Structural Characterization of (±)-N-Chloro-2,2-bis(methoxycarbonyl)aziridine by X-Ray Crystallography and 2D NMR Spectroscopy

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The X-ray crystal structure analysis for racemic N-chloro-2,2-bis(methoxycarbonyl)aziridine is reported. The complete assignments of the ¹H, ¹³C and ¹⁷O chemical shifts are performed using 2D NMR techniques (C–H COSY, COLOC) to establish unequivocally the relative configuration of the aziridine.

Racemic N-chloro-2,2-bis(methoxycarbonyl)aziridine (1) was synthesized by chlorination of the corresponding NH-aziridine as reported in the literature.[1] Compound 1 shows interesting oxidizing properties and is a good unnatural substrate for enzymatic reactions[2] as well as a versatile intermediate for the synthesis of chiral 2-amidoaziridines.[3]

We now report on the structural characterization of (±)-1 by X-ray diffraction analysis and 2D NMR spectroscopy.

Results and Discussion

Synthesis.—The NH-2,2-bis(methoxycarbonyl)aziridine was obtained by reaction of dimethyl 2-bromo-2-bromomethyl-malonate with ammonia in dried acetonitrile (51% yield) by analogy with the synthesis of the NH-2,2-bis(ethoxycarbonyl)-aziridine.[4] The crude NH-aziridine was halogenated with *tert*-butyl hypochlorite in dichloromethane solution to give the corresponding N-chloroaziridine 1 in 80% yield (Scheme 1). The

COOCH₃ | CH₂Br — NH₃/CH₃CN → COOCH₃ — NH — Bu'OCl/CH₂Cl₂ → COOCH₃ — N—Cl
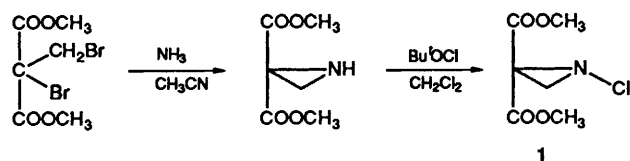
Scheme 1

compound, which is a colourless crystalline solid, was subjected to X-ray diffraction analysis after crystallization from diethyl ether–pentane.

X-Ray Crystal Structure.—The crystal structure of 1 is built up of racemic pairs of discrete molecules, whose bond distances and angles are reported in Table 1, the atoms being labelled as shown in Fig. 1. The dimensions of the aziridine ring compare well with those previously observed in other N-substituted chloro derivatives, such as the racemic 1-chloro-2,2-diphenylaziridine (2)[5] and (−)-(E)-1-chloro-2-methoxy-carbonyl-2-methylcarbamoylaziridine (3).[6] A common feature of these compounds appears to be the marked lengthening of only one of the two C–N ring bond distances [1.501(2), 1.510(5) and 1.508(2) Å in 1, 2 and 3, respectively] with respect to the value of 1.474(3) Å retrieved from the Cambridge Crystallographic Database for saturated C₂N rings.[7] Since there is a linear relationship between the heteroatom electronegativity and the ring bond distances,[7] this lengthening may be attributed to an increased electronegativity at the N atom determined by the Cl substituent. Nevertheless, the expected parallel shortening of the C–C bond distance[7] [1.488(2), 1.474(6) and 1.486(3) Å in 1, 2 and 3, respectively, which compare well with the values of 1.484(4) Å from CCD[7]] was not observed. There was also very good agreement between the Cl–N bond

Table 1 Bond distances/Å and bond angles/° involving non-hydrogen atoms

Cl–N	1.757(1)	N–C(1)	1.469(2)
N–C(2)	1.501(2)	C(1)–C(2)	1.488(2)
C(2)–C(3)	1.504(2)	C(3)–O(1)	1.190(2)
C(3)–O(2)	1.330(2)	O(2)–C(4)	1.442(2)
C(2)–C(5)	1.498(2)	C(5)–O(3)	1.198(2)
C(5)–O(4)	1.314(2)	O(4)–C(6)	1.443(2)

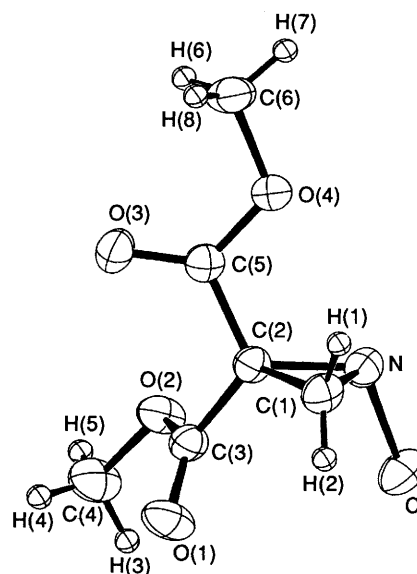| Cl–N–C(1)	112.5(1)	Cl–N–C(2)	112.1(1)
C(1)–N–C(2)	60.1(1)	N–C(1)–C(2)	61.0(1)
N–C(2)–C(1)	58.9(1)	N–C(2)–C(3)	118.3(1)
N–C(2)–C(5)	116.1(1)	C(1)–C(2)–C(3)	118.8(1)
C(1)–C(2)–C(5)	118.5(1)	C(3)–C(2)–C(5)	114.9(1)
C(2)–C(3)–O(1)	125.0(1)	C(2)–C(3)–O(2)	109.9(1)
O(1)–C(3)–O(2)	125.1(1)	C(3)–O(2)–C(4)	116.2(1)
C(2)–C(5)–O(3)	122.2(1)	C(2)–C(5)–O(4)	112.0(1)
O(3)–C(5)–O(4)	125.6(1)	C(5)–O(4)–C(6)	115.7(1)

Fig. 1 ORTEP[21] plot of the molecule with atom numbering scheme. Thermal ellipsoids for non-H atoms enclose 40% probability.

distances, which range from 1.757(1) Å in 1 to 1.755(4) and 1.758(1) Å in 2 and 3. In the present case, the N-substituent bond makes an angle of 64.0° with the ring plane and has valence angles of 112.5(1)° and 112.1(1)°, which are very close to those observed in 2 and 3. These values are significantly different from that of 55.5(5)° for the bond-plane and of 119.3(6)° for the valence angle, averaged over many other N-substituted aziridines.[7] It is interesting to note that, in all cases,

Table 2 ^{1}H, ^{13}C and ^{17}O NMR spectral parameters for ($\pm$)-N-chloro-2,2-bis(methoxycarbonyl)aziridine (1)
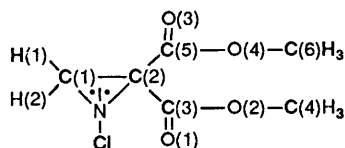
	$\delta(^{1}H)^{a}$		$\delta(^{13}C)^{b}$		$\delta(^{17}O)^{c}$
H(1)	2.91	C(1)	46.90		
H(2)	3.06	C(2)	52.43		
		C(3)	164.05	O(1)	349.1
C(4)H	3.97	C(4)	54.56	O(2)	136.5
		C(5)	166.48	O(3)	364.2
C(6)H	3.87	C(6)	54.39	O(4)	143.2

^{a} ppm downfield from TMS as internal standard; solution 0.1 mol dm^{-3} in CDCl$_{3}$ at 300 K. ^{b} ppm downfield from TMS as internal standard; solution 0.5 mol dm^{-3} in CDCl$_{3}$ at 300 K. ^{c} ppm downfield from H$_{2}$O as external reference in a coaxial tube; solution 0.5 mol dm^{-3} in CDCl$_{3}$ at 300 K; signal width $\Delta w_{1/2} = 300$ Hz.

Table 3 Coupling constants ^{n}J (C–H) and J (H–H) in Hz of ($\pm$)-N-chloro-2,2-bis(methoxycarbonyl)aziridine

$^{1}J_{(C-H)}$		$^{2}J_{(C-H)}$		$^{3}J_{(C-H)}$		$J_{(H-H)}$	
C(1)–H(1)	180.17	C(2)–H(1)	2.71	C(3)–H(1)	4.04	H(1)–H(2)	2.97
C(1)–H(2)	176.01	C(2)–H(2)	2.71	C(3)–H(2)	2.85		
C(4)–H	148.50			C(3)–Me	4.04		
C(6)–H	148.50			C(5)–H(1)	2.71		
				C(5)–H(2)	3.30		
				C(5)–Me	3.94		

the chlorine substituent is involved in short van der Waals contacts, which range from 2.950 Å in **2** to 3.273 Å in **1**. The pyramidal N atom lies 0.782 Å out of the plane defined by its three bonded atoms. The orientation of the planar methoxy-carbonyl groups appears to be determined by crystal packing requirements; their mean planes make dihedral angles of 63.2° and 79.7° with the aziridine ring plane and of 64.4° with each other. The molecular packing is determined by many (18) short (< 3.60 Å) van der Waals interactions involving mainly carbonyl oxygens. The shortest one [O(3)···C(5)] corresponds to 3.170(2) Å.

NMR Spectra.—The ^{1}H, ^{13}C and ^{17}O NMR spectra of aziridine **1** were recorded in order to assign the proper signal to each group or atom in the molecule and so establish unequivocally the relative configuration between the substituents on the aziridine ring; complete and unambiguous assignments of ^{1}H, ^{13}C and ^{17}O chemical shifts of aziridine **1** are listed in Table 2. ^{13}C Assignments were carried out using a 2D-heteronuclear chemical shift correlated spectrum (C–H COSY)[8] and a heteronuclear correlated spectrum *via* long-range coupling (COLOC spectra);[9] ^{17}O assignments were performed by the analysis of the induced shifts measured on the spectrum recorded in the presence of the shift reagent tris(8,8,8,7,7,6,6-heptafluoro-2,2-dimethyl-3,5-octanedionato)-ytterbium, Yb(fod)$_{3}$.

Chemical shifts of groups or atoms in small heterocycles, like aziridines and oxaziridines, are reported[10] to depend on the shielding effect of the nitrogen lone-pair electrons and the magnetically anisotropic effects of the nitrogen substituents. It is from the combinations of the two effects that the observed chemical shift arises. It seems that the effect of the nitrogen lone-pair on the chemical shift of adjacent groups or atoms in the aziridine ring is reversed on passing from N-unsubstituted to N-

substituted aziridine. It has been observed[10] that the shielding effect of the nitrogen lone-pair on the *cis*-related ring protons predominates in N-unsubstituted aziridines, while a shielding effect by the N-substituent on the ring protons *cis* to the N-bond and *trans* to the lone-pair is observed in N-alkyl and N-chloroaziridines.[11] Nevertheless, in N-alkoxyaziridines it has been observed that the shielding effect of the nitrogen lone-pair predominates over the effect of the N–OR substituent.[11]

The ^{1}H NMR spectrum of **1** in deuteriochloroform solution showed two signals at 3.87 and 3.97 ppm for the two diastereotopic methyl groups and two signals at 2.91 and 3.06 ppm, each resolved into a doublet (J 2.97 Hz), for the two geminal diastereotopic protons of the aziridine ring. From the ^{1}H NMR spectra of the corresponding *cis* and *trans* mono-amidic derivatives,[3] we would assign the upfield methyl group to the ester substituent *cis* to the nitrogen lone-pair in spite of the known[10] shielding effect of the N-substituent. In order to make the correct assignments and to evaluate the relative shielding effect of the nitrogen lone-pair and/or of the N-chloro substituent on the observed chemical shifts, two-dimensional NMR methods (C–H COSY, COLOC) were employed. From the 1D-^{13}C NMR spectrum, the chemical shifts of each carbon atom of the molecule **1** were determined and reported in Table 2. The chemical shift assignments of the carbons attached to protons were performed using the 2D heteronuclear chemical-shift correlated spectrum (C–H COSY): C(4) and C(6) methyl carbons at 54.56 and 54.39 ppm, respectively, were correlated with the proton chemical shifts at 3.97 and 3.87 ppm, respectively. At the same time, the signals of the C(3) and C(5) carbonyl carbons at 164.05 and 166.48 ppm, respectively, were correlated with the proton methyl chemical shifts by using the COLOC spectrum: it was found that the more-shielded carbonyl carbon, at 164.05 ppm, is bonded to the more-deshielded methoxy group. On the basis of the literature,[12] and the known shielding effect of the N-chloro substituent,[13] we assigned the ^{13}C upfield carbonyl carbon signal to the group *cis* to the N-substituent and *trans* to the nitrogen lone-pair. This assignment was supported by the coupling constant analysis. The direct coupling constants ^{1}J (C–H) and the long-range coupling constants ^{n}J (C–H), measured from ^{13}C 1D-NMR spectrum, are reported in Table 3. Direct coupling constants were assigned using the 1D-inverse HMQC technique,[14] while the long-range coupling constants were assigned by the 2D-heteronuclear long-range correlation spectrum (COLOC). It has been reported[15] that the magnitude of nuclear spin coupling constants are affected by the presence of lone-pair electrons: in the case of N-alkyl aziridines,[16] a larger ^{1}J (C–H) has been observed for the ring proton *cis* to the nitrogen lone-pair than for the *trans* ring proton. Therefore, from the experimental values of the direct coupling constants ^{1}J [C(1)–H(1)] and ^{1}J [C(1)–H(2)] of 180.17 and 176.01 Hz, respectively, we assigned the *cis* orientation of H(1) at 2.91 ppm with respect to the nitrogen lone-pair and the *trans* relationship between H(2) at 3.06 ppm and the lone-pair. This assignment also agrees with the observed ^{3}J (C–H) coupling constants between the carbonyl carbons and the ring protons H(1) and H(2). The long-range coupling constant ^{3}J (C–H) values depend on the dihedral angles delineated by the atoms in question, according to a Karplus-like relationship.[17,18] Although ring strain effects and high perturbations of the electronegative ester substituents made a theoretical ^{3}J calculation for **1** difficult, the experimental values are consistent with the X-ray determined dihedral angles. Corresponding to the dihedral angles $\angle$ H(1)–C(1)–C(2)–C(3) and $\angle$ H(2)–C(1)–C(2)–C(5) of 152.4 and 211.4°, respectively, a ^{3}J [C(3)–H(1)] of 4.04 Hz and a ^{3}J [C(5)–H(2)] of 3.30 Hz were measured. Coupling constants, ^{3}J [C(3)–H(2)] of 2.85 Hz and ^{3}J [C(5)–H(1)] of 2.71 Hz, were determined between atoms related by dihedral angles

∠ H(1)–C(1)–C(2)–C(5) of 4.3° and ∠ H(2)–C(1)–C(2)–C(3) of −0.4°. The largest ^3J values suggest a transoid orientation of H(1) and H(2) with respect to C(3) and C(5), respectively.

The ^{17}O NMR spectrum of 1 displayed a signal for each oxygen of the two diastereotopic carboxylic groups (Table 2). ^{17}O Assignments were performed by correlations of the reagent-shift Yb(fod)$_3$-induced effect on the ^{17}O chemical shifts as well as on the ^{13}C and ^1H chemical shifts of 1. The LIS measurements (molar ratio shift reagent/substrate, 0.02) showed a more evident downfield shift of the ^{17}O signals at 364.2 and 143.2 ppm as well as for the carbon signals C(5) and C(6) and the C(6)–H proton and the ring proton H(1) signals. Accordingly, we were able to ascertain that the downfield carbonyl and methoxy oxygens were attributable to the carboxylic group cis to the nitrogen lone-pair.

Thus, the NMR assignments reported in Table 2 show that the carbonyl carbon and oxygen signals of the carboxylic group cis to the nitrogen lone-pair are deshielded with respect to the trans ones, while the chemical shifts of protons cis to the lone-pair are shielded, as already observed for N-methoxy-2,2-bis(methoxycarbonyl)aziridine.[11]

These results seem to indicate that the anisotropic effects of the carbon ring substituents, together with the nitrogen lone-pair and N-substituent, also play an important role on the observed proton chemical shifts.

Experimental

NMR Measurements.—^1H, ^{13}C and ^{17}O NMR spectra were recorded on a Bruker AMX-400Wb spectrometer at 400.13, 100.61 and 54.25 MHz, respectively, and at 300 K. ^1H and ^{13}C chemical shifts are reported in δ values from TMS as internal standard (s singlet, d doublet, m multiplet). ^1H and ^{13}C spectra were recorded, respectively, on a 0.1 mol dm^{-3} and a 0.5 mol dm^{-3} solution of compound 1 in CDCl$_3$: a spectral width of 2000 Hz with 32 K data points, 45° pulse angle and 64 scans were used for ^{13}C. Coupling constant values J are given in Hz. No attempts were made to determine the relative sign of ^nJ (C–H) coupling constants.

The ^{17}O spectrum (natural abundance) was recorded on the same solution as employed for ^{13}C measurement without sample spinning and with the lock on. The chemical shifts are given in δ values from H$_2$O as external reference in a coaxial tube. The instrument settings were: spectral width 33 kHz, acquisition time 250 ms, 90° pulse angle and 2.10^4 scans.

COSY.—The 2D-heterocorrelated spectrum was performed using the standard Bruker software (hxcobi) with H–H decoupling in F$_1$ using BIRD pulse and a one-bond coupling constant value of 160 Hz. The following parameters were adopted: SW$_2$ 30.5 ppm in 2 K data points; SW$_1$ 1.3 ppm and 1 s relaxation delay; 256 t_1 increments were sampled using 32 scans (4 dummy) for each of the t_1 increments to a maximum value of 0.245 76 s.

COLOC.—The COLOC sequence (standard Bruker software) was employed to obtain correlations through long-range coupling constants ^nJ (C–H), using a delay value for the long-range correlation selected in order to follow the evolution of a J of 4 Hz. The spectrum was acquired with a spectral range of 30.5 ppm in 4 K data points, a SW$_1$ of 1.36 ppm, a relaxation delay of 1 s and using 128 scans (4 dummy) for each of the t_1 increments to a maximum value of 0.117 63 s.

HMQC.—The sequence employed in the inverse-detection HMQC method was that performed by the standard Bruker software (inv4nd1d) in the 1D-version. A delay of 2.78 ms and a relaxation delay of 1 s were used.

LIS Measurements.—LIS measurements on ^1H, ^{13}C and ^{17}O were performed with the shift reagent Yb(fod)$_3$, dried *in vacuo* over phosphorus pentaoxide and added in known and increasing amounts to the CDCl$_3$ solution (0.5 mol dm^{-3}) of the substrate 1. The maximum molar ratio between Yb(fod)$_3$ and the substrate was 0.02.

Syntheses.—GLC analyses were performed on a Hewlett-Packard 5890 A gas-chromatograph (capillary column DB-1, 5 μm, 30 m × 0.53 mm I.D.). Mass spectra were determined on a Hewlett-Packard 5970 mass selective detector. Melting points are uncorrected. Light petroleum refers to the fraction boiling at 30–50 °C.

Dimethyl methylenemalonate. This was synthesised from dimethyl malonate and formaldehyde as described in the literature[4] for the synthesis of diethyl methylenemalonate; yield 60%, b.p. 155–160 °C (20 mmHg).

Dimethyl α,β-dibromomethylenemalonate. This was obtained by bromination[4] of the dimethyl methylenemalonate in tetrachloromethane solution at 0–5 °C; yield 60%; m/z 223 (M$^+$ − HBr).

NH-2,2-Bis(methoxycarbonyl)aziridine. To a solution of NH$_3$ (6.7 g, 0.4 mol) in dried acetonitrile (200 cm^3) was added dimethyl α,β-dibromomethylenemalonate (30 g, 0.1 mol) at 0 °C. The mixture was kept at room temperature for 24 h, then the solvent was removed and the product extracted with diethyl ether. After removal of the solvent, the residue was purified by column chromatography (silica gel, 50:50 light petroleum–diethyl ether as eluent) to obtain the aziridine as an oil (8 g, 51%), b.p. 82–84 °C (0.04 mm Hg); δ$_H$ 1.85 (1 H, m), 2.24 (1 H, m), 2.3 (1 H, m) and 3.83 (6 H, s); m/z 159 (M$^+$).

N-Chloro-2,2-bis(methoxycarbonyl)aziridine (1). *tert*-Butyl hypochlorite (0.01 mol) was added dropwise to a stirred solution of the NH-aziridine (1.6 g, 0.01 mol) in dichloromethane (30 cm^3) cooled to −5 °C. After 1 h, the reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (silica gel, 50:50 light petroleum–diethyl ether as eluent) to yield the racemic derivative 1 (1.6 g, 80%). Crystallization from diethyl ether–pentane afforded pure crystals, m.p. 52–53 °C; δ$_H$ 2.91 (1 H, d), 3.06 (1 H, d), 3.87 (3 H, s) and 3.97 (3 H, s); m/z 193 (M$^+$).

Crystal Data.—C$_6$H$_8$ClNO$_4$, M = 189.59, monoclinic, a = 23.286(2), b = 5.996(1), c = 13.532(1) Å, $β$ = 117.81(1)°, V = 1671.1 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically-centred reflections, $λ$ = 0.710 69 Å), space group C2/c (no. 15), Z = 8, D_m = 1.49 g cm^{-3}, D_c = 1.507 g cm^{-3}, $F(000)$ = 800. Colourless, air-stable prisms. Crystal dimensions 0.38 × 0.30 × 0.28 mm, $μ$(Mo-Kα) = 3.7 cm^{-1}.

Data Collection and Processing.—CAD4 diffractometer, ω/2θ mode with ω scan width = 0.70 + 0.35 tanθ. ω scan speed 1.2–4.1 deg min^{-1}, graphite-monochromated Mo-Kα radiation; 1893 reflections measured (1.5 ≤ θ ≤ 26°, ±h,k,l) giving 1386 with I > 3σ(I); 1296 unique [merging R = 0.006] used, without absorption correction, in the structure analysis. No crystal decay during collection.

Structure Analysis and Refinement.—Direct methods (SHELX 86)[19] followed by full-matrix least-squares refinement (SHELX 76).[20] All non-hydrogen atoms anisotropic, and hydrogens (located in ΔF Fourier maps) isotropic, with common temperature factors for those bonded to the same atom. The weighting scheme w = 1/[σ^2(F_0 + 0.0008 F_0^2)], with σ(F_o) from counting statistics gave satisfactory agreement analyses. Final R and R_w values are 0.027 and 0.032. Scattering factors from SHELX 76.[19] All calculations carried out on a VAX 6310 computer. Final atomic coordinates are given in Table 4. A full

Table 4 Final fractional coordinates

Atom	x	y	z
Cl	0.914 33(2)	0.323 63(7)	0.599 08(4)
N	0.835 95(6)	0.353 7(2)	0.585 6(1)
C(1)	0.823 45(8)	0.198 8(2)	0.657 4(1)
C(2)	0.837 25(6)	0.437 0(2)	0.691 2(1)
C(3)	0.901 83(7)	0.497 3(2)	0.787 6(1)
O(1)	0.936 04(6)	0.372 2(2)	0.859 2(1)
O(2)	0.915 50(5)	0.709 7(2)	0.779 6(1)
C(4)	0.974 23(9)	0.795 9(3)	0.870 5(2)
C(5)	0.781 94(6)	0.584 2(2)	0.677 0(1)
O(3)	0.783 75(6)	0.696 7(2)	0.751 6(1)
O(4)	0.732 14(5)	0.565 8(2)	0.576 81(9)
C(6)	0.673 75(8)	0.679 7(3)	0.560 4(2)

list of hydrogen atom coordinates, thermal parameters, bond lengths and angles involving H atoms, least-squares planes, torsion angles, and shortest intermolecular distances has been deposited at the Cambridge Crystallographic Data Centre.*

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

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