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THE MOLECULAR STRUCTURE OF (1′-t-BUTYL-2′,2′-DIMETHYLPROPYL)-π-(TRICARBONYLCHROMIUM)-BENZENE

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Summary

The molecular structure of (1′-t-butyl-2′,2′-dimetnylpropyl)-π-(tricarbonylchromium)benzene, $CrC_{18}H_{24}O_3$, has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$. The unit-cell, of dimensions a 8.321(3), b 14.741(5), c 14.369(5) Å and β 98.85(3)°, contains four molecules. The structure has been solved using the heavy-atom method. Least-squares refinement converged to a final R index of 3.2% for 2738 independent non-zero reflexions.

The molecular strain is relieved by a deviation of the CH-t-Bu_2 group and the $Cr(CO)_3$ group from their usual position. The α-carbon atom is forced out of the arene ring plane by 0.41 Å. The dihedral angle between the aromatic plane and the plane through the oxygen atoms is 8.0°. The octahedral symmetry around the chromium atom is almost maintained. The average twist of the $Cr(CO)_3$ group from the electronically favoured conformation (i.c. eclipsed with respect to the alkyl group) is 44.4°.

Introduction

The X-ray analysis of 4-t-butyl-π-(tricarbonylchromium)benzoic acid [1] (Fig. 1, R_1 = t-Bu, R_2 = COOH) shows that steric effects play an important role on the conformational preference of the $Cr(CO)_3$ group with respect to the arene ring. In this compound steric effects in favour of conformer I are opposed by electronic effects favouring conformer II. Another example of a compound, in which these competing effects are operative, is (1′-t-butyl-2′,2′-dimethylpropyl) π-(tricarbonylchromium)benzene (Fig. 1, R_1 = CH-t-Bu_2, R_2 = H). The IR spectrum of this compound [2] points to the existence of a small perturbation of the geometry around the chromium atom. In a recent ^{1}H NMR paper on the conformational preference in alkyl-substituted π-(tricarbonylchromium)benzenes

Fig. 1. The conformers I and II.

[3] the conformation around the sp^3—sp^2 carbon—carbon bond was discussed. In that paper the title compound was used as a model substance for conformer I.

Since a proper interpretation of the spectral data requires a detailed knowledge of the molecular structure of (1′-t-butyl-2′,2′-dimethylpropyl)-π-(tricarbonylchromium)benzene, we have performed the necessary X-ray investigation.

Experimental

The preparation and some physical properties of (1′-t-butyl-2′,2′-dimethylpropyl)-π-(tricarbonylchromium)benzene have been described previously [2,3]. Yellow crystals were grown from nonane at room temperature. The crystal selected for X-ray analysis measured approximately $0.40 \times 0.20 \times 0.35$ mm along the *a*, *b* and *c* directions, respectively.

Preliminary Weissenberg photographs, taken with Cu-K_α radiation, showed monoclinic diffraction symmetry and the systematic extinctions of $P2_1/c$. The unit-cell dimensions, deduced from measurements on a Nonius automatic single-crystal diffractometer CAD-3, are *a* 8.321(3), *b* 14.741(5), *c* 14.369(5) Å and β 98.85(3)° (Mo-$K_{\alpha 1}$ 0.70926 Å). The unit-cell contains four molecules.

The crystal was mounted about the *a*-axis. The intensities were measured using Mo-K_α radiation and a graphite monochromator. High intensities were reduced by nickel filters. From the 3667 measured reflexions 2741 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) 6.9 cm^{-1}].

Structure determination and refinement

All computations were made on an IBM 370/158 computer, using the computer programs from XRAY72 [4]. The atomic scattering factors used were taken from The International Tables for X-ray Crystallography [5] for chromium-(0) and from XRAY72 for all other atoms.

The structure has been solved using the heavy-atom method. All hydrogen atoms could be located in a difference map. Three very strong low order reflexions, which were subject to extinction, were rejected. Blocked refinement * of posi-

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* Block 1, 2×2 containing the overall temperature and scaling factor; block 2, 132×132 containing the thermal and positional parameters of the atoms of the $Cr(CO)_3C_6H_5$ fragment; block 3, 138×138 containing the thermal and positional parameters of the atoms of the alkyl group.

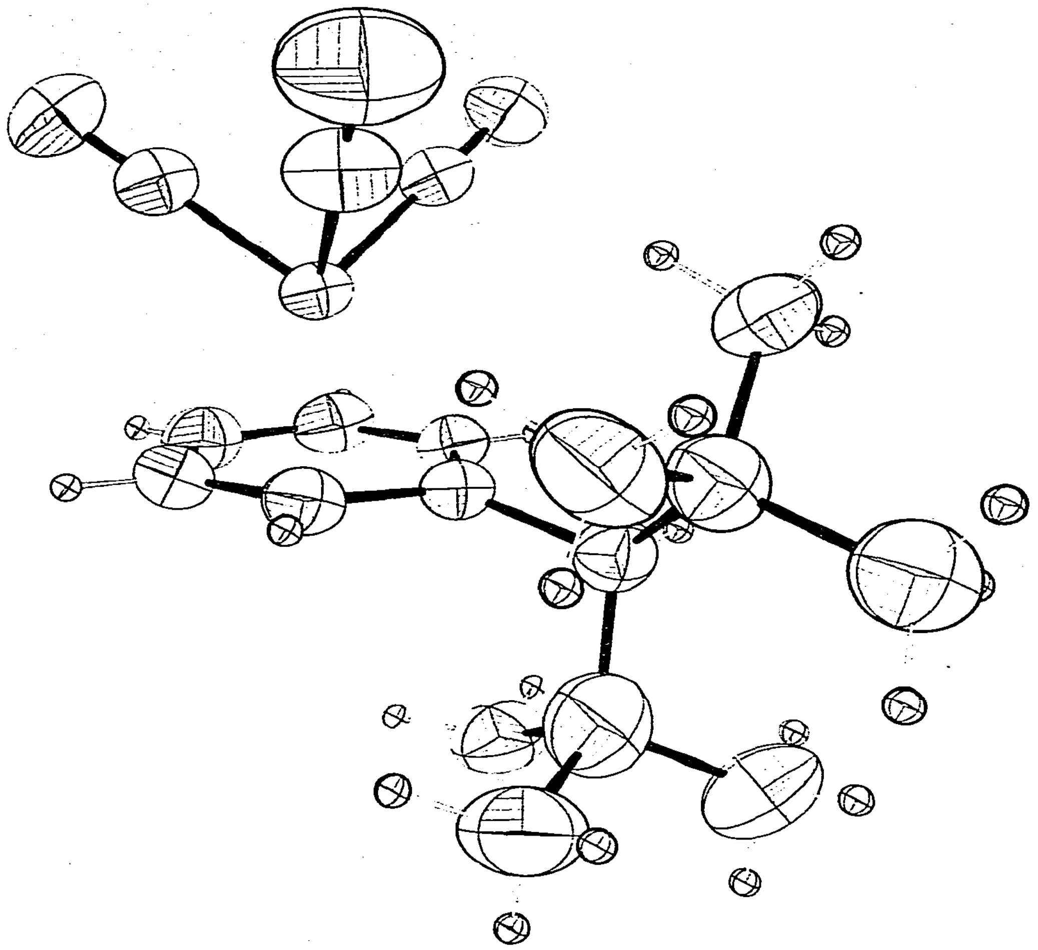

Fig. 2. Thermal ellipsoids scaled to enclose 50% probability for the non-hydrogen atoms (prepared with program ORTEP [10]).

tional 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 3.2 for 2738 independent non-zero reflexions *. A final difference Fourier synthesis showed a residual density between −0.26 and +0.20 eÅ^{-3}. The positional and thermal parameters of the atoms and their estimated standard deviations are listed in Table 1. The anisotropic temperature movement for the non-hydrogen atoms is illustrated in Fig. 2.

Structure description and discussion

General

Bond lengths, valence angles and some interatomic distances in (1′-t-butyl-

(continued on p. 300)

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* The Table of F_0 and final F_c values is available from the authors.

TABLE 1

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS

The fractional atomic coordinates have been multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the hydrogen atoms. The isotropic factors U are in $Å^2 \times 10^3$. The U_{ij} coefficients ($Å^2 \times 10^3$) 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	225.0(0.5)	1642.2(0.3)	922.2(0.3)	38.2(0.2)	49.6(0.2)	39.7(0.2)	−2.1(0.2)	2.2(0.2)	−0.6(0.2)
C(1)	2686(3)	2228(1)	1679(1)	39(1)	42(1)	37(1)	−1(1)	2(1)	−2(1)
C(2)	1450(3)	2269(2)	2259(2)	46(1)	51(1)	39(1)	−1(1)	6(1)	−3(1)
C(3)	618(3)	1490(2)	2474(2)	53(1)	75(2)	40(1)	−9(1)	7(1)	6(1)
C(4)	922(4)	655(2)	2070(2)	59(2)	59(2)	52(2)	−14(1)	0(1)	11(1)
C(5)	2043(3)	604(2)	1451(2)	55(2)	40(1)	62(2)	1(1)	−5(1)	−3(1)
C(6)	2887(3)	1389(2)	1251(2)	41(1)	49(1)	45(1)	2(1)	3(1)	−5(1)
C(7)	384(3)	1409(2)	−309(2)	42(1)	60(2)	50(1)	−8(1)	0(1)	2(1)
C(8)	−871(4)	2675(2)	508(2)	68(2)	71(2)	65(2)	11(2)	−8(2)	−5(2)
C(9)	−1770(3)	1093(2)	760(2)	49(2)	94(2)	54(2)	−7(2)	5(1)	3(2)
C(11)	3954(3)	2966(2)	1638(2)	50(1)	47(1)	48(1)	−7(1)	18(1)	−11(1)
C(12)	3305(4)	3888(2)	1171(2)	78(2)	45(1)	59(2)	−10(1)	22(1)	−2(1)
C(13)	5155(3)	2952(2)	2617(2)	46(1)	68(2)	61(2)	−11(1)	3(1)	−18(1)
C(121)	2728(5)	3695(2)	125(2)	108(3)	66(2)	58(2)	−7(2)	23(2)	9(2)
C(122)	1890(5)	4311(2)	1588(3)	92(2)	51(2)	75(2)	10(2)	16(2)	−1(2)
C(123)	4648(6)	4606(2)	1215(3)	109(3)	57(2)	101(3)	−25(2)	35(3)	−2(2)
C(131)	4568(5)	3518(3)	3388(2)	72(2)	110(3)	63(2)	−4(2)	−2(2)	−36(2)
C(132)	5409(4)	1975(3)	2971(2)	60(2)	85(2)	72(2)	−2(2)	−14(2)	0(2)
C(133)	6863(4)	3273(3)	2492(3)	55(2)	94(3)	113(3)	−19(2)	−9(2)	−26(3)
O(7)	493(2)	1265(1)	−1085(1)	73(1)	96(2)	44(1)	−14(1)	10(1)	−3(1)

O(8)	—1623(3)	3296(2)	205(2)	108(2)	93(2)	108(2)	41(2)	—23(2)	7(2)
O(9)	—3025(3)	751(2)	660(2)	50(1)	152(2)	99(2)	—32(1)	2(1)	11(2)
H(2)	117(3)	283(2)	251(2)	48					
H(3)	—19(3)	157(2)	288(2)	56					
H(4)	44(3)	12(2)	219(2)	57					
H(5)	221(3)	7(2)	116(2)	53					
H(6)	364(3)	136(2)	85(2)	46					
H(11)	461(3)	272(2)	121(2)	47					
H(211)	364(4)	348(2)	—16(2)	77					
H(212)	186(4)	321(2)	—1(2)	77					
H(213)	226(4)	425(2)	—19(2)	77					
H(221)	167(4)	487(2)	129(2)	73					
H(222)	83(4)	396(2)	149(2)	73					
H(223)	219(4)	447(2)	222(2)	73					
H(231)	498(4)	487(2)	190(2)	84					
H(232)	558(4)	439(2)	99(2)	84					
H(233)	413(4)	511(2)	85(2)	84					
H(311)	343(4)	331(2)	353(2)	80					
H(312)	442(4)	418(2)	324(2)	80					
H(313)	532(4)	341(2)	392(2)	80					
H(321)	444(4)	174(2)	318(2)	72					
H(322)	626(4)	198(2)	355(2)	72					
H(323)	573(4)	159(2)	252(2)	72					
H(331)	760(4)	318(2)	306(2)	89					
H(332)	685(4)	392(2)	232(2)	89					
H(333)	725(4)	293(2)	201(2)	89					

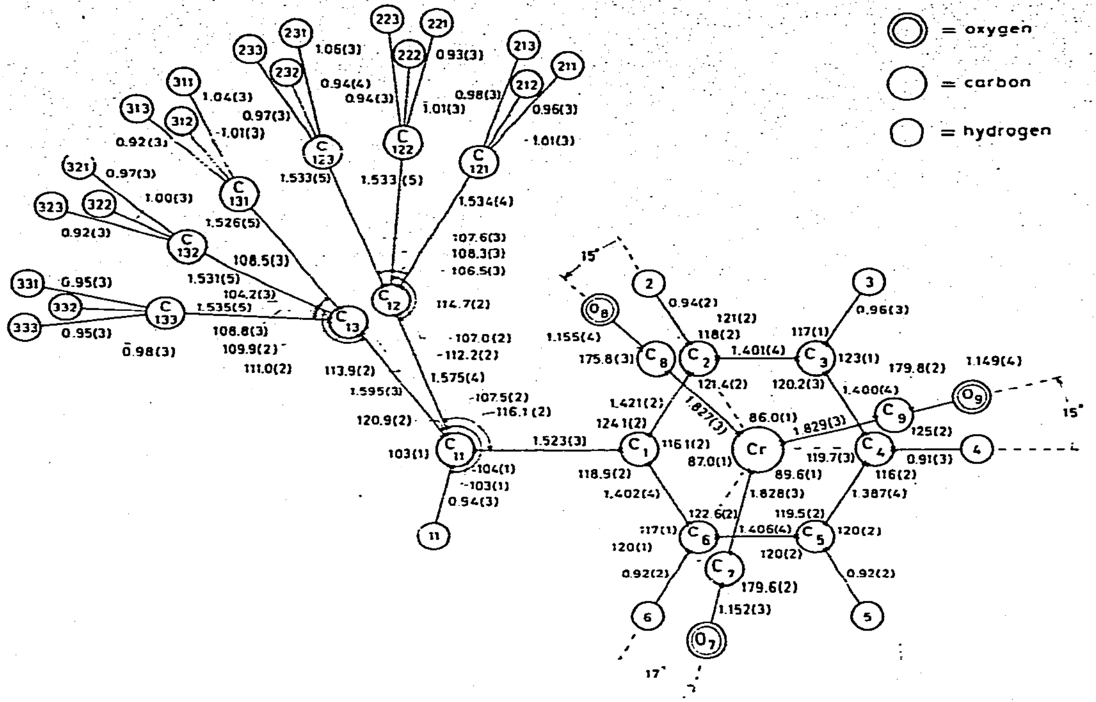

Fig. 3. Bond lengths and angles in (1'-t-butyl-2',2'-dimethylpropyl)-π-(tricarbonylchromium)benzene.

2',2'-dimethylpropyl)-π-(tricarbonylchromium)benzene are given in Fig. 3 and Table 2. The aromatic C—C bond lengths averages 1.403 Å. Some of the bond lengths (C(1)—C(11), C(11)—C(12) and C(11)—C(13)) and the valence angles of the atoms concerned are unusually large. In 1-(4-methoxyphenyl)-2,2,6,6-tetramethylcyclohexanol ($C_{17}H_{26}O_2$) [6], which resembles closely the free aromatic ligand, the same anomalies are found. However, in $C_{17}H_{26}O_2$, the aromatic ring is planar within experimental error. Therefore, the observed displacement of C(1) from the aromatic plane is probably due to unfavourable interaction of the $Cr(CO)_3$ group with the aromatic ligand *. The deviations of the atoms

TABLE 2

SOME INTERATOMIC DISTANCES IN (1'-t-BUTYL-2',2'-DIMETHYLPROPYL)-π-(TRICARBONYLCHROMIUM)BENZENE (e.s.d.'s in parentheses)

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
Cr—C(1)	2.332(2)	Cr—C(4)	2.210(3)	Cr—O(7)	2.979(2)
Cr—C(2)	2.231(2)	Cr—C(5)	2.203(3)	Cr—O(8)	2.981(3)
Cr—C(3)	2.215(3)	Cr—C(6)	2.224(3)	Cr—O(9)	2.978(2)

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* Another model compound to study the geometry of the free ligand is 1-t-butyl-2,2-dimethyl-1-(4-methoxyphenyl)propanol, the X-ray analysis of which will be started in future.

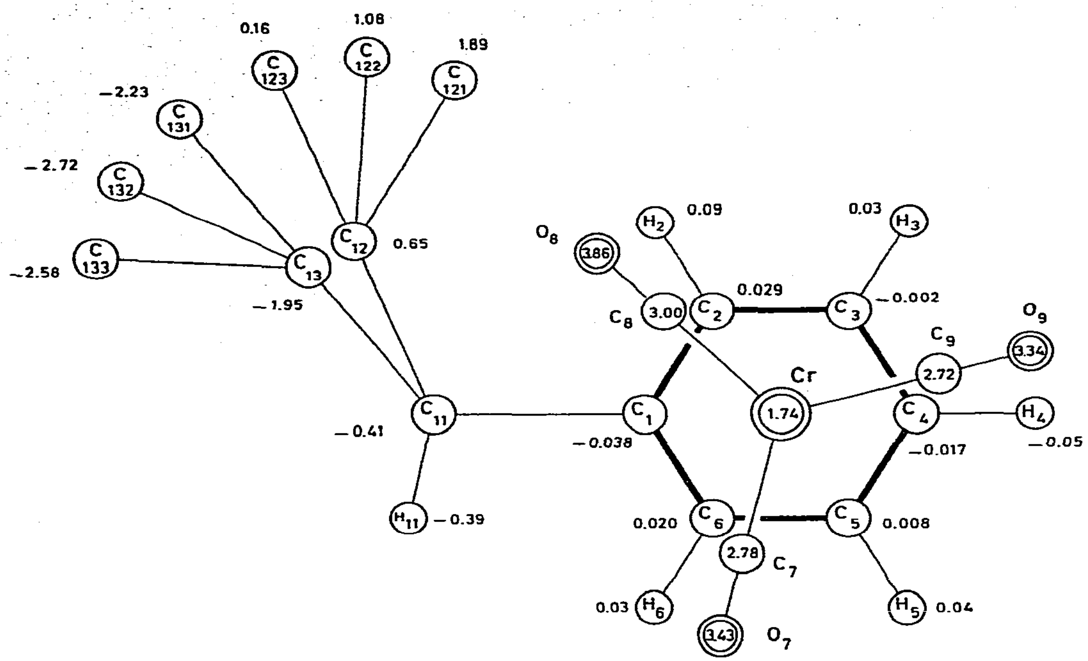


Fig. 4. Distance of the atoms from the least-squares plane through the aromatic ring carbon atoms (in Å).

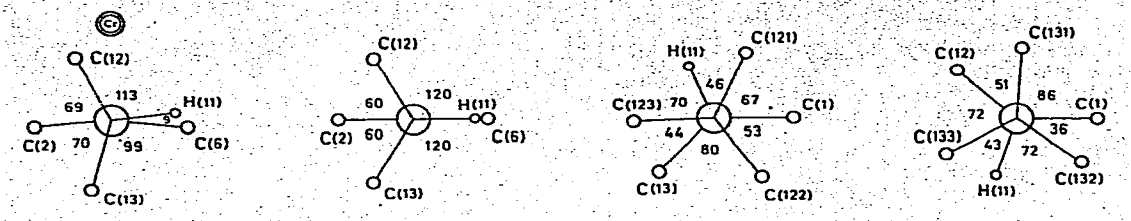
from the least-squares plane through the ring carbon atoms are given in Fig. 4. The aromatic ligand is folded slightly around the C(1)—C(4) direction. This is in accordance with earlier observations in π-Cr(CO)$_3$ complexes of fused ring systems [7]. The chromium—ring distance is 1.74 Å; this value is in close agreement with the value reported previously for the corresponding distance in related compounds [1,7,8].

Geometry around the chromium atom

The chromium atom lies almost central with respect to the ring carbon atoms (except to C(1)). The valence angles around Cr approximate an octahedral symmetry. The Cr—C(CO) as well as the C—O bond lengths are equal within experimental error. The deviation from linearity of Cr—C(8)—O(8), which is mainly localised in the direction perpendicular to and away from the arene ring, is apparent. The angle between the plane through the aromatic carbon atoms and the plane through the oxygen atoms is 8.0°. This geometry can explain the perturbation of C_{3v} symmetry deduced from the IR spectrum of the title compound [2].

Conformation around the C(11)—C(1) bond and geometry of the t-Bu groups

The α-carbon atom is forced out of the ring plane by 0.41 Å away from the Cr(CO)$_3$ group. The angle between the ring plane and the C(11)—C(1) bond is 15.4°. A Newman projection along this bond is given in Fig. 5a. The suggested conformation [9] around the C(11)—C(1) bond in the free ligand is depicted in Fig. 5b, and is close to the conformation found in the complex. Therefore,



a: along C(11)–C(1) b: along C(11)–C(1) c: along C(12)–C(11) d: along C(13)–C(11)

Fig. 5. Newman projections along (a) C(11)—C(1), (b) C(11)—C(1) in the free ligand [9], (c) C(12)—C(11) and (d) C(13)—C(11).

we take the present data as evidence for the correctness of the suggested conformation in the free ligand. The conformations around the C(12)—C(11) and the C(13)—C(11) bonds are shown in Figs. 5c and 5d, respectively. The average twist from perfect staggering amounts to 12° for the C(12) t-Bu group and to 17° for the C(13) t-Bu group. All methyl protons are oriented approximately staggered (see Fig. 2).

Conformational preference of the tricarbonylchromium group

The $Cr(CO)_3$ group is twisted away from the electronically favoured conformer II by 44.4°. The CO(8) ligand is embedded in a cavity formed by two of the methyl groups. The C(8)—C(121) and C(8)—C(122) distances are 3.47 and 3.54 Å, respectively; the Cr—C(8)—O(8) angle is 175.8°. It seems noteworthy, that similar interactions are present in 4-t-butyl-π-(tricarbonylchromium)-benzoic acid * [1]. Possibly these interactions determine to a large extent the conformation of the tricarbonylchromium group in the crystalline state. It may be noted, that the orientation of the $Cr(CO)_3$ group departs from the orientation assumed in our ^1H NMR study [3] by 15.6°. Therefore, if the orientation of the $Cr(CO)_3$ group observed in the solid state is retained in solution, the actual conformational preference in the alkyl-substituted π-(tricarbonylchromium)benzenes might be somewhat less pronounced than indicated by the values obtained in that study.

Acknowledgements

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* In this structure the corresponding distances C(8)—C(11) and C(8)—C(13) are 3.51 and 3.55 Å, respectively; the Cr—C(8)—O(8) angle is 177.4°.

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