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About Intermolecular Interaction, Submolecular Structure, and Paramagnetism of Polyconjugated Systems

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SUMMARY

It is shown that macromolecules with polyconjugated systems are capable of forming strong π-complex associates. The paramagnetic centers cause intercombinative transitions in auto- or π-complexes with other molecules and increase their reactivity ("effect of local activation").

At the present time it has been determined that an increase of polyconjugated chains leads to a decrease of the energy slits and the energy of excited states.

At the same time ionization potentials (I) are decreased, but electron affinity (A) and electron polarizability are increased. One can show that the change of the difference I - A correlates with the change in the physicochemical properties of polyconjugated homologs [1, 2]. Some data concerning aromatic hydrocarbons, wherein the polarization and space influence of groups and heteroatoms are excluded, may be illustrative. As we can see from Figs. 1 and 2, in the cases of polyacene and poly-p-phenylene the melting points and the heat of sublimations increase with a decrease in I - A. At the same time the solubility and activation energy of conductivity of these compounds decrease.

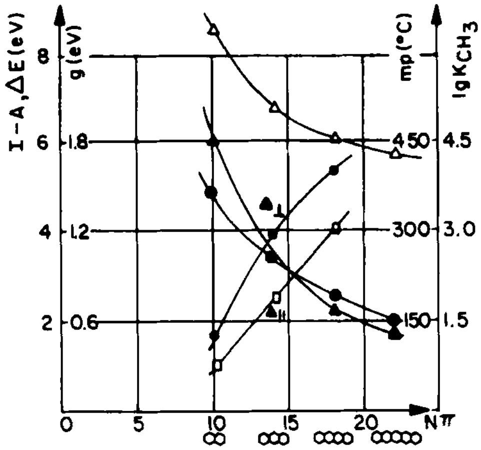
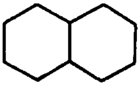
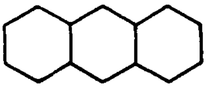
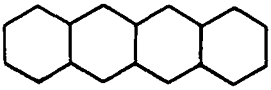
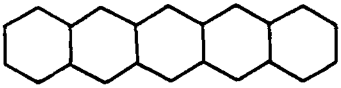


Fig. 1. The dependence of physicochemical properties of acene hydrocarbons on the number of π-electrons. (△) Difference of ionization potential value and electron affinity, I - A (eV). (⊗) Value of energy slip (eV). (▲) Activation energy of electroconductivity (eV). (□) Melting point (°C). (●) Logarithm of methyl affinity rate (arbitrary units).

Compound	ΔH_{subl} (kcal/mole)	ΔS_{subl} (cal/mole deg)	T_{subl} at 10^{-2} Torr (°C)	Solubility
	17	41	27	Readily
	23	42	87	1.8 g/100 ml
	28	39	186	Difficultly
	–	–	–	Trace

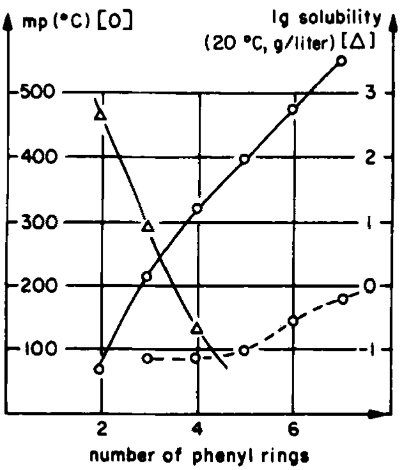
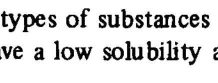
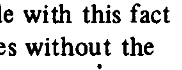


Fig. 2. The dependence of the change of melting point and solubility for individual polyphenylenes on the number of phenylene nuclei. (o) Melting point of phenylenes. (Δ) Logarithm of solubility for p-phenylenes in benzene (g/ml), T = 70°. (– –) For . (——) For .

These data show that the melting points for crystals of linear and chain polycyclic aromatic hydrocarbons with 4-5 cycles exceed the same physical parameters for such metals as zinc, lead, and tin. Side by side with this fact it is known that both these types of substances and some dyes without the capacity for substituents have a low solubility and form associates in solutions.

According to our point of view, the above-mentioned correlations are connected with the formation of intermolecular π-complexes [3], whose polarizability increases with the growth of the conjugated chain and with the decrease of difference I - A. Taking into account that the polarizability of atoms at the ened of the polyconjugated chain (linear polyenes, poly-p-phenylenes, molecules with end heteroatoms) or atomic centers within molecule (polyacenes, heterochain PCS) takes place in the chain, one can assume that the most favorable conditions for intermolecular π-electron interaction will be displayed with bundle packing and rapprochement of chain ends. In such associates with the corresponding chain length, polarizability is favorable to the decrease of intermolecular distances in comparison with the first members of homologous series. Such increases of packing density with decreases of I - A crystal complexes has been experimentally shown for some systems [3].

The rapprochement of chains in polarized π-complex associates of a polyconjugated system has an additional energy advantage at the expense of intermolecular π-electron orbits crossing in the direction perpendicular to σ-bonds and in the direction of the molecular axis for end heteroatoms.

Anomalously high melting points, the heats of sublimation, difficulties in solubility, association in solutions, and some other properties of polyconjugated systems (see Figs. 1 and 2) are the consequences of the peculiarity in intermolecular interaction mentioned.

Both the deflection from linear or series dispostion of conjugated nuclei, the presence of capacious side substituents, causing the steric difficulties, and the absence of structural order in the conjugated chain decreases or disturbs the regular variation of I - A with the growth of the number of conjugated π-bonds and reduces the possibility of dense molecular packing. Such systems must therefore be less thermostable, have a lower thermal shock resistance and higher solubility, and differ from the compounds considered above by other properties. All the aforesaid is in good agreement with experimental data.

Although the question of the particular intermolecular forces in PCS and their great part in the physics and chemistry of polyconjugated systems was considered as long ago as 1958 [4], it has not attracted the proper attention of scientific workers. This problem has arisen only recently in connection with the peculiarity of conjugated chain formation [1, 5] and the structure of organic semiconductors [6]. To elucidate this question, calorimetric investigations in the determination of the energy of conjugation and the role of intermolecular π-electron interaction in individual or polymer hydrocarbons with main chain, containing conjugated bonds (oligoarylvinylenes) or aromatic nuclei (polyarylenes) [5] has been carried out.

In these works the difference between total energy of conjugation and energy of conjugation in aromatic rings has been taken as a criterion for estimation of the intermolecular exchangable π-electron interaction in polyconjugated chains and has been named "the energy of structure stabilization" ΔH_π (see Table 1).

As we can see, there is an additional contribution of stabilization energy, $-\Delta H_\pi$ = 6.0-12.0 kcal/mole, in individual polyene hydrocarbons. This value considerably exceeded all known data of the energy of conjugation for butadiene-1,3 and its vinyl analogs (2-4 kcal/mole). It is incorrect to explain this difference by intramolecular delocalization. It is reasonable to consider that the observed values of ΔH_π are caused in the main by intermolecular interaction.

It follows from the data cited in Table 1 that anomalously high values of stabilization energy, which are equal to dozens or hundreds of kilocalories, calculated on one link or average macromole, are observed with the transition to the polymers with the system of conjugation. It is obvious that such high values of ΔH_π are the consequence of particular intermolecular forces, displayed even in the case of polymer hydrocarbons—substances without heteroatoms and dipole groups or hydrogen bonds.

It is interesting to note that it is characteristic for such polymers as 1,4-diphenylbutadiene-1,3, obtained by thermal polymerization, the decrease of experimental values of ΔH_π in comparison with calculated ones for linear structure, which may be formed by polymerization along one triple bond, are 23.5 to 54.4 kcal/mole. This fact confirms the data that the thermal polymerization of diphenylbutadiene passes through two triple bonds. Such a mechanism leads to the formation of polyconjugated polymers with strained rubrenelike fragments.

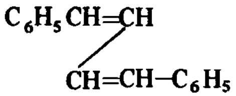
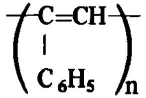
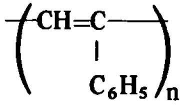
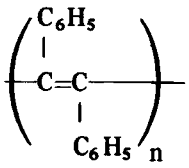
As has been shown, ΔH_π has a positive value for rubrene, equal to 44-46 kcal/mole. It is associated with reciprocal repulsion of the closely situated phenyl nuclei. It follows from this that the rather high negative value of ΔH_π in the case of polydiphenylbutadiene indicates the considerable contribution of π-electron interaction.

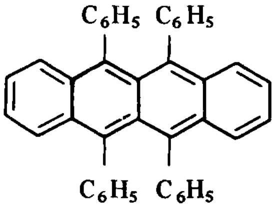
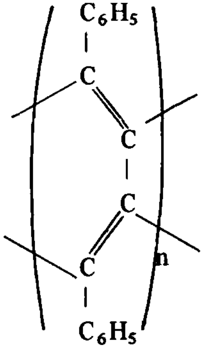
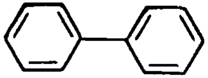
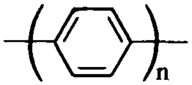
Thus experimental confirmation is found of stable intermolecular interaction in polyconjugated systems, and which are responsible to a considerable degree for their thermostability and specific properties. Apparently, π-electron interaction makes an even greater contribution than does the energy of intramolecular delocalization in the case of spacialy uncomplicated polyconjugated systems. A high tendency of polymers with conjugation systems to form stable associates, which follows from the above-mentioned data, gives grounds for the assumption of microheterogeneous structures for such compounds [1, 7].

Electronomicroscopical investigations confirm this conclusion [7] (see Fig. 3). Shading replicas from the breaking of monolithic samples and particles of amorphous polyphenylacetylene and polytolane show the presence of secondary spherical formations with dimension of about 10-50 nm (100-500 Å).

Analogous substructural formations have been observed by us for some other PCS (polytolane, polydiphenylbutadiene). It is logical to assume that the presence of secondary spherical formations indicates that associates of macromolecules represent microphases of the system. With the formation

Table 1

No.	Name	Link	$\bar{M}_n$	$-\Delta U_{exp}$ (kcal/mole)	$-\Delta U_{calc}$ (kcal/mole)	$-\Delta H_{\pi}^*$ (kcal/mole) (link)	$-\Delta H_{\pi}^*$ (kcal/mole) (macromole)
1	Styrene	$C_6H_5CH{=}CH_2$	104.15	1048.2	1050.0	1.8	
2	trans-Stilbene	$C_6H_5CH{=}CH{-}C_6H_5$	180.25	1762.1 ± 0.9 (1758.2 ± 0.2)	1768.8	6.1	
3	trans-trans-1,4-diphenylbutadiene-1,3		206.29	2027.5 ± 0.5 (2024.7 ± 0.3)	2039.4	11.9 (14.7)	
4	Polyphenylacetylene (thermal polymerization)a	 $\left(-C(C_6H_5){=}CH-\right)_n$	1100.0	984 ± 0.7	993.5	9.1	97.4
5	Polyphenylacetylene (catalytic polymerization)b	 $\left(-CH{=}C(C_6H_5)-\right)_n$	5700.0	977.1 ± 0.2	994.4	17.3	960
6	Polytolan	 $\left(-C(C_6H_5){=}C(C_6H_5)-\right)_n$	890.0	1695.2 ± 0.1	1717.9	22.7	113.5

7	Rubrene		535.69	5059.7 (5057.5)	5013.7	-41.6 (-43.8)	
8	Polydiphenyl-butadiene-1,3		2150.0	1901.4± 1.4	1924.9	23.5	249.1
9	4,4-Diphenyl		154.0	1492.7	1495.7	3.0	
10	p-Polyphenylene (Kovachič)		6000	672.0	716.8	45.0	3600

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[a]Conjugated block with n conjugations = 2-3 links. Reference or calculated data in parentheses.

[b]Conjugated block with n conjugations = 5-7 links. Reference or calculated data in parentheses.

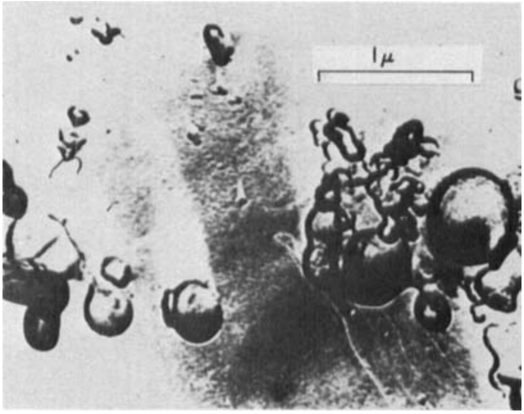
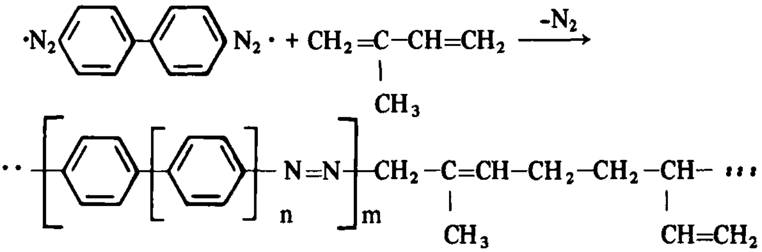


Fig. 3. Submolecular formations of polytolane replicas, shading by Pt-C, 33,000 X.

of polymer such particles tend to decrease the interface by packing in spherical aggregates.

Recently it was successfully shown that if polyconjugated blocks are introduced into elastomer molecule, more dense packing of associates may be achieved than in the case of "pure" PCS with the same structure. For example, in the polymerization of isoprene by bisdiazonium in the presence of reductant or nitroazodiacetate of aromatic diamines (for example, benzidine), block copolymers, including polyazophenylene fragments, are formed [8]



Such block copolymers with small amount of PCS-blocks (m = 15-20%) are thermoelastoplastics, with EPR signals characteristic for polyazophenylene and with an anomalous form of the curve for the dependence of reduced viscosity on the concentration with increased η/c at $c \leqslant 0.2$-0.3 g/100 ml, peculiar to associated substances. Such elastomers have a violet color

color while polyazophenylene, obtained under the same conditions, is yellow or light-brown.

As can be seen from Fig. 4, elastomer containing only 15% of polyazophenylene blocks has, in contrast to pure polyazophenylene, a maximum of absorption spectra at λ = 560 nm and is characterized by a considerably higher extinction coefficient value in the long wave region ($\lambda > 500$ nm).

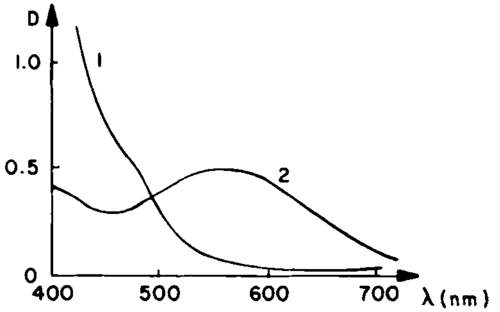


Fig. 4. The absorption spectrum for polyazophenylene ($\bar{M}_n$ = 2200) (Curve 1) and block copolymer of polyazophenylene (PAP) and polyisoprene (the PAP content = 15%, $\bar{M}_n$ = 22,000).

It must be added that an increase of polyazophenylene block content above 60% leads to light-colored yellow-brown products which are not elastomers at t = 20-50°. Their absorption spectra are similar to polyazophenylene. Apparently the reason for such anomalous regularities are the following. The packing into bundles of associates is greatly facilitated if we place a hard polyconjugated block into a flexible matrix (caoutchone). As a result, intermolecular π-electron interaction is more complete and this, in a certain sense, is equivalent to the growth of a conjugated chain and, hence, is connected with a decrease of energy gap and bathochromic shift in absorption spectra.

The ideas about the microheterogeneous structure of polymers with the system of conjugation are in a perfect agreement with the heterogeneous model of polymer semiconductors proposed in previous works [9, 10].

As a result of EPR-spectra investigations, investigations of frequency and temperature dependences activation energy of conductivity, thermoelectromotive force and application of carrier injection method for polytetraacyanoethylene, its chelate complexes and thermolized irradiated polyethylene, it was convincingly shown that there are regions of polyconjugation in such systems where the conductivity is a few orders greater than the average value and the activation energy of conductivity tends to zero. Therefore estimates have been made of high carrier mobility in the regions of polyconjugation (10-100 cm^2/V sec), while the average mobility for the same polymers does not exceed 10^{-2} to 10^{-6} cm^2/V sec. The minimum linear dimension of conducting regions for polytetra-acyanoethylene is about 40 Å. As a result of thermal treatment of polymer (higher than t = 350°), the increase of conductivity and dimensions of such regions up to 300 Å has been observed.

Thus we have every reason to believe that the structure of PCS includes "metal-like" associates, formed microphase of the system. Such associates unite into more friable spherical formations, randomly situated among weakly associated macromolecules. Apparently low mobility and lifetime of carriers in polymer semiconductors are connected with their random microheterogeneous structure. Some recently published data [11] giving the increase of drift carrier mobility as 4-5 orders by a corresponding treatment of polyphenylacetylene to change its submolecular structure are confirmation of the above-mentioned ideas.

ABOUT PARAMAGNETISM OF POLYMERS WITH THE SYSTEM OF CONJUGATION, "SPIN" COMPLEXES, AND "THE EFFECT OF LOCAL ACTIVATION"

The most general property of PCS which makes them different from "saturated" polymer is the presence of spins, which were discovered by EPR methods.

Paramagnetic centers (PMC) influence the physical and physicochemical properties of PCS, including dark and photoinduced electroconductivity, absorption spectra, luminescence, and reactivity. The PMC influence on the properties of complexed molecules with conjugated system was discovered in our laboratory and called "the local activation effect" in 1962 [12-15].

Nevertheless, the question of the nature and formation conditions of PMC cannot be considered as settled at present. There are two basic points of view on the nature of PCS paramagnetism: 1) The biradical hypothesis [12, 15], according to which paramagnetic centers arise due to a local unpairing of π-bonds in the longest conjugated macromolecules. It is assumed that S-T transition takes place due to thermal excitation and triplet formed turns into a stable double radical. The possibility of such transitions is determined by insignificant energetic gaps in the bundle-packed associates of polymer homologous fractions with long conjugated chains, broken coplanarity in these systems, and sufficient energy gain from the unpaired spin delocalization along the conjugated system. 2) The hypothesis that the charge transfer complexes are determinative [16, 17]. It assumes that there are closely situated polar states realized by the one-electron intermolecular transfer with the formation of stable ion-radical complexes.

The hypotheses mentioned are able more or less to explain the experimental facts concerning PMC generation and their influence on PCS properties [18, 19].

The biradical hypothesis received its present status through quantum chemistry calculations of polyenes as sums of =CH− groups possessing an odd number of electrons [20]. An interaction of the two nearest neighbors depends on their electrons summary spin. There are two possible cases: 1) neighbor summary spin $S = 0$ and interaction energy is equal to Q; 2) summary spin $S = 1$ and interaction energy is equal to R. Case 1 is preferable (antiparallel orientation of spins) for organic molecules. Energy $R - Q$ must be spent to violate this order at any place in a chain and to produce the triplet excitation ($S = 1$). If we take into consideration that this excitation is not localized at one link but is spread over the entire conjugation chain, then we get an energetic band $E_{max}(P_{max}) - E_{min}(P_{min})$ instead of one level with energy of excitation $R - Q$. The width of this band is determined by the probability of the triplet excitation jumping over. It is worth mentioning that this jumping over and the bandwidth are conditioned by the electron exchange interaction, hence the energy of triplet excitation is washed away and forms a band, the lower edge of which sides with the basic level.

Quantum chemical calculations have shown that the energetic spectrum (E_n) of the lowest triplet excitations of the polyene chain which is of quasihomopolar character are

$$E_n = \delta \, | n | / N$$

where

$$\delta = 4\pi\beta \frac{I_1\left(\frac{2\pi\beta}{\gamma}\right)}{I_0\left(\frac{2\pi\beta}{\gamma}\right)}$$

and $n = \pm 1, \pm 2, \pm 3, \ldots$. Here β is the resonance integral, γ is the Coulomb integral and determines the repulsion of two electrons at one center, I_0 and I_1 are the Bessel functions of imaginary argument of the zero and the first orders, and N is the number of π-electrons. If we further take into consideration that according to Refs. 21 and 22 there is no bond alternation in polyene and analogous structures, only one value of β must be taken into account. Then the energetic spectrum of the lowest triplet excitations is

$$E_n \simeq \frac{|n|}{N} \; \frac{4\pi^2\beta^2}{\gamma}$$

if $2\pi\beta/\gamma$ is small.

The smaller β is the lower the spectrum is when N and γ are constant. The diminition of β is probable when coplanarity of structural elements of PCS macromolecules is broken as is really observed [23, 24] but large values of N can take place in the longest high molecular fractions.

The number of the conjugated π-electrons increases greatly if we take into account an intermolecular π-electron exchange interaction.

From all that has been said above it follows that there are low-lying triplet excitations in most polymeric fractions of PCS and the probability of these states increases together with the number of exchange-interacted π-electrons.

Calculations show that the energy of the singlet-triplet transition in PCS is of order of kT, and excitation is stabilized by the delocalization along the conjugated chain and interacts very weakly with the lattice acoustic oscillations.

The triplet excitation which arises is therefore characterized by a long existence. The one-electron intermolecular transfer of triplet spins is valid when the ionized state formation is preferable (existence of polar groups and heteroatoms, solvation by a medium with large ϵ, etc.).

All that has been said above about low-lying triplet states in PCS makes clear the origin of the PMC appearance during the soft conditions of synthesis. These data supplement our earlier biradical hypothesis [12-15] and are of great importance for a general theory of paramagnetism of PCS. Recently discovered thermally excited paramagnetism in PCS [23] is in good agreement with everything stated above.

Figure 5 illustrates the temperature behavior of the EPR signal intensity of the oligophenylacetylene (OPA) treated briefly at 400°C. It is seen that raising the temperature for 5-10 min causes a growth in the intensity of as much as 2.5 times (a-b) and subsequent cooling for about 30 min is not

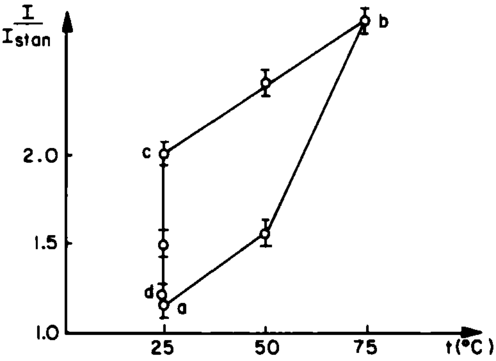


Fig. 5. The dependence of EPR-signal intensity on temperature for oligophenylacetylene. Ordinate: Ratio of EPR-signal intensity to standard signal.

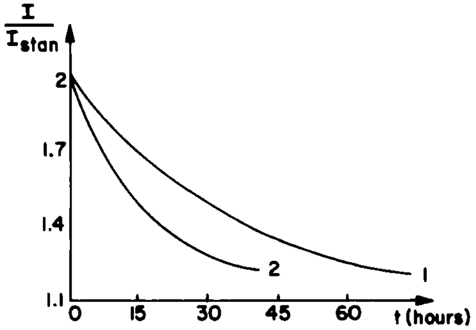


Fig. 6. The rate of change in EPR-signal intensity for oligophenylacetylene (OPA) at room temperature. The time scale is stretched for segment "c-d" of Fig. 5. Curve 1: Solid sample of OPA. Curve 2: OPA in benzene solution. (c = 0.3 mole/l.)

followed by a return to the initial intensity (b-c). Further, at room temperature (c-d and Curve 1 of Fig. 6) a diminishing of the intensity practically to the initial value was observed. This time dependence of the EPR signal intensity is characteristic for a OPA-benzene solution as well (benzene is degassed). But the time for return to the initial value (relaxation time) is shorter for solution than for the solid state (Curve 2, Fig. 6). It has been shown that this phenomenon is not connected with SHF saturation.

Taking into consideration all that has been said above, we can assume that part of the EPR signal observable in PCS at room temperature is due to thermal excitation. This assumption was confirmed by decreasing of the EPR signal intensity in a pattern which was held for 3 months at -78°C. The fact that the Curie law is valid for lower than room temperatures may be connected with the great relaxation time of EPR signal intensity.

As has been pointed out before, it is typical of PCS that there exist strong macromolecular associations where intermolecular π-electron delocalization takes place. If we allow three-dimensional (intermolecular) π-electron delocalization, we can suppose the intermolecular transfer of spin-magnon in PCS associations.* Therefore diamagnetic and paramagnetic associations must be considered as particular types of intermolecular complexes which can be named "the spin transfer complexes" (STC) or "magnon complexes."

We consider that STC are widespread and of great frequency in chemistry and biology. Such complexes, besides paramagnetic PCS, are complexes of aromatic and conjugated hydrocarbons with stable radicals, NO, O_2, etc.

The question of particular interest is in the transfer of excitation from triplet particles to molecules complexed with them: What must change the triplet excitation probability and hence change the reactivity and physicochemical properties (the "effect of local activation") [13-15]?

The role of "the effect of local activation" has been proved at present for thermolysis [24, 25], thermal and photooxidative destruction [26-28], initiation [29-32] of polymerization, radical reactivity of PCS [32-35], catalysis by PCS [36], and activation of cis-trans isomerization [37].

PMC influences the physical properties of PCS, for example, the fluorescence yield, the photocarrier lifetime, and the conduction energy activation [38-43].

The effect of local activation involves a great number of phenomena, many of which are of great scientific and practical interest.

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