144. TADDOLs Under Closer Scrutiny – Why Bulky Substituents Make It All Different

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Homage to Professor *Dieter Seebach* on the occasion of his 60th birthday

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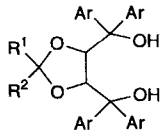
A systematic investigation of the rotational behavior of aryl substituents in α,α,α′,α′-*t*etra*a*ryl-1,3-*d*ioxolane-4,5-*d*imethan*o*ls (TADDOLs) is presented. In the use as chiral ligands for enantioselective metal-catalyzed reactions, a change from phenyl to bulkier substituents, *e.g.*, 1-naphthyl, gives rise to an astounding alteration of the selectivity. The possible existence of preferred rotamers of TADDOLs has so far not been given due attention, which encouraged us to look at the validity of the *Knowles* model, originally formulated for diaryl substituted bisphosphines. ^{1}H-NMR Investigations at various temperatures as well as X-ray powder diffraction were employed to study the rotation in the case of tetra(1-naphthyl) TADDOL **1**. To support the interpretation of the experimental results, molecular mechanics, semiempirical, and *ab initio* calculations were performed. For comparison, the energy surface of tetraphenyl TADDOL **2** was calculated as well. Our results lead to the conclusion that for **1**, only one major conformation is present in both solution and solid state, which determines the stereochemical outcome of the catalyzed reactions.

1. Introduction. – The family of chiral diarylmethanol compounds introduced by *Seebach* and coworkers in 1983 [1][2] and referred to as TADDOLs (α,α,α′,α′-*t*etra*a*ryl-1,3-*d*ioxolane-4,5-*d*imethan*o*ls; **A**) [3] has proven to be a pool of versatile auxiliaries applicable to various methods for the preparation of enantiomerically pure compounds [4]. On the one hand, TADDOLs were originally used as chiral ligands at Ti^{IV} in nucleophilic additions (stoichiometrically) and as chiral *Lewis* acids for mediating *Diels-Alder* reactions [5]. This methodology has evolved into a number of synthetically useful metal-catalyzed reactions, both stoichiometric and catalytic, *e.g.*, pericyclic, *Grignard*, aldol, and transesterification reactions. On the other hand, the TADDOLs themselves have proved to be useful as NMR shift reagents, as components for enantioselective formation of inclusion compounds, and for enantioselective solid-state reactions. (For a comprehensive list of applications, see [4].) The easy preparation of TADDOLs from tartrate esters, which are acetalized and then reacted with aryl *Grignard* agents, allows the introduction of various substituents in the 2-position of the dioxolane ring and a great variety of aryl groups in the diarylmethanol moieties. To date, more than 70 different TADDOLs have been prepared by various groups [6].

The question then arose whether a correlation between structural features of the ligand **A** and the observed selectivities in the metal-catalyzed reactions could be established. The great number of crystal structures reported by various groups allowed the



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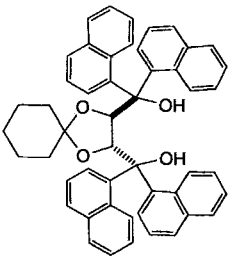

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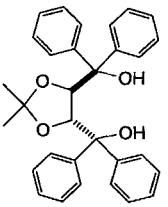

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identification of common structural features[1]). A comprehensive survey was published in 1992 [7]. This study revealed that the dioxolane rings are always in a non-planar, strongly puckered conformation, and thus force the diarylmethanol substituents of **A** in the pseudo-equatorial positions (for (*R*,*R*)- and (*S*,*S*)-configuration, resp.). In all cases[2]), a seven-membered ring is formed by an intramolecular H-bond between the two OH groups. The aryl (Ar) substituents occupy pseudo-axial and pseudo-equatorial positions of this seven-membered ring, forming a chiral array around the position taken by a metal in the case of coordination. It has been demonstrated that because of the intramolecular H-bond, the TADDOLs themselves are excellent models for their respective metal complexes[3]) [7][10]. Based on this array, a number of models explaining the stereochemical course of various metal-TADDOLate-mediated reactions has been proposed [7]. These models were further refined and extended in subsequent publications [9–11].

Generally, high enantioselectivities are obtained in metal-TADDOLate-mediated reactions [6]. There is, however, a remarkable exception, in that reactions employing TADDOLs with bulky aryl substituents, *e.g.*, the 1-naphthyl derivative **1** or the phenanthryl derivative **A** ($R^1 = R^2 =$ Me, Ar = 9-phenanthryl), either give low selectivities (addition of Et_2Zn to benzaldehyde [7]), or result in a reversal of the stereochemical course (*Diels-Alder* reaction of cyclopentadiene and 3-[(*E*)-but-2-enoyl]-1,3-oxazolidin-2-one [10][11]). The crystal structure of **1** (*Fig. 1*) shows that, in comparison to the tetraphenyl-substituted derivatives **A**, steric hindrance is increased by fusing the additional benzene ring on the pseudo-equatorial phenyl substituents on the side of the reaction center, whereas with the pseudo-axial substituents, the additional benzene ring points towards the dioxolane moiety. From this crystal structure, it was deduced that rotation around the C–aryl bond should be highly hindered, in accordance with ^{1}H-NMR data. At room temperature, only broad, unresolved signals were observed. At 120°, most signals became sharp [3].

At this point, it is useful to mention an earlier concept discussed by *Knowles* and coworkers [12] to rationalize the discrimination between enantiotopic faces in the hydrogenation of dehydroamino acids catalyzed by chiral bisphosphine-rhodium complexes. From a number of crystal structures of bisphosphine complexes, they concluded that the

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[1]) In June 1997, the *CSD* reports 41 crystal structures of TADDOLs.

[2]) There is, however, a notable exception: in the case of hexaphenyl-substituted **A** ($R^1 = R^2 =$ Ar = Ph), both OH groups point towards the phenyl substituents on the dioxolane ring [8].

[3]) The conclusions we draw from the calculations in the present study can, therefore, be extended to the actual catalysts bearing the TADDOL ligand.

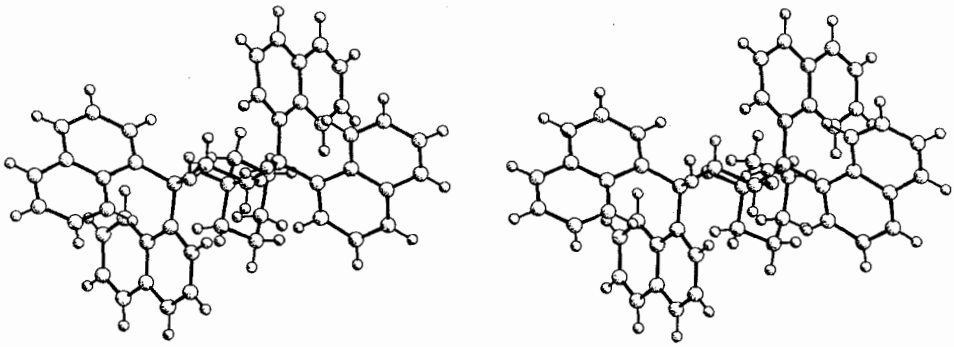

Fig. 1. *Stereoplot of the crystal structure of the tetra(1-naphthyl) TADDOL* **1** *as present in the inclusion complex with EtOH* [10]. The EtOH molecule is not shown.

coordination of the substrate is determined by an alternating 'edge-on' and 'face-on' arrangement of the aryl rings (*Fig. 2, a*). Later, more comprehensive studies showed only a weak preference for the pseudo-axial substituents to adopt 'edge-on' and the pseudo-equatorial 'face-on' conformations [13].

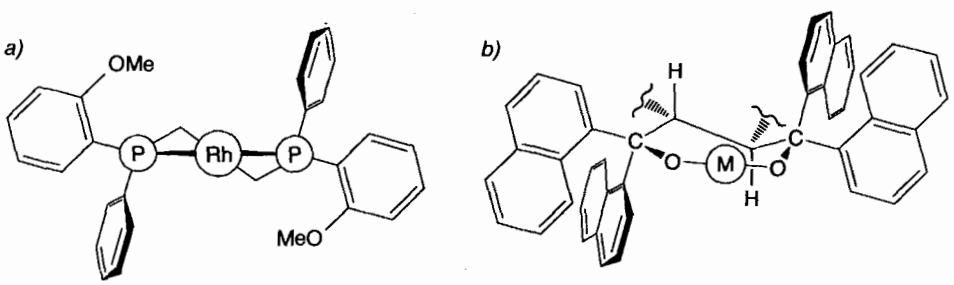

Fig. 2. *Schematic representation of* a) *a [Rh{(*R,R*)-DIPAMP}] and* b) *a [metal{(*R,R*)-TADDOL}] complex with Ar = 1-naphthyl according to the* Knowles *'edge-on/face-on' concept* [12]. (*R,R*)-DIPAMP = (*R,R*)-(ethane-1,2-diyl)bis[(2-methoxyphenyl)phenylphosphine]. The conformation for the TADDOL complex was adopted from the crystal structure depicted in *Fig. 1*.

This 'edge-on/face-on' concept was not considered important in the case of tetraphenyl TADDOLs because free rotation around the C–phenyl bond was assumed. With tetra(1-naphthyl) TADDOLs, however, the hindered rotation around the C-naphthyl bonds could 'freeze' a specific conformation (*Fig. 2,b*); thus, it may be useful to reconsider the original *Knowles* concept to rationalize the stereochemical course of several metal-TADDOLate-catalyzed reactions involving the tetra(1-naphthyl)-substituted ligand **1**. Our present study investigates the relevance of the *Knowles* effect in TADDOLs both by experiments and calculations.

2. NMR Spectra and X-Ray Powder Diffraction Data. – The appearance of the ^{1}H-NMR spectra of the tetra(1-naphthyl) TADDOLs at room temperature is characterized by rather broad signals, somewhat varying with solvent and magnetic-field strength [3][10]. In a first interpretation, it was assumed that this behavior was due to hindered

rotation of the sterically demanding aryl groups[4]). The rotational behavior was further examined by high-temperature ^{1}H-NMR. At 500 MHz (*Bruker AMX 500*) in (D_6)DMSO, the aromatic signals of TADDOL **1** · EtOH, already somewhat structured at room temperature, became better resolved upon heating, showing completely resolved bands at 167° (see *Fig. 3*). To correlate the solid-state conformation of **1** (*Fig. 1*) with the NMR spectra, attempts were made to obtain low-temperature NMR data. In a first step, **1** · EtOH was dissolved in CD_2Cl_2 at room temperature, and ^{1}H-NMR spectra were collected down to −80° in 20° steps at 200 MHz (*Varian Gemini 200*). The resonance signals for the aromatic H-atoms became more resolved upon cooling, reaching an optimum at *ca.* −40°, while on further cooling to −80°, some of the resolution was lost again. Since these results did not allow an unambiguous assignment of the signals to a specific conformation, we decided to reverse the experiment. Unfortunately, when we attempted to dissolve **1** · EtOH in CD_2Cl_2 at −78°, the solubility proved to be too low for practical reasons. We, therefore, had to switch to (D_8)THF as the solvent of choice. Up to *ca.* −30°, only slight changes in the resolution of the broadened aromatic signals were observed. On further heating to room temperature, the familiar broadening (indicating the beginning of coalescence) reappeared. We interpret these results as follows. From room temperature down to −80°, the ^{1}H-NMR spectra showed essentially the same number of signal groups in the aromatic region, both in CD_2Cl_2 and (D_8)THF. This indicates that only one conformation dominates in this temperature range. The finding that essentially identical spectra were obtained when cooling the solution starting from room temperature or dissolving the sample at −78° suggests that some residual dynamics is still preserved at low temperatures. The high-temperature spectrum, on the other hand, displayed completely resolved signals in the aromatic region (see *Fig. 3,b*) corresponding to two diastereotopic naphthyl groups, as expected for unhindered rotation while retaining C_2 symmetry.

The sample used for the NMR experiments was obtained by dissolving the tetra-(1-naphthyl) TADDOL **1** (2 g) in toluene (15 ml) and heating to *ca.* 80° before addition of EtOH (30 ml). Within minutes, the 1:1 inclusion compound **1** · EtOH precipitated as a white crystalline powder. The single crystal used for the structure determination of **1** · EtOH, however, had been grown over a period of weeks [10]. We had to take into account the possibility that the conformer of the X-ray structure was not necessarily identical to the major solution conformer. The fast precipitation of the **1** · EtOH powder, on the other hand, would seem to guarantee that the dominant solution conformer is also present in the solid sample. The quality of the powder sample justified collection of powder diffraction data at room temperature (*Fig. 4*). The data could be unambiguously indexed with the space group and cell constants of the single crystal[5]). All reflections were well defined and sharp with no additional, unindexed peaks. Polymorphism can thus be excluded within the limits of the sensitivity of the method. We conclude that the conformations in the single crystal and the crystalline powder are identical. Of course we cannot exclude strictly the possibility of exact isomorphism, *i.e.*, the crystallization of a

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[4]) In contrast to the tetra(1-naphthyl) TADDOL, the 2-naphthyl analog shows sharp and structured signals at room temperature [3].

[5]) Slight adjustments of the cell constants were necessary because the single-crystal structure data was collected at −40°.

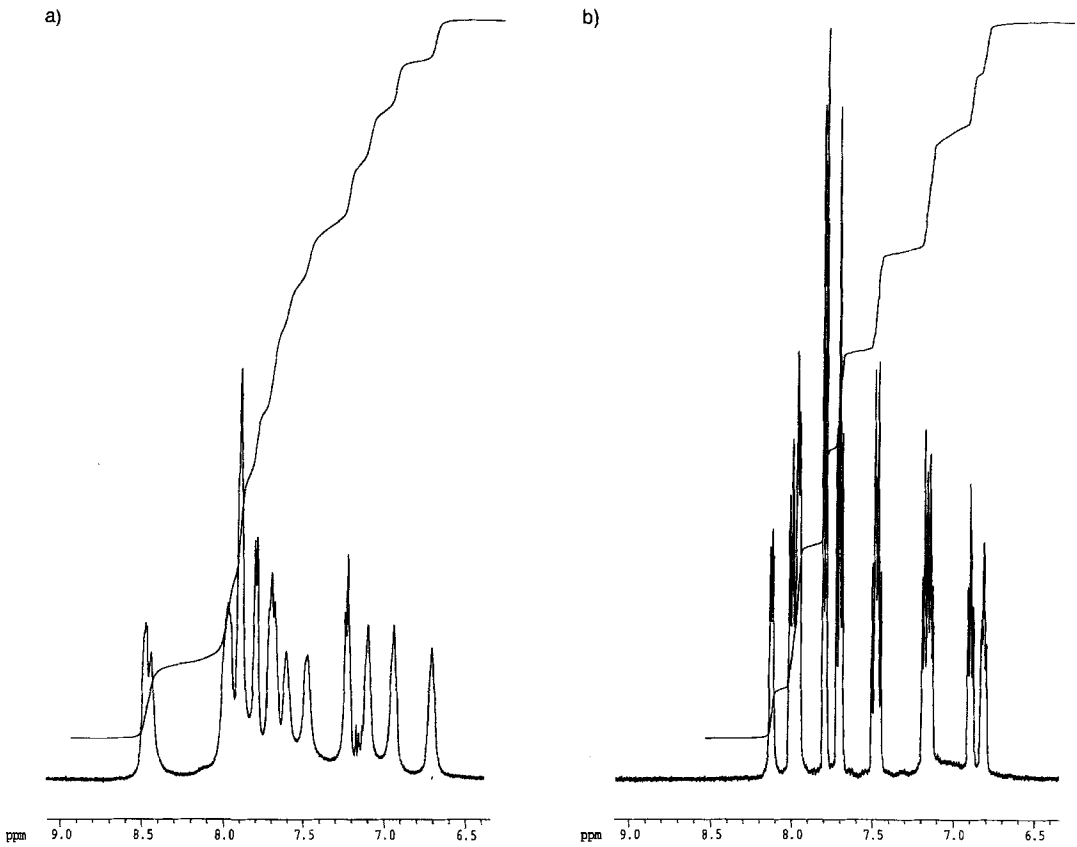

Fig. 3. *^{1}H-NMR Spectra* (500 MHz, (D_6)DMSO) *of the aromatic region of* **1** · *EtOH* a) *at room temperature and* b) *at 167°*

different conformer in the same cell and space group. Since no broadening of the reflection profiles is observed, we consider this as highly improbable.

3. Calculations. – To get a quantitative estimate of the energy barriers for the rotation around the C–aryl bonds, and the absolute energy differences between the rotamers, a number of calculations employing empirical, semiempirical, and *ab initio* methods were performed. Starting with the crystal structure of **1** (*Fig. 1*), a *Ramachandran*-type plot of two geminal C–aryl bond torsion angles was calculated using the MM2 force field [14] as implemented in the program MacroModel [15]. The two torsion angles were varied from -180 to $+180°$ with a step size of 15°. They were kept frozen at the grid points by applying an artificially high rotational barrier of 1000 kJ/mol. Each conformation obtained by this procedure was energy-minimized. The result is shown in *Fig. 5*. The lowest-energy conformer is the MM2-minimized crystal structure with torsion angles of *ca.* -90 and 0°. This orthogonal arrangement of the naphthyl groups seems to be favorable, as indicated by similar minima at the three additional orthogonal settings.

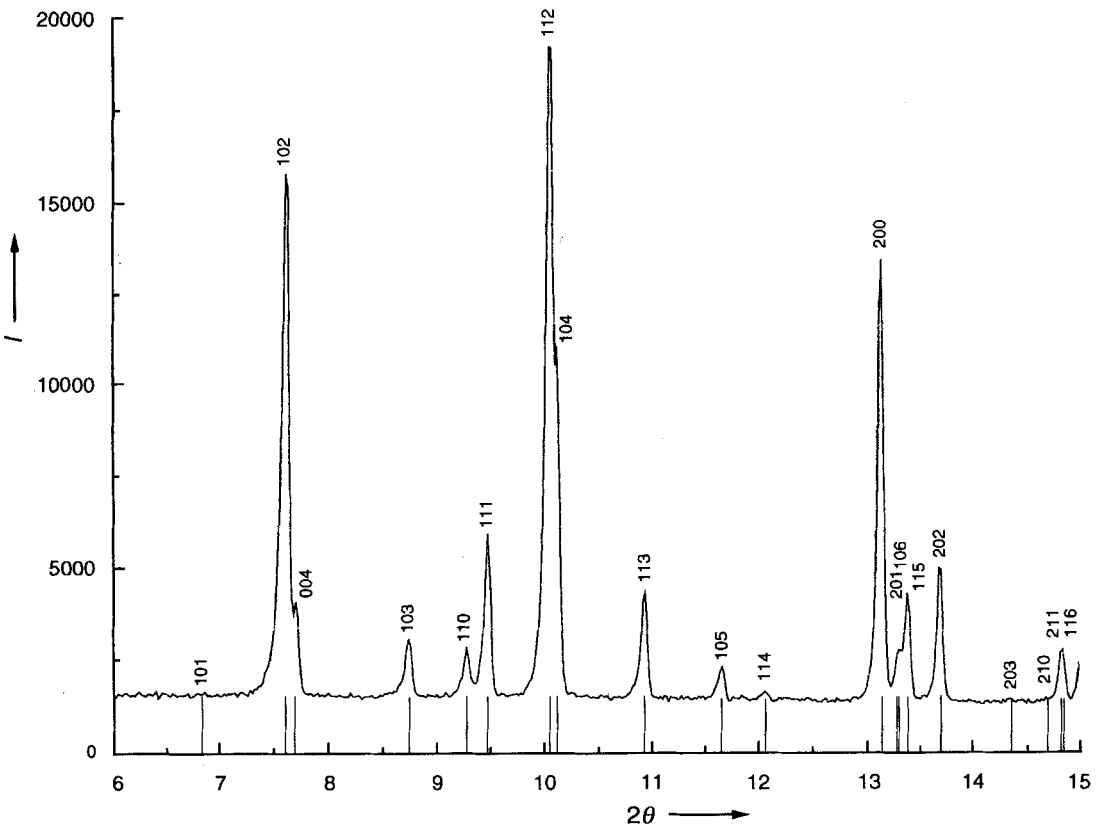

Fig. 4. *A representative part of the X-ray powder diffraction pattern of* **1** · *EtOH* ($6° < 2\Theta < 15°$). Data was collected to $2\Theta = 35°$. Indexing (marked with thin lines along the 2Θ axis) is based on a tetragonal cell, space group $P4_12_12$, $a = b = 13.4648$, $c = 45.9075$ Å. In the single-crystal structure analysis, data was collected at $-40°$, with $a = b = 13.418$, $c = 45.784$ Å.

All minima are separated by high barriers, so that interconversion must be very slow at room temperature. It must be added, though, that due to severe steric crowding in the course of mutual rotation of the naphthyl groups, the absolute energy values in the barrier regions are unreliable because the torsional restrictions lead to highly distorted geometries.

In a further step, we extended the scope of the investigation to include all 16 combinations of orthogonal arrangements of the naphthyl groups. These model rotamers were fully minimized without constraints.

The energy differences between the rotamers are in the range of 10 to 40 kJ/mol (see *Table*). The analysis of the different energy contributions shows that the conformers differ mainly in the *van der Waals* and angle-bending constituents. The lowest-energy conformation (*Table*, *Entry 1*) corresponds to the conformation as present in the solid state (see *Fig. 6,a*). The three next-lowest-energy conformations are within 10 kJ/mol (*Entries 4*, *8*, and *12*; see *Fig. 6,b–d*).

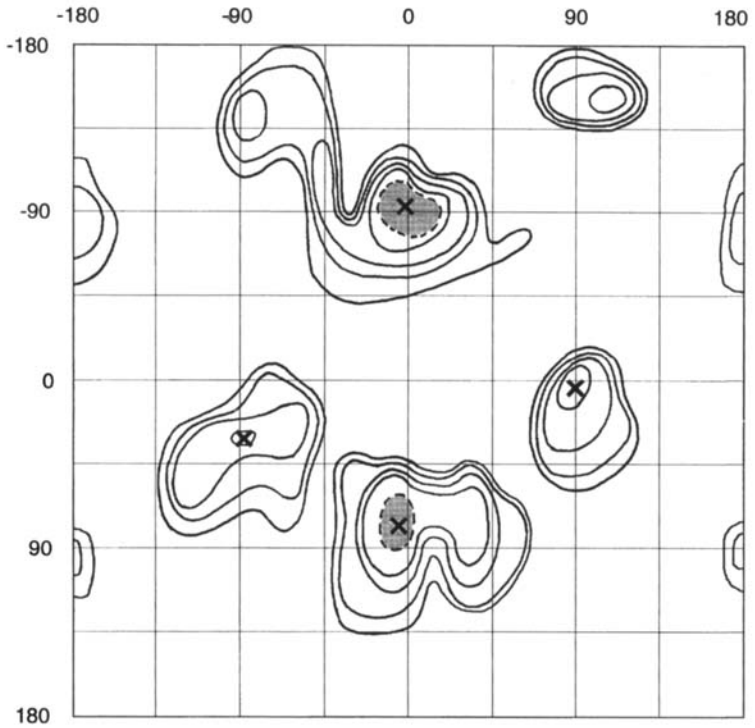

Fig. 5. Ramachandran *plot for the rotation of the 1-naphthyl substituents in* **1**. The dashed lines enclose regions with energies from 0 to 10 kJ/mol (gray). The full contour lines are at 20, 40, 60, and 80 kJ/mol. The lowest calculated energy is defined as 0 kJ/mol and is represented by the cross at 0°/ – 90°. The other crosses mark the three next-lowest-energy minima, roughly corresponding to orthogonal arrangements of the geminal naphthyl substituents.

Table. *Calculated Energies* [kJ/mol] *and Torsion Angles* [°] *of All Possible Rotamers of* **1**. Optimization was started from the optimized X-ray structure, using the force field MM2 [14] in MacroModel [15].

Entry	Torsion 1	Torsion 2	Torsion 3	Torsion 4	*E* [kJ/mol]	Structure
1	95.0	−6.6	−6.3	93.2	134.1	*Fig. 6,a*
2	96.3	−6.8	96.3	−7.7	152.5	
3	93.5	−6.8	−89.9	8.5	148.5	
4	94.9	−5.6	0.0	−88.0	142.3	*Fig. 6,b*
5	−89.6	3.0	85.5	1.9	163.9	
6	−89.8	0.6	−91.8	7.3	153.0	
7	−86.0	−1.3	−2.3	−88.2	151.8	
8	−85.7	−1.6	−4.5	92.8	144.2	*Fig. 6,c*
9	3.6	−90.1	98.6	−9.6	169.0	
10	4.2	−90.1	−89.8	−2.7	168.7	
11	7.4	−92.1	0.2	−88.4	148.4	
12	7.5	−90.6	−6.2	92.4	144.1	*Fig. 6,d*
13	−7.6	100.8	98.7	−11.5	170.8	
14	−5.4	99.8	−90.3	−4.5	171.6	
15	1.8	85.8	2.4	−87.5	160.2	
16	−7.1	96.0	−6.4	94.5	150.8	

It was of particular interest to compare the differences in energy of the X-ray structure (*Fig. 6,a*) and of the rotamer of *Entry 12* (*Fig. 6,d*), where in one of the diarylmethanol moieties, both naphthyl groups are rotated against each other. To this purpose, and to compare the calculations with experimental findings, additional calculations applying semiempirical and *ab initio* methods were employed. Much to our surprise, the semiempirical AM1 [16] and PM3 [17] methods failed. Starting from the MM2-optimized geometries of the two conformers of *Entries 1* and *12*, a full geometry optimization lead to essentially planar dioxolane rings, in striking contrast to all experimental findings [18]. As a result, the difference between axial and equatorial substituents vanishes. Consequently, the diarylmethanol branches drift apart, leading to structures with only a vague resemblance to the solid-state geometries. The energy differences obtained by AM1 and PM3 are 3.3 and 15.1 kJ/mol, respectively, and are not regarded meaningful in the light of the above shortcomings. More reliable results were expected from an *ab initio* RHF calculation using the 3-21G basis set [19]. Starting again from the MM2-optimized models, a full geometry optimization was performed. Fortunately, even at this modest level of theory, the geometrical features of the solid-state structures are well reproduced. Therefore, the calculated energy difference of 15.5 kJ/mol is regarded to be a good estimate for the energy difference between the two rotamers. In accordance with the experimental results presented above, the force-field and *ab initio* calculations indicate the presence of a major conformer in solution at room temperature. Thus, possible interconversion is expected to be very slow, and the equilibrium concentration of other conformers low, at best.

Intrigued by this result, we decided to extend this investigation to include tetraphenyl TADDOLs. An earlier study by *Landis* and coworkers [20] using NMR and molecular-

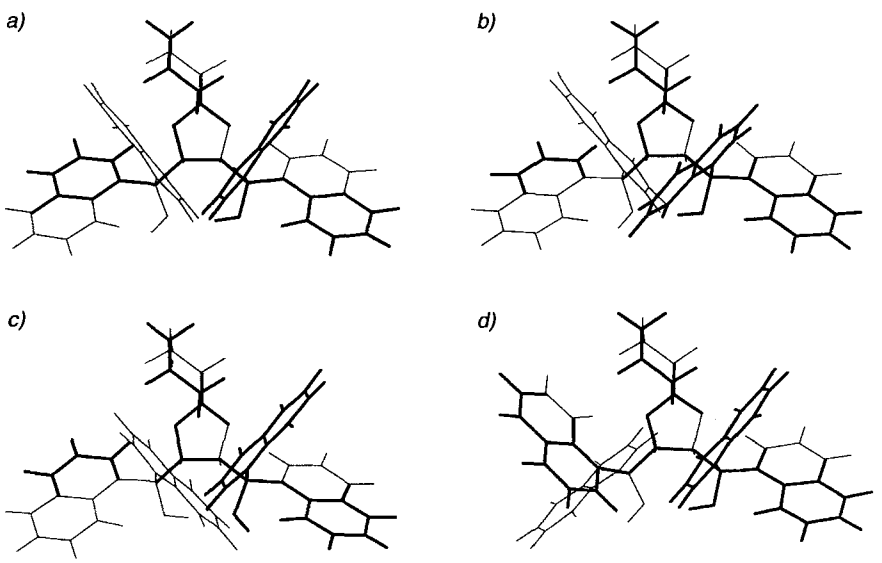

Fig. 6. *Top view of the MM2-optimized structures of the four lowest-energy rotamers of the tetra(1-naphthyl) TADDOL* **1**. The structures *a*), *b*), *c*), and *d*) correspond to *Entries 1*, *4*, *8*, and *12*, respectively, in the *Table*. The drawing plane is the least-squares plane through the dioxolane ring atoms.

mechanics methods concentrated on chiral bisphosphines with diaryl substitution at the P-atoms, making it difficult to relate their results to the TADDOL case[6]). A *Ramachandran*-type plot (*Fig. 7*) for the rotation around two geminal C–phenyl bonds was calculated starting from the MM2-optimized crystal structure of α,α,α′,α′-tetraphenyl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (**2**; *CSD* code KOGJAR). The most striking contrasts to the *Ramachandran* plot of the tetra(1-naphthyl) TADDOL **1** (*Fig. 5*) are much broader minima and the overall flatness of the energy surface[7]). While the rotation of one phenyl group with respect to its fixed geminal partner would have to overcome substantial barriers (horizontal and vertical connector lines between the marked minima, *Fig. 7*), a concerted rotation is easily possible within an energy range of 20 kJ/mol.

The minimum structure of **2** resembles the experimental geometry very closely. The position of the phenyl groups show a tendency towards an 'edge on' for the axial and a 'face on' orientation for the equatorial substituents. Whereas the exact 'edge on/face on' positions are within 10 kJ/mol of the minimum, the axial 'face on', equatorial 'edge on' orientations are at least two times higher in energy. Interestingly, the orientation of the naphthyl groups in the MM2-optimized structure of **1** is the same as in the phenyl case, but here small deviations from the minima lead to steep increases in energy.

Conclusions. – Our results suggest that the original *Knowles* concept [12] is not meaningful for tetraphenyl TADDOLs, as already demonstrated by *Landis* and coworkers [20] for the chiral bisphosphines. The concerted rotation of the geminal phenyl substituents does not have to overcome barriers higher than *ca.* 20 kJ/mol (*Fig. 7*), ensuring that a variety of rotamers is present in solution even down to relatively low temperatures. In contrast, only one major rotamer has to be considered for the tetra(1-naphthyl) TADDOL **1** for two reasons. Firstly, our calculations show that the differences between the solid-state structure and other local energy minima representing different rotamers are so high that their population is negligible under realistic conditions. Secondly, rotation of the geminal 1-naphthyl groups is prohibited by high barriers, slowing down a possible interconversion. For the tetra(1-naphthyl) TADDOLs, the *Knowles* concept seems to be a valuable tool to understand and predict the stereochemical oddities in reactions employing this ligand. In a way, this result confirms the mnemonic device developed by *Seebach* and coworkers for the stereochemical course of metal-TADDOLate-mediated reactions [4][7][9–11]. In the case of 1-naphthyl substituents, the frozen conformation reverses the effective size of the equatorial and axial aryl groups, thus supporting the tentative interpretation given earlier [10].

We would like to express our gratitude to *Joachim Glaus* for the preparation of a sample of the TADDOL · EtOH complex as well as for assistance with the low-temperature NMR measurements. Moreover, we thank Ms. *B. Brandenberg* for recording the 500-MHz NMR spectra, and Prof. Dr. *B. Jaun* for helpful discussions on the interpretation of these data. Finally, the collection of the X-ray powder diffraction data by *Simon Brenner* and Dr. *Ch. Bärlocher* (Laboratorium für Kristallographie, ETH-Zürich) is gratefully acknowledged.

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[6]) On the one hand, the average P-aryl bond (1.836 Å) is much longer than the C–aryl bond (1.513 Å) [21]. On the other hand, the diaryl-bearing atoms are somewhat farther from the reaction center in the TADDOL case.

[7]) The four marked minima in *Fig. 7* are equivalent since rotation around 180° leads to identical structures.

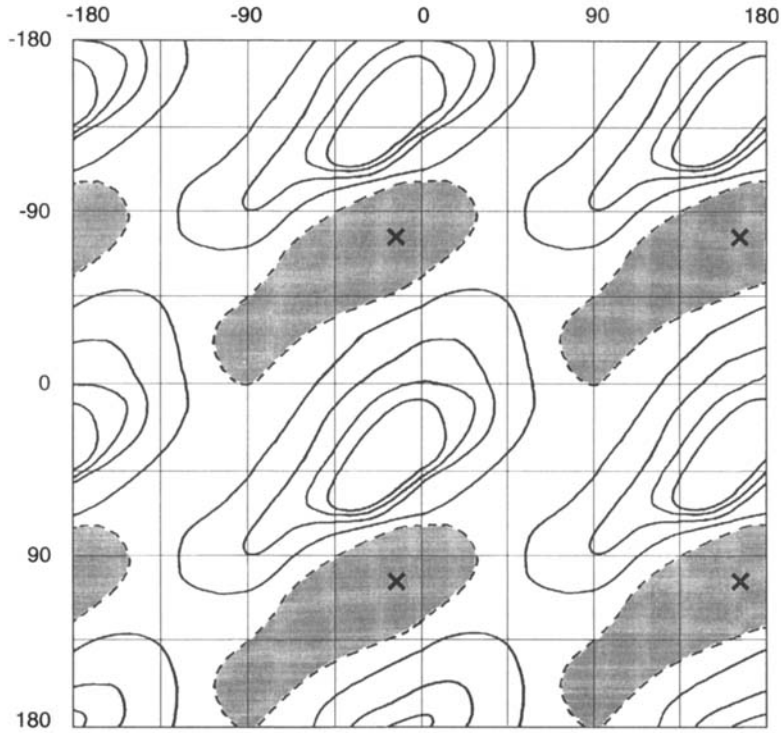

Fig. 7. Ramachandran *plot for the rotation of two geminal phenyl substituents in* **2**. The energy levels indicated by the contour lines are the same as in *Fig. 5*. In the case of phenyl substituents, the crosses, indicating the absolute energy minimum, represent identical structures.

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