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Theory and Calculation of Carbon-Nitrogen Spin-Spin Coupling Constants

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Abstract: Nuclear spin-spin coupling constants for ^{13}C and ^{15}N are treated theoretically in a framework of coupled Hartree-Fock theory using localized and delocalized molecular orbitals. Calculations implemented in the INDO integral approximation in this model have been performed for one-, two-, and three-bond couplings in some simple nitrogen-containing organic molecules. It is demonstrated that orbital and dipolar contributions are important in cyanides and nitriles, and furthermore that molecules can be divided into two classes depending on the presence or absence of lone pairs which may contribute to $^1J_{\mathrm{CN}}$.

I. Introduction

As is well known,[2a] indirect isotropic nuclear spin-spin coupling constants result from three types of electron coupling mechanisms: (1) Fermi contact interaction between the electron and nuclear spins, J^{Fc}, (2) interaction between the magnetic field arising from the orbital motion of the electron and the nuclear magnetic dipole, J^{o}, and (3) interaction between the nuclear and electron spin dipoles, J^{sd}. Recently self-consistent field calculations including the effect of the "noncontact" terms, (2) and (3), for first row atoms have been made by Blizzard and Santry,[2b] Towl and Schaumburg,[3] and Schulman and Newton.[4] The latter study of CC one-bond coupling constants found that the Fermi contact term is usually dominant and is related to the product of the hybrids in the bonding orbitals. However, the orbital and spin-dipolar terms are not necessarily negligible and in a few cases, most notably bicyclobutane (C_1C_3) bonds, they are actually more important than the contact term. This led to the unusual prediction of a negative value for $^1J_{C_1C_3}$[5] which has been recently confirmed by an elegant experiment.[6] For CF coupling constants the orbital terms have been found to be comparable to the contact term.[2b,3]

The present study deals with the case of $\mathrm{C}^{13}\mathrm{N}^{15}$ coupling constants which has not been systematically studied previously and for which there are a wide variety of bonding situations, e.g., amines, amides, nitriles, isocyanides, imines, protonated nitrogen species, etc. In view of the variations in both magnitude and signs obtained even for one-bond coupling constants, the accurate calculation of J_{CN} is an interesting problem and one which provides a stringent test of any theory of coupling constants.

II. Theory

The scalar nuclear spin–spin coupling constant, J_{AB}, between spin (vectors) $\mathbf{I}_{\mathrm{A}}$ and $\mathbf{I}_{\mathrm{B}}$ is the coefficient of the interaction energy bilinear in the nuclear spins, and is given in hertz by[2a]

$$E_{\mathrm{AB}} = hJ_{\mathrm{AB}}\mathbf{I}_{\mathrm{A}} \cdot \mathbf{I}_{\mathrm{B}} \tag{1}$$

where $J_{\mathrm{AB}} = J_{\mathrm{AB}}{}^{\mathrm{Fc}} + J_{\mathrm{AB}}{}^{\mathrm{o}} + J_{\mathrm{AB}}{}^{\mathrm{sd}}$. Since E_{AB} is a second-order energy it is amenable to calculation by coupled Hartree–Fock perturbation theory[7] which is known to be correct through first order in correlation while containing parts of higher-order terms as well.[7,8] Adapting the theory to the calculation of J_{AB} for each of the three terms, in turn (i.e., p = Fc, o, sd), we obtain J_{AB} as the sum of contributions from the N occupied spin orbitals of the system:[8]

$$J_{\mathrm{AB}}{}^{\mathrm{p}} = (3h)^{-1}\sum_{i=1}^{N} \langle \chi_i{}^0|\mathbf{h}_{\mathrm{A}}{}^{\mathrm{p}}\cdot|\chi_i{}^{\mathrm{C}}\rangle + \text{complex conjugate} \tag{2}$$

Here, $\chi_i{}^0$ is a molecular spin orbital appearing in the zeroth order or unperturbed N-electron determinantal wave function ($N/2$ spatial orbitals are doubly occupied); $\chi_i{}^{\mathrm{C}}$ is the first-order perturbation correction due to the interaction, $\mathbf{h}_{\mathrm{B}}{}^{\mathrm{p}}$, between its electron and the nuclear spin $\mathbf{I}_{\mathrm{B}}$, which is constructed to be orthogonal to the occupied spin orbitals $\chi_j{}^0$. Since the perturbations are vector operators, $\chi_i{}^{\mathrm{C}}$ is a vector perturbed function and the factor of $1/3$ appearing in eq 2 corresponds to an average taken over the possible orientations of $\mathbf{I}_{\mathrm{B}}$ in a molecule-fixed coordinate system (the contact contribution is independent of $\mathbf{I}_{\mathrm{B}}$ orientation).

The three perturbing operators $\mathbf{h}_{\mathrm{B}}{}^{\mathrm{p}}$, summed over the electrons, are

$$\mathbf{h}_{\mathrm{B}}{}^{\mathrm{Fc}} = \frac{16\beta\gamma_{\mathrm{B}}\hbar}{3}\sum_{k} \delta(\mathbf{r}_{k\mathrm{B}})\mathbf{s}_{k\mathrm{B}} \tag{3a}$$

$$\mathbf{h}_{\mathrm{B}}{}^{\mathrm{o}} = 2\beta\hbar\gamma_{\mathrm{B}}\sum_{k} r_{k\mathrm{B}}{}^{-3}\mathbf{L}_k{}^{\mathrm{B}} \tag{3b}$$

$$\mathbf{h}_{\mathrm{B}}{}^{\mathrm{sd}} = 2\beta\hbar\gamma_{\mathrm{B}}\sum_{k} [3(\mathbf{s}_k \cdot \mathbf{r}_{k\mathrm{B}})\mathbf{r}_{k\mathrm{B}}r_{k\mathrm{B}}{}^{-5} - \mathbf{s}_k r_{k\mathrm{B}}{}^{-3}] \tag{3c}$$

with similar expressions holding for $\mathbf{h}_{\mathrm{A}}{}^{\mathrm{p}}$.

The $\chi_i{}^{\mathrm{C}}$ are obtained as solutions to the set of coupled first-order (in $\mathbf{I}_{\mathrm{B}}$) equations

$$\begin{aligned}(h^0(1) - e_i{}^0)\chi_i{}^{\mathrm{C}}(1) + (\mathbf{h}_{\mathrm{B}} + \mathbf{w} - \langle\chi_i{}^0|\mathbf{h}_{\mathrm{B}} + \mathbf{w}|\chi_i{}^0\rangle)&\\ \times \chi_i{}^0 = 0 \qquad i = 1, 2, \ldots, N&\end{aligned} \tag{4}$$

where $\mathbf{w}(1)$ is the nonlocal self-consistency operator

$$\begin{aligned}\mathbf{w}(1) = \sum_{j=1}^{N} (\langle\chi_j{}^{\mathrm{C}}|r_{12}{}^{-1}(1 - P_{12})|\chi_j{}^0\rangle&\\ + \langle\chi_j{}^0|r_{12}{}^{-1}(1 - P_{12})|\chi_j{}^{\mathrm{C}}\rangle)&\end{aligned} \tag{5}$$

While eq 2 involving the $\chi_i{}^{\mathrm{C}}$ determined from eq 4 is an expression based on delocalized orbitals it is also possible to write J_{AB} in terms of a set of localized orbitals, $\eta_i{}^0$, and the coupled-perturbed counterparts, $\eta_i{}^{\mathrm{C}}$, as the analogous sum[9]

$$J_{\mathrm{AB}} = (3h)^{-1}\sum_{i=1}^{N} \langle \eta_i{}^0|\mathbf{h}_{\mathrm{A}}{}^{\mathrm{p}}\cdot|\eta_i{}^{\mathrm{C}}\rangle + \text{complex conjugate} \tag{2$'$}$$

The $\eta_i{}^{\mathrm{C}}$ satisfy an equation slightly more complicated than eq 4 and although there are no reported calculations that have obtained the localized contributions directly, eq 2′ is important in expressing the relationship between the electronic structure of a molecule and its coupling constants. The first example of a localized orbital analysis is given in section IV.

Equation 4 can be rewritten in terms of the unperturbed spin orbitals, $\chi_p{}^0$, of orbital energy $e_p{}^0$

$$\chi_i{}^{\mathrm{C}} = \sum_{p} |\chi_p{}^0\rangle\langle\chi_p{}^0|\mathbf{h}_{\mathrm{B}} + \mathbf{w}|\chi_i{}^0\rangle(e_i{}^0 - e_p{}^0)^{-1} \tag{6}$$

Only the unoccupied spin orbitals need be included in the sum since the occupied orbitals do not contribute to J_{AB}, the denominator $(e_i{}^0 - e_p{}^0)^{-1}$ being antisymmetric in i and p. We may further expand the $\chi_i{}^0$ and their perturbation corrections in an atomic orbital basis set $\{\phi_u\}$[10]

$$\chi_i{}^0 = \sum_{u} \phi_u C_{ui} \tag{7a}$$

$$\chi_i{}^{\mathrm{C}} = \sum_{u} \phi_u \mathbf{D}_{ui} \tag{7b}$$

where the vector coefficient $\mathbf{D}_{ui}$ is given by

$$\begin{aligned}\mathbf{D}_{ui} = \sum_{p}^{\text{unocc}}\sum_{v,z}^{\text{AO's}} C_{up}C_{vp}{}^*C_{zi}(e_i{}^0 - e_p{}^0)^{-1}&\\ \times \left\langle v||\mathbf{h}_{\mathrm{B}} + \sum_{x,y}^{\text{AO's}} \mathbf{P}_{xy}{}^1\langle x|r_{12}{}^{-1}(1 - P_{12})|y\rangle_2||z\right\rangle_1&\end{aligned} \tag{8}$$

the subscripts indicating electron coordinate integrations. The quantity

$$\mathbf{P}_{xy}{}^1 = \sum_{j=1}^{\text{occ}} (\mathbf{D}_{xj}{}^*C_{yj} + C_{xj}{}^*\mathbf{D}_{yj}) \tag{9}$$

is the vector correction to the density matrix first order in $\mathbf{I}_{\mathrm{B}}$, and is proportional to the atomic orbital matrix element $\langle v|\mathbf{h}_{\mathrm{B}}|z\rangle$. Should an iteration scheme for the $\mathbf{D}_{ui}$ converge, J_{AB} is obtained from eq 2, 7, 8, and 9 as

$$J_{\mathrm{AB}} = (3h)^{-1}\sum_{tu}^{\text{AO's}} \mathbf{P}_{tu}{}^1 \cdot \langle t|\mathbf{h}_{\mathrm{A}}|u\rangle \tag{10}$$

Thus J_{AB} is proportional to the product of atomic orbital matrix elements $\langle t|\mathbf{h}_{\mathrm{A}}|u\rangle$ and $\langle v|\mathbf{h}_{\mathrm{B}}|z\rangle$ explicitly and implicitly, respectively. That both matrix elements of $\mathbf{h}_{\mathrm{A}}$ and $\mathbf{h}_{\mathrm{B}}$ should appear symmetrically in J_{AB} is clear from the a priori equivalence of nuclear spins $\mathbf{I}_{\mathrm{A}}$ and $\mathbf{I}_{\mathrm{B}}$ in eq 1.

While an ab initio evaluation of J_{AB} in the present formalism is possible for small molecules[11] it would be quite expensive for a molecule with say six first-row atoms as in an aromatic; the corresponding calculation at an INDO level, on the other hand, is reasonably inexpensive. This method has been programmed by Blizzard and Santry[2b] and it is equivalent, in principle, to the finite perturbation method which has been applied to the Fermi contact term[12] but not the orbital and dipolar terms. (At a more approximate level yet are calculations employing average energy denominators.)

In the spirit of the differential overlap approximation only one-center integrals $\langle t|\mathbf{h}_{\mathrm{A}}|u\rangle$ are included in the present treatment; thus ϕ_t and ϕ_u are valence s orbitals on atom A with exponents adjusted for agreement with experiment. The final expression for $J_{\mathrm{AB}}{}^{\mathrm{Fc}}$ contains the factor $S_{\mathrm{A}}{}^2(0)S_{\mathrm{B}}{}^2(0)$, the product of valence s densities at the two nuclei. The expressions for $J_{\mathrm{AB}}{}^{\mathrm{o}}$ and $J_{\mathrm{AB}}{}^{\mathrm{sd}}$ are each proportional to $\langle r^{-3}\rangle_{\mathrm{A}}\langle r^{-3}\rangle_{\mathrm{B}}$, the averages being over the p valence electrons. While the approximations made in employing the INDO method (i.e., differential overlap, spherically averaged two-electron integrals, and the retention of solely one-center perturbation integrals) are not negligible, it is assumed that by treating $S_{\mathrm{A}}{}^2(0)S_{\mathrm{B}}{}^2(0)$ and $\langle r^{-3}\rangle_{\mathrm{A}}\langle r^{-3}\rangle_{\mathrm{B}}$ (hereafter referred to as a and b, respectively) as least-squares-determined parameters the basic accuracy of the coupled Hartree–Fock theory can be recovered.[13]

Table I. Calculated Values for J_{CN} (Hz) in Nitrogen-Containing Carbon Compounds[a]

Molecule	Bond	J_{CN}^{Fc}	J_{CN}^{o}	J_{CN}^{sd}	J_{CN}(total)	J_{CN}(exptl.)[f]
Hydrogen cyanide	CN	3.3	−9.4	−12.7	−18.8	
Cyanide ion (1.15 Å)[b]	CN	−0.7	15.8	−8.0	7.1	(5.9)[g]
Acetonitrile	C≡N	3.7	−7.9	−12.7	−16.8	−17.5[h]
	CN	3.1	0.3	0.1	3.5	3.0[h]
Methyl isocyanide	N≡C	24.0	−6.0	−10.2	7.8	(9.1)[i]
	CN	−11.9	0.2	−0.1	−11.8	−10.7[j]
Methylamine	CN	−2.7	0.2	−0.1	−2.6[c]	−4.5[k]
Pyrrole	C_1N	−14.8	0.9	0.0	−13.9	−13.0[l]
	C_2N	−0.6	−0.1	−0.1	−0.8	−3.9
Pyridine	C_1N	−0.7	1.6	−0.3	0.6	0.6[l]
	C_2N	2.9	−0.1	0.3	3.1	2.5
	C_3N	−3.2	−0.1	−0.4	−3.7	−3.9
Pyridinium ion	C_1N	−13.5	1.2	−0.2	−12.5	−11.9[l]
	C_2N	3.6	0.0	0.1	3.7	2.0
	C_3N	−4.3	−0.1	−0.3	−4.4	−5.3
Pyridine *N*-oxide	C_1N	−18.3	1.2	−0.8	−17.9	−15.2[l]
	C_2N	5.4	−0.1	0.5	5.8	1.4
	C_3N	−6.2	2.1	−0.9	−5.0	−5.2
Aniline	C_1N	−8.0	0.4	−0.1	−7.7[d]	−11.4[l]
	C_2N	−0.1	0.0	−0.2	−0.3	−2.7
	C_3N	−1.6	0.0	0.0	−1.6	−1.3
	C_4N	−0.7	0.0	−0.1	−0.8	(0.3)
Azirane (C_2NH_5)	CN	3.7	0.4	0.0	4.1	
Formamide	CN	−11.4	0.7	0.0	−10.7	
Formaldoxime	CN	0.5	1.9	−0.9	1.5	⟨2.96⟩[m]
Nitromethane	CN	−17.8	0.2	−0.1	−17.7[e]	−10.5[n]
Methylenimine (CH_2NH)	CN	−2.1	2.1	−0.8	−0.8	

[a] The parameters employed were $S_C^2(0)S_N^2(0) = 13.79a_0^{-3}$ and $\langle r^{-3}\rangle_C\langle r^{-3}\rangle_N = 1.77a_0^{-3}$ except for CN^-, CH_3CN, and the CH_3NC isocyanide bond where 17.08 and 15.34 were the respective values. [b] The experimental bond length of NaCN. [c] The experimental geometry of Nishikawa et al., *J. Chem. Phys.*, **23,** 1735 (1955), was used. The results for a planar nitrogen geometry are $J^{Fc} = -13.5$, $J^o = 0.4$, and $J^{sd} = -0.1$, and for a tetrahedral nitrogen, $J^{FC} = -2.3$, $J^o = 0.3$, and $J^{sd} = -0.1$. [d] The experimental geometry of Lister and Tyler, *Chem. Commun.*, 152 (1966), was used. The corresponding one-bond terms for planar aniline are $J^{Fc} = -13.5$, $J^o = 0.3$, and $J^{sd} = 0.0$. [e] This is the value obtained from 17 iterations after which divergence occurred. In general, the presence of oxygen attached to the nitrogen seems to impede convergence. [f] Values in parentheses are of unknown signs. For the purposes of obtaining least-squares fits the CN^- and N≡C constants were taken to be positive as predicted by the calculations. [g] G. A. Gray, Ph.D. Dissertation, University of California, Davis, 1967. [h] W. McFarlane, *Mol. Phys.*, **10,** 603 (1966). [i] W. McFarlane, *J. Chem. Soc. A,* 1660 (1967). [j] I. Morishima, A. Mizuno, and T. Yonezawa, *Chem. Commun.*, 1321 (1970). [k] L. Paolillo and E. D. Becker, *J. Magn. Reson.*, **3,** 200 (1970). [l] T. Bundegaard and H. J. Jakobsen, *J. Magn. Reson.*, **19,** 345 (1975). [m] R. L. Lichter, D. E. Dorman, and R. Wasylishen, *J. Am. Chem. Soc.*, **96,** 930 (1974). [n] E. D. Becker and R. B. Bradley, cited in T. Axenrod, "Nitrogen NMR", G. Webb and M. Witanowski, Ed., Plenum Press, New York, N.Y. 1972, p. 261.

III. **Results**

In analyzing the results for J_{CN} for the molecules in Table I *a* and *b* were treated as least-squares parameters obtained by fitting the experimental $^1J_{CN}$ values of nine carbon-nitrogen bonds. The best agreement with experiment came from treating the triple and isocyanide bonds separately so that one fit, using the multiple CN bonds of CN^- and $CH_3N{\equiv}C$ assuming positive coupling constants and acetonitrile, furnished $a = 17.08$ and $b = 15.34$ (in a_0^{-3})[20] with a standard deviation of 1.1 Hz. For the remaining coupling constants in Table I, *a* and *b* values of 13.79 and 1.77, respectively, obtained by fitting $^1J_{CN}$ of methylisocyanide, methylamine, pyrrole, pyridine, pyridinium ion, and aniline (six in all), were used. Here, the standard deviation was 1.2 Hz (14% of the average). In all cases the experimental geometry or a close approximate was used.

From the results in Table I it can be seen that the calculations correctly predict the known signs of J_{CN} in every case, including a wide variety of bonding situations and an appreciable range of experimental values (−18 to +9 Hz). The reasonably good quantitative agreement with experiment allows some statements to be made regarding individual terms and trends.

Examination of the Fermi contact terms in Table I shows that $^1J^{Fc}$ is large and negative in the aromatics except pyridine, small and negative in methylamine, nearly zero in CN^- and pyridine, small and positive in the nitriles, and large and positive in the isocyanide bond. In acetonitrile and pyridine the calculated Fermi contact term is smaller than the orbital and dipolar terms and it is *opposite in sign* to the experimental value.

The orbital contribution $^1J^o$ is positive except for the C≡N and N≡C bonds and curiously, in almost all cases it has a sign opposite that of the contact term (as is the case for $^1J_{CC}$ as well[4]). $^1J^o$ is the dominant contributor to J_{CN} for CN^-, which our calculation suggests is positive.

The dipolar term $^1J^{sd}$ is negligible with the exception of C≡N and N≡C bonds. It makes the largest contribution in CH_3CN where it combines with the orbital term of like sign to give a large negative $^1J_{CN}$. In CH_3NC and CN^- $^1J^{sd}$ is also large and negative, although not the dominant term. Thus, it is found that within Table I there are instances in which *each of the three terms may make the largest contribution to* $^1J_{CN}$. It might also be noted that of the three terms $^1J^{Fc}$ is very sensitive to the geometry used whereas $^1J^o$ and $^1J^{sd}$ are not. An example of this are the three respective contributions to ^1J for the cyanide ion at a bond length of 1.07 Å (−6.0, +12.9, and −4.1); here there is a tenfold increase in the contact term. A second example is the sensitivity of $^1J^{Fc}$ in amines to the extent of pyrimidization as evidenced from the values for methylamine at the experimental and assumed planar and tetrahedral nitrogen geometries. The effect of vibrational averaging is currently under investigation.

In contrast to the one-bond constants, $^2J_{CN}$ and $^3J_{CN}$ are always dominated by the Fermi contact term. The calculated results are in good agreement with experiment except for $^2J_{CN}$ in pyrrole and aniline where the error in magnitude is large.

Finally, Table I contains calculated coupling constants for several molecules for which there are no experimental results, although related systems have been studied. For the three-membered ring-molecule azirane we obtain $J_{CN} = +4.1$ Hz; a sign determination of J_{CN} in a substituted oxazirane furnished +4.9 Hz.[14] The calculated value for J_{CN} in formamide was −10.7 Hz. As the measured magnitude of J_{CN} in acetamide and similar systems is 14 Hz,[15] this result seems reasonable and we assign their signs to be negative.

There is no experimental value of $^1J_{CN}$ in methylenimine which, using an ab initio optimized geometry, we calculate to be −0.8 Hz. An experimental determination of $^1J_{CN}$ has recently been made for the syn and anti isomers of the *N-tert*-butylimine of 9-anthraldehyde.[16] In both cases the value obtained was −5.0 Hz. It seems likely that the negative sign for methylenimine is correct. In this regard it is interesting to note that a positive $^1J_{CN}$ is calculated for formaldoxime due principally to the fact that the Fermi contact term is much smaller (and positive) than in methylenimine. It is not clear whether the difference in contact terms arises from the oxygen or from differences in geometry of the two molecules.

IV. Discussion

The present study supplies answers to the questions: (1) do the orbital and spin-dipolar terms make significant contributions to J_{CN}; and (2) what is the utility and scope of the Binsch relation[17] between $^1J_{CN}$ and the product of percent s characters in the bonding hybrids

$$J_{CN} = -0.0125 S_C S_N \qquad (11)$$

(minus sign supplied here)? As we have seen, the answer to the first question is yes for nitriles, isocyanides and pyridine, where $^1J^{o}$ and $^1J^{sd}$ are inherently large and the contact terms are small. Also noteworthy is the fact that the contact term is frequently positive in these systems (though it is of the correct sign in the other couplings) and this immediately provides counterexamples to eq 11 whose right-hand side must be negative by the definition of percent s character. In fact, there is nothing particularly anomalous about the hybridizations in pyridine, for example, both atoms use nearly sp^2 orbitals as shown from a localization of the INDO orbitals.[18] We turn then to the origin of these seemingly unusual contact terms.

Examination of the sum over occupied molecular orbitals in eq 2 shows, for pyridine, that the small value $^1J^{Fc} = -0.7$ arises from a cancellation of terms. A large positive contribution arises from the highest occupied molecular orbital which is largely lone pair in character. In contrast, no such cancellation is found in the calculation of $^1J^{Fc}$ for the pyridinium ion, the result being a large negative value. Similar cancellations occur for the other entries of Table I which have small contact terms. The common feature in each of these cases is the presence of a lone pair containing s character. Thus, it appears that large negative values of $^1J^{Fc}$ occur in molecules having no such lone pairs (class I molecules), while smaller negative or positive $^1J^{Fc}$, values depending on the extent of the cancellation, are found when a σ lone pair is present on the nitrogen (class II molecules) or carbon in the case of an isocyanide. This *one-bond lone-pair effect* is particularly pronounced in methylisocyanide where the presence of a lone pair on carbon leads to a large positive $^1J^{Fc}$.

It appears that the Binsch relationship might retain its validity if applied strictly to class I molecules where the cancellation does not occur and the contact term is therefore also dominant. Thus substituting the nominal value of 33.3% for both carbon and nitrogen into eq 11 (i.e., sp^2 bonding hybrids) leads to $^1J_{CN}$ of ca. −13 Hz, which is indeed nearly the case for pyrrole and planar aniline whose lone pairs are pure p, pyridinium ion, and the predicted value for formamide (as well as the experimental values in magnitude of other amides[16]). Whether the predicted linearity will hold up awaits more refined calculation of the hybrizations.

It is of interest to try to make a closer connection between the presence of a lone pair and the resultant coupling constant. Thus we seek to examine the origin of $^1J^{Fc}$ from the vantage point of the localized orbital description, eq 2′. First, consider the role of the localized CN bond orbital in the sum over states. The σ orbital of α spin, $\eta_{\sigma\alpha}{}^0$, when perturbed by the operator $s_z\delta(\vec{r}_N)$ is modified by mixing in some antibonding component $\eta_{\sigma^*\alpha}{}^0$. Since the carbon and nitrogen 2s coefficients are of the same sign in $\eta_{\sigma\alpha}{}^0$ and opposite sign in $\eta_{\sigma^*\alpha}{}^0$, given the negative effective energy denominator and the negative γ_N, $\eta_{\sigma\alpha}{}^0$ makes a negative contribution to $^1J^{Fc}$. A similar argument leading to a negative contribution from $\eta_{\sigma\beta}{}^0$ can readily be constructed.

For class II molecules, however, an additional contribution to $^1J^{Fc}$ from the lone pair must be considered. At first glance it might be thought that no contribution would be made from $\eta_{lp}{}^0$ since if it were fully localized on nitrogen there would be no contact interaction with the carbon nucleus. However, the small "tail" of the lone pair on the other atoms, needed for its orthogonality to the other localized orbitals, supplies the carbon density. To determine the sign of the contribution in eq 2′ of the lone pair one must again follow the relative signs of C_{2s} and N_{2s} in $\eta_{lp}{}^0$ and $\eta_{lp}{}^C$. Briefly, it appears that the perturbation correction will be derived principally from the $\eta_{\sigma^*}{}^0$ virtual orbital as the lone pair has no antibonding counterpart. Also, in the examples we have examined, $\eta_{lp}{}^0$ has oppositely signed C_{2s} and N_{2s} coefficients unlike the $\eta_\sigma{}^0$ case and therefore it makes a positive contribution to $^1J^{Fc}$. Of course, when the lone pair has no s content, no contact contribution from it exists. It appears to be difficult to prove that the lone-pair contribution will, in general, be positive as this depends on the sign of C_{2s} in the lone pair tail which could, in principle, be influenced by nitrogen substituents and perhaps geometry. Thus there may ultimately be found examples in which both the $\eta_\sigma{}^0$ and $\eta_{lp}{}^0$ lead to negative terms in eq 2′ for an exhaltation of the Binsch prediction.

The above argument is a qualitative interpretation of the one-bond lone-pair effect based on uncoupled perturbation theory arguments. In order to obtain a quantitative interpretation based on the coupled Hartree-Fock theory, a localized orbital analysis has been made for the Fermi contact term of the one-bond constant of pyridine according to eq 2′. The second term of this equation was written in the form $\Sigma_j\langle\eta_i{}^0|\mathbf{h}_B{}^{Fc}\cdot\eta_i{}^C\rangle$ where $|\eta_i{}^C\rangle$ is the localized coupled Hartree-Fock correction due to the perturbation $\mathbf{h}_A{}^{Fc}$. The results, given in Table II, confirm that the net, small coupling constant $^1J_{CN}{}^{Fc}$ of pyridine arises from extensive cancellation among the various terms in the sum over occupied localized molecular orbitals, the principal contributors being the localized CN σ bond, the lone pair, and those localized orbitals proximate to the CN bond. This seems physically reasonable.

The sum of the localized orbital contributions excluding that of the lone pair is −16.5 Hz, reasonably close to the value appearing in our discussion of the Binsch relationship vide supra, while the lone pair contribution, 15.5 Hz, provides the nearly complete cancellation inferred previously from the delocalized orbital results, according to eq 2. It thus seems fair to speculate that the localized contributions *sans* the lone pair are to some extent transferable within molecules of the same type bond, i.e., single, double, and perhaps triple CN bonds, while the lone-pair contribution will vary independently and significantly

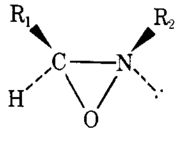
Table II. Localized Orbital Contributions to $^{1}J_{\mathrm{C_1N}}{}^{\mathrm{Fc}}$ in Pyridine (Hz)

Localized orbital[a,b]	Contribution to $^{1}J_{\mathrm{C_1N}}{}^{\mathrm{Fc}}$	Localized orbital[a,b]	Contribution to $^{1}J_{\mathrm{C_1N}}{}^{\mathrm{Fc}}$
C_1N	−24.3	C_2C_3	−0.1
Lone pair	15.5	C_3C_4	−0.1
C_1H_1	9.9	C_2H_2	0.1
C_1C_2	−4.9	C_3H_3	−0.1
NC_5	2.2	C_4C_5	0.1
C_5H_5	0.7	C_4H_4	0.0
Total			−1.0

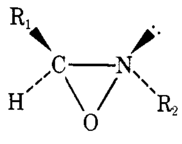
[a] The orbitals, localized according to the Edmiston-Ruedenberg criterion, were of σ and π symmetry; the latter make no contribution to the coupling constant. [b] The molecular geometry was slightly different from that used for the pyridine calculation of Table I.

from case to case, disappearing to a large extent on protonation and loss of its s character.

The existence of an explicit contribution to $^{1}J_{\mathrm{CN}}{}^{\mathrm{Fc}}$ from the lone pair allows an explanation of several observations which have appeared in the literature. For example, the oxazirane with coupling constant +4.9 is in the Z configuration with its CH bond and lone pair cis.[14] The corresponding E isomer with lone pair and p-nitrophenyl group cis has a coupling constant of magnitude 3.1 (presumably positive). The difference in J for the two isomers could accounted for by a larger amount of p character in the E lone pair to reduce its greater steric repulsion, the result being a smaller positive contribution. Of course, a concomitant increase in the s character of the nitrogen hybrid in the CN bond would lead to the same result, and only a detailed calculation would predict which effect was the more important (and to some extent they are not independent). However, the overall net positive sign of J indicates that the lone pair is making a contribution which is important.



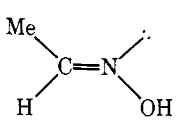
Z



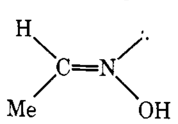
E

R_1 = *p*-nitrophenyl
R_2 = isopropyl

The same kind of argument can be made for the Z and E isomers of acetaldoxime, J = 2.3 and 4.0, respectively, and presumably positive from the calculations reported.[19] Here the lone pair of the Z isomer should have more p character to diminish its repulsion by the methyl group leading again to a smaller $^{1}J_{\mathrm{CN}}{}^{\mathrm{Fc}}$.



Z



E

Finally, the one-bond lone-pair effect can be expected to appear for nuclei other than nitrogen (e.g., P) bonded to nuclei other than carbon (e.g., H). Thus, a positive lone-pair contribution explains the anomalously small value of $^{1}J_{\mathrm{NH}}$ observed in diphenylketimine, and an orbital mechanism need not be invoked.

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(20) NOTE ADDED IN PROOF. J_{CN} for $^{14}N{\equiv}C$ of methyl isocyanide has recently been determined to be positive, +6.33 Hz [N. J. Koole, D. Knol, and M. J. A. DeBie, *J. Magn. Reson.*, **21**, 499 (1976)] contrary to the assumption made here; this requires a modification of *a* and *b* for CN triple bonds. Using the corresponding isocyanide $J_{^{15}\mathrm{NC}}$, −8.9 Hz, $J = -17.5$ Hz for acetonitrile, and $|J_{\mathrm{CN}}| = 77.5$ Hz for 2,4,6-trimethylbenzonitrile oxide [M. Christl, J. P. Warren, B. L. Hawkins, and J. D. Roberts, *J. Am. Chem. Soc.*, **95**, 4392 (1973)], presumably negative, $a = 13.10$ and $b = 20.85$ are obtained. The four triple bond values of Table I should be so modified, leading to no change in the conclusions reached heretofore. For benzonitrile oxide, the model for the latter compound, the calculated $J_{\mathrm{CN}} = -75.2$ Hz arises from $J^{\mathrm{Fc}} = -34.4$, $J^{\circ} = -23.0$, and $J^{\mathrm{sd}} = -17.8$ Hz.