

(146, 23H) give the major contributions. Histidine (64, 7E) is the so-called distal histidine which is near the sixth ligand of the iron. The fifth ligand, histidine (93, 8F), gives only a small effect, because the imidazole sits in a rather symmetrical position with respect to the heme.

The two components of the Soret band, B_x and B_y , have opposite signs for the rotational strength (Table I). This raises the question of why only a single positive band is observed. That the two components are not completely degenerate has been shown by Eaton and Hochstrasser.¹³ Their single-crystal polarization measurements indicate a splitting of about 200 cm^{-1} . Such a splitting would lead to two distinct CD bands of opposite sign if the intensities were comparable in magnitude, but even a 2:1 disparity in magnitude can obscure the presence of two bands.¹⁴ The magnitudes of the two individual components depend on the orientation of the Soret transition moments in the heme plane, but the total Soret rotational strength is independent of the direction of polarization. The calculations on which Table I is based assume polarization parallel to the opposing N-N lines. Rotating the transition moments by 45° leads to $R_{B_x} = -0.127$ and $R_{B_y} = 0.434$. Thus the shape of the Soret CD band of heme proteins may be rather sensitive to substituent and conformational changes, leading to variation in the direction of polarization of the Soret components.

Details of these calculations will be published. We are also investigating other heme transitions, and a study of hemoglobin is in progress.

Acknowledgment. The authors wish to thank Dr. J. C. Kendrew and Dr. H. C. Watson for providing their unpublished atomic coordinates of myoglobin, and Dr. G. Willick for communication of his results on the CD of myoglobin. This work was supported by U. S. Public Health Service Grant GM-13910.

(13) W. A. Eaton and R. M. Hochstrasser, *J. Chem. Phys.*, **49**, 985 (1968).

(14) K. M. Wellman, P. H. A. Laur, W. S. Briggs, A. Moscowitz, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 66 (1965).

(15) University of Illinois Fellow, 1966-1968.

Ming-Chu Hsu,¹⁶ Robert W. Woody
W. A. Noyes Laboratory of Chemistry
University of Illinois, Urbana, Illinois 61801
Received February 24, 1969

Nitrogen-15 Magnetic Resonance Spectroscopy. A Correlation of the ^{15}N -H Coupling Constants in Aniline Derivatives with Hammett σ Constants

Sir:

We wish to report the observation of a linear correlation between the magnitude of the directly bonded ^{15}N -H coupling constants and the appropriate Hammett σ constants in a series of aniline- ^{15}N derivatives. The chemical shifts of the amino protons¹ and the N-H stretching frequencies² in a series of anilines have recently been shown to be directly proportional to the Hammett substituent constants, as have the ^{13}C -H coupling constants³ and chemical shifts of the methyl protons in a series of toluene derivatives.⁴

(1) B. M. Lynch, B. C. Macdonald, and J. G. Webb, *Tetrahedron*, **24**, 3598 (1968).

(2) E. V. Titov, L. M. Litvinenko, and N. A. Izmailov, *Ukr. Khim. Zh.*, **27**, 87 (1961); *Chem. Abstr.*, **55**, 20624d (1961).

(3) C. H. Yoder, R. H. Tuck, and R. E. Hess, *J. Amer. Chem. Soc.*, **91**, 539 (1969).

The magnitude of the ^{13}C -H coupling constant is generally believed to be related to the hybridization and polarity of the C-H bond.⁵ An empirical equation, $\% s = 0.43(J_{^{13}\text{C}-\text{H}}) - 6$, relating the hybridization of the nitrogen atom to the directly bonded ^{15}N -H coupling constant, has been proposed⁶ based on compounds in which the nitrogen hybridization is reliably known (e.g., NH_4^+ , sp^3 , $J = 73.2$ Hz; $(\text{C}_6\text{H}_5)_2\text{C}=\text{NH}_2^+$, sp^2 , $J = 92.6$ Hz).⁷ This relationship is further supported by the recently reported coupling constants involving the sp-hybridized nitrogen atom in protonated nitriles.⁸

The ^{15}N -H coupling constants measured in CDCl_3 and $\text{DMSO}-d_6$ are summarized in Table I. Although

Table I. ^{15}N -H Coupling Constants in Aniline Derivatives^a

X	$J_{^{15}\text{N}-\text{H}}^b$	
	$\text{DMSO}-d_6^c$	CDCl_3^c
4-NO ₂	89.4	86.4
3,5-Me ₂ ,4-NO ₂	87.0	83.2
3-Br	85.3	80.5
3-Cl	85.1	80.9
3-I	84.4	80.4
4-I	84.0	79.7
4-Br	84.0	79.6
4-Cl	83.7	78.9
3-MeO	83.0	79.4
H	82.6	78.6
3-Me	82.0	78.2
3,5-Me ₂	82.1	77.5
4-F	81.6	77.8
4-Me	81.4	76.5
4-MeO	79.4	75.6

^a All anilines were prepared with a ^{15}N enrichment of at least 95% by Hofmann rearrangement of the corresponding amides.

^b All constants are expressed in hertz and are accurate to ± 0.2 Hz. All measurements were made from pmr spectra. ^c All measurements were made with approximately 1 *m* solutions where possible. Otherwise saturated solutions were used. In ^{15}N -aniline, the coupling constant was independent of concentration between 0.4 and 2.2 *m* in CDCl_3 .

the observed trends correspond well with those reported by Bramwell and Randall,⁹ their measurements on CDCl_3 solutions differ considerably from ours. The source of this discrepancy is not clear.

Essentially parallel trends are seen in the two different solvents, although, as has been previously observed,¹⁰ the magnitude of the coupling is larger in $\text{DMSO}-d_6$. The observed ^{15}N -H coupling constant in aniline is intermediate between those observed for typical systems containing sp^3 - and sp^2 -hybridized nitrogen. This may be attributed to delocalization of the nitrogen lone pair by orbital overlap with the π system of the aromatic ring, resulting in enhanced s character in the N-H bond compared to a normal sp^3 -hybridized ammonium ion.

(4) S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).

(5) J. W. Emsley, J. Feeney, and L. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Pergamon Press, New York, N. Y., 1965, Chapters 5 and 12.

(6) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5564 (1964).

(7) An equivalent expression has been suggested by A. J. Bourn and E. W. Randall, *Mol. Phys.*, **8**, 567 (1964).

(8) H. Hogeveen, *Rec. Trav. Chim.*, **86**, 1288 (1968); G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 4666 (1968).

(9) M. R. Bramwell and E. W. Randall, *Chem. Commun.*, 250 (1969).

(10) E. D. Becker, H. T. Miles, and R. B. Bradley, *J. Amer. Chem. Soc.*, **87**, 5575 (1965), and personal communication.

The ^{15}N -H coupling is increased by the introduction of electron-withdrawing substituents, whereas electron-donating substituents can be seen to have the reverse effect. Similar explanations are generally advanced to account for the difference in basicity between aromatic and aliphatic amines.¹¹

A plot of the ^{15}N -H coupling constants for *meta* and *para* aniline- ^{15}N derivatives against the appropriate Hammett substituent constants is shown in Figure 1.

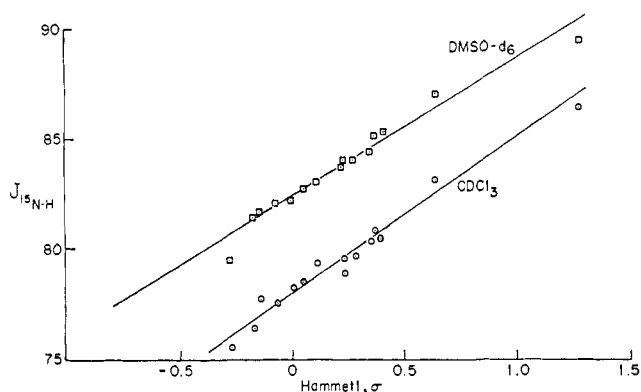


Figure 1.

Reasonably good linear correlations are observed using either $\text{DMSO-}d_6$ or CDCl_3 as solvent, although the fit is somewhat better in the former solvent case.

Effective conjugation of a mesomerically interacting substituent requires that both the amino group and the substituent be approximately coplanar with the benzene ring. This condition is subject to steric influences, and it is interesting to note that while 4-nitroaniline is correlated by the use of the σ^- value,¹² a poor correlation is obtained when this value is used in the case of 3,5-dimethyl-4-nitroaniline. Considerable evidence indicates that in the latter compound the nitro group is twisted out of the plane of the ring to the extent of 56° , leading to suppression of its resonance interaction with the amino group.¹³ The observed coupling constant reflects this steric inhibition of resonance, and its correlation with the usual σ value for the nitro group seems justified.

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

Acknowledgment. This work was supported in part by a grant from The General Faculty Research Committee of The City College. We acknowledge the assistance of Mr. E. Sokoloski.

- (11) P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. I W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 3.
 (12) H. H. Jaffé, *Chem. Rev.*, **53**, 250 (1953).
 (13) J. P. Schaefer and T. J. Miraglia, *J. Amer. Chem. Soc.*, **86**, 64 (1964).

T. Axenrod, P. S. Pregosin, M. J. Wieder

Department of Chemistry, The City College
 of the City University of New York, New York, New York 10031

G. W. A. Milne

Molecular Disease Branch, National Heart Institute
 Bethesda, Maryland 20014

Received March 21, 1969

Chemical Ionization Mass Spectrometry of Complex Molecules

Sir:

Despite the spectacular advances of mass spectrometry during the past decade, some of the basic problems attendant in its application still remain. Of these, perhaps the most serious from the point of view of the organic chemist is the failure on the part of many complex organic molecules to yield a stable molecular ion. This in turn is due to the instability of either the

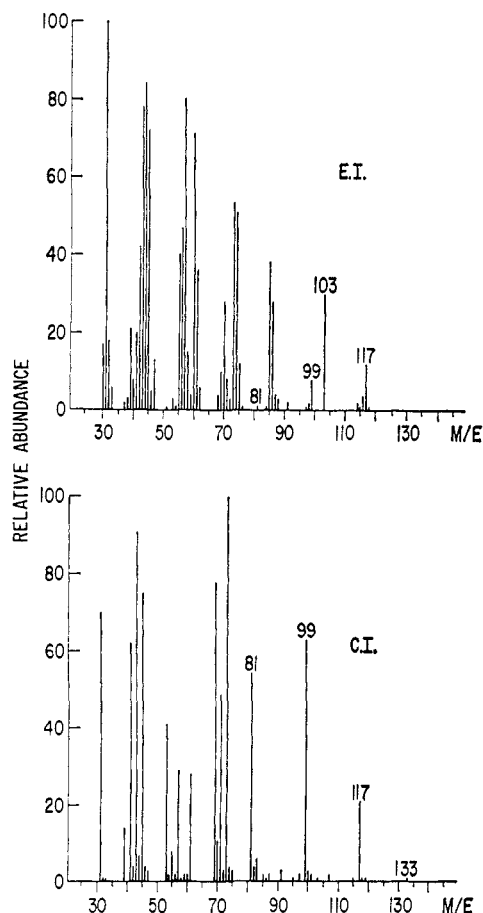


Figure 1. Mass spectra of 2-deoxy-D-ribose above m/e 30.

molecule itself or of the molecular ion which in normal electron impact (EI) mass spectrometry may be produced in a highly excited state. In an attempt to ameliorate the difficulties arising from the latter of these, we have investigated the potential of chemical ionization (CI) mass spectrometry in organic chemistry. The purpose of this communication is to report preliminary results of this work.

High-pressure mass spectrometry has been studied for many years by groups interested in ion-molecule reactions,¹ and recently Field, Munson, and coworkers have pioneered the technique of CI mass spectrometry.²

(1) "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966.

(2) (a) F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968); (b) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966); (c) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 4337 (1968); (d) M. S. B. Munson and F. D. Field, *ibid.*, **89**, 1047 (1967); (e) M. S. B. Munson and F. H. Field, *ibid.*, **89**, 4274 (1967); (f) F. H. Field, *ibid.*, **89**,