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An Electron Paramagnetic Resonance Study of Electron Exchange Effects in Reduced Aromatic Hydrocarbon Polymers

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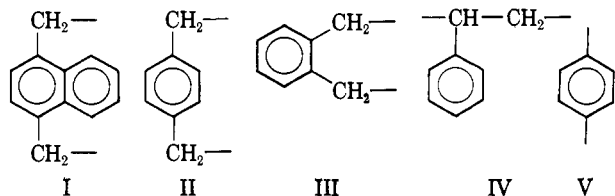
The effects of metal reduction of several aromatic hydrocarbon polymers has been investigated by means of e.p.r. Two such polymers containing high electron-affinity aromatic centers were found to become solvated in dimethoxyethane with concurrent production of high color and a strong, narrow e.p.r. resonance signal. Some implications of conjugation and intramolecular electron exchange are discussed. Also, electron storage and electron exchange resin possibilities were explored.

The technique of metal reduction of hydrocarbon molecules has recently found wide application in electron paramagnetic resonance (e.p.r.) studies.¹ Free electron conjugation between aromatic moieties separated by heteroatomic or alkyl substituents such as diaryl ethers, diarylalkanes, and paracyclophanes has been investigated by several workers.²

Since several aromatic hydrocarbon polymers possess a high number of centers which in smaller molecules have a relatively high electron affinity, the possibility of metal reduction of a significant number of these centers in each polymer molecule was considered. Should a large number of aromatic rings become reduced, high molecular weight and normally insoluble polymers might be brought into solution as poly-electrolyte anion radicals.

The concept of electron exchange resins in which each aromatic center of polyhydroquinone derivatives might participate in the storage of electrons has been approached by Cassidy.³ These polymers were chemically oxidized, possibly to a nonradical quinhydrone,^{3b} and were found to be insoluble in the oxidized form in the usual organic solvents. Recent studies of several vinyl-type polyaromatic molecules⁴ (see type IV below), have shown that metal reduction of these polymers in ethereal solvents is indeed possible.

In order to determine the structures necessary for a large scale retention of electrons from alkali metals within the polymer chain, reduction of the aromatic polymers polybenzo-*p*-xylylene (I), poly-*p*-xylylene (II), poly-*o*-xylylene (III), polystyrene (IV), and polyphenyl (V) was attempted over potassium in dimethoxyethane at -70° and the decomposition products were studied in the e.p.r. spectrometer at temperatures ranging from -70° to $+25^{\circ}$.



(1) (a) S. I. Weissman, J. Townsend, D. E. Paul, and G. E. Pake, *J. Chem. Phys.*, **21**, 2227 (1953); (b) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956); (c) T. Tuttle and S. I. Weissman, *ibid.*, **80**, 5342 (1958).

(2) (a) H. S. Jarrett, C. J. Sloan, and W. R. Vaughn, *J. Chem. Phys.*, **25**, 697 (1956); (b) D. C. Reitz and S. I. Weissman, *ibid.*, **27**, 158 (1955); (c) D. H. Eargle, Jr., and S. I. Weissman, *ibid.*, **34**, 1840 (1961); (d) S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 6462 (1958).

(3) (a) H. G. Cassidy, *ibid.*, **71**, 402 (1949); (b) M. Ezrin, I. H. Updegraff, and H. G. Cassidy, *ibid.*, **75**, 1610 (1953); (c) M. Ezrin and H. G. Cassidy, *Ann. N. Y. Acad. Sci.*, **57**, 67 (1953).

(4) A. Rembaum and J. Moacanin, *J. Polymer Sci.*, **B1**, 41 (1963); A. Rembaum, *ibid.*, **B2**, 117 (1964).

The relatively low electron affinity of molecules containing isolated monocyclic aromatic hydrocarbon rings such as benzene, toluene, and benzenoid paracyclophanes is well known.^{2a,5} The anion radicals of these molecules are stable only at lowered temperatures, whereas polycyclic aromatic molecules such as naphthalene and biphenyl possess a much greater electron affinity, even at room temperature.^{5a} Polymers I and V possess structures related to the latter, while II, III, and IV are of the more simple benzenoid structures. Studies have shown some conjugative properties of the electron through alkyl "insulating barriers" such as the $-\text{CH}_2-\text{CH}_2-$ group.^{2a} The group of polymers I-V was chosen in order to test the possibility of odd electron retention by conjugative stabilization through the ethylene linkage. The results of the attempted reductions are to be seen in Table I.

TABLE I

Polymer	Soln. color (25°)	Line width initial, gauss	Line width 1 week, gauss
I	Blue-violet	0.58 ^a	32.5
II	Pale blue	0	0
III	Pale blue	0	0
IV	Very pale blue	0.25 ^b	0
V	Violet → black	0.58 ^a	0.1
K, DME	Pale blue	0	0
VI	Green → violet	23.6	35

^a Measured at -40° , much broader (~ 1.75 gauss) at 25° .
^b Measured at -70° at ca. $1/50$ the intensity of V; no signal at 25° .

Of the polymers listed only one, polystyrene, is soluble to any extent in dimethoxyethane. After the initial reduction attempt, two of the polymers, I and V, produced highly colored solutions which resulted in strong e.p.r. lines. The solid polymeric material not in solution accumulated at the bottom of the spectrometer tube (A, Fig. 1) and was not in the resonance cavity. Polymers I and V produced a single, very intense, almost symmetrical, and narrow e.p.r. line; polymers II and III gave only pale blue solutions with no detectable e.p.r. signal; IV produced an extremely weak (about $1/50$ as intense as V) signal at -70° which disappeared at room temperature.

There are several implications of these findings:

(1) The pale blue color observed in samples II, III, and possibly IV was in all probability due to the well-known blue color of solvated potassium in ethereal solvents (Table I).⁶ On the other hand, the polymers which gave a very strong e.p.r. signal produced considerably more highly colored solutions. These high

(5) (a) G. J. Hoijtink, *et al.*, *Rec. trav. chim.*, **75**, 487 (1956); (b) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961).

(6) F. Cafasso and B. R. Sundheim, *J. Chem. Phys.*, **81**, 809 (1959).

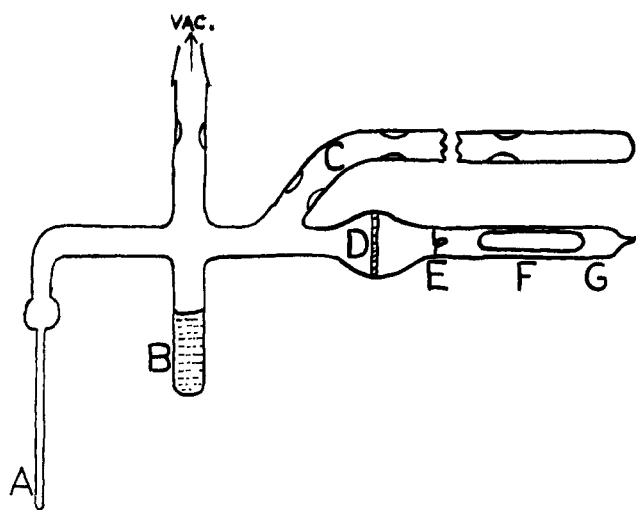


Fig. 1.—A, spectrometer tube; B, sample and solvent; C, potassium mirror; D, sintered glass filter; E, break-seal; F, hammer; G, biphenyl sample.

molecular weight polymers, unreduced, are insoluble in most organic solvents, and are quite insoluble in the dimethoxyethane solvent used in these experiments. Therefore, it is indicated by the colors and e.p.r. signals of the solutions that solvation by reduction of the polymer molecules themselves has occurred and thus may be considered evidence of the formation of a radical-anionic polyelectrolyte.

(2) A polycyclic structure within each unit is necessary for formation of the polyelectrolyte. A chain consisting of single benzene rings separated by $-\text{CH}_2-\text{CH}_2-$ does not possess sufficient electron affinity to stabilize electrons within the chain. Stabilization through $>\text{CH}-\text{CH}_2-$ is very slight, if it occurs at all.

(3) There is apparently very rapid electron exchange among all possible proton positions within the reduced polymers. The development of a single narrow line indicates that fairly localized intramolecular electron exchange *via* a conjugative mechanism is not occurring to a large extent between adjacent aromatic moieties, in which case a great deal of electron spin pairing and, hence, no e.p.r. signal would likely result. On the other hand, there is probably rapid "external" exchange of the electron from one relatively remote π -system to another in the polymer chain or to an adjacent polymer molecule. Fairly slow ("retention time" *ca.* 10^{-7} sec.) electron exchange should have resulted in a considerably wider spectrum and in the possible development of some hyperfine structure.

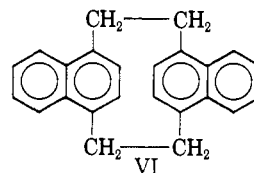
(4) A polyradical of this nature might easily serve as a method of "storing" electrons.

Approximately 1 week after the initial generation of the anion radicals, the spectra of the cold-stored (*ca.* $+5^\circ$) samples were restudied. The violet polyphenyl solution (V) had turned black but still retained a small amount of radical activity.

In the initial reduction of I and V, not all the polymeric material (*ca.* 5 mg. in *ca.* 2 cc. of DME) had gone into solution by any means; however, the remaining particles which were not soluble in the limited amount of solvent adopted the color of the solution above them. Such was also the case after the 1-week storage. Upon breaking open the sample tube of the polyphenyl and exposing the solution and particles to the air, the

black color disappeared after several seconds and left a tan-colored residue (no radical activity).

The behavior of I after 1 week was notably different from the other four polymers. This polymer apparently decomposed into simpler segments which possessed a markedly changed spectrum of high radical activity. This spectrum was some 33 gauss wide and consisted of 21 groups of several hyperfine lines each. It is of interest that reduction of the cyclic dimer of polymer I and [2.2]paracyclonaphthane (VI)⁷



results in precisely the same decomposition product (as determined by the e.p.r. spectra) after standing for about 1 week. This common decomposition product has not been further identified.

The possibility that the reduced polymer I might serve as a source of stored electrons was investigated. Upon removal of the potassium metal source (see Fig. 1), unreduced biphenyl was introduced into the sample tube from behind a breakseal.

The polymer promptly delivered up its supply of electrons to the biphenyl—evidenced by the intense blue-green color and the strong characteristic spectrum of biphenyl negative ion. A "blank" of poly-*o*-xylylene (III) similarly conducted failed to produce any biphenyl negative ion. Thus it is believed that a polyanion-radical solution may act as a "gentle" electron donor possibly somewhat less severe to sensitive compounds than an alkali metal surface would be. Results indicate that the polymer I in solution is retained upon a coarse sintered glass filter (D, Fig. 1). Utilizing larger amounts of reduced polymer, it is clearly possible that the material might be retained upon such a filter and function much as an electron exchange resin (see ref. 3) for use in flow systems.

It is anticipated that reduction of several polymers of similar structure will be reported upon in the future and that determinations of the extent and limitations of exchange between aromatic moieties may be made.

Experimental⁸

Polymers.—Polybenzo-*p*-xylylene (I) was obtained by a procedure quite similar to that for the preparation of [2.2]paracyclonaphthane and poly-*p*-xylylene by Winberg, *et al.*,⁹ and for the preparation of [2.2]paracyclonaphthane by Cram, *et al.*⁷ Ten grams of 1-chloromethyl-4-methylnaphthalene (Aldrich Chemical Co.) dissolved in 160 ml. of dry ether was treated for 1 hr. with trimethylamine by bubbling the gas into the solution. The yield (unrecrystallized, but dried under vacuum) of the precipitated white chloride salt was 11.93 g., m.p. 233–234° dec. A solution of 5.00 g. of the quaternary ammonium salt in 50 ml. of water was stirred for 1 hr. with 4.64 g. of silver oxide. The resulting mixture was filtered under nitrogen and the filtrate was placed in a flask containing 250 ml. of toluene. The water was distilled off (as an azeotrope) with stirring. The resulting mixture was

(7) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963).

(8) Polymer I and dimer VI were prepared by the author in the laboratories of Prof. S. I. Weissman, Department of Chemistry, Washington University, St. Louis, Mo.

(9) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960).

refluxed about 10 min. and cooled. The white solid material remaining was extracted for several hours with toluene in a Soxhlet extractor and then was washed with acetone, chloroform, and finally toluene again. The solvents from the washings were evaporated and the residue saved for recovery of the paracyclonaphthene VI (see below). The polymeric material remaining was slightly grayish white and did not soften or melt at 310°.

Poly-*p*-xylylene (II) was prepared by treatment of α -bromoxylene in a manner analogous to that of the preparation of I, with the exception that the quaternary amine was treated directly by hot concentrated sodium hydroxide overnight.¹⁰ The polymer was obtained after cooling the hot solution and diluting it with water, followed by filtration of the solid. The crude polymer was triturated many times with hot toluene and acetone and was dried to a white lumpy powder. No attempt was made to recover any paracyclonaphthene.

Poly-*o*-xylylene (III) was obtained as a generous gift of Dr. L. A. Errede, Central Research Laboratories, 3M Co., St. Paul, Minn.

Polystyrene (IV) was whittled from a large mass of polystyrene. Freshly distilled styrene was allowed to polymerize slowly for several years to form this mass.

Polyphenyl (V) was provided in liberal quantity by Dr. Peter Kovacic, Case Institute of Technology, Cleveland, Ohio.

[2.2] **Paracyclonaphthene (VI)**.—The extraction residue from the preparation of polybenzo-*p*-xylylene (see above) was recrystallized from a mixture of nitrobenzene-acetic acid solvent thinned with a little benzene and water; this crude material melted at 292–297°. The crude crystals were sublimed under vacuum (210° (0.05 mm.)) and 0.14 g. (45%) of white needles was obtained, m.p. 292–297°. The needles were sublimed thrice more, m.p. 291–293° (Cram, m.p. 299–301°). *Anal.* Calcd. for C₂₄H₂₀: C, 93.46; H, 6.54. Found: C, 93.17; H, 6.77.

Sample Preparation.—All polymer reductions were carried out under as nearly identical conditions as possible. The initial polymer suspensions were allowed to stand over the potassium mirrors at –70° for about 0.5 hr. before a full e.p.r. signal was obtained. This is somewhat longer than the time required for the simpler aromatic hydrocarbons; however, the difficulty of

(10) This procedure was suggested by Dr. L. A. Errede in a private communication.

reduction was no doubt due to the polymer chain size and insolubility. Sample sizes were about 5–10 mg. in about 2 ml. of solvent.

A sample of polyphenyl in DME (no potassium) was examined for an e.p.r. signal, since its method of preparation¹¹ might have involved the inclusion of magnetic impurities. No paramagnetism was observed in the sample.

In the investigation of the electron "storage" of polymer I, the solvent containing the polymer solution was frozen with liquid nitrogen and the tube containing the potassium mirror (C, Fig. 1) was subsequently removed so as not to provide a continuing reducing source. The colored polymeric solution was melted, but the entire sample tube was kept bathed in a cold viscous isopropyl alcohol-Dry Ice mixture, whereupon the biphenyl compartment was broken open to the solution and the solution was filtered into this section (G) of the tube. The polymer and all of the colored material were retained upon the filter and a clear solution was brought into section G, indicating that no potential electron-donor material had been introduced. The colorless DME-biphenyl solution was then filtered back through the sintered glass, at which time the solution assumed the characteristic dark blue-green of biphenyl negative ion and produced the strong biphenyl negative ion e.p.r. spectrum. Since the system had been thoroughly degassed and flamed out prior to introduction of the samples, it is unlikely that the decolorization of the solution resulted from reaction of the radical with a radical-scavenging material adsorbed upon the filter. To be sure, the polymeric material upon the filter retained its characteristic dark color and subsequently discharged its supply of electrons to the biphenyl solution when the latter was brought into the tube section D.

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(11) P. Kovacic and F. W. Koch, *J. Org. Chem.*, **28**, 1864 (1963).

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Nitrogen-14 Nuclear Magnetic Resonance in Nitro Compounds

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Nonaromatic nitro groups were shown to give rather narrow N¹⁴ n.m.r. peaks. Their chemical shifts are characterized by a very regular dependence on the electronegativity of the rest of the molecule. Spectral identification of nitramines and primary, secondary, and tertiary nitroalkanes is possible. Nitromethane is suggested as an internal standard for calibration of N¹⁴ n.m.r. spectra.

N¹⁴ magnetic resonance spectra are characterized by very low sensitivity and broadness of the signals. This is probably the main reason why relatively little work has so far been done^{1,2} in this field in spite of the fact that the first nuclear magnetic resonance spectrum to be observed was the N¹⁴ spectrum of ammonium nitrate.³ Applicability of N¹⁴ spectra to chemical structure determination was even questioned.²

Results of our investigation of the N¹⁴ n.m.r. spectra of aliphatic nitro compounds seem to be promising as far as identification and localization of nitro groups in saturated systems are concerned. The resonance peaks

of aliphatic NO₂ groups are narrow and show regular changes of chemical shifts with structural changes in the remaining part of the molecule.

The N¹⁴ n.m.r. shifts (at 4.3 Mc.) of fifteen aliphatic nitro compounds and also of nitrobenzene are presented in Table I. Sample spectra are shown in Fig. 1.

The observed range of the chemical shifts is 344 c.p.s. (78 p.p.m.) and the average half-width of the peaks is about 40 c.p.s. so that the N¹⁴ signals of different types of nitro groups may be easily resolved.

Thus far saturated aqueous ammonium nitrate solution has been used as an external reference for calibrating N¹⁴ n.m.r. spectra.^{1,2} It has serious drawbacks as a standard for accurate work with narrow signals because of relatively low concentration per volume of nitrogen nuclei and disturbances in the n.m.r. probe characteristic of every external standard, resulting in decreased effective sensitivity, increased base line drift, and inaccuracy of measured shifts. We suggest nitromethane

(1) 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, pp. 313–315; see also B. M. Schmidt, L. C. Brown, and D. Williams, *J. Mol. Spectry.*, **2**, 539 (1958); *ibid.*, **3**, 30 (1959); B. Holder and M. P. Klein, *J. Chem. Phys.*, **23**, 1956 (1955).

(2) P. C. Lauterbur, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, Inc., New York, N. Y., 1962, pp. 506–509.

(3) W. G. Proctor and F. C. Yu, *Phys. Rev.*, **81**, 20 (1951).