stituted[4] derivatives has been previously observed, and we report here a solvent study of $^1J(^{15}NH)$ in a series of ortho-substituted anilines, which may serve as a basis for assessing the intramolecular hydrogen bonding abilities of the various ortho substituents.

A series of ortho-substituted anilines having an ^{15}N enrichment of 99 atom % was prepared and the one-bond ^{15}N–H coupling constants in $CDCl_3$ and DMSO were measured. A summary of $^1J(^{15}NH)$ values and amino proton chemical shifts is presented in Table I.

Table I. ^{15}N–H Coupling Constants and Amino Proton Chemical Shifts in Some Ortho-Substituted Anilines

Substituent[c]	$^1J(^{15}NH)^a$ CDCl$_3$	$^1J(^{15}NH)^a$ DMSO	$\Delta ^1J$-(^{15}NH)	$\delta_{NH_2}{}^b$ CDCl$_3$	$\delta_{NH_2}{}^b$ DMSO
2-NO_2, 4-Cl	91.1	91.8	0.7	6.11	7.56
2-NO_2	90.3	91.0	0.7	6.16	7.40
2-COPh	88.1	89.3	1.2	6.15	7.16
2-Cl, 4-NO_2	89.2	90.5	1.3	4.91	6.86
2,4,6-$(Br)_3$	85.5	87.4	1.9	4.30	5.48
2-CF_3	83.6	86.5	2.9	4.11	5.46
2-Br	81.4	84.3	2.9	4.01	5.16
2-OCH_3	79.4	82.3	2.9	3.75	4.60
2-F	80.1	83.5	3.4	3.66	4.98
2-H	78.6	82.6	4.0	3.56	4.80

[a] All coupling constants are expressed in hertz and are accurate to ±0.2 Hz. [b] Amino proton chemical shifts are expressed in parts per million relative to TMS. [c] Where possible, measurements were made with *ca.* 1 *M* solutions; otherwise, saturated solutions were used.

It is readily apparent from an examination of Table I that, as had been the case in the meta and para series of ^{15}N anilines, $^1J(^{15}NH)$ values in the ortho series of anilines are also substituent and solvent dependent. Thus, the ability of the solvent or the ring substituent to foster delocalization of the amino nitrogen lone pair of electrons and enhance the sp^2 character of the ^{15}N–H bond is reflected in the magnitude of ^{15}N–H coupling.

Of particular interest, however, is the set of $\Delta ^1J$-(^{15}NH) values.[5] It will be noted that as the electron-withdrawing ability of the ortho substituent increases, the difference between the coupling constants observed in $CDCl_3$ and DMSO decreases. For example, $\Delta ^1J$-(^{15}NH) for *o*-nitroaniline is 0.7 Hz, whereas for *m*- and *p*-nitroaniline $\Delta ^1J(^{15}NH)$ is 3.2 and 3.0 Hz, respectively.[6]

Significantly, since it is generally acknowledged that *o*-nitroanilines are *intramolecularly* hydrogen bonded in $CDCl_3$ and *intermolecularly* hydrogen bonded in DMSO,[7] and since it has also been reported that both intra-[8] and intermolecular[9] hydrogen bonding in ring-substituted anilines enhance the electron-donating ability of the amino group, the $\Delta ^1J(^{15}NH)$ values of Table I may be considered to reflect the strength of the *intramolecular* hydrogen bond in $CDCl_3$. Thus, for a strongly electron-withdrawing ortho substituent, the enhancement of sp^2 character in the ^{15}N–H bond due to *intramolecular* hydrogen bonding in $CDCl_3$ will be comparable to that due to *intermolecular* hydrogen bonding in DMSO, and consequently, $\Delta ^1J(^{15}NH)$ for that substituent will be small. On this basis, the order of substituent hydrogen bonding abilities may be seen to be: $NO_2 > C{=}O > CF_3$, Br, $OCH_3 > F$.

It is interesting to note that a moderately strong intramolecular hydrogen bond exists in 2-chloro-4-nitroaniline, whereas only a very weak interaction, if any, is indicated in *o*-fluoroaniline. In the former case, this undoubtedly arises due to the resonance interaction between the amino group and the para nitro group. Infrared evidence supports this view.[10] In the latter case, the small size of the fluorine atom presumably prevents the close approach of the amino proton to the fluorine lone pair of electrons.

Studies are currently in progress to determine the nitrogen-15 chemical shifts in these systems.

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(5) $\Delta ^1J(^{15}NH) = {}^1J(^{15}NH)_{DMSO} - {}^1J(^{15}NH)_{CDCl_3}$.

(6) T. Axenrod, P. S. Pregosin, M. J. Wieder, E. D. Becker, R. B. Bradley, and G. W. A. Milne, *J. Amer. Chem. Soc.*, in press.

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Symmetry Considerations Concerning d-Orbital Participation in Chemical Bonding of Second-Row Elements

Sir:

As large-scale digital computation of molecular wave functions has become routinely available to chemists, there has been considerable interest and activity involving the use of extended basis sets to describe molecular bonding. In particular, d orbitals have often been utilized in the construction of wave functions for molecules including second-row atoms. For second-row atoms, early consideration of 3d-orbital contributions to binding were given by Pauling,[1] Mulliken,[2] Moffitt,[3] and Longuet-Higgins,[4] among others. Coulson, in an important and timely review,[5] has stressed the fact that chemical importance cannot always be attached to small contributions to the wave function arising from d-orbital inclusion in the basis set. Coulson stresses the suitability of d functions for effecting polarization of p orbitals, but notes that little or no chemical relevance should be attached to the small d-orbital populations arising from this.

Coulson[5] also mentions the obvious but important fact that expansion of a minimal basis set to include d, f. . . functions will of course provide a variationally improved wave function, but that "There is little if any chemical significance in such members." Certain recent calculations, particularly on molecules containing sulfur, have utilized d functions,[6] while others have

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(1) L. Pauling, *J. Amer. Chem. Soc.*, **53**, 1367 (1931).

(2) R. S. Mulliken, *ibid.*, **72**, 4493 (1950).

(3) W. Moffitt, *Proc. Roy. Soc., Ser. A*, **200**, 409 (1950).

(4) C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

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(6) *Cf.*, *e.g.*, (a) D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 601 (1962); (b) A. Rauk, and I. G. Csizmadia, *Can. J. Chem.*, **46**, 1205 (1968); (c) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967); (d) D. B. Boyd, *ibid.*, **52**, 4846 (1970); (e) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 199 (1970); (f) F. P. Boer and W. N. Lipscomb, *J. Chem. Phys.*, **50**, 989 (1969); (g) I. H. Hillier and V. R. Saunders, *Chem. Phys. Lett.*, **5**, 384 (1970).

not,[7] and questions have arisen concerning the necessity of including such orbitals.[6b,c,7a] We feel that the symmetry of the state in question often provides a good criterion for estimating the stereochemical, as opposed to merely numerical, importance of such basis functions.

If an occupied molecular orbital transforms according to an irreducible representation of the point group of the nuclear configuration for which the usual s and p functions do not provide a basis, it then becomes crucial to include orbitals of higher azimuthal quantum number in the description of the molecular bonding. Alternatively, if the s and p functions do provide such a basis, the energy lowering provided by the inclusion of higher orbitals is due to such factors as polarization and is therefore not of fundamental importance in the qualitative bonding picture. In the case of molecules involving second-row atoms, these higher orbitals will be principally the 3d functions.

As a simple example consider the pyramidal inversion of phosphine. In the pyramidal (C_{3v}) ground-state configuration, all occupied molecular orbitals have A_1- or E-type symmetry. Bases for these irreducible representations are provided by s- and p-type functions. Therefore, d functions are not qualitatively significant in the bonding of this state. On the other hand, for the maximum-potential, planar (D_{3h}) transition state, occupied molecular orbitals, especially in configuration interaction calculations, may have A_1', A_2'', E', or E'' symmetry. Of these, only the E'' irreducible representation does not have a basis in s- and p-type phosphorus orbitals. Therefore, for this state, the d functions are important if there is any occupied molecular orbital of E'' symmetry. Kari[8] has, in fact, reached more or less the same conclusion by means of a CI calculation on NH_3.

The simple question of whether d orbitals are qualitatively important in sulfur bonding becomes meaningless with respect to this symmetry criterion. For a molecule such as H_2S (C_{2v}), calculations have shown that d orbitals, while providing polarization effects, are unimportant in understanding the actual bonding scheme.[6b,e] In the octahedral case (O_h) of SF_6, however, there are occupied molecular orbitals of T_{2g} and E_g symmetries.[6c] These irreducible representations do not have a basis in the s- and p-type functions, and therefore d-type functions are qualitatively necessary for understanding their bonding structure.

The cases of H_2S and SF_6 are well-known extremes for the contribution of d orbitals and symmetry considerations. There are also many intermediate cases,[9] and these have been treated by a variety of methods. A survey of some representative calculations is given by Rauk, Wolfe, and Csizmadia,[10] and the role of d orbitals in various compounds is discussed. Recently, Maclagan[11] has discussed the symmetry criterion for d-orbital participation from a valence-bond point of view.

We feel that this symmetry criterion, used in conjunction with the usual overlap considerations,[12] should aid in evaluating the importance of higher orbitals in the description of molecular orbital bonding.

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Reactivity of Trialkylphosphine Complexes of Platinum(0)

Sir:

We find the reactivity of trialkylphosphine complexes of platinum(0) to be surprisingly greater than that of the established triarylphosphine analogs.[1] The exemplar is the facile cleavage of carbon–carbon bonds in aryl nitriles.

The new trialkylphosphine–platinum complexes were prepared through displacement of the π-borallyl ligand[2] from $PtB_3H_7(R_3P)_2$[4] by excess phosphine. In this fashion, we isolated colorless crystals of the tetrakis-triethylphosphine and -trimethylphosphine complexes.[5] The triethylphosphine complex dissolved in hydrocarbons with ligand dissociation to give red-orange solutions. On heating $Pt[P(C_2H_5)_3]_4$ at 50–60° *in vacuo*, $Pt[P(C_2H_5)_3]_3$ was isolated as a red-orange oil. In contrast, the tetrakis-trimethylphosphine complex did not dissociate up to 70–80°.

The ^{31}P nmr spectra of solutions of $Pt[P(C_2H_5)_3]_3$ and $Pt[P(C_2H_5)_3]_4$ at $-55°$ consist of singlets flanked by ^{31}P–^{195}Pt satellites. Chemical shifts and ^{31}P–^{195}Pt coupling constant data for these compounds and for $Pt[P(p\text{-}C_7H_7)_3]_3$ and $Pt[P(p\text{-}C_7H_7)_3]_4$ are set forth in Table I. The coupling constants for PtL_3 complexes are significantly larger than those for PtL_4 complexes. This is consistent with the presumed greater s character in Pt–P bonds of tris-phosphine complexes.[6] Ligand ex-

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[2] This reaction is strikingly similar to the displacement of the π-allyl ligand from $\{Pt(\pi\text{-}C_3H_5)[P(C_6H_5)_3]_2\}^+$ by excess triphenylphosphine[3] and is consistent with our formulation of the B_3H_7 ligand as a π-allyl analog.

[3] H. C. Volger and K. Vrieze, *J. Organometal. Chem.*, **9**, 527 (1967).

[4] A. R. Kane and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 1041 (1971).

[5] Satisfactory elemental analyses were obtained for all new compounds. *E.g. Anal.* Calcd for $Pt[P(C_2H_5)_3]_4$: C, 43.2; H, 9.06; P, 18.5; Pt, 29.2. Found: C, 43.3; H, 9.28; P, 18.5; Pt, 29.2.

[6] Formally sp^2 and sp^3 hybridization may be assumed for the tris and tetrakis complexes, as was done for the analogous AgL_3^+ and AgL_4^+