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## A Highly Strained Tertiary Alcohol: *anti*-Di(1-adamantyl)[2,5-di(isopropyl)phenyl]-methanol

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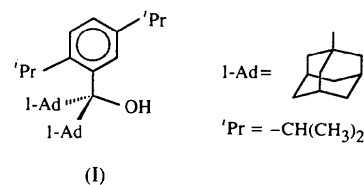
### Abstract

Steric interactions between the *ortho* isopropyl group and the adamantyl groups in the title compound, C<sub>33</sub>H<sub>48</sub>O, result in very large in-plane deformations of the benzene ring.

### Comment

Though other aryldi(*tert*-alkyl)methanols have been described, notably 3,4,5-trimethoxyphenyldi(*tert*-butyl)-

methanol (van Koningsveld & van Meurs, 1977), *syn*-4-methoxy-2-methylphenyldi(*tert*-butyl)methanol (Hough & Lomas, 1984) and, more recently, the *anti/syn* rotamer pair of 3-(*tert*-butyl)phenyldi(1-adamantyl)-methanol (Lomas & Vaissermann, 1996a), no *anti* rotamer bearing a substituent in the *ortho* position has been investigated. Though they are substantially less thermodynamically stable than the *syn* isomers, the *anti* isomers are the major product of the addition of *ortho*-alkyl-substituted phenyllithiums to bulky ketones (Lomas, Luong & Dubois, 1977). Rotamer interconversion is, moreover, very slow when large *tert*-alkyl substituents are present (Lomas & Dubois, 1981). We now report an X-ray study of the title compound, (I), the most sterically congested *anti-ortho*-substituted aryldi(*tert*-alkyl)methanol yet synthesized (Lomas & Vaissermann, 1996b).



The main features of this molecule are consistent with data from previous studies of aryldi(1-adamantyl)-methyl derivatives, notably the very large C101—C10—C201 angle subtended by the adamantyl (Ad) groups at the C—OH carbon and the long bonds to this C atom. In a di-1-adamantylmethane derivative, the corresponding bonds are substantially shorter (1.554 Å) but non-bonded interactions are reduced by opening of the Ad—C—Ad angle to 125.0° (Ermer & Bödecker, 1981). Though the C10—O11 bond is not far from the plane of the benzene ring, the two adamantyl groups are quite distinct; that which is further from the benzene plane, in terms of the torsion angles with respect to *ortho* C atoms, is approximately staggered with respect to the C1—C10 bond. The other is about 30° out of the staggered position. Both adamantyl groups are somewhat compressed, the mean of the internal angles at the quaternary C atoms, C101 and C201, being 106.6(10)°.

The benzene ring is normal as far as planarity is concerned (greatest deviation of any one C atom from the mean plane: 0.012 Å) but shows considerable deformation within the plane, notably, the rather long C1—C2 bond and internal angles ranging from 116.1(3) to 125.4(3)°. The external angles subtended by the pair of *ortho* substituents to C1 and C2 are also remarkably large and are comparable to those found in compounds bearing *ortho*-related pairs of *tert*-butyl groups (Stam, 1972; Watanabe, Kawashima, Tokitoh & Okazaki, 1995). Further deformation to reduce steric interaction between the *ortho*-isopropyl and the adamantyl groups includes lengthening of the C1—C10 bond. The

displacement ellipsoids are much larger for the 'free' isopropyl group than for the one constrained by the proximity of the adamantyl substituents.

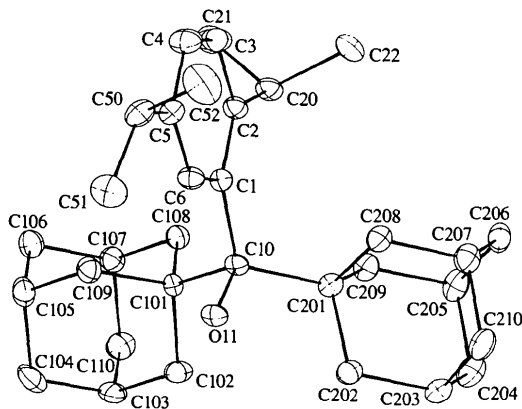


Fig. 1. CAMERON (Pearce, Watkin & Prout, 1996) diagram of the molecular structure of the title compound showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

## Experimental

The title compound was prepared by the reaction of 2,5-di(isopropyl)phenyllithium with di(1-adamantyl) ketone in diethyl ether (Lomas & Vaissermann, 1996b). Recrystallization was from acetone (m.p. 503–504 K).

### Crystal data

C<sub>33</sub>H<sub>48</sub>O

$M_r = 460.75$

Monoclinic

$P2_1/n$

$a = 11.081(3) \text{ \AA}$

$b = 15.147(8) \text{ \AA}$

$c = 15.668(8) \text{ \AA}$

$\beta = 96.14(3)^\circ$

$V = 2615(2) \text{ \AA}^3$

$Z = 4$

$D_x = 1.17 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 10.34\text{--}11.56^\circ$

$\mu = 0.06 \text{ mm}^{-1}$

$T = 203 \text{ K}$

Prismatic

$0.32 \times 0.26 \times 0.21 \text{ mm}$

Colourless

### Data collection

Enraf–Nonius CAD-4 diffractometer

$2\theta/\omega$  scans

Absorption correction: none

4938 measured reflections

4495 independent reflections

3081 reflections with

$I > \sigma(I)$

$R_{int} = 0.04$

$\theta_{max} = 25.0^\circ$

$h = -13 \rightarrow 13$

$k = 0 \rightarrow 17$

$l = 0 \rightarrow 16$

2 standard reflections

frequency: 60 min

intensity decay: 3.5%

### Refinement

Refinement on  $F^2$

$R = 0.088$

$wR = 0.089$

$(\Delta/\sigma)_{max} = 0.019$

$\Delta\rho_{max} = 0.49 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.27 \text{ e \AA}^{-3}$

$S = 1.141$

3081 reflections

309 parameters

H atoms not refined

Weighting by Chebychev polynomial (Carruthers & Watkin, 1979)

Extinction correction: Larson

[1970, equation (22)]

Extinction coefficient:

$1.3(5) \times 10^2$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C1—C2	1.414 (5)	C10—C101	1.617 (5)
C1—C10	1.588 (4)	C10—C201	1.617 (5)
C2—C1—C6	116.1 (3)	C1—C2—C3	118.0 (3)
C2—C1—C10	129.2 (3)	C1—C2—C20	129.6 (3)
C6—C1—C10	114.7 (3)	C3—C2—C20	112.4 (3)
C2—C1—C10—O11	177.3 (3)	C1—C10—C101—C109	-52.9 (3)
C2—C1—C10—C101	-72.6 (4)	C1—C10—C201—C202	146.0 (3)
C2—C1—C10—C201	66.5 (4)	C1—C10—C201—C208	29.7 (3)
C6—C1—C10—O11	-0.7 (4)	C1—C10—C201—C209	-92.0 (3)
C6—C1—C10—C101	109.4 (3)	C1—C2—C20—C21	121.3 (4)
C6—C1—C10—C201	-111.5 (3)	C1—C2—C20—C22	-114.9 (4)
C1—C10—C101—C102	-170.2 (3)	C6—C5—C50—C51	-16.5 (5)
C1—C10—C101—C108	66.6 (3)	C6—C5—C50—C52	108.7 (4)

H atoms were located in a  $\Delta\rho$  map and introduced in the final refinements with one overall refinable isotropic displacement parameter. The high  $R$  value is probably due to thermal agitation of the terminal C atoms of the isopropyl groups, in particular C51 and C52.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *RC93* (Watkin, Prout & Lilley, 1994). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996). Molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996). Software used to prepare material for publication: *CRYSTALS* and *PARST97* (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1450). Services for accessing these data are described at the back of the journal.

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## *N*-(*p*-Hydroxybenzylidene)phenylamine *N*-Oxide

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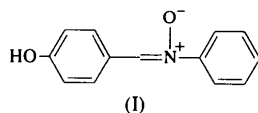
(Received 26 November 1996; accepted 10 April 1997)

### Abstract

The crystal structure of the title compound, C<sub>13</sub>H<sub>11</sub>NO<sub>2</sub>, confirms that it exists as a nitron. The geometry about C=N is *Z*. The torsion angles O8—N8—C7—H7 [174.55 (2)°] and C8—N8—C7—H7 [−0.89 (4)°] indicate the *trans* and *cis* positions around the nitron moiety.

### Comment

The title compound, (I), has been analysed as part of crystallographic studies on substituted *N*-phenylnitrones.



The molecule exists as a nitron. The C=N distance of 1.304 (3) Å is within 3σ of 1.279 (8) Å reported by Allen *et al.* (1987). The dihedral angle between the C8, N8, C7 and N8, C7, C1 planes is 2.61 (2)°. The nitron group formed by atoms C8, N8, C7 and C1 attached to two phenyl rings is nearly planar. Atoms N8, C8, C7 and C1 deviate from the least-squares plane by −0.008 (2), −0.013 (2), −0.017 (2) and −0.015 (2) Å, respectively. The C1—C7 distance of 1.440 (3) Å is nearly equal to the value of 1.438 (4) Å reported by Bedford, Chaloner & Hitchcock (1991). The phenyl

bond lengths and angles are in agreement with the expected values reported by Allen *et al.* (1987). The dihedral angle between the two phenyl rings is 55.3 (1)°.

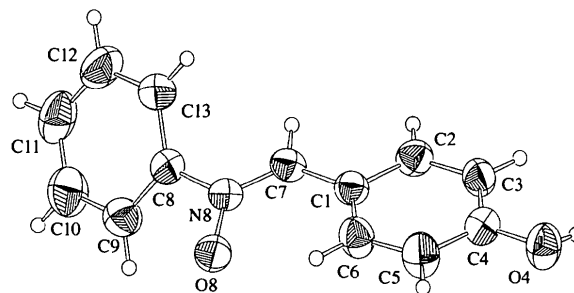


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

### Experimental

A solution of 4-hydroxybenzaldehyde (1.22 g) in ethanol (25 ml) was added dropwise with stirring to a solution of *N*-phenylhydroxylamine (1.09 g) in ethanol (10 ml). The mixture was warmed for about 1 h at 333 K. On cooling, crude crystals of the title compound separated and were recrystallized from ethanol [m.p. 487 K; yield 1.76 g (83%)]. The title compound was prepared in the Department of Industrial Chemistry, Alagappa University, Karaikudi, India.

### Crystal data

C<sub>13</sub>H<sub>11</sub>NO<sub>2</sub>  
M<sub>r</sub> = 213.23  
Orthorhombic  
*Pbca*  
a = 18.033 (9) Å  
b = 14.019 (9) Å  
c = 8.973 (5) Å  
V = 2269 (2) Å<sup>3</sup>  
Z = 8  
D<sub>x</sub> = 1.249 Mg m<sup>−3</sup>  
D<sub>m</sub> not measured

Mo Kα radiation  
λ = 0.7107 Å  
Cell parameters from 25 reflections  
θ = 5–25°  
μ = 0.085 mm<sup>−1</sup>  
T = 293 K  
Rectangular  
0.25 × 0.20 × 0.10 mm  
Yellow

### Data collection

Rigaku AFC-7S diffractometer  
ω–2θ scans  
Absorption correction:  
ψ scan (North, Phillips & Mathews, 1968)  
T<sub>min</sub> = 0.922, T<sub>max</sub> = 1.000  
1875 measured reflections  
1874 independent reflections  
843 reflections with  
I > 2σ(I)

R<sub>int</sub> = 0.032  
θ<sub>max</sub> = 24.87°  
h = 0 → 21  
k = 0 → 16  
l = −10 → 0  
3 standard reflections every 100 reflections  
frequency: 150 min  
intensity decay:  
negligible

### Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.035  
wR(F<sup>2</sup>) = 0.115

(Δ/σ)<sub>max</sub> = 0.048  
Δρ<sub>max</sub> = 0.127 e Å<sup>−3</sup>  
Δρ<sub>min</sub> = −0.117 e Å<sup>−3</sup>