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Characterization of *meta*-substituted phenyldi(1-adamantyl)methanol rotamers by X-ray crystallography and ^{13}C NMR spectroscopy

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Summary – The rotameric *syn-* and *anti,meta*-(*tert*-butyl)phenyldi(1-adamantyl)methanols have been unambiguously identified by X-ray crystallographic structure determination. Application of the additivity rule to the ^{13}C NMR spectra confirms the previous attribution of the *syn-* and *anti,meta*-tolyldi(1-adamantyl)methanols.

alcohol rotamer / X-ray crystallography / NMR spectroscopy / molecular mechanics

Résumé – Caractérisation de rotamères phényldi(1-adamantyl)méthanol substitués en *méta* par cristallographie aux rayons-X et spectroscopie RMN ^{13}C. *Deux rotamères,* syn- *et* anti,méta-*(tert-butyl)phényldi(1-adamantyl)méthanol, ont été caractérisés sans ambiguïté par la détermination de leur structure cristallographique. L'application de la règle d'additivité des déplacements chimiques en RMN du carbone-13 aux rotamères analogues,* syn- *et* anti,méta-*tolyldi(1-adamantyl)méthanol, permet de vérifier leur attribution.*

alcool rotamère / cristallographie aux rayons-X / spectroscopie RMN / mécanique moléculaire

Introduction

In previous work on the rotational isomers of disubstituted benzenes one of us isolated five isomers (*para*, two *meta* and two *ortho*) of tolyldi(1-adamantyl)methanol and three isomers (*para* and two *meta*) of (*tert*-butyl)phenyldi(1-adamantyl)methanol [1]. These could be converted by successive treatment with oxalyl bromide and tri-*n*-butyltin hydride to alkanes. In the case of the *meta*-substituted derivatives, mixtures of rotameric alkanes were obtained, while the *anti,ortho*-tolyl derivative gave only the corresponding *syn,ortho*-tolyl methane. In more recent work, *anti,ortho*-tolyldi(1-adamantyl)methane has been obtained by ionic hydrogenation of either of the *ortho*-tolyldiadamantylmethanols with trifluoroacetic acid and triethylsilane [2].

Whereas the *anti-* and *syn,ortho*-tolyldiadamantylmethanols, **1A** and **1S**, respectively, are readily separated and characterized by comparison with the known [3] *ortho*-tolyldi(*tert*-butyl)methanols, **2A** and **2S**, differentiation of the *meta*-substituted alcohols, **3** and **4**, is less easy. However, on the basis of ^1H and ^{13}C NMR studies [1] we came to the conclusion that the *anti* isomer of the *meta*-(*tert*-butyl)phenyldiadamantylmethanols, **3A**, was the more stable, this isomer being associated with a *tert*-butyl proton chemical shift (in $CDCl_3$, relative to TMS) of 1.35 ppm. The corresponding chemical shift for the other isomer, **3S**, is 1.32 ppm. For the *meta*-tolyl derivatives the relative stabilities are reversed, the *syn* **4S** (methyl shift 2.35 ppm) being more stable than the *anti* **4A** (2.39 ppm).

The NMR assignments of the structures depend ultimately upon analogy with *meta-* and *para*-substituted phenyldi(*tert*-butyl)methanols investigated by Sternhell [4], and we have therefore sought unambiguous confirmation of our conclusions. This has now been possible through X-ray crystallographic study of both *meta*-(*tert*-butyl)phenyldi(1-adamantyl)methanols.

Results and discussion

The rotameric alcohols were prepared and separated as described previously [1]. Adequate crystals of the 1.35 ppm rotamer were obtained by crystallization from a solution in *n*-hexane, no particular precautions being taken. It was more difficult to obtain suitable crystals of the other isomer, but slow partial evaporation of an *n*-hexane solution at room temperature finally gave a few specimens of adequate quality. Both samples were

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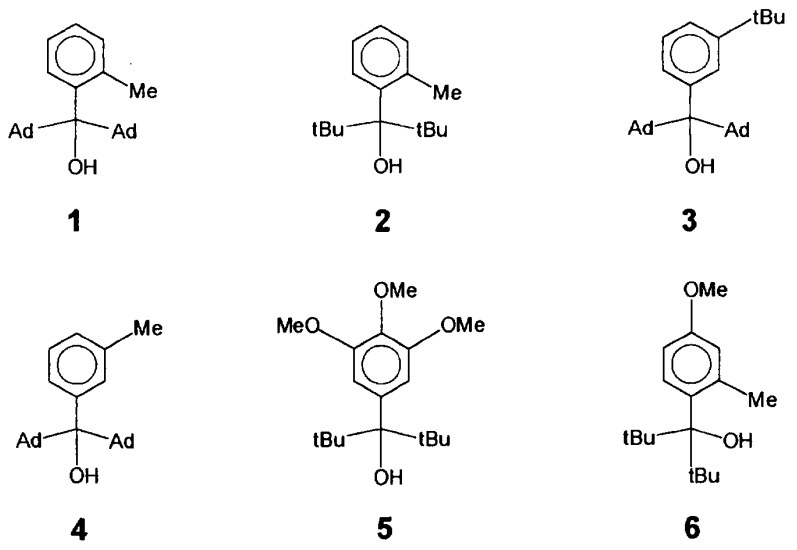


Fig 1

100% pure by the ^{1}H NMR criterion. The crystal data are given in the *Experimental section*. All carbon atoms and the oxygen atom were located; the hydrogen atoms were not systematically located from the diffraction diagrams but were placed at standard distances for optimization. Atom coordinates and isotropic thermal parameters for compounds **3A** and **3S** are listed in tables I–IV. Other crystallographic data can be found in the supplementary material. The main features of the structures (bond lengths, bond angles and torsion angles) are listed in table V, together with the results of molecular mechanics (MM) calculations (see below) [5, 6]. In some cases, values for particular internal coordinates are given, in which case the atoms are fully specified. In other cases only average values are listed.

Description of anti *isomer,* **3A***: crystallographic results*

The general features of this type of molecule have been described in previous studies on 3,4,5-trimethoxyphenyldi(*tert*-butyl)methanol, **5** [7], and *syn*-4-methoxy-2-methylphenyldi(*tert*-butyl)methanol, **6** [8]. However, in both these cases the C-OH bond was out of the plane of the benzene ring by about 12°, whereas in the present case this angle is not significantly different from zero. Furthermore, the symmetry of the molecule is close to C_s, in agreement with Olah's assumption for the *para*-substituted phenyldi(1-adamantyl)methanols [9]. The *tert*-butyl groups in the di(*tert*-butyl) derivatives are quite distinct in terms of their torsion angles with respect to the ring plane and the orientation of the constituent methyl groups with respect to the sp^2-sp^3 bond. In the *anti* di(1-adamantyl) derivative, **3A**, however, such dissymmetry is to a large extent absent. Thus, the torsion angle between the tertiary carbon of the adamantyl group and an *ortho* carbon of the aryl group differs by only 3° (66° and −69°), and the orientations of the adamantyl groups differ by an average of 4°, as compared to some 24° for the *tert*-butyl groups in *syn*-4-methoxy-2-methylphenyldi(*tert*-butyl)methanol, **6**. In the latter the *tert*-butyl group furthest from the plane, in terms of angle, has the shortest C-C_{OH} bond and the methyl groups are very nearly staggered with respect to the sp^2-sp^3 bond. In the present case, the slightly more remote Ad, in terms of the torsion angle, is the more staggered but the bond

Table I. Fractional atomic coordinates for *anti,meta*-(*tert*-butyl)phenyldi(1-adamantyl)methanol, **3A**.

Atom	x/a	y/b	z/c	U*(eq)*
O(11)	0.4555(1)	0.5888(5)	0.1359(2)	0.0531
C(1)	0.3896(2)	0.5071(6)	0.2220(3)	0.0410
C(2)	0.3576(2)	0.3975(7)	0.2661(3)	0.0414
C(3)	0.3204(2)	0.4650(7)	0.3140(3)	0.0429
C(4)	0.3145(2)	0.6542(8)	0.3182(4)	0.0549
C(5)	0.3451(3)	0.7665(7)	0.2739(5)	0.0637
C(6)	0.3820(2)	0.6950(7)	0.2274(4)	0.0549
C(10)	0.4320(2)	0.4307(6)	0.1706(3)	0.0420
C(30)	0.2875(2)	0.3321(7)	0.3597(4)	0.0501
C(31)	0.2499(2)	0.4288(9)	0.4128(5)	0.0774
C(32)	0.3285(2)	0.2085(8)	0.4340(4)	0.0653
C(33)	0.2500(2)	0.2096(8)	0.2805(4)	0.0645
C(101)	0.4844(2)	0.3410(7)	0.2512(3)	0.0426
C(102)	0.5344(2)	0.3041(9)	0.2100(4)	0.0645
C(103)	0.5864(2)	0.239(1)	0.2901(4)	0.0706
C(104)	0.6044(2)	0.381(1)	0.3697(5)	0.0839
C(105)	0.5562(3)	0.412(1)	0.4134(4)	0.0739
C(106)	0.5421(2)	0.234(1)	0.4566(4)	0.0729
C(107)	0.5247(2)	0.0936(9)	0.3767(4)	0.0684
C(108)	0.4724(2)	0.1619(8)	0.2982(4)	0.0629
C(109)	0.5046(2)	0.4797(8)	0.3352(4)	0.0656
C(110)	0.5728(3)	0.062(1)	0.3325(5)	0.0786
C(201)	0.3997(2)	0.3171(7)	0.0753(3)	0.0422
C(202)	0.4360(2)	0.289(1)	0.0059(4)	0.0843
C(203)	0.4028(3)	0.200(2)	−0.0891(6)	0.0892
C(204)	0.3835(4)	0.013(1)	−0.0674(6)	0.0897
C(205)	0.3446(3)	0.0380(8)	−0.0026(4)	0.0680
C(206)	0.2948(3)	0.154(1)	−0.0552(4)	0.0755
C(207)	0.3159(3)	0.335(1)	−0.0765(5)	0.0771
C(208)	0.3482(2)	0.4314(8)	0.0178(4)	0.0676
C(209)	0.3771(3)	0.1318(8)	0.0925(4)	0.0665
C(210)	0.3530(4)	0.312(1)	−0.1407(5)	0.0945

Table II. Anisotropic thermal parameters for *anti,meta*-(*tert*-butyl)phenyldi(1-adamantyl)methanol, **3A**.

Atom	U*(11)*	U*(22)*	U*(33)*	U*(23)*	U*(13)*	U*(12)*
O(11)	0.072(2)	0.044(2)	0.064(2)	0.008(2)	0.030(2)	−0.015(2)
C(1)	0.044(3)	0.035(3)	0.046(3)	−0.004(2)	0.014(2)	0.002(2)
C(2)	0.042(3)	0.039(3)	0.047(3)	−0.002(3)	0.017(2)	−0.001(2)
C(3)	0.041(3)	0.044(3)	0.045(3)	−0.004(2)	0.014(2)	−0.001(2)
C(4)	0.057(3)	0.049(4)	0.070(4)	−0.014(3)	0.021(3)	0.008(3)
C(5)	0.088(4)	0.036(3)	0.095(5)	0.002(3)	0.038(4)	0.010(3)
C(6)	0.072(4)	0.034(3)	0.075(4)	0.004(3)	0.029(3)	0.002(3)
C(10)	0.047(3)	0.034(3)	0.050(3)	0.001(3)	0.017(2)	−0.006(2)
C(30)	0.043(3)	0.056(3)	0.060(3)	−0.011(3)	0.020(3)	−0.002(3)
C(31)	0.083(4)	0.081(5)	0.114(5)	−0.018(4)	0.063(4)	−0.007(4)
C(32)	0.070(4)	0.076(4)	0.061(4)	0.007(3)	0.027(3)	−0.009(3)
C(33)	0.049(3)	0.067(4)	0.086(4)	−0.010(3)	0.019(3)	−0.007(3)
C(101)	0.041(3)	0.046(3)	0.043(3)	−0.004(2)	0.014(2)	−0.004(2)
C(102)	0.054(3)	0.101(5)	0.055(3)	−0.001(4)	0.021(3)	0.011(3)
C(103)	0.049(3)	0.138(7)	0.065(4)	0.002(5)	0.023(3)	0.025(4)
C(104)	0.048(3)	0.135(7)	0.087(5)	0.003(5)	0.002(3)	−0.013(4)
C(105)	0.071(4)	0.100(6)	0.061(4)	−0.029(4)	0.002(3)	−0.001(4)
C(106)	0.055(4)	0.144(7)	0.049(4)	0.008(4)	0.009(3)	0.020(4)
C(107)	0.065(4)	0.074(4)	0.070(4)	0.024(4)	0.005(3)	0.004(4)
C(108)	0.056(3)	0.066(4)	0.069(4)	0.019(3)	0.002(3)	−0.007(3)
C(109)	0.064(4)	0.072(4)	0.063(4)	−0.017(3)	0.013(3)	0.000(3)
C(110)	0.074(4)	0.109(6)	0.073(4)	−0.012(4)	−0.002(4)	0.043(4)
C(201)	0.046(3)	0.042(3)	0.040(3)	0.003(2)	0.015(2)	−0.001(2)
C(202)	0.067(4)	0.176(8)	0.071(4)	−0.054(5)	0.026(3)	−0.025(5)
C(203)	0.075(5)	0.23(1)	0.087(6)	−0.090(7)	0.043(5)	−0.045(7)
C(204)	0.108(6)	0.148(8)	0.095(6)	−0.081(6)	−0.032(5)	0.055(6)
C(205)	0.125(6)	0.048(4)	0.056(4)	−0.003(3)	−0.003(4)	−0.027(4)
C(206)	0.072(4)	0.098(6)	0.066(4)	−0.022(4)	0.016(3)	−0.019(4)
C(207)	0.085(5)	0.084(5)	0.065(4)	0.018(4)	−0.013(4)	0.004(4)
C(208)	0.075(4)	0.057(4)	0.069(4)	0.008(3)	−0.005(3)	0.006(3)
C(209)	0.122(5)	0.045(4)	0.055(4)	0.004(3)	0.000(3)	−0.023(4)
C(210)	0.123(6)	0.180(9)	0.051(4)	0.007(5)	0.007(4)	−0.081(7)

Table III. Fractional atomic coordinates for *syn,meta*-(*tert*-butyl)phenyldi(1-adamantyl)methanol, **3S**.

Atom	x/a	y/b	z/c	U*(eq)*
O(11)	0.7258(2)	0.8022(3)	0.1907(7)	0.0394
C(1)	0.7618(3)	0.7745(5)	−0.123(1)	0.0318
C(2)	0.8193(3)	0.7882(5)	−0.031(1)	0.0301
C(3)	0.8723(3)	0.7793(5)	−0.123(1)	0.0326
C(4)	0.8664(3)	0.7578(6)	−0.322(1)	0.0393
C(5)	0.8105(4)	0.7446(5)	−0.417(1)	0.0368
C(6)	0.7580(3)	0.7517(5)	−0.322(1)	0.0348
C(10)	0.7052(3)	0.7802(5)	−0.0080(9)	0.0251
C(30)	0.9332(3)	0.7953(6)	−0.015(1)	0.0383
C(31)	0.9830(4)	0.7446(7)	−0.099(1)	0.0657
C(32)	0.9506(4)	0.8879(7)	−0.041(2)	0.0752
C(33)	0.9340(4)	0.7781(8)	0.205(1)	0.0727
C(101)	0.6631(3)	0.8572(5)	−0.087(1)	0.0307
C(102)	0.6079(4)	0.8665(5)	0.031(1)	0.0414
C(103)	0.5719(4)	0.9456(6)	−0.027(1)	0.0441
C(104)	0.6118(5)	1.0225(6)	0.006(1)	0.0616
C(105)	0.6649(5)	1.0138(5)	−0.122(2)	0.0541
C(106)	0.6415(4)	1.0101(6)	−0.339(1)	0.0556
C(107)	0.6020(4)	0.9321(6)	−0.367(1)	0.0478
C(108)	0.6399(3)	0.8541(5)	−0.310(1)	0.0379
C(109)	0.7019(4)	0.9365(6)	−0.062(1)	0.0479
C(110)	0.5488(4)	0.9401(6)	−0.242(1)	0.0468
C(201)	0.6757(3)	0.6882(5)	0.012(1)	0.0300
C(202)	0.6400(4)	0.6826(5)	0.200(1)	0.0410
C(203)	0.6166(4)	0.5940(6)	0.230(1)	0.0487
C(204)	0.5749(4)	0.5676(6)	0.053(2)	0.0533
C(205)	0.6094(4)	0.5704(6)	−0.129(1)	0.0516
C(206)	0.6631(5)	0.5112(6)	−0.105(1)	0.0579
C(207)	0.7032(4)	0.5363(6)	0.073(2)	0.0508
C(208)	0.7273(3)	0.6244(5)	0.043(1)	0.0384
C(209)	0.6329(3)	0.6596(5)	−0.163(1)	0.0394
C(210)	0.6686(4)	0.5332(6)	0.258(1)	0.0564

length is 0.01 Å the greater. In all cases, the bonds to the C_{OH} carbon are substantially longer than normal, averaging 1.61, 1.60 and 1.61 Å for **3A**, **5** and **6**, respectively, for the *tert*-alkyl groups, and 1.55, 1.55 and 1.54 Å for the bond to the aryl group.

The benzene ring is planar, the standard deviation of the carbon atoms with respect to the mean plane being 0.005 Å. Bond lengths are normal, with an average of 1.39 Å. As is usual in this type of compound, the internal bond angles at the points of attachment of the substituents are smaller than average, being 116° and 118° for the Ad_2COH and *t*-Bu groups, respectively. In the highly strained *ortho*-tolyldi(*tert*-butyl)methanol, **6**, the corresponding angle for the $(t\text{-Bu})_2COH$ group is 115° while the external angles at this point are 119° and 126°, with those for the methyl group 127.5° and 113°, these angular deformations allowing better separation of the methyl and hydroxy groups. In the present case, however, the degree of dissymmetry is smaller and tends to increase the separation between the *tert*-butyl group and the adamantyls, the external angles being 124° and 120°.

Table IV. Anisotropic thermal parameters for *syn,meta*-(*tert*-butyl)phenyldi(1-adamantyl)methanol, **3S**.

Atom	U*(11)*	U*(22)*	U*(33)*	U*(23)*	U*(13)*	U*(12)*
O(11)	0.046(3)	0.054(4)	0.025(3)	−0.002(3)	0.003(2)	0.000(3)
C(1)	0.027(4)	0.030(5)	0.041(5)	0.003(4)	−0.000(4)	0.005(4)
C(2)	0.029(4)	0.028(5)	0.035(4)	0.003(4)	−0.004(4)	−0.000(4)
C(3)	0.034(4)	0.032(5)	0.035(4)	0.008(4)	0.001(4)	0.006(4)
C(4)	0.039(5)	0.058(6)	0.030(5)	0.002(4)	0.010(4)	0.008(5)
C(5)	0.046(5)	0.039(5)	0.028(4)	0.000(4)	0.000(4)	−0.000(4)
C(6)	0.037(5)	0.038(5)	0.030(4)	0.002(4)	0.000(4)	−0.000(4)
C(10)	0.028(4)	0.043(5)	0.015(4)	−0.009(4)	0.000(3)	−0.002(4)
C(30)	0.029(4)	0.060(7)	0.034(5)	0.005(4)	0.002(4)	−0.007(4)
C(31)	0.043(5)	0.099(9)	0.071(7)	−0.007(7)	−0.006(5)	0.014(6)
C(32)	0.053(7)	0.084(8)	0.103(9)	−0.014(7)	−0.001(6)	−0.013(6)
C(33)	0.047(6)	0.13(1)	0.063(7)	0.019(7)	−0.005(5)	0.001(6)
C(101)	0.042(5)	0.025(5)	0.028(4)	−0.003(4)	0.002(4)	−0.004(4)
C(102)	0.042(5)	0.048(6)	0.044(5)	−0.008(4)	0.009(4)	0.015(5)
C(103)	0.046(5)	0.053(6)	0.046(5)	−0.005(5)	0.013(4)	0.017(5)
C(104)	0.089(8)	0.058(7)	0.067(7)	−0.026(6)	−0.004(6)	0.029(6)
C(105)	0.067(7)	0.033(6)	0.078(8)	−0.010(5)	0.007(6)	−0.011(5)
C(106)	0.064(7)	0.047(6)	0.075(8)	0.023(5)	0.021(6)	0.011(5)
C(107)	0.053(6)	0.051(6)	0.042(5)	0.007(5)	0.004(4)	0.010(5)
C(108)	0.041(5)	0.035(5)	0.040(5)	0.004(4)	0.004(4)	0.007(4)
C(109)	0.044(5)	0.040(6)	0.064(6)	0.005(5)	0.002(4)	−0.006(5)
C(110)	0.035(5)	0.061(7)	0.058(6)	0.017(5)	0.005(4)	0.014(5)
C(201)	0.023(4)	0.035(5)	0.033(4)	0.003(4)	0.000(3)	−0.001(4)
C(202)	0.047(5)	0.045(6)	0.034(5)	0.010(4)	0.003(4)	−0.003(4)
C(203)	0.044(6)	0.062(7)	0.048(5)	0.006(5)	0.014(4)	0.000(5)
C(204)	0.039(5)	0.050(6)	0.089(7)	0.018(6)	0.011(5)	−0.004(5)
C(205)	0.052(6)	0.044(6)	0.064(6)	0.004(5)	−0.009(5)	−0.009(5)
C(206)	0.076(7)	0.043(6)	0.060(7)	0.004(5)	0.005(6)	−0.004(5)
C(207)	0.047(6)	0.046(6)	0.078(7)	0.020(6)	0.015(5)	0.016(5)
C(208)	0.037(5)	0.039(5)	0.038(5)	−0.002(4)	0.002(4)	0.003(4)
C(209)	0.041(5)	0.042(6)	0.036(5)	0.000(4)	−0.005(4)	−0.001(4)
C(210)	0.055(6)	0.064(7)	0.060(6)	0.023(6)	0.003(5)	0.003(5)

Table V. Principal bond lengths (Å), bond angles (°) and torsion angles (°) for *anti*- and *syn,meta*-(*tert*-butyl)phenyldi(1-adamantyl)methanols, **3A** and **3S**. Comparison of crystallographic data and MM3-calculated values.

	anti, ***3A***		syn, ***3S***			anti, ***3A***		syn, ***3S***	
Bond length[a]	*MM3*	*Found*	*MM3*	*Found*	*Torsion angle*[b]	*MM3*	*Found*	*MM3*	*Found*
C(1)-C(10)	1.538	1.543(6)	1.539	1.54(1)	O(11)-C(10)-C(1)-C(2)	−170	180	−8	1
C(10)-O(11)	1.443	1.442(5)	1.443	1.44(1)	C(101)-C(10)-C(1)-C(2)	−57	−68	103	115
C(10)-C_q (Ad)	1.602	1.61	1.600	1.625	C(201)-C(10)-C(1)-C(2)	79	66	−121	−111
CH_2-C_q (Ad)	1.558	1.54	1.553	1.54	O(11)-C(10)-C(1)-C(6)	10	−1	−170	178
C–C (aromatic)	1.402	1.39	1.401	1.39	C(101)-C(10)-C(1)-C(6)	124	111	−79	−68
C(3)-C(30)	1.526	1.526(6)	1.526	1.51(1)	C(201)-C(10)-C(1)-C(6)	−100	−115	57	66
C_q-Me (*t*-Bu)	1.546	1.53	1.546	1.53	C(1)-C(10)-C(101)-C(102)	−151	−166	−178	−178
Bond angle[a]	*MM3*	*Found*	*MM3*	*Found*	C(1)-C(10)-C(101)-C(108)	87	70	58	59
C(10)-C_q-CH_2 (Ad)	112.3	112	112.3	112	C(1)-C(10)-C(101)-C(109)	−34	−49	−60	−58
CH_2-C_q-CH_2 (Ad)	106.5	107	106.5	107	C(1)-C(10)-C(201)-C(202)	178	162	152	153
C(101)-C(10)-C(201)	120.2	120.4(4)	120.4	119.5(5)	C(1)-C(10)-C(201)-C(208)	59	46	35	37
C(1)-C(10)-C_q	110.7	110	110.7	110	C(1)-C(10)-C(201)-C(209)	−59	−73	−86	−85
O(11)-C(10)-C_q	103.8	105	103.7	104.5	C(2)-C(3)-C(30)-C(31)	179	178	−179	152
C(1)-C(10)-C(11)	106.1	105.6(4)	106.3	106.3(5)	C(2)-C(3)-C(30)-C(32)	59	58	61	−91
C(10)-C(1)-C(2)	122.1	123.8(4)	121.1	121.5(6)	C(2)-C(3)-C(30)-C(33)	−61	−61	−59	29
C(10)-C(1)-C(6)	121.2	120.3(4)	122.2	121.4(6)					
C(2)-C(1)-C(6)	116.7	116.0(4)	116.7	117.1(7)					
C(2)-C(3)-C(4)	117.9	117.9(5)	117.9	116.6(7)					
C(3)-C(30)-Me	109.7	111	110.0	111					
Me-C(30)-Me	107.9	108	107.9	107					

[a] Single values are taken directly from the crystallographic data with the standard error in parentheses; other values are averages reduced to three significant figures. [b] All values reduced to three significant figures.

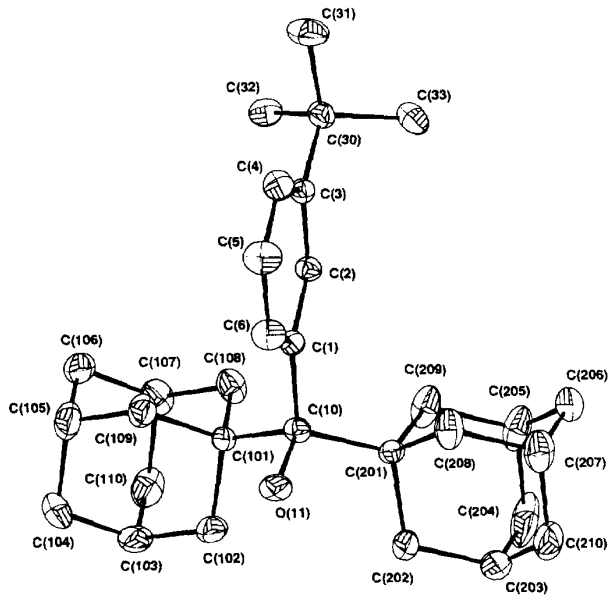


Fig 2. CAMERON diagram for *anti,meta*-(*tert*-butyl)phenyldi(1-adamantyl)methanol, **3A**.

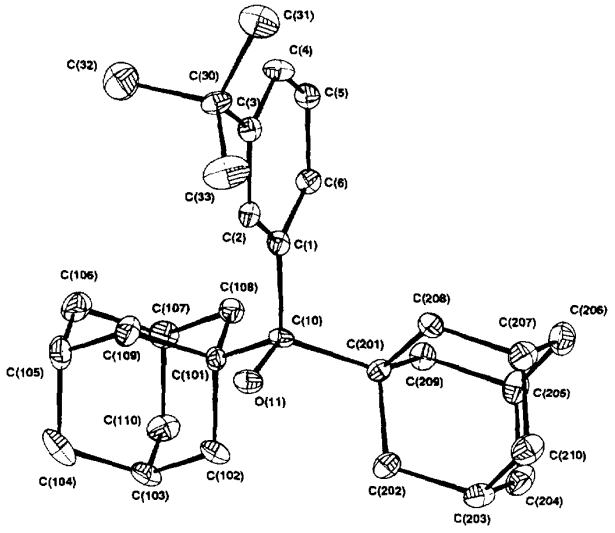


Fig 3. CAMERON diagram for *syn,meta*-(*tert*-butyl)phenyldi(1-adamantyl)methanol, **3S**.

The *meta tert*-butyl substituent is oriented so that one methyl group is virtually eclipsed with the *para* carbon, the other two being directed towards the two adamantyl groups. From a conventional steric point of view, this would seem to be the less favorable orientation, as it would maximize repulsive interactions between Ad and *t*-Bu. However, MM calculations suggest that at the distances prevailing between the relevant atoms, attractive interactions (the negative part of the van der Waals energy plot) are larger [1, 10].

The Ad-C-Ad bond angle is very large, 121°, slightly larger than for previously studied *tert*-butyl analogues, 119° for both **5** and **6**. Not unexpectedly, the adamantyl groups are somewhat deformed, the angles subtended by the methylene groups adjacent to the quaternary carbon being on average 107° rather than 109.5°. This is not significantly different from the angles between the methyl groups of the *tert*-butyls in related structures (107° for both **5** and **6**). Furthermore, the C-C distances between the quaternary carbons and the methylenes in **3A** are the same as those between methyl and quaternary carbon in **5** and **6**, 1.54 Å. The greater 'rigidity' of the adamantyl group [3b], as compared to *tert*-butyl, is not therefore expressed by any notable differences in the carbon skeleton in the vicinity of the quaternary carbon.

Description of syn *isomer,* **3S**: *crystallographic results*

The crystals being of poorer quality, the precision of the measurements is not so high as for the *anti* isomer, but the salient features are quite clear. Unlike the *anti* isomer, the *syn* isomer is truly dissymmetric, despite the fact that the C–OH bond is once again virtually in the plane of the benzene ring. One of the adamantyl groups is now staggered with respect to the sp^2-sp^3 bond (to within 2°) while the other is 25° from the staggered conformation. The *tert*-butyl group no longer has a C-methyl bond in the plane of the benzene ring, the whole group being rotated through an angle of about 30°. The other main features are much the same as for the *anti* isomer.

The C-Ad bonds are surprisingly long, 1.62 and 1.63 Å; the group which is staggered is slightly closer in terms of bond length but slightly further from the benzene ring in terms of its torsion angle (−68° vs 66°). The Ad-C-Ad bond angle is slightly smaller (119.5°) than in the *anti* isomer.

The benzene ring is planar. The standard deviation of the carbon atoms with respect to the mean plane is 0.008 Å. Again, the internal bond angles are small, 117°, at the point of attachment of the Ad_2COH and *t*-Bu substituents but the external angles are the same, 121–122°.

The Ad-C-Ad bond angle is large (119.5°) and the deformation of the adamantyl groups is similar to that in the *anti* isomer, the internal angles being not significantly different (average 107°) and the quaternary carbon to methylene bonds being very similar to that in **3A**, 1.54 Å.

Comparison of crystallographic results and those of molecular mechanics calculations

Molecular mechanics (MM) is normally designed to calculate the energies and geometries of molecules in the gas phase, though the importance of non-bonded interactions has led to the development of applications to the determination of crystal packing. MM has also been used as a tool for the solution of X-ray crystallographic problems [5]. However, since the structures of molecules obtained by gas phase measurements generally agree very well with those found in crystals, one frequently encounters comparisons of crystallographic structures with MM calculations on isolated molecules, deviations being most often attributed to crystal packing effects.

Table VI. ^{13}C NMR shift increments (relative to benzene δ_C = 128 ppm) for aromatic carbons in aryldi-(1-adamantyl)methanols, **3**, **4** and **7**.

Carbon	***3A***	***3A**(corr)*[a]	***3S***	***3S**(corr)*[a]	**7**	*Mean*[b]	***4A**(calc)*[c]	***4**(δ_H = 2.39)*[d]	***4S**(calc)*[c]	***4S**(δ_H = 2.35)*[d]
a	15.6	15.6	15.2	15.2	15.9	15.6	16.0	16.0	15.8	15.7
b	−3.1	−0.5	−3.2	−0.4	−0.1	−0.3	−3.0	−3.0	0.7	0.6
c	−1.3	−1.3	21.8	−1.2	−0.7	−1.1	−0.9	−0.9	8.7	8.6
d	−5.8	−3.0	−6.0	−3.2	−2.3	−2.8	−1.8	−1.4	−1.8	−1.8
e	19.6	−3.4	−2.8	−2.8	−2.7	−3.0	6.8	6.3	−2.8	−2.7
f	−1.9	0.9	−2.3	0.3	0.4	0.5	1.5	1.2	−2.2	−2.4

[a] Increments corrected for the contribution of the *tert*-butyl group. [b] Mean of the values for **3A** (corr), **3S** (corr) and **7**. [c] Calculated by addition of the methyl group contributions to 'Mean'. [d] Values are ordered so as to obtain the best match.

In this context, the comparison of MM2 [11] calculations and crystallographic data for two strained hydrocarbons containing adamantyl groups is interesting. For 2,3-di(1-adamantyl)-2,3-dimethylbutane [12], the 'structure determined by X-ray analysis is matched with high precision by MM2 force field calculations'. For the closely related, but more strained, 3,4-di-(1-adamantyl)-2,2,5,5-tetramethylhexane DL rotamers [13] the bond length and bond angle agreement is considered good (within 0.015 Å and 3°), while torsion angles differ by not more than 10° and up to 28° for the M and P rotamers, respectively.

In the present case, such a comparison is encouraged by the fact that the main features of the *ortho*-tolyldi(*tert*-butyl)methanol derivative, **6**, previously investigated [8] were very well reproduced by an early version of MM2 supplemented with benzene parameters proposed by Beckhaus [14]. The non-planar structure with the two *tert*-butyl groups in different orientations is correctly predicted. A more recent version, MM2(85) [11], and MM3(89) [15] reproduce these features equally well.

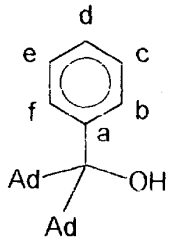
For a comparison of the crystallographic results with those of molecular mechanics calculations, MM3 was used in preference to MM2 since the former, more recent, force field has been found to give better agreement with the relative energies of the *syn*- and *anti,meta*-(*tert*-butyl) rotamers, predicting a difference of 0.7 kcal mol^{-1} in favor of the *anti* isomer, as against 0.3 kcal mol^{-1} determined experimentally [1, 10].

The outstanding but, unfortunately, rather negative result of this comparison is that MM3 completely fails to account for either the symmetry of the *anti* isomer or the coplanarity of the C–O bond and the aryl ring in the *syn* isomer. The geometries predicted by MM3 remain very close to those for the *tert*-butyl analogues. While the different orientations of the adamantyl groups in the *syn* isomer are correctly described, the *meta tert*-butyl group is calculated to have one C-methyl bond in the plane of the ring, and the C–OH bond is some 8° out of plane.

Bond lengths involving the C_{OH} carbon or related to the benzene ring are generally underestimated, while those related to the adamantyls or the *tert*-butyl group are somewhat too long. Bond angles are within 2° of those found, but these do not normally show such wide deviations from the standard values as do torsion angles and, to a lesser degree, bond lengths.

Additivity of substituent effects in ^{13}C NMR: verification of the assignment of the meta*-tolyldi(1-adamantyl)methanols*

In our previous work [1] the assignment of the *anti*- and *syn,meta*-substituted alcohols were based on the assumption that substituents effects on the ^{13}C NMR shifts are additive [16]. Complete assignment of the aromatic carbons in phenyldi(1-adamantyl)methanol, **7**, by correlation experiments gave the contributions of the -CAd_2OH substituent, and those of *tert*-butyl and methyl were taken from the corresponding alkylbenzenes. Now that we have unambiguous evidence for the structures of the two *meta*-(*tert*-butyl) derivatives we can check the assignments of **7** and somewhat refine the calculation of the shifts for the two *meta*-tolyl derivatives.



7

Fig 4

For the sake of simplicity, substituent effects are expressed in terms of increments relative to a standard value of 128.0 ppm for the shift of the carbon atoms in benzene. Using the notation previously adopted to designate the aromatic carbons (see **7**) [1], we obtained the series of increments listed in column 2 of table VI for *anti,meta*-(*tert*-butyl)phenyldiadamantylmethanol, **3A**. These values, however, include the contributions from the *tert*-butyl group; when these are subtracted we obtain the values in column 3. Appplying the same treatment to the *syn* isomer, **3S**, gives, after correction, the values in column 5. Not only do these two sets

Table VII. Crystallographic data for *anti-* and *syn,meta-*(*tert*-butyl)phenyldi(1-adamantyl)methanols, **3A** and **3S**.

	anti-$C_{31}H_{44}O$	syn-$C_{31}H_{44}O$
Fw	432.7	432.7
a (Å)	24.732(8)	22.296(10)
b (Å)	7.297(1)	16.037(5)
c (Å)	14.320(4)	6.812(4)
α (°)	90.	90.
β (°)	106.3(2)	94.71(4)
γ (°)	90.	90.
V (Å^3)	2 480	2 427
Z	4	4
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/a$	$P\ 2_1/n$
Linear absorption coefficient μ (cm^{-1})	0.63	0.64
Density ρ (g cm^{-3})	1.16	1.18
Diffractometer	Philips PW 1100	Philips PW 1100
Radiation	Mo$K\alpha$ (λ = 0.71069 Å)	Mo$K\alpha$ (λ = 0.71069 Å)
Scan type	$\omega/2\theta$	$\omega/2\theta$
Scan range (°)	0.9 + 0.345 tgθ	1.2 + 0.345 tgθ
θ limits (°)	2–25	2–25
Temperature of measurement	Room temperature	Room temperature
Octants collected	−29.28; 0.8; 0.17	−26.26; 0.19; 0.8
No of data collected	4 946	4 832
No of unique data collected	4 256	4 261
No of unique data used for refinement	1 784 $(Fo)^2 > 3\sigma(Fo)^2$	1 517 $(Fo)^2 > 3\sigma(Fo)^2$
R (int)	1.37	2.39
$R = \Sigma\|\|Fo\| - \|Fc\|\|/\Sigma\|Fo\|$	0.0489	0.0715
$Rw = \Sigma w(\|Fo\| - \|Fc\|)^2/\Sigma wFo^2$	0.0448 w = 1.0	0.0714 w = 1.0
Absorption correction	DIFABS (min = 0.87, max = 1.03)	DIFABS (min = 0.89, max = 1.15)
Extinction parameter ($\times 10^{-6}$)	371	64
Goodness of fit s	0.68	1.50
No of variables	291	291
$\Delta\rho$min (e Å^{-3})	−0.15	−0.25
$\Delta\rho$max (e Å^{-3})	0.17	0.24

agree well with each other but also with that for **7** (column 6), thus confirming the previous assignment and the additivity assumption.

Now we can average these three sets of values, which express the effect of the -CAd_2OH substituent, and calculate shifts for the *meta*-tolyl derivatives. In this way, for the *anti* isomer, **4A**, we obtain the increments given in column 8, and for the *syn* isomer, **4S**, those in column 10. Corresponding increments for the more stable isomer, associated with a methyl proton shift of 2.35 ppm (column 11) closely match those in column 10, leaving no doubt that this is the *syn* isomer. The agreement for the other isomer, associated with a methyl proton shift of 2.39 ppm, is not quite so good (compare columns 8 and 9). The root mean square value of the deviations is ±0.3 ppm, as against ±0.1 for the *syn* isomer, but is clearly consistent with this being the *anti* isomer. The previous identification of the *meta*-tolyl derivatives is therefore confirmed by this study.

Conclusions

By X-ray crystallography the rotameric *meta*-(*tert*-butyl)phenyldi(1- adamantyl)methanols associated with *tert*-butyl ^{1}H NMR shifts (in $CDCl_3$, relative to TMS) of 1.35 and 1.32 ppm have been identified as the *anti* and *syn* isomers, respectively, thus confirming the assignments based on analysis of their ^{1}H NMR spectra and analogy with previous work by Sternhell [4]. This is the first time that both members of a rotamer pair have been unambiguously characterized. This result also confirms the association of the methyl shifts of 2.35 and 2.39 ppm for the corresponding *meta*-tolyl derivatives with the *syn* and *anti* isomers, respectively.

The highly unusual feature of the structure of the *anti* isomer is its approximate C_s symmetry, while the *syn* isomer is dissymmetric, however, with the C–O bond approximately in the plane of the benzene ring. These features are in sharp contrast to previous findings on di(*tert*-butyl) analogues, where the C–O bond is something like 12° out of the ring plane. MM calculations reproduce this aspect of the geometry of *tert*-butyl derivatives correctly, but fail to foresee the different structure for the adamantyl derivatives in the crystalline state.

Experimental section

X-ray crystallography

Crystallographic data and other pertinent information concerning the compounds are summarized in table VII. Both structures were solved by the direct method (SHELXS86)

[17]. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, and hydrogens in calculated positions with one, overall, refined isotropic thermal parameter (291 refinable parameters). Absorption correction applied (DIFABS) [18]. Program used is the PC version of CRYSTALS [19] for refinements and CAMERON [20] for views.

Relevant NMR data (from reference [1], in ppm relative to TMS)

- meta-*(*tert*-Butyl)phenyldi(1-adamantyl)methanols*

3A: δ_H 1.35 (*t*-Bu); δ_C 147.6, 143.6, 126.7, 126.1, 124.9, 122.2 (aromatics). **3S**: δ_H 1.32; δ_C 149.8, 143.2, 125.7, 125.2, 124.8, 122.0.

- meta-*Tolyldi(1-adamantyl)methanols*

4A: δ_H 2.39 (Me); δ_C 144.0, 134.3, 129.2, 127.1, 126.6, 125.0 (aromatics). **4S**: δ_H 2.35; δ_C 143.7, 136.6, 128.6, 126.2, 125.6, 125.3.

- *Phenyldi(1-adamantyl)methanol* **7**

δ_C 143.9 (a), 128.4 (f), 127.9 (b), 127.3 (c), 125.7 (d), 125.3 (e).

- *(*tert*-Butyl)benzene*

δ_C 151.0 (*ipso*), 128.0 (*meta*), 125.4 (*para*), 125.2 (*ortho*).

- *Toluene*

δ_C 137.8 (*ipso*), 129.0 (*ortho*), 128.2 (*meta*), 125.3 (*para*).

Acknowledgment

We are grateful to JM Brégeault for helpful discussion and constructive criticism.

Supplementary material available

X-ray characterization data for compounds **3A** and **3S** including tables of final fractional coordinates, thermal parameters, bond distances and bond angles, calculated and observed structure factors (24 pages) have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK as Supplementary Publication No SUP 9404 and is available on request from the Document Supply Centre.

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