM ANISOTROPIC LEAST-SQUARES REFINEMENT

Bond Lengths

Atoms	Distance, Å.	σ, Å.	Atoms	Distance, Å.	σ, Å.
Cr–C$_1$	2.230	0.009	C$_1'$–C$_1$	1.371	0.011
Cr–C$_2$	2.218	0.008	C$_1$–C$_2$	1.402	0.008
Cr–C$_3$	2.216	0.008	C$_2$–C$_3$	1.404	0.008
Cr–C$_4$	1.841	0.010	C$_3$–C$_3'$	1.421	0.011
Cr–C$_5$	1.842	0.008	C$_3'$–C$_2'^a$	1.404	0.008
Cr–O$_4$	2.976	0.011	C$_2'$–C$_1'^a$	1.402	0.008
Cr–O$_5$	2.992	0.009	C$_1$–H$_1^b$	1.080	. . .
C$_4$–O$_4$	1.135	0.008	C$_2$–H$_2^b$	1.080	. . .
C$_5$–O$_5$	1.150	0.006	C$_3$–H$_3^b$	1.080	. . .

Angles

Atoms	Angle, deg.	σ, deg.	Atoms	Angle, deg.	σ, deg.
Cr–C$_4$–O$_4$	179.7	0.6	O$_4$–Cr–O$_5$	89.0	0.3
Cr–C$_5$–O$_5$	178.8	0.4	O$_5$–Cr–O$_5'$	85.9	0.4
C$_4$–Cr–C$_5$	89.4	0.3	C$_1'$–C$_1$–C$_2$	120.9	0.3
C$_5$–Cr–C$_5'$	86.7	0.4	C$_1$–C$_2$–C$_3$	119.5	0.5
			C$_2$–C$_3$–C$_3'$	119.6	0.3

^{a} The bond distances C$_3'$–C$_2'$ and C$_2'$–C$_1'$ are symmetry-related by a mirror plane to the bond distances C$_2$–C$_3$ and C$_1$–C$_2$, respectively. ^{b} The carbon–hydrogen distances were constrained to be 1.08 Å.

TABLE V
DEVIATIONS (Å.) OF ALL ATOMS FROM
THE MEAN PLANE OF THE SIX RING CARBON
ATOMS: $0.365X - 3.931Z = 2.327^a$

Atom	Distance, Å.	Atom	Distance, Å.
C$_1$	−0.004	Cr	1.724
C$_2$	0.008	C$_4$	2.733
C$_3$	−0.004	C$_5$	2.856
H$_1$	−0.004	O$_4$	3.361
H$_2$	0.008	O$_5$	3.580
H$_3$	−0.004		

^{a} The equation is expressed in orthogonal coordinates X, Y, and Z, which are related to the monoclinic cell coordinates by the transformation $X = ax + cz \cos \beta$, $Y = by$, and $Z = cz \sin \beta$.

The Patterson and electron density maps were calculated on the CDC 1604 computer with the Blount program.[18] The full-matrix least-squares nonrigid-body refinements (isotropic and anisotropic) were carried out on the CDC 1604 computer with the Busing–Martin–Levy ORFLS program,[19] whereas the rigid-body isotropic refinement was obtained with Scheringer's full-matrix least-squares Fortran program for the IBM 704.[16] All bond lengths and angles were calculated with the Busing–Martin–Levy ORFFE program with errors obtained from the full inverse matrix.[20]

(18) J. Blount, "A Fourier Program for the CDC 1604," University of Wisconsin, 1963.
(19) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS—A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1963.
(20) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE—A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

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.[21]

Discussion

One three-dimensional X-ray analysis of benzene-chromium tricarbonyl gives no indication of a threefold distortion of the π-bonded benzene ring in this tricarbonyl chromium complex. The four independent carbon–carbon bond distances range in value from 1.370 ± 0.011 to 1.421 ± 0.011 Å., and each is within 3 standard deviations of the average bond distance of 1.40$_1$ Å. This average distance is in good agreement with the average arene carbon–carbon bond length of 1.42 Å. found in hexamethylbenzenechromium tricarbonyl[8] and 1.39 Å. reported for dibenzenechromium.[6] The averages of each of the two sets of alternate bond lengths are 1.39$_3$ and 1.40$_8$ Å. Since these last two averages are equal within the estimated error, it is concluded that no threefold distortion toward a triene system is observed in this π-bonded benzene ring. This result for benzenechromium tricarbonyl gives strong support to earlier indications that within the estimated error dibenzenechromium possesses D$_{6h}$ symmetry.[5-7]

The three chromium to ring carbon distances range from 2.21$_6$ to 2.23$_0$ Å. (individual e.s.d., 0.009 Å.). The average value of 2.22$_1$ Å. agrees well with the corresponding average distance of 2.23 Å. (individual e.s.d., 0.011 Å.) for hexamethylbenzenechromium tricarbonyl[8] but is significantly greater than the 2.13 Å. (individual e.s.d., 0.006 Å.) average chromium to ring carbon distance found for dibenzenechromium.[6] The perpendicular distance of the chromium atom from the plane of the six ring carbons shows the same trend for these three complexes with 1.72$_4$ Å. for benzenechromium tricarbonyl (Table V), 1.72$_6$ Å. for hexamethyl-benzenechromium tricarbonyl,[8] and 1.60 Å. (av.) for dibenzenechromium.[6] Comparison of the perpendicular distances of the chromium atom from the ring plane in each of these three complexes thus indicates that the metal to ring bond in benzenechromium tricarbonyl is approximately as strong as that in hexamethylbenzene-chromium tricarbonyl, but is weaker than each of the chromium to ring bonds in dibenzenechromium. The six ring carbon atoms of benzenechromium tricarbonyl are coplanar (Table V), and their mean plane is essentially parallel to that of the three oxygen atoms (dihedral angle of 3.4°).

The chromium tricarbonyl fragment possesses approximately C$_{3v}$ symmetry, with two symmetry related C–Cr–C angles of 89.4° and a third C–Cr–C angle of 86.7°. For the anisotropic refinement the average bond distances in the chromium tricarbonyl moiety are: Cr–C, 1.84$_2$ Å.; C–O, 1.14$_5$ Å.; Cr$\cdots$O, 2.98$_7$ Å. In contrast, the isotropic refinement which included the hydrogen atoms gave the following averaged dis-

(21) D. L. Smith, "A Least-Squares Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.
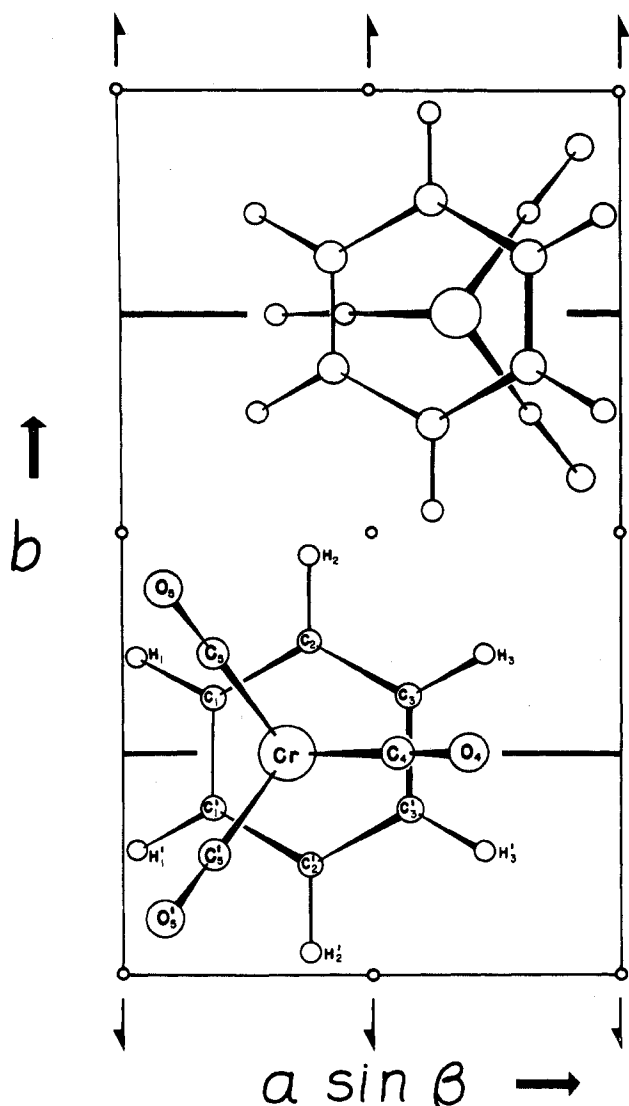
Figure 2.—[001] projection of the unit cell of benzenechromium tricarbonyl.

tances in the chromium tricarbonyl fragment: Cr–C, 1.80_2 Å.; C–O, 1.18_4 Å.; Cr $\cdots$ O, 2.98_6 Å. The C–Cr–C angles for the isotropic refinement, however, are within 0.2° of those obtained in the anisotropic refinement. Thus, the net average change in the chromium tricarbonyl positional coordinates during the anisotropic refinement was a 0.04 Å. shift of the carbonyl carbons toward the chromium atom.

The [001] projection (Figure 2) indicates the arrangement of the two molecules of the unit cell. Shortest intermolecular nonbonding distances (2.58 Å. for H to O, 2.68 Å. for H to H, and 3.19 Å. for O to ring carbon in a direction nearly perpendicular to the ring) indicate no unusually close approaches between the basic molecule and its nearest neighbors.

A comparison of the crystal structure of this compound with that of thiophenechromium tricarbonyl is informative.[22] Lattice constants and chromium tricarbonyl positions for the thiophene complex are given in Table VI. The isomorphism is quite evident and includes the rings as well. The thiophene rings, however, were found to possess a crystallographic threefold disorder with the sulfur atom of any given ring always *trans* to one of the three carbonyl groups. Nonetheless, the crystal plane which contains the three "one-third" thiophene rings is essentially the same as the crystal plane of the benzene ring. An extension of this isomorphism to crystals of "free" benzene and "free" thiophene has been discussed elsewhere.[22]

TABLE VI

CRYSTAL DATA AND CHROMIUM TRICARBONYL FRACTIONAL
COORDINATES FOR THIOPHENECHROMIUM TRICARBONYL[22]
CRYSTAL DATA[a]

Atom	Chromium tricarbonyl coordinates		
	x	y	z
Cr	0.3279	0.2500	0.0372
C_4	0.551	0.2500	0.256
O_4	0.691	0.2500	0.415
C_5	0.181	0.364	0.148
O_5	0.082	0.438	0.237

[a] a = 6.06 Å., b = 10.79 Å., c = 6.65 Å., and β = 102.2°; space group $P2_1/m$; 2 molecules per unit cell.

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