Chaudret, P. Fau, L. Lescouzères, A. Peyre-Lavigne, *Adv. Mater.* **1999**, *11*, 61.
[10] Q. Chen, M. Tanaka, K. Furuya, *J. Surf. Anal.* **1999**, *5*, 348.
[11] a) T. Douglas, K. Theopold, *Inorg. Chem.* **1991**, *30*, 596; b) R. L. Wells, S. R. Aubuchon, S. S. Kher, M. S. Lube, P. S. White, *Chem. Mater.* **1995**, *7*, 793.
[12] a) H. Uchida, T. Matsunaga, H. Yoneyama, T. Sakata, H. Mori, T. Sasaki, *Chem. Mater.* **1993**, *5*, 716; b) Y.-D. Li, X.-F. Duan, Y.-T. Qian, L. Yang, M.-R. Ji, C.-W. Li, *J. Am. Chem. Soc.* **1997**, *119*, 7869.
[13] see H. K. Kim, C. C. Li, G. Nykolak, P. C. Becker, *J. Appl. Phys.* **1994**, *76*, 8209, and references therein.
[14] G. T. Cardenas, E. C. Salgado, J. Morales, H. Z. Soto, *J. Appl. Polym. Sci.* **1999**, *73*, 1239.
[15] K.-L. Tsai, J. L. Dye, *J. Am. Chem. Soc.* **1991**, *113*, 1650.
[16] For example, see:a) T. J. Trentler, S. C. Goel, K. M. Hickman, A. M. Viano, M. Y. Chiang, A. M. Beatty, P. C. Gibbons, W. E. Buhro, *J. Am. Chem. Soc.* **1997**, *119*, 2172; b) X. Duan, C. M. Lieber, *Adv. Mater.* **2000**, *12*, 298.
[17] H. Zhou, W. Cai, L. Zhang, *Appl. Phys. Lett.* **1999**, *75*, 495.
[18] O. T. Beachley, Jr., J. C. Pazik, T. E. Glassman, M. R. Churchill, J. C. Fettinger, R. Blom, *Organometallics* **1988**, *7*, 1051.
[19] For the use of TOPO for stabilizing nanoparticles and inducing self-assembly, see ref. [5b] and a) B. O. Dabbousi, C. B. Murray, M. F. Rubner, M. G. Bawendi, *Chem. Mater.* **1994**, *6*, 216; b) T. Cassagneau, T. E. Mallouk, J. H. Fendler, *J. Am. Chem. Soc.* **1998**, *120*, 7848.

Induction of a Preferred Twist in a Biphenyl Core by Stereogenic Centers: A Novel Approach to the Absolute Configuration of 1,2- and 1,3-Diols**

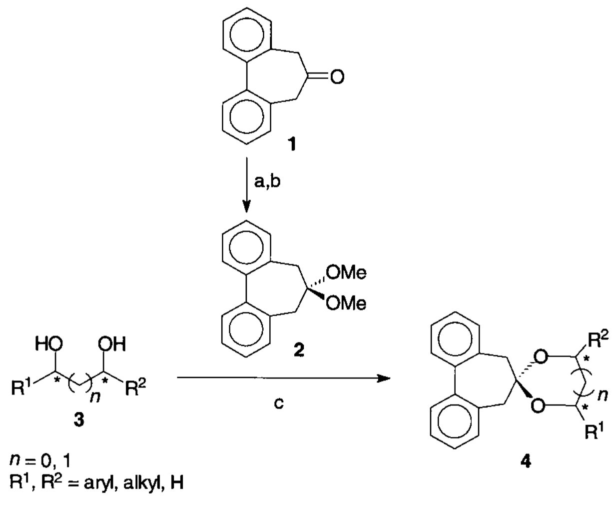
Stefano Superchi, Daniele Casarini,
Alessandro Laurita, Alfonso Bavoso, and Carlo Rosini*

2,2′,6,6′-Tetrasubstituted biphenyls and 2,2′-disubstituted-1,1′-binaphthyls are the paradigms of atropisomeric[1] chiral substances because the steric hindrance to rotation around the C_{Ar}–C_{Ar} bond means that they can exist as a stable pair of enantiomers *P* and *M*.[1, 2] These configurationally stable biaryls have enjoyed a lot of attention in natural products chemistry,[3] asymmetric synthesis,[4] materials science,[5] and molecular recognition,[6] while only very recently nonatropisomerically stable, flexible biaryl compounds have also been used in asymmetric catalysis[7] and molecular recognition.[8] These latter compounds are usually present as racemic (*P,M*) mixtures because the free rotation around the C_{Ar}–C_{Ar} bond does not allow the isolation of a single enantiomer. A preferred enantiomeric conformation can be, however, stabilized through interaction with chiral metal complexes[7a] and/or substitution with chiral auxiliaries.[7b–e]

We present herein a novel application of flexible biphenyl compounds for the nonempirical determination of the absolute configuration of 1,2- and 1,3-diols by CD spectroscopy. This is a task of great importance considering the wide use of such diols as chiral building blocks[9] and chiral controllers in asymmetric processes.[4a, 10] Although CD spectroscopy has been already employed for this purpose, such as in the dibenzoate-[11] and in the metal-induced CD methods,[12] the former nonempirical approach often involves difficult conformational assignments, while the latter, being an empirical method, does not allow an immediate and completely reliable correlation between the CD spectrum and configuration. For these reasons we recently developed alternative nonempirical CD approaches to the assignment of the absolute configuration of 1,2-diarylethane-[13] and 1-arylethane-1,2-diols,[14] in which the problem of the conformational determination is overcome by transforming the original flexible diols into their 2,2-dimethyl-1,3-dioxolanes or 4-biphenylboronates, respectively (that is, cyclic, conformationally defined derivatives).

We were looking for a more general method that would also be suitable for nonchromophoric alkyl-substituted diols, and have developed the approach described herein which is based on the formation of conformationally defined derivatives between a diol and a pro-atropisomeric[7a] flexible biphenyl moiety. In order to determine the absolute configuration of aliphatic (and hence UV transparent) diols by CD analysis it is necessary to introduce suitable chromophores which are sensitive to the chirality of the diol and give rise to Cotton effects in the CD spectrum. Moreover, the mechanism by which the diol stereogenic centers induce optical activity in the chromophore must be known in order to obtain a nonempirical correlation between the CD spectrum and the absolute configuration of the diol.

Following our previous approaches,[13, 14] we thought that the dioxolanes **4** (Scheme 1), derived from chiral diols **3** and the dimethylacetal **2** (which in turn is obtained from the 2,2′-bridged biphenyl ketone **1**)[15] would constitute suitable



Scheme 1. Synthesis of biphenyldioxolanes **4**. a) $CH(OCH_3)_3$, *p*TsOH, MeOH, RT; b) NH_3 2 M in EtOH; c) $CHCl_3$, 4-Å MS, RT. Ts = toluene-4-sulfonyl; MS = molecular sieve.

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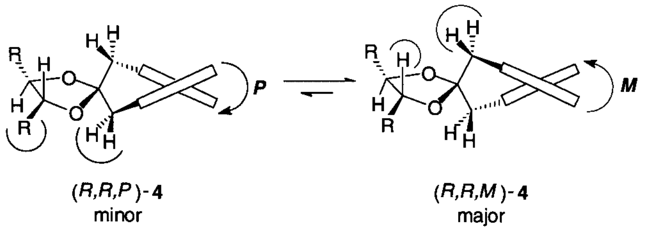
[*] Prof. Dr. C. Rosini, Dr. S. Superchi, Prof. Dr. D. Casarini,
A. Laurita,[+] Prof. Dr. A. Bavoso[+]
Dipartimento di Chimica
Università della Basilicata
Via Nazario Sauro 85, 85100 Potenza (Italy)
Fax:(+39) 971-202223
E-mail: Rosini@Unibas.It

[+] Crystal structure analysis

[**] This work was supported by MURST and Università della Basilicata. We thank Prof. Jan Sandström, University of Lund (Sweden), for helpful comments in the preparation of the manuscript.

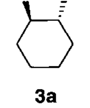
derivatives for our purposes. Several authors reported[16] that in seven-membered 2,2′-bridged biphenyl derivatives such as **4** the inversion barrier is about 14 kcal mol^{-1} and that a conformational equilibrium resulting from rotation around the C_{Ar}–C_{Ar} bond occurs at room temperature. This fact ensures that if we obtain a pair of dioxolanes (*R*,*R*,*P*)-**4** and (*R*,*R*,*M*)-**4** (Scheme 2) from nonracemic 1,2-diols (*R*,*R*)-**3** (R^1, R^2 = alkyl, aryl; $n = 0$; Scheme 1) their diastereoisomeric ratio is determined only by their thermodynamic stability and is independent of their mechanism of formation.



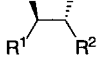
Scheme 2. Conformations of the dioxolanes **4** as derived from molecular mechanics calculations. In the isomer (*R*,*R*,*P*)-**4** the benzyl protons are close to a R residue, while in (*R*,*R*,*M*)-**4** they face a smaller hydrogen atom.

Molecular mechanics calculations[17] revealed that in dioxolanes **4** derived from chiral *threo*-(*R*,*R*)-1,2- or -1,3-diols,[18] the most stable diastereoisomer, independent of the diol structure, is the one having an *M* torsion of the biphenyl moiety. From the structures in Scheme 2 it can be clearly seen that in (*R*,*R*,*P*)-**4** both the benzylic CH_2 moieties face a bulky R substituent, while in (*R*,*R*,*M*)-**4** the benzylic residues are opposite hydrogen atoms and only minor steric interactions then result. In this system an efficient transfer of chirality from the diol (central chirality) to the twisted biphenyl (axial chirality) should occur[7d] and then the absolute configuration of the diols can be determined simply by recognizing the prevailing sense of twist of the biphenyl moiety. The relationship between the sense and angle of torsion of a biphenyl moiety and its CD spectrum is clearly and reliably established,[16c, 19, 20] so the use of such a system as a probe allows the chirality of the diol to be directly related to the features in the CD spectrum.

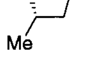
The ketone **1** was prepared in high yield according to two different literature procedures,[21] starting from commercially available 2,2′-biphenyldicarboxylic acid, and transformed in its dimethyl acetal **2** by treatment with trimethyl orthoformate in the presence of *p*TsOH, followed by neutralization with ethanolic ammonia (Scheme 1).[22] Solutions of crude **2** in $CHCl_3$ were treated directly with the diols **3a**–**h**[23] in the presence of traces of *p*TsOH and 4-Å molecular sieves.[24]



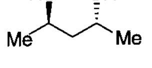
3a



3b $R^1 = R^2 = C_6H_{11}$
3c $R^1 = R^2 = Ph$
3d $R^1 = R^2 = Me$
3e $R^1 = Ph$, $R^2 = H$
3f $R^1 = C_3H_7$, $R^2 = H$



3g



3h

After filtration, evaporation of the solvent, and column chromatography the dioxolanes **4a**–**h** were isolated and their CD and UV spectra recorded (THF) between 200–330 nm.

The absorption spectrum of **4a** (Figure 1) shows the typical bands of a biphenyl chromophore: the A band at 250 nm ($\varepsilon \sim 15000$) and a more intense absorption at 215 nm ($\varepsilon \sim 30000$) which is referred to the C band.[25] It is known[19, 20] that the A band is very sensitive to the biphenyl torsion angle θ and Suzuki has calculated[25] θ values of 44–47° for its present wavelength position. This value of θ is in agreement with our molecular mechanics calculations and with the values determined by Sandström and co-workers for similar seven-membered 2,2′-bridged biphenyls.[16c, 20] A positive Cotton effect ($\Delta\varepsilon = 15$) occurs in the CD spectrum at 250 nm (that is, corresponding to the A band), followed by a positive couplet-like feature centered at 220 nm. As shown by Mislow and co-workers[19] and Sandström and co-workers,[16c, 20] a positive Cotton effect arising from the A band is related to an *M* torsion of the C_{Ar}–C_{Ar} bond. Thus the CD spectrum of **4a** experimentally confirms that the (*R*,*R*)-diol really induces *M* torsion in the biphenyl chromophore.

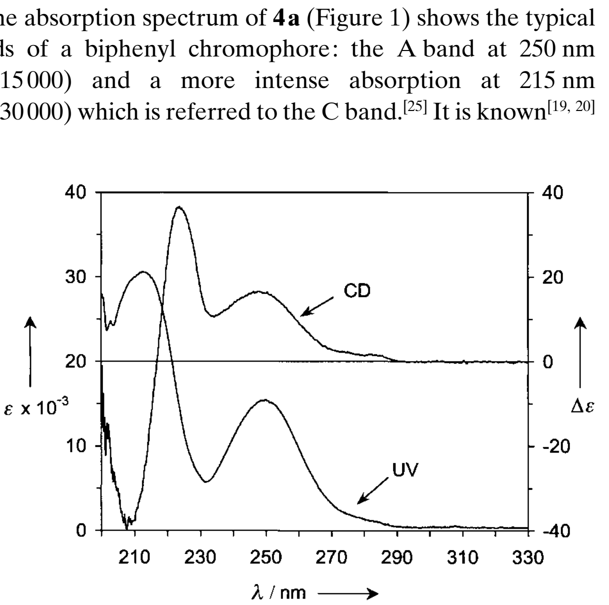


Figure 1. UV and CD spectra (THF) of dioxolane **4a**.

In order to confirm and extend this correlation to more flexible acyclic diols and to determine the effect of the bulkiness of the diol substituents on the diastereoisomeric ratio we tested our approach with 1,2-disubstituted diols **3b**–**d** (with decreasing size of substituents) with the less sterically hindered monosubstituted 1,2-diols **3e**–**g** and with the 1,3-diol **3h**, which gives rise to a more-flexible six-membered ring dioxolane. The absorption and CD spectra of the dioxolanes **4a**–**f**, **h** show the same sequence in wavelength, sign, and shape of bands while **4g**, which is derived from an *S*-configurated diol, gives rise to a mirror image CD spectrum. The CD spectra of compounds **4** only differ in the intensities of the Cotton effects. These results confirm that in all the derivatives tested we have the same expected correlation of *R*,*R*-diol and *M* torsion of the biphenyl. In addition, almost the same angle of twist of the biphenyl occurs as evidenced by the A band always occuring at 250 nm. These results show that this induction model is not limited to *threo*-dialkyl- or -diaryl-1,2-disubstituted diols **3a**–**d**, but works very well also with the 1,3-diol **3h** and even with the less sterically demanding monoaryl diol **3e** and monoalkyl diols **3f**, **g**. It is important to point out the sensitivity of this method: a small group, such as the methyl in **4g**, is sufficient to induce enough population difference between the diastereoisomers to give rise to an intense and clearly interpretable CD spectrum. This method is also of general validity because it can be applied to all those systems having negligible absorption at 250 nm (for example, **3c** and **3e**).

The crystal structure analysis of **4c** (Figure 2) confirms the stereochemical correlation between the absolute configuration of the carbon stereocenter of the diol and the sense of twist of the biphenyl moiety.[26] In fact, the *R*,*R* absolute configuration of the two stereocenters gives a negative (*M*) torsion of the biphenyl moiety and the absolute value of the torsion angle C_3-C_8-C_9-C_{14} is 46.2°, which is in excellent agreement with the values proposed by the Suzuki analysis[27] and with literature values for similar biphenyl derivatives.[16c, 28]

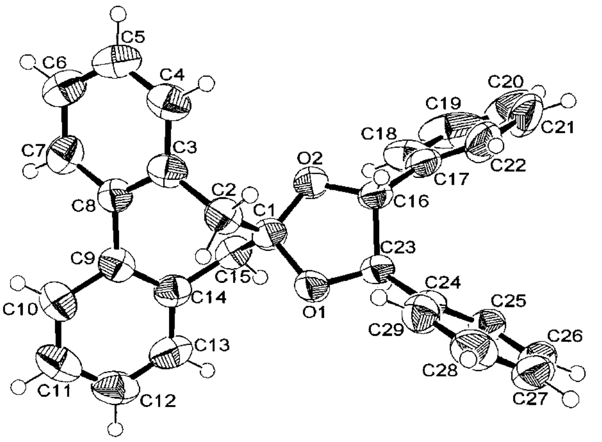


Figure 2. Crystal structure of (*R*,*R*,*M*)-**4c**; torsion angle C3-C8-C9-C14: 46.2°.

In order to confirm the presence of a thermodynamic equilibrium between the two stereoisomers (*R*,*R*,*P*)-**4** and (*R*,*R*,*M*)-**4**, the rotational process about the pivotal axis of the biphenyl moiety for the representative dioxolanes **4a**, **c**, **e**, **g**, **h** was monitored by dynamic NMR spectroscopy (DNMR; Table 1), and by freezing the exchange process at low temperature the diastereoisomeric ratio was measured. Changes in the line shape with the temperature for both the benzylic and the dioxolane ring protons were observed in the ^{1}H NMR experiments.[29] In derivative **4e**, for instance, the diastereomerization process was easily monitored by lowering the temperature and observing the decoalescence of the OCH signals belonging to the dioxolane ring at 3.83, 4.40 (Figure 3), and 5.2 ppm. Indeed the sharp multiplets detected at +45 °C broadened upon cooling, decoalesced at about 0 °C, and at −30 °C appeared clearly split into a set of signals having an approximate 75:25 ratio. An analysis of the kinetic process for the transformation of the more- into the less-stable stereoisomer afforded a first-order rate constant and a $\Delta G^{\neq}$ value of 14.4(±0.15) kcal mol^{-1}. Similar values of $\Delta G^{\neq}$ were found for the other ketals examined (Table 1) and ranged from 14.0 to 14.8 kcal mol^{-1}, while d.r. values ranging from 74:26 to 92:8 were determined.[30] These measurements, which confirm the presence of a low activation barrier for the atropisomeric interconversion of the dioxolanes **4**, demonstrate with certainty that the diastereoisomer ratio is only determined by their thermodynamic stability and that the structure of the major diastereoisomer is nonempirically predictable.

Table 1. Diastereoisomeric ratios d.r., coalescence temperatures, rate constants, and free energies of activation involved in the (*R*,*R*,*M*)-**4** to (*R*,*R*,*P*)-**4** interconversion.[a]

Compound	*R*,*R*,*M*:*R*,*R*,*P*	*T* [K]	*k* [s^{-1}]	$\Delta\nu^{[b]}$ [Hz]	$\Delta G^{\neq}$ [kcal mol^{-1}]
4a	92: 8	278	14	34	14.8
4c	90:10	268	8	30	14.5
4e	78:22	273	18	37	14.4
4g	74:26	258	7	12	14.0
4h	90:10	265	4	32	14.7

[a] All the activation parameters of the dioxolanes were measured from the ^{1}H NMR spectra recorded in CD_2Cl_2. [b] Signal separation in ^{1}H NMR spectra.

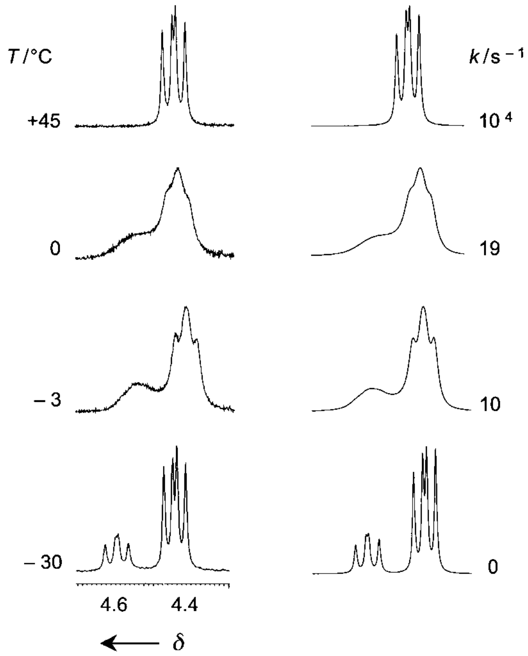


Figure 3. ^{1}H NMR spectra at 300 MHz in CD_2Cl_2 for the signal of the OCH group of dioxolane **4e**. On the left are shown the experimental traces, and on the right the computer simulated ones.

In summary, we have described a novel CD method for determining the absolute configuration of 1,2- and 1,3-diols based on a chirality transfer from the diol to a biphenyl chromophore. According to our protocol, to determine the absolute configuration of a diol it is simply necessary to prepare its biphenyldioxolane derivative **4**, to measure the CD spectrum, and to look at the sign of the A band (at 250 nm): A positive A band corresponds to an *M* torsion of the biphenyl and to a *R* or *R*,*R* configuration of the diol and vice versa. This method is quite simple, straightforward, and general, being applicable to many classes of 1,2- and 1,3-diols: cyclic, acyclic, mono- and disubstituted.

Experimental Section

Compounds **4a**–**h** show analytical and spectral (^{1}H, ^{13}CNMR, MS) data in agreement with the assigned structures. Absorption and CD spectra were recorded on a JASCO J600 spectropolarimeter at RT in THF ($c \sim 6 \times 10^{-3}$ M) in 0.1 and 1.0-mm cells. During the measurement the instrument was thoroughly purged with N_2. Low temperature ^{1}H and ^{13}CNMR spectra were recorded in solution at 300 and 75.5 MHz, respectively. The cooling of the samples was achieved by means of a precooled flow of dry nitrogen in a standard NMR-VT device. The accuracy of the real temperature in the NMR probe was checked before the VT experiments with a calibrated thermocouple. The computer simulations of the line shapes were performed by a computer program based on the Bloch equations, and the best fit was visually checked by direct superimposition of the simulated and experimental traces.

Received: July 10, 2000 [Z15422]

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[1] E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**, p. 1142.

[2] For examples of non-biaryl atropisomers, see J. Clayden, L. W. Lai, *Angew. Chem.* **1999**, *111*, 2755; *Angew. Chem. Int. Ed.* **1999**, *38*, 2556 and references therein.

[3] See for example: a) M. Kitamura, K. Ohmori, T. Kawase, K. Suzuki, *Angew. Chem.* **1999**, *111*, 1308; *Angew. Chem. Int. Ed.* **1999**, *38*, 1229; b) B. H. Lipshutz, J. M. Keith, *Angew. Chem.* **1999**, *111*, 3743; *Angew. Chem. Int. Ed.* **1999**, *38*, 3530; c) G. Bringmann, M. Breuning, S. Tasler, *Synthesis* **1999**, 525; d) G. Bringmann, R. Walter, R. Weinrich, *Angew. Chem.* **1990**, *102*, 1006; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 977.

[4] a) J. K. Whitesell, *Chem. Rev.* **1989**, *89*, 1581; b) C. Rosini, L. Franzini, A. Raffaelli, P. Salvadori, *Synthesis* **1992**, 503; c) J. Bao, W. D. Wulff, J. B. Dominy, M. J. Fasno, E. B. Grant, A. C. Robb, M. C. Whitcomb, S. Yeung, R. L. Ostrander, A. L. Rheingold, *J. Am. Chem. Soc.* **1996**, *118*, 3392; d) L. Pu, *Chem. Rev.* **1998**, *98*, 2405; e) D. Yang, Y.-C. Yip, M.-W. Tang, M.-K. Wong, K.-K. Cheung, *J. Org. Chem.* **1998**, *63*, 9888.

[5] H. Deussen, C. Boutton, N. Thorup, T. Geisler, E. Hendrickx, K. Bechgaard, A. Persoons, T. Bjoernholm, *Chem. Eur. J.* **1998**, *4*, 240; H. Deussen, P. V. Shibaev, R. Vinocour, T. Bjoernholm, K. Schaumburg, K. Beechgaards, V. P. Shibaev, *Liq. Cryst.* **1996**, *21*, 327; G Solladiè, P. Hugelè, R. Bartsch, *J. Org. Chem.* **1998**, *63*, 3895.

[6] See for example: a) D. J. Cram, J. M. Cram, *Acc. Chem. Res.* **1978**, *11*, 8; b) D. J. Cram, K. V. Trueblood, *Top. Curr. Chem.* **1981**, *98*, 43; c) D. J. Cram, *Angew. Chem.* **1986**, *98*, 1041; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1039; d) F. Diederich, M. R. Hester, M. A. Uyeki, *Angew. Chem.* **1988**, *100*, 1775; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1705; e) P. P. Castro, T. M. Georgiadis, F. Diederich, *J. Org. Chem.* **1989**, *50*, 5835; f) J. Reeder, P. P. Castro, C. B. Knobler, E. Martinborough, L. Owens, F. Diederich, *J. Org. Chem.* **1994**, *59*, 3151; g) P. Lustenberg, E. Martinborough, T. Mordasini-Denti, F. Diederich, *J. Chem. Soc. Perkin 2* **1998**, 747.

[7] a) K. Mikami, T. Kirenaga, M. Terada, T. Ohkuma, T. Pham, R. Noyori, *Angew. Chem.* **1999**, *111*, 517; *Angew. Chem. Int. Ed.* **1999**, *38*, 495; b) Y. Imai, W. Zhang, T. Kida, Y. Nakatsuji, I. Ikeda, *Tetrahedron Lett.* **1997**, *38*, 2681; c) Y. Imai, W. Zhang, T. Kida, Y. Nakatsuji, I. Ikeda, *Synlett* **1999**, *8*, 1319; d) F. Fabris, O. De Lucchi, V. Lucchini, *J. Org. Chem.* **1997**, *62*, 7156; e) M. Chavarot, J. J. Byrne, P. Y. Chavant, J. Pardillos-Guindet, Y. Vallée, *Tetrahedron: Asymmetry* **1998**, *9*, 3889.

[8] T. Mizutani, H. Takagi, O. Hara, T. Horiguchi, H. Ogoshi, *Tetrahedron Lett.* **1997**, *38*, 1991.

[9] S. Hanessian, *Total Synthesis of Natural Products: The Chiron Approach*, Pergamon, New York, **1983**.

[10] a) C. Rosini, S. Superchi, M. I. Donnoli, *Enantiomer* **1999**, *4*, 3; b) H. C. Kolb, M. S. Van Nieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483.

[11] N. Harada, K. Nakanishi, *Acc. Chem. Res.* **1972**, *5*, 257; N. Harada, K. Nakanishi, *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*, University Science Books, Mill Valley, CA, **1983**; K. Nakanishi, N. Berova in *Circular Dichroism: Principles and Applications* (Eds.: K. Nakanishi, N. Berova, R. W. Woody), VCH, New York, **1994**, p. 361; N. Harada, A. Saito, H. Ono, S. Murai, H.-Y. Li, J. Gawronski, K. Gawronska, T. Sugioka, H. Uda, *Enantiomer* **1996**, *1*, 119; M. Hartl, H. Humpf, *Tetrahedron: Asymmetry* **1998**, *9*, 1549.

[12] To this end several metal atoms have been employed: a) Cu: S. T. K. Bukhari, R. D. Wrixon, A. I. Scott, A. D. Wrixon, *Tetrahedron* **1970**, *26*, 3653; W. L. Nelson, J. E. Wennerstrom, S. R. Sankar, *J. Org. Chem.* **1977**, *42*, 1006; b) Os: A. I. Scott, A. D. Wrixon, *J. Chem. Soc. Chem. Commun.* **1969**, 1184; c) Ni: J. Dillon, K. Nakanishi, *J. Am. Chem. Soc.* **1975**, *97*, 5409; d) Pr: J. Dillon, K. Nakanishi, *J. Am. Chem. Soc.* **1975**, *97*, 5417; e) Mo: J. Frelek, N. Ikegawa, S. Takatsuto, G. Snatzke, *Chirality* **1997**, *9*, 578 and references therein; f) J. Frelek, M. Geiger, W. Voelter, *Curr. Org. Chem.* **1999**, *3*, 117.

[13] a) C. Rosini, S. Scamuzzi, G. Uccello-Barretta, P. Salvadori, *J. Org. Chem.* **1994**, *59*, 7395; b) C. Rosini, S. Scamuzzi, M. Pisani-Focati, P. Salvadori, *J. Org. Chem.* **1995**, *60*, 8289; c) C. Rosini, G. P. Spada, G. Proni, S. Masiero, S. Scamuzzi, *J. Am. Chem. Soc.* **1997**, *119*, 506.

[14] S. Superchi, M. I. Donnoli, C. Rosini, *Org. Lett.* **1999**, *1*, 2093.

[15] Under our conditions ketone **1** did not directly react with the diols to give the dioxolanes, so it was necessary to transform **1** into its more reactive dimethyl acetal **2**.

[16] a) I. O. Sutherland, M. V. J. Ramsay, *Tetrahedron* **1965**, *21*, 3401; b) R. E. Carter, K.-I. Dahlqvist, P. Berntsson, *Org. Magn. Reson.* **1977**, *9*, 44; c) P. Rashidi-Ranjbar, J. Sandström, *Proc. 4th Int. Conf. on CD* (Bochum, Germany), **1991**, p. 152.

[17] MMX, Serena Software, P. O. Box 3076, Bloomington IN 47402, USA.

[18] Formal inversions according to the Cahn–Ingold–Prelog (CIP) rules can occur.

[19] a) E. Bunnenberg, C. Djerassi, K. Mislow, A. Moscowitz, *J. Am. Chem. Soc.* **1962**, *84*, 2823; b) K. Mislow, E. Bunnenberg, R. Records, K. Wellman, C. Djerassi, *J. Am. Chem. Soc.* **1963**, *85*, 1342.

[20] a) B. Borecka, T. S. Cameron, A. Linden, P. Rashidi-Ranjbar, J. Sandström, *J. Am. Chem. Soc.* **1990**, *112*, 1185; b) P. Rashidi-Ranjbar, J. Sandström, *J. Mol. Struct.* **1991**, *246*, 25; c) R. Isaksson, P. Rashidi-Ranjbar, J. Sandström, *J. Chem. Soc. Perkin Trans. 1* **1991**, 1147; d) L. Loncar-Tomascovic, R. Sarac-Arneri, A. Hergold-Brundic, A. Nagl, M. Mintas, J. Sandström, *Helv. Chim. Acta* **2000**, *83*, 479.

[21] a) L. M. Tolbert, M. Z. Ali, *J. Org. Chem.* **1982**, *47*, 4793; b) M. Tichy, J. Holanova, J. Zavada, *Tetrahedron: Asymmetry* **1998**, *9*, 3497.

[22] V. Bakthavachalam, L.-G. Lin, X. M. Cherian, A. W. Czarnik, *Carbohydr. Res.* **1987**, *170*, 124.

[23] Enantiopure diols **3a**–**e**, **g**, **h** are commercially available (Aldrich) and were used as purchased, while diol **3f** (75% ee) was a generous gift of Prof. C. Bonini, Università della Basilicata.

[24] S. Superchi, M. I. Donnoli, G. Proni, G. P. Spada, C. Rosini, *J. Org. Chem.* **1999**, *64*, 4762.

[25] For such a definition of biphenyl absorption bands, see H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules*, Academic Press, New York, **1967**, p. 262 and p. 272.

[26] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147198. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[27] See ref. [25], p. 285.

[28] B. Kiupel, C. Niederalt, M. Nieger, S. Grimme, F. Vögtle, *Angew. Chem.* **1998**, *110*, 1308; *Angew. Chem. Int. Ed.* **1998**, *37*, 3031.

[29] In principle all the signals are split as a consequence of the diastereomerization process. However the benzylic methylene and ketal methyne signals were the most suitable for monitoring the dynamic process because of their separation from the remaining signals.

[30] In order to check the influence of the solvent polarity on the diastereoisomer ratios, two samples of **4e** were left to equilibrate overnight at RT in [D$_8$]toluene and [D$_4$]methanol, then cooled at -40°C and the diastereoisomer ratios were measured. The ratios were 78:22 in CD_2Cl_2, the solvent used for VT experiments, 80:20 in [D$_8$]toluene, and 74:26 in [D$_4$]methanol, thus indicating only a modest solvent effect on the diastereoisomer stabilization.