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Abstract

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On the Relation of the Electrical Conductivity of Organic Substances with Conjugated Bonds to Their Electron Magnetic Resonance Spectra

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It is known that a number of organic substances possess enhanced electrical conductivity of a nonionic type at room temperature and a clearly expressed photoconductivity effect (^{1,2}).

Recently, in connection with the preparation of a number of polymers with enhanced electrical conductivity, interest in organic semiconductors has greatly increased ($^{3-5}$). Substances possessing enhanced electrical conductivity consist, as a rule, of molecules with conjugated double bonds.

In work by one of us with coauthors (^{6}), a series of polymers with conjugated double bonds was studied, and substances were also found that possess enhanced electrical conductivity at room temperature. However, it turned out that most of the substances investigated are, at room temperature, typical insulators, with values of the "activation energy" E and of the pre-exponential factor σ_0 of the electrical conductivity σ varying, depending on the substance and on the conditions of preparation of the specimen, over very wide limits. It was found, moreover, that σ_0 and E are related by an approximately linear dependence, expressed less distinctly in the region of substances with low E and especially clearly in the region of large E.

At the same time, in works ($^{7-9}$) it was shown that these compounds possess anomalous magnetic properties, which reduce to the following. In all polymers with a sufficiently developed system of conjugated double bonds, narrow (4-8 Oe) symmetric lines of electron paramagnetic resonance are observed, with the g-factor of a free spin. The signal intensity does not depend on the method of preparation of the polymer, but is completely determined by the degree of conjugation. In the polymers studied, the intensity of the signals formally corresponds to a content of 10^{16}–10^{20} unpaired electrons per gram of specimen, or 10^{-4}–10^{-1} unpaired electron per molecule. The effect is retained upon dissolution, and the number of unpaired electrons per gram does not depend on dilution. The temperature dependence of the intensity of the resonance signals shows that for these compounds the Curie law is strictly obeyed, i.e., that the state of the system responsible for the appearance of the resonance signal is the ground state.

Graph showing relation between E and $\lg \sigma_0$

Figure 1: Graph showing relation between E and $\lg \sigma_0$

In addition, for some of the polymers with conjugated bonds, containing heteroatoms, electron-donor and electron-acceptor groups in the conjugation chain, extremely broad (500–1000 Oe) asymmetric magnetic-resonance lines with a g-factor shifted toward larger values relative to the g-factor of a free electron are observed in the solid state. The integral intensity of these "broad" lines corresponds (assuming true paramagnetism) to the presence of 10^{21}–10^{22} unpaired electrons per gram of specimen. However, the sharp dependence of the static magnetic susceptibility on the intensity of the external magnetic field (pronounced saturation effects) indicates that in this case it is not paramagnetism but an effect associated—

connected with collective spin interaction. In work (^{10}), the name "pseudoferromagnetism" of organic structures was proposed for these phenomena. The effect of the broad line disappears upon dissolution and is sharply enhanced by treatments of the sample that lead to a more ordered packing of the macromolecules (^{9}).

It is of interest to compare the magnetic properties and electrical conductivity of the substances investigated by the authors. In Fig. 1 data are given on σ_0 and E for these substances, as well as for several substances about which information is available in the literature. At the same time, Fig. 1 shows the type of magnetic-resonance spectra that

Fig. 1. Relation between the pre-exponential factor and the activation energy of electrical conductivity *

* In Fig. 1, samples giving only narrow EPR lines are denoted by a plus sign; samples giving broad EPR lines by a dot. 1 —polyphenylacetylene: a mixture of yellow (obtained by polymerization at the boiling temperature of phenylacetylene) and black (yellow, heated to 400°). 2 —the same as 1, but another sample. 7 —

[structural formula shown]

$$[-\mathrm{C_6H_4} - \mathrm{NH}-]_n$$

(with COOH substituent on the aromatic ring)

(All structural formulas are given tentatively, according to (^{6})). 9 —the same as 7, but another sample. 10 —

[structural formula shown]

$$[\text{quinone-biphenyl dicarboxylic-acid unit}]_n\, [\text{quinone-N} =] = [\text{N} - \text{biphenyl dicarboxylic-acid unit}]_m\,.$$

11 –

$$[-C_6H_4 - C_6H_4 - NH - N = N-]_n \, .$$

12 –unfractionated 11, of lower molecular weight; 14 –

[structural formula shown]

$$[\text{quinone-phenylene unit}]_n \, .$$

[structural formula shown]

$$[\text{quinone} - N = N - C_6H_4-]_m \, .$$

16 –

$$[-C_6H_4 - C_6H_4-]_n \, [-N = N - C_6H_4-]$$

(with COOH substituents as shown).

give the indicated substances. As can be seen, all substances that give broad electron-magnetic-resonance lines are shifted, in electrical conductivity, toward larger values at the given E, which corresponds to increased conductivities at room temperature. At the same time, the linear dependence of σ_0 on E becomes still more clearly visible; moreover, one may note that it also well covers all substances without broad magnetic-resonance lines. The results presented clearly testify to the existence of a correlation, above all, not between electrical conductivity and the appearance of the e.p.r. spectrum of a conjugated system in general, but to a correlation between the pseudoferromagnetic properties of organic structures and their electrical conductivity.

At present, a rigorous theoretical interpretation of the indicated correlation cannot be given. It can only be pointed out that the appearance of "broad lines" apparently indicates the presence in the sample of regions of order with a large number of unpaired electrons. It may be supposed that charge motion in such regions takes place practically without resistance. The factor limiting the electrical conductivity in this case is charge transfer between the "regions of order."

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$$-\langle\text{phenylene unit with COOH}\rangle_m$$

unfractionated. 17 –insoluble fraction 16. 18

$$\mathrm{Cl}\,[-\langle\text{biphenylene unit}\rangle-]_n\,[-N=N-\langle\text{biphenylene unit with } CH_3, CH_3\rangle-]_m\,\mathrm{Cl}$$

(heated at 200°). 19 –the same as 18, but unheated. 20

$$\mathrm{Cl}\,[\,\langle\text{dimethyl biphenylene unit with O}\rangle\,]_n[-N=N-\langle\text{biphenylene unit}\rangle-]_m\,\mathrm{Cl}$$

(heated). 21

$$[\,\langle\text{dichloroquinone unit}\rangle-N-\langle\text{biphenylene unit}\rangle\,]_n.$$

22 –complex of 21 with copper acetate. 26 –complex of tetrasalicylideneferrocene with Fe^{++}. 29 –copolymer of polyphenylacetylene with hexine. 31 –polytetracyanoethylene. 32 –polytetracyanoethylene with cyanethylene. 34 –polyphenylacetylene (yellow, pressing conditions 200°, 2000 kg/cm^2). 35 –polyphenylacetylene (black, pressing conditions 200°, 2000 kg/cm^2); 36 –copolymer of yellow polyphenylacetylene with *p*-diethynylbenzene. 37 –complex of

acenaphthene with chloranil (1 : 1). 39 –the same as 37; ratio 1 : 2. 74 – polyphenylene.

Note: Figure translations are in progress. See original paper for figures.

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