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THE ELECTRICAL CONDUCTIVITY OF BENZALDAZINE AND ITS *o*-, *m*- AND *p*-HYDROXY SUBSTITUENTS

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ABSTRACT

The electrical conductivity of benzaldazine and its *o*-, *m*- and *p*-hydroxy substituents has been measured over a temperature range with included their phase transition temperatures. The effect of intermolecular overlapping as well as hydrogen bonding on the conduction mechanism in the low and high temperature regions was studied using IR spectra and conductivity data. The activation energy values obtained showed that all the compounds behaved as semiconducting materials.

INTRODUCTION

Recently much effort has been devoted to relating the chemical structures of organic compounds to their electrical properties [1–3]. It has been pointed out by Garrett [4] that the condensed aromatic hydrocarbons are superconductors on the molecular scale, since there are no obstacles to the flow of electrons within the molecules. The reason for the extremely low conductivities and relatively high energy gaps of these hydrocarbons must be sought in the processes involved in the transport of charges across intermolecular barriers. In view of these barriers, it is perhaps surprising that organic molecular solids display any conductivity at all. The explanation may lie in mechanisms which allow electronic interaction across the barriers, leading to overlapping of the molecular orbitals of adjacent molecules.

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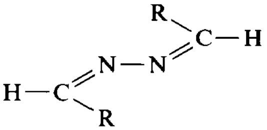

Scheme I. Structural formulae of benzaldazine and its hydroxy substituents: **1**, R = C_6H_5; **2**, R = *o*-OH-C_6H_4; **3**, R = *m*-OH-C_6H_4; **4**, R = *p*-OH-C_6H_4.

In polar as well as dielectric materials, ionic conductivity may occur as a result of impurities or defects within the structure. This behaviour is observed mainly in the ferroelectric materials with ordered structures.

For some organic materials containing hydrogen bonds [4], it is necessary to consider the possibility that interionic conductivity may occur at the same time as electronic conduction. Imidazole and benzimidazole have been selected as examples for a study of the effect of hydrogen bonding on the conduction mechanism, to explore the significance of this role in the azine compounds [5]. The azine compounds (**1**–**4**, Scheme I) containing nitrogen atoms of C = N– double bonds occur readily in Schiff's bases and related compounds [6]. The presence of double bonds as well as hydrogen bonds led us to design the present work, a study of the effect of both on the electrical conductivity of azine compounds. Like the compounds under investigation, phenazine has been used [7] to show the influence of the two pairs of unshared electrons on the two nitrogen substituents; in positions 9 and 10 of anthracene; on the orbital overlapping.

EXPERIMENTAL

The chemicals used in this study were B.D.H. and Merck pure reagents. The azines were prepared according to known procedures [8]. IR spectra were recorded with a Shimadzu-IR-440, the samples compressed with KBr (1%) discs.

Chemical analysis of the samples was carried out before the electrical data were collected.

The d.c. conductivity of the samples was measured at constant d.c. voltage using the potential probe method [9]. The sample temperature was measured using a calibrated copper–constantan thermocouple in the range 300–400 K for different samples. All the data were checked several times, and good reproducibility was obtained. The electrical conductivity σ was measured for the solids as compressed discs, 6 mm in diameter and 1 mm in thickness, at a pressure of 5 tons cm^{-2}. The two surfaces were polished, coated with silver paste (B.D.H., England), and checked for good contact.

RESULTS AND DISCUSSION

A qualitative change in the temperature dependence of the d.c. conductivity is shown in Fig. 1. From the figure it is clear that the data reveal a linear trend except for one shoulder, which appears at different positions, depending on the sample. This shoulder in the conductivity line indicates the presence of two conducting mechanisms with two activation energies. The values of the activation energies and the transition temperatures are listed in Table 1. From the data obtained it is clear that the general behaviour of the electrical conductivity obeys the equation $\sigma = \sigma_0 \exp(-E/KT)$, where σ_0 is a constant, E is the activation energy, and K is the Boltzmann constant. The low temperature conducting phase is distinguished by a higher activation energy (E_{I}) than the high temperature phase (E_{II}). This is because at low temperature the possibility of molecular orbital overlapping between neighbouring molecules isolates the conduction between them, and this in turn raises the conduction energy. This rule enhances the obtained data.

At low temperature phase, the electrical conductivities of the *ortho* and *para* compounds are greater than those of the *meta* compound and benz-

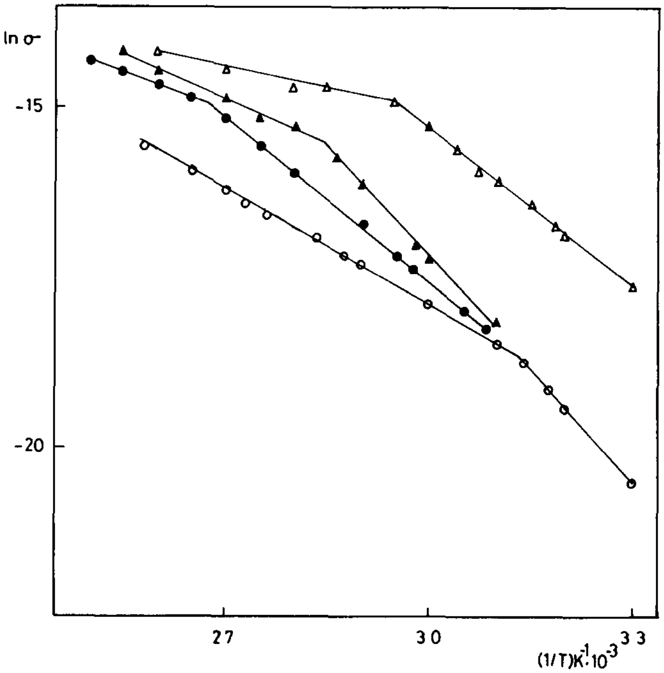

Fig. 1. The relation between ln σ (σ = conductivity) and the reciprocal of the absolute temperature $1/T$ for the four compounds: △ *o*-OH compound, ● *p*-OH compound, ▲ *m*-OH compound, ○ benzaldazine compound.

TABLE 1

Values of activation energy and conductivity for *o*-OH, *p*-OH, *m*-OH and benzaldazine samples at low and high temperature phases

Sample	T	E_{II} (eV) high	E_I (eV) low	σ_{II} (10^{-7}) high	σ_I (10^{-9}) low
o-OH	339	0.19	0.65	7.16	22.7
p-OH	375	0.37	0.68	4.20	2.1
m-OH	351	0.28	0.90	5.36	1.5
Benzaldazine	320	0.51	0.91	1.70	1.2

aldazine. This may be due to the hydroxyl substituent having a greater effect on the electrical conductivity of the *ortho* and *para* compounds, increasing the resistance effect of increasing delocalization of π-electrons [10]. The azine molecule contains two nitrogen atoms which are considered as centres for hydrogen bonding. So one can say that intra- and intermolecular hydrogen bonding will greatly reduce the energy of the ground state of the basic benzaldazine skeleton of *o*-hydroxybenzaldazine and *p*-hydroxybenzaldazine compared to that of benzaldazine itself (see Fig. 2). In the case of *m*-hydroxybenzaldazine, there is less opportunity for hydrogen bonding than in the case of the *ortho* and *para* compounds. This leads to a decrease in conductivity values and an increase in the activation energy, to a value which is similar to that obtained for unsubstituted benzaldazine.

It is important to explain the data obtained by proposing a suitable configuration model to account for the increased conduction of electricity in substituted compared to unsubstituted benzaldazine. In such a model the benzaldazine skeleton may be considered as the basic structural skeleton, while the hydroxyl substituents may be regarded as perturbation [10]. One can trace the conducting processes in both low and high temperature phases as follows. On the basis of the electronic transitions within molecules, two pathways for the conduction of electricity, from ground electronic state up to excited states, may be expected. Important work on the electronic absorption spectra of benzaldazine and *o*-, *m*- and *p*-hydroxybenzaldazines in different solvents has confirmed these two pathways of conduction mechanism [10]. By the first pathway, all $n \rightarrow \pi^*$ transitions are out-of-plane (z) polarized. Less activation energy is required for the transitions to be performed, and the charges are able to participate in the mechanism of electronic conduction. The second pathway of conduction at higher temperature phase can be attributed to all $\pi \rightarrow \pi^*$ transitions, which are in-plane (x, y) polarized. This stage of conduction is distinguished by a drastically low activation energy (E_{II}), with enhanced conduction of electricity compared to E_I. This would allow the participation of $\pi \rightarrow \pi^*$ transitions as well as $n \rightarrow \pi^*$ transitions in the conduction of electricity at higher tempera-

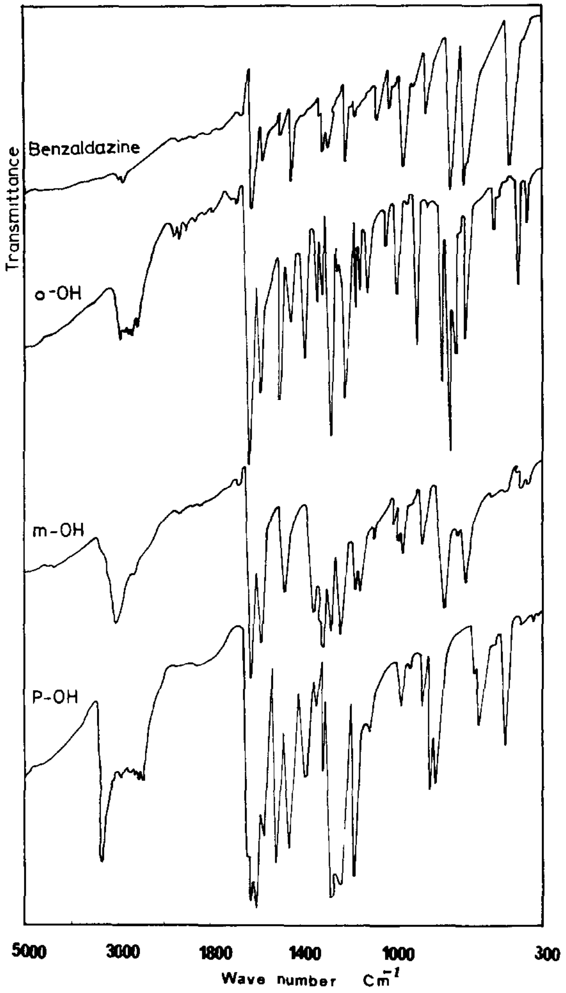

Fig. 2. IR spectra of the *o*-OH, *p*-OH, *m*-OH and benzaldazine compounds.

ture. The observed enhancement of conduction may be due to interactions between n–π^* and π–π^* electronic transitions, which would increase delocalization, with reduction of activation energy (E_{II}) and higher values of conductivity. On the basis of the activation energy values obtained for the low and high temperature phases, one can say that these compounds have semiconducting properties [11].

The structures and dielectric constants of the azine compounds are now under further investigation, and more details will be published later.

In conclusion, one can safely say that in the high temperature region the possibility of overlapping between molecular orbitals as well as weak hydrogen bonding increases the conductivity values compared to those obtained in the low temperature region.

REFERENCES

1 J. James Brophy and W. John Buttrey (Eds.), Organic Semiconductors, Proceedings of an Inter-Industry Conference, Macmillan, New York, 1962, p. 79.
2 A. Herbert Pohl, in H. Reiss (Ed.), Progress in Solid State Chemistry Vol. 1, Pergamon Press, 1964, pp. 316–346.
3 K. Shigekazu, T. Akimasa and M. Hiroshi, Bulletin (Japan), 39 (1966) 1344.
4 C.G.B. Garrett, in N.B. Hannay (Ed.), Semiconductors, Reinhold Publishing Corp., New York, 1959, Chap. 15.
5 B. Rosenberg, J. Chem. Phys., 31 (1959) 238.
6 B. Michel and D. Gilles, Can. J. Chem., 57 (1979) 2540.
7 D.C. Northrop, Proc. Phys. Soc., 74 (1959) 756.
8 D. Kolbah and D. Korunav, in Houben Weyl (Ed.), Methoden der Organischen Chemie, X/2, G. Thieme Verlag, Stuttgart, 4th edn., 1967.
9 M.A. Mousa, A.M. Summan, M.A. Ahmed and A.M. Badawy, J. Mat. Sci., 24 (1989) 346.
10 E.C. Okafor, Spectrochim. Acta, 36A (1980) 207.
11 T. Tager, Physical Chemistry of Polymers, Mir, Moscow, 1972.