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STEREOSPECIFIC GEMINAL $^{15}N,H$ COUPLING CONSTANTS IN 2-(α-NAPHTHYL)AZIRIDINE-^{15}N *[1]

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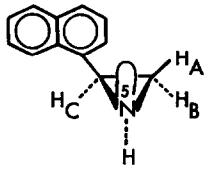
Lehn and co-workers have recently reported that the magnitude of $J_{N,H(gem)}$ strongly depends upon the orientation of lone-pair electrons on the nitrogen (1-3). Absolute values of $J_{^{15}N,H(gem)}$ were found to be much larger for an anti proton (10-16 Hz) than for a syn proton (2-4 Hz) in several oximes and related compounds (1, 2); the two $J_{^{15}N,H(gem)}$ values have opposite signs in formaldoxime-^{15}N (2). In tetrahydro-1,3-oxazine-^{15}N, $|J_{^{15}N,H(4-eq)}|$ has a larger value (~1.5 Hz) than $|J_{^{15}N,H(4-ax)}|$ (~0 Hz) (3).

Such stereospecific $J_{N,H(gem)}$ can be expected to occur also in aziridines in which the hybridizations of the N and intervening C atoms are different from those in the compounds studied so far. In previous papers (4), we suggested the contribution of lone-pair orientation to the magnitudes of $J_{N,H(gem)}$ in 1-alkylaziridines. Recent papers on the results with 1-chloroaziridine (5) and oxazine-^{15}N (6) have prompted us to report here our results on 2-(α-naphthyl)aziridine-^{15}N (I), which was obtained by treatment (7) of the α-acetylnaphthalene oxime-^{15}N (97% ^{15}N) with LAH in refluxing THF.



(I)

$^{15}N,H$ spin couplings between ^{15}N and 3-membered ring protons in I were clearly seen to determine their relative signs in the 100 MHz spectra, while the N-H signal appears as a singlet showing that the exchange of N-H is rapid. The signals of ring protons were assigned on the basis of the fact that

*[1] NMR Studies of Aliphatic Nitrogen-Containing Compounds. Part X. For Part IX, see Ref. 4b.

$J_{H,H(cis)} > J_{H,H(trans)} > J_{H,H(gem)}$ in aziridine rings (4). The population of the N-H configuration anti to the naphthyl group is inferred to be much larger than that of the syn configuration by taking account of the benzene-induced shifts of the ring protons (see the Table) (4b, 8) and by the analogy of 2-methylaziridine.*2 This inference determined the assignments of $J_{^{15}N,H}$'s, which depend on the orientation of the lone-pair on ^{15}N.

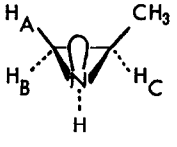
TABLE
PMR Parameters of 2-(α-Naphthyl)aziridine-^{15}N[a]

Solvent	Chemical shift (τ) H_A	H_B	H_C	J_{H_A,H_B}	J_{H_A,H_C}	J_{H_B,H_C}	$J_{^{15}N,H_A}$	$J_{^{15}N,H_B}$	$J_{^{15}N,H_C}$
$CDCl_3$	8.22	7.74	6.54	0.7	3.6	5.9	(-)3.6	(-)1.4	(-)1.7
C_6D_6	8.65	8.32	7.01	1.1	3.4	6.0	(-)4.6	(-)0.8	(-)1.1
	(0.43)[b]	(0.58)[b]	(0.47)[b]						
CD_3CN	8.46	7.76	6.53	1.2	3.5	6.1	(-)4.8	(-)0.4	>(-)0.6
$(CD_3)_2SO$	8.52	7.78	6.53	1.4	3.3	6.1	(-)4.9	>(-)0.3	>(-)0.7

[a] All spectra were taken with a Varian HA-100 spectrometer operating at 100 MHz in the frequency-swept and TMS-locked mode. Proton double resonance experiments were performed by using a Hewlett-Packard HP-200ABR audio-oscillator and HP-5212A electronic counter. [b] Benzene-induced shifts, $\Delta\tau = \tau_{C_6D_6} - \tau_{CDCl_3}$.

PMR parameters of I thus obtained are listed in the Table. The relative signs of the $J_{^{15}N,H}$ values were found to be the same. As seen from the Table, $|J_{^{15}N,H_C}|$ values are always larger than $|J_{^{15}N,H_B}|$ values. This fact results from the higher electronegativity of the naphthyl group than that of the hydrogen atom, and suggests that the $J_{^{15}N,H(gem)}$ values are absolutely negative on the assumption that the trend of the change in $J_{^{15}N,H(gem)}$ induced by electronegative α-substituents is similar to that of the change in $J_{H,H(gem)}$ (9). Theoretically calculated $J_{^{15}N,H(gem)}$ values previously reported (10) agree with the

*2 $J_{^{13}CH}$ values in 2-methylaziridine (II) indicate that the anti configuration of the N-H is more stable than the syn configuration; $J_{^{13}CH_A}$ and $J_{^{13}CH_B}$ were observed to be 168.6 and 166.8 Hz, respectively (our unpublished results). The larger $J_{^{13}CH}$ value has been confirmed to correspond to that between ^{13}C and the proton cis to the nitrogen lone-pair in 1-alkylaziridines (4a).



(II)

present result. Solvent dependence of $J_{^{15}N,H(gem)}$ values is probably due to both the solvent effect as seen in oximes (2) and to the differences in the population of the N-H configurations in various solvents.

The observation that the $J_{^{15}N,H(gem)}$ values in I lie between those for $^{15}N{=}CH$ (1, 2) and $^{15}N{-}CH$ (3) is suggestive of the π-bond character of N-C bonds in aziridine, although $J_{N,H(gem)}$ values depend also upon their bond angles. Studies of N,H spin couplings in other aziridines are now in progress in this laboratory.

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