The Relationship between Allylic or Homoallylic-coupling Constants and Electron Localization on C=N Double Bonds in Some Schiff Bases and Their *N*-Oxides

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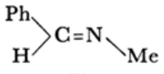
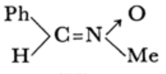
It is well known that the magnitude of an allylic or a homoallylic coupling constant⁽¹⁾ depends upon the degree of σ-π overlaps⁽¹,²⁾ and the amount of electron localization on the intervening double bond.⁽¹,³,⁴⁾ A similar situation is also seen when the central double bond is C=N.⁽¹,³,⁵,⁶⁾

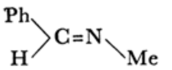
We have recently observed the PMR spectra of benzal-*N*-methylamine (I),⁽⁷⁾ its *N*-oxide (II),⁽⁷⁾ methylbenzal-*N*-methylamine (III),⁽⁸⁾ and its *N*-oxide (IV).⁽⁹⁾ The spectral data obtained by the first-order approximation are listed in Table I.



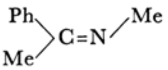
(I)



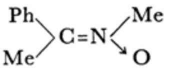
(II)



(IIIa)



(IIIb)



(IV)

The introduction of the N→O bond into I extends the conjugation and causes an electron delocalization on the C=N double bond, as our previous study by ultraviolet absorption spectroscopy proved.⁽⁷⁾ Therefore, it may readily be expected that the allylic or the homoallylic coupling constants vary from compound to compound and with the protonation occurring in such an acid solvent as trifluoroacetic acid. The fairly large $|J_{\mathrm{H,CH_3}}|$ value in I becomes smaller in a deuterotrifluoroacetic acid solution and much smaller in II, in spite of the increase in the electronegativity of the nitrogen atom by the protonation to I and also by introducing an N→O group into I. These decreases in the $|J_{\mathrm{H,CH_3}}|$ value should, accordingly, be attributed to the decreasing double-bond character of the C=N bond. In fact, π-bond orders calculated by Hückel MO method⁽¹⁰⁾ are consistent with these results (Table I). However, the $J_{\mathrm{CH_3,CH_3}}$ value in IV, which is considerably larger than the $|J_{\mathrm{H,CH_3}}|$ value in II, does not decrease appreciably in comparison with the $J_{\mathrm{CH_3,CH_3}}$ value in IIIb. These facts can be ascribed to the steric hindrance of the phenyl group with the methyl groups, which interrupts the conjugation of the benzene ring with the C=N bond. These conclusions are consistent with the results obtained by the earlier ultraviolet absorption spectroscopic study.⁽⁷⁾ A study of the solvent effects and a theoretical study of the chemical shifts of these and other related compounds in connection with electron densities and other factors are now in progress.

TABLE I. PMR SPECTRAL DATA*¹ AND RESULUS OF HÜCKEL MO CALCULATION*²

Compound	Chemical shift (τ)		Coupling constant*³, (c.p.s.)		π-Bond order of C=N
	=CH or =C-CH_3	=N-CH_3	$J_{\mathrm{H,CH_3}}$	$J_{\mathrm{CH_3,CH_3}}$	
I	1.81 (1.18)*⁴	6.53 (6.03)*⁴	−1.6 (−1.1)*⁴	—	0.873 (0.529)*⁵
II	2.76	6.21	−0.5	—	0.732
IIIa	7.82 (7.06)*⁴	6.69 (6.33)*⁴	—	+0.8 (+0.6)*⁴	
IIIb	7.82 (∼7.05)*⁴	7.03 (6.42)*⁴	—	+1.4 (+0.9)*⁴	
IV	7.69	6.45	—	+1.2	

*¹ The spectra were recorded on a Varian A-60 spectrometer by using solutions in CCl_4 containing Me_4Si as an internal reference, unless otherwise noted.

*² See, Ref. 10.

*³ For the signs of these coupling constants, see Refs. 1, 2 and 11.

*⁴ Observed in CF_3COOD solutions.

*⁵ Calculated for $-C=N^+$ system.

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1) For a review, see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

2) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

3) H. Rottendorf and S. Sternhell, *Australian J. Chem.*, **17**, 1315 (1964).

4) P. M. Nair and G. Gopakumar, *Tetrahedron Letters*, **1964**, 709.

5) G. O. Dudek, *J. Am. Chem. Soc.*, **85**, 694 (1963); G. O. Dudek and G. F. Volpp, ibid., **85**, 2697 (1963).

6) H. A. Staab, F. Vögtle and A. Mannschreck, *Tetrahedron Letters*, **1965**, 697.

7) T. Kubota, M. Yamakawa and Y. Mori, This Bulletin, **36**, 1552 (1963).

8) We have obtained this compound as a mixture of *syn*- (IIIa) and *anti*- (IIIb) isomers in a ratio of 18 : 1. The assignment of each isomer in the spectra was made according to Ref. 6.

9) Y. Mori, unpublished results; we are also indebted to Dr. Mori for supplying us with a specimen of IV.

10) T. Kubota and M. Yamakawa, This Bulletin, **36**, 1564 (1963).

11) D. Gagnaire, A. Rouseau and P. Servoz-Gavin, *J. Chim. Phys.*, **61**, 1207 (1964).