^{15}N CHEMICAL SHIFTS OF 2-SUBSTITUTED AZIRIDINES

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The ^{15}N NMR spectra of 2-substituted aziridines were studied, and a linear dependence between the ^{15}N and $^{13}C_3$ resonances was observed. The ^{15}N chemical shifts correlate with the Taft σ^* inductive constants and the E_S steric constants.

The ^{15}N resonance of aziridines has not been studied. Only the ^{15}N chemical shift for an undiluted solution of aziridine itself (δ ^{15}N 387.2 ppm) is known [1]. In order to investigate the factors that affect the shielding of the ^{15}N nucleus we studied the NMR spectra of some 2-substituted aziridines (Table 1).

The shielding of the ^{15}N nucleus in the aziridine ring is appreciably greater than in other cyclic amines [1, 2]; this is explained [1] by the effect of the diamagnetic ring currents in the aziridine ring. The ^{13}C chemical shifts in aziridine have been similarly interpreted [3]. The observation of a linear relationship between the ^{15}N and ^{13}C resonances in the spectra of 2-substituted aziridines constitutes evidence for the similarity in the factors that affect the shielding of the ^{13}C and ^{15}N nuclei in the aziridine ring:

$$\delta\,^{13}C_3 = -438.84 + 2.71\delta\,^{15}N;\ r = 0.992;\ s = 1.1.$$

It is apparent that the ^{15}N resonance is 2.7 times more sensitive than the ^{13}C resonance to the effects of substituents. This may be due in part to the differences in the lengths of the C–N and C–C bonds in aziridines [4]. However, a greater sensitivity of the ^{15}N resonance to the effects of substituents has also been observed in other cyclic amines [2].

The ^{15}N chemical shifts correlate with the Taft σ^* inductive constants and the E_S steric constants:

$$\delta\,^{15}N = -393.3 - 15.6E_s + 5.2\sigma^*;\ r = 0.945;\ s = 2.3.$$

TABLE 1. ^{15}N and ^{13}C Chemical Shifts (ppm) of 2-Substituted Aziridines

Compound[a]	Substituent	δ ^{15}N of aziridine	δ ^{15}N of the substituent	δ $^{13}C_3$
I	H	−390,4	—	18,2
II [9]	CH_3	−370,7	—	25,8
III [9]	C_2H_5	−372,8	—	24,7
IV [12][b]	$CONH_2$	−366,4	−273,3	26,8
V [12][b]	$CONHNH_2$	−367,2	−248,8 (NH), −324,5 (NH_2)	25,7[c]
VI [13]	CH_2NH_2	−375,3	−363,6	23,4[d]
VII [10]	CN	−367,0	−138,4	25,8
VIII [11]	$COOCH_3$	−364,3	—	27,4[e]
IX [9]	2,2-$(CH_3)_2$	−351,9	—	32,5

[a] The literature citations to the method of synthesis are presented. [b] The spectra were obtained from solutions in d_6-DMSO. [c] Other signals: 29.3 (C_2) and 171.4 ppm (C=O). [d] Other signals: 32.5 (C_2) and 45.6 ppm (CH_2). [e] Other signals: 29.2 (C_2), 174.5 (C=O), and 52.9 ppm (CH_3).

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Consequently, the ^{13}C chemical shifts in 2-substituted aziridines also depend both on σ^* and the volume of the substituents.

EXPERIMENTAL

The ^{13}C and ^{15}N NMR spectra were obtained with a WH 90/DS spectrometer under pulse conditions with noise decoupling of the protons. The pulse durations were 5 μsec for ^{13}C and 15 μsec for ^{15}N, and the time lag between pulses was 2 μsec. The substances were studied in the form of 50% solutions in deuterochloroform, and the ^{13}C chemical shifts were measured relative to cyclohexane (δ 27.44 ppm) as the internal standard, whereas the ^{15}N chemical shifts were measured relative to nitromethane as the external standard. The accuracies in the measurements for ^{13}C and ^{15}N were ±0.06 ppm and ±0.2 ppm, respectively. The ^{13}C chemical shifts for I-IV, VI, and IX were borrowed from [5, 6]. The E_S and σ^* constants were taken from [7, 8].

LITERATURE CITED

1. R. L. Lichter and J. D. Roberts, J. Am. Chem. Soc., 94, 2495 (1972).
2. R. O. Duthaler, K. L. Williamson, D. D. Gianni, W. H. Bearden, and J. D. Roberts, J. Am. Chem. Soc., 99, 8406 (1977).
3. G. E. Maciel and G. B. Savitsky, J. Phys. Chem., 69, 3925 (1965).
4. P. A. Gembitskii, D. S. Zhuk, and V. A. Kargin, The Chemistry of Ethyleneimine [in Russian], Nauka, Moscow (1966), p. 48.
5. P. Mison, R. Chaabouni, Y. Diab, R. Martino, A. Lopez, A. Lattes, F. W. Wehrli, and T. Wirthlin, Org. Magn. Reson., 8, 79 (1976).
6. K. Jaehnisch, E. Schmitz, and G. Gruendeman, J. Prakt. Chem., 321, 712 (1979).
7. S. H. Unger and C. Hansch, in: Physical Methods in Organic Chemistry, Vol. 12, New York (1976), p. 91.
8. Yu. A. Zhdanov and V. I. Minkin, Correlation Analysis in Organic Chemistry, Izd. Rostovsk. Univ. (1966), p. 312.
9. G. D. Jones, J. Org. Chem., 9, 484 (1944).
10. Z. Burzin and K. Enderer, Angew. Chem., 84, 108 (1972).
11. S. A. Giller, A. V. Eremeev, I. Ya. Kalvin'sh, É. É. Liepin'sh, and V. G. Semenikhina, Khim. Geterotsikl. Soedin., No. 12, 1625 (1975).
12. I. Ya. Kal'vin'sh and E. B. Astapenok, Belgian Patent No. 860239; Chem. Abstr., 90, 34103 (1978).
13. J. D. Spivack, U.S. Patent No. 2931804; Chem. Abstr., 55, 1651 (1960).