Structural Studies of *N*-Chloroaziridinecarboxylates by Multinuclear NMR Spectroscopy

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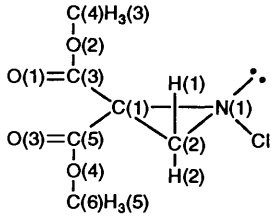
A systematic multinuclear (^{1}H, ^{13}C, ^{15}N, ^{17}O) magnetic resonance study provides an easy method of determining relative configurations of *N*-chloroaziridinecarboxylates.

Aziridinecarboxylates at the ring carbon atoms are of significant practical importance as synthetic intermediates in the preparation of α- and β-amino acids,[1] β-lactams,[2] or in biological and pharmacological applications.[3] Of particular interest are the chiral aziridines, which may form chiral derivatives through nucleophilic ring-opening reactions.[4] Accordingly, it would be useful to correlate the structure of the aziridines with the stereochemistry of the ring-opening reactions.

Recently, we reported[5] a structural characterization of *N*-chloro-2,2-bismethoxycarbonylaziridine (**1**) by 2D-NMR spectroscopy and X-ray diffraction analysis. To see if the NMR data of some related *N*-chloroaziridines, like **2**–**5**, could provide an easy and reliable method of determining relative configurations, a systematic multinuclear (^{1}H, ^{13}C, ^{15}N, ^{17}O) magnetic resonance study was performed. In this paper we report the NMR results in terms of relative configurations of aziridines **1**–**5**.



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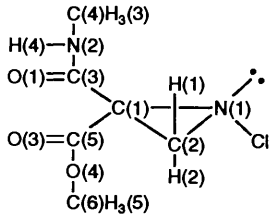

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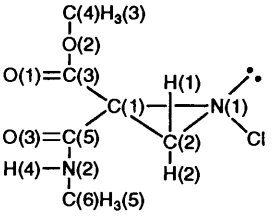

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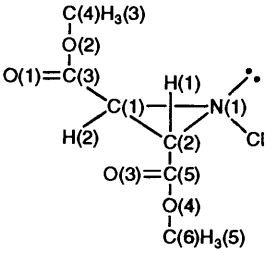

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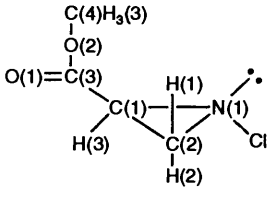

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Results and Discussion

The synthesis of aziridine **1** and of isomeric *cis*- and *trans*-*N*-chloro-2-methoxycarbonyl-2-methylcarbamoylaziridines **2** and **3** was carried out as described elsewhere.[5,6] The *trans* and *cis* structures of compounds **2** and **3** were unequivocally determined by X-ray crystallography.[6]

Table 1 ^{1}H NMR chemical shifts[a] of *N*-chloroaziridines **1**–**5**

Compd.	1-H	2-H	3-H	4-H	3-CH_3	5-CH_3
1[b]	2.91 ($J_{1,2}$ 2.97)	3.06	—	—	3.87	3.97
2	2.79 ($J_{1,2}$ 3.01)	3.12	—	6.63	2.90 ($J_{3,4}$ 5.01)[c]	3.96
3	3.10 ($J_{1,2}$ 2.5)	3.32	—	7.79	3.85	3.05 ($J_{5,4}$ 4.9)[c]
4	3.48 ($J_{1,2}$ 4.8)	3.54	—	—	3.86	3.95
5	2.76 ($J_{1,2}$ 2.6)	2.61	3.06 ($J_{1,3}$ 5.4) ($J_{2,3}$ 7.95)		3.86	—

[a] Chemical shifts (δ) downfield of $SiMe_4$ as internal standard; solutions 0.1–0.3 mol dm^{-3} in $CDCl_3$ at 300 K and 400 MHz. In parentheses *J*(H,H) coupling constants (Hz) are reported. [b] Data from ref. 5. [c] Coupling constants between the methyl protons and the NH proton.

N-Chloro-2,3-bismethoxycarbonylaziridine (**4**) and *N*-chloro-2-methoxycarbonylaziridine (**5**) were synthesized from the corresponding NH derivatives by halogenation with *tert*-butyl hypochlorite.[7] In particular, halogenation of 2-methoxycarbonylaziridine afforded the corresponding aziridine **5** as a single diastereoisomer, as indicated by the ^{1}H NMR spectrum. The aziridine-2- and -2,3-(di)carboxylates were synthesized following the procedures reported in ref. 7.

All compounds **1**–**5** exhibited a fairly high inversion barrier at nitrogen: in particular, their configurational stability enabled us to isolate epimers **2** and **3** and obtain NMR spectra without noticeable interconversion occurring.[6,†]

^{1}H and ^{13}C Chemical Shift Assignments.—The assignments of the observed resonances to the corresponding protons and carbons were carried out using 2D-heteronuclear correlation spectroscopy (H,C-COSY)[8] and 2D-heteronuclear correlated spectroscopy *via* long-range coupling constants (COLOC).[9] The ^{1}H and ^{13}C chemical shifts of aziridines **1**–**5** are reported in Tables 1 and 2, respectively.

The direct coupling constants ^1J(C,H) were assigned and determined using an HMQC experiment in 1D version.[10] The long-range coupling constants ^nJ(C,H) were determined through a COLOC experiment and a 2D-inverse HMBC technique.[11] The correct numerical values were determined from high resolution ^{13}C coupled spectra. The direct and long-range coupling constants ^nJ(C,H) are reported in Table 3.

In the light of published data,[12] the geminal ring-proton was assigned on the assumption that the direct coupling constant ^1J(C,H) was greater for the ring protons *cis* related to the

† After 24 h at 27 °C the $CDCl_3$ solution of the *trans* derivative showed traces of the *cis* isomer.

nitrogen lone-pair than that for the *trans* ones. The relative positions of the substituent group at the ring carbon atoms with respect to the nitrogen lone-pair were inferred from the coupling-constant determinations and from analysis of the lanthanide induced shifts (LIS) measured on the spectra recorded in the presence of the shift reagents tris(8,8,8,7,7,6,6-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium, Eu(fod)$_3$ and tris(8,8,8,7,7,6,6-heptafluoro-2,2-dimethyl-3,5-octanedionato)ytterbium, Yb(fod)$_3$.[13]

^{17}O *and* ^{15}N *Chemical Shift Assignments.*—The ^{17}O and ^{15}N chemical-shift assignments of aziridines **1–5** are reported in Table 4. The ^{17}O chemical shifts for derivatives **1** and **4** were assigned on the basis of the LIS effects measured in the presence of Eu(fod)$_3$, since the dominant perturbations induced by Eu(fod)$_3$ are contact effects on ^{17}O signals and prevalently dipolar effects on proton and carbon signals.[14] The ^{17}O signals were assigned to the appropriate ester group by measuring the induced shifts on ^{17}O as well as on ^{13}C and ^{1}H signals and assuming that the more coordinated oxygens should be the less crowded.

^{15}N-signal assignments for aziridines **1–5** were performed using the heteronuclear polarization transfer technique (INEPT).[15–17]

N-*Chloro*-2,2-*bismethoxycarbonylaziridine* (**1**)—The ^{1}H and ^{13}C assignments are reported in ref. 5. The LIS measurements, carried out in the presence of Eu(fod)$_3$, showed an evident shielding effect on the ^{17}O signals at 349.1 and 136.5 ppm and a remarkable deshielding effect on carbons at 166.48 and 54.39 ppm and protons at 3.87 and 2.91 ppm. Since these ^{13}C and ^{1}H signals were connected and attributed to the ester group and to the ring proton *cis* to the nitrogen lone-pair, we deduced that the ^{17}O signals at 349.1 and 136.5 ppm were also attributable to the same carboxylic group *cis* to the nitrogen lone-pair. In the light of these results, for derivative **1** the ^{17}O assignment, reported by us previously in this journal,[5] must be reversed.

N-*Chloro*-2-*methoxycarbonyl*-2-*methylcarbamoylaziridine* (**2**).—The relative *cis* configuration of **2** is known from the X-ray diffraction analysis.[6] Inspection of the ^{1}J(C,H) coupling constants obtained from a 1D-HMQC experiment enabled the *cis* position to the nitrogen lone-pair to be assigned to the ring proton at 2.79 ppm disclosing the higher ^{1}J(C,H). The carbonyl carbons were assigned by means of a 2D experiment (COLOC) based on the evolution of the long-range coupling constants with the methyl protons, which were easily assigned from the proton spectrum; the carbonyl signals at 164.84 and at 165.52 ppm were therefore correlated, respectively, with the methyl protons at 3.96 and 2.90 ppm.

N-*Chloro*-2-*methoxycarbonyl*-2-*methylcarbamoylaziridine* (**3**).—The relative *trans* configuration of **3** is known from the X-ray diffraction analysis.[18] The ring proton at 3.10 ppm, showing the higher direct coupling constant ^{1}J(C,H), was *cis* related to the nitrogen lone pair. From the COLOC spectra, the ^{13}C signals at 169.0 and 161.82 ppm were correlated with the ester and amidic methyl groups, respectively, at 3.85 and 3.05 ppm. The assignment of the ^{17}O chemical shifts for isomers **2** and **3** is straightforward.[19]

N-*Chloro*-2,3-*bismethoxycarbonylaziridine* (**4**).—The *cis* position to the nitrogen lone-pair was assigned to the proton at 3.48 ppm with the higher direct coupling constant ^{1}J(C,H). Direct correlations between ^{13}C and ^{1}H signals allowed us to assign the ring carbons and to connect methyl carbon signals with the corresponding proton signals. The COLOC experiment enabled us to assign the proper carbon and proton signals to each ester group. The relative position of each ester group with respect to the nitrogen lone-pair was inferred from the analysis of the LIS effects as well as from the ^{2}J(C,H) and

Table 2 ^{13}C NMR chemical shifts[a] of *N*-chloroaziridines **1–5**

Compd.	C-1	C-2	C-3	C-4	C-5	C-6
1[b]	52.43	46.90	166.48	54.39	164.05	54.56
2	53.42	46.63	165.52	26.99	164.84	54.48
3	50.25	45.65	169.00	54.48	161.82	28.12
4	49.34	48.03	167.44	53.97	164.69	54.26
5	45.50	43.17	169.09	53.63	—	—

[a] Chemical shifts (δ) downfield of $SiMe_4$ as internal standard; solutions 0.1–0.3 mol dm^{-3} in $CDCl_3$ at 300 K and 100.61 MHz. [b] Data from ref. 5.

Table 4 ^{15}N and ^{17}O NMR chemical shifts[a] of *N*-chloroaziridines **1–5**

Compd.	N-1	N-2	O-1	O-2	O-3	O-4
1	−308.8	—	349.1	136.5	364.2	143.2
2	−313.8	−279.3	311.9	—	364.6	143.8
3	−300.6	−269.6	359.1	132.7	323.8	—
4	−308.3	—	350.6	136.6	361.5	144.8
5	−319.0	—	345.8	136.6	—	—

[a] ^{15}N chemical shifts (δ) upfield of CH_3NO_2 in $CDCl_3$ in a coaxial tube as external reference; solutions 0.1–0.3 mol dm^{-3} in $CDCl_3$ at 300 K and 100.61 MHz. ^{17}O chemical shifts (δ) downfield of H_2O as external reference in a coaxial tube; solutions 0.1–0.3 mol dm^{-3} in $CDCl_3$ at 300 K and 54.25 MHz.

Table 3 ^{n}J(C,H) coupling constants (Hz) of *N*-chloroaziridines **1–5**

Compd.	^{1}J(C-2,*x*-H)	^{2}J(C-1,*x*-H)	^{3}J(C-3,*x*-H)	^{1}J(C-4,*x*-H)	^{3}J(C-5,*x*-H)	^{1}J(C-6,*x*-H)
1	180.17 (1-H) 176.01 (2-H)	2.7 (1-H) 2.7 (2-H)	2.7 (1-H) 3.3 (2-H) 3.94 (3-CH_3)	148.5 (3-CH_3)	4.04 (1-H) 2.85 (2-H) 4.04 (5-CH_3)	148.5 (5-CH_3)
2	179.23 (1-H) 175.77 (2-H)	2.68 (1-H) 2.68 (2-H)	3.07 (1-H) 2.42 (2-H) 3.61 (3-CH_3) ^{2}J 1.78 (4-H)	139.26 (3-CH_3) ^{2}J 2.91 (4-H)	2.99 (1-H) 4.35 (2-H) 3.95 (5-CH_3)	148.7 (5-CH_3)
3	180.39 (1-H) 174.73 (2-H)	2.68 (1-H) 2.68 (2-H)	3.09 (1-H) 2.86 (2-H) 3.92 (3-CH_3)	148.71 (3-CH_3)	2.40 (1-H) 3.63 (2-H) 3.82 (5-CH_3) ^{2}J 1.78 (4-H)	139.16 (5-CH_3) ^{2}J 2.83 (4-H)
4	183.75 (1-H) ^{2}J 2.93 (2-H)	2.58 (1-H) ^{1}J 180.49 (2-H)	3.01 (1-H) 3.94 (3-CH_3) ^{2}J 1.51 (2-H)	148.25 (3-CH_3)	3.93 (2-H) 3.93 (5-CH_3) ^{2}J 0.66 (1-H)	148.25 (5-CH_3)
5	178.28 (1-H) 174.97 (2-H) ^{2}J 1.3 (3-H)	2.63 (1-H) 1.66 (2-H) ^{1}J 179.97 (3-H)	3.97 (1-H) 3.3 (2-H) 3.97 (3-CH_3) ^{2}J 1.57 (3-H)	147.9 (3-CH_3) ^{4}J 0.47 (3-H)	—	—

^3J(C,H) coupling constants between the carbonyl-carbon atoms and the ring protons. In the presence of $Yb(fod)_3$, the observed downfield shift of the ring carbon signal at 49.34 ppm and of the methoxycarbonyl-carbon signals at 167.44 and 53.97 ppm indicated the *cis* position of this group with respect to the nitrogen lone-pair.

The ^{17}O signals were assigned on the basis of the LIS effects measured in the presence of $Eu(fod)_3$, using the same arguments described before for compound **1**: we assigned the more shielded ^{17}O signals at 350.6 and 136.6 ppm to the ester group *cis* to the nitrogen lone-pair.

N-*Chloro*-2-*methoxycarbonylaziridine* (**5**).—The ^1H ring-proton signals were assigned on the basis[20] of the relation between the spin–spin coupling constants $J(H,H)_{cis} > J(H,H)_{trans} \gg J(H,H)_{gem}$. Following the findings discussed above, we observed that the coupling constant ^1J(C,H) between the proton at 2.76 ppm and the ring carbon at 43.17 ppm was higher (178.28 Hz) than that of the proton at 2.61 ppm (174.97 Hz); accordingly, to the proton at 2.76 ppm we assigned the *cis* orientation to the nitrogen lone-pair.[12] Consequently, it follows that the proton at 3.06 ppm, producing a *cis* and a *trans* ^1J(H,H), is in the *trans* position. Analysis of the ^1H and ^{13}C spectra and the signal assignments attest to the *trans* configuration of the sole isomer obtained by halogenation of the corresponding NH-aziridine.[7]

These results compare well with the *trans* configuration reported in the literature[20] for the *N*-methyl-2-[$^2H_3$]methoxycarbonylaziridine. Furthermore, the ^{13}C and ^{17}O chemical shifts of the ester group in aziridine **5** compared well with those of the ester group *cis* related to the nitrogen lone-pair in aziridines **1**–**4**.

Examination of the ^1H data, reported in Table 1, shows that in all the aziridines **1**–**4** the chemical shifts of the ring-protons (1-H) and of the methyl groups (3-CH_3) *cis* related to the nitrogen lone-pair are upfield of those (2-H and 5-CH_3) in the *trans* position. On the other hand, in derivative **5**, where only one carboxylic group is present, the geminal ring-proton (2-H), *trans* related to the lone-pair, is the more shielded one. In all the compounds examined, the methyl groups display constant chemical shift values, relative to their *cis* or *trans* orientation to the nitrogen lone-pair. Furthermore, ^1H NMR comparison of aziridines **1**, **4** and **5** reveals that the ester groups exert a higher deshielding effect (0.72 ppm) over the geminal ring-proton than over the *cis* ring-proton (0.48 ppm) or the *trans* ring-proton (0.15 ppm).

The ^{13}C chemical shifts of Table 2 indicate that the behaviour noted for ^1H nuclei is also observed for the amidic and ester methyl carbon atoms of aziridines **1**–**5**, namely that the ^{13}C signals relative to the methyl groups *cis* to the nitrogen lone-pair are more shielded than the *trans* ones. An opposite trend appears for the carbonyl carbons: the carbon signals *cis* related to the nitrogen lone-pair are downfield of the *trans* ones. Moreover, all C-5 carbonyl carbons, *trans* to lone-pair, show the same chemical shift close to 164 ppm, while more changes are observed for the C-3 carbonyl carbons *cis* to nitrogen lone-pair. These effects could be closely connected to steric and electronic interactions between the ring-substituents and therefore to changes in molecular geometry.

Larger variations in the C-3 carbonyl carbon chemical shifts could reflect a greater conformational mobility of these carboxylic groups in aziridines **1**–**5** with respect to the C-5 carbonyl carbon ester groups, which are more rigidly orientated. X-ray diffraction analysis[5,6,18] of aziridines **1**–**3** and recent studies into the chiroptical properties of aziridines **4** and **5**,[21] as well as the higher reactivity of the lone-pair *cis* related ester groups towards amidation and hydrolysis reactions,[6] suggest a similar conclusion.

The chemical shift behaviour of the ^{17}O atoms in aziridines **1**–**5**, Table 4, parallels the trend observed for the ring proton signals and for the methyl-proton and carbon signals. ^{17}O signals relative to the carboxylic group *cis* related to the nitrogen lone-pair are more shielded than those in *trans* positions and larger variations in chemical shifts are observed for the *cis* oxygens than for the *trans* ones. These variations would indicate that the *cis* ester group can present a greater variety of conformations than the *trans* group. The deshielding of the latter is probably due to their greater steric interactions with the *cis* chlorine atom.[19]

Comparison between the ^{15}N chemical shifts of aziridines **1**–**5**, Table 4, and that reported for the *N*-chloroaziridine (−330.9 ppm)[22] shows the presence of a deshielding effect due to the electron-withdrawing ring-substituents. In aziridines **1**, **4** and **5**, it seems that each ester group contributes to the deshielding effect on the ^{15}N signals to the same extent (*ca.* 11 ppm) and, in particular for compounds **1** and **4**, irrespective of their position in the ring, while different ^{15}N resonances for isomers **2** and **3** are observed.

Conclusions

The ^1H, ^{13}C, ^{17}O and ^{15}N chemical shift data of aziridines **1**–**5** have been rationalized in terms of their molecular structure. ^nJ(C,H) Coupling constants as well as heteronuclear NMR chemical shift correlations are all consistent and provided detailed configurational and conformational information. In particular, the results indicate that the chemical shift parameters reflect the stereochemistry of the investigated compounds, that is, in all aziridines **1**–**5** the ester group *cis* to the nitrogen lone pair is more shielded than that in *trans*; larger variations of ^1H, ^{13}C and ^{17}O chemical shifts reflect more conformational mobility of the relative carboxylic group. So they can be used to establish the relative configuration of unknown related aziridines.

Experimental

Compounds.—Syntheses of compounds **1**–**5** have been reported previously.[5–7]

NMR Measurements.—The ^1H, ^{13}C, ^{17}O and ^{15}N NMR data were obtained at 300 K on 0.1–0.3 mol dm^{-3} solutions in $CDCl_3$, using a Bruker AMX 400 WB spectrometer operating at 400.13, 100.61, 54.25 and 40.56 MHz, respectively. ^1H and ^{13}C chemical shifts are quoted relative to internal $SiMe_4$. For ^{17}O and ^{15}N the external references are H_2O and CH_3NO_2 (in $CDCl_3$ at 50% w/w), respectively. A typical resolution for ^1H NMR spectra was 0.05 Hz; for decoupled ^{13}C spectra we used a spectral width of 20 kHz with 32 K data points, 45° pulse angle and relaxation delay of 1 s. The ^{17}O spectra (natural abundance) were recorded on the same sample as was used for ^{13}C measurements, without sample spinning. The following parameters were used: spectral width 30 kHz, acquisition time 250 ms, 90° pulse angle and 2–4 × 10^4 scans. Natural abundance ^{15}N NMR spectra were obtained using a refocused INEPT for protonated nitrogens and a modified INEPT for non-protonated nitrogen atoms. For the INEPT experiments the acquisition parameters were as follows: spectral width of 20 kHz with 32 K data points, a relaxation delay of 1–2 s and 5000–10 000 scans. The 90° pulse angle was 22 and 17 μs, respectively, for ^1H and ^{15}N. The delay for the coherence transfer was selected corresponding to a ^1J(N,H) of 90 Hz (refocused INEPT) and a long-range of 4 Hz (modified INEPT).

COSY. The 2D-heterocorrelated spectra were obtained using the standard Bruker software (hxcobi) with H–H decoupling in

F1 with BIRD pulse. The following parameters were used: SW_2 of 25 ppm with 1 K data points; SW_1 of 1.3 ppm with 128 t_1 increments and a relaxation delay of 1 s; 128 scans were used for each of the t_1 increments.

COLOC. The COLOC sequence (standard Bruker software) was employed in order to obtain correlation through a long-range coupling constant of 4 Hz. Two spectra were acquired, one corresponding to the aliphatic region and one to the carbonyl region. The following parameters were used: SW_2 of 20–10 ppm in 2–1 K data points with 128 or 64 scans (4 dummy) and a relaxation delay of 1 or 3 s, respectively. SW_1 of 2 ppm with 128 increments.

HMQC. The sequence was employed in 1D version. A delay of 2.78 ms and a relaxation delay of 1 s were used, with a spectral width and a time domain suitable in order to achieve a resolution of 0.1 Hz.

HMBC. The 2D inverse experiment was performed in order to assign the long-range coupling constants ^nJ(C,H) of each proton to the carbonyl groups. The following parameters were used: SW_2 of 2 ppm with 2 K data points, SW_1 of 10 ppm with 80 increments, a relaxation delay of 1 s and 64 scans for each of the t_1 increments.

LIS Measurements. The LISs on ^1H, ^{13}C and ^{17}O signals were measured in the presence of Yb(fod)$_3$ and Eu(fod)$_3$. The shift reagents, dried *in vacuo* over P_2O_5, were added in known and increasing amounts to the $CDCl_3$ solution. The maximum molar ratio between the shift reagent and the substrate was 0.02.

Acknowledgements

The Authors thank the *Ministero dell'Università e della Ricerca Scientifica e Tecnologica*, Rome, for financial support and the *Centro Strumenti*, University of Modena, for instrumental measurements.

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Paper 4/02370F
Received 21*st April* 1994
Accepted 9*th June* 1994