Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 3, 775–782

ELECTRICAL AND THERMAL STUDIES ON SOME ACETYLACETONE- AND BENZOYLACETONE –ARYLHYDRAZONES

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The electrical and thermal properties of some acetylacetone- (I) and benzoylacetone-(II) arylhydrazone derivatives have been investigated. The results obtained show semiconductor behavior as evident from the positive temperature coefficient of electrical conductivity (dG/dT). Values of activation energy (ΔE) have been calculated in each case. The electrical conductivity increases with the introduction of either electron-donating or electron-withdrawing substituents to the phenyl ring. Differential thermal analysis curves showed sharp well-defined peaks at the melting point of the investigated compounds. The latent heats of fusion were calculated from these thermograms.

Keywords: *arylhydrazone, DTA, electrical conductivity, semiconductor behavior*

Introduction

Coupling of aryldiazonium salts with β-dicarbonyl compounds led to the formation of a series of compounds that has shown to exist as the intramoleculary H-bonded arylhydrazone tautomers rather than in any other tautomeric forms. Previous structural and spectroscopic data [1–3] for 1,3-diketone-arylhydrazones derived from benzoylacetone have indicated that the strength of the NH······O hydrogen bond formed is essentially determined by the degree of resonance within the heterodienic system modulated by the inductive effects of the aryl substituents. A model called RAHB [4, 5] [Resonance Assist Hydrogen Bond] has been successfully employed to interpret the intra- and inter-molecular hydrogen bonds in all the compounds containing β-diketo-enol fragment. Bertolassi *et al*. [6] have reported the crystal structures and spectroscopic data for five 1,3-diketone- arylhydrazones derived from dibenzoylmethane. They were able to prove that the interplay between N······O hydrogen bond strength and π-delocalization in all the structures is a general phenomenon in the whole class of investigated compounds. The same studies were performed on six β-diketone-arylhydrazones derived from benzoylacetone or acetylacetone in a detailed investigation of the nature of intramolecular hydrogen bond formed by the HN–N=C–C=O moiety in these compounds [7]. The authors showed that the magnitude of the strong hydrogen bond was essentially determined by the degree of π-delocalization within the ketohydrazone hetero conjugated system and modulated by all other factors that can affect the degree of conjugation including inductive effects and non-bonded intermolecular interactions.

The electrical and spectral properties of ethyl-cyanoacetate-phenylhydrazone derivatives have been investigated [8]. The results obtained show anomalous metallic-like and semiconducting behaviors. β-diketones are still very interesting goals to analytical chemists, their arylhydrazones are known to be promising in many applications [9, 10]. Potentiometric studies of dissociation constants of their metal complexes were reported [11–13].

Superconduction of some metals was the subject of recent studies [14, 15]. Some new superconductors were discovered. Studies were based on thermodynamic and thermal conductance measurements.

The aim of the present work is to investigate the electrical and thermal properties of some acetylacetone- and benzoylacetone-phenylhydrazone derivatives. Some thermodynamic functions for the investigated compounds were calculated from DTA measurements.

Experimental

All chemicals used were of the chemical pure grade from Aldrich. The arylhydrazones under investigation were prepared by coupling of acetylacetone and benzoylacetone with substituted benzenediazonium salts in cold solution of sodium acetate. The compounds prepared have the general formula:

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1388–6150/$20.00

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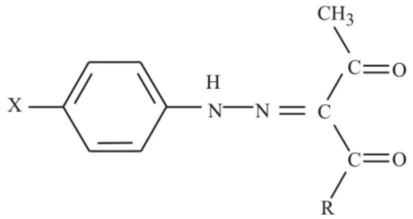


where R=CH_3 (I, AAAH), C_6H_5 (II, BAAH), X=H (a), CH_3 (b), OCH_3 (c), $N(CH_3)_2$ (d), Cl (e) and NO_2 (f)

The *m.p.* values which are in agreement with those previously reported [6, 16, 17], solvent of crystallization, color and main IR-bands are given in Table 1.

For electrical measurements the samples were pressed into pellets 13 mm in diameter and 3 mm in thickness. The two parallel opposite faces of each disc were coated with silver paste to contact the current leads to the sample cell. A regulated electrical oven was used to control the surrounding temperature in the range 35–70°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 ±2–4%.

DTA measurements were carried out by a DTA system type TA 500 manufactured by Heraeus Company, Germany using Al_2O_3 as inert reference material in nitrogen atmosphere. It is provided with thermoanalyzer, fitted with a temperature programmer, a differential amplifier and an automatic voltage stabilizer. The linear heating or cooling process was determined by a digital reference voltage generator to which a DTA converter, linearised for NiCr–Ni thermocouples, was connected.

Results and discussion

Electrical conduction in organic molecular solids differs in several important ways from that of metals and typical semiconductors. Structurally, arylhydrazone derivatives fall in the category of conjugated chains conductive organic solids.

The temperature dependence of the electrical conductivity of some of the investigated compounds is shown, Fig. 1. It is obvious from the curves that electrical conductivity increases with continuous rise in temperature reaching a maximum value (σ_p). In almost all cases the conductance then decreases with continuous increase of temperature reaching a minimum value depending on the compound investigated. A peculiar behavior is observed for Ia and IIb for heating cycle and IId for the reheating cycle. The positive temperature coefficient of electrical conductivity for all the investigated compounds is an evidence for the semiconducting character within the range of temperature studied (35–70°C). It is clear that the increase of conductivity with increase of temperature obeys the usual exponential law:

$$\sigma = \sigma_0 \exp(-\Delta E/KT)$$

Table 1 Melting point, solvent of crystallization, colors and main IR absorption frequencies of the investigated compounds

Compd. No.	X	Solvent of crystallization	Color	*m.p.*/ °C		$^{\nu}$NH/cm^{-1}	C=O		COCH$_3$
				Exp.	Lit.		Free	H-bonded	
I) acetylacetone arylhydrazone (AAAH)									
a	H	CCl_4	yellow	83	–	3100w	1678	1625	622
b	CH_3	cyclopentane	yellow	94–95	98	3080w	1670	1628	620
c	OCH_3	EtOH+MeOH	brown	95	98	3080w	1675	1620	620
d	$N(CH_3)_2$	EtOH	reddish	125–128	–	3010w	1660	1610	615
e	Cl	EtOH	yellow	128–130	122	3065w	1670	1628	610
f	NO_2	EtOH+MeOH	orange	202–204	–	3100	1675	1600	605
II) benzoylacetone arylhydrazone (BAAH)									
a	H	MeOH	yellow	93	98	3062w	1645	1600	620
b	CH_3	EtOH	yellow	63–65	65	3070w	1635	1587	617
c	OCH_3	EtOH	orange	87	82	3060w	1650	1625	615
d	$N(CH_3)_2$	MeOH	faint brown	53	–	3065w	*	1600	610
e	Cl	EtOH	yellowish brown	105	110	3060w	1655	1595	625
f	NO_2	EtOH	yellowish brown	142–144	–	3097w	1660	1598	615

*not detected

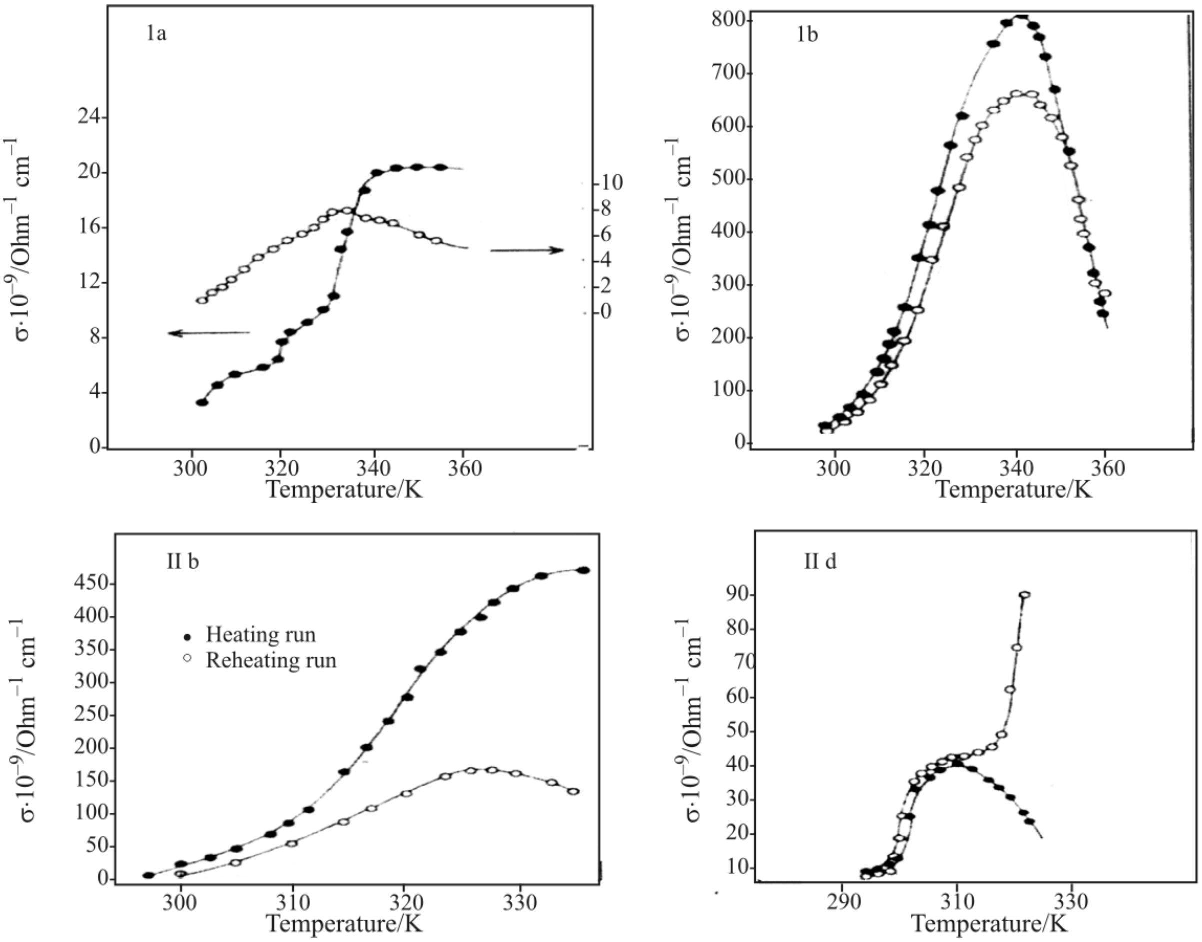


Fig. 1 Temperature dependence of the electrical conductivity of some of the investigated compounds Ia, Ib – AAAH and II b, IId – BAAH

where σ is the electrical conductivity at a given absolute temperature T, σ_0 is the initial conductivity, ΔE is the activation energy of conduction and K is the Boltzman constant ($1.37 \cdot 10^{-16}$ erg degree^{-1}).

The activation energy is estimated from this exponential relation. Most of the temperature dependence electrical conductivity curves ($\ln\sigma$ *vs.* $1/T$, Fig. 2) are characterized by two activation energy values. This indicates that the mode of conduction is changed during the conductivity measurements. It is thus assumed that the first step in the conduction process (i.e. at low temperature), is essentially due to electronic conduction through the delocalization of the π-electrons. In other words, a pure extrinsic mechanism is predominant where the conduction is mainly due to the empty states (positive holes) formed by transition of electrons to the acceptor levels. In the second step that occurs at relatively higher temperatures, the conduction occurs by an intrinsic semiconducting mechanism. This is attributed to the transition of π-electrons from the valence band to the lowest empty π-state in the conduction band.

Thus the electron is assumed to tunnel to an equivalent empty level of a neighboring molecule in the anodic direction whereas the positive hole moves to a molecule in the cathodic direction. It is clear from Fig. 1 that during the reheating of the sample, the maximum conductivity, as well as, the peak conductivity temperature are reduced with respect to those obtained during the heating cycle, with but few exceptions. Table 2 lists the numerical data of peak conductivity, σ_p, temperature of peak conductivity and activation energy before and after heating for the two series I and II. The activation energy values for reheating are more than those of heating cycle at the same temperature.

The aforementioned phenomena could be ascribed to the fact that after heating an ordering crystallographic symmetry is reached, thus delocalization of π-electrons in the lattice decreases leading to a decrease in conductivity and an increase in the activation energy. In fact the higher the energy barrier value obtained for almost all reheating measurements is attributed to a less cooperative phenomenon taking place at the relatively high temperature. Hence, a remarkable increase in the energy barrier and so a decrease in the conductivity will accom-

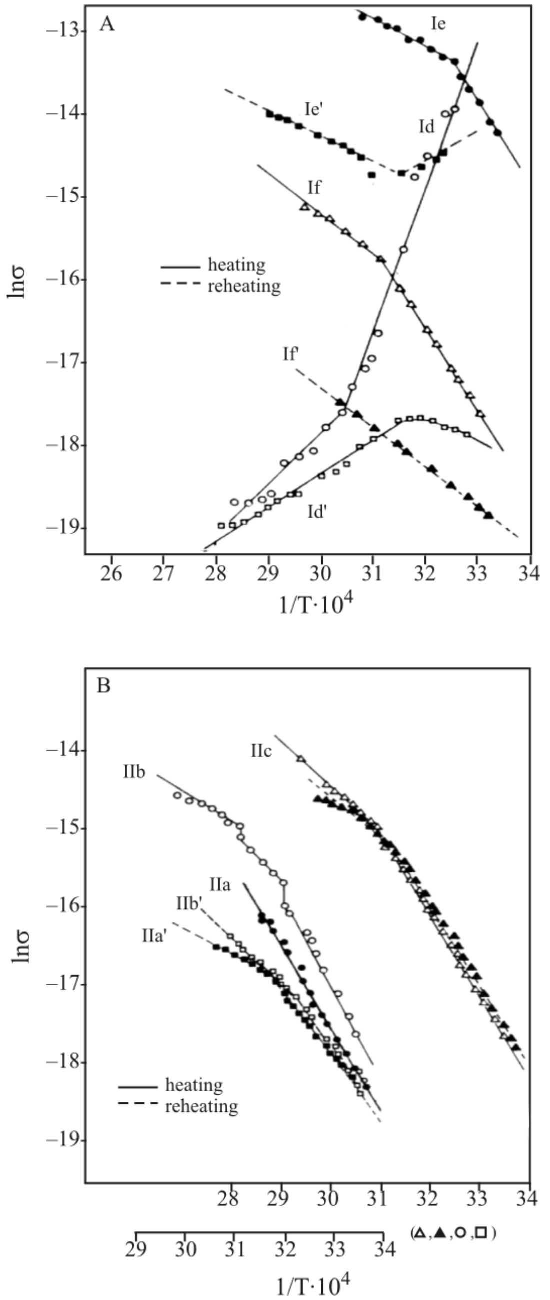


Fig. 2 Variation in conductivity *vs*. 1/*T* for some of the investigated compounds A – AAAH (Id, Ie and If) and B – BAAH (IIa, IIb and IIc)

pany this process. In general, the variation of the conductance of the polycrystalline sample during thermal agitation depends on the ordering and disordering of molecules that in turn cause the lattice dipole to distort. Mention is to be made to the fact that the investigated compounds can exist in two tautomeric forms mainly hydrazone and the azo tautomers. It was proved from IR measurements that most of these compounds are found mainly in the hydrazone form thus facilitating hydrogen bond formation.

On comparing the conductivity of acetylacetone (la) and benzoylacetone (IIa) phenylhydrazone (Table 2), it is obvious that conductivity is improved in the later. This may be due to the presence of the second phenyl group leading to the increase of the π-electrons thus causing an increase in the delocalization of electrons and hence the conduction increases.

Also according to McConnel [18, 19], the self-trapping energy for intramolecular trapping of electrons in flight can be expected to be inversely proportional to the number of conjugated aromatic C=C bonds. To this extent, the activation energy for resonance transfer of electrons can be expected to decrease with the increase of the size of the aromatic molecules i.e. the conduction increases.

For the investigated derivatives, the change of conductance is largely dependent on the nature of the substituents, (Ic<IIc, Id>IId, Ie>IIe and If>IIf). This behavior can be explained on the basis that the electrical properties of solids such as organic semiconductors are determined not only by the properties of their molecules, but also by the possibility of intermolecular interactions as well, since crystallized organic substances form molecular crystal lattices in which the molecules are spaced several angstroms apart. The high intermolecular energy barriers hindering the movement of electrons in a solid are responsible for the low conductivity of most organic semiconductors.

In the case of electron-withdrawing groups, the phenyl as well as, the carbonyl groups attract the electrons in opposite direction to that of the Cl or NO_2 groups, this results in the increase of localization of π-electrons on the center of the molecule, conjugation decreases and consequently conductivity decreases.

The fact that IId has a much lower conductivity than Id may be due to the presence of the $N(CH_3)_2$ group leading to the formation of the azo form rather than the hydrazo form in addition to the presence of the extra phenyl group.

Effect of substituents on electrical conductivities

It is obvious from the values of σ_p, Table 2, that the substitution in the para position generally improves the conductivity whether the substituent is electron donating group (CH_3, OCH_3 and $N(CH_3)_2$) or electron attracting group (Cl and NO_2).

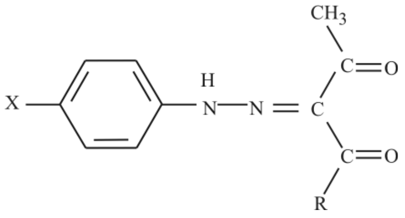
The d.c. electrical conductivity of the *p*-methoxyphenylhydrazone (c) is improved compared with that of (a). This is attributed to the high donating effect of the methoxy group ($\sigma_x = -0.268$) in addition to the presence of non-bonding electrons on its oxygen atom. This leads to an increase in electron (charge) delocalization, thus lowering the activation energy of the system and consequently the electrical

Table 2 Electrical and thermal properties of acetyleacetone (I) and benzoylacetone (II) arylhydrazones

Compd. No.	$\sigma_p\cdot10^7/\Omega^{-1}$ cm^{-1}	T_p /°C	E_{a_1} /kJ mol^{-1}	E_{a_2} /kJ mol^{-1}	T_s/°C
Acetylacetone-arylhydrazone (I)					
Heating cycle					
a	0.21	67	30.87	21.23	47
b	8.00	71	51.13	41.49	49
c	1.60	61	81.05	36.67	49
d	8.20	33	103.24	54.03	54
e	2.65	64	82.98	41.49	48
f	25.70	51	81.05	32.81	35
Reheating cycle					
a	0.18	60	31.84	37.63	–
b	6.60	71	60.79	32.81	51
c	1.30	60	76.23	38.60	51
d	5.80	41	17.37	34.74	42
e	0.29	67	38.60	–	–
f	7.80	70	30.88	25.09	45
Benzoylacetone-arylhydrazone (II)					
Heating cycle					
a	0.94	35	90.70	–	30
b	4.62	62	183.33	83.00*	49
c	5.02	67	82.98	35.70	31
d	0.41	37	128.33	41.49	47
e	2.25	62	85.88	47.28	52
f	5.10	68	73.33	23.16	
Reheating cycle					
a	0.70	36	65.61	31.84	41
b	1.70	54	83.00	42.46	34
c	4.20	64	106.14	38.60	49
d	–	–	132.19	19.30	32
e	1.70	67	82.02	51.14	47
f	3.75	70	70.44	27.98	33

σ_p: maximum peak conductivity; T_p: temperature of maximum peak conductivity; E_a: activation energy (kJ mole^{-1}); T_s: transition temperature from DTA; *Ea_3=32.81 kJ mol^{-1}

conduction increases. For the p-(N(CH$_3$)$_2$) derivative (d) the conductance of Id»Ia while lId«IIa. The high electrical conductivity values for Id and the fact that peak conductivity is attained at a rather low temperature, ≈33°C, Table 2, may be attributed to the existence of the strong donating group $N(CH_3)_2$ and the presence of non-bonding electrons on the nitrogen atom. These two factors increase the delocalization of π-electrons, lower the activation energy and consequently increase the electrical conduction of the system. In addition, the strong donating power of the $N(CH_3)_2$ groups causes the break of the intramolecular H-bonding and consequently ordering to occur at earlier temperatures.



In other words, to account for the peak behavior of conductivity characterizing the present results, one must look for ordering and disordering during thermal history of the sample. At low temperature the molecules are disordered. This disordering configuration of molecules gives resultant charges that increase the conductivity of the molecules and hence, of the crystals as the temperature increases. At a certain temperature (33°C), the energy is sufficient to rotate (packing) the organic groups, i.e., an ordering state may take place and increases of the temperature. The ordering state here increases the electrical resistivity of the sample [20].

The observed low conduction value for IId with respect to IIa (Table 2) although it bears the strong donating group, $N(CH_3)_2$, may be attributed to the predominance of the azo form rather than the hydrazo one [21]. The curve of the reheating run of IId (Fig. 1) is different than those of the other investigated compounds. A broad shoulder with a maximum conductivity of $0.41\cdot10^{-7}$ ohm^{-1} cm^{-1} at 37°C is observed then the conductance increases extremely with temperature. This behavior may be explained according to Eleye *et al*. [22] who predicted zero activation energy for a free radical possessing an unpaired electron in the $[(n/2)+1]$ level. So the conduction changes from tunneling to free radical conduction.

From Table 2, it is obvious that electron-withdrawing substituents increase the electric conduction in the order a<e<f. For the *p*-chlorophenylhydrazone derivative (e), chlorine being an electron withdrawing substituent will attract the charge density towards its direction; also the carbonyl groups tend to attract the charge density towards their direction. Thus, the net result is the increase of delocalization of the π-electrons which leads to an increase of electrical conductivity with increase of temperature till the maximum conduction is reached.

The highest conductivity is observed for the *p*-nitrophenylhydrazone derivative (f), a fact that is attributed to the presence of strong electron withdrawing substituent on the phenyl moiety and consequently, the π-electrons delocalization increases.

Differential thermal analysis (DTA)

DTA for the different investigated compounds was carried out in an attempt to record changes in lattice energy or order–disorder state which is detectable on the differential thermal analysis curves unless the reaction is extremely sluggish. The differential change in temperature ΔT was recorded in the temperature range 40–95°C with a heating rate of 2°C min^{-1}. The DTA curves, Fig. 3, do not indicate structural changes in the same temperature range of conductivity measurements and a clear endothermic signal is obtained in the heating cycle which is due to the melting process. An exothermic signal is observed during the cooling cycle. The observed difference in the peak height in the forward and reverse directions is due to the difference in the heat of transformation while heating and that evolved during cooling. According to these DTA results one might easily suggest that there was no appreciable phase transition except the solid–melt transformation. Generally, the sudden sharp changes of differential temperature, ΔT max. (Table 3), were taken as a measure of the endothermicity and the rate of transition, while the location of the peak along the temperature axis was related to the estimated activation energy provided.

For phenylhydrazone-acetylacetone (Ia) Fig. 3, the endothermic signal obtained during the heating cycle is observed at 83°C while the exothermic signal appeared at 74°C during cooling indicating thermal hysteresis of 9°C.

Table 3 Numerical analysis of the change of d.c. conductivity in acetylacetone (I) and benzoylacetone(II) arylhydrazone

Compd. No.	$\Delta\sigma_p/\Omega^{-1}$	T_p/°C	σ^*/Ω^{-1} cm^{-1}	Decrease of conductivity by reheating/%
Acetylacetone-arylhydrazone (I)				
a	$1.30\cdot10^{-8}$	7	0.62	62
b	$1.40\cdot10^{-8}$	0	0.18	18
c	$2.70\cdot10^{-8}$	3	0.17	17
d	$7.90\cdot10^{-7}$	8	0.97	97
e	$2.36\cdot10^{-7}$	3	0.89	89
f	$1.74\cdot10^{-6}$	1	0.68	68
Benzoylacetone-arylhydrazone (II)				
a	$0.24\cdot10^{-7}$	4	0.26	26
b	$1.92\cdot10^{-7}$	8	0.42	42
c	$0.82\cdot10^{-7}$	3	0.16	16
d	–	–	–	increased extremely
e	$0.55\cdot10^{-7}$	5	0.24	24
f	$1.35\cdot10^{-7}$	2	0.24	27

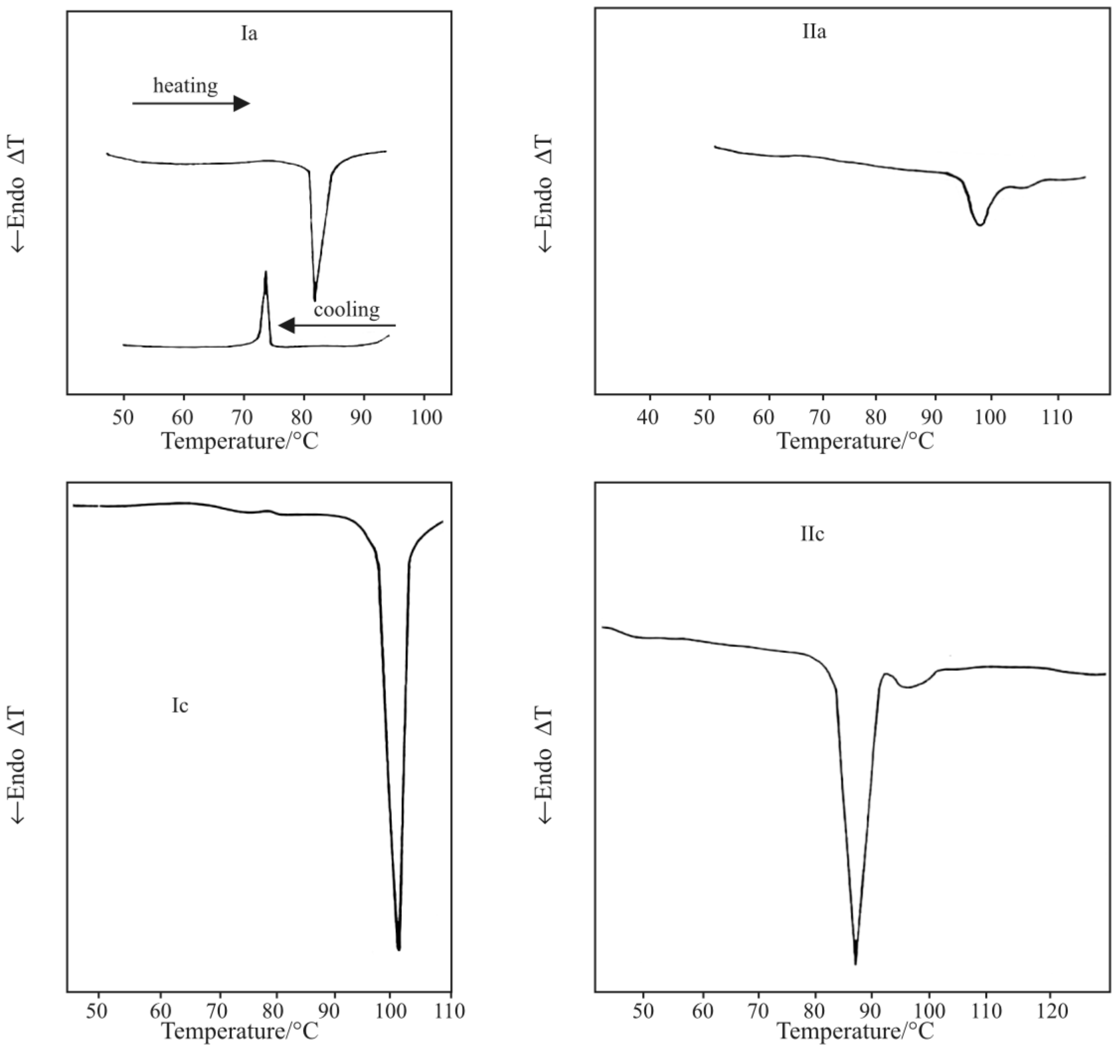


Fig. 3 DTA curves of the compounds indicated

$$T^h = T^f - T^r$$

where T^h=hysteresis width, T^f=forward temperature of transition and T^r=reverse temperature of transition.

The mechanism and physical basis for the phenomena of thermal hysteresis are well known and explained thermodynamically on the assumption that there is a potential barrier between the atomic arrangements of any two phases.

Table 4 Calculated values of enthalpy of fusion for AAAH and BAAH derivatives

No.	ΔH/kJ mol^{-1}	
	AAAH (I)	BAAH (II)
a	0.25	4.60
b	7.52	5.43
c	6.69	2.09
d	6.69	1.25
e	3.76	2.51

The latent heat of fusion (ΔH) for each of the investigated compounds has been calculated using the peak area of the band in the DTA curves. The calculated enthalpy changes (ΔH) of the melting process are listed in Table 4. It is clear that for the AAAH series (I), the substitution process increases the enthalpy and a maximum value is obtained for p-CH_3. But for BAAH (II) series, the substitution reduces ΔH values and the minimum values are obtained for both p-CH_3 and p-N–$(CH_3)_2$ derivatives.

Conclusions

The investigated compounds, acetylacetone- arylhydrazones and their bezoylacetone analogue (I and II) exhibit semi-conductivity behavior within the temperature range studied (35–70°C). Two modes of conduction predominate, extrinsic and intrinsic mechanisms at low and high temperatures, respectively. Electrical conductance generally is improved by the presence of substituent regardless of its nature (electron withdrawing or electron donating).

Differential curves does not indicate any structural changes within the temperature range of conductivity measurements.

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Received: April 19, 2007
Accepted: October 30, 2007

DOI: 10.1007/s10973-007-8514-9