Journal of Organometallic Chemistry, 78 (1974) 229—235

THE MOLECULAR STRUCTURE OF 4-tert-BUTYL-π-(TRICARBONYLCHROMIUM)BENZOIC ACID

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(Received April 29th, 1974)

Summary

The molecular structure of 4-tert-butyl-π-(tricarbonylchromium)benzoic acid, $CrC_{14}O_5H_{14}$, has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$. The unit-cell, of dimensions a = 12.230(5), b = 7.509(3), c = 18.099(6) Å and β = 117.91(4)°, contains four molecules. The structure has been solved using the heavy-atom method. Refinement by the least-squares method converged to a final R index of 4.8% for 1717 independent non-zero reflexions. 4-tert-Butyl-π-(tricarbonylchromium)benzoic acid adopts a conformation which departs from perfect staggering by about seven degrees.

Introduction

Several structure determinations [1—6] of π-(tricarbonylchromium)arenes indicate that the orientation of the $Cr(CO)_3$ group is mainly controlled by inductive and mesomeric electron repulsion or withdrawal by the substituents in the arene ring. To obtain maximum $\pi \rightarrow d^2sp^3$ donation, the empty hybrid orbitals of the chromium atom point towards regions of high electron density of the arene ring. CNDO calculations [4—6] on some free arenes support the application of the above approximation.

In addition to these electronic effects, steric influences may also play an important role*. As an example of a system in which steric factors can predominate over electronic effects, we have carried out an X-ray analysis of 4-tert-butyl-π-(tricarbonylchromium)benzoic acid. In this compound the tert-butyl and the carboxyl group together give rise to a charge distribution in the arene ring

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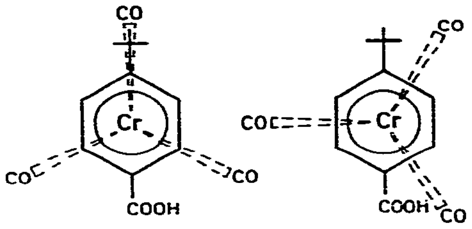
* This is confirmed by the temperature dependence of the ^1H NMR spectra of some alkyl-π-(tricarbonylchromium)benzenes [7] (cf. also refs. 8—10).

which would favour an eclipsed conformation (I). However, in this conformation serious steric interaction between the tert-butyl and a carbonyl group is involved. The actual molecular structure is described below.



(I) (II)

Experimental

4-tert-Butyl-π-(tricarbonylchromium)benzoic acid was prepared as described by Ashraf and Jackson [11]. Orange-coloured monoclinic crystals of the compound were obtained by recrystallization from carbon tetrachloride at 4°. The space group, $P2_1/c$, was determined from systematic extinctions on Weissenberg photographs (Mo-K_α, Cu-K_α). The unit-cell dimensions, deduced from measurements on a Nonius automatic single-crystal diffractometer CAD-3, are $a = 12.350(5)$, $b = 7.509(3)$, $c = 18.099(6)$ Å and $\beta = 117.91(4)°$ (Mo-K_{α_1} = 0.70926 Å). The unit-cell contains four molecules.

Three-dimensional intensity data were collected with the automatic diffractometer using Mo-K_α radiation with a zirconium filter. High intensities were reduced by nickel filters. From the 3234 measured reflexions 1721 were significantly different from the background intensity. The crystal was directed along the c-axis and had approximate dimensions of 0.2 × 0.1 × 0.5 mm, in the a, b and c direction, respectively. In the reduction of intensities to structure factors no correction was made for absorption [μ(Mo-K_α) = 8.3 cm^{-1}].

Structure determination and refinement

All computations were made using the computer programs from XRAY70 [12] on an IBM 360/65. The atomic scattering factors used were those of C, O, H and Cr, as given in the International Tables for X-ray Crystallography (1969) [13].

The coordinates of the chromium atom were deduced from a three-dimensional Patterson function. A Fourier synthesis, based on the refined coordinates of the chromium atom, revealed the position of all non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic temperature factors of the form exp $-2\pi^2 (U_{11}h^2a^{*2} + \ldots$ etc.) were made, resulting in a discrepancy index R ($= \Sigma||F_o|-|F_c||/\Sigma|F_o| \times 100$) of 6.4. At this stage a difference Fourier synthesis was calculated, in which the hydrogen atoms [except H(133)] were located.

After repetition of the sequence of refinements, including isotropic refinement on the located hydrogen atoms, a difference Fourier synthesis revealed the

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 $\text{Å}^2 \times 10^3$. The U_{ij} coefficients ($\text{Å}^2 \times 10^3$) are given by the expression: $\exp[-2\pi(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})]$

	x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	2587(1)	2672(1)	1351(1)	47(0)	38(1)	40(0)	0(0)	21(0)	0(0)
C(1)	3786(5)	4788(7)	1337(3)	55(3)	47(3)	46(3)	−4(3)	27(3)	2(3)
C(2)	2642(5)	5527(7)	1142(3)	65(4)	37(3)	49(3)	3(3)	28(3)	6(3)
C(3)	2114(5)	5309(7)	1686(3)	55(3)	44(3)	58(4)	5(3)	34(3)	2(3)
C(4)	2723(5)	4321(7)	2430(3)	59(3)	39(3)	43(3)	0(2)	26(3)	0(3)
C(5)	3889(5)	3607(7)	2621(3)	50(3)	53(3)	39(3)	2(3)	20(3)	4(3)
C(6)	4427(5)	3823(7)	2094(3)	48(3)	54(3)	48(3)	−3(3)	24(3)	−3(3)
C(7)	1165(6)	2518(10)	370(4)	70(4)	66(4)	77(4)	11(4)	7(4)	−7(4)
C(8)	2045(6)	763(8)	1727(4)	104(5)	51(4)	83(5)	−19(4)	62(4)	−15(4)
C(9)	3265(6)	1008(8)	949(3)	76(4)	57(4)	45(3)	8(3)	26(3)	1(3)
C(10)	2148(5)	4206(7)	3025(3)	75(4)	50(3)	56(3)	1(3)	46(3)	−1(3)
C(11)	2738(8)	2712(12)	3658(5)	130(7)	84(5)	86(5)	23(6)	83(5)	28(5)
C(12)	2449(9)	5971(11)	3492(5)	134(8)	71(5)	79(6)	−6(5)	73(6)	−15(4)
C(13)	765(8)	3934(12)	2356(5)	85(6)	99(6)	91(6)	−1(5)	66(5)	−2(5)
C(14)	4322(6)	4880(7)	749(3)	67(4)	45(3)	53(3)	−9(3)	35(3)	2(3)
O(1)	3674(4)	5786(6)	78(3)	101(4)	70(3)	69(3)	13(3)	59(3)	19(3)
O(2)	5299(4)	4147(6)	918(2)	67(3)	98(4)	68(3)	7(3)	45(3)	16(3)
O(7)	263(5)	2433(10)	−250(3)	100(4)	139(5)	107(4)	14(5)	−34(4)	−25(5)
O(8)	1715(6)	−463(7)	1941(4)	194(6)	65(4)	143(5)	−45(4)	120(5)	−15(4)
O(9)	3712(4)	−28(7)	703(3)	126(5)	93(4)	80(3)	38(3)	49(3)	−17(3)
H(1)	404(7)	580(12)	−15(5)	86					
H(2)	213(5)	609(8)	63(4)	50					
H(3)	125(5)	571(8)	147(4)	52					
H(5)	431(5)	289(8)	308(3)	47					
H(6)	521(5)	320(8)	224(3)	50					
H(111)	231(7)	265(12)	390(5)	101					
H(112)	263(7)	152(12)	338(5)	101					
H(113)	382(7)	303(11)	406(5)	101					
H(121)	339(7)	624(11)	382(5)	95					
H(122)	217(8)	600(12)	381(5)	95					
H(123)	215(7)	705(11)	315(5)	95					
H(131)	43(8)	399(11)	290(5)	92					
H(132)	54(8)	303(12)	224(5)	92					
H(133)	34(8)	487(12)	218(5)	92					

position of H(133). Four very strong low order reflexions, which were subject to extinction, were rejected. Further blocked anisotropic refinements* with assigned isotropic temperature factors to the hydrogen atoms led to a final R-index of 4.76 for all 1717 non-zero reflexions**.

The ratios of shifts to the estimated standard deviations in the last least-squares cycle, including all parameters refined, were less than 0.53. A final difference Fourier synthesis showed a residual density between −0.33 and +0.40 $e\,\text{Å}^{-3}$. Final positional and thermal parameters and corresponding estimated standard deviations are listed in Table 1. The anisotropic temperature movement for the non-hydrogen atoms is illustrated in Fig. 1.

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* Block 1, 2 × 2 containing the overall temperature and scaling factor; block 2, 63 × 63 containing thermal and positional parameters of Cr, C(7), O(7), C(8), O(8), C(9) and O(9); block 3, 159 × 159 containing the thermal and positional parameters of the remaining atoms; the assigned temperature factors of the hydrogen atoms were kept invariant during these cycles.

** The table of F_{obs} and final F_{calc} values is available on request.

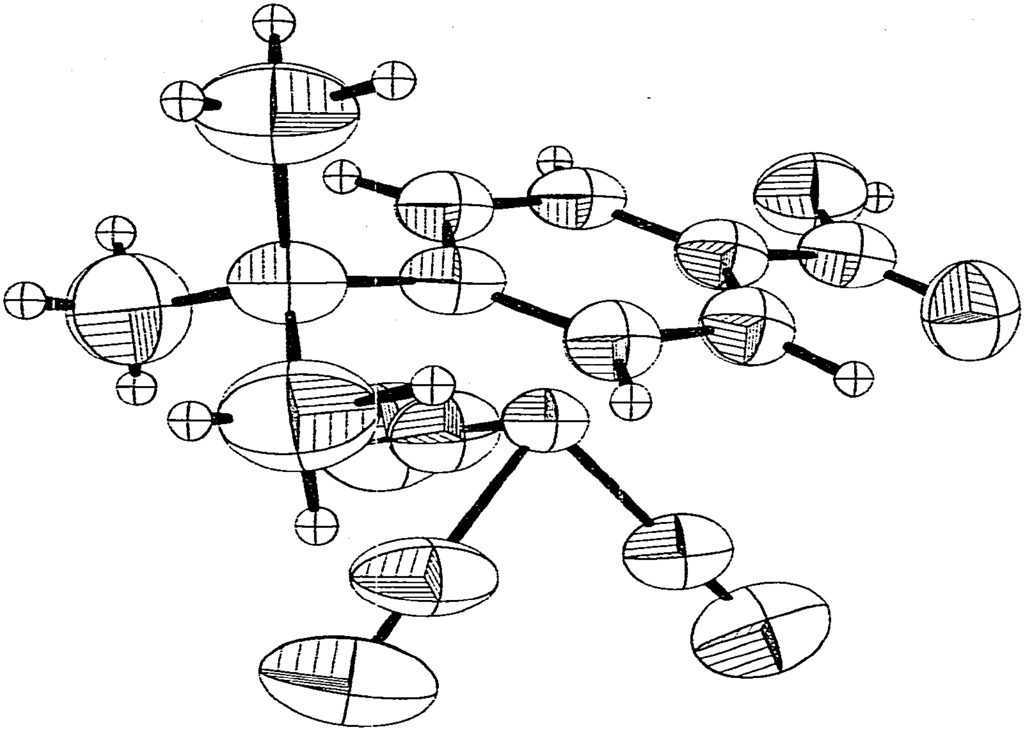

Fig. 1. Thermal ellipsoids scaled to enclose 50% probability for non-hydrogen atoms (prepared with program ORTEP) [14].

Results

Bond lengths, valence angles and some interatomic distances are given in Fig. 2 and Table 2 respectively.

The carboxyl group is planar within experimental error. The least-squares planes through the carboxyl group and the benzene ring are inclined at about four degrees, whilst torsion around the C(1)—C(14) bond is negligible.

The torsional angles around the C(4)—C(10) bond are shown in a Newman projection (Fig. 3). The C(4)—C(10) bond is rather long for an sp^2—sp^3 bond.

TABLE 2

SOME INTERATOMIC DISTANCES IN 4-tert-BUTYL-π-(TRICARBONYLCHROMIUM)BENZOIC ACID (E.S.D.'s IN PARENTHESES)

Atoms	Distance (Å)
Cr—C(1)	2.170(6)
Cr—C(2)	2.184(5)
Cr—C(3)	2.225(6)
Cr—C(4)	2.251(6)
Cr—C(5)	2.210(5)
Cr—C(6)	2.187(5)
Cr—O(7)	2.967(5)
Cr—O(8)	2.980(7)
Cr—O(9)	2.982(6)

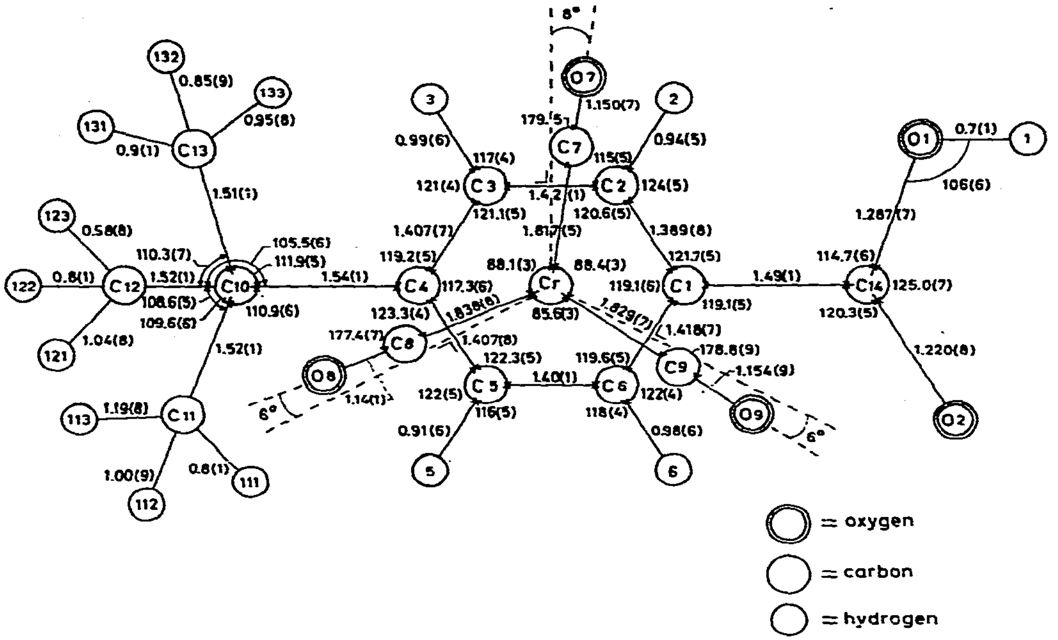

Fig. 2. Bond lengths and angles in 4-tert-butyl-π-(tricarbonylchromium)benzoic acid.

The average twist of the tert-butyl group from the position predicted from simplified calculations on tert-butylbenzene [15] is about 20 degrees.

The arene ring, which is sandwich-bonded to the $Cr(CO)_3$ group, is planar within experimental error. The distances of all atoms (except the methyl-hydrogen atoms) from the least-squares plane of the aromatic carbon atoms are given in Fig. 4. The distance of the chromium atom from this least-squares plane is 1.70 Å. This value is in close agreement with the corresponding chromium—ring distances in π-(tricarbonylchromium)benzene [16] (1.72 Å) (from neutron diffraction [18], 1.73 Å), hexamethyl-π-(tricarbonylchromium)benzene [17] (1.73 Å) and methyl π-(tricarbonylchromium)benzoate [3] (1.70 Å).

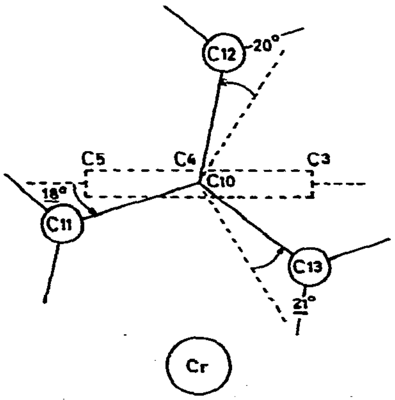

Fig. 3. Newman projection along the C(10)—C(4) bond showing the orientation of the tert-butyl group.

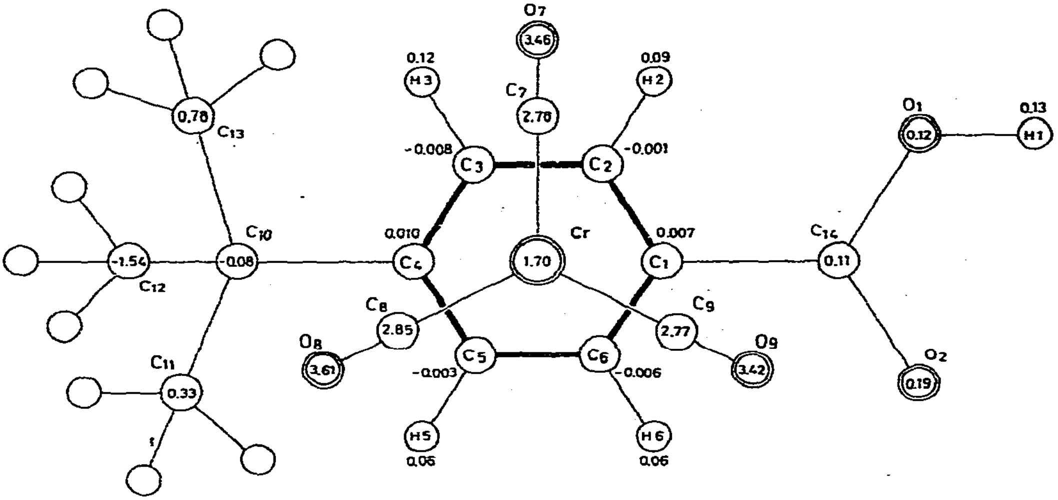

Fig. 4. Distances of the atoms (except the methyl-hydrogen atoms) from the least-squares plane through the aromatic ring (in Å).

For hexamethyl-π-(tricarbonylchromium)benzene Bailey and Dahl [13] found a small bending of the methyl-carbons out of the ring plane and away from the chromium atom (with a maximum of 0.09 Å). The same holds in 4-tert-butyl-π-(tricarbonylchromium)benzoic acid for C(10), while the aromatic protons as well as C(14) are bent towards the chromium atom. The average aromatic C—C bond length is 1.41 Å, which is a normal value for this type of compound.

As indicated in the Introduction, the eclipsed conformation I should be favoured on the basis of valence-bond considerations. Actually the system prefers a nearly staggered conformation II, with a small deviation (7 degrees) from perfect staggering. Apparently the preferred geometry of 4-tert-butyl-π-(tricarbonylchromium)benzoic acid is mainly governed by steric factors. Steric repulsion is minimized by rotation of the tert-butyl group* as well as by the $Cr(CO)_3$ group and by elongation of the C(4)—C(10) bond.

In a forthcoming paper [19] the observed conformation of 4-tert-butyl-π-(tricarbonylchromium)benzoic acid will be used to account for some anomalies in physical properties.

Acknowledgements

This investigation was supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We are indebted to Prof. H. van Bekkum for his interest and discussions.

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* In order to establish the "normal" conformation of the tert-butyl group with respect to the benzene ring, one of us (H.v.K.) has started an X-ray investigation of some model compounds.

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