Chiroptical Properties of C_2-Symmetric *N*-Haloaziridines. Chiral Rules for the *N*-Haloaziridine Chromophore

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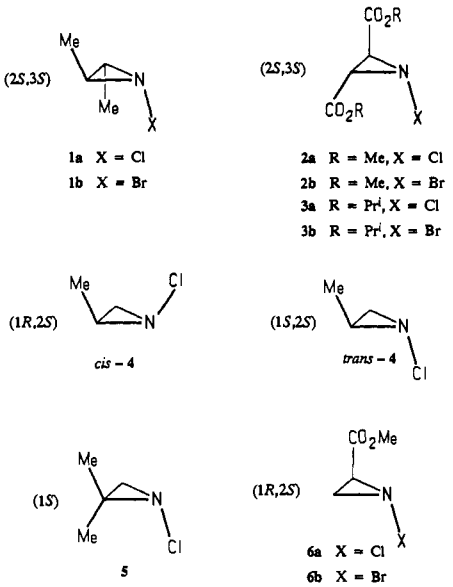
Abstract: *N*-Chloro (**a**) and *N*-bromo (**b**) derivatives of C_2-symmetric aziridines (2*S*,3*S*)-1-halogen-2,3-dimethylaziridines **1a,b** and (2*S*,3*S*)-1-halogen-2,3-bis(alkoxycarbonyl)aziridines **2a,b** and **3a,b** were obtained. Haloaziridines **1a,b** are an example of the "pure" *N*-haloaziridine chromophore which has the first Cotton effect (CE) in the region of 260–300 nm. A quadrant rule which connects the first CE sign with the stereochemical environment of the chromophore is offered. Haloaziridinecarboxylic esters are a specific case of the *N*-haloaziridine chromophore. The second CE sign at 220–230 nm in the CD spectra of these compounds obeys a reverse quadrant rule.

Introduction

Optically active aziridines are synthons for the preparation of amino acids[1] and β-lactams,[2] are used as chiral reagents,[3] and show various biological activity.[4] Optically active aziridines are often obtained by such methods as asymmetrical synthesis,[5] kinetic resolution (fermentative catalysis),[6] or resolution of racemates.[7] In such cases the problem of the determination of absolute stereochemistry usually arises. This problem could be easily solved by means of circular dichroism (CD) spectroscopy. However, the aziridine chromophore proper has its first dichroic absorption in the short-wavelength region (<200 nm[8]), which makes it difficult to measure the aziridine Cotton effect (CE) in the usual organic solvents as well as in the presence of other chromophoric groups in the molecule. This obstacle is removed by the introduction of a halogen (chlorine or bromine) to the aziridine nitrogen atom. The first CE of the *N*-haloaziridine chromophore is observed about 250 (Cl) or 290 nm (Br)[9] and is not covered by the dichroic bands of some other chromophores, for example, ester groups.[9b] As an added advantage, the *N*-haloaziridine chromophore is possessed of a certain stereochemical rigidity owing to the high nitrogen inversion barrier (25–27 kcal mol^{-1} for *N*-chloroaziridines[6a,9]). These features as well as the availability and the relative stability of *N*-haloaziridines engender hope for a practical usefulness of the *N*-haloaziridine chromophore for the determination of the absolute stereochemistry of optically active aziridines by means of CD spectroscopy.

Chart I



Earlier we have studied the origin of the optically active electronic transitions in the *N*-haloaziridine chromophore.[9b] In the present work, we investigate the chiroptical properties of 2,3-symmetrically substituted *N*-haloaziridines, henceforth described as "C_2-symmetric". In these compounds, unlike the 2-substituted analogs, the nitrogen center is not an additional element of stereochemistry. Thus a study of *N*-haloaziridines, **1–3**, is undertaken with the purpose of finding a qualitative relation of the CE signs of the *N*-haloaziridine chromophore with the absolute stereochemistry of the carbon centers. Also, the CD data of 2-substituted *N*-haloaziridines, **4–6**,[9b-d] are used.

Results and Discussion

Optically active C_2-symmetric NH-aziridines **10** and **14**—the precursors of *N*-haloaziridines **1–3**, have been obtained from the corresponding 1,2-glycols **7** and **11** through the 1,3,2-dioxathiolane derivatives **8** and **12** (Scheme I).[10] Practically, these syntheses are more efficient than through optically active oxiranes.[2,11]

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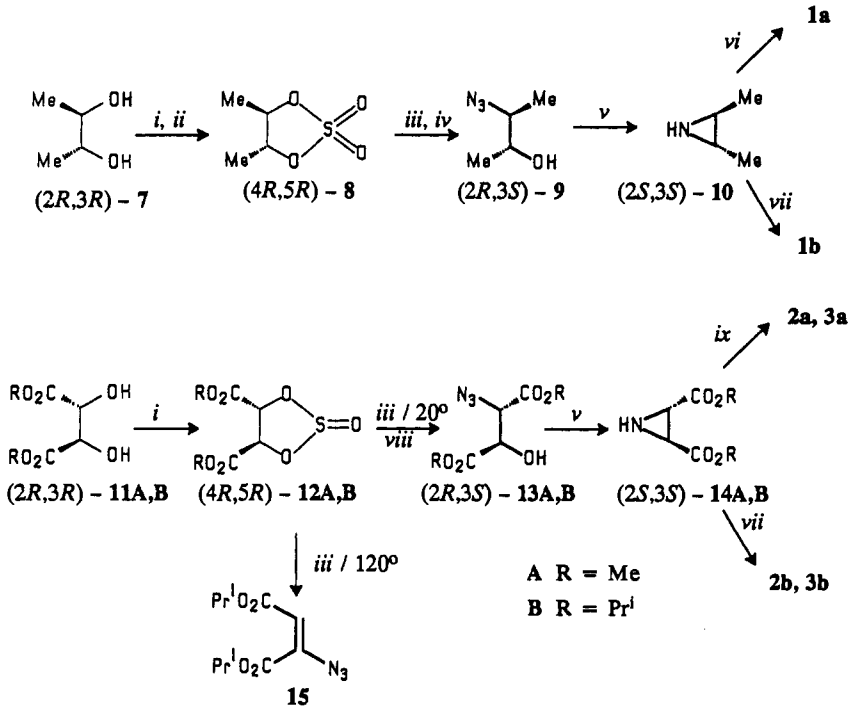
Scheme I[a]



[a] Reagents: *i*, $SOCl_2$; *ii*, $NaIO_4/RuCl_3$; *iii*, NaN_3; *iv*, aqueous H_2SO_4; *v*, Ph_3P; *vi*, NaOCl; *vii*, NBS, *viii*, H_2O; *ix*, Bu^{t}OCl.

Table I. CD Spectra of C_2-Symmetric *N*-Haloaziridines **1–3**[a]

compd	solvent[b]	
1a	H	261 (–0.742), 216 (0.682)
	M	259 (–0.591), 212 (0.606)
1b	H	303 (–0.918), 249 (0.732)
2a	H	253 (–2.151), 220 (–3.727)
	M	249 (–1.788), 220 (–3.121)
2b	H	302 (–0.873), 234 (–7.211), 209 (4.394)
	M	290 (–0.703), 233 (–5.818), 207 (4.181)
3a	H	255 (–2.151), 220 (–3.333)
	M	253 (–1.788), 220 (–2.757)
3b	H	305 (–0.715), 236 (–5.030), 210 (3.636)
	M	291 (–0.521), 233 (–4.000), 208 (3.151)

[a] Wavelengths of apparent maxima in nm, $\Delta\epsilon$ values in parentheses. [b] H, *n*-heptane; M, methanol.

However, it is necessary to note that only general procedures for the synthesis of different optically active aziridines, not specifically **10** and **14**, were given in ref 10. Therefore we have decided to describe the detailed experimental conditions of the synthesis of aziridines **10** and **14A,B**. The attempt to carry out the reaction of sulfite **12B** with NaN_3 in DMF at 120 °C according to ref 10b afforded azidomaleate **15** only. The structure of this compound was confirmed by its ^{1}H NMR spectrum by the comparison with previously described dimethyl azidomaleate.[12] Azidoalcohols **13A,B** are smoothly obtained by keeping the reaction mixtures at 20 °C.

2,3-Dimethyl-substituted *N*-haloaziridines **1a,b** as well as the earlier studied *N*-chloroaziridines **4**, **5**, and **9b** can be considered as models of the "pure" *N*-haloaziridine chromophore because these compounds do not contain other functional (chromophoric) groups and have the well-known rigid orientation of the halogen in relation to the carbon substituents. Two dichroic absorption bands of the opposite signs are observed in the CD spectra of *N*-haloaziridines **1a,b** (Table I, Figure 1). According to ab initio calculations on *cis*- and *trans*-**4**,[9b] and on **1a** and **5** (see below), these bands are assigned to the π^*_{NHal}–σ^*_{NHal} (long-wavelength CE) and the $3p_{Hal}$–σ^*_{NHal} (short-wavelength CE) transitions. Decreasing of the halogen electronegativity from *N*-chloro **1a** to *N*-bromo derivative **1b** causes a bathochromic shift of both bands. This is due to raising of the π^*_{NHal} and $3p_{Hal}$ occupied orbital energies and lowering of the σ^*_{NHal} unoccupied orbital energy. The hypsochromic shift of the bands for *N*-chloroaziridine **1a** in MeOH confirms the participation of the nonbonding electrons in the first two transitions.

The CD spectrum of *N*-chloroaziridine **1a** (Table I, Figure 1) is very close to the spectrum of *cis*-**4** and differs from the spectrum of its *trans* isomer.[9b] Hence it follows that the perturbative influence of the *cis* methyl group on the first and possibly second optically active electronic transition in the *N*-haloaziridine chromophore is decisive. The results of a computational study of **1a** and **5** are listed in Table II, and the structures of (2*S*,3*S*)-**1a** and (1*S*)-**5** are shown in Figure 2. Plots of the molecular orbitals involved in the first two electronic transitions, both of which terminate in valence states, are shown in Figure 3. The descriptions, π^*_{NCl}–σ^*_{NCl} (long-wavelength) and the $3p_{Cl}$–σ^*_{NCl} (short-wavelength), are identical to those previously found for **4**.[9b] The rotational strengths of the first two transitions are calculated to be very low. This is in part due to fact that the transitions are only weakly allowed, i.e., the electric dipole transition moments are small (see the oscillator strengths in Table II), and the fact that the magnetic and electric dipole transition moments are close to perpendicular. For (2*S*,3*S*)-**1a**, the calculated angles are 116.0° and 96.6° for the first and second transitions, respectively, and the computed signs of the rotatory strengths are both negative. The calculated sign of the first transition is in agreement with the observed long-wavelength CE. The calculated CE of the second transition appears to be incorrect in sign, as was the case also for *cis*- and *trans*-**4**,[9b] a failure attributed to the quality of the electronic wave functions and the nearly perpendicular nature of the transition dipole moments. We note, however, that the next electronic transitions are to Rydberg states and, in aggregate, have a relatively large positive rotational strength. If the strong positive CE observed to shorter wavelengths in the experimental spectra (Figure 1 and ref 9b) is due to Rydberg transitions, it is possible that the negative CE

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Table II. Energies,[a] Ionization Potentials, Dipole Moments, Excitation Energies, Rotatory Strengths, and Oscillator Strengths for **1a**, **5**, and **6a**

property	*N*-chloro-2,3-dimethylaziridine (2*S*,3*S*)-**1a**	*N*-chloro-2,2-dimethylaziridine (1*S*)-**5**	*N*-chloro-2-carbomethoxyaziridine, **6a** (1*R*,2*S*,*E*) *trans*	(1*R*,2*S*,*Z*) *trans*	(1*S*,2*S*,*E*) *cis*	(1*S*,2*S*,*Z*) *cis*
rel energy (kJ mol^{-1})	0.0[b]	0.0[b]	0.0[b]	0.2	16.8	12.8
IP,[c] eV 1	9.2	9.2	10.2	10.2	10.1	10.0
2	10.5	10.6	11.2	11.3	11.3	11.3
3	11.7	11.8	12.2	11.9	11.8	12.0
μ, *D*	2.92	2.89	2.66	3.24	3.29	2.86
$S_o \rightarrow S_1$ *E*, eV	6.06	6.11	6.23	6.21	6.10	6.12
$[R]'([R])^p$	−3.3 (−3.1)	1.7 (3.2)	+1.3 (+0.4)	−0.7 (−2.4)	+0.8 (+2.7)	−0.5 (+1.5)
f	0.0173	0.0187	0.0145	0.0136	0.0158	0.0158
$\angle\langle r\rangle\cdot\langle m\rangle$[d]	116.1	81.0	92.4	88.4	94.3	87.8
description[e]	$\pi^*_{NCl} \rightarrow \sigma^*_{NCl}$	$\pi^*_{NCl} \rightarrow \sigma^*_{NCl}$	$\pi^*_{NCl} \rightarrow \sigma^*_{NCl}$	$\pi^*_{NCl} \rightarrow \sigma^*_{NCl}$	$\pi^*_{NCl} \rightarrow \sigma^*_{NCl}$	$\pi^*_{NCl} \rightarrow \sigma^*_{NCl}$
$S_o \rightarrow S_2$ *E*, eV	7.02	7.00	7.01	7.00	7.05	7.05
$[R]'([R]^p)$	−1.3 (−0.7)	−0.8 (−1.4)	−1.8 (−2.0)	−2.2 (−2.0)	−4.9 (−3.6)	−4.1 (−2.3)
f	0.0025	0.0005	0.0004	0.0002	0.0002	0.0002
$\angle\langle r\rangle\cdot\langle m\rangle$[d]	96.6	100.0	82.2	78.6	19.4	48.7
description[e]	$3p_{Cl} \rightarrow \sigma^*_{NCl}$	$3p_{Cl} \rightarrow \sigma^*_{NCl}$	$3p_{Cl} \rightarrow \sigma^*_{NCl}$	$3p_{Cl} \rightarrow \sigma^*_{NCl}$	$3p_{Cl} \rightarrow \sigma^*_{NCl}$	$3p_{Cl} \rightarrow \sigma^*_{NCl}$
$S_o \rightarrow S_n$ *E*, eV	8.3–9.0	8.3–9.0	7.46	7.50	7.33	7.38
$[R]'([R]^p)$	14.5[f] (12.4[f])	−14.0[f] (−10.9[f])	−36.8 (−31.4)	−6.8 (−7.2)	−14.5 (−14.7)	−4.83 (+0.2)
f	0.029[f]	0.0411[f]	0.0103	0.0015	0.0016	0.0030
$\angle\langle r\rangle\cdot\langle m\rangle$[d]			4.5	67.7	32.1	81.5
description[e]	$\pi^*_{NCl} \rightarrow 4s,4p$	$\pi^*_{NCl} \rightarrow 4s, 4p$	$\pi^*_{NCl} \rightarrow \pi^*$	$\pi^*_{NCl} \rightarrow \pi^*$	$\pi^*_{NCl} \rightarrow \pi^*$	$\pi^*_{NCl} \rightarrow \pi^*$

[a] The geometries (Figure 2) and relative energies were obtained with the 6-31G* basis set; all other properties were calculated with the 6-31+G* basis set. [b] *E*(RHF, 6-31G*): **1a**, −669.978 518; **5**, −669.977 056; **6a**, −818.542 381. [c] By the method of ref 16. [d] Angle between the electric and magnetic dipole transition moments, in degs. [e] See Figures 3 and 5 for orbital plots. [f] Sum of four Rydberg transitions.

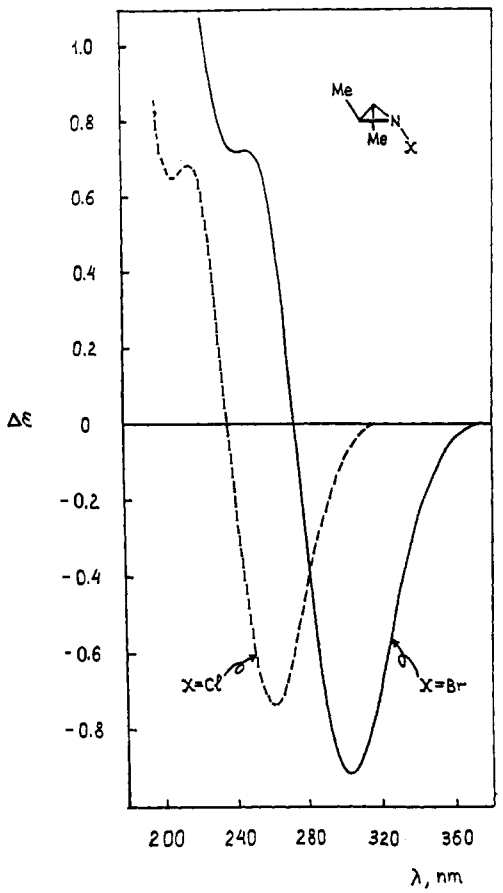

Figure 1. The CD spectra of *N*-haloaziridines **1a,b** in heptane.

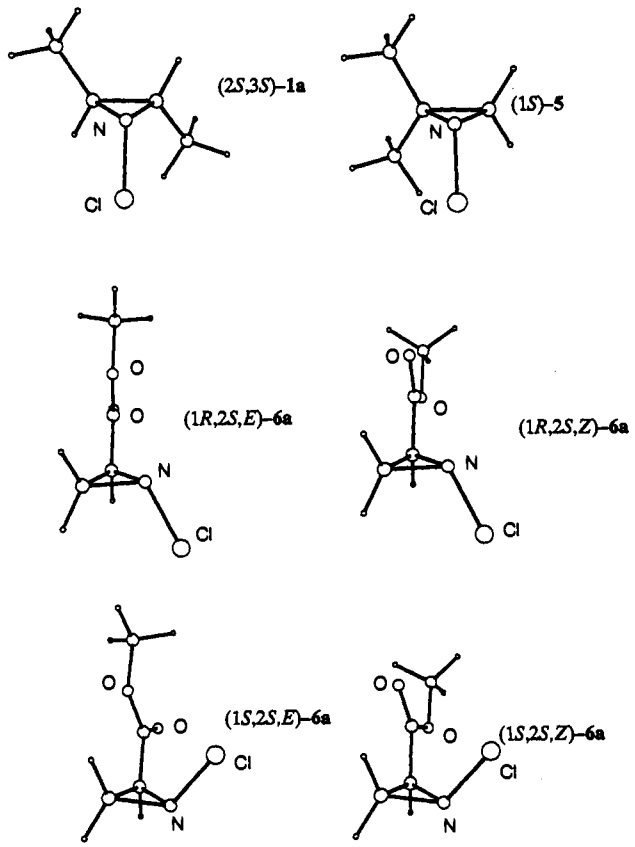

Figure 2. 6-31G* structures of (2*S*,3*S*)-1-chloro-2,3-dimethylaziridine (2*S*,3*S*)-**1a**, (1*S*)-1-chloro-2,2-dimethylaziridine (1*S*)-**5**, and (2*R*)-1-chloro-2-carbomethoxyaziridine **6a**.

of the second valence transition is partially obscured, manifesting itself only as a depression in the region of positive ellipticity. The unambiguous resolution of the sign of the second valence transition awaits the capability to perform more accurate calculations. In any case, the first electronic transition is well characterized and may serve as a diagnostic of the absolute configuration of the *N*-haloaziridine chromophore. The computations on **5** (Table II) agree with experimental observations[9b] and support this conclusion.

Chiral rules have previously been suggested for the first (long-wavelength) CE of the *N*-haloaziridine chromophore: a quadrant rule[9a] and a planar rule.[13] It is evident from Table III that both rules incorrectly predict the first CE sign of methyl-substituted *N*-haloaziridines **1**, *cis*-**4**, and **5**. The reason is, evidently, an incorrect interpretation of the ORD spectrum of (1*R*,2*S*)-*cis*-**4**[9a] in the first case and an unsuccessful choice of model, i.e., (1*R*)-

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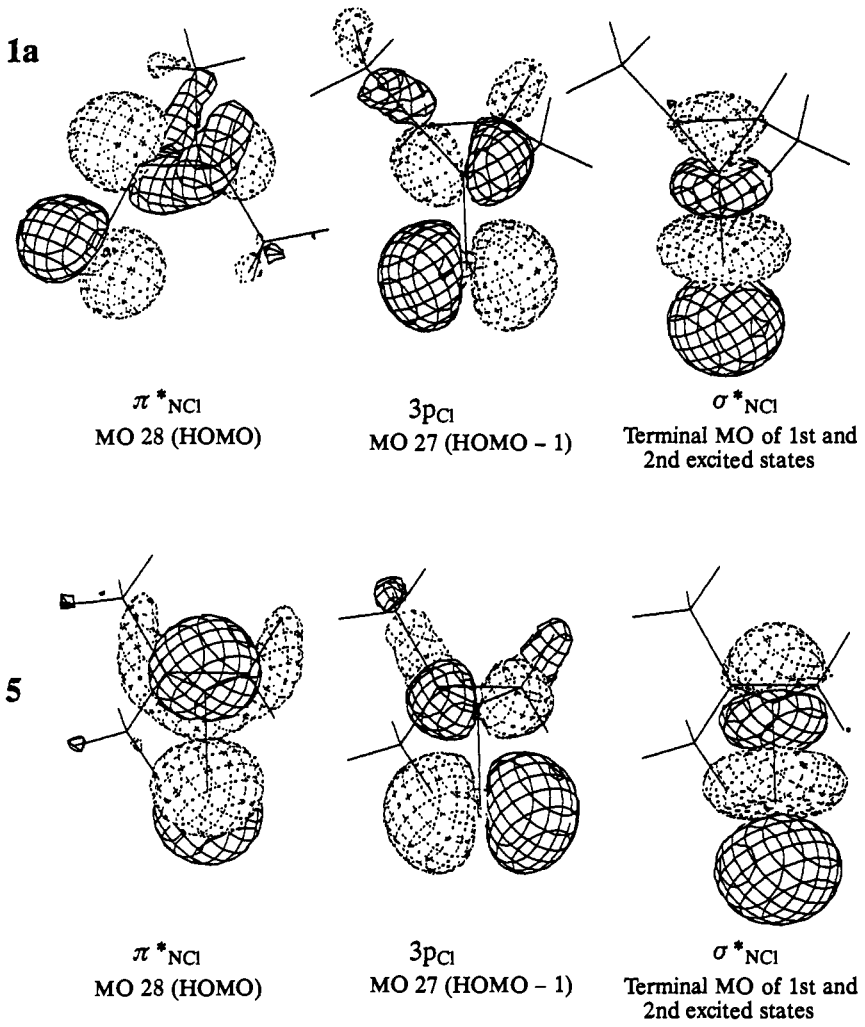

Figure 3. Molecular orbitals involved in the two lowest energy electronic transitions of the chlorodimethylaziridines **1a** and **5**. Contour level 0.05.

1-chloro-2,2-diphenylaziridine,[13] in the second instance. It is possible that for the latter compound, interaction may occur between the phenyl and *N*-chloroaziridine chromophores, thereby altering the nature of the chromophore. Even in the absence of direct coupling, a superposition of their CEs in the region, 240–270 nm, is also likely. From the CD data of methyl-substituted *N*-haloaziridines, **1**, **4**, and **5**, we propose a new quadrant rule for the *first* CE of the "pure" *N*-haloaziridine chromophore (Table III). A space around the chromophore is divided by two surfaces: the vertical surface, which is the plane of the local symmetry of the chromophore, and a horizontal surface—the nodal surface of the nitrogen lone pair or, more accurately, of the π^*_{NHal} orbital (HOMO, e.g., Figure 3). We approximate the latter surface as the plane which passes through the nitrogen atom and is parallel to the base of the nitrogen pyramid.

The proposed quadrant rule correctly predicts not only the CE sign of the π^*_{NHal}–σ^*_{NHal} transition but reflects also such features as the relative influence of the *cis* and *trans* alkyl substituents at the aziridine carbons on this transition. Actually, the *trans* methyl group lies near to the horizontal surface, and perturbative influence of this group is considerably smaller than the influence of the *cis* methyl group, which is located far from both the surfaces. Therefore, for example, a positive first CE is observed for *N*-chloroaziridine (1*S*)-**5**[9b] containing the *cis* Me group in the positive quadrant and the *trans* Me group in the negative one (Table III).

Table III. Chiral rules for the Pure *N*-Haloaziridine Chromophore[a]

The first CE sign of *N*-haloaziridines	**1a**	**1b**	*cis*-**4**	*trans*-**4**	**5**
observed	–	–	–	–	+
Predicted by					
'old' quadrant rule 	0	0	+	–	–
planar rule 	0	0	+	–	–
'new' quadrant rule 	–	–	–	–	+

A replacement of the methyl groups by the ester groups substantially alters the chiroptical properties of *N*-haloaziridines. A reverse relation of the first CE sign with the absolute stereochemistry is observed for the dicarboxylic esters **2** and **3** (Table I, Figure 4) as in the case of the monoesters **6a,b**.[9b] The second CE has a relatively high intensity and the same sign as the first one.

We have examined the optical activity of 1-chloro-2-carbomethoxyaziridine, **6a**, computationally in an attempt to determine the origin of the anomalous behavior caused by the ester substitution. The *cis* and *trans* invertomers, (1*S*,2*S*)- and

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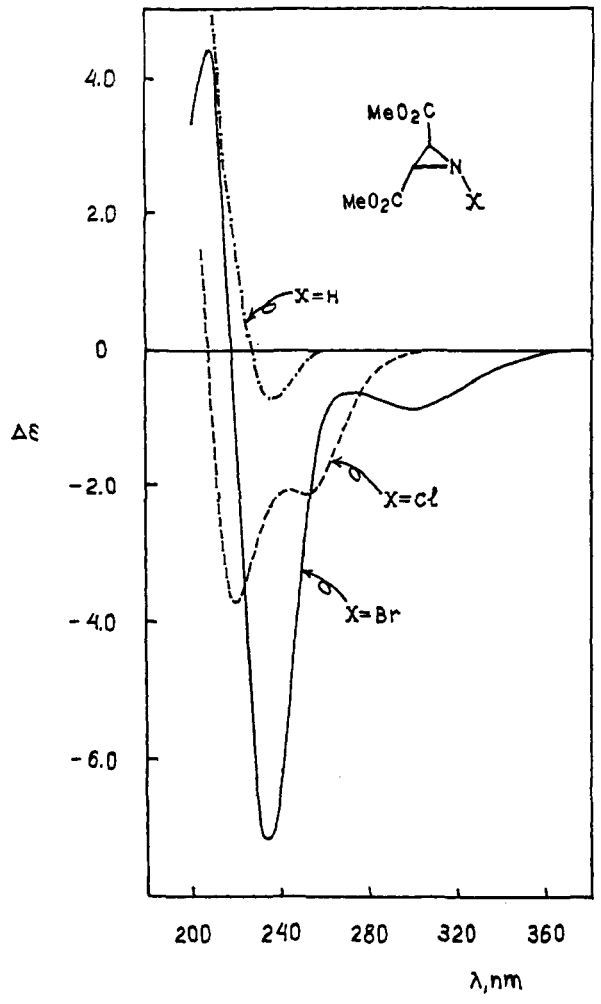


Figure 4. The CD spectra of dimethyl 1-haloaziridine-2,3-dicarboxylates **2a,b** and of dimethylaziridine-2,3-dicarboxylate **14A** in heptane.

(1*R*,2*S*)-**6a**, were calculated for modeling of the influence of *cis*- and *trans*-oriented ester groups on the optical active electronic transitions in the *N*-haloaziridine chromophore. It was found that each of the invertomers has two relatively stable rotamers with the *E*- and *Z*-orientation of the carbonyl to the aziridine ring (Figure 2, Table II). The near bisected conformation of the CO_2Me group in all four stereoisomers is caused, evidently, by the interaction of the π^* orbital of this group with the Walsh orbital of the aziridine ring. The same conformation (*Z*) of a *trans*-CO_2Me group has been found for 1-chloro-2-(methoxycarbonyl)-2-(methylcarbamoyl)aziridine by means of X-ray diffraction measurements.[6b] The difference in the *E*,*Z*-rotamer energies is predicted to be almost zero for the *trans* invertomer of **6a** and is more appreciable in the case of *cis*-**6a**. Therefore one may expect similar populations of the *E*- and *Z*-rotamers for the *trans*-CO_2Me group, and a preference of the *Z*-rotamer for the *cis*-CO_2Me group in the dicarboxylic esters **2** and **3**. The *cis*- and *trans*-invertomer energies are substantially different owing to steric repulsion of the CO_2Me group and the N–Cl bond in the *cis* invertomer of **6a**. This result agrees with experimental data,[9b] according to which 1-haloaziridine-2-carboxylic esters exist only as the *trans* invertomers under conditions of thermodynamic equilibrium.

1-Chloroaziridine-2-carboxylic ester **6a** has the same orbital origin of the first and second CEs as methyl-substituted *N*-chloroaziridines **1a**, **4**,[9b] and **5** (Table II). Inspection of the molecular orbitals (Figure 5) shows that neither the π^*_{NCl} orbital nor the σ^*_{NCl} orbital has any significant extension into the carbomethoxy group, even at orbital contours as low as 0.03. The initial $3p_{Cl}$ orbital of the second electronic transition is an exception. A small amount of admixture of the n_O orbital to the *trans*-CO_2Me group is observed for this orbital. Such admixture is absent in the case of the *cis* invertomer of **6a**.

The calculations qualitatively correctly reproduce the ratio of the intensities of the first and second CEs in the CD spectra of *trans*-**6a**[9b] as well as the small hypsochromic shift of the first CE which is caused by introduction of the electronegative ester group. The first CE sign, in substantial extent, is determined by the conformation of the CO_2Me group. Evidently the rotation of this group around the C–C bond is the lowest energy process, and such factors as the introduction of other substituents or even solvation can affect the equilibrium population of the rotamers. Furthermore, in all four stereoisomers, the electric and magnetic dipole transition moments are close to perpendicular, suggesting that the computation may be unreliable even with respect to sign, and also that the observed first CE may be sensitive to the above-mentioned extrachromophoric perturbations. Indeed, when the C–N–Cl angles of *trans*-**6a** (specifically (1*R*,2*S*,*E*)-**6a**) were modified to coincide with the corresponding angles of the *cis* isomer (specifically (1*S*,2*S*,*Z*)-**6a**), changes of only +4.7° and −1.9°, the predicted CE of the first calculated rotatory strength changed sign (to −0.6 from +1.3, Table II). This deformation simulates the local geometry expected in the 2,3-dicarbomethoxy system, **2a**, which is too large for direct computation.

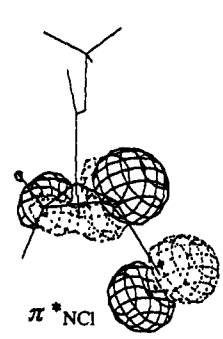
Unlike the first CE, the calculated second CE signs of **6a** do not depend on the CO_2Me group conformation and coincide with the experimental one.[9b] The angles between the electric and magnetic dipole transition moments differ more appreciably from 90° than the angles of the first electronic transition and, correspondingly, the second CE has higher intensity. Therefore it is preferable to take into consideration the second CE sign for the determination of absolute configuration of 1-haloaziridinecarboxylic esters. According to the calculations, the *cis* invertomers of **6a** have larger rotational strengths of the second electronic transition than *trans*-**6a** (Table II). This result is reminiscent of the decisive influence of the *cis*-methyl group on the values of the first CEs in the methyl-substituted *N*-haloaziridines **1**, **4**,[9b] and **5** (*vide supra*). Hence, the experimental and calculated data for the *second* CE of haloaziridinecarboxylic esters **2**, **3**, and **6** may be generalized by the same empirical quadrant rule as in the case of the *first* CE of the pure haloaziridine chromophore (Table III) but with the opposite quadrant signs, i.e., by a reverse quadrant rule (Scheme IIa).

The proposed chiral rules could be used with some prudence for other *N*-haloamines. For example, the "new" quadrant rule for the pure chromophore correctly predicts the negative first CE sign for (+)-*N*-chlorocamphidine[14a] (Scheme IIb) and the reverse quadrant rule—negative second CE sign in the case of methyl (2*S*)-1-chloroproline[14b] (Scheme IIc). However, it will be necessary to assume a higher population of the isomers with the equatorial orientation of the chlorine atom and their dominant contribution to the observed rotational strength of the corresponding electronic transitions.

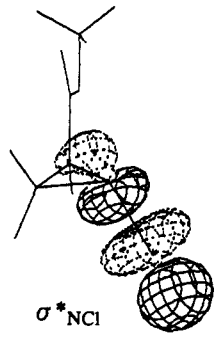
It is clear that, in contrast to the stereochemically rigid *N*-haloaziridines, problems may arise in assignment of relative populations of the rotamers and invertomers, and their contributions to the rotational strength, in the case of *N*-haloamines with larger rings.

Methods

Theoretical. The geometries of (2*S*,3*S*)-1-chloro-2,3-dimethylaziridine **1a**, (1*S*)-1-chloro-2,2-dimethylaziridine **5**, (1*R*,2*R*)-1-chloro-2-carbomethoxyaziridine, *trans*-**6a**, and its *cis* diastereomer, (1*S*,2*R*)-1-chloro-2-carbomethoxyaziridine, *cis*-**6a**, were fully optimized by Hartree–Fock SCF calculations at the 6–31G*

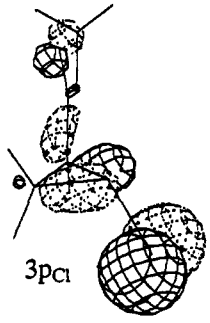


MO 35 (HOMO)

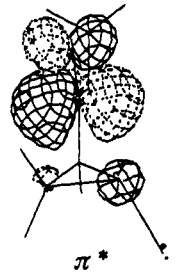


Terminal MO of 1st and 2nd excited states

(1R,2S,E)-6a

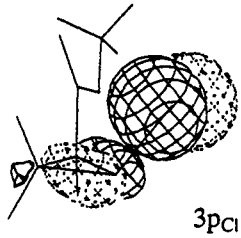


MO 34 (HOMO - 1)



Terminal MO of 3rd excited state

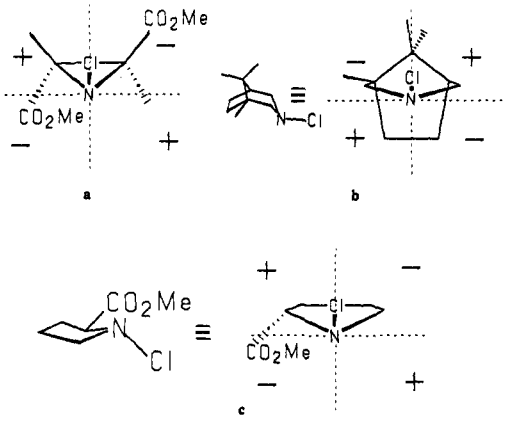
(1S,2S,Z)-6a



MO 34 (HOMO - 1)

Figure 5. Molecular orbitals involved in the lowest energy electronic transitions of the 1-chloro-2-carbomethoxyaziridine, **6a**. Contour level 0.075.

Scheme II



level by using the GAUSSIAN 90 system of programs.[15] In the case of the 2-carbomethoxyaziridine **6a**, two rotamers, corresponding to reorientation of the plane of the carbomethoxy group, were found. For the purpose of determining the transition properties, the wave functions were redetermined using the internal 6-31+G* basis set, which includes additional diffuse *s* and *p* functions in the basis set. Addition of these diffuse functions permits a better description of the lowest few valence states and the identification of Rydberg states. Ionization potentials are calculated using a many body perturbation theory correction to Koopmans' theorem based on the work of Pickup and Goscinski.[16] The frontier orbitals are displayed as modified Jorgensen–Salem plots.[17]

The method used to calculate oscillator and optical rotatory strengths is the same as was used previously[9b,18-20] and has been described in detail elsewhere.[21] Partially correlated wave functions for the ground and excited states are determined to first order

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in Rayleigh–Schrödinger perturbation theory

$$\Psi_n = \Psi_n^o - \sum\nolimits_j a_{nj}\Phi_j^o \tag{1}$$

where

$$a_{nj} = \langle\Psi_n^o|H|\Phi_j^o\rangle/(\langle\Phi_j^o|H|\Phi_j^o\rangle - \langle\Psi_n^o|H|\Psi_n^o\rangle) \tag{2}$$

H is the exact Hamiltonian, Φ_j^o is a singlet singly or more highly excited configuration derived from the Hartree–Fock determinant, Φ_{HF}, and Ψ_n^o is a linear combination of strongly interacting Φ_l^o ($l \neq j$) selected from at most singly excited configurations. Thus, for the ground state, $\Psi_o^o = \Phi_{HF}$. All configurations for which the interaction coefficient a_{nj} (eq 2) was greater than 0.05 were included in the zero-order part of the CI wave function. For reasons of expediency, the CI calculation was restricted to a window of 14 occupied orbitals and 48 unoccupied orbitals for each system.

Electric dipole transition moments in the length $\langle r\rangle_{on}$ and velocity $\langle v\rangle_{on}$ formalism and magnetic dipole transition moments $\langle m\rangle_{on}$ are explicitly evaluated from

$$\langle r\rangle_{on} = \langle\Psi_o|\mu|\Psi_n\rangle \tag{3}$$

$$\langle v\rangle_{on} = \langle\Psi_o|\nabla|\Psi_n\rangle/(E_n - E_o) \tag{4}$$

$$\langle m\rangle_{no} = -i\,\langle\Psi_n|m|\Psi_o\rangle \tag{5}$$

where the dipole, gradient, and magnetic moment operators, μ, ∇, and m, have their usual definitions and

$$E_n = \langle\Psi_n|H|\Psi_n\rangle \tag{6}$$

Oscillator strengths f_{on} are calculated by the "mixed" formalism

$$f_{on} = \frac{2}{3}\langle\Psi_o|\nabla|\Psi_n\rangle\cdot\langle r\rangle_{no} \tag{7}$$

Optical rotatory strengths are evaluated as

$$[R_{on}]^r = \langle r\rangle_{on}\cdot\langle m\rangle_{no} \tag{8}$$

and in the origin independent form

$$[R_{on}]^v = \langle v\rangle_{on}\cdot\langle m\rangle_{no} \tag{9}$$

The extent of the deviation of $\langle r\rangle$ and $\langle v\rangle$ from collinearity and in magnitude is a measure of the quality of the wave function for the particular states and of the origin dependence of $[R]^r$.

Experimental Section

The CD spectra were measured on a JASCO J-500A spectropolarimeter with a DP-500N data processor, the ^{1}H NMR spectra on a Bruker WM-400 (400 MHz) and a Varian XL-200 (200 MHz) spectrometers, and the optical rotation angles on an Autopol III and a Polamat A polarimeters.

(4*R*,5*R*)-2,2-Dioxo-4,5-dimethyl-1,3,2-dioxathiolane (8). Thionyl chloride (26.4 g, 0.222 mol) was added dropwise to glycol (–)-**7** (10.0 g, 0.111 mol) in CCl_4 (50 mL), and the resulting solution was refluxed for 1 h. The reaction mixture was evaporated in vacuo, and the residual clear liquid (15.8 g) was dissolved in MeCN (70 mL). $RuCl_3\cdot 3H_2O$ (37 mg, 0.14 mmol) and a solution of $NaIO_4$ (35.7 g, 0.167 mol) in H_2O (200 mL) were added to the MeCN solution with cooling (15 °C) and stirring. After 2 h at 20 °C, the precipitate was filtered off, the filtrate was diluted with ether (500 mL), and the two phases were separated. The organic layer was washed with water (50 mL), saturated aqueous $NaHCO_3$ (2 × 50 mL), and brine (50 mL). After drying over $CaCl_2$, the solution was evaporated in vacuo. The residue was distilled, providing sulfate **8** (15.13 g, 90%): bp 114–116 °C (6 mm), $[\alpha]^{20}_D$ +1.8° (neat) (lit.[22] bp 93 °C (2 mm); $[\alpha]^{25}_D$ +1.75° (neat)); ^{1}H NMR (200 MHz) in $CDCl_3$ (*J*, Hz) δ 1.55 (6 H, d, Me, ^3J = 6.0), 4.69 (2 H, m, CH).

(2*R*,3*S*)-3-Azidobutanol-2 (9). A saturated aqueous solution of NaN_3 (13.0 g, 0.2 mol) was added to sulfate **8** (15.0 g, 0.099 mol) in acetone (130 mL), and the resulting mixture was stirred at 20 °C for 10 h. The precipitate was filtered off, and the filtrate was evaporated in vacuo. The residual white solid (21.5 g) was stirred with ether (100 mL) and 3 M H_2SO_4 (15 mL) at 20 °C for 72 h. After the separation of the organic layer, the aqueous solution was extracted with CH_2Cl_2 (4 × 20 mL). After stirring with $NaHCO_3$ (5.0 g), the combined extract was dried over $MgSO_4$ and evaporated in vacuo. The residue was distilled, providing azidoalcohol **9** (8.7 g, 76%): bp 79–80 °C (20 mm); $[\alpha]^{20}_D$ +43.1° (*c* 2.5, heptane) (lit.[23] bp 83–84 °C (31 mm)); ^{1}H NMR (200 MHz) in $CDCl_3$ (*J*, Hz): δ 1.19 (3 H, d, 2-Me, $^3J \approx 6.4$), 1.25 (3 H, d, 3-Me, ^3J = 6.7), 1.82 (1 H, d, OH, ^3J = 4.7), 3.55 (1 H, dq, 3-CH, ^3J = 6.7, 3.9), 3.8 (1 H, br dq, 2-CH).

(2*S*,3*S*)-2,3-Dimethylaziridine (10). A 50-mL, three-necked flask equipped with a condenser connected to a dry-ice trap, a stopper, and a rubber septum was charged with Ph_3P (15.7 g, 0.06 mol) which was then cooled with a dry-ice–acetone bath. Azidoalcohol **9** (4.61 g, 0.04 mol) was added via a syringe to the flask, and the resulting mixture was warmed up carefully to melting and the beginning of the nitrogen gas evolution. The product was collected in the trap and then distilled, providing aziridine **10** (2.02 g, 71%): bp 74–75 °C; $[\alpha]^{20}_D$ –101.6° (*c* 1.7, heptane) (lit.[11a] bp 74.5–74.8 °C; $[\alpha]^{20}_D$ –103.8° (*c* 0.22, heptane)); ^{1}H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 0.16 (1 H, br s, NH), 1.18 (6 H, d, Me, ^3J = 5.3), 1.64 (2 H, m, CH, ^3J = 5.3, 3.4).

(2*S*,3*S*)-1-Chloro-2,3-dimethylaziridine (1a). Aziridine **10** (0.36 g, 5 mmol) was added to a solution of NaOCl (10 mmol) in H_2O (5 mL) with cooling (0 °C). After 15 min at 10 °C, the organic layer was separated and then dried over $MgSO_4$ and distilled in vacuo, providing *N*-chloroaziridine **1a** (0.36 g, 68%): bp 30–31 °C (30 mm); $[\alpha]^{20}_D$ +16.8° (*c* 3.2, heptane); ^{1}H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 1.23 and 1.49 (6 H, dd, Me, ^3J = 5.8), 1.94 and 1.99 (2 H, m, CH_ACH_B, ^3J = 5.8, 5.8). Anal. Found: C, 45.7; H, 7.8; N, 13.1. Calcd for C_4H_8ClN: C, 45.5; H, 7.6; N, 13.3.

(2*S*,3*S*)-1-Bromo-2,3-dimethylaziridine (1b). *N*-Bromosuccinimide (0.38 g, 2.11 mmol) was added to a solution of aziridine **10** (0.1 g, 1.41 mmol) in CH_2Cl_2 (2 mL) with cooling (0 °C) and stirring. After 15 min at 20 °C, the solvent was evaporated in vacuo, and the product was extracted from the residue with pentane. After removal of pentane the yellow liquid was distilled, providing *N*-bromoaziridine **1b** (0.11 g, 53%): bp 47–48 °C (30 mm); $[\alpha]^{20}_D$ +1.3°, $[\alpha]^{20}_{406}$ –52.8° (*c* 1.8, heptane); ^{1}H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 1.22 and 1.48 (6 H, dd, Me, ^3J = 5.8), 1.44 and 1.95 (2 H, dm, CH_ACH_B, ^3J = 5.8, 5.8). Anal. Found: C, 32.3; H, 5.5; N, 9.2. Calcd for C_4H_8BrN: C, 32.0; H, 5.4; N, 9.3.

2-Oxo-1,3,2-dioxathiolanes 12A,B. A solution of (+)-dialkyl tartrate **11** (0.05 mol) and $SOCl_2$ (17.85 g, 0.15 mol) in CCl_4 (50 mL) was refluxed for 1 h. After removal of the solvent in vacuo, the residual clear liquid was distilled, providing sulfite **12**.

(4*R*,5*R*)-4,5-Bis(methoxycarbonyl)-2-oxo-1,3,2-dioxathiolane (12A): yield 93%; bp 114–115 °C (1 mm); $[\alpha]^{20}_D$ –164.9° (*c*, 2.8, $CHCl_3$); ^{1}H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 3.83 and 3.84 (6 H, ds, MeO), 5.22 and 5.67 (2 H, dd, CH_ACH_B, ^3J = 4.2). Anal. Found: C, 32.0, H, 3.8. Calcd for $C_6H_8O_7S$: C, 32.15; H, 3.6.

(4*R*,5*R*)-4,5-Bis((isopropyloxy)carbonyl)-2-oxo-1,3,2-dioxathiolane (12B): yield 96%; bp 120–121 °C (1 mm); $[\alpha]^{20}_D$ –151.0° (*c* 2.9, $CHCl_3$); ^{1}H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 1.33 (12 H, td, Me, ^3J = 6.1), 5.15 (2 H, m, CHO), 5.15 and 5.65 (2 H, dd, CH_ACH_B, ^3J = 4.3). Anal. Found: C, 42.7; H, 5.5. Calcd for $C_{10}H_{16}O_7S$: C, 42.85; H, 5.75.

Azidoalcohols 13A,B. A mixture of sulfite **12** (0.04 mol) and NaN_3 (5.2 g, 0.08 mol) in absolute DMF (75 mL) was stirred for 48 h at 20 °C and then poured into ice water (150 mL). The product was extracted with ether (4 × 50 mL) and dried over $MgSO_4$. After removal of solvent in vacuo, the residue was distilled, providing azidoalcohol **13**.

Dimethyl (2*R*,3*S*)-2-hydroxy-3-azidosuccinate (13A): yield 65%; bp 112–113 °C (1 mm); $[\alpha]^{20}_D$ –12.2° (*c* 2.7, $CHCl_3$); ^{1}H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 3.28 (1 H, br s, OH), 3.83 and 3.84 (6 H, ds, MeO), 4.28 (1 H, d, 3-CH, ^3J = 2.7), 4.63 (1 H, d, 2-CH). Anal. Found: C, 35.7; H, 4.6; N, 20.4. Calcd for $C_6H_9N_3O_5$: C, 35.5; H, 4.5; N, 20.7.

Diisopropyl (2*R*,3*S*)-2-hydroxy-3-azidosuccinate (13B): yield 60%; bp 114–115 °C (1 mm); $[\alpha]^{20}_D$ +7.2° (*c* 2.4, $CHCl_3$); ^{1}H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 1.30 (12 H, dd, Me, ^3J = 6.3), 3.23 (1 H, d, 3J = 3.2), 4.20 (1 H, d, 3-CH, 3J = 2.6), 4.54 (1 H, dd, 2-CH), 5.12 (2 H, m, CHO). Anal. Found: C, 46.5; H, 6.8; N, 16.1. Calcd for $C_{10}H_{17}N_3O_5$: C, 46.3; H, 6.6; N, 16.2.

Aziridinedicarboxylates 14A,B. A solution of azidoalcohol **13** (0.02 mol) in absolute MeCN (15 mL) was added dropwise to Ph_3P (5.5 g, 0.021 mol) in absolute MeCN (25 mL) with cooling (20 °C) and stirring.

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After 6 h at 20 °C, the solution was evaporated in vacuo, and the residue was then heated at 110–140 °C at 0.8 mm in a distillation apparatus (Kugelrohr). This gave the aziridinecarboxylate **14** as an oil. Purification by chromatography on silica ($CHCl_3$) gave an analytically pure sample.

(2*S*,3*S*)-2,3-Bis(methoxycarbonyl)aziridine (14A): yield 58%; $[\alpha]^{20}_D$ +134.0° (*c* 2.1, $CHCl_3$); ^1H NMR (400 MHz) in C_6D_6 (*J*, Hz) δ 1.60 (1 H, br m, NH), 2.66 (1 H, dd, CH_A, ^3J = 9.5, 2.2), 2.90 (1 H, dd, CH_B, ^3J = 8.5, 2.2), 3.14 and 3.20 (6 H, ds, MeO). Anal. Found: C, 45.1; H, 5.9; N, 8.7. Calcd for $C_6H_9NO_4$: C, 45.3; H, 5.7; N, 8.8.

(2*S*,3*S*)-2,3-Bis((isopropyloxy)carbonyl)aziridine (14B): yield 81%; $[\alpha]^{20}_D$ +115.0° (*c* 2.4, heptane); ^1H NMR (400 MHz) in toluene-d_8 (*J*, Hz) δ 0.90 and 0.92 (6 H, dd, Me, ^3J = 6.3), 0.96 (6 H, d, Me, ^3J = 6.3), 1.60 (1 H, br m, NH), 2.70 (1 H, dd, CH_A, ^3J = 9.6, 2.3), 2.94 (1 H, dd, CH_B, ^3J = 8.5, 2.3), 4.81 and 4.87 (2 H, dm, CHO). Anal. Found: C, 55.6; H, 8.1; N, 6.3. Calcd for $C_{10}H_{17}NO_4$: C, 55.8; H, 8.0; N, 6.5.

Diisopropyl Azidomaleate (15). A mixture of sulfite **12B** (2.8 g, 0.01 mol) and NaN_3 (1.3 g, 0.02 mol) in absolute DMF (20 mL) was stirred for 4 h at 120 °C and, after cooling (20 °C), was poured into ice water (50 mL). The product was extracted with ether (3 × 20 mL) and dried over $MgSO_4$. After removal of ether, the residue was purified by chromatography on silica ($CHCl_3$), giving azidomaleate **15** (1.23 g, 51%). ^1H NMR (400 MHz) in $CDCl_3$ (*J*, Hz): δ 1.23 and 1.29 (12 H, dd, Me, ^3J = 6.4), 5.0 and 5.10 (2 H, dm, CHO), 5.38 (1 H, s, CH). Anal. Found: C, 50.0; H, 6.4; N, 17.1. Calcd for $C_{10}H_{15}N_3O_4$: C, 49.8; H, 6.3; N, 17.4.

***N*-Chloroaziridinedicarboxylates 2a and 3a.** A solution of Bu^{t}OCl (0.163 g, 1.5 mmol) in CH_2Cl_2 (1 mL) was added dropwise to aziridinecarboxylate **14** (1.0 mmol) in CH_2Cl_2 (5 mL) with cooling (–70 °C). The resulting solution was evaporated in vacuo, and the product was extracted with pentane. After removal of pentane, *N*-chloroaziridine was obtained.

(2*S*,3*S*)-1-Chloro-2,3-bis(methoxycarbonyl)aziridine (2a): yield 96%; $[\alpha]^{20}_D$ –101.1° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) d 3.37 and 3.43 (2 H, dd, CH_ACH_B, ^3J = 4.9), 3.79 and 3.88 (6 H, ds, MeO).

(2*S*,3*S*)-1-Chloro-2,3-bis(isopropyloxycarbonyl)aziridine (3a): yield 98%; $[\alpha]^{20}_D$ –44.2° (*c* 2.1 MeOH); ^1H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 1.29 and 1.31 (6 H, dd, Me, ^3J = 6.4), 1.35 (6 H, d, Me, ^3J = 6.4), 3.31 and 3.36 (2 H, dd, CH_ACH_B, ^3J = 4.9), 5.05 and 5.15 (2 H, dm, CHO).

***N*-Bromoaziridinedicarboxylates 2b and 3b.** *N*-Bromosuccinimide (0.27 g, 1.5 mmol) was added to a solution of aziridinecarboxylate **14** (1.0 mmol) in CH_2Cl_2 (5 mL) with cooling and stirring. After 1 h at 20 °C, the solvent was evaporated in vacuo, and the product was extracted from the residue with pentane. After removal of pentane, *N*-bromoaziridine was obtained.

(2*S*,3*S*)-1-Bromo-2,3-bis(methoxycarbonyl)aziridine (2b): yield 80%; $[\alpha]^{20}_D$ –117.4° (*c* 4.5, $CHCl_3$); ^1H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 3.00 and 3.22 (2 H, dd, CH_ACH_B, ^3J = 4.4), 3.79 and 3.89 (6 H, ds, MeO).

(2*S*,3*S*)-1-Bromo-2,3-bis((isopropyloxy)carbonyl)aziridine (3b): yield 88%; $[\alpha]^{20}_D$ –56.4° (*c* 2.9, heptane); ^1H NMR (400 MHz) in $CDCl_3$ (*J*, Hz): δ 1.29, 1.31, 1.35, and 1.36 (12 H, qd, Me, ^3J = 6.4), 2.92 and 3.16 (2 H, dd, CH_ACH_B, ^3J = 4.3), 5.04 and 5.16 (2 H, dm, CHO).

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