Optically Active *cis*- and *trans*-1-Chloro-2-methoxycarbonyl-2-methylcarbamoylaziridines. Stereochemical Properties

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The synthesis of optically active *cis*- and *trans*-1-chloro-2-methoxycarbonyl-2-methylcarbamoylaziridines (**2**) is described and their relative stability determined by thermal equilibration. The crystal structure of (±)-*cis*-**2** was determined by X-ray diffraction analysis and compared with that of (−)-*trans*-**2**. The chiroptical properties and configurational correlations with the parent compound (+)-1-chloro-2,2-bismethoxycarbonylaziridine (**1**) are reported.

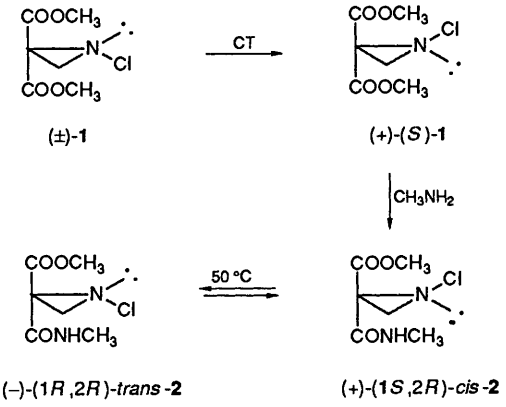
Suitably-functionalized aziridines, such as aziridine-2-carboxylates, play an important role in organic and bioorganic synthesis:[1] for instance, they may be used as key intermediates for the synthesis of amino acids[2] and β-lactam antibiotics.[3] Furthermore, besides the intrinsic high reactivity of the three-membered ring,[4] aziridine-2-carboxylates are also characterized by the presence of reactive ester groups on the ring carbon atom which make for easy transformations.

Recently, we resolved the racemic 1-chloro-2,2-bismethoxycarbonylaziridine (**1**) *via* the stereospecific and stereoselective enzymatic hydrolysis of the ester groups[5] and, more recently,[6] we assigned the absolute configuration at the chiral nitrogen atom of (+)-**1** by chemical correlation with that determined by X-ray diffraction analysis of the related compound, (−)-*trans*-1-chloro-2-methoxycarbonyl-2-methylcarbamoylaziridine (**2**).

In this paper we report experimental details of the synthesis of the isomeric optically pure compounds *cis*- and *trans*-1-chloro-2-methoxycarbonyl-2-methylcarbamoylaziridine (**2**) from the corresponding optically active aziridine (+)-**1**. The X-ray structure analyses of (±)-*cis*- and (−)-*trans*-**2** and the X-ray absolute configuration determination of crystalline (−)-*trans*-**2** afford an unambiguous picture of the transformation of (+)-**1** into (−)-*trans*-**2**. CD spectra of (+)-**1**, (+)-*cis*-**2** and (−)-*trans*-**2** indicate that the chiroptical properties of these compounds can be correlated with the assigned configurations.

Results and Discussion

Synthesis of Optically Pure (+)-cis-**2** *and* (−)-trans-**2**.—Optically pure epimers *cis*- and *trans*-1-chloro-2-methoxycarbonyl-2-methylcarbamoylaziridines (**2**) were synthesized according to Scheme 1. Optically active aziridine (+)-**1** was obtained in 50% enantiomeric excess (ee%) through the diastereospecific and enantioselective α-chymotrypsin (CT)-catalysed hydrolysis of the ester groups.[5] Despite a half-life for racemization of 32 h at 20 °C,[5] (+)-**1** can be quickly and stereospecifically amidated, *i.e.* it affords in nearly quantitative yield (80%) the corresponding 1-chloro-2,2-dicarboxyaziridine monomethylester monomethylamide (**2**) when treated with an excess of methylamine at −5 °C in dichloromethane solution. It is well known[4] that aziridines react differently towards nucleophilic reagents depending on the nature of the nitrogen atom substituents. So, it is worth comparing this result with others reported in the literature for aziridine-2-carboxylates: strong electron-accepting groups at the ring nitrogen atom cause direct ring opening when treated with heteroatomic nucleophiles (*e.g.* amines),[7] whereas 1-alkoxyaziridine-2-carboxylic or -2,2-dicarboxylic esters show stereospecific nucleophilic substitution at the ester group *trans* to the nitrogen-atom substituent.[8]



Scheme 1

The monomethylamide **2**, recovered from the amidation reaction as an optically active low melting solid (ee *ca.* 51%), appears in ^{1}H NMR spectroscopy as a single diastereoisomer. Crystallization of crude (+)-**2** from diethyl ether at −30 °C yields the racemic form as the main crystalline product and the enantiomerically enriched compound as the oily residue. Attempts to crystallize the (+)-**2** enantiomer failed. The ^{1}H NMR spectrum of this residue, recorded in the presence of (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluoroethanol, indicates that its enantiomeric purity is not less than 90%. The X-ray structure analysis of crystalline racemic **2** enables us to assign the *cis* relative configuration, showing that the amidation reaction occurs at the ester group *trans* to the substituent on the ring nitrogen atom.

When heated at 50 °C for 5 h, the tetrachloromethane solution of (+)-*cis*-**2** reveals the presence in the ^{1}H NMR spectrum of both the invertomers at the aziridine-ring nitrogen atom. The resultant *trans* epimer (*cis*/*trans* ratio 4:1) is a solid which is less soluble than the *cis*-isomer in tetrachloromethane; it was therefore possible to obtain the *trans* isomer through the asymmetric transformation induced by crystallization.[9] A further purification by crystallization from dichloromethane/hexane afforded the diastereoisomerically and enantiomerically pure (−)-*trans* epimer. X-Ray diffraction analysis[6] afforded the (1*R*,2*R*) absolute configuration of this compound.

Crystal Structure of (±)-cis-**2**.—The crystal structure of (±)-*cis*-**2**, Fig. 1,[10] is made up of racemic pairs of discrete molecules with (1*S*,2*R*) and (1*R*,2*S*) configurations at the chiral N(1) and C(2) atoms.

Final atomic co-ordinates are given in Table 1. Bond distances and bond angles are reported in Table 2, which contains, for the sake of easier comparison, the corresponding values found for the (−)-*trans*-**2** form.[6] There are no significant differences between the corresponding bond distances of (±)-

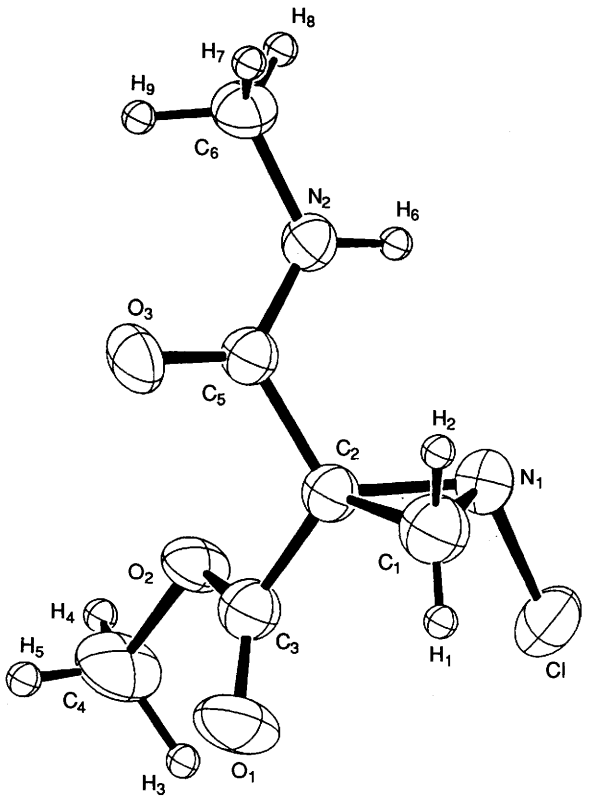


Fig. 1 ORTEP[11] drawing of (±)-*cis*-**2** with atom numbering scheme. Thermal ellipsoids for non-H atoms enclose 40% probability.

Table 1 Final non-hydrogen atom fractional co-ordinates for the (±)-*cis*-1-chloro-2-methoxycarbonyl-2-methylcarbamoylaziridine

Atom	*x*	*y*	*z*
Cl	0.531 4(2)	0.017 6(1)	0.122 54(9)
N(1)	0.377 2(4)	0.049 6(3)	0.184 4(2)
C(1)	0.230 9(6)	−0.013 1(4)	0.165 8(3)
C(2)	0.240 9(5)	0.106 7(4)	0.146 8(2)
C(3)	0.257 7(5)	0.139 1(4)	0.065 4(3)
O(1)	0.227 8(5)	0.080 4(3)	0.013 9(2)
O(2)	0.311 7(4)	0.242 9(2)	0.061 3(2)
C(4)	0.341 2(8)	0.286 4(5)	−0.014 0(3)
C(5)	0.150 9(5)	0.190 7(3)	0.193 2(3)
O(3)	0.019 9(3)	0.218 4(3)	0.171 9(2)
N(2)	0.218 7(4)	0.226 9(3)	0.255 2(2)
C(6)	0.140 2(5)	0.303 1(4)	0.305 8(3)

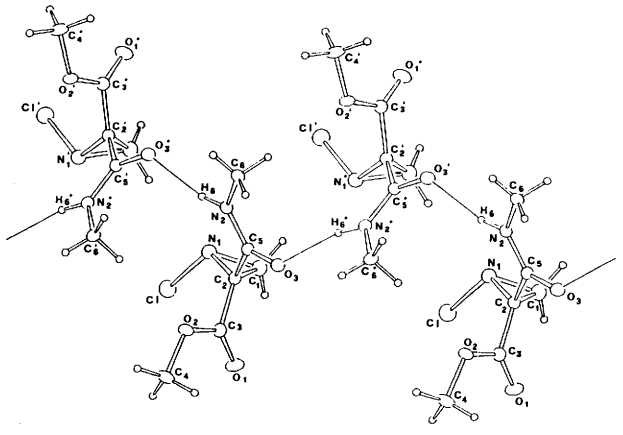


Fig. 2 Molecular packing in (±)-*cis*-**2**

cis-**2** and (−)-*trans*-**2**, which compare well with those previously observed in other *N*-substituted chloroaziridines.[11] The only

Table 2 Bond distances (Å) and bond angles (°) involving non-hydrogen atoms

	(±)-*cis*-**2**	(−)-*trans*-**2**
C(1)–N(1)	1.753(4)	1.758(2)
N(1)–C(1)	1.485(6)	1.472(3)
N(1)–C(2)	1.499(6)	1.508(2)
C(1)–C(2)	1.478(7)	1.486(3)
C(2)–C(3)	1.514(7)	1.512(3)
C(3)–O(1)	1.186(6)	1.190(2)
C(3)–O(2)	1.327(5)	1.334(2)
O(2)–C(4)	1.464(6)	1.448(3)
C(2)–C(5)	1.510(6)	1.513(3)
C(5)–N(2)	1.322(6)	1.320(3)
C(5)–O(3)	1.218(5)	1.215(2)
N(2)–C(6)	1.447(6)	1.450(3)
Cl–N(1)–C(1)	111.6(3)	112.6(1)
Cl–N(1)–C(2)	112.9(3)	112.2(1)
C(1)–N(1)–C(2)	59.4(3)	59.8(1)
N(1)–C(1)–C(2)	60.8(3)	61.3(1)
N(1)–C(2)–C(1)	59.9(3)	58.9(1)
N(1)–C(2)–C(3)	118.4(4)	110.7(2)
N(1)–C(2)–C(5)	116.5(4)	119.5(2)
C(1)–C(2)–C(3)	118.5(4)	116.3(2)
C(1)–C(2)–C(5)	119.5(4)	117.8(2)
C(3)–C(2)–C(5)	113.8(4)	119.3(2)
C(2)–C(3)–O(1)	125.0(4)	124.1(2)
C(2)–C(3)–O(2)	109.0(4)	110.8(2)
O(1)–C(3)–O(2)	125.9(5)	125.1(2)
C(3)–O(2)–C(4)	116.3(4)	115.2(2)
C(2)–C(5)–O(3)	118.0(4)	120.8(2)
C(2)–C(5)–N(2)	117.5(4)	115.5(2)
O(3)–C(5)–N(2)	124.5(4)	123.7(2)
C(5)–N(2)–C(6)	122.2(4)	122.8(2)

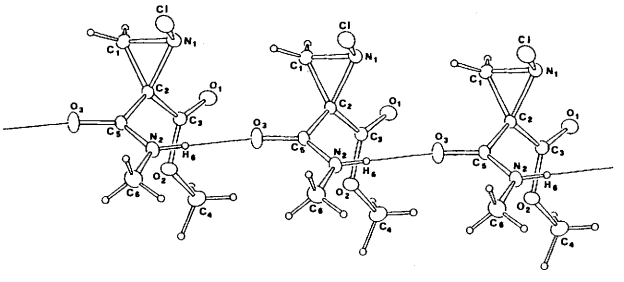


Fig. 3 Molecular packing in (−)-*trans*-**2**

point of note is the lengthening of the C(1)–N(1) bonds with respect to the mean value of 1.474(3) retrieved from the Cambridge Crystallographic Database for saturated C_2N rings.[12] A significant difference exists between the N(1)–C(2)–C(3) bond angles of the two isomers [118.4(4)° in (±)-*cis*-**2** and 110.7(2)° in (−)-*trans*-**2**]. This appears to be due to a strong intramolecular interaction between the chlorine and the carbon of the carbonyl group *cis* to the Cl atom [Cl • • • C(3) = 2.920(5) Å]. Also the Cl–N–C valence angles [from 111.6(3) to 112.9(3)°] are in both cases significantly smaller than the mean value of 119.3(6)° averaged over many other *N*-substituted aziridines.[12] As a consequence, the angles between the ring plane and the *N*-substituent bond [64.2° in (±)-*cis*-**2**, and 63.9° in (−)-*trans*-**2**] are larger than the mean reported value of 55.5(5)°.[12] As expected, the ring nitrogen atom is acutely pyramidal, and lies 0.789 Å in (±)-*cis*-**2**, and 0.785 Å in (−)-*trans*-**2** out of the plane defined by the three atoms bonded to it. The ester and amide units of (±)-*cis*-**2** are planar within ±0.009 Å, and are at dihedral angles of 64° and 63.6°, respectively, to the aziridine ring plane, and 82.5° to each other.

Their orientations appear to be determined by intermolecular crystal-packing requirements. The major contributor to the molecular packing of (±)-*cis*-**2** (Fig. 2) is one hydrogen bond

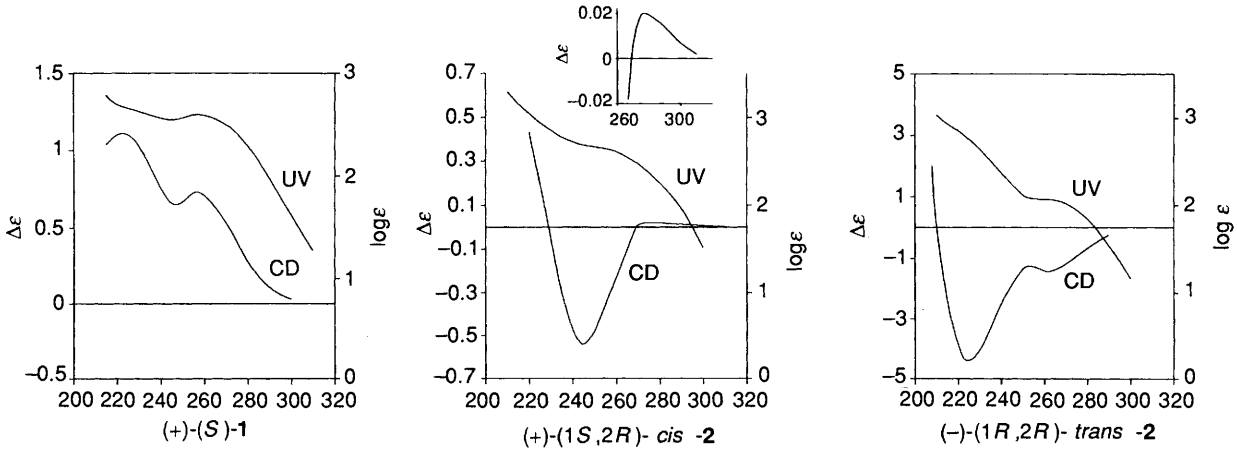


Fig. 4 UV and CD spectra of (+)-(*S*)-1-chloro-2,2-bismethoxycarbonylaziridine, (+)-(1*S*,2*R*)-*cis*- and (−)-(1*R*,2*R*)-*trans*-1-chloro-2-methoxycarbonyl-2-methylcarbamoyl aziridines in isooctane solution

Table 3 Chiroptical properties and UV absorptions of aziridines (+)-(*S*)-**1**, (+)-(1*S*,2*R*)-*cis*-**2** and (−)-(1*R*,2*R*)-*trans*-**2** in isooctane solution

Aziridine	UV and CD maxima: nm (log ε or Δε)		
(+)-(*S*)-**1**	UV	257 (2.60)	220 (2.70)[a]
	CD	255 (+0.73)	220 (+1.1)
(+)-(1*S*,2*R*)-*cis*-**2**	UV	250 (2.66)[b]	
	CD	278 (+0.02)	244 (−0.54)
(−)-(1*R*,2*R*)-*trans*-**2**	UV	262 (2.07)[b]	220 (2.85)[a]
	CD	264 (−1.43)	223 (−4.35)

[a] Inflexion point. [b] Shoulder.

involving the amidic functions of racemic pairs, which are thus arrayed in linear chains [N···O = 2.863(5) Å, ∠N–H···O = 156°]. A few (7) short van der Waals contracts [from 3.204(6) to 3.528(6) Å], involving mainly oxygen atoms, were found to be present. In (−)-*trans*-**2** as well, the molecules are arrayed in linear chains by one hydrogen bonding interaction involving the amidic function (Fig. 3). But, in this case, the packing of molecules with the same chirality favours shorter [N···O = 2.792(2) Å] and more linear [∠N–H···O = 165(2)°] hydrogen bonding contacts. Furthermore, the molecular packing is characterized by more (17 less than 3.6 Å), and stronger van der Waals interactions (there are three contacts shorter than 3.10 Å). This can explain the relevant difference in calculated density [1.411 and 1.460 g cm^{-3} for (±)-*cis*-**2** and (−)-*trans*-**2**, respectively], and, perhaps, the fast intensity decay observed during X-ray data collection for the racemic compound.

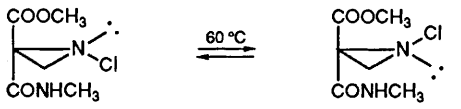
Absolute Configuration of Aziridines (+)-**1** *and* (+)-cis-**2**.—The knowledge of the absolute configuration of (−)-*trans*-**2** enabled us to assign the absolute configuration to (+)-**1** and (+)-*cis*-**2** through the chemical correlations of Scheme 1.[6] In particular, the amidation reaction of (+)-**1** affording (+)-*cis*-**2** does not involve the nitrogen chiral centre, so compounds (+)-**1** and (+)-*cis*-**2** must have the same configuration at the nitrogen atom. On the other hand, thermal epimerization of (+)-*cis*-**2** into (−)-*trans*-**2** involves nitrogen inversion. Since X-ray analysis established the (1*R*,2*R*) absolute configuration of (−)-*trans*-**2**, we were able to infer the (1*S*,2*R*) absolute configuration for (+)-*cis*-**2** and, consequently, the (*S*) configuration at the chiral nitrogen atom of (+)-**1**.

Chiroptical Properties of Aziridines (+)-**1**, (+)-cis-**2** *and* (−)-trans-**2**.—The absorption (UV) and circular dichroism (CD) spectra of the aziridines (+)-**1**, (+)-*cis*-**2** and (−)-*trans*-**2** were recorded in isooctane solution. The corresponding UV and CD data are depicted in Fig. 4 and summarized in Table 3.

For the two isomers (+)-*cis*-**2** and (−)-*trans*-**2**, a significant difference is observed in the form and position of UV and CD spectral bands. The circular dichroism spectrum of (−)-(1*R*,2*R*)-*trans*-**2** reveals the presence of two negative Cotton effects (CE), at 264 nm and 220 nm respectively, corresponding to weak absorptions in the UV spectrum. The (+)-(1*S*,2*R*)-*cis*-**2** derivative shows a very weak positive CE at 278 nm and a negative one at 244 nm, not corresponding to absorption maxima. The UV spectrum shows only a maximum at 250 nm. For compound (+)-**1**, two positive CE, corresponding to weak UV absorptions at 255 nm and 220 nm, are observed.

In the light of theoretical and experimental studies[13] of the chiroptical properties of the N–X chromophore in *N*-halogen-substituted aziridines, we were able to assign the CE observed at the longer wavelength (250–280 nm) to the lowest N–X electronic transition π^*_{NCl}–σ^*_{NCl} and the CE at the shorter wavelength (220 nm) to the methoxycarbonyl and/or the carbamoyl group transitions. Although the dichroic absorbances of the methoxycarbonyl group could overlap the N–Cl transition, as reported for *N*-chloro-2-methoxycarbonylaziridine,[13] the CD behaviour of the spectra in Fig. 4 clearly shows that the sign of the CE of the long-wavelength band is governed by the chirality of the nitrogen atom, *i.e.* it changes sign upon inversion of the configuration at the halogenated nitrogen atom. We observed a negative CE at 264 nm for the aziridine (−)-*trans*-**2** having the *R* configuration at the chiral nitrogen atom and a positive CE at 278 nm and 255 nm, respectively, for aziridines (+)-*cis*-**2** and (+)-**1**, whose *S* configuration at the ring-nitrogen atom has been assigned as described above. These results agree, and further confirm the configurational correlation carried out through the chemical transformations depicted in Scheme 1.

Thermal Epimerization.—In order to study the relative stabilities of the *cis* and *trans* isomers of **2**, their standard free energy difference ($\Delta G°$) was determined by thermal equilibration. Thermal isomerizations of both (+)-*cis*-**2** and (−)-*trans*-**2** were conducted in benzene solution at 60 °C and followed by polarimetry. The equilibrium *cis*/*trans* ratio was determined from ^{1}H NMR spectra of the equilibrated solutions. The results are reported in Scheme 2. No evidence for the decompositon of compounds *trans*- and *cis*-**2** during the kinetic experiments was found by ^{1}H NMR spectroscopy. This result suggests that the



(−)-*trans*-**2** 13% (+)-*cis*-**2** 87%

Scheme 2 Thermal epimerization data for aziridines (−)-*trans*-**2** and (+)-*cis*-**2** at 333.15 K: % *cis* at equilibrium, 87; K_{eq} 6.7 ± 0.01; $\Delta G°$ 1.26 kcal mol^{-1};* k (8.34 ± 0.08) 10^{-4} s^{-1}; k' (1.24 ± 0.01) 10^{-4} s^{-1}; $\Delta G^{\ddagger}_{tc}$ 24.26 kcal mol^{-1}; $\Delta G^{\ddagger}_{ct}$ 25.52 kcal mol^{-1}

isomerization does not involve any measurable degree of bond cleavage, but only a nitrogen inversion mechanism. The slow change of *cis*-**2** compared with the rapid isomerization of *trans*-**2** and the very high *cis*/*trans* ratio at equilibrium prove the superior stability of the *cis* isomer.

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ on a VARIAN XL-200 spectrometer. Chemical shifts are reported as δ values from tetramethylsilane (TMS) as internal standard (s singlet, d doublet, br broad signal). Coupling constant values are given in Hz. Optical rotations were measured on a Perkin-Elmer 241 polarimeter in $CHCl_3$ solution and are in 10^{-1} deg cm^2 g^{-1}. All enantiomeric purities (ee. %) were determined by ^{1}H NMR spectra recorded in the presence of the chiral solvating agent (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluoroethanol. Accuracy was within ±2%. CD and UV measurements were carried out in isooctane solution on a Jobin-Yvon Mark IV spectropolarimeter and a Perkin-Elmer Lambda 15 spectrophotometer, respectively. Mass spectra were determined on a Hewlett-Packard 5970 mass selective detector. GLC analyses were performed on a Hewlett-Packard 5890 A gas chromatograph (capillary column DB-1, 5 μm, 30 m × 0.53 mm I.D.). Elemental analyses were performed with a Carlo Erba Elemental Analyser model 1106. Melting points are uncorrected.

(*R*)-(−)-1-(9-anthryl)-2,2,2-trifluoroethanol, $[\alpha]_D^{25}$ −29 ($CHCl_3$), was purchased from Ega-Chemie and used without additional purification. α-Chymotrypsin was purchased from Fluka and used without additional purification.

Racemic 1-chloro-2,2-bismethoxycarbonylaziridine (**1**) was synthesized as described elsewhere.[5]

Enzymatic Hydrolysis of (±)-1-*Chloro*-2,2-*bismethoxycarbonylaziridine* (**1**) *with* α-*Chymotrypsin*.—(±)-**1** (4 g, 0.02 mol) was added to 180 cm^3 of 0.1 mol dm^{-3} potassium phosphate buffer (containing NaCl 0.1 mol dm^{-3}), pH 7.5, and treated with α-chymotrypsin (1 g) under vigorous stirring at room temperature. Ester hydrolysis was followed by GLC and TLC. After 5 h (approximately 50% conversion) the reaction mixture was extracted with dichloromethane and the organic extract was washed with water and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (silica gel, 50:50 light petroleum–diethyl ether as eluent) to obtain the unreacted ester as a thick oil (1.83 g, 46%) $[\alpha]_D^{20}$ +53.7 (*c* 0.43).

Fractional crystallization of partially optically active **1** at −20 °C from diethyl ether/pentane afforded the racemic derivative **1** as the main crystalline product, m.p. 52–53 °C. The oily residue to the last crystallization had $[\alpha]_D^{20}$ +109.1 (*c* 0.65) ee ≥ 98%. Both racemic and optically active **1** exhibit the following properties: δ_H 2.85 (1 H, d, *J* 2.9), 3.0 (1 H, d), 3.82 (3 H, s), 3.91 (3 H, s); *m*/*z* 193 (M^+).

(+)-cis-1-*Chloro*-2-*methoxycarbonyl*-2-*methylcarbamoylaziridine* (**2**).—To a stirred solution of crude (+)-**1** ee 50% (1.93 g, 0.01 mol) in dichloromethane (20 cm^3) cooled to −5 °C, methylamine (3 g, 0.1 mol) was rapidly added. After 15 min the reaction mixture was concentrated *in vacuo* and the residue purified by SiO_2 column chromatography (50:50 dichloromethane–diethyl ether as eluent) to yield 1.5 g (78%) $[\alpha]_D^{20}$ +59.5 (*c* 1.5). The crystallization of (+)-*cis*-**2** from diethyl ether at −30 °C afforded the racemic derivative *cis*-**2** as the main crystalline product, m.p. 44–45 °C. The oily residue of the last crystallization had $[\alpha]_D^{20}$ +103.9 (*c* 0.6) ee ≥ 90%. Both racemic and optically-active *cis*-**2** exhibit the following properties [Found: C, 37.75; N, 14.15; H, 4.75%; (M^+ − Cl, 157). $C_6H_9N_2O_3Cl$ requires C, 37.41; N, 14.55; H, 4.71%; *M*, 192]; δ_H 2.76 (1 H, d, *J* 3.04), 2.84 (3 H, d, *J* 5.03, NMe), 3.06 (1 H, d), 3.9 (3 H, s, COOMe), 6.52 (1 H, br, NH).

(−)-trans-1-*Chloro*-2-*methoxycarbonyl*-2-*methylcarbamoylaziridine* (**2**).—A solution of optically pure (+)-*cis*-**2** (1 g) in tetrachloromethane (5 cm^3) was heated in a sealed tube at 60 °C. After 5 h the mixture was cooled at −20 °C and the solid, the less soluble *trans* epimer (0.32 g) removed by filtration. Crystallization from dichloromethane/hexane afforded the diastereoisomerically and enantiomerically pure *trans*-**2** isomer m.p. 125–126 °C [Found: C, 37.35; N, 14.35; H, 4.7%; (M^+ − Cl, 157). $C_6H_9N_2O_3Cl$ requires C, 37.41; N, 14.55; H, 4.71%; *M*, 192]; $[\alpha]_D^{20}$ −92.6 (*c* 0.28); δ_H 2.99 (3 H, d, *J* 4.9, NMe), 3.05 (1 H, d, *J* 2.5), 3.27 (1 H, d), 3.8 (3 H, s, COOMe), 7.75 (1 H, br, NH).

Thermal Epimerization.—Thermal equilibration of (+)-*cis*-**2** and (−)-*trans*-**2** was monitored in a thermostatically-controlled polarimeter cell (±0.1 K). On completion of the readings, the solutions were rechecked for decomposition by TLC and ^{1}H NMR spectroscopy. The rate of epimerization and the equilibrium constant K_{eq} were determined by polarimetry and ^{1}H NMR spectroscopy. At 60 °C the kinetic data fit eqn. (1),

$$(\alpha_t - \alpha_\infty) = (\alpha_0 - \alpha_\infty)\exp(-kt) \quad (1)$$

where α_0 is the rotation at time 0, α_∞ the rotation at equilibrium and α_t the rotation at time *t*. The standard free energy difference was calculated from the relationship $\Delta G^0 = -RT \ln K_{eq}$. The barrier to pyramidal inversion was determined from eqn. (2),

$$k = (KT/h)\exp(-\Delta G^{\ddagger}/RT) \quad (2)$$

where *k* is the rate constant of epimerization, *K* is the Boltzmann constant and *h* the Planck constant.

Crystal Data.—$C_6H_9ClN_2O_3$, *M* = 192.602, orthorhombic, *a* = 8.457(2), *b* = 11.985(3), *c* = 17.884(3) Å, *V* = 1812.7(7) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group *P bca* (no. 61), *Z* = 8, D_m = 1.40 g cm^{-3}, D_c = 1.411 g cm^{-3}, *F*(000) = 800, colourless, air stable prisms. Crystal dimensions 0.40 × 0.30 × 0.30 mm, μ(Mo-Kα) = 3.4 cm^{-1}.

Data Collection and Processing.—Enraf-Nonius CAD4 diffractometer, ω/2θ mode with ω scan width = 0.60 + 0.35 tan θ, ω scan speed 1.27–8.24° min^{-1}, graphite-monochromated Mo-Kα radiation; 1975 unique reflections measured ($1.5 \leq \theta \leq 27°$, $+h$, $+k$, $+l$) giving 797 with $I > 2\sigma(I)$ used, without absorption correction, in the structure analysis. Linear and approximate isotropic crystal decay (46.1% during 12.3 h of exposure time) corrected during processing.

* 1 cal = 4.184 J.

Structure Analysis and Refinement.—Direct methods (SHELX 86)[14] followed by full-matrix least-squares refinement (SHELX 76).[15] Cl, O, N, and methyl C atoms anisotropic, other C atoms isotropic; H atoms, located in ΔF maps, refined isotropically through some least-squares cycles, and then held fixed (because of the low reflection/parameter ratio).

The weighting scheme $w = 1.17/[\sigma^2(F_o) + 0.000\,71F_o^2]$ gave satisfactory agreement analyses. Final R and R_W values are 0.050 and 0.053. Scattering factors from SHELX 76.[15] Major calculations were carried out on a VAX 6310 computer. Full lists of thermal parameters, bond lengths and angles involving H atoms, least-squares planes, torsion angles, hydrogen atom coordinates and shortest intermolecular distances have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1.

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