

character than in C-H<sub>A</sub> (the C-H<sub>B</sub> bond is shorter than the C-H<sub>A</sub>). Analogous results were obtained with formamide<sup>5</sup> (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 C<sup>13</sup> 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<sub>A</sub> = 1.002 ± 0.005 Å, and the N-H<sub>B</sub> = 1.014 ± 0.005 Å, according to C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

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### $\pi$ -Electron Densities in Arylmethyl Carbanions by Nuclear Magnetic Resonance Spectroscopy

Sir:

Nuclear magnetic resonance spectroscopy offers a unique approach toward the explication of  $\pi$ -electron densities in aromatic molecules. It has been amply demonstrated<sup>1-10</sup> that, in general, the chemical shift ( $\delta$ ) of an aromatic proton is approximately proportional

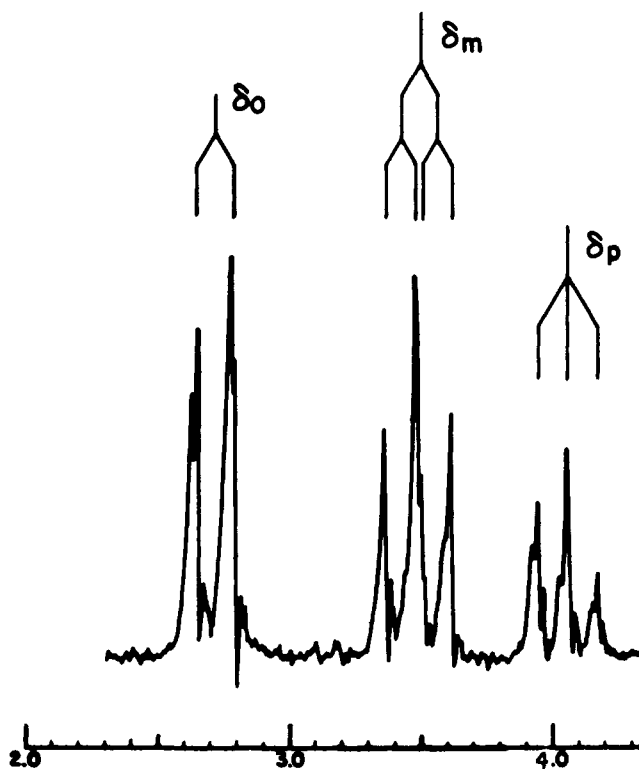


Fig. 1.—Proton n.m.r. spectrum of triphenylmethyl lithium in THF.

- (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.*, **35**, 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).

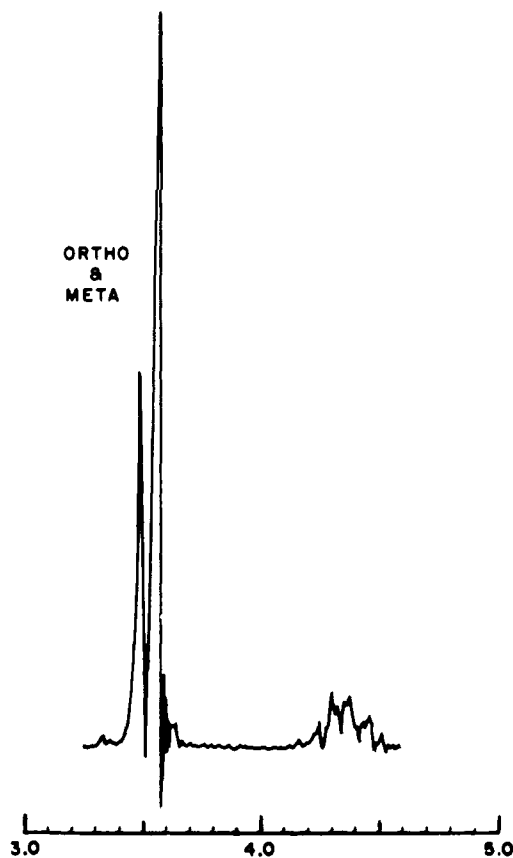


Fig. 2.—Proton n.m.r. spectrum of diphenylmethyl lithium in THF.

to the  $\pi$ -electron density on the carbon to which it is attached. Using this principle, the electronic structures of various aromatics,<sup>1-10</sup> including arylmethyl carbonium ions,<sup>2,3,10</sup> 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  $\pi$ -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.<sup>11</sup>

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  $\tau$ , 3.48  $\tau$ , and 4.04  $\tau$  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,<sup>12</sup> in accord with the conclusion of Ziegler and Wollschitt<sup>13</sup> 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).

TABLE I  
CHARGE DISTRIBUTION IN PHENYL-SUBSTITUTED METHYL CARBANIONS

Carbanion	N.m.r. method <sup>a</sup>	S.c.f. MO <sup>a</sup>	LCAO MO <sup>a</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C <sup>-</sup> Li <sup>+</sup>	<i>ortho</i>	0.00	-0.05
	<i>meta</i>	-.08	-.06
	<i>para</i>	-.13	-.19
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH <sup>-</sup> Li <sup>+</sup>	<i>ortho</i>	-.08	-.08 <sup>b</sup>
	<i>meta</i>	-.07	-.06 <sup>b</sup>
	<i>para</i>	-.16	-.23
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> <sup>-</sup> Li <sup>+</sup>	<i>ortho</i>	-.12	-.14
	<i>meta</i>	-.10	-.07
	<i>para</i>	-.18	-.23

<sup>a</sup> In units of the absolute value of the charge of an electron.

<sup>b</sup> These are average values since the two *ortho* and *meta* positions in each ring are not equivalent.

Diphenylmethyl lithium in THF yields a spectrum which consists of a doublet and a multiplet centered at 3.48 and 4.35  $\tau$ , respectively, with relative areas of 4:1 (Fig. 2).<sup>14</sup> The conclusion that we are dealing here with an A<sub>2</sub>B<sub>2</sub>C system in which the A and B chemical shifts are nearly identical<sup>15</sup> follows from an examination of the spectrum of *p,p'*-dideuteriodiphenylmethyl lithium in THF which consists of a single band at 3.48  $\tau$ . Thus, the high-field multiplet in the diphenylmethyl lithium spectrum is assigned to the *para* protons and the low-field doublet to the *ortho* and *meta* protons, and a preliminary mathematical analysis (using an A<sub>2</sub>B<sub>2</sub>X approximation) gives the following approximate parameters:  $\delta_o = 3.49 \tau$ ,  $\delta_m = 3.46 \tau$ ,  $\delta_p = 4.35 \tau$ ,  $J_{o-m} = 8.2$  c.p.s.,  $J_{o-p} = 1.3$  c.p.s.,  $J_{o-o'} = 2.0$  c.p.s.,  $J_{o-m'} = 0.5$  c.p.s.,  $J_{m-p} = 6.9$  c.p.s., and  $J_{m-m'} = 2.0$  c.p.s. A more precise calculation is in progress and will be published elsewhere.

The spectrum of benzyl lithium in THF (Fig. 3) consists of two multiplets with relative areas of four (low-field) to one (high-field). A first-order interpretation yields coupling constants of  $J_{o-m} = 8.0$  c.p.s. and  $J_{m-p} = 6.2$  c.p.s. and a chemical shift of 4.50  $\tau$  for the *para* proton. Upon substitution of deuterium for hydrogen in the *para* position, the spectrum collapsed to a typical A<sub>2</sub>B<sub>2</sub> quartet with  $J_{o-m} = 8.0$  c.p.s., thus confirming the assignment for the *ortho* and *meta* protons and allowing a more precise determination of their chemical shifts. Since  $J_{o-o'}$ ,  $J_{m-m'}$ , and  $J_{o-m'}$  are small, the spectrum approximated that of two separate but identical AB systems with chemical shifts of  $\delta_o = 3.91 \tau$  and  $\delta_m = 3.70 \tau$ .

Charge distributions in the phenyl rings of the above carbanions were calculated from the proton chemical shifts relative to benzene ( $\delta_B = 2.72 \tau$ ) in THF using the proportionality constant of Fraenkel, *et al.*,<sup>4</sup> of 10 p.p.m./electron. In Table I these results are compared with similar data of Brickstock and Pople<sup>11</sup> calculated by a s.c.f. molecular orbital method and that of Streitwieser<sup>16</sup> using the Hückel LCAO molecular orbital method. In general there is good qualitative agreement between the n.m.r. data and the s.c.f. calculations but not with the LCAO results.

The charge distribution in the triphenylmethyl carbanion is particularly interesting in that the *meta* ring positions bear more negative charge than do the *ortho*.<sup>17</sup> An analogous situation has been reported for the triphenylmethyl carbonium ion by Dehl, Vaughan, and Berry<sup>18</sup> and by Schaefer and Schneider.<sup>10</sup> This is contrary to the predictions of both LCAO calculations

(14) The  $\alpha$  protons of diphenylmethyl lithium and benzyl lithium were not observed in the n.m.r. spectra. Presumably these bands are masked by the solvent.

(15) The possibility of an anomalous interaction between the  $\alpha$  and ring protons was eliminated by the observation that the spectrum of  $\alpha$ -deuteriodiphenylmethyl lithium was identical to that of the undeuterated compound.

(16) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **74**, 5290 (1952).

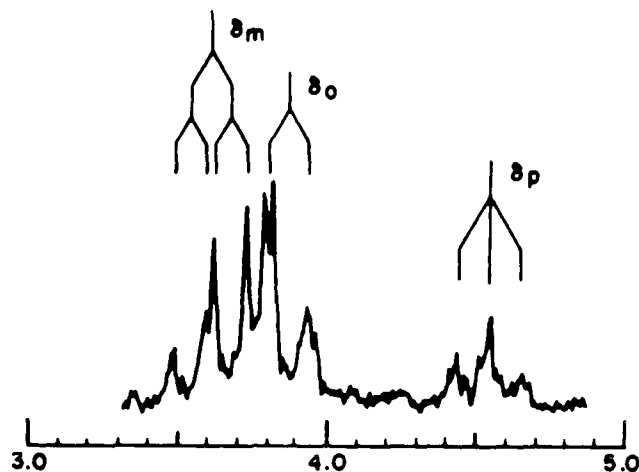


Fig. 3.—Proton n.m.r. spectrum of benzyl lithium in THF.

(Table I) and resonance theory.<sup>19</sup> Inter-electron repulsion causes a dispersion of charge to the extremities of the ion, resulting in a high concentration of negative charge on the *meta* and *para* carbons, this effect becoming progressively less important in the diphenylmethyl and benzyl carbanions. The success of Pople's s.c.f. method in treating all three ions attests to its usefulness in dealing with inter-electron repulsion.

A comparison of the spectra of the triphenylmethyl anion and cation is interesting at this point since theoretical calculations<sup>11,16</sup> indicate that the charge distribution should be identical but opposite in sign, and on this basis one would expect the carbonium ion spectrum to be a mirror image of that of the anion. The carbonium ion spectrum has been recorded by several workers,<sup>2,8,10,18</sup> and it bears no resemblance to the carbanion spectrum. Any explanation given for this difference at the present time would be largely speculative.

The examination of these and related ionic species by the n.m.r. method is continuing and will be reported in detail later.

**Acknowledgment.**—We gratefully acknowledge helpful discussions with Jerry Heesch and George Olah during the course of this work.

(17) In triphenylmethyl lithium and diphenylmethyl lithium there is a possibility of an anomalous chemical shift, particularly of the *ortho* protons, due to the ring currents in adjacent rings. If the triphenylmethyl carbanion is assumed to be a propeller-shaped molecule with an  $sp^2$   $\alpha$  carbon atom, ring dimensions of benzene, and ring hydrogens with van der Waals radii of 1.2 Å, the contribution of the inter-ring anisotropic effect to the chemical shift of the *ortho* protons amounts to only +0.03 p.p.m., based upon the point dipole ring current model. The more refined model of Waugh and Fessenden [*J. Am. Chem. Soc.*, **79**, 846 (1957); *ibid.*, **80**, 6697 (1958)] yields an equally insignificant value of -0.03 p.p.m. (unpublished results of John Wahr, Dow Chemical Company, Midland, Michigan). Inter-ring anisotropic shifts in the diphenylmethyl carbanion might be expected to be even smaller than those of the triphenylmethyl carbanion, since at any instant, only one *ortho* hydrogen per ring is affected.

(18) (a) R. Dehl, W. R. Vaughan, and R. S. Berry, *J. Org. Chem.*, **24**, 1616 (1959); (b) R. S. Berry, R. Dehl, and W. R. Vaughan, *J. Chem. Phys.*, **34**, 1460 (1961).

(19) Since reasonable resonance structures cannot be drawn with the negative charge on the *meta* ring positions, resonance theory predicts delocalization of the negative charge to the *ortho* and *para* positions only.

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### Cotton Effects in Optically Active Sulfoxides<sup>1</sup>

Sir:

In their classic paper of 1926, Harrison, Kenyon and Phillips recorded the optical rotatory dispersion of two sulfoxides in the visible region.<sup>2</sup> Since that time

(1) We gratefully acknowledge support by the National Science Foundation (GP-757).