cooperative complex calculated with the parameters $\epsilon_b = -4500$ cal/mol, $S_0 = 1.6 \times 10^{-4}$, and $\sigma = 3.2 \times 10^{-3}$. For illustrative purposes, we may define an entropy of nucleation, $\Delta S_n = R \ln \sigma = -11.4$ eV and an entropy of bond formation, $\Delta S_b \equiv R \ln S_0 = -17.3$ eu. The model with $N = 5$ and these parameters obviously generates a cooperative melting curve that closely mimics the transition reported here (Figures 7, 8, and 10). Within the spirit of this model, the parameters do not violate reasonable ideas of the strength of the entropy change for localizing opposing segments of the interface.

Future work will address such features as the structural differences that cause the high-temperature forms of the complex to exhibit quenching whereas the low-temperature form(s) do not. It will further seek a realistic picture of the interfacial interactions in both types of forms, as well as a kinetic mechanism that embodies the ideas proposed here.

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(58) The fraction of broken bonds is defined as $(\langle N(0)\rangle - \langle N(T)\rangle)/\langle N(0)\rangle$, where $\langle N(T)\rangle$ is the average number of bonds and is given by eqs 16–93 of ref 57 and $N(0) = N - 1$ in the model as formulated (ref 57). We have explored a range of $N$ and find this makes no difference to the qualitative features of this approach. However, the magnitudes of $\epsilon_b$, $\Delta S_b$, and $\Delta S_n$ decrease with increasing $N$.

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# Direct Evidence of a Bipolaron Charge Carrier in Conducting Polyazines from $^{13}C$ and $^{15}N$ Solid-State NMR Spectroscopy: Detection of a Nitrenium Cation by Natural Abundance $^{15}N$ Solid-State NMR Spectroscopy

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**Abstract:** Natural abundance $^{13}C$ and $^{15}N$ solid-state NMR experiments were performed on undoped and doped samples of polyazine, $(-N{=}C(R){-}C(R){=}N-)_x$. The topology of the polymer requires that doping-induced charge carriers must be either polarons (radical cations) or bipolarons (dications). Magnetic susceptibility measurements shows that the iodine-doped polymers are diamagnetic, so the charge carriers must be bipolarons. The specific bipolaron charge carrier in polyazines has been identified; the nitrogens bear the charge primarily in the form of a nitrenium cation. This is the first report of a nitrenium cation detected by $^{15}N$ solid-state NMR spectroscopy. Independent of the substitution of the polyazine, R = H or $CH_3$, the same charge carrier is present.

## Introduction

The field of conducting polymers has generated tremendous interest in the past decade.[1] The prototype conducting polymer is polyacetylene,[2-13] which has alternating double and single bonds along the all-carbon backbone. Analogous to polyacetylene is polyazine, $(-N{=}C(R_1){-}C(R_2){=}N-)_x$, which emulates polyacetylene but inserts an azine bond, $=N{-}N=$, at every other diene site. Unlike polyacetylene, polyazines are not oxidized in air. The presence of the heteroatom also likens polyazine to other heteroatom-containing conducting polymers: polypyrrole,[14-18] polythiophene,[19-26] and polyaniline.[27-36]

The oxidation (doping) of polymers with halogens has been widely used since polyacetylene was doped with iodine to give high levels of conductance.[37] The same behavior is seen in polypyrrole.[18] Permethylpolyazine doped with iodine only shows conductance levels similar to those of a semiconductor, with its highest level of conductance being $10^{-1}$ S cm$^{-1}$.[37] Examination of the spectroscopy should indicate what type of charge carrier is present within each polymer system. In this work, we present details of the NMR spectra of iodine-doped polyazines.

If the $^{13}C$ NMR spectra of an undoped and a doped polymer (or a nonconductive and a conductive form) are compared, no-

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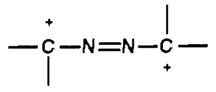
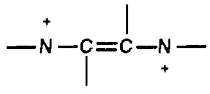
ticeable differences are observed. For example, the $^{13}C$ NMR spectra of both undoped polyacetylene[7] and undoped polypyrrole[15] exhibit a resonance due to alkene double bonds. Upon doping, the growth of a new resonance is observed. The new band, also due to alkenes, is more deshielded than the original resonance and is significantly broader.

Polyacetylene possesses a different type of charge carrier in comparison to polypyrrole, polythiophene, and polyazine. Polyacetylene has a degenerate ground state[3] and consequently a soliton charge carrier. In contrast, polypyrrole[14] and polythiophene[22] both have bipolaron charge carriers. A previous study[39] of the IR spectra and conductivity as a function of iodine doping showed that the charge carrier had a vibrational band at 1500 cm$^{-1}$, leading to two possible bipolaron structures: either the carbons bear the charge, structure A, or the nitrogens bear the charge, structure B, as shown. Neither the IR results nor a later theoretical study[40] was able to distinguish which carrier would be of lower energy.



A



B

The subject of this report is to identify the specific charge carrier, structure A or B, present in oxidized polyazines by $^{13}C$ and $^{15}N$ solid-state NMR spectroscopy. We find that the doped polyazines are diamagnetic, as required for bipolarons, so that excessive line broadening from unpaired spins is not a problem. A detailed analysis of the NMR data will show that structure B is the charge carrier; the nitrogens bear the positive charge. This article reports the first finding of a nitrenium cation, $-N^+-$, by solid-state $^{15}N$ NMR spectroscopy.

## Experimental Section

Solid-state NMR spectra were obtained at Lehigh University on a General Electric NMR Instruments GN-300 spectrometer operating at 75.4 MHz for $^{13}C$ and 30.4 MHz for $^{15}N$. A 7-mm Doty Scientific, Inc., probe was utilized at ambient temperature with sapphire rotors and Kel-F endcaps containing a sample volume of up to 0.35 cm$^3$. Spectra were obtained with cross polarization[41] and magic angle sample spinning.[42] Spinning speeds were measured between 3 and 5.3 kHz. Typical conditions included a single cross-polarization contact time of 1.0 ms and an acquisition time of 10–41 ms. Signal averaging of approximately 2000–41 000 transients improved the signal-to-noise ratio with a 2–4-s recycle time. Exponential line broadening equivalent to 100–200 Hz was applied before zero-filling and Fourier transformation. Maximum radio frequency field strengths were 1.6, 6.3, and 12.9 mT for protons, carbon, and nitrogen, respectively. $^{13}C$ chemical shifts are relative to TMS referenced to external adamantane,[43] with an estimated error of ±0.2 ppm for narrow peaks. For the broader peaks, chemical shift errors are correspondingly larger. $^{15}N$ chemical shifts are relative to $^{15}NH_4Cl$. Approximately 1 mg of $^{15}NH_4Cl$ was added to the doped permethylpolyazine as an internal reference for the $^{15}N$ NMR experiments.

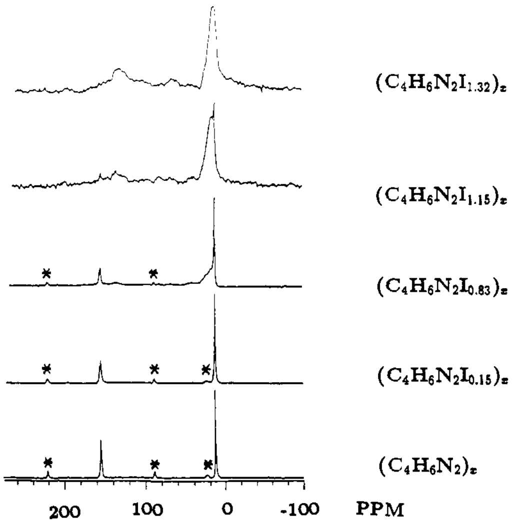


Figure 1. $^{13}C$ solid-state NMR spectra of $(-C_4H_6N_2I_{1.32}-)_x$, $(-C_4H_6N_2I_{1.18}-)_x$, $(-C_4H_6N_2I_{0.826}-)_x$, $(-C_4H_6N_2I_{0.148}-)_x$, and $(-C_4H_6N_2I_0-)_x$. Stars denote rotational sidebands. As the amount of iodine is increased, bands due to the polyazine segments decrease in intensity while features due to the bipolaron charge carrier increase in intensity.

Unsubstituted polyazine,[44] $(-N{=}CH{-}CH{=}N-)_x$, and permethylpolyazine, $(-N{=}C(CH_3){-}C(CH_3){=}N)_x$, and doped polymers[38] were prepared according to literature procedures.

Magnetic susceptibility measurements were conducted on a home-built Gouy balance at room temperature, using $Hg[Co(SCN)_4]$ as a reference. All of the doped polymers were found to be diamagnetic.

## Results

The doped permethylpolyazine has the general formula $(C_4H_6N_2I_y)_x$ with $y = 0$–$1.60$. Doping levels were found from elemental analysis. The chemical composition of the unsubstituted doped polyazine is rather complicated, having the general formula $[C_2H_2N_2(C_4H_8N_2O_4)_zI_y]_x$. The $C_4H_8N_2O_4$ moiety is 2,3,5,6-tetrahydroxypiperazine, a saturated defect or "bubble" found on about 15% ($z = 0.15$) of the repeat units along the polymer chain. This defect structure restricts the mobility of a charge carrier, so that these materials have very low conductivities. Nonetheless, the spectral characteristics of the iodine-doped unsubstituted polyazine in the double-bond region are analogous to those of the similarly prepared permethyl polymer.

It should be noted that the iodine-doping level, $y$, does not reflect the amount of charge on the polymer chain. Presumably, the iodine is in the form of $I_3^-$ (analogous to polyacetylene[6]), so that the charge per repeat unit is $y/3$. However, the structure of the iodine has not been verified, as yet. Furthermore, addition of

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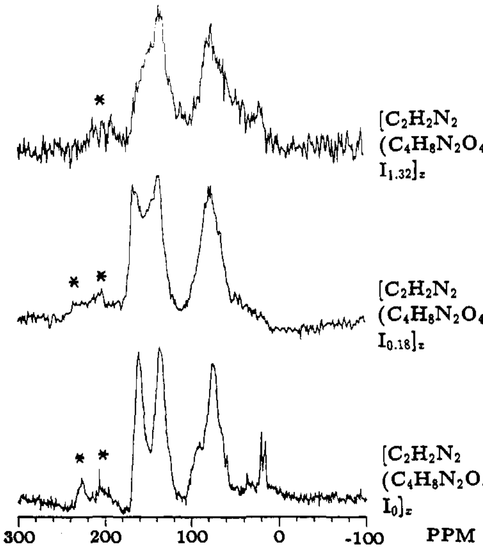

**Figure 2.** $^{13}C$ solid-state NMR spectra of $[-C_2H_2N_2(C_4H_8N_2O_4)_{0.15}I_{1.32}-]_x$, $[-C_2H_2N_2(C_4H_8N_2O_4)_{0.15}I_{0.18}-]_x$, and $[-C_2H_2N_2(C_4H_8N_2O_4)_{0.15}I_0-]_x$. Stars denote rotational sidebands. Increasing iodine content causes a decrease in the intensity of bands due to imines and an increase in intensity of features due to bipolarons. The resonances due to the sp$^3$ defect are unaffected by oxidation.

iodine is not reversible: some iodine can be removed by pumping on the more highly doped samples, but in no case can the iodine be removed entirely.

**$^{13}C$ Solid-State NMR Spectroscopy. Permethylpolyazine.** Undoped permethylpolyazine has been previously studied by $^{13}C$ solid-state NMR spectroscopy.[45,46] The spectrum of the permethylpolyazine, $y = 0$, exhibits two main features: one due to imine carbons at 155.2 ppm and one due to methyl groups at 12.6 ppm, as seen at the bottom of Figure 1.

A lightly doped sample, $y = 0.15$, has nearly the same spectrum as the undoped material. The resonance due to imines is centered at 155 ppm, and the feature due to methyls is centered at 12.5 ppm. The only difference is a slight broadening of the peaks in the doped polymer.

The spectrum in the middle of Figure 1, $y = 0.83$, shows both line width and chemical shift differences when compared to the previous two spectra. The intensity of the peak due to imines at 155 ppm has diminished, while a weak feature begins to appear at ~130 ppm, associated with charge carriers that have been formed. In the methyl region, a sharp peak due to methyls in unoxidized portions of the polymer is found at 12.1 ppm and a broader shoulder centered around 14 ppm due to methyls in oxidized portions of the polymer is observed.

The spectrum labeled $y = 1.15$ also shows the further evolution of the features associated with the charge carrier: a diminution of the intensity of the 155 ppm peak and an increase of intensity at 133 ppm. In the methyl region of the spectrum, the methyl peak is much broader and is clearly split into two peaks.

The final spectrum in the permethyl series has the highest doping level shown, with $y = 1.32$. This spectrum shows two major features. The double-bond region shows only *one* broad resonance centered at 133 ppm. The methyl region corroborates what is seen in the double-bond region, exhibiting the presence of only one peak centered at 16 ppm. The lack of sharp peaks at 12.4 and 155 ppm indicates that the polymer is close to "completely" oxidized; i.e., the majority of the chain can be structurally characterized as being in the bipolaron state.

Table I. $^{13}C$ NMR Chemical Shifts[a]

| polymer | $y$ | imine | methyl | charge carrier |
|---|---|---|---|---|
| permethyl- | 0 | 155.2 | 12.6 | |
| polyazine | 0.15 | 155 | 12.5 | |
| $(C_4H_6H_2I_y)_x$ | 0.83 | 155 | 12.1 | 133 |
| | 1.15 | 155 | 12.7 | 133 |
| | | | 15 | |
| | 1.32 | | 16 | 133 |
| unsubstituted | 0 | 161 | *b* | |
| polyazine | | 137 | | |
| $[C_2H_2N_2(C_4H_8N_2O_4)_{0.15}I_y]_x$ | 0.18 | 166 | *b* | |
| | | 138 | | |
| | 1.32 | | *b* | 135 |

[a] The last digit indicates errors in the chemical shift: ±0.2 or ±2 ppm. [b] Not applicable.

**Unsubstituted Polyazine.** A detailed $^{13}C$ solid-state NMR spectrum of unsubstituted polyazine has previously been reported.[43] The $^{13}C$ solid-state NMR spectrum of unsubstituted polyazine is shown at the bottom of Figure 2. The existence of a resonance in the sp$^3$ region of the spectrum at 75 ppm is due to a 2,3,5,6-tetrahydroxypiperazine (THP) defect contained within the polymer. A consequence of this is that the resonance due to imines has been split into two peaks: 137 and 161 ppm. The peak at 161 ppm is due to imines in the conjugated region whereas the peak at 137 ppm is due to imines that are located nearer the THP defect sites, the less conjugated region. The small peaks below 50 ppm are due to occluded solvent and end groups.

The middle spectrum in Figure 2, $y = 0.18$, depicts little difference when compared to the spectrum of the undoped sample. The feature due to THP has been unaffected at this low doping level. The final spectrum of Figure 2, $y = 1.32$, exhibits a single, broad, asymmetric resonance at 135 ppm, which is due to the formation of charge carriers. The resonance due to the THP defect is, again, affected very little, an indication that the structural integrity of the polymer is maintained upon iodine oxidation. The imine peak at 161 ppm is virtually gone, also indicating that the entire conjugated region of the polymer is in the bipolaron form.

Table I summarizes the $^{13}C$ NMR data for the two polymers. Upon doping, both polymers exhibit line broadening and most importantly they both possess a feature due to the presence of a charge carrier appearing in the same region of the spectrum, ~130 ppm. The unchanging nature of the defect peak in the $^{13}C$ NMR spectra of the unsubstituted polyazine is an indication that degradation of the polymer chain is minimal. In the methyl-substituted polymer, the methyl groups' chemical shifts change from about 12 ppm with low doping to about 16 ppm with high doping. Despite the differences in permethylated and unsubstituted polyazine, they both undergo oxidation (with iodine) and react in the same way. The oxidation removes imines from the polymer while a new band appears at ~130 ppm, due to the formation of the charge carrier.

**$^{15}N$ Solid-State NMR Spectroscopy.** Figure 3 shows the $^{15}N$ natural abundance spectra of undoped permethylpolyazine, $y = 0$, and the most heavily doped permethylpolyazine, $y = 1.60$. The undoped polyazine exhibits a single resonance at 324.8 ppm due to an imine nitrogen.[47] This is consistent with observing only one kind of carbon resonance in the imine region of the $^{13}C$ NMR spectrum. The spectrum of the doped polyazine exhibits a broad peak at 103 ppm due to formation of the nitrenium charge carrier. There also is evidence for additional shoulders at 115 and 140 ppm, although the signal-to-noise ratio does not permit unambiguous identification of these features. A peak is not observed in the imine region of the spectrum, ~320 ppm.

## Discussion

Upon doping, the peaks associated with the carbons in the delocalized $\pi$-electron system both shift and broaden. This can be interpreted in either of two ways. If the oxidation depletes the $\pi$ band to form a metal, the chemical shift changes are due to Knight shifts and the line broadening is due to Korringa type processes.[48] An alternate possibility is that the new chemical species are formed, i.e., bipolaron formation. In this case, the

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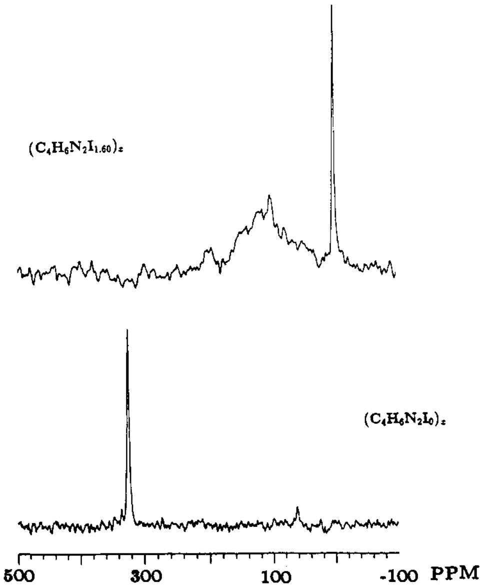

**Figure 3.** $^{15}N$ solid-state NMR spectra of $(-C_4H_6N_2I_{1.60}-)_x$ and $(-C_4H_6N_2I_0-)_x$. The sharp feature at 0 ppm is that of the internal reference, $^{15}NH_4Cl$. The spectrum of the undoped polymer exhibits a weak rotational sideband at 63 ppm; rotational sidebands should appear near 0 and 190 ppm in the spectrum of the doped material. The presence of the broad feature centered at 103 ppm confirms that the charge carrier is based on a nitrenium ion.

changes in chemical shift are due to the new chemical bonding and the increased line width is a result of the mobility of the charge carrier and possibly some heterogeneity in the polymer sample. The diamagnetism found in these samples eliminates the possibility of a partially filled band and supports the latter interpretation.

The oxidation of the polyazine with $I_2$ produces a new band in the IR spectrum at about 1500 cm$^{-1}$,[38,49] associated with charge-carrier formation. This band could be associated with either a N=N (A) or a C=C (B) bond.[39] From the IR data, then, it was only possible to propose that one of these two bipolaron charge carriers was formed. The $^{13}C$ NMR spectra should easily distinguish which charge carrier is present. If the charge carrier is A, a resonance due to the 3° carbocation should appear. On the other hand, if the carrier is B, then a resonance due to the alkene should appear. Tertiary alkyl carbocations[50] resonate at ~330 ppm vs TMS, while alkenes have resonances nearer 130 ppm. Clearly, our results indicate alkene formation, structure B.

This conclusion can be corroborated by the $^{15}N$ NMR spectrum. If an azo bond were present, A, a resonance at ~480 ppm (or at ~360 ppm, as seen for protonated diazo bonds vs $^{15}NH_4Cl$)[51] would be expected. However, if B were the bipolaron charge carrier, a nitrenium cation would be detected. The $^{15}N$ NMR spectrum of nitrenium cation has not been previously reported in the literature. The chemical shift of the nitrenium cation is expected to be shielded due to the nature of the electropositive charge present on the nitrogen. The presence of resonances in the 100–140 ppm region and the absence of a peak in the 300–500 ppm region confirms structure B as the charge carrier.

**Figure 4.** Calculated charge distribution of an isolated bipolaron in polyazine. The diameter of the circles is proportional to the amount of positive charge at that site. Closed circles are nitrogen atoms, and open circles are carbon atoms. Results are from the extended Hückel calculation of ref 40.

Extended Hückel calculations[40] predict that the bipolarons in polyazines should extend over three to four repeat units. Assuming the iodine is in the form of triiodide, $I_3^-$, and the average chain length is about 45 repeat units, the maximum doping level should be $y \simeq 1.5$–2. The $^{15}N$ spectrum for $y = 1.60$ has no peak in the 320 ppm region, indicating that no pure imine remains and that this is near a maximum doping level. But it is possible that at least three features are observed in the 100–150 ppm region. This is explained by the charge distribution of the bipolaron, as depicted in Figure 4. The positive charge is distributed primarily onto the nitrogen atoms, with about four different types of nitrogens expected. The $^{15}N$ NMR spectrum suggests evidence for three of these types of nitrogens.

This depiction of the bipolaron also explains the $^{13}C$ NMR spectrum. The bipolaron structure implies the presence of a few alkene moieties with only a small amount of charge localized at carbon sites. Thus, only small chemical shift changes around the alkene resonance can be expected. Given the smaller chemical shift range of carbon, the observation of only a single broad peak is in agreement with the $^{15}N$ results.

## Conclusion

Polyazines can be oxidized with iodine to form bipolaron charge carriers. The bipolaron has been studied by natural abundance $^{13}C$ and $^{15}N$ solid-state NMR spectroscopy, which explicitly shows that the nitrogens bear the charge. This is the first report of a nitrenium cation detected by $^{15}N$ NMR spectroscopy. Both the $^{13}C$ and $^{15}N$ NMR spectra suggest that the charge is delocalized over a number of repeat units, in accord with the usual depiction of charge carriers in polymers with delocalized electronic systems.

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