TABLE I

Copolymer	Monomer ratio in the copolymer	λ_{max} (ϵ per unit of monomer as given in the monomer ratio)	Solvent
TNS-4-VP	1:2	460, 530 (6400, 4200)	Acetone
		464, 520 (6400, 4200)	DMF
TNS-4-VP	1:1	460, 516 (5350, 3500)	Acetone
		464, 520 (5350, 3500)	DMF
TNS-2-VP	1:1	452, 493, 583 (10,400, 4850, 4800) 460, 505,	Acetone
		585 (10,400, 5850, 5000)	DMF
TNS-DMAS	2:1	445 (4400)	Acetone

hydrocarbons. We have also successfully prepared copolymers of TNS with 2-vinylpyridine (2-VP, III) and with p-dimethylaminostyrene (DMAS, IV).

The charge-transfer interactions in these copolymers of TNS were subsequently investigated. Charge-transfer complexes from trinitrotoluene (TNT) and amines were selected as model systems to compare with these copolymers. The copolymers displayed two unusual and interesting properties when compared with the model complexes: (1) these copolymers exhibit strong and broad charge-transfer transitions near 450 mμ which obey Beers Law, and (2) the extinction coefficients of the charge-transfer transitions are anomalously high. The complexes of TNT and amines dissociate rapidly upon dilution and their equilibrium constants for complex formation are low, e.g., TNT and 4-picoline form a 1:2 complex in solution [$\lambda_{max}^{CH_2Cl_2}$ 474 mμ (ϵ 800), $K = 0.13$ l.^{2} mole^{-2}], TNT and N,N-dimethyl-p-toluidine form a 1:1 complex in solution [$\lambda_{max}^{CH_2Cl_2}$ 460 mμ (ϵ 700), $K = 0.60$ l. mole^{-1}], and TNT forms a red solution in 2-picoline but the K for complex formation is too small to be determined by the variable concentration method. The charge-transfer interactions in our copolymers were not perturbed by the solvent environment and exhibited no visible dissociation over a concentration range of 5×10^{-4} to 1×10^{-6} M in acetone or dimethylformamide. This phenomenon may be rationalized by the explanation that the donating and accepting groups in our copolymers were held together by the polymer network and thus were unaffected by the solvent. In relation to the second property, the extinction coefficients of these copolymers per an appropriate unit of TNS and donor monomer were found to be of the order of 5,000-10,000, and several such examples are listed in Table I. Intensification of the charge-transfer transitions in the copolymers may be due to the coupling of adjacent donor–acceptor oscillators or to the delocalization of an excited donor–acceptor couple to the adjacent donor–acceptor couples (eq. 1). These observations suggest that we may have achieved the stacking of alternating donor (D) and acceptor (A) groups along the polymer chain.

$$-[D-A-D-A-D-A]- \xrightarrow{h\nu} -[D^+A^- -D-A-D-A]-$$
$$\longleftrightarrow -[D-A-D^+A^- -D-A]-; \text{ etc. } (1)$$

Reactions of other types of vinyl monomers as well as the conductivity and the photoconductivity of these copolymers are being investigated.

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Analysis of the Proton Nuclear Magnetic Resonance Spectrum of Benzene in a Nematic Liquid Crystal

Sir:

An n.m.r. spectrum of benzene in a liquid crystal nematic phase[1] was recently published.[2] The major features of that spectrum were attributed to direct magnetic dipole–dipole interactions of protons.[2] We have reproduced that spectrum and wish to present an analysis based on computer simulations. Our proton n.m.r. spectrum of ~ 15 mole % benzene in the nematic phase of p,p'-di-n-hexyloxyazoxybenzene was obtained at 79° on a Varian DP-60 n.m.r. spectrometer. It is displayed on the right side of Fig. 1. The spectrum is symmetrical.

Fig. 1.—Proton n.m.r. spectrum of benzene in nematic p,p'-di-n-hexyloxyazoxybenzene: computer simulation on left, experimental on right.

Our program to simulate n.m.r. spectra[3] was easily modified to incorporate the constants D_{ij}, which represent the direct nuclear magnetic dipole–dipole interaction of nuclei i and j, into the spin Hamiltonian[4] of eq. 1. Here ν_0 is the spectrometer frequency, and

$$\mathcal{H}_s = \sum_{i=1}^{6} \nu_0 I_z(i)\left(1 + \frac{\Delta H_z}{H_z^0}\right) +$$
$$\sum_{i>j}(J_{ij} + D_{ij})I_z(i)I_z(j) + \sum_{i>j}(1/2 J_{ij} - 1/4 D_{ij}) \cdot$$
$$(I_+(i)I_-(j) + I_-(i)I_+(j)) \quad (1)$$

the resonant frequency of an uncoupled proton in the

(1) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962. This is a comprehensive review on the occurrence and properties of liquid crystals.

(2) A. Saupe and G. Englert, Z. Naturforsch., 19a, 172 (1964). These authors concluded in a footnote that J_{ortho} and J_{meta} are positive; see also A. Saupe, ibid., 19a, 161 (1964).

(3) P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kronegay, J. Am. Chem. Soc., 85, 3630 (1963).

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

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.

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

Here θ_{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 $\overline{(1 - 3 \cos^2 \theta_{ij})}$ 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.,[4] 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.,[a] c.p.s.	Computed,[b] 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

[a] 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. [b] 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 $D_{ortho} = \pm639.45$ 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[1] 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,[1] then $D_{ortho} = -639.45$ c.p.s., and J_{ortho} and J_{meta} are positive.[2] 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.

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

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A Novel Approach to Studies of Triple-Ion Formation

Sir:

It was pointed out by Fuoss[1] 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 Cs^+ as counterion suggested an alternative approach to the problem of triple-ion formation. Dissociation of such a polymer produces a styryl⁻ ion ($\sim S^-$) linked by a chain to a $\sim S^-, Cs^+$ ion pair, viz.

$$Cs^+, {}^-S\sim S^-, Cs^+ \xrightleftharpoons{K_{S-,Cs+}} Cs^+, {}^-S\sim S^- + Cs^+$$
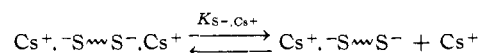
(1) R. M. Fuoss and C. A. Krauss, *J. Am. Chem. Soc.*, **55**, 21, 476, 1019, 2387 (1933).