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THE MOLECULAR STRUCTURE OF π-(TRICARBONYLCHROMIUM)-TOLUENE

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Summary

The molecular structure of π-(tricarbonylchromium)toluene, $CrC_{10}H_8O_3$, has been determined from three-dimensional X-ray data. The orthorhombic unit-cell, $P2_12_12_1$ with a = 11.109(4), b = 7.231(3) and c = 12.206(4) Å, contains four molecules. Refinement converged to a final weighted R-index of 4.1% for 1163 observed reflexions. The orientation of the tricarbonylchromium group is nearly eclipsed with respect to the carbon atoms C(1), C(3) and C(5).

Introduction

NMR data of monoalkylsubstituted π-(tricarbonylchromium)benzenes have been analysed in terms of a rapid equilibrium between conformers I and II [1—3]. As a reference compound for conformer II (1′-t-butyl-2′,2′-dimethylpropyl)-π-(tricarbonylchromium)benzene (R = CH-t-Bu_2) was used [3]; a recent X-ray analysis of this compound [4] showed the orientation of the $Cr(CO)_3$ group with respect to the arene ring to deviate by about 15° from the assumed position. The ^{1}H NMR study [3] revealed that the population of conformer I in the conformational mixture is most predominant if R = Me ($\Delta G^0 \sim 0.5$ kcal mol^{-1}). To compare this result with the conformation of the $Cr(CO)_3$ group in π-(tricarbonylchromium)toluene in the solid state, the present X-ray investigation was started.

TABLE 1

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS

The fractional atomic coordinates have been multiplied by 10^5 for Cr, by 10^4 for C and O, and by 10^3 for H. The isotropic factors U are in $Å^2 \times 10^3$. The U_{ij} coefficients ($Å^2 \times 10^4$ for Cr and $Å^2 \times 10^3$ for C and 0) are given by the expression: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})]$

	x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	22490(5)	9634(7)	18393(4)	378(3)	319(3)	360(3)	40(2)	35(2)	−2(2)
C(1)	2738(4)	3959(5)	1740(3)	68(2)	31(2)	65(2)	0(2)	14(2)	2(2)
C(2)	2636(5)	3446(6)	2833(3)	67(3)	42(2)	47(2)	1(2)	−7(2)	−10(2)
C(3)	1614(5)	2617(6)	3223(4)	98(4)	46(2)	49(2)	8(2)	24(3)	−5(2)
C(4)	634(5)	2288(7)	2560(4)	54(2)	51(3)	92(4)	10(2)	28(3)	−10(3)
C(5)	717(5)	2792(7)	1466(4)	55(3)	57(3)	88(4)	22(2)	−18(3)	−10(3)
C(6)	1730(5)	3622(6)	1044(4)	85(3)	40(2)	48(2)	21(2)	−5(2)	4(2)
C(7)	3711(4)	465(6)	1227(4)	52(2)	42(2)	66(3)	7(2)	15(2)	4(2)
C(8)	2471(4)	−918(6)	2805(3)	65(3)	44(2)	43(2)	8(2)	3(2)	−3(2)
C(9)	1597(4)	−696(6)	872(3)	53(2)	45(2)	43(2)	1(2)	3(2)	−6(2)
C(11)	3854(7)	4873(8)	1306(8)	103(5)	52(3)	134(6)	−16(3)	51(5)	0(4)
O(7)	4043(3)	153(5)	848(4)	60(2)	87(3)	121(3)	14(2)	43(2)	10(2)
O(8)	2605(4)	−2126(5)	3411(3)	141(4)	57(2)	68(2)	18(2)	2(2)	22(2)
O(9)	1208(4)	−1744(5)	268(3)	95(2)	74(2)	62(2)	−13(2)	−3(2)	−23(2)
H(2)	322(4)	363(6)	310(4)	52					
H(3)	141(4)	220(7)	387(4)	64					
H(4)	−4(4)	173(6)	302(3)	65					
H(5)	8(4)	262(7)	115(4)	67					
H(6)	186(4)	384(6)	29(4)	57					
H(111)	398(6)	604(8)	144(5)	97					
H(112)	405(6)	447(10)	71(5)	97					
H(113)	468(6)	425(8)	145(5)	97					

Experimental

The preparation and some physical properties of π-(tricarbonylchromium)-toluene have been previously described [3,5]. Crystals of the title compound were grown from nonane at room temperature. The crystal selected for X-ray analysis measured approximately 0.4 mm along the *a*, *b* and *c* directions.

Preliminary Weissenberg photographs, taken with Cu-K_α radiation, showed orthorhombic diffraction symmetry and the systematic extinctions of $P2_12_12_1$. The unit-cell dimensions, deduced from measurements on a Nonius automatic single-crystal diffractometer CAD-3, are a = 11.109(4), b = 7.231(3) and c = 12.206(4) Å (Mo-$K_{\alpha 1}$ = 0.70926 Å). The unit-cell contains four molecules.

The crystal was mounted about the *b*-axis. The intensities were measured, up to $\theta = 27°$, using Mo-K_α radiation and a graphite monochromator. High intensities were reduced by nickel filters. From the 1259 measured reflexions 1168 were significantly ($>2.85\sigma(I)$) different from the background intensity. In the reduction of intensities to structure factors no correction for absorption was made (μ(Mo-K_α) = 11.81 cm^{-1}).

Structure determination and refinement

All computations were made on an IBM 370/158 computer, using the computer programs from XRAY 72 [6]. The atomic scattering factors used were taken from The International Tables for X-ray Crystallography [7] for chromium(0) and from XRAY 72 for the other atoms. Anomalous scattering factors of chromium(0) [8] were used in the final stages of the refinement.

The structure has been determined using the heavy atom method. All hydrogen atoms were located in a difference map. Five strong low-order reflexions, which were subject to extinction, were rejected. Full matrix refinement of positional parameters of all atoms, anisotropic thermal parameters for the non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms led to a final R index ($\Sigma||F_0| - |F_c||/\Sigma|F_0| \times 100$) of 4.1 for 1163 independent non-zero reflexions. However, refinement of the positional parameters of the hydrogen atoms resulted in C—H distances ranging from 0.57 to 1.21 Å. The refinement was repeated using weights equal to $1/\sigma^2(F_0)$. The positional parameters of the hydrogen atoms changed drastically, resulting in more realistic C—H distances: from 0.73 to 1.03 Å. The positional parameters of Cr changed less than 0.001 Å and those of C and O less than 0.03 Å. The standard deviations of the bond lengths decreased by about 45%. Therefore, we believe this refinement to be more reliable than the refinement using unit-weights. The ratios of shifts to estimated standard deviations in the last least-squares cycle (weighted R = 4.1%), including all parameters refined, were less than 0.63. A final difference Fourier synthesis showed a residual density between —0.44 and +0.23 eÅ^{-3}. Final positional and thermal parameters of the atoms in the absolute configuration * and their estimated standard deviations are listed in Table 1 **.

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* An analogous refinement using positional parameters $-x$, $-y$, $-z$ yields an R index of 4.5%.

** A table of structure factors may be obtained from the authors.

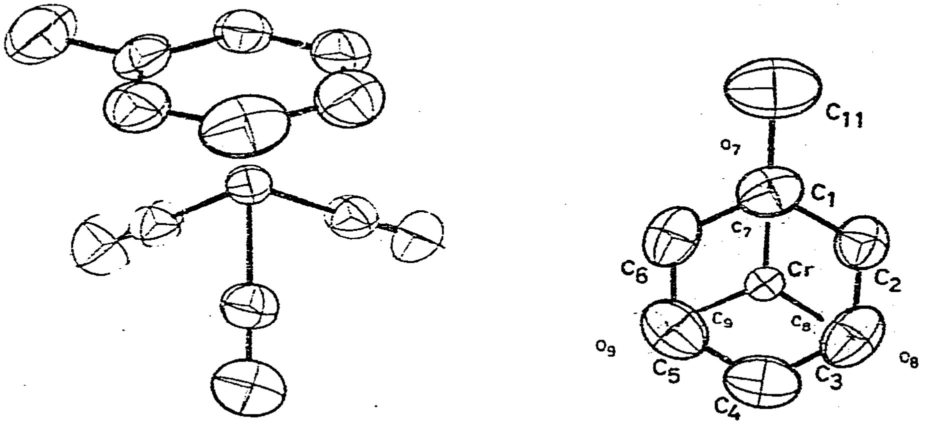

Fig. 1. ORTEP drawings of π-(tricarbonylchromium)toluene in the absolute configuration. Ellipsoids are 50% probability surfaces.

Structure description and discussion

General

The geometry of the molecule, $C_6H_5CH_3Cr(CO)_3$, is depicted in Fig. 1, which also illustrates the anisotropy of the thermal motions of the toluene ligand. Ignoring the anomalous thermal behaviour of C(2) *, it looks like the aromatic ligand librates around the threefold axis of the $Cr(CO)_3$ moiety. No correction for the suggested libration was applied, because the data obtained are considered to be sufficiently accurate for our purpose.

The bond lengths, valence angles and some interatomic distances in π-(tricarbonylchromium)toluene are given in Fig. 2 and Table 2.

The aromatic ring is planar within experimental error. The distances of the atoms from the least-squares plane through the ring carbon atoms are given in Fig. 3. The angle between the plane through the oxygen atoms and the ring plane is 0.9°. The local symmetry of the $Cr(CO)_3$ group is nearly C_{3v} **.

Conformational preference of the tricarbonylchromium group

The $Cr(CO)_3$ group adopts a nearly eclipsed conformation (I) with respect to the carbon atoms C(1), C(3) and C(5). The average deviation from perfect eclipsing is 2.2°. It is promising that the conformation found in the crystal is in agreement with both valence-bond considerations [4,9] and results obtained from NMR [1—3] for solutions.

In order to investigate whether a conformational equilibrium between conformations I and II or merely a vibration around an intermediate conformation (depending on the size of R) is involved in solution, we have started the X-ray analysis of some other compounds in this class (R = i-Pr and R = t-Bu).

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* We were unable to explain the very short C(2)—H(2) bond length (0.73 Å), which might affect the thermal behaviour of C(2).

** Cf. also ref. 5.

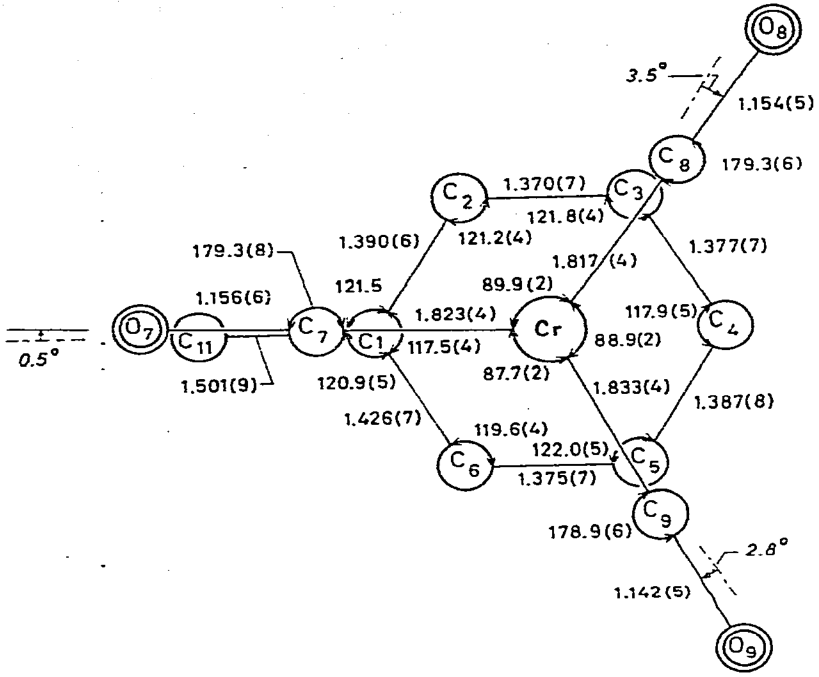

Fig. 2. Bond lengths and angles in π-(tricarbonylchromium)toluene.

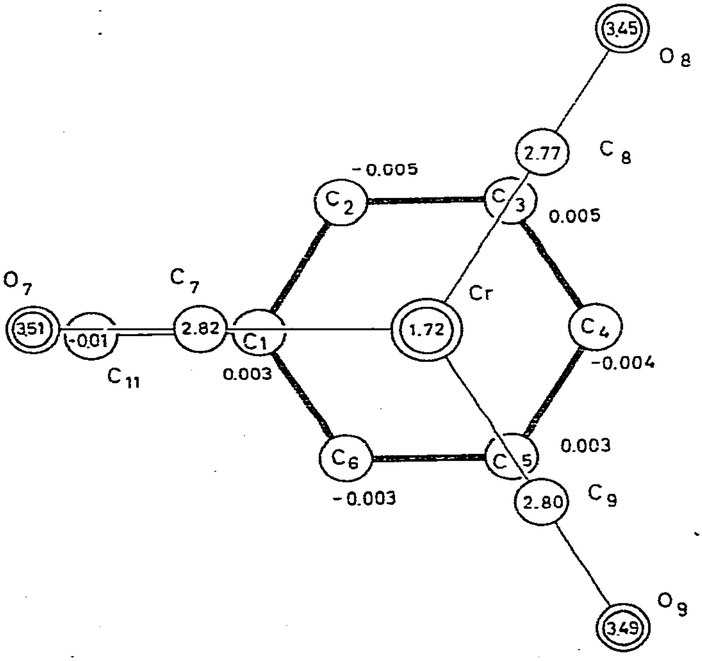

Fig. 3. Distances of the atoms from the least-squares plane through the ring carbons in π-(tricarbonylchromium)toluene.

TABLE 2

SOME INTERATOMIC DISTANCES IN π-(TRICARBONYLCHROMIUM)TOLUENE
(esd's in parentheses)

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
Cr—C(1)	2.236(4)	Cr—C(4)	2.217(5)	Cr—O(7)	2.979(4)
Cr—C(2)	2.209(4)	Cr—C(5)	2.203(5)	Cr—O(8)	2.971(4)
Cr—C(3)	2.186(5)	Cr—C(6)	2.229(4)	Cr—O(9)	2.975(4)

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