2. É. A. Mistryukov, N. I. Aronova, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 932 (1961).
3. I. N. Nazarov and V. A. Rudenko, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 6, 610 (1948).
4. G. Ellies and R. G. Jones, J. Chem. Soc., Perkin Trans, 2, No. 4, 437 (1972).
5. J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, J. Am. Chem. Soc., 92, 1338 (1970).
6. A. J. Jones, A. F. Casy, and V. M. McErlane, J. Can. Chem., 51, 1782 (1973).
7. É. A. Mistryukov and N. I. Aronova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2171 (1966).
8. S. Biniecki and B. Gutkowska, Acta Pol. Pharm., 23, 201 (1966).

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^{13}C–^{13}C SPIN-SPIN COUPLING CONSTANTS IN THE SPECTRA OF MONOSUBSTITUTED PYRIDINES

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The ^{13}C–{^{1}H} NMR spectra of pyridine and a number of monosubstituted pyridines for compounds with the natural percentage of the ^{13}C isotope were analyzed. The direct, geminal, and vicinal ^{13}C–^{13}C spin-spin coupling constants (SSCC) were determined. Linear relationships that link the ^{13}C–^{13}C SSCC in the spectra of monosubstituted pyridines and benzenes were obtained.

Researchers have recently become interested in ^{13}C–^{13}C spin-spin coupling constants (SSCC) for the study of structures and electronic structures [1-4]. The ^{13}C–^{13}C SSCC depend on the degree of hybridization of the coupling carbon atoms, the nature of the substituents, and the three-dimensional structure of the molecule and vary over a wide range from −20 Hz in the case of bicyclobutanes to +200 Hz in the case of acetylenes [4].

Systematic investigations of the ^{13}C–^{13}C SSCC have not been made for heteroaromatic compounds, and constants for only individual heterocycles (for example, furan, thiophene, pyrrole, and pyridine [5]) have been presented in the literature. Theoretical calculations of the ^{13}C–^{13}C SSCC in the spectra of aromatic compounds [6, 7] are in poor agreement with the experimental values, and this makes it necessary to use empirical rules that are frequently based on additive equations. Their effectiveness for nitrogen-containing heterocycles has been demonstrated in the case of ^{13}C–^{1}H SSCC [8].

The aim of the present research was to measure the ^{13}C–^{13}C SSCC in the spectra of monosubstituted pyridines and to search for empirical relationships between the constants for pyridines and benzenes.

The ^{13}C NMR spectrum of pyridine (with complete spin decoupling of the protons) is presented in Fig. 1. The set of lines in the vicinity of the principal signals of the ^{13}C isotopmers corresponds to the signals for molecules that contain two ^{13}C isotopes. In the general case the amplitude of the signals is on the order of 1/200 of the principal signal, and the ^{13}C–^{13}C SSCC are readily determined as the distances between the lines of the doublets.

The ^{13}C–^{13}C SSCC found for monosubstituted pyridines are presented in Table 1. In analogy with benzenes [4, 7], the direct and vicinal constants are assumed to be positive. The geminal ($^{2}J_{CC}$) constants were obtained only in some cases due to their small values (less than 3.5 Hz, except for $^{2}J_{2,6}$) and superimposition of the lines of these signals on the principal signal of the ^{13}C isotopomer. The $^{2}J_{2,6}$ values are two times greater than the geminal constants observed for benzenes.

The results of a comparison of the ^{13}C–^{13}C SSCC for monosubstituted pyridines and benzenes [7] (for the direct and vicinal constants) are presented in Table 2. For methyl benzo-

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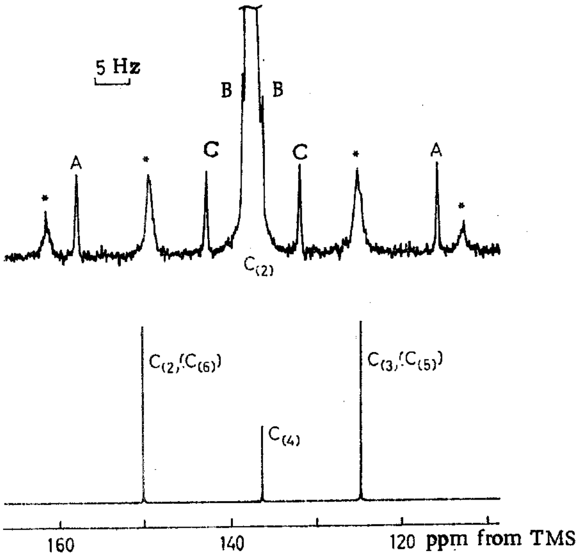

Fig. 1. $^{13}C-\{^{1}H\}$ NMR spectrum of pyridine [the complete spectrum and the region in the vicinity of the signal of the $^{13}C_{(2)}$ isotopomer]. The distances between the identically designated signals in the upper spectrum correspond to: A) $^{1}J_{2,3}$; B) $^{2}J_{2,4}$; C) $^{3}J_{2,5}$ (the rotational satellites are denoted by asterisks).

TABLE 1. $^{13}C-^{13}C$ SSCC (Hz) for Monosubstituted Pyridines

m*	Substituent	$^{1}J_{2,3}$	$^{1}J_{3,4}$	$^{1}J_{4,5}$	$^{4}J_{5,6}$	$^{3}J_{2,5}$	$^{3}J_{3,6}$	$^{2}J_{CC}$
—	H	54,26	53,68	53,68	54,26	13,95	13,95	$J_{2,4}=2,87$
2	Me†	56,2	54,7	54,2	54,7	13,2	12,4	$J_{2,6}=5,8$
	CN	61,6	53,6	53,9	52,9	14,6	12,1	—
	CO_2Me	59,6	53,8	53,7	53,5	12,9	12,2	—
	OMe	70,7	57,6	53,6	57,0	11,7	9,7	$J_{3,5}=3,5$
	F	75,4	55,7	54,4	56,0	12,2	8,8	—
	Cl	67,4	54,1	54,3	55,3	13,1	10,5	$J_{3,5}=3,3$
	Br	64,9	53,3	54,4	55,4	13,1	10,9	$J_{2,6}=5,6$
3	Me	55,4	55,1	54,3	54,6	12,6	13,3	$J_{2,6}=6,5$
	CN	58,6	58,4	54,6	53,4	13,0	15,6	$J_{2,6}=6,8$
	CO_2Me	57,4	56,8	54,3	53,5	12,6	13,2	—
	OMe	66,1	64,6	55,2	54,9	10,5	13,6	$J_{2,6}=6,8$
	F	70,3	68,8	54,2	54,2	9,9	15,5	$J_{2,6}=6,8$
	Cl	62,4	63,0	53,5	54,3	11,2	16,1	$J_{2,6}=6,8$
	Br	59,9	61,4	52,9	54,3	11,8	16,2	$J_{2,6}=6,7$
4	Me	54,9	54,7	54,7	54,9	12,6	12,6	—
	CN	54,3	58,5	58,5	54,3	13,3	13,3	—
	CO_2Me	54,4	57,1	57,1	54,4	12,7	12,7	—
	OMe	56,2	64,2	64,2	56,2	10,5	10,5	—
	Cl	53,6	62,5	62,5	53,6	11,3	11,3	—
	Br	52,7	60,8	60,8	52,7	11,8	11,8	—

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*Here and subsequently, m is the position of the substituent in pyridine.

†The $^{1}J_{CC}$ constants for spin-spin coupling with the carbon atom of the substituent are as follows: 51.4, 44.2, and 42.9 Hz for Me (m = 2, 3, 4) and 75.7 and 74.5 Hz for CO_2Me (m = 3, 4) (not determined for CN).

ate, to supplement the data in [7], we obtained the $^{3}J_{2,5}$ (8.8 Hz) and $^{2}J_{2,4}$ (2.5 Hz) constants and refined the $^{1}J_{1,2}$ constant (58.7 Hz). The best linear dependences were found for the direct $^{1}J_{CC}$ constants with participation of the substituted carbon atoms (the $^{1}J_{1,2}$ type in benzenes), which have the greatest ranges of change, as well as for the vicinal constants, which correspond (with respect to the substituent) to $^{3}J_{2,5}$ for monosubstituted benzenes. Certain deviations for chloro and bromo substituents are observed in the case of the correlation of the $^{1}J_{2,3}$ constants for 3-substituted pyridines and the $^{1}J_{1,2}$ constants for benzenes, and exclusion of these values from the correlation substantially increases its quality (Table 2); such effects are not observed in the remaining cases. The ranges of change in the direct $^{1}J_{CC}$ con-

TABLE 2. Linear Correlations of the Direct and Vicinal ^{13}C–^{13}C SSCC for Monosubstituted Pyridines (J^{pyr}) and Benzenes (J^{benz}) [7] of the Type $J^{pyr} = a \cdot J^{benz} + b$ (Hz)

m	J^{pyr}	R	S	J^{benz}	a	b	J^{pyr} (ΔJ^{pyr})*
2	$^1J_{2,3}$	0,996	0,70	$^1J_{1,2}$	1,383	−22,38	63,8 (21,1)
	$^1J_{3,4}$	0,846	—	$^4J_{2,3}$	—	—	54,6 (4,3)
	$^1J_{4,5}$	0,443	—	$^1J_{3,4}$	—	—	54,0 (0,8)
	$^1J_{5,6}$	0,824	—	$^1J_{3,4}$	—	—	54,9 (4,1)
	$^3J_{2,5}$	0,526	—	$^3J_{1,4}$	—	—	13,1 (2,9)
	$^3J_{3,6}$	0,995	0,18	$^3J_{2,5}$	1,503	−1,17	11,3 (5,2)
3	$^1J_{2,3}$†	0,982	1,11	$^1J_{1,2}$	1,029	−3,59	60,5 (16,0)
		(0,999)	(0,11)		(1,075)	(−5,87)	
	$^1J_{3,4}$	0,999	0,26	$^1J_{1,2}$	0,986	−1,22	60,2 (15,1)
	$^1J_{4,5}$	0,960	0,21	$^1J_{2,3}$	0,823	7,77	54,1 (2,3)
	$^1J_{5,6}$	0,895	—	$^1J_{3,4}$	—	—	54,2 (1,5)
	$^3J_{2,5}$	0,997	0,11	$^3J_{2,5}$	1,229	1,72	11,9 (4,0)
	$^3J_{3,6}$	0,925	—	$^3J_{1,4}$	—	—	14,7 (3,0)
4	$^1J_{2,3}$	0,983	0,22	$^1J_{2,3}$	1,210	−13,68	54,3 (3,5)
	$^1J_{3,4}$	0,994	0,47	$^1J_{1,2}$	0,921	2,54	58,8 (10,5)
	$^3J_{2,5}$	0,986	0,22	$^3J_{2,5}$	1,237	1,72	12,3 (3,5)

*The average J^{pyr} value and the range of change (in parentheses) in hertz.

†Data for the case of exclusion from the correlation of the constants for the chloro and bromo derivatives are given in parentheses.

stants for pyridines that do not include substituted carbon atoms are relatively small, and their average values are numerically close to the constants for pyridine. The vicinal $^3J_{1,4}$ constants for benzenes and the corresponding constants for pyridines correlate poorly with one another. It must be noted that the data were obtained for highly concentrated solutions of the compounds and that the effect of the solvents and the concentration on the ^{13}C–^{13}C SSCC was not investigated (according to the data in [4], a difference of 0.5 Hz is permissible for the direct constants).

Thus we have demonstrated a linear interrelationship for the ^{13}C–^{13}C SSCC for pyridines and benzenes that can be used to predict the constants for nitrogen-containing heteroaromatic compounds.

EXPERIMENTAL

The ^{13}C–{^1H} NMR spectra were recorded with a Bruker WP-200 SY spectrometer operating under pulse conditions at a frequency of 50.33 MHz. Stabilization was realized with respect to the NMR signal of the deuterium of the solvent (d_6-acetone). The concentration of the solutions for most of the compounds was 80% (by volume). Lower concentrations were used for a number of the compounds: 60% for 3-Br-, 3-CN-, and 3-OMe-pyridines and 40% for 2-CO_2Me-, 3-CO_2Me-, 2-CN-, and 4-CN-pyridines and methyl benzoate.

The spectra were recorded under the following conditions: a 10-mm ampul was used, the volume of the sample was 2 ml, the width of the spectra was up to 2 kHz (the digital resolution was better than 0.12 Hz), the number of accumulations ranged from 400 to 2500, the lag between pulses was 10 sec, the spectra were obtained under conditions of complete spin decoupling of the protons, and the temperature was 28 ± 2°C.

The spectra of each isotopomer that contained two ^{13}C nuclei were calculated as AB spin systems, where A and B are ^{13}C nuclei. The initial chemical shifts of the ^{13}C nuclei were taken from [9, 10]. The isotopic chemical shifts due to replacement of a second ^{12}C nucleus were determined from calculations and ranged from 0.005 to 0.035 ppm to strong field for the directly bonded atoms and were less than ±0.005 ppm for the atoms through two or three bonds. The error in the determination of the ^{13}C–^{13}C SSCC was on the order of 0.1 Hz (0.05 Hz for pyridine).

The investigated compounds were obtained by the method in [11]; their physical constants were in agreement with the values presented in the literature.

LITERATURE CITED

1. V. Wray, in: Progress in NMR Spectroscopy, Vol. 13, Pergamon Press, Oxford (1979), p. 177.
2. P. E. Hansen, Org. Magn. Reson., 11, 215 (1978).
3. P. E. Hansen and V. Wray, Org. Magn. Reson., 15, 102 (1981).
4. L. B. Krivdin, Master's Dissertation, Irkutsk (1982), p. 170.
5. F. J. Weigert and J. D. Roberts, J. Am. Chem. Soc., 94, 6021 (1972).
6. S. A. T. Long and J. D. Memory, J. Magn. Reson., 44, 355 (1981).
7. V. Wray, L. Ernst, T. Lund, and H. J. Jakobsen, J. Magn. Reson., 40, 55 (1980).
8. A. Yu. Denisov, V. I. Mamatyuk, and O. P. Shkurko, Khim. Geterotsikl. Soedin., No. 7, 986 (1985).
9. A. Yu. Denisov, V. I. Mamatyuk, and O. P. Shkurko, Khim. Geterotsikl. Soedin., No. 9, 1223 (1984).
10. A. Yu. Denisov, V. I. Mamatyuk, and O. P. Shkurko, Khim. Geterotsikl. Soedin., No. 7, 948 (1984).
11. A. Weissberger (editor), The Chemistry of Heterocyclic Compounds, Vol. 14, Interscience, New York—London (1960).

QUANTUM-CHEMICAL INVESTIGATION OF THE RECYCLIZATION OF 1,2,4,6-TETRAMETHYL-3-NITROPYRIDINIUM IODIDE

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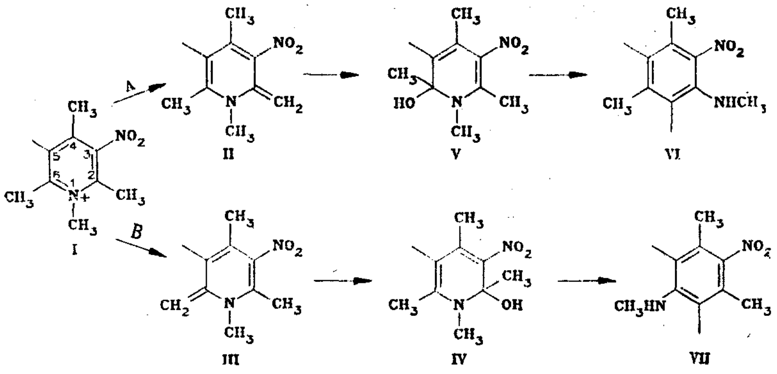
The recyclization of 1,2,4,6-tetramethyl-3-nitropyridinium iodide was examined within the framework of the CNDO/2 (complete neglect of differential overlap) approximation. The electronic structures of the starting, final, and intermediate structures of two competitive processes were evaluated. The primary formation of one of the products was explained.

Two competitive processes (A and B), which, according to [1], take place through the formation of the corresponding anhydro bases II and III, are possible in the recyclization of 1,2,4,6-tetramethyl-3-nitropyridinium iodide.



The aim of the present research was to ascertain the possibility of description of the recyclization within the CNDO/2 (complete neglect of differential overlap) approximation [2]. The calculations were made by means of the program in [3] with an EC-1022 computer. It has been shown [4, 5] that it is sufficient to use the "averaged" geometrical parameters to esti-

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