3'-Amino-spiro-[4-azafluorene-9,1'-indane] (IX). A solution of 0.18 g (0.6 mmole) oxime VIII and 1 ml hydrazine hydrate in 10 ml ethanol was stirred for 72 h in the presence of a catalytic quantity of Raney nickel. After the catalyst was removed 20 ml water was added to the solution and the precipitate was removed by filtration. Yield 0.12 g (70.6%) of amine IX, mp 202-204°C (from heptane). IR spectrum: 3365 cm^{-1} (NH_2). Found, %: N 9.6, M^+ 284. $C_{20}H_{16}N_2$. Calculated, %: N 9.9, M 284.

3'-Acetylamino-spiro-[4-azafluorene-9,1'-indane] (X). A mixture of 0.05 g (0.18 mmole) amine IX and 5 ml acetic anhydride was heated for 20 min at 60°C. The reaction mixture was poured into water (20 ml) and neutralized with sodium bicarbonate. the precipitate was filtered and washed with 30 ml water and 5 ml ether and then dried over phosphorus pentoxide. Yield 0.025 g (44%), mp 277-279°C. IR spectrum: 3210, 3110 (NH), 1685 cm^{-1} (CO). Found, %: N 8.8, M^+ 326. $C_{22}H_{18}N_2O$. Calculated, %: N 8.6, M 326.

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^{13}C-^{13}C SPIN-SPIN COUPLING CONSTANTS IN SIX-MEMBERED RING AZAAROMATIC COMPOUNDS

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and O. P. Shkurko

UDC 543.422.25:547.853.4'823'821.411

The ^{13}C-{^1H} NMR spectra of monomethyl substituted diazines, protonated at the picoline and 2-methylopyrimidine nitrogen atoms,have been analyzed, along with that of pyridine N-oxide and its 2-methyl derivatives protonated at the oxygen atom. Direct and vicinal ^{13}C-^{13}C spin-spin coupling constants (SSCC) have been measured. It was found that the ^{13}C-^{13}C SSCC in diazines follow additivity rules which are based on consideration of the number and mutual orientation or distribution of nitrogen atoms in the ring. It has also been demonstrated that increased direct $^1J_{CC}$ values involving methyl group carbon atoms in α-positions to nitrogen atoms in the aromatic ring are due to effects associated with unshared electron pairs.

The recent development of pulse NMR techniques has made the measurement of ^{13}C-^{13}C SSCC values practical and convenient; these SSCC values, in turn, can provide valuable information concerning the structure, both three-dimensional and electronic, of organic compounds [1-4]. We have previously analyzed [5] the ^{13}C-^{13}C SSCC in monosubstituted pyridines and have established linear correlations between the corresponding direct and vicinal constants in monosubstituted pyridines and benzenes (changes in these parameters are determined primarily by the electronegativities of substituents). These results, together with data concerning additivity effects of substituents on both direct and vicinal coupling constant values in benzenes [6], can be used to predict the ^{13}C-^{13}C SSCC values in six-membered

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ring azaaromatic compounds. The present paper details a systematic investigation of ^{13}C-^{13}C SSCC values in aromatic heterocycles.

It was of interest to us to examine the relationship between the additivity characteristics of ^{13}C-^{13}C SSCC values in azines and the number and mutual orientation of nitrogen atoms in the heterocycle, in analogy with a previously reported study of ^{13}C-^{1}H and ^{1}H-^{1}H SSCC [7]. Since it is difficult in the case of unsubstituted azines to determine many ^{13}C-^{13}C SSCC values, due to the absence of splitting in ^{13}C-$\{^{1}H\}$ NMR spectra for magnetically equivalent ^{13}C nuclei, we examined their monomethyl-substituted derivatives in order to analyze the additivity characteristics of their SSCC. In the case of unsubstituted azines, $^{1}J_{3,4}$ (in pyridazine) and $^{1}J_{4,5}$ (in pyrimidine) are known [1]. In the present paper we have determined the values of both direct and vicinal ^{13}C-^{13}C SSCC in methyldiazines (see Table 1): 3- and 4-methylpyridazines (I and II), 2- and 4-methylpyrimidines (III and IV), and have also used for comparison the data reported in [8] for 2-methylpyrazine (V). We have also reported in Table 1, in addition to the experimentally determined SSCC values, the calculated values of these parameters obtained from the following linear additivity equation:

$$^{n}J^{az}(X) = {}^{n}J^{bz}(X) + \sum_{N_i} [{}^{n}J_i^{pyr}(X) - {}^{n}J^{bz}(X)], \qquad (1)$$

where $^{n}J^{az, pyr, bz}$ are the corresponding coupling constant values for monosubstituted azine, pyridine, and benzene, respectively (in our case X = Me); the summation is carried out relative to the number and positions of nitrogen atoms in the azine ring. The observed direct and vicinal ^{13}C-^{13}C SSCC values are regarded as positive, in agreement with the data in [1].

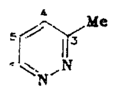
The values of experimentally determined and calculated, based on the additivity Eq. (1), direct and vicinal ^{13}C-^{13}C SSCC in pyrimidines and pyrazine overlap one another, within 0.6 Hz limits (with the exception of $^{1}J_{C_{(2)},C_{Me}}$ in compound III, which will be discussed further). This leads us to conclude that additivity calculations based on Eq. (1) are valid and useful for predicting ^{13}C-^{13}C SSCC in azines. Somewhat larger deviations (1.1-2.1 Hz) were detected in the case of coupling constant values involving the ring ^{13}C nuclei in pyridazines, in which the values of $^{1}J_{3,4}$ and $^{1}J_{5,6}$ were less than the additivity values, and $^{1}J_{4,5}$ and $^{3}J_{3,6}$ were greater than the calculated values. The data indicate the existence of stronger nonlinear effects in pyridazines compared to pyrimidines and pyrazine. Based on the theory [10] of spin-spin interaction of ^{13}C nuclei for directly bonded atoms, coupling is transmitted primarily via the σ-bond electrons; the observed deviation, therefore, can be attributed to changes in the σ-bond system of the pyridazine molecule, which are themselves due to interaction of two neighboring nitrogen atoms. This has previously been noted as well in studies of ionization potentials, basicity constants, and rates of N-methylation and other reactions of these compounds [11]. We cannot exclude the possibility, however that the observed deviations from additivity are associated with changes in the π-electron contribution to $^{1}J_{CC}$ [12, 13], since the state of the pyridazine molecule reflects a large contribution of resonance structure A, and only a negligible contribution of B [14], in contrast to pyridine, pyrimidine, and pyrazine.

A B

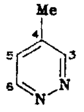
Similar explanations, based on comparison of $^{1}J_{CC}$ values and C-C π-bond orders, have previously been applied in analyses of these parameters for monosubstituted anilines [6], heteroaromatic cations [15], and benzoyl and carboxonium cations [16]; however, it has been accurately stated [13] that the results cannot be regarded as an unequivocal indication of changes in the π-electron contribution toward the values of direct $^{1}J_{CC}$ constants in these compounds. A rigorous interpretation of the nature of these nonlinear deviations in pyridazines requires elucidation by accurate quantum mechanical calculations of ^{13}C-^{13}C SSCC; this is, of course, difficult to achieve at the present time.

Analysis of the data in Table 1 concerning the values of direct $^{1}J_{C,C_{Me}}$ coupling constants involving methyl group carbon atoms reveals that there is a large increase in these parameters for methyl groups located in positions α to aromatic ring nitrogen atoms. An analogous observation has been made previously [5] for picolines. This increase in $^{1}J_{C,C_{Me}}$

TABLE 1. Direct and Vicinal $^{13}C-^{13}C$ SSCC Values in Methyl-Substituted Diazines I-V*



I



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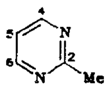
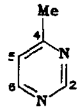
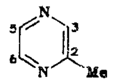


III



IV



V

Compound	$^nJ_{CC}$, Hz						
	$^1J_{2,3}$	$^1J_{3,4}$	$^1J_{4,5}$	$^1J_{5,6}$	$^3J_{2,5}$	$^3J_{3,6}$	$^1J_{C,C_{Me}}$
I	—	52,2 (54,3)	—** (52,5)	50,7 (52,1)	—	18,5 (16,9)	51,5 (51,3)
II	—	51,0 (53,1)	53,9 (52,8)	51,2 (52,7)	—	17,8 (16,2)	43,3 (42,8)
III	—	—	53,1 (52,6)	53,1 (52,6)	17,3 (16,8)	—	59,8 (58,5)
IV	—	—	54,3 (53,9)	53,7 (53,4)	16,4 (16,8)	—	49,7 (50,0)
V***	54,6 (54,6)	—	—	53,6 (53,0)	17,3 (16,9)	16,4 (16,0)	51,2 (51,3)

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*The experimental (±0.1 Hz) and calculated (based on the additivity equation (1) (in parentheses)) SSCC values are given; the calculations also used values for picolines [5] and toluene [9].

**Example of a strongly coupled AB spin system.

***Experimental values from [8].

can be attributed not only to the electronegativity of the heteroatom, but also to the effect of the unshared electron pair on the ring nitrogen atom on the adjacent C—C bond. Similar effects due to the influence of unshared electron pairs on nitrogen and oxygen atoms has been noted earlier in studies of $^1J_{CC}$ and $^1J_{CH}$ values in oximes, imines, aziridines, vinyl ethers, and other heteroatomic compounds [17-19]. We have also found that upon protonation of the nitrogen atoms in 2-picoline and 2-methylpyrimidine the values of $^1J_{C(2),C(Me)}$ decrease, just as would be expected due to the disappearance of unshared electron pair effects (for the preliminary communication, see Ref. [20]; analogous results were reported for acetone oxime in [21]). According to NMR theory [10, 12], the values of such $^1J_{CC}$ constants are determined by a Fermi contact term, which to a first approximation is proportional to the squared matrix elements for the $P_{2s_C,2s_C}$ bond orders (i.e., the s-bond order of the C—C bond). The changes observed in the $^1J_{C,C_{Me}}$ direct coupling constant values in neutral and nitrogen-protonated picolines and 2-methylpyrimidine, relative to the values of this constant in toluene, are qualitatively consistent with changes in the s-bond orders of the respective $C—C_{Me}$ bonds, as calculated using the INDO molecular orbital method.

In the case of 4-picoline and its protonated form VI a small decrease is observed for $^1J_{C(4),C_{Me}}$, apparently due to the appearance of positive charge on the $C_{(4)}$ atom (cf. data in [22] for $^1J_{C,C(Me)}$ in the tert-butyl cation). In addition, the value of $^1J_{C(2),C(Me)}$ in the methylpyrimidinium dication (IX) is close to its additive (calculated) value (46.9 Hz), estimated from Eq. (1), and also to the values of $^1J_{C,C(Me)}$ for the 2-picolinium cation (VIII) in toluene solution. Apparently, therefore, the nonlinear deviation of this coupling constant value in compound III, which was noted earlier in this discussion, can be attributed to nonadditivity effects due to the two unshared pairs of electrons on the ring nitrogen atoms.

According to the data presented above, the increased values of the direct $^1J_{C,C(Me)}$ coupling constants for methyl group carbon atoms located in positions α to aromatic ring nitrogen atoms are determined primarily by the effects of unshared electron pairs on the nitrogen atoms; one of these effects is the influence (of unshared electron pairs) on the $C—C_{Me}$ s-bond orders. Based on calculations of s-bond orders for C—H bonds [20], the observed influence of unshared electron pairs on direct $^1J_{CH}$ coupling constants for the

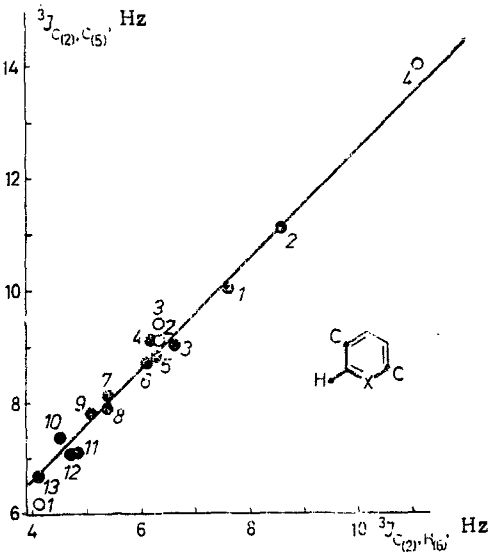
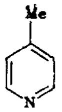


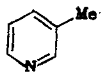
Fig. 1. Linear relationship between the values of the vicinal constants $^3J_{C(2),C(5)}$ and $^3J_{C(2),H(6)}$ in heteroatomic compounds (pyridine, pyridinium and pyrylium cations, pyridine N-oxide [15, 26]) and in monosubstituted benzenes [9, 27].

●: X=C—Y. *1* — Y=H, *2* — Y=SiH$_3$, *3* — Y=Me, *4* — Y=CN, *5* — Y=CHO, *6* — Y=I, *7* — Y=Br, *8* — Y=NH$_2$, *9* — Y=Cl, *10* — Y=NO$_2$, *11* — Y=OMe, *12* — Y=OH, *13* — Y=F. ○: *1* — X=N$^+$—O$^-$; *2* — X==N$^+$—H; *3* — X=O$^+$; *4* — X=N.

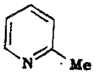
$^1J_{C,C_{Me}}=44.26$ Hz [9]
$P_{2s_C2s_C}=0.263$



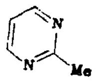
$^1J_{C,C_{Me}}=42.9$ Hz [5]
$P_{2s_C2s_C}=0.263$



$^1J_{C,C_{Me}}=44.2$ Hz [5]
$P_{2s_C2s_C}=0.264$

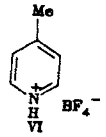


$^1J_{C,C_{Me}}=51.4$ Hz [5]
$P_{2s_C2s_C}=0.270$



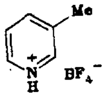
III

$^1J_{C,C_{Me}}=59.8$ Hz
$P_{2s_C2s_C}=0.282$



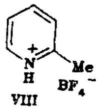
VI

$^1J_{C,C_{Me}}=41.8$ Hz
$P_{2s_C2s_C}=0.261$



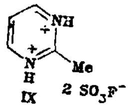
VII

$^1J_{C,C_{Me}}=44.5$ Hz
$P_{2s_C2s_C}=0.266$



VIII

$^1J_{C,C_{Me}}=45.6$ Hz
$P_{2s_C2s_C}=0.266$



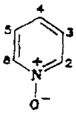
IX

$^1J_{C,C_{Me}}=47.1$ Hz
$P_{2s_C2s_C}=0.270$

α-positions in pyridines is a weaker (or comparable) effect than that associated with the effective electronegativity of the heteroatom. Comparison of the experimental $^1J_{CH}$ data in this case is difficult, since these parameters, in addition to the s-bond orders, depend to a significant degree on the charges on the hydrogen atoms [23, 24]. The observed $^1J_{C,C(Me)}$ data are of practical interest from the point of view of structural studies and reactivity of azaaromatic compounds (reactivity with respect to protonation, alkylation, prototropic tautomerism, and other reactions involving the heterocyclic nitrogen atoms). This method might be especially suitable for studies of polysubstituted azaaromatic compounds, where it is not possible to utilize ^{1}H-NMR spectral data and ^{13}C-^{1}H SSCC values. It should also be noted that the presence of unshared electron pairs on nitrogen atoms influences not only $^1J_{CC}$ values involving carbon atoms in a substituent, but also affects the values of these parameters for ^{13}C nuclei in the rings themselves, such as in the case of condensed aromatic compounds. For example, the value of the direct $^1J_{8,9}$ coupling constant in quinoline is equal to 64.4 Hz [8], while the analogous $^1J_{CC}$ constant in naphthalene is equal to 55.87 Hz [25].

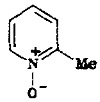
The values of $^1J_{CC}$ involving ring carbon nuclei in the picolinium cations (VI-VIII) are in agreement with the data reported in [15], based on a study of these coupling constants in the pyridinium cation (upon protonation the values of $^1J_{2,3}$ and $^1J_{5,6}$ in picolines increase by 4-5 Hz, while the values of $^1J_{3,4}$ and $^1J_{4,5}$ decrease by 2 Hz; the coupling constant values for compounds VI-VIII are summarized in Table 2). The observed decrease in $^1J_{CC}$ values, based on the results of theoretical calculations [13], can be explained in terms of a change in the atomic charges [to a first approximation the positive charge on $C_{(4)}$], which is analogous with the data obtained for carbocations [22]; the change in atomic charge apparently affects the atom-atom polarizability of the s-orbitals $\pi_{2s_C,2s_C}$ (the Fermi contact contribution term to $^1J_{CC}$ is proportional to $\pi_{2s_C,2s_C}$ [10]).

It was therefore important to compare the ^{13}C-^{13}C SSCC values in the pyridinium cation and in pyridine N-oxide (X); interesting results had been reported earlier by comparison of the ^{13}C-^1H coupling constant values in these two compounds [24, 26]. In the present paper we have measured the direct and vicinal ^{13}C-^{13}C SSCC values in compound X, and in light of the effects discussed above have also examined the effect of quaternization of the nitrogen atom on the $C{-}C_{Me}$ bond, using 2-methylpyridine N-oxide (XI) and its protonated form (XII) as examples.



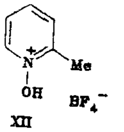
X

$^1J_{2,3} = 60.00$ Hz;
$^1J_{3,4} = 54.44$ Hz;
$^3J_{2,5} = 6.22$ Hz;



XI

$^1J_{C_{(2)},C_{Me}} = 51.1$ Hz



XII

$^1J_{C_{(2)},C_{Me}} = 49.0$ Hz

The values of the direct coupling constant $^1J_{2,3}$ are similar in compound X and in the pyridinium cation (59.1 Hz [15]), while the value of $^1J_{3,4}$ is 2.3 Hz higher for compound X than for the corresponding coupling constant (in the pyridinium cation); based on the data in [13] this may be due to compensation of the positive charge on $C_{(4)}$ in pyridine N-oxide compared to in the pyridinium cation. Analysis of the direct $^1J_{C_{(2)},C_{(Me)}}$ constants in compounds XI and XII reveals that these parameters exceed the value of the analogous constant in 2-picoline. We cannot exclude the possibility that in this case the unshared electron pairs on the oxygen atoms exert a supplementary effect on $^1J_{C,C_{Me}}$ [18]. These results illustrate that extreme care must be taken when analyzing the structures of methyl-substituted derivatives of azaaromatic N-oxides and their protonated forms based on studies of $^1J_{C,C_{(Me)}}$, or in other studies as well.

The value of the vicinal constant $^3J_{2,5}$ in pyridine N-oxide (X) is substantially greater than the values of the vicinal constants $^3J_{CC}$ in pyridine itself (13.95 Hz [5]) or in the pyridinium cation (9.1 Hz [15]); the changes in these parameters correlate very well with changes in the vicinal coupling constants $^3J_{C_{(2)},H_{(6)}}$ (for interaction via the heteroatom) (Fig. 1). A relationship was demonstrated between $^3J_{C_{(2)},C_{(5)}}$ and $^3J_{C_{(2)},C_{(6)}}$ in monosubstituted benzenes; these were found to decrease linearly as the electronegativity of the first atom in the substituent increased [9, 27]:

$$^3J^{\mathrm{bz}}_{C_{(2)},C_{(5)}} = 0.959\ ^3J^{\mathrm{bz}}_{C_{(2)},H_{(6)}} + 2.82 \qquad (2)$$
$$(r = 0.989,\ s = 0.19\ \mathrm{Hz},\ n = 13).$$

The coupling constant data for aromatic heterocycles follow practically the same linear relationships as observed for these parameters in monosubstituted benzenes. This result suggests that the changes in $^3J_{2,5}$ in pyridine, the pyridinium cation, and in pyridine N-oxide relative to the value in benzene are determined primarily by changes in the system of σ-bonds in these compounds. This is also indicated by the changes in $^3J_{CC}$ for nonaromatic molecular fragments reported in [28] (C—C—C—C 4–5, C—C=C—C 4–5, C—C=N—C 8, C—N=N—C 14–15 and C—N=N—C 3–4 Hz), which are comparable with the corresponding changes in vicinal $^3J_{CC}$ coupling constants in azaaromatic compounds. The π-electron contribution to $^3J_{CC}$ in

TABLE 2. Additional $^{13}C-\{^1H\}$ NMR Spectral Parameters for Compounds I-IV, VI-XII

Compound	δ_C, ppm from TMS						$^nJ_{CC}$, Hz					
	δ_2	δ_3	δ_4	δ_5	δ_6	δ_{Me}	$^1J_{2,3}$	$^1J_{3,4}$	$^1J_{4,5}$	$^1J_{5,6}$	$^3J_{2,5}$	$^3J_{3,6}$
I	—	160,7	127,3	127,1	150,2	22,3	—	—	—	—	—	—
II	—	153,9	138,3	127,4	151,6	18,1	—	—	—	—	—	—
III	168,6	—	157,4	118,8	157,4	26,1	—	—	—	—	—	—
IV	159,1	—	167,3	121,5	157,0	24,0	—	—	—	—	—	—
VIII	155,1	129,1	148,0	125,6	141,6	20,0	59,8	53,0	51,9	60,0	8,6	8,4
VII	141,9	140,2	149,0	127,9	139,7	18,3	—	—	52,5	59,4	8,1	—
VI	142,1	128,6	161,3	128,6	142,1	22,2	59,1	52,9	52,9	59,1	8,3	8,3
IX*	164,4	—	158,9	124,9	158,9	19,5	—	—	56,1	56,1	—	—
X	139,9	127,2	125,7	127,2	139,9	—	—	—	—	—	—	—
XI	149,0	127,3	126,0	124,6	139,7	17,6	62,6	55,3	53,8	60,4	—	—
XII	151,0	129,2	135,4	126,0	140,2	17,5	61,3	54,6	52,9	60,3	—	—

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*Relative to δ_C for CD_2Cl_2: 53.6 [30].

the compounds studied herein and in benzene is apparently practically constant and relatively small, in contrast to the results of quantum mechanical calculations [12]. Our data further indicate that the previously observed correlation between $^3J_{CC}$ and π-bond orders in aromatic compounds [25] cannot be considered as due to changes in the π-electron contribution alone (analogous predictions have been reported elsewhere [2, 15]). The increase in geminal constants $^2J_{2,6}$ (interaction via the heteroatom) in the transition from benzene (−2.46 Hz [9]) to pyridine (~−6.5 Hz [5]) can also be explained in terms of changes in the σ-bond system. The signs of $^2J_{CC}$ were chosen to be consistent with the conclusion reached in [2] for this constant in benzene and also by comparison with the nature of the changes in these constants in monosubstituted pyridines and benzenes [5, 9].

The increased σ-contributions to the $^3J_{CC}$ vicinal constants in pyridines compared to benzenes is reflected in the increased sensitivity of these parameters to substituent effects, as was found for $^3J_{3,6}$ in 2-substituted pyridines [5]. The previously discussed deviations from additivity noted for $^3J_{3,6}$ values in pyridazines I and II can also be rationalized in an analogous manner, if one regards the influence of the second nitrogen atom in the ring as simply the effect of an equivalent substituent. Comparison of these $^3J_{CC}$ values with those shown for nonaromatic fragments [28] provides additional evidence in favor of increased transmission of spin-spin coupling of interaction via the σ-bond system. The deviations from additivity for $^3J_{3,6}$ in ortho-substituted anilines [6] can also be interpreted similarly if one assumes that the amino group, along with the decreased σ-contribution to $^3J_{3,6}$, lessens the sensitivity of these parameters to substituent electronegativity effects, compared to monosubstituted benzenes.

EXPERIMENTAL

$^{13}C-^{1}H$ NMR spectra were recorded on a Bruker WP-200SY (50.32 MHz) spectrometer in a pulse mode for samples containing natural abundance ^{13}C isotope. The signals were stabilized relative to deuterium solvent NMR signals; the temperature was 25-30°C. Solutions of compunds I-IV, X, and XI (in acetone-D_6) having concentrations of 50-80% were used; the concentrations of solutions of VI-VIII and XII (in acetonitrile-D_3) were 40-70%. TMS was added to these solutions as internal standard. Compound IX was prepared by dissolving at low temperature 2-methylpyrimidine in fluorosulfonic acid HSO_3F at a ratio of 1:6, followed by the addition of methylene chloride-D_2 to the solution. The indicated compounds were prepared according to [14]; salts (tetrafluoroborates) VI-VIII and XII were obtained in an analogous manner to [26].

The $^{13}C-\{^{1}H\}$ NMR spectral acquisition conditions and subsequent analysis to determine $^{13}C-^{13}C$ SSCC values were analogous to those reported in [5] (Table 2). The accuracy of the $^{13}C-^{13}C$ SSCC measurements was ±0.1 Hz, ±0.05 Hz for compound X. ^{13}C isotopic shifts, due to exchange interaction of a second ^{12}C nucleus on ^{13}C, were on the order of −0.040 to −0.010 ppm for directly bonded atoms and −0.004 to 0.008 ppm for atoms bound across three chemical bonds (positive downfield shift). In the case of compounds VI-XII, as was noted in earlier works [24, 26], signal broadening was observed for the carbon atoms directly bonded to ^{14}N atoms in the rings, on the order of 1-6 Hz.

Quantum mechanical calculations of s-bond orders using the INDO approximation were carried out on a BESM-6 computer using the VIKING program [29]. The calculations were based on accurate geometric information for pyridine and pyrimidine molecules [14]; in the case of cations, the geometries of neutral molecules were used (N^+–H bond length of 1.03 Å [24]).

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