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Compensation effect in the electrical conduction process in a series of pyrenyl polyenes

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Abstract. The semiconductive properties of a series of pyrenyl polyenes of the type R–(CH=CH)$_n$–R, are studied as a function of the adsorption of different amount of a vapour. With regard to the compensation temperature (T_0) the compounds are divided into two groups. For compounds which have odd number of double bonds, T_0 is infinite and in compounds having even number double bonds, T_0 is finite. T_0 for II_2 is higher while that of II_4 is lower than the experimental temperature. Different T_0 for the compounds having odd or even number of double bonds suggests a physical basis for the compensation rule, which we believe, is related to the molecular and crystalline structure of the compounds.

Keywords. Pyrenyl polyenes; electrical conduction; compensation effect.

1. Introduction

Earlier investigations (Mallik *et al* 1979, 1980a) in some linear conjugated polyenes revealed that the compensation temperature (T_0) of an organic semiconductor plays an important role in the dark conduction process. The decrease or increase in activation energy (E) with concomitant increase in conductivity (σ) as a result of adsorption of vapours on the polyene crystallites depends on whether T_0 is higher or lower than the experimental temperatures. As for example in vitamin A (alcohol and acetate) (Mallik *et al* 1979) a decrease in activation energy (E) with increase in σ on adsorption of vapours were observed and the compensation temperature for these compounds were at much higher value than the experimental temperatures. On the other hand the compensation temperatures of polyenes (Mallik *et al* 1980a) β-apo-8′-carotenal, astacene and methyl bixin being lower than the experimental temperatures, an increase in activation energy with a simultaneous increase in σ were observed on adsorption of vapours. It has been pointed out (Rosenberg *et al* 1968; Waclawck and Zabcowska 1980) that T_0 depends on the molecular property of the semiconductors. But it is still not clear which factors control the T_0 value. Recently it has been shown (Sircar *et al* 1982) that the observed compensation behaviour as well as the kinetics of adsorption and desorption for a series of naphthyl polyene compounds with odd number of double bonds are distinctly different from those having even number of double bonds. We have extended such investigations on a series of pyrenyl polyenes, with increasing number of double bonds to study the effect of the polyene end group and also the number of double bonds on the compensation temperature. In this paper we present the results of our investigations.

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2. Experimental

Highly pure samples of α,ω-di-2-pyrenyl polyenes of the type R–$(CH=CH)_n$–R, where R stands for the pyrenyl group and $n = 1$ to 4, were used for study. The samples were gifted to us by Prof. Nakagawa of Osaka University, Japan, who synthesised these chemicals and performed spectral studies (Nakasuji *et al* 1972). We have followed their convention of denoting the samples II_n. Sandwitch cell technique (Mallik *et al* 1979) was employed with a conducting glass and a stainless steel electrode. Organic solvents of spectrograde quality (E Merck, BDH) were used for adsorption studies. Dry nitrogen gas was used as carrier to pass the reagent vapour in the chamber. Repeated heating and cooling of the sample initially in vacuum and finally in dry nitrogen atmosphere ensured desorption of water vapour or any other adsorbed gases. The currents were measured with an electrometer amplifier EA 815 of the Electronic Corporation of India Ltd. The details of the experimental arrangement are as described earlier (Mallik *et al* 1979).

3. Results and discussions

As in other polyenes (Mallik *et al* 1979, 1980a), in pyrenyl polyenes also, the current starts increasing on adsorption of vapours and finally attains a saturation value. The maximum value of the current reached at equilibrium, under a particular experimental condition, depends on the vapour pressure of the reagent chemical and the temperature of the sample cell. The time required to attain this maximum equilibrium value at a fixed vapour pressure depends on the rate of flow. With increase in semiconduction current, the activation energy also changed significantly. The log σ (T) vs $1/T$ plot for any sample studied gives two distinct straight lines: One in the low temperature region after complete adsorption and the other in the high temperature region after complete desorption. The slope of the line in the low temperature region gives the activation energy in the adsorbed stage and that in the high temperature region reproduces the activation energy of the original sample. Such a plot of log σ and $1/T$ for II_1 on adsorption of ethyl acetate vapour is shown in figure 1.

4. Semiconductive properties

We have studied the effect of adsorption of different amount of a particular vapour on the activation energy of these polyene semiconductors in the usual manner (Mallik *et al* 1979, 1980b). The change in E is different for different amount of the same vapour adsorbed. In figures 2 and 3 change in E for II_1 and II_2 compounds on adsorption of different amount of ethyl acetate vapours are shown. For II_1 compound almost parallel extrapolated lines for different amount of adsorption are obtained. In II_2 compound the change in E is appreciable and the extrapolated lines all pass through a single point corresponding to a temperature T_0. At this point the σ (T_0) value is called σ'_0 which is a constant. Excellent plot of log σ_0 vs E was obtained for II_2 compound and is shown in figure 4. σ'_0 and T_0 values as obtained from figures 3 and 4 are $2{\cdot}4 \times 10^{-7}$ ohm^{-1} cm^{-1} and 310·5 K. Agreement between the set of values obtained from figures 3 and 4 confirm the high degree of correlation between the two parameters.

The log σ vs $1/T$ plot for ethyl acetate vapour adsorption in II_3 and II_4 compounds are shown in figures 5 and 6 respectively. In II_3 the change in E on vapour adsorption is

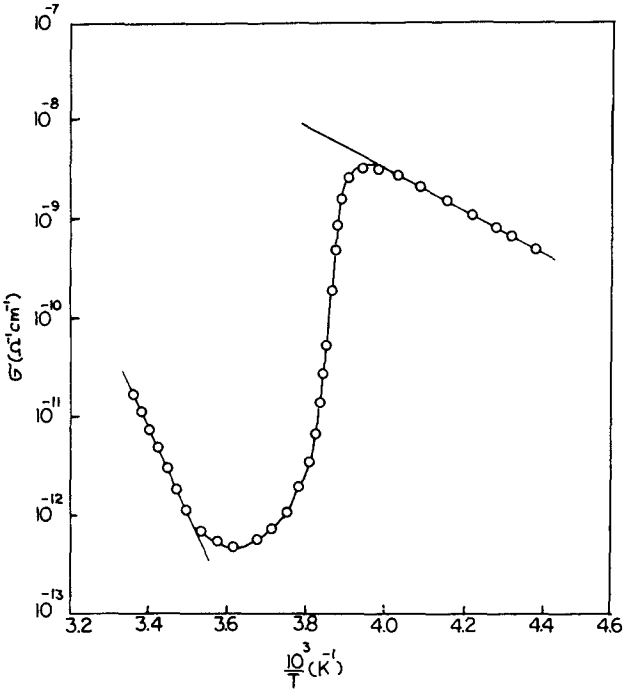

Figure 1. Semiconductivity data in an ethyl acetate adsorbed powder cell of II_1 compound as a function of temperature. Ambient vapour pressure at 60 torr; sample temperature 250 K.

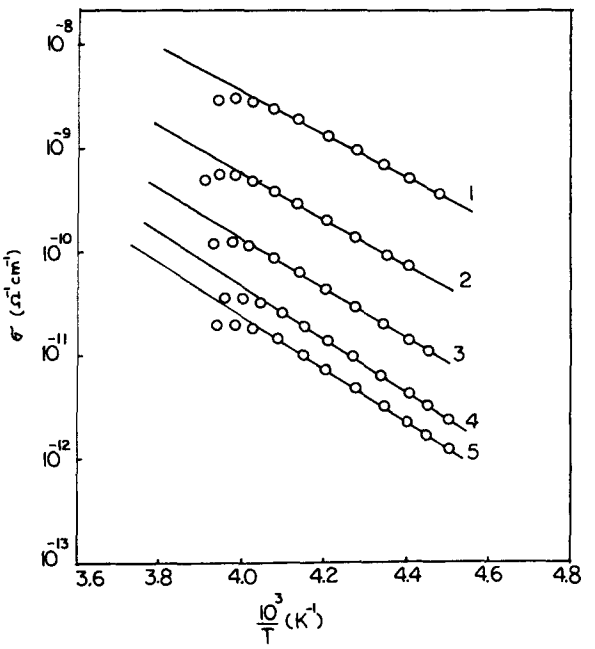

Figure 2. Semiconductivity data for II_1 compound with the adsorption of different amount of ethyl acetate vapour at 60 torr pressure and at a sample temperature of 250 K. The curves (1) to (5) refer to the states with decreasing amount of adsorbed vapour.

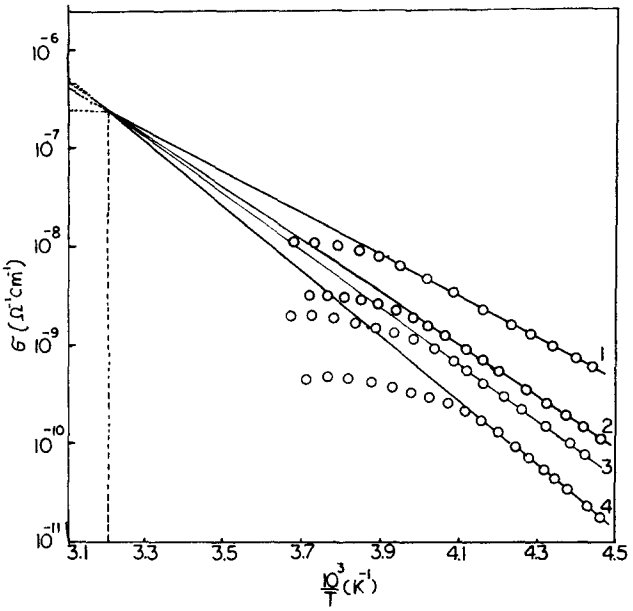

Figure 3. Semiconductivity data for II_2 compound with the adsorption of different amount of ethyl acetate vapour at 60 torr pressure and at sample temperature of 263·5 K. The curves (1) to (4) refer to the states with decreasing amount of adsorbed vapour.

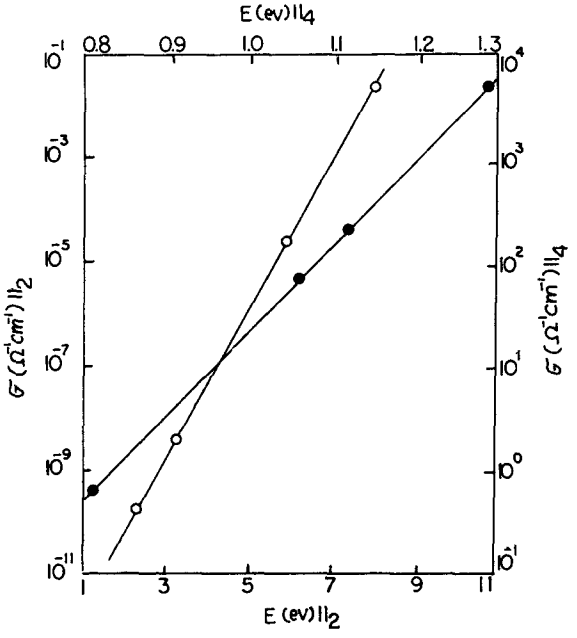

Figure 4. Plots of $\log \sigma_0$ at constant $T_1[1/T_1 = 4{\cdot}2 \times 10^{-3}\mathrm{K}^{-1}]$ versus activation energy (E) for II_2 and II_4. ——○—— for II_2; ——●—— for II_4.

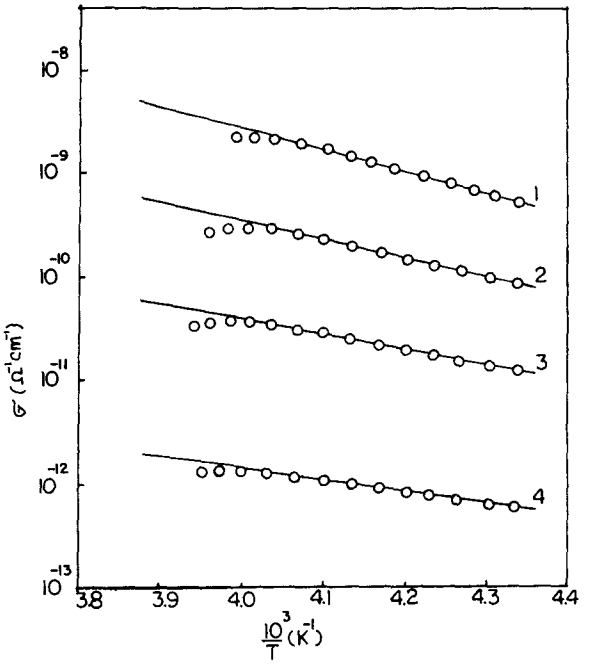

Figure 5. Semiconductivity data for II_3 compound with the adsorption of different amount of ethyl acetate vapour at 60 torr pressure and at a sample temperature of 250 K. The curves (1) to (4) refer to the decreasing amount of adsorbed vapour.

small and the extrapolated lines are almost parallel whereas for II_4 the extrapolated lines meet at a fixed point. Contrary to that in II_2, in II_4 compound the slope of log σ vs $1/T$ plot increases as the amount of adsorbed vapour increases. The plot of log σ_0 vs E for II_4 is shown in figure 4; T_0 and σ'_0 values as obtained from figures 4 and 6 for II_4 ($T_0 = 172{\cdot}7$ K; $\sigma'_0 = 4{\cdot}7 \times 10^{-14}$ ohm^{-1} cm^{-1}) are also in good agreement. Thus the conductivity equation for II_2 and II_4 takes the form $\sigma(T) = \sigma'_0 \exp E/2k(1/T_0 - 1/T)$ i.e. compensation rule is also valid in these cases. It is obvious from the equation that if $T_0 \gg T$ (or $T_0 \ll T$) a small change in E compared to (T) is expected as is observed for II_1 and II_3 respectively in our limited experimental range. Experimentally observed set of parallel lines in ln σ vs $1/T$ plots in figures 2 and 5 suggests T_0 of the above equation is either ∞ or 0. However, T_0 cannot be zero, for in that case, $\sigma(T)$ becomes infinite. On the other hand, $T_0 = \infty$, gives $\sigma(T) = \sigma_0 \exp(-E/2kT)$ which is the operational definition of semiconductor. These results indicate that in these polyene semiconductors compensation temperature T_0 is finite only for compounds with even number of double bonds. For compounds with odd number of double bonds T_0 becomes infinite.

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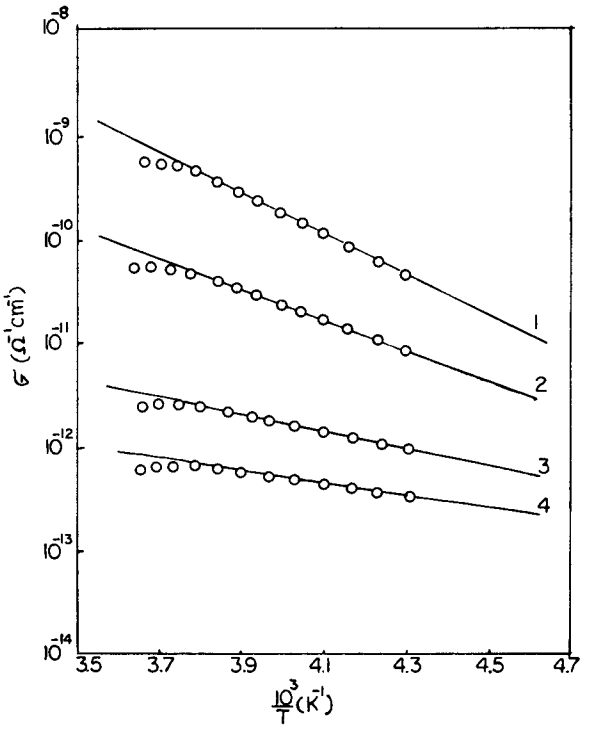

Figure 6. Semiconductivity data for II_4 compound with the adsorption of different amount of ethyl acetate vapour at 60 torr pressure and at sample temperature 263·5 K. The curves (1) to (4) refer to the states with decreasing amount of adsorbed vapour.

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