Two pathways for the stereomutation of 2-substituted 1-(*tert*-butylsulfinyl)naphthalenes

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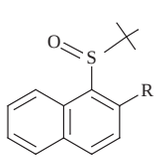
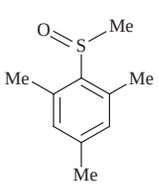
The synthesis of a number of 2-substituted 1-(*tert*-butylsulfinyl)naphthalenes is described and the free energies of activation ($\Delta G^{\ddagger}$ = 50.0–80.7 kJ mol^{-1}) for their stereomutation about the S–Ar bonds have been determined. It is shown that two pathways operate for this process. For the smaller 2-substituents (F, OMe, CO_2Pr^i), the *tert*-butyl group passes over the 2-position, and for larger substituents (Cl, Me, Br) it passes over the 8-position of the naphthalene ring.

Introduction

Atropisomerism in 1,8-disubstituted naphthalenes[1] and 1,1′-binaphthyls,[2] where the atropisomers are capable of isolation at room temperature, has been known for almost 70 years. During work related to the atropisomer selective synthesis of 1,1′-binaphthyls we have observed examples of conformational atropisomerism in 1,2-disubstituted naphthalenes where the 1-substituent is a *tert*-butylsulfinyl group.[3] Thus the ^{1}H NMR spectra of the sulfoxides **1** and **2** each showed at room temperature two signals for the *peri*-proton (8-H) which was ascribed to restricted rotation about the S–Ar bond, a stereogenic axis, giving rise to enantiomeric conformational atropisomers. This phenomenon had been observed previously by Lunazzi and co-workers[4] for 1-naphthyl sulfoxides substituted with a methyl group at the 2-position of the naphthalene ring. These workers measured the free energy of activation ($\Delta G^{\ddagger}$) for the stereomutation of the enantiomers by ^{1}H NMR line shape analysis at various temperatures. They studied sulfoxides with a variety of sulfur ligands keeping the 2-substituent constant as a methyl group. For all the sulfur ligands examined the 2-methyl ^{1}H NMR signal was at higher field for the more populated conformer and the opposite trend was observed for the *peri*-proton signal. The more highly populated conformer was assigned the conformation **A** (Fig. 1) since the SO entity is known to shift hydrogens affected by its anisotropy to lower field.[5] Lunazzi and co-workers[4] designated this conformation as (*Z*) but a more proper designation is synperiplanar when the 2-substituent is an alkyl group. The less populated conformation is thus **D** which was designated (*E*) by these workers but is more properly designated antiperiplanar. For halo substituents at the 2-position the designations will be reversed because of the reversal of substituent priorities. It was proposed that the stereomutation could occur by two possible pathways which involve the strained intermediates where the *tert*-butyl group in Fig. 1 passes over the *peri*-position (conformation **B**) or over the 2-substituent (conformation **C**). Molecular mechanics calculations were used to estimate the energy differences between the two pathways and the results, which were in good agreement with the experimental values of $\Delta G^{\ddagger}$ for sulfur alkyl ligands, indicated that for isopropyl or *tert*-butyl ligands the lower energy pathway involves the passage of the alkyl group over the *peri*-position but for less bulky groups such as methyl and ethyl the alternative pathway is of lower energy. However, the computed energy difference between the two pathways is small (3.8–10.1 kJ mol^{-1}). More recent results[6] have confirmed this estimate. The difference in $\Delta G^{\ddagger}$ values for the similar stereomutations in compounds **3** and **4** indicates that it is easier by 10.5 kJ mol^{-1} for an *S*-methyl group to pass over the *o*-methyl group in compound **3** than a *peri*-hydrogen in compound **4**.



1 R = $CONMe_2$
2 R = CO_2Pr^i



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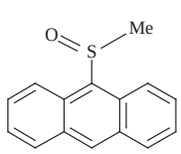

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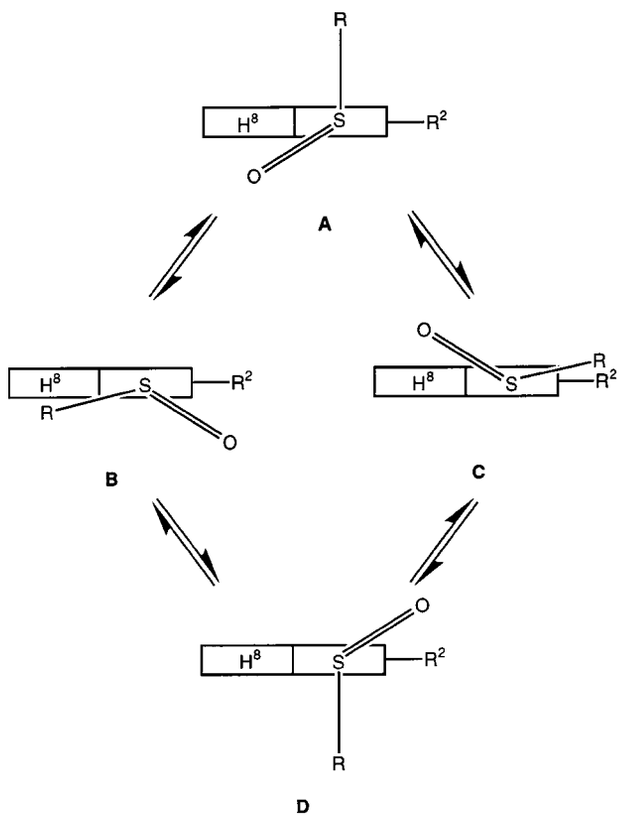


Fig. 1 Newman projections of the top view of the naphthalene ring for conformers of sulfoxides

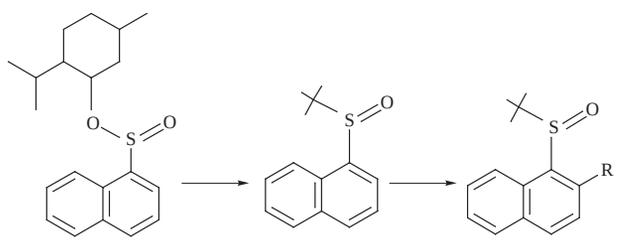
It appeared obvious that the two pathways could be more readily differentiated by choosing a bulky sulfur ligand such as *tert*-butyl at the naphthalene 1-position and varying the

size of the 2-substituent. We therefore synthesised a range of 1-naphthyl *tert*-butyl sulfoxides with different 2-substituents in order to further investigate this phenomenon.

Results and discussion

Synthesis

We have previously shown [3] that the sulfoxide **6**, in enantiomerically pure form, will undergo lithiation at the 2-position and subsequent reaction with the appropriate electrophiles afforded the sulfoxides **1** and **2**. The sulfoxide **6** was thus prepared in racemic form by allowing the sulfinate **5** (Scheme 1), prepared

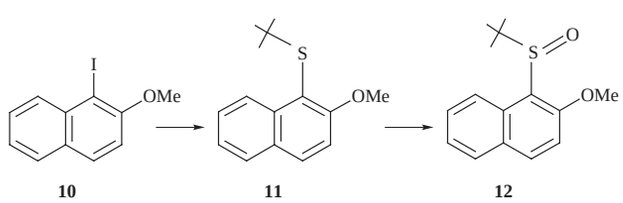


5 **6** **7** R = Br **8** R = Cl **9** R = Me

Scheme 1

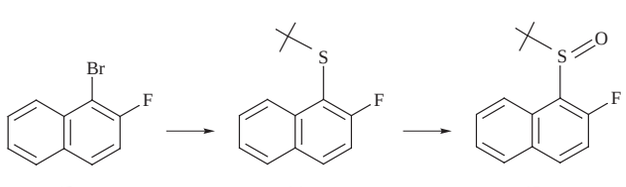
from racemic menthol, to react with butylmagnesium chloride. When the lithiated sulfoxide **6** was treated separately with 1,2-dibromotetrafluoroethane, hexachloroethane and iodomethane the substituted compounds **7**, **8** and **9** were obtained.

For the synthesis of the methoxy compound **12** (Scheme 2)



10 **11** **12**

Scheme 2



13 **14** **15**

Scheme 3

and the fluoro compound **15** (Scheme 3) we adopted an alternative method. Thus treatment of 1-iodo-2-methoxynaphthalene **10** (Scheme 2) with sodium *tert*-butylthiolate in boiling butanol in the presence of palladium tetrakis(triphenylphosphine) afforded the thioether **11**.[7] This was oxidised to the sulfoxide **12** by the agency of 3-chloroperoxybenzoic acid. A similar method starting from 1-bromo-2-fluoronaphthalene **13**[8] gave the sulfoxide **15** by way of the thioether **14** (Scheme 3).

Stereodynamics

It is known that sulfoxides having at least one alkyl substituent with a hydrogen atom attached to a β-carbon atom can undergo thermal decomposition by an E_i mechanism to yield alkenes and sulfinic acids.[9] The sulfoxides used in this investigation being *tert*-butyl sulfoxides are particularly prone to this reaction [3] and for compounds with bulky 2-substituents this elimination of isobutene occurs at temperatures near the coalescence temperature for the stereomutation. This circumstance precludes the use of the variable temperature line shape analysis method for the determination of the rotational barriers so that the saturation transfer method [10] was adopted since lower temperatures could be used.

Table 1 Thermodynamic data for stereomutation of 2-substituted 1-(*tert*-butylsulfinyl)naphthalenes in [$^2H_8$]toluene solution

2-Substituent	$\Delta G^{\ddagger}$/kJ mol^{-1}	T/K [a]	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	δ_H [b]
F	50.0 ± 0.5	216			7.90
OMe [c]	63.6 ± 0.5	259			8.20
CO_2Pr^i	73.2 ± 0.5	294	70.3 ± 3.8	−10.5 ± 13.0	7.86
Cl	72.9 ± 0.5	293	61.0 ± 10.8	−40.3 ± 37.7	8.10
Me	75.8 ± 0.5	292	71.3 ± 8.1	−15.6 ± 27.2	2.97 [d]
Br	80.7 ± 0.5	313			8.10

[a] Temperature at which $\Delta G^{\ddagger}$ was measured. [b] Chemical shift of irradiation. [c] Data for $CDCl_3$ solution. [d] The methyl signal was irradiated.

In the case of the ester **2**[3] and the methyl compound **9**[4] the ^{1}H NMR spectra determined near room temperature showed signals for the presence of both conformers, the most highly populated being conformer **A**. For the ester **2** at 11 °C the ratio **A**:**D** was 2.14:1 and for the methyl compound **9** it was 2.3:1 at 24 °C both in [$^2H_8$]toluene solution. In the case of the fluoro compound **15** a broad signal at δ 8.20, attributed to the *peri*-proton of the minor conformer **D**, could be detected at −30 °C in deuteriochloroform solution. The signal gradually sharpened on lowering the temperature and at −50 °C the **A**:**D** ratio was *ca.* 1.2:1. In the case of the methoxy compound **12** a signal at δ 8.24 due to the *peri*-proton of the minor conformer **D** (8% of the major conformer **A**) was detected in deuteriochloroform solution at −30 °C. However, the behaviour of the *peri*-proton signal of the major conformer of **12** was as expected.[10] At −40 °C it was sharp ($Wh_{/2}$ 11.6 Hz) and on raising the temperature it broadened so that at −10 °C width at half height ($Wh_{/2}$) = 21.7 Hz. On further raising the temperature the signal again sharpened and at 18 °C it had $Wh_{/2}$ = 13.0 Hz.

Neither the bromo compound **7** nor the chloro compound **8** gave evidence of signals for the minor conformer at room temperature nor could such signals be detected on raising or lowering the temperature. This presumably reflects the destabilisation of the minor conformer **D** by dipole–dipole interaction between the 2-substituent and the SO bond. In the case of the chloro compound **8** raising the temperature from room temperature to 40 °C resulted in significant broadening of the *peri*-proton signal.

The saturation transfer experiments were performed by first identifying the chemical shift of the *peri*-proton of the minor conformer at a temperature where approximately 50% saturation transfer could be obtained and then varying the frequency of irradiation by steps of 0.01 ppm until maximum saturation transfer was observed. In all cases the chemical shift of the *peri*-proton of the minor conformer was at a higher field than that for the major conformer so that the major conformer must be **A**. Since all the experiments involved irradiation of the minor conformer the value of $\Delta G^{\ddagger}$ which is determined is for the conversion of the major into the minor conformer which is, of course, the highest energy barrier in the stereomutation.

In the cases of compounds **2**, **8** and **9** measurements were carried out at several temperatures so that the enthalpy ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) could be computed. The data are shown in Table 1. The quoted errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined by least squares plots and represent the 95% confidence level. Dynamic NMR spectroscopy usually results in large errors in $\Delta S^{\ddagger}$ and the only conclusion that can be drawn from the present values is that they are small and negative. Hence the enthalpies and free energies of activation are almost coincident and can be equated with each other within the experimental error over the temperature ranges involved.[12]

The $\Delta G^{\ddagger}$ values are also shown in Table 1. The errors in $\Delta G^{\ddagger}$

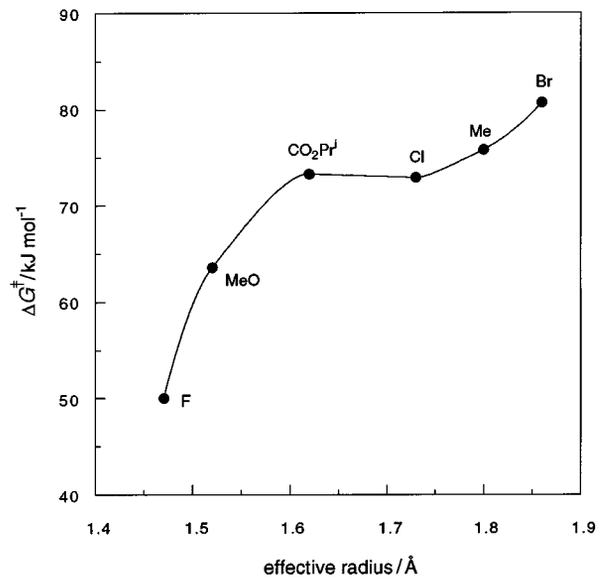


Fig. 2 Plot of $\Delta G^{\ddagger}$ (kJ mol^{-1}) for 2-substituted 1-(*tert*-butylsulfinyl)-naphthalenes against effective radius (Å) of 2-substituent

were estimated from the errors of observation in the measurement of saturation transfer, relaxation time constant and temperature. The $\Delta G^{\ddagger}$ value obtained for the methyl compound **9** (75.8 kJ mol^{-1}) in [$^2H_8$]toluene solution at 292 K is in close agreement with the value (77.1 kJ mol^{-1}) determined by Lunazzi and co-workers[4] over the temperature range 353–373 K in tetrachloromethane solution in agreement with a low entropy of activation and the negligible effect of solvent interactions on stereomutations of this type.[12]

Given the assumption that the enthalpies and free energies of activation can be equated over the small temperature range involved, a plot of $\Delta G^{\ddagger}$ for the various compounds against the effective radii[12] of the 2-substituents is given in Fig. 2. The value used for the effective radius of the CO_2Pr^i group is that given by Sternhell and co-workers[12] for the CO_2Me group, it being assumed that they would be identical.

It is seen that on passing from F to OMe to CO_2Pr^i the value of $\Delta G^{\ddagger}$ rises sharply consistent with the bulky *tert*-butyl group passing directly over these groups (intermediate **C** in Fig. 1). There is a discontinuity between CO_2Pr^i and Cl and this suggests that a change of mechanism occurs here with the *tert*-butyl group now passing over the *peri*-proton (intermediate **B** in Fig. 1). If we assume that the intermediate for the CO_2Pr^i group is **C** and that for Cl is **B** and note that although the effective radii are different the two values of $\Delta G^{\ddagger}$ are similar it follows that the effective radius of the *peri*-position must approximate that of the CO_2Pr^i group. Were this effective radius to be greater than that of the CO_2Pr^i group but smaller than that for Cl a higher value for $\Delta G^{\ddagger}$ might be expected.

On passing from Cl to Me to Br the value of $\Delta G^{\ddagger}$ continues to rise but less sharply than before. This behaviour is consistent with the major interaction in **B**, *i.e.* that between the *tert*-butyl group and the *peri*-position, remaining constant. It is only a weaker *gauche* interaction between the sulfoxide oxygen and the 2-substituent which changes.

Experimental

Syntheses

General directions have been given before.[3] NMR spectra were determined in deuteriochloroform. The assignment of ^{13}C NMR spectra was assisted by the DEPT and HMQC techniques. ^{19}F NMR spectra were determined at 282.4 MHz with hexafluorobenzene (δ_F −162.0) as internal standard. δ Values are given in ppm; J values are given in Hz.

Menthyl naphthalene-1-sulfinate 5. Racemic menthol (900 mg, 5.8 mmol) and triethylamine (879 mg, 8.7 mmol) were added in turn to a stirred solution of naphthalene-1-sulfonyl chloride (2.0 g, 8.7 mmol) in dichloromethane (25 cm^3). Trimethyl phosphite (1.44 g, 1.16 mmol) was then added dropwise and the mixture was stirred and boiled under reflux for 20 h. The cooled solution was diluted with dichloromethane and washed in turn with saturated aqueous sodium hydrogen carbonate and with saturated brine. The residue left on removal of the solvent from the dried ($MgSO_4$) solution was crystallized first from aqueous acetone and then from light petroleum which afforded the sulfinate **5** as prisms (565 mg, 20%), mp 109 °C [lit.,[3] 118–119 °C for (1*R*,*S*)-form] (Found: C, 72.55, H, 8.3, S, 9.5. $C_{20}H_{26}O_2S$ requires C, 72.7; H, 7.9; S, 9.7%); δ_H(300 MHz) 0.44 and 0.76 (each 3H, d, J 6.9, Me_2CH), 0.78–0.87 and 0.93–1.01 (each 1H, m), 0.97 (3H, d, *Me*CH), 1.22–1.32 (2H, m), 1.48 (1H, m, 3′-H), 1.59–1.66 (2H, m), 1.96 (1H, dd, J 2.5, 6.9, Me_2CH), 2.44 (1H, dddd, J 2.5, 4.5, 10.5, 10.5, 6′-H), 4.16 (1H, ddd, J 4.5, 10.5, 10.5, 1′-H), 7.54–7.62 (2H, m, 6- and 7-H), 7.61 (1H, dd, $J_{3,2} = J_{3,4}$ 8.2, 3-H), 7.93 (1H, dd, $J_{5,7}$ 0.6, $J_{5,6}$ 8.2, 5-H), 7.99 (1H, d, $J_{2,3}$ 8.2, 2-H), 8.22 (1H, dd, J 1.2, $J_{4,3}$ 9.2, 4-H) and 8.34 (1H, dd, $J_{8,6}$ 0.6, $J_{8,7}$ 8.3, 8-H); δ_C(75.5 MHz) 15.0, 20.7 and 21.9 (each Me), 22.9, 33.8 and 42.8 (each CH_2), 24.9, 31.4, 47.7 and 79.3 (each CH), 122.4, 123.3, 124.8, 126.5, 127.0 and 128.6 (each CH), 129.1 (C), 132.5 (CH) and 133.7 and 140.6 (C); ν_{max}(KBr)/cm^{-1} 1145, 1129; *m*/*z* 193 (37%), 138 (25), 128 (34), 127 (26), 97 (23), 83 (100).

1-(*tert*-Butylsulfinyl)naphthalene 6. A solution of *tert*-butylmagnesium chloride (0.36 mol dm^{-3} in THF, 4.5 cm^3, 1.52 mmol) was added dropwise over 30 min to a stirred solution of the sulfinate **5** (500 mg, 1.52 mmol) in THF (10 cm^3) at 0 °C. After a further 3 h an excess of 10% aqueous ammonium chloride was added and the crude product was isolated by extraction with dichloromethane. It was purified by radial chromatography over silica with 30% ethyl acetate–light petroleum as eluent which gave the sulfoxide **4** (215 mg, 61%) as pale yellow prisms, mp 99 °C (decomp.) [lit.,[3] 61–63 °C (decomp.) for (+)-enantiomer)]. The ^1H NMR spectrum was identical to that recorded for the (+)-enantiomer.[3] δ_C(125 MHz) 23.28 (3 × Me), 57.99 (C), 123.27 (8-C), 124.93 (3-C), 125.56 (2-C), 126.24 and 126.62 (6- and 7-C), 128.54 (5-C), 131.39 (4-C), 131.53 (8a-C), 133.07 (4a-C) and 136.67 (1-C).

2-Bromo-1-(*tert*-butylsulfinyl)naphthalene 7. A solution of butyllithium (5.2 mmol; 1.81 mol dm^{-3}) in hexane (2.9 cm^3) was added dropwise at −78 °C to a stirred solution of the sulfoxide **6** (1.00 g, 4.3 mmol) in THF (25 cm^3) under an atmosphere of argon. After 15 min at −78 °C this solution was added *via* a cannula to a stirred solution of 1,2-dibromotetrafluoroethane (0.6 cm^3, 4.7 mmol) in THF (15 cm^3) at −78 °C. After a further 30 min an excess of 10% aqueous ammonium chloride was added and the crude product was isolated by extraction with dichloromethane and purified by radial chromatography over silica with 20% ethyl acetate–light petroleum as eluent. The sulfoxide **7** (568 mg, 43%) was obtained as prisms, mp 75–77 °C [lit.,[3] 79–80 °C for (+)-enantiomer]; δ_H(500 MHz) 1.37 (3H, s, 3 × Me), 7.49 (1H, ddd, $J_{6,8}$ 1.6, $J_{6,7}$ 6.8, $J_{6,5}$ 7.5, 6-H), 7.51 (1H, ddd, $J_{7,5}$ 2.1, $J_{7,6}$ 6.8, $J_{7,8}$ 7.6, 7-H), 7.54 (1H, d, $J_{3,4}$ 8.7, 3-H) 7.69 (1H, br d, $J_{4,3}$ 8.7, 4-H), 7.77 (1H, br dd, $J_{5,7}$ 2.1, $J_{5,6}$ 7.5, 5-H) and 9.46 (1H, br dd, $J_{8,6}$ 1.6, $J_{8,7}$ 7.6, 8-H); δ_C(125 MHz) 23.39 (3 × Me), 62.95 (C), 124.10 (2-C), 124.85 (8-C), 126.79 and 126.94 (6- and 7-C), 128.40 (C-5), 130.12 (3-C), 132.91 (4-C), 132.94 (8a-C), 133.41 (4a-C) and 133.92 (1-C).

2-Chloro-1-(*tert*-butylsulfinyl)naphthalene 8. This was prepared in a similar manner to the bromo-compound **7** from the sulfoxide **6** and hexachloroethane. The sulfoxide **8** (50%) was obtained as prisms, mp 86 °C (Found: C, 63.25; H, 5.85; S, 12.25. $C_{14}H_{15}ClOS$ requires C, 63.05; H, 5.65; S, 12.0%); δ_H(500 MHz) 1.39 (9H, s, 3 × Me), 7.39 and 7.82 (2 H, AB, $J_{3,4}$ 8.8, 3- and 4-H), 7.51 (1H, ddd, $J_{6,8}$ 1.0, $J_{6,5} = J_{6,7}$ 8.4, 6-H), 7.54 (1H, ddd, $J_{7,5}$ 1.6, $J_{7,6}$ 8.4, $J_{7,8}$ 8.6, 7-H), 7.81 (1H, dd, $J_{5,7}$ 1.6, $J_{5,6}$ 8.4, 5-H) and 9.47 (1H, dd, $J_{8,6}$ 1.0, $J_{8,7}$ 8.6, 8-H); δ_C(125

MHz) 24.40 (3 × Me), 61.55 (C), 125.23 (8-C), 126.71 (6- or 7-C), 127.10 (3-C), 127.21 (6- or 7-C), 128.44 (5-C), 131.15 (4a-C), 133.03 (8a-C), 133.08 (4-C), 133.80 (2-C) and 134.21 (1-C); ν_{max}(KBr)/cm^{-1} 1046 (S=O); *m*/*z* 210 (M − C_4H_8, 100%), 162 (50), 57 (42).

2-Methyl-1-(*tert*-butylsulfinyl)naphthalene 9. This was prepared in a similar manner to the bromo-compound **7** from the sulfoxide **6** and iodomethane. It was obtained as prisms, mp 84 °C (lit.,[4] no mp given); δ_H(500 MHz) major rotamer: *inter alia*., 1.31 (9H, s, 3 × Me), 2.64 (3H, s, ArMe), 7.24 and 7.79 (2H, AB, $J_{3,4}$ 8.5, 3- and 4-H) and 9.47 (1H, m, 8-H); minor rotamer: *inter alia*., 1.28 (9H, s, 3 × Me), 2.96 (3H, s, ArMe), 7.28 (1H, part AB, $J_{3,4}$ 8.5, 3-H) and 8.34 (1H, m, 8-H); δ_C(125 MHz) major rotamer: 21.33 (ArMe), 25.03 (3 × Me), 60.51 (C), 125.78 (6- or 7-C), 126.04 (8-C), 126.34 (6- or 7-C), 128.19 (5-C), 128.55 (3-C), 130.47 (4a-C), 131.87 (4-C), 133.16 (8a-C), 133.32 (2-C) and 139.11 (1-C); minor rotamer: 19.66 (ArMe), 24.76 (3 × Me), 60.70 (C), 123.53 (8-C), 125.46 (6- or 7-C), 126.38 (6- or 7-C), 128.29 (5-C), 130.39 (4a-C), 130.83 (4-C), 131.67 (8a-C), 131.74 (3-C), 133.41 (2-C) and 140.89 (1-C).

1-Iodo-2-methoxynaphthalene 10. A solution of iodine (8.8 g, 34.8 mmol) in chloroform (200 cm^3) was added dropwise over 2 h to a stirred solution of 2-methoxynaphthalene (5.5 g, 34.7 mmol) and silver trifluoroacetate (7.66 g, 34.7 mmol) in chloroform (25 cm^3). After a further 1 h the precipitated silver iodide was separated by filtration and washed with chloroform. The crude product was flash chromatographed over silica gel with 1–2% ethyl acetate–light petroleum as eluent and then crystallised from light petroleum which gave the iodo-compound **10** (5.01 g, 51%) as shining plates, mp 88–89 °C (lit.,[13] 88–89 °C).

2-Methoxy-1-(*tert*-butylthio)naphthalene 11. Sodium *tert*-butylthiolate (1.18 g, 10.5 mmol)[14] and palladium tetrakis-(triphenylphosphine) (0.13 g, 0.12 mmol)[15] were added to a stirred solution of the iodo-compound **10** (2.5 g, 8.8 mmol) in anhydrous butanol (30 cm^3) under argon. The solution was boiled under reflux for 5 h and the solvent was removed under reduced pressure. The crude product was dissolved in pentane and the solution was washed with water and with saturated brine and dried ($MgSO_4$). The crude product was purified by flash chromatography with 5% ethyl acetate–light petroleum as eluent and then crystallised from light petroleum which gave the sulfide **11** (1.2 g, 46%) as needles, mp 98 °C (Found: C, 72.95; H, 7.5; S, 12.9. $C_{15}H_{18}OS$ requires C, 73.15; H, 7.35; S, 13.0%); δ_H(300 MHz) 1.29 (9H, s, 3 × Me), 3.96 (3H, s, OMe), 7.29 and 7.88 (2H, AB, $J_{3,4}$ 9.0, 3- and 4-H), 7.33 (1H, ddd, $J_{6,5} = J_{6,7}$ 9.0, $J_{6,8}$ 1.0, 6-H), 7.50 (1H, ddd, $J_{7,6} = J_{7,8}$ 9.0, $J_{7,5}$ 1.5, 7-H), 7.75 (1H, m, 5-H) and 8.35 (dd, $J_{8,6}$ 1.0, $J_{8,7}$ 9.0, 8-H); δ_C(75 MHz) 31.5 (3 × Me), 48.9 (C), 56.2 (OMe), 112.8 (CH), 114.7 (C), 123.6, 126.7 (× 2) and 127.9 (each CH), 129.3 (C), 131.3 (CH), 138.2 and 159.9 (each C); *m*/*z* 206 (22%, M − C_4H_8), 190 (100), 175 (30), 149 (46), 147 (24), 115 (33), 71 (25), 57 (41).

2-Methoxy-1-(*tert*-butylsulfinyl)naphthalene 12. 3-Chloroperoxybenzoic acid (500 mg, 2.8 mmol) was added to a stirred solution of the sulfide **9** (700 mg, 2.8 mmol) in dichloromethane (15 cm^3) at 0 °C and stirring was continued for 2 h at 0 °C and the solution was diluted with dichloromethane and then extracted exhaustively with saturated aqueous sodium hydrogen carbonate. The dried ($MgSO_4$) solution was concentrated and subjected to radial chromatography with 30% ethyl acetate–light petroleum as eluent which afforded the sulfoxide **12** (620 mg, 85%) as prisms, mp 124 °C (Found: C, 68.85; H, 7.25; S, 12.1. $C_{15}H_{18}O_2S$ requires C, 68.65; H, 6.9; S, 12.2%); δ_H(500 MHz) 1.35 (9H, s, 3 × Me), 3.94 (3H, s, OMe), 7.22 and 7.92 (2H, AB, $J_{3,4}$ 9.0, 3- and 4-H), 7.37 (1H, ddd, *J* 8.3, 8.3, 1.1, 6- or 7-H), 7.49 (1H, ddd, *J* 8.3, 8.3, 1.4, 6- or 7-H) 7.76 (ddd, $J_{5,6}$ 8.3, $J_{5,7}$ 1.4, *J* 0.7, 5-H) and 9.26 (1H, br s, 8-H); δ_C(125 MHz) 24.52 (3 × Me), 56.53 (OMe), 59.93 (C), 112.46 (3-C), 118.40 (1-C), 124.17 (6- or 7-C), 124.68 (8-C), 127.08 (6- or 7-C), 128.32 (5-C), 129.64 (4a-C), 133.80 (8a-C), 134.02 (4-C) and 157.19 (2-C); ν_{max}(KBr)/cm^{-1} 1273 (C–O), 1250 (C–O), 1036 (S=O); *m*/*z* 206 (100%, M − C_4H_8), 191 (32), 115 (23), 57 (20).

2-Fluoro-1-(*tert*-butylthio)naphthalene 14. This was prepared in a similar manner to the sulfide **11** from 1-bromo-2-fluoronaphthalene **13** (200 mg, 0.89 mmol),[8] sodium *tert*-butylthiolate (126 mg, 1.2 mmol) and palladium tetrakis-(triphenylphosphine) (13.4 mg, 0.012 mmol) in butanol (6 cm^3) during 18 h. The crude product was flash chromatographed over silica with light petroleum as eluent and then crystallised from light petroleum where upon the sulfide **14** (87 mg, 44%) formed prisms, mp 43–44 °C (Found: C, 72.0; H, 6.35; S, 13.8. $C_{14}H_{15}FS$ requires C, 71.75; H, 6.45; S, 13.7%); δ_H(500 MHz) 1.34 (9H, d, $J_{Me,F}$ 0.8, 3 × Me), 7.34 (1H, dd, $J_{3,4}$ 8.9, $J_{3,F}$ 8.2, 3-H), 7.48 (1H, dd, *J* 8.1, 1.1, 6- or 7-H), 7.60 (1H, m, 6- or 7-H), 7.84 (1H, ddd, $J_{5,6}$ 8.1, $J_{5,7}$ 1.2, $J_{5,F}$ 0.6, 5-H), 7.89 (1H, dd, $J_{4,3}$ 8.9, $J_{4,F}$ 5.5, 4-H) and 8.74 (1 H, m, 8-H); δ_C(125 MHz) 31.44 (3 × Me), 49.26 (C), 114.55 (1-C, J_{CF} 17.9), 115.98 (3-C, J_{CF} 29.6), 125.14 (CH, $J_{C,F}$ 6.6), 127.22 and 128.16 (each CH), 130.92 (C) 131.94 (CH, $J_{C,F}$ 10.1) and 162.76 (2-C, $J_{C,F}$ 245.7); δ_F −99.05 (br dd, $J_{F,3}$ 38.2, $J_{F,4}$ 5.5); *m*/*z* 234 (M^+, 9%), 178 (100), 146 (10), 133 (26).

2-Fluoro-1-(*tert*-butylsulfinyl)naphthalene 15. Oxidation of the foregoing sulfide **14** in a manner similar to that described above gave the sulfoxide **15** (68%) as prisms, mp 65–66 °C (Found: C, 66.7; H, 5.8; S, 12.8. $C_{14}H_{15}FOS$ requires C, 67.15; H, 6.05; S, 12.8%); δ_H(500 MHz) 1.34 (9H, d, $J_{Me,F}$ 1.6, 3 × Me), 7.23 (1H, dd, $J_{3,F}$ 10.0, $J_{3,4}$ 9.0, 3-H), 7.47 (1H, ddd, $J_{6,5}$ 8.1, $J_{6,7}$ 6.9, $J_{6,8}$ 1.2, 6-H), 7.54 (1H, dddd, $J_{7,8}$ 8.4, $J_{7,6}$ 6.9, $J_{7,5}$ 1.4, $J_{7,F}$ 0.8, 7-H), 7.82 (1H, ddd, $J_{5,6}$ 8.1, $J_{5,7}$ 1.4, $J_{5,F}$ 0.7, 5-H), 7.93 (1H, dd, $J_{4,3}$ 9.0, $J_{4,F}$ 5.4, 4-H) and 9.01 (1H, br s, 8-H); δ_F −94.62 (br dd, $J_{F,3}$ 10.0, $J_{F,4}$ 5.4); δ_C(125 MHz) 24.09 (3 × Me, $J_{Me,F}$ 1.92), 59.78 (C), 115.66 (3-C, $J_{C,F}$ 27.6), 118.86 (1-C, $J_{C,F}$ 10.8), 125.04 (8-C, $J_{C,F}$ 6.2), 125.72 (6-C, $J_{C,F}$ 2.3), 127.68 (7-C), 128.56 (5-C, $J_{C,F}$ 1.4), 130.99 (4a-C), 133.32 (8a-C, $J_{C,F}$ 2.8), 134.52 (4-C, $J_{C,F}$ 10.5), 159.54 (2-C, $J_{C,F}$ 253.4); ν_{max}(KBr)/cm^{-1} 1227 (C–F), 1046 (S=O); *m*/*z* 194 (M − C_4H_8, 25%), 178 (100), 167 (27), 146 (27).

Dynamic NMR experiments

A Bruker AM-300 spectrometer operating at 300 MHz was used with solutions of the sulfoxides (0.12 mmol) in 0.5 cm^3 of solvent. Temperatures were measured by using the chemical shift dependence of methanol. Rate constants for the dynamic process were determined by the Forsen–Hoffman spin saturation transfer method in which the relaxation time constant under the condition of saturation of one of the exchange sites is measured by the inversion recovery method with the sequence: relaxation time delay (15 s) −180° pulse − τ (incrementable delay 0.01 − 15 s) −90° pulse (width 10.8 μs) − FID acquisition (4.227 s). Seven different values of τ were chosen and 16 transients were acquired for each. The rate constants were calculated using the modified Bloch equation which relates the relaxation time constant to the magnetisation (intensity) of the observed site. Intensities were calibrated by measuring relative intensity changes of signals (with and without irradiation) compared with solvent signals. For those spectra with sharp signals the FIDs were zero filled from 32 to 128 kbyte and the intensities were measured with line broadening equal to 0.2 Hz. $\Delta H^‡$ and $\Delta S^‡$ were obtained by measuring $\Delta G^‡$ at intervals of 5 K over the range 270–310 K and then using the Eyring equation with least squares fitting of the data to linear plots.

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