Sign Determinations and INDO-MO Calculations of ^{13}C–^{15}N and ^{15}N–^{15}N Spin–Spin Coupling Constants of 3-Methyl- and 3,6-Dimethyl-pyridazines

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^{13}C–^{15}N Nuclear spin-coupling constants, ${}^nJ$(C–N), of 3-methyl- and 3,6-dimethyl-pyridazines and one-bond ^{15}N–^{15}N spin-coupling constant of 3-methylpyridazine have been observed with the intention of investigating the influence of the two nitrogen lone pairs on the magnitudes and signs of ${}^nJ$(C–N) and ${}^1J$(N–N). Signs of ${}^nJ$(C–N) were determined by comparing the splittings of each carbon atom in the 3-methylpyridazine with those in the 3,6-dimethylpyridazine or by the single-frequency off-resonance proton-decoupling technique. The ${}^1J$(C–N) values were found to be large and positive (+6.0 and +6.4 Hz), in marked contrast to the case of pyridine (+0.6 Hz). Although C–C–N two-bond coupling constants in the pyridazine ring (+1.3 Hz) are roughly similar to the corresponding coupling in pyridine (+2.5 Hz), C–N–N two-bond coupling constants were also large and positive (+4.8 Hz). INDO-MO calculations of ${}^nJ$(C–N) reproduced well not only the observed trends of the differences between 3-methylpyridazine and pyridine but also the absolute magnitude and the sign of each spin-coupling constant. The magnitude of ${}^1J$(N–N) was also found to be large (22.1 Hz), and its sign was concluded to be negative on the basis of selective ^{15}N decoupling experiments.

^{13}C–^{15}N Spin–spin coupling constants, ${}^nJ$(C–N), are of interest in that their magnitudes and signs depend on the hybridization state of the nitrogen atom and also on the proximity of its lone pair to the spin-coupled carbon atom. Hence, the magnitudes and signs of ${}^nJ$(C–N) would be expected to provide valuable information on the electronic structures of organic molecules which contain nitrogen atoms and therefore have been investigated extensively.[1–3] However, only a small amount of work has been done, without sign determinations, for compounds containing an N=N bond.[4,5]

Previously, in the course of our studies on ^{13}C–^{15}N spin-coupling constants of *trans*- and *cis*-azobenzenes and benzo[*c*]cinnoline,[6,7] we found that ${}^1J$(C–N) is large and positive for *cis*-azobenzene (+10.0 Hz) and benzo[*c*]cinnoline (+7.3 Hz), in contrast to our expectation of a small value in the light of the one-bond lone-pair effect.[8] Since the corresponding coupling constant of the *trans*-isomer of azobenzene is relatively small (+1.9 Hz), the anomalously large values of *cis*-azobenzene and benzo[*c*]cinnoline can be ascribed to the two *s*-hybridized lone pairs adjoining each other with a *cis*-configuration, and not to the electronegativity of one nitrogen atom.

Recently, Simova *et al.* have observed ${}^1J$(C–N) for such azo compounds as 4-methylazobenzene, diazocyanides, and triazenes.[5] They also found in these molecules that ${}^1J$(C–N) is large in the *cis*-isomers (7.7—18.3 Hz), in contrast to the *trans*-isomers (0—1.2 Hz). However, since experimental sign determinations of ${}^nJ$(C–N) have been made only for benzo[*c*]cinnoline,[6,7] we felt it necessary to study further the signs and magnitudes of the ^{13}C–^{15}N spin-coupling constants for another compound which contains an N–N bond in a *cis*-form.

In this work, 3-methyl[^{15}N$_2$]pyridazine and 3,6-dimethyl-[^{15}N$_2$]pyridazine were chosen for this purpose. The signs of ${}^nJ$(C–N) were determined by comparing observed splittings between these molecules. This approach can be considered to be a modified version of the symmetrical double-labeling method.[9] The spin system of the ^{13}C resonances in the 3,6-dimethyl-[^{15}N$_2$]pyridazine can be considered to be AA′X (AA′ for ^{15}N-enriched nitrogens and X for natural abundance ^{13}C). Thus, the ^{13}C spectrum of each carbon atom appears as a triplet, giving half the sum of two coupling constants, $1/2(J_{AX} + J_{A'X})$. Therefore, the relative signs of J_{AX} and $J_{A'X}$ can be determined by comparing the sum with the ^{13}C–^{15}N splittings of each carbon atom in 3-methyl[^{15}N$_2$]pyridazine, which gives the absolute magnitudes of J_{AX} and $J_{A'X}$ as a good approximation. The single-frequency off-resonance proton-decoupling technique[10] was used to determine the absolute sign of ${}^1J$(C–N). ^{15}N N.m.r. spectra were also observed, since ${}^1J$(N–N) is also of interest in relation to the lone pair orientation. The sign was determined by selective ^{15}N decoupling experiments in ^{1}H n.m.r. INDO-MO calculations were carried out to test whether the theory can reproduce the magnitudes and signs of ${}^nJ$(C–N) and ${}^1J$(N–N). Observed and calculated ${}^nJ$(C–N) values were compared with the corresponding spin-coupling constants of pyridine.

Experimental

Materials.—3-Methyl- and 3,6-dimethyl-[^{15}N$_2$]pyridazine were synthesized according to the method described by Clauson-Kaas[11] and Levisalles,[12] respectively, using [^{15}N$_2$]-hydrazine sulphate (95% enriched; CEA).

Measurements.—The ^{1}H (199.6 MHz), ^{13}C (50.2 MHz), and ^{15}N (20.2 MHz) n.m.r. spectra were recorded with a JEOL FX-200 spectrometer. All spin-coupling constants were measured with a digital resolution of 0.12 Hz per point. Triple-resonance ^{13}C–{^{1}H(noise),^{15}N(selective)} and ^{1}H–{^{1}H(selective),^{15}N(selective)} experiments were performed by the method described elsewhere.[13] Solutions were prepared in CDCl$_3$ in the concentration range 1.0—1.5 mol dm^{-3} for observing ^{1}H and ^{13}C n.m.r. and 0.4—0.5 mol dm^{-3} for ^{15}N n.m.r. The chemical shifts of ^{13}C resonances were determined from internal tetramethylsilane and those of ^{15}N resonances were determined by comparing the observed ^{15}N resonance frequencies with that of NO$_3^-$ of ^{15}NH$_4$^{15}NO$_3$ (10 mol dm^{-3} in 2 mol dm^{-3} HNO$_3$) contained in a coaxial capillary tube; downfield values are taken as positive.

INDO-MO Calculations of Spin–Spin Coupling Constants of 3-Methylpyridazine and Pyridine.—The molecular orbital calculations were made with the standard INDO parametrization.[14] The spin-coupling constants were calculated by the method developed by Blizzard and Santry.[15] In order to maintain internal consistency throughout our calculations for the related compounds,[6,16,17] one-centre integrals used were taken from those reported by Towl and Schaumburg,[18] and no refinement of these parameters was attempted. The structural parameters related to the pyridazine ring were transferred from 3,6-dichloropyridazine[19] and those related to the methyl group were constructed by assuming the C–C bond length as 1.50 Å, with tetrahedral bond angles. The structural parameters for pyridine were taken from the microwave results reported by Bak *et al.*[20] All C–H bond lengths were assumed to be 1.0 Å.

Results

As a typical example of the ^{13}C n.m.r. spectra, Figures 1(a) and (b) show those of C(4) and C(5) of 3,6-dimethyl[$^{15}N_2$]pyridazine and 3-methyl[$^{15}N_2$]pyridazine, respectively. As expected, the C(4) and C(5) signals in the former case appear as a triplet, whereas in the latter they appear as a doublet of doublets. Signs can be determined from their spacings by a simple mathematical consideration of the sum and each absolute value. The assignments for C(4) and C(5) were determined by the substituent-induced chemical shift of a methyl group for aromatic carbons[21] and also by a selective decoupling experiment for the methyl protons; the assignments for the other carbon atoms were straightforward from the expected chemical shifts. The coupling assignments were made by selective irradiation at the ^{15}N resonance frequency of either N(1) or N(2) in the ^{13}C–{^{1}H,^{15}N} triple-resonance experiments. Figure 1(c) shows the result of this triple-resonance experiment, where N(1) transitions were irradiated selectively. Although the smaller splitting (1.3 Hz) in the double doublet of C(4) is not resolved, it is obvious that both for C(4) and C(5) the larger splitting (6—6.5 Hz) corresponds to the three-bond coupling, and the smaller one (1.3 Hz) to the two-bond coupling. Observed ^{13}C–^{15}N splittings assigned in this way are summarized in Table 1 together with ^{13}C chemical shifts, ^{15}N chemical shifts, and the ^{15}N–^{15}N spin-coupling constant.

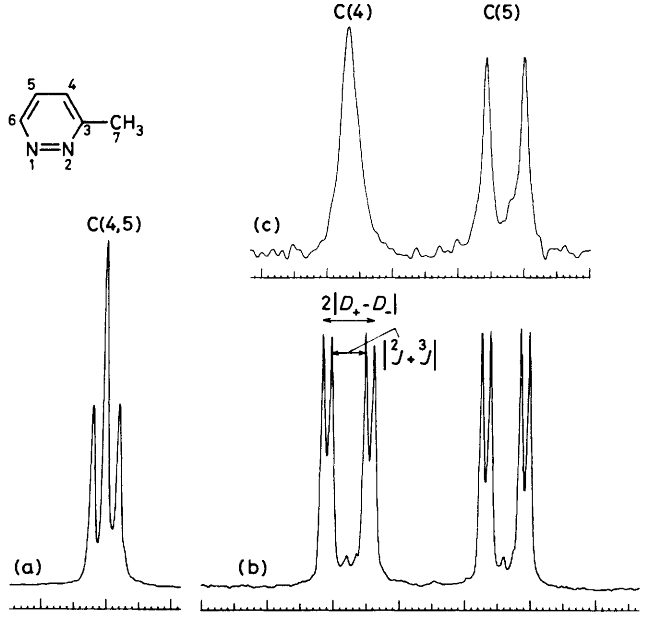

Figure 1. ^{13}C N.m.r. spectra of C(4) and C(5) of 3,6-dimethyl[$^{15}N_2$]pyridazine [spectrum (a)] and 3-methyl[$^{15}N_2$]pyridazine [spectra (b) and (c)] in $CDCl_3$; (a) and (b) were obtained under conditions of complete proton decoupling and (c) was obtained on further irradiating N(1) transitions selectively. One division is equal to 1 Hz. Structure and numbering of 3-methylpyridazine are also shown.

The assignments for N(1) and N(2) in the ^{15}N n.m.r. spectrum of 3-methylpyridazine were determined unequivocally by the ^{13}C–{^{1}H,^{15}N} triple-resonance experiments. Selective irradiation of the ^{15}N transitions corresponding to the high-field doublet, which originates from the ^{15}N–^{15}N one-bond coupling, caused collapse of a large splitting of 9.6 Hz exhibited by the methyl carbon atom, C(7). Thus, the high-field doublet in the ^{15}N spectrum is due to N(2) and the remaining low-field doublet to N(1), since the large splitting is undoubtedly due to ^2J[C(7)–N(2)] on account of the *cis* orientation of the lone pair on N(2) with respect to C(7). Interestingly, this order of the ^{15}N chemical shifts relative to the methyl-substituent position is opposite to that of the ^{13}C chemical shifts, where the C(4) signal appeared to lower field than that of C(5).

Further, the ^{15}N n.m.r. spectrum of 3-methyl[$^{15}N_2$]pyridazine appeared as an AB-type quartet with ^1J(N–N) 22.1 Hz and with a chemical shift separation of 68.4 Hz. Accordingly, observed splittings in the ^{13}C n.m.r. spectra at 50.2 MHz are not necessarily the spin-coupling constants. However, we regard the observed splittings as good substitutes for the true coupling constants. This is because values of $2|D_+ - D_-|$[22] calculated by using the apparent ^nJ(C–N) values agree well with the observed separations, as shown in the last two columns in Table 1. The $2|D_+ - D_-|$ value corresponds to the separation between inner or outer lines of the double doublet [*e.g.* see C(4) in Figure 1(b)].

Table 1. Observed ^{13}C–^{15}N splittings, ^{13}C chemical shifts, ^{15}N chemical shifts, and ^{15}N–^{15}N spin–spin coupling constant of 3,6-dimethyl[$^{15}N_2$]pyridazine and 3-methyl[$^{15}N_2$]pyridazine in $CDCl_3$

	Chemical shifts[a]			3,6-Dimethyl	3-Methyl			$2\|D_+ - D_-\|$[e]	
	3,6-Dimethyl	3-Methyl	*n*	$\|^nJ + ^{n+1}J\|$[b]	^nJ[c]	^{n+1}J[c]	$\|\Delta\|$[d]	Calc.	Obs.
C(3)	157.6	160.2	1	10.3	+6.0	+4.8	0.5	1.1	1.2
C(4)	126.8	126.9	2	4.0	+1.3	−6.5	1.2	7.4	7.8
C(5)	126.8	126.4	2	4.0	+1.3	−6.0	0.7	7.0	7.3
C(6)	157.6	149.4	1	10.3	+6.4	+4.8	0.9	1.5	1.6
C(7)	21.9	22.3	2	11.5	−9.6	−1.8	0.1	7.4	7.8
N(1)	16.7	22.2	1		−22.1				
N(2)	16.7	18.9	1		−22.1				

[a] In p.p.m. from internal Me_4Si for ^{13}C and from external NO_3^- for ^{15}N, ±0.1 p.p.m. [b] Separations between the outer lines of a triplet observed in 3,6-dimethyl[$^{15}N_2$]pyridazine; in Hz, ±0.1 Hz. [c] ^{13}C–^{15}N Splittings observed in 3-methyl[$^{15}N_2$]pyridazine; in Hz, ±0.1 Hz. For nitrogen atoms, ^1J(N–N) is shown here. [d] Differences between $|^nJ + ^{n+1}J|$ of 3,6-dimethyl[$^{15}N_2$]pyridazine and that of 3-methyl[$^{15}N_2$]pyridazine. [e] Separations between inner lines of a double doublet for C(3), C(6), and C(7), and those between outer lines for C(4) and C(5) in 3-methyl[$^{15}N_2$]pyridazine; D_+ and D_- have their usual meanings.[22] In Hz, ±0.1 Hz for observed values.

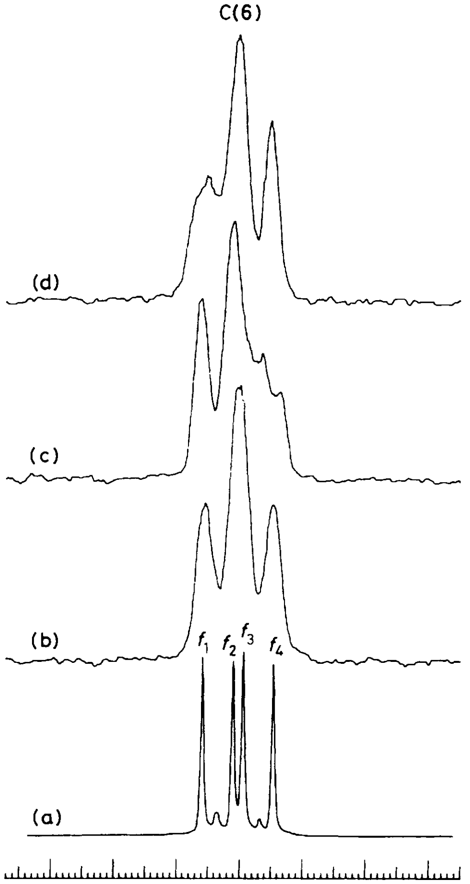

Figure 2. ^{13}C N.m.r. spectra of C(6) of 3-methyl[$^{15}N_2$]pyridazine in $CDCl_3$: (a) complete proton-decoupled spectrum; (b) with selective irradiation just at the H(6) resonance frequency; (c) with selective irradiation at the frequency which was shifted by 10 Hz from the H(6) resonance frequency to higher field; (d) as in (c), but shifted by 10 Hz to lower field. In (b), (c), and (d), irradiation power ($\gamma H_2/2\pi$) was *ca.* 1350 Hz. One division is equal to 1 Hz.

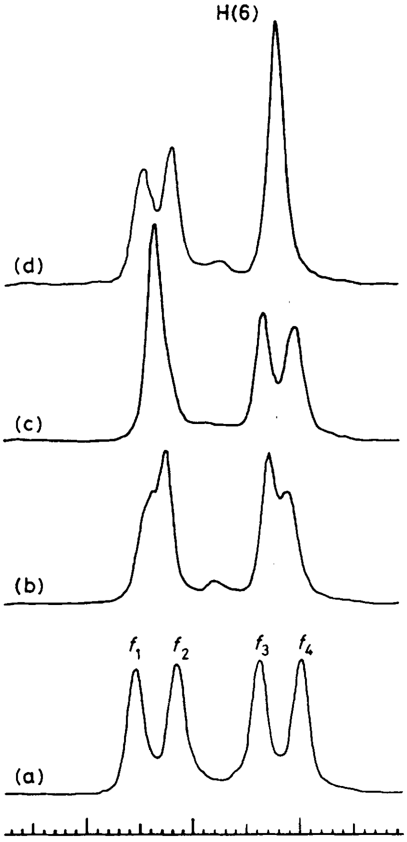

Figure 3. ^{1}H N.m.r. spectra of H(6) of 3-methyl[$^{15}N_2$]pyridazine in $CDCl_3$: (a) ^{1}H-{^{1}H} double-resonance spectrum, where H(4) and H(5) resonances were irradiated; (b) ^{1}H-{^{1}H,^{15}N} triple-resonance spectrum, where in addition to the irradiation at H(4) and H(5) resonances, N(2) resonance was also selectively irradiated approximately at its chemical shift position; (c) and (d) as in (b), but ^{15}N irradiation frequencies shifted by 10 Hz to high and low field, respectively. One division is equal to 1 Hz.

Relative signs could be determined unequivocally, since the differences (|Δ| values in Table 1) between the sum of ^nJ and ^{n+1}J obtained from 3,6-dimethylpyridazine and that from 3-methylpyridazine were satisfactorily small. Absolute signs were determined by assuming that in a ^2J(C–N) coupling, when the lone pair lies *cis* to the coupled carbon, the sign is negative, and that when the lone pair lies in a *trans* orientation the sign is positive. These assumptions may be rationalized by considering signs determined for (*E*)- and (*Z*)-acetophenone oxime[23] and pyridine.[24] However, in order to offer further corroborating evidence for the signs, we have tried the single-frequency off-resonance proton-decoupling technique.[10] In order that this technique should operate effectively, we chose the H(6)–C(6)–N(1) moiety of 3-methylpyridazine, since the sign of ^2J[H(6)–N(1)] is undoubtedly negative in view of the lone pair orientation.[2] As shown in Figure 2(a), the complete proton-decoupled spectrum of C(6) appears as a doublet (6.4 Hz) of doublets (4.8 Hz), lines f_1—f_4. If the irradiation power was lowered and selectively applied to H(6), the C(6) signal appeared as a somewhat broadened triplet [Figure 2(b)]. At the same irradiation power, when the decoupling frequency was shifted to the high field side, the effective reduction in the residual J^r[C(6)–H(6)] coupling was observed for lines f_1 and f_2 [Figure 2(c)], whereas if it was shifted to the low-field side, the effective reduction of J^r[C(6)–H(6)] was noted for lines f_3 and f_4 [Figure 2(d)]. These observations indicate that the sign of ^1J[C(6)–N(1)] is opposite to that of ^2J[H(6)–N(1)], *i.e.* positive.

The sign of ^1J[N(1)–N(2)] could also be determined by applying a similar concept to H(6), N(1), and N(2), and by performing ^{1}H-{^{1}H,^{15}N} triple resonance experiments. The ^{1}H n.m.r. spectrum of H(6) appeared as a doublet (11.7 Hz) of doublets (3.9 Hz), lines f_1—f_4, when both H(4) and H(5) resonances were simultaneously irradiated [Figure 3(a)]. The larger splitting corresponds to ^2J[H(6)–N(1)], and the smaller one to ^3J[H(6)–N(2)]. Each peak is somewhat broad owing to the still remaining spin-coupling with methyl protons. Selective irradiation at an ^{15}N frequency slightly off-resonance at high field from the N(2) chemical shift caused effective decoupling for lines f_1 and f_2 [Figure 3(c)], and similar irradiation at low field for lines f_3 and f_4 [Figure 3(d)]. The irradiation power used was such that could partially decouple ^3J[H(6)–N(2)], when applied approximately at the frequency of the N(2) chemical shift [Figure 3(b)]. By considering the combination of the signs of magnetogyric ratios of nuclei involved in J(N–N) and J(H–N), the sign of ^1J[N(1)–N(2)] can be concluded to be the same as that of ^2J[H(6)–N(1)], *i.e.* negative.

Discussion

The characteristics of the spin-coupling constants noted in Table 1 are as follows:

(1) The sign of ^{1}J(C–N) is positive and the absolute magnitude much larger than expected in view of the one-bond lone-pair effect.[8] For example, in pyridine, ^{1}J(C–N) is only + 0.6 Hz.[24]

(2) In the pyridazine ring, ^{2}J(C–N–N) is larger than ^{2}J(C–C–N).

(3) The absolute magnitude of ^{3}J(C–N) within the pyridazine ring is larger than that of the corresponding coupling constant in pyridine.

(4) The absolute magnitude of ^{3}J(C–N) is also larger than that of the three-bond coupling constant between the methyl carbon atom and N(1).

(5) The sign of ^{1}J(N–N) is negative and the absolute magnitude fairly large; in fact, it is the largest so far reported for diazenes.[1,2]

Although the characteristic (3) can be explained by the presence of two unsymmetrical coupling pathways, (1), (2), and (5) can be explained only as being due to the presence of two adjacent lone pairs with a *cis*-configuration. The case of (4) may be the differences in geometry of coupling pathways; indeed, similar findings have been reported.[25]

It is of interest to calculate the spin-coupling constants of 3-methylpyridazine having these characteristics and to compare the results with those for pyridine. The results are shown in Table 2. Overall agreement between calculated and experimental values is satisfactory for both cases in 3-methylpyridazine and pyridine, except for ^{2}J[C(7)–N(2)] in the former, for which the calculations give somewhat too positive a value; similar trends have been pointed out by Wasylishen for quinoline[1] and by us for azobenzene and benzo[*c*]cinnoline.[6] Interestingly, however, all the characteristics listed above are fully reproduced. Table 2 informs us that these good correspondences are due solely to the Fermi contact term. For example, the calculation can follow the difference in ^{1}J[C–N) between 3-methylpyridazine and pyridine only by changes in the Fermi contact term; the remaining terms assume nearly identical values. The success in reproducing the trend noted in (4) encourages us to use the INDO-MO level of approximation for future predictions of torsion angle and lone-pair orientation dependences in ^{3}J(C–N) couplings. It is also interesting that although no refinement of one-centre integrals was made, the calculation gave a close frequency fit for the ^{1}J(N–N) coupling, showing a negative sign for it. Khin and Webb.[26] and Schulman *et al.*[27] have also reported negative signs in their calculations of ^{1}J(N–N) for other compounds which have two *s*-hybridized lone pairs in a *cis*-configuration. The present determination of negative sign by selective ^{15}N decoupling experiments justifies the theory employed in these calculations. Again, both the negative sign and the large absolute magnitude of ^{1}J(N–N) are responsible for the large negative contribution from the Fermi contact term. However, Table 2 indicates that in addition to the Fermi contact term, the orbital–dipole term plays an important role in the spin-coupling mechanism of the one-bond ^{13}C–^{15}N and ^{15}N–^{15}N couplings, giving a good fit with the observed values, *e.g.* ^{1}J(N–N).

Table 2. Calculated and experimental coupling constants (Hz)

	FC[a]	OB[a]	SD[a]	*J*(total)	*J*(expt.)
			3-Methylpyridazine		
^{1}J[C(3)–N(2)]	4.9	3.4	−1.0	7.3	+6.0
^{1}J[C(6)–N(1)]	3.6	3.5	−1.1	6.0	+6.4
^{2}J[C(3)–N(1)]	4.1	−0.0	1.0	5.1	+4.8
^{2}J[C(6)–N(2)]	4.6	0.0	1.1	5.7	+4.8
^{2}J[C(4)–N(2)]	3.5	−0.7	1.1	3.9	+1.3
^{2}J[C(5)–N(1)]	3.4	−0.7	1.1	3.8	+1.3
^{2}J[C(7)–N(2)]	−2.9	−0.1	0.0	−3.0	−9.6
^{3}J[C(4)–N(1)]	−6.7	−0.5	−1.6	−8.8	−6.5
^{3}J[C(5)–N(2)]	−6.5	−0.5	−1.6	−8.6	−6.0
^{3}J[C(7)–N(1)]	−1.0	−0.0	−0.1	−1.1	−1.8
^{1}J[N(1)–N(2)]	−17.9	−4.0	0.7	−21.2	−22.1
			Pyridine		
^{1}J[C(2)–N]	−1.4	3.4	−0.7	1.3	+0.6[b]
^{2}J[C(3)–N]	3.2	−0.2	0.5	3.5	+2.5[b]
^{3}J[C(4)–N]	−3.7	−0.2	−0.9	−4.8	−3.9[b]

[a] FC = Fermi contact term; OB = orbital–dipole term; SD = spin–dipole term. The parameters employed were $S_N^2(O) = 5.246$, $S_C^2(O) = 3.012$, $<r^{-3}>_N = 2.472$, and $<r^{-3}>_C = 1.430$.[18] [b] Taken from ref. 24.

In conclusion, ^{1}J(C–N) is large and positive in sign when there are two *s*-hybridized lone pairs with a *cis*-configuration in the N=N bond. These two *s*-hybridized lone pairs make ^{2}J(C–N–N) more positive than ^{2}J(C–C–N), and also increase the absolute magnitude of ^{1}J(N–N). INDO-MO calculations of spin-coupling constants can mimic well not only the differences in ^{n}J(C–N) between 3-methylpyridazine and pyridine but also the observed magnitudes and signs of ^{n}J(C–N) and ^{1}J(N–N) in these molecules.

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