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STEREOSPECIFIC CHEMICAL SHIFTS AND COUPLING CONSTANTS IN ^{15}N-OXAZIRIDINES

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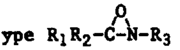
Oxaziridines of the type  $R_1R_2\text{-}C\text{-}N\text{-}R_3$ are known to exist in *cis*- and *trans*-isomeric forms due solely to noninversion at the pyramidal nitrogen center.[3] However, unequivocal assignment of relative stereochemistry between the substituents on the oxaziridine ring has not yet been possible. We present a method for assignment for oxaziridines having a hydrogen substituent at C-3 on the oxaziridine ring based on i) proton nmr line position of the 3-CH, ii) previously unreported stereospecificity of ^{15}N coupling to the 3-CH, and iii) correlation with two oxaziridines whose structures are known from x-ray crystallography.

Synthesis of oxaziridines containing ^{15}N (Table 1) was achieved by oxidation of the corresponding ^{15}N-imines with (+)-peroxycamphoric acid or *m*-chloroperoxybenzoic acid. Condensation of ^{15}N-amine hydrochlorides (methyl, *i*-propyl, *t*-butyl) with aldehydes (4-nitro or 4-bromo-2,6-dimethylbenzaldehyde) in triethylamine solvent (sealed tube, 15 hrs., 100°) provided the required ^{15}N-imines in high yield. The ^{15}N-amines[4] were obtained by Hoffman reaction on the appropriate amides derived initially from $^{15}NH_3$ (97% ^{15}N).

Chemical shifts and coupling constants for the ^{15}N-oxaziridines are given in Table 1. The structures of both **5** *trans*[5] and **2** *cis*[6] have been determined by x-ray crystallography. The earlier x-ray study was done when only the single isomer of **5** was available and before it was recognized that oxaziridines do not readily invert at the nitrogen center.

For all structures assigned the *cis*-configuration, the chemical shift for the 3-CH falls in the region δ = 5.1 - 5.4 ppm; for the four compounds possessing the nitrophenyl substituent the value is almost constant at 5.35 ppm. For the *trans* compounds the 3-CH chemical shift is in the range 4.5 - 4.8 ppm. Apparently the line position of the 3-CH can thus be used as a general method for distinguishing between such isomeric pairs; the signal for the *trans*-isomers always appearing at higher field by 0.5 - 0.8 ppm.

For all examples investigated the 3-CH is coupled to the ^{15}N with J = 4.8 - 5.4 Hz for the *cis*-isomers, while J $\sim$ 0 for the *trans*-isomers. This striking dependence of $^2J_{^{15}N\text{-}H}$ upon the orientation of the 3-CH relative to the nitrogen lone pair electrons has parallel in other systems. For example, Lehn and co-workers showed that in several oximes and related molecules containing the grouping $H\text{-}C{=}^{15}N$ $^2J_{^{15}N\text{-}H}$ was much larger for the *anti* configuration than for *syn*,[7] and that in ^{15}N-formaldoxime the two geminal $H\text{-}C{=}^{15}N$ coupling constants are opposite in sign.[8] They attributed the large coupling constant primarily to the *cis* arrangement of the proton and the nitrogen lone-pair electrons. The importance of lone pair orientation on coupling constants in three-membered ^{14}N containing rings was suggested for aziridines[9] but had not previously been demonstrated unequivocally.

Experiments are under way to determine the sign of $^2J_{^{15}N-H}$ in the *cis*-oxaziridines.

Table 1. Chemical shifts in *cis* and *trans*-oxaziridines[a]

$R_1HC\overset{O}{-}N-R_2$		δ(3-CH) (ppm)[b]		$^2J_{^{15}N-H}$ (Hz)[c]	
R_1	R_2	*cis*	*trans*	*cis*	*trans*
1 4-nitrophenyl	methyl	5.34	4.60	5.4	0
2 4-nitrophenyl	*i*-propyl[d]	5.36	4.61	5.0	0
3 4-nitrophenyl	*t*-butyl[e]	----	4.79	---	0
4 4-nitrophenyl	benzyl	5.37	4.78	5.3	0
5 4-bromo-2,6-dimethylphenyl	methyl[d]	5.08	4.55	4.8	0

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[a] Compounds 1 *cis*, 4 *cis*, and 5 *cis* have not been reported previously. Their assigned structures are consistent with their uv, ir, and nmr spectra, as well as their high active oxygen content (>90%).[10] Physical data for the remaining compounds compared favorably with those of the known ^{14}N-analogues. [b] From TMS (internal). [c] No splitting observed; apparently J < 0.5 Hz for all *trans* isomers. [d] Structures of 2 *cis* and 5 *trans* determined by x-ray crystallography. [e] *Cis* isomer has never been observed.

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