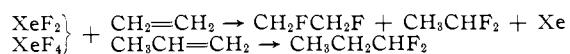Purified reactants were condensed at $-195°$ into a 130-ml. nickel vessel. The vessel was allowed to warm to room temperature and the course of the reaction was followed by observing the change in pressure. It was assumed that the reaction had reached completion when no further pressure change was noted. The reaction products were separated at the vacuum line by trapping at different temperature and by gas chromatography. They were identified by their infrared, n.m.r., and/or mass spectra.

In a typical experiment a mixture of XeF_4 (0.75 mmole) and perfluoropropene (1.28 mmoles) was allowed to react in a nickel vessel at room temperature. The products were removed from unreacted XeF_4 *in vacuo* at $-78°$ and trapped at $-195°$. They were shown to be perfluoropropane and xenon in stoichiometric amounts. Perfluoropropane was identified by comparison with an authentic sample. We observed that XeF_6 is considerably more reactive than XeF_4 while XeF_2 is less reactive. Under similar conditions, XeF_6 reacts with perfluoropropane to give both C_2F_6 and CF_4 as the major products, indicating extensive cleavage, while XeF_2 is unreactive even after six days.

$$XeF_4 + 2CF_3CF=CF_2 \rightarrow 2CF_3CF_2CF_3 + Xe$$
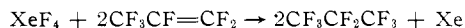
An interesting rearrangement occurs when xenon fluorides react with aliphatic olefins. At room temperature, ethylene reacts with XeF_2 or XeF_4 to give 1,1- and 1,2-difluoroethane in 35 and 45% yields, respectively, together with a minor component which is not yet identified. However the reaction of propylene with XeF_2 or XeF_4 gives 1,1-difluoropropane as the main product (*ca.* 65% yield). Allylic fluorination may have occurred also to a certain extent as hydrogen fluoride was detected in the reaction mixture.

$$\begin{matrix} XeF_2 \\ XeF_4 \end{matrix} \Big\} + \begin{matrix} CH_2=CH_2 \rightarrow CH_2FCH_2F + CH_3CHF_2 + Xe \\ CH_3CH=CH_2 \rightarrow CH_3CH_2CHF_2 \end{matrix}$$

The relative instability of secondary fluorides[6] and the increasing stability of compounds with fluorine atoms attached on the same carbon[7] suggest a possible pathway for formation of the *gem*-difluorides; the *vic*-difluorides, presumably the initial products of the reactions, isomerize under the reaction conditions to give the *gem*-difluorides. We detected a slow isomerization of 1,2-difluoroethane to 1,1-difluoroethane in CCl_4 solution upon standing at room temperature, which is in agreement with the suggested pathway.

The reactions studied so far indicate the potential of the xenon fluorides as fluorinating agents in organic chemistry. The mechanism of the reactions and further studies extending the work to acetylenic and aromatic systems are in progress.

(6) For example, see A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 12.

(7) J. Hine, *J. Am. Chem. Soc.*, **85**, 3239 (1963).

(8) Alfred P. Sloan Foundation Fellow, 1960–1964.

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Charge-Transfer Interaction in Organic Polymers[1]

Sir:

The charge-transfer interaction between electron donors and acceptors has been a subject of both theoretical and experimental interest.[2] Certain types of charge-transfer complexes of simple organic compounds exhibit semiconducting properties,[3] and charge-transfer interaction has been suggested as an intermediate stage in biological reactions.[4] The present communication deals with the intramolecular interaction of electron-donating and electron-accepting groups in organic polymers.

One major difficulty in the preparation of organic polymers containing both electron-donating and electron-accepting functional groups is that organic monomers containing strong electron-accepting groups, *e.g.*, trinitrostyrene (TNS, I), are excellent inhibitors to both ionic and free-radical polymerizations.[5] Apparently, the reactive intermediates in the polymerizations, ions or radicals, are rendered inactive by interaction with the electron-accepting groups. Several attempts made to prepare polymers and copolymers of TNS have been unsuccessful.[5]

Although TNS could not be polymerized in previous attempts, it might be copolymerized with monomers containing electron-donating groups. The electron-donating group may interact with the strong electron-accepting trinitrophenyl function, thus freeing the vinyl group for polymerization. The copolymerization of TNS with nitrogen-containing vinyl monomers was thus attempted with the nonbonding electrons of the nitrogen atom acting as the electron donor. The copolymerization of TNS and 4-vinylpyridine (4-VP, II) occurred exothermically upon mixing at room temperature. After the mixture was dissolved in pyridine and treated with ether, copolymers of molecular weight ranging from 6000 to 8000 were obtained in about 60% yield. The presence or absence of oxygen made no difference. Apparently sufficient delocalization occurred during the charge-transfer process to initiate the polymerization.[7] The relative proportion of the two monomers in the copolymers could be varied by adjusting the mole ratio of the two monomers in the polymerization mixture, *e.g.*, a 1:1 mixture of the monomers reacted to give a 1:2 (TNS–4-VP) copolymer while a 2:1 (TNS–4-VP) mixture gave a 1:1 copolymer. The copolymers formed were somewhat soluble in chloroform, acetone, or dimethylformamide but were insoluble in ether or aliphatic

(1) The work is supported in part by the U. S. Atomic Energy Commission, Contract No. AT(11-1)-1043, and by the Alfred P. Sloan Foundation.

(2) For a review on the interaction of electron donors and acceptors, see R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962). For applications of charge-transfer complexes, see L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, pp. 122–125.

(3) D. S. Acker, *et al.*, *J. Am. Chem. Soc.*, **82**, 6508 (1960), and later papers; M. M. Labes, R. Sehr, and M. Bose, *J. Chem. Phys.*, **33**, 868 (1960).

(4) For discussions on the charge-transfer interactions in biological systems, see A. Szent-Gyorgyi, "Introduction to a Submolecular Biology," Academic Press Inc., New York, 1960, p. 76; E. Kosower, "Molecular Biochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 180.

(5) R. H. Wiley and L. C. Behr, *J. Am. Chem. Soc.*, **72**, 1822 (1950).

(6) The molecular weights were determined with a Mechrolab vapor phase osmometer.

(7) Polymerizations initiated by charge-transfer interactions have been reported by H. Scott, G. A. Miller, and M. M. Labes, *Tetrahedron Letters*, 1073 (1963).

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).

CH=CH$_2$ CH=CH$_2$ CH=CH$_2$ CH=CH$_2$

O$_2$N ⟋⟍ NO$_2$

NO$_2$ N   N   N(CH$_3$)$_2$

I   II   III   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

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

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.