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Abstract

Full Text

Physical Chemistry

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Electron Paramagnetic Resonance Spectra of Cyanine Dyes

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In the investigation by the method of electron paramagnetic resonance (e.p.r.) of compounds having a system of conjugated bonds, resonance absorption was observed in some cases (1,7), caused by the fact that the molecules have an uncompensated electronic magnetic moment. Thus, in substances which, according to modern concepts, have fully saturated chemical bonds, radical states appear; the study of these states can, on the one hand, explain certain chemical features of molecules with a large number of conjugated double bonds and, on the other hand, clarify the mechanism—still unclear at the present time—by which paramagnetism arises in them.

A convenient object for the study of e.p.r. spectra of conjugated systems may be cyanine dyes, which have found wide practical application for the optical sensitization of photographic emulsions. In the present work the influence on the e.p.r. spectrum of the number of conjugated double bonds between heterocyclic nuclei, the structure of the heterocyclic nuclei, and the nature of the dye anion was studied. The following symmetrical cyanine dyes served as the objects of measurement:

1. Symmetrical cyanine dyes with two quinoline-type heterocyclic nuclei bearing N-ethyl substituents; the polymethine chain is

$$-\mathrm{CH} = (\mathrm{CH} - \mathrm{CH})_n =$$

with iodide counterion J^-, where

$$n = 0;\ 1;\ 2;\ 3;\ 4.$$

2. A symmetrical dye with two quinoline-type heterocyclic nuclei bearing N-ethyl substituents; the chain is

$$-\mathrm{CH} = \mathrm{CH} - \mathrm{CH} =$$

with chloride counterion Cl^-.

Fig. 1. EPR spectra.

Figure 1: Fig. 1. EPR spectra.

3. Symmetrical cyanine dyes with two benzothiazole-type heterocyclic nuclei bearing *N*-ethyl substituents; the polymethine chain is

$$-\mathrm{CH} = (\mathrm{CH} - \mathrm{CH})_n =$$

with iodide counterion J$^-$, where

$$n = 0;\ 1;\ 2;\ 3;\ 4.$$

4. Symmetrical cyanine dyes with two dimethyl-substituted indolenine-type heterocyclic nuclei bearing *N*-ethyl substituents; the polymethine chain is

$$-\mathrm{CH} = (\mathrm{CH} - \mathrm{CH})_n =$$

with iodide counterion J$^-$, where

$$n = 3;\ 4.$$

All the dyes were pure preparations, with the exception of dye 1 with $n = 4$.

The measurements were carried out with dye powders in amounts from 20 to 90 mg on a spectrometer [2] using a frequency of $9 \cdot 10^9$ Hz, double magnetic modulation, synchronous detection, amplification at a frequency of 975 kHz, and a circuit for automatic tuning of the klystron frequency to the working resonator. The absorption curve was recorded in the form of the first derivative by an EPP-09 recorder.

The EPR signal was not obtained for all the dyes investigated. However, when resonance absorption was observed, the line was a symmetric singlet with g-factor 2.003 (Fig. 1,a). The line width varied depending on the structure of the dye. One of the dyes investigated (2 with $n = 3$), in addition to the narrow singlet, had a second, rather broad singlet with g-factor 2.24 (Fig. 1,c). The line width, determined between the points of maximum slope of the absorption curve, in the latter case was equal to $\Delta H_{\mathrm{mn}} = 130$ G.

Fig. 1. EPR spectra. *a*—dye 1, $n = 3$; *b*—dye 3, $n = 3$, 1—$T = 290^\circ$ K, 2—$T = 90^\circ$ K; *c*—dye 1, $n = 3$.

The concentration of unpaired electrons was determined against a known standard (diphenylpicrylhydrazyl) and corresponded approximately to one free electron per 10^4 dye molecules. Because of the low intensity of the EPR spectrum

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and the small quantities of the preparations, the determination of the concentration of unpaired electrons had an accuracy within one order of magnitude.

The results obtained are summarized in Table 1, from which it is evident that, for this homologous series of dyes, resonance absorption arises only at a certain number of conjugated double bonds. With increasing conjugation the EPR line width decreases. Another factor determining the occurrence of the radical state is the nature of the heterocyclic nucleus. In the case of quinoline derivatives the EPR spectrum arises at a conjugation corresponding to three CH groups, whereas in benzothiazole derivatives no fewer than five CH groups are necessary for the appearance of a signal, and in indole derivatives even seven CH groups. Apparently, the formation of the radical state is influenced by the basicity of the heterocyclic nucleus, which decreases in the same order. It is interesting to note that the anion (replacement of J^- by Cl^-) does not play an essential role in the resonance absorption of the dye. This is evidence in favor of the radical state arising in the system of conjugated bonds of the dye cation.

It may be assumed that the EPR spectrum in the dyes investigated is caused by a thermally excited triplet state, the energy of which, with sufficient conjugation, becomes comparable with kT. However, this is contradicted by experiments at low temperatures. The EPR signal at the temperature of liquid nitrogen does not decrease, but increases by approximately a factor of 2 (Fig. 1,b), as is observed in paramagnetic substances. Thus, the presence of an uncompensated electronic magnetic moment in the substances studied is associated not with the excited state, but with the ground state of the dye molecules.

As can be seen from Fig. 1,b, lowering the temperature to 90° K does not decrease the width of the EPR line. Consequently, in our case the broadening of the EPR line is not limited by spin-lattice interaction. Apparently, the decrease in the EPR line width with increasing chain length is—

conjugated bonds is due to the increasing delocalization of the electron over many centers (4).

A very characteristic circumstance is that the radical states we have observed arise in those dyes that absorb light in the red and near-infrared regions of the spectrum. These dyes usually bleach very rapidly in aqueous solutions. On the other hand, during the optical sensitization of photographic emulsions by readily destructible dyes, an increased instability of the photographic properties is often observed. There are indications that atmospheric oxygen plays an essential role in these processes (4–6). In this connection it was of definite interest to determine the influence of atmospheric oxygen on the EPR spectrum. It turned out that evacuation of dye 2 with $n = 3$ for 4 hours to a vacuum of $2 \cdot 10^{-6}$ mm Hg causes the signal to increase by 20–30%. After air is admitted into the ampoule with the dye, the EPR signal correspondingly decreases, which indicates interaction of the dye molecules with atmospheric oxygen. Unfortunately, we were unable to obtain EPR spectra of solutions of the dyes because of their poor solubility. However, the results indicating the preservation of a very similar EPR signal upon dissolution of polyphenylvinylene, as well as the regular influence on the EPR spectra of changes in the structure of the cyanine dyes, make it possible to assert with considerable certainty that the radical states are a property of the molecules of the compounds studied, and not of their crystalline structure.

Table 1

Dye no.	n	Mol. wt.	Abs. max.	ΔH_{mn}, G	g-factor
1	0	454	523	–	–
1	1	480	603	8.4	2.003
1	2	506	707	4.6	2.003
1	3	532	820	4.3	2.003
1	4	680	–	8.0	2.003
2	1	388	605	9.5	2.003
3	0	478	424	–	–
3	1	504	559	–	–
3	2	530	652	15	2.003
3	3	556	762	7.3	2.003
3	3	556	762	130	2.240
3	4	582	870	5.7	2.003
4	2	630	639	–	–
4	3	656	730	15	2.003

The results of the investigation carried out show that the appearance of an uncompensated electronic magnetic moment in cyanine dyes is connected not with thermal excitation, but with the ground state of the dye molecules; moreover, each molecule has a spin density of 10^{-4}.

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