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Stereomutation of the Enantiomers of Hindered *O*-Substituted Oximes

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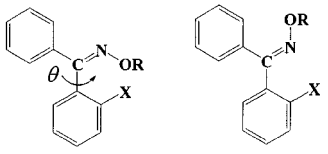
As anticipated by Molecular Mechanics calculations, the (*E*) and (*Z*) isomers of diaryl ketone oximes containing a bulky substituent (PhS or Ph_2N) in the *ortho* position of the phenyl ring, display different conformational preferences. Whereas the (*E*) isomers exhibit a plane of symmetry at any accessible temperature, the (*Z*) isomers exist as a pair of stereolabile enantiomers that were detected by low-temperature NMR spectroscopy in a chiral environment. In a number of *O*-substituted oximes, the enantiomerisation barriers of the (*Z*) isomers were determined by monitoring the line shape of the NMR signals of diastereotopic methylene hydrogen atoms as a function of temperature. The four stereoisomers, generated by the combination of the conformational axial chirality with the configurationally stable chirality of a stereogenic centre, have been all detected in a specifically substituted oxime and monitored in an appropriate chiral environment. The NMR results in solution were confirmed by X-ray diffraction measurements in the solid state.

Introduction

The prototype of diaryl ketone oximes, namely benzophenone oxime ($Ph_2C{=}NOH$), is expected to display two different values for the dihedral angles formed by the plane of the C=NO moiety with that of each phenyl ring, owing to the different steric hindrance experienced by the two aromatic groups. Although an X-ray structure analysis of benzophenone oxime itself is not available, molecular mechanics calculations[2] suggest that in the isolated molecule, the ring in the (*E*) configuration should be nearly coplanar and the ring in the (*Z*) configuration significantly twisted with respect to the C=NO moiety plane, the calculated dihedral angles being 20° and 54°, respectively. The crystal structures obtained for related molecules such as *O*-[1-(benzotriazol-1-yl)-2-methylpropyl]benzophenone oxime,[3a] benzophenone *O*-(2,3,5,6-tetrafluoro-4-pyridyl)oxime[3b] and the two isomeric forms of *para*-bromobenzophenone *O*-picryloxime,[3c] confirm that the (*Z*) rings are twisted much more than the (*E*) rings. As a further example, the two isomeric *para*-chlorobenzaldehyde oximes [3d] have the (*E*) ring coplanar with the plane of the C=NO moiety whereas the (*Z*) ring is twisted out of that plane.

Benzophenone oximes bearing an *ortho* substituent in one of the two phenyl groups can also exist as (*E*) or (*Z*) isomers. In the latter case the substituted ring should be twisted to the point of becoming essentially orthogonal to the C=NO plane. In the (*E*) isomer, on the contrary, the substituted ring might still be accommodated in an arrangement nearly coplanar to the C=NO moiety. Such a qualitative prediction has been substantiated by calculations[2] carried out on diaryl ketone oximes bearing quite a bulky substituent in the *ortho* position of one of the two phenyl rings, as in the case of **1**, **2**.



Z (**a**) E (**b**)

X = SPh ; R = H (**1**)
X= NPh_2 ; R = H (**2**)
X = SPh ; R = Me (**3**)
X = SPh ; R = CH_2-Bu^t (**4**)
X = SPh ; R = CH_2-$COBu^t$ (**5**)
X = SPh ; R = CH_2-$COOBu^t$ (**6**)
X = NPh_2 ; R = CH_2-$COOBu^t$ (**7**)
X = SPh ; R = CHMeEt (**10**)

Whereas in the calculated ground state (GS) conformation of the (*E*) isomers (**1b, 2b**) the plane of the *ortho*-substituted phenyl group turns out to be coplanar with that of the C=NOH moiety, in the GS conformation of the (*Z*) isomers (**1a**, **2a**) the *ortho*-substituted phenyl group is calculated to lie in a plane orthogonal to that of the C=NOH moiety. Contrary to the (*E*) isomers, the (*Z*) isomers are therefore chiral molecules and should exhibit a pair of (*M*)/(*P*) conformational enantiomers if the corresponding interconversion barriers are sufficiently large to be amenable to an experimental verification. A similar situation has been reported to occur in the (*Z*) isomers of some *ortho*-substituted *N*-alkyl-*C*-arylimines.[4]

The calculated[2] energy profile for the rotation about the Ar−CN bond (Ar being the *ortho*-substituted phenyl group) of **1** and **2** indicates that there are two different

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transition states (TS) for such an enantiomerisation process in the (*Z*) isomers. One (i.e. TS_1) corresponds to a planar situation where the X substituent is *syn* (= 0°). The other transition state (i.e. TS_2) corresponds to a planar situation where the X substituent is *anti* (= 180 °) with respect to the OH group (Table 1). In order to detect these stereolabile enantiomers, the rotation rate corresponding to the lower one of the two barriers has to be made sufficiently slow with respect to the time scale of the technique employed for their detection. Depending on the nature of the substituent X, either TS_1 or TS_2 may correspond to the energy level yielding the rate-determining step. In the case of **1a** (X = SPh), for instance, the calculated enantiomerisation barrier is 9.4 kcal mol^{-1} (Table 1): Accordingly, at temperatures close to −90 °C the corresponding life-time should be long enough to allow detection by NMR spectroscopy. Clearly, only in an appropriate chiral environment would separate NMR signals become observable for these enantiomers.

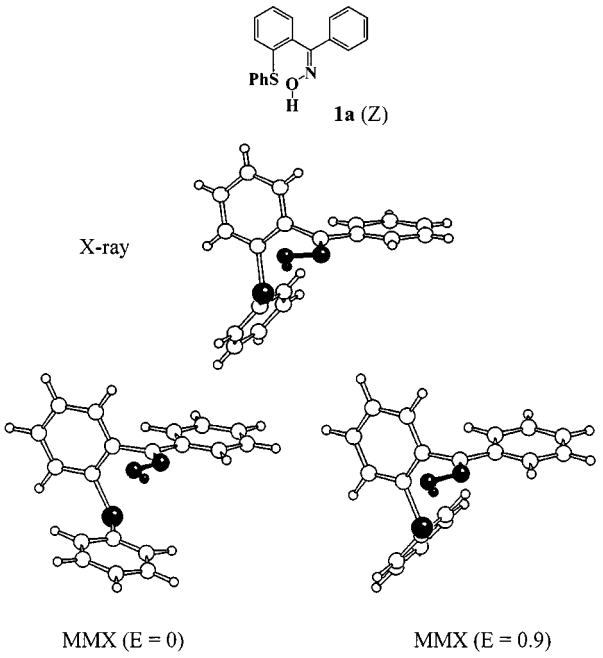
Table 1. Relative energies (*E*, in kcal mol^{-1}) and dihedral angles (θ) between the *ortho*-substituted ring and the C=NO plane in the ground (GS) and transitions states (TS) of the (*Z*) isomers **1a** and **2a** as obtained by MM calculations, see ref.[2]

Compound	GS *E* (θ)	TS_1 *E* (θ)	TS_2 *E* (θ)
1a	0 (97 °)	13.5 (0 °)	9.4 (180 °)
2a	0 (−102 °)	10.2 (0 °)	11.7 (180 °)

Results and Discussion

Both the (*E*) and (*Z*) isomers of oxime **1** were obtained approximately in a 1:5 proportion, by treating hydroxylamine with the corresponding ketone (see Experimental Section). An X-ray diffraction determination did show that the more abundant isomer (m.p. 139 °C) corresponds to the (*Z*) isomer **1a**. In Scheme 1 (top) it is shown how the plane of the *ortho*-substituted phenyl group is indeed orthogonal to that of the C=NOH moiety, as indicated by calculations. The calculated structure corresponding to the absolute energy minimum is essentially equal to that experimentally determined, the only difference concerning the position of the phenyl ring of the SPh substituent (Scheme 1, bottom left). Actually, a theoretical structure identical to the experimental one was also found to correspond to a conformational minimum (Scheme 1, bottom right), but its energy value appeared to be slightly higher (by 0.9 kcal mol^{-1}). The barrier to rotation about the Ph−S bonds is quite low, so that the crystal packing apparently favours a conformation which is expected to be moderately less stable in the isolated molecule. As can be seen in Scheme 1, the steric effects of the more crowded conformer adopted in the crystal are undoubtedly larger than those of the most stable theoretical conformer, but its more compact shape probably fits better into the crystal cell.

The energy value calculated for the (*E*) isomer **1b** is much higher (by 3.7 kcal mol^{-1}) than for the (*Z*) isomer **1a**. The



Scheme 1. Top: X-ray diffraction structure of **1a**; bottom: MMX-calculated structures for the two most stable conformational minima of **1a**; the relative energies *E* are in kcal mol^{-1}

90° torsion angle between the C=NOH moiety and the substituted phenyl in the (*Z*) isomer is likely to relieve the strain which occurs in the (*E*) isomer **1b**, where the substituted phenyl remains coplanar, while the less encumbering unsubstituted phenyl ring becomes orthogonal. Under thermodynamic equilibrium conditions, such a large energy difference would lead to a negligible amount of the (*E*) isomer so that the relatively large yield of the minor isomer (about 20%) seems to indicate that kinetic control is somehow operating in the reaction process. This is supported by the observation that once the isolated isomer **1b** is dissolved in a chlorinated solvent (chloroform or dichloromethane), a rapid isomerisation does take place and only the more stable form **1a** can be observed (both isomers apparently display, in these solvents, identical ^1H and ^{13}C NMR spectra). The *syn*−*anti* interconversion of oximes is known to be an acid-catalysed process [5] so that traces of HCl, likely to be present in chlorinated solvents, greatly accelerate such interconversions. On the other hand, when hydrocarbons are used as solvents, this process is much slower and in [D_8]toluene for instance, the isomer **1b** exists sufficiently long to yield NMR spectra different from those of **1a**.

In CD_2Cl_2, the ^{13}C NMR spectrum of the (*Z*) isomer **1a** displays a single line for the quaternary C=N carbon atom at any temperature down to −85° C. However, in the chiral environment generated by the addition of an appropriate amount of an enantiomerically pure Pirkle's alcohol, such as (*R*)-*l*-Ar−CH(OH)CF_3 (Ar = 9-anthryl), [6] this line splits into a 1:1 doublet (line separation 0.1 ppm) at about −85 °C. On warming to 20 °C, a single line is observed again: this proves that the (*Z*) isomer **1a** is comprised of two stereolabile enantiomers that can be detected only at

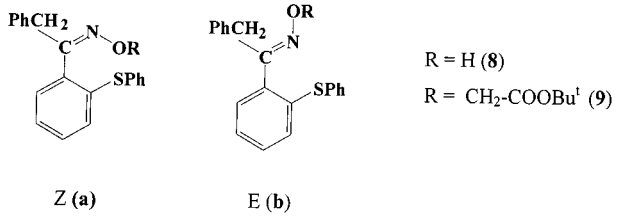
low temperatures because they interconvert too rapidly at ambient temperature. This type of experiment, however, could not be carried out in the case of the (*E*) isomer **1b** because the Pirkle's alcohol turned out to be sufficiently acid to catalyse the rapid interconversion of **1b** into **1a** even in [D_8]toluene.

Contrary to the case of oxime **1**, the (*E*) isomer **2** does not interconvert into the (*Z*) isomer (see Experimental Section) in chlorinated solvents. It might be argued that the catalytic process is hampered by the presence of the amino group which neutralises possible traces of acid present in these solutions. Due to this occurrence, we could check that in a CD_2Cl_2 solution of the (*E*) isomer **2b**, the signal of the C=N carbon atom does not split at −85 °C in the presence of excess enantiomerically pure Pirkle's alcohol, whereas under the same conditions, the corresponding signal of the (*Z*) isomer **2a** does split (separation of 0.6 ppm), much in the same way as reported for the (*Z*) isomer **1a**. It is thus conclusively ascertained that the (*Z*) isomers adopt a chiral conformation whilst the (*E*) isomers do not.

Although we have proved the existence of two stereolabile enantiomers for the (*Z*) isomers **1a** and **2a**, we were not able to determine the corresponding enantiomerisation barriers, owing to the very low signal to noise ratio of the C=N quaternary carbon lines. To overcome this difficulty, we prepared the *O*-methyl derivatives of both the isomers of **1** (i.e. **3a** and **3b**), which are quite stable and do not interconvert so easily into each other. Incidentally this fact seems to support the hypothesis that the interconversion of **1b** into **1a** is facilitated by the intermediacy of a *C*-nitroso tautomeric form,[7] that obviously cannot occur in *O*-alkyl derivatives.

In the presence of the mentioned Pirkle's alcohol,[6] one of the two *O*-methyl isomers (**3a**) displays a methyl ^{1}H signal which broadens on lowering the temperature and eventually splits into a pair of lines below −15 °C, whereas the corresponding signal of the other isomer (**3b**) does not split even at −100 °C. Thus the chiral structure (*Z*) and the achiral structure (*E*) could be confidently assigned to **3a** and to **3b**. The spectral simulation (Figure 1) yields the rate constants, hence the free energy of activation, for the enantiomerisation process (14.9 ± 0.3 kcal mol^{-1}, as in Table 2).

An alternative method to measure the enantiomerisation barriers requires the introduction of a probe sensitive to the chirality, for instance the methylene moiety, which displays diastereotopic hydrogen atoms in asymmetric molecules. For this reason we synthesised a number of (*Z*) isomers (**4a−9a**) containing a CH_2 group and prepared, for comparison, the corresponding (*E*) isomers **6b−9b**.



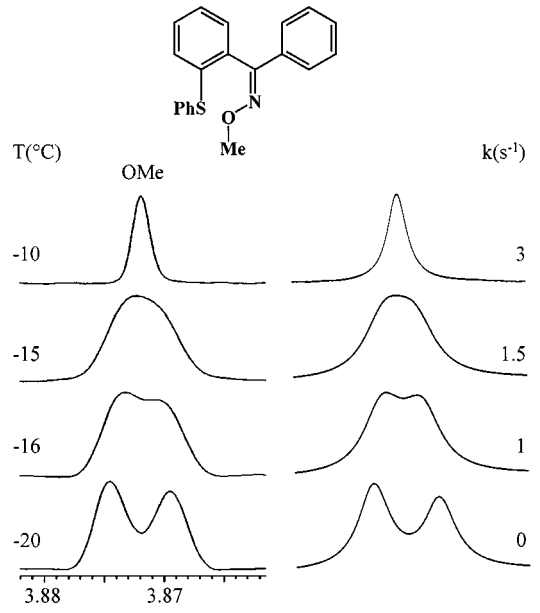


Figure 1. Temperature dependence of the 400-MHz ^{1}H NMR spectrum of **3a** in a CD_2Cl_2 solution containing a 300:1 molar excess of an enantiomerically pure Pirkle's alcohol (see text); on the right, the computer simulation is shown

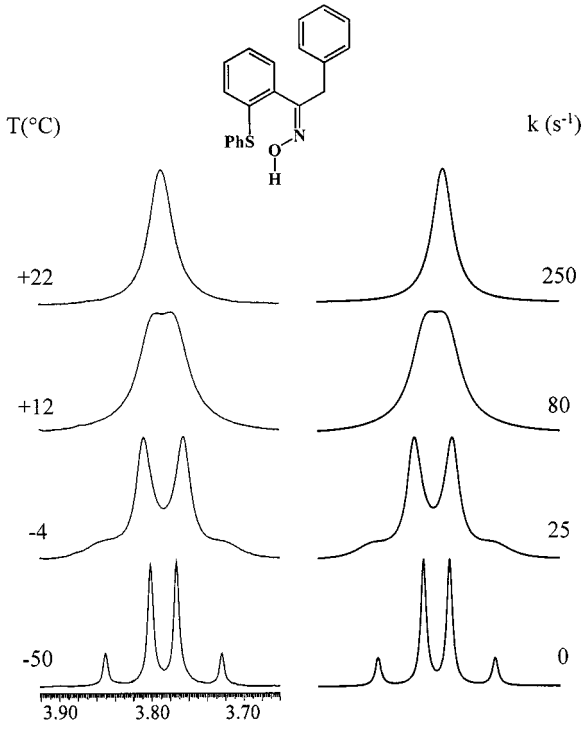


Figure 2. Experimental (left) and computer-simulated (right) ^{1}H methylene signal of **8a** as a function of temperature in $CDCl_3$ at 300 MHz

It is worth mentioning that contrary to the case of oximes **1** and **2**, the reaction leading to oxime **8** yields an amount of the (*E*) isomer larger than that of the (*Z*) isomer (see Experimental Section): a further indication that the reaction is under kinetic control.

The ^{1}H NMR spectra of the (*E*) isomers **6b−9b** always display a single line for the CH_2 hydrogen atoms at any

Table 2. Experimental free energies of activation ($\Delta G^{\neq}$ in kcal mol^{-1}) for the enantiomerisation of the (*Z*) isomers **3a−10a**; the shift separations ($\Delta\nu$) are in Hz at the appropriate temperature (°C)

Compound	$\Delta G^{\neq}$	Monitored signal	$\Delta\nu$ (*T*)	*J* [Hz]	Solvent	Frequency [MHz]
3a	14.9	CH_3	4.8 (−30°)	−	CD_2Cl_2[a]	400
4a	14.4	CH_2	8.5 (−30°)	−10.2	CD_2Cl_2	400
5a	14.8	CH_2	92 (−20°)	−17.3	$CDCl_3$	300
6a	14.8	CH_2	70 (−10°)	−16.2	$CDCl_3$	400
7a	14.9	CH_2	26 (−20°)	−16.6	$CDCl_3$	400
8a	14.2	CH_2	18 (−50°)	−14.8	CD_2Cl_2	300
9a	14.5	CH_2−COO	53 (−20°)	−16.4	$CDCl_3$	300
	14.5	CH_2−Ph	22 (−20°)	−14.2		
10a	14.7[b]	CH_3−CH	13.1 (−20°)	+6.3	CD_2Cl_2	400

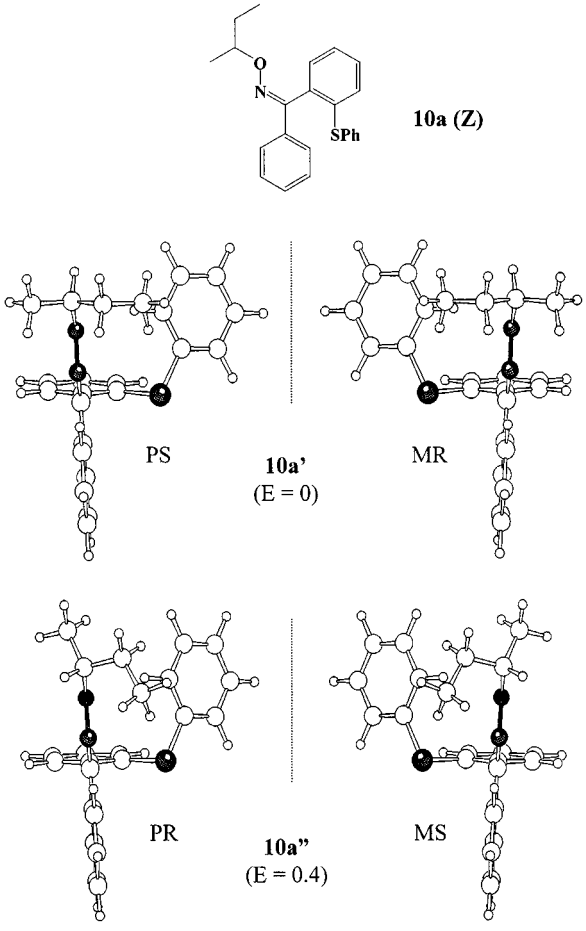
[a] In the presence of a 300:1 molar excess of an enantiopure Pirkle's alcohol (see text). − [b] In this case the barrier actually refers to an epimerisation process about the chiral axis.

attainable temperature: For instance even at −135 °C in dimethyl ether, the 400-MHz NMR spectrum of 8**b** showed that these hydrogen atoms remain enantiotopic, as expected for a nonchiral molecule. On the contrary, in all the (*Z*) isomers **4a−9a** anisochronous methylene signals were observed on cooling, since the molecular asymmetry renders these hydrogen atoms diastereotopic. In a typical example, reported in Figure 2, the single CH_2 line of 8**a** splits into an AB-type spectrum below −20 °C, and the accompanying computer simulation allowed us to determine the appropriate rate constants for the enantiomerisation process. X-ray diffraction confirmed that **8a** corresponds to a (*Z*) structure where the *ortho*-substituted phenyl group has its plane orthogonal to that of the C=NO moiety.

The free energies of activation ($\Delta G^{\neq}$) for these compounds are given in Table 2. Within the experimental errors they are temperature-independent, suggesting that the activation entropy is negligible, as is usually observed in conformational processes. Also, the barriers measured by monitoring the CH_2 signals cover a very restricted range of values (from 14.2 to 14.8 kcal mol^{-1}) for all the examined derivatives containing the PhS substituent (i.e. **4a−6a**, **8a**, **9a**), regardless of the group bonded to the oxygen atom of the oxime. This is a clear indication that the same motion, i.e. rotation of the *ortho*-substituted phenyl ring, is responsible for the observed dynamic processes.

When the diphenylamino derivative **7a** is investigated, its enantiomerisation barrier appears to be essentially equal to that of the corresponding derivative **6a** (Table 2), despite the apparent larger dimension of the Ph_2N with respect to the PhS moiety. The theoretical study of the rotation pathway carried out on the simpler corresponding oxime **2a** (Table 1), had shown that the transitions state TS_1 was the one related to the lowest energy level, rather than TS_2 as in the case of the PhS-substituted oxime **1a**. The inter-system crossing of the transition states thus makes the corresponding barrier lower than that expected if the same TS_2 transition state had been adopted by both **1a** and **2a**. The calculated difference between the two barriers (Table 1) in fact becomes only 0.8 (i.e. 10.2−9.4), rather than 2.3 (i.e. 11.7−9.4) kcal mol^{-1}. Within the approximations of this type of calculations a theoretical difference as small as 0.8 kcal mol^{-1} compares reasonably well with the negligible difference (0.1 kcal mol^{-1}) experimentally observed for the analogous pair **6a** and **7a**.

Having demonstrated that the (*Z*) isomers are chiral and have enantiomerisation barriers high enough to be experimentally measurable, it can consequently be anticipated that the introduction of a configurationally stable chiral centre would generate a pair of diastereoisomers in unequal proportions. For instance, if the OH hydrogen atom of the oxime **1a** is replaced by a CHMeEt group, yielding the cor-



Scheme 2. Theoretical structures of the enantiomers (*PS*), (*MR*) of diastereoisomer **10a**′ (top) and of the enantiomers (*PR*), (*MS*) of the diastereoisomer **10a"** (bottom); the calculated relative energies *E* are in kcal mol^{-1}

responding derivative **10a**, calculations predict that both such diastereoisomers (**10a′** and **10a"**) correspond to a minimum energy. These diastereoisomers result from the combination of the stereolabile axial chirality (*M*) with the configurationally stable chirality (*R*) or (*S*) of the stereogenic centre at the asymmetric carbon atom:[8] They are enantiomerically related, to the pair derived from the combination of the (*P*) with the (*S*) or (*R*) chirality, as shown in Scheme 2.

According to the theory, the diastereoisomer **10a′**, comprising the enantiomers (*PS*) and (*MR*) (Scheme 2, top), should be slightly more stable (by only 0.4 kcal mol^{-1}) than

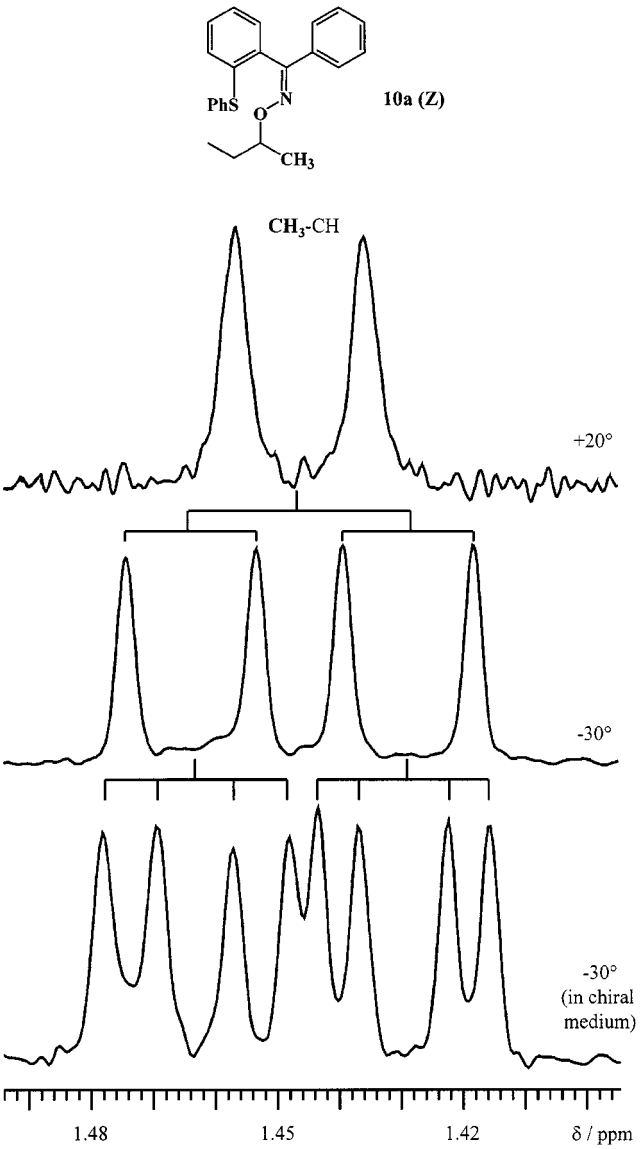


Figure 3. At ambient temperature, the ^1H NMR spectrum (in CD_2Cl_2 at 300 MHz) of the (*Z*) isomer **10a** displays a doublet (J = 6.3 Hz) for the methyl group bonded to the CHEt moiety (top); at −30 °C, two doublets (separated by 0.035 ppm) due to the diastereoisomers **10a′** and **10a"** are observed (middle trace); underneath is reported the spectrum (also at −30 °C) in a chiral environment (15:1 molar excess of Pirkle's alcohol[6] showing the four doublets expected for the four stereoisomers of Scheme 2; the two doublets (downfield) due to the pair of enantiomers of the minor (49%) diastereoisomer are separated by 0.009 ppm, those for the major (51%) diastereoisomer (upfield) are separated by 0.007 ppm

10a", which comprises the pair (*PR*)/(*MS*). Indeed most of the ^1H NMR aliphatic signals of **10a** in CD_2Cl_2 broaden on cooling, eventually yielding two almost equally intense spectra below 0 °C. Computer line-shape simulation indicated that the barrier for the interconversion of the more (51%) into the less (49%) stable[9] diastereoisomer (14.7 kcal mol^{-1} as in Table 2) is essentially the same as those measured for the other derivatives. In Figure 3 it is shown how the doublet ($J_{Me,CH}$ = 6.3 Hz) observed at ambient temperature for the methyl group bonded to the CHEt moiety of **10a** splits at −30 °C into two doublets separated by 0.035 ppm. When at the same temperature the environment is rendered chiral by addition of an appropriate amount of the mentioned Pirkle's alcohol, [6] the two pairs split further, yielding four pairs of lines since all four stereoisomers (*PS*), (*MR*), (*PR*), (*MS*), as in Scheme 2, now display distinguishable NMR spectra.

Experimental Section

Materials: The oximes **1**, **2**, and **8** were prepared by treacting the appropriate ketone with hydroxylamine hydrochloride in EtOH and pyridine.[10] After heating at reflux for a few hours, the volume was reduced and the residue poured into iced water, extracted with diethyl ether and dried (sodium sulfate). After removal of the solvent, the residue was crystallised from light petroleum ether/benzene. Typical yields were in the range 70−80%.

Phenyl[(2-phenylsulfanyl)phenyl]methanone Oxime (1): Two isomers (*E*), (*Z*), in a 1:5 proportion, were obtained (total yield 85%) from phenyl[(2-phenylsulfanyl)phenyl]methanone [11] (26.1 g, 90 mmol) and hydroxylamine hydrochloride (23.3 g, 76.4 mmol). They were separated by chromatography; eluent: light petroleum ether (40−70 °C)/diethyl ether. − **(*Z*) Isomer (1a):** M.p. 138−140° C. − MS; *m/z* (%): 305 (23) [M^+], 288 (100), 212 (22), 77 (25). − ^1H NMR ($CDCl_3$, 200 MHz): δ_H = 7.16−7.40 (m, 12 H, aromatic), 7.42−7.50 (m, 2 H, aromatic), 9.12 (br. s, 1 H, OH). − ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ_C = 126.8, 127.2, 127.81, 128.77, 128.9, 129.4, 129.9, 130.1, 131.5, 132.3, 133.7, 134.2, 134.5, 135.3, 156.5. − ^1H NMR ([D_8]toluene, 75.5 MHz, at −30 °C): δ_C = 157.30 (C=N). − **(*E*) Isomer (1b):** M.p. 111−113 °C. − MS; *m/z* (%): 305 (23) [M^+], 288 (100), 212 (22), 77 (25). − ^{13}C NMR ([D_8]toluene, 75.5 MHz, at −30 °C): δ_C = 156.7 (C=N). The difference of 0.6 ppm between the C=N signals of **1a** and **1b** was also checked by recording the spectrum of a [D_8]toluene solution containing a mixture of both isomers. − $C_{19}H_{15}NOS$ (305.4): calcd. C 74.73, H 4.95, N 4.59, S 10.50; found C 74.65, H 4.92, N 4.65, S 10.46.

[(2-Diphenylamino)phenyl]phenylmethanone Oxime (2): Two isomers (*E*), (*Z*), in a 1:3 proportion, were obtained (total yield 82%) from [(2-diphenylamino)phenyl]phenylmethanone [12] (10.5 g, 30 mmol) and hydroxylamine hydrochloride (8.9 g, 24.6 mmol). They were separated by chromatography; eluent: light petroleum ether (40−70 °C)/diethyl ether. − **(*Z*) Isomer (2a):** M.p. 150−152 °C. − MS; *m/z* (%): 364 (92) [M^+], 347 (36), 332 (100), 272 (20), 167 (12), 77 (16). − ^1H NMR ($CDCl_3$, 300 MHz): δ_H = 6.86−6.78 (m, 5 H, aromatic), 7.00−7.06 (m, 4 H, aromatic), 7.12−7.26 (m, 6 H, aromatic), 7.32−7.40 (m, 4 H, aromatic), 8.30 (br. s, 1 H, OH). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C = 122.5, 123.69, 123.74, 127.1, 127.7, 127.8, 128.6, 129.1, 129.5, 130.1, 131.6, 135.5, 146.5, 147.5, 156.5. − IR: $\tilde{\nu}_{max}$ = 3560 cm^{-1}. − $C_{25}H_{20}N_2O$ (364.4): calcd. C 82.39, H 5.53, N 7.69; found C 82.33, H 5.50, N 7.73. − **(*E*) Isomer (2b):** M.p. 161−163 °C. − MS; *m/z* (%): 364 (98) [M^+], 347 (39),

332 (100), 272 (22), 167 (11), 77 (13). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H = 6.64−6.70 (m, 3 H, aromatic), 6.80−7.36 (m, 15 H, aromatic), 7.42−7.48 (dd, 1 H, aromatic), 8.74 (br. s, 1 H, OH). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C = 122.2, 123.2, 124.7, 127.4, 128.68, 128.72, 129.3, 129.5, 130.4, 132.2, 132.6, 134.4, 146.4, 147.6, 156.2. − IR: $\tilde{\nu}_{max}$ = 3560 cm^{-1}.

2-Phenyl-1-[2-(phenylsulfanyl)phenyl]-1-ethanone Oxime (8): Two isomers (*E*), (*Z*), in a 3:1 proportion (total yield 75%) were obtained from 2-phenyl-1-[2-(phenylsulfanyl)phenyl]-1-ethanone (6.1 g, 20 mmol) and hydroxylamine hydrochloride (4.8 g, 15.0 mmol). They were separated by chromatography; eluent: light petroleum ether (40−70 °C)/diethyl ether. − **(*Z*) Isomer (8a):** M.p. 100−101° C. − MS; *m/z* (%): 319 (25) [M$^+$], 302 (100), 224 (35), 212 (9), 211(15), 210 (13), 92 (8), 91 (85), 77 (17). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ_H = 3.80 (2 H, br. s, CH_2), 6.81−6.88 (m, 1 H aromatic), 7−10−7.30 (m, 13 H, aromatic), 8.28 (br. s, 1 H, OH). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 40.6, 125.5, 125.70, 125.76, 127.19, 127.23, 127.9, 128.0, 128.4, 129.8, 131.5, 132.4, 134.6, 134.9, 135.1, 156.5. − **(*E*) Isomer (8b):** M.p. 90−91 °C. − MS; *m/z* (%): 319 (23) [M$^+$], 302 (100), 224 (19), 212 (19), 211(28), 210 (25), 92 (53), 91 (89), 77 (36). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ_H = 4.18 (s, 2 H, CH_2), 7.08−7.30 (m, 14 H, aromatic), 9.18 (br. s, 1 H, OH). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 33.9, 125.1, 125.5, 126.1, 127.1, 128.04, 128.11, 128.2, 128.8, 130.3, 130.9, 134.3, 134.6, 134.8, 136.1, 157.1. − $C_{20}H_{17}NOS$ (319.4): calcd. C 75.20, H 5.36, N 4.38, S 10.04; found C 75.26, H 5.39, N 4.34, S 10.07.

2-Phenyl-1-[2-(phenylsulfanyl)phenyl]-1-ethanone: Thiophenol (13.4 g, 122 mmol) was added dropwise to an EtOH solution of sodium ethoxide (6.8 g, 100 mmol), and the mixture was warmed for 20 min at 50 °C. The solvent was removed and the residue dissolved in dimethylformamide. Subsequently 1-(2-chlorophenyl)-2-phenyl-1-ethanone[13] (23.2 g, 100 mmol) was added dropwise and the solution was heated at reflux for 3 h. The volume of the solution was reduced and, after addition of water, the organic residue was extracted with diethyl ether, dried, treated with carbon and filtered. The compound (16.7 g, yield 55%) was crystallised from light petroleum ether/benzene. − M.p. 72−73 °C. − MS; *m/z* (%): 304 (14) [M$^+$], 213 (100), 184 (28). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ_H = 4.28 (s, 2 H, CH_2), 6.93 (dd, 1 H, J_1 = 7.9 Hz, J_2 = 1.4 Hz, aromatic), 7.08−7.49 (m, 12 H, aromatic), 7.80 (dd, 1 H, J_1 = 7.4 Hz, J_2 = 1.9 Hz, aromatic). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 47.8, 125.3, 127.5, 129.2, 129.3, 129.5, 130.1, 130.2, 130.6, 132.5, 134.1, 135.0, 135.1, 135.6, 142.1, 199.6. − IR: $\tilde{\nu}_{max}$ = 3000, 1660 cm^{-1}. − $C_{20}H_{16}OS$ (304.4): calcd. C 78.91, H 5.30, S 10.53; found C 78.86, H 5.33, S 10.49.

Phenyl[2-(phenylsulfanyl)phenyl]methanone *O*-Methyloxime (3): Two isomers (*E*), (*Z*) in a 1:5 proportion (yield 85%) were obtained by treating phenyl[(2-phenylsulfanyl)phenyl]methanone [11] (2.9 g, 10 mmmol) with *O*-methylhydroxylamine hydrochloride[10] (2.7 g, 8.5 mmol) in EtOH and pyridine. They were separated by chromatography; eluent: light petroleum ether(40−70 °C)/diethyl ether. − **(*Z*) Isomer (3a):** MS; *m/z* (%): 319 (16) [M$^+$], 288 (100), 184 (15), 77(13). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H = 3.92 (s, 3 H, Me), 7−18−7.60 (m, 14 H, aromatic). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C = 62.6, 126.4, 127.3, 127.8, 129.0, 129.2, 129.3, 129.9, 130.8, 131.7, 132.2, 134.64, 135.3, 135.9, 136.5, 155.6. − $C_{20}H_{17}NOS$ (319.4): calcd. C 75.20, H 5.36, N 4.38, S 10.04; found C 75.22, H 5.32, N 4.43, S 10.01. − **(*E*) Isomer (3b):** MS; *m/z* (%): 319 (9) [M$^+$], 288 (100), 184 (16), 77(11). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H = 3.99 (s, 3 H, Me), 7.15−7.58 (m, 14 H, aromatic). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C = 62.4, 126.4, 127.80, 127.83, 129.0, 129.2, 129.3, 129.9, 130.9, 131.7, 132.2, 133.1, 135.6, 137.1, 137.7, 155.5. − All the other *O*-substituted oximes were prepared by treating the (*E*) or the (*Z*) isomer of the appropriate oxime with a selected halide in DMSO with K_2CO_3. The temperature varied depending on the reactants: typical yields were in the range 70−80%.

(*Z*)-Phenyl[(2-phenylsulfanyl)phenyl]methanone *O*-Neopentyloxime (4a): The reaction (yield 80%) was carried out at 80 °C using 1-bromo-2,2-dimethylpropane (1.7 g, 4.5 mmol) and oxime **1a** (1.5 g, 5 mmol). − MS; *m/z* (%): 375 (14) [M$^+$], 288 (100), 212 (12), 184 (13), 77 (41). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ_H = 0.89 (s, 9 H, *t*Bu), 3.90 (s, 2 H, CH_2), 7.13−7.38 (m, 12 H, aromatic), 7.47−7.55 (m, 2 H, aromatic). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 27.52, 32.86, 85.34, 127.44, 127.59, 127.66, 128.96, 129.63, 129.74, 129.89, 132.23, 132.89, 135.51, 136.23, 136.50, 136.99, 155.44. − $C_{24}H_{25}NOS$ (375.5): calcd. C 76.76, H 6.71, N 3.73, S 8.54; found C 76.81, H 6.74, N 3.68, S 8.51.

(*Z*)-Phenyl[(2-phenylsulfanyl)phenyl]methanone *O*-(3,3-Dimethyl-2-oxobutyl)oxime (5a): The reaction (yield 84%) was carried out at 20 °C using 1-bromo-3,3-dimethylbutan-2-one (1.75 g, 4.2 mmol) and oxime **1a** (1.5 g, 5 mmol). − MS; *m/z* (%): 403 (15) [M$^+$], 290 (21), 289 (29), 288 (100), 212 (34), 184 (25), 77 (39), 57 (85). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H = 1.13 (s, 9 H, *t*Bu), 4.86 (br. m, 2 H, CH_2), 7.12−7.40 (m, 11 H, aromatic), 7.41−7.50 (m, 3 H, aromatic). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C = 26.9, 41.8, 75.2, 127.5, 127.7, 127.94, 128.86, 129.5, 130.00, 130.06, 130.2, 132.1, 133.2, 135.1, 135.7, 136.5, 136.6, 157.4, 211.1. − IR: $\tilde{\nu}_{max}$ = 1720 (C=O) cm^{-1}. − $C_{25}H_{25}NO_2S$ (403.5): calcd. C 74.41, H 6.24, N 3.47, S 7.95; found C 74.36, H 6.21, N 3.50, S 7.99.

(*Z*)-*tert*-Butyl 2-[({Phenyl[2-(phenylsulfanyl)phenyl]methylidene}-amino)oxy]acetate (6a): The reaction (yield 91%) was carried out at 20 °C using *tert*-butyl chloroacetate (1.9 g, 4.53 mmol) and oxime **1a** (1.5 g, 5 mmol). − MS; *m/z* (%):419 (16) [M$^+$], 288 (100), 212 (13), 184 (14), 77 (15), 57 (33). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H = 1.48 (s, 9 H, *t*Bu), 4.50 (br. m, 2 H, CH_2), 7.12−7.39 (m, 12 H, aromatic), 7.43−7.50 (m, 2 H, aromatic. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 28.2, 71.7, 81.5, 127.04, 127.11, 127.2, 128.3, 128.9, 129.41, 129.45, 129.55, 131.5, 132.6, 134.7, 135.1, 135.7, 135.8, 156.7, 169.0. − IR: $\tilde{\nu}_{max}$ = 1750 (C=O) cm^{-1}. − $C_{25}H_{25}NO_3S$ (419.5): calcd. C 71.57, H 6.01, N 3.34, S 7.64; found C 71.62, H 6.05, N 3.37, S 7.58.

***tert*-Butyl (*E*)-2-[({Phenyl[2-(phenylsulfanyl)phenyl]methylidene}-amino)oxy]acetate (6b):** The reaction was carried out at 50 °C using *tert*-butyl chloroacetate and oxime **1b** in the same proportion as in the previous case. − MS; *m/z* (%): 419 (15) [M$^+$], 288 (100), 212 (10), 184 (24), 77 (12), 57 (33). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ_H = 1.47 (s, 9 H, *t*Bu), 4.62 (s, 2 H, CH_2), 7.10−7.40 (m, 12 H, m, aromatic), 7.58−7.65 (m, 2 H, aromatic). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 28.1, 71.8, 81.6, 126.3, 127.4, 127.8, 129.1, 129.4, 129.5, 130.1, 130.9, 131.5, 132.4, 133.0, 135.4, 137.2, 137.4, 147.0, 169.0. − IR: $\tilde{\nu}_{max}$ = 1745 (C=O) cm^{-1}.

***tert*-Butyl (*Z*)-2-[({[2-(Diphenylamino)phenyl]phenylmethylidene}-amino)oxy]acetate (7a):** The reaction (yield 80%) was carried out at 40 °C using *tert*-butyl chloroacetate (3.8 g, 8.0 mmol) and oxime **2a**. − MS; *m/z* (%): 478 (85) [M$^+$], 422 (35), 347 (100), 243 (28), 167 (16), 57 (49). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H =1.42 (s, 9 H, *t*Bu), 4.23 (br. s, 2 H, CH_2), 6.74−6.90 (m, 6 H, aromatic), 7.05−7.36 (m, 12 H, aromatic), 7.49−7.54 (dd, 1 H, aromatic). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C = 28.1, 71.1, 81.3, 122.2, 123.6, 123.7, 127.30, 127.35, 127.6, 128.4, 129.0, 129.8, 130.2, 131.9, 135.5, 146.0, 147.5, 156.3, 169.0. − $C_{31}H_{30}N_2O_3$ (478.6): calcd. C 77.80, H 6.32, N 5.85; found C 77.76, H 6.29, N 5.90.

***tert*-Butyl (*E*)-2-[({[2-Diphenylamino)phenyl]phenylmethylidene}-amino)oxy]acetate (7b):** The reaction was carried out as above at 40 °C using *tert*-butyl chloroacetate and oxime **2b**. − MS; *m*/*z* (%): 478 (80) [M^+], 422 (35), 347 (100), 243 (25), 167 (11), 57 (48). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H = 1.42 (s, 9 H, *t*Bu), 4.38 (s, 2 H, CH_2), 6.68−6.75 (m, 4 H aromatic), 6.84−6.92 (m, 2 H, aromatic), 7.02−7.36 (m, 12 H, aromatic), 7.44−7.49 (dd, 1 H, aromatic). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C = 28.1, 71.3, 81.2, 122.0, 123.0, 124.7, 127.2, 128.5, 128.9, 129.1, 129.5, 130.3, 132.3, 132.8, 134.3, 146.3, 147.5, 156.4, 168.5.

***tert*-Butyl (*Z*)-2-[({Phenyl[2-(phenylsulfanyl)phenyl]ethylidene}-amino)oxy]acetate (9a):** The reaction (yield 80%) was carried out at 80 °C using *tert*-butyl chloroacetate (1.7 g, 3.98 mmol) and oxime **1a** (1.5 g, 5 mmol). − MS; *m*/*z* (%): 433 (5) [M^+], 302 (100), 224 (10), 211 (10), 91 (67), 57 (26). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ_H = 1.50 (s, 9 H, *t*Bu), 3.84 (br. s, 2 H, CH_2), 4.38 (br. s, 2 H, CH_2), 6.92−6.98 (m, 1 H, aromatic), 7.10−7.35 (m, 13 H, aromatic). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 27.9, 41.3, 71.0, 81.2, 126.4, 126.9, 128.1, 128.6, 128.7, 128.8, 129.3, 130.3, 132.4, 132.9, 135.7, 136.34 136.6, 157.4, 168.9. − IR: $\tilde{\nu}_{max}$ = 1750 (C=O) cm^{-1}. − $C_{26}H_{27}NO_3S$ (433.6): calcd. C 72.03, H 6.28, N 3.23, S 7.39; found C 72.00, H 6.25, N 3.20, S 7.44.

***tert*-Butyl (*E*)-2-[({Phenyl[2-(phenylsulfanyl)phenyl]ethylidene}-amino)oxy]acetate (9b):** The reaction was carried out as above at 60 °C by using *tert*-butyl chloroacetate and oxime **1b**. − M.p. 68−69 °C**.** − MS; *m*/*z* (%): 433 (6) [M^+], 302 (100), 224 (7), 211 (9), 91 (55), 57 (18). − ^{1}H NMR ($CDCl_3$, 200 MHz): δ_H = 1.52 (s, 9 H, *t*Bu), 4.28 (s, 2 H, CH_2), 4.68 (s, 2 H, CH_2), 6.90−7.38 (m, 14 H, aromatic). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ_C = 28.2, 35.8, 71.5, 81.6, 126.4, 126.5, 127.3, 128.4, 129.20, 129.28, 129.5, 129.9, 131.8, 131.9, 135.86, 135.91, 135.99, 136.7, 159.0, 169.1. − IR: $\tilde{\nu}_{max}$ = 1745 (C=O) cm^{-1}.

(*Z*)-Phenyl[2-(phenylsulfanyl)phenyl]methanone *O*-(1-Methylpropyl)oxime (10a): The reaction was carried out at 40 °C using 2-bromobutane (2.65 g, 7.3 mmol) and oxime **1a** (3.0 g, 10 mmol). − MS; *m*/*z* (%): 361 (12) [M^+], 288 (100), 212 (7), 197 (15), 184 (20), 77 (23). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H = 0.88 (t, 3 H, Me), 1.20, (d, 3 H, Me), 1−40−1.78 (m, 2 H, CH_2), 4.18−4.25 (m, 1 H, CH), 7.10−7.38 (m, 12 H, aromatic), 7.45−7.55 (m, 2 H, aromatic). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C = 9.8, 19.3, 28.4, 81.2, 126.71, 126.76, 127.0, 128.2, 128.8 (probably comprising two carbon atoms), 128.9, 129.3, 131.3, 132.5, 134.8, 136.03, 136.2, 136.8, 154.3. − $C_{23}H_{23}NOS$ (361.5): calcd. C 76.42, H 6.41, N 3.87, S 8.87; found C 76.35, H 6.38, N 3.84, S 8.92.

NMR Measurements: Spectra were recorded at 200, 300 (Gemini, Varian) or 400 MHz (Mercury, Varian) for the ^{1}H frequency. The temperatures were calibrated by means of an Ni/Cu thermocouple inserted in the probe before the measurements. Line-shape simulations were performed by means of a PC version of the DNMR 6 program.[14] In the spectra obtained in the presence of a chiral solvating agent (CSA), the shift separation ($\Delta\nu$) is temperature-dependent. By means of an empirical equation this separation was related to the temperature in the range where the rotation rate was undoubtedly negligible. The $\Delta\nu$ values were subsequently extrapolated into the temperature range where the exchange rate occurs, allowing one to obtain reliable line-shape simulations. In order to observe sufficiently separated ^{1}H NMR signals for the enantiomers, a very large molar excess (up to 300:1) of the Pirkle's alcohol[6] used as CSA was needed. Thus in these experiments, the concentration of the substrate had to be quite low (typically 10^{-3} M) in order to have a concentration of CSA lower than the saturation point.

X-ray Diffraction

Crystal Data of 1a: $C_{19}H_{15}NOS$ (305.38), triclinic, $P\bar{1}$, Z = 2, a = 7.6341(5), b = 8.9532(6), c = 12.3720(8) Å, α = 71.584(2), β = 87.455(2), γ = 87.344(2)°, V = 801.06(9) Å^3, $D_{calcd.}$ = 1.266 g cm^{-3}, $F(000)$ = 320, μ_{Mo}= 0.203 cm^{-1}, T = 293 K. Data were collected using a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) range $1.74° < \theta < 25.00°$. Of 6741 reflections measured, 2825 were found to be independent (R_{int} = 0.0303), 2227 of which were considered as observed [$I > 2\sigma(I)$], and were used in the refinement of 160 parameters leading to a final R_1 of 0.0472 and a final R_{all} of 0.0593. The structure was solved by direct methods and refined by full-matrix least squares on F^2, using SHELXTL 97 program packages. In refinements weights according to the scheme $w = [\sigma^2(F_o^2) + (0.0948P)^2 + 0.0360P]^{-1}$ were used where $P = (F_o^2 + 2F_c^2)/3$. The hydrogen atoms, including the OH hydrogen atom, were located by geometric calculations and refined using a "riding" method; wR_{obs} and wR_2 were equal to 0.1411 and 0.1472, respectively. The goodness of fit parameter S was 1.087. Largest difference peak and hole was 0.256 and −0.256 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-141678. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Data of 8a: $C_{20}H_{17}NOS$ (319.41), monoclinic, $P2_1/c$, Z = 4, a = 9.0807(5), b = 13.4441(8), c = 13.7268(8) Å, β = 95.878(2)°, V = 1680.75(12) Å^3, $D_{calcd.}$ = 1.262 g cm^{-3}, $F(000)$ = 672, μ_{Mo}= 0.196 cm^{-1}, T = 293 K. Data were collected using a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) range $2.12° < \theta < 25.00°$. Of 13827 reflections measured, 2963 were found to be independent (R_{int} = 0.0462), 2241 of which were considered as observed [$I > 2\sigma(I)$], and were used in the refinement of 172 parameters leading to a final R_1 of 0.0494 and a final R_{all} of 0.0628. The structure was solved by direct methods and refined by full-matrix least squares on F^2, using SHELXTL 97 program packages. In refinements weights according to the scheme $w = [\sigma^2(F_o^2) + (0.0827P)^2]^{-1}$ were used, where $P = (F_o^2 + 2F_c^2)/3$. The hydrogen atoms were located by geometric calculations and refined using a "riding" method; wR_{obs} and wR_2 were equal to 0.1572 and 0.1636, respectively. The goodness of fit parameter S was 1.250. Largest difference peak and hole was 0.279 and −0.263 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-141678 (**1a**) and CCDC-141679 (**8a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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