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Polyazacetylene: Metallic conductor versus Mott insulator

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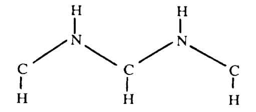
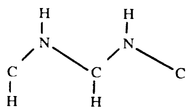
Polyazacetylene, $(CHNH)_n$, has been recently proposed as a tentative metallic conductor. The present work suggests that it should be considered as an antiferromagnetic Mott insulator. A Heisenberg Hamiltonian has been extracted from *ab initio* molecular-orbital configuration-interaction calculations on the (H)CH-NH-HC(H) unit and used to treat finite linear chains. Both effective Hamiltonian and *ab initio* calculations show that a dimerization takes place in this model system.

A recent paper[1] suggests that polyazacetylene (PAzA) (scheme 1) could be an organic metallic conductor. This system differs from polyacetylene (PA) by substituting one CH group among two by a NH group. The π band is then $\frac{3}{4}$ filled. The authors have performed self-consistent-field (SCF) crystal-orbital complete neglect of differential overlap calculations on a regular planar *trans* chain and they found no bond alternation, i.e., no Peierls distortion of the type in scheme 2:



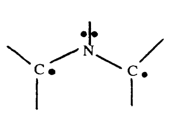
Scheme I



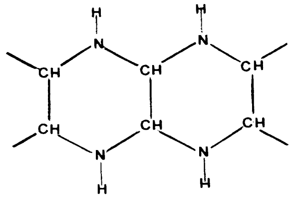
Scheme 2

All bonds are equal to 1.372 Å. Furthermore, the monoelectronic levels exhibited no band gap between occupied and vacant molecular orbitals (MO's), and the density of states at the Fermi level was nonnegligible. The authors therefore concluded that this system should be a metallic conductor (if it might exist as a stable planar system).

From a chemist point of view, this chain is essentially a polyradicalar system,



with two π electrons on each nitrogen atom, and one unpaired electron on each carbon atom. The nitrogen lone pair should break or restrain the π delocalization, while the carbon atoms should keep a large radicalar character. This weaker delocalization may result in two effects: (i) a nonplanarity of the system to diminish the repulsion between adjacent and second-neighbor groups, and (ii) a high chemical reactivity leading to the construction of saturated polymers by constituting, for instance, six-membered rings between adjacent chains:



Besides these "practical" problems, the main basic question concerns the electronic properties of this hypothetic linear chain. Multiradicalar systems are known to give a zero band gap in the monoelectronic picture, and even a high density of states at the Fermi level, but they are also known to be strongly correlated. The Mott insulators cannot be treated through monoelectronic pictures, and their properties are better described by Heisenberg Hamiltonians.[2]

The above-mentioned biradicalar character of the CH-NH-CH unit led us to research the relevant Heisenberg Hamiltonian for the study of PAzA. One should remember first that conjugated hydrocarbons, such as polyacetylene, may be treated efficiently through *ab initio* Heisenberg Hamiltonians.[3] Such Heisenberg Hamiltonians restricted to exchange couplings between adjacent atoms have been extracted from accurate *ab initio* molecular-orbital configuration-interaction (MO-CI) calculations on ethylene. Two distance-dependent parameters, $R(r)$ and $g(r)$, are sufficient to define a tight-bonded Heisenberg Hamiltonian:

$$H=\sum_{\substack{i<j\\ \text{bonded}}} R(r_{ij})+g(r_{ij})(\,|\,i\bar{j}-\bar{i}j\,\rangle\langle\, i\bar{j}-\bar{i}j\,|\,) \qquad (1)$$

valid for any conjugated hydrocarbon. The ground-state conformation may be optimized by minimizing the energy and the neutral excited states may be determined as well. The accuracy for calculated bond lengths and spectra is excellent, and asymptotic behaviors for PA have been extrapolated from the study of finite linear polymers.

Since Heisenberg Hamiltonians may be applied to linear polymers which are more conjugated than PAzA, the treatment of the later system through a magnetic model should be relevant. Accurate MO-CI calculations have been performed on the two lowest eigenstates of the

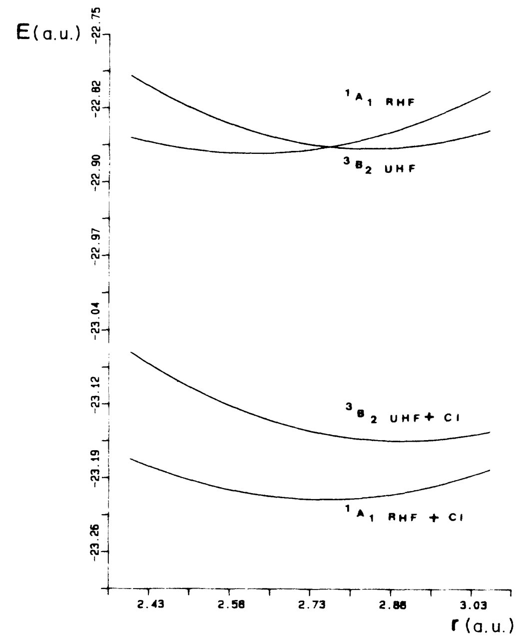


FIG. 1. Lowest potential energy curves for the CH_2-NH-CH_2 fragment. Upper part: monoelectronic description. Lower part: correlated description.

CH_2-NH-CH_2 planar diradical. These two states are the singlet (b^2a^2) $^1A_1$ state and triplet (baa') $^3B_2$ state. They are essentially neutral in the sense of valence-band (VB) theory and their potential-energy surfaces define a Heisenberg Hamiltonian [Eq. (1)] with

$$R(r_1,r_2)=E_3(r_1,r_2)$$

and

$$2g(r_1,r_2)=E_3(r_1,r_2)-E_1(r_1,r_2)$$

depending on the two C-N distances (or on their mean value r and difference Δr). Parabolic fittings are given in Fig. 1.

The ground state is singlet, and the exchange coupling is therefore antiferromagnetic. The singlet-triplet separation is rather weak (1.77 eV for the adiabatic transition), weaker than in ethylene.

This effective Hamiltonian has been constructed and exactly diagonalized in a study of the planar geometry of H_2C-$(NH$-$CH)_nH$ chains. We actually verified that there was no tendency to dimerize according to scheme 2, but a dimerization involving larger subunits takes place (scheme 3).

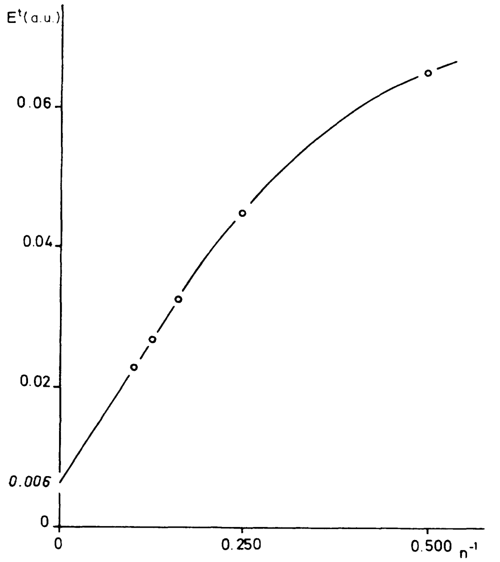
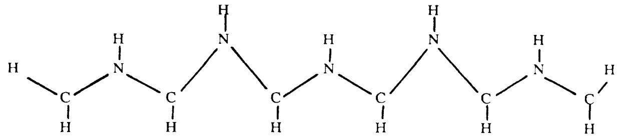
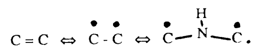


FIG. 2. Chain length dependence of the $^1A_1 \rightarrow {}^3B_2$ lowest vertical transition energy in the $H(CH$-$NH)_{n-1}CH_2$ series.



Scheme 3

The optimized distances up to C_{10} are reported in Table I. This dimerization is rather weak, but it should again create a band gap in the monoelectronic picture. One may notice that it is isomorphic to the PA Peierls distortion since the C-N-C unit is analogous to a C=C double bond:



$$C{=}C \Leftrightarrow \dot{C}\text{-}\dot{C} \Leftrightarrow \dot{C}\text{—}\overset{H}{N}\text{—}\dot{C}.$$

In order to check these results, restricted Hartree-Fock *ab initio* calculations have been performed on the butadiene analog

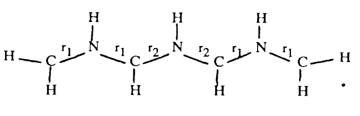


TABLE I. Optimized C-N interatomic distances in a $H_2C(N$-$CH)_nH$ linear chain. $R_{i(i+1)}$ is related to the C—N bond lengths of the C_i-N-C_{i+1} subunit.

			R (Å)		
n	R_{12}	R_{23}	R_{34}	R_{45}	R_{56}
4	1.477	1.505			
6	1.478	1.504	1.481		
8	1.478	1.504	1.482	1.502	
10	1.479	1.504	1.483	1.502	1.484

TABLE II. RHF *ab initio* energies obtained on the butadiene analog H_2C-NH-CH-NH-CH-NH-CH_2 as a function of r_1 and r_2.

r_2 (Å) \ r_1 (Å)	Energy (a.u.) 1.35	1.40	1.45
1.35	−54.1712	−54.1826	−54.1758
1.40	−54.1870	−54.1975	−54.1899
1.45	−54.1936	−54.2033	−54.1949
1.50	−54.1930	−54.2021	−54.1930

as a function of the bond lengths (r_1 and r_2) of internal and external subunits (keeping the CH and NH bond lengths at their optimized value for H_2C-NH-CH_2). The results appear in Table II and confirm the tendency to dimerization predicted by the Heisenberg Hamiltonian. The bond-length alternation at the SCF level ($r_2 - r_1 = 0.07$ Å) is longer than the one predicted from the Heisenberg Hamiltonian ($r_2 - r_1 = 0.03$ Å) which is extracted from CI calculations. This discrepancy simply reflects the larger difference between the triplet and the singlet equilibrium bond lengths in the elementary subunit [r(triplet)$-r$(singlet) is 0.15 Å at the SCF level and 0.07 Å at the CI level].

This unusual dimerization distortion has been already predicted from general considerations by Bozovic[4] who assigned such distortion to Q_1 and Q_2 modes. The author suggested a substantial bond length alternation ($\Delta R > 0.05$ Å). This value falls between our Heisenberg and SCF estimates.

Even with equal bond lengths PAzA would not be a conducting system, as demonstrated by Lieb and Wu,[4] due to the electronic correlation: the first dipolarly allowed excited state would be at a nonzero distance from the ground state. Heisenberg Hamiltonians cannot provide such ionic excited states but we have calculated the energy for the lowest triplet state as a function of chain lengths and vertical transition energies are pictured in Fig. 2. One may see that even the lowest neutral triplet state remains at a nonzero energy above the ground-state singlet. The asymptotic limit for large n is however quite small (0.16 eV versus 0.87 eV for polyacetylene).[3] The ionic singlet excited state would necessarily be above that energy, which confirms that the model chain cannot be viewed as a monodimensional metallic conductor.

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