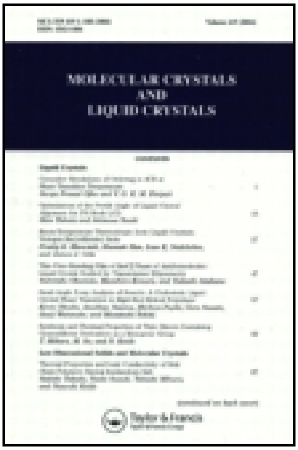

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Electrical Conductivity of Some Ethylenes and Butadienes

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The effect of electron repelling groups on the conductivity of some pure aromatic semiconductors has been investigated by an electrometer method. Ethylenes and butadienes (which are ethylenes with their mirrorimages) in the form of compressed tablets have been chosen for this purpose. In case of ethylenes, it has been found that the resistivity increases markedly as the electron repelling effect increases, but the activation energy (1.4 eV) remains constant. Butadienes show a similar behavior, though the relative increase in resistivity is much smaller than that of ethylenes, and the activation energy is about half as much (0.71 eV)

INTRODUCTION

In the last few decades, extensive studies on the electrical properties of organic semiconductors [1,2,3] have been made, but as yet there appears to be no complete picture of the factors governing the conductivity and its type[4] in organic semiconductors. However, up to our knowlegde there is no previous work dealing with such problem.

This work is an attempt to study the effect of electron-repelling groups on the electrical conductivities of some ethylenes and butadienes to which different groups with different electron-repelling forces could be attached to the molecules.

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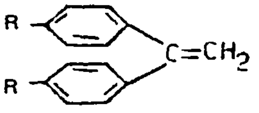
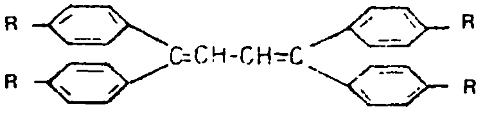
EXPERIMENTAL

Materials

–a– 1,1-bis-p-alkoxyphenylethylenes and –b– 1,1,4,4-tetrakis-p-alkoxyphenyl buta-1,3 dienes





were selected in view of thier high stability with time and with temperature. Moreover, the physical properties of annealed specimens are remarkably reproducable. (*R* stands for the electron-repelling groups which may be OCH_3, OC_2H_5 or OC_3H_7).

1– Preparation of 1,1-bis-p-alkoxy phenyl ethylenes. These were prepared from chemically pure materials (BDH), by the addition of the corresponding di-p-alkoxy benzophenone to methyl magnesium iodide ethereal solution, followed by hydrolysis of the product using aqueous ammonium chloride. Thus, we prepared

a 1,1-bis-p-methoxyphenylethylene with m.p.[5] 142°C, crystallized from acetic acid.

b 1,1-bis-p-ethoxyphenylethylene crystallized from acetic acid, m.p.[6] 142-143°C.

c 1,1-bis-p-isopropoxyphenylethylene crystallized from acetic acid, m.p.[7] 84°C.

2– Preparation of 1,1,4,4-tetrakis-p-alkoxy phenyl buta-1,3 dienes. a– 1,1,4,4,-tetrakis-p-methoxy phenyl buta-1,3 dienes.

A solution of 1,1,4,4-tetrakis-p-methoxyphenylethylene (2.4 gm, 0.01 mole) and 2-bromo-1,1-bis-p-methoxyphenylethylene (3.19 gm, 001 mole) in glacial acetic acid (20 cc) was boiled for two minutes. The solution acquired a deep olive green color and hydrogen bromide was libarated. The product separated on cooling was filtered off, and crystallized from glacial acetic acid to give 1,1,4,4-tetrakis-p-methoxyphenylbuta-1,3 diene (4.6 gm) with m.p.[8] 204-205°C.

b– Similarly we prepare:

i 1,1,4,4-tetrakis-p-ethoxy phenyl buta-1,3 diene crystallized from acetic acid with m.p.[6] 206-207°C.

ii 1,1,4,4-tetrakis-p-isopropoxyphenyl-buta-1,3 diene crystallized from acetic acid, m.p.[7] 187°C.

Throughout this work, these materials will be denoted by methoxy ethylene, ethoxy ethylene, isopropoxy ethylene, methoxy butadiene, ethoxy butadiene and isopropoxy butadiene respectively.

PURIFICATION OF THE MATERIALS

The test materials have been recrystallized several times from glacial acetic acid and measurements were performed after each crystallization. The purity of the sample is regarded as satisfactory if further recrystallization does not change the resistivity.

ELECTRICAL MEASUREMENTS

Compressed powder specimens of dimension 1 x 1 x 0.2 cm have been used. Samples prepared under pressures of 1000kg/cm^2, 2000 kg/cm^2 and 4000 kg/cm^2 respectively have been tested but no appreciable changes in conductivity could be detected for these packings. Inokuchi[9] in connection with the work on isoviolanthrone, observed rather rapid increase of conductivity at low pressures followed by approach to a levelled-off value at about 80 kg/cm^2, while Samara and Drickamer[10] reported a levelling-off value at about 200-250 kg/cm^2. In the present work, pressures of 1000 kg/cm^2 were used in order to insure freedom from voids.

Tests were made using different types of electrodes, such as silver-paste, Aquadag and thin layer of powdered metal (Cu) applied to the sample ends during compression. Alle these electrodes were found to be good enough and ohmic showing linear current-voltage relationship. The electrical measurements were carried out by means of vibrating reed electrometer (type VA-J-52, enabling current measurements down to 10^{-14} A) in a vacuum of $\approx 10^{-3}$ mmHg, using electric fields ranging from 20 to 1000 V/cm.[2]

The cell used is teflon insulated, and is otherwise similar to that of Brown and Aftergut[11] with slight modifications as shown in Figure 1.

RESULTS AND DISCUSSIONS

The variation of the dark log d.c. resistivity with the resiprocal of the absolute temperature for the ethylenes and butadienes is shown in fig. 2 in the temperature range from 25°C up to 20°C below the melting point. The temperature

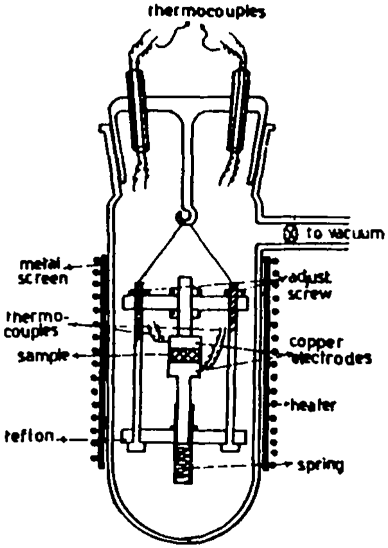


FIGURE 1 The conductivity cell for d.c. meqsurements

dependence of ρ was recorded during both heating and cooling cycles and in both directions of the current, concordant results were obtained for heat treated samples.

An increase with time in the conductivity, especially at high temperatures, is observed in fresh samples which is probably due to annealing.[12] Provided each specimen is first annealed (up to several days) higher by about 5°C than the maximum temperature used in the measurements, the results show reproducibility in successive runs.

The temperature dependence of resistivity, for both ethylenes and butadienes is found to be of the form

$$\rho = \rho_0 \exp (E/kT)$$

where ρ_0 is a constant, E is the activation energy for conductivity.

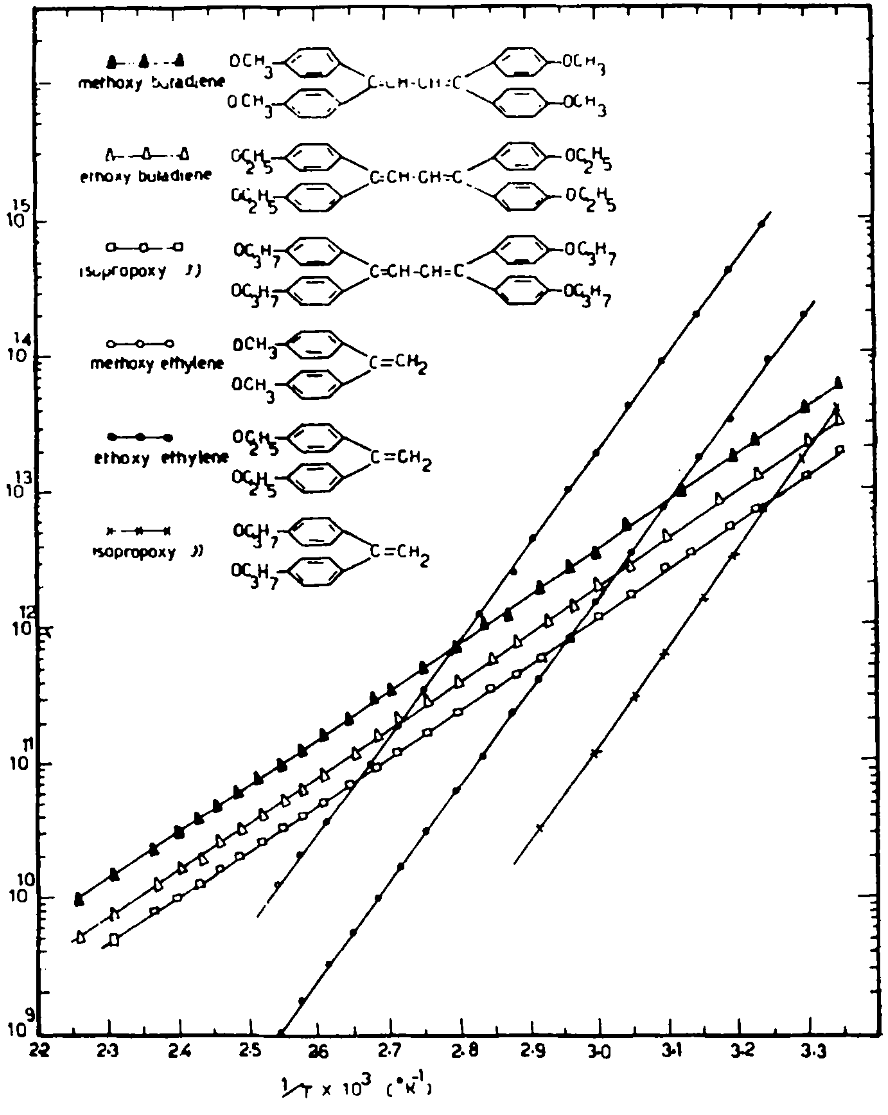


FIGURE 2 Log specific resistivities of ethylenes and butadienes against 1000/T.

Table I summarizes the main results:

TABLE 1

Compound	ρ 300°KΩcm	ρ_0 Ωcm	E eV
methoxy ethylene	2.4×10^{15}	6.6×10^{-9}	1.4
ethoxy ethylene	2.0×10^{14}	5.4×10^{-10}	1.4
isopropoxy ethylene	1.8×10^{13}	5.0×10^{-11}	1.4
methoxy butadiene	4.0×10^{13}	6.6	0.71
ethoxy butadiene	2.2×10^{13}	3.6	0.71
isopropoxy butadiene	1.2×10^{13}	1.95	0.71

Qualitatively the electron repelling force in the molecule increases in the direction $OCH_3 \longrightarrow OC_2H_5 \longrightarrow OC_3H_7$ [13]. This is also the direction in which the resistivity increases in ethylenes and butadienes, while the activation energies for both remain unchanged, being 1.4 and 0.71 eV respectively.

It is remarable that in case of ethylenes as the force of the electron repelling group increases the resistivity increases markedly, being more than one order of magnitude, while the changes in butadienes (which is douple the ethylenes) is much smaller than the corresponding ethylenes.

A probable explanation of the effect of the electron repelling groups is that it reduces the conductivity by reducing the carrier mobility.

According to a previous work[2a], the activation energy decreases as the number of π-electrons increases. This is in accordance with our results since the activation energy of butadienes (4 benzene rings) is nearly half that of ethylenes (2 benzene ring).

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