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Kiyoshi Matsumoto[a]; Mitsuo Toda[b]; Naoto Hayashi[a]; Jong Chul Kim[a]; Akikazu Kakehic[c]
[a] Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan [b] Faculty of Engineering, Shizuoka University, Hamamatsu, Japan [c] Faculty of Engineering, Shinshu University, Nagano, Japan

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Conformational Stability of 2,2′-Dialkoxybenzpinacols in Solid State

KIYOSHI MATSUMOTO[a,*], MITSUO TODA[b], NAOTO HAYASHI[a], JONG CHUL KIM[a] and AKIKAZU KAKEHI[c]

[a]*Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan;* [b]*Faculty of Engineering, Shizuoka University, Hamamatsu 432-8561, Japan;* [c]*Faculty of Engineering, Shinshu University, Nagano 380-8553, Japan*

X-ray analyses of the 2,2′-dialkoxybenzpinacols have established that the previously tentative assignment of configuration is incorrect. For example, the *dl*- and *meso*-isomer of 2,2′-dimethoxy-, 2,2′-diethoxy-, and 2,2′-dibutoxybenzpinacols proved to have a rigid conformation (1aα, 1bα, 1cα) and (1aβ, 1bβ, 1cβ) where hydroxy groups are always in an *anti* fashion, in the solid state, respectively. MM2 and semi-empirical molecular orbital calculations for possible conformations were performed, suggesting that the conformational stability of the present pinacols is controlled by repulsive *gauche* interactions between aryl groups associated with intramolecular hydrogen bondings.

Keywords: Pinacol; X-ray analysis; Conformational analysis MO calculations

INTRODUCTION

Twenty years ago, with the object of studying the effect of ortho-substituent and configuration upon the mechanism of pinacol rearrangement, several 2,2′-disubstituted benzpinacols were synthesized [1]. The 2,2′-dialkoxybenzpinacol, which is usually obtained as a mixture of *meso*- and *dl*-isomer in comparable proportion, was successfully separated into each isomer by means of column chromatography. Tentative assignment of configuration was made based upon the results obtained by the relative reaction rates with $Pb(OAc)_4$, IR spectra, and classical NMR spectra [2]. Assuming this configuration of *dl*- and *meso*-2,2′-dialkoxybenzpinacols, the kinetics and mechanism of these pinacols were intensively studied [3]. A recent report by Toda *et al.* on pinacol rearrangement in the solid state [4] has prompted us to reinvestigate pinacol rearrangement of the title compounds in the solid state. Before starting this project, it might be essential to learn the molecular and crystal structures and conformational properties of the title compounds. This is the subject of the present communication.

RESULTS AND DISCUSSION

There are an infinite number of conformations (around the C1—C2 bond) in acyclic 1,2-diols such as ethylene glycol and 1,2-dimethoxyethane for which an *ab initio* molecular orbital conformational analysis has been reported [5].

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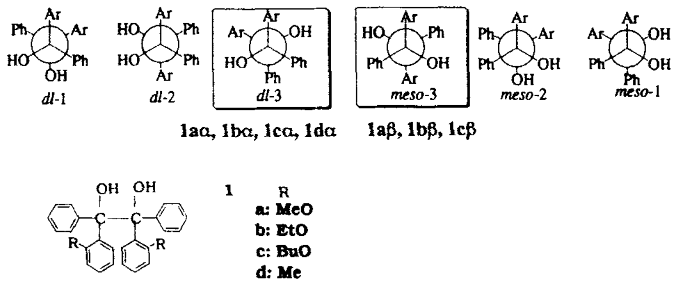
*Corresponding author.

The 1,2-dihalogenoethanes, XCH_2-CH_2X, and a variety of other substituted ethanes are found as mixtures of *anti* and *gauche* conformers in the liquid and gas phases, but only *anti* in the crystal [6]. In contrast, both the pure *gauche* and *anti* conformers of 1,1,2,2-tetrachloro- and tetrabromoethane have been isolated in the solid [7]. This does not seem to be so in the present case even in solution, probably because 2,2′-dialkoxybenzpinacols are highly crowded based upon an inspection of their molecular models and their NMR and IR spectral analyses [2].



SCHEME 1

TABLE I Crystal data for *dl*- and *meso*-2,2′-dimethoxybenzpinacols **1aα**, **1aβ**

Formula	$C_{28}H_{26}O_4$	
Crystal dimensions (mm)	0.060 × 0.280 × 0.420	0.200 × 0.440 × 0.620
M(amu)	426.51	
Space group	$P\bar{1}$(no.2), triclinic	$P2_1/a$ (no.14), monoclinic
a (Å)	10.09 (2)	16.084 (2)
b (Å)	18.92 (1)	8.445 (3)
c (Å)	6.164 (4)	16.860 (3)
α/deg.	96.88 (5)	90
β/deg.	99.3 (1)	91.34 (1)
γ/deg.	75.9 (1)	90
U (Å^3)	2526 (3)	2289.3 (9)
Z	2	4
D_c (g cm^{-3})	1.262	1.237
μ(cm^{-1})	0.78	0.76
F (000)	454	904
Radiation Mo-Kα graphite monochromatized	$\lambda = 0.71069$ Å	
Diffratometer	Rigaku AFC5S	
Orienting reflections, range	$19.91° < 2\theta < 35.84°$	$24.95° < 2\theta < 35.24°$
T (K)		293
Scan method	$\omega-2\theta$	
Data collection range	$6.0° < 2\theta < 55.3°$	
No. unique reflections	4462	4896
No. of observed reflextions with $I > 2\sigma(I)$	1821	1769
No. of parameters	289	320
R[a]	8.9%	6.7%
R_w[b]	9.3%	6.6%
Largest shift/esd, final cycle	0.05	0.00
Largest positive peak(e Å^{-3})	0.28	0.27
Largest negative peak(e Å^{-3})	−0.41	−0.27

Weighting scheme: $w = 4F_0^2/\sigma^2(F_0^2)$.

[a] $R = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|$.

[b] $R_w = \{[\Sigma w(|F_o| - |F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{1/2}$.

TABLE II Crystal data for *dl*- and *meso*-2,2′-dimethoxybenzpinacols **1bα**, **1bβ**

Formula	$C_{30}H_{30}O_4$	
Crystal dimensions (mm)	0.220 × 0.180 × 0.460	0.100 × 0.460 × 0.720
M(amu)	454.56	
Space group	$P2_1/c$(no.14), monoclinic	$P2_1/a$ (no.14), monoclinic
a (Å)	15.106 (8)	16.284 (3)
b (Å)	8.879 (8)	8.539 (4)
c (Å)	18.599 (6)	19.234 (4)
α/deg.	90	90
β/deg.	94.02 (3)	114.27 (1)
γ/deg.	90	
U (Å^3)	2489 (3)	2438 (1)
Z	4	4
D_c (g cm^{-3})	1.213	1.238
μ(cm^{-4})	0.74	0.76
F (000)	968	968
Radiation Mo-Kα graphite monochromatized	$\lambda = 0.71069$ Å	
Diffratometer	Rigaku AFC5S	
Orienting reflections, range	$22.47° < 2\theta < 34.73°$	$24.46° < 2\theta < 36.27°$
T (K)	297	
Scan method	$\omega - 2\theta$	
Data collection range	$6.0° < 2\theta < 55.3°$	
No. unique reflections	5723	5986
No. of observed reflextions with $I > 2\sigma$(I)	1514	1852
No. of parameters	307	340
R^a	7.7%	7.2%
$R_w{}^b$	7.6%	6.9%
Largest shift/esd, final cycle	0.03	0.00
Largest positive peak(e Å^{-3})	0.26	0.38
Largest negative peak(e Å^{-3})	−0.26	−0.26

Weighting scheme: $w = 4F_0^2/\sigma^2(F_0^2)$.

[a] $R = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|$.

[b] $R_w = \{[\Sigma w(|F_o| - |F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{1/2}$.

The X-ray analyses of the 2,2′-dialkoxybenzpinacols **1a–c** have established that they take only one conformation in each *dl*- and *meso*-isomer in the solid state, the previously tentative assignment of configuration being proven unfortunately *incorrect* [2]. For example, the *dl*- and *meso*-isomer of 2,2′-dimethoxy-, 2,2′-diethoxy- and 2,2′-dibutoxybenzpinacols proved to have a rigid conformation (**1aα**, **1bα**, **1cα**) and (**1aβ**, **1bβ**, **1cβ**), respectively (Scheme 1). In the case of 2,2′-dimethylbenzpinacol **1d**, only the *dl*-isomer **1d**α was isolated in our hands, the reason being not yet clear. Their crystal data are summarized in Tables I–IV. Their molecular and crystal structures are depicted in Figure 1. It is interesting to note that the hydroxy group is always at the *anti* position in these isomers. This is not surprising because, in the isomers (***dl*-1**, ***dl*-2**, ***meso*-1** and ***meso*-2**), there are severely repulsive *gauche* interactions [8] between *four* aromatic rings, whereas the isomers (***dl*-3** and ***meso*-3**) have a pair of *gauche* interactions between two aromatic rings. An inspection of the ORTEP drawings (Fig. 1) shows that there exist *intramolecular* hydrogen bondings between hydroxy hydrogen and ether oxygen at the δ position (that is, the interacting Ar and OH groups are bonded in a *geminal* fashion) which forms a cyclic six-membered structure (Scheme 2). Alternatively, there can exist a similar hydrogen bonding at the ε position (that is, the interacting Ar and OH groups are connected in a *vicinal* fashion) that would form a seven-membered ring, being more unfavorable than those at the δ

TABLE III Crystal data for *dl*- and *meso*-2,2′-dimethoxybenzpinacols **1cα**, **lcβ**

Formula	$C_{34}H_{38}O_4$	
Crystal dimensions (mm)	0.320 × 0.740 × 1.000	0.440 × 0.660 × 1.000
M(amu)	510.67	
Space group	$P\bar{1}$(no.2), triclinic	$P\bar{1}$(no.2), triclinic
a (Å)	11.268 (3)	12.180 (5)
b (Å)	13.495 (8)	13.602 (6)
c (Å)	9.818 (2)	9.592 (2)
α/deg.	94.16 (2)	99.93 (3)
β/deg.	103.91 (2)	104.84 (2)
γ/deg.	87.60 (2)	69.39 (3)
U (Å^3)	1444.8 (6)	1431.9 (9)
Z	2	2
D_c (g cm^{-3})	1.174	1.184
μ(cm^{-1})	0.70	0.71
F (000)	548	548
Radiation Mo-Kα graphite monochromatized	$\lambda = 0.71069$ Å	
Diffratometer	Rigaku AFC5S	
Orienting reflections, range	$38.08° < 2\theta < 39.76°$	$38.21° < 2\theta < 40.00°$
T (K)	293	
Scan method	$\omega - 2\theta$	
Data collection range	$6.0° < 2\theta < 55.0°$	
No. unique reflections	6646 ($R_{int} = 0.016$)	6604 ($R_{int} = 0.024$)
No. of observed reflextions with $I > 2\sigma(I)$	3899	4116
No. of parameters	343	343
R[a]	6.8%	7.4%
R_w[b]	8.1%	8.9%
Largest shift/esd, final cycle	0.01	3.16
Largest positive peak(e Å^{-3})	0.23	0.64
Largest negative peak(e Å^{-3})	−0.29	−0.62

Weighting scheme: $w = 4F_0^2/\sigma^2(F_0^2)$.

[a] $R = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|$.

[b] $R_w = \{[\Sigma w(|F_o| - |F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{1/2}$.

position, and consequently this was not the case (Scheme 2). In the case of ***meso*-3**, 2-akoxyphenyl groups are at an anti conformation, thus reducing steric hindrance, through the hydrogen bonding between alkoxy oxygen and hydroxy hydrogen atoms described above, due to alkyl moieties of alkoxy substituents, whereas this is not the case for ***meso*-1** and ***meso*-2**. From an inspection of the crystal structures in Figures 1–3, no *intermolecular* hydrogen bondings seem to be important.

Finally, MM2 and semi-empirical molecular orbital calculations [9] were carried out. For ***dl*-3** and ***meso*-3**, geometry optimizations were performed for the conformations obtained by X-ray analyses, while, in other isomers (***dl*-1**, ***dl*-2**, ***meso*-1**, ***meso*-2**), the calculations were done for a variety of possible conformations (for each of the rigid staggered conformations shown in Scheme 1, taking into account such hydrogen bondings as OH—OH, RO—HO, *et al.*) and the values of heat of formation were taken from the most stable geometries. Some of the results are summarized in Tables V–IX.

The results of MM2 calculations are always in agreement with the experimentally obtained conformations (***dl*-3**, and ***meso*-3**), confirming that *gauche* interactions between aryl groups are most important in impeding the conformational stability of the present pinacols; dihedral energy contributions were larger than those of hydrogen bonding. Semi-empirical MO calculations were also, in most cases but *not always*, in agreement with the experimentally obtained

TABLE IV Crystal data for *dl*-2,2′-dimethoxybenzpinacol **1dα**

Formula	$C_{28}H_{26}O_2$
Crystal dimensions (mm)	0.340 × 0.660 × 0.800
M(amu)	394.51
Space group	$P\bar{1}$ (no.2) triclinic
a (Å)	10.642 (2)
b (Å)	12.028 (2)
c (Å)	9.935 (4)
α/deg.	106.88 (2)
β/deg.	102.71 (3)
γ/deg.	110.68 (2)
U (Å^3)	1062.1 (6)
Z	2
D_c (g cm^{-3})	1.234
μ(cm^{-4})	0.71
F (000)	420
Radiation Mo-Kα graphite monochromatized	$\lambda = 0.71069$ Å
Diffratometer	Rigaku AFC5S
Orienting reflections, range	39.6° $< 2\theta <$ 40.0°
T (K)	293
Scan method	$\omega - 2\theta$
Data collection range	6.0° $< 2\theta <$ 55.0°
No. unique reflections	4863 ($R_{\text{int}} = 0.019$)
No. of observed reflextions with $I > 2\sigma$(I)	3230
No. of parameters	271
R^a	6.1%
$R_w{}^b$	7.4%
Largest shift/esd, final cycle	0.03
Largest positive peak(e Å^{-3})	0.35
Largest negative peak(e Å^{-3})	−0.39

Weighting scheme: $w = 4F_0^2/\sigma^2(F_0^2)$.
[a] $R = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|$.
[b] $R_w = \{[\Sigma w(|F_o| - |F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{1/2}$.

conformations. This may not be strange because there are a variety of conformations associated with intramolecular hydrogen bonding in the hypothetical conformations (***dl*-1**, ***dl*-2**, ***meso*-1**, ***meso*-2**) that would contribute the stabilization energy term in MO calculations. 2,2′-Dimethylbenzpinacol **1d**, which cannot participate in RO—HO hydrogen bonding, takes exclusively **1dα** conformation, although no *meso*-isomer was isolated in our hands. Thus, semi-empirical MO calculations of **1d** predicted the ***dl*-3** isomer (and ***meso*-3** isomer) to be most unstable, in contrast with the results of the MM2 calculations, presumably because *gauche* hydrogen bondings are important in the conformations ***dl*-1** and ***dl*-2** (***meso*-1** and ***meso*-2**). For comparison, the results of semi-empirical MO calculations of 4,4′-dimethoxybenzpinacol, which cannot participate in RO—HO hydrogen-bonding, are shown in Table IX, again suggesting that repulsive *gauche* interactions are most important since the ***dl*-3** and ***meso*-3** isomers are estimated to be most stable even if hydroxy groups are constrained in an *anti* manner; no intramolecular hydrogen bond is contributed in calculations. Furthermore, in agreement with this, MINDO/3 and MNDO calculations in which no hydrogen-bonding contributions are believed to be reproduced, qualitatively better predict, in irony but naturally, the experimental results shown in Tables V–VII.

Further studies on pinacol rearrangement of the title compounds in the solid state under Toda conditions [4, 10], along with their

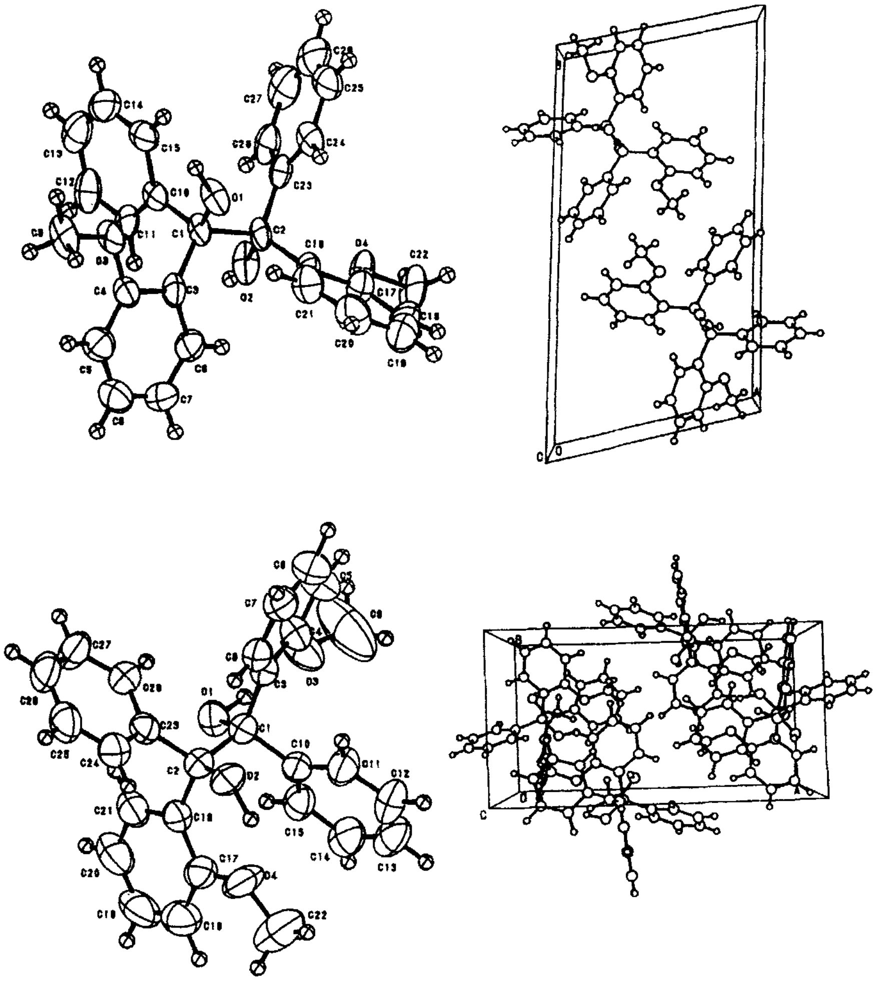
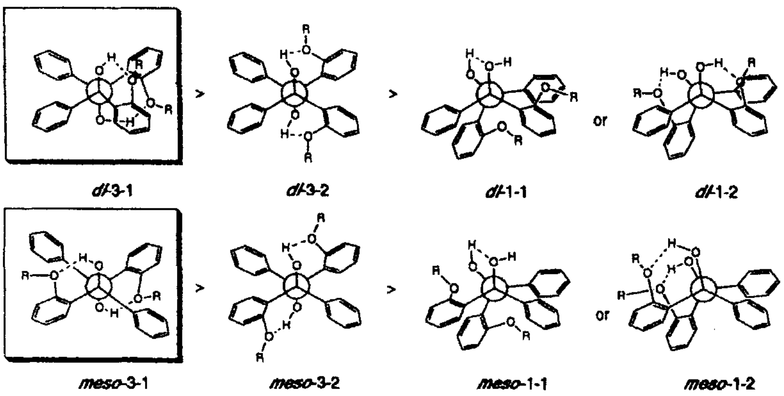


FIGURE 1 Molecular and crystal structure of *dl*- and *meso*-2,2′-dimiethoxybenzpinacols **1aα**, **1aβ**; above: **1aα**, below: **1aβ**.



SCHEME 2

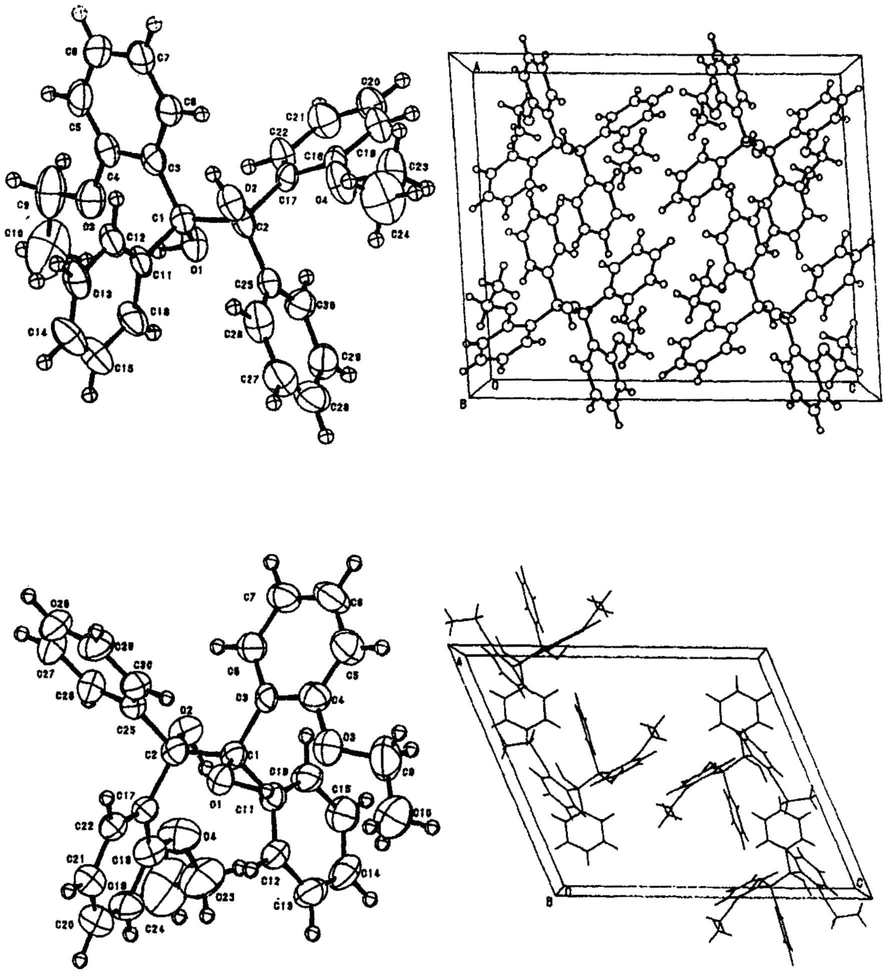


FIGURE 2 Molecular and crystal structure of *dl*- and *meso*-2,2′-dimethoxybenzpinacols **1bα**, **1bβ**; above: **1bα**, below: **1bβ**.

inclusion properties [11] and packing motifs [12], are in progress and will be reported in due course.

EXPERIMENTAL SECTION

Preparation and separation, along with their physical data, of the 2,2′-dialkoxybenzpinacols **1a–c** into each *dl*- and *meso*-isomer by means of column chromatography, have been described previously [2].

Crystal Structure Determination

Summaries of the crystal data and structure refinement details are given in Tables I–IV. The structure was solved by a direct method [13], and refined by full-matrix least squares. The atoms other than hydrogen were refined anisotropically. The atomic scattering factors for all atoms and the anomalous dispersion correction factors for atoms other than hydrogen were taken from the literature [14–16]. All calculations were performed using the TEXSAN [17]

TABLE V Calculated heat of formation (kcal/mol) of *dl*- and *meso*-2,2′-dimethoxybenzpinacol **1a**

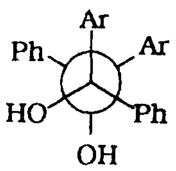
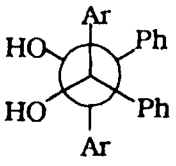
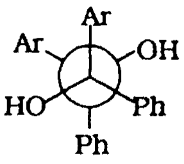
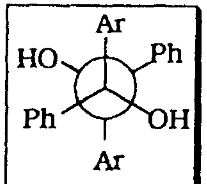
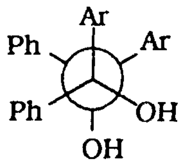
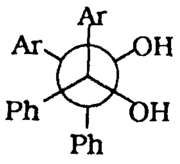
	dl-**1a**			*meso*-**1a**		
						
Method	***dl*-1**	***dl*-2**	***dl*-3**	***meso*-3**	***meso*-2**	***meso*-1**
MM2	−23.319	−19.247	−29.755	−26.526	−21.597	−20.564
AM 1	−30.449	−32.153	−38.926	−34.595	−32.399	−34.319
PM3	−27.187	−25.809	−34.591	−28.156	−30.247	−24.531
MINDO/3	15.583	6.916	−5.534	−2.499	1.884	4.574
MNDO	4.772	7.953	−6.225	3.239	4.920	8.435

TABLE VI Calculated heat of formation (kcal/mol) of *dl*- and *meso*-2,2′-dimethoxybenzpinacol **1b**

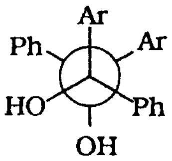
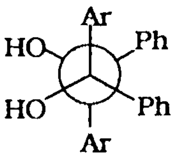
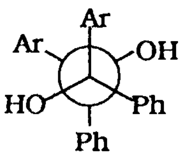
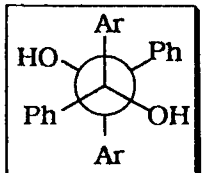
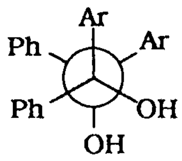
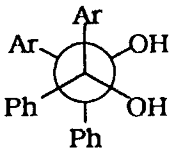
	dl-**1b**			*meso*-**1b**		
						
Method	***dl*-1**	***dl*-2**	***dl*-3**	**meso-3**	***meso*-2**	***meso*-1**
MM2	−20.491	−19.208	−30.306	−27.874	−24.698	−19.346
AM 1	−40.974	−44.095	−49.779	−45.797	−44.623	−45.652
PM3	−40.415	−35.257	−46.207	−40.590	−41.201	−42.085
MINDO/3	−11.202	1.321	−19.615	−19.099	−11.139	−3.212
MNDO	8.825	−1.059	−14.178	−9.873	−7.414	−5.026

TABLE VII Calculated heat of formation (kcal/mol) of *dl*- and *meso*-2,2′-dimethoxybenzpinacol **1c**

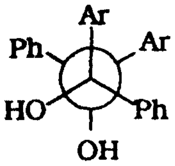
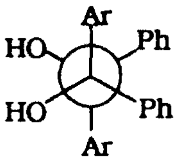
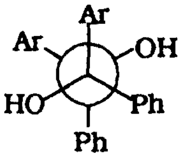
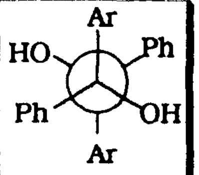
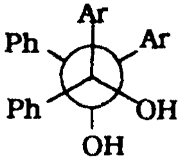
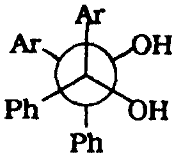
	dl-**1c**			*meso*-**1c**		
						
Method	***dl*-1**	***dl*-2**	***dl*-3**	**meso-3**	***meso*-2**	***meso*-1**
MM2	−15.131	−17.064	−27.915	−25.251	−21.813	−15.617
AM 1	−62.419	−69.165	−76.196	−69.687	−68.189	−67.828
PM3	−48.864	−56.796	−66.387	−61.901	−58.836	−59.667
MINDO/3	−31.082	−15.429	−42.760	−42.336	−33.012	−23.978
MNDO	−4.953	−14.800	−29.946	−29.244	−24.445	−19.863

TABLE VIII Calculated heat of formation (kcal/mol) of *dl*- and *meso*-2,2′-dimethylbenzpinacol **1d**

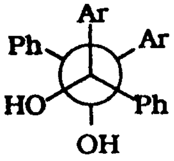
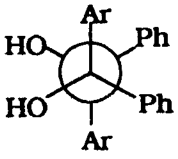
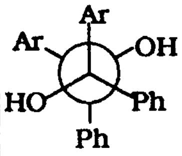
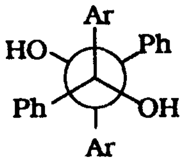
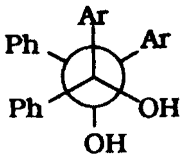
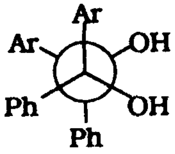
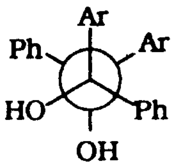
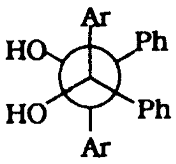
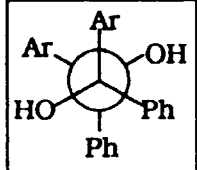
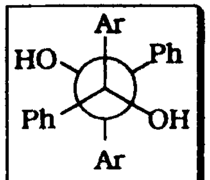
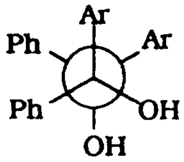
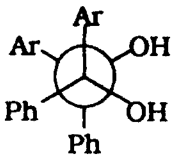
	dl-**1d**			*meso*-**1d**		
						
Method	**dl -1**	**dl -2**	**dl -3**	**meso-3**	**meso-2**	**meso-1**
MM2	−13.836	−14.239	−21.930	−16.319	−15.869	−15.154
AM 1	30.714	32.214	26.676	31.862	32.592	28.596
PM3	32.597	33.297	24.501	31.755	31.797	30.117

TABLE IX Calculated heat of formation (kcal/mol) of *dl*- and *meso*-4,4′-dimethoxybenzpinacol **1e**

	dl-1e			*meso*-1e		
						
Method	**dl -1**	**dl -2**	**dl -3**	**meso-3**	**meso-2**	**meso-1**
MM2	−16.056	−15.126	−20.706	−20.290	−14.406	−15.080
AM 1	−39.005	−37.636	−40.463	−43.863	−37.551	−37.551
PM 3	−36.249	−36.257	−38.516	−40.353	−36.015	−36.268

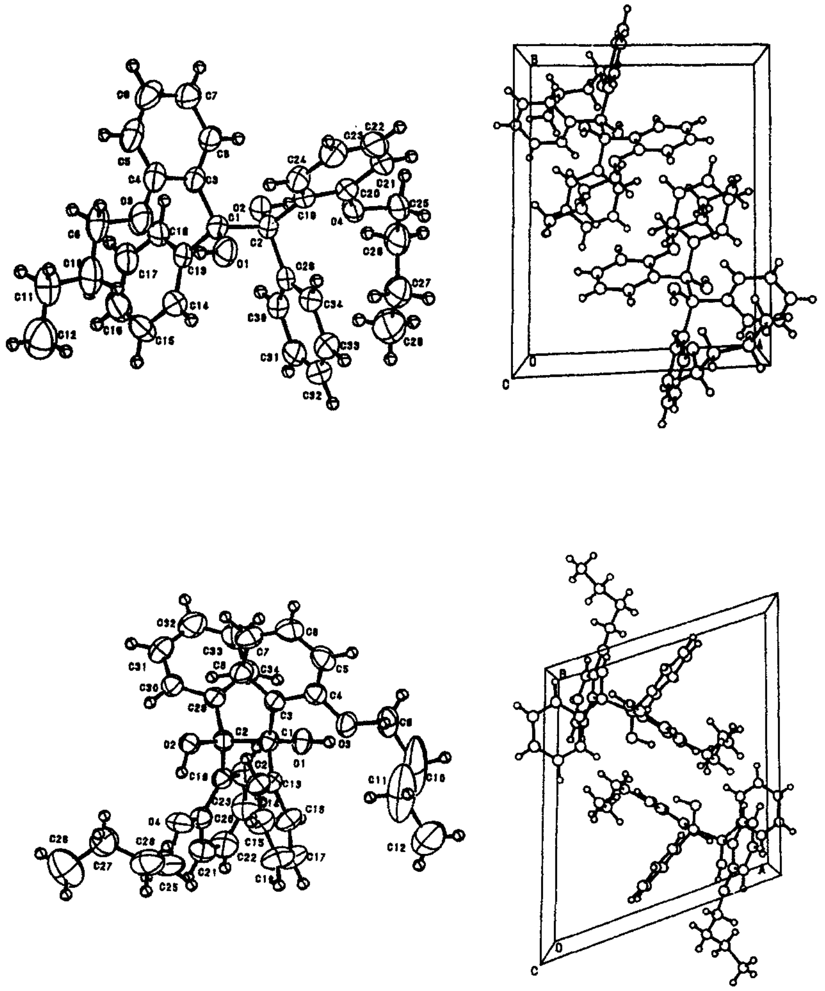


FIGURE 3 Molecular and crystal structure of *dl*- and *meso*-2,2′-dibutoxybenzpinacols **1cα**, **1cβ**; above: **1cα**, below: **1cβ**.

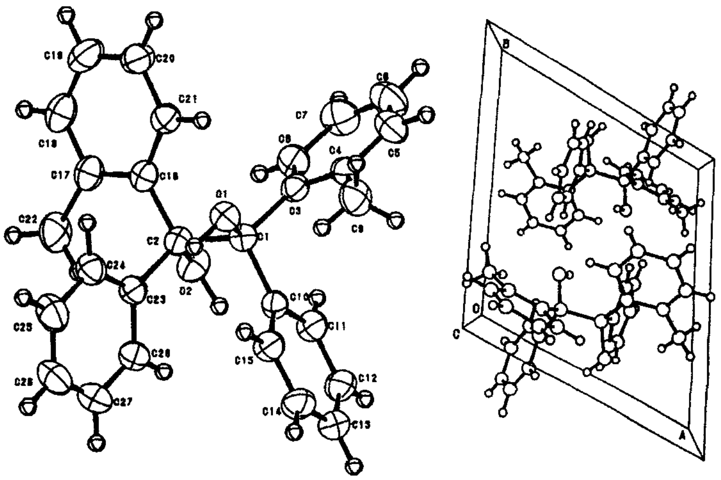


FIGURE 4 Molecular and crystal structure of *dl*-2,2′-dimethylbenzpinacol **1dα**.

crystallographic software package from the Molecular Structure Corporation.

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