

X-RAY, IR AND ¹H-NMR STRUCTURAL AND CONFORMATIONAL STUDY OF
HIGHLY CONGESTED 2-ALKYL-1,3-DIOLS AND OF 3-(1-ADAMANTYL)PENTANE-2,4-DIONE

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Abstract.— Configuration of *meso* diols produced by LiAlH₄ reduction of symmetric α-(1-adamantyl)-β-diketones has been determined by X-ray diffraction. Large C-C distances and C-C-C angles have been measured for these strained molecules. Most of the studied 1,3-diols, both *meso* and *d,l*, exist in solution in conformations possessing intramolecular hydrogen bond. The conformations of two diols were also studied in the crystal phase.

INTRODUCTION

Some of us have investigated the use of transition metal complexes of β-dicarbonyl compounds as substrates for C-alkylation. Co(II)¹ and Cu(II)² complexes have been particularly useful to prepare severely hindered diketones bearing bulky substituents at the central carbon atom (Ox). 3-(1-Adamantyl)-3-methylpentane-2,4-dione, **1**, (Fig. 1) prepared by copper mediated alkylation of 3-methylpentane-2,4-dione,² has two consecutive quaternary centers and therefore peculiar properties were expected both from the viewpoints of structure and reactivity. Some information about **1** is available. Thus, its conformational preferences in liquid phase are known^{1d} and its reaction with LiAlH₄ gives, in a highly diastereoselective manner, a *meso* diol of 3-(1-adamantyl)-3-methylpentane-2,4-diol general constitution, for which configuration at the central carbon atom could not be assigned on spectroscopic basis.³ A similar reduction of 3-(1-adamantyl)pentane-2,4-dione afforded two diols, one of them of the *meso* type. Again, configuration at the central carbon atom could not be assigned.³ Assignment of configuration to both *meso* diols was essential in order to understand the mechanism of the reduction of severely hindered diketones such as **1** and its demethyl congener.³ We wish to present in this paper the features of diketone **1** in solid phase, as well as to assign the configurations to both *meso* diols⁴ that were therefore identified as (2R,3R,4S)-3-(1-adamantyl)pentane-2,4-diol, **2a**, and (2R,3R,4S)-3-(1-adamantyl)-3-

methylpentane-2,4-diol, **3a**, by X-Ray diffraction. We have also performed a conformational analysis of compounds **1**, **2a** and **3a** in the solid state. In order to get more information on the conformational preferences of diols belonging to the **a** and **b** families, we have also registered variable concentration infrared spectra of the following products: **2a**, its (*2RS,4RS*) diastereoisomer **2b**, **3a**, (*2R,3r,4S*)-3-(1-adamantyl)-3-ethylpentane-2,4-diol, **4a**, (*2R,3r,4S*)- and (*2RS,4RS*)-3-*t*-butylpentane-2,4-diol, **5a** and **5b**, (*2R,3r,4S*)-3-cyclohexylpentane-2,4-diol, **6a**, and (*3R,4s,5S*)- and (*3RS,5RS*)-4-(1-adamantyl)-2,2,6,6-tetramethylheptane-3,5-diol, **7a** and **7b**. All diols (Fig. 1) have been previously described.³

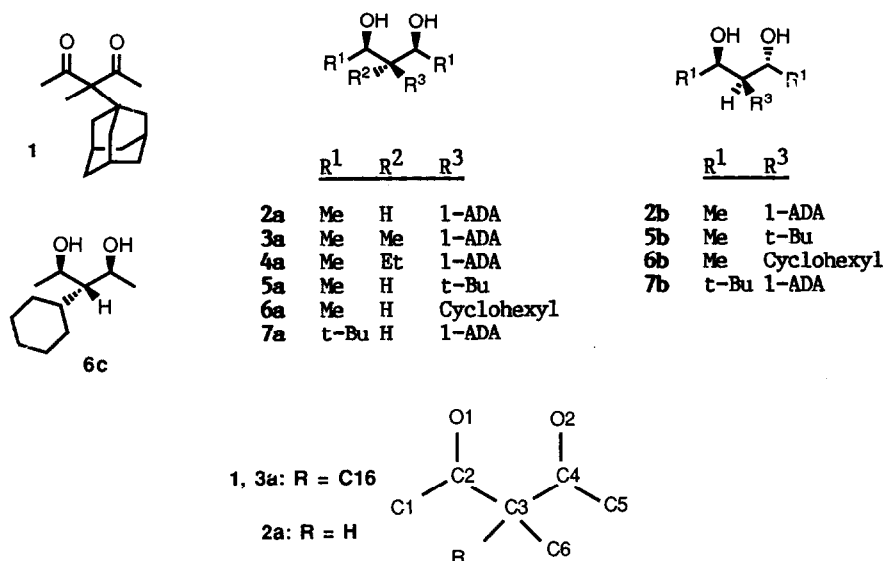


Figure 1.— Compounds **1–7** and Atomic Numbering for **1**, **2a** and **3a**

X-RAY STUDIES

Figure 1 contains the general crystallographic numbering for **1**, **2a** and **3a**. From the X-Ray diffraction study we have determined the configuration (*2R,3r,4S*) for **2a** and **3a** as depicted in figure 2. The pertinent bond distances and angles are collected in Tables 1 and 2. The steric hindrance present in **1** and in **3a** is reflected by bond length C3–C6 around 1.60 Å. The corresponding bond for the less strained diol **2a** is shorter (1.55–1.58 Å). Bond angles also show unusual values; thus, C4–C3–C6 is larger than 119° in diol **2a**. Angles C1–C2–C3 and C3–C4–C5, for a crystal conformation of **2a** and for both crystal conformations of **3a**, are close to 120°. These angle values are unusually large for carbon atoms in sp³ hybridization. Figure 2 contains representations of **1**, **2a** and **3a** made using the PC-PLUTO program.⁵

TABLE 1.- Selected Bond Distances for Compounds 1, 2a and 3a.^a

	1	2a (a, b, c and d)					3a (e and f)	
C1-C2	1.521(9)	1.525(8)	1.529(7)	1.513(9)	1.512(9)	1.524(8)	1.544(10)	
C2-C3	1.544(8)	1.550(7)	1.547(7)	1.562(8)	1.547(8)	1.557(8)	1.554(5)	
C3-C4	1.537(14)	1.533(8)	1.548(7)	1.555(8)	1.536(8)	1.584(7)	1.558(7)	
C4-C5	1.508(10)	1.524(9)	1.530(8)	1.521(9)	1.522(9)	1.533(6)	1.517(7)	
C3-C6	1.595(8)	1.577(7)	1.563(7)	1.552(7)	1.571(8)	1.608(8)	1.589(5)	
C3-C16	1.568(11)	-----	-----	-----	-----	1.550(6)	1.533(11)	
C2-O1	1.186(9)	1.447(6)	1.439(7)	1.422(7)	1.446(8)	1.445(6)	1.444(9)	
C4-O2	1.214(11)	1.430(7)	1.450(7)	1.431(7)	1.449(7)	1.441(4)	1.451(11)	

^a Four and two crystal conformations have been observed for 2a and 3aTABLE 2.- Selected Bond Angles for Compounds 1, 2a and 3a.^a

	1	2a (a, b, c and d)					3a (e and f)	
C1-C2-O1	119.0(5)	110.2(4)	108.3(4)	109.1(5)	108.5(5)	106.7(4)	108.6(4)	
C1-C2-C3	116.5(5)	116.3(4)	116.6(4)	117.1(5)	118.4(5)	119.4(5)	118.3(5)	
O1-C2-C3	124.4(6)	105.7(4)	106.1(4)	108.4(5)	109.1(5)	110.8(4)	109.2(4)	
C2-C3-C4	106.9(5)	110.4(4)	111.2(4)	113.5(5)	115.6(5)	103.5(3)	103.4(4)	
C2-C3-C6	114.0(5)	113.4(4)	112.8(4)	114.9(5)	113.1(4)	116.4(4)	115.9(3)	
C2-C3-C16	103.9(5)	-----	-----	-----	-----	105.1(4)	104.6(4)	
C3-C4-C5	120.9(8)	115.0(5)	113.1(5)	119.4(5)	118.9(5)	121.3(4)	120.6(5)	
C3-C4-O2	119.3(6)	111.1(4)	113.6(4)	106.3(5)	107.8(5)	112.4(4)	112.6(4)	
O2-C4-C5	119.8(9)	110.7(5)	107.1(4)	109.2(5)	107.1(5)	106.1(4)	105.1(6)	
C4-C3-C6	107.9(6)	119.1(4)	119.9(4)	117.7(5)	117.1(5)	115.5(4)	116.0(4)	
C4-C3-C16	112.5(5)	-----	-----	-----	-----	103.7(4)	104.3(4)	
C6-C3-C16	111.5(5)	-----	-----	-----	-----	111.3(4)	111.3(4)	

^a Four and two crystal conformations have been observed for 2a and 3a.TABLE 3.- Selected Torsion Angles for Conformations of 1, 2a and 3a.^a

	1	2a (a, b, c and d)					3a (e and f)	
C1-C2-C3-C4	-51.5(8)	-44.9(6)	44.7(6)	-49.5(7)	-39.6(7)	177.7(5)	-169.6(5)	
C1-C2-C3-C6	-170.7(6)	91.7(5)	-93.3(6)	90.0(6)	99.5(6)	49.8(7)	62.4(6)	
C1-C2-C3-X ^b	67.7(7)	-158.1(5)	156.4(6)	-160.6(6)	-148.5(6)	-73.8(6)	-60.6(6)	
O1-C2-C3-C4	132.8(8)	77.7(5)	-75.9(5)	74.4(6)	85.1(6)	53.1(5)	65.6(5)	
O1-C2-C3-C6	13.6(10)	-145.7(4)	146.0(4)	-146.1(5)	-135.9(5)	-74.8(6)	-62.5(5)	
O1-C2-C3-X ^b	-108.0(8)	-35.5(6)	35.8(7)	-36.6(7)	-23.8(7)	161.6(4)	174.5(4)	
C5-C4-C3-C2	135.9(7)	-140.8(5)	136.1(5)	80.1(7)	74.7(7)	154.9(5)	164.6(5)	
C5-C4-C3-C6	-101.0(8)	85.4(6)	-89.2(6)	-58.3(7)	-62.6(7)	-76.6(6)	-67.4(7)	
C5-C4-C3-X ^b	22.4(10)	-23.0(7)	18.4(7)	-166.6(6)	-173.0(6)	45.4(6)	55.4(7)	
O2-C4-C3-C2	-42.9(9)	92.5(5)	-101.5(5)	-43.9(6)	-47.3(6)	-78.1(5)	-70.3(5)	
O2-C4-C3-C6	80.2(9)	-41.3(6)	33.2(7)	177.7(5)	175.3(4)	50.4(5)	57.7(6)	
O2-C4-C3-X ^b	-156.3(7)	-149.7(5)	140.8(5)	69.5(6)	65.0(6)	172.4(4)	-179.5(5)	

^a Four and two crystal conformations have been observed for 2a and 3a.^b X = C16 for 1 and 3a; X = H for 2a.

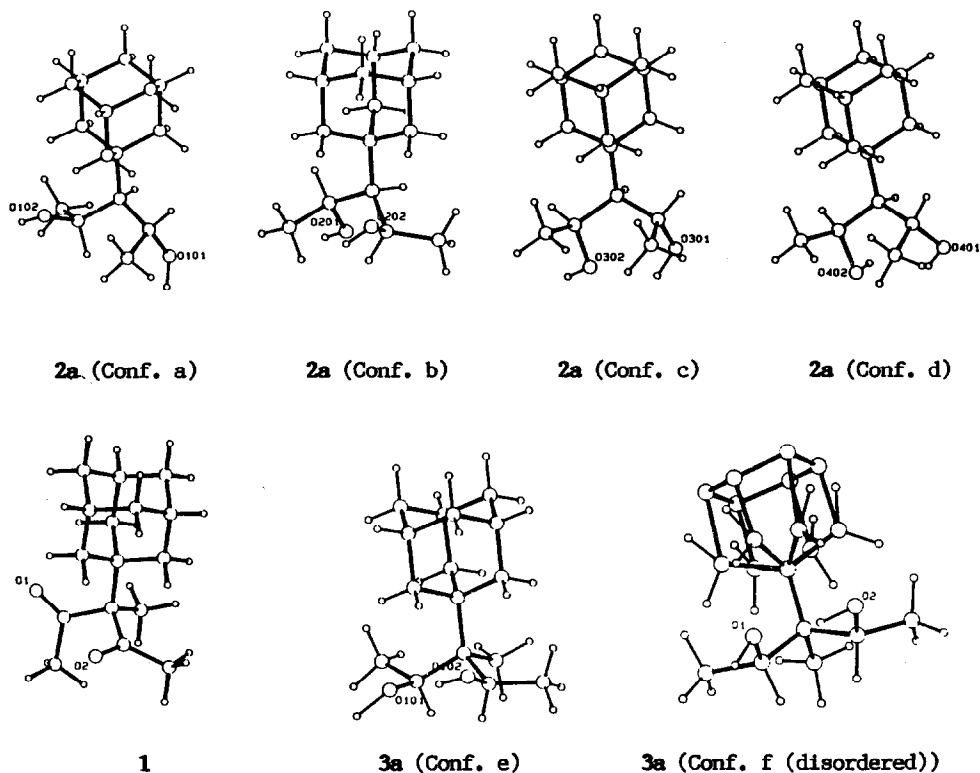


Figure 2.— Representations of **1**, **2a** and **3a** using PC-PLUTO program

A unique crystal conformation is observed for diketone **1**. The angle between the dipoles defined by both carbonyl groups is $75.1(6)^\circ$. Torsion angles C1–C2–C3–C4 and C2–C3–C4–C5 are respectively $-51.5(8)$ and $135.9(7)^\circ$. This compound presents three conformations in cyclohexane solution,^{1d} one of them having a high dipole moment and populated to an extent of 20%, and having values for the three parameters of 87.3, 29.6 and -128.3° . The other two populated conformations in solution are very different, having lower dipole moments. The high dipole moment conformation is the only one present in the crystal. The molecules of **1** are packed forming layers, perpendicular to the *c* axis, containing the carbonyl and adamantyl moieties (Fig. 3).

Diol **2a** has four molecules in the asymmetric unit with different conformations in the pentane-2,4-diol part of the molecule. Two of the conformations are approximately mirror images (a and b) and the two other are similar (c and d) (Fig. 2) as reflected in Table

3. The molecules of diol **2a** are linked by hydrogen bonds as described in Table 4.

Diol **3a** has two molecules in the asymmetric unit having similar conformations in the 2,4-diol part of the molecule (Table 3, e and f, and Fig 2). One of the molecules (f) presents disorder in the adamantyl radical. Peaks of residual electron density are localized in this part of the molecule (Table 5). The conformation of the open chain part of the molecule can be described as a deformed chair containing C102, C103, C104, O102-H and O101. The adamantyl group occupies an axial position on C103 but lacking 1,3-diaxial interactions. The three methyl groups are equatorial. The molecules of diol **3a** are linked by hydrogen bonds as described in Table 4.

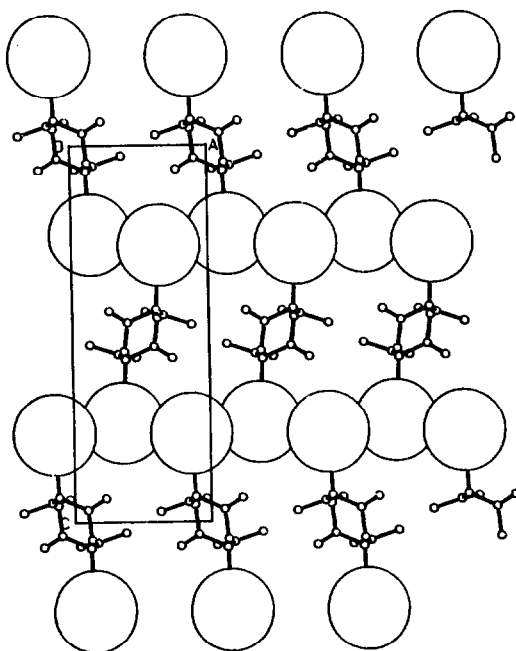


Figure 3.- Molecular Packing of Diketone 1. The circles represent adamantyl groups.

TABLE 4.- Hydrogen Bonding in **2a** and **3a**

Diol 2a

	d(O-O)	d(O-H)	d(H-O)	Angle OHO
O101-H...O402 (-x,-y+1,-z+1)	2.791(6)	1.02(7)	1.81(7)	160(6)
O101...H-O201 (x,y-1,z)	2.771(6)	1.91(7)	0.87(7)	170(7)
O102-H...O202	3.088(6)	0.82(8)	2.30(8)	163(7)
O201-H...O101 (x,y+1,z)	2.771(6)	0.87(7)	1.91(7)	170(7)
O201...H-O302 (-x+1,-y+2,-z+1)	2.734(6)	1.95(6)	0.84(6)	154(6)
O202-H...O401	2.793(6)	0.88(7)	2.00(7)	151(7)
O202...H-O102	3.088(6)	2.30(8)	0.82(8)	163(7)

0301-H...0302	2.648(7)	1.00(6)	2.04(5)	117(4)
0301...H-0402 (-x, -y+2, -z+1)	2.671(6)	1.74(6)	0.96(6)	163(5)
0302-H...0201 (-x+1, -y+2, -z+1)	2.734(6)	0.84(6)	1.95(5)	154(6)
0302...H-0301	2.648(7)	2.04(5)	1.00(6)	117(4)
0401-H...0402	2.924(6)	0.81(6)	2.28(6)	137(6)
0401...H-0202	2.793(6)	2.00(7)	0.88(7)	151(7)
0402-H...0301 (-x, -y+2, -z+1)	2.671(6)	0.96(6)	1.74(6)	163(5)
0402...H-0401	2.924(6)	2.28(6)	0.81(6)	137(6)
0402...H-0101 (-x, -y+1, -z+1)	2.791(6)	1.81(7)	1.02(7)	160(6)

Diol 3a

0101-H...02 (x, y+1, z)	2.757(9)	1.3(1)	2.0(1)	115(6)
0101...H-0102	2.667(5)	1.81(9)	1.0(1)	145(8)
0102-H...0101	2.667(5)	1.0(1)	1.81(9)	145(8)
0102...H-01 (-x+1/2, y+1/2, -z+1/2)	2.717(4)	1.59(8)	1.15(8)	166(11)
01 -H...0102 (-x+1/2, y-1/2, -z+1/2)	2.717(4)	1.15(8)	1.59(8)	166(11)
01...H- 02	2.623(6)	1.8(1)	1.0(1)	138(9)
02- H...01	2.623(6)	1.0(1)	1.8(1)	138(9)
02...H- 0101 (x, y-1, z)	2.757(9)	2.0(1)	1.3(1)	115(6)

TABLE 5.- Crystal Data for 1, 2a and 3a

	1	2a	3a
Formula	C ₁₆ H ₂₄ O ₂	C ₁₅ H ₂₆ O ₂	C ₁₆ H ₂₈ O ₂
Molecular weight	248.35	238.36	252.38
Crystal system	orthorhombic	triclinic	monoclinic
Space group	Pc2 ₁ n (33)	P-1 (2)	C2/c (15)
a (Å)	6.638(1)	11.631(1)	27.952(3)
b (Å)	11.224(4)	13.210(3)	14.855(2)
c (Å)	18.438(2)	17.594(2)	18.308(5)
α	90	92.73(1)	90
β	90	90.83(1)	130.22(2)
γ	90	90.20(1)	90
V (Å ³)	1373.7(6)	2699.9(7)	5805(3)
D _c (g/cm ³)	1.201	1.173	1.156
Z	4	8	16
μ (mm ⁻¹)	0.07	0.07	0.07
F(000)	544	1056	2240
Unique reflections	1210	9472	4688
Observed reflections (I ≥ 2.5 σ(I))	732	2905	3607
hkl range	0/7, 0/13, 0/21	-13/13, -15/15, 0/20	-33/33, 0/17, 0/21
R	0.046	0.051	0.112
R _w	0.052	0.055	0.162
w = 1/(σ ² (F) + kF ²)	0.00726	0.00490	0.24446
Parameters	163	639	365
Residual electron density (e · Å ⁻³)	0.15/-0.21	0.18/-0.21	0.54/-0.50

IR AND ¹H-NMR STUDIES

Stereochemistry of meso-diols **2a** and **3a** was determined by X-Ray diffraction. However, this was not done for **4a-7a**. Although assignment of the same stereochemistry to **4a-7a** as for **2a** and **3a** is more palatable than assignment of the opposite one, we decided to examine the behaviour of all meso-diols by a common technique to check whether the responses were similar or not.

Variable concentration IR studies have been applied to determine the presence of intra and intermolecular hydrogen bonds. This is a useful technique in conformational analysis of 1,3-difunctional compounds bearing -OH and -NHR groups.⁶

IR Spectra of diols **2a-7a**, **2b**, **5b** and **7b** were registered in 0.2M solutions in CDCl₃ and in 0.02M solutions in CDCl₃/CCl₄ (1:5) (Table 6). Meso-diols **2a-6a** behave similarly. At 0.2M concentrations two rather sharp peaks (Fig. 4) are observed. The higher frequency corresponds to the free O-H group and the lower one corresponds to the intramolecularly associated O-H. A shoulder at even lower frequencies is an evidence for some molecules being engaged in intermolecular hydrogen bonds. The shoulder is no longer present in the IR spectra registered at 0.002M concentrations, the two sharp peaks remaining instead (Table 6). This similar behaviour supports that all compounds **2a-6a** have the same stereochemistry. For compounds **2a**, **5a** and **6a** the coupling constants -CH(OH)-CHR³- were in the range 3-4 Hz. All the above data suggest that compounds **2a-6a** have the same stereochemistry and exist predominantly in a conformation having intramolecular hydrogen bond and gauche -CH(OH)-CR²R³- dihedral angles. This is fulfilled by conformations C and E (Fig. 5). The available experimental data do not permit any further decision. However, conformation E presents a destabilizing Me-Me 1,3-diaxial interaction, not present in conformation C. Therefore, products **2a-6a** most probably exist predominantly in conformation C. This conformation is the only found for **3a** in the crystal phase. On the other hand, compound **2a** has, in the crystal, one conformation close to E (c and d of Fig. 2), presenting also conformations not detected in liquid phase: B and D (b and a respectively in Fig. 2)

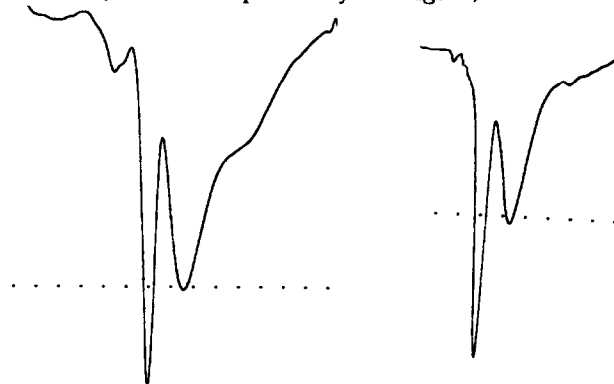


Figure 4.- IR Spectra of Compound **2a** at 0.02 and 0.002M Concentrations.

TABLE 6.- IR^a and 1H-NMR Data of Diols 2a-7a, 2b, 5b-7b and 6c.

			O-H stretching				
R ¹	R ²	R ³	0.2M	0.02	0.002	J(-CH(OH)-CHR ³ -)	
2a	Me	H	1-ADA	3616, 3506	3622, 3538	3623, 3552	3.09
3a	Me	Me	1-ADA	3620, 3506	3625, 3530	-----	-----
4a	Me	Et	1-ADA	3614, 3494	3624, 3498	-----	-----
5a	Me	H	t-Bu	3617, 3505	3626, 3546	-----	3.24
6a	Me	H	c-C ₆ H ₁₁	3616, 3474	3625, 3525	-----	4.07
7a	t-Bu	H	1-ADA	3624	3629	-----	2.4
2b	Me	H	1-ADA	3618, 3518	3626, 3556	3624, 3567	1.26, 1.98
5b	Me	H	t-Bu	3621, 3531	3627, 3547	-----	1.80, 2.89
6b	Me	H	c-C ₆ H ₁₁	not studied			2.19, 6.17
7b	t-Bu	H	1-ADA	3634, 3611	3639, 3611	-----	< 1.0
				3551	3578	-----	
6c	Me	H	c-C ₆ H ₁₁	not studied			6.44

a ± 2 cm⁻¹; b solutions in CDCl₃ for 0.2 M concentrations and in CDCl₃:CCl₄ (1:5) for all other concentrations.

Diol 7a exhibits a different behaviour. Thus, only a sharp O-H stretching absorption at ca. 3626 cm⁻¹ is observed in all the concentration range. Therefore, no intramolecular hydrogen bond is present. Also, a coupling constant of 2.4 Hz rules out conformations such as A (and H) and F (and I) (Fig. 5). In summary, assuming the same stereochemistry for 7a as for 2a-6a, it exists in the enantiomeric conformations B and D. The presence of two gauche 1-adamantyl-t-butyl interactions in B and E renders these conformations less stable despite of the hydrogen bond in E.

The d,l-diols 2b and 5b exist predominantly in conformation C (Fig. 6), the only one presenting intramolecular hydrogen bond and two gauche -CH(OH)-CHR³-coupling constants. Compound 6b was not studied by IR spectroscopy since a pure sample was not available.³ However, its 1H-NMR behaviour (Table 6) points out to a general trend already insinuated in the series 2a, 5a, 6a. Thus, the coupling constant increases as the size of R³ decreases. d,l-Diol 6b exists probably in an equilibrium between hydrogen bond forming conformations C and E. In E a coupling constant is of the axial-axial type (ca. 12 Hz). One of the observed coupling constants (6.17 Hz) should be an averaged value between a gauche and an anti situations (conformations C and E).

Diol 7b presents two sharp peaks at 3634 and 3611 cm⁻¹ as well as a third peak somehow broader at 3551 cm⁻¹. It is difficult to explain this fact but in any case conformations close to C account for both the IR data and the observed coupling constants, that are very close to zero.

Diols 6a and 6b were formed³ together with a third diol exhibiting only a methyl doublet. On this basis it is assigned the structure (2R,3S,4S)-3-cyclohexyl-3-methylpentane-2,4-diol, 6c. This product shows a -CH(OH)-CHR³- coupling constant of 6.44 Hz, quite apart from the range 3-4 Hz observed for 2a-6a, thus giving further support for the idea that compounds 2a-6a belong to the same stereochemical family.

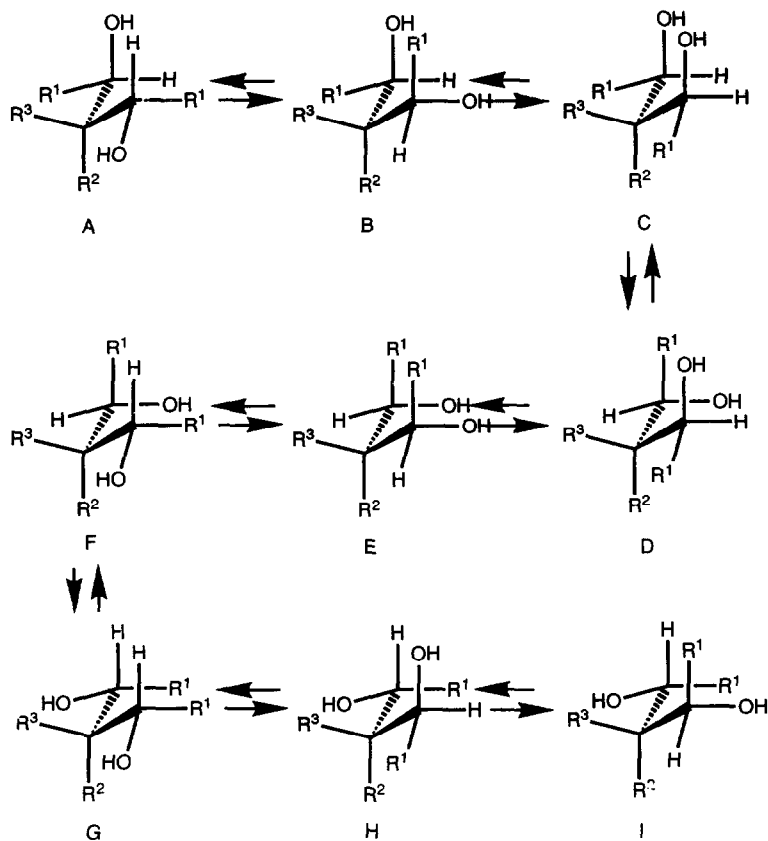


Figure 5.— Conformers of meso-diols **2a-7a**. Pairs B/D; A/H; and F/I are enantioisomeric. C, E and G are meso conformers

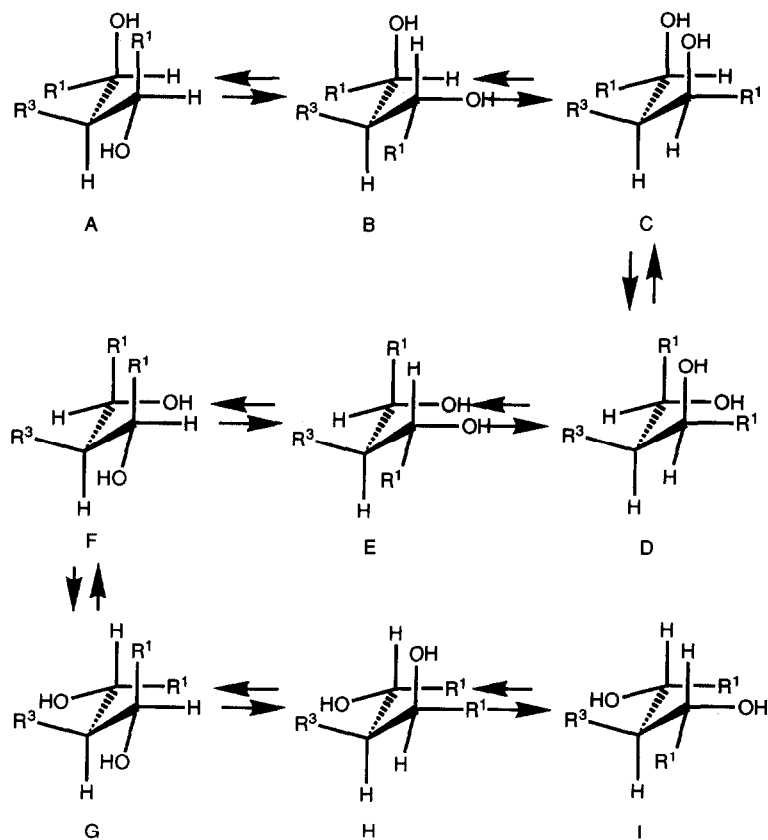


Figure 6.— Conformers of d,l diols **2b** and **5b-7b**. Only one enantiomer is shown.

EXPERIMENTAL PART

X-Ray structure analysis. Suitable monocrystals were grown from dichloromethane-hexane solutions and mounted on an Enraf-Nonius CAD4 diffractometer. Graphite monochromated Mo-K α radiation, ($\lambda = 0.71069$ Å) was used. Lattice parameters were obtained from least-squares refinement of 25 well centered reflections. Intensity measurements were done at room temperature using the $\omega/2\theta$ scan technique. Standard reflections monitored every 200 measurements showed no significant decay. Lorentz and polarization corrections were applied but no absorption corrections were made. The structures were solved by direct methods using the SHELXS⁷ program and were refined anisotropically by the least-squares method.⁸ The atomic scattering factors were taken from the International Tables for X-Ray Crystallography. The full matrix method was used for **1** and **3a**; block matrix was used for **2a** because of the great number of parameters to be refined. The positions of all hydrogen atoms bound to carbon were calculated and refined with an overall isotropic temperature factor. The hydrogen atoms bound to oxygen were located in Fourier difference maps and refined with a different overall isotropic temperature factor. The full set of coordinates, anisotropic thermal parameters and additional geometrical data have been deposited at the Cambridge Crystallographic Data Centre.

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