TABLE I

CHARGE DISTRIBUTION IN PHENYL-SUBSTITUTED METHYL CARBANIONS

Carbanion		N.m.r. method[a]	S.c.f. MO[a]	LCAO MO[a]
$(C_6H_5)_3C^-Li^+$	*ortho*	0.00	−0.05	−0.08
	meta	− .08	− .06	.00
	para	− .13	− .19	− .08
$(C_6H_5)_2CH^-Li^+$	*ortho*	− .08	− .08[b]	− .10
	meta	− .07	− .06[b]	.00
	para	− .16	− .23	− .10
$C_6H_5CH_2^-Li^+$	*ortho*	− .12	− .14	− .14
	meta	− .10	− .07	.00
	para	− .18	− .23	− .14

[a] In units of the absolute value of the charge of an electron. [b] These are average values since the two *ortho* and *meta* positions in each ring are not equivalent.

Diphenylmethyllithium in THF yields a spectrum which consists of a doublet and a multiplet centered at 3.48 and 4.35 τ, respectively, with relative areas of 4:1 (Fig. 2).[14] The conclusion that we are dealing here with an A_2B_2C system in which the A and B chemical shifts are nearly identical[15] follows from an examination of the spectrum of *p,p'*-dideuteriodiphenylmethyllithium in THF which consists of a single band at 3.48 τ. Thus, the high-field multiplet in the diphenylmethyllithium 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_2B_2X 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 benzyllithium 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 τ for the *para* proton. Upon substitution of deuterium for hydrogen in the *para* position, the spectrum collapsed to a typical A_2B_2 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.*,[4] of 10 p.p.m./electron. In Table I these results are compared with similar data of Brickstock and Pople[11] calculated by a s.c.f. molecular orbital method and that of Streitwieser[16] 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*.[17] An analogous situation has been reported for the triphenylmethyl carbonium ion by Dehl, Vaughan, and Berry[18] and by Schaefer and Schneider.[10] This is contrary to the predictions of both LCAO calculations (Table I) and resonance theory.[19] 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.

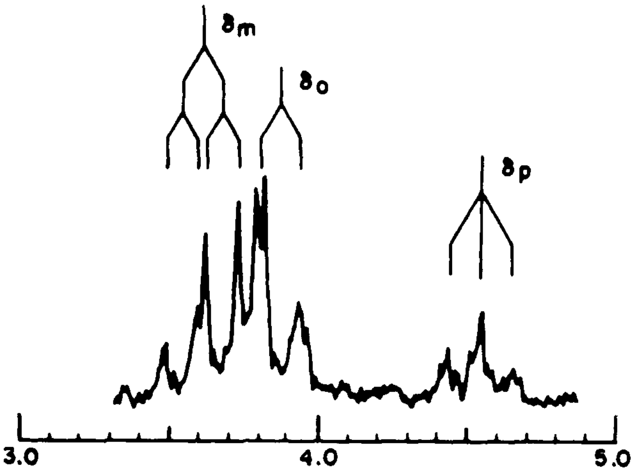

Fig. 3.—Proton n.m.r. spectrum of benzyllithium in THF.

A comparison of the spectra of the triphenylmethyl anion and cation is interesting at this point since theoretical calculations[11,16] 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,[2,3,10,18] 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 Heeschen and George Olah during the course of this work.

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(14) The α protons of diphenylmethyllithium and benzyllithium 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 α and ring protons was eliminated by the observation that the spectrum of α-deuteriodiphenylmethyllithium was identical to that of the undeuterated compound.

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

(17) In triphenylmethyllithium and diphenylmethyllithium 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 α 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[1]

Sir:

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

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

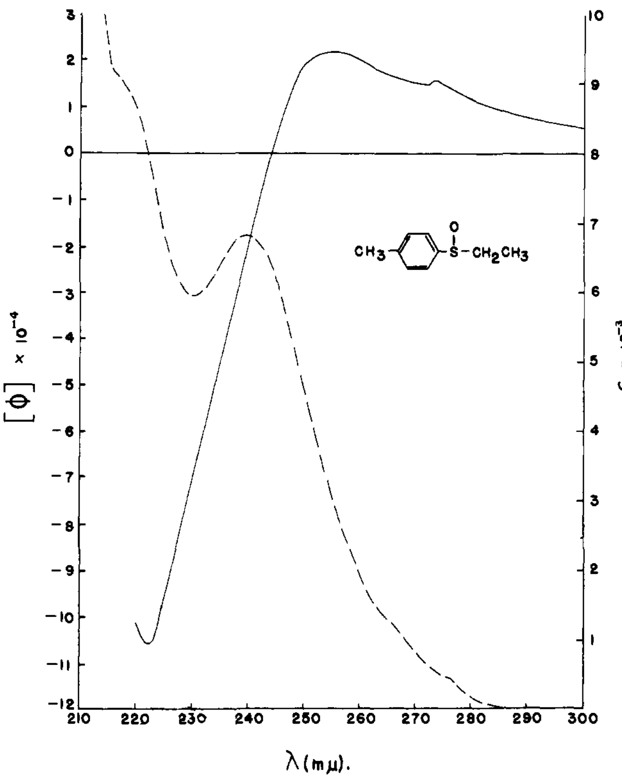

Fig. 1.—Optical rotatory dispersion (solid line) and absorption (dashed line) of (+)-ethyl *p*-tolyl sulfoxide in 95% ethanol.

numerous publications have appeared describing the o.r.d. of dialkyl, diaryl and aryl alkyl sulfoxides in the visible and ultraviolet regions[3–9]; however, all of the reported curves are plain[10] and it has not been clear which transitions are responsible for the optical activity. We now report our finding that the long wave length absorption maximum of aryl alkyl sulfoxides is associated with a high-amplitude Cotton effect and our conclusion that these sulfoxides may be regarded as inherently dissymmetric chromophores.

The sulfoxide transition in dissymmetric dialkyl sulfoxides is presumed to be only weakly perturbed by the alkyl groups and the chromophore is therefore essentially symmetric. The same is true of symmetrical diaryl sulfoxides which are unsymmetrically substituted by an alkyl group, such as phenyl *p*-tolyl sulfoxide. In both instances it is therefore safe to assume that the rotational strength of the transition is small. By contrast, the ultraviolet spectra of simple aryl alkyl sulfoxides display an intense (log $\epsilon \sim 3.5$–3.8) band in the range $\lambda_{\max}^{\text{EtOH}}$ 235–250 mμ[11,12] and while the nature of this band is still subject to debate[13] it may be taken as evidence for strong coupling between the local benzene $\pi \rightarrow \pi^*$ and sulfoxide $n \rightarrow \pi$ exitations.[11] The chromophore may thus be viewed as an extended dissymmetric array which is expected to manifest high rotational strength.[14,15] In fact, the large amplitude (Table I) of the Cotton effects of aryl alkyl sulfoxides, a typical example of which is illustrated in Fig. 1, permits classification of these substances as inherently dissymmetric chromophores.

TABLE I

SOME PROPERTIES OF OPTICALLY ACTIVE *p*-$CH_3C_6H_4SOR$

R	Solvent	Absorption $\lambda_{\max}$, mμ	Cotton effect: Amplitude,[a] $[\varphi] \times 10^{-5}$	Cotton effect: Estd. mid-point, mμ
$-CH_2CH_3$	95% EtOH	240	+1.28	237
$-CH(CH_3)_2$	95% EtOH	244	+1.27	242
$-C(CH_3)_3$	95% EtOH	250	+2.06	244
$-C(CH_3)_3$	Isoöctane	261	+1.54	254
–O–Menthyl (–)	95% EtOH	246	−0.75	244

[a] Since optical purities are unknown, these are *minimum* values.

The absolute chirality of inherently dissymmetric chromophores is expressed in the sign of the relevant Cotton effect.[14,15] The (+)-sulfoxides were prepared from (–)-menthyl *p*-toluenesulfinate by the method of Andersen[9] and this transformation is accompanied by a change in the sign of the Cotton effect. Assuming that *both* the conformations *and* the nature of the electronic transitions are comparable in the sulfinates and sulfoxides, it is possible to conclude that the configuration has been inverted, as has been suggested by Andersen.[9]

Contrasting with the above results, the low rotation of phenyl *p*-tolyl sulfoxide (in ethanol, $[\phi]_{589}$ +58° and $[\phi]_{280}$ +3230°)[16] reflects the essential symmetry of the diphenyl sulfoxide chromophore.[17] We shall reserve for the full paper a detailed account of the effects of conformation and configuration on sign and magnitude of Cotton effects in these and related optically active sulfoxides, but we wish to point at this time to a discrepancy which was uncovered in the course of our work. Previously, Andersen[9] and Montanari, *et al.*,[4,6] on the one hand and Cram and Pine[18] on the other, had independently assigned (*R*)- and (S)-configurations, respectively, to asymmetric sulfur in closely related dextrorotatory aryl alkyl sulfoxides. Our preliminary results have clearly shown that the Cotton effect is not greatly modified by minor variations in structure of the basic chromophore (such as branching in the alkyl side chain) and therefore we are forced to conclude that the two claims are mutually incompatible.

The optically active sulfoxides prepared in this study were shown to be free of menthol by g.l.c. and gave elemental analyses (C, H, S) in agreement with calculated values. The asymmetry of the sulfur is also revealed in the n.m.r. spectra of the ethyl and isopropyl *p*-tolyl sulfoxides, which exhibit complex methylene and methine multiplets at τ 7.2.[19]

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(2) P. W. B. Harrison, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 2079 (1926).

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(7) R. M. Dodson, N. Newman and H. M. Tsuchiya, *J. Org. Chem.*, **27**, 2707 (1962).

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(9) K. K. Andersen, *Tetrahedron Letters*, **No. 3**, 93 (1962).

(10) Andersen[9] has reported Cotton effects for ethyl *p*-tolyl sulfoxide and for menthyl *p*-toluenesulfinate. We observe (a) for the sulfoxide in ethanol, a shoulder at 273 mμ with $[\varphi]$ +15,600; (b) for the ester in ethanol a shoulder or shallow maximum at 276 mμ with $[\varphi]$ −14,150.

(11) G. Leandri, A. Mangini and R. Passerini, *J. Chem. Soc.*, 1386 (1957).

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(13) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 461 ff.

(14) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

(15) K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962).

(16) Prepared in this Laboratory by Mr. T. Simmons.

(17) The reasonable assumption is made that the various sulfoxides prepared by the method of Andersen[9] are of comparable optical purity.

(18) D. J. Cram and S. H. Pine, *J. Am. Chem. Soc.*, **85**, 1096 (1963).

(19) For related examples, *cf.* F. Kaplan and J. D. Roberts, *ibid.*, **83**, 4666 (1961), and references cited therein.

(20) Fellow of the Alfred P. Sloan Foundation.