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Electrical conductivity studies on some dibenzoylmethane arylhydrazones (DBMAH)

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Abstract Electrical conductivity of some dibenzoylmethane arylhydrazones (DBMAH) were measured during heating and reheating runs. The observed variation of the conductance of the polycrystalline sample during thermal agitation was found to depend on the ordering and disordering of molecules which in turn cause the lattice dipole to distort. A semiconducting behavior was detected for these systems as it was deduced from their conductance values ($1.7 \times 10^{-6} - 8.25 \times 10^{-7}$ ohm^{-1} cm^{-1}). The presence of substituents affects markedly the measured electrical conductivity and calculated activation energy values.

Keywords Hydrazones · Dibenzoylmethane · Electrical conductivity · Activation energy

Introduction

Hydrazo and azo compounds are concerned with a number of important biological reactions [1]. Some hydrazo alkanes are known to be alkylating agents having carcinogenic properties [2, 3], others are reported as antifungal agents [4]. El-Nagdi et al. [5, 6] prepared a number of ethylcyanoacetate-arylhydrazones. The authors measured their IR and UV spectra and determined their dissociation and isomerization constants. The hydrazone rather than the azo structure was confirmed.

Previous structural and spectroscopic data [7–10] for 1,3-diketone arylhydrazones derived from benzoylacetone and acetylacetone have indicated that the strength of the NH···O hydrogen bond is determined by the degree of resonance within the hetero dienic system modulated by the inductive effects of the aryl substituents.

Bertolasi et al. [11] have reported the crystal structures and spectroscopic data for five 1,3-diketone-arylhydrazones derived from dibenzoylmethane. They used the RAHB model [Resonance Assisted Hydrogen Bond] to prove that the interplay between N–H···O hydrogen bond strength and π-delocalization in all the structures is a general phenomenon in the whole class of the investigated compounds. The same studies were performed on six β-diketo-arylhydrazones derived from benzoylacetone or acetylacetone [12]. The authors showed that the magnitude of the strong hydrogen bond was essentially determined by the degree of π-delocalization within the keto-hydrazone heteroconjugated system and modulated by all other factors that can affect the degree of π-conjugation, including inductive effects and non-bonded intermolecular interactions.

Elctrical conductivity, electronic, IR and NMR spectra were measured [13], for some ethylcyanoacetate-phenylhydrazone derivatives and their lanthanide complexes in the temperature range 20–200 °C. A semi-conducting behavior was detected for these systems, and the mechanism of the conduction process was evaluated.

Recently, the electrical and thermal properties of acetylacetone-, and benzoylacetone-arylhydrazones have been studied and found to exhibit positive temperature coefficient (dG/dT) [14]. On the contrary, superconduction of metals was the subject of several studies based on thermodynamic and thermal conductance measurements [15, 16].

Dibenzoylmethane derivatives have been the subject of several investigations in the recent years. These include, ion-selective optode for UO_2^{2+} [17], preparation of pH-responsive luminescent complexes [18], and use of Fe(III), Co(II), Ni(II), and Cu(II) mixed complexes as catalysts [19]. The

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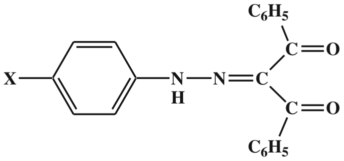
modeling of the relative intensity ratio of DBM –Eu(III) complex was reported [20]. Binuclear complexes of DBM-Schiff base with Cu(II), Ni(II), and Co(II) were investigated using several techniques including elemental analysis, conductivity measurements, spectral and thermal analyses [21].

The major goal of the present investigation is to study the mechanism of electrical conductivity of some dibenzoylmethane-arylhydrazones during heating and reheating runs. The effect of different substituents on the aryl group on the conductivity values as well as on the activation energy is studied.

Experimental

All chemicals used in this investigation were of the highest purity grade provided by B.D.H. The water was always twice distilled from all glass equipment.

The general method of preparation of the investigated compounds is based on the coupling of dibenzoylmethane with substituted benzenediazonium salt in cold solution of sodium acetate [22]. The compounds prepared have the general formulae:



where X = H (a), CH_3 (b), OCH_3 (c), $N(CH_3)_2$ (d), Cl (e) and NO_2 (f).

The m.p.°C, solvent of crystallization, color and main IR bands are listed in Table 1.

The IR absorption spectra were obtained by the KBr disc technique using a PYE UNICAM SP 1100 spectrophotometer within the wave number range 4000–400 cm^{-1}.

Compressed pellets of the investigated compounds (a–f) of 1.3 cm diameter and 0.3 cm thickness were molded for conductivity measurements. The two parallel opposite faces of each disc were coated with silver paste to conduct the current leads of the sample cell. The experimental technique was previously published [23].

A regulated electrical oven was used to control the surrounding temperature in the range from 35 to m.p. −20 °C. The measurements were carried out while the sample is being heated at a rate of 1 °C min^{-1}. Prior to measurements the samples were subjected to moderate heating for 1 h in order to minimize surface conductivity. The conduction current was measured using a 610 C electrometer (Keithley instruments). The minimum current that can be measured by this instrument is 10^{-4} A with an accuracy of ±2 to 4%.

Results and discussion

The studies on electrical conductivity of the different derivatives of dibenzoylmethane-arylhydrazones (DBMAH) give direct information about the mode of electric conduction in these derivatives and the effect of substitution on electrical conductivity and activation energies. The electrical conductivities of DBMAH derivatives at different temperatures are shown in Fig. 1, during heating and reheating cycles. It is apparent that the conductivity increases with elevation of temperature during heating and reheating cycles to reach a maximum value, then the conductivity decreases gradually with continuous increase of temperature reaching a certain minimum value, except for f (p-NO_2) where the conductivity continues to increase with the increase of temperature in the heating and reheating cycles. The maximum peak conductivities for the heating and reheating cycles are listed in Table 2. It is clear that the electrical conductivities during the reheating measurements have lower values than the heating runs with variable amounts. The only exception is the unsubstituted derivative (a) in which the electrical conductivity during reheating is higher than that in the heating cycle by 54%.

In order to estimate the activation energy and to account for the charge transfer mechanism, the relation between ln σ and $1/T$ was obtained as shown in Fig. 2, for heating and reheating runs. The activation energies have been computed from the slope of the curves and collected in Table 2. The $+d\sigma/dT$ is indicative of a semiconducting behavior of these systems. The curves obtained show discontinuity at

Table 1 Melting points, solvents of cryctallization, colours and main IR absorption bands (cm^{-1})

Cpd No.	X	Solvent of crystallization	Color	m.p./°C	NH	CO free	H-bonded
a	H	EtOH	YB	138	3067w	1655	1600
b	CH_3	EtOH	Y	127	3040	1640	1610
c	OCH_3	EtOH	B	72	3062	1640	1600
d	$N(CH_3)_2$	EtOH	DB	74	3065	–	1600(b)
e	Cl	MeOH	Y	137	3060	1660	1610
f	NO_2	EtOH	YB	69	3080	1630	1600

YB yellow brown, *Y* yellow, *B* brown, *DB* dark brown, – Not detected

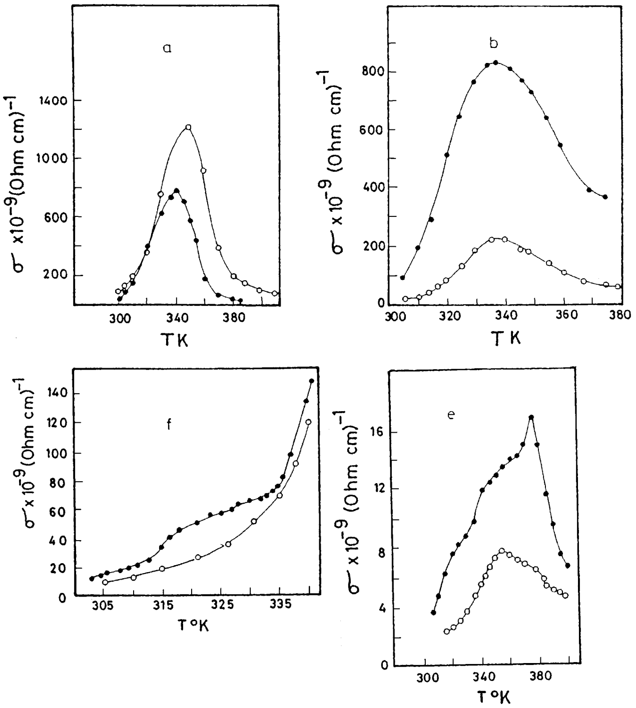
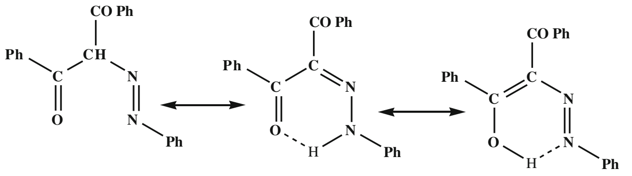


Fig. 1 Variation of electrical conductivity with temperature

certain transition temperatures "Ts" during heating and reheating cycles. It is apparent that the activation energy at low temperatures is higher than that at high temperatures. For (a) the activation energy during the heating cycle has the values of 0.93 and 0.64 eV within the temperature range 25–60 °C and that for the reheating cycle has the values of 0.78 and 0.57 eV within the same temperature range. This is due to the higher conductivity value obtained during the reheating run. These results illustrate the well known fact that the lower the activation, the easier the conduction process.

Prior to discussion of the results, one may recall that IR measurements have proved the existence of these compounds as intramolecular H-bonded arylhydrazone rather than the tautomeric azo compound. This fact is revealed by the shift and broadening of the NH stretching band appearing in the range 3040–3080 cm^{-1}, Table 1, and the shift and decrease of C=O stretching band (1655–1600 cm^{-1}). The latter is believed to arise from a carbonyl group which has its double bond character reduced by resonance between the forms B and C.



A
Azo form

B
Hydrazo form

C
Enol Form

Table 2 Electrical properties of dibenzoylmethane-arylhydrazone (DBMAH)

Compd	$\sigma_p \times 10^7$	T_p/°C	eV	
			Ea$_1$	Ea$_2$
Heating cycle				
a	7.80	67	0.93	0.64
b	8.25	64	0.81	0.3
c	0.62	59	0.74	0.3
d	2.20	60	1.16	0.48
e	0.17	102	1.14	0.21
f	1.48	70	0.78	0.3
Reheating cycle				
a	12.00	77	0.78	0.57
b	2.25	64	0.86	–
c	0.22	57	0.79	0.57
d	0.20	60	0.93	0.52
e	0.08	102	0.38	0.4
f	1.20	70	0.45	1.2

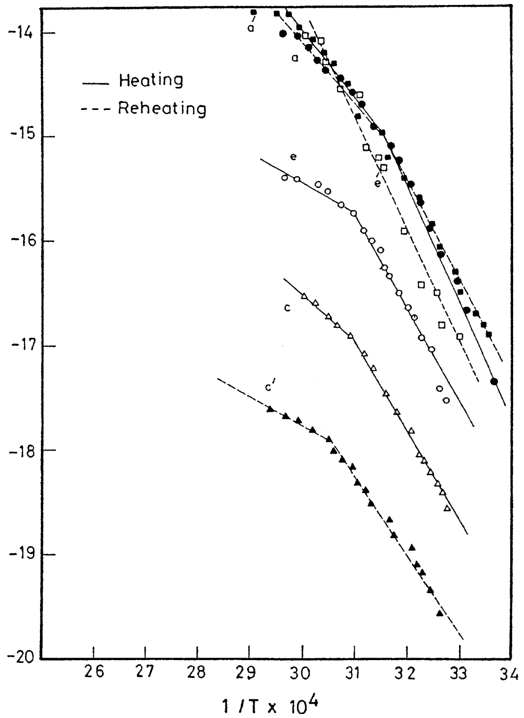


Fig. 2 Electrical conductivity as a function of reciprocal of temperature

The peak behavior of conductivity characterizing the present obtained results (except f) is explained on the basis of ordering and disordering taking place during thermal history of the sample. At low temperature the molecules are disordered. This disordering configuration of molecules gives up resultant charges that increase the conductivity of the molecules and hence, of the crystals as the temperature increases. At a certain temperature (T_p) the energy is enough to rotate (paking) the organic groups i.e. an ordering state may take place and increases with the increase of temperature. The ordering state here increases the resistivity of the sample for electric conductivity. In addition, the increase of conductivity at temperatures below T_p is enhanced by the rupture of the intramolecular hydrogen bond. Accordingly, the delocalization of π-electrons increases and this facilitates their transfer from the valence band to the conduction band and hence the electrical conductivity increases.

Table 2 shows the presence of two activation energy values (Ea_1 and Ea_2), thus indicating change of conduction mode during conductivity measurements. At low temperature, a pure extrinsic mechanism is predominant where the conduction is mainly due to the empty state (positive holes) formed by transition of electrons to the acceptor levels. This process is strongly attributed to the enhanced delocalization of the π-electrons. At higher temperature than Tp, the conductivity is controlled by the number of holes which are primarily intrinsic, i.e. which are produced by thermal agitation. This is attributed to the excitation of π-electrons from the valence band to the lowest empty π-states in the conduction band.

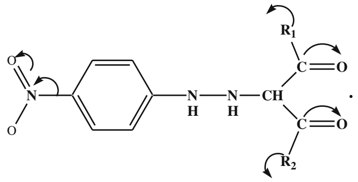
The increase of conductivity observed in the reheating cycle of (a), Fig. 1; may be attributed to decrease of strength or rupture of the hydrogen bond. Such behavior can be confirmed from the IR spectra of the samples before and after heating. The υ_{OH} (3480 cm^{-1}) appearing as a very weak band of low intensity before heating becomes more intense broad one (3500 cm^{-1}). This change of υ_{OH} band appearance can be attributed to decreased hydrogen bond strength.

Effect of substituent on electrical conductivity

In the case of introduction of electron-donating substituent [CH_3(b), OCH_3(c) and p-$N(CH_3)_2$ (d)], the heating run curve shows a broad peak which indicates the slow rate of change of conduction during the rise of temperature. On reheating, the broad peak is also observed but the conductivity is reduced. It is clear that change of conductance follows the order $b > c < d$. The small conductivity values obtained for c may be ascribed to the introduction of the methoxy group which causes oxidation of impurities near the surface of the sample thus decreasing the probability of holes formation and consequently it results in high resistivity. Thus, the introduction of the methoxy group reduces the conduction free pass, leading to reduced conductivity. On the other band, for compound d, the presence of the strong electron donating and bulky p-$N(CH_3)_2$ group with the two phenyl groups leads to the formation of the azo form rather than the hydrazo form [24] so the conductivity decreases.

The variation of electrical conductivity of e (p-Cl) with temperature during heating and reheating runs, Fig. 1, indicates that the conductivity curves are not simple peak bands as obtained with the other derivatives, but both the two bands are distorted specially that for heating run. The value of the peak conductivity is very low compared to that for a (H). Thus, the introduction of chlorine atom reduces the electric conduction remarkably. This may be explained on the basis of the +ve mesomeric effect and −ve inductive effect of the chorine atom. The former partially equalizes the latter causing a lowering of the resonance energy compared to that of the un-chlorinated derivatives.

The variation of electrical conductivity of f (p-NO_2); with temperature is shown in Fig. 1. It is clear from Table 2 that the introduction of p-nitro group decreases the conductivity. This behavior is explained on the basis of increased localization of the π-electron withdrawing effects of the phenyl groups ($R_1 + R_2$) and the two carbonyl groups in addition to the electron withdrawal properties of the NO_2 group



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