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ASYMMETRICAL NONBRIDGEHEAD NITROGEN—XXIV

COMPLETE SEPARATION INTO ANTIPODES AND ABSOLUTE CONFIGURATION OF CHIRALIC N-ALKOXYAZIRIDINES

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Abstract—Optically active derivatives of 1 - methoxyaziridine - 2,2 - dicarboxylic acid have been obtained: the diethyl ester *S*-(−**1a**) by kinetic enrichment under the action of l-ephedrine; the diamides *R*-(+**2d**) and *S*-(−**2f**) by crystallization from l-methyllactate; the diamide *S*-(−**2g**) by asymmetric inversion reaction at the N atom while heating in l-methyllactate. The basic possibility of 1-alkoxyaziridine reactions with retention of optical activity (ammonolysis and reduction with LAH_4) has been demonstrated for *S*-(−**1a**) and *R*-(+**1**). 1-Methoxy - aziridine - 2,2 - dicarboxylic acid cis-ethyl ester **4** has been completely separated into antipodes 1*R*, 2*S*-(+**4**) and 1*S*, 2*R*-(−**4**) which under the effect of diazoethane afford diethyl esters *R*-(+**1**) and *S*-(−**1**) with optical purity of 96.2 and 93.8% (determined by PMR using a chiralic shift-reagent). On the basis of X-ray analysis of monoamides of 1 - methoxyaziridine - 2,2 - dicarboxylic acid ethyl ester and of salt **+7** the *trans*-specificity of ammonolysis and hydrolysis of **1** and the absolute configurations of all the optically active derivatives obtained were established.

The first optically active aziridines with a stable N pyramid to be obtained were optically pure diastereomers of 1*S*,2*S* - *trans* - 1 - chloro (and bromo) - 2 - methyl (and n-propyl) - aziridines; 1 - chloro - 2 - methylaziridine was separated into 1*R*,2*S* - *cis* - and 1*S*,2*S* - *trans* - diastereomers.[2,3] Partially enriched readily racemizating enantiomer (−) - 1 - chloro - 2,2 - diphenylaziridine was then synthesised by asymmetric chlorination.[4] After 10 years of unsuccessful attempts[5,6] a more stable partially enriched *R* - (+) - 1 - chloro - 2,2 - dimethylaziridine was obtained according to Scheme 1.

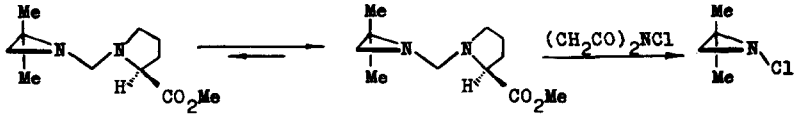
Due to the restricted configurational (Table 1) and thermal stability of 1-haloaziridines it was decided to study the more stable 1-alkoxyaziridines with electronegative substituents (CF_3 and CO_2R) at the cycle carbon.[10,14,15] Attempts to kinetically enrich 2,2 - bis - trifluoromethyl - aziridine derivatives $(CF_3)_2CCH_2NOX$ (X=Ts) and to separate diastereomers (X=CO_2R, where R is the residue of an optically active alcohol) failed.[16] The drawing together of asymmetric centres in the case of X=$MeCHCONH_2$ allows to separate the diastereomers by crystallization[17] and in the case of X=Me_2CCO_2H the enantiomers via the salt with *R*-(+)- and *S* - (−) - α - phenylethylamine (PEA).[9] Comparison of the configurational stability of these types of compounds shows the advantage of 1-alkoxyaziridinedicarboxylic esters (Table 1). The proximity of easily solvating and sufficiently reactive ester groups to the N chiralic center in the case of 1 - alkoxyaziridine - 2 - carboxylic esters makes it possible to carry out asymmetric reactions, to separate diastereomeric derivatives,[18] and for $TsONCH_2C(CO_2Me)_2$ to perform partial separation by crystallization from l-methyllactate.[19] For 1-alkoxyaziridine - 2 - carboxylic[12,18] and -2,2-dicarboxylic esters[6,20] the trans-specificity (with respect to the substituent at N) of nucleophilic substitution at the ester group was established and confirmed by X-ray analysis of the *trans*-amide of 1-methoxy-aziridine-2,2-dicarboxylic acid ethyl ester[21] and by data presented here. This stereospecificity is of a general nature. It was later observed in saponification and amidation reactions of esters of 1-methyldiaziridine-3,3-dicarboxylic,[22,23] 2 - methoxy - isoxazolidine - 3,3 - dicarboxylic[24,25] and 1 - ethylcyclopropane - 2,2 - dicarboxylic[26] acids. A method for complete separation into antipodes which makes use of this stereospecificity and the stability of 1 - alkoxyaziridine - 2,2 - dicarboxylic monoesters and of their salts was developed[6]. In this paper data on the synthesis of optically active 1-alkoxyaziridines[6,11,27] and on their absolute configuration[28] are supplemented and summarized.

A simple preparative method of optical activation consists in asymmetric amidation of 1 - methoxyaziridine - 2,2 - dicarboxylic ester **1** in the presence of half-molar amounts of l-ephedrine(EPH) (Scheme 2, Table 2).[6,11]

The first optically active 1-alkoxyaziridines were thus obtained. The possibility of carrying out reactions with retention of optical activity was demonstrated on the example of exhaustive ammonolysis and reduction of −**1a**.

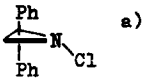
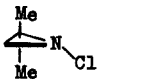
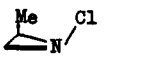
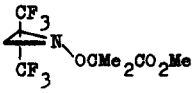
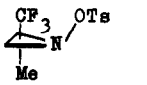
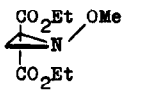
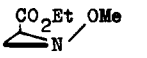
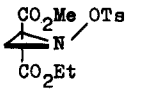
The racemate of crystalline 1 - methoxyaziridine - 2,2 - dicarboxylic acid diamide was separated into antipodes

†See Ref. 1 for Part XXIII.

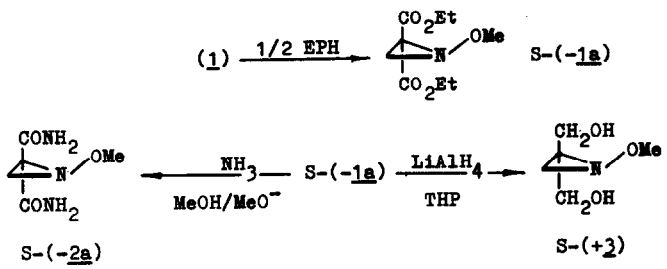


Scheme 1.

Table 1. Configurational stability of aziridines according to data on racemization and epimerization under normal conditions (20°)

Aziridine	$\Delta G^{\neq}$ inv. kcal/mole (KJ/mole)	$\tau_{1/2}$ years	Ref.
 a)	-	-	4
R-(+)- 	26.7 (111.8)	0.16	7
	26.8 (112.2)	0.19	8
(+)- 	29.8 (124.8)	35.2	9
	30.2 (126.4)	63.4	10
S-(-)- 	31.1 (130.2)	323	11
	31.3 (131.0)	412	12
	31.5 (131.9)	602.2	13

a) Racemizates in 4 days at 0°.



Scheme 2.

by fractional crystallization from 1-methyllactate (Scheme 3), yielding antipodes with a high degree of optical purity (Table 2). It is noteworthy that one-time crystallization of a partially enriched sample of −**2e** from MeOH affords a 2.5-fold increase in optical purity of −**2f**.

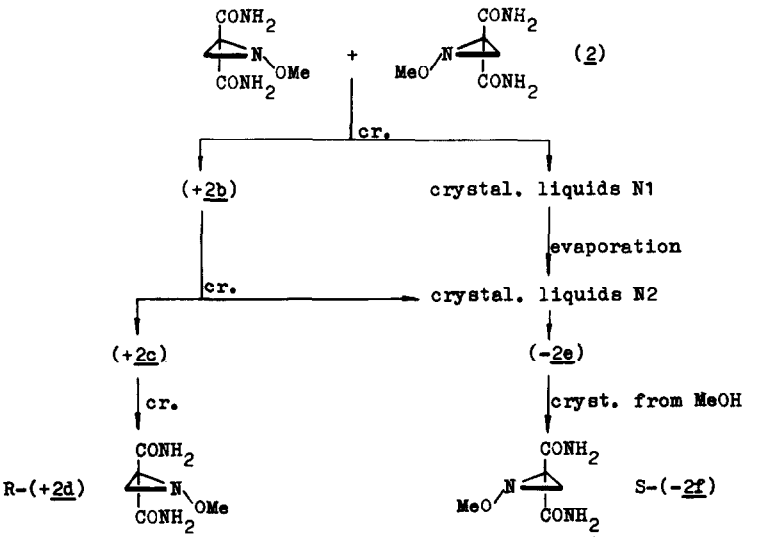
The meaning of separation of **2** during crystallization from a chiralic solvent becomes clear when considering the asymmetric inversion reaction which we briefly described in.[29] Heating of **2** in 1-methyllactate with subsequent removal of the solvent in vacuo results in 7% enrichment of the sample with the levorotatory antipode (Scheme 4, Table 2). Thus the inversional equilibrium is shifted towards the most solvate *S*-(−) antipode, while during crystallization the less solvate and therefore less soluble *R*-(+) antipode is mainly precipitated (Scheme 3).

Complete separation of **1** into antipodes was conducted via diastereomeric salts of 1 - methoxyaziridine - 2,2 - dicarboxylic acid *cis*-ethyl ester **4**[20] with *R*-(+) and *S* - (−) - α - phenylethylamine (PEA) (Scheme 5, Tables 2 and 3). Crystallization of these salts +**5a** and −**5a** from CCl_4 up to constant m.ps and rotation angles renders diastereomerically pure +**5** and −**5** (Table 3). Diastereomeric purity was also monitored by the MeO signals in the PMR spectra (Table 3). Under the action of *p*-toluenesulphonicacid (TsOH) from +**5** and −**5** optically active acids +**4** and −**4** were isolated, the esterification of which yields antipods +**1** and −**1** (Table 2). All steps in Scheme 5 were carried out under con-

Table 2. Optically active derivatives of 1-methoxyaziridine-2,2-dicarboxylic acid

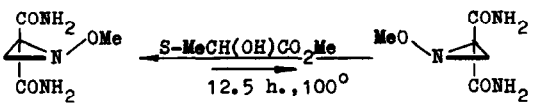
Compound	Yield[a] %	B.p. °C (mm Hg)	$[\alpha]_D^{20}$ (deg.)	$[M]_{max}^{20}$, deg. (λ nm)	$\Delta\varepsilon$ (λ nm)	Concentration, vol.%(solvent)	Optical purity,%
R-(+1)	100	65-68(0.5)	59.5	4700(240)	4.53(207)	0.56(EtOH)	96.2
S-(-1)	100	65-68(0.5)	-55.9	-4570(240)	-3.96(207)	0.67(EtOH)	93.8
S-(-1a)	60	-[b]	-3.1	-	-	2.10(EtOH)	5.2[c]
R-(+2)	66	m.p.150	45.6 55.9(546 nm)	-	5.60(202)	0.50(MeOH)	96.2[d]
S-(-2a)	50	m.p.158	-2.4	-	-	4.66(MeOH)	5.1[e]
R-(+2b)	68	m.p.158	1.1(546 nm)	-	-	4.50(MeOH)	1.9[e]
R-(+2c)	12.8	-	9.6(546 nm)	-	-	2.10(MeOH)	16.5[e]
R-(+2d)	2.1	m.p.151	36.7(546 nm)	-	-	1.70(MeOH)	63.1[e]
S-(-2e)	10.8	m.p.157-158	-10.0(546 nm)	-	-	2.00(MeOH)	17.2[e]
S-(-2f)	35	-	-25.2(546 nm)	-	-	0.40(MeOH)	43.4[e]
S-(-2g)	100	-	- 4.0(546 nm)	-	-	0.50(MeOH)	7.0[e]
S-(+3)	70.2	-[b]	1.1	-	-	1.62(MeOH)	5.2[f]
(1R,2S)-(+4)	93	oil	72.4	-	-	0.60(MeOH)	96.2[g]
(1S,2R)-(-4)	93	oil	74.4	-4270(238)	-4.26(206.5)	0.60(MeOH)	93.8[h]

a) Yield of (2b-2e) with respect to racemate (2), of (2f) with respect to (2e); b) isolated by chromatography; c) determined by correlation with rotation angle of (-1); d) taken equal to optical puriyy of (+1); e) determined by correlation with rotation angle of (+2); f) taken equal to optical purity of (-1a); g) taken equal to optical purity of (+1); h) taken equal to optical purity of (-1).

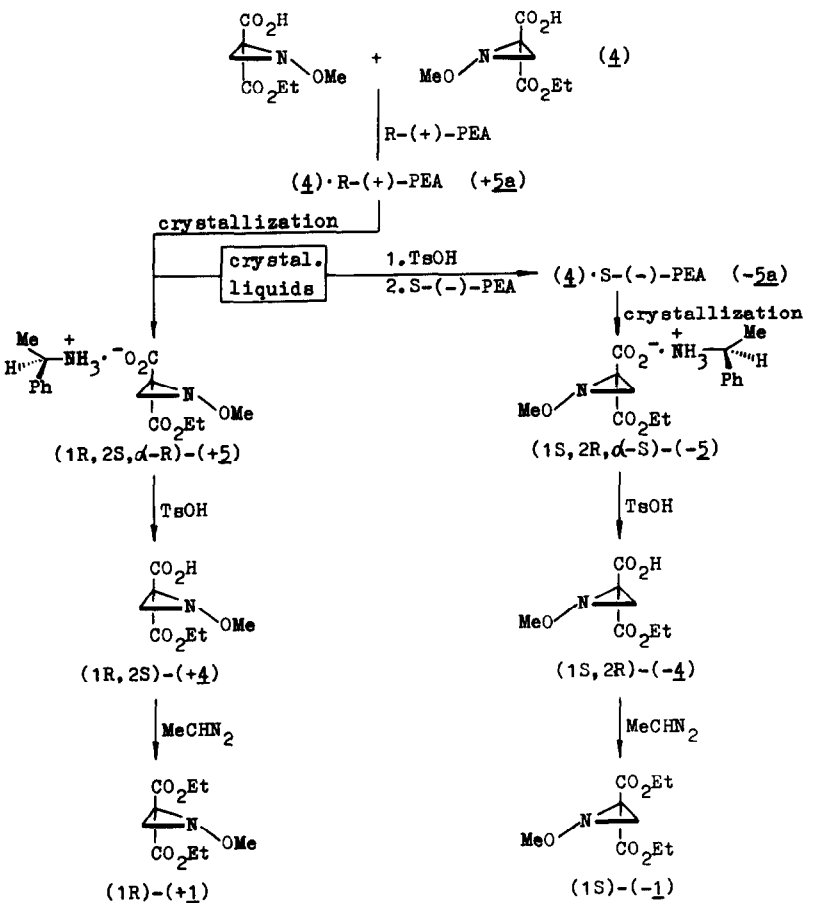


cr. - crystallization from l-methyllactate

Scheme 3.



Scheme 4.



Scheme 5.

Table 3. Optically active salts of 1 - methoxyaziridiie - 2,2 - dicarboxylic acid *cis*-ethyl ester 4

Comp.	Yield	M.p., °C	$[\alpha]^{20}$(nm) deg.	$\Delta\varepsilon$ (λnm)	Conc. vol.% MeOH	PMR (100 MHz, C_6H_6, δ ppm from TMS, J Hz)[a]					
						EtO	MeCH	CH_2 cycle	MeO	Ar	NH_3^+
(+5a)	99.0	92-115	6.62(546)	-	3.02	0.93;4.10 J=7.0	1.65;4.40[b]	2.11;2.21; 2.60;2.65[b]	3.51 3.59	-	-
(-5a)	36.7[c]	133	-18.30(546)	-	3.27	PMR spectrum is similar to that of (+5a)					
(+5)	43.8[d]	141	23.69(546) 19.90(589)	-0.09(266) -0.06(260) 1.39(222) 1.59(213) -1.30(200)	1.59	1.05;4.10 J=7.0	1.57;4.39 J=7.0	2.08;2.55 J=-2.0	3.50	-	-
(-5)	43.4[d]	141	-23.00(546) -19.90(589)	0.03(266) -0.03(263) -1.45(222) -1.60(213) +1.18(200)	1.68	PMR spectrum is similar to that of (+5)					
(+7)	65.8	155	7.38(589)	-	2.50	1.18;4.11 J=7.0	1.46;4.21 J=7.0	1.76;2.34 J=-2.5	3.44	7.24;7.44 J=8.0	7.71
(-7)	45.5	163-164	-19.80(589)	-	0.30	1.28;4.19 J=7.0	1.58;4.29 J=7.0	1.98;2.48 J=-2.5	3.50	7.35;7.53 J=8.0	7.65

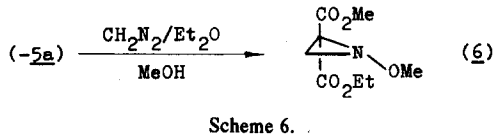
a) PMR of (+7) and (-7) (80 MHz, $CDCl_3$, HMDS); b) multiplet centres; c) from (+5a); d) from (+5a), diastereomerically pure form.

ditions excluding epimerization and racemization. It should be noted that *trans-cis* isomerization of acid **4** is considerably hindered while its salt does not isomerize at all.[20] Scheme 5 may be considerably simplified by directly passing from salts **+5** and **−5** to esters **+1** and **−1** avoiding isolation of acids **+4** and **−4**. Earlier we devised a preparative method for esterification of carboxylic acids involving interaction of an diazoalkane with their ammonium salts.[24,25] Its applicability to the given case is illustrated by the quantitative conversion according to Scheme 6.

Optical purity of **+1** and **−1** was determined from PMR spectra in the presence of an optically active shift-reagent, europium tris - (3 - trifluoromethyloxymethylene - d - camphorate) $Eu(tfc)_3$[6] (Fig. 1, Table 4). It practically coincides with that of the initial chiralic amines (94.1% for *S*-(−)-PEA and 97% for *R*-(+)-PEA). The degree of kinetic enrichment of **−1a** and of products of its conversion, **−2a** and **+3**, was estimated from optical purity of **−1** (Scheme 2, Table 2). In order to correlate the optical purity of the diamides (**2a–g**) exhaustive ammonolysis of **+1** was carried out (Scheme 7, Table 2). Taking into account the absence of isomerization under conditions of monoamidation of **1**[20] the optical purities of **+2** and **+1** may be considered equal.

Diastereomerically pure salts of 1 - methoxyaziridine - 2,2 - dicarboxylic acid cis-ethyl ester enantiomers with *S* - (−) - α - (p-bromophenyl) ethylamine (*S*-(−)-BPEA) were obtained following Scheme 8.[30]

By X-ray analysis of salt **+7** the absolute 1*R*,2*S*-configuration of the anion in coordinates of the known S-configuration of the cation was determined[28] (see below). The absolute 1*R*-configuration is exhibited by **+5**, **+4**, **+1** and **+2** since in conversions **+7**←**+5**→



Scheme 6.

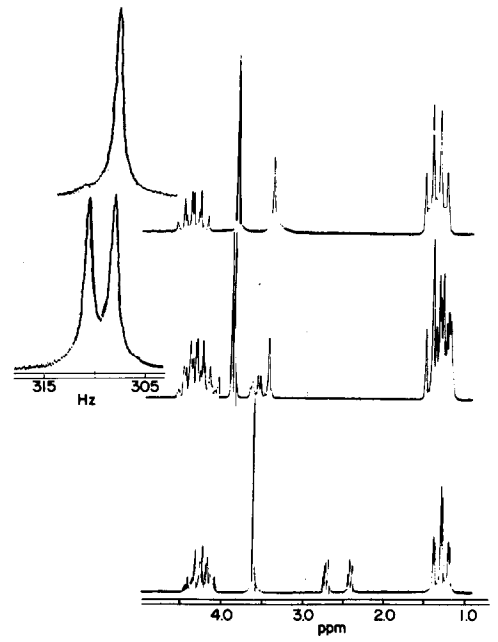
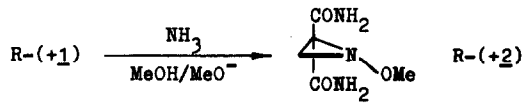


Fig. 1. PMR spectra (parameters are listed in Table 4): (a) **+1**, normal spectrum; (b) racemate **1** with $Eu(tfc)_3$ additive, molar ratio $C_{p/s} = 0.07$; (c) **+1** with $Eu(tfc)_3$ additive, $C_{p/s} = 0.139$; in (b) and (c) the left part—MeO signals of antipodes, the ratio of integral intensities of which was used to determine optical purity of **+1**.

Table 4. PMR spectral parameters of racemate (**1**) and (**+1**) and (**−1**) antipodes in the presence of $Eu(tfc)_3$ (80 MHz, δ ppm from HMDS, J Hz).

Comp.	Optical purity	$C_{p/s}$ [a]	Cycle protons			EtO_2C			MeO
			H_A	H_B	$J_{H_AH_B}$	Me	CH_2	J	
(1)	0	0	2.39	2.69	-2.6	1.26	4.21	7.1	3.60
						1.28	4.27		
(1)	0	0.070	3.41[b]	3.54[c]	-	1.25	4.27	7.1	3.85
				3.63[c]		1.30	4.40		3.88
						1.38	4.59		
(−1)	93.8	0.192	3.46[b]		-	1.33	4.40	7.1	3.86[d]
						1.40	4.46		3.90
(+1)	96.2	0.139	3.41[b]		-	1.27	4.28	7.1	3.80
						1.36	4.39		3.83[d]

a) $C_{p/s}$ is the molar ratio shift-reagent/substrate. For racemat (1) at $C_{p/s}$=0.07 maximal resolution of signals is achieved for MeO groups of antipodes and signals of cycle protons coalesce into a singlet. Accordingly, in determination of optical purity of (+1) and (−1) such a value of $C_{p/s}$ was elected so as to ensure coalescence of cycle proton signals and thus maximal resolution of MeO signals of antipodes; b) singlet signal; c) multiplet centre; d) signal corresponding to admixture of the second antipode.



Scheme 7.

+4→+1→+2 the N chiralic centre is not involved. Thus the dextrorotary antipode +1 has a *R*-configuration and a positive Cotton effect (Fig. 2, Table 2), while the levorotary −1 has a *S*-configuration and a negative Cotton effect.

The absolute configuration of asymmetric nitrogen in non-bridgehead structures was first determined for diaziridines[22,23,33] then for diastereomeric[32–34] and enantiomeric[35] oxaziridines, and enantiomeric N-alkoxyisoxazolidines[25] and now for aziridine.

Preliminary crystallographic studies showed that in the independent part of the crystal cell of −5 and −7 the number of molecules is equal to 6 while for +7 it is equal to 1 (Table 5). Accordingly we conducted a detailed X-ray analysis of salt +7, which crystallizes from MeCN in rhombical syngony with parameters listed in Table 5.

Intensities of 1309 independent nonzero ($1>2\sigma$ (I)) hko–hkl reflections were measured on a $0.4\times0.15\times0.2\,mm^3$ crystal using a DAR-UM automatic diffractometer (Cu–K_α radiation, graphite monochromator) in the region of θ from 3.5° to 74°. Absorption was ignored (μCu, $K_\alpha = 35.3\,cm^{-1}$). The structure was determined by the heavy atom method. H atoms were localised on difference syntheses. Due to intensive thermal vibrations of the C(6) atoms we were unable to determine the coordinates of the three H atoms bonded to it. The structure was refined according to the UMNKSA[37] programme taking into account anomalous scattering on Br, O, N and C atoms using anisotropic-isotropic (H-atoms) approximation up to R = 0.50. Cruickshank's weights scheme[38] was used in the refinement. Atomic coordinates and temperature corrections are listed in Tables 6 and 7, bond lengths and bond angles in Table 8 and geometrical data in Table 9. The molecular structures of the cation and anion of salt +7 with 30% probabilities of nonhydrogen thermal vibration ellipsoids are shown in Figs. 3 and 4. The anions and cations are bonded in the crystal structure by H-bonds into infinite chains directed along axis "C" (Fig. 5). The main structural parameters of the hydrogen bonds are given in Table 10.

The structure of the anion of +7 (Fig. 3) indicates *trans*-orientation of CO_2^- and MeO groups. It is presented in coordinates of the cationic chiralic centre C(14) (Fig. 4), therefore the absolute *R*-configuration of the N chiralic centre N(1) directly follows. The absolute configuration was also confirmed by refinement of the absorption correction for the Br atom, $\Delta f''_{Br}$.[39] The experimental value of $\Delta''_{Br} = 1.1$ (1) is in good agreement with the theoretical value of 1.280.[40]

Structural parameters of the aziridine cycle in +7 conform with results of recent X-ray analyses (Table 11). Some data obtained up to 1975 are summarized in Ref.[44] In accordance with known correlations[47] the tendency in

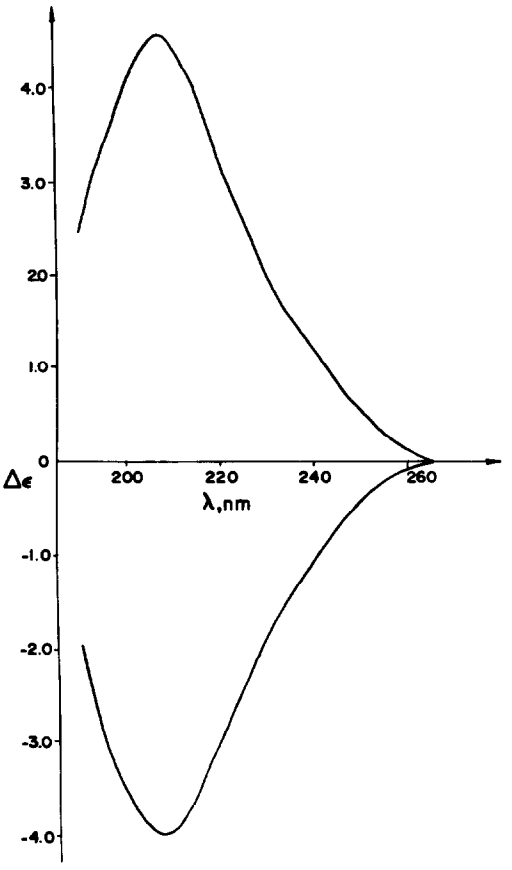


Fig. 2. Spectra of CD of antipodes +1 (above) and −1 (below).

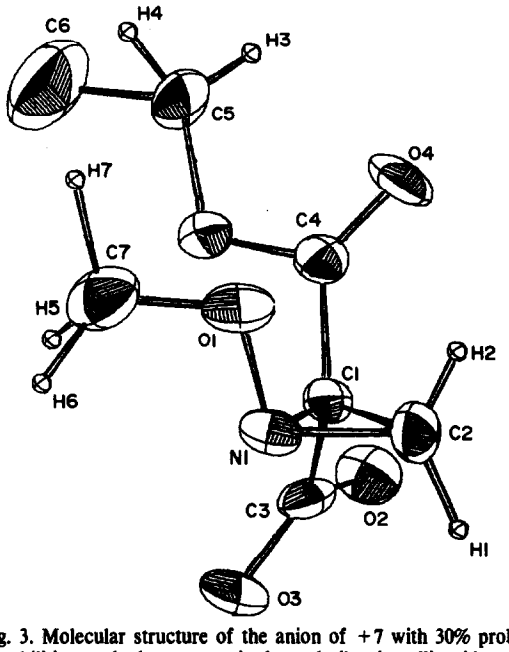
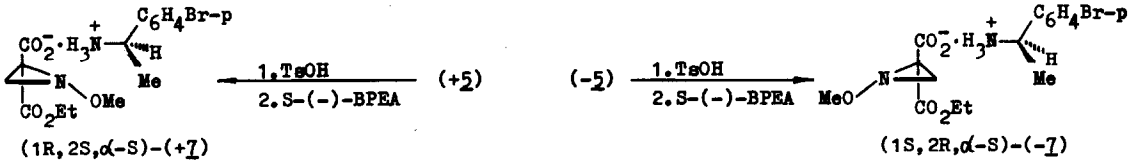


Fig. 3. Molecular structure of the anion of +7 with 30% probabilities nonhydrogen atomic thermal vibration ellipsoids.



(1R, 2S, α-S)-(+7)

(1S, 2R, α-S)-(-7)

Scheme 8.

Table 5. Crystallographic data for salts −5, −7 and +7

Atomic comp.	M.p., °C	M	a, Å	b, Å	c, Å	α°	β°	γ°	V. Å^3	ρ_{cal} g/cm^3	Z[a]	Space group	N[b]
(-5)$C_{15}H_{22}N_2O_5$	141	310.35	15.611(6)	23.310(8)	12.808(6)	90	90	107.83	4436.55	1.17	10	P 2_1	5x22=110
(-7)$C_{15}H_{21}N_2O_5Br$	163-164	389.25	13.605(10)	21.677(17)	38.880(16)	90	90	90	11466.30	1.36	24	$P2_12_12_1$	6x23=138
(+7)$C_{15}H_{21}N_2O_5Br$	155	389.25	25.121(6)	10.512(3)	7.062(3)	90	90	90	1864.87	1.394	4	$P2_12_12_1$	1x23=23

a) When determining Z for (-5) and (-7) atomic increments were taken from Ref.36 ;

b) Number of nonhydrogen atoms in the independent part of the cell.

Table 6. Coordinates and thermal parameters of Br, O and N atoms. Temperature factor $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$, standard deviations are given in parentheses

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0.47718(4)	0.00281(1)	0.8444(2)	0.00294(2)	0.0243(2)	0.0465(3)	-0.00139(9)	-0.0138(1)	-0.0143(4)
O(1)	0.1696(2)	-0.4455(4)	-0.6367(6)	0.0025(1)	0.0111(4)	0.016(1)	-0.0033(3)	-0.0014(5)	-0.008(1)
O(2)	0.2165(2)	-0.2275(4)	-0.0844(6)	0.0024(1)	0.0117(4)	0.0094(9)	-0.0018(3)	-0.0009(4)	-0,0049(9)
O(3)	0.2342(2)	-0.1372(4)	-0.3632(6)	0.0024(1)	0.0078(4)	0.017(1)	-0.0032(3)	0.0026(5)	-0.003(1)
O(4)	0.1470(2)	-0.5106(4)	-0.2149(7)	0.0025(1)	0.0079(4)	0.031(1)	-0.0014(3)	0.0044(5)	0.012(1)
O(5)	0.1124(1)	-0.3219(4)	-0.2906(6)	0.0013(1)	0.0098(4)	0.025(1)	0.0003(3)	0.0016(4)	0.006(1)
N(1)	0.2100(2)	-0.3618(4)	-0.5624(6)	0.0017(1)	0.0090(4)	0.005(1)	-0.0015(3)	0.0017(4)	-0.000(1)
N(2)	0.2647(2)	-0.1205(4)	0.2449(6)	0.0015(1)	0.0064(4)	0.013(1)	-0.0013(3)	-0.0004(4)	0.000(1)
C(1)	0.2022(2)	-0.3503(4)	-0.3540(8)	0.0013(1)	0.0055(4)	0.014(1)	-0.0001(3)	0.0009(5)	0.001(1)
C(2)	0.2428(2)	-0.4386(5)	-0.4325(9)	0.0018(1)	0.0077(5)	0.016(1)	0.0008(4)	0.0010(6)	-0.001(1)
C(3)	0.2189(2)	-0.2254(5)	-0.2594(8)	0.0010(1)	0.0083(5)	0.016(1)	-0.0009(3)	0.0002(5)	-0.004(1)
C(4)	0.1525(2)	-0.4059(4)	-0.2769(8)	0.0016(1)	0.0060(4)	0.011(1)	-0.0009(3)	-0.0004(6)	0.002(1)
C(5)	0.0600(2)	-0.3664(8)	-0.237(1)	0.0012(1)	0.023(1)	0.033(2)	-0.0010(5)	0.0023(8)	0.021(3)
C(6)	0.0211(3)	-0.271(2)	-0.272(2)	0.0021(2)	0.049(3)	0.079(5)	0.004(1)	0.001(2)	0.035(8)
C(7)	0.1360(3)	-0.3756(8)	-0.750(1)	0.0025(1)	0.0218(9)	0.017(2)	-0.0041(6)	-0.0037(8)	0.003(2)
C(8)	0.4271(2)	-0.0560(7)	0.661(1)	0.0015(1)	0.0140(7)	0.027(2)	-0.0009(4)	-0.0048(7)	-0.011(2)
C(9)	0.4195(3)	-0.1820(6)	0.639(1)	0.0023(1)	0.0116(7)	0.027(2)	0.0012(5)	-0.0042(8)	0.007(2)
C(10)	0.3834(3)	-0.2244(6)	0.503(1)	0.0021(1)	0.0077(6)	0.025(2)	0.0002(4)	-0.0014(8)	-0.002(2)
C(11)	0.3548(2)	-0.1392(5)	0.3939(9)	0.0014(1)	0.0083(5)	0.015(1)	-0.0002(4)	-0.0006(5)	-0.006(1)
C(12)	0.3643(3)	-0.0112(6)	0.422(1)	0.0030(1)	0.0084(6)	0.052(3)	0.0009(6)	-0.015(1)	0.002(2)
C(13)	0.4000(3)	0.0298(7)	0.562(2)	0.0036(2)	0.0095(8)	0.068(3)	-0.0001(6)	-0.023(1)	-0.002(3)
C(14)	0.3185(2)	-0.1852(6)	0.241(1)	0.0016(1)	0.0091(5)	0.022(2)	-0.0003(4)	0.0011(6)	-0.006(2)
C(15)	0.3423(3)	-0.167(1)	0.047(1)	0.0020(1)	0.033(2)	0.018(2)	0.0005(8)	0.0052(8)	-0.012(3)