

# Iodine-Doped Polyazines: Evidence against Bipolarons and Nitrenium Ions<sup>1</sup>

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**Abstract:** The recent claim of the first isolation and <sup>15</sup>N NMR observation of the long-sought nitrenium ion has been revisited through extensive molecular-orbital calculations at the AM1, RHF/6-31G\*, and MP2/6-31G\* levels on neutral and cationic polyazine model systems. These data as well as a careful analysis of the available spectroscopic and conductivity data lead to the conclusion that no such nitrenium ions (bipolarons) are present. Oxidative doping of polyazines leads to irreversible reaction or structural rearrangement of the polymer through nearly collinear diazoalkane-like -C=N<sup>+</sup>=N- moieties. Formation of the latter, in which all atoms have complete octets, is energetically favored over a six-electron nitrenium ion. However, experimental evidence suggests this species undergoes further reaction or rearrangement. Calculations suggest that a dicationic nitrenium charge carrier, as originally proposed, would cause fragmentation of the polymer to nitrogen and acetylene, disfavoring this conductivity mechanism. Other possibilities are explored.

## Introduction

Nitrenium ions are of broad interest because of their importance as reactive intermediates,<sup>3,4</sup> their fundamental and mechanistic relevance as basic chemical moieties,<sup>3,5</sup> their implications in carcinogenesis,<sup>6</sup> and their spin interactions in triplet-singlet interconversions.<sup>7</sup> Like the more stable isoelectronic carbenium ions, nitrenium ions are highly reactive and usually inferred from reaction products and stereochemistries. Unlike carbenium ions, simple nitrenium ions had not been directly observed,<sup>8</sup> until a recent article claimed their isolation and first direct <sup>15</sup>N NMR observation.<sup>12</sup> Remarkably, these nitrenium ions were stable indefinitely at ambient temperature to atmospheric moisture and air.

Polyazine (-N=CH-CH=N-) <sub>x</sub> and permethylpolyazine (-N=C(CH<sub>3</sub>)-C(CH<sub>3</sub>)=N-) <sub>x</sub> react with iodine to form elec-



trically conductive materials.<sup>12,13</sup> Several experiments have probed the nature of the charge carrier in these systems. Magnetic susceptibility data show the doped materials are diamagnetic, which suggests dication (bipolaron)<sup>14</sup> formation rather than radical cation (polaron) formation. Two structural types of bipolarons in these materials are: a carbenium ion (A) or a nitrenium ion (B).<sup>15</sup> From <sup>13</sup>C and <sup>15</sup>N NMR chemical shifts, Chaloner-Gill et al.<sup>12</sup> assigned the carrier as B, a nitrenium based bipolaronic charge carrier.

Nevertheless, this assignment suffers in that carbenium ions are more stable than nitrenium ions, as evidenced by prior definitive NMR spectral observations of the former but not the latter. Indeed, the facile formation of carbocations from nitrenium ions by C → N alkyl migration is believed to be driven by the greater stability of the former.<sup>3</sup> In the polyazines a nitrenium ion implies oxidation of the more electronegative nitrogen, whereas the less electronegative carbon would intuitively be the preferred site of oxidation. To test the relative stability of carbenium versus nitrenium based dications in iodine-doped polyazines and to explore their structures, energetics, as well as conduction mechanism, we performed quantum mechanical calculations on model systems of the undoped and doped material.

## Results and Discussion

**a. Oxidation.** Initially 1, all-trans-1,4,5,8,9-pentaaza-1,3,5,7,9-decapentaene, was chosen as a balanced, unbiased model to add

(1) For a preliminary account, see: Dudis, D. S.; Yeates, A. T.; Kost, D.; Smith, D. A.; Medrano, J. *Polym. Prepr.* **1992**, *33*, 1166.

(2) (a) Wright Laboratories. (b) Ben Gurion University. (c) University of Toledo. (d) Adtech Corp.

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(6) Gassman, P. G.; Granrud, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1498 and references cited therein.

(7) (a) Gassman, P. G.; Cryberg, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 5176.

(b) Falvey, D. E.; Cramer, C. J. *Tetrahedron Lett.* **1992**, *33*, 1705. (c) Ford, G. P.; Herman, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 3987.

(8) The only reported directly observed nitrenium ions are highly resonance stabilized species, which may better be described as carbenium ions in superacid medium,<sup>9</sup> or as the filled-octet oxonium ions<sup>10</sup> and ammonium or iminium ions<sup>11</sup> in electrochemical oxidations leading to formal nitrenium ions.

(9) Olah, G. A.; Arvanaghi, M.; Surya Prakash, G. K. *J. Am. Chem. Soc.* **1982**, *104*, 1628.

(10) (a) Serve, D. *J. Am. Chem. Soc.* **1975**, *97*, 432. (b) Svanholm, U.; Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 1234.

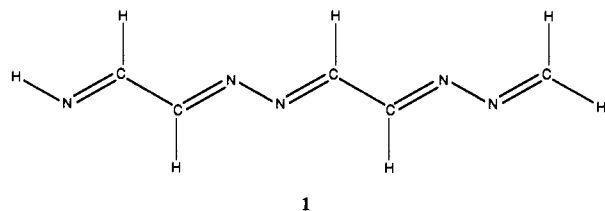
(11) Rieker, A.; Speiser, B. *Tetrahedron Lett.* **1990**, *31*, 5013.

(12) Chaloner-Gill, B.; Euler, W. B.; Mumbauer, P. D.; Roberts, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 6831.

(13) Euler, W. B. *Solid State Commun.* **1988**, *68*, 291.

(14) For general references on charge carriers in conducting polymers, see: (a) Brédas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309. (b) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183.

(15) Alternatively, one could envision one positive charge centered on a carbon and one on a nitrogen, but presumably one site is preferred over another due to such factors as electronegativity. This implies that only one type of atom will bear the charge in the polymer, to the extent that the charge is localized. Should a mixed charge situation arise, the calculations reported herein should be adequate to reveal that. Charge centers in structural types A and B could have more than one intervening double bond.



evidence to either carbon or nitrogen centered dication formation upon oxidation. It is balanced in two respects. First, as shown in Scheme I (vertically), the formal charges of the dication in **1** could be either completely internal (i.e., on nonterminal atoms) or internal-terminal.<sup>16</sup> Second, the horizontal relationships show that the number of intervening bonds between formal charge sites are identical (balanced) for carbon- or nitrogen-based dications (the structures in the right column are the same as in the left but rotated 180° to emphasize this point). As far as possible, the model was designed to be computationally tractable and unbiased with respect to charge separation and discrimination in favor of one site over another for charge centering. Furthermore, it seems reasonable that this is an adequately long segment to model polymeric structural properties; it contains two completely internal C—C and N—N units, minimizing end effects.<sup>17</sup> The nature of the charge centers is addressed herein by examination of the fully optimized neutral and dicationic **1**.

Simple double vertical ionization of **1**, as outlined above, is not sufficient to test for bipolaron formation. Double ionization (oxidation) corresponds to removal of two electrons from the delocalized highest occupied molecular orbital (HOMO), neglecting orbital relaxation. Since the conjugated molecular orbitals are delocalized over the entire molecule, the charge in the doubly ionized species would also be delocalized. Electronic and geometric relaxation subsequent to ionization, with charge pinning, are mandatory for carbenium or nitrenium formation.

Neutral **1** (Tables I and II) has distinctly short C=N double bonds and correspondingly long C—C and N—N single bonds. All three levels of theory, AM1, RHF/6-31G\*, and MP2/6-31G\*, are in good agreement for both neutral and dicationic **1**. Correlation slightly lengthens the N—N bond and shortens the C—C bond, making them more equivalent. It also lengthens the short C=N bonds, tending to even out the overall structure. The same effect is observed in polyene oligomers<sup>18</sup> and infinite *trans*-polyacetylene,<sup>19</sup> where correlation lengthens the double bonds and shortens the single bonds, thereby decreasing the bond length alternation. Optimizations at the MP2/6-31G\* level for molecules composed of second-row elements are generally of experimental accuracy.<sup>20</sup> The agreement of the self-consistent field (SCF) and post-SCF results, their consistency with results for *trans*-polyacetylene, and their faithful reproduction of model compound parameters (see Computational Details) strongly validate the computational results.

Surprisingly, the dicationic species showed gross differences from the neutral molecule. Neither one of the suggested models A and B provides a suitable structural description. The N—N bond lengths (Table I) of the dication are substantially shorter than those in the neutral species, within the range of a nitrogen-nitrogen double bond; furthermore, two of the C—N—N bond angles

(16) An internal-terminal charge centering could reflect Coulombic repulsion in the short oligomer rather than inherent stability of an ionic charge at terminal positions, but this would still be balanced for the question of nitrogen versus carbon based bipolarons.

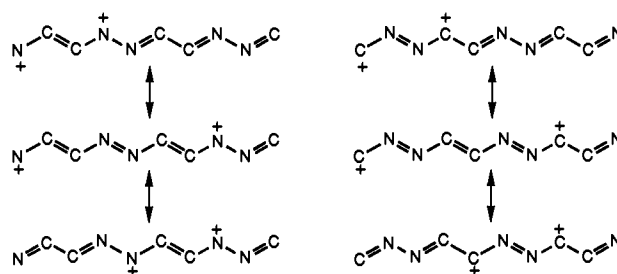
(17) For comparison, the C=C length of *trans*-polyacetylene at the C<sub>10</sub> oligomer length (same model length as used here) is within 0.001 Å of the polymeric value calculated at the RHF/6-31G\* level, indicating the internal geometry of **1** is close to that of an infinite system: Dudis, D. S.; Yeates, A. T. In preparation.

(18) Dudis, D. S. Unpublished results.

(19) Suhai, S. *Chem. Phys. Lett.* **1982**, *96*, 619.

(20) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

## Scheme I

Table I. Optimized Bond Lengths (Å) in Neutral and Dicationic **1**

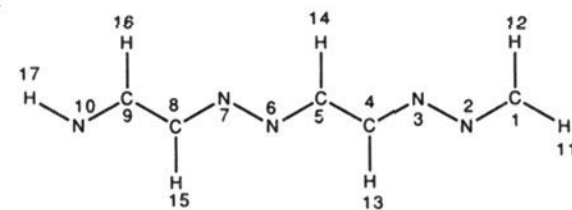
bond <sup>a</sup>	neutral			dication		
	AM1	6-31G*		AM1	6-31G*	
		RHF	MP2		RHF	MP2
1-2	1.2919	1.2544	1.2872	1.2756	1.2380	1.2584
2-3	1.3523	1.3885	1.4181	1.2039	1.1789	1.2119
3-4	1.3032	1.2580	1.2950	1.4393	1.4181	1.4120
4-5	1.4869	1.4671	1.4496	1.3639	1.3232	1.3535
5-6	1.3047	1.2588	1.2965	1.4444	1.4204	1.4122
6-7	1.3492	1.3831	1.4090	1.2017	1.1795	1.2136
7-8	1.3038	1.2582	1.2945	1.2886	1.2434	1.2628
8-9	1.4917	1.4744	1.4599	1.4967	1.5047	1.5064
9-10	1.2806	1.2538	1.2879	1.2743	1.2440	1.2758
1-11	1.1056	1.0754	1.0858	1.1215	1.0789	1.0924
1-12	1.1057	1.0786	1.0903	1.1214	1.0789	1.0925
4-13	1.1128	1.0781	1.0921	1.1151	1.0749	1.0901
5-14	1.1129	1.0782	1.0922	1.1158	1.0750	1.0901
8-15	1.1129	1.0784	1.0923	1.1240	1.0794	1.0914
9-16	1.1136	1.0824	1.0954	1.1161	1.0783	1.0920
10-17	0.9991	1.005	1.0267	1.0025	1.0070	1.0269

<sup>a</sup> Bonds between atoms numbered as in the structure above.

(those defined by the atoms labeled 1-2-3 and 6-7-8, respectively; Table II) have opened up considerably relative to the uncharged molecule to become almost collinear. The three-dimensional perspective drawing (Figure 1) shows the molecule is no longer planar. These structural features can be understood using the paradigm in Figure 2. The C=N=N functionalities resemble a diazo compound, with two adjacent (cumulative) double bonds.<sup>21</sup> The immediate implication of this structure can be seen in Figure 2; since the two cumulative double bonds lie in perpendicular planes, they force the other  $\pi$ -bonds to which they are conjugated to likewise occupy perpendicular planes. Thus, the oligomer (or polymer) chain can no longer have a single extended conjugated  $\pi$ -system, but rather is composed of short conjugated  $\pi$ -segments, perpendicular to each other.

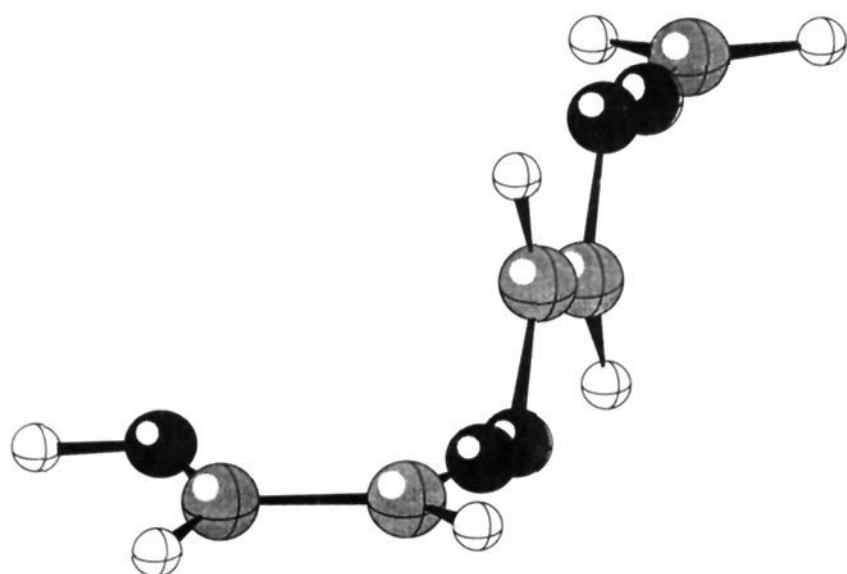
The formation of the diazoalkane-like moieties requires positive charge development on nitrogen, but with no electron-deficient nitrenium ions. Rather, a new bond is formed which satisfies the octet of the positively charged nitrogen. In the neutral oligomer, each nitrogen contributes one electron to the  $\pi$ -conjugation along the chain, but also possesses an additional nonbonding pair of electrons. Upon doping, a positively charged "hole" is first created on carbon or on nitrogen. However, this hole is an unstable electron-deficient center, which is "filled" by an adjacent nonbonding pair of electrons to form a new double bond with the adjacent nitrogen, as depicted in Figure 2. Consequently the

(21) This structure could best be described as an *N*-alkyldiazoalkane cation. A somewhat similar structure,  $[-C(C)=N=N=C(R)]_n^{2+}$ , with three cumulative double bonds and two adjacent positive charges on neighboring nitrogens, was suggested as a result of MNDO and VEH calculations: Burke, L. A.; Butler, R. N. Private communication, W. B. Euler.<sup>13</sup>

**Table II.** Optimized Bond Angles (degrees) in Neutral and Dicationic **1**


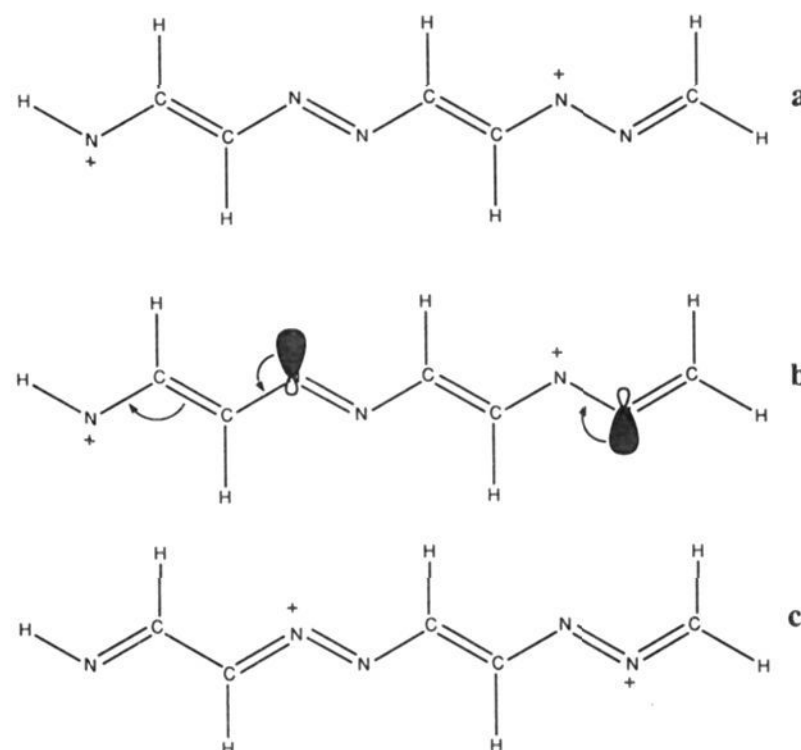
angle <sup>a</sup>	neutral			dication		
	6-31G*			6-31G*		
	AM1	RHF	MP2	AM1	RHF	MP2
1-2-3	119.375	112.402	110.080	166.589	170.889	170.934
2-3-4	118.600	112.683	110.346	123.449	118.981	119.013
3-4-5	118.451	118.912	118.236	116.768	115.226	114.387
4-5-6	118.474	119.066	118.306	117.057	115.380	114.443
5-6-7	118.361	112.722	110.444	122.788	118.147	118.278
6-7-8	118.392	112.814	110.620	165.811	167.272	161.974
7-8-9	118.658	119.068	118.419	124.656	119.555	114.846
8-9-10	120.103	119.492	118.561	120.225	116.206	115.647
11-1-2	115.590	118.275	117.625	119.938	118.712	118.442
12-1-2	127.988	122.574	122.516	119.927	118.736	118.428
13-4-3	125.273	122.658	122.365	120.114	119.823	121.257
14-5-4	116.318	118.348	119.394	123.128	124.836	124.343
15-8-7	125.469	122.859	122.670	117.425	117.055	119.189
16-9-8	115.053	115.596	115.960	110.683	115.358	115.096
17-10-9	115.340	111.767	109.927	119.262	113.719	112.118

<sup>a</sup> Angle defined by the three atoms numbered as in the structure above.

**Figure 1.** A perspective view of optimized dicationic **1** featuring the collinear C=N=N moieties and the mutually perpendicular conjugated segments.

doped polyazine would not be expected to show enhanced conductivity of the same order of magnitude as *trans*-polyacetylene or support mobile dicationic charge carriers. Indeed, the conductivity levels shown by iodine-doped permethylpolyazine are lower than those of the presumably analogous polyacetylene.<sup>22,23</sup>

While clearly the diazoalkane-like compound with its complete octets is more plausible than a nitrenium ion, the stability of the product remains an open question. Alkyl diazonium compounds are exceedingly unstable. The first crystal structure of a vinyl diazonium salt was only recently reported.<sup>24</sup> Aryl diazonium salts are stable and isolable. However, *N*-alkylated diazonium compounds or *N*-alkylated diazoalkanes are unknown.<sup>25</sup> Our results show that the *N*-alkyldiazoalkane structure in the present case is at least a locally stable stationary point on the potential-energy hypersurface. The calculations do not indicate the

**Figure 2.** Model-doped polyazine: (a) doubly charged **1**, initial charges may be on nitrogen or carbon; (b) nonbonding lone pairs on nitrogens form new double bonds with electron-deficient atoms; (c) resulting (calculated) structure of dication **1**, featuring "diazoalkane-like" moieties.

activation barrier separating this species from its decomposition products. Some stability may be gained by the conjugation of the diazoalkane-like carbon (when it is not a terminal carbon) with the adjacent C=N bond, in analogy to the relative stability of diazo ketones. Nonetheless, the possibility that the doped polymer may undergo further chemical modification cannot be ruled out. Indeed the irreversibility reported for the doping,<sup>12</sup> in contrast to reversibility in polyacetylene, suggests rearrangement or reaction may be occurring. Furthermore, the pristine polymer is reported<sup>26</sup> to melt by 320 °C, but the iodine-doped material loses iodine and decomposes at 320 °C without melting. This also suggests that doping is disrupting the polymer.<sup>27</sup>

The <sup>13</sup>C NMR imine signal shifts upfield upon addition of iodine to the permethylpolyazine.<sup>12</sup> Since carbenium ion resonances are farthest downfield of all <sup>13</sup>C resonances (*vide infra*),<sup>28a</sup> the observed shift rules out the carbenium charge carrier, A. From this shift Chaloner-Gill et al. concluded that the doubly-bonded carbons do not suffer major changes upon doping, assigning model B as the carrier. However, in B the carbons have electron-deficient nitrenium ions as next neighbors and would, therefore, be subject to substantial electron withdrawal and consequent significant downfield shifts. Such shifts are well documented for carbons adjacent to carbenium ions.<sup>28a</sup> The <sup>13</sup>C NMR results thus exclude A and B.

The formation of a diazoalkane-like structure, as suggested by the calculations, is in better agreement with the experimental result. This structure contains a well-defined C=C bond. The major <sup>13</sup>C NMR peak (133 ppm) for the doped polymer is in excellent agreement with shifts from other alkenes substituted with electronegative elements. For example, the reported shifts for the  $\alpha$  and  $\beta$  carbons of (CH<sub>2</sub>=CH)<sub>2</sub>SO<sub>2</sub> are 137.7 and 131.3 ppm, respectively.<sup>28b</sup> The calculated structure also has a carbon

(25) An *N*-alkylated diazoalkane has been mentioned in the literature once, as a postulated unstable intermediate in the oxidation of azines: Paredes, R.; Bastos, H.; Montoya, R.; Chaves, A. L. *Tetrahedron* **1988**, *44*, 6821. Analogous *N*-metal rather than *N*-alkyl complexes do exist, and have been reported recently for Rh and Ir: Wolf, J.; Brandt, L.; Fries, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 510. Only few other such complexes have been described: (a) Albini, A.; Kisch, H. *Top. Curr. Chem.* **1976**, *65*, 105. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.

(26) Hauer, C. R.; King, G. S.; McCool, E. L.; Euler, W. B.; Ferrera, J. D.; Youngs, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5760.

(27) The melting behavior would also be consistent with other processes; e.g., the release of iodine (or HI) in the thermal process is accompanied by cross-linking or further reaction resulting in decomposition rather than melting.

(28) Levy, G. C.; Nelson, C. L. *Carbon-13 NMR for Organic Chemists*; Wiley: New York, 1972: (a) p 136; (b) p 63.

(22) Hasegawa, S.; Oku, M.; Shimizu, M.; Tanaka, J. *Synth. Met.* **1990**, *38*, 37.

(23) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chaing, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578.

(24) Glaser, R.; Chen, G. S.; Barnes, C. L. *Abstracts of Papers*, 203rd National Meeting of the American Chemical Society, San Francisco; American Chemical Society: Washington, DC, 1992; ORG-221.

which remains part of a C=N bond. It is subject to two opposing effects: the proximity of a positively charged nitrogen which may cause deshielding, and allyl-type resonance  $[-C=N^+ \leftrightarrow N^+ \leftrightarrow -C-N^+ \equiv N^+]$  which may place some of the lone-pair electron density from nitrogen on carbon, producing an opposing shielding effect. As a result, a smaller change in  $^{13}\text{C}$  chemical shift is anticipated. The observed spectra support formation of C=C in the polymer and consumption of C=N. The signal is broad enough to contain C=N=N as well as residual C=N, which should also be present.

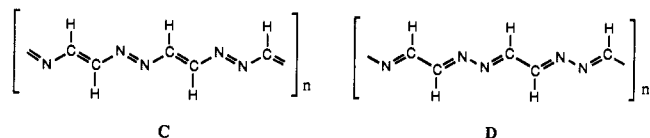
Infrared spectral evidence corroborates the formation of C=C in the doped materials. The infrared spectra of several per-C-methylated polyazine oligomers, the pristine polymer, and the iodine-doped material have been reported.<sup>13,26</sup> The pre- and postdoping spectra are virtually identical, which argues against gross degradation of the polymer upon doping. The vibrations related to the CH<sub>3</sub> groups could be discounted since they would probably not be very perturbed in cross-linking or other reactions. However, the peak assigned to the N-N stretch remains intact, and a new peak 65 cm<sup>-1</sup> lower than the C=N stretch frequency appears, precisely where one would anticipate a C=C stretch band for such compounds.

The most troubling observation for a nitrenium ion assignment is, in fact, the  $^{15}\text{N}$  NMR, upon which this assignment was originally made. There are no previously reported  $^{15}\text{N}$  NMR spectra for conventional nitrenium ions.<sup>29</sup> However, by analogy with carbenium ions, the reported shift rules out such a nitrenium ion. Carbenium ions are the most deshielded of all carbons.<sup>28a</sup> That their  $^{13}\text{C}$  NMR resonances are further downfield than any other type of carbon makes intuitive sense, since they have only six valence electrons and are positively charged. The  $^{13}\text{C}$  NMR of oxidatively doped polyacetylene shows just such a downfield shift from 127 ppm (undoped) to ca. 165 ppm (doped).<sup>30</sup> Thus, one would expect a nitrenium ion to be shifted substantially downfield from its precursor. The reported  $^{15}\text{N}$  shift is, in fact, upfield by  $\sim 200$  ppm. The  $^{15}\text{N}$  NMR spectrum for a mesomerically stabilized nitrenium ion has been reported ( $\text{Ph}_2\text{C}^+ \leftrightarrow \text{C}=\text{N} \leftrightarrow \text{Ph}_2\text{C}=\text{C}=\text{N}^+$ ).<sup>9</sup> In this example, all of the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  resonances shifted downfield relative to the cyanohydrin precursor. Since there is little geometric change from cyanohydrin to its nitrenium ion and little postulated change in B, similar changes in the chemical shifts would be anticipated. The  $^{15}\text{N}$  NMR also strongly argues against a nitrenium ion.

The assignment of the (experimental)  $^{15}\text{N}$  NMR chemical shifts are ambiguous for (calculated) dicationic 1. Those for linear, dicoordinate nitrogens of diazo compounds (with formal positive charges on the nitrogens) range from 220 to 310 ppm.<sup>31</sup> The shifts for the terminal nitrogens in such compounds (similar to the N-alkyl nitrogen of dicationic 1 but without the alkyl) range from 300 to 450 ppm, while shifts for diazobenzenes are  $>500$  ppm. Dicationic 1 might thus have two  $^{15}\text{N}$  NMR signals, one around 220–310 ppm and one substantially farther downfield. Chaloner-Gill et al. reported a normal azine signal at 324.8 ppm for the undoped polymer and a  $\sim 200$ -ppm upfield shift to 103 ppm for the doped material, although the latter is significantly broadened. While the upfield shift of the  $^{15}\text{N}$  NMR signal rules out a nitrenium ion, the spectrum is not unequivocally consistent with dicationic 1. Since  $^{15}\text{N}$  NMR resonances are very sensitive to coordination number and hybridization of the nitrogen, and since no suitable models are available for dicationic 1, a definitive analysis of the spectrum cannot presently be made.

**b. Conduction Mechanism.** Mobile bipolaronic charge carriers, such as the nitrenium ions previously invoked, necessarily entail

molecular switching which would interconvert the two forms of the polymer, C and D, in the vicinity of the carrier. Analogous



switching occurs via dicationic (bipolaronic) charge migration in *trans*-polyacetylene.<sup>32</sup> Thus the relative stabilities of C and D are critical to the viability of this conduction mechanism. A facile switch would be noteworthy since molecular switches are of great interest for use in opto-electronic signal processing.<sup>33</sup>

The relative stabilities of C and D were investigated by AM1 calculations employing periodic boundary conditions (i.e., the infinite limit) to examine the possibility of molecular switching. Form D gave the following parameters: C-C 1.478 Å, N-N 1.353 Å, C=N 1.308 Å, C-N-N 119.02°, and N-C-C 118.75°, in good agreement with the central portions of 1. The alternate form C proved more troublesome. Attempts to optimize all structural variables converged to D, even if set initially to those values anticipated for C. Use of fixed, reasonable C=C and N=N values (1.341 Å and 1.233 Å, respectively, obtained as described in Computational Details) with unconstrained C-N distances disrupted the molecule during optimization. Analysis showed that the optimization terminated with a C-N distance of 4.78 Å and that the polymer had fragmented into N<sub>2</sub> and acetylene. Computationally the polymer prefers form D and no molecular switching seems viable. Average experimental thermochemical bond energies give backbone enthalpies per unit cell of 393 (from C) and 415 (from D) kcal mol<sup>-1</sup>,<sup>34</sup> corroborating the theoretical results. Since unstable species are amenable to study by quantum methods, fragmentation in such a calculation argues strongly against the existence of C. More importantly, conductivity via migration of dicationic (bipolaron) charge centers would imply such switching and likely lead to decomposition of the material. This result casts doubt on the original interpretation of the conduction mechanism.<sup>12</sup>

If doping disrupts conjugation in polyazines, the mechanism of conductivity remains a question. However, we note that electrically conductive iodine-doped systems need not have extensively conjugated polymer backbones. Nonconjugated polymers, such as polyisoprene, can be doped by iodine to conductivity levels similar to those reported for the polyazines ( $\sim 10^{-1}$  s cm<sup>-1</sup>).<sup>36</sup> The conduction mechanism in these systems has been the subject of dispute,<sup>37</sup> but it is clear that the materials are not conjugated. The computational,  $^{13}\text{C}$  NMR, and IR data given above all indicate the formation of C=C bonds upon iodine doping. These nonconjugated C=C bonds could react with additional iodine to yield conducting materials analogous to iodine-doped polyisoprene. This scenario implies an induction in the conductivity versus dopant concentration curves. Indeed, this plot for permethylpolyazine<sup>26</sup> is very suggestive of such an induction during which double bonds could be forming, whereas that for poly(dimethylbutadiene)<sup>36</sup> shows no such induction. The presence of nonconjugated double bonds with iodine dopant would be sufficient to account for the conductivity without recourse to mobile nitrenium ions (bipolarons) in a conjugated polyazine backbone.

(32) Medrano, J. A.; Dudis, D. S. *Synth. Met.* **1992**, *49*, 231.

(33) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztoła, D.; Gaines, G. L., III; Wasielewski, M. R. *Science* **1992**, *257*, 63.

(34) Form C has one N=N, one C=C, and two C-N per cell, while D has two C=N, one N-N, and one C-C. One arrives at the quoted backbone enthalpies by using the following bond energies (kcal mol<sup>-1</sup>):<sup>35</sup> C=C 147, N=N 100, C=N 147, C-C 83, N-N 38, C-N 73.

(35) Jolly, W. L. *Modern Inorganic Chemistry*; McGraw-Hill: New York, 1984.

(36) Thakur, M. *Macromolecules* **1988**, *21*, 661.

(37) Shang, Q.-Y.; Pramanick, S.; Hudson, B. *Macromolecules* **1990**, *23*, 1886. Suh, D. M.; Wnek, G. F. *Polym. Prepr.* **1990**, *31*, 410. Calvert, P. *Nature* **1988**, *333*, 296.

(29) Cf., however, ref 9, in which the  $^{15}\text{N}$  NMR spectrum of  $\text{Ph}_2\text{C}=\text{C}=\text{N}^+$  was reported.

(30) Peo, M.; Foerster, H.; Menke, K.; Hocker, J.; Gardner, J. A.; Roth, S.; Dransfeld, K. *Solid State Commun.* **1981**, *38*, 467.

(31) Levy, G. C.; Lichter, R. L. *Nitrogen-15 NMR Spectroscopy*; Wiley: New York, 1979.

## Conclusion

The structural resemblance of polyazine to polyacetylene, combined with its superior stability toward oxygen, made this polymer an ideal target for the search of better conducting materials. However, the reported conductivity of doped polyazine does not approach that for polyacetylene. Our results show that the presence of nonbonding electrons in the polymer chain of polyazine circumvents the formation of bipolarons which might have been expected upon doping. Rather than the postulated nitrenium ion, our results indicate oxidation lead to diazoalkane-like collinear  $C=N^+=N$  moieties, which apparently react further. The data (experimental and computational) indicate  $C=C$  bonds in the doped product. The overwhelming propensity of second-row elements to obey the octet rule seems to preclude nitrenium ion formation in these systems. We are exploring the implications of these results for other systems. The conduction mechanism requires further study. Nevertheless, conductivity in organic systems is not necessarily an indication of ionic charge carriers or extended conjugation.

## Computational Details

Semiempirical AM1 calculations were performed using MOPAC 6.0.<sup>38</sup> The optimized geometries<sup>39</sup> were utilized as the starting geometries for

(38) MOPAC 6.0 Version 6, 1990, A General Molecular Orbital Package. Stewart, J. J. P. *QCPE* 1983, 455.

(39) Neutral **1**, at the AM1 level, tended to coil and lose its coplanarity. At the ab initio levels, however, neutral **1** converged to a coplanar geometry. Therefore, in the AM1 calculations of this species, planar geometry was imposed. There were no geometric constraints imposed on dicationic **1** at any level of theory.

(40) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90*; Gaussian, Inc.: Pittsburgh, PA, 1990.

ab initio optimizations with the Gaussian-90 suite of programs.<sup>40</sup> These utilized the 6-31G\* basis set<sup>41</sup> for neutral and dicationic species. The restricted Hartree-Fock (RHF) formalism was used throughout since both the neutral and the doped polymers are reported to be diamagnetic.<sup>12,42</sup> Calculated frequencies were all positive, indicating the structures are minima. Both the neutral and dicationic species were further optimized with corrections for electronic correlation via second-order Moller-Plesset perturbation theory (MP2).<sup>43</sup>

To validate the structural results, the polyazine model compound (*E*)-2,3-butanedione dihydrazone,  $H_2NN=C(CH_3)C(CH_3)=NNH_2$ , was optimized at the AM1 and RHF/6-31G\* levels. The results are in excellent agreement with the structure found in a crystallographic study.<sup>26</sup> Details will be published elsewhere.

Polymeric (infinite chain) calculations on C and D were performed at the AM1 level using MOSOL,<sup>44</sup> the solid-state analogue of MOPAC. Form C reverted to form D spontaneously in a number of different attempts. Finally, the  $N=N$  and  $C=C$  distances were obtained by optimizing (AM1) the geometries of (all-trans)  $H_2C=CH-N=N-CH=CH_2$  and  $HN=N-CH=CH-N=NH$  and utilizing the central  $N=N$  (1.233 Å) and  $C=C$  (1.341 Å) distances, respectively. These distances were then held constant in the polymer and all other geometrical variables optimized with the molecule held planar.

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(41) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* 1973, 28, 213.

(42) In general, nitrenium ions, like carbenes, can be singlets or triplets. See ref 7 for discussions of the stabilities of various singlet and triplet nitrenium ions.

(43) Moeller, C.; Plesset, M. S. *Phys. Rev.* 1934, 46, 818. Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* 1975, 9, 229.

(44) Dewar, M. J. S.; Yamaguchi, Y.; Suck, S. H. *Chem. Phys.* 1979, 43, 145. The implementation used herein was modified by J. Medrano and R. Bohicchio to include the AM1 Hamiltonian.