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Relation between the thermal activation energy of conduction and the first excited singlet state energy—a case of photo-conducting organic materials

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Abstract

The thermal activation energy of dark conductivity has been measured for a new series of cationic cyanine dyes (seven in numbers) derived from different heterocyclic nuclei. The thin layers of the dyes were obtained by vacuum deposition on a surface type raster cell in a vacuum of the order of 10^{-4} Torr. The results concerning the nature of charge transport have been discussed. A relationship between the thermal activation energy (ΔE_D) and the first excited singlet state energy of the molecules (^1E) has also been attempted.

Keywords: Conductivity; Activation energy; First excited singlet state energy; Organic semiconductors

1. Introduction

The level of sophistication of research in the field of electrical properties of organic semiconductors has increased steeply both in experimental techniques and theoretical analysis. Several theories have been proposed to explain the generation and transport of charge carriers through these materials [1]. This is not surprising because the structural organization of organic semiconductors is not as clear-cut as for inorganic semiconductors. These materials (specially organic dyes) form an important group of materials on account of their conduction properties, narrow absorption profile in the visible region and due to the fact that its spectral response can easily be changed by chemical substitution [2]. These compounds fabricated in thin layers have shown very useful properties with various potential applications in diode laser printers [3], photovoltaic devices [4], vidicon pick-up tubes [5] and xerographic photoreceptors [6]. The electrical properties of conjugated polycyclic molecular solids are related to the number of condensed aromatic rings and to the number of π-electrons in the molecules. Early results of Inokuchi et al. [7] on a series of polycyclic aromatic differing in condensed rings suggest that the electrical resistivity and energy gap decrease with larger number of condensed aromatic rings. The correlation between the energy gap with the number of π-electrons for linear polycenes and condensed naphthalene has been attempted [8]. In both cases, the energy gap decreases with greater number of π-electrons and conductivity increases. Systems such as naphthalene and anthracene containing a few rings have large energy gaps, low carrier mobilities and, consequently, high resistivities.

In elemental semiconductors, it is now well established that the activation energy for electrical conduction is theoretically expected to be half the band gap and this theoretical result is in agreement with the experimental observations. In the case of organic semiconductors, the picture is not quite clear. Akamatu and Sano [9] reported that the optical threshold energies for photoconduction were nearly in accord with the large wavelengths edge of optical absorption spectra of crystals and also in agreement with the values of energy gaps, which were estimated from the

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temperature dependence of electrical conductivity. Because of little difference between the band structure and the molecular energy levels in the case of organic semiconductors, a correlation between the activation energy (ΔE_D) and the first excited singlet state energy (^1E) has been proposed in the literature for many compounds [10–12] and in some, no such correlation exists [1,13,14]. The existence of correlation between ΔE_D and ^1E is still a matter of speculation. However, a large number of investigations for finding a relation between the spectroscopic data and activation energy continue [15–23].

Yadav et al. [22] and Raghavan et al. [23] have reported their data on two different series of dyes and shown that there is a correspondence between the thermal activation energy and first excited singlet state energy of the molecules. Here in this paper, an attempt has been made to investigate any such relation between the spectroscopic data and activation energy for the dark conduction. The photoconduction and photovoltaic properties of these dyes have been reported elsewhere [24,25].

2. Experimental

The cationic styryl dyes (seven in numbers) were derived by the condensation of *p*-dimethylamino benzaldehyde with four different bases, namely, ethylquinoline, methylpyridine, ethylbenzothiazole and ethylphenylthiazole to get the dyes *p*-dimethylamino styryl dye from *N*-ethylquinoline-4 (dye I), *N*-ethylquinoline-2 (dye II), *N*-ethylbenzothiazole (dye III), *N*-ethylphenylthiazole (dye IV), *N*-ethylpyridine-2 (dye V) and *N*-ethylpyridine-4 (dye VII), all with iodide anion and *p*-dimethylamino styryl dye from benzothiapyran (dye VI) with chlorate anion. The synthesis and purification of the dyes were done in the laboratory by soxhelet extraction, repeated re-crystallization and, finally, by column chromatography. The structures of the dyes are shown in Fig. 1.

The dc conductivity of thin layers of the dyes has been measured on a raster-type multi-electrode surface cell [25] having 35 gaps of 0.02 cm width among each other, prepared by etching out pure aluminum (BDH, UK, 99.99% pure) coated on a previously cleaned transparent quartz plate by the vacuum deposition technique in the vacuum of the order of 10^{-4} Torr. The conductivity was measured at different applied potentials in the range of 0–200 V between 288 and 333 K. The samples could not be studied beyond 333 K as they started deforming and the measurements were not consistent. The measurements for dark current have been made in the vacuum of the order of 10^{-5} Torr. The details about the block diagram of the experimental setup have been reported elsewhere [23–25].

A Perkin-Elmer Lambda 4B Spectrophotometer has been used to record the absorption spectra in solution form. A non-polar solvent, *n*-hexane is taken for solution spectra. Saturated hydrocarbon solvents (like *n*-hexane, cyclohexane, etc.) are said to be good spectroscopic solvents because they have comparatively low refractive indices and dielectric constants and hence give spectra nearly resembling the solid state and vapour spectra [26]. The method of Eley and Williams [27] has been adopted to calculate the photon energy corresponding to the higher wavelengths edge of the absorption spectra of these dyes.

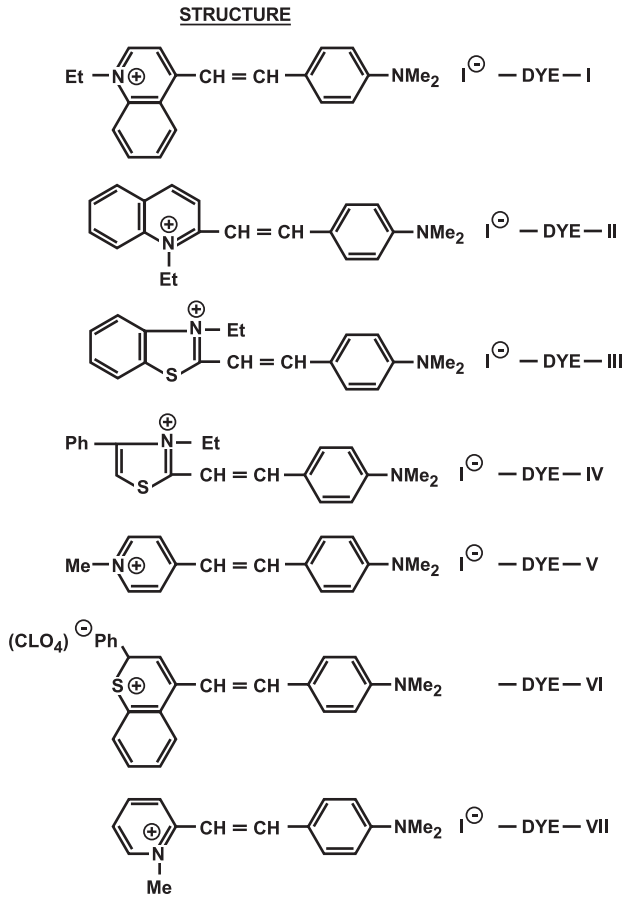

Fig. 1. Structures of the dyes studied.

3. Results and discussion

Electrical measurements on the current–voltage (*I–V*) dependence at different temperatures and in a vacuum of the order of 10^{-5} Torr were accomplished. The results that have been obtained are represented in Fig. 2 in a log I_D vs. log V graph (a representative plot is given for dye VII). It was observed that in all samples for applied potentials, an ohmic characteristic is followed throughout the temperature range studied. Hence, the electrode effect leading to the space charge does not seem to be present in the present series of dyes. The dark current found, ranged between 10^{-13} and 10^{-10} amp. Evidently, a few charge carriers can be thermally excited, possibly due to a relatively broad forbidden zone between the conduction and valence bands. The observed dark current might be due to the iodide ion acting as a donor impurity. The ions may be lying near or above the