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THE MOLECULAR STRUCTURE OF 2,2,4,4-TETRAMETHYL-3-(3,4,5-TRIMETHOXYPHENYL)PENTAN-3-OL

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Abstract—The molecular structure of 2,2,4,4-tetramethyl-3-(3,4,5-trimethoxyphenyl)pentan-3-ol, $C_{18}H_{30}O_4$, has been determined from 3-dimensional X-ray data. The monoclinic unit-cell, $P2_1/c$ with a = 14.420(6), b = 8.629(4) and c = 15.003(6) Å and β = 109.45(3)°, contains four molecules. Refinement converged to a final conventional R-index 4.6% for 2662 observed reflexions.

The orientation of the C(OH)–t-Bu_2 group and the OMe groups with respect to the benzene nucleus is discussed and compared with the orientations found in related compounds.

As part of an investigation on the conformational preference of the $Cr(CO)_3$ group[1] in alkylsubstituted π-(tricarbonylchromium)benzenes, the molecular structure of (1-t-butyl-2,2-dimethylpropyl)-π-(tricarbonylchromium)benzene (**1**) has been reported.[2] The aromatic ligand of **1** was compared with 1-(4-methoxyphenyl)-2,2,6,6-tetramethylcyclohexanol (**2**).[3] However, the comparison is obscured because in **2** C_1, C_2 and C_6 are members of a cyclohexane ring. We therefore searched for a genuine di-t-butylphenylcarbinol as a subject for an X-ray study. For this purpose the compound 2,2,4,4-tetramethyl-3-(3,4,5-trimethoxyphenyl)pentan-3-ol (**3**) was selected.

The three OMe groups on adjacent sites in the phenyl ring of **3** allow a comparison with the geometric assumptions of Zweig.[4] The rotation around the sp^3–sp^2 C–C bond in **3**, was studied by ^{1}H NMR.[5,6]

These studies point to a geometry, in which the angle (ϕ) between the C–O(H) bond and the ring plane is small. However, Lomas and Dubois[7] obtain from dehydration and solvolysis rates ϕ-values of 34° and 39° for **4A** and **4B**, respectively. This inconsistency† served as an additional argument to study **3** by X-ray diffraction.

EXPERIMENTAL

A sample of the compound $C_{18}H_{30}O_4$, was kindly provided by Dr. S. Sternhell from the Department of Organic Chemistry, University of Sydney, Australia.[5]

Monoclinic crystals, space group $P2_1/c$ and Z = 4, were grown from petroleum ether (b.p. 40–60°). The unit-cell dimensions, deduced from measurements on a single-crystal diffractometer ($MoK_{\alpha 1}$ = 0.70926 Å), are a = 14.420(3), b = 8.629(4), c = 15.003(6) Å and β = 109.45(3)°. Three dimensional intensity data were collected up to θ = 27° with the CAD-3-Nonius diffractometer using MoK_α radiation and a graphite monochromator. High intensities were reduced by Ni filters. No absorption correction was applied. The crystal had approximate dimensions of 0.50 × 0.45 × 0.30 mm in the a, b and c direction respectively and was mounted about the b-axis.

Structure determination. All calculations were done on an IBM 370/158 computer using the X-ray system.[9] The structure was solved by direct methods. The E-map did reveal all heavy atoms. After three cycles of blocked full-matrix refinement the H atoms were located in a difference map. The last cycle of blocked full-matrix anisotropic least-squares refinement, with fixed isotropic thermal parameters for the hydrogen atoms, converged to a final conventional R-index of 4.6% for 2662 observed (>2.85 σ (I)) reflexions. The final difference map did not show any special features. The final atomic coordinates, the temperature factors and their standard deviations (ESD's) as calculated from the refinement are given in Table 1. A list of F_0 and final F_c values is available on request.

RESULTS AND DISCUSSION

General. Figure 1 shows the bond distances and angles in the title compound (**3**). For the sake of clarity the bond angles involving the H atoms are left out. The aromatic ring is planar within experimental error. The distances of the atoms from the least-squares plane through the ring C atoms of **3** are given in Fig. 2.

Conformation around the C_1–C_{11} *bond and geometry of the* C(OH)–t-Bu_2 *group.* The conformation around C_1–C_{11} is given in Fig. 3a. The angle between the ring plane and the C_1–C_{11}–O_{11} plane is 12.5°. Since this angle is in close agreement with the corresponding angles reported for **2** (ϕ = 12.9°)[3] and **5** (ϕ = 11.6°),[8] the interpretation of the kinetic data for **4** (leading to ϕ = 34° and 39°) looks doubtful.

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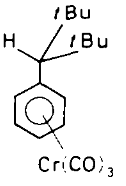
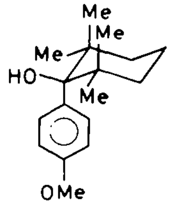
† While our work on **3** was in progress, Lomas and Dubois[8] reported ϕ to be only 11.6° for compound **5**.



1



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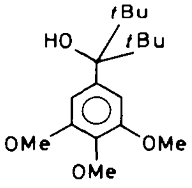
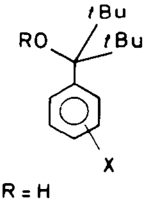
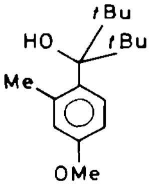


3



A, R = H
B, R = p-$NO_2C_6H_4CO$-

4



5

Table 1. Final parameters with ESD's in parentheses. The fractional atomic coordinates are multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the hydrogen atoms. The expression for the anisotropic thermal parameters (Å × 10^3) is

$$\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+a^*b^*khU_{12}+c^*a^*lhU_{13}+b^*c^*klU_{23})]$$

The isotropic factors (U) are in Å × 10^3.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	7802(1)	2869(2)	3932(1)	42(1)	36(1)	33(1)	−2(1)	18(1)	−2(1)
C2	8818(2)	2738(3)	4313(1)	42(1)	43(1)	38(1)	−1(1)	17(1)	2(1)
C3	9429(2)	3470(3)	3899(2)	44(1)	46(1)	49(1)	−7(1)	23(1)	−5(1)
C4	9029(2)	4346(2)	3077(2)	61(1)	37(1)	50(1)	−11(1)	34(1)	−4(1)
C5	8020(2)	4439(2)	2686(4)	64(1)	35(1)	34(1)	−1(1)	23(1)	−1(1)
C6	7411(2)	3726(2)	3108(1)	44(1)	44(1)	35(1)	0(1)	15(1)	−1(1)
C11	7154(1)	2079(2)	4441(1)	34(1)	37(1)	30(1)	1(1)	12(1)	2(1)
C12	6783(1)	3365(2)	5008(1)	42(1)	42(1)	36(1)	1(1)	18(1)	−2(1)
C13	6363(2)	943(3)	3742(1)	48(1)	46(1)	38(1)	−10(1)	16(1)	−7(1)
C31	10,881(2)	2582(4)	5094(2)	41(1)	86(2)	84(2)	−4(1)	16(1)	4(1)
C41	10,028(2)	4359(4)	2111(2)	63(2)	90(2)	68(2)	−2(2)	42(1)	6(2)
C51	7589(4)	6808(4)	1855(3)	146(4)	48(2)	71(2)	18(2)	1(2)	−1(2)
C121	7683(2)	3985(3)	5803(2)	58(1)	54(1)	46(1)	−10(1)	22(1)	−13(1)
C122	6068(2)	2718(3)	5481(2)	49(1)	59(2)	48(1)	2(1)	28(1)	−1(1)
C123	6281(2)	4768(3)	4416(2)	74(2)	50(1)	57(1)	20(1)	31(1)	5(1)
C131	5421(2)	1713(4)	3093(2)	49(1)	79(2)	53(2)	−12(1)	1(1)	−5(1)
C132	6856(2)	101(3)	3118(2)	77(2)	54(2)	49(1)	−13(1)	28(1)	−16(1)
C133	6038(2)	−336(3)	4287(2)	73(2)	60(2)	60(2)	−29(1)	29(1)	−11(1)
O3	10,432(1)	3419(2)	4250(1)	43(1)	81(1)	70(1)	−11(1)	23(1)	10(1)
O4	9625(1)	5182(2)	2702(1)	90(1)	50(1)	85(1)	−18(1)	62(1)	−1(1)
O5	7582(1)	5208(2)	1834(1)	95(1)	41(1)	38(1)	0(1)	28(1)	5(1)
O11	7821(1)	1077(2)	5119(1)	43(1)	47(1)	38(1)	6(1)	18(1)	12(1)
H2	908(1)	217(3)	486(1)	43					
H6	67(1)	388(2)	280(1)	43					
H11	763(2)	86(3)	554(1)	44					
H31	1069(2)	149(3)	499(2)	63					
H32	1159(2)	269(3)	523(2)	63					
H33	1067(2)	302(3)	562(2)	63					
H41	1051(2)	498(3)	198(2)	70					
H42	1034(2)	347(3)	242(2)	70					
H43	956(2)	422(3)	154(2)	70					
H51	798(2)	730(3)	238(2)	82					
H52	716(2)	721(3)	128(2)	82					
H53	713(2)	689(3)	220(2)	82					
H211	802(2)	320(3)	628(2)	52					
H212	818(2)	442(3)	557(1)	52					
H213	748(2)	483(3)	613(2)	52					
H221	541(2)	244(3)	500(2)	56					
H222	633(2)	181(3)	588(1)	56					
H223	593(2)	349(3)	587(2)	56					
H231	673(2)	539(3)	417(2)	59					
H232	607(2)	542(3)	481(2)	59					
H233	569(2)	448(3)	385(2)	59					
H311	501(2)	92(3)	266(2)	56					
H312	554(2)	253(3)	270(2)	56					
H313	500(2)	217(3)	344(2)	56					
H321	750(2)	−32(3)	351(2)	61					
H322	700(2)	78(3)	268(2)	61					
H323	640(2)	−70(3)	275(2)	61					
H331	662(2)	−96(3)	468(2)	62					
H332	570(2)	4(3)	472(2)	62					
H333	559(2)	−102(3)	385(2)	62					

The geometry around C_{11} is in accordance with the geometries reported for **1**[2] and **2**;[3] the corresponding bond lengths in **1**, **2** and **3** are approximately equal, whereas the bond angles indicate the C_2–C_1–C_6 angle in **2** to be influenced by the cyclohexane ring geometry. The conformations around the C_{12}–C_{11} and C_{13}–C_{11} bonds are given in Figs. 3b and 3c, respectively. The average twist from perfect staggering amounts to 11° for the C_{12} t-Bu group and to 18° for the C_{13} t-Bu group.

Conformation of the methoxy groups. Zweig[4] has investigated the correlation of the HFMO energies with the frequencies of the charge-transfer band of molecular complexes of several OMe-substituted benzenes. The correlation is very poor for complexes carrying more than two OMe groups on adjacent sites in the benzene ring. This was explained by assuming the central methoxy group(s) to be non-coplanar with the benzene ring. More recently, this assumption has been confirmed by X-ray analyses of mescaline·HBr,[10] mescaline·HCl,[11] reserpine[12] and 2,4-diamino-5-(3,4,5-trimethoxybenzyl)-pyrimidine-1-oxid-dihydrate.[13]

The orientations of the OMe groups with respect to

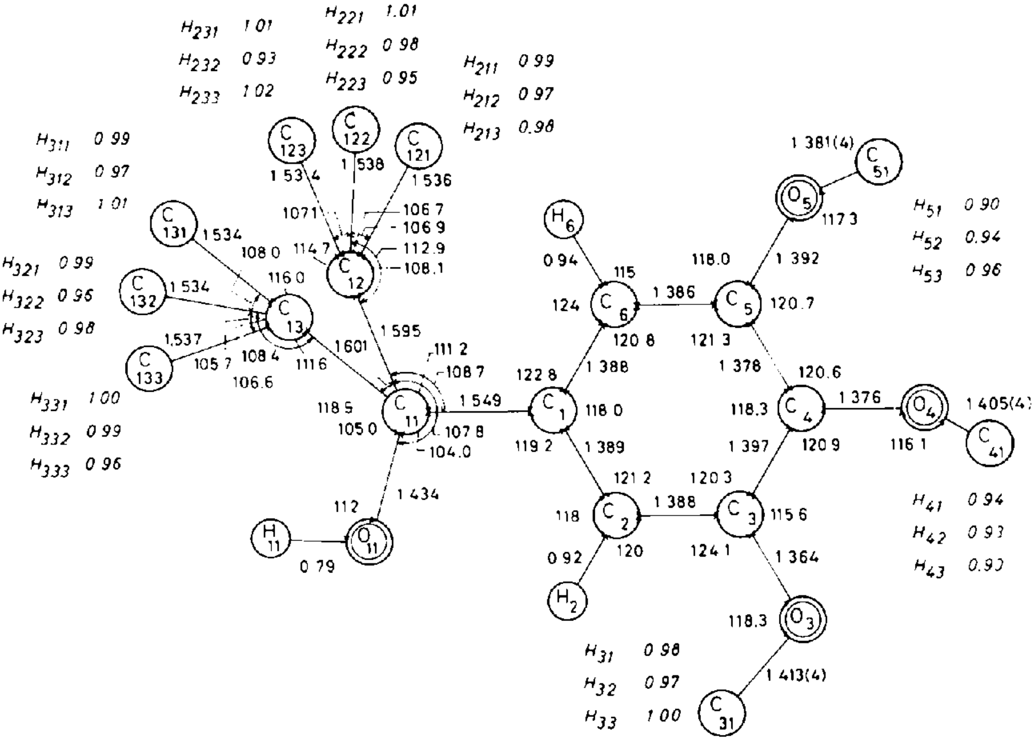


Fig. 1. Bond lengths (Å) and bond angles (°) in 3. The estimated standard deviations (ESD's) are 0.003 Å for distances between non-hydrogen atoms and 0.04 Å for distances to hydrogen atoms. The ESD's of the angles given are 0.2°.

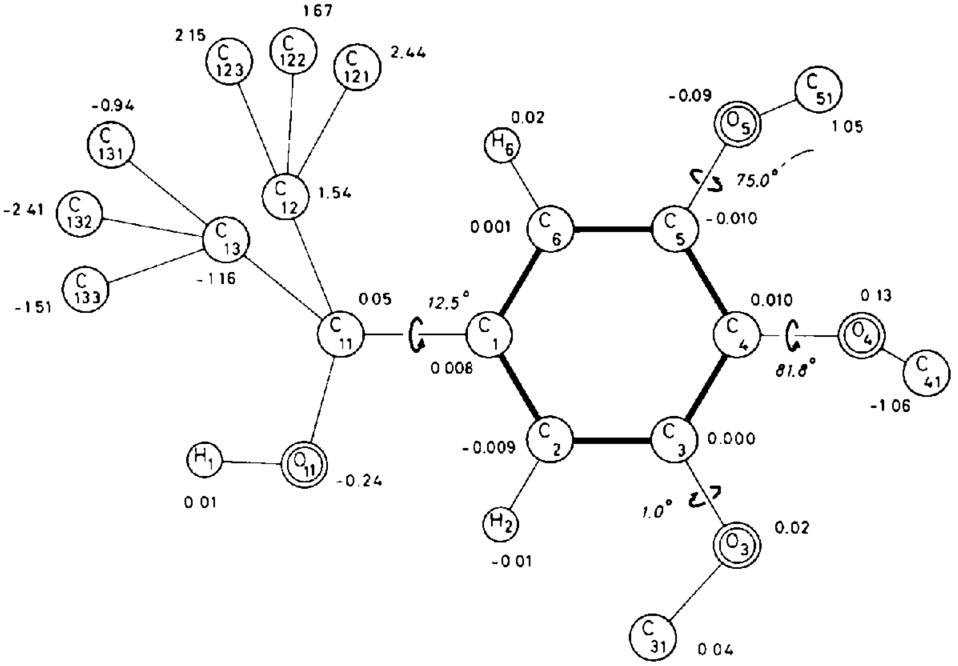
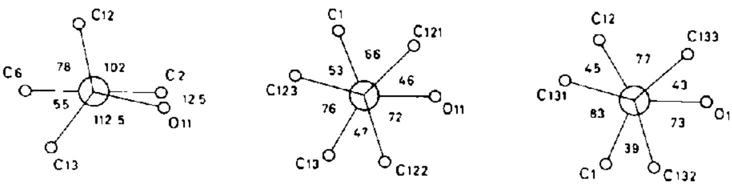


Fig. 2. Deviation (in Å) of the atoms for the least-squares plane through the ring carbon atoms.



a along C11-C1 b along C12-C11 c along C13-C11

Fig. 3. Newman projections along C_{11}–C_1, C_{12}–C_{11} and C_{13}–C_{11}.

the benzene ring in the title compound are given in Fig. 2. The orientations of the 3- and 4-OMe groups are in agreement with those found in the literature.[10–13] The 5-OMe group, however, has a different orientation, which is probably due to directing effects of the C(OH)–t-Bu_2 group. These three orientations can explain the separate ^1H NMR signals observed by Gall *et al.*[5] for the OMe groups of 3.

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