



Figure 3. Suggested variation of molecular orbital energies for $M(NO)X_3$.

geometries for $Ni(N_3)(NO)(PPh_3)_2$,¹⁸ $Ir(NO)_2(PPh_3)_2^+$,¹⁹ and $[Co(NO)_2I]_n$ ²⁰ which have M-N-O bond angles between 166 and 153°. To date no complexes with the extreme square-planar bent nitrosyl geometry have been reported.

It is of interest to note that the feasibility of distorting the metal-nitrosyl geometry for the four-, five-, and six-coordinate complexes discussed above could have also been predicted on the basis of the second-order Jahn-Teller effect, which relates the symmetries of the ground and first excited states of the complex to the symmetry of the distorting vibrational mode.²¹ The valence-bond formulation of bent nitrosyl complexes as Lewis acid adducts of NO^+ also bears a resemblance to the molecular orbital model because it emphasizes donation of a lone pair from a metal d_{z^2} orbital to the empty ligand π^* orbital.²² The previous molecular orbital model¹ did not emphasize the strong interactions between $a_1(d_{z^2})$ and $e(\pi^*(NO), d_{xz})$ in the bent molecule and consequently cannot be generalized to all transition metal-nitrosyl complexes.²³ In particular it would be difficult to explain the observed linear nitrosyl geometries in certain d^{10} complexes according to the Eisenberg-Pierpont model¹ which associates bending with occupation of a strongly antibonding σ wave function. In a d^{10} complex a σ^* orbital must be occupied by two electrons, yet d^{10} complexes with linear metal-nitrosyl

(18) J. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971).

(19) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **9**, 1105 (1970).

(20) L. F. Dahl, E. R. deGil, and R. D. Feltham, *J. Amer. Chem. Soc.*, **91**, 1653 (1969).

(21) D. M. P. Mingos, *Nature Phys. Sci.*, **229**, 193 (1971); **230**, 154 (1971).

(22) D. J. Hodgson, N. C. Payne, J. A. McGinney, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **90**, 4486 (1968).

(23) It is interesting to note that calculations of overlap populations for $[Co(NO)(NH_3)_5]^{2+}$ show that the long Co-NH₃(trans) bond also results from mixing of the $a_1(d_{z^2})$ and $e(\pi^*(NO), d_{xz})$ orbitals. The former molecular orbital, which is unoccupied when Co-N-O = 180°, is particularly antibonding between the metal and the nitrogen atom trans to the nitrosyl ligand and this antibonding character is imparted to the occupied $a_1(\pi^*(NO), d_{z^2})$ orbital in the complex when Co-N-O \neq 180°.

geometries are well established, e.g., $Ir(NO)(PPh_3)_3$. Also their localized assignment of orbitals according to $sp^2(N)$ lone pair, $sp^2(O)$ lone pair, etc., leads to an unduly complicated and formal correlation diagram. Such a scheme neglects the important point that nitric oxide, unlike carbon monoxide and dinitrogen, forms linear and bent complexes primarily because it has a low-lying π^* orbital.

Registry No. $[Co(NO)(NH_3)_5]^{2+}$, 38402-80-1.

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Received May 26, 1972

Spin Delocalization in σ Systems.

An Analysis of INDO Calculations

Sir:

In an appendage, inserted in proof to a recent article, DeSimone and Drago¹ (DeS and D) averred that in our INDO calculations² on a simulated pyridine σ radical³ we failed to "factor out"⁴ the spin polarization (SP) of the π system and that this negated our criticism of Cramer and Drago's⁵ (C and D) extended Huckel molecular orbital (EHMO) analysis of spin delocalization in pyridine-type ligands coordinated to nickel(II). The purpose of this letter is to clarify the situation and to present additional insight into σ spin delocalization in these systems by further analysis of the INDO results.

The controversy is to some extent a semantic one over what exactly is meant by the description σ or π radical or σ or π spin delocalization. By σ radical we mean that the unpaired electron is contained in a one electron MO which has no out-of-plane (p_z) components. For the phenyl radical model employed in our calculations^{3,6} this is the case, and the probability of finding the unpaired electron in the highest bonding σ orbital is unity. This unpaired electron of course influences the spin *distribution* in the remaining filled MO's by SP. This applies to filled MO's of both π and σ symmetries. An analysis of our INDO results reveals the presence of three filled π levels (these occur in pairs of α and β spin⁷ containing MO's in the open-shell INDO calculation) centered at 2.12, 2.32, and 11.65 eV below the α -spin-containing σ level. Taken as α, β pairs none of these π levels contains any

(1) R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, **11**, 668 (1972).

(2) Intermediate neglect of differential overlap: J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968); P. A. Dobosh, CNINDO, Program 141, Quantum Chemistry Program Exchange, Indiana University, 1969.

(3) W. DeW. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, **10**, 1835 (1971).

(4) Just how this factorization was to be achieved in a rigorous manner was not specified.

(5) R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 66 (1970).

(6) A rationale and partial justification for our use of the hydrocarbon radicals as models for spin delocalization in coordinated pyridines is given at some length in the fourth paragraph and footnote 13 of ref 3. A further comment on this point is made in the final paragraph of the present article.

(7) α spin is here taken to indicate that the electron magnetic moment is parallel to the applied magnetic field, while β spin indicates the opposite.

net unpaired spin, nor does the π system as a whole.⁸ There is, however, a redistribution of spin among the atomic centers of the π system as a result of SP by the unpaired σ electron. Our INDO results show spin densities of +0.066, -0.043, +0.028, and -0.036 in the p_z orbitals of carbon atoms 1, 2, 3, and 4, respectively⁹ (a positive number signifies α spin). The bulk of this polarization occurs in the two highest lying π levels. The sense of this polarization is in perfect agreement with the methyl proton isotropic shifts¹⁰ of coordinated picolines¹¹ which are upfield for methyl groups attached to positions 2 and 4 and downfield for the 3-methyl group (this agreement may, however, be largely fortuitous, *vide infra*). A semiempirical treatment of π system polarization by an unpaired σ electron using a variation of the McLachlan method¹² has been presented by Zhidomirov, *et al.*,¹³ with results in qualitative agreement with ours. It is, of course, neither correct nor desirable to subtract the SP of the π system in our INDO calculations on the phenyl radical as suggested by DeS and D,¹ anymore than it is to factor out the in-plane σ SP which accounts for the observed hyperfine interaction of in-plane protons with the unpaired electron in π radicals. The phenyl radical is a σ radical involving σ spin delocalization in the same sense as the benzene anion radical is a π radical involving π spin delocalization.

The C and D analysis⁵ of spin delocalization in coordinated pyridine-type ligands is nowise equivalent to our interpretation³ of this phenomenon. They attribute the observed proton isotropic shift behavior to a linear combination of direct delocalization of α spin in the σ system and delocalization of β spin in either a particular π or π^* orbital. As indicated above, SP of the π system by the unpaired σ electron does not correspond to any particular π MO, indeed there is no net unpaired spin in any of them. Moreover, the C and D⁵ analysis implies a metal-ligand π interaction while our simpler σ -only model does not.

It is appropriate at this point to consider the relative contributions of direct *vs.* indirect (SP) mechanisms in determining the proton isotropic shifts as obtained from our INDO calculations. One of the salient features of the pyridine isotropic shifts is that they fall off in the ratios 1.00:0.303:0.091 for the 2, 3, and 4 protons respectively.^{3,14} The C and D⁵ EHMO analysis of direct σ spin delocalization predicts the ratios to be 1.00:0.38:1.01, in poor agreement with experiment at the 4 position. The inclusion of a π or π^* β spin contribution in linear combination worsens the agreement at the 4 position. Our INDO results show that *direct* delocalization yields spin densities of 0.034, 0.021, and 0.034 (ratios, 1.00:0.617:1.00) for the 2, 3, and 4 positions

(8) This point has been made in a recent review of spin delocalization and electronic structure: G. N. La Mar in "NMR of Paramagnetic Molecules: Principles and Applications," G. N. La Mar, W. DeW. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York, N. Y., 1973, Chapter 3.

(9) Carbon atom number 1 of the phenyl radical corresponds to the nitrogen atom of pyridine. Atoms 2, 3, and 4 correspond to the ortho, meta, and para positions, respectively.

(10) Isotropic shift refers to the nuclear resonance displacement in a paramagnetic system with respect to its position in a corresponding diamagnetic system. A downfield shift corresponds to a positive spin density and a positive electronic-nuclear interaction constant for the resonating nucleus.

(11) D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 6839 (1970); J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

(12) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

(13) G. M. Zhidomirov, P. V. Schastnev, and N. D. Chuvylkin, *J. Struct. Chem.*, **10**, 800 (1969); **11**, 458 (1970).

(14) The ratios quoted are for the $Ni(C_5H_5O_2)_2(C_6H_5N)_2$ systems.¹¹ For the $Ni(C_5H_5N)_6^{2+}$ system the corresponding ratios are 1.00:0.372:0.117.⁵

respectively. SP yields spin density contributions of 0.001, -0.010, and -0.026 at the same respective positions, leading to net calculated spin densities and hyperfine constants in the ratios, 1.00:0.33:0.21. It is noteworthy that the observed falloff of coupling constant with distance from the coordination site is caused in large measure by SP effects at the 3 and 4 protons rather than by attenuation of the wave function for direct delocalization as is commonly supposed.

For methyl groups at the 2, 3, and 4 positions our INDO calculations show that *direct* delocalization leads to average spin densities at the methyl protons of 0.0026, 0.0041, and 0.0007, respectively, while the average *total* s-orbital spin densities at these sites are -0.0034, 0.0030, and -0.0022. For methyl proton coupling constants *direct* delocalization is seen to be unimportant compared with SP at the 4 position, dominant but counteracted to some extent by SP effects (contrary to the prediction of the π SP model) at the 3 position and significant but unable to overcome a large SP contribution of opposite sign at the 2 position. While at first sight the qualitative picture of SP of the π system appears to explain the methyl proton results,¹¹ the analysis of the INDO calculations presented above shows that the total SP contributions to the proton shifts are in qualitative disagreement with this picture for the 4-position proton and the 3-position methyl hydrogens, rendering this qualitative model of dubious predictive value.

In summary, we offer the following observations. (1) As noted before,³ INDO calculations appear capable of rendering a semiquantitative account of the contact shift behavior of ¹H and ¹³C nuclei in coordinated pyridine-type bases, whereas EHMO calculations have little or no predictive or interpretive value in this regard. (2) This shift behavior is adequately described in terms of σ spin delocalization (with concomitant SP of both σ and π systems), there being no evidence for any metal-ligand π interaction. (3) Analysis of the calculations shows that both direct delocalization and SP contribute importantly to the contact shifts, with the latter quantity being highly variable and in most cases providing an upfield contribution to the net proton contact shifts. (4) The electrons in the π system are indeed spin polarized by the unpaired σ electron, but detailed analysis fails to reveal a necessary causal relationship between this polarization and the ring proton and methyl proton shift behavior.

Finally we offer the following rationale for why the phenyl radical appears to be a better model of σ spin delocalization in coordinated pyridine than is the pyridine cation radical used by others.¹⁵ A quantitative evaluation of spin densities from the observed shifts and a comparison with those calculated for the phenyl radical indicate that only ~0.05 of an unpaired spin is delocalized in each pyridine ligand. Thus, the neutral phenyl radical may more closely approximate the situation in the complex, where some degree of electroneutrality is achieved, than does the pyridine cation radical which has a net positive charge.

Registry No. C₅H₅N, 110-86-1.

(15) M. J. Scarlett, A. T. Casey, and R. A. Craig, *Aust. J. Chem.*, **23**, 1333 (1970).

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Received May 20, 1972