Noncovalent Polymer-like Structures of 1,1′-Bicyclohexylidene-4,4′-dione Dioxime and 1,1′-Bicyclohexyl-4,4′-dione Dioxime. Chiral Recognition in the Solid State

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As a consequence of the high activation barrier for oxime nitrogen inversion, the dioximes 1,1′-bicyclohexylidene-4,4′-dione dioxime (**1**) and 1,1′-bicyclohexyl-4,4′-dione dioxime (**2**) as well as their related monooximes 1,1′-bicyclohexylidene-4-one oxime (**3**) and 1,1′-bicyclohexyl-4-one oxime (**4**) consist of a mixture of stereoisomers. For **1**, the configurational stereoisomers **1**-*E* and **1**-*Z* were identified in solution in a ratio 1:1 (^{13}C NMR). Moreover, in the solid state, **1**-*Z* as well as **3** also consist of conformational enantiomers, viz. **1**-*Z*(*RR*)/**1**-*Z*(*SS*) and **3**-*R*/**3**-*S*, respectively, which rapidly interconvert in solution due to ring inversions of the cyclohexyl moieties. Whereas dioxime **2** consists of an enantiomer pair (**2**-*RR*/**2**-*SS*) and a *meso* form (**2**-*RS*/**2**-*SR*) in a ratio 1:1:2, for monooxime **4** an enantiomer pair (**4**-*R*/**4**-*S*) in a ratio 1:1 is found (chiral HPLC). Upon recrystallization of crude **1**−**4** no segregation of stereoisomers occurs [^{1}H and ^{13}C NMR, FT-IR, (chiral) HPLC, and WAXD]. Both dioximes **1** and **2** crystallize in the achiral $P2_1/c$ space group and possess nearly identical structures build up from stacked layers consisting of parallel oriented noncovalent polymer-like chains formed via intermolecular oxime dimer formation by (self) complementary hydrogen bonding [$R_2^2(6)$ motif in graph-set notation]. In the unit cell both molecules possess C_i symmetry. In addition, C_i symmetry is found in the six-membered rings resulting from hydrogen bonding of two oxime groups. Similar centrosymmetric oxime dimerization is also observed for **3** and **4** in the solid state. The C_i symmetry and the presence of multiple stereoisomers can be reconciled if chiral recognition is operational in the solid state, i.e. intermolecular dimeric hydrogen bonding occurs only between oxime groups of units possessing opposite configurations. This poses restrictions on the stereoisomer distribution within the noncovalent polymer-like chains, viz. it dictates their linear rodlike topology. The oxime disorder observed in all crystal structures is attributed to random stacking of differently oriented noncovalent polymer-like chains (**1** and **2**) or dimers (**3** and **4**).

Introduction

The design of compounds that form well-defined supramolecular structures in the solid state with the use of directional noncovalent intermolecular interactions is referred to as crystal engineering.[1] Among the available noncovalent interactions, intermolecular hydrogen bonding has received considerable attention.[2] It combines moderate strength and directionality.[3] One-, two-, and three-dimensional solid-state packing motifs, i.e. ribbons, tapes, chains, layers, sheets, stacks,[2b,c] and diamondoids,[4] have been prepared, taking advantage of

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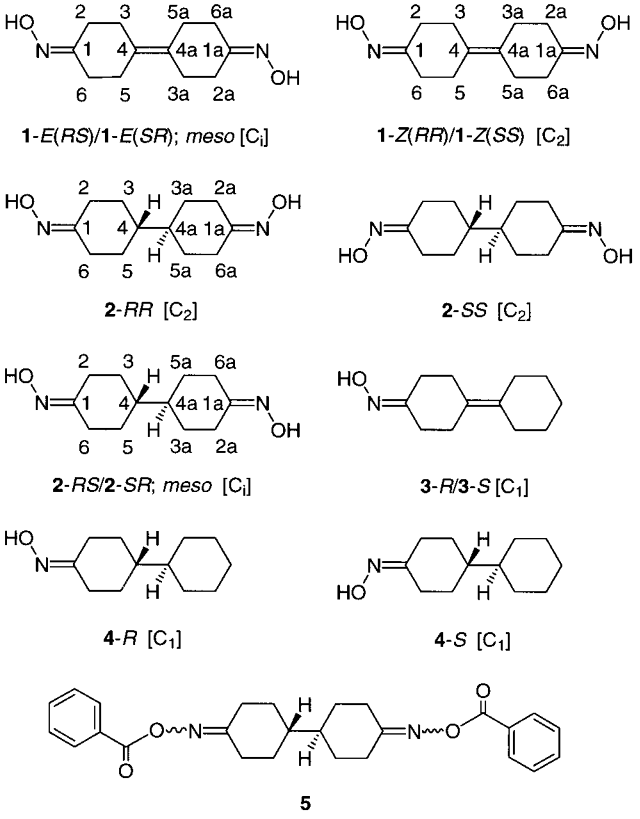
the hydrogen bonding capabilities of hydroxyl, amine, amide, and carboxylic acid functionalities. Remarkably, oxime (−C=N−OH) groups, which possess stronger hydrogen bonding capabilities than alcohols, phenols, and carboxylic acids,[5] have only been rarely applied.[6]

Recently, end-functionalized semirigid rodlike oligo(cyclohexylidenes), which consist of cyclohexyl-type rings linked at the 1,4-positions by carbon−carbon double bonds, were identified as molecular building blocks for supramolecular systems.[7] Single-crystal X-ray structure analyses of derivatives bearing one oxime moiety showed that exclusively dimers [$R_2^2(6)$ motif in graph-set notation][2a,f] are formed due to (self) complementary intermolecular hydrogen bonding.[8−10a] In addition, these oligo(cyclohexylidenes) and their (partly) saturated analogues bearing an oxime headgroup were found to possess amphiphilic properties. Stable Langmuir films at the air/water interface, which can be transferred to hydrophilic silicon substrates, could be prepared.[8] Furthermore, microcrystals were obtained after deposition by spin-coating on hydrophilic silicon wafers enabling the study of microcrystal nucleation and growth using atomic force microscopy.[9]

Here we report and discuss the single-crystal X-ray structures of 1,1′-bicyclohexylidene-4,4′-dione dioxime (**1**) and its saturated analogue 1,1′-bicyclohexyl-4,4′-dione dioxime (**2**, Chart 1). In the solid-state noncovalent polymer-like chains are formed due to self-complementary intermolecular hydrogen bonding. Since oxime nitrogen inversion has a high activation barrier,[10] both **1** and **2** exist as a number of distinct stereoisomers. For **1** both its *E* (**1**-*E*) and *Z* stereoisomer (**1**-*Z*) are discernible in solution. In addition, **1**-*Z* is present as a conformational enantiomer pair [**1**-*Z(RR)*/**1**-*Z(SS)*] in the solid state. In contrast, **2** is present as a configurational enantiomer pair (**2**-*RR*/**2**-*SS*) and a diasteromeric *meso* form (**2**-*RS*/**2**-*SR*) both in solution and the solid state. It is shown that chiral recognition in the solid state determines the noncovalent polymer-like topology of both **1** and **2**.

Chart 1. Structures and PM3[16] Point Groups (between Square Brackets) of the Possible Stereoisomers of **1**−**4**[a]



1-*E*(*RS*)/**1**-*E*(*SR*); *meso* [C$_i$]

1-*Z*(*RR*)/**1**-*Z*(*SS*) [C$_2$]

2-*RR* [C$_2$]

2-*SS* [C$_2$]

2-*RS*/**2**-*SR*; *meso* [C$_i$]

3-*R*/**3**-*S* [C$_1$]

4-*R* [C$_1$]

4-*S* [C$_1$]

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[a] For **1** and **2** the atom numbering corresponds to that in Figure 5.

Single-crystal X-ray structural analyses of the monooximes 1,1′-bicyclohexylidene-4-one oxime (**3**)[10a] and 1,1′-bicyclohexyl-4-one oxime (**4**)[11] (Chart 1) revealed that exclusively dimers [$R_2^2(6)$ motif in graph-set notation][2a,2f] are formed due to self-complementary intermolecular hydrogen bonding of the oxime groups. Hence, for the bifunctional 1,1-bicyclohexylidene-4,4′-dione dioxime (**1**) and 1,1′-bicyclohexyl-4,4′-dione dioxime (**2**) noncovalent polymer-like, viz. rodlike, structures were anticipated in the solid state. This notion was corroborated by a comparison of the physical and spectroscopic properties of **1** and **3**,[10a] as well as of **2** and **4**, respectively. Whereas **1** lacks a clear melting point (DSC) and is thermally stable up to 220 °C (TGA), **3** melts at 114 °C (DSC). Furthermore, **1** is only sparingly soluble in polar protic (CH_3OH, CH_3CH_2OH) and polar aprotic (DMSO, pyridine) solvents, while **3** is soluble in all common organic solvents. The occurrence of intermolecular oxime dimer formation was unequivocally established using solid-state FT-IR. For **1** and **3,** free oxime OH groups (3606 cm^{-1}; CCl_4 solution) are absent; only broad O−H stretch vibrations indicative for intermolecular hydrogen bonding were found (**1**: 3400−3000 cm^{-1} and **3**: 3350−3100 cm^{-1}). The position of the out-of-plane O−H···N (bend) vibrations (**1**: 757 cm^{-1} and **3**: 756 cm^{-1}) is characteristic for intermolecular dimer formation [out-of-plane O−H···N (bend) vibrations: dimer 756 cm^{-1} and trimer 800 cm^{-1}].[10]

Similar results were found for **2** and **4**. Whereas the properties of **2** [sparingly soluble in all common organic

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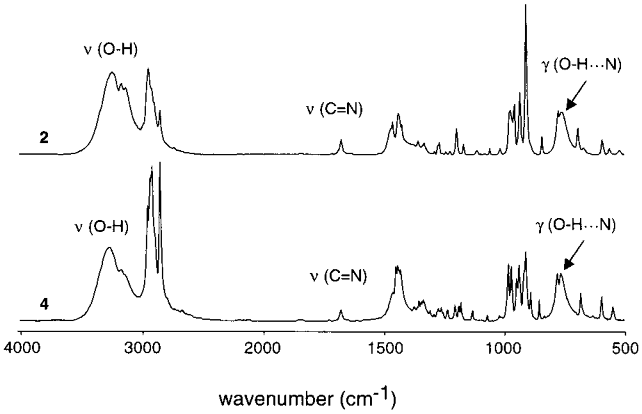

Figure 1. Solid-state FT-IR spectra of crystalline racemic **2** and **4**.

solvents, lack of a clear melting point (DSC) and thermal stability up to 230 °C (TGA)] closely resemble those of **1**, the properties of **4** [mp 97 °C (DSC)[12] and soluble in all common organic solvents] are almost identical to those of **3**. Again intermolecular oxime dimer formation is supported by the observed O—H stretch (**2** and **4**: 3500—3000 cm^{-1}) and out-of-plane O—H···N (bend) vibrations (**2**: 761 cm^{-1} and **4**:[12] 763 cm^{-1}; Figure 1). For compounds **1**—**4**, the assignment of these vibrations was supported by deuteration experiments (see Experimental Section for procedure).

Stereochemistry of Compounds 1—4. As a consequence of the high activation barrier for oxime nitrogen inversion ($\Delta H^{\ddagger}$40—50 kcal/mol[10,13]), stereoisomerism has to be taken into account for compounds **1**—**4**. In the case of 1,1′-bicyclohexylidene-4,4′-dione dioxime (**1**), *E* (**1**-*E*) and *Z* stereoisomers (**1**-*Z*) are expected.[14] Whereas in **1**-*E* the oxime—OH groups are located on opposite sides of the bicyclohexylidene skeleton, which possesses an *anti* conformation,[15] in the **1**-*Z* they are positioned on the same side (Chart 1). Semiempirical PM3[16] calculations gave molecular C_i (**1**-*E*) and C_2 symmetry (**1**-*Z*) [ΔH_f^0 (**1**-*E* and **1**-*Z*): −9.0 kcal/mol, see Experimental Section and Supporting Information]. The presence of both stereoisomers in a ratio 1:1 was unequivocally established using ^{13}C NMR (DMSO-d_6);[10a,17]in line with the high activation barrier for oxime nitrogen inversion, no coalescence phenomena were observed upon heating of the sample up to 159 °C.

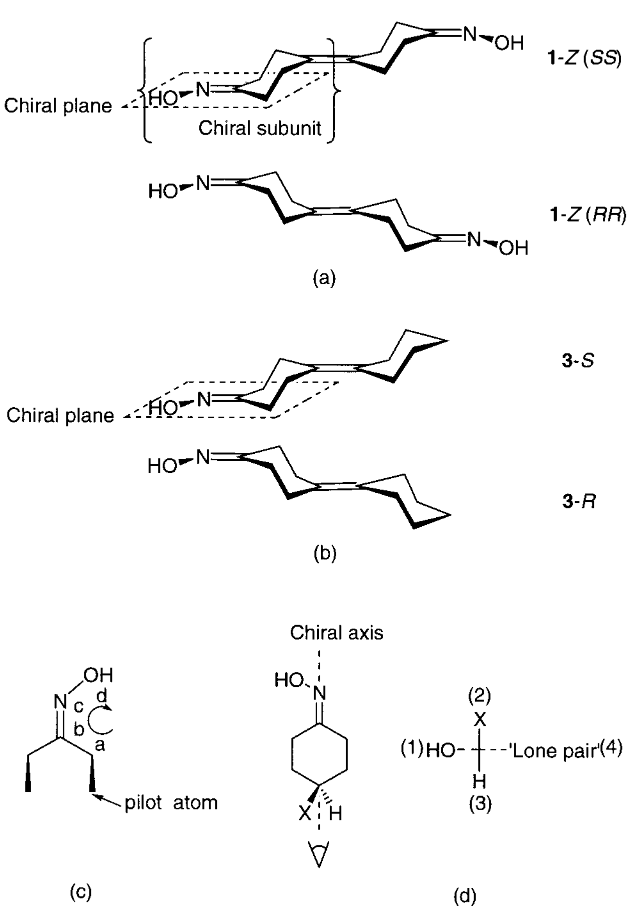

Figure 2. Structures of (a) conformational enantiomer pair of **1**-*Z* [**1**-*Z(RR)*/**1**-*Z*(*SS*)], (b) conformational enantiomer pair of **3** (**3**-*R*/**3**-*S*), (c) configurational assignment for subunits of **1**-*Z* and **3** having a chiral plane (*R* configuration shown),[18] and (d) configurational assignment for an axially dissymmetric cyclohexanone oxime with a substituent X at C4 (precedences in parentheses; *R* configuration shown).

It should be stipulated, that for **1**-*Z* and **3** besides configurational *E*/*Z* stereoisomerism, also conformational stereoisomerism has to be taken into consideration in the solid state.[14] Due to a number of possible conformations of the bicyclohexylidene skeleton of **1**-*Z* (C_2) as well as monooxime **3** (C_1) both compounds will be present as conformational enantiomers pairs in the solid state [**1**-*Z* [**1**-*Z(RR)*/**1**-*Z*(*SS*)] and **3** (**3**-*R*/**3**-*S*), Figure 2, parts a and b][13] For **1**-*Z* and **3** chirality is a consequence of a stereogenic (chiral) plane, which contains the nitrogen and oxygen atoms as well as C1, C2, and C6 (Chart 1; see also Figure 2c for the assignment of configuration according to the Cahn, Ingold, and Prelog rules).[18] Accordingly, **1**-*E* represents the *meso* form [**1**-*E(RS)*/**1**-*E*(*SR*)].

Although the configurational stereoisomers **1**-*E* (C_i) and **1**-*Z* (C_2) can be distinghuished in solution, this is not the case for the conformational enantiomers of **1**-*Z* [**1**-*Z(RR)*/**1**-*Z*(*SS*)] and **3** (**3**-*R*/**3**-*S*). ^{1}H NMR spectroscopy shows that rapid interconversions of the cyclohexyl moieties take place; the equatorial and axial protons of

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(13) The OH group can occupy two positions with respect to the C—C=N plane related by a 180° rotation around the C=N bond: Lambert, J. B.; Takeuchi, Y. *Acyclic Organonitrogen Stereodynamics*; VCH: Weinheim, 1991; Chapters 2 and 6 and references therein.

(14) Definitions regarding the basic terminology of stereochemistry are used as described in: Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; John Wiley and Sons: New York, 1994.

(15) In the *anti* conformation both cyclohexyl-type rings adopt chairlike conformations in such a way that the bicyclohexylidene skeleton has a stairlike geometry.[7]

(16) Stewart, J. J. P. MOPAC: A Semiempirical Molecular Orbital Program, Version 7.0, 1993. PM3: Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(17) ^{1}H and ^{13}C NMR spectroscopy, in combination with single-crystal X-ray analysis, showed that in cocrystals of **1** and DMSO molecules (ratio 1:2) only **1**-*E* is present.[10a]

(18) To obtain the descriptor for the sense of chirality (configuration) of plane chiral stereoisomers one views the chiral plane from the out-of-plane atom (pilot atom) closest to the plane (Figure 2c). If multiple pilot atom candidates are present, the atom of higher precedence according to the sequence rules is chosen. Subsequently, the configuration is determined by the array that is described by the adjacent three atoms a, b, and c (chosen by precedence, if there is a choice) on the chiral plane (clockwise array: *R*) However, in case of **1**-*Z* as well as **3** a fourth atom besides a, b, and c is necessary to be able to choose the pilot atom (C3 or C5). Thus assigning the oxygen atom with d, the configuration shown in Figure 2c is *R* (see ref 14, Chapter 14).

C2/C2a, C3/C3a, C5/C5a, and C6/C6a of both **1** and **3**[12] are isochronous at room temperature (Chart 1).[19] Moreover, upon cooling of an NMR solution (acetone-d_6) of **3** to −34 °C, where **3** precipitates, no decoalescence phenomena were observed. Unfortunately, due to the poor solubility of **1** (vide supra) similar experiments were impossible.

In the case of **2** and **4**, configurational *E*/*Z*-stereoisomerism does not contribute. However, due to the presence of the single carbon−carbon bond between the 4 and 4a positions in **2** and **4** these compounds are axially dissymmetric, viz. they possess a chiral axis parallel to the imino bond (see Figure 2d for their configurational assignment according to the Cahn, Ingold, and Prelog rules[20−23]). For 1,1′-bicyclohexyl-4,4′-dione dioxime (**2**), an enantiomer pair (**2**-*RR*/**2**-*SS*) and a *meso* form (**2**-*RS*/**2**-*SR*) can be distinguished. Whereas **2**-*RR*/**2**-*SS* possess C_2 symmetry [PM3: ΔH_f^o (**2**-*RR*/**2**-*SS*) −28.0 kcal/mol, see Experimental Section and Supporting Information], **2**-*RS*/**2**-*SR* has C_i symmetry [PM3: ΔH_f^o (**2**-*RS*/**2**-*SR*) −28.0 kcal/mol]. Depending on the amount of overlap between corresponding ^{13}C NMR resonances of the diastereomers, a maximum of 12 and a minimum of 6 distinct signals for an isomeric mixture of **2** is expected. Unfortunately only C2, C2a, C6, and C6a are partly resolved (Chart 1 and Supporting Information).[24] Analogous to **1**,[10a] variable-temperature ^{1}H and ^{13}C NMR spectroscopy (DMSO-d_6) up to 102 °C of **2** revealed that oxime nitrogen inversion does not occur. Unequivocal evidence for the presence of the enantiomer pair (**2**-*RR*/**2**-*SS*) and the *meso* form (**2**-*RS*/**2**-*SR*) as well as the enantiomer pair (**4**-*R*/**4**-*S*) for **2** and **4**, respectively, was obtained using chiral HPLC (see Experimental Section). Whereas for **4** two peaks (t'_R, 29.2 and 36.6 min, ratio 1:1) were found,[25] no resolution could be obtained for **2** (**2**-*RR*:**2**-*SS*:**2**-*SR*/**2**-*RS* ratio 1:1:2).[26] However, the HPLC trace for its dibenzoate derivative **5** shows the three expected stereoisomers (t'_R, 20.4, 28.0, and 38.0 min, ratio 2:1:1; Chart 1 and Figure 3). The peak of highest intensity represents the *meso* form (**5**-*RS*/**5**-*SR*) while the two peaks of equal intensity are assigned to the enantiomer pair (**5**-*RR*/**5**-*SS*).

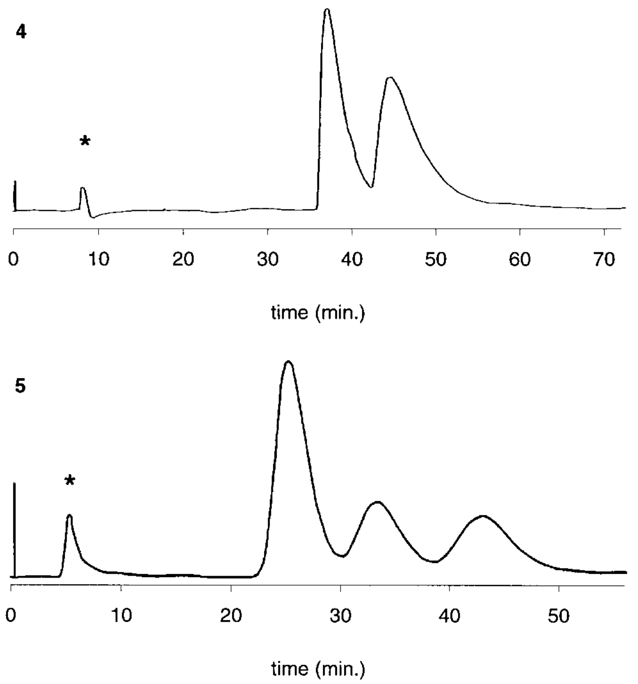

Figure 3. Chiral HPLC traces of racemic mixtures of **4** and **5**. Peaks due to sample solvent are marked with an asterisk (∗). Compound **5** is a dibenzoate derivative of racemic **2** (see Text and Chart 1). Adjusted retention times (t'_R) are reported in the text.

Table 1. Crystallographic Data for 1,1′-Bicyclohexylidene-4,4′-dione Dioxime (1) and 1,1′-Bicyclohexyl-4,4′-dione Dioxime (2)

	1	**2**
formula	$C_{12}H_{18}N_2O_2$	$C_{12}H_{20}N_2O_2$
molecular weight	222.28	224.30
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
T (°C)	−123	−123
A (Å)	7.5343(11)	7.7595(12)
B (Å)	9.222(2)	9.5618(7)
C (Å)	10.509(2)	10.5280(15)
β (deg)	128.361(14)	129.662(10)
V (Å^3)	572.5(2)	601.33(16
D_{calc} (g cm^{-3})	1.289	1.239
Z	2	2
R_1, wR_2	0.0713, 0.180	0.0523, 0.124

[a] $R_1 = [\Sigma|F_0| - |F_c|]/\Sigma|F_0|$ and $wR_2 = [\Sigma w(|F_0|^2 - |F_c|^2)^2/\Sigma w|F_0 2|^2]^{1/2}$.

Single-Crystal X-ray Structures of Dioximes 1 and 2. Suitable crystals for single-crystal X-ray analysis were grown from saturated methanol solutions (Table 1). Both **1** and **2** crystallize in the $P2_1/c$ space group and contain two symmetry related molecules in the unit cell. A crystallographic center of inversion located at the center of the C4−C4a bond, i.e. the carbon frameworks of **1** and **2** possess C_i symmetry, is found in the solid state (Figure 4). In agreement with results reported earlier,[8−11,27] molecules of **1** and **2** possess a rodlike shape, viz. the cyclohexyl-type rings adopt chairlike conformations. Hence, the bicyclohexylidene skeleton of **1** as well as the bicyclohexyl skeleton of **2** adopt *anti* conformations (Figure 4). Bond lengths and valence angles are in agreement with those previously found for

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[19] PM3[16] calculations suggest that for **1**-*Z* a *syn* conformer (bicyclohexylidene skeleton: *syn* conformation) is accessible [C_s symmetry, ΔH_f^o (**1**-*Z*, *syn*) −9.0 kcal/mol] which possesses a mirror plane (*meso* form). See also: Havenith, R. W. A.; Jenneskens, L. W.; van Lenthe, J. H. *Chem. Phys. Lett.* **1998**, *282*, 39.

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[22] Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill Book Company, Inc: New York; Chapter 11. The nitrogen lone pair represents the second substituent at nitrogen and the *R*/*S* configuration is determined by substituent ranking at nitrogen and C4 according to the sequence rules with the lone pair possessing the lowest precedence.

[23] Compound **2** consists of two cyclohexanone oxime subunits connected via their C4 atoms. In contrast to **1** and **3**, where both configurational and conformational stereoisomers are found, for **2** and **4** only configurational stereoisomerism independent of the conformation of the bicyclohexylidene skeleton will apply.[14]

[24] Unequivocal assignment of the four resolved ^{13}C NMR resonances of **2** to two diastereoisomeric species (enantiomer pair and *meso* form) using ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY spectroscopy, failed due to the lack of an appropriate reference and overlap of the proton signals of C2, C2a, C6, and C6a (Chart 1) in the 1D ^{1}H- and the 2D ^{1}H,^{1}H-COSY spectra. Resolution enhancement by chemical modification of racemic **2**, viz. by using the dibenzoate **5**, also gave partially resolved ^{13}C NMR signals only.

[25] Increased ratios *n*-hexane/2-propanol gave enhanced resolution.

[26] Although **2** has low solubility in the eluent, high-sensitivity UV detection allowed the use of dilute samples.

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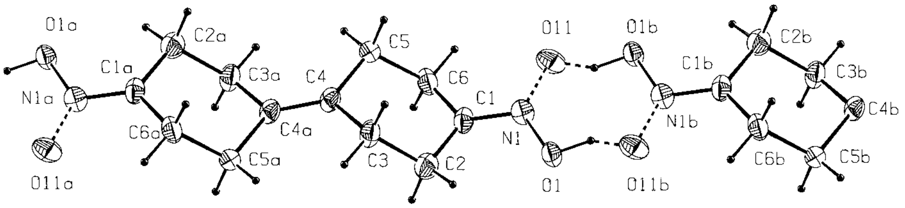

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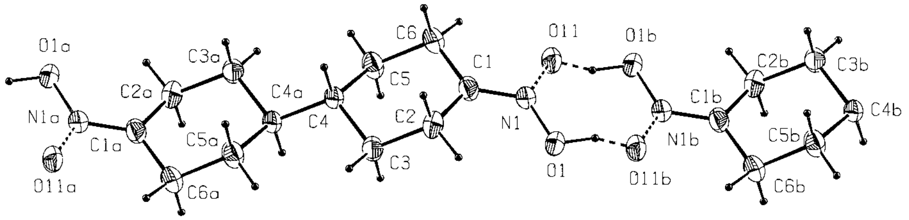

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Figure 4. ORTEP representations (50% probability level) of **1** and **2** with oxime disorder (O11 represents the minor disorder form).

Table 2. Selected Bond Lengths and Valence Angles for 1,1′-Bicyclohexylidene-4,4′-dione Dioxime (1) and 1,1′-Bicyclohexyl-4,4′-dione Dioxime (2)[a]

	bond length (Å)			valence angle (deg)	
bond	**1**	**2**	angle	**1**	**2**
C4−C4^b	1.329(6)	1.539(3)	N1−C1−C2	123.2(4)	122.99(15)
C1−N1	1.273(5)	1.279(2)	N1−C1−C6	120.6(4)	120.74(17)
N1−O1	1.448(5)	1.464(2)	C2−C1−C6	116.2(3)	116.27(15)
N1−O11	1.478(12)	1.521(3)	C1−N1−O1	114.2(4)	114.17(15)
C1−C2	1.498(5)	1.494(3)	C1−N1−O11	116.1(6)	114.71(18)
C1−C6	1.491(5)	1.489(2)	C3−C4−C5	110.2(3)	108.95(14)
C2−C3	1.527(7)	1.531(3)	C3−C4−C4^b	125.5(4)	111.94(16)
C5−C6	1.530(7)	1.531(3)	C1−C2−C3	110.2(4)	110.85(18)
C3−C4	1.508(6)	1.530(2)	C2−C3−C4	111.7(4)	112.68(17)
C4−C5	1.522(5)	1.530(2)	C5−C4−C4^b	124.3(4)	112.34(18)
O1···N1^c	2.736(7)	2.747(2)			

[a] For atom numbering see Figure 5. [b] $2 - x, -y, 1 - z$. [c] $1 - x, 1 - y, -z$.

oligo(cyclohexylidene) compounds bearing only one oxime headgroup (Table 2).[8−11] Note that due to the presence of all stereoisomers in the solid state (vide infra), all structural data of **1**−**4** will be weighted. Furthermore, the hydrogen-bonded oxime groups of dioximes **1** and **2** are disordered over two positions related by a 180° rotation with respect to the imino bond (disorder ratio: **1** 0.69:0.31 and **2** 0.63:0.37, Figure 4). It should be noted that there is no symmetry restriction imposed on the disorder ratio by the inversion center. Hence, it might deviate from 0.50:0.50 if the disorder ratio depends on the mode of incorporation of the various stereoisomers as well as their packing modes in the solid state (vide infra). Similar disorder was found in the single-crystal X-ray structures of monooximes **3** and **4** (disorder ratio: **3**, 0.53:0.47 and **4**, 0.61:0.39), as well as of other derivatives.[8−11]

Indeed, both **1** and **2** form noncovalent polymer-like chains by (self) complementary intermolecular hydrogen bonding in the solid state (Figure 5). Two oxime groups of neighboring molecules form centrosymmetric, nearly planar[28] six-membered rings consisting of two O−H···N hydrogen bonds [$R_2^2(6)$ motif in graph-set notation[2a,f]]. An antiperiplanar conformation is found for the oxime groups.[6,10a] Each six-membered ring contains a crystallographic center of inversion, which is also found for the dimers of the monooximes **3** and **4** in the solid state.[8−11] The hydrogen bond (D···A) distances [**1**: 2.736(7) Å and **2**: 2.747(**2**) Å] are in agreement with the occurrence of intermolecular hydrogen bonding. They are significantly smaller than the sum of the isotropic van der Waals radii for nitrogen and oxygen (N: 1.55 Å and O: 1.52 Å)[29] as well as the average N···O distance (2.822 Å) observed for other oxime dimers.[6]

Although the solid-state packing motifs of **1** and **2** are nearly identical, they differ significantly from those found for oligo(cyclohexylidenes) bearing only one oxime group, viz. **3** and **4**.[10a,11] Whereas in the case of **3** and **4** the dimers stack parallel on top of each other, the linear rodlike, noncovalent polymer-like chains of **1** and **2** stack close to perpendicularly. The chains extend along two body diagonals (1, 1, 1) and (1, −1, 1) of the unit cell (Figure 6). Densely packed layers in which parallel neighboring chains are shifted with respect to each other over a distance equal to half the length of a molecule are formed. Subsequently, these layers are stacked on top of each other along the *a* axis. The angles between the vectors (1, 1, 1) and (1, −1, 1) along which the polymer-like chains of successive layers extend are 84° and 81° for **1** and **2**, respectively. Efficient packing is reflected by their densities [X-ray: **1**, 1.289 g cm^{-3} and **2**, 1.239 g cm^{-3}; and picnometry: **1**, 1.30 g cm^{-3} and **2**, 1.20 g cm^{-3}].[30]

Stereoisomer Distribution, Oxime Disorder, and Solid-State Topology. Although both **1** and **2** give noncovalent polymer-like chains in the solid state, several issues remain to be addressed. For example, to what extent do stereoisomer distribution and oxime disorder affect the solid-state packing motifs in general and the polymer-like chain topologies in particular?

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(28) In every six-membered ring formed by hydrogen bonding, one nitrogen atom is located below and the other above [distances: **1**, 0.129(5) Å and **2**, 0.110(2) Å] a plane containing all four positions of the disordered oxygen atoms.

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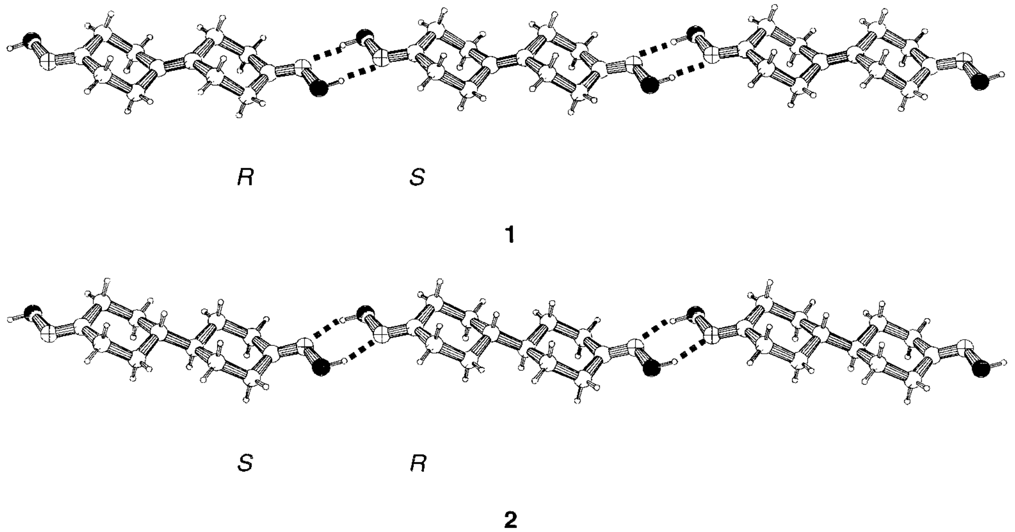

Figure 5. Noncovalent polymer-like chains of **1** and **2** in the solid state. For clarity only the **1**-*E(RS/SR)* and **2**-*RS/SR* stereoisomers, respectively, are shown.

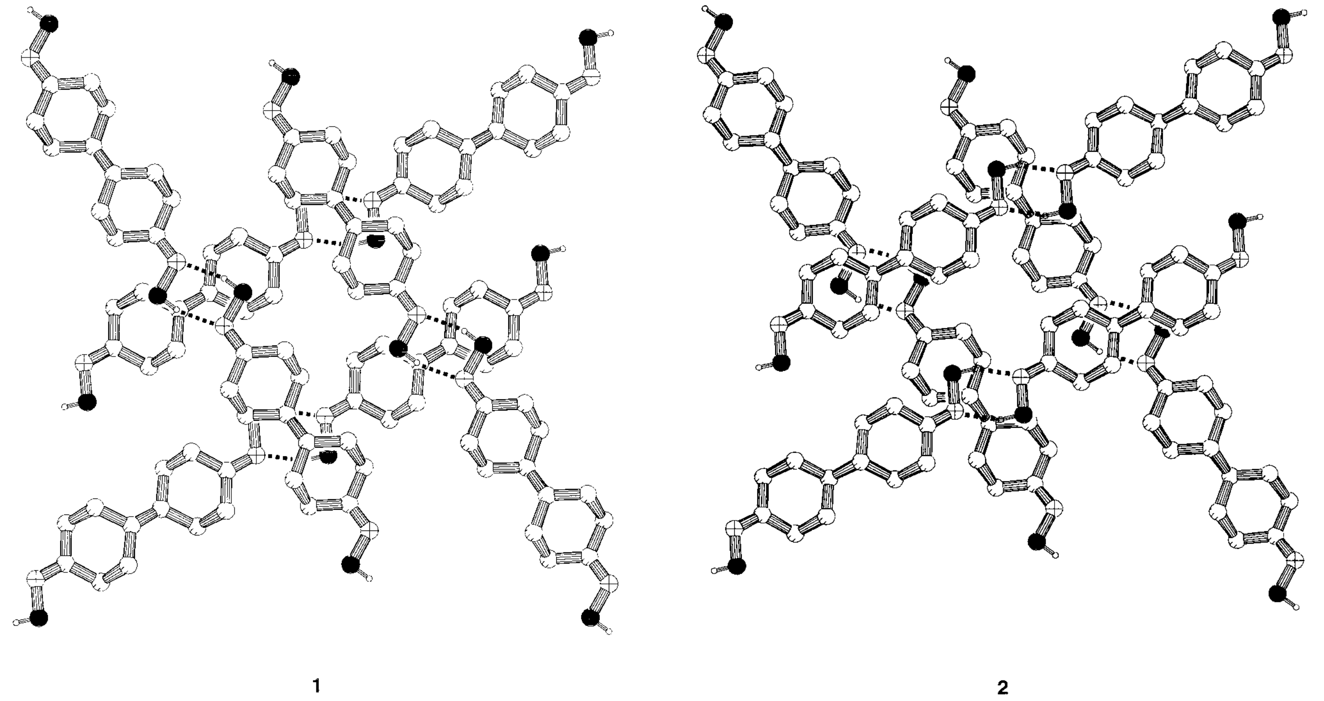

Figure 6. Solid-state packing motifs of **1** and **2** of the noncovalent polymer-like chains. For clarity only the **1**-*E(RS/SR)* and **2**-*RS/SR* stereoisomers, respectively, are shown.

Insight can be obtained by a comparison of ^{13}C NMR, (chiral) HPLC as well as WAXD data of crude and recrystallized **1** and **2**, in combination with a reexamination of the single-crystal X-ray structural data of **3** and **4**.

The ^{13}C NMR data of crude and recrystallized **1** and **2**, respectively, reveal the presence of two stereoisomers in a ratio 1:1. Whereas for **1** they are the configurational stereoisomers **1**-*E* and **1**-*Z*,[10a] in the case of **2** they represent the enantiomer pair **2**-*RR*/**2**-*SS* and the *meso* form **2**-*RS*/*SR*. For **2** this is supported by chiral HPLC (**2**-*RR*:**2**-*SS*:**2**-*RS*/*SR* ratio 1:1:2, vide supra). These results strongly indicate that both in crude as well as recrystallized **1** and **2,** all stereoisomers are present in identical ratios. This is confirmed by the achiral $P2_1/c$ space group of **1** and **2**. Furthermore, the identical positions and intensities of reflections in powder diffraction patterns (WAXD) of crude **1** and **2** and those calculated from the single-crystal X-ray structures, respectively, rule out stereoisomer segregation during recrystallization.

Furthermore, a reexamination of the single-crystal X-ray structures of 1,1′-bicyclohexylidene-4-one oxime (**3**)[10a] and 1,1′-bicyclohexyl-4-one oxime (**4**)[11] revealed that the dimer structure will be markedly affected by chiral recognition between the *R* an *S* enantiomer in the case of **3** and **4**, i.e., hydrogen bonding between two molecules of **3** or **4** with either an *R* or *S* conformation would give dimers possessing C_2 symmetry and a bent geometry, instead of the centrosymmetric, linear, rod-like dimers formed by combining molecules that have opposite conformations (see Supporting Information).

The occurrence of oxime disorder in the centrosymmetric dimers of **3** and **4** is rationalized by random stacking of differently oriented dimers. Rotation (180°)

of a dimer around its long axis followed by a second rotation (180°) around an axis parallel to the stacking direction leaves the average atomic positions of the bicyclohexylidene skeleton as well as of the imino nitrogens nearly unaffected, whereas the OH groups become disordered (see Supporting Information).[10a,31−33]

These results indicate that chiral recognition will also play an important role in determining the stereoisomer distribution and the topology of the noncovalent polymer-like chains of **1** and **2**. Note that for **1** and **2** three stereoisomers have to be taken into account. Since **1** consists of *E* and *Z* stereoisomers (ratio 1:1), the molecular C_i symmetry in the unit cell indicates that **1**-*Z* [enantiomer pair **1**-*Z(RR)*/**1**-*Z(*SS), C_2 symmetry] has to be randomly distributed. However, because of the inversion center found in the six-membered rings formed by the intermolecularly hydrogen-bonded oxime groups, chiral recognition has to be operational. This poses restrictions on the stereoisomer distribution; intermolecular hydrogen bonding has to occur between subunits possessing a *R* and a *S* configuration. The other two stereogenic units of the coupled stereoisomers are allowed to have either a *R* or a *S* configuration as long as the overall molecular *anti* conformation of the bicyclohexylidene skeleton is maintained. Using similar arguments, the distribution of **1**-*E* [**1**-*E(RS)*/**1**-*E*(*SR*), C_i symmetry] cannot be resolved. It is likely to be random, albeit with the restriction that only *R* and *S* subunits participate in intermolecular oxime hydrogen bonding with a *S* and *R* subunit, respectively, of a molecule **1**-*E* or any of its other stereoisomers.

In the case of 1,1′-bicyclohexyl-4,4′-dione dioxime (**2**) the distribution of the *meso* form (**2**-*RS*/**2**-*SR*, C_i symmetry) in the noncovalent polymer-like chains remains unresolved. Furthermore, both enantiomers (**2**-*RR*/**2**-*SS*, C_2 symmetry) have to be randomly distributed in a ratio 1:1. The center of inversion in the six-membered rings obtained by intermolecular oxime hydrogen bonding indicates that chiral recognition is again operational. In contrast to **1**, compound **2** possesses methine hydrogens at C4 and C4a, which can be conveniently utilized as a probe for the determination of the stereoisomer distribution (Chart 1). In going from one side to the other along a noncovalent polymer-like chain, the methine hydrogens alternately point "up" and "down" with respect to the plane bisecting the bicyclohexyl carbon framework, i.e., they possess an "up−down−up−down" pattern (Figure 5). This is only possible, if **2**-*RR* (**2**-*SS*) forms an intermolecular hydrogen bond with a cyclohexanone oxime subunit[23] possessing an *S* (*R*) configuration. The latter subunit has to belong either to **2**-*SS* (**2**-*RR*) or the *meso* compound (**2**-*RS*/**2**-*SR*). If an oxime moiety of **2**-*RR* hydrogen bonds with a cyclohexanone oxime subunit also possessing a *R* configuration, the methine hydrogens would show an "up−down−down−up" pattern, which corresponds to the pattern of a bent dimer of **4** (**4**-*S*/**4**-*S* or **4**-*R*/**4**-*R*, see Supporting Information). Importantly, as was found for the dimers of **3** and **4**, chiral recognition by subunits of both **1** and **2** also controls intermolecular oxime hydrogen bonding and consequently dictates the topology of the noncovalent polymer-like chains.[34]

With respect to the oxime disorder in the case of **1** and **2,** we anticipate that it is either a consequence of random stacking of differently oriented chains analogous to the stacking of dimers of **3** and **4** or resulting from stacking of chains that have different stereoisomer sequences. Therefore, we predict that oxime disorder will only be absent in crystals derived from pure enantiomers. However in that case, curved instead of rodlike chain topologies will be obtained as a consequence of the molecular C_2 symmetry of the enantiomers. Experiments are in progress.

Conclusions

In the solid state, dioximes **1** and **2** form noncovalent polymer-like chains via oxime dimer formation due to (self) complementary intermolecular hydrogen bonding. Identical hydrogen bonding occurs for the monooximes **3** and **4** in the solid state. Both crude and recrystallized **1** contain configurational *E* and *Z* stereoisomers randomly distributed in a ratio 1:1. Evidence is presented that in the solid state **1**-*Z* and the related monooxime **3** consists of conformational enantiomers [**1**-*Z*(*RR*)/**1**-*Z*(*SS*) and **3**-*R*/**3**-*S*] in a ratio 1:1, which rapidly interconvert in solution. Crude **2** as well as its single crystals consist of two configurational enantiomers (**2**-*RR* and **2**-*SS*) and a *meso* form (**2**-*SR*/**2**-*RS*) in a ratio 1:1:2, respectively. Similarly, configurational enantiomers (**4**-*R*/**4**-*S*, ratio 1:1) are observed for monooxime **4**. For all compounds, chiral recognition is operational in the solid state. In the case of **3** and **4** intermolecular hydrogen bonding takes place exclusively between enantiomers having an opposite configuration, giving centrosymmetric dimers (C_i symmetry) that possess a rodlike topology. Also for **1** and **2** intermolecular hydrogen bonding only occurs between subunits having opposite configurations (*R* or *S*) of two coupled stereoisomers. Despite the overall random distribution of stereoisomers in the solid state, chiral recognition poses restrictions on the sequence of stereoisomers within the noncovalent polymer-like chains and controls the noncovalent polymer-like topology of the chains. Oxime disorder is observed in the crystal structures of **1**−**4**. It originates from random stacking of differently oriented dimers (**3** and **4**) or noncovalent polymer-like chains (**1** and **2**).

Experimental Section

Analytical Techniques. NMR spectra were recorded on a Bruker AC 300 spectrometer (^{1}H 300.13 MHz; ^{13}C 75.47 MHz) using $CDCl_3$ as the solvent, except for the dioximes, which were measured in DMSO-d_6 (internal standard: TMS). ^{13}C APT, ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY experiments were performed using standard Bruker pulse sequences. FT-IR spectra were

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[31] The double rotation operation is identical to that of dimer inversion followed by a 180° rotation around its long axis.

[32] In the crystal structure of **3** alternate stacking of two crystallographically independent centrosymmetric dimers is found.[10a] However, for each type of dimer a similar disorder ratio is found, which can be rationalized independently by orientational freedom during dimer stacking.

[33] Dimers found in single crystals of other racemic, axially dissymmetric monooxime derivatives[8,9] are always formed by intermolecular hydrogen bonding between opposite enantiomers. Apparently, chiral recognition is a general phenomenon for oligo(cyclohexylidenes) bearing an oxime headgroup as well as their saturated analogues.

[34] For another example of chiral directed self-assembly, see: Brienne, M.-J.; Gabard, J.; Leclerq, M.; Lehn, J.-M.; Cesario, M.; Pascard, C.; Chevé, M.; Dutruc-Rosset, G. *Tetrahedron Lett.* **1994**, *35*, 8157.

recorded on a Nicolet Magna-IR 860 or a Perkin-Elmer System 2000 spectrometer using the KBr pelleting technique. Samples were diluted with optically pure KBr. Oxygen-deuterated analogues of compounds **1**−**4** were obtained by dissolving 0.1 mmol **1**−**4** in CH_3OD (0.5 mL) followed by removal of the solvent in vacuo; this procedure was done twice. Powder wide-angle X-ray diffraction (WAXD) patterns were measured at room temperature with 1.5405 Å Cu Kα radiation using a Delft Instruments Guinnier Johanssen FR 552 camera. Differential scanning calorimetry (DSC) was done on a Mettler DSC 12E (samples ∼10 mg in sealed aluminum pans, N_2, heating and cooling rate 5 °C/min). Thermogravimetric Analyses (TGA) were done using a Perkin-Elmer TGS-2 apparatus equipped with an AR-2 autobalance (N_2, temperature program: 50 → 850 °C, heating rate 20 °C/min). Picnometry[30] was performed in triplicate (picnometer volume 10 mL, solvent degassed cyclohexane, $T = 25.0 \pm 0.1$ °C), and the results were averaged. Chiral HPLC was performed using a Pharmacia Fine Chemicals Liquid Chromatography Controller LCC-500 equipped with two Pharmacia Fine Chemicals Liquid Pumps P 3500, a Kratos Analytical Spectroflow 757 absorbance detector (filter rise time: 1.0 s) and a Diacel Chemical Industries Chiralcel OD column [eluent: *n*-hexane/2-propanol (**4**, 19/1 v/v; and **5**, 3/2 v/v), flow rate (**4**, 0.5 mL/min; and **5**, 1.0 mL/min.), UV detection (**4**, $\lambda = 218$ nm; and **5**, $\lambda = 232$ nm)]. Adjusted retention times (t'_R) were obtained by subtraction of t_{solv} from t_R. From Elemental analysis was performed by Dornis u. Kolbe, Microanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Syntheses. *1,1′-Bicyclohexyl-4,4′-dione* was prepared in a Parr apparatus by catalytic hydrogenation (0.2 g 10% Pd/C, 4 atm H_2) of 1,1′-bicyclohexylidene-4,4′-dione[6] (1.75 g, 19.1 mmol) dissolved in ethyl acetate (150 mL). After filtration through Celite and removal of the solvent in vacuo, pure product was obtained in quantitative yield: ^{1}H NMR δ 1,55 (m, 4H), 1.73 (m, 2H), 2.10 (m, 4H), 2.36 (m, 8H) ppm; ^{13}C NMR δ 29.85, 40.25, 40.80, 211.54 ppm; IR ν 567, 950, 1145, 1174, 1338, 1710, 2891, 2922, 2941, 2955 cm^{-1}.

*1,1′-Bicyclohexylidene-4,4′-dione dioxime (**1**)* was synthesized from the corresponding ketone according to a procedure described elsewhere.[10a]

*1,1′-Bicyclohexyl-4,4′-dione dioxime (**2**)* was synthesized from 1,1′-bicyclohexyl-4,4′-dione (1.14 g, 5.10 mmol) using a similar procedure as for **1**.[10a] Compound **2**: yield 1.00 g (4.44 mmol, 87%); mp 230 °C (dec); ^{1}H NMR δ 1.08 (m, 4H), 1.39 (m, 2H), 1.64 (m, 2H), 1.79 (m, 4H), 2.00 (m, 2H), 2.25 (m, 2H), 3.13 (m, 2H), 10.09 (s, 2H) ppm; ^{13}C NMR δ 23.20, 28.24, 28.27, 29.58, 29.61, 30.97, 40.98, 157.03 ppm; IR ν 593, 694, 756, 908, 934, 957, 975, 1197, 1424, 1437, 1463, 1676, 2849, 2946, 3247 cm^{-1}; WAXD (2θ) 14.25, 14.60, 16.65, 17.25, 19.10, 22.60, 24.50, 25.60, 28.10, 28.80, 30.25. Calc for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.99; N, 12.49; O, 14.26. Found: C, 63.63; H, 9.14; N, 12.34.

*1,1′-Bicyclohexylidene-4-one Oxime (**3**) and 1,1′-Bicyclohexyl-4-one Oxime (**4**)* were synthesized according to procedures described elsewhere.[10a,12]

*Bisbenzoate of 1,1′-Bicyclohexyl-4,4′-dione Dioxime (**5**).* To a stirred solution of **2** (100 mg, 0.446 mmol) in dry pyridine (3.5 mL) cooled to 0 °C (ice bath) was added benzoyl chloride (0.114 mL, 0.892 mmol) with a syringe. The temperature was slowly raised to room temperature after which the reaction mixture was stirred for an additional 24 h. Following removal of the solvent in vacuo, the residue was dissolved in CH_2Cl_2 (10 mL) and washed with a saturated, aqueous $NaHCO_3$ solution (10 mL) and water (10 mL). After drying ($MgSO_4$), filtration over activated carbon and concentration in vacuo, a colorless oil remained (300 mg) which solidified upon standing. The crude material was flash chromatographed using silica 60 (eluent: 200 mL of *n*-hexane/CH_2Cl_2, 1/1 v/v). The filtrate was discarded, and pure **5** was obtained as a white solid by eluting the column with acetone (80 mL) followed by evaporation of solvent: yield 193 mg (0.446 mmol, 100%); ^{1}H NMR δ 1.25−1.53 (m, 6H), 1.90−2.10 (m, 6H), 2.20−2.31 (m, 2H), 2.78 (m, 2H), 3.40 (m, 2H), 7.46 (m, 4H), 7.56 (m, 2H), 8.06 (d, 4H) ppm; ^{13}C NMR δ 26.47, 28.77, 28.88, 29.79, 29.84, 31.56,41.09, 128.50, 129.29, 129.51, 133.18, 164.17, 168.97, 197.48 ppm; IR ν 712, 860, 899, 1022, 1065, 1086, 1175, 1265, 1452, 1599, 1632, 1738, 2864, 2953, 3065 cm^{-1}; chiral HPLC, adjusted retention times (t'_R) 20.4, 28.0, and 38.0 min.

PM3 Calculations. Semiempirical calculations were performed with MOPAC 7.0.[16] Geometry optimizations were done using the PM3[16] Hamiltonian, the eigenvector following routine with initial Hessian calculation, and increased convergence criteria (keywords: EF, HESS=1, RECALC=1, and PRECISE); a GNORM < 0.03 was obtained. All minima were characterized by a Hessian calculation (keywords: FORCE and LARGE); no imaginary frequencies were found (see Supporting Information).

Single-Crystal X-ray Determinations of 1 and 2. Crystals of dioximes **1** and **2** suitable for single-crystal X-ray structure determination were grown from filtered, saturated methanol solutions by slow evaporation of the solvent. X-ray data were collected on an Enraf-Nonius CAD4T diffractometer on a rotating anode using graphite-monochromated MoKα radiation for colorless transparent crystals at a temperature of −123 °C. Unit-cell dimensions were derived from the setting angles of 25 SET4 reflections.[35] Reflection data were reduced using the HELENA[36] program. The structures were solved by direct methods (SHELXS86[37]) and refined on F2 (SHELXL93[38]). The oxime moieties show their usual disorder over two configurations, which was taken into account with a disorder model. The disorder ratios for **1** and **2** were refined to 0.69:0.31 and 0.63:0.37, respectively (cf. text). For compound **1**, hydrogen atoms were taken into account at calculated positions except for the hydrogen-bonded one, which was refined freely. All hydrogen atom positions were refined for compound **2**. Geometrical calculations and illustrations were done with PLATON.[39]

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Supporting Information Available: Stereoisomer distribution of compounds **3** and **4** in the solid state and its consequences on the geometry of the dimers (Figure 7); part of the ^{13}C NMR (solvent DMSO-d_6, 300 K) of racemic **2** showing the partially resolved resonances of C2, C2a, C6, and C6a (Figure 8); PM3 archive files for compounds **1**-*Z(RR/SS)* [C_2], **1**-*E(RS/SR)* [C_i], **2**-*RR*/**2**-*SS* [C_2], **2**-*RS*/**2**-*SR* [C_i], and **1**-*Z(RS/SR)* [C_s] with the bicyclohexylidene skeleton in a *syn* conformation as well as the dimers **3**-*R*/**3**-*S* [C_i], **3**-*R(S)*/**3**-*R(S)* [C_2], **4**-*R*/**4**-*S* [C_i], and **4**-*S(R)*/**4**-*S(R)* [C_2]; single-crystal X-ray structure data of **1** and **2**; and observed and calculated structure factors of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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