

of the $=\text{NNHX}$ structure indicates that the conformation of aliphatic oximes in benzene is VI, not VII. Microwave spectroscopy has shown⁴ that the conformation of formaldoxime in the gas phase is VI. For $=\text{NNHX}$ compounds conformation IV is preferred over the one which is analogous to VI, because of unfavorable interactions between X and R₁ in VI.

Acknowledgment.—We thank the United States Atomic Energy Commission for financial support, Grant AT(11-1)-1189.

(4) I. N. Levine, *J. Mol. Spectry*, **8**, 276 (1962).

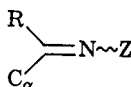
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Structural Studies by Nuclear Magnetic Resonance. IV. Conformations of *syn-anti* Isomers from Chemical Shifts and Spin-Spin Coupling Constants

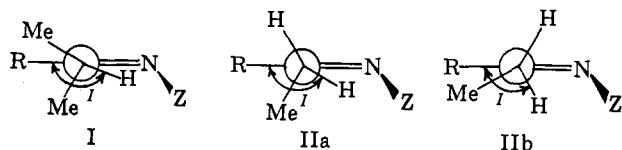
Sir:

We reported¹ in our n.m.r. studies on structural assignments to *syn* and *anti* isomers that α -methyl hydrogens when *cis* to Z resonate at higher fields (*shielded*) than when *trans*; for α -methylene hydrogens the chemi-



cal shift difference between *cis* and *trans* hydrogens is smaller than it is for α -methyl hydrogens, and in many cases this difference is zero; α -methine hydrogens when *cis* to Z resonate at *appreciably lower fields* (*deshielded*) than when *trans*. In this respect α -methine hydrogens behave as hydrogens directly bonded to the imino carbon.²

This puzzling behavior of α -hydrogens is explicable from conformational considerations. Because of steric interactions between Z and isopropyl when *cis* to each other, the preferred conformation of the isopropyl group might be I ($I \sim 180^\circ$ or slightly smaller). Conformation I places the methine hydrogen in or near the $\text{C}=\text{N}-\text{Z}$



plane and explains the similarity in behavior between methine and hydrogens directly bonded to the imino carbon (deshielded). The angle I will depend on the size of R, *i.e.*, as R increases in size I will increase and approach 180° . As I increases, the methine hydrogen will become more deshielded. Our data support this hypothesis, *e.g.*, in oximes ($\text{Z} = \text{OH}$), when R = H, $\tau(\text{trans}) = 7.55$ and $\tau(\text{cis}) = 6.87$; when R = Me, $\tau(\text{trans}) = 7.52$ and $\tau(\text{cis}) = 6.55$. From similar arguments the important conformations of the ethyl group

(1) G. J. Karabatsos, R. A. Tallier, and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 2326 (1963).

(2) We also observed the same behavior in nitrosamines. In cases such as oximes where all α -hydrogens are deshielded (*cis* lower than *trans*), we find the same trend; *i.e.* α -methine hydrogens are more deshielded (0.7–1.0 p.p.m. in carbon tetrachloride) than α -methyl hydrogens (0.03–0.05 p.p.m. in carbon tetrachloride).

should be those where I varies from 180° (IIa) to 125° (IIb).

We could test further the above hypothesis by measuring $J_{\text{H}\alpha\text{H}_\beta}$ for *cis* (III) and *trans* (V) isomers provided $J_{\text{H}\alpha\text{H}_\beta}$ were a function of the dihedral angle, as J is



in ethane derivatives.³

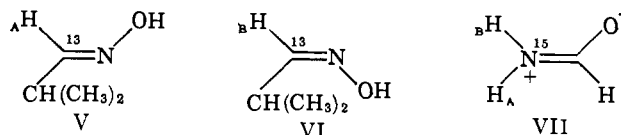
The data summarized in Table I are consonant with the advanced explanation. As expected from a dihedral angle of about 180° , J_{cis} for isopropyl compounds is large (7.6 c.p.s.). For ethyl compounds II_a predicts J_{cis} larger than J_{cis} for methyl compounds, while II_b predicts the reverse. The data indicate that both II_a and II_b are important contributors, but do not allow assignment of relative contributions. J 's, especially J_{trans} of oximes, are solvent dependent. In addition, J_{trans} of oximes depends on concentration, *e.g.*, J_{trans} of isobutyraldoxime = 6.55, 6.35, 6.30 c.p.s. in carbon tetrachloride solutions of 20%, 10%, and 5% concentration, respectively. Preliminary temperature studies also show that J_{cis} of isobutyraldoxime (neat) decreases by 0.10 c.p.s. and J_{trans} by about 0.20 c.p.s. as the temperature is raised from 38° to about 70° . These results are easily understood in terms of self-association and hydrogen bonding between solute and solvent.

TABLE I

Compound	Solvent (Concd., 5–10%)	$J_{\text{H}\alpha\text{H}_\beta}$ (<i>cis</i>)	$J_{\text{H}\alpha\text{H}_\beta}$ (<i>trans</i>)
MeHC=N-NHC ₆ H ₅ (NO ₂) ₂	b, c, d, e, f	5.60 ± 0.05	5.40 ± 0.05
MeHC=N-NHC ₆ H ₅ (NO ₂) ₁	g, h	5.50 ± 0.05	5.30 ± 0.05
EtHC=N-NHC ₆ H ₅ (NO ₂) ₂	b	5.4 ± 0.1	5.0 ± 0.1
<i>i</i> -PrHC=N-NHC ₆ H ₅ (NO ₂) ₂	b	7.6 ± 0.1	4.9 ± 0.1
MeHC=N-NH ϕ	g, i, k, l	5.75 ± 0.05	5.55 ± 0.05
MeHC=N-NH ϕ	m	5.80 ± 0.05	5.60 ± 0.05
EtHC=N-NH ϕ	a	5.2 ± 0.1	5.2 ± 0.1
<i>i</i> -PrHC=N-NH ϕ	a, i, k, n	7.6 ± 0.1	5.0 ± 0.1
MeHC=N-NC ₆ H ₄ NO ₂ (<i>o</i>)	b	5.50 ± 0.05	5.30 ± 0.05
MeHC=N-NHMe	a, i	5.80 ± 0.05	5.50 ± 0.05
MeHC=N-NHMe	k, l	5.80 ± 0.05	5.60 ± 0.05
MeHC=N-NHCONH ₂	b	5.80 ± 0.05	5.50 ± 0.05
MeHC=N-NHCSNH ₂	b	5.80 ± 0.05	5.50 ± 0.05
MeHC=N-OH	a, b, i, k	5.80 ± 0.05	6.30 ± 0.05
MeHC=N-OH	e, g, l	5.75 ± 0.05	6.10 ± 0.05
EtHC=N-OH	a	5.75 ± 0.05	6.10 ± 0.05
EtHC=N-OH	b, k, l	5.75 ± 0.05	5.90 ± 0.05
EtHC=N-OH	g	5.75 ± 0.05	6.00 ± 0.05
<i>i</i> -PrHC=N-OH	a	7.65 ± 0.05	6.65 ± 0.05
<i>i</i> -PrHC=N-OH	g	7.60 ± 0.05	6.15 ± 0.05
<i>i</i> -PrHC=N-OH	k	7.55 ± 0.05	6.30 ± 0.05
<i>i</i> -PrHC=N-OH	l	7.50 ± 0.05	6.0 ± 0.1

^a Neat. ^b Methylene bromide. ^c Nitrobenzene. ^d Dioxane. ^e Pyridine. ^f Dimethylformamide. ^g Acetone. ^h Quinoline. ⁱ Benzene. ^k Carbon tetrachloride. ^l Dimethyl sulfoxide. ^m Methanol. ⁿ Isodurene.

Exceptionally high J_{trans} values for oximes⁴ result in $J_{\text{trans}} > J_{\text{cis}}$ for acetaldoxime and propionaldoxime. We find $J_{\text{C}^{13}\text{H}_\alpha}$ (V) = 162 ± 2 c.p.s. and $J_{\text{C}^{13}\text{H}_\beta}$ (VI) = 174 ± 2 c.p.s. From the dependence of $J_{\text{C}^{13}-\text{H}}$ on the % s-character of the carbon atomic orbitals we conclude



that the imino carbon orbital in C-H_B has more s

(3) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Phys. Chem.*, **64**, 1793 (1960).

(4) Our studies confirm the correctness of oxime assignments by W. P. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958); E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).

character than in C-H_A (the C-H_B bond is shorter than the C-H_A). Analogous results were obtained with formamide⁵ (VII), $J_{N^{15}H_A} = 92$ c.p.s., $J_{N^{15}H_B} = 88$ c.p.s.

Part of the difference, therefore, between J_{cis} and J_{trans} (Table I) could be due to changes in the hybridization of the imino carbon. Evaluation of conformational and hybridization contributions must await temperature studies and C¹³ labeling.

Acknowledgment.—We thank the United States Atomic Energy Commission for financial support, Grant AT(11-1)-1189.

(5) B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38**, 681 (1960). The N-H_A = 1.002 ± 0.005 Å, and the N-H_B = 1.014 ± 0.005 Å, according to C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

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π -Electron Densities in Arylmethyl Carbanions by Nuclear Magnetic Resonance Spectroscopy

Sir:

Nuclear magnetic resonance spectroscopy offers a unique approach toward the explication of π -electron densities in aromatic molecules. It has been amply demonstrated¹⁻¹⁰ that, in general, the chemical shift (δ) of an aromatic proton is approximately proportional

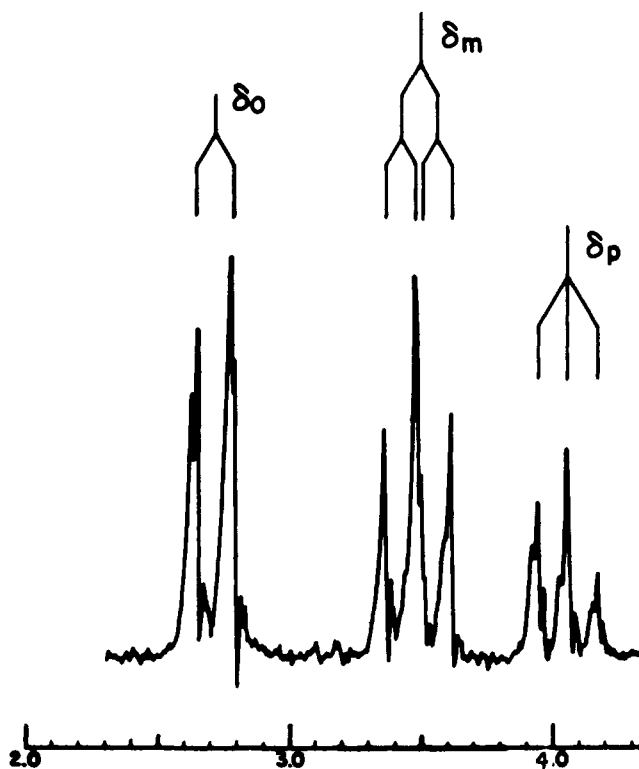


Fig. 1.—Proton n.m.r. spectrum of triphenylmethyl lithium in THF.

- (1) P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956).
- (2) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959).
- (3) D. E. O'Reilly and H. P. Leftin, *J. Phys. Chem.*, **64**, 1555 (1960); according to Berry, Dehl, and Vaughn (see ref. 18b) the chemical shifts assigned to the *ortho* and *meta* protons of the triphenylmethyl carbonium ion are reversed.
- (4) G. Fraenkel, et al., *J. Am. Chem. Soc.*, **82**, 5846 (1960).
- (5) I. C. Smith and W. G. Schneider, *Can. J. Chem.*, **39**, 1158 (1961).
- (6) H. Spiesscke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).
- (7) H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **36**, 731 (1961).
- (8) W. Seiffert, H. Zimmermann, and G. Scheibe, *Angew. Chem., Intern. Ed. Engl.*, **1**, 265 (1962).
- (9) J. C. Schug and J. C. Deck, *J. Chem. Phys.*, **37**, 2618 (1962).
- (10) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

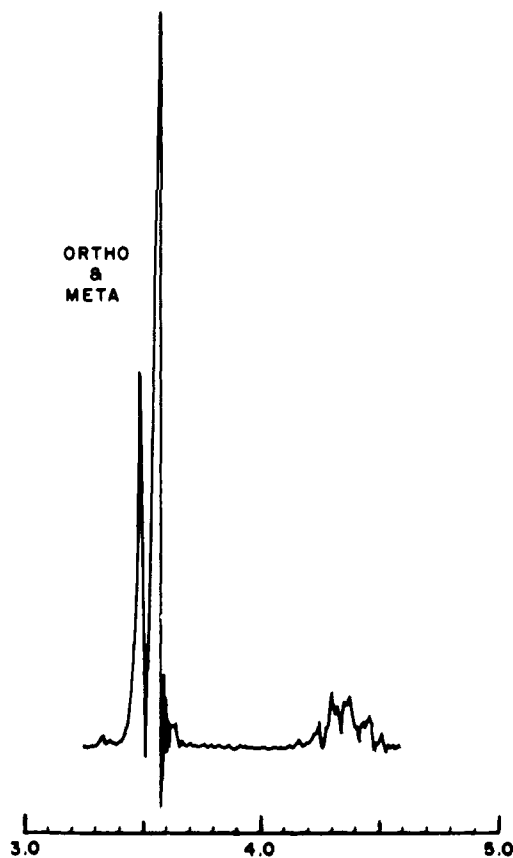


Fig. 2.—Proton n.m.r. spectrum of diphenylmethyl lithium in THF.

to the π -electron density on the carbon to which it is attached. Using this principle, the electronic structures of various aromatics,¹⁻¹⁰ including arylmethyl carbonium ions,^{2,3,10} have been investigated. We now have been able to show this technique to be particularly useful for arylmethyl carbanions, with triphenylmethyl lithium exhibiting the first spectrum of a monosubstituted benzene readily interpretable by first-order analysis. The π -electron densities of such carbanions have not been experimentally available previously. Our results are contrary to the predictions of classical resonance theory or Hückel LCAO molecular orbital calculations, and strongly support the self-consistent field (s.c.f.) calculations of Brickstock and Pople.¹¹

The 60 Mc.p.s. proton n.m.r. spectra of triphenylmethyl lithium, diphenylmethyl lithium, and benzyl lithium in tetrahydrofuran (THF) are shown in Fig. 1, 2, and 3. The spectrum of triphenylmethyl lithium is surprisingly uncomplicated, consisting of three discrete multiplets with integrated intensities of 2:2:1. First-order analysis gives chemical shifts of 2.69 τ , 3.48 τ , and 4.04 τ for the *ortho*, *meta*, and *para* protons, respectively, with coupling constants of $J_{o-m} = 7.9$ c.p.s. and $J_{m-p} = 6.6$ c.p.s. Further, the spectrum is neither solvent nor cation sensitive; only minor shifts were observed between spectra run in THF, hexamethylphosphoramide, and dimethyl sulfoxide, and between the spectra of triphenylmethylsodium and triphenylmethyl lithium in THF. Thus, the alkali triphenylmethyls must be essentially completely ionized,¹² in accord with the conclusion of Ziegler and Wollschitt¹³ derived from conductance data.

- (11) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).
- (12) This conclusion cannot be extrapolated to diphenylmethyl lithium and benzyl lithium until the proper experiments have been completed.
- (13) K. Ziegler and H. Wollschitt, *Ann.*, **479**, 123 (1930).