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INVERTOMERS AT NITROGEN IN AZIRIDINE CARBOXYLATES BY MULTINUCLEAR (^{1}H, ^{13}C, ^{17}O, AND ^{15}N) NMR STUDY

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A configurational and conformational study of NH, N-acetyl- and N-sulfonylaziridine carboxylates is performed by ^{1}H, ^{13}C, ^{17}O, and ^{15}N NMR spectroscopy. The presence of acetyl and sulfonyl groups on the ring nitrogen atom seems to reduce greatly the configurational stability at nitrogen.

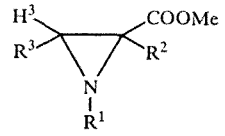
KEY WORDS: NMR; ^{1}H NMR; ^{13}C NMR; ^{17}O NMR; ^{15}N NMR; aziridine-carboxylates; configurational analysis; conformational analysis

INTRODUCTION

Many reports in the literature point out that small heterocycles, such as aziridines, show high ring-strain that strongly influences the nitrogen pyramidal inversion, as well as the electronic, conjugative, and steric effects of the nitrogen substituents [1]. Several methods have been used to determine the nitrogen pyramidal inversion barrier, e.g., microwave and vibrational spectroscopy, dynamic nuclear magnetic resonance (DNMR) spectroscopy, kinetic methods, or molecular orbital (MO) calculations. The reliability of each method depends on the applicability to the particular problem of the theory on which the method itself is based [1].

In this paper, the classical ^{1}H and ^{13}C NMR approach is used and compared with the ^{17}O and ^{15}N NMR approach, in order to study the configurational and conformational stability of NH, N-acetyl and N-sulfonylaziridine-carboxylates **1-8** (Scheme 1).

Scheme 1



1–8

1	$R^1 = H^1$	$R^2 = H^2$	$R^3 = H^{3'}$
2	$R^1 = H^1$	$R^2 = COOMe$	$R^3 = H^{3'}$
3	$R^1 = H^1$	$R^2 = H^2$	$R^3 = COOMe$
4	$R^1 = COMe$	$R^2 = H^2$	$R^3 = H^{3'}$
5	$R^1 = COMe$	$R^2 = COOMe$	$R^3 = H^{3'}$
6	$R^1 = COMe$	$R^2 = H^2$	$R^3 = COOMe$
7	$R^1 = SO_2Me$	$R^2 = H^2$	$R^3 = H^{3'}$
8	$R^1 = SO_2Me$	$R^2 = H^2$	$R^3 = COOMe$

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TABLE 1. ^1H Chemical Shifts (δ, ppm) of Compounds **1-8** at the Highest and the Lowest Measured Temperatures

Compd.	Temp. K	δ_{H-1}	δ_{H-2}	δ_{H-3}	$\delta_{H-3'}$	δ_{OCH_3}	δ other signals[a]
1	320		2,62	2,09	1,96	3,86	
	230	1,20	2,64	2,13	1,98	3,87	
2	320	1,91		2,38[b]		3,90	
	250	2,01		2,41[c]	2,41c	3,92/3,87	
3	320	1,86	2,94[b]			3,84	
	240	2,00	2,97/2,95			3,86/3,81	
4	300		3,22	2,65	2,57	3,87	2,23
	230		3,30	2,69	2,67	3,88	2,29
5	300			2,83[b]		3,85	2,16
	210			2,97[b]		3,92	2,27
	170[d]			3,00[e]		3,87	2,22[f]
6	300		3,45[b]			3,81	2,13
7	300		3,40	2,71	2,85	3,89	3,22
	230		3,46	2,76	2,88	3,90	3,28
8	300		3,74[b]			3,81	3,22

a) Chemical shifts of the nitrogen substituents.

b) Observed signal for both the indicated protons.

c) Values obtained from a simulated spectrum (PCPMR) with $\Delta\nu$ = 3 Hz.

d) In CD_2Cl_2.

e) Very broad.

f) Broad.

TABLE 2. ^{13}C Chemical Shifts (δ, ppm) of Compounds **1-8** at the Highest and the Lowest Measured Temperatures

Compd.	Temp. K	δ_{C-2}	δ_{C-3}	δ_{CO}		δ_{OCH_3}	δ other signals[a]
1	320	29,66	27,98	174,32		53,46	
	230	30,05	28,99	175,08		54,22	
2	320	40,81	33,95	168,4[b]	170,7[b]	53,71/54,29	
	250	40,84	34,64	168,53	170,85	54,44/55,08	
3	320	36,91/36,04		169,93	171,86	53,68/53,43[c]	
	240	37,11/36,37		170,49[d]	172,10[e]	54,59/54,16	
4	300	35,23	31,70	169,68		53,66	181,35/24,52
	220	34,89	32,09	169,98		54,18	182,40/24,90
5	300	45,44	35,90	165,56		53,53	178,41/23,67
	210	45,05	36,59	165,51		54,29	179,71/24,01
	170[f]	45,52	37,34[g]	166,03		54,82	180,12[g]/24,38[g]
6	300	40,90		167,74		54,02	178,37/24,63
7	300	36,11	32,57	168,16		54,00	40,73
	230	35,64	33,50	168,79		54,79	40,76
8	300	43,61		166,45		54,60	42,51

a) Chemical shifts of the nitrogen substituents.

b) At 300 K.

c) Near coalescence.

d) $^3J_{^{13}C,H-1}$ = 5.1 Hz.

e) $^3J_{^{13}C,H-1}$ = 6.2 Hz.

f) In CD_2Cl_2.

g) Very broad signal.

TABLE 3. Coupling Constants [$^{n}J_{^{1}H,^{1}H}$ and $^{1}J_{^{13}C,^{1}H}$] for Aziridines **1-8** at 300 K

Compd.	Temp. K	H-1,H-2	H-1,H-3	H-1,H-3'	H-2,H-3	H-2,H-3'	H-3,H-3'	C-2,H-2	C-3,H-3	C-3,H-3'
1[a]	230	7,31	10,33	8,04	2,87	5,40	1,29	183,8	171,0	178,9
2	250	—	10,5/9,5[b]		—	—	1,0[b]	—	171,7	181,6
3	240	8,88[b]	9,31[b]	—	1,56[b]	—	—	188,1	179,6	—
4	300	—	—	—	2,93	5,49	1,68	180,6	177,4	175,6
5	300	—	—	—	—	—	—	—	178,5	
6	300	—	—	—	—	—	—	178,7		—
7	300	—	—	—	4,17	7,15	0,25	178,3	183,0	173,8
8	300	—	—	—	—	—	—	—	—	—

a) At 300 K no $^{n}J_{^{1}H,^{1}H}$ are evident; a $^{1}J_{C\text{-}2,H\text{-}2}$ of 182.5 Hz and a mean value of 172.3 Hz for the $^{1}J_{^{13}C,^{1}H}$ coupling constant between C-3 and the protons H-3 and H-3′ are observed.

b) Values obtained from simulated spectra (PCPMR).

TABLE 4. ^{17}O[a] and ^{15}N[b] NMR Chemical Shifts of Derivatives **1-8** at 300 K and $^{1}J_{^{15}N,^{1}H}$ Coupling Constants (Hz)

Compd.	^{17}O (δ, ppm)[c]			^{15}N (δ, ppm)
	C=O	C=O	OCH_3	δ / J
1	—	316	135	-362,5/-62
2	355	326	135	-345,0/-65
3	342	324	135	-347,4/-61
4	332[d]		156	-289,9
5	344[d]		138	-279,3
6	342[d]		139	-278,4
7	346	—	155[e]	-296,3
8	349	365	173/165[f]	-281,7

a) ^{17}O chemical shifts (δ) referred to H_2O as external reference.

b) ^{15}N chemical shifts (δ) referred to CH_3NO_2 as external reference.

c) ^{17}O NMR signals of the ring-ester groups.

d) Overlapped resonances of the signals relative to the ester groups and the nitrogen substituents.

e) Overlap to the resonance of the sulfonyl group.

f) Relative to the sulfonyl and methoxy groups.

RESULTS AND DISCUSSION

The ^{1}H, ^{13}C, ^{17}O, and ^{15}N measurements are carried out in $CDCl_3$ solutions in non-anhydrous conditions. Protic impurities or water in trace could be expected to influence the inversion rate of NH-aziridines **1-3**, in particular [1, 2].

^{1}H and ^{13}C chemical shift data (*d*) and coupling constants (*J*) of derivatives **1-8** are reported in Tables 1-3. The relative signal assignments are made on the assumption that the $^{1}J(^{13}C,^{1}H)$ coupling constants are ~ 10 Hz greater for the ring-protons *cis* than those *trans* to the nitrogen lone-pair [2] and on the basis of the relation between the $J(^{1}H, ^{1}H)$ coupling constants $^{3}J(cis) > {}^{3}J(trans) > {}^{2}J(gem)$ [2, 3].

The direct coupling constants $^{1}J(^{13}C,^{1}H)$ were assigned and determined using HMQC experiments in 1D and 2D versions. The correct numerical values were determined from high-resolution ^{13}C-coupled spectra.

The ^{17}O and ^{15}N NMR chemical shifts of aziridines **1-8** are reported in Table 4.

NH-2-methoxycarbonylaziridine (1). At 320 K the ^1H NMR spectrum of compound **1** (Table 1) displays a broad signal at 1.15 ppm for H-1, a doublet at 1.96 ppm for H-3′, a sharp quartet at 2.09 ppm for H-3, a broad quartet at 2.62 ppm for H-2 and a sharp signal at 3.86 ppm for the methyl group. The lack of $^3J(^1H, ^1H)$ coupling constants between the ring protons and H-1 in the spectrum is the evident consequence of a process of exchange with residual water. On lowering the sample temperature to 270 K, the proton signals broaden. At 230 K, the ^1H spectrum displays one set of signals for each proton and allows $^3J(^1H, ^1H)$ coupling constants of 7.31, 10.33, and 8.04 Hz between H-1 and H-2, H-3, and H-3′, respectively, to be detected (Table 3). The ^3J values are consistent with a *cis* relationship between the nitrogen substituent (H-1) and the ester group, thus indicating the main presence of a *cis* invertomer at 230 K, as reported in the literature for **1** at room temperature in $C_6D_5CD_3$ and in anhydrous conditions [2].

The $\{^1H\}$-^{13}C NMR spectra of aziridine **1**, recorded in $CDCl_3$ in the range 320-230 K (Table 2), display an inversion process. At 320 K the C-3 signal at 27.98 ppm is broader than that of the C-2 at 29.66 ppm and the acyl carbon signal at 174.32 ppm is so broad that is difficult to detect. A $^1J(^{13}C, ^1H)$ coupling constant of 182.5 Hz, between C-2 and H-2 and a mean value of 172.3 Hz for the $^1J(^{13}C, ^1H)$ coupling constant between C-3 and H-3 and H-3,′ are determined.

At low temperature (230 K), sharp signals for each carbon are detected and three distinct $^1J(^{13}C, ^1H)$ coupling constants measured: 183.8 Hz between C-2 and H-2; 178.9 Hz between C-3 and H-3′ and 171.0 Hz between C-3 and H-3 (Table 3). The spectrum clearly shows that only one invertomer is largely predominant at low temperature and, from the $^1J(^{13}C, ^1H)$ values, that we are in the presence of a *cis* invertomer [2].

The ^{17}O NMR measurement at 300 K supplies a signal at 316 ppm relative to acyl oxygen and a signal at 135 ppm for methoxy oxygen (Table 4).

The ^{17}O chemical shift values assigned the ester group in a *cis* position with respect to the NH proton by comparison with the data obtained for derivatives **2** and **3**. The ^{17}O measurements seem to indicate that the *cis* invertomer is already predominant at room temperature; this could be not inferred from ^1H and ^{13}C data. The ^{15}N NMR measurement at 300 K gives a signal at -362.5 ppm with a $^1J(^{15}N, ^1H)$ coupling constant of -62 Hz (Table 4).

NH-2,2-bismethoxycarbonylaziridine (2). The ^1H NMR spectrum of **2,** recorded at 320 K in non-anhydrous conditions, shows the presence of two related dynamic processes: the exchange of H-1 with residual water or protic impurities and nitrogen inversion. A signal at 1.91 ppm for the nitrogen substituent (H-1), at 2.38 ppm for the H-3 and H-3′ ring-protons and at 3.90 ppm for the two methyls are observed at 320 K. The shape of these signals is influenced by the non-anhydrous environment, as indicated by the loss of the vicinal coupling constants between H-3 and H-3′ with H-1 above 300 K. At a lower temperature (250 K), the methyl signal splits into two signals of equal intensity at 3.92 and 3.87 ppm, as expected from a process of slow inversion. On cooling to 250 K, the ring-protons H-3 and H-3′, which are indistinguishable at 320 K, form the AB part of an ABX system with a chemical shift difference of 3 Hz and register $^3J(^1H, ^1H)$ coupling constants of 10.5 Hz and 9.5 Hz with H-1.

In order to monitor the nitrogen inversion barrier in **2**, we referred to the ^1H methyl signals, whose shape is unaffected by the intermolecular exchange process. ΔG^* was estimated [4] to be 15.5 ± 0.3 kcal·mole^{-1} at 305 K ($\Delta\nu$ CH_3 = 22.9 Hz; coalescence temperature is between 300 K and 310 K). This value agrees well with that reported in the literature [5] in anhydrous conditions.

In the ^{13}C NMR timescale the inversion process is already slow at 320 K: in the $\{^1H\}$-^{13}C spectrum two broad signals of equal intensity at 53.71 and 54.29 ppm for the methyl carbon atoms and two very broad signals (at the detection limit), at 168.4 and 170.7 ppm, for the acyl carbon atoms are detected. On the basis of the downfield effect of the intramolecular hydrogen bond [6] the signal at 170.7 ppm was assigned to the ester group *cis* to the NH bond. The methyl and acyl carbon atom signals become sharper on cooling to 250 K and the presence of two different $^1J(^{13}C, ^1H)$ coupling constants of 171.7 and 181.6 Hz between C-3 and H-3 and H-3′, respectively, reflects a slow inversion process. The ΔG^* for the nitrogen inversion barrier was calculated from a total line-shape analysis, performed with the DNMR3 software [7] in the range 270-320 K. This afforded a value of 15.6 ± 0.7 kcal·mole^{-1} at 300 K, as obtained from the above-reported ^1H-DNMR analysis.

The ^{17}O NMR chemical shifts reported in Table 4 indicate a slow inversion process at 300 K on the ^{17}O timescale. Two different signals of equal intensity, at 355 and 326 ppm, are observed for the acyl oxygens and only one, at 135 ppm, for the methoxy oxygens. Since the hydrogen bond has a shielding effect on the resonance of the involved oxygen [8] the assignment of the two acyl oxygens is straightforward. The resonances at 355 and 326 ppm were assigned to the ester groups *trans* and *cis*, respectively, to the NH bond.

The ^{15}N NMR measurement at 300 K affords a signal at -345 ppm with a $^1J(^{15}N, ^1H)$ coupling constant of -65 Hz.

NH-2,3-bismethoxycarbonylaziridine (3). The behavior of derivative **3**, in the temperature range 240-320 K, parallels that of derivative **2**. Between 320 K and 290 K, the averaged ^{1}H NMR spectrum displays three singlets, corresponding to the different protons: δH-1 at 1.86 ppm, δH-2 and δH-3 at 2.94 ppm and the methyl protons at 3.84 ppm. On cooling to 240 K, the methyl signal splits into two lines of equal intensity at 3.86 and 3.81 ppm and the ring-protons display chemical shifts at 2.97 and 2.95 ppm. From the simulated spectrum (PCPMR) a ^3J(H-1, H-2) coupling constant of 8.88 Hz and a ^3J(H-1, H-3) coupling constant of 9.31 Hz are calculated.

The ^{13}C NMR spectrum of **3** at 320 K displays two signals, at 36.91 and 36.04 ppm, for the C-2 and C-3 ring-carbon atoms, two signals at 169.93 and 171.86 ppm for the two acyl-carbon atoms and two signals at 53.68 and 53.43 ppm for the methoxy groups. At 240 K it is possible to measure a $^1J(^{13}C, ^1H)$ coupling constant of 179.6 Hz for the carbon atom at 37.11 ppm and one of 188.1 Hz for the carbon atom at 36.37 ppm. These values indicate that the carbon atom at 36.37 ppm bears the ring-proton *cis* to the nitrogen lone-pair.

The ΔG^*, obtained from the total line-shape analysis of the ^{13}C carbomethoxy-carbon signals in the range 240-320 K, is of 15 $\pm$ 1 kcal·mole^{-1}.

The inversion process is slow on the ^{17}O timescale at 300 K, as already noted for aziridine **2**: two different signals of equal intensity at 342 and 324 ppm for the acyl oxygens and a signal at 135 ppm for the methoxy oxygens are observed. The signal at 342 ppm was assigned to the ester group *trans* to the NH bond.

The ^{15}N NMR measurement of **3** at 300 K affords a signal at −347.4 ppm with a $^1J(^{15}N, ^1H)$ coupling constant of −61 Hz.

The comparison of ^{15}N NMR chemical shifts of aziridines **1-3** shows that the introduction of a further electron-withdrawing substituent, such as a carboxylic group, in the ring of **1** leads to a deshielding of about 10-18 ppm of the nitrogen signal [9].

N-Acetyl-2-methoxycarbonylaziridine (4). At room temperature, the ^{1}H NMR spectrum of **4** displays a signal at 3.22 ppm for H-2, at 2.65 ppm for H-3 and at 2.57 ppm for H-3′. Two singlets, one at 3.87 and the other at 2.23 ppm, are observed for the methyl protons of the ester and acetyl groups, respectively. At the same time, the ^{13}C NMR spectrum displays a signal at 35.23 ppm for C-2, at 31.7 ppm for C-3, at 169.68 and at 53.66 ppm for the carbon atoms of the ester group and at 181.35 and 24.52 ppm for the carbon atoms of the acetyl group. When **4** was studied in $CDCl_3$ in the range 300-230 K and in C_6D_6 in the range 300-330 K, temperature variation failed to bring about a nitrogen inversion process in either the ^{1}H or the ^{13}C NMR timescale, nor were any significant changes in the spectra observed. At room temperature, the $^1J(^{13}C, ^1H)$ coupling constants between the C-3 ring-carbon atom and the geminal protons H-3 and H-3′ are 177.4 and 175.6 Hz, respectively: this slight difference (2 Hz) could result from the competition of several effects, e.g., the nitrogen lone-pair and the nitrogen substituent effects [3] or from a fast nitrogen inversion [10].

The ^{17}O NMR spectrum of **4** displays a signal at 332 ppm due to the overlapping of the acetyl- and acyl-oxygen resonances, and a signal at 156 ppm relative to methoxy-oxygen. The ^{15}N NMR spectrum displays a signal at −289.9 ppm.

N-Acetyl-2,2-bismethoxycarbonylaziridine (5). The spectra of aziridine **5**, studied in $CDCl_3$ in the range 300-210 K, do not reveal any variation related to a nitrogen inversion process. At 300 K, only a^{1}H NMR signal at 2.83 ppm (2.97 ppm at 210 K) for the two geminal ring protons and at 3.85 ppm (3.92 ppm at 210 K) for the two methyl-ester groups are detected. The ^{13}C NMR spectrum displays only one signal at 165.56 ppm for the two acyl carbon atoms and another at 53.53 ppm for the two methoxy carbons. A $^1J(^{13}C, ^1H)$ coupling constant of 178.5 Hz is evident.

Measurements in CD_2Cl_2 reveal hindered rotation about the N-C(O) bond in the temperature range 210-170 K. On cooling, the ^{13}C acetyl signal at 179.71 ppm and the C-3 signal at 36.59 ppm progressively broaden, whereas the ^{13}C signal of the ester groups and the C-2 carbon signal are only slightly affected. The ^{1}H NMR spectrum indicates the broadening of the geminal-proton signal and, to a lesser extent, of the acetyl proton signals. No variation in the ester-group resonances is noted, which probably indicates that the rotation process could be part of the nitrogen inversion. No more information was obtained from the ^{17}O measurements owing to the overlap of the ^{17}O acetyl- and carboxy-oxygen signals: only one signal at 344 ppm for these oxygens and another at 138 ppm for the methoxy oxygens are detected.

The ^{15}N NMR chemical shift of aziridine **5** is at −279.3 ppm.

N-Acetyl-2,3-bismethoxycarbonylaziridine (6). The ^{1}H NMR spectrum of **6**, recorded at 300 K, displays only one signal at 3.45 ppm for the ring-protons and another at 3.81 for the methoxy groups. The ^{13}C NMR spectrum, at the same temperature, displays a signal at 40.90 ppm relative to the ring-carbon atoms and a $^1J(^{13}C, ^1H)$ of 178.7 Hz. Two signals, at 167.74 and 54.02 ppm, respectively, for the carbomethoxy carbon atoms and at 178.34 and 24.63 ppm, respectively, for the

acetyl carbon atoms, are detected. The ^{17}O NMR spectrum displays a signal at 342 ppm relative to both the acyl and the acetyl oxygens and one at 139 ppm for the methoxy oxygens. The ^{15}N NMR spectrum displays a signal at −278.4 ppm.

The ^{15}N chemical-shift values of aziridines **4-6**, compared with those of aziridines **1-3**, reveal a marked deshielding effect of the nitrogen substituent: this could indicate a conjugative effect between the nitrogen and the acetyl group, as supported by the ^{17}O chemical shift value of 344 ppm for the acetyl oxygen, typical of an amidic oxygen [8].

1-Methylsulfonyl-2-methoxycarbonylaziridine (7). The ^1H and ^{13}C NMR spectra of this derivative, studied in $CDCl_3$ in the temperature range 300-230 K and in C_6D_6 in the temperature range 300-350 K, do not reveal the presence of different isomers. At room temperature, the ^1H NMR spectrum of **7** displays a signal at 3.40 ppm for H-2, at 2.71 ppm for H-3, at 2.85 for H-3′ and at 3.89 and 3.22 ppm for the methyl protons. The^{13}C NMR spectrum displays a signal at 36.11 ppm for C-2, at 32.57 ppm for C-3, at 168.16 and 54.00 ppm for the carbomethoxy carbon atoms and at 40.73 ppm for the methylsulfonyl carbon atom. No linewidth or $^1J(^{13}C, ^1H)$ significant changes are observed in the examined temperature range. In particular, at 300 K the ^{13}C NMR spectrum displays a $^1J(^{13}C, ^1H)$ coupling constant of 178.3 Hz between C-2 and H-2 and two $^1J(^{13}C, ^1H)$ coupling constants of 183.0 Hz and 173.8 Hz between C-3 and the geminal protons H-3 and H-3′, respectively. This enables us to assign to the proton H-3, which displays higher $^1J(^{13}C, ^1H)$, a *cis* relationship with the nitrogen lone-pair,[2,3] indicating the presence of a predominant *trans*- invertomer. This result agrees with that reported in literature for aziridine **7** on the basis of the $^2J(^{15}N, ^1H)$ coupling constant [2].

The ^{17}O NMR spectrum displays a signal at 346 ppm for acyl oxygen and a signal at 155 ppm due to the overlap of the resonances of the sulfonyl and methoxy groups.

The ^{15}N NMR spectrum displays a signal at −296.3 ppm.

1-Methylsulfonyl-2,3-bismethoxycarbonylaziridine (8). The ^1H and ^{13}C NMR spectra of **8** at 300 K display average signals owing to rapid interconversion between two invertomers. A signal at 3.74 ppm for the ring-protons H-2 and H-3 and another at 3.81 ppm for the two methyl-ester groups are detected. The ^{13}C NMR spectrum displays a signal at 43.61 ppm for the C-2 and C-3 ring-carbon atoms and two signals, at 166.45 and 54.6 ppm, respectively, for the carbomethoxy carbon atoms. At 300 K the ^{17}O NMR spectrum shows two signals of equal intensity at 349 and 365 ppm, respectively, for the two CO's and two signals, at 173 and 165 ppm, respectively, for the methoxy and the sulfonyl groups. The downfield acyl oxygen signal is assigned to the ester group *cis* to the N-sulfonyl substituent on the basis of the deshielding due to steric compression [8, 9].

The ^{15}N NMR spectrum displays a signal at −281.7 ppm.

CONCLUSION

The results of the ^1H, ^{13}C, ^{17}O, and ^{15}N NMR measurements of aziridines **1-8** show that the stereodynamic processes are generally slower in the ^{17}O than in the ^1H and ^{13}C NMR timescales. The nitrogen inversion barriers in NH aziridines **1-3** are calculated to be of about 15.6 kcal·mole^{-1}. The ^1H and ^{13}C NMR spectra at 230 K and the ^{17}O measurements, at room temperature, reveal the presence of a predominant *cis* invertomer for aziridine **1**.

It is well known that an acyl substituent at the ring nitrogen atom in three-membered heterocycles, such as aziridines [11] or oxaziridines [12], greatly reduce the nitrogen inversion barrier. Nevertheless, the ground state configuration of nitrogen in N-acylaziridines is reported to be strongly pyramidal and the barrier to N-C(O) rotations much lower than that for amides [11]. The ^1H, ^{13}C and ^{17}O NMR measurements of N-acetylaziridines **4-6** reveal average spectra, even at low temperature, with variations that can be attributable to a slower rotation about the N-C(O) bond. On cooling, we observed a slowing down of the rotation around the N-C(O) bond before the presence of an inversion process was apparent. The ^{17}O and ^{15}N chemical shift values of the amido group in aziridines **4-6** seem to indicate, at room temperature, a conjugation between the nitrogen and the acetyl substituent. This effect could drastically lower the nitrogen inversion barrier of these derivatives to NH aziridines **1-3**, thus stabilizing the planar transition state. Nevertheless, amide conjugation in aziridines **4-6** seems weaker than that of conventional amides, which increases the degree of pyramidality of the nitrogen atom in the ground state: on cooling to 170 K, there is no coalescence to afford the torsional barriers about the N-C(O) bond. The stereochemical lability of the nonplanar amide group is confirmed by the observation that the optically active compound **4** does not display thermal epimerization [13].

An N-sulfonyl substituent seems to reduce the configurational stability of nitrogen in aziridines. The ^1H and ^{13}C NMR measurements of N-sulfonylaziridines **7-8** reveal averaged spectra at room temperature, which would indicate a rapid interconversion between the invertomers at nitrogen. Nevertheless, the ^{13}C NMR spectra of aziridine **7** seem to suggest the

presence of a predominant *trans* invertomer. Since there is no *trans-cis* thermal isomerization of optically active aziridine **7** [13], the *trans* isomer would appear to represent a thermodynamic product control rather than a kinetic preference, as reported in the literature for N-sulfonyl oxaziridines [14].

EXPERIMENTAL

Syntheses. Racemic compounds **1-8** and optically active compounds **4** and **7** were synthesized as reported elsewhere [15]. Aziridine **5** (R 95%) was obtained by acetylation of **2** with acetic anhydride in pyridine at 40°C, following the procedure already described for compound **4** [15].

NMR measurements. The ^{1}H, ^{13}C, ^{17}O, and ^{15}N NMR spectra were obtained on 0.1 mol dm^{-3} solutions in $CDCl_3$ (unless specified), at 400.13, 100.61, 54.25, and 40.56 MHz, respectively, using a Bruker AMX 400 WB spectrometer equipped with a variable temperature controller unit (Eurotherm).

^{1}H and ^{13}C are quoted relative to $SiMe_4$. ^{17}O and ^{15}N NMR measurements refer to the H_2O and CH_3NO_2 (in $CDCl_3$ 50% v/v), respectively, as external references.

For coupled and proton-decoupled ^{13}C spectra, typical conditions were: 0.8-1 s for relaxation delay; 60° pulse angle; spectral widths of 18 kHz with 32k data points.

The sequence employed in the inverse-detection HMQC [16] method was that performed by the standard Bruker software in 1D and 2D version. A delay of 2.78 ms and a relaxation delay of 1 s were used for the 1D experiments; for the 2D experiments the following parameters were adopted: SW_2 of 3 ppm with 2k data points; SW_1 of 60 ppm with 128 increments; a relaxation delay of 1s and 16 scans (4 dummy) for each t_1 increment.

The ^{17}O NMR spectra (natural abundance) were recorded on the same solution as employed for ^{13}C measurements without sample spinning and with the lock on. The instrumental settings were: spectral width, 33 kHz; acquisition time, 250 ms; 90° pulse angle and 20-60 $\times$ 10^3 scans.

Natural abundance ^{15}N NMR spectra were obtained using different procedures including INEPT for protonated nitrogen and a modified INEPT [17] for nonprotonated nitrogen atoms. For the INEPT experiments the acquisition parameters were the following: spectral width of 20 kHz with 32k data point; a relaxation delay of 1-2 s and a number of 5000-10,000 scans. ^{1}H $P_w(90°)$ = 22 ms, ^{15}N $P_w(90°)$ = 17 ms. The delay for the coherence transfer corresponded to $^{1}J(^{15}N,^{1}H)$ of 90 Hz (for INEPT) and a long range of 4 Hz (for modified INEPT).

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