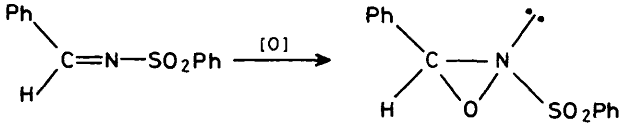
X-Ray Absolute Configuration and Circular Dichroic Properties of a Chiral Oxaziridine containing Two Phenyl Chromophores in a *trans* Configuration. Application of the Circular Dichroism Exciton Chirality Method to the Optical Activity of (*S*,*S*)-(−)-3-Phenyl-2-phenylsulphonyloxaziridine

Maria Bucciarelli, Arrigo Forni,* Irene Moretti, and Giovanni Torre
Dipartimento di Chimica, Università di Modena, via Campi 183, 41100 Modena, Italy
Sergio Brückner and Luciana Malpezzi
Dipartimento di Chimica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

Bijvoet *X*-ray diffraction analysis of crystalline, optically pure 3-phenyl-2-phenylsulphonyloxaziridine (−)-(**2**), obtained by asymmetric oxidation of the corresponding prochiral *N*-benzylidenephenylsulphonylimine (**1**) with (1*S*)-(+)-peroxycamphoric acid, followed by fractional crystallization of the crude reaction product, shows that the absolute configuration at the chiral nitrogen and carbon atoms of the oxaziridine ring is (2*S*,3*S*). Absolute configuration of (**2**) was also determined independently by application of the circular dichroism exciton chirality method.

The circular dichroism (c.d.) exciton chirality method is a powerful non-empirical tool for the determination of the absolute configuration of chiral organic compounds containing two or more chromophores in a dissymmetric array[1] and has been widely applied to the study of the optical activity of *trans*-1,2-diphenyl three-membered-ring derivatives such as (−)-*trans*-1,2-diphenylcyclopropane,[2] (+)-*trans*-stilbene oxide (α,α′-epoxybibenzyl),[3] and (−)-*trans*-stilbene episulphide (α,α′-epithiobibenzyl).[4] Unfortunately, this same method is not applicable to aziridine or oxaziridine derivatives carrying an *N*-phenyl substituent, owing to the low value of the energy barrier to inversion at the nitrogen of these systems which, at least at room temperature, prevents optically active compounds from being obtained.[5]

In a previous work we reported that optically pure (−)-3-phenyl-2-phenylsulphonyloxaziridine (**2**) can be obtained by oxidation of the corresponding imine (**1**) with (*S*)-(+)-peroxycamphoric acid followed by crystallization of the reaction crude product.[6]



(**1**) (**2**)

X-Ray and stereochemical studies indicate that 2-arenesulphonyl-3-aryloxaziridines like (**2**) possess a stable pyramidal nitrogen atom and are obtained only in the *E* diastereoisomeric form.[7,8] Here we report the absolute configuration of (−)-(**2**) determined by the Bijvoet method through *X*-ray analysis and by application of the c.d. exciton chirality method.

Results and Discussion

X-*Ray Structural Analysis.—Molecular geometry.* The crystal structure of the optically pure (−)-(**2**) (Figure 1) was determined by single-crystal *X*-ray analysis and the absolute configuration (*S*,*S*) assigned to both chiral carbon and nitrogen ring atoms was obtained on the basis of selected pairs. Atomic co-ordinates are reported in Table 1, while some bond distances and angles are listed in Table 2.

The oxaziridine entity can be suitably compared with that of very similar compounds previously studied by us.[9] The geometry of the small ring agrees well with that already observed[9–13] and expected[14] in three-membered substituted heterocycles, showing a decrease in bond lengths in the order: N–O(3), N–C(1), and O(3)–C(1).

The S–N bond length of 1.729(7) Å is typical of a pure single bond indicating no significant interaction between the lone pair at nitrogen and the *d* or σ^*–π orbital of the sulphur. Accordingly, the N atom appears strongly pyramidal lying 0.788(7) Å out of the plane of its three substituents and the S–N bond makes an angle of 25.1(4)° with the normal to the oxaziridine plane. The S–O bond lengths [mean value 1.428(6) Å] are typical double bond distances.

The O(1)–O(2) direction lies fairly parallel to the phenyl ring bonded to the S atom, giving rise to two short intramolecular contacts O(1)···C(9) and O(2)···C(13) of 2.918(8) and 2.972(7) Å, respectively. The S–O(1) bond is *trans* to the N lone pair and the O(1) atom is almost equidistant from C(1) and O(3) with two short intramolecular contacts of 2.875(10) and 2.852(9) Å, respectively. The conformation of the phenylsulphonyl group and its orientation relative to the three-membered ring closely resembles that found in diethyl 1-(*p*-

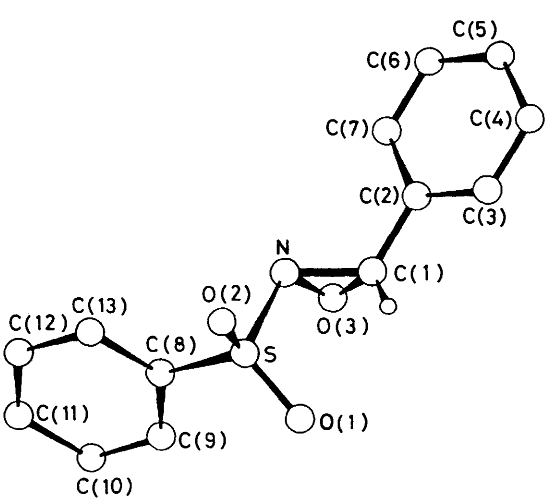


Figure 1. *X*-Ray structure and numbering scheme of oxaziridine (**2**)

Table 1. Fractional atomic co-ordinates (× 10^4) of (**2**)

Atom	*x*	*y*	*z*
S	−977(3)	−15 220(0)	−9 315(3)
O(1)	1 465(7)	−1 458(4)	−9 054(7)
O(2)	−2 086(10)	−1 180(4)	−10 881(7)
O(3)	−915(11)	−846(5)	−6 157(7)
N	−2 272(10)	−816(5)	−7 809(8)
C(1)	−873(12)	10(5)	−7 180(10)
C(2)	−1 950(7)	907(3)	−6 631(6)
C(3)	−3 987(7)	884(3)	−5 800(6)
C(4)	−4 999(7)	1 758(3)	−5 309(6)
C(5)	−3 974(7)	2 656(3)	−5 649(6)
C(6)	−1 937(7)	2 679(3)	−6 480(6)
C(7)	−925(7)	1 805(3)	−6 971(6)
C(8)	−1 867(6)	−2 687(4)	−8 847(6)
C(9)	−360(6)	−3 338(4)	−7 976(6)
C(10)	−1 000(6)	−4 313(4)	−7 746(6)
C(11)	−3 147(6)	−4 638(4)	−8 388(6)
C(12)	−4 655(6)	−3 987(4)	−9 259(6)
C(13)	−4 015(6)	−3 012(4)	−9 488(6)

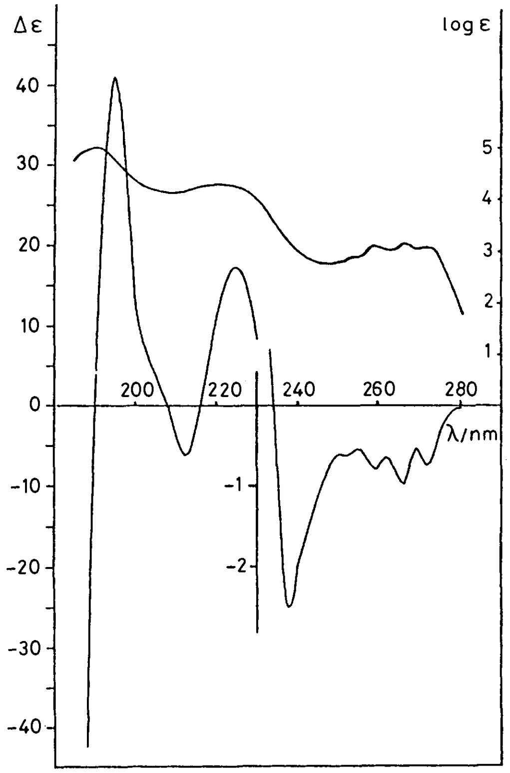


Figure 2. C.d. and u.v. spectra of oxaziridine (−)-(**2**) in iso-octane solution

Table 2. Molecular dimensions

Bond lengths (Å)

S–O(1)	1.435(6)	O(3)–N	1.467(8)
S–O(2)	1.421(6)	O(3)–C(1)	1.413(10)
S–N	1.729(7)	N–C(1)	1.458(10)
S–C(8)	1.716(5)	C(1)–C(2)	1.451(8)

Bond angles (°)

N–S–C(8)	102.5(3)	S–N–C(1)	113.2(5)
O(2)–S–C(8)	110.9(3)	O(3)–C(1)–N	61.4(5)
O(2)–S–N	101.7(4)	N–C(1)–C(2)	120.1(6)
O(1)–S–C(8)	109.9(4)	O(3)–C(1)–C(2)	120.3(6)
O(1)–S–N	110.4(4)	C(1)–C(2)–C(7)	118.7(5)
O(1)–S–O(2)	119.8(4)	C(1)–C(2)–C(3)	121.3(5)
N–O(3)–C(1)	60.8(5)	S–C(8)–C(13)	119.8(4)
S–N–O(3)	110.0(5)	S–C(8)–C(9)	119.9(4)
O(3)–N–C(1)	57.8(5)		

Selected torsion angles (°)

N–S–C(8)–C(9)	−104.2(5)
O(2)–S–C(8)–C(9)	147.9(4)
O(1)–S–C(8)–C(9)	13.2(6)
N–S–C(8)–C(13)	82.2(5)
O(2)–S–C(8)–C(13)	−25.7(6)
O(1)–S–C(8)–C(13)	−160.4(4)
O(2)–S–N–C(1)	−101.0(6)
O(1)–S–N–C(1)	27.3(6)
C(8)–S–N–O(3)	81.8(5)
O(2)–S–N–O(3)	−163.5(5)
O(1)–S–N–O(3)	−35.2(6)
C(8)–S–N–C(1)	144.3(5)
C(1)–O(3)–N–S	105.5(6)
N–O(3)–C(1)–C(2)	110.1(7)
S–N–C(1)–O(3)	−99.7(6)
O(3)–N–C(1)–C(2)	−110.4(7)
S–N–C(1)–C(2)	149.9(5)
N–C(1)–C(2)–C(3)	35.4(9)
O(3)–C(1)–C(2)–C(3)	−37.0(9)
N–C(1)–C(2)–C(7)	−143.7(6)
O(3)–C(1)–C(2)–C(7)	143.8(6)
C(4)–C(3)–C(2)–C(1)	−179.1(5)
C(6)–C(7)–C(2)–C(1)	179.1(5)
C(10)–C(9)–C(8)–S	−173.6(4)
C(12)–C(13)–C(8)–S	173.6(4)

Table 3. Some short non-bonded distances

Atoms	O ··· C (Å)	Symmetry operation for *c*
O(1) ··· C(1)	2.875(9)	*x*, *y*, *z*
O(1) ··· C(9)	2.918(8)	*x*, *y*, *z*
O(2) ··· C(13)	2.972(7)	*x*, *y*, *z*
O(3) ··· C(3)	2.988(8)	*x*, *y*, *z*
O(1) ··· C(13)	3.424(9)	*x* + 1, *y*, *z*
O(3) ··· C(6)	3.253(8)	−*x*, *y* − 1, −*z* − 1

methoxyphenylsulphonyl)aziridine-2,2-dicarboxylate[15] as indicated also by the torsion angles around the S–C(8) bond, which are very similar in both compounds. The orientation of the phenyl ring bonded to C(1) relative to the oxaziridine plane is defined[16] by the acute angle θ between the normal to the phenyl ring and the distal N–O(3) bond, the bisector (b) conformation being defined by θ = 0° and the perpendicular (p) one by θ = 90°. Compound (**2**) shows the (b) conformation [θ = 1.6(3)°]. Orientation of this phenyl ring is *trans* to the N–S bond through N–C(1) and the acute angle between the two phenyl rings is 56.5(1)°.

The molecule undergoes some intra- and inter-molecular short contacts of the type O ··· C(Ph). A list of the most significant interactions is given in Table 3.

C.D. Spectra and Absolute Stereochemistry as determined by the C.D. Exciton Chirality Method.—The u.v. and c.d. spectra for (−)-3-phenyl-2-phenylsulphonyloxaziridine (**2**), were recorded in iso-octane (2,2,4-trimethylpentane) solution and in the 185—350 nm spectral range.

As shown in Figure 2, the isotropic absorption spectrum of (**2**) exhibits weak, moderate, and high intensity bands at 250—280, 222, and 192 nm, respectively. Using Platt's[17] terminology

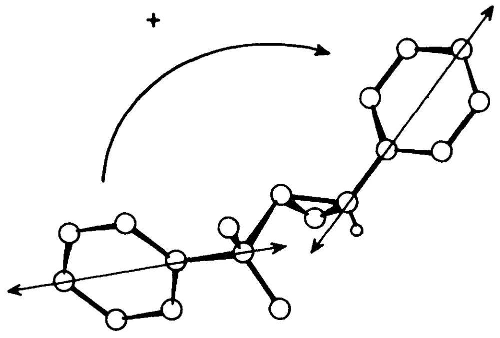


Figure 3. Positive exciton chirality between the long-axis-polarized transition moments of benzene chromophores

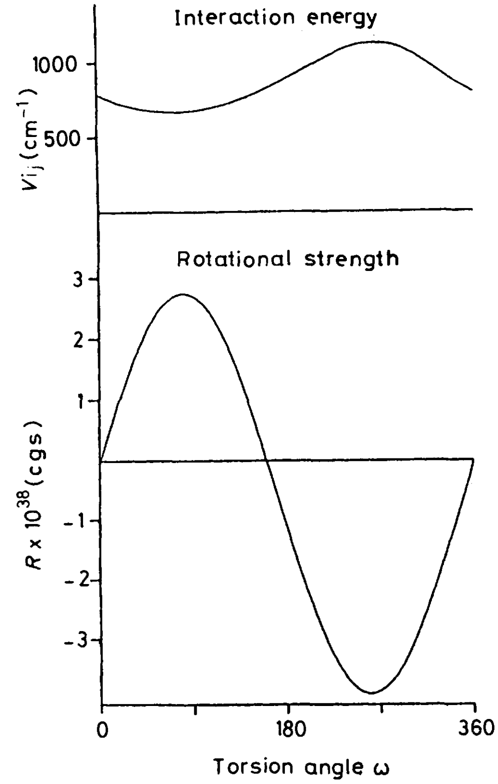


Figure 4. Angular dependence of the interaction energy and rotational strength (R at low energy) of (−)-(**2**)

these are the ^1L_b, ^1L_a, and $^1B_{a,b}$ electronic transitions of both the phenyl substituents of (**2**). The c.d. spectrum of (−)-(**2**) indicates multiple weak negative bands in the 250—280 nm range corresponding to the absorption bands, whereas the Cotton effects related to the u.v. transitions at 221.6 and 191.8 nm show for each absorption maximum the characteristic exciton form, consisting of positive and negative circular dichroism behaviour at lower and higher energy, respectively.* According to the molecular exciton theory, these two circular dichroism bands of opposite sign arise from the in-phase and out-of-phase coupling mode of the excitation moments of the two interacting benzene chromophores of (−)-(**2**). Therefore, by assuming that these two coupled electric transition moments are long-axis polarized in both benzene rings,† simple qualitative application of the exciton chirality method[1] to the conformation depicted in Figure 1 for (−)-(**2**) leads to a right-handed screw relationship between these dipoles (Figure 3), *i.e.*, to a positive chirality consisting of positive (first) and negative (second) Cotton effects. The same trend, namely positive and negative circular dichroism bands at lower and higher frequency, is experimentally observed in the region of both ^1L_a and $^1B_{a,b}$ band absorptions of (−)-(**2**) (Figure 2). Thus, the *X*-ray Bijvoet method and the exciton treatment assign the same (2*S*,3*S*) absolute configuration to oxaziridine (−)-(**2**).

As already mentioned, the exciton treatment was qualitatively applied to oxaziridine (**2**) on the basis of the molecular conformation reported in Figure 1. In order to study the influence of the conformational possibilities of the PhSO$_2$ substituent on the exciton behaviour of (−)-(**2**), the rotational strength R [equation (1)] and the corresponding exciton splitting energy V_{ij} [equation (2)] related to the ^1B_a transition

$$R = \pm(\pi/2)\sigma_0\vec{R}_{ij}\cdot(\vec{\mu}_{i0a}\cdot\vec{\mu}_{j0a}) \qquad (1)$$

$$V_{ij} = \mu_{i0a}\mu_{j0a}R_{ij}{}^{-3}[\vec{e}_i\cdot\vec{e}_j - 3(\vec{e}_i\cdot\vec{e}_{ij})(\vec{e}_j\cdot\vec{e}_{ij})] \qquad (2)$$

at 191.8 nm were calculated for each conformation obtained on rotation around the N–S bond with a Molecular Graphics PCMODEL program, by using the point dipole approximation[1] and by assuming that the benzene chromophores are degenerate.

In equation (1), R_{ij} is the interchromophoric distance vector between the centres of the two benzene rings, σ_0 the excitation wavenumber (cm^{-1}), and μ_{i0a} and μ_{j0a} the electric dipole moments of the transitions of the two interacting chromophores. In equation (2), e_i, e_j, and e_{ij} are unit vectors of μ_{i0a}, μ_{j0a}, and R_{ij}, respectively. The geometric parameters were taken from the crystallographic data of (**2**), whereas the value of σ_0 (52.138 cm^{-1}) and the absolute value of the electric transition moments $\mu_{i0a} = \mu_{j0a}$ were estimated from numerical evaluation of the dipole strength $D = \mu^2 = 3.5 \times 10^{-35}$ (cgs units) corresponding to the u.v. transition at 191.8 nm of Figure 2.‡

For the ^1B_a transition the angular dependence of the rotational strength, R at low energy, and of the exciton splitting energy V_{ij}, on the torsion angle ω, defined by rotation around the N–SO$_2$Ph bond, are depicted in Figure 4. The picture clearly shows that the rotational strength at 191.8 nm remains positive when the torsion angle ω is gradually changed counterclockwise from 0—160° (0 refers to a co-planar geometry of the transition dipole moments). In contrast, the interaction energy V_{ij} is always positive in the 0—360° angular range. Moreover, the rotational strength shows its positive maximum around 80°, which is relative to the structure of the solid-state conformation of (**2**) reported in Figure 1. This same conformation is indicated as the most stable one by CNDO/2 calculations.§

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* The c.d. spectrum of Figure 2 clearly reveals another optically active electronic transition in the 230—245 nm spectral range, *i.e.* in a spectral region which is noticeably distant from any absorption maximum. The nature of this optically active band is uncertain, though it seems reasonable to assign the origin of this transition to the oxazaridine chromophore.

† Following Platt's theory of spectroscopic moments in a monosubstituted benzene ring, in both the benzene rings of (**2**) the reported bands at 250—280 and 221.6 nm can be attributed to the short-axis ^1L_b and long-axis ^1L_a polarized electronic transitions, respectively, whilst the high-energy band at 191.8 nm is attributable to the doubly degenerate $^1B_{a,b}$ transition having a transition moment with both short- and long-axis components.[18] Long-axis polarization of the ^1L_a transition for the PhSO$_2$ chromophore was verified in our laboratory by the liquid crystal-linear dichroism (l.c.-l.d.) technique applied to the phenylmethyl sulphone.

‡ 1 D = $3.335\,64 \times 10^{-30}$ C m.

§ The energy barrier (8 kcal mol^{-1}) for rotation around the N–S bond was calculated with a CNDO/2 program on a basis set of hybrid AOs according to ref. 19, and by introducing different screening parameters for π–π and σ–π interactions, according to ref. 20.

From all these results one should expect the exhibited Cotton effects of (**2**) to reflect its absolute stereochemistry in a fairly large range of preferred conformations and this allows the use of the simple qualitative exciton chirality treatment[1] for the purpose of absolute configuration assignments to oxaziridines and, more generally, to three-membered-ring derivatives of type (**2**).

Experimental

Oxaziridine (**2**), $[\alpha]_D$ −130.8 (*c* 1—2 in $CHCl_3$), m.p. 60—61 °C (from diethyl ether), was prepared as previously described.[6] The u.v. spectrum was measured with a JASCO UVDEC-650 u.v.–visible spectrometer; the c.d. spectrum was recorded with a JOBIN-YVON Mark IV dichrograph.

X-Ray Structural Analysis.—Intensity measurements were collected on a Philips PW1100 diffractometer at room temperature with Cu-K_α radiation, using $\theta/2\theta$ scan technique. Cell dimensions were obtained by least-squares refinement carried out over 18 $(\theta,\chi,\psi)_{h,k,l}$ measurements.

Crystal Data.—$C_{13}H_{11}NO_3S$, $M = 261.3$. Monoclinic $P2_1$, $a = 5.860(15)$, $b = 13.615(8)$, $c = 7.780(2)$ Å, $\beta = 93.77(12)°$, $V = 619(1)$ Å^3, $Z = 2$, $D_c = 1.401$ g cm^{-3}, $F(000) = 272$, $\lambda = 1.5418$ A, $\mu(\text{Cu-}K_\alpha) = 22.8$ cm^{-1}. 707 Independent reflections out of 1 429, collected in the range $6 \leq \theta \leq 75°$, were observed having $I \geq 2.5\sigma(I)$.

During data collection two standard reflections, measured every 120 min to monitor crystal stability, showed no significant change. Semiempirical absorption correction was applied on the basis of ψ-scan data with two different 2θ values according to the program of Immirzi.[21] Data were corrected for Lorentz and polarization effects.

Structure Analysis and Refinement.—The structure was solved by direct method with MULTAN80[22] and refined with SHELX-76[23] program using the full-matrix method. During refinement the geometry of both phenyl rings was kept fixed at standard values in order to minimize the number of parameters. Hydrogen atoms were located on difference Fourier maps or by theoretical calculation. Least-squares refinement with anisotropic thermal parameters for sulphur, oxygen, nitrogen, and carbon (C1) atoms converged at R and R_w values both of 0.048. A weighting scheme of the form $w = 1/(\sigma^2(F) + 0.000\,283|F|^2)$ was employed in the final cycle. Maximum and minimum peak heights in final difference Fourier maps were ± 0.21 e Å^{-3}.

The absolute configuration was determined with the aid of the most enantiomer-sensitive Friedel pairs. The two antipodal sets of atomic co-ordinates, individually refined, were used in a structure factor calculation limited to 27 Bijvoet pairs. The two weighted R_w factors are 0.081 for the (*S*,*S*) model and 0.107 for the (*R*,*R*) model.*

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* *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). Fractional atomic co-ordinates with thermal parameters, and hydrogen atom co-ordinates with thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.