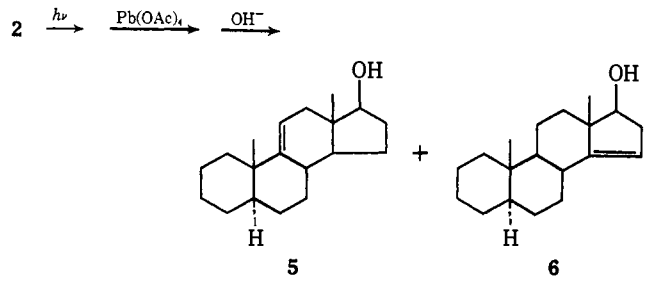
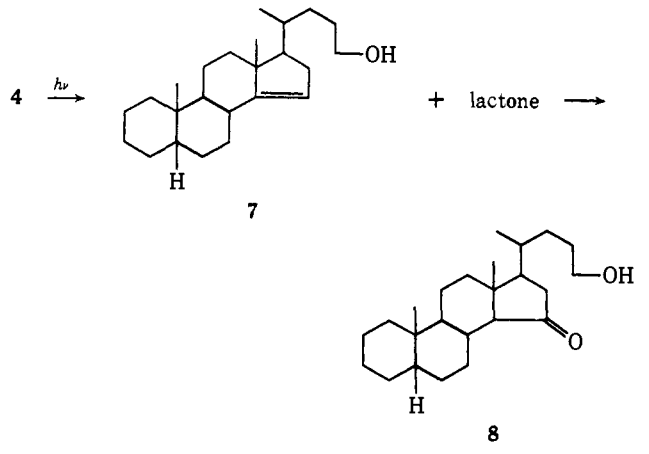


The structure of **5**, *m/e* 274, is indicated by its mp, 158–159° (lit.[8] 160.5–162°), and its highly characteristic nmr spectrum. The vinyl proton is centered at δ 5.34 (expected[9a] value δ 5.27). Angular methyl resonance positions for the C-18 and C-19 groups vary characteristically with the double bond position,[9b] and our signals (60 MHz) at 42.0 and 56.0 Hz agree with the predicted[9b] values of 40.5 and 56.5 Hz.[10] The closest methyl signals for an alternative position of the double bond, Δ^{14}, are predicted at 48.5 and 59.5 Hz, in poor agreement with the values above but in excellent agreement with the values of 48.0 and 58.0 observed for the compound assigned structure **6**. The vinyl proton of **6** has its characteristic signal at δ 5.07 (predicted[9a] δ 5.04), quite different from other[9a] steroid vinyl positions.

Photolysis of a 10^{-3} *M* solution of **4** in purified benzene (450-W medium-pressure lamp, uranium glass filter) followed by basic hydrolysis affords a 25% yield of the hitherto unreported Δ^{14}-cholen-24-ol (**7**), mp 99–100° (*m/e* 344), and a 45% yield of a lactone fraction.[11] This lactone was reduced with lithium aluminum hydride, acetylated with acetic anhydride in pyridine, and dehydrated with thionyl chloride in pyridine. The resulting diphenylethylene derived from **4** was submitted to oxidation with ruthenium tetroxide and sodium periodate, followed by chromatography. The only steroidal ketone detectable, isolated in 16% yield based on the total lactone fraction, was the hitherto unreported 15-keto-cholan-24-ol (**8**) (*m/e* 360).



(8) W. Klyne and S. Palmer, *J. Chem. Soc.*, 4545 (1958). Their multistep synthesis starts with a cortisone derivative.

(9) (a) G. M. L. Cragg, C. W. Davey, D. N. Hall, G. D. Meakins, E. E. Richards, and T. L. Whateley, *J. Chem. Soc.*, 1266 (1966); (b) calculated from the tables in N. Bhacca and D. H. Williams, "Application of Nmr Spectroscopy in Organic Chemistry; Illustrations from the Steroid Field," Holden-Day, San Francisco, Calif., 1964.

(10) These data also agree with those for other $\Delta^{9(11)}$ steroids prepared in unpublished remote oxidation work by W. Washburn.

(11) Oxidation of this lactone with lead tetraacetate produces no olefinic cleavage products.

The structure of **7** is indicated by its vinyl nmr resonance at δ 5.15, and its C-18 and C-19 resonances at 54.0 and 56.0 Hz. For this skeleton the predicted[9b] values for **7** are 55.0 and 56.0 Hz, while the closest alternative (excluded also by the vinyl nmr), Δ^{11}, would come at 45.0 and 53.5 Hz. The structure of **8** is indicated by the infrared band for a cyclopentanone at 1740 cm^{-1}, and methyl nmr signals at 44.5 and 55.5 Hz (predicted[9b] 44.5 and 56 Hz). The alternative 16-oxo structure would have[5,12] these signals at 50.5 and 57 Hz.

It is interesting that, in the previous examples,[2,3,5] attachment of a benzophenone residue to the rigid steroid nucleus by a flexible chain of atoms led to attack quite remote from the position of attachment at 3α. By contrast, in **4** we may consider that the benzophenone is attached by a long chain, partly from the reagent and partly the side chain of the steroid, leading from C-17 of the steroid nucleus; however, attack occurs at C-14 and C-15, only a few atoms from the point of attachment of the flexible chain. Apparently in this case the chain doubles back under itself as a loop, and the flat benzophenone system lies underneath ring D of the steroid. In the photolysis of **2** the two products arise from initial attack of the benzophenone carbonyl group on carbon–hydrogen bonds at C-9 and C-14, again on the α side of the steroid even though the chain was attached β. The flexibility in **2** and **4** makes *a priori* predictions of these positions of attack difficult. However, the observation that in **2** the major product, in respectable conversion, is the $\Delta^{9(11)}$ olefin **5** indicates further the synthetic potential of remote oxidation.

(12) J. Jacques, M. Minssen, D. Varech, and J. Basselier, *Bull. Soc. Chim. Fr.*, 77 (1965).

(13) NIH Predoctoral Trainee. Support of this work by the National Institutes of Health is gratefully acknowledged.

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Nitrogen-15 Magnetic Resonance Spectroscopy. Solvent Effects on $^1J(^{15}NH)$ and Hydrogen Bonding in Ortho-Substituted Anilines

Sir:

Nmr evidence for the existence of hydrogen bonding has come primarily from chemical shift investigations of the proton(s) involved in the hydrogen-bonded complex X—H···Y,[1] although recent reports indicate that new insights may be provided by chemical shift studies of the heteronuclei which serve as the hydrogen donors (X) and acceptors (Y).[2]

To the extent that hydrogen bonding alters the nature of the X–H bond, one might expect this to be reflected in the one-bond X–H spin coupling. Solvent dependence of $^1J(^{15}NH)$ in aniline[3] and its ring-sub-

(1) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1965, p 534.

(2) A. E. Florin and M. Alei, Jr., *J. Chem. Phys.*, 47, 4268 (1967); A. E. Florin and M. Alei, Jr., *J. Phys. Chem.*, 73, 863 (1969); J. Reuben, *J. Amer. Chem. Soc.*, 91, 5725 (1969); W. M. Litchman, M. Alei, Jr., and A. E. Florin, *ibid.*, 91, 6574 (1969); 92, 4828 (1970); H. Saito and K. Nukada, *ibid.*, 93, 1072 (1971); H. Saito, Y. Tanaka, and K. Nukada, *ibid.*, 93, 1077 (1971).

(3) L. Paolillo and E. D. Becker, *J. Magn. Resonance*, 2, 168 (1970).

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	Δ^1J- (^{15}NH)	δ_{NH_2}[b] $CDCl_3$	δ_{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.

(10) L. K. Dyall, *Aust. J. Chem.*, 23, 947 (1970).

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(4) T. Axenrod, P. S. Pregosin, M. J. Wieder, and G. W. A. Milne, *J. Amer. Chem. Soc.*, 91, 3681 (1969).
(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.
(7) I. D. Rae, *Chem. Commun.*, 519 (1966); *Aust. J. Chem.*, 20, 1173 (1967); V. Bekarek, J. Kavalek, J. Socha, and S. Andrysek, *Chem. Commun.*, 630 (1968).
(8) P. J. Krueger, *Can. J. Chem.*, 40, 2300 (1962).
(9) B. M. Lynch, B. C. Macdonald, and J. G. K. Webb, *Tetrahedron*, 24, 3595 (1968).

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

(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).
(5) C. A. Coulson, *Nature (London)*, 221, 1106 (1969).
(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).