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Phase transition study of some selected azine compounds

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Abstract

The dielectric constants (real and imaginary) of benzaldazine and its hydroxy derivatives have been measured at different frequencies up to 100 kHz. The measurements were also carried out at different temperatures up to near the melting point of each sample. Two phase transitions were obtained during measurements at 320 and 370 K. The rotation of the benzene ring around the –C=N– axis was responsible for these transitions. The effect of variation of the OH substituent between *o*-, *p*- and *m*-positions on the dielectric loss was discussed. The a.c. conductivities for the different samples were measured and explained.

INTRODUCTION

Dielectric materials are in many respects playing a central role in microwave instrumentation. Considerable work is being done in the field of microwave or millimeter-wave integrated circuits and applications for microwave heating [1]. Materials with ionic, covalent or mixed ionic and covalent bonding are normally either insulators or intrinsic semiconductors, whereas polar materials are considered as extrinsic semiconductors because the charges may be due to impurities or defects that exist in them [2,3]. As previously reported [3], organic materials containing a benzene ring can be considered as semiconductors. Theoretical studies have shown that in semiconductors, such as those under investigation, a significant change in dielectric constant can occur at relatively low temperatures as a result of photoexcitation of impurities from the ground state to an excited state with larger polarizability [4]. Compounds containing benzene rings can have a high degree of symmetry, and the replacement of even one substituent will decrease this symmetry to an extent that the molecular symmetry will no

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longer define the coordinates of the normal vibrations. In this case, the individual normal coordinates which depend on the substituent will appear [5]. Introduction of the OH substituent in different positions, ortho, meta and para, in benzaldazine will affect the symmetry as well as the polarization. At the same time, the dielectric constant for the benzaldazine substituent will be affected. The presence of the –C=N– group, hydrogen bonding and the change of symmetry due to the OH group have led us to study the temperature dependence of the complex dielectric constant and the a.c. conductivity.

EXPERIMENTAL

The samples under study were prepared [6] using chemicals of AnalaR grade from BDH (UK). After drying the samples, they were pressed into pellet form of 14 mm diameter and 1 mm thickness. The pressure used for all samples was 4 ton cm^{-2}. The two surfaces of each sample were polished, coated with silver paint and checked for good contact.

The dielectric constant measurements were carried out using a Schering bridge [7]. This method is used for measuring the capacitance and loss angle of the samples by comparison with a standard capacitor of negligible loss value. The temperature of the samples was measured using a digital multimeter (DEL-JAP, HC-5010 EC) with a Ni–NiAl thermocouple.

RESULTS AND DISCUSSION

The temperature dependence of the dielectric constant for the OH derivatives of benzaldazine is shown in Fig. 1. The data were obtained in the temperature range from 250 up to 490 K. From the figure it is clear that the gradual structural changes which we expect to occur in the compounds appear in the form of two peaks. This may be due to the change in electronic configuration of the main skeleton of benzaldazine. Varying the temperature of the sample will help one of the two benzene rings to rotate around the –C=N–axis and become fixed in a plane nearly perpendicular to the original plane of polarization. This may cause a decrease in the polarized charges and in turn affect the dielectric constant ε of the samples. The transition which appeared in the ε vs. T diagram is similar to those in the case of $(NH_4)_2SO_4$ and NH_4NO_3 [8,9]. Increasing the temperature of the sample after the first phase transition may cause inclination of the two benzene rings to the original plane of polarization, as mentioned above; and give what we may call a canting angle, which causes the appearance of the second phase transition. Taking into consideration the stereochemistry of the main skeleton, one can find that the OH group in the *o*- and *m*-positions will help the polarization process more than in the case of benzaldazine and *p*-OH. Since the probability of hydrogen

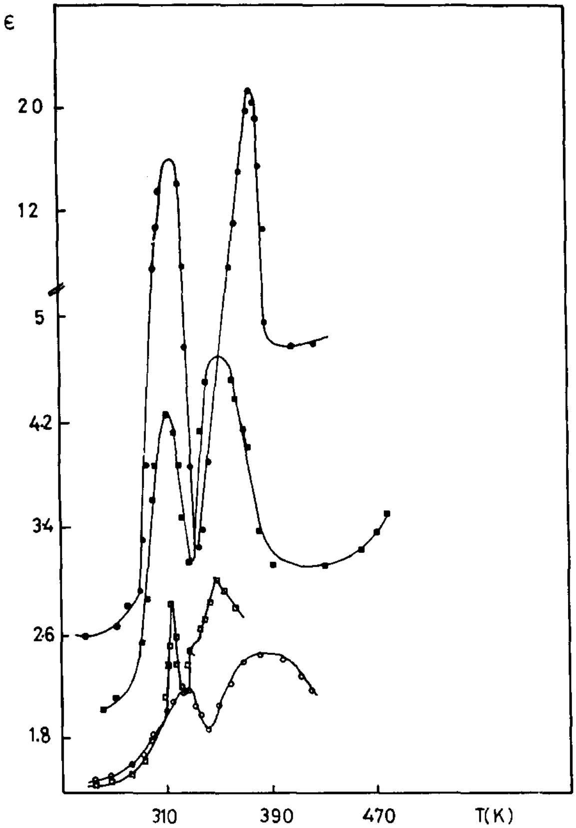

Fig. 1. Correlation of the complex dielectric constant ε and absolute temperature T for the benzaldazine (BA) compounds: ●, *m*-OH; ■, *o*-OH; ○, *p*-OH; □, BA.

bonding in the case of *o*-OH is greater than that for *m*-OH [3], therefore, one may expect the dielectric constant of *m*-hydroxy- to be larger than that of *o*-hydroxybenzaldazine (Fig. 1). The *p*-hydroxybenzaldazine will be inserted into the x–y plane of polarization. At the same time the OH groups attached to the rings will be inserted in two opposing directions. This may decrease the polarization to a certain limit at which the dielectric constant of *p*-hydroxybenzaldazine is less than that of benzaldazine itself.

The values of the electric dipole moments are calculated at the peak positions from the relationship of ref. 10. The data obtained for *o*-OH, *m*-OH and *p*-OH are $(2.45, 2.71) \times 10^{-21}$, $(4.99, 6.31) \times 10^{-21}$ and $(2.02, 2.28) \times 10^{-21}$ respectively. These values enhance our expectation about the framework of the discussion.

In the samples under investigation we expect, as discussed here, that the ionic vibration and deformation losses, as well as the electron polarization losses, are the main factors affecting the dielectric constant. This is clear

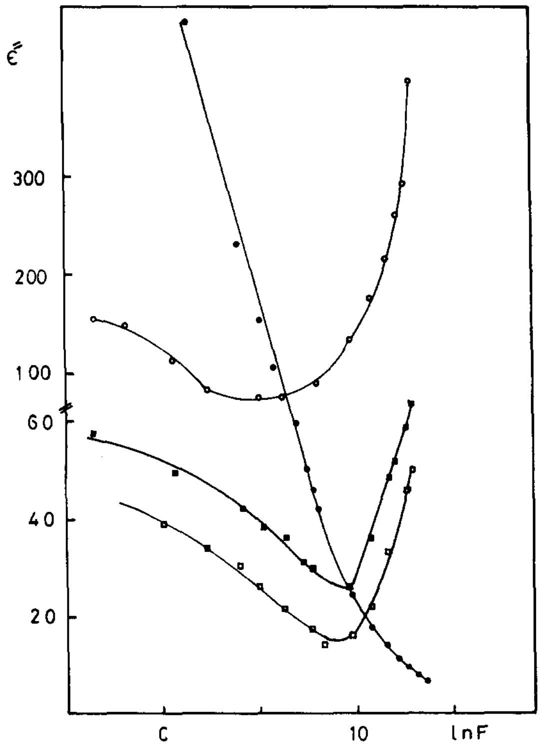

Fig. 2. Correlation of the imaginary part of the dielectric (ε'') and the frequency (ln f) for benzaldazine compounds: ●, m – OH; ■, o-OH; ○, p-OH; □, BA.

from Fig. 2, which correlates the imaginary part of the dielectric constant ε'' vs. ln f (f = applied frequency). From the figure, it is obvious that in the case of o-, and p-OH substitution, the dielectric loss factor ε' tan δ (ε' tan $\delta = \varepsilon''$) decreases with the frequency down to a minimum value at about 13.3 kHz. This may be due to the fact that the applied alternating frequency of the source is much smaller than the jump frequency of the atoms in the compounds. After that, if the applied frequency is much larger than the jump frequency, the atoms do not have the opportunity to jump. This will cause an increase in the dielectric loss after about 13.3 kHz, as shown in Fig. 2. In the case of m-OH, the dielectric loss shows different behaviour, with the disappearance of the minimum that is clear for o-OH and p-OH. The trend shows almost a continuous decrease in the dielectric loss up to a frequency of about 36 kHz except for a flattening in the curve from 36 up to 100 kHz. The presence of an OH group in the m-position does not help the pumping of electrons in the same direction as for the main skeleton, and a very large value of ε'' in comparison with o-OH and p-OH benzaldazine at the threshold applied frequency (about 0.4 kHz) is obtained. Figure 3 shows the dependence of the a.c. conductivity on the frequency (ln f). From the figure it is clear that the conduction behaviour

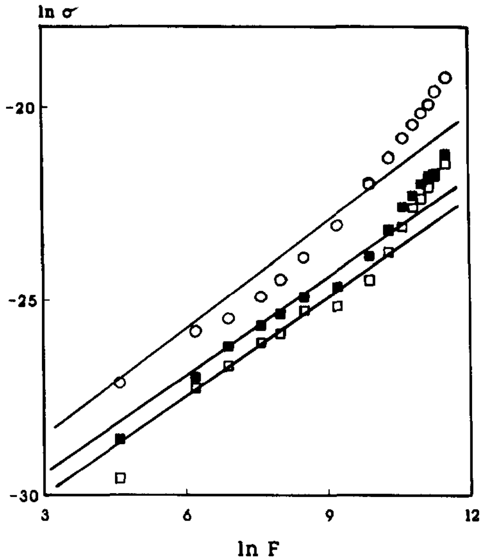

Fig. 3. Correlation of the a.c. conductivity (ln σ) versus the frequency (ln f) for benzaldazine compounds: ■, *o*-OH, ○, *p*-OH; □ BA.

increases with increasing applied frequency. This is because of the effect of the frequency in pushing more charges to participate in the conduction process. Also, it is clear that the slopes S for the different samples are less than unity, which agrees well with the expected values published in ref. 3. The behaviour shown in Fig. 3 agrees with that obtained by Mansingh and Dhawan [11]. This behaviour can be interpreted as the hopping of charge carriers over the barrier rather than tunnelling, as suggested previously [3]. In general, the conduction processes in the compounds under investigation may be due to the *S–trans* (E–Z) isomer, which is the more stable isomer.

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