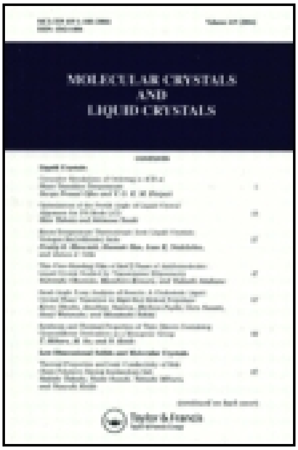

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On Trapping of Phase Kinks in Polyacetylene

M. Kertesz [a] , P. R. Surján [a] [c] & K. Holczer [b]

[a] Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525, Budapest, Hungary

[b] Central Research Institute for Physics, Hungarian Academy of Sciences, H-1525, Budapest, Hungary

[c] CHINOIN pharm. and chem. works, H-1325, Budapest, P.O.B. 110, Hungary

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ON TRAPPING OF PHASE KINKS IN POLYACETYLENE

M. KERTÉSZ, and P.R. SURJÁN*
Central Research Institute for Chemistry,
Hungarian Academy of Sciences, H-1525 Budapest, Hungary

K. HOLCZER
Central Research Institute for Physics,
Hungarian Academy of Sciences, H-1525 Budapest, Hungary

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A microscopic mechanism for trapping of solitons in polyacetylene is given. Molecular orbital calculations with full geometry optimization using semi-empirical tight-binding Hamiltonian for finite chain indicate that the neutral spin-caying phase kink is attracted by an energy on the meV scale to carbon atoms having a non-hydrogen side-group in accordance with recent magnetic resonance experiments. The oxygen induced trapping of the spins is also discussed.

Energetics of soliton-like phase-kinks in all-*trans*-polyacetylene[1-3] /bond-length alternation defects[4]/ is relevant with respect to phenomena involving the dynamics of these mobile defects. Recent magnetic resonance experiments revealed the coexistence of two types of spins in the undoped $/CH/_x$[5], namely:

i. highly mobile spins whose properties can be described by the proposed neutral soliton picture[1,2].

ii. static spins whose mobility is several orders of magnitude smaller than those of the mobile ones.

However, both spins have EPR lineshapes indicative of a large degree of delocalization over several C atoms. Their relative concentration in a given sample depends on the preparation conditions, mainly on the oxygen content[5], and on temperature, too. It has been shown that at low temperatures the mobile spins are trapped with a trapping energy around 4 meV[6]. Exposure to air causes two distinct effects:

a. For short time a rapid decrease of the total number of spins is observed. The fast increase of the linewidth indicates that the number of mobile spins is the one which is decreasing.

b. After a few hours the total number of spins starts to increase slowly. This increase has been monitored up to three days when the process still did not stop. The depth of the minimum /about one hour after opening to air/ was around 30%, and after three days the susceptibility value was around the same as originally. Meanwhile the static spin concentration raised to about 50% from the original 7%. The final oxygen concentration is supposed to be a few per cent.

The exposure to air results in complicated reactions among which these experiments could distinguish two processes[7]. The first fast one resembles the proposed soliton doping process[1,2] /the initial reversibility favours this picture, too/. The second slow process is probably an oxidation of conjugated bonds,thus it is reducing the conjugation length.

In this paper we discuss a possible microscopic mechanism of trapping which explains the above experimental findings. We use the molecular tight-binding Hamiltonian of Longuet--Higgins and Salem[8] /LS/ and determine all C-C bond lengths fully variationally. We show that the soliton in a $/CH/_x$ chain treated in this way can be trapped by a carbon atom whose hydrogen is substituted by another group.

LS treat only the $2p_z$ orbitals explicitly and represent the σ-orbitals by an effective potential. Their extension of the classical Hückel Hamiltonian is capable of describing the Peierls-distortion of $/CH/_x$ as well as the structure of conjugated hydrocarbons realistically[8]. The π-transfer integrals of the n-th bond between atom n and n+1 depends on the length of this bond r_n in an exponential way[8]. r_n is taken proportional to the n-th bond order

/a quantity calculated from the molecular orbitals characterizing the charge density in the bond region/. Bonding due to σ-electrons is represented by the potential f/r/ which is added to the usual Hückel Hamiltonian of the π-electrons

$$H = \sum_{n,\sigma} \beta_n a^{+}_{n,\sigma} a_{n+1,\sigma} + \sum_{n} f/r_n/$$

where $a^{+}_{n,\sigma}$ is a reaction operator for an electron in orbital $\chi_n/r/$ with spin σ.

We have applied this method to finite chains of $/CH/_{2m+1}$ with closed end boundary condition for m = 40[9]. A few calculations have been performed by optimizing <u>all</u> r_n-s. Using this model a soliton is locked in the chain. If we define the size of the soliton by counting the number of C atoms involved in the soliton formation we find the soliton size is around 30-40 atoms.

It is not easy to define unambigous model for calculating the total energy of the system as the soliton moves in the chain. We have studied the effect of an impurity atom at the p-th site /<u>Fig. 1.</u>/ in order to estimate total energy changes as the phase kink approaches this atom. We have frozen in the fully optimized geometry of a phase kink and than perturbed the p-th atom changing the ionization potential $/\alpha_p/$ of the perturbed C atom, by adding

$$V = \sum_{\sigma=1,2} \alpha_p a^{+}_{p\sigma} a_{p\sigma}$$

to the Hamiltonian. Than the distance between the soliton and the impurity was changed. This

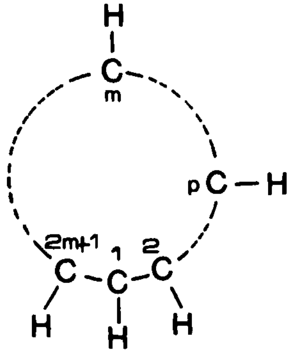

Figure 1 Perturbed chain at the p-th site. Perturbation is due to a non-conjugated side group attached to the p-th carbon of the chain. R stands e.g. for $-CH_3$, $-CH_2CH_3$, or -OH.

brought about an energy gain, until the perturbed atom concided with the soliton center. A further energy gain resulted from relaxation of the soliton shape around the perturbed atom. The results obtained for some model values of α are given in Table 1., where E_D is the sum of the above two energy gains. It is remarkable that E_D turns out to be always negative[9]. This universality may be explained by taking into account a resonance effect of the alternation of charges due to Friedel oscillations[10] around the perturbed atom, and the charge alternation /i.e. bond alternation/ in polyacetylene. Namely, the charge alternations have a similar phase kink around an impurity[11] as the soliton has around

Table 1 The attraction of a soliton by different impurities in a $/CH/_x$ chain. E_D is the attraction energy, α_p is the model value of the impurity ionization potential

α_p /eV/	0.5[a]	1.0[b]	-0.5[c]
E_D /meV/	-6.0	-13.0	-0.7

[a] Methyl or ethyl side group, inductive model
[b] OH side group, inductive model
[c] Model side group with opposite sign of relative electronegativity

its center.

The most striking result of our calculations is that a small energy on the meV scale has occurred naturally. It is likely that in $/CH/_x$ samples, prepared by the Shirakawa technique[12], a few tenth of a per cent hydrogen are replaced by other groups /as e.g. ethylene groups from catalyst solution/, giving rise to the kind of trapping centers discussed in this paper. The observed 4 meV trapping energy compares well with the calculated binding energies, E_D.

It is, however, unlikely that the oxygen would form this kind of side group. The initial fast decrease of the mobile spin concentration of oxygen and charge transfer reaction between the soliton and the oxygen. As oxidation goes further the oxygen reacts with chains, cutting the conjugation. At a level of a few per cent oxygen content the conjugation length thus becomes equal or smaller than the soliton size, prohibiting their motion. The fact that the thermally trapped spins are nearly undistinguishable from the excess static spins, due to oxidation[6], supports this picture.

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* Permanent address: CHINOIN Pharm. and Chem. Works, H-1325 Budapest, P.O.B. 110, Hungary

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