TABLE I

Compound[a]	$|J|_{HH}$(gem)[b] (c.p.s.)	Solvent[c]	$|J|$"average"[d] (c.p.s.)
CH₂=N—OH (or D)	7.63 to 9.95[e]	[e]	
CH₂=N—OCH₃	6.96 to 9.22[e]	[e]	} 8.5
CH₂=N—N(CH₃)₂	10.3 ± 0.2	50% in D₂O	
	11.7 to 12.0 ± 0.2	C₆H₆[f]	
CH₂=N—N—C₆H₄—NO₂(4) H	11.6 ± 0.2	Me₂CO, Me₂SO	
CH₂=N—N—C₆H₃—(NO₂)₂(2,4) (or D) H (or D)	11.0 to 11.4[g]	[g]	} 11
CH₂=N—N—C₆H₄—NO₂(4) CH₃	12. ± 0.2	Me₂CO	
CH₂=N—C(CH₃)₃	16.11	MeCN	
	16.52	(neat)	
CH₂=N—C(CH₃)₂CH₂C(CH₃)₃[h]	16.08	Me₂SO	
	16.20	MeCN	} 16.5
	16.34	ClCH₂CH₂Cl	
	16.86	CCl₄	
	16.97	(neat)	

[a] All compounds were prepared in standard fashion by the reaction of formaldehyde with the appropriate H₂N–R compound. [b] All J values were measured on carefully calibrated Varian Associates Model A-60 spectrometers, radiofrequency 60 Mc./sec., sample temp. 36 ± 2°. Unless otherwise specified, the P.E. of the values given is 0.05 c.p.s. or less. [c] Unless otherwise noted, dilute (~5% or less) solutions were used. [d] A rough "average" value, convenient for indicating the general sizes of the couplings. [e] Strongly solvent dependent. For a more detailed account, see B. L. Shapiro, S. J. Ebersole, and R. M. Kopchik, J. Mol. Spectry., 11, 326 (1963). [f] Small concentration dependence. [g] Small solvent dependence. See G. J. Karabatsos, B. L. Shapiro, F. M. Vane, J. S. Fleming, and J. S. Ratka, J. Am. Chem. Soc., 85, 2784 (1963). [h] We thank Dr. P. L. de Benneville of the Rohm and Haas Co., Bristol, Pa., for generous samples of this compound and for helpful discussions.

side the range 0 ± 3.5 c.p.s. only for the cases of substitution by elements of very low electronegativity, such as Al, Li, and Mg,[3] where values in the range (+) 6 to 8 c.p.s. are observed. In Table I, we report our observations of $|J_{HH}|$(gem) in a number of CH₂=N— compounds, in which very different values are obtained.

Among other interesting features[4] of the spectra, the magnitudes and (in some cases) solvent dependences[4] of the J values are noteworthy. In these CH₂=N—Y compounds, $|J|$ increases markedly as the electronegativity of Y decreases. The trend observed here, taken together with that reported for the olefins,[2h] suggests that the sign of these CH₂=N—Y J values is negative, and various sign determination experiments are in progress.

It may be noted at this stage, however, that the range of magnitudes of these sp²-type J(gem) values overlaps extensively with the range of values hitherto associated with sp³-type J(gem) values.[5] Thus, regardless of the signs of the J values reported here, a theoretical picture which gives major importance to the H–C–H bond angles[6] will clearly be inapplicable, since it is evident that in our sp²-type cases, substituent effects (to put the matter in the most general terms) are dominant, as has already been pointed out for sp³-type CH₂ systems and suggested strongly for vinylic sp² cases as well.[7]

Regardless of the detailed nature of the dominant factors controlling the spin–spin coupling constants, the observed monotonic trend in $|J|$(gem) with β-

atom electronegativity (cf. vinyl-X[2h]) suggests that resonance form B, which is certainly unimportant in the azomethines, is also probably not very significant in the oxime and hydrazone derivatives. Resonance contributors of type A, however, could well be involved to some significant extent in all three types of compound. One possible and plausible implication of

$$\overset{+}{C}H_2—\overset{-}{N}—Y \qquad \overset{-}{C}H_2—\overset{+}{N}=Y$$
$$A \qquad\qquad B$$

this is that the more "positive" the carbon atom of the CH₂, the larger the $|J|$. However, other factors (such as the involvement of the π-system, and especially the availability of electron pairs on X of the CH₂=X system) may well be important. These and other matters are currently being investigated.

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(3) (a) D. W. Moore and J. A. Happe, J. Phys. Chem., 65, 224 (1961); (b) C. S. Johnson, Jr., M. A. Weiner, J. S. Waugh, and D. Seyferth, J. Am. Chem. Soc., 83, 1306 (1961); (c) R. T. Hobgood, Jr., and J. H. Goldstein, Spectrochim. Acta, 18, 1280 (1962); (d) G. Fraenkel, D. G. Adams, and J. Williams, Tetrahedron Letters, No. 12, 767 (1963).

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(6) Cf. M. Karplus and D. H. Anderson, J. Chem. Phys., 30, 6 (1959); H. S. Gutowsky, M. Karplus, and D. M. Grant, ibid., 31, 1278 (1959); H. S. Gutowsky, V. D. Mochel, and B. G. Somers, ibid., 36, 1153 (1962); M. Karplus, J. Am. Chem. Soc., 84, 2458 (1962).

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Complexes of Organolithium Compounds with Vacant Orbital Acceptors. II. Determination of Electron-Density Changes by Proton Magnetic Resonance

Sir:

We wish to report that changes in electron density of an aromatic organolithium compound, brought about by dative-bond formation with a Lewis acid, can be determined from changes occurring in its proton magnetic resonance (p.m.r.) spectra on complexing. Organolithium compounds form reversible dative complexes
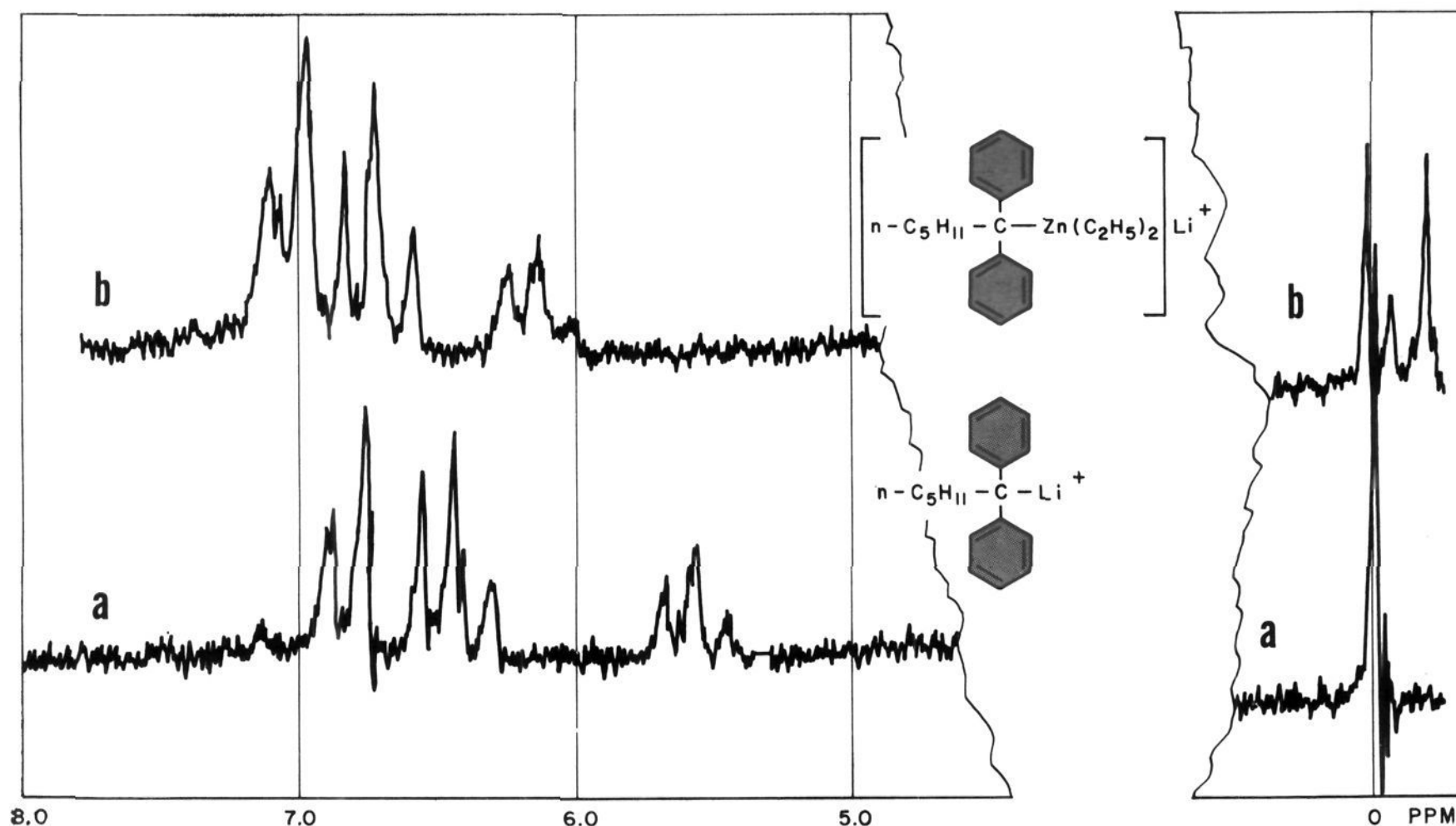
Fig. 1.—Proton magnetic resonance spectra of 1,1-diphenyl-n-hexyllithium and its diethylzinc complex.

with weak Lewis acids, *e.g.*, $R^-Li^+ + Et_2Zn \rightleftarrows [R \rightarrow ZnEt_2^-]Li^+$. The chemistry of complexes of this type has been investigated principally by Wittig and co-workers,[1] but there is little information on their physical properties. Recently, we have shown that such properties as association constant and bond energy can be obtained from the ultraviolet and visible spectrum of the complex.[2] Since nuclear screening in molecules is determined by electron distribution in the vicinity of the nucleus, the protons of the organolithium compound move to lower field on complexing and those of the Lewis acid to higher field. We believe this to be the first quantitative observation of electron-density changes occurring in dative-bond formation.

We report data for the p.m.r. of the complex formed between 1,1-diphenyl-n-hexyllithium (I) and diethylzinc in tetrahydrofuran solution. In this odd alternant organolithium compound the negative charge is extensively delocalized onto the phenyl rings.[3] Because the electron densities at the *ortho*, *meta*, and *para* positions are different,[4] the aromatic protons at each position experience a different upfield chemical shift. The spectrum of I is shown in Fig. 1a with internal TMS zero. The downfield shift of the aromatic protons owing to the electron density lost to diethylzinc on complex formation is shown in Fig. 1b for the ratio of ZnEt₂/RLi = 0.82. The spectral pattern of I is identical with that of triphenylmethyllithium.[6]

Several workers[7,8] have established that there is a

(1) G. Wittig, *Angew. Chem.*, **70**, 65 (1958), and references therein. See ref. 2 for a more complete summary of previous preparative work.

(2) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 2861 (1963).

(3) Evidence indicates I exists in THF solution as free ions or as very loose ion-pairs having only weak interaction.

(4) Hückel LCAO calculations predict equal charge densities at the *o-*, *p*-positions and zero at the *m*-position, but calculations including electron repulsion predict different charge densities at each position, which increase in the order *o-*, *m-*, *p-*.[5]

(5) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

(6) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

(7) G. Fraenkel, R. E. Carter, A. McLachlin, and J. H. Richards, *ibid.*, **82**, 5846 (1960).

(8) T. Schaefer and W. G. Schneider. *Can. J. Chem.*, **41**, 96 (1963), and references therein.

direct relation between proton chemical shift (δ) and electron density at the carbon atom to which the proton is attached. From the difference between δ of free RLi and completely complexed RLi, the actual amount of electron density change ($\Delta\rho$) occurring at each of the aromatic protons on dative-bond formation can be determined. Or similarly, absolute charge densities (ρ) may be determined from $\Delta\delta$ benzene[6-8] (benzene δ = 7.25 p.p.m. in THF). These values are summarized in Table I. Because the central carbon atom in I has no attached proton, ρ at this position cannot be experimentally obtained. Complexes of other organolithium compounds having α-protons are under study.

TABLE I

NEGATIVE CHARGE DENSITIES DETERMINED FROM CHEMICAL SHIFTS[a]

Position	1,1-Diphenyl-n-hexyllithium	I–diethylzinc complex	$\Delta\rho$/proton on complexing	Total $\Delta\rho$ on complexing	$\Delta\rho^b$ fractional
ortho	0.040	0.019	0.021	0.084	0.53
meta	.077	.043	.034	.136	.44
para	.158	.089	.069	.138	.44
Total charge on rings	.784	.426	...	.358	...

[a] Using the relationship, $\Delta\delta = 10.7 \cdot \Delta\rho$ from reference 8.

[b] $\Delta\rho_{fractional} = \dfrac{\Delta\rho \text{ (on complexing)}}{\rho \text{ (free RLi)}}$.

The total observable electron-density change caused by complexing with diethylzinc is 0.358 electron. Since it seems unlikely that the central C-atom will have a higher incipient charge in the dative complex than in the free ion, at least this amount of electron density is acquired by the diethylzinc during dative bonding. The largest change in electron density occurs at the *para* position, which in the free organolithium is the position having the largest fraction of negative charge. The largest fractional change in charge density on complexing occurs at the *ortho* position.

The charge densities are in reasonable agreement with SCF calculated values,[5] although no corrections were

made for contributions other than ρ to δ.[8] Presumably the protons of I and its complex are subject to the same effects so their difference is independent of correction factors. The order of chemical shift with increasing field strength, i.e., increasing charge density, is o-, m-, p-, and as predicted by MO theory is a mirror image of triphenylmethyl carbonium ion.[9] By difference, the charge on the central carbon in I is 0.216 electron.

When there is insufficient Et_2Zn to complex all the RLi, a discrete spectrum is not observed for the complexed and uncomplexed RLi. There must, therefore, be rapid exchange between complexed and uncomplexed species. Because the average spectrum is sharp, the lifetime[10] in each state is <0.008 sec. In a rapidly equilibrating system the δ obsd. is the sum of δ of the individual species multiplied by their respective mole fractions,[10] which for this system are obtained from the known association constant.[2] The average δ calculated from ten experiments with a range of fraction of RLi complexed of $0.29 \rightarrow 0.95$ are in excellent agreement with the observed chemical shifts.

The methylenes of diethylzinc in THF produce a quartet centered at 0.03 p.p.m. downfield from TMS with splitting of 8 c.p.s., which is shifted upfield by complex formation, centering at 0.32 p.p.m. above TMS for complete complexing. The shift of the complexed $—CH_2–Zn$ is equivalent to 38% of $\Delta\rho$ of the aromatic protons, showing the larger share of the charge of the dative bond is localized on zinc.

The reversibility of these complexes is readily observed from their p.m.r. spectrum, in that adding excess n-butyllithium to complex the diethylzinc, the original spectrum of I is recovered.

With stronger Lewis acids, e.g., triethylaluminum, the downfield shifts of I are considerably larger for a given Lewis acid/RLi ratio. Thus, studies of this type should provide a quantitative measure of Lewis acid strengths.

(9) R. Dehl, W. R. Vaughn, and R. S. Berry, J. Org. Chem., 24, 1616 (1959).

(10) H. S. Gutowsky and A. Saika, J. Chem. Phys., 21, 1688 (1953).

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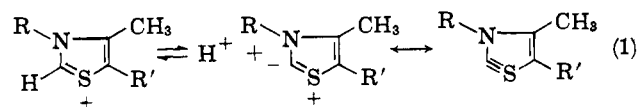FRAMINGHAM, MASSACHUSETTS

A Comparison of Thiazoles and Oxazoles[1]

Sir:

The importance in thiamine action of ionization of the 2-hydrogen of the thiazolium ring system, eq. 1, seems well established.[2] We have studied thiazoles, thiazol-

$$\text{(1)}$$

ium ions, oxazoles, and oxazolium ions and have found that molecular orbital calculations, p.m.r. spectra, and exchange rates provide some highly interesting comparisons and some unusually large $C^{13}–H$ coupling constants.

The positioning of charge in thiazolium ions (eq. 1 and structure C) is based upon molecular orbital calculations carried to internal consistency by means of the ω technique.[3] These calculations result in π densities

(1) This research was supported in part by Grant No. AM-6870 from the U. S. Public Health Service. W. B. M. was a participant in the National Science Foundation program for research by undergraduates.

(2) (a) R. Breslow, J. Am. Chem. Soc., 79, 1762 (1957); (b) F. H. Westheimer, Advan. Enzymol., 24, 467 (1962); (c) R. Breslow, Ciba Foundation Study Group 11. "The Mechanism of Action of Water Soluble Vitamins," Little, Brown, and Co., Boston, p. 18.

(3) Our LCAO-MO calculations used the ω method[4] ($\omega = 1.4$) for adjustment of coulomb integrals until successive calculations showed insignificant

a, R = H
b, R = CH₃

a, R = H
b, R = CH₃
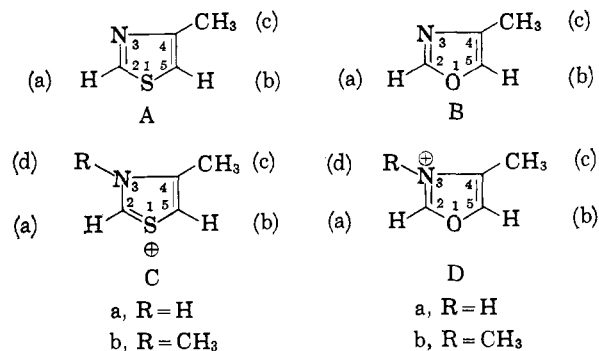
which indicate partial positive charges at both sulfur and nitrogen, but most of the charge is on sulfur; therefore the best single representation of thiazolium ions is C. Qualitative reasoning based on electronegativities and polarizabilities dictates the same conclusion. The partial positive charge on sulfur might cause sufficient d-orbital contraction so that the benzyne-type structure shown in eq. 1 could make an important contribution to the structure of the intermediate in ionization of thiazolium ions.

Table I gives the chemical shifts which we have observed in our studies of 4-methylthiazole, 4-methyloxazole, and some onium ions derived therefrom. Although the signals for the 5-hydrogens come consistently at lower field in the oxazoles than in the thiazoles, the reverse is true for the 2-hydrogens; in 4-methylthiazole (A) the chemical shift for the 2-hydrogen is considerably lower than in 4-methyloxazole (B), although the gap is considerably lowered on methylation or protonation. The very low chemical shifts for the 2-hydrogen in the thiazolium (C) and oxazolium (D) ions indicate that this hydrogen is unusually deshielded in both of these onium ions and is therefore an unusually acidic aromatic hydrogen.

TABLE I
CHEMICAL SHIFTS IN OXAZOLES AND THIAZOLES[a]

Compd.	Solvent	T_a	T_b	T_c	T_d
A	CCl₄	1.36	3.13	7.53	
A	D₂O	1.33	3.05	7.60	
B	CCl₄	2.25	2.59	7.82	
B	D₂O	1.95	2.50	7.78	
Ca	CF₃CO₂H	0.17	2.19	7.25	
Cb	D₂O	0.12	2.06	7.25	5.72
Da	CF₃CO₂H	0.47	1.88	7.46	
Db[b]	D₂O	0.21	1.75	7.48	5.95

[a] Spectra taken with Varian A-60 n.m.r. spectrometer; chemical shifts are relative to Me₄Si except for those spectra in D₂O where the HOD peak (taken as 5.25T) was used as an internal standard. [b] The ion, Db, was isolated as the iodide salt; it is apparently a new compound and a satisfactory analysis was obtained.

Some of the coupling constants found for these heterocyclic systems are listed in Table II. The H–H coupling constants found in the thiazoles and thiazolium ions are consistent with previous results on other thiazoles,[7] although the J_{ac} observed here is a longer-

change in π density. A variety of coulomb integrals for neutral atoms and resonance integrals were used including those selected by Streitwieser[4b] and Kreevoy.[5] The S–C resonance integral, $0.6\beta_0$, suggested by Pullman and Pullman[6] seems too low considering overlap integrals and the polarizability of sulfur; we prefer Kreevoy's value[5] of $0.93\beta_0$. Our results indicate positive charges of about 0.6 on sulfur and 0.4 on nitrogen.

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