Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Effect of Electron Repelling and Electron Attracting Groups on the Electrical Conductivity and Thermoelctric Power of some Ethylenes and Butadienes

B. S. Farag [a] & J. E. Rizk [a]
[a] Semiconductor Unit, Physics Department, National Research Centre, Dokki, Cairo, Egypt

Version of record first published: 21 Mar 2007.

To cite this article: B. S. Farag & J. E. Rizk (1975): Effect of Electron Repelling and Electron Attracting Groups on the Electrical Conductivity and Thermoelctric Power of some Ethylenes and Butadienes, Molecular Crystals and Liquid Crystals, 31:1-2, 1-8

To link to this article: http://dx.doi.org/10.1080/15421407508082853

Mol. Cryst. Liq. Cryst., 1975, Vol. 31, pp. 1–8

Printed in Holland

Effect of Electron Repelling and Electron Attracting Groups on the Electrical Conductivity and Thermoelectric Power of some Ethylenes and Butadienes

B. S. FARAG and J. E. RIZK

Semiconductor Unit, Physics Department, National Research Centre, Dokki, Cairo, Egypt

(*Received December 6, 1974*)

Conductivity and thermoelectric power of some ethylenes and butadienes have been examined, with the aim of investigating the possible effect of attaching electron repelling or electron attracting groups either to one end of the molecule (as in case of ethylenes) or to the opposite ends (as in case of butadienes). In case of ethylenes, it has been found that both the type and magnitude of the conductivity and thermoelectric power are sensitive to the character of the attaching groups, but the activation energy for conductivity remains constant (1.4 eV). On the other hand, butadienes (which are douple ethylenes) do not seem to be much affected by the groups, and the activation energy remains close to 0.71 eV, while the thermoelectric power at a given temperature remains positive and practically unchanged in magnitude. It would appear possible to control the type of conductivity in ethylenes, electron repelling groups leading to *p*-type while electron attracting groups leading to *n*-type conduction.

INTRODUCTION

Recently, interest in organic semiconductors has been increasing rapidly, and extensive research is being done in this field[1,2,3] because of the attractive possibilities of using them in practice.[4,5] For technical applications, the important point in organic materials is the possibilities to control both the type and magnitude of the conductivity, as in the case of inorganic semiconductors.

Semiconducting organic solid materials are frequently grouped into three categories: molecular crystal of aromatic ring structure, polymers and charge transfer complexes. In molecular complexes[6] the resistivity depends on the stoichiometric composition for both electron donor and acceptor groups. It has also been recently found that it is possible by complex formation to govern the type of conductivity.[7] Semiconducting polymers[8] can now be made with resitivities extending from 10^4 to 10^{12} ohm cm by mere changes in the position or types of substituents of the aromatic compound.

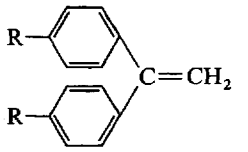
In molecular complexes, on the other hand, it is only quite recently that Eley[9] has demonstrated the possible effects of a donor and acceptor groups attached to opposite ends of the same molecule, even though this does not induce a large solid state conductivity. The present authors[10] have studied the effect on conductivity of electron repelling groups attached either to one end of the molecule (as in case of ethylenes) or to both ends (as in case of butadienes). A remarkable change was noticed in the first but not in the second.

The present work is an attempt to clarify the factors governing both the type and magnitude of conductivity in molecular crystals. This is made by studying the effects of both electron repelling and electron attracting groups on the electrical conductivity and thermoelectric power of some aromatic hydrocarbons e.g. ethylenes and butadienes to which different groups with different electron repelling and electron attracting forces could be attached.

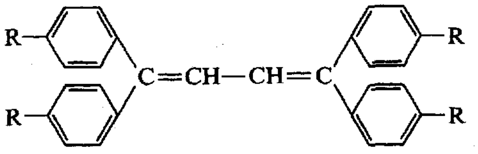
Materials

a) 1,1-bis-*p*-alkoxyphenylethylenes and

b) 1,1,4,4-tetrakis-*p*-alkoxyphenylbuta-1,3-dienes



a) Ethylenes



b) Butadienes

were chosen as shown in the previous work,[10] where R stands for either electron repelling groups (e.g. OCH_3, OC_2H_5, OC_3H_7) or electron attracting groups (e.g. Br and Cl). With the substitution of R by electron repelling groups, the following compounds were obtained by the method outlined in reference.[10]

a) -1- 1,1-bis-*p*-methoxyphenylethylene
   -2- 1,1-bis-*p*-ethoxyphenylethylene
   -3- 1,1-bis-*p*-isopropoxyphenylethylene

b) -4- 1,1,4,4-tetrakis-*p*-methoxyphenylbuta-1,3 diene
   -5- 1,1,4,4-tetrakis-*p*-ethoxyphenylbuta-1,3 diene
   -6- 1,1,4,4-tetrakis-*p*-isopropoxyphenylbuta-1,3 diene

Throughout the present work the materials listed above will be respectively denoted for brevity by:

a) methoxy-, ethoxy-, isopropoxy-ethylene and
b) methoxy-, ethoxy-, isopropoxy-butadiene.

With the substitution of R by electron attracting groups, the following compounds were prepared by the method described by Tadros and coworkers[11,12]

a) -7- 1,1-bis-*p*-bromophenylethylene
   -8- 1,1-bis-*p*-chlorophenylethylene
b) -9- 1,1,4,4-tetrakis-*p*-bromophenylbuta-1,3 diene
   -10- 1,1,4,4-tetrakis-*p*-chlorophenylbuta-1,3 diene

This will be denoted respectively by:

a) bromo-, chloro-ethylene and
b) bromo-, chloro-butadiene.

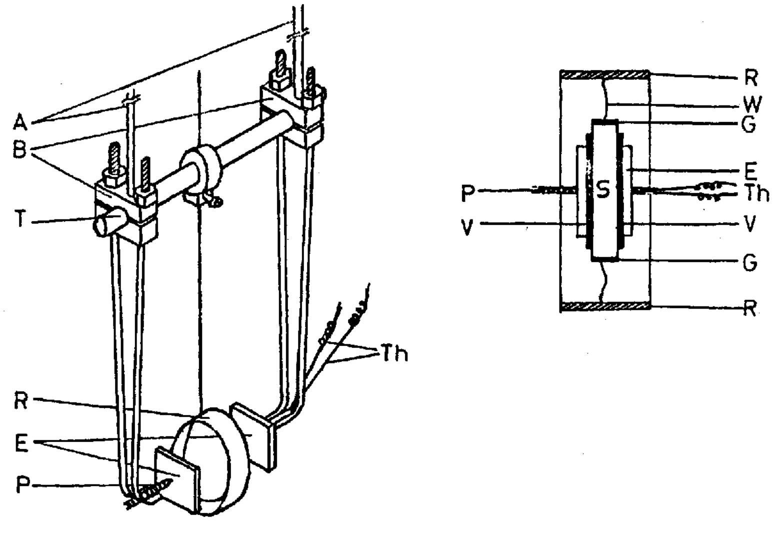
Purification of the materials

The tested materials have been recrystallized several times from BDH acetic acid, and measurements of conductivity on compressed tablets were performed after each crystallization. The purity of the sample is regarded as satisfactory if further recrystallization does not change the resistivity beyond the limits of the experimental error (± 10%).

Measuring Cells and Procedures

For electrical conductivity, a cell with a guard ring similar to that of Eley,[13] with some modifications, was used and is shown in Figure 1a. Powder samples $\approx 1 \times 1 \times 0.2$ cm^3 compressed at 1500 Kg/cm^2 were mounted in the cell as shown in Figure 1b., and the measurements were conducted as described in a previous work.[10]

For thermoelectric power measurements (against copper) a cell similar to that of Eley,[14] was used, shown in Figure 2, in conjunction with a vibrating reed electrometer type VA-J-52, R.F.T. The temperature difference between the two ends of the sample ranged from 5–20 °C (as measured by isolated and earthed Cu-constantan thermocouples). Each experimental point was taken as an average of several consistent readings at the same ambient temperature. The same samples used for electrical conductivity were also used for the measurements of the thermoelectric power.



1a 1b

FIGURE 1 1a—Separated electrodes conductivity cell with guard ring, 1b—Mounting the specimen.
S—sample, A—current leads, B—movable holders, T—teflon rod, R—earthed shielding cylinder, E—pt coated current electrodes, P—pressure spring, Th—thermocouple, V—silver paste, G—guard ring silver paste, and W—connecting wire between G and R.

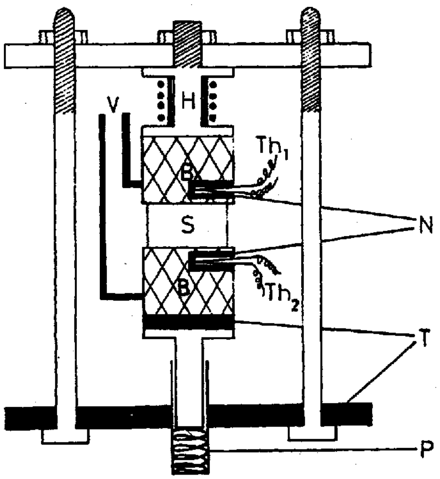


FIGURE 2 A cell for thermo e.m.f. measurements.
S—sample, T—teflon insulator, P—pressure spring, H—noninductive highly insulated heater, B—copper blocks, N—teflon tubes, V—thermo e.m.f. leads and Th$_1$,and Th$_2$—thermocouples.

Results and Discussions

Figure 3 shows the variation of the dark log d.c. conductivity with the reciprocal of the absolute temperature for some ethylenes and butadienes to which electron attracting groups (i.e. Bromo and Chloro groups) were attached. The authors' previous results with methoxy-, ethoxy-, and isopropoxy- groups are also reproduced as dotted lines for comparison with the new materials.

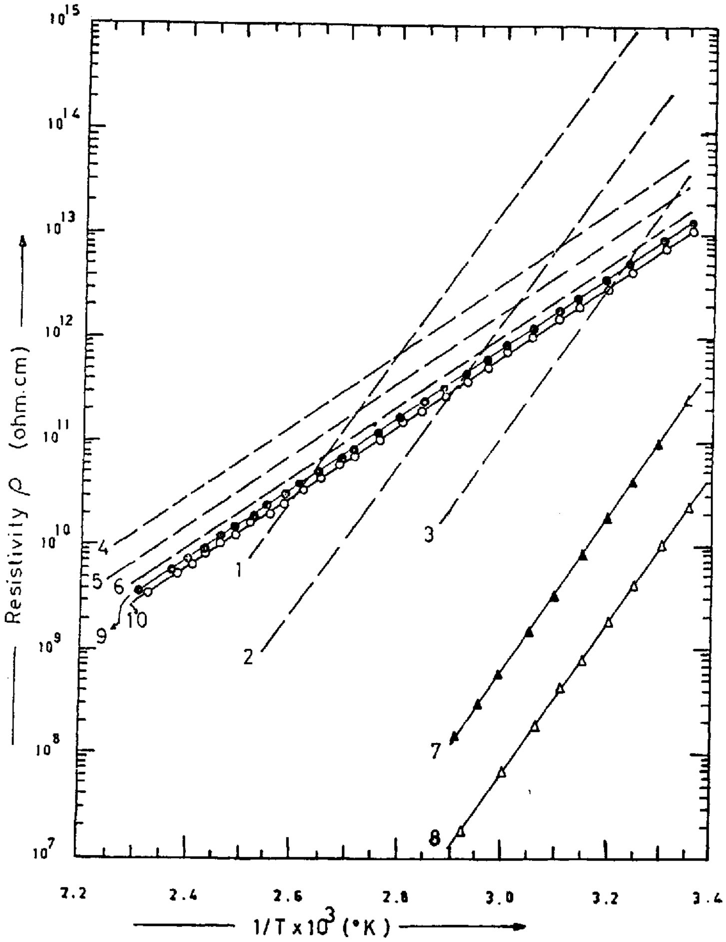


FIGURE 3 Temperature dependence of resistivity for, 7—bromoethylene, 8—chloroethylene, 9—bromobutadiene, 10—chlorobutadiene and 1, 2, 3, 4, 5, and 6 are after Farag[10] for methoxy-, ethoxy-, and isopropoxy- ethylenes and butadienes respectively.

The temperature dependence of resistivity, as indicated in Figure 3 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, T the absolute temperature, k Boltzmann's constant, and ρ the specific resistivity at T.

Figure 3 indicates also that as the electron repelling character of the group in the molecules increases in the direction $OC_3H_7 \rightarrow OC_2H_5 \rightarrow OCH_3$,[15] the resistivity also increases in the same direction. In case of ethylenes and butadienes to which electron attracting groups were attached the resistivity on the other hand decreases as the electron attracting character increases in the direction Br → Cl.[16]

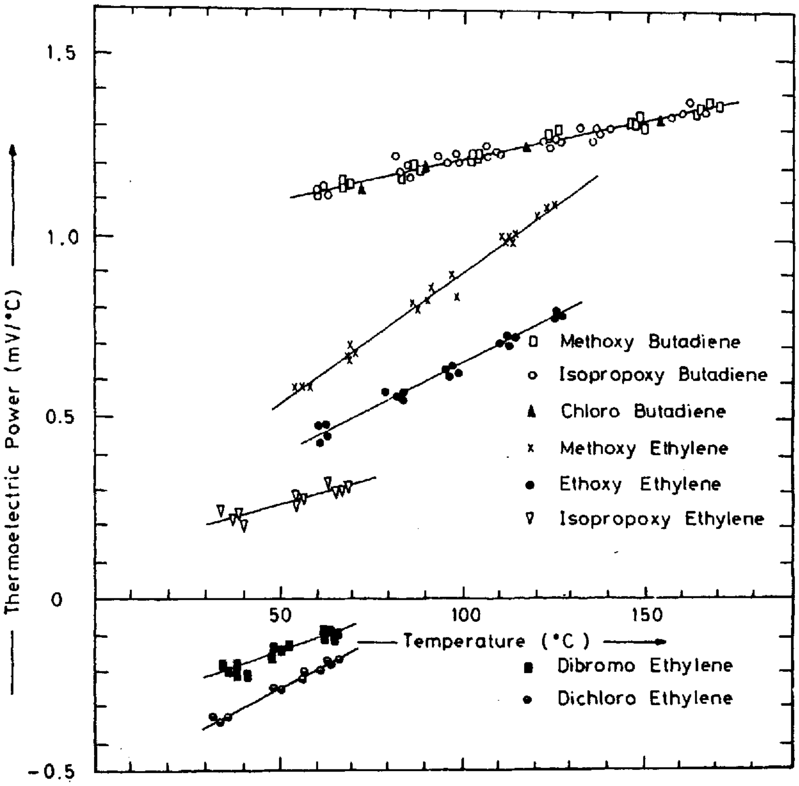


FIGURE 4 Temperature dependence of thermoelectric power for ethylenes and buta-dienes. In the curve for butadienes (the upper one) the experimental points for ethoxy-, and bromo-butadienes are not included for clarity of the curve.

It is remarkable that in case of ethylenes to which the groups (either attracting or repelling) were attached to one end of the molecule, the resistivity changes may be several orders of magnitude, while in butadienes (which are douple ethylenes) to which the groups were attached to both ends of the molecule the changes are much smaller.

The addition of the group does not seem to affect the activation energy which remains 1.4 and 0.71 eV for the ethylenes and butadienes respectively.

Figure 4 shows the variation with temperature of the thermoelectric power of the investigated materials from which it may be seen that the thermoelectric powers of all butadienes (including those with electron repelling as well as electron attracting groups) are positive and have essentially the same value, within the limits of the experimental error (about ±15%). In case of ethylenes, the thermoelectric power may be positive or negative depending respectively on whether an electron repelling or an electron attracting group has been attached to the molecule. The magnitude of the thermoelectric power depends on the degree of repelling or attracting character.

We may thus conclude that the electron repelling and electron attracting groups attached to one end of the molecule behave in some way as acceptors and donors respectively in inorganic semiconductors. On the other hand, groups attached to opposite ends of the molecule have no obvious effect on the type or magnitude of conductivity and thermoelectric power. The present results on butadienes are in agreement with those of Eley[9] who demonstrated the minute effect of donor and acceptor groups attached to opposite ends of diphenyl butadiene and four analogues stilbene.

Conclusion

We conclude that the type and magnitude of conductivity in organic semiconductors could be controlled by attaching either an electron repelling group to one end of the molecule, thus giving *p*-type conductivity, or an electron attracting group, thus leading to *n*-type conductivity. The degree with which electrons and holes shares in the conductivity depends on the amount of the force between the groups and π electrons. This shows that their is a possibility to control both type and magnitude of conductivity.

Acknowledgement

The authors would like to express their gratitude to Prof. Dr. W. Tadros and Dr. S. A. Abdou of the Chemistry Department, Faculty of Science, University of Cairo for their kind assistance in the preparation of the materials investigated.

References

1. C. Sharma, *Sci. Ind. Res.*, **31**, no. 10, 510–14 (1972).
2. R. Pething, *Electronic and Power* (GB), **14**, 271–4 (1968).
3. P. K. Datta, *J. Sci. Ind. Res.* (India), **30**, no. 5, 222–227 (1971).
4. S. Matsumoto, *J. Inst. Electron and Commun. Eng. Jap.* (Japan), **55**, no. 3, 397–408 (1972).
5. D. D. Eley, *Electronic Compon.* (GB) **9**, no. 10, 1145–6 (1969).
6. Y. Okomoto and W. Bernner, Organic semiconductors, Reinhold Publishing Corporation, New York (1964) p. 63.
7. V. Hadek, *Phys. Status Solidi*, **30**, no. 1, 275–282 (1968).
8. H. A. Pohl, J. A. Bornmann and W. Itoh, Organic semiconductors, edited by J. J. Brophy and J. W. Buttery, The Macmillan Company, New York (1962) p. 142.
9. D. D. Eley and O. M. G. Newman, *Trans. Faraday Soc.*, **66**, no. 569, 1106 (1970).
10. B. S. Farag, J. E. Rizk and S. E. Abdou, *J. Molec. Crys. and liquid Crys.* (USA) Under Publication (1974).
11. W. Tadros and G. Aziz, *J. Chem. Soc.*, 2684–7 (1961).
12. W. Tadros, A. Badie and M. Sadek, *J. Chem. Soc.*, 4210–12, 1958.
13. D. D. Eley and W. P. Williams; *Trans. Farad. Soc.*, **64**, Part 6, 1528, 1968.
14. D. D. Eley and B. M. Pacini, *Polymer* **9(3)**, 159–72, 1968.
15. C. K. Ingold, Structure and mechanism in organic chemistry, Ithac and New York, Cornell University Press, 1957.
16. O. Reutov, Theoretical principles of organic chemistry, Mir Publishers, Moscow, 1967.