Relationships between Solid-state Structures of Enantiomers and the Corresponding Racemic Compounds in Small Ring Derivatives. Comparison of Crystal Structures and Solid-state Properties of (*R*)-(−)- and Racemic 1-Chloro-2,2-diphenylaziridine. Solvent Effect on the Racemization of (*R*)-(−)-1-Chloro-2,2-diphenylaziridine

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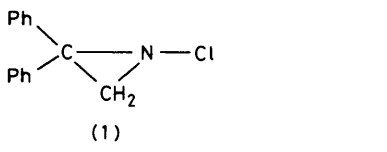
The synthesis of highly optically pure *N*-chloro-2,2-diphenylaziridine, in a crystalline form and sufficiently stable at room temperature, has enabled the study and the comparison to be carried out of the solid-state properties (*e.g.*, the m.p. phase diagram, the crystal and molecular structures, and the i.r. spectra) of the enantiomer and racemic species of this small ring derivative. The solvent effect on the racemization of the optically active *N*-chloro-2,2-diphenylaziridine is relatively small, and this is attributed to the low basicity of the nitrogen atom of the *N*-chloroaziridine ring.

There are several reports in the literature which indicate that fractional crystallization of partially optically pure three-membered heterocycles containing a chiral nitrogen atom, such as *N*-alkyloxaziridines,[1] *N*-sulphonyloxaziridines,[2] *N*-alkoxyaziridines,[3] and *N*-chloroaziridines,[4] allows the separation of highly optically pure crystals from the corresponding solid racemates. This behaviour prompted us to undertake a programme devoted to a study of the relationships between the solid-state structures and the properties of the enantiomeric and corresponding racemic forms of three-membered-ring compounds.

We now report the m.p. phase diagram, the crystal and molecular structures, and the i.r. spectra of solid (*R*)-(−)- and racemic 1-chloro-2,2-diphenylaziridine (1). Crystals of optically active (1), $[\alpha]_D^{20}$ −304.7° ($CHCl_3$), were obtained by fractional crystallization from pentane of a sample of (1) with $[\alpha]_D$ −67.9° ($CHCl_3$), which was itself synthesized by chlorination of 2,2-diphenylaziridine with t-butyl hypochlorite at −60 °C, in the presence of (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol, as previously reported.[4] The ^1H n.m.r. spectrum of this enantiomerically enriched *N*-chloroaziridine (1), recorded in the presence of the chiral shift reagent (+)-Eu(hfc)$_3$,† suggests that its enantiomeric purity is not less than 94%. The (*R*) absolute configuration at the asymmetric nitrogen atom of (−)-(1) was assigned by means of *X*-ray crystallographic studies.[4] The solvent effect on the rate of racemization of (*R*)-(−)-(1) is also reported.



(1)

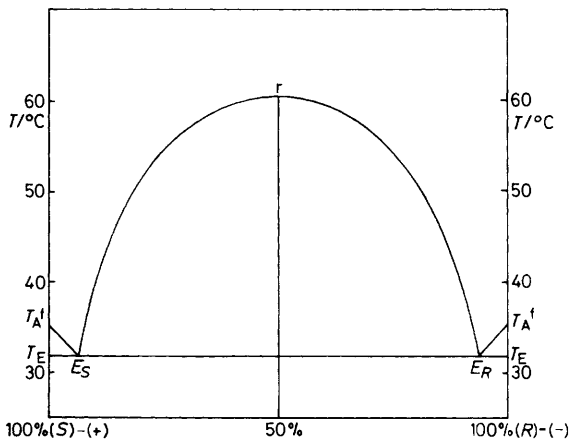


Figure 1. Melting point phase diagram of 1-chloro-2,2-diphenylaziridine (1)

Results and Discussion

Phase Diagram.—Melting points and enthalpies of fusion of (*R*)- and racemic (1) were determined by calorimetry, and used to calculate the melting point phase diagram of (1) shown in Figure 1. The m.p. of the eutectic mixture (T_E) was also verified experimentally by using a partially optically active sample of (1). Attempts to obtain other experimental points of the diagram by using derivatives of (1) of known enantiomeric composition were hindered by the concomitant racemization of the samples used.

The E_Rr–$T_A^f E_R$ parts of the curve were calculated by using the Prigogine–Defay and Schröder–Van Laar equations (1) and (2), respectively,[5a] where x is the mole fraction of one

$$\ln 4x(1 - x) = 2\,\Delta H_r^f/R(1/T_r^f - 1/T^f) \quad (1)$$

$$\ln x = \Delta H_A^f/R(1/T_A^f - 1/T^f) \quad (2)$$

of the enantiomers in the mixture whose m.p. is T^f; ΔH_A^f (3.7 kcal mol^{-1}) ‡ and ΔH_r^f (5.1 kcal mol^{-1}) are the enthalpies of fusion of the (*R*) and racemic form of (1), respectively; T_A^f (308.5 K) and T_r^f (333.7 K) are the corresponding melting points, and R is the gas constant (1.986 9 cal mol^{-1} K^{-1}).

† hfc = tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato].

‡ 1 cal = 4.184 J.

Table 1. Fractional co-ordinates ($\times 10^4$ for non-hydrogen and $\times 10^3$ for hydrogen atoms) of the four independent molecules A, B, C, and D of optically active (*R*)-(−)-1-chloro-2,2-diphenylaziridine (structure I in the text, see Figure 2)

	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Cl	9 536(2)	11 118(4)	5 613(3)	231(2)	6 154(4)	8 784(3)
N	9 548(4)	9 145(10)	5 611(8)	195(4)	4 158(10)	8 724(8)
C(1)	9 935(5)	8 646(19)	6 678(11)	−18(6)	3 725(17)	7 588(9)
C(2)	9 211(4)	8 501(12)	6 390(7)	693(5)	3 551(11)	8 266(7)
C(3)	8 843(4)	9 481(9)	6 853(5)	1 206(4)	4 500(9)	8 078(5)
C(4)	9 105(4)	9 871(9)	7 901(5)	1 174(4)	4 991(9)	7 084(5)
C(5)	8 747(4)	10 781(9)	8 362(5)	1 672(4)	5 894(9)	6 952(5)
C(6)	8 126(4)	11 302(9)	7 774(5)	2 203(4)	6 307(9)	7 813(5)
C(7)	7 863(4)	10 913(9)	6 726(5)	2 235(4)	5 817(9)	8 806(5)
C(8)	8 222(4)	10 002(9)	6 265(5)	1 737(4)	4 913(9)	8 939(5)
C(9)	8 890(4)	7 024(9)	5 964(6)	938(3)	2 030(8)	8 699(5)
C(10)	8 930(4)	6 392(9)	5 044(6)	767(3)	1 413(8)	9 525(5)
C(11)	8 651(4)	4 997(9)	4 727(6)	987(3)	−7(8)	9 888(5)
C(12)	8 334(4)	4 236(9)	5 331(6)	1 380(3)	−810(8)	9 425(5)
C(13)	8 294(4)	4 869(9)	6 251(6)	1 551(3)	−193(8)	8 600(5)
C(14)	8 572(4)	6 263(9)	6 567(6)	1 330(3)	1 226(8)	8 237(5)
H(1C1)	1 005(7)	787(18)	659(10)	−34(7)	265(20)	795(11)
H(2C1)	1 020(7)	793(17)	714(10)	−6(7)	459(18)	663(10)

	Molecule C			Molecule D		
	x	*y*	*z*	*x*	*y*	*z*
Cl	5 261(1)	7 353(3)	6 528(2)	4 485(2)	2 530(3)	8 990(2)
N	5 234(4)	9 305(10)	6 561(7)	4 531(4)	4 458(10)	9 007(6)
C(1)	5 073(5)	9 804(15)	7 519(11)	4 984(5)	5 003(16)	8 421(9)
C(2)	5 771(5)	9 948(11)	7 452(7)	4 250(4)	5 188(11)	7 905(7)
C(3)	6 297(4)	8 994(9)	8 113(6)	3 909(3)	4 188(9)	7 014(6)
C(4)	6 306(4)	8 493(9)	9 093(6)	4 203(3)	3 735(9)	6 278(6)
C(5)	6 821(4)	7 595(9)	9 682(6)	3 855(3)	2 835(9)	5 445(6)
C(6)	7 329(4)	7 198(9)	9 291(6)	3 213(3)	2 388(9)	5 349(6)
C(7)	7 321(4)	7 699(9)	8 310(6)	2 919(3)	2 841(9)	6 084(6)
C(8)	6 805(4)	8 597(9)	7 722(6)	3 267(3)	3 741(9)	6 917(6)
C(9)	5 993(4)	11 456(8)	7 218(4)	3 946(3)	6 654(8)	7 934(4)
C(10)	5 835(4)	11 961(8)	6 193(4)	3 977(3)	7 333(8)	8 875(4)
C(11)	6 045(4)	13 363(8)	5 987(4)	3 712(3)	8 752(8)	8 878(4)
C(12)	6 412(4)	14 261(8)	6 806(4)	3 417(3)	9 491(8)	7 939(4)
C(13)	6 570(4)	13 757(8)	7 831(4)	3 386(3)	8 812(8)	6 998(4)
C(14)	6 361(4)	12 354(8)	8 037(4)	3 651(3)	7 393(8)	6 995(4)
H(1C1)	504(6)	421(16)	1 139(10)	508(5)	416(14)	794(8)
H(2C1)	521(6)	616(17)	1 277(10)	521(5)	603(15)	852(8)

As shown in Figure 1, the phase diagram of 1-chloro-2,2-diphenylaziridine is relevant to enantiomeric mixtures showing the formation of racemic compounds. Moreover, the m.p. of the racemate is 25 °C higher than the m.p. of the (*R*)-enantiomer, and the eutectic points are very close to the edges of the diagram.

Crystal Structures.—A comparison of the crystal structures of (*R*)-(−)- and racemic (1) shows two points of interest. The first is the greater number of crystallographically independent molecules in (*R*)-(1), which may indicate, together with a significant difference in density [1.238 g cm^{-3} for the enantiomer and 1.289 g cm^{-3} for the racemate form of (1)], that it is more difficult for molecules of the same chirality to pack together. The second point is that, contrary to what is frequently found in these systems,[5b] in this case no obvious relationship exists between the molecular packing of the enantiomer and that of the racemic compound. In fact, molecules of the same chirality face each other, within the crystal, in a quite different way in the optically active and in the racemic derivative of (1).

Molecular Geometry.—Final positional parameters are

Table 2. Fractional co-ordinates ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogens) of racemic 1-chloro-2,2-diphenylaziridine (structure II in the text, see Figure 3)

	x	*y*	*z*
Cl	2 104(1)	1 033(1)	3 626(1)
N	4 007(4)	985(3)	3 519(3)
C(1)	4 144(6)	1 172(4)	2 324(4)
C(2)	4 567(4)	2 146(3)	3 157(3)
C(3)	3 599(3)	3 235(2)	3 073(2)
C(4)	2 745(3)	3 657(2)	2 016(2)
C(5)	1 859(3)	4 672(2)	1 974(2)
C(6)	1 828(3)	5 266(2)	2 989(2)
C(7)	2 682(3)	4 844(2)	4 046(2)
C(8)	3 568(3)	3 828(2)	4 088(2)
C(9)	6 234(3)	2 355(2)	3 708(2)
C(10)	6 946(3)	1 845(2)	4 763(2)
C(11)	8 488(3)	2 066(2)	5 256(2)
C(12)	9 316(3)	2 797(2)	4 694(2)
C(13)	8 604(3)	3 307(2)	3 639(2)
C(14)	7 062(3)	3 086(2)	3 145(2)
H(1C1)	315(5)	123(4)	180(3)
H(2C1)	493(5)	67(4)	209(3)

Table 3. Bond lengths and angles and some selected torsion angles for structure (I). E.s.d.s are in parentheses. Phenyl rings have standard geometrical features

	Bond distance/Å			
	Mol. A	Mol. B	Mol. C	Mol. D
Cl–N	1.77(1)	1.80(1)	1.76(1)	1.73(1)
N–C(1)	1.49(2)	1.51(2)	1.51(2)	1.51(2)
N–C(2)	1.56(2)	1.49(2)	1.49(1)	1.56(1)
C(1)–C(2)	1.48(1)	1.51(1)	1.53(2)	1.51(1)
C(2)–C(3)	1.45(1)	1.47(1)	1.47(1)	1.50(1)
C(2)–C(9)	1.52(1)	1.51(1)	1.50(1)	1.47(1)
	Bond angle/°			
	Mol. A	Mol. B	Mol. C	Mol. D
Cl–N–C(2)	111.1(7)	111.0(7)	112.6(6)	113.8(6)
Cl–N–C(1)	107.6(8)	107.3(7)	109.6(7)	111.1(7)
C(1)–N–C(2)	57.8(7)	60.6(8)	61.2(7)	58.8(6)
N–C(1)–C(2)	63.6(8)	59.1(7)	58.8(7)	62.2(7)
N–C(2)–C(1)	58.6(7)	60.3(8)	59.9(7)	58.9(6)
C(1)–C(2)–C(9)	119.1(10)	119.1(9)	117.9(9)	119.2(8)
C(1)–C(2)–C(3)	119.9(9)	119.6(9)	119.2(9)	118.5(8)
N–C(2)–C(9)	108.5(7)	112.0(8)	113.1(7)	113.0(7)
N–C(2)–C(3)	119.7(8)	121.8(8)	120.7(8)	117.3(7)
C(3)–C(2)–C(9)	116.9(8)	113.8(8)	115.0(8)	116.8(7)
C(2)–C(3)–C(8)	120.4(7)	120.0(7)	117.1(7)	117.6(7)
C(2)–C(3)–C(4)	119.5(7)	122.4(7)	122.9(8)	122.4(7)
C(2)–C(9)–C(10)	123.1(8)	120.0(6)	120.6(7)	121.4(6)
C(2)–C(9)–C(14)	116.8(7)	118.5(6)	119.4(6)	118.6(6)
	Torsion angle/°			
	Mol. A	Mol. B	Mol. C	Mol. D
C(1)–C(2)–C(9)–C(10)	−62(1)	−75(1)	−84(1)	−61(1)
N–C(2)–C(9)–C(10)	2(1)	−8(1)	−17(1)	6(1)
C(1)–C(2)–C(9)–C(14)	115(1)	104(1)	97(1)	117(1)
N–C(2)–C(9)–C(14)	179(1)	171(1)	164(1)	183(1)
C(1)–C(2)–C(3)–C(4)	−39(1)	−33(1)	−31(1)	−37(1)
N–C(2)–C(3)–C(4)	−107(1)	−104(1)	−101(1)	−104(1)
C(1)–C(2)–C(3)–C(8)	143(1)	147(1)	149(1)	145(1)
N–C(2)–C(3)–C(8)	74(1)	75(1)	79(1)	77(1)

reported in Table 1 for the (*R*)-(1)-enantiomer (structure I), and in Table 2 for the racemate of (1) (structure II). Bond lengths, angles, and some selected torsion angles for structures (I) and (II) are shown in Table 3 and 4, respectively, the numbering scheme being that shown in Figures 2 and 3. Structural data for (II) are more accurate but data which refer to the four independent molecules of (I) are of some interest because they reflect different intermolecular environments and therefore give some idea of the flexibility of the molecular conformation.

The average C–C bond length within the three-membered ring is 1.49 Å, which is shorter than a single C–C bond. This effect has already been observed in other small rings and is in good agreement with the value expected for a saturated NCC ring.[3,6] In both structures, the bond angle N–C(2)–C(3) is significantly larger than the expected value (*ca.* 112°) owing to a severe intramolecular interaction between one phenyl ring and chlorine [C(3) · · · Cl = 2.95 Å]. This interaction may also explain the narrow range spanned by the orientation of this phenyl ring in both structures [*e.g.*, the C(1)–C(2)–C(3)–C(8) torsion angle ranges from 143 to 149°] in contrast with the twisting flexibility of the second phenyl ring, whose orientation, with respect to the aziridine ring, changes over a range of about 30°. This situation is also illustrated in Table 5 where the angles between the planes of the phenyl rings and of the three-membered ring are reported. The pyramidal structure of nitrogen may be conveniently described in terms of the angle between the N–Cl bond and the aziridine ring plane, this angle being 116.6(2)° in (II) and 112.5(7), 112.6(7), 114.9(6), and 116.1(5)° in the four independent molecules of (I). These values compare well with the 115.2° found in the gas phase from microwave spectra of 1-chloroaziridine,[7] and are also comparable with data observed when a methoxy group is bound to nitrogen (see Table 11 of ref. 3, values of 180 − α). The packing is consistent with commonly accepted van der Waals interactions in both structures.

I.r. Spectra.—I.r. spectra of (*R*)-(−)- and racemic (1) were registered for CCl_4 solutions, for suspensions in Nujol, and for KBr pellets. Raman spectra of both compounds in CCl_4 were also recorded. The i.r. spectra for solutions and for KBr pellets are shown in Figure 4. As expected, the i.r. spectra of the enantiomeric and racemic forms of *N*-chloro-2,2-diphenylaziridine (1) are identical in CCl_4 solution (Figure 4A), whereas they show differences in both the intensities (at 1 070 and 920 cm^{-1}) and the number of related bands (at 700 and 550 cm^{-1}) when recorded for KBr pellets or Nujol mulls. These differences may be due to bending and low-frequence radial skeletal vibrations of the monosubstituted benzene rings of (1),[8] and to stretching mode of the N–Cl bond.[9]

Moreover, in the 4 000—300 cm^{-1} spectral range, the spectrum of solid (*R*)-(1) appears to be less well resolved and more similar to that observed in solution than the corresponding spectrum of racemic (1). This behaviour is in agreement

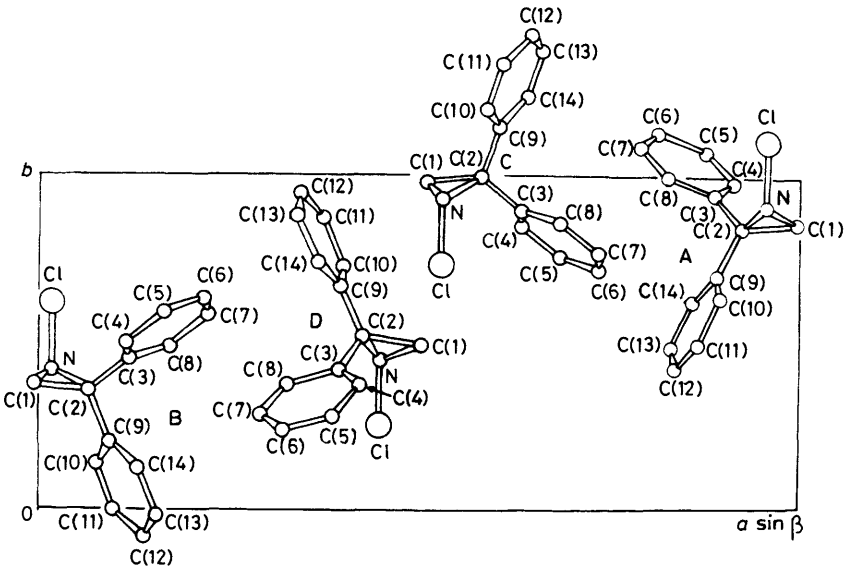


Figure 2. *X*-Ray structure (structure I) of (*R*)-(−)-1-chloro-2,2-diphenylaziridine

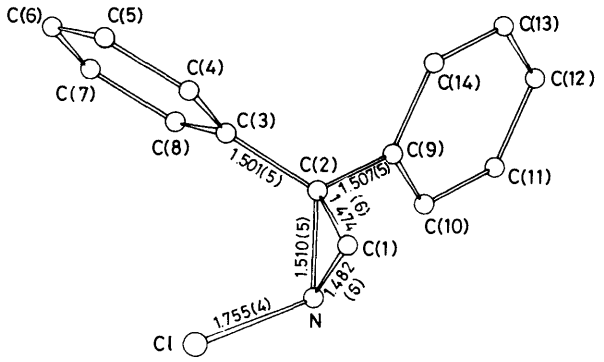


Figure 3. *X*-Ray structure (structure II) of racemic 1-chloro-2,2-diphenylaziridine

with the *X*-ray data, which indicate different organizations in the solid state of the two derivatives of (1), and stronger interactions in the solid racemate than in the solid enantiomer.

Solvent Effect on the Nitrogen Inversion Barriers.—First-order rate constants for racemization of (*R*)-(−)-(1) in several solvents are given in Table 6. These results show that the rate of nitrogen inversion in *N*-chloroaziridine (1) is relatively insensitive to the solvent. In particular, the three non-polar solvents (cyclohexane, carbon tetrachloride, benzene), as well as the polar protic ethanol and t-butyl alcohol,* give small and similar solvent effects, to within 0.2 kcal mol^{-1}. An increase of 0.4—0.7 kcal mol^{-1} for the barrier value was observed with the polar non-protic solvent acetonitrile.†

Table 4. Bond lengths and angles, and some selected torsion angles for structure (II). E.s.d.s are in parentheses. Phenyl rings have standard geometrical features

	Bond distance/Å
Cl–N	1.755(4)
N–C(1)	1.482(6)
N–C(2)	1.510(5)
C(1)–C(2)	1.474(6)
C(2)–C(3)	1.501(5)
C(2)–C(9)	1.507(5)
	Bond angle/°
Cl–N–C(2)	113.4(3)
Cl–N–C(1)	112.4(3)
C(1)–N–C(2)	59.0(3)
N–C(1)–C(2)	61.5(3)
N–C(2)–C(1)	59.5(3)
C(1)–C(2)–C(9)	118.6(3)
C(1)–C(2)–C(3)	121.4(3)
N–C(2)–C(9)	112.3(3)
N–C(2)–C(3)	120.3(3)
C(3)–C(2)–C(9)	113.8(3)
C(2)–C(3)–C(8)	118.3(2)
C(2)–C(3)–C(4)	121.7(2)
C(2)–C(9)–C(14)	118.6(2)
C(2)–C(9)–C(10)	121.4(3)
	Torsion angle/°
C(1)–C(2)–C(9)–C(10)	−93.0(4)
N–C(2)–C(9)–C(10)	−26.6(4)
C(1)–C(2)–C(9)–C(14)	87.7(4)
N–C(2)–C(9)–C(14)	154.1(3)
C(1)–C(2)–C(3)–C(4)	−30.6(5)
N–C(2)–C(3)–C(4)	−101.3(3)
C(1)–C(2)–C(3)–C(8)	149.3(3)
N–C(2)–C(3)–C(8)	78.7(4)

The best racemization conditions, *i.e.*, relatively low temperatures and without decomposition by or interaction of (*R*)-(1) with solvents, were for cyclohexane, acetonitrile, and t-butyl alcohol solution. The corresponding activation parameters and rate constants at different temperatures are reported

* It should be noted that racemizations of chiral *N*-chloroaziridines in polar alcohols may be accompanied by solvolytic cleavage of the three-membered ring.[10] Indeed, this was the case when the racemizations of (*R*)-(−)-(1) were carried out in methanol solution and also, although to a smaller extent, in ethanol. On the other hand, solvolytic effects were not found in racemizations carried out in t-butyl alcohol.

† Attempts to study racemizations of (*R*)-(−)-(1) in dimethyl sulphoxide solution failed owing to reactions between the solvent and the *N*-chloroaziridine substrate.

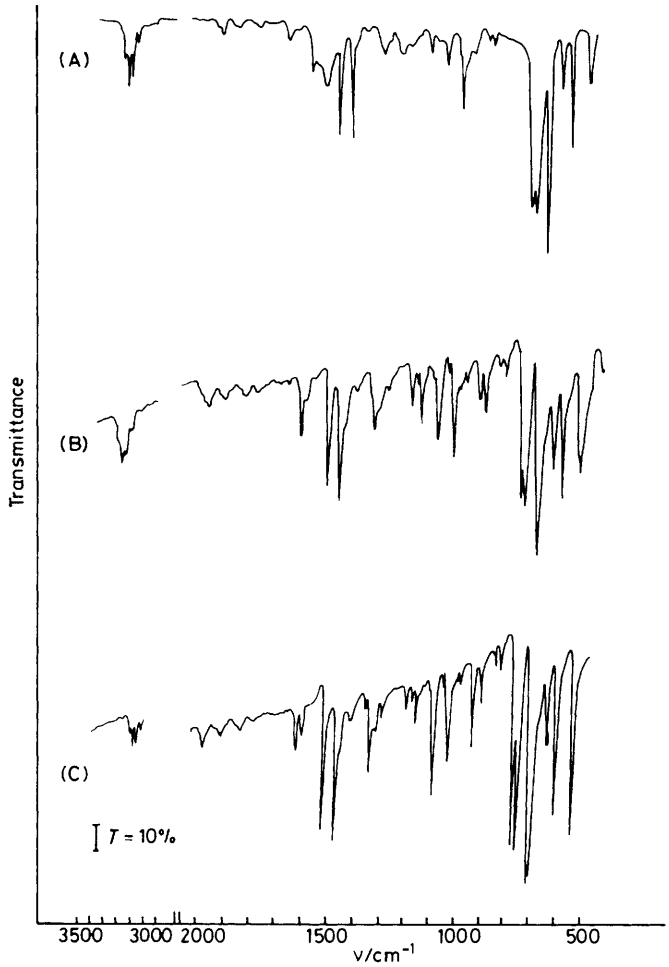


Figure 4. I.r. spectra of (*R*)-(−)- and racemic 1-chloro-2,2-diphenylaziridine: (A), in CCl_4 solution; (B), solid (*R*)-(−)-(1) in KBr pellet; (C), solid racemate (1) in KBr pellet

in Table 7. In cyclohexane and acetonitrile solution, the activation energy (E_a) and the frequency factor (A) as well as the $\Delta S^{\ddagger}$ values, are in accord with expectations for an intramolecular pyramidal inversion process in the absence of any appreciable differential solvent effects. The influence of the $\Delta S^{\ddagger}$ parameter seems more important in the racemization carried out in t-butyl alcohol. Polar or hydroxylic solvents have been reported to increase the barriers to nitrogen inversion in aziridines by *ca.* 2 kcal mol^{-1}.[11] On the other hand, no significant solvent effect has been observed in nitrogen pyramidal inversion studies in acyclic chloramines [12] and in oxaziridines.[13] As in the latter cases, the present results may be attributed mainly to the low basicity of the nitrogen atom in *N*-chloroaziridine derivatives.

Experimental

Optical rotations were measured with a Perkin-Elmer 141 automatic polarimeter with 1 or 10 cm path-length cells. ^{1}H N.m.r. spectra were measured for carbon tetrachloride solutions, with tetramethylsilane as internal standard, with a Varian XL-200 spectrometer. Thermal analyses were performed with a Mettler TA 2000 instrument. I.r. and Raman spectra were recorded on a Perkin-Elmer IR 180 and Raman Jobin-Yvon HG 2S spectrometer, respectively. 2,2-Diphenylaziridine was prepared as described in the literature.[14] (*S*)-2,2,2-Trifluoro-1-(9-anthryl)ethanol, $[\alpha]_D$ +30.73° ($CHCl_3$), was purchased from Ega-Chemie and used without additional purification.

Table 5. Angles between planes defined by the two phenyl rings and the aziridine ring

Plane	Atoms
AZ	N, C(1), C(2)
PH1	C(3), C(4), C(5), C(6), C(7), C(8)
PH2	C(9), C(10), C(11), C(12), C(13), C(14)

Interplanar angles (°)

	Structure (I)				Structure (II)
	Mol. A	Mol. B	Mol. C	Mol. D	
AZ–PH1	55.7(7)	56.0(6)	57.4(6)	58.7(4)	57.9(2)
AZ–PH2	69.3(7)	66.4(7)	64.4(6)	72.8(7)	60.8(2)
PH1–PH2	84.8(2)	88.1(2)	89.5(2)	82.8(2)	84.9(1)

Table 6. Dependence on solvent of the first-order rate constants for racemization of (*R*)-(−)-(1) at 333.15 K

Solvent	$10^6 k$/s^{-1}	$\Delta G^{\ddagger}$/ kcal mol^{-1} [a]
Cyclohexane	787 ± 3	24.7
Carbon tetrachloride	655 ± 2	24.8
Benzene	481 ± 2	25.0
Acetonitrile	270 ± 0.6	25.4
t-Butyl alcohol	663 ± 2	24.8
Ethanol	563 ± 4	25.0 [b]

[a] The error in $\Delta G^{\ddagger}$ is ≤0.3 kcal mol^{-1}. [b] Experimental error is ±1. In this case solvolysis of the *N*-chloroaziridine (*R*)-(1) accompanies the racemization process.

Synthesis of Optically Active and Racemic 1-*Chloro*-2,2-*diphenylaziridine*.—A mixture of 2,2-diphenylaziridine (10 mmol) and (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol (20 mmol) was diluted with CH_2Cl_2 (25 ml) and treated at −40 °C with a solution of freshly prepared Bu^{t}OCl (10 mmol). The mixture was kept for 3 h at −40 °C and the CH_2Cl_2 solvent was then evaporated off *in vacuo*. Optically active *N*-chloro-2,2-diphenylaziridine (1), $[\alpha]_D$ −67.83° ($CHCl_3$), was recovered in 85—90% yield, free from traces of the optically active alcohol, by column chromatography on silica gel using n-hexane–ether (9 : 1) as eluant. Crystallization of the crude product at −20 °C from ether–light petroleum (b.p. 40—60 °C) gave the racemic derivative of (1) as the main crystalline product, m.p. 60.5 °C. The oily residue of the crystallizations, having $[\alpha]_D$ −207.29 °C ($CHCl_3$) was crystallized from pentane at low temperature (−20 to 0 °C) until it showed m.p. 35.3 °C and $[\alpha]_D^{20}$ −304.7° (*c* 0.49, $CHCl_3$). The optically active residue (1) of the last crystallization had $[\alpha]_D^{20}$ −293.2° (*c* 0.41, $CHCl_3$). Both racemic and optically active (1) exhibit the following ^{1}H n.m.r. properties: δ (CCl_4) 7.35 (5 H, s), 7.18 (5 H, s), 3.03 (1 H, d), and 2.76 (1 H, d).

Kinetics.—The progress of the racemization of (*R*)-(−)-(1) was followed in a thermostatically controlled polarimeter cell (±0.1 K). On completion of the readings, the solutions were rechecked for decomposition by t.l.c. and n.m.r. spectroscopy. Rate constants were calculated from the slope ($-k/2.303$) obtained from the best straight line (linear least squares) plot of $\log_{10} \alpha$ *vs.* time. Kinetic parameters were obtained from the slope and intercept on the ordinate of the best straight line plot of ln k *vs.* T^{-1}. Rate constants used in the Arrhenius and

Table 7. First-order rate constants and kinetic parameters for thermal racemization of (*R*)-(−)-(1) in cyclohexane, acetonitrile, and t-butyl alcohol [a]

Solvent	*T*/K	$10^6k/s^{-1}$	$\Delta H^{\ddagger}$/kcal mol^{-1}	E_a/kcal mol^{-1}	$\log_{10}(A/s^{-1})$	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
Cyclohexane	333.15	786 ± 3	24.8 ± 0.5	25.4 ± 0.5	13.3 ± 0.3	0.2 ± 1
	323.15	260 ± 0.7				
	313.15	68 ± 0.3				
Acetonitrile	333.15	270 ± 0.6	25.3 ± 0.2	26.1 ± 0.2	13.25 ± 0.1	−0.35 ± 0.5
	323.15	82 ± 0.2				
	313.15	22 ± 0.1				
t-Butyl alcohol	333.15	663 ± 2	23.8 ± 0.3	24.5 ± 0.3	12.6 ± 0.2	−3.0 ± 1
	323.15	220 ± 2				
	313.15	63 ± 0.2				

[a] All activation parameters refer to nitrogen inversion.

Eyring equations were the rate constants for nitrogen inversion and not the rate constants for racemization, the latter being twice the former.[15]

X-Ray Structural Analyses.—(R)-(−)-1-*Chloro*-2,2-*diphenylaziridine.* Intensity measurements were collected on a Philips PW1100 diffractometer. Cell dimensions were obtained by least-squares refinement carried out over 20 $(\theta,\chi,\varphi)_{hkl}$ measurements.

Crystal data. $C_{14}H_{12}NCl$, $M = 229.7$, monoclinic, space group $P2_1$, $a = 21.370\ 5(8)$, $b = 8.986\ 7(2)$, $c = 13.522\ 4(7)$ Å, $\beta = 108.40(1)°$, $Z = 8$, $D_c = 1.238$ g cm^{-3}, $U = 2\ 464.1(3)$ Å^3, $F(000) = 960$, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 23.8 cm^{-1}. 3 681 Independent reflections were collected in the range $4 \leqslant \theta \leqslant 58°$ while 1 729 Friedel pairs were collected in the range $10 \leqslant \theta \leqslant 42°$ with a θ–2θ scan using a scan width of 1.3° and a speed of 0.05° s^{-1}. During data collection the intensities of two reference reflections, monitored every 100 min, decreased to 85% of their original value; the data were scaled accordingly. Semiempirical absorption corrections were made on the basis of ψ scan data with three different 2θ values.

Structure analysis and refinement. The structure, composed of four independent molecules, was solved with the MULTAN-80[16] system while refinement was carried out with the SHELX-76[17] program using the blocked full-matrix method. One molecule was refined at a time while the contributions to the calculated structure factors of the other three molecules were kept constant. For this reason all positional parameters in Table 1 appear with e.s.d.s in spite of the requirement in the $P2_1$ space group for the origin to be fixed by fixing the *y* co-ordinate of one atom. During refinement the geometry of both phenyl rings was kept fixed at standard values in order to keep the number of parameters as low as possible. Hydrogen atoms bound to C(2) were located on a difference Fourier map and refined in the last cycles. The final *R* factor was 0.071 and was obtained with a weighting function of the form $1/w = \sigma^2(F_o) + 0.0002\ F_o^2$.

The absolute configuration was determined by selecting the 316 Friedel pairs which showed absolute values of the Bijvoet ratio greater than 0.04 and by making use of these most enantiomer-sensitive reflections in a structure factor calculation to discriminate between the two enantiomers. The (*R*)-model gave a conventional *R* factor of 0.064 ($R_w = 0.095$) while the (*S*)-model gave an *R* factor of 0.088 ($R_w = 0.121$).

Racemic 1-*Chloro*-2,2-*diphenylaziridine.*—Intensity measurements were collected on a Philips PW1100 diffractometer. Cell dimensions were obtained by least-squares refinement carried out over 18 $(\theta,\chi,\varphi)_{hkl}$ measurements.

Crystal data. $C_{14}H_{12}NCl$, $M = 229.7$, monoclinic, space group $P2_1/c$, $a = 9.030(1)$, $b = 11.330(2)$, $c = 11.973(2)$ Å, $\beta = 104.19(1)°$, $Z = 4$, $D_c = 1.289$ g cm^{-3}, $U = 1\ 187.6(3)$ Å^3, $F(000) = 480$, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 25.9 cm^{-1}. 1 595 Reflections were collected in the range $4 \leqslant \theta \leqslant 57°$ with a θ–2θ scan technique using a scan width of 1.2° and a speed of 0.06° s^{-1}. The intensities of two reference reflections, monitored every 60 min, showed no significant change. No absorption correction was made on observed data.

Structure analysis and refinement. The structure was solved with the MULTAN-80[16] system and refinement was carried out with the SHELX-76[17] program using the blocked full-matrix method, the internal co-ordinates of both phenyl rings being fixed at standard values. Hydrogen atoms bound to C(2) were located on a difference Fourier map and refined in the last cycles. The final *R* factor, calculated with anisotropic thermal parameters for all non-hydrogen atoms, was 0.057 (0.063 with 201 unobserved reflections included) and was obtained with a weighting function of the form $1/w = \sigma^2(F_o) + 0.0003\ F_o^2$. Tables of observed and calculated structure factors for the two structure determinations, together with anisotropic thermal parameters non-hydrogen atoms and hydrogen atom parameters have been deposited as Supplementary Publication No. 23852 (34 pp.).*

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