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Spin Polarization and Localized Molecular Orbitals of Amino Radicals

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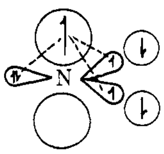
Abstract: Energy localized orbitals are generated from INDO wave functions for the π radicals NH_2, $N(CH_3)_2$, NC_2H_4, and NH_3^+ to test the currently used model for π–σ orbital polarization. In addition, vibronic contributions to a_N for NH_2 and NH_3^+ were examined and found to be smaller than those from *ab initio* methods. Conversely, the energy minimum a_N values are somewhat larger for the semiempirical method. Analyses of localized lone-pair and bond-pair orbital polarizations for the NX_2 radicals reveal the bond pairs to be the major source of positive nitrogen atom (that is, total s and p) spin density. The nitrogen s orbital spin density, however, gets its main contribution (positive) from the lone pair while the bond pairs give negative contributions. The origin of the latter is a direct result of minimized π–σ electron repulsion. The increase in nitrogen s spin density with increasing HNH angle of NH_2 is analyzed in terms of lone and bond hybrid variations as is the substituent effect of replacing H with CH_3.

For quite some time now the chemist has used the concept of $\pi \rightarrow \sigma$ spin polarization as a model or mechanism by which nonzero orbital spin density (used here to mean $P_{aa}{}^{\alpha} - P_{aa}{}^{\beta}$, where P^{α} and P^{β} are the α and β electron density matrices) may be introduced into the σ orbitals of π radicals. Mathematical formulation of the polarization has been achieved by use of configuration interaction refinement of independent electron approximations[1] and more directly by use of the unrestricted Hartree–Fock–Roothan method.[2] For a qualitative, working model, one often visualizes the effects of spin correlation in terms of localized molecular orbitals formed by overlapping atomic hybrid orbitals. Propagation of σ spin density is predicted[3] by spin correlation between σ orbitals. For the amino radical, a diagram such as the following would be used



where the dotted lines identify the spin correlation forces causing the accumulation of nonzero spin density about each atom. The basic physical phenomenon at play in spin-polarization is the greater repulsion between two electrons of opposite spin than between two electrons of the same spin.

At present, the most popular method for studying spin polarization is the unrestricted, self-consistent field method outlined by Pople and Nesbet.[2] The one-electron wave functions of this method, however, are highly delocalized over several nuclei and make impossible a direct analysis of $\pi \rightarrow \sigma$ spin polarization in terms of the localized σ pairs model mentioned above. To bring the two schemes into closer perspective, we apply the localization procedure developed by Edmiston and Ruedenberg[4] for closed-shell molecules to some simple nitrogen radicals: NH_2, NH_3^+, $N(CH_3)_2$, and NC_2H_4. To our knowledge, the Edmiston–Ruedenberg method has been applied[5] to only two other odd-electron species, NO and O_2.

The choice of nitrogen radicals was suggested by recent experimental work[6] on them and by their simplicity of structure and size. The primary goal is to examine $\pi \rightarrow \sigma$ spin polarization where the σ electrons may be treated as localized, but polarized, pairs and

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(1) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

(2) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 22, 571 (1954).

(3) J. P. Copla and E. de Boer, *Mol. Phys.*, 7, 333 (1963).

(4) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963); *J. Chem. Phys.*, **43**, S97 (1965); in "Quantum Theory of Atoms, Molecules, and the Solid State," P. O. Lowdin, Ed., Academic Press, New York, N. Y., 1966; J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc., London*, **202**, 166 (1950).

(5) D. M. Hirst and M. E. Linington, *Theor. Chim. Acta*, **16**, 55 (1970).

(6) W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970).

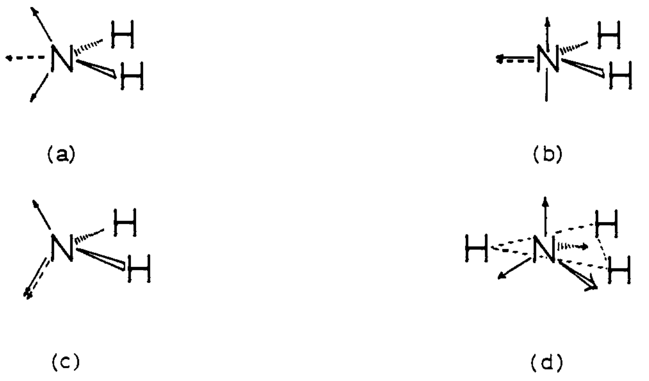

Figure 1. Vector sketches of localized orbitals. For the unshared electrons, solid vectors represent α-spin and dashed vectors represent β-spin hybrids. Shared electrons are not distinguished by α and β spin in these sketches.

at the same time stay within the constraints of a mathematically consistent formulation of the molecular electron distribution. The Edmiston–Ruedenberg criterion for localized orbitals (that of minimum e,e repulsions) is truly objective among those methods proposed for generating localized orbitals from delocalized ones. A further advantage is that Newton[7] has worked out a procedure for testing satisfactory convergence of the search for a true minimum in e,e repulsions. In those cases where highly localized wave functions can be generated, we are justified in examining the nonzero spin density about each atom in terms of α- and β-spin hybrid atomic orbitals, the partitioning of atomic orbital (in particular the valence s orbital) spin density among the several atomic hybrids, and the operation of substituent and bond angle effects on atomic spin densities. At the outset we recognize a potential interplay of spin correlation forces and "substituent effects" in controlling the s characters and s orbital spin density contributions of the various hybrid atomic orbitals about a given atom.

Theoretical Methods and Results

The calculations for all the radicals were of the INDO variety using a program originally obtained from the Quantum Chemistry Program Exchange.[8] The wave functions and repulsion integrals for these molecules at their energy minimized geometries[9] (see Table I for the geometries and a comparison of calculated[10] and observed a_N values) were used in a locally written program to generate the localized orbitals of minimum interorbital repulsion. The details of the localization procedure are given elsewhere.[11] Briefly, the energy localized orbitals are generated by successive pair-wise transformation of the INDO canonical orbitals (symmetry orbitals) in the manner to minimize the repulsions between electrons in different orbitals. The convergence criterion used here (different from that used previously[11]) is that the quantity B_{ij}^3 be less than 10^{-5} for all possible pair-wise orbital mixings. Following the methodology of the unrestricted INDO technique, the energy localized α and β spin orbitals are generated separately.[5] All converged wave functions were subjected to Newton's localization test[7] and found to correspond to true minima in e,e repulsion.

Table I. Radical Geometries

	NH_2	NH_3^+	$N(CH_3)_2$	NC_2H_4
r_{NX}, Å	1.07	1.08	1.39	1.43
∠XNX, deg	104.8	120	117	61.39
r_{XX}, Å				1.46
r_{XH}, Å			1.12	1.12
∠HXH, deg			107.15	110.7
				158.5[a]
a_N, G	12.4	21.6	13.8	10.3
(Obsd)	10.3	19.5	14.8[b]	12.5[c]
	13.3[d]	18.1[d]		

[a] The angle defined by a CH_2 plane and the C–C axis. [b] Reference 6. [c] Reference 13. [d] See Table III.

The localized orbitals for the amino radicals (NX_2) can be described in general terms as follows. For the nitrogen atom, for which there are nominally four α spin orbitals, the α localized orbitals can be crudely described as sp^3 or tetrahedral in type. Since the nitrogen has only three β spin electrons in its vicinity, the expected (approximately trigonal planar) β spin localized orbitals result from the localization procedure. These orbitals are qualitatively those expected from the Pauli principle and are schematically described in Figure 1a.

Rather than use the four hybrid α orbitals as developed by the localization technique, we have chosen to transform the two localized lone α orbitals of NX_2 back into a $p\pi$ and an sp^2 type σ orbital. The reason for doing this is that the working model of spin polarization with which we want to compare the SCF results adopts this orbital pattern. The important point is that the reversion to a $\sigma + \pi$ scheme *does not alter the distribution of nitrogen s character between lone and bond hybrids.* As will be discussed later, these final orbitals are *not* the same as those from localization of σ orbitals alone. The back transformation is simply done by applying the unitary transformation

$$\begin{vmatrix} a & -a \\ a & a \end{vmatrix}$$

with $a = 1/\sqrt{2}$, to these orbitals. The final orbital description for the nitrogen atoms in these radicals is that of one $p\pi$ atomic orbital and a set of trigonal planar α and a set of trigonal planar β spin orbitals (Figure 1b). The final orbitals are characterized in Table II.[12] (The molecular skeletons lie in the yz plane with the z and C_2 symmetry axes coincident.)

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(7) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970); M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 2645 (1970).

(8) P. A. Dobosh, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind., No. 141.

(9) C_{3v} symmetry was assumed for NH_3^+. The other radicals were constrained to C_{2v} symmetry. All angles and distances were varied for NC_2H_4 while local C_{3v} symmetry was imposed on the CH_3 groups of $N(CH_3)_2$.

(10) A referee has expressed a general concern that the nitrogen 1s orbitals have not been explicitly included in the INDO computations. The core electrons can be quite safely ignored as far as the localized orbitals are concerned as numerous *ab initio* calculations[4,7] on many molecules have shown these orbitals to be highly localized and pure. The contribution to a_N of 1s polarization is, under the INDO scheme, accounted for by the parameterization of $\rho_s(0)$. To include the 1s orbital of nitrogen specifically would, in view of the highly localized nature of core electrons, require using different 1s radial functions for α and β spin electrons—a refinement not made for the valence 2s functions.

(11) T. G. M. Dolph, M. J. Schultz, and K. F. Purcell, Program No. 198, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.; K. F. Purcell and T. G. M. Dolph, *J. Amer. Chem. Soc.*, **94**, 2693 (1972).

(12) Tables of the final eigenvectors will appear following these pages in the microfilm edition of this volume of the journal. Single

Table II. Localized σ Orbitals about Nitrogen as Linear Combinations of Normalized Atomic Hybrids: $\Psi = C_N\chi_N + C_x\chi_x$, $\chi_N = a\phi_s + b\phi_p$

		C_N	C_x	a	b	sp^x	Angle,[a] deg
NH_2							
α spin	lp	1.000	−0.019	0.819	0.573	$sp^{0.49}$	
	NH	0.751	0.660	0.423	0.906	$sp^{4.59}$	101
β spin	lp	0.993	−0.081	0.728	0.685	$sp^{0.89}$	
	NH	0.727	0.687	0.548	0.837	$sp^{2.33}$	111
$N(CH_3)_2$							
α spin	lp	0.987	−0.094	0.738	0.675	$sp^{0.84}$	
	NC	0.745	0.659	0.467	0.884	$sp^{3.58}$ ($sp^{2.46}$)[b]	107
β spin	lp	0.987	−0.097	0.651	0.759	$sp^{1.36}$	
	NC	0.728	0.679	0.553	0.833	$sp^{2.27}$ ($sp^{2.55}$)[b]	117
NC_2H_4							
α spin	lp	0.999	−0.033	0.844	0.537	$sp^{0.40}$	
	NC	0.739	0.657	0.366	0.931	$sp^{6.47}$ ($sp^{4.69}$)[b]	113
β spin	lp	0.990	−0.100	0.770	0.638	$sp^{0.69}$	
	NC	0.727	0.671	0.484	0.875	$sp^{3.27}$ ($sp^{4.79}$)[b]	123
NH_3^+							
α spin	NH	0.819	0.572	0.606	0.796	$sp^{1.73}$	120
β spin	NH	0.788	0.614	0.605	0.797	$sp^{1.74}$	120

[a] The angle between bond hybrids at nitrogen. [b] These values are for the carbon hybrids.

While on the subject of alternate orbital patterns we would like to mention that a structure such as 1c in Figure 1 is not permissible for the ground-state NH_2 radical. Missing is the mirror image resonance structure which is of equal importance to the one shown. The superposition of both structures produces a molecular wave function which is no different from that given for b in Figure 1. It is inappropriate to consider[13] only structure c as a possible structure for amino radicals, just as is the use of only one Kekulé structure for benzene.

The energy localized α spin orbitals of NH_3^+ are surprisingly like those of NH_3, even though NH_3^+ has an energy minimum planar structure. The N α spin hybrids to be identified as those used for NH bonding are *not* trigonal planar but make angles of 112° with the threefold axis (Figure 1d). This situation leads to about 6% delocalization of the lone orbital over the three hydrogen orbitals. Because of the difficulties[7] reported in obtaining a unique set of localized orbitals for planar NH_3, it is important to note that Newton's curvature analysis[7] confirms that these orbitals correspond to a true minimum in interelectron repulsions (to second order). A unitary transformation to a pπ + trigonal planar orbital pattern is possible and has been applied to give the orbitals to be used in later discussions. The transformed set of hybrids are characterized in Table II.[12]

In order to estimate the success of localization of the one-electron orbitals in these radicals, we have computed the probability with which each electron is to be found on atoms other than that defining the lone orbital or those defining the bond orbital; it was found that the delocalization of the NX and N lone pair orbitals never amounted to more than 2% in any of the four molecules. Thus we find it is possible to obtain highly localized orbitals for these radicals.

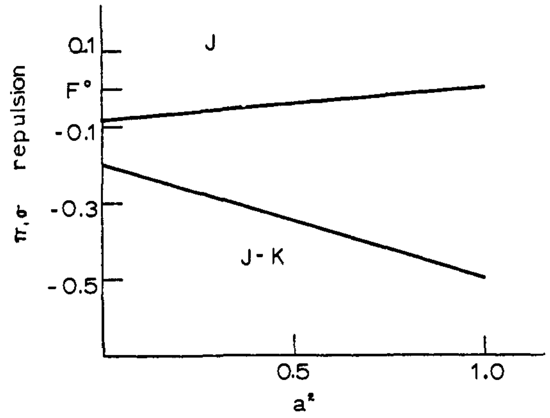

Figure 2. The π,σ repulsions $J_{\pi,sp}$ and $J_{\pi,sp}$, $-$ $K_{\pi,sp}$, in units of F^2, as a function of a^2, the fractional 2s character of the sp hybrid.

A point of some significance in the spin polarization process concerns how the INDO technique allows for the difference in electron-electron repulsion energy between an α pπ electron and an α sp^n σ electron on the one hand and between an α pπ electron and a β sp^n σ electron on the other. This is of importance to our goal of assessing the distribution of nitrogen valence s character and spin density between lone and bond hybrids. Representing the sp^n orbital as follows

$$\chi_{sp} = a\phi_s + b\phi_p$$

the repulsion energies are computed as simply the coulombic energy for the α,β pair and difference in coulombic and exchange energies for the α,α pair

$$J_{\pi,sp} = F^0 + \frac{2}{25}F^2(a^2 - 1)$$

$$K_{\pi,sp} = \frac{3}{25}F^2\left(1 + \frac{19}{6}a^2\right)$$

since $G^1 \sim {}^3/_2F^2$ for second-row elements.[14] (F^0, F^2, and G^1 are the usual Slater–Condon parameters.) The

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(13) W. C. Danen and T. Kensler, *Tetrahedron Lett.*, 2247 (1971).

(14) J. A. Pople D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967); *J. Amer. Chem. Soc.*, 90, 4201 (1968).

Table III. Calculated and Experimental Hyperfine Constants for NH_2 and NH_3^+

Radical	a_N, G		a_H, G	
	Exptl	Calcd	Exptl	Calcd
NH_2	10.3^a	$(12.4, 12.5^c)^h$	23.9	$(-22.5, -22.7^c)^h$
	13.3^b	$(8.5, \ldots)^d$		
NH_3^+	18.1^e	$(21.6, 23.2^c)^h$	25^e	$(-26.6, -25.4^c)^h$
	19.5^e	$(10.6, 16.9^c)^g$	25.9^f	$(-22.7, -20.0^c)^g$

[a] At 4°K, Ar matrix; S. Foner, E. Cochran, V. Bowers, and C. Jen, *Phys. Rev. Lett.*, **1**, 91 (1958). [b] 77°K, KNH_2SO_3: J. R. Morton and D. R. Smith, *Can. J. Chem.*, **44**, 1951 (1966). [c] Corrected for vibronic contribution. [d] Reference 15a. [e] J. S. Hyde and E. S. Freeman, *J. Phys. Chem.*, **65**, 1636 (1961). [f] T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961). [g] Reference 15 b. [h] This work.

variations in $J_{\pi,\mathrm{sp}}$ and $J_{\pi,\mathrm{sp}} - K_{\pi,\mathrm{sp}}$ are shown in Figure 2 as a function of a^2, the s character of the sp^n orbital. The graphical presentation makes clear that the (π,sp) electron exchange energy *markedly* favors high s character of α spin hybrids about a second row atom whereas p character is favored, albeit modestly, for the β spin hybrids. Consequently, π,σ spin polarization is expected to make *all* hybrids contribute positive nitrogen s spin density. While this is believed to be *generally* true by most esr spectroscopists, our results challenge the *generality* of this effect as dominant. No difficulties are encountered for three σ *bond* pairs about nitrogen (NH_3^+), but, in the cases of one lone and two bond pairs (NR_2), we find negative s orbital spin density in the bond hybrids.

Discussion

Calculated *vs.* Experimental Hyperfine Constants. Table III compares the calculated and experimental values of the hyperfine constants for NH_2 and NH_3^+. Two values have been computed for each. The first value cited in each case is that for the energy minimum geometry while the second is that obtained after allowance for zero-point vibrational distortion of the radicals. Only the lowest energy bending modes were considered in each case (A_1 for NH_2 and A_2'' for NH_3^+; the bending normal coordinates were approximated as pure bending symmetry coordinates). The vibronic contribution to a_N is negligible (~0.1 G) for NH_2 and an order of magnitude greater for NH_3^+ (~1.6 G).

In comparing the INDO and experimental values it appears that the approximate MO method overestimates a_N somewhat. Better agreement with experiment could be achieved for NH_2 and NH_3^+ if the adjustable parameter[14] $\rho_s(0)$ were decreased in magnitude.

In comparing these values of a_N with those computed by Claxton,[15] we find the INDO values to be 50–100% larger than the *ab initio* values for the static structures. In the case of NH_3^+ the INDO vibronic correction is about 25% of the *ab initio* value (6.3 G). Consequently, the vibronic corrected values of a_N for both calculations are reasonably close to the experimental value but for different reasons. That using a smaller value for $\rho_s(0)$ in the INDO scheme[14] would mean an even smaller vibronic contribution to a_N is worth noting. For a_H, the INDO results are in even better agreement with experiment than are the a_N values. For NH_2, the vibronic correction to a_H is small (~0.15 G) but slightly larger than that computed for a_N. For NH_3^+ the correction to a_H is larger (~1.2 G) both because of the greater value of $\langle \Delta\theta^2 \rangle$ and because of a greater change in a_H with θ. Again, the vibronic correction for a_H of NH_3^+ is about the same magnitude as that computed for a_N. Also, the INDO vibronic correction to a_H agrees somewhat better with that from the *ab initio* study (2.7 G) than does the correction to a_N.

Spin-Polarized σ Orbitals of NH_2. By writing the localized σ orbital functions for NH_2 as linear combinations of (normalized) atomic hybrids on N and the H 1s function (Table II) we can examine the spin polarization of the σ orbitals at two levels: the

$$\Psi_i^\alpha = C_{Ni}{}^\alpha \chi_{Ni}{}^\alpha + C_{Hi}{}^\alpha \chi_H$$

$$\Psi_i^\beta = C_{Ni}{}^\beta \chi_{Ni}{}^\beta + C_{Hi}{}^\beta \chi_H$$

polarization of the σ electron *pairs*, in terms of the coefficients C_N for α and β spin, and the s, p characters of the nitrogen *hybrids*, in terms of the coefficients a for α and β spin. The spin density assigned to the ith nitrogen electron pair is

$$\rho_N(i) = (C_{Ni}{}^\alpha)^2 - (C_{Ni}{}^\beta)^2$$

The total nitrogen atom spin density is, therefore

$$\rho_N = \sum_i \rho_N(i)$$

Similarly, the total nitrogen valence s orbital spin density consists of a contribution from each hybrid

$$\rho_s = \sum_i \rho_s(i)$$

where the $\rho_s(i)$'s are given by

$$\rho_s(i) = (C_{Ni}{}^\alpha)^2(a_i^\alpha)^2 - (C_{Ni}{}^\beta)^2(a_i^\beta)^2$$

The latter expression follows from the definitions of Ψ_i^α and Ψ_i^β and the definition of the normalized atomic hybrids

$$\chi_{Ni}{}^\alpha = a_i^\alpha \phi_s + b_i^\alpha \phi_p$$

$$\chi_{Ni}{}^\beta = a_i^\beta \phi_s + b_i^\beta \phi_p$$

The left-most structures in Figure 3a,b summarize the results. First of all, Figure 3a, the σ pairs are polarized to leave net positive spin density on nitrogen with the bond pairs showing three times the polarization of the lone pair. The unpairing of the σ pairs ($C_{Ni}{}^\alpha \neq C_{Ni}{}^\beta$) is well understood to be due to the greater repulsion between the α pπ electron and the β σ electrons than between the α pπ electron and the α σ electrons. The exchange energy difference here may be thought of as more strongly forcing the β spin electron away from the nitrogen onto the substituent H. The polarization is, of course, greater for the bond pairs than the lone pair which would not be polarized *at all* if both α and β spin orbitals were perfectly localized on nitrogen.

The second effect of σ,π spin correlation is to make the s characters of corresponding α and β spin hybrids

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(15) (a) T. A. Claxton, *Trans. Faraday Soc.*, **66**, 1537 (1970); (b) *ibid.*, **66**, 1825 (1970).

different ($a_i^\alpha \neq a_i^\beta$). The discussion associated with Figure 2 would lead one to expect $a(\alpha \text{ spin}) > a(\beta \text{ spin})$ for each electron pair about nitrogen. Such is the case for the bond pairs of NH_3^+ and the lone pairs of the three NX_2 radicals. The bond pairs of NH_2 (and the other NX_2 radicals) clearly are an exception (Figure 3b and Table II). Thus the total nitrogen s orbital spin density, while positive, is the net result of considerable positive spin density from the lone pair and less than half that amount of *negative* spin density from each bond pair. Clearly, the lone pair contribution is dominant, but barely so. The finding that a bond hybrid can be polarized to contain + spin density while the atomic s and p components of the hybrid are polarized − and +, respectively, is quite unexpected and in complete disagreement with the simple models used by chemists.

From the canonical orbital description we know the total nitrogen s α spin density to be greater than the β spin density. The question is why, on localization, is the distribution of this total density between the lone and bond pairs so unsymmetrical. In fact, and in spite of the predictions of Figure 2, the role of π,σ repulsions is of great importance here. To begin with, localization of *only* the canonical α and β σ spin orbitals (that is, temporarily ignoring the $p\pi$ electron) reveals very little difference in the distribution of α and β spin hybrid s characters, and each σ pair contributes +s orbital spin density ($a(\alpha \text{ spin}) > a(\beta \text{ spin})$). (Note that the lone hybrid is polarized to give an almost negligible negative N atom spin density.)

	Lone pair		Bond pair	
	α	β	α	β
C_N	0.989	0.993	0.758	0.727
a	0.730	0.728	0.553	0.548

Upon inclusion of π,σ repulsion for α spin electrons, however, there is a pronounced redistribution of s character from bond to lone hybrids. As a consequence of minimizing the π,σ repulsion the bond-pair α electrons are slightly more delocalized onto the substituent atoms. Since the total α density on nitrogen is conserved in the localization process, the lone pair α electron becomes more localized on nitrogen. This accounts for the changes in lone and bond hybrid C_N values. Conservation of total electronic energy and individual AO densities requires that a and b for each hybrid also change. To facilitate the displacement of α density in the bond pair onto H, the p character of the bond χ_N^α must increase. Consequently the s character of the lone-pair α hybrid must increase. In this way we find a suitable explanation for the localized orbital result that $a(\alpha) < a(\beta)$ for each bond χ_N and consequently $a(\alpha) \gg a(\beta)$ for the lone χ_N.

Effect of Coordination of NH_2. It has been suggested that solvent effects on amino radical hyperfine constants might be traced to a specific interaction between an acidic site of the solvent molecule and the NR_2 lone-pair electrons.[16] A comparison of NH_2 and NH_3^+ allows an examination of this coordination effect in the limit of strong interaction. The analysis will be given in terms of localized orbitals for which lone pairs can be readily identified.

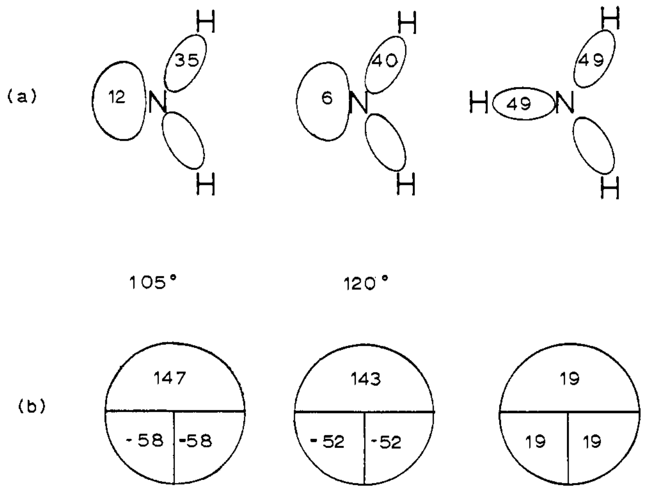

Figure 3. (a) The spin polarization of the normalized atomic hybrids about nitrogen of NH_2 and NH_3^+ (units are 10^{-3} electron). (b) The hybrid components of total nitrogen 2s spin density.

Using the normalized atomic hybrids about N in each molecule, the spin polarization of σ orbitals can be examined at two levels: the polarization of the electron pairs and the basis AO characters of the nitrogen hybrids. Considering the electron pairs first, the changes in spin polarization can be examined in two steps. First, the change due to increasing the HNH angle from 104.8 to 120° and, secondly, the effect of protonation of the distorted NH_2. The contents of Figure 3a illustrate the changes. The effect of angle opening is to decrease the polarization of the lone pair (which is only *ca.* one-third that of the bond pairs) and increase that of the bond pairs. Protonation of the lone pair then dramatically increases the polarizations of both types of orbitals—particularly that of the lone pair. The overall N atom spin density (s + p) increases only modestly (+0.004) on opening the HNH angle but more drastically on protonation (+0.061) (compare the C_N in Table II). There are, of course, corresponding increases of negative spin density on the protons (*cf.* C_X of Table II) which should be reflected in increases in $|a_H|$.

Of considerable interest to esr investigators are the contributions of these orbitals to the changes in N s spin density. The results for NH_2 are intriguing (Figure 3b). As discussed above, the lone-pair contribution to ρ_s is quite large and positive while that of each bond pair is *negative* and less than half that of the lone pair. Angle opening decreases the magnitudes of both contributions slightly with the greater decrease occurring for the bond pairs, which results in a net increase in ρ_s of +0.008. Protonation of the lone pair drastically reduces (by 0.124) the lone-pair contribution to ρ_s while increasing (by 0.142) the bond-pair contribution to ρ_s. The net result is an increase of 0.018 in ρ_s. In a qualitative sense only, there is diversion of N_s character from lone to bond hybrids. (Compare the coefficients labeled a in Table II.)

This brings us to examine another qualitative bonding model, that of isovalent hybridization and the prediction of central atom valence s orbital distribution among several σ hybrids as a function of structural changes. The basic idea in common usage is that the nitrogen atom valence s orbital is completely utilized in the three σ orbitals and that a change of the HNH angle or coordination of the lone pair simply redistributes

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(16) See, for example, K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc.*, 2163 (1971).

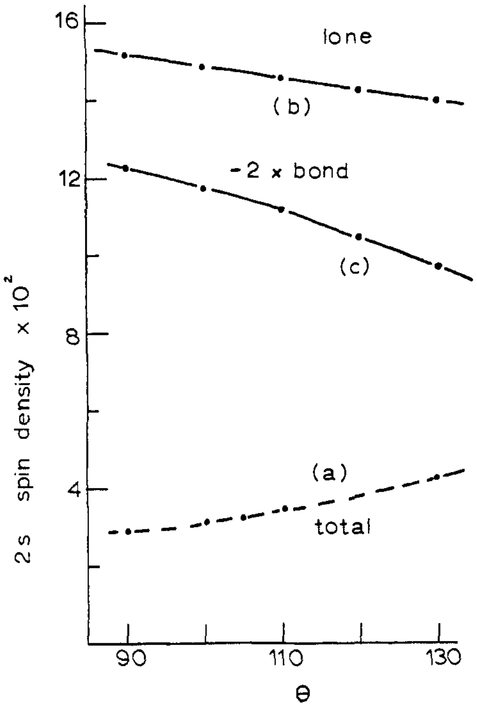

Figure 4. The lone-pair (b), bond-pair (c), and total (a) nitrogen 2s spin density of NH_2 as a function of the HNH angle.

the s orbital among the various hybrids. While this idea may be qualitatively useful for closed-shell molecules, it is clearly inconsistent with the LCAO–SCF method. The orthonormality requirements imposed on the AO coefficients require full s orbital involvement over both *virtual* and occupied MO's, not just over the occupied MO's. Any change as a result of structural or coordination changes in s orbital contribution to occupied MO's is achieved by change of s orbital involvement in virtual orbitals. Thus, while s character is often thought to be simply diverted from lone to bond hybrids as the HNH angle is increased, the situation is more complex than this. In an unrestricted calculation the α and β spin isovalencies are not simply and directly related. More specifically, loss of α spin s character does not lead to an equal increase in β spin s character. Additionally, if the s orbital involvement in the occupied spin hybrids did not change with coordination or HNH angle change, there could be *no* change calculated for a_N. Simple redistribution of α spin and β spin s character between lone and bond hybrids cannot explain the variation in a_N with coordination, HNH angle change, or substitution for H.

a_N as a Function of Bond Angle. As there have been attempts to correlate the nitrogen hyperfine constants of amino radicals with the bond angle at nitrogen,[17] we carried out INDO calculations for NH_2 over the bond angle range 90–130° and have subsequently analyzed the σ orbital polarization as a function of angle. The results are summarized in Figure 4. The total nitrogen atomic s orbital spin density (4a) varies nearly linearly over the range (100–120°) pertinent to most radicals. The increase is clearly due to the greater increase in N s orbital involvement in the occupied α spin orbitals than in the β spin orbitals. Translating this into localized hybrids, the gradual increase in ρ_s can be traced to a slowly decreasing net positive contribution from the lone pair (4b) and a rapidly decreasing (in magnitude) contribution from the bond pairs (4c). Clearly, the change in total ρ_s is dominated by the changes in the bond pairs whose contributions steadily increase toward positive values. The decrease (4b) in lone-pair contribution is due to two factors: (a) decreasing s character in both α and β hybrids and (b) greater localization of the β spin function onto the nitrogen as the hydrogens approach the p_z orbital nodal plane. Curve 4c for the bond hybrids shows that N s character enters these hybrids more easily for α than β spin.

To account for these results, we need to make use of the principles behind the curves of Figure 2 and the increase and decrease, respectively, expected for the s characters of bond and lone hybrids as NH_2 approaches a linear geometry.

1. Spin correlation favors increasing s involvement in α spin orbitals.
2. Angle opening favors increasing s involvement in bond hybrids and decreasing s involvement in the lone pair.

These then act synergically and antisynergically, respectively, for the α spin bond and lone hybrid changes with increasing HNH angle.

3. For β spin, the s orbital involvement in occupied MO's is opposed by spin correlation.

The increase in bond hybrid s character with increasing HNH angle is opposed by spin correlation while the decrease in lone hybrid s character is favored.

4. Generally, the role of spin correlation is greater for α than for β spin.

In this way, it is clear that the bond hybrids' contribution to ρ_s should be a more sensitive function of HNH angle than are the lone hybrids'. Consequently, the bond hybrids should rapidly tend toward more positive contributions while the lone hybrid contribution should slowly diminish, and a_N should increase.

In this way, we find a synergic relation between electron repulsion control of N s orbital involvement and the usual angle–s character relationship is at the heart of the increased a_N and nitrogen valence s orbital polarization as the XNX angle increases.

While the trends in lone-pair and bond-pair contributions to ρ_s as a function of XNX angle can probably be extended to molecules with X other than hydrogen, the σ bonding of X to N is likely to be as important as the XNX angle in determining the lone-pair and bond-pair contributions to ρ_s. That is, not only will Q_N, in the expression $\rho_s = Q_N\rho_\pi$, be a function of an angle but also a function of X. Furthermore, Q_N will show different angle and X dependences for the lone-pair and bond-pair polarizations ($\rho_s = (Q_N^{lp} + Q_N^{bp})\rho_\pi$). This is evident in a comparison of NH_2 and $N(CH_3)_2$. The lone-pair contribution to ρ_s is in the order $N(CH_3)_2 < NH_2$ while the bond pair contribution follows $NH_2 < N(CH_3)_2$ with an overall trend of $NH_2 < N(CH_3)_2$.

To ascertain the magnitude of the substituent effect of replacing H with CH_3, we may factor out the effect of the XNX angle difference by using Figure 4. At 117°, the NH_2 curves predict ρ_s contributions of 0.144 and −0.107 from the lone and bond pairs. The theoretical values for $N(CH_3)_2$ are 0.119 and −0.082. This leaves

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[17] See, for example, D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, 75, 3486 (1971).

an overall substituent effect of −0.025 for the lone pair and +0.025 for the bond pairs. By correcting the angle adjusted values of 0.144 and −0.107 for the methyl hyperconjugative effect (the nitrogen pπ spin density of $N(CH_3)_2$ is only 0.838), the σ effect of replacing H with CH_3 is only −0.002 for the lone pair and +0.009 for the bond hybrids. In summary, for the lone pair

$$\underset{(\mathrm{NH_2})}{+0.147} \xrightarrow[-0.003]{\text{angle change}} 0.144 \xrightarrow[-0.023]{\text{hyper}} 0.121 \xrightarrow[-0.002]{\sigma} \underset{(\mathrm{N(CH_3)_2})}{0.119}$$

and for the bond pairs

$$\underset{(\mathrm{NH_2})}{-0.116} \xrightarrow[+0.009]{\text{angle change}} -0.107 \xrightarrow[+0.016]{\text{hyper}} -0.091 \xrightarrow[+0.009]{\sigma} \underset{(\mathrm{N(CH_3)_2})}{-0.082}$$

It is very clear that the σ orbital effects of angle opening and rehybridization are responsible for a greater part (+0.013) of the ρ_s change than is the hyperconjugation effect (−0.007). Also, with reference to the first sentence of the preceding paragraph, σ rehybridization exclusive of the angle change is as important as the rehybridization from the angle change. Interestingly, it is fortuitous that the increase in ρ_s occasioned by replacement of H by CH_3 can be thought of as arising from the angle change only.

Summary

The broader goal of this research has been to examine the concept of π–σ spin correlation as commonly discussed in terms of the rigorous framework of the unrestricted self-consistent model for molecular electronic structure. The energy localization criterion was employed to generate from the delocalized symmetry MO's a set of equivalent localized orbitals for spin density analyses in terms of lone and bond hybrid orbitals. The qualitative concept of π–σ polarization of hybrid atomic orbitals to yield positive hybrid spin density at the π center is borne out for both lone and bond hybrids, with the latter, understandably, exhibiting the greater polarization. The origin of the total nitrogen valence s orbital spin density as the sum of lone and bond hybrid components was examined, with the unexpected result that the bond hybrid components are *negative* when a valence shell lone pair is present. This could be explained in terms of electron–electron repulsion forces at the π center. An important finding is that capriciously ignoring minimization of π,σ repulsions while minimizing σ,σ repulsions drastically alters the roles to be assigned to the lone and bond pairs in the spin polarization phenomenon. Clarification of the variation of total valence s orbital spin density with XNX angle resulted when it was found that the variation is dominated by changes in the bond hybrid components, a result arising from the synergic relation between spin-correlation and bonding forces. The concept of atomic orbital isovalency was examined to show that, as normally applied, the concept is too restrictive to account for variation in nitrogen valence s orbital spin density with XNX angle. Finally, analysis of the substituent effect of replacing H and CH_3 at the nitrogen radical center showed that σ orbital inductive effects are as important to the nitrogen valence s orbital spin density as the nitrogen rehybridization consequent to the change of XNX angle. CH_3 hyperconjugation also plays an important role.

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