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Circular dichroism spectra and absolute configuration of some aryl methyl sulfoxides

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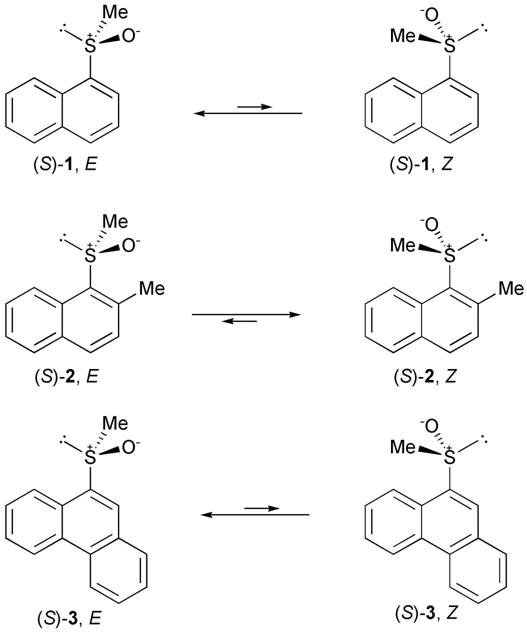
The absorption and circular dichroism (CD) spectra of three aryl sulfoxides, *i.e.* (−)-(*S*)-1-naphthyl methyl sulfoxide, (*S*)-**1**, (−)-(*S*)-1-(2-methyl)naphthyl methyl sulfoxide, (*S*)-**2** and (−)-(*S*)-9-phenanthryl methyl sulfoxide, (*S*)-**3**, have been interpreted by means of the coupled oscillator model formulated by DeVoe. Theoretical spectra have been calculated starting from input geometries provided by molecular mechanics (MMX) calculations and by employing standard spectroscopic parameters to describe the allowed transitions of the aromatic and the sulfoxide chromophores. The satisfactory agreement between the predicted and experimental spectra allows us to confirm the configurational assignment of these compounds as (−)/(*S*). The analysis of CD spectra, affording the right assignment of the absolute configuration (AC) of the alkyl aryl sulfoxides, then offers a practical alternative to the more complex vibrational circular dichroism spectroscopy and *ab initio* optical rotation calculation techniques that have been used very recently to assign the AC of (−)-**2** and (−)-**3**.

Introduction

In spite of the significant role played by optically active sulfoxides in organic chemistry[1] the absolute configuration (AC) of these compounds has been assigned so far only on the basis of mechanistic consideration[2] or by X-ray analysis.[3] Very recently, vibrational circular dichroism spectroscopy (VCD)[4] and induction of cholesteric mesophases[5] began to be used to solve this problem, while, surprisingly, electronic circular dichroism spectroscopy (ECD) (*i.e.* the most popular chiroptical method amongst the experimentalists) has been used to this end only in a few instances. In fact, after the seminal papers of Mislow[6] and Gottarelli,[7] and their co-workers only one investigation appeared in the literature[8] aimed at establishing a nonempirical correlation between ECD spectral data and absolute configuration of alkyl aryl sulfoxides. In this investigation a qualitative but nonempirical spectrum/structure correlation for (*S*)-1-naphthyl methyl sulfoxide, (*S*)-**1**, (Scheme 1) was established. In this compound the chromophores determining the optical activity, *i.e.* the aromatic and sulfoxide ones, do not exchange electrons because (*S*)-**1** assumes a preferential conformation where the lone pair on the sulfur atom is almost coplanar with the naphthalene nucleus, pointing toward the *peri* proton (structure *E* of Scheme 1). Therefore the ECD spectrum (at least in the 260–190 nm region) can be interpreted in terms of non-degenerate exciton coupling[9] between the naphthalene ^{1}B transition (220 nm) and the lowest energy $\sigma \rightarrow \sigma^*$ transition of the S=O chromophore, allowing a non-empirical correlation between CD and the structure. In order to verify the validity of this approach and to extend its scope, we decided to study the case of other suitable aryl methyl sulfoxides.



Scheme 1

The exciton chirality approach can be rigorously applied only when the coupled moieties are not exchanging electrons. We believed that, similarly to (*S*)-**1**, also in other aryl methyl sulfoxides such as (*S*)-1-(2-methyl)naphthyl methyl sulfoxide (**2**), and (*S*)-9-phenanthryl methyl sulfoxide (**3**) (Scheme 1), analogous conformational situations could prevent electronic exchange between the sulfoxide and the aryl moieties. Casarini *et al.* showed,[10] by dynamic NMR analysis, that the prevailing conformation of (*S*)-**2** is the *Z* one (Scheme 1), where the lone pair points towards the Me of the naphthalene ring. Such a conformation differs from the *E* one observed for **1**, showing that the introduction of the methyl group at the 2-position of the naphthalene nucleus reverses the relative stability of the two conformers. On the other hand, since in (*S*)-**3** and (*S*)-**1** the main structural feature determining the conformational equilibrium is the presence of the *peri* hydrogen, we can expect for both these compounds the same conformational prevalence of the *E* conformer (Scheme 1). Such considerations suggest that in **2** and **3** the aryl and sulfoxide chromophores are not exchanging electrons and therefore their AC could be deduced from a coupled oscillator analysis of ECD spectra.

The AC of **2** was previously assigned as (−)/(*S*) by means of VCD spectroscopy,[4b] while the AC of **3** was assigned as (−)/(*S*) only very recently by DFT calculation of its optical rotatory power (OR) at the sodium D line.[11] Both the VCD method and the OR *ab initio* calculations constitute powerful but, however, not widely used techniques, because the latter requires practice in computational methods while the former needs expensive instrumentation. Therefore it would be useful to provide the

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experimental organic chemist with a simpler and reliable technique to obtain the AC of alkyl aryl sulfoxides from the analysis of their ECD spectra. The aim of this paper is then to carry out a nonempirical interpretation of the ECD spectra of **2** and **3** in order to extract their AC's. A more detailed quantitative analysis of the CD spectra of **1** will be also provided. In particular, our interest was to show that the apparently complex ECD spectra of **1**–**3** can be profitably interpreted by coupled oscillator calculations. An important starting point for such analysis is that the *E*–*Z* equilibria of compounds **1** and **2** are already experimentally[10] and theoretically[11] defined and that for all compounds **1**–**3** the *E* and *Z* structures and energies can be straightforwardly determined by simple molecular mechanics calculations.

Results and discussion

Synthesis

The synthesis of compounds (−)-(*S*)-**1**[12] and (−)-(*S*)-**2**[4b] has been described elsewhere. Optically active (−)-(*S*)-**3** was prepared in 74% ee by catalytic asymmetric oxidation of the corresponding sulfide using *t*-BuOOH (TBHP) in the presence of a complex formed *in situ* between Ti(*i*-PrO)$_4$, H$_2$O and enantiopure (*R*,*R*)-1,2-diphenylethane-1,2-diol.[12] Earlier syntheses of alkyl aryl sulfoxides using this catalytic sulfoxidation protocol have uniformly yielded sulfoxides of (*S*) AC by using (*R*,*R*)-1,2-diphenylethane-1,2-diol as the catalytic precursor.[12,13] Such (−)/(*S*) AC assignment is confirmed in the present cases. To the best of our knowledge, there is only one report about the synthesis of optically active **3**. Sakuraba *et al.*[14] prepared optically active **3** in 37% ee by asymmetric oxidation of 9-phenanthryl methyl sulfide included in crystalline cyclodextrin. However they did not propose any configurational assignment for this compound.

Absorption and CD spectra

As the UV and CD analyses of these sulfoxides will be performed following the approach previously reported in the AC assignment of **1**,[8] recall of its spectral features is needed. The conformational equilibrium described for the 1-naphthyl substituted compound (*S*)-**1** was confirmed by the analysis of its absorption and CD spectra.[8] The lack of the so-called conjugation band at 250 nm in both spectra clearly showed that the aromatic and sulfoxide chromophores are separated. In fact the UV spectrum of (*S*)-**1** reveals a band at 290 nm, corresponding to the allowed short-axis polarized ^1L_a transition,[15] and an intense absorption at about 220 nm associated with the allowed long-axis ^1B_b transition. The CD spectrum of (*S*)-**1** shows a negative Cotton effect corresponding to the ^1L_a transition (288 nm), followed by an intense negative Cotton effect (at 225 nm) allied to the naphthalene ^{1}B transition, and by a positive band at 200 nm ascribed to the $\sigma\longrightarrow\sigma^*$ transition of the S=O chromophore, directed along the C$_1$–C$_2$ direction of the C$_1$–(S=O)–C$_2$ moiety.[7,8] These two CD bands can be considered the two branches of a negative, non-degenerate couplet-like feature. Therefore application of the Harada–Nakanishi exciton chirality rules[9] is possible and the above negative/positive sequence of bands at 225/200 nm probes the (*S*) configuration at the sulfur stereogenic centre (Fig. 1).[8]

The absorption and CD spectra of (*S*)-**2** are reported in Fig. 2. As expected, the typical features of the 1-naphthyl chromophore can be easily recognized: in fact, bands at 295 nm ($\varepsilon \approx 6000$ dm^3 mol^{-1} cm^{-1}, ^1L_a transition), 230 nm ($\varepsilon \approx 45000$ dm^3 mol^{-1} cm^{-1}, ^{1}B transition), and 210 nm ($\varepsilon \approx 35000$ dm^3 mol^{-1} cm^{-1}) are present. The absorption spectrum of (*S*)-**2** is very similar to that of (*S*)-**1**, showing the same absence of the so-called conjugation band[8] at 250 nm and therefore the lack of 2p(C)/3sp^3(S) overlap. This is in keeping with a prevailing *Z* conformation (Scheme 1) for **2**, as previously showed by NMR results.[10] Also in this case we have a non-conjugated sulfoxide chromophore, and the 210 nm band, on the high energy side of the naphthalene ^{1}B band, can be ascribed to the $\sigma\longrightarrow\sigma^*$ sulfoxide transition. Such assignment is experimentally confirmed because by changing the solvent from CH$_3$CN to methanol, a blue shift of the strong negative Cotton effect at 210 nm is observed in the CD spectrum. The case of (*S*)-**2** is similar to that of (*S*)-**1** but a striking difference is clearly shown in the CD spectrum where, between 250 and 200 nm, for the same (*S*) configuration, (*S*)-**1** presents a negative CD couplet and (*S*)-**2** a positive one. In the most stable *Z* conformation of compound (*S*)-**2**,[10] the naphthalene ^{1}B transition dipole and the sulfoxide transition dipole define, for an (*S*) configured sulfoxide, a positive chirality (Fig. 1), and then a positive couplet is expected, as experimentally found. In summary, (*S*)-**1** and (*S*)-**2** although having the same (*S*) AC and possessing the same non-conjugated sulfoxide chromophore, show oppositely signed CD couplets between 250 and 200 nm, simply because they assume different conformations where the electric dipoles of the ^{1}B transition and that of the $\sigma\longrightarrow\sigma^*$ SO transition define opposite chirality.

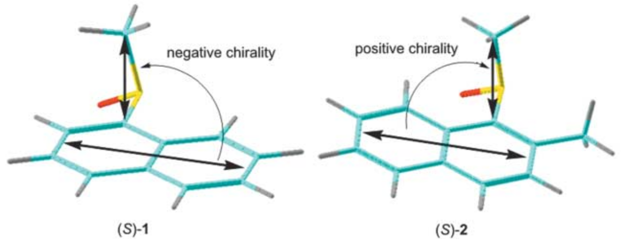

Fig. 1 Exciton chiralities defined by the allowed ^{1}B transitions of the naphthalene and S=O chromophores in (*E*,*S*)-**1** and (*Z*,*S*)-**2** respectively.

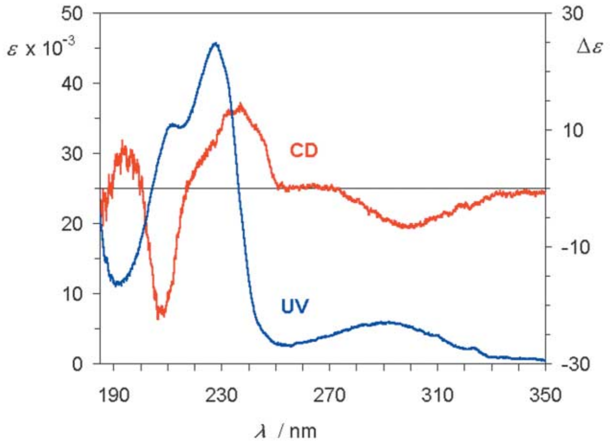

Fig. 2 UV (blue line) and CD (red line) spectra of (−)-**2** in acetonitrile.

The absorption and CD spectra of (*S*)-**3** are collected in Fig. 3. In the absorption spectrum three different ranges can be easily identified: between 400–330 nm, 330–270 nm, and 270–190 nm. The first spectral range is dominated by a structured absorption band with low molar absorption coefficient: taking into account frequency, intensity and vibrational fine structure it can be assigned[15a] to the ^1L_b transition of the phenanthrene chromophore. In the region of 330–270 nm the ^1L_a band can be observed, while the high-energy zone is dominated by a strong band at about 260 nm (reasonably the ^{1}B band of the phenanthrene chromophore[15a]), followed by two other intense ($\varepsilon \approx 25000$ dm^3 mol^{-1} cm^{-1}) absorption bands at 225 and 210 nm. In the CD spectrum between 400–270 nm weak negative ^1L_b and ^1L_a Cotton effects can be observed. At

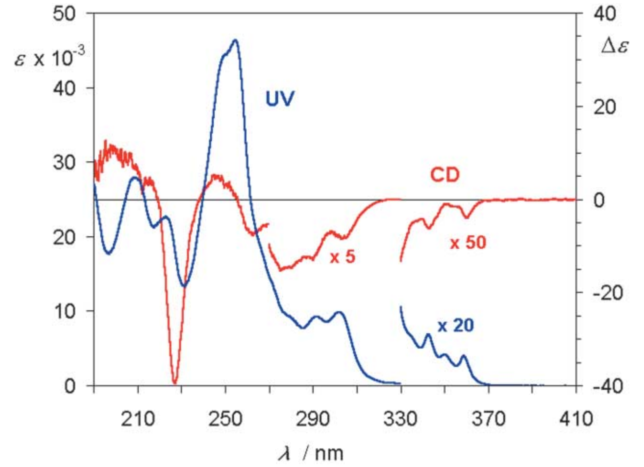

Fig. 3 UV (blue line) and CD (red line) spectra of (−)-**3** in acetonitrile.

shorter wavelengths the shape of the spectrum becomes particularly complex: a sequence of negative ($\Delta\varepsilon$ −10 dm^3 mol^{-1} cm^{-1}), positive ($\Delta\varepsilon$ +10 dm^3 mol^{-1} cm^{-1}), negative ($\Delta\varepsilon$ −40 dm^3 mol^{-1} cm^{-1}), and positive ($\Delta\varepsilon$ +10 dm^3 mol^{-1} cm^{-1}) bands can be measured at 265, 250, 225, and 200 nm, respectively. The most striking feature of the ECD spectrum of (−)-**3** is that, in contrast to what happens in the CD spectra of **1** and **2**, no clear exciton couplet is visible. Therefore the absolute configuration of (−)-**3** cannot be obtained by the simple application of the exciton chirality rules and a quantitative analysis of its ECD spectrum is then required to assign its absolute configuration (*vide infra*).

DeVoe calculations

In order to provide a detailed, quantitative and nonempirical interpretation of the absorption and CD spectra of compounds **1**–**3**, calculations of CD intensities in the range of the strongly allowed transitions (250–200 nm for **1** and **2**, 270–190 nm for **3**) have been carried out. The DeVoe coupled oscillator approach[16] has been successfully applied to the AC assignment of organic molecules[17] and the main features of the method have been fully discussed elsewhere.[16,17] Calculation of the CD spectrum of an optically active molecule within the DeVoe model requires both geometrical and spectroscopic parameters. The geometrical data can be obtained once a molecular AC has been (arbitrarily) assumed and the conformational analysis has been carried out, experimentally (by NMR spectroscopy, for instance) or theoretically (by molecular mechanics or *ab initio* calculations). The spectroscopic parameters are taken from the spectral properties of the chromophores, which constitute the overall molecular aggregate. They are obtained from the UV-VIS spectra of the constituent elements. Compounds **1**–**3** can be considered as being constituted by an aryl (1-naphthyl, 9-phenanthryl) chromophore and by a sulfoxide one. The allowed transitions of these systems are well characterized as far as intensity, energy, position and polarization direction are concerned (*vide infra*).

1-Naphthyl derivatives (*S*)-1 and (*S*)-2

The calculations related to these two compounds are discussed together: in fact they possess very similar electronic features having essentially the same aryl chromophore.[18] Therefore, to provide a satisfactory description of the UV spectrum of **1** in the 250–190 nm range, the intense absorption band of the naphthalene chromophore of (*S*)-**1** in this range (^{1}B spectral range) was represented by two oscillators polarized along the long axis of the naphthalene nucleus and carrying a dipolar strength of 30 D^2 (at 220 nm) and 10 D^2 (at 215 nm), respectively. The allowed SO $\sigma \longrightarrow \sigma^*$ transition was described by a single oscillator, directed along the C_{Ar}–CH_3 direction[8] and carrying a polarizability of 10 D^2 (at 215 nm). The (*S*) AC at the sulfur stereogenic center was assumed in all the cases and the input structures were generated by molecular mechanics (MMX routine[19]) calculations. For (*S*)-**1** the structures *E*,*Z* provided by the MMX calculations differ by about 0.94 kcal mol^{-1} (*E* being the most stable), which corresponds to a Boltzmann population at 298 K of 83% *E* and 17% *Z*. In Fig. 4 are represented the absorption and CD spectra obtained by a weighted average of the calculated ones, taking into account the relative populations of the two conformers: a satisfactory fit of the experimental data is clearly obtained. These results provide a quantitative support for the (−)/(*S*) assignment[8] of the configuration of **1** based only on a qualitative analysis. The same considerations can be applied to treat the case of (−)-**2**, **1** and **2** being very similar from a spectroscopic point of view. The only difference is that here the *Z* conformer is the most populated one. MMX calculations provided an 88 : 12 *Z* : *E* ratio for (*S*)-**2**, while a more sophisticated conformational analysis carried out at the DFT/B3PW91/TZ2P level by Stephens *et al.*[4b] gave a 70 : 30 *Z* : *E* ratio. By using the Boltzmann population derived from the MMX conformational analysis a good qualitative fit of both the absorption and CD data of (−)-**2** in the 250–190 nm range was obtained (Fig. 5b, red line), strongly supporting the (−)/(*S*) assignment, in keeping with the results obtained by *ab initio* calculation of the VCD spectrum of (−)-**2**.[4b] An even better quantitative agreement between the calculated and experimental spectra was however obtained using the more accurate *ab initio* population distribution (Fig. 5b, green line). The experimental and predicted ECD spectra reported in Fig. 5 clearly show that correct knowledge of the concentration of the *E*/*Z* conformers is a critical parameter for quantitative agreement between experimental and predicted spectra. In this case it has to be noted that, even if the *ab initio* conformational analysis, requiring a heavy computational effort, leads to a better agreement with the experimental data than MMX, the simple MMX input geometries also afford a satisfactory result.

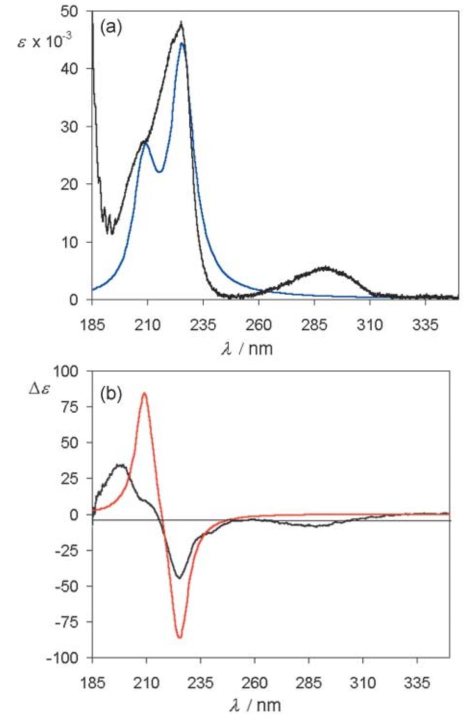

Fig. 4 (a) Experimental (black line) and theoretical (blue line) absorption spectra of (*S*)-**1**. (b) Experimental (black line) and theoretical (red line) CD spectra of (*S*)-**1**.

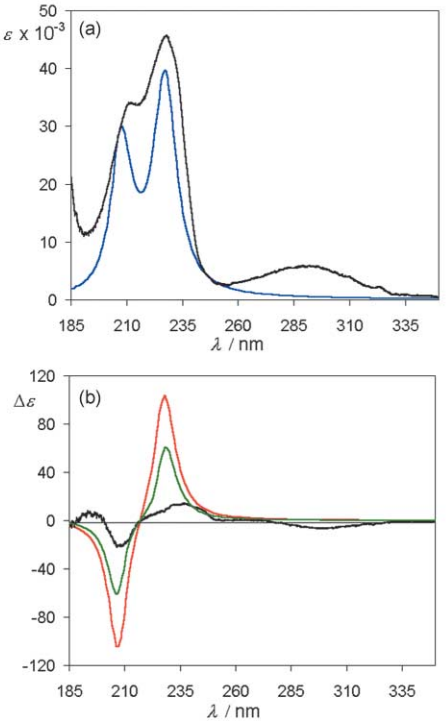

Fig. 5 (a) Experimental (black line) and theoretical (blue line) absorption spectra of (*S*)-**2**. (b) Experimental (black line) and theoretical CD spectra of (*S*)-**2**. Red line obtained using the *Z* : *E* ratio provided by MMX calculations, green line obtained using the *Z* : *E* ratio provided by *ab initio* calculations.[4b]

9-Phenanthryl derivative (*S*)-3

Analogous calculations have been also carried out for the 9-phenanthryl methyl sulfoxide **3**, in order to verify if the interpretation of its CD spectrum could lead to the assignment of the absolute configuration. (*S*) AC has been assumed for the sulfur stereogenic centre. Also in this case, the equilibrium between the *E* and *Z* conformers (Scheme 1) must be taken into account and a 90 : 10 *E* : *Z* ratio was determined by MMX calculations. In order to get the required information about the allowed transitions of the phenanthrene chromophore a CNDO/S-CI calculation, with standard parameters, was carried out,[20] using a MMX phenanthrene geometry. The calculated allowed transitions are reported in Table 1.

In order to keep the calculations at an acceptable level of simplicity (without reducing their reliability) we used a set of three oscillators to describe the allowed transitions of the phenanthrene chromophore. We were interested in reproducing the ECD spectrum of (−)-**3** in the shortest wavelength region and therefore no transitions at wavelengths longer than 270 nm were taken into account (transition no. 1 was disregarded). Moreover the region of intense absorption between 270 and 240 nm was represented by an oscillator located at 250 nm (28 D^2, long-axis polarization, Fig. 6) and a second one located at 240 nm (10 D^2, short-axis polarization, Fig. 6), representing transitions 2 and 3, respectively. Finally, for the sake of simplicity, the group of transitions 4–7 were described by a single oscillator placed at 205 nm (carrying 10 D^2, short-axis polarization, Fig. 6). It has been recently[21] pointed out that the centre of gravity of the ^{1}B allowed transition of the phenanthrene chromophore is not in the middle of the central ring, but it is shifted toward the centre of the 4a–4b bond: the bonds of 8a–9, 9–10, 10–10a do not contribute to the overall transition dipole moment. So in the present work we placed all the oscillators used to describe the phenanthrene chromophore in the middle of the 4a–4b bond (Fig. 6). A weighted average of the spectra of the two pure *E* and *Z* conformers affords the calculated spectra reported in Fig. 7. Inspection of such spectra clearly indicates that the main features of the experimental CD spectrum (*i.e.* the correct sequence of the positive, negative, positive Cotton effects and also the right order of magnitude of the intensity between 270 and 185 nm) are quite well reproduced by the present calculations. Only some differences in wavelength position of the CD bands can be observed and, obviously, Cotton effects at $\lambda > 270$ nm could not be reproduced, since allowed transitions in that range have been not considered. A consequence of this approximation is that the positive zone around 250 nm is more intense than the experimental one. Such differences between experimental and calculated spectra are not relevant from the point of view of the configurational assignment and therefore we can safely conclude that the (−) antipode of **3** indeed possesses (*S*) absolute configuration.

Table 1 CNDO/S-CI calculated[20] transitions of phenanthrene chromophore

Transition no.	λ/nm	Oscillator strength	Polarization[a]
1	285	0.22	l
2	246	1.77	l
3	240	0.51	s
4	232	0.22	s
5	216	0.10	s
6	213	0.10	l
7	203	0.10	s

[a] l: long axis polarization; s: short axis polarization.

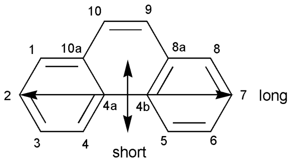

Fig. 6 Direction and location of the main transitions of the phenanthrene chromophore.

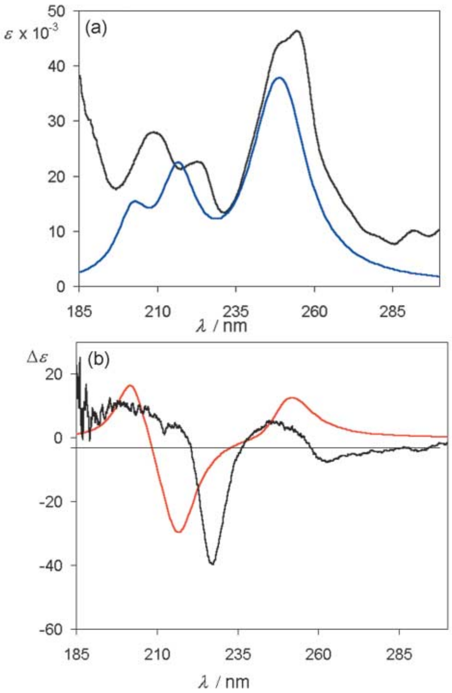

Fig. 7 (a) Experimental (black line) and theoretical (blue line) absorption spectra of (*S*)-**3**. (b) Experimental (black line) and theoretical (red line) CD spectra of (*S*)-**3**.

Conclusions

In this paper the analysis of CD spectra of three alkyl aryl sulfoxides **1**–**3** has been carried out, allowing a nonempirical AC assignment of these compounds. It is noteworthy that the goal of a safe configurational assignment has been achieved by a coupled oscillator analysis of the ECD spectra based on input geometries obtained by a conformational analysis carried out by a molecular mechanics technique. Taking into account that use of molecular mechanics analysis is now widespread among experimental organic chemists and that also the coupled oscillator interpretation of an ECD spectrum is also becoming popular in organic chemistry, it is to be expected that the AC assignment based on the study of the ECD spectra will shortly become an area of research open to non-specialists. The case of (*S*)-**3** seems particularly relevant from the point of view of AC assignment using ECD data. In fact, in this case it is important to note that it is possible to do such spectroscopic analysis even if a couplet-like feature is not present in its complex CD spectrum. The lack of couplet features prevents a simple two dipoles analysis (*i.e.* a simple application of the Harada–Nakanishi rules) and requires a more detailed treatment, dealing with several simultaneously interacting oscillators. As a final result, the exciton coupling model can also be successful in the case of a compound containing the complex phenanthrene chromophore. Recently two reports appeared in the literature[22] showing that this particular chromophore cannot be submitted to such analysis, owing to the complexity of its absorption spectrum. The use of the DeVoe model, which allows several oscillators to be dealt with simultaneously, helps in solving this problem. In fact, taking into account all the electronic transitions in the range 250–200 nm, the coupled oscillator treatment gives the right answer also in the case of this apparently anomalous chromophore. A second important result of this work is that even the analysis of the ECD spectrum affords the right assignment of the AC of alkyl aryl sulfoxides, and therefore this method constitutes an attractive alternative to the more complex techniques based on the use of VCD spectroscopy or on the *ab initio* calculation of the optical rotatory power.

Experimental

Equipment

HPLC analyses were performed at room temperature using a Hewlett Packard 1050 pump with a Varian 2550 UV detector and a Daicel CHIRALCEL OJ (cellulose tris(*p*-methylbenzoate)) column. Mobile phases were prepared from HPLC-grade solvents (Fluka). ^{1}H NMR (300 MHz) spectra were recorded in $CDCl_3$ on a Bruker Aspect 300 spectrometer using TMS as internal standard. Optical rotations were measured with a JASCO DIP-370 digital polarimeter and are given in units of deg dm^{-1} g^{-1} mL. Absorption and CD spectra were recorded on a JASCO J600 spectropolarimeter at rt using acetonitrile solutions ($c \approx 1 \times 10^{-3}$ M) in 0.1 and 1.0 mm cells. During the measurement the instrument was thoroughly purged with N_2.

Chemicals

CCl_4 was distilled from CaH_2 and stored over activated 4 Å molecular sieves. Ti(*i*-PrO)$_4$ was distilled prior to use under an N_2 atmosphere. Commercially available *tert*-butyl hydroperoxide (TBHP) (70% in water) (Aldrich) was used as purchased. Enantiomerically pure (*R*,*R*)-1,2-diphenylethane-1,2-diol was prepared by asymmetric dihydroxylation of (*E*)-stilbene.[23] Racemic sulfoxides were prepared by oxidation of the corresponding sulfides with 35% hydrogen peroxide, according to literature procedures.[24] Analytical and preparative TLC were performed, respectively, on 0.2 mm × 2.0 mm Merck 60 F-254 silica gel plates, and column chromatography was carried out with Merck 60 (80–230 mesh) silica gel. Compounds **1**[12] and **2**[4a] have been prepared as previously described. 9-Phenanthryl methyl sulfide was prepared from 9-phenanthryl bromide according to a literature procedure.[25]

9-Phenanthryl methyl sulfide. Yield 68%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.6 (s, 3H), 7.5–7.6 (m, 3H), 7.6–7.7 (m, 2H), 7.8–7.9 (m, 1H), 8.35 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 8.6 (dd, J_1 = 5.3 Hz, J_2 = 4.0 Hz, 1H), 8.7 (dd, J_1 = 6.9 Hz, J_2 = 2.5 Hz, 1H).

(−)-(*S*)-Phenanthryl methyl sulfoxide (3). To a suspension of (*R*,*R*)-1,2-diphenylethane-1,2-diol (34.3 mg, 0.16 mmol) in CCl_4 (5 mL) were added dropwise Ti(*i*-PrO)$_4$ (23.6 µL, 0.08 mmol) and H_2O (28.8 µL, 1.6 mmol) in sequence. To the resulting homogeneous solution was added phenanthryl methyl sulfide (360 mg, 1.61 mmol), and the solution was stirred at room temperature for 15 min. It was then cooled to 0 °C and TBHP (70% in water, 440 µL, 3.22 mmol) was added. The mixture was left stirring at 0 °C for 2 hours, then diluted with CH_2Cl_2 and dried over Na_2SO_4 for a few minutes. After filtration and evaporation of the solvent, the residue was immediately purified by column chromatography (EtOAc) isolating (**3**) as white needles (65% yield).

$[\alpha]_D^{20}$ = −171 (*c* = 0.66, acetonitrile), ee 74% Chiralcel OJ, hexane–isopropanol = 95 : 5, flow = 0.5 mL min^{-1}, t_1 = 39.5 s, t_2 = 46.7 s; lit.[14] $[\alpha]_D^{25}$ = +99.4 (*c* = 0.50, $CHCl_3$), ee 37%; mp 119–121 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.90 (s, 3H), 7.6–7.9 (m, 4H), 7.90 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 8.46 (s, 1H), 8.70 (d, *J* = 8.2 Hz, 1H), 8.77 (d, *J* = 7.7 Hz, 1H); MS (EI): *m*/*z*, 240 (M$^+$, 38), 225 (100), 224 (48), 197 (14), 181 (22), 176 (30), 165 (63), 151 (10), 28 (48).

Calculations

CNDO/S-CI calculations have been carried out, using the standard parameters,[20] by means of a routine kindly provided by the late Professor T. D. Bouman, University of Southern Illinois, USA. For a short description of the DeVoe coupled oscillator calculations see ref. 8. Such calculations were performed by means of a program written by Hug *et al.*[26] Both the programs are available, free of charge, from the authors of the present paper.

Acknowledgements

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