Doping of AlN with Si or O (supercells $Al_{15}SiN_{16}$ and $Al_{16}N_{15}O$) is accompanied by an increase in the concentration of valent electrons, due to which high-energy antibonding states are populated, *i.e.*, the system is destabilized (see Fig. 1). "Reconstruction" of stability requires hole donors, such as vacancies of Al and N or doped Group II elements. For example, the presence of the aluminum vacancy (V_{Al}, calculation of the $Al_{15}V_{Al}N_{16}$ supercell, see Fig. 1) results in the "devastation" of some near-Fermi bonding bands. The type of filling of the energy levels of the spectrum can be reproduced, and the optimum balance of the bonding and antibonding states inherent in AlN can be achieved in the presence of electron and hole donors in a ratio of Si : 2O : V_{Al} ($Al_{14}SiV_{Al}N_{14}O_2$ supercell). This cell corresponds to the $13(AlN)(AlNSiO_2)$ polytype belonging to the family of $Al_{x+y}Si_{6-x}O_xN_{8-x}$ sialones under discussion. All known[2] compositions of wurtzite-like polytypes in the Si—Al—O—N system can be reproduced by variation of the supercell size and concentration of the elements.

Thus, the general scheme of band simulation of the composition of concentration polytypes is evident. The band spectrum is calculated using the quantum theory methods, and the chemical bond is analyzed for probable compositions after the determination of EES of the basis phase for which polytype formation is expected. The criterion of selection of specific compositions of polytypes is their conformity to EES and conditions of chemical bonding with similar values for the starting phase as the most stable in the polytype series formed.

Possibilities of this approach are not restricted by the problem of determination on the element composition of polytypes.[4,5] Information on fundamental EES of polytypes defines challenges on description of the concentration polytypism phenomenon in the electronic structure—composition—structure—properties interrelation.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-32512).

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Received November 20, 1998

Intramolecular electron transfer and spin exchange in molecules with two electrophoric moieties. Bis(2,4,6-triphenylpyridinium)-1,ω-alkanes

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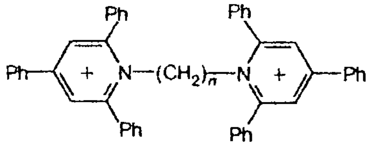
We have previously[1] obtained stable bridged radical cations and biradicals of bis(2,4,6-triphenylpyridinium)-1,ω-alkanes by the electroreduction of dications.

These paramagnetic species serve as the 1e⁻- and 2e⁻-carriers in electrocatalytic reduction of the S—S and Te—Te groups in organic dichalcogenides.[2] Since the intermolecular electron transfer depends on the interaction of electrophoric centers in the carrier molecule, we studied in this work the intramolecular electron transfer and spin exchange in molecules with short ethylene (**1**, $n = 2$) and butylene (**2**, $n = 4$) bridges.



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 823—824, April, 1999.

The ESR spectra of the electrochemically generated[3] radical cations, biradicals of systems **1** and **2**, and the neutral radical of *N*-methyl-2,4,6-triphenylpyridinium ($\mathbf{3}^{\cdot}$) are characterized by equal *g* factors of 2.0026 but different linewidths. For molecule **1**, the potentials of formation of the radical cation (−0.82 V) and biradical (−0.95 V) differ.[1] The reduction of molecule **2** occurs *via* one two-electron stage (−1.0 V)[1]; therefore, the radical cations were obtained at −0.85 V (in the region of the predominant generation of monoradicals).

The shape of the ESR line of $\mathbf{3}^{\cdot}$ is due to the unresolved HFS from one N nucleus and protons. The main contribution to the linewidth is made by the splitting from the N nuclei with spin $I = 1$, and the ESR line is well simulated by three Gaussian lines with the width $D = 0.45$ mT with the splitting $a_N = 0.5$ mT. The Gaussian shape of the line indicates the unresolved HFS from protons, and low HFS constants indicate that the unpaired electron is mainly located on the N atom. For radical cation $\mathbf{1}^{\cdot+}$ and biradical $\mathbf{1}^{\cdot\cdot}$, the ESR spectra are narrowed as compared to that of radical $\mathbf{3}^{\cdot}$. Intramolecular collisions of the triphenylpyridinium rings result in narrowing, and the narrowing mechanisms for $\mathbf{1}^{\cdot+}$ and $\mathbf{1}^{\cdot\cdot}$ are different. In the case of $\mathbf{1}^{\cdot+}$, the narrowing is due to hole/electron hopping. If the time τ between the hops is sufficiently short, so that the condition is fulfilled:

$$\gamma^2 a_N{}^2 \tau^2 \ll 1, \qquad (1)$$

where γ is the electron gyromagnetic ratio ($1.77 \cdot 10^8$ s^{-1} mT^{-1}), the HFS from two equivalent protons with the constant $a_N{}' = a_N/2$ should be observed. In fact, the spectrum for $\mathbf{1}^{\cdot+}$ is well simulated by the HFS from two equivalent protons with $a_N{}' = 0.2$ mT and $D = 0.44$ mT. Condition (1) is fulfilled at $\tau < 10^{-8}$ s.

In the case of biradical $\mathbf{1}^{\cdot\cdot}$, the narrowing is due to the spin exchange between the triphenylpyridinium radicals at the moment of their intramolecular collisions. This mechanism is characterized by several parameters, such as the value of exchange interaction J and the contact time τ_c of the radicals; therefore, the efficiency of the spin exchange in the narrowing of the ESR line can differ from that of the electron transfer. In fact, the ESR spectrum of biradical $\mathbf{1}^{\cdot\cdot}$, unlike that of radical cation $\mathbf{1}^{\cdot+}$, is sufficiently close to the spectrum of radical $\mathbf{3}^{\cdot}$.

When the temperature decreases from room to −40 °C, the splitting of the a_N lines of both radical cation $\mathbf{1}^{\cdot+}$ and biradical $\mathbf{1}^{\cdot\cdot}$ increases to the a_N value characteristic of radical $\mathbf{3}^{\cdot}$, which agrees with a decrease in the frequency of collisions of the triphenylpyridinium rings.

The temperature changes in the ESR linewidths of system **2** are similar to those of system **1**. It is of interest that, as compared to system **1**, intramolecular electron transfer in radical cation $\mathbf{2}^{\cdot+}$ occurs more slowly because of a longer bridge, while the spin exchange in biradical $\mathbf{2}^{\cdot\cdot}$ results in the same efficient narrowing of the ESR lines.

Analysis of the ESR spectra of the biradicals in frozen solutions makes it possible to determine the exchange interaction value and the distance between spins; therefore, we are planning further experiments in glassy solvents (for example, in ethanol).

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Received December 11, 1998

Carbonylation of methyl acetate in the presence of rhodium catalysts based on pyrrolidinopyridine polymers

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Previously,[1] we have studied the hydroformylation of olefins in the presence of a catalytic system based on $\mathrm{RhCl_3}$ and the pyrrolidinopyridine polymer (**1**).

This system exhibits high activity in hydroformylation

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 824—825, April, 1999.

1066-5285/99/4804-0818 $22.00 © 1999 Kluwer Academic/Plenum Publishers