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Poly(*p*-phenyleneamineimine): Synthesis and Comparison to Polyaniline

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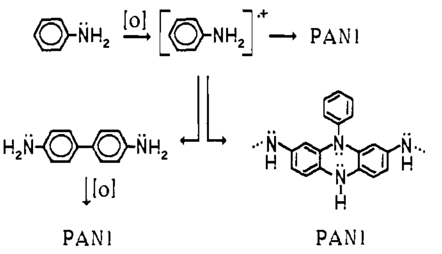
Abstract: We present a complete account of results on the preparation of a polymer which could only be a poly(*p*-phenyleneamineimine) (PPAI) and which, by several criteria, has the same properties of polyaniline (PANI). We also present detailed results of comparative studies of not only PANI with PPAI but of PANI with phenyl-capped octaaniline (COA), a discrete length, fully characterized molecule. Finally, we present support for the hypothesis that acid doping of PANI involves the proton induced spin unpairing mechanism for protonated quinoneimine moieties. We conclude that magnetic and transport data are qualitatively consistent with that of a Fermi "glass" model and not with that of a metal.

I. Introduction

In 1826, two years before the official birth of organic chemistry, aniline was obtained for the first time from the pyrolytic distillation of indigo and was called "Krystallin" because it produced well-formed crystalline salts with sulfuric and phosphoric acid.[1] In 1840, Fritzsche also obtained a colorless oil from indigo, called it aniline ostensibly from the spanish añil (indigo), and oxidized it to polyaniline (PANI); the oldest electroactive synthetic polymer.[2] In its neutral form, the latter is blue, but upon protonation it turns green; hence, the name emeraldine for the hydrochloride salt and emeraldine base for its blue precursor. Between the first half of the nineteenth century and ca. 1907, frequent discussions about the structure of PANI appeared in the literature. Between 1907 and 1910, an English[3] and a German[4] group concluded, on the basis of extensive investigations, that polyaniline was an octamer whose color depended on the number of quinoneimine (Q) moieties in the backbone. Thus, "leucoemeraldine" had no Q, "protoemeraldine" had one Q, "emeraldine" had two Q's, "nigraniline" had three Q's, and "pernigraniline" had four Q's. Various inorganic and organic redox reagents were employed to correlate the above names with the various oxidation states. Within the last few years, MacDiarmid[5a] has reinvestigated previous work of Josefowicz[6] and has found potential application of this polymer to lightweight, high energy density batteries.[5c] Their initial interpretations on "protonic acid doping" stated that the fully reduced form, when protonated, was practically an insulator; whereas the fully oxidized form (maximum number of Q in the backbone), when protonated, was a good conductor.[5a] In the more recent publications from the same group, the authors concluded that the highest conductivity form of polyaniline is the protonated form of a material that, on the average, has a 3:1 ratio of benzenoid (B) and Q moieties linking the nitrogen atoms of the backbone,[5b] i.e., a mixed valent system, a conclusion consonant with other workers' results.[7]

We became intrigued by the fact that these authors and, to some extent, others[7] had taken for granted that the structure of polyaniline was a linear, strictly para linked, set of phenyleneamineimines. While the early evidence[3,4] was in favor of that structure, it was by no means an absolute proof. Other attempts to unambiguously establish the structure, for example, by spectroscopy,[8] were not incontrovertible.

Scheme I



Our main concern arose from the fact that the first intermediate in a plausible mechanism of polymerization of aniline, the radical cation [(PhNH$_2$)$^{\bullet+}$], could be attacked by (or could attack) another aniline molecule through the ortho positions as well as (with a much lower probability) through the meta positions. Besides, carbon-carbon bond formation to introduce benzidine moieties in the backbone could also occur. These and other possibilities are depicted in Scheme I.

Another problem which induced us to investigate PANI was the discrepancy between the interpretations of the results of Bronsted acid (hence known as "acid doping") doping of PANI. One group's results implied that there were no open shell intermediates produced upon acidification[5b] of PANI, and another

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(3) Green, A. G.; Woodhead, A. E. *J. Chem. Soc.* **1910**, *97*, 2388; **1912**, *101*, 1117.

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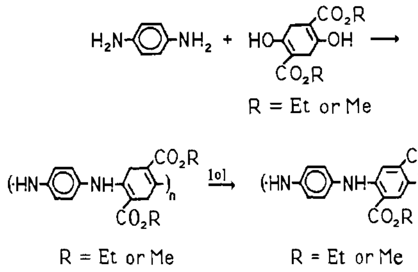
Scheme II



group reported a large increase in magnetic susceptibility with protonation.[9] However, while our work was in progress, the large increase in number of spins upon HCl treatment of PANI was reported by Epstein et al.[10]

In view of the above, there was a need for (a) an unambiguous proof of structure of PANI and (b) a complete investigation of the physical properties, analogous to our previous work on conducting polymers (correlation of transport, spectroscopy, and magnetism as a function of doping), to clarify the problem of acid doping of PANI.

Upon considering all previous attempts and potential problems with modern methods of structure proof of polymers in general, we decided to honor the oldest organic polymer with the oldest method of structure proof: synthesis. A synthetic route had to be devised which (1) would have as starting materials compounds whose linkage through nitrogen atoms could occur only at the para positions of aromatic or incipient aromatic rings, (2) would proceed under mild conditions conducive to high molecular weight polymer, and (3) would have a known mechanism of polymerization which could be supported by ample precedence.

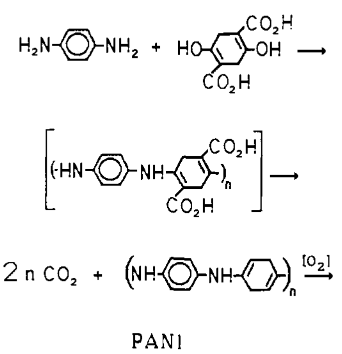
In this paper we present a complete account[11,12] of results on the preparation of a polymer which could only be a poly(*p*-phenyleneamineimine) (PPAI) and which, by several criteria, has the same properties of PANI. We also detail results of comparative studies of not only PANI with PPAI but also PANI with phenyl-capped octaaniline (COA), a discrete, fully characterized molecule.[13] Finally, we present support for the hypothesis that acid doping of PANI involves a proton induced spin unpairing of protonated quinoneimine moieties.[11-13]

II. Results and Discussion

A. Development of the Modified Honzl Scheme. Investigation of the literature revealed that Honzl in 1968 had prepared small PANI oligomers by a double condensation of *p*-phenylamino-substituted anilines with diethyl succinoylsuccinate[14] and that other workers had employed the same diester for the preparation of poly(*p*-phenyleneamines).[15] Indeed poly(*p*-phenylenediaminoterephthalate) could be prepared from a series of solvents by using the above methodology[16] as shown in Scheme II.

Unfortunately the polymeric esters could not be hydrolyzed under mild conditions required for an unambiguous comparison with polyaniline. In fact, it appears as though Honzl may have had trouble with the hydrolysis–decarboxylation sequence of the octamer.[14,17] We therefore decided to explore the possibility of employing succinoylsuccinic acid as the condensation partner, as shown in Scheme III.

Scheme III



We were aware that this was a double-barreled β-keto acid which had the potential problem of decarboxylation before imine formation. It was also known that imino carboxylic acids tend to decarboxylate more readily than their keto analogues. The diacid had been prepared as far back as 1882,[18] and it was known to decarboxylate readily when heated in aqueous solution to produce 1,4-cyclohexanedione.[19] In accordance with Moore's work,[15] we expected the air oxidation of the intermediate "poly(2,6-dihydro-*p*-phenylenediamine)" to proceed smoothly to produce a leucoemeraldine analogue as depicted in Scheme III. Preliminary experiments indicated that the polymerization could be carried out in *m*-cresol, and we called this the "MH approach" (for "modified Honzl" or "Moore–Honzl").

B. Poly(*p*-phenyleneamineimine). 1. Synthesis. In the MH approach, temperature and solvent had already been optimized; all that remained to do was a qualitative determination of reaction rates (condensation and oxidation). It was found that as the reaction proceeded, and before the diacid dissolved slowly and completely at 65 °C, a tan solid began to separate. Disappearance of the diamine was complete after 48 h as determined by TLC (silica gel, 50% hexane in ethyl acetate). Parenthetically, this reaction is an excellent test of laboratory technique; unless the condensation is carried out under *strict anaerobic* conditions, within a short time the mixture turns green and then blue. When all the starting materials were consumed, the reaction mixture was exposed to the atmosphere at 65 °C for 12–24 h. Within the first few minutes the heterogeneous reaction mixture turned green and soon thereafter blue. The product was isolated by simple filtration, followed by the usual washings (cf. Experimental Section).

In a control experiment, the reaction mixture was exposed to the atmosphere at the outset. Within ca. $^1/_2$ h the mixture turned green, and after 18 h a copious blue-black precipitate had formed. The product (isolated as above) showed both IR and UV–vis spectra similar to PANI. However, acid doping of this product failed to produce a conductor, as determined by transport and spectroscopic measurements.

The PPAI prepared as described above, is a blue-black powder which is insoluble in most common organic solvents and in 80% acetic acid (in which PANI is reported to be soluble) but moerately soluble in DMF. Films cast from DMF on a substrate (e.g., ITO glass) can be employed for the determination of cyclic voltammetry, conductivity, etc. Differential scanning calorimetry (DSC)[20] and thermal gravimetric analysis (TGA)[20] reveal that the polymer is stable up to 460 °C and that it loses up to 35% weight when heated to 700 °C. In contrast, while PANI is stable to 460 °C, it loses up to 53% weight, and the fully reduced

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[9] Travers, J. P.; Chroboczek, J.; Devreux, F.; Genoud, F.; Nechtschein, M.; Syed, A.; Genies, E. M.; Tsintavis, C. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 195.

[10] Epstein, A. J.; Ginder, J. M.; Zuo, F.; Bigelow, R. W.; Woo, H. S.; Tanner, D. B.; Richter, A. F.; Huang, W. S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *18*, 303.

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[19] *Organic Syntheses*; Wiley: New York, Collect. Vol. V, p 288.

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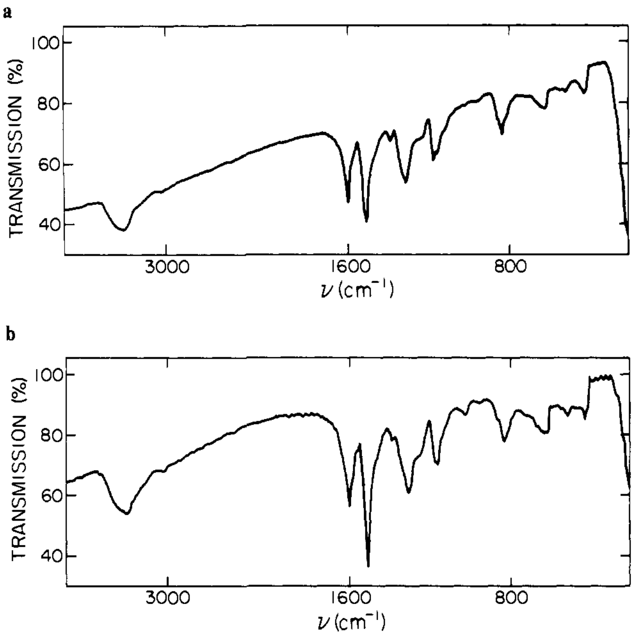

Figure 1. (a) Infrared spectrum of PANI as a KBr mull. (b) Infrared spectrum of PPAI as a KBr mull.

phenyl-capped octaaniline (B_7) decomposes at 385 °C with 76% loss in weight.

Treatment of solid PPAI or DMF solutions with HCl gas produces the familiar green color ("emeraldine hydrochloride"). As described below, there are concomitant dramatic changes in magnetic and transport properties, in qualitative agreement with the same changes observed in PANI.

Other aromatic diamines can be employed, and the preparation of a number of polymers is possible.[20] Suffice it to say that the condensation step is very sensitivie to electronic effects; for example, benzidine requires over 6 days for completion of the condensation step!

2. Comparative Spectroscopy. Since the main aim of the work on PPAI was to prove the structure of PANI by synthesis, all the remaining topics in this report, spectroscopy, transport, etc., will be presented in comparison to the properties of PANI. In Figures 1–4 we show the comparative IR and solution UV–vis spectra of neutral and acid-doped polymers.

a. Infrared Spectroscopy. It is clear from Figures 1 and 2 that the infrared spectra of both polymers, in the neutral- and acid-doped states, can be superimposed on a peak-by-peak basis. A closer look at the relative intensities of the 1598 and 1500 cm^{-1} reveals that PPAI is in a different oxidation state (fewer Q's) than PANI. The only differences between the infrared spectra of PANI and PPAI are that the latter exhibits peaks which are somewhat sharper and also shows some absorption in the OH region (3600–3100 cm^{-1}). Elemental analysis revealed that PPAI retained one molecule of *m*-cresol (confirmed by warming a sample into the inlet of a mass spectrometer and observing only peaks due to *m*-cresol, $P = 108$) for every 12 aromatic rings even after evacuation at 80 °C for 48 h; hence, the broad absorption centered at 3300 cm^{-1}. More recent results[21] on the synthesis of poly(*o*-*p*-phenyleneamineimine) reveal that, to the limits of our infrared spectrophotometer, PANI *is devoid of incorporation of o-phenylenediamine moieties in the backbone* as evidenced from the absence of a diagnostic absorption at 750 cm^{-1}, which is prominent in the deliberately prepared *o-p* polymer.

b. Ultraviolet Spectroscopy. In Figure 3 we show the solution electronic absorption spectra of PANI and PPAI in the neutral state. It is clear from the low intensity of the ~620-nm band of PPAI that the soluble fraction of this polymer consists mostly of the leuco form. This is probably due to the higher molecular weight and lower quinoneimine content of PPAI relative to PANI.

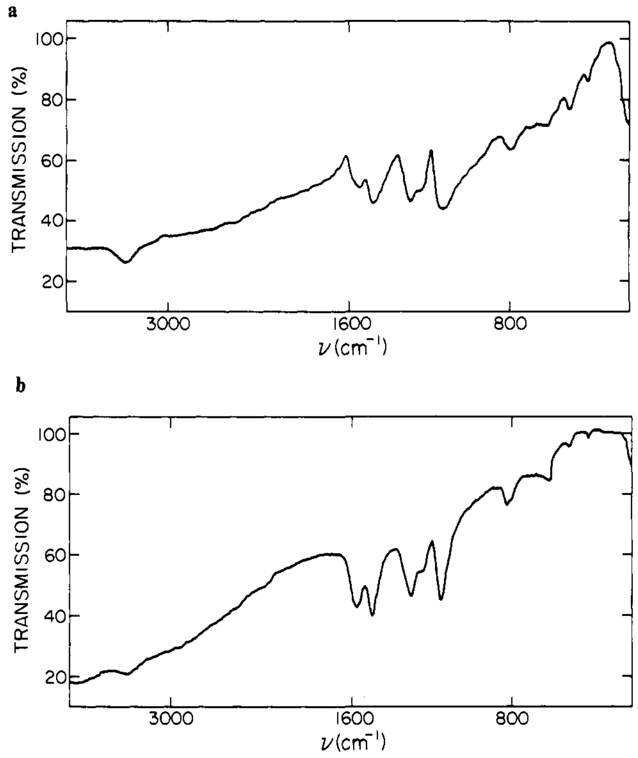

Figure 2. (a) Infrared spectrum of PANI·HCl. (b) Infrared spectrum of PPAI·HCl.

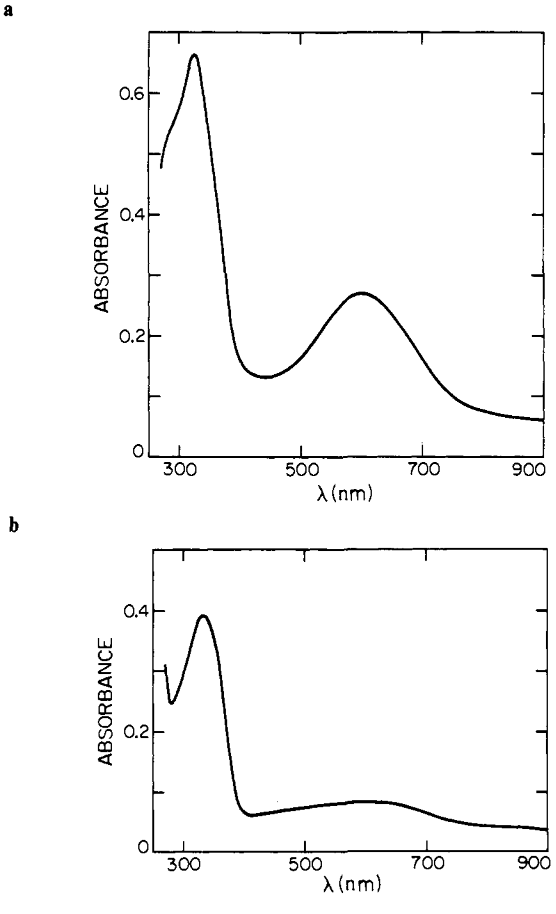

Figure 3. (a) UV–vis spectrum of PANI in DMF solution. (b) UV–vis spectrum of PPAI in DMF solution.

The spectra of the hydrochloride salts of PANI and PPAI are shown in Figure 4. Although the two look somewhat different (e.g., the shoulder at 450 nm is more pronounced in PANI·HCl whereas the structure near 350 nm is more pronounced in

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[21] Allemand, P. M.; Nowak, M.; Wudl, F., unpublished paper in preparation.

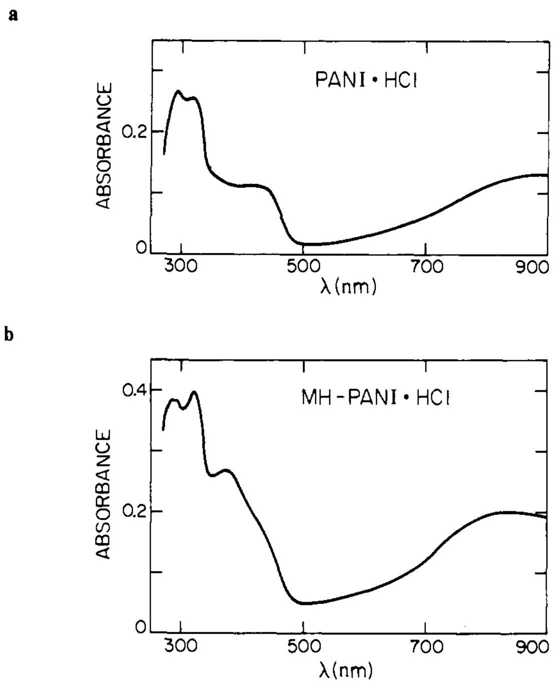


Figure 4. (a) UV–vis spectrum of PANI·HCl in DMF "solution" (colloidal suspension). (b) UV–vis spectrum of PPAI·HCl in DMF "solution".

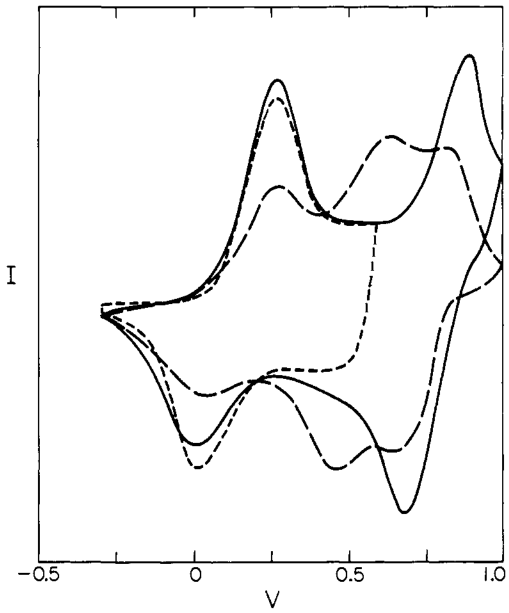


Figure 5. Cyclic voltammograms of PANI on ITO (working electrode) in 1.0 molar aqueous hydrochloric acid (potentials relative to SCE): second cycle, —; tenth cycle — — —; 20 reproducible cycles, - - -.

PPAI·HCl), a spectrum of doped PANI very similar to that shown for PPAI can be generated electrochemically at pH 5.9 and 0.04 V vs. SCE.[7c] These solution spectra are actually those of colloidal suspensions as evidenced by the fact that a green "solution" of PANI·HCl deposited a green, flaky precipitate (leaving a completely colorless solution) when standing overnight undisturbed. Brief, vigorous shaking caused the solid to completely "redissolve". The spectrum of PPAI·HCl shown in Figure 4 is then due to lower doping level in PPAI relative to PANI. To test this, a sample of PPAI was oxidized with ammonium persulfate under conditions which produce PANI from aniline. The results were disappointing in that we discovered that both PANI and PPAI are irreversibly decomposed under these conditions.

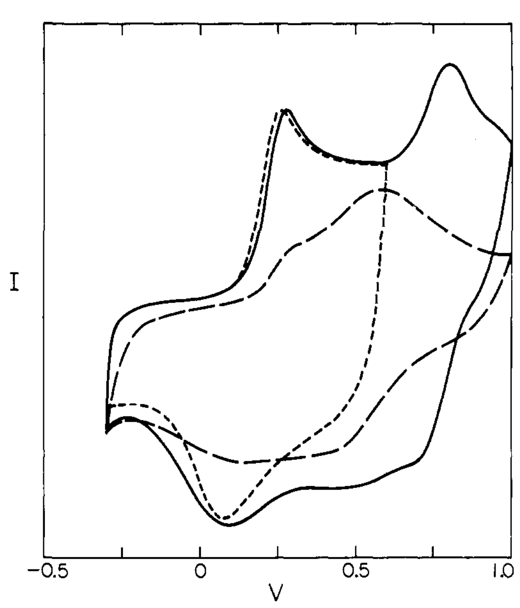


Figure 6. Cyclic voltammograms of PPAI, same conditions as above: second cycle, —; thirtieth cycle, — — —; 20 reproducible cycles, - - -.

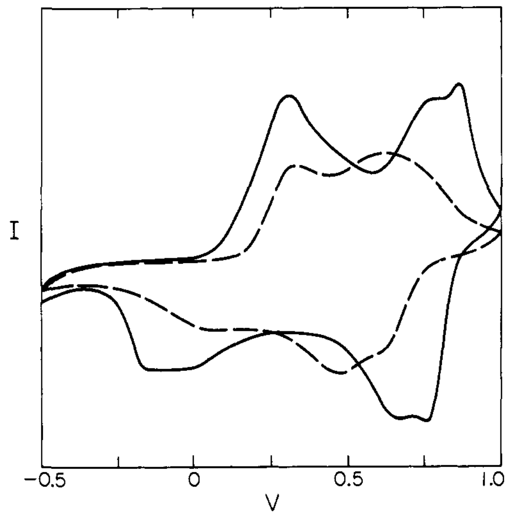


Figure 7. Cyclic voltammograms of B_5Q_2, same conditions as above: second cycle, —; thirtieth cycle, — — —.

3. Comparative Electrochemistry. The cyclic voltammograms shown in Figures 5–7 were recorded by using thin films cast onto ITO glass from DMF solution. The initial appearance of the films was blue. The films were cycled at a given pH in deionized water at room temperature in the range −0.300 to +1.00 V vs. SCE. We basically observe, for all three systems, what had previously reported for PANI;[5-7,22] namely, four regions (T, G, B, and M) bracketed by potentials (vs. SCE) of −1 to +0.05 V, +0.05 to +0.4 V, +0.4 to +0.6 V, and +0.6 to 1 V, respectively. Below −0.05 V, the materials are colorles and transparent: in region G, they are green, in region B, they are blue, and in region M, they are dark blue–magenta.

After a number of cycles, the two polymers exhibit qualitatively the same oxidation peaks at $E_p = 0.30 \pm 0.02$ V (A) and $E_p = {\sim}0.6 \pm 0.03$ V (B), and the octamer exhibits oxidations at $E_p = 0.31$ V (A), $E_p = 0.60$ V (B), and $E_p = 0.78$ V (C). The main difference between PANI and PPAI is that the later, after the first cycle, is electrochemically more robust; i.e., it took only 10 cycles for PANI to reach the same CV as a 30-cycle PPAI. On the other hand, considering the most positive voltage oxidation peak (PANI 0.89 V, PPAI 0.74 V), the difference between the first and second cycles is much more dramatic for PPAI than for PANI. Also, in the first cycle of PPAI, there is already a hint of oxidation peak B; i.e., the first wave of PPAI looks like the second wave of PANI. The origin of the highest oxidation potential wave in aqueous medium in the case of PANI has been interpreted as arising from oxidative degradation. However, since the same high oxidation potential wave is observed without at-

Table I. Magnetism Data

	χ (emu/mol-octaaniline)	Ns/(spin/octaaniline)
PANI	0	$6.4 \times 10^{-3\,a}$
PPAI	0	$4.7 \times 10^{-3\,a}$
B_5Q_2	0	$4.0 \times 10^{-3\,a}$
PANI·HCl	$4.8 \times 10^{-4\,b}$	$8.6 \times 10^{-2\,b}$
PPAI·HCl	$4.0 \times 10^{-4\,b}$	$1.6 \times 10^{-1\,b}$
B_5Q_2·HCl	$4.0 \times 10^{-4\,b}$	$1.1 \times 10^{-1\,b}$

[a] Measurements carried out by integration of the ESR signal and calibrated against a ruby standard. [b] Measurements carried out with a SQUID Magnetometer (Figure 8) and checked against ESR data on similar samples (see text).

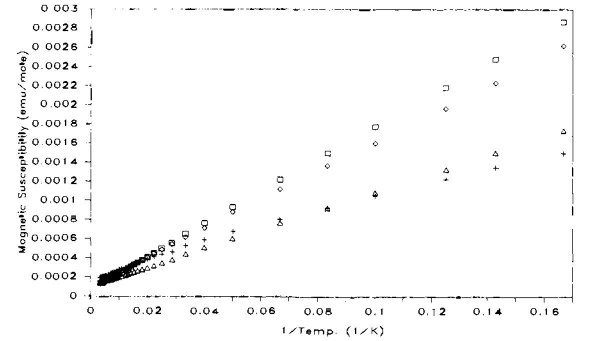


Figure 8. Magnetic susceptibility as a function of inverse temperature of "wet doped" PANI·HCl (□), PPAI·HCl (◇), extracted, dry doped PANI·HCl (+), and B_5Q_2·HCl hydrate[23] (△). The accuracy of the measurements is ±0.5% in χ as well as *T*; i.e., error bars are within the width and height of the symbols used in the figure.

tendant degradation in a nonnucleophilic solvent ($NH_4F{\cdot}2.3HF$),[22] the source of the E_p ~0.6 V wave in aqueous acid remains to be established.

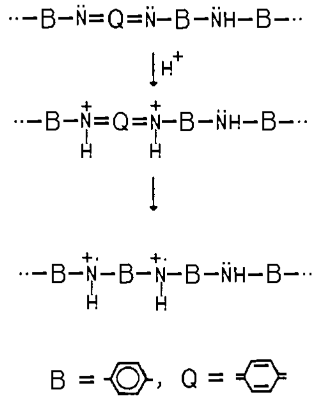
4. Comparative Magnetic Properties. The magnetic properties of the pristine and protonated forms of PANI, PPAI, and B_5Q_2 were determined by means of a combination of Electron Spin Resonance (ESR) and static magnetic susceptibility measurements (the latter utilized a superconducting quantum interference device, SQUID, magnetometer). In the ESR case, the quantitative susceptibility measurements (and spin counts) involved double integration of the ESR signal and utilized a Ruby standard for calibration. The results are summarized in Table I and in Figure 8.

ESR studies of the neutral PANI, PPAI, and B_5Q_2 indicated a small number of unpaired spins. In each case, plots of χ vs. $^1/_T$ demonstrated Curie Law behavior with a high temperature intercept that was zero to within the experimental accuracy. These results indicate high quality material with relatively few magnetic impurities and/or spin-carrying defects. Upon protonation, all three materials show a major increase in the strength of the ESR signal concomitant with a decrease in line width (from 1.9–0.6 G for PANI; from 8.8–1.1 G for PPAI; and from 10–0.54 G for B_5Q_2). A detailed quantitative study of the susceptibilities (and their temperature dependences) was carried out by using the higher accuracy available with the SQUID technique.

The results of static susceptibility (SQUID) measurements of PANI·HCl, PPAI·HCl, and B_5Q_2·HCl are shown in Figure 8. In each case, a core diamagnetic contribution of $\chi_{dia} = -5.24 \times 10^{-4}$ emu/mol-octaaniline was subtracted from the data. This value was estimated by using Pascal's constants for the molecular units in the polymer backbone and for the chloride counterion. The results indicate that protonation leads to a temperature independent paramagnetic contribution of about $\chi_P = 4 \times 10^{-4}$ emu/mol-octaaniline and a major increase in the number of Curie spins. ESR data on the protonated materials gave results consistent with the static susceptibility measurements. In particular, after correcting for the diamagnetic contribution, the room temperature SQUID and ESR susceptibilities were in agreement.

We found some variability in the data from sample to sample. For PANI·HCl and PPAI·HCl, the results were consistent for all of the independently prepared samples. For the protonated B_5Q_2·HCl, the values of χ_P were quite consistent, $\chi_P = 4 \times 10^{-4}$ emu/mol-octaaniline. However, the number of Curie spins was observed to vary from sample to sample by as much as a factor of four (from 0.1–0.2 spins/octaaniline to about 0.5 spins/octaaniline). The origin of this variability is uncertain. We note in this context that there is other evidence that the number of Curie spins is sensitive to details of sample preparation. For example, PANI·HCl as prepared by the procedure of MacDiarmid et al. (doped wet) has nearly twice the number of Curie spins as PANI·HCl doped after extensive extraction with THF to remove low molecular weight components (see Figure 8).

Scheme IV



The results presented in Table I and Figure 8 are in qualitative agreement with those reported by Epstein et al.[10] The only major difference is in the detailed temperature dependence. Our results on the protonated samples are well-represented by the sum of two contributions

$$\chi = \chi_P + C/T$$

There is excellent agreement between our χ_P values for the protonated PANI, PPAI, and B_5Q_2 (see Table I), and this value is in good agreement with that reported by Epstein et al. Although Epstein et al. find a similar increase in the magnitude of the temperature dependent contribution, they report a significant deviation from Curie Law behavior with the number of spins (or the Curie constant) first increasing and then decreasing as the temperature is lowered.[10] By contrast, the data of Figure 8 show *C* to be nearly constant (a small decrease in slope is observed for PANI·HCl and B_5Q_2·HCl at low temperatures). Although the origin of these differences is not known, the simpler behavior demonstrated in Figure 8 gives confidence in the separation of the susceptibility into the traditional contributions.

It is clear from the magnetic susceptibility results that acid treatment of neutral PANI, PPAI, and B_5Q_2 leads to the generation of a combination of itinerant and localized or semilocalized spins. This is of interest and importance since electrons are neither added nor subtracted by protonation. A plausible mechanism for such a proton induced spin generation is shown in Scheme IV.

The driving force for converting $[\text{—HN=Q=NH—}]^{2+}$ to $[\text{—HN—B—NH—}]^{2\bullet 2+}$ is expected to be provided by the gain in resonance energy obtained in going from a quinoneimine to a diaminobenzene. The $B\text{–}\ddot{N}H\text{–}B$ moieties in Scheme IV are not shown protonated, not because we do not believe they are, but because equilibrium protonation–deprotonation of these units is not expected to have the same energetic consequences as protonation of the —N=Q=N— groups. Also, according to Genies,[22] and contrary to intuition and what had been reported previously,[6a] the pK_a of the $(\text{B—NH}_2\text{—B})^+$ moieties was found to be lower than that of the $(\text{Q=NH—B})^+$ groups by ca. 2 units.

The same outcome is expected if only one of the quinoneimine nitrogens is protonated first, followed by a second proton as shown in Scheme V.

The radical cations (polarons) are not expected to remain strictly localized as depicted, for heuristic reason, in the schemes. Bredas has shown that in the idealized case of uniform protonation of

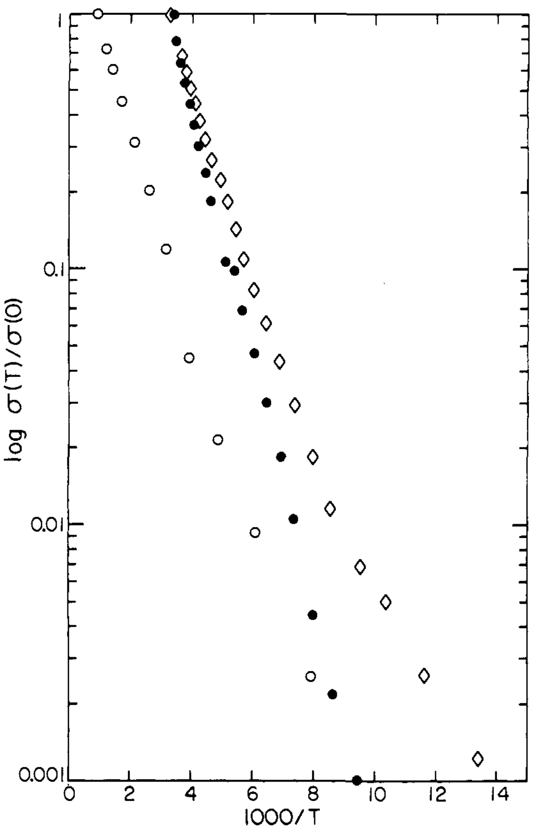
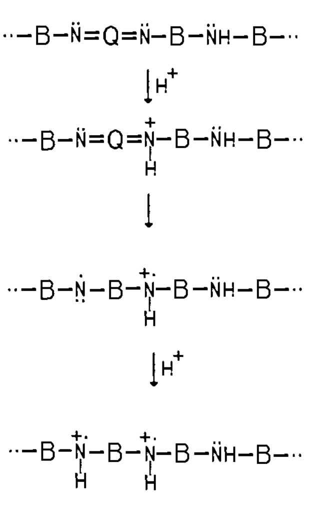


Figure 9. Four probe compressed pellet log of conductivity as a function of inverse temperature of dry doped PANI·HCl (◇), PPAI·HCl (●), and B_5Q_2·HCl hydrate[18] (○). The accuracy of the measurements is ±0.5% in ρ and ±0.1 K in T; i.e., error bars are within the width and height of the symbols used in the figure.

Scheme V



the pernigraniline (B—N═Q═N—B···) polymer, a half-filled polaron band would result. However, we defer a detailed discussion of the electronic structure of the highly conducting PANI·HCl and PPAI·HCl to section 6.

5. Comparative Transport Properties. With a conductivity of ~5 s cm^{-1}, polyaniline hydrate hydrochloride (PANI·HCl) is a relatively poor organic polymeric conductor, the anhydrous material exhibits a conductivity which is lower by at least a factor of 5–10 (see curve due to B_5Q_2 in Figure 9). As can be seen from Figure 9, conductivities of polyaniline hydrochloride as well as PPAI and B_5Q_2 all decrease with temperature. Although the plots of log σ vs. $^1/_T$ are not precisely straight, the materials can be characterized as semiconductors with an activation energy of 0.08 eV.

Since the backbone is positively charged, material with these characteristics might be expected to have a rather high, positive thermopower. Instead (see Figure 10), the thermopower of PANI·HCl is small and negative. The thermopower of the protonated B_5Q_2 has a similar temperature dependence; it is also negative but with a magnitude approximately 10 times larger than the value for PANI·HCl.

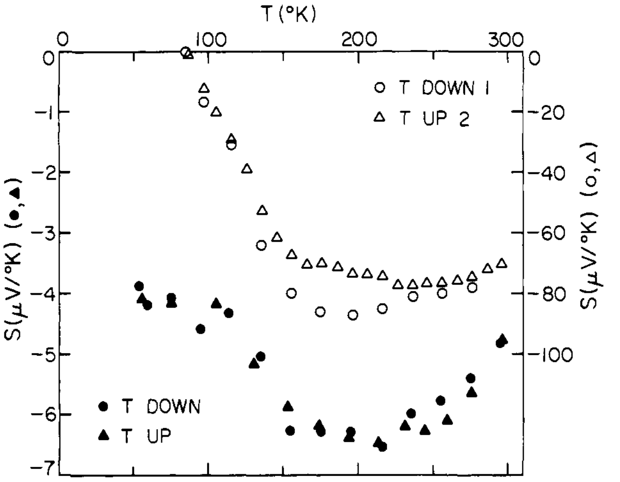


Figure 10. Compressed pellet thermopower of dry doped PANI·HCl (●, ▲ left ordinate) and B_5Q_2·HCl hydrate[18] (○, △ *right ordinate*). The accuracy of the measurements is ±0.5% in s and ±0.1 K in T; i.e., error bars are within the width and height of the symbols used in the figure.

6. The Electronic Structure of Protonated PANI, PPAI, and B_5Q_2. The comparison of the data presented in the previous sections provides convincing evidence that the electronic structures of these three materials are essentially identical. The similarity of the properties of B_5Q_2·HCl to those of protonated PANI and protonated PPAI provides important new evidence that the dominant transport mechanism is via *inter*molecular (or *inter*chain) hopping. Evidently, the intrachain bandwidths and/or the molecular weights are simply not large enough to lead to significant delocalization along the polymer backbone.

Although it has been argued that protonated PANI is truly a metal,[22,23] we do not believe that this is the case. The large number of Curie spins in the protonated samples is not consistent with genuine metallic behavior. In our view a more proper description is that of a relatively high density of localized states which originate from the proton induced spin unpairing mechanism described above. Alternately, one may think of this continuous density of localized states as arising from the effect of severe disorder on the band structure[24] of the polaron metal.[25] Unpaired electrons can hop from site to site (primarily by interchain transfer) giving rise to the activated transport. The picture which we propose is qualitatively that of a Fermi "glass",[26] i.e., a continuous density of localized states which are occupied according to the Pauli Exclusion Principle. The magnetic susceptibility of the interacting Fermi glass exhibits behavior similar to our observations (Figure 8): a Curie-like temperature dependence at low temperature and a temperature independent regime at higher temperature.[27] The origin of this temperature dependence can be understood qualitatively in terms of the occupancy of the localized states. Well

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below the Fermi energy (E_F) the states are doubly occupied, and well above E_F the states are empty. Near E_F, the Coulomb interaction will cause some of the states to be singly occupied, resulting in a number of Curie spins approximately equal to $U_{eff}N(E_F)$ where U_{eff} is the effective Coulomb interaction, and $N(E_F)$ is the density of localized states at the Fermi energy. Taking into account, as well, the repopulation of the doubly occupied states in the presence of a magnetic field leads to a temperature independent contribution to the susceptibility, $\chi_P = \mu_B^2N(E_F)$ where μ_B is the Bohr magneton. Thus, the magnetic data and the transport data are qualitatively consistent with a Fermi "glass" model.

The dominance of interchain transport between localized states in "polyaniline" is to be contrasted with the genuine metallic behavior inferred for other conducting polymers where a true Pauli susceptibility is observed[28] (with no significant number of localized spins) over a broad temperature range. In this context, we note that electrical conductivities in the range of 1 s/cm are relatively easy to achieve by simple hopping mechanisms whereas conductivities of several hundred s/cm or greater begin to demand mean free paths consistent with delocalized states and metallic transport.

III. Experimental Section

Unless otherwise stated, all preparations were carried out in an inert atmosphere (usually Ar). NMR spectra were recorded with a Varian EM-360, 60-MHz spectrometer, infrared spectra were obtained with a Perkin Elmer Model 1300 spectrophotometer, and UV-vis spectra were obtained with a Perkin Elmer Model Lambda 5 spectrophotometer. Elemental analyses were performed by Spang Microanalysis and University of California Microanalysis Laboratory, Berkeley, CA. ESR spectra were recorded with an IBM Instruments (Bruker) E-200 D ESR spectrometer (9.3 GHz). Magnetic susceptibility measurements were carried out on a SQUID susceptometer located at the regional facility of the Department of Chemistry of the University of Southern California, Professor C. Reed, Director.

2,5-Dioxo-1,4-cyclohexanedicarboxylic Acid (Succinosuccinic Acid). While under a blanket of N_2, 2,5-dihydroxyterephthalic acid (5.00 g, 25.2 mmol) was dissolved in 5% aqueous NaOH (125 mL) and cooled to 0 °C. To this yellow solution was added powdered 3% Na(Hg) all at once. During the next 30 min, the mixture was stirred vigorously to suspend the amalgam. The resulting pale yellow solution was decanted, and the Hg was rinsed with 0 °C water (10 mL). The combined basic solutions were added dropwise during 20 min to a 0 °C solution of 10% aqueous HCl (300 mL). The copious pale yellow precipitate which formed was collected on a frit (10–15 μm), rinsed with ice water (3 × 25 mL), and dried overnight at reduced pressure to give 3.61 g of a pale yellow solid mp, 155–6 °C. The diacid decomposes readily at ~110 °C losing 82% (theoretical, 78%) of the original weight. The white sublimate collected from the cool apparatus proved to contain only 1,4-cyclohexanedione. The diacid is unstable in most solvents (Me_2SO, DMF, pyridine), and the product decomposes readily with gas evolution. The ^1H NMR spectrum was recorded in acetone-d_6/Me_2SO-d_6 (3:1). However, the spectrum of 1,4-cyclohexanedione was soon observed. The spectrum revealed 10% of 2,5-dihydroxyterephthalic acid. Even the act of pressing a KBr pellet for IR analysis caused the formation of some 1,4-cyclohexanedione: ^1H NMR (acetone-d_6/Me_2SO-d_6, relative to Me_4Si) (3:1) δ 8.8 (br s, 4 H, COOH, OH) 3.1 (s, 4 H, allyl CH_2); IR (KBr, cm^{-1}) 3410 br m, 3300–2600 br m, 2335 m, 1650 s, 1545 s, 1450 s, 1350 m, 1295 m, 1215 s, 1058 m, 905 w, 695 w, 658 w, 505 w.

PPAI Model System: *N,N′-p*-Phenylenediamine. Succinosuccinic acid 75% (150 mg, 0.75 mmol) was added to a flame and vacuum dried 100-mL Morton flask. The flask was evacuated and back flushed with Ar 3 times and then charged with *m*-cresol (50 mL, Ar degassed). Most of the diacid did not dissolve, yet the solution became pale yellow. Freshly distilled aniline (183 μL, 2.01 mmol) was added all at once, and the mixture was warmed to 73 ± 2 °C, stirred vigorously, and monitored periodically by TLC. (TLC samples were prepared by withdrawing 0.5 mL of the mixture, diluting it with ether (0.5–1 mL), and extracting the organic solution with 10% NaOH (6 × 2 mL).) During the reaction, the mixture became orange and almost homogeneous. No 1,4-cyclohexanedione was observed by TLC at any time, and aniline was always present. After 150 h, the mixture was poured into ether (100 mL) and washed with 10% aqueous NaOH (5 × 50 mL) and then H_2O (50 mL), dried ($MgSO_4$), and concentrated to a pale tan solid (139 mg, 53%), mp 128–131 °C. The isolated solid has the same IR and NMR spectrum as commercial *N,N′*-diphenyl-*p*-phenylenediamine (lit. mp 146–148 °C).

Poly(*p*-phenyleneamineimine) (PPAI). To a flamed and vacuum dried Morton flask back flushed with Ar were quickly added succinosuccinic acid 75% (760 mg, 3.79 mmol) and *p*-phenylenediamine (410 mg, 3.79 mmol). After evacuating and back flushing with argon 3 times, *m*-cresol (80 mL, argon degassed) was added via cannula. The resulting slurry of diacid was warmed to 65–70 °C and stirred vigorously for 2–3 days. During this time, the slurry became orange and almost homogeneous. Soon, a tan precipitate fell. TLC analysis showed the absence of both *p*-phenylenediamine and 1,4-cyclohexanedione. The flask was then opened to the atmosphere. Heating and vigorous stirring were maintained for an additional day. Exposure to atmospheric O_2 immediately caused some of the tan precipitate to turn green and soon the entire mixture was dark blue-black. The mixture was filtered (10–15 μm glass frit) and washed with THF (50 mL). The residue was extracted continuously (Soxhlet) with THF until the extract was clear (1 day) and then dried overnight at reduced pressure to afford 644 mg (93%) of PPAI, mp > 290 °C: IR (KBr pellet cm^{-1}) 1595 m br, 1515 s h, 1505 s br, 1300 m br, 1165 m br, 825 m br (see Figure 1b); UV–vis (DMF) λ_{max} 330, 620 nm (see Figure 3b). Anal. Calcd for $C_{18}H_{15}N_3(C_7H_8O)_{0.083}$: C, 79.00; H, 5.56; N, 14.89. Found: C, 79.14; H, 5.59; N, 14.70.

Aqueous Acid Doping of PPAI. Finely pulverized PPAI (100 mg) was suspended in 1.0 M aqueous HCl (10 mL), stirred vigorously for $^1/_2$ h, filtered (10–15-μm glass frit), and dried overnight at reduced pressure. The doping afforded a fine green-black powder: IR (KBr, cm^{-1}) 4000–2000 s br, 1590 m, 1495 m, 1500 m, 1160 m (see Figure 2b); UV–vis (DMF solution, λ_{max}) 875, 435 (sh), 345 nm (see Figure 4b); $\sigma \sim 1.2 \times 10^{-2}$ s/cm, ESR 1.2 G_{pp}, $g = 2.0036$.

Acid Doping of PPAI in Methylene Chloride. Finely pulverized PPAI (100 mg) was suspended in CH_2Cl_2 saturated with anhydrous $HCl_{(g)}$ (10 mL). The slurry was shaken for 15 min or longer. The supernatant was decanted, and the polymer was dried at reduced pressure. ESR measurements were made in both the acidic slurry and the dried polymer, and all other physical measurements were made only on the dried polymer, mp > 290 °C, $\sigma \sim 3 \times 10^{-3}$ s/cm. Other properties are shown in Figures 8–10 and Table I.

Electrochemistry. Electrochemical experiments were carried out by using an EG&G PARC Model 174A polarographic analyzer, an EG&G PARC 175 universal programmer, and a RE0098 X-Y recorder.

Cyclic voltammograms were recorded by using a three electrode cell with a Pt wire as a counter electrode and SCE as the reference electrode in 1 M HCl at room temperature under noncontrolled atmosphere. Working electrodes were made by casting thin films of PANI, PPAI, and B_5Q_2 onto ITO glass (surface = 1–2 cm^2) from saturated DMF solutions.

When the films were cycled at 100 mV/s from −0.3 to +1.0 V/SCE, three redox systems were observed. After about 50 cycles, only one discernible wave at intermediate potential remained. However, if the films were cycled from −0.3 to +0.4/0.5 V, the first redox wave of the three polymers exhibited a good stability for 10–20 cycles. The cyclic voltammograms were found to depend on the thickness of the films, i.e., the redox waves were very broad for a thick film (at this scan rate), but, on the other hand, the color changes were easier to observe with thick films. CV's were also pH-dependent. For example, the CV of a B_5Q_2 film recorded in 0.01 M HCl showed only one redox wave ($E_p^{ox} = +0.55$ V/SCE).

Doping Studies. (a) Polyaniline prepared as described was worked up to the point where it was a wet cake in a suction filter,[5b] was suspended in 1 M HCl, and was allowed to dope over a few hours. The resulting green solid was then isolated by filtration and dried under dynamic vacuum overnight. This was the sample labeled "wet doped" in Figure 8. Anal. Calcd for $C_{12}H_{10}Cl_{0.9}N_2(H_2O)_{0.4}$: C, 65.11; H, 4.85; Cl, 14.45; N, 12.66; O 2.89. Found: C, 64.87; H, 4.85; Cl, 14.48; N, 13.08; O (by diff), 2.71.

(b) Polyaniline prepared as described[5b] was dried under dynamic vacuum overnight and extracted with THF under an inert atmosphere until no more color was observed in the extracts (48-h Soxhlet). The resulting finely powdered blue-black solid was suspended in methylene chloride and treated with anhydrous HCl gas until the solution was saturated and the reaction mixture was stirred overnight. Filtration under an inert atmosphere followed by washing with dry methylene chloride and 48-h evacuation at room temperature afforded the sample labeled "extracted, dry doped" in Figure 8. Anal. Calcd for $C_{12}H_{10.5}ClN_2(H_2O)_{0.2}$: C, 64.98; H, 4.92; Cl, 16.02; N, 12.63; O, 1.45. Found: C, 64.71; H, 4.94; Cl, 16.01; N, 13.13; O (by diff), 1.36.

(c) Polyaniline was prepared by the MH method as described above and was doped as in (b) above. This was the sample labeled PPAI·HCl

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[28] (a) Moraes, F.; Chen, J.; Chung, T. C.; Heeger, A. J. *Synth. Met.* **1985**, *11*, 271. (b) Moraes, F.; Davidov, D.; Kobayashi, M.; Chung, T. C.; Chen, J.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1985**, *10*, 169.

in Figure 8. Anal. Calcd for $C_{19}H_{17}ClN_3O$ [$C_{18}H_{16}ClN_3O_{0.86}\cdot(C_7H_8O)_{0.14}$]: C, 67.35; H, 5.02; Cl, 10.49; N, 12.40; O, 4.72. Found: C, 67.78; H, 4.97; Cl, 10.62; N, 12.24; O (by diff), 4.39. Indicating that the sample was slightly contaminated with *m*-cresol and water.

Degradation Studies. A thick film of PANI deposited on ITO glass was cycled in 1 M HCl from −0.3 to +1.0 V/SCE at 10 mV/s for 6 h. The film was black and seemed to be partially dissolved on the edges of the glass electrode. The electrode was dried under vacuum, but the black material was oily, and no IR spectrum was recorded. Moreover, other control experiments under these conditions showed that the ITO layer was dissolved (this could explain the absence of current at the end of the experiment).

Acknowledgment. We are indebted to the Office of Naval Research and the Naval Research Laboratory for support. ESR and magnetic susceptibility studies were supported by NSF DMR85-21392. We thank Dr. Hugh Webb for mass spectrometry and Carol Koch and Jerry Wuenschell for their help with the SQUID susceptometer.

Total Synthesis of 7,7-, 10,10-, and 13,13-Difluoroarachidonic Acids

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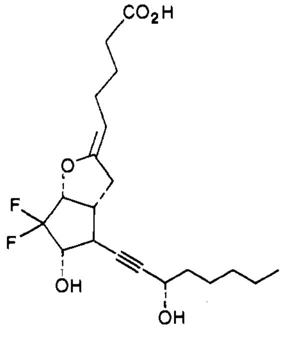
Abstract: General methodology is described for the synthesis of polyunsaturated fatty acids, in which one of the methylene groups between cis double bonds is replaced by a CF_2 group. This is exemplified by the preparation of 7,7-, 10,10-, and 13,13-difluoroarachidonic acids **22**, **18a**, and **30**, respectively. Crucial to the synthesis is the preparation of the fluorodiacetylenic system **7** by a chain reaction involving an acetylenic anion containing the substituent X and CF_2ClBr to form the bromides **4**, followed by reaction of the corresponding iodides with a second acetylenic anion bearing Y. After reduction of **7** to the diallylic system **3** the substituents X and Y are employed in the construction of the tetraunsaturated arachidonate system. In the 10,10-case two separate chain extensions are performed by sequentially converting X and Y to Br and condensing the allylic bromides with the cuprous acetylides **10** and **12a**. In the 7,7- and 13,13-cases X possesses the required carbon skeleton, and Y is provided by coupling with the cuprates of 1,4-decadiyne and methyl nona-5,8-diynoate, respectively. The synthesis is completed by semihydrogenation and enzymatic hydrolysis.

1. Introduction

During the last few years this laboratory has been engaged in the synthesis of fluorinated derivatives of the unstable prostacyclin (PGI_2) and thromboxane A_2 (TXA_2), in which fluorine is substituted for hydrogen in strategic positions of the molecule so as to destabilize, by virtue of the powerful inductive effect of fluorine, the transition states for hydrolysis. At the same time because of the similarity in the van der Waals radii between hydrogen (1.20 Å) and fluorine (1.35 Å) biological activity should be preserved. Indeed, 10,10-difluoro-13-dehydroprostacylin (**1**) was hydrolyzed at 1/100 the rate and possessed biological activity of the same order as that of the natural product.[1,2] More dramatically, compound **2** containing the ring system of 10,10-difluoro TXA_2 was shown to undergo hydrolysis at 10^{-8} times the rate of TXA_2 itself.[3]



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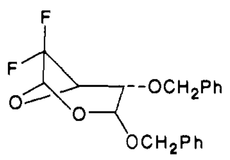

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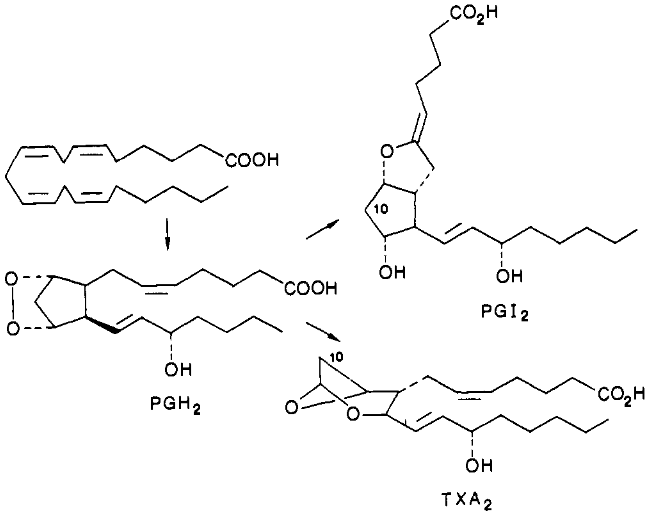
It occurred to us that if the enzymatic processes leading to PGI_2 and TXA_2 could be made to operate on the appropriately substituted fluorinated substrates,[4] the corresponding fluoro derivatives could be obtained rapidly by biosynthetic means. The precursor in the biosynthesis of all the prostaglandins and thromboxanes is the tetraunsaturated acid arachidonic acid which is converted to PGH_2 by PGH synthase.[5] PGH_2 is in turn rearranged to PGI_2 and TXA_2 by prostacyclin and thromboxane synthase, respectively.[6] For fluorine to be substituted at C-10 of PGI_2 or TXA_2 requires 10,10-difluoroarachidonic acid (10,10-DFAA) as a precursor.



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