

applied field  $H_z^0$ ; and  $\Delta H = H_z - H_z^0$ . The  $J_{ij}$  values are the well-known indirect spin-coupling constants. The  $D_{ij}$  values are an average of the direct dipole-dipole interaction over the motion of the molecule in its anisotropic liquid crystal environment.

$$D_{ij} = \gamma_i \gamma_j \frac{\hbar}{2\pi} r_{ij}^{-3} (1 - 3 \cos^2 \theta_{ij}) \quad (2)$$

Here  $\theta_{ij}$  is the angle between the internuclear vector and the applied field  $H_z^0$ . The internuclear distance is  $r_{ij}$ . Because benzene is planar and hexagonal, it may be shown that  $(1 - 3 \cos^2 \theta_{ij})$  is the same for all pairs of protons. Thus we anticipate that the  $D_{ij}$  will be proportional to  $r_{ij}^{-3}$ ; and  $D_{meta} = 1/(3\sqrt{3})D_{ortho}$ , with  $D_{para} = 1/8 D_{ortho}$ .

Since the indirect couplings are known to be 10 or less c.p.s.,<sup>4</sup> the main features of the spectrum are determined by the single constant,  $D_{ortho}$ , and the benzene geometry. As is illustrated in Table I, the position of

TABLE I  
COMPARISON OF COMPUTED AND EXPERIMENTAL N.M.R.  
LINE POSITIONS

Line	Expt., <sup>a</sup> c.p.s.	Computed, <sup>b</sup> c.p.s.			
		I	II	III	IV
A	21.6	20.8	23.9	10.9	20.8
B	55.0	55.6	55.2	54.2	54.5
C	188.8	189.5	189.7	191.4	189.5
D	350.8	349.5	349.0	349.0	350.2
E	431.3	431.1	435.0	432.3	429.1
F	483.6	483.7	484.9	483.6	481.6
G	1019.6	1019.1	1019.1	1019.1	1019.1
H	1091.9	1088.2	1088.5	1089.6	1089.2
I	1203.3	1203.7	1203.7	1203.7	1203.7

<sup>a</sup> The experimental line positions are the average from five spectra of the splitting of the high- and low-field lines from the center of the spectrum. <sup>b</sup> In each calculation  $D_{ortho} = -639.45$ ,  $D_{meta} = -123.06$ , and  $D_{para} = -79.93$  c.p.s. In calculation I,  $J_{ortho} = +6.0$ ,  $J_{meta} = +2.0$ , and  $J_{para} = +1.0$  c.p.s. In calculation II,  $J_{ortho} = +7.45$ ,  $J_{meta} = +2.0$ , and  $J_{para} = +1.0$  c.p.s. In calculation III,  $J_{ortho} = +6.0$ ,  $J_{meta} = -2.0$ , and  $J_{para} = +1.0$  c.p.s. In calculation IV,  $J_{ortho} = +6.0$ ,  $J_{meta} = +2.0$ , and  $J_{para} = -1.0$  c.p.s.

the outermost intense line I of Fig. 1 is dependent only on  $D_{ortho}$ . Thus by taking  $D_{ortho} = \pm 639.45$  c.p.s., all major features of the spectrum may be computer simulated. There are two important exceptions: the lines A are merged at the center of the spectrum, and line E is merged with line D. If  $J_{ortho}$  of magnitude 7 c.p.s. and of sign opposite that of  $D_{ortho}$  is introduced, then lines A and E move to their experimentally observed regions. If the same sign is employed, A splits correctly, but line E remains under line D. Thus we conclude that the sign of  $J_{ortho}$  is opposite to that of  $D_{ortho}$ . We have fit the observed spectrum by varying  $J_{ortho}$  and giving approximate values having the same sign as  $J_{ortho}$  to the smaller indirect interactions  $J_{meta}$  and  $J_{para}$ . The experimental line positions may be compared with those computed after this fitting, which is calculation I in Table I. All major lines which are not groups of closely overlapping lines have been compared. The variation of  $J_{ortho}$  in calculation II moves line E greatly and line A to a lesser degree.

The calculation III shows that a change in sign of  $J_{meta}$  moves line A almost 10 c.p.s. Calculation IV shows that the position of most lines is insensitive to the sign of  $J_{para}$ ; thus we have nothing to say on its sign now.

A computer-simulated theoretical spectrum with the constants of calculation I of Table I is displayed on the left side of Fig. 1. It is constructed as a sum of Lorentzian lines of half-width at half-height 4.5 c.p.s. It appears that the line width in the experimental spectrum increases from the center to the wings of the spectrum, a phenomenon we attribute to a distribution of liquid crystal domain or swarm<sup>1</sup> orientations with respect to the applied field. Otherwise, the computed relative line intensities are in good agreement with those observed.

We conclude that the Hamiltonian (eq. 1) is adequate to explain the position and relative intensity of the lines in our spectrum. We believe  $J_{ortho}$  and  $J_{meta}$  have a sign opposite to that of  $D_{ortho}$ . If we assume that the planes of dissolved benzene molecules tend to be parallel to those in the liquid crystal molecules and thus parallel to the applied field,<sup>1</sup> then  $D_{ortho} = -639.45$  c.p.s., and  $J_{ortho}$  and  $J_{meta}$  are positive.<sup>2</sup> We also note that the mean geometry of the protons of benzene must be on the corners of a plane hexagon; otherwise, the assumed relative sizes of  $D_{meta}$  and  $D_{para}$  would have been incorrect, and major errors in computed relative line positions would have been expected.

It may be shown that  $P(\theta, \varphi)$ , the probability density per unit solid angle of orientations of the applied field with respect to the sixfold symmetry axis of the benzene, when expanded in real spherical harmonics to  $l = 2$ , is determined by our observed value of  $D_{ortho}$ , which we assume to be negative. Having done this, we obtain eq. 3.

$$P(\theta, \varphi) = 0.10 - 0.05 \cos^2 \theta \quad (3)$$

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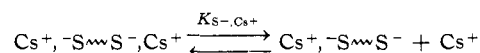
BELL TELEPHONE LABORATORIES, INC. LAWRENCE C. SNYDER  
MURRAY HILL, NEW JERSEY ERNEST W. ANDERSON

RECEIVED OCTOBER 2, 1964

## A Novel Approach to Studies of Triple-Ion Formation

Sir:

It was pointed out by Fuoss<sup>1</sup> that in solvents of a low dielectric constant, free ions may associate with ion pairs into triple ions if the concentration of ion pairs is sufficiently high. Our recent studies of living polystyrene possessing two active ends per chain and  $\text{Cs}^+$  as counterion suggested an alternative approach to the problem of triple-ion formation. Dissociation of such a polymer produces a styryl<sup>-</sup> ion ( $\sim\text{S}^-$ ) linked by a chain to a  $\sim\text{S}^-, \text{Cs}^+$  ion pair, viz.

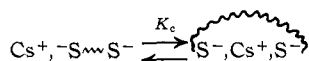


(1) R. M. Fuoss and C. A. Krauss, *J. Am. Chem. Soc.*, **55**, 21, 476, 1019, 2387 (1933).

TABLE I  
 REACTIVITIES AND CONDUCTIVITIES OF LIVING POLYSTYRENES IN THF AT 25°

	Counterion					
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup> (one-ended)	Cs <sup>+</sup> (two-ended)
10 <sup>5</sup> × K <sub>B<sup>-</sup>,M<sup>+</sup></sub> , moles/l.	7.96	8.52	3.22	...	...	0.187
Δ <sub>0</sub> <sup>+</sup>	36.6	48.2	49.8	...	...	68.4
β = k''(K <sub>S<sup>-</sup>,M<sup>+</sup></sub> ) <sup>1/2</sup> , l. <sup>1/2</sup> /mole <sup>1/2</sup> sec.	30.3	25.2	18.0	6.7	3.0	1.4
10 <sup>3</sup> × γ = 1/Δ <sub>0</sub> <sup>2</sup> (K <sub>S<sup>-</sup>,M<sup>+</sup></sub> )	2.14	1.74	3.52	...	53.0	9.0
10 <sup>7</sup> × K <sub>S<sup>-</sup>,M<sup>+</sup></sub> from β, moles/l.	2.18	1.52	0.77	0.107	0.021	0.00465
10 <sup>7</sup> × K <sub>S<sup>-</sup>,M<sup>+</sup></sub> from γ, moles/l.	1.86	(1.52)	0.71	...	0.028	0.165

Even in the most dilute solutions, such an ion has to remain in the vicinity of an ion pair, and therefore it may associate with its neighbor forming a triple ion by closing the chain, *viz.*



The equilibrium constant,  $K_c$ , of cyclization depends on the length of the chain, or the degree of polymerization,  $\overline{DP}$ , as well as on its flexibility.

The equilibrium constant  $K_c$  was determined for a  $\overline{DP} \sim 25$  in THF by the following method. The propagation of anionic polymerization of styrene in tetrahydrofuran (THF) arises from the growth of the ion pairs,  $\sim\text{S}^-, \text{M}^+$ , and of the free polystyryl ions<sup>2,3</sup> ( $\sim\text{S}^-$ ). The apparent rate constants of propagation,  $k_p$ , are linear with  $1/[\text{living polymer}]^{1/2}$ , the slopes of the lines,  $\beta$ , being  $k_s''(K_{S^-,M^+})^{1/2}$ , where  $k_s''$  is the propagation rate constant of the free  $\sim\text{S}^-$  ion, and  $K_{S^-,M^+}$  the dissociation constant of the respective ion pair. The kinetic data of  $\sim\text{S}^-, \text{Na}^+$  polymerization in the presence and absence of  $\text{Na}^+(\text{BPh}_4)^-$  led to the values  $k_s'' = 65,000$  l. mole<sup>-1</sup> sec.<sup>-1</sup> and  $K_{S^-,\text{Na}^+} = 1.52 \times 10^{-7}$  mole/l., both referring to 25°. The calculation requires knowledge of the dissociation constant of sodium tetraphenylboride in THF, and that constant, as well as those for other alkali salts, was determined in this laboratory<sup>4</sup> (see Table I for the respective  $K_{B^-,M^+}$  and  $\Delta_0^+$  calculated from Fuoss plots). Having the  $\beta$  values for other salts of living polystyrene, we could calculate the respective  $K_{S^-,M^+}$  for  $M^+ = \text{Li}^+, \text{K}^+, \text{Rb}^+, \text{and Cs}^+$ , all the data and results being given in Table I.

Studies of conductivity of living polystyrenes in THF led to Fuoss lines, their slopes,  $\gamma$ , being  $1/\Delta_0^2(K_{S^-,M^+})$ . Now,  $\Delta_0 = \Delta_0^+ + \Delta_0^-$ , and the  $\Delta_0^-$  for polystyryl ion was found from the value of  $K_{S^-,\text{Na}^+}$  to be 13.5. Thus, the respective  $K_{S^-,M^+}$  were calculated again from the  $\gamma$ -values (see Table I). The agreement between both sets of data is most satisfactory, the two-ended  $\text{Cs}^+, \sim\text{S}^-, \text{Cs}^+$  being the striking exception. The conductivity gives a " $K_{S^-,\text{Cs}^+}$ " much larger than that determined for the one-ended  $\sim\text{S}^-, \text{Cs}^+$ , whereas the value derived from the reactivity study is much too small.

Accepting the idea of cyclization, we derived the following equations for the two-ended  $\sim\text{S}^-, \text{Cs}^+$ . The slope of its  $k_p$  vs.  $1/[\text{living ends}]^{1/2}$  relation is

$$\beta' = k_s''[1 + (k^*/k_s'')K_c] \{(K_{S^-,\text{Cs}^+})/(1 + K_c)\}^{1/2}$$

where  $k^*$  is the rate constant of growth of the triple

$\text{S}^-, \text{Cs}^+, \text{S}^-$  ion. The slope of  $\Lambda^{-1}$  vs.  $\Delta_c$  relation is

$$\gamma' = 1/(K_{S^-,\text{Cs}^+}(1 + K_c)[\Delta_{0,\text{Cs}^+} + \Lambda_{0,\text{t}}[K_c/(1 + K_c)] + \Delta_0^-(1 + K_c)]$$

where  $\Lambda_{0,\text{t}} < \Delta_0^-$  is the limiting conductivity of the triple ions. The total  $\Lambda_{0,\text{total}}$  is assumed to be 10, and thus

$$1 + K_c = (\gamma/\gamma')(\Delta_{0,\text{one-ended}}/\Delta_{0,\text{two-ended}})^2 = 6.5$$

where  $\gamma$  refers to one-ended  $\sim\text{S}^-, \text{Cs}^+$ . Any reasonable change in the assumed value of  $\Lambda_{0,\text{total}}$  has a negligible effect on the final value of  $1 + K_c$ . On the other hand,  $1 + K_c = (\beta/\beta')^2[1 + (k^*/k_s'')K_c]^2$ , where  $\beta$  refers again to the one-ended  $\sim\text{S}^-, \text{Cs}^+$ . Hence, one finds  $k^* = 2000$  l./mole<sup>-1</sup> sec.<sup>-1</sup>. Thus, the triple ion is 30 times less reactive than the free  $\sim\text{S}^-$  ion and about 100 times more reactive than the  $\sim\text{S}^-, \text{Cs}^+$  ion pair ( $k_{S^-,\text{Cs}^+} = 22$  l./mole<sup>-1</sup> sec.<sup>-1</sup>)—a most reasonable result. At 25° no triple-ion formation was noticed in a two-ended  $\text{Na}^+$  and  $\text{K}^+$  living polystyrene ( $\overline{DP} \sim 25$ ). Apparently the strong solvation of these ions in THF prevents the association. Moreover, the triple-ion formation is favored by a high  $\sim\text{S}^-, \text{Cs}^+$  dipole, and hence the outstanding position of polymers possessing  $\text{Cs}^+$  counterions. Increase of the polymer length decreases  $K_c$  and this is seen in Fig. 1, which is self-explanatory.

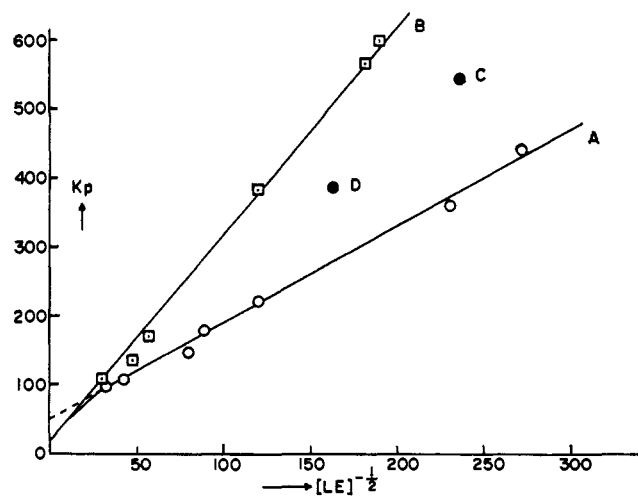


Figure 1.

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