2026 *Russian Chemical Bulletin, International Edition, Vol. 56, No. 10, pp. 2026—2033, October, 2007*

Spin crossover in polyaniline

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Solutions of the basic form of polyaniline in *m*-cresol were studied by ESR and optical spectroscopy in the visible region. *m*-Cresol can slowly (during one month) protonate polyaniline. For the first time characteristic features of spin crossover were found: sharp changes in the magnetic susceptibility and the ESR line width of polyaniline at ~200 and 250 K, a smooth decrease in the susceptibility and absorption with the temperature increase from 293 to 423 K, and the temperature hysteresis. The temperature-induced structural rearrangements of polyaniline are caused, most likely, by singlet-triplet transitions in relatively short sections of the polymer chain. The model of short sections permits to explain the origin of the temperature-independent part of susceptibility. Quantum-chemical calculations for the aniline dimers and tetramers describe correctly the singlet-triplet splitting value, thermochromism, and HFS constants in the spectrum of polyaniline.

Key words: polyaniline, ESR spectroscopy, spin crossover, quantum chemistry.

The term "spin crossover" (SC) or "spin transition" is used for the description of characteristic phenomena in samples, where transitions between the high- and low-spin states of the centers of the sample occur upon the temperature change or under pressure or irradiation and lead to the structural rearrangement of the sample.

Most systems manifesting SC contain iron(II).[1,2] The systems containing no iron but including, for example, Cu atoms and nitroxy radicals are also known.[3] The energy of low-spin states of the centers is usually lower than that of the high-spin states and, hence, the fraction of the low-spin states increases with the temperature decrease. The geometry of the low-spin and high-spin centers is different and, therefore, strains accelerating the conversion of the high-spin to low-spin states increase with an increase in the fraction of the low-spin states in the samples, and the phase transition occurs at some temperature. The sharpness of the transition is determined by the degree of cooperativity of the system and, as a rule, the temperature hysteresis is observed. Investigation of the nature of this phenomenon, including establishing conditions for the appearance of cooperativity and the mechanism of an irradiation effect and search for new systems manifesting SC is the matter of numerous studies. The high sensitivity of parameters of the systems under study, especially absorption in the visible region and magnetic susceptibility, to slight changes in the temperature, pressure, and irradiation makes it possible to use them as sensors, displays, and information storage devices. To increase the sharpness of the transition, the centers are bound through ligands into polymer structures; however, no true polymers exhibiting SC are known. The SC term is applied to both solid-state systems with sharp temperature-induced transitions and solutions with smooth transitions reflecting the change in the Boltzmann populations of spin states. The systems manifesting SC are rather few, because they need to fulfill several conditions; in particular, the singlet-triplet splitting should be comparable with kT.

The increase in the population of singlet states with the temperature decrease is also characteristic of antiferromagnetically coupled spins. Antiferromagnetism was observed for the polythiophene derivatives[4]; the origin of the temperature-independent part of the polyaniline susceptibility was explained[5—7] using antiferromagnetically coupled spin pairs; the decrease in the polyacetylene susceptibility of polyacetylene with the temperature decrease below 200 K can also be related to antiferromagnetic spin coupling.[8] Therefore, it is probable that the conducting polyconjugated polymers (polyaniline, polythiophene, polyacetylene, and others) manifest SC. However, no characteristic properties of SC, such as sharp changes in the susceptibility and hysteresis during the temperature change, were observed. We know only two works in which SC can be assumed. In one of them the authors observed[9] sharp non-reproducible and remained unexplained changes in the ESR line width of the stretched polyaniline film at 10 K, and in another study the temperature hysteresis of the polyacetylene susceptibility was observed[8] at ~20 K and ascribed to phase separation into the metallic phase and the phase of charged solitons.

We found for the first time distinct properties of SC in polyaniline. In the present work, we studied solutions of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1959—1966, October, 2007.

1066-5285/07/5610-2026

the basic form of polyaniline in *m*-cresol. *m*-Cresol itself, without acid additives, can protonate (dope) polyaniline.[10] Complete protonation requires ~1 month. Sharp conformational transitions occur at ~200 and 250 K in solutions of partially doped polyaniline in *m*-cresol. They are detected by a change in the ESR line width and magnetic susceptibility, and the temperature hysteresis is observed. The susceptibility and optical spectra change smoothly in solutions at 293—423 K. We believe that the temperature-induced structural rearrangements of polyaniline are caused by singlet-triplet transitions, in particular, rather short sections of the polymer chain. This model of short sections can also explain the origin of the temperature-independent component of the magnetic susceptibility. The quantum chemical calculations for the aniline dimer and tetramer describe correctly the singlet-triplet splitting value, thermochromism, and HFS constants in the ESR spectra of polyaniline.

Experimental

Aniline (Reakhim, pure grade), *m*-cresol (Aldrich, 98%), and $HClO_4$ and $(NH_4)_2S_2O_8$ (Reakhim, reagent grade) were used. Polyaniline was synthesized by oxidative polymerization at −20 °C as described earlier.[10]

ESR spectra were recorded on a Radiopan SE/X 2544 (3-cm range) spectrometer (Poland) equipped with a magnetometer, a frequency meter, and a temperature control unit.

Oxygen was removed from samples using a known procedure.[10] A solution in a thin-wall polyethylene ampule with a diameter of ~1 mm and gas-permeable walls was kept for 2—3 h in an argon flow at room temperature.

The magnetic susceptibility was determined by comparing the second integrals of the ESR spectra of the polyaniline sample under study and a standard sample with a known concentration of spins. A 1 m*M* solution of the free stable nitroxy radical in ethanol was used as the standard sample. The molar magnetic susceptibility of the nitroxy radical at room temperature was accepted as $1.5 \cdot 10^{-3}$ electromagnetic unit (emu). The molar susceptibility of polyaniline was calculated based on 1 mole of two rings. The relative error of measurement of the second integral was at most 5—10%. The absolute error of measurements of the magnetic susceptibility was estimated by comparing the second integrals of the ESR samples with the known concentration of the paramagnetic centers, nitroxy radicals, $CuCl_2 \cdot 6H_2O$, and several iron nitrosyl complexes. This error does not exceed 15—20%.

Optical spectra in a range of 400—900 nm were recorded on a Specord M-40 spectrophotometer (Germany). Pure *m*-cresol was placed in a reference cell, and the time interval between measurements at different temperatures was ~25 min.

Quantum chemical calculations were performed using the GAUSSIAN-98 program package.[11]

Results and Discussion

Dissolution of the basic form of polyaniline in *m*-cresol. A freshly prepared blue solution of polyaniline in *m*-cresol gives the optical spectrum with a band at 690 nm, which is characteristic of the basic form of emeraldine, and a very weak ESR signal with a width of ~0.15 mT. During several days the solution gradually turned green, the intensity of the band at 690 nm decreased and that of the band at 450 nm increased, and the intensity of the ESR signal with a width of ~1 mT increased. These changes in the properties of the solution are due to the fact that polyaniline is slowly protonated by *m*-cresol (for 1 month). The optical spectra were published.[10] The second moment of the ESR spectrum of the solution, *viz.*, mean-square width, is ~0.6 mT^2 and virtually independent of the duration of dissolution and temperature. According to published data,[10] the second moment is caused by the unresolved HFS from the protons and nitrogen nuclei, and the ESR line width is determined by averaging of this HFS simultaneously by the exchange interaction of the paramagnetic centers of the adjacent chains and jumps of electrons along or between the chains.

Temperature plots of the susceptibility and ESR line width. The temperature plots of the product of susceptibility by temperature (χT) and the ESR line width (ΔH) for a solution of completely protonated polyaniline in *m*-cresol are shown in Fig. 1. The temperature was decreased from room temperature to a minimum, then increased to the maximum temperature, and returned to

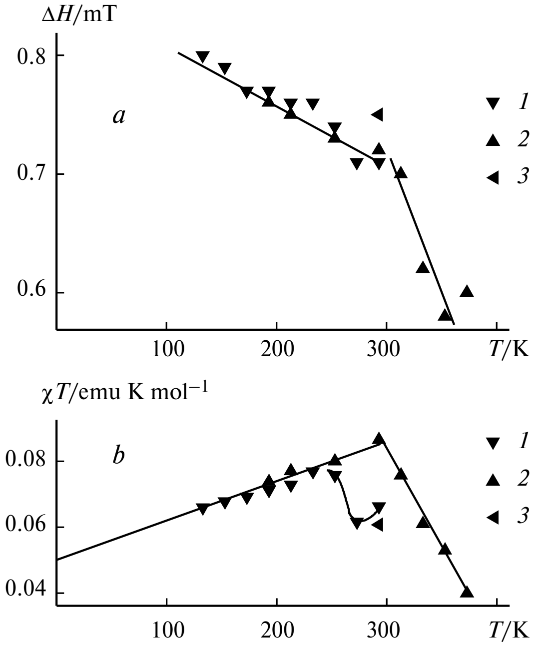

Fig. 1. Temperature plots of the ESR line width (*a*) and the product of susceptibility by temperature (*b*) for a solution of completely protonated polyaniline in *m*-cresol. The solution was stored at room temperature for 1 month after the dissolution onset. The measurements were carried out in air: *1*, the temperature was decreased from room temperature, *2*, increasing from the minimum temperature, and *3*, returning to room temperature.

room temperature. At temperatures below room temperature, the temperature plots of the line width and susceptibility are virtually reversible. The distinct break in the curves of the temperature dependences of both the susceptibility and ESR line width at room temperature can be attributed to the melting—freezing of *m*-cresol at ~283 K.

At temperatures below room temperature, the χT value depends linearly on temperature. The temperature-independent section of susceptibility equal to ~$1.2 \cdot 10^{-4}$ emu mol^{-1} can be determined from the slope of this straight line, and the temperature-dependent section of susceptibility as $1/T$ (Curie susceptibility) can be determined from the section cut by the straight line on the ordinate at $T = 0$. The Curie susceptibility, to which 0.11 spin per 1 mole of two rings corresponds, is ~$1.7 \cdot 10^{-4}$ emu mol^{-1} at room temperature.

Numerous linear temperature plots of χT for powders and films of conducting polymers have been published earlier.[9,12,13] It is commonly accepted that the temperature-independent susceptibility is the Pauli susceptibility characteristic of metals with the perfect periodical lattice, and the Curie susceptibility is due to rather rare lattice defects. In our case, this linear dependence was obtained for a frozen solution in which polyaniline exists as unfolded globules without structural regularity. Our explanation of the origin of two components of susceptibility is based on the model of short periodical sections of the polymer chain (see below).

When the temperature increases above room temperature, the susceptibility decreases and does not return to the initial value at room temperature. This decrease in susceptibility is not due to polymer deprotonation on heating, because no band at 690 nm characteristic of the undoped polyaniline form appears in the absorption spectra, and the addition of formic acid does not increase the susceptibility. The susceptibility returns to the initial value on storage of the sample at room temperature for one week. It can be assumed that the susceptibility decrease on heating above room temperature and the slow return to the initial value are related to conformational changes in the polymer. The ESR line width decreases with the temperature change from 133 to 373 K due to the acceleration of electron jumps averaging the HFS. The influence of conformational changes on the susceptibility and ESR line width will be considered in detail below after an analysis of the data on the temperature dependence of the absorption spectra of the solution in the visible region.

The hysteresis of the χT value at room temperature is seen in Fig. 1. The hysteresis of the susceptibility and line width becomes distinct for solutions of partially protonated polyaniline (Figs 2 and 3). The measurements were carried out in air (see Fig. 2) and under argon (see Fig. 3). Experiments in argon were carried out to reveal the effect of molecular oxygen with the spin 1 in the ground state on the ESR line width and susceptibility. It was found that

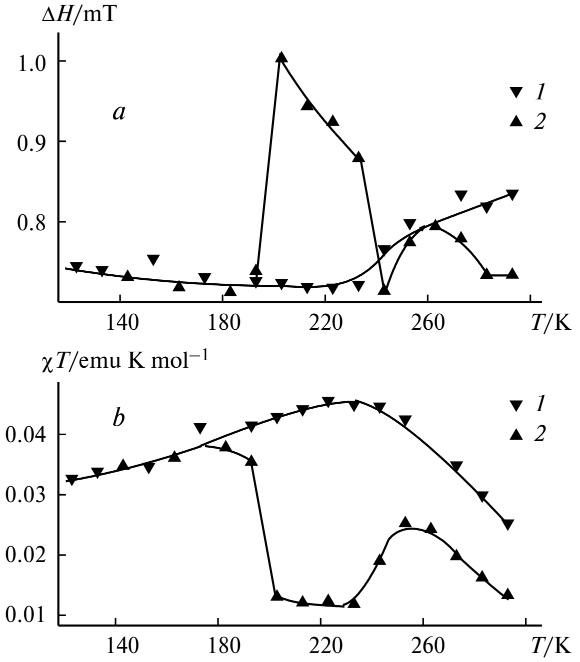

Fig. 2. Temperature plots of the ESR line width (*a*) and the product of susceptibility by temperature (*b*) for a solution of partially protonated polyaniline in *m*-cresol. The solution was kept at room temperature for 8 days after the dissolution onset. The measurements were carried out in air: *1*, the temperature was decreased from room temperature and *2*, increasing from the minimum temperature.

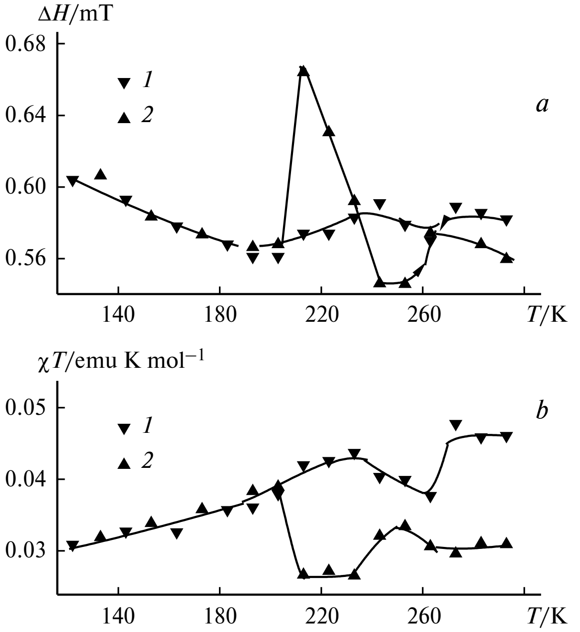

Fig. 3. Temperature plots of the ESR line width (*a*) and the product of susceptibility by temperature (*b*) for a solution of partially protonated polyaniline in *m*-cresol. The solution was kept at room temperature for 9 days after the dissolution onset. The measurements were carried out under argon: *1*, the temperature was decreased from room temperature and *2*, increasing from the minimum temperature.

the removal of oxygen (see Experimental) did not narrow the ESR line width and, therefore, differences in the temperature plots of the susceptibility (see Figs 2 and 3) are due to different times of polyaniline dissolution in *m*-cresol (8 and 9 days) rather than to the oxygen effect.

Sharp changes in the susceptibility and line width and the temperature hysteresis are characteristic of the SC phenomenon. In the case of known systems that manifest SC mainly for the Fe^{II} compounds, the sharp changes in the parameters are induced by the difference in equilibrium geometry of the high- and low-spin centers, an increase in the fraction of low-spin centers with the temperature decrease, and the cooperative effect. We believe that rather short sections with approximately equal angles between the planes of the adjacent rings act in polyaniline as centers that can exist in the states with different multiplicities. The results of quantum chemical calculations for the aniline tetramers (see below) show that the tetramers in the singlet and triplet states are of different geometry.

Model of short periodical sections of the polymer. According to a popular point of view,[9,12,13] powders and films of doped polyaniline represent highly ordered metallic regions immersed into amorphous regions. The high conductivity and Pauli susceptibility are due to the metallic regions. Distortions of the lattice periodicity result in the formation of a minor number of localized electrons, *i.e.*, polarons with the spin 1/2, whose susceptibility obeys the Curie law. The periodic lattice model was used to explain thermochromism.[13]

The linear dependence of χT on T for the basic forms of polyaniline and aniline tetramers with a low conductivity was explained[5,6] using the model of exchange-coupled polaron pairs. It was shown that the averaging of the susceptibility of antiferromagnetically coupled pairs described by the Bowers—Bleaney formula over a wide distribution of exchange interaction (from 0 to the maximum one, with a constant weight) gives the quasi-Pauli susceptibility. Further this model was applied to doped polyaniline.[7] The model can explain the nonlinear plots of χT *vs* T, which are sometimes observed experimentally. In the framework of this model, high values of the maximum exchange interaction are observed: from 100 to 1000 K, respectively (from 0.8 to 8 kJ mol^{-1}). In our opinion, these values are highly overestimated. We proposed[10] the method for determination of the exchange interaction by the temperature dependence of the ESR line width. The maximum known value of the exchange interaction is ~1 K at a distance between polarons of ~0.6 nm. The model described[5,6] is valid, if we accept that the singlet-triplet splitting is not caused by the exchange interaction of two isolated centers but is an intrinsic property of a particular section of the polyaniline chain, for example, tetramer. Our quantum chemical calculations of the tetramer dication show (see below) that the singlet-triplet splitting value can vary from 0 to 1000 K for different conformations.

We assume that polyaniline molecules consist of rather short periodical sections with close angles between the planes of the adjacent rings; the sections are separated from each other by a sharp change in these angles, and there is a set of conformations of these sections. An idea that chains of conducting polymers are divided by defects into conjugated fragments of finite length has first been advanced in Refs 14 and 15.

These concepts are close to those developed for polythiophene.[4] The magnetic susceptibility of polythiophene can be divided into three sections: the Curie susceptibility, Pauli susceptibility, and antiferromagnetic susceptibility; thermochromism and the influence of a prolong heating (at 453 K) on the characteristics of the polymer are observed. After heating, the characteristics of the polymer relax slowly to the initial values for several weeks. These facts are explained[4] by the structure of the polymer consisting of sections with parallel adjacent rings, and coplanarity of the rings is violated by their turns relative to each other. When the temperature increases, the violations of the coplanarities become more frequent and the sections are shortened. Antiferromagnetism is due to possible transformations of paramagnetic polarons in long sections into diamagnetic bipolarons. The authors[4] do not explain the origin of the Pauli and Curie susceptibilities and present no detailed mechanism of conversion of polarons to bipolarons. In our opinion, antiferromagnetism in polythiophene at temperatures below room temperature is caused by singlet-triplet transitions in particular sections without a considerable change in their geometry, and heating to 453 K results in the substantial conformational rearrangement.

Temperature dependences of the magnetic susceptibility and optical absorption of a polyaniline solution in the 293—363 K interval. The temperature dependences of the optical absorption spectra of a solution of completely protonated polyaniline in *m*-cresol are shown in Fig. 4. The temperature plots of the absorption at three wavelengths normalized to the corresponding absorption values at room temperature are shown in Fig. 5. On heating from room temperature to 363 K, the normalized absorption at all wavelengths decreases, and the spectrum is recovered when returning to room temperature.

The temperature plots of the product of susceptibility by temperature are also shown in Fig. 5. The values of this product on heating are higher than the values observed on cooling. On storage of the sample at room temperature after heating, the susceptibility is recovered only in several days. We believe that the slow return of the susceptibility is caused by slow large-scale conformational changes in the polymer, and the reversibility of the absorption changes is due to the fact that these changes are not associated with considerable conformational changes.

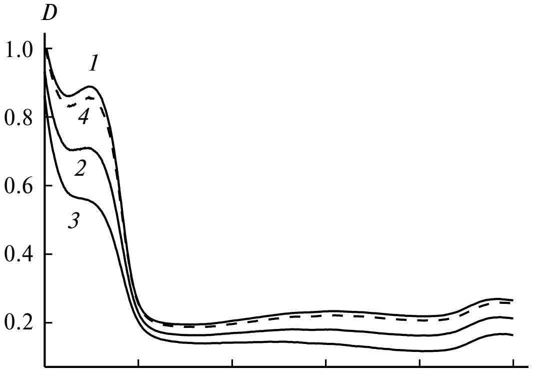

Fig. 4. Optical absorption spectra of a solution of completely protonated polyaniline in *m*-cresol at 292 (*1*), 333 (*2*), 363 (*3*), and 293 K (after heating to 363 K) (*4*). The solution was kept at room temperature for 6 months after the onset of dissolution of the basic form of the polymer.

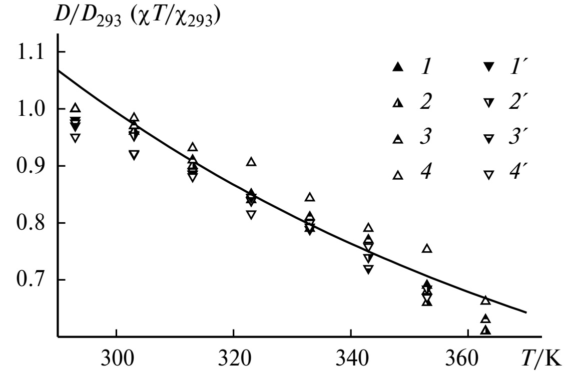

Fig. 5. Temperature plots of the optical absorption at 450 (*1*, *1´*), 690 (*2*, *2´*) and 890 nm (*3*, *3´*) and the products of susceptibility by temperature (*4*, *4´*) for a solution of completely protonated polyaniline in *m*-cresol. The solution was kept at room temperature for 6 months after the onset of dissolution of the basic form of the polymer. The temperature was increased from 293 K to the maximum temperature (*1*—*4*) and then decreased (*1´*—*4´*).

It can be assumed that the reversible absorption changes on heating to a moderate temperature (363 K) are due to the equilibrium shift between the singlet and triplet states in short periodical sections with an even number of positive charges without a substantial change in the conformation of these sections. With the temperature increase the equilibrium shifts toward the singlet states, which do not absorb in the visible region and do not contribute to the magnetization, *i.e.*, the absorption and susceptibility are proportional to the number of sections existing in the triplet state. The change in this number depending on temperature can be described by the equation

$$A_t/A_s = K \equiv \exp[\Delta F/(kT)], \qquad (1)$$

where A_t and A_s are the numbers of sections in the triplet and singlet state, respectively; K is the equilibrium constant; $\Delta F = \Delta H - T\Delta S$ is the difference between the free energy of the singlet and triplet states of the polyaniline section. Taking into account that the $A_t + A_s$ sum is constant and equal to A_0, we have

$$A_t = A_0K/(1 + K). \qquad (2)$$

The temperature plots of D and χT are shown in Fig. 5. The solid line corresponds (see Fig. 5) to Eq. (2) with $A_0 = 3.1$, $\Delta H = +7.8$ kJ mol^{-1}, and $\Delta S = +32$ J K^{-1} mol^{-1}. At room temperature $A_s/A_t = 2.1$.

The temperature dependence of the product of susceptibility by temperature is also shown in Fig. 5. This was made in order to compensate susceptibility changes with temperature variation according to the Curie law. These changes are due to the changes in populations of the spin levels, the splitting between which are considerably lower than kT. In the case of absorption of a photon with the energy strongly exceeding kT, the highest level is virtually unoccupied and corrections to the population changes upon temperature variation are insignificant for absorption.

Relaxation of the magnetic susceptibility and optical absorption after heating at 423 K. On heating to 363 K the temperature changes in the absorption and susceptibility are virtually reversible (during the time of experiment). After heating of the solution at 423 K for 15 min, both the absorption and susceptibility values at room temperature are lower than the initial values (Fig. 6). The absorption returns to the initial value within 5—6 days. The susceptibility returns to the initial value after several weeks. The slow return of the absorption and susceptibility indicates considerable conformational changes induced by heating, and the higher is the heating temperature, the slower is the return to the initial values.

Quantum chemical analysis of the aniline tetramers and dimers. To check the quantum chemical results, we first calculated the HFS constants for the radical cation of the aniline dimer. It was found that the results of the B3LYP calculations agree with the experimental data. The geom-

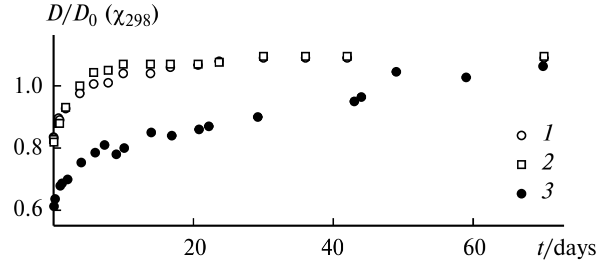

Fig. 6. Time plots of the optical absorption at 450 (*1*) and 690 nm (*2*) and the susceptibility at room temperature (*3*) after heating of solution of completely protonated polyaniline in *m*-cresol at 423 K for 15 min. The absorption and susceptibility values were normalized to the corresponding initial values before heating.

etry was optimized by this method as well. The HFS constants obtained by the HF method turned out to be almost an order of magnitude higher than the experimental values.

It was found[16] that a polyaniline solution in concentrated sulfuric acid containing NaCl gives a multicomponent spectrum with the g factor 2.0035, which is well simulated assuming that polyaniline decomposes to the $[—C_6H_4—NH—C_6H_4—]^{+\bullet}$ fragments with the HFS constants $a_H(1\ H) = 0.79$ mT, $a_N(1\ N) = 0.79$ mT, $a_H(4\ H) = 0.16$ mT, and $a_H(4\ H) = 0.086$ mT. The second moment of the ESR line, *viz.*, mean-square line width, can be calculated by the formula

$$M_2 = \frac{2}{3}\sum a_N^2 + \frac{1}{4}\sum a_H^2. \qquad (3)$$

The second moment corresponding to the above presented HFS constants is 0.58 mT^2 and virtually coincides with the experimentally determined second moment of polyaniline solutions in *m*-cresol, being 0.6 mT^2. The HFS constants for the radical cation of the symmetric $[NH_2—C_6H_4—NH—C_6H_4—NH_2]^{+\bullet}$ dimer were calculated by the B3LYP/6-311++g method: $a_H(1\ H) = 0.84$ mT, $a_N(1\ N) = 0.44$ mT, $a_H(4\ H) = 0.20$ mT, $a_H(4\ H) = 0.016$ mT, $a_N(2\ N) = 0.14$ mT, and $a_H(4\ H) = 0.37$ mT. The two latter are attributed to two NH_2 groups and are not observed experimentally. The calculated HFS constants agree well with the experimental values, except for the calculated $a_N(1\ N)$ constant, which is twofold lower than the experimental value. This is related, most likely, to the fact that the calculation did not take into account hydrogen bonds with the NH group affecting substantially the conductivity of polyaniline.[17,18] Thus, the calculated HFS constants of the dimers are well consistent with the experimental values (except for the constants for the NH_2 groups, which are absent in the polyaniline fragments in concentrated sulfuric acid). If the HFS constants for the NH_2 groups are ignored, the calculated constants correspond to the second moment equal to 0.35 mT^2.

The quantum chemical calculations were also performed for the $[C_6H_5—NH—C_6H_4—NH—C_6H_4—NH—C_6H_4—NH_2]^{2+}$ dication of the polyaniline tetramer. The results of calculations are given in Table 1 and in Fig. 7 (symbol * in the names of conformations designates the optimized geometry, and the last letter denotes the singlet (s) or triplet (t) state).

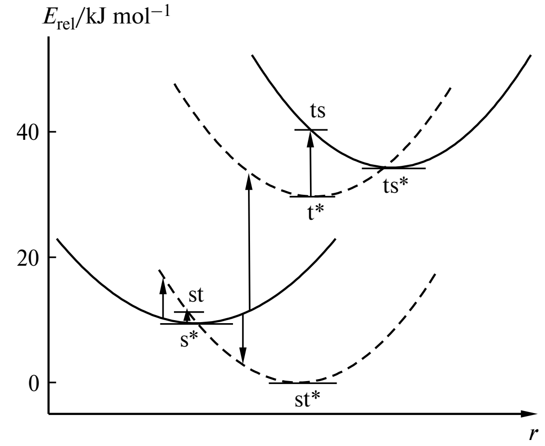

Fig. 7. Relative energies (E_{rel}) of the singlet and triplet states of the dication of the aniline tetramer in different conformations obtained by the B3LYP/6-31g method; r is the reaction coordinate.

At first the geometry of the tetramer dication in the singlet and triplet states was optimized by the semiempirical AM1 method using the HyperChem program package. It turned out that the structure of the tetramer dication in the triplet state is almost planar, whereas in the singlet state it is twisted with angles between the planes of the adjacent rings of ~30°. Then these structures were optimized by the B3LYP/6-31g method to obtain the conformations s* and t*. The s* and t* conformations are close to those obtained by the AM1 method. The nonoptimized states ts and st were obtained from the optimized t* and s* states, respectively, with the multiplicity change but without geometry changes. The triplet t* conformation is higher in energy than the singlet conformation s*; however, there are triplet conformations lying lower in energy than the singlet conformations. For instance, the st* state was obtained by the search for a

Table 1. Results of the B3LYP and CIS quantum chemical calculations in the 6-31g basis set for the aniline tetramer with the charge 2+

Conformation	Multiplicity	−E/au	λ/nm (oscillator strength)	
			B3LYP	CIS
Planar t*	3	1146.026454	239, 274, 281, 293, 567, 758	—
Planar ts	1	1146.022689	295, 301, 1597	—
Planar ts*	1	1146.024643	261, 304, 1435	—
Twisted s*	1	1146.034151	290, 302, 1402	382 (0.0027), 532 (0.34), 952 (1.83)
Twisted st	3	1146.034049	243, 277, 281, 300, 563, 810	435 (0.32), 483 (0.54)
Twisted st*	3	1146.037661	240, 270, 276, 290, 564, 707	373 (0.25), 409 (0.20), 565 (0.56)

local minimum from the st state (gdiis option in the GAUSSIAN-98 program package). The ts* state was obtained analogously.

The relative energies of different states of the tetramer dication are presented in Fig. 7. These energies were calculated from the energies given in Table 7 using the equality 1 au = 2629.3 kJ mol^{-1}. The aniline tetramer consists of 50 atoms, and the abscissa in Fig. 7 is a generalized coordinate in the 144-dimensional space. The parabola slopes in Fig. 7 are given arbitrarily.

At temperatures <200 K, only vertical transitions occur, most likely, between the singlet and triplet states without changing the tetramer geometry in frozen solutions of polyaniline in *m*-cresol. Some transitions are shown in Fig. 7 by vertical arrows. According to published data,[5—7] the energy distribution of just these vertical transitions from 0 to 10 kJ mol^{-1} (from 0 to ~1000 K) can result in the pseudo-Pauli susceptibility.

For the singlet states, one can find solutions with the violated symmetry (stable=opt option), whose energies lie lower by ~10 kJ mol^{-1}; however, this does not change the qualitative conclusion about the wide distribution of the singlet-triplet splitting.

At temperatures >200 K, transitions of the st* $\rightleftharpoons$ s* type occur with the conformation change. The difference in bond lengths and angles of the s* and st* conformations reach 0.005 nm and 6°, respectively. Just this difference in geometry of the singlet and triplet states can serve as a reason for the temperature-induced structural transitions at ~200 and 250 K (see Figs 2 and 3).

The wavelengths of the absorption bands calculated from the difference between the energy of the lowest occupied and highest unoccupied orbitals and using the CIS method are listed in Table 1. The CIS method makes it possible to calculate the wavelengths of the lines and also their intensities (oscillator strengths). For the planar conformations, the use of the CIS method did not allow one to obtain a consistent result. According to the experimental spectra, the calculations for all states give the absorption at λ ~500—600 nm, whereas the absorption at $\lambda > 600$ nm depends on both the conformation and multiplicity and, as a rule, the singlet states give the absorption only at $\lambda > 900$ nm.

It seems that the merging of two sections into one section on heating can be considered to explain the heating effect on the absorption and susceptibility (see Figs 4—6). Upon this recombination the number of sections decreases and the heating should decrease the susceptibility, because the susceptibility, according to the Bowers—Bleaney formula, is independent of the section length. Perhaps, the quantum-chemical analysis of this recombination of the sections will make it possible to explain both the absorption decrease on heating and experimental values $\Delta H = +7.8$ kJ mol^{-1} and $\Delta S = +32$ J K^{-1} mol^{-1}.

Thus, thermochromism of polyaniline can be due to the temperature-induced conformational transitions.

The second moment of the t* and st* states calculated by formula (3) is 0.24 and 0.26 mT^2, respectively, which is lower than an experimental value of 0.6 mT^2. The low value of the calculated second moment is caused, most likely, by ignoring hydrogen bonding in the calculation.

Thus, the characteristic features of SC, such as sharp changes in the magnetic susceptibility and ESR line width of polyaniline at ~200 and 250 K, their smooth decrease with the temperature increase from 293 to 423 K, and the temperature hysteresis, have been found for the first time in polyaniline solutions in *m*-cresol. After heating to 423 K and returning to 293 K, the susceptibility and absorption take the initial values only in several weeks. The slow return indicates considerable conformational changes induced by heating.

We believe that the temperature-induced structural rearrangements of polyaniline are caused by singlet-triplet transitions in rather short sections of the polymer chain. The conformations of the sections in the singlet and triplet states differ, and the change in the population of these states with a temperature change result in sharp changes in the absorption and susceptibility at ~200 and 250 K and their smooth changes at temperatures higher than room temperature. The temperature hysteresis in both frozen solutions at temperatures below room temperature and in solutions is explained by a low rate of conformational transformations of the polymer chain. The model of short sections explains the origin of the temperature-independent component of the magnetic susceptibility.

The quantum chemical calculations show that the optimized conformations of the singlet and triplet states differ substantially and this difference results in temperature-induced structural rearrangements in polyaniline. The quantum chemical calculations for the aniline dimer and tetramer describe correctly the singlet-triplet splitting value, thermochromism, and HFS constants in the ESR spectra of polyaniline.

This work was financially supported by the Program "Development of Scientific Potential of the Higher School" (Grant RNP 2.2.1.1.7181).

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Received November 16, 2006;
in revised form April 27, 2007