

A Study the Phase Transformations in Amorphous Diphenyl Carbazide (C₁₃H₁₄N₄O)

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Abstract: Thermal and electrical properties of amorphous diphenyl carbazide (DPC) are studied between room temperature and its melting point 435 K. The study includes a set of measurements DTA, DSC, dielectric constant (ϵ'), electrical resistance (R), the pyroelectric current (I) and X-ray diffraction analysis. The results obtained are strongly supported each other and indicate that the amorphous DPC samples undergo four different phase transitions at 323 K, 363 K, 395 K and 415 K respectively. It is found that each phase transition belongs to a certain definite crystal structure. These crystal structure variations are found to be amorphous, monoclinic, tetragonal, orthorhombic and amorphous within the temperature range of this study. Thermal analysis revealed that the thermal energies for these four different phase transitions are 10.92 J/g, 7.63 J/g, 79.3 J/g and 31.77 J/g respectively. The electrical measurements showed that the conduction in these phases is activated by energies of 0.22, 0.3, 0.16 and 0.47 eV respectively. The first phase transition is attributed to the variation in hydrogen bonding N-H to the carbonyl group C=O, which is leading to a twisted intermolecular charge transfer (TICT) in the temperature region of this phase transition. The second phase transition is mainly due to the weakening of the N-H hydrogen bonding with increasing temperature. Beside that, it may be due to the reorientational molecular motion to another equivalent position. The third phase transition is attributed to a changing in the intermolecular hydrogen bonding with -CO as well as -N-H groups. These changes can greatly affect the charge distribution and in turn affect the transition process (populated locally excited states). The fourth phase transition is due to the weakening of the hydrogen bond of N-H group. [Journal of American Science. 2010;6(9):470-476]. (ISSN: 1545-1003).

Keywords: Diphenyl carbazide; Polymorphism, thermal and electrical properties.

1. Introduction

Diphenyl carbazide (DPC) is an organic compound usually used in analytical chemistry for colorimetric measurements. It exhibits many useful properties [1]. It is used as an artificial donor during charge separation in photochemical reactions and also photosynthesis electron transport [2]. It can be used for determination of trace amounts of copper (II) in water matrices [3]. It is also used for determination of trace mercury (II) in waste water [4] and to identify chlorine ions in liquid phase in mineral inclusion where DPC is used as a complexing agent [5]. It is helpful for measuring methods of chromium (VI) in leather and in dyes and determination of trace Cr (VI) and Cr (II) in water [6-8]. It is important in DNA unwinding assay's principle and application where DNA damage prevented by compounds, one of these compounds is diphenyl carbazide which is powerful one [9]. The photophysical characteristics of diphenyl carbazide (DPC) have been investigated in various protic and aprotic polar solvents in which the results showed that DPC behaves like a keto compound than a hydrazide derivative [10]. At room temperature, it has orthorhombic crystal structure and melts at 435 K and after melting and on cooling DPC

transforms to an amorphous structure as detected by X-ray analysis [11] as shown in fig. 1. According to De Ranter et al [12], DPC has an orthorhombic structure with space group pbnm with $a = 5.7171$, $b = 8.4121$ and $c = 25.6982 \text{ \AA}$.

In a previous work on amorphous DPC, an exothermic phase transition has been previously detected at 363 K by thermal analysis (DSC and DTA) and electrical measurements [1]. The presence of this phase transition in DPC is strongly confirmed by an accurate infrared study [11]. This complex compound has two phenyl hydrazide groups lie on either side of a crystallographic symmetry plane passing along the bond direction of the carbonyl group fig.1 [1]. The previous measurements which was carried out on this compound by some thermal (DTA & DSC) and electrical (d.c resistance, pyroelectric current and dielectric constants) measurements of DPC samples during the heat treatment runs to investigate the kinetics responsible for variations and the probable phase changes in this organic compound. [1].

In the present work, it is thought that the study of temperature dependence of the variation of d.c resistivity and dielectric constant as well as

pyroelectric current in addition to DTA & DSC studies might help in understanding of the mechanism of each phase transition process in this complex compound.

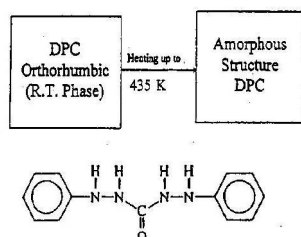


Fig. 1. The structure of the diphenyl carbazide compound.

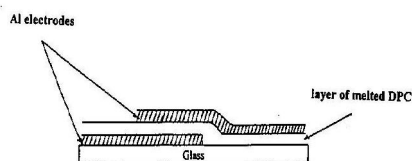


Fig. 2. Schematic diagram of cross section of the sandwich structures.

2. Experimental

The material used in the present work was ultra pure diphenyl carbazide powder $C_{13}H_{14}N_4O$ obtained from PDH, England. For thermal analysis measurements (DTA and DSC) a Shimadzu system type 50 was used to perform high precision thermal analysis. All functions are incorporated into a single compact instrument including detector, temperature, gas control and computer interface. The heating rate used for DTA is $10^\circ\text{C}/\text{min}$ while for DSC is $5^\circ\text{C}/\text{min}$.

For electrical measurements the samples were prepared in the form of a thin layer. Thin layer of DPC was prepared by melting it on the surface of the glass substrate as shown in fig.2. Aluminum electrodes were used here as a contact terminals of the sample. The electrical measurement (the capacitance C and electrical resistance R), are carried out by an RLC bridge type (Philips 6304). Also, a picoammeter was used for measuring the pyroelectric current (type Keithley 485). X-ray diffraction patterns are carried out by X-ray machine type, Bruker axs D8, Germany with Cu-K ($\lambda = 1.5406 \text{ \AA}$)

radiation and secondary monochromator in the 2 range from 20 to 70° .

3. Results

The results of a set of electrical and thermal parameters measurements of DPC samples are given below in a temperature range between room temperature (303 K) and the melting point (435 K).

Fig.(3a-d) shows the DTA and DSC thermograms for amorphous DPC samples during heating runs starting from room temperature up to 433 K. The two thermograms indicate a new endothermic phase transition at 323 K. The thermal energy of transformation is found to be 10.92 J/g, as indicated in fig. (3a). In fig. (3b), one can easily see that an exothermic phase transition has been recorded near 363 K, and the energy required for such exothermic transformation is found to be 7.63 J/g. Fig.(3c) indicates another new exothermic phase transition takes place at 395 K with heat of transformation is 79.3 J/g. Finally, fig.(3d) shows a new endothermic phase transition at 415 K, with energy of transformation process equals to 31.77 J/g.

All of these phase transformations detected here by thermal analysis (DTA & DSC) are also checked by studying the variations in electric and the dielectric properties of amorphous DPC. Fig.(4a-c) shows the temperature dependence of the d.c resistance (R), the dielectric constant (ϵ') and the pyroelectric current of amorphous DPC during the phase transformation which takes place near 323 K, as seen in fig.(4a). It is clear that the variation of the sample resistance with temperature showed a minimum value at 323 K. But with respect to the dielectric constant and the pyroelectric current, the behavior is completely different. Both of ϵ' & I_p showed maximum values at the critical temperature 323 K. The behavior of R , ϵ' & I_p with temperature strongly confirm each other and indicate the presence of a phase transition at 323 K. The activation energy of such phase transformation has been calculated in the present study and found to be 0.22 eV. It must be noticed here that this phase transformation observed here at 323 K is accompanied by a change in crystal structure. According to our X-ray measurements, it is found that the crystal structure has been changed from amorphous state to monoclinic crystal structure. This phase transformation is mainly due to the variation in hydrogen bonding (N-H) to the carbonyl group C=O, which is leading to a twisted intramolecular charge transfer (TICT) in the temperature region of this phase transition [13-15].

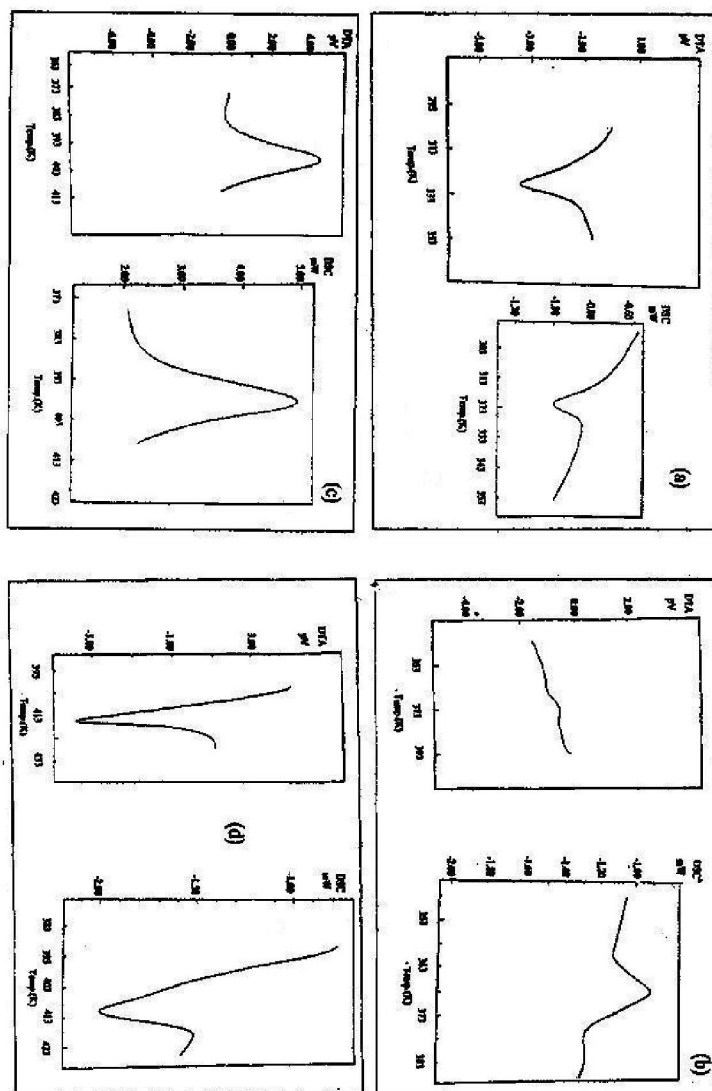


Fig.(3a-d): The DTA and DSC thermograms for released DPC through the polymorphism regions.

Fig. (5a-c) shows the temperature dependence of these electric parameters (R , ρ , and I) as the temperature elevated to 373 K. One can observe best similarity with fig.(4a-c). These parameters showed minima for (R) and maxima for (ρ & I) at a new critical temperature 363 K. Such behavior implies the presence of two different phase states before and after 363 K. This conclusion is strongly supported by the results obtained by thermal analysis as seen in fig. (3b). X-ray measurements showed that during this phase transition at 363 K, the crystal structure is changed from monoclinic to

tetragonal state. The activation energy of this phase transition process is calculated and is found to be 0.3 eV. Such transition may be due to a change in the hydrogen bonding of amino ions (N-H) to the carbonyl group (C=O) ions. This means that it is possible to attribute this observed transition to the weakening of the N-H hydrogen bonding with increasing temperature. Also the thermal energy during this phase transformation is sufficient to stimulate the reorientational molecular motion to another equivalent position which resulting in the observed structural phase transition [16].

When the DPC sample temperature exceeds 373 K, the electric parameters (R , & I) showed new variations with temperature. Maximum and minimum values has been recorded at 395 K, fig.6 (a, b& c). This critical change with temperature can be considered as a good evidence for the presence of a structure phase change. The X-ray analysis for such phase change indicates a structural change from tetragonal system to orthorhombic state system. However, this phase transition may be mainly due to a change in the intermolecular hydrogen bonding with $-CO$ as well as $-N-H$ groups [17]. These changes can be strongly affect the charge distribution and in turn the transition process (populated locally excited states) and also may be assigned to a TICT state which is generated via twisting in the higher excited state [13-15]. The energy activated this high temperature phase transition is calculated and found to be 0.16 eV. When the DPC sample temperature approaches the melting point, the three electric parameters (R , & I) showed clear anomalies with temperature fig.7 (a, b& c). Each of these parameters denotes a new critical temperature point at 415 K at which different behavior can be easily observed. Such trend is strongly supported by endothermic peak shown in the DTA & DSC thermograms fig. (3d). According to X-ray analysis, the crystal structure in this case has been changed from orthorhombic to amorphous state. Also, this transition may be due to the weakening of the hydrogen bond of N-H group during the elevation of temperature and hence stimulate the reorientational molecular motion to another equivalent position (due to the sufficient thermal energy) [16]. The activated energy required for this phase transformation is calculated and found to be 0.47 eV. The energy diagram for the conduction process during the different phase transformations is given in fig. 8.

4. Discussions

According to the present investigation of amorphous DPC, all of the obtained results (thermal analysis DTA & DSC and electrical measurements R ,

& I) are clearly confirmed the presence of four different independent phase transformations at 323 K, 363 K, 395 K and 415 K respectively. In fact, the phase transformation at 363 K has been previously detected [1]. But the other three transformations at 323 K, 395 K and 415 K are completely new and detected here for the first time. According to the present analysis, each of these phases belongs to a new a crystal structure. A set of X-ray diffraction curves is obtained for these phases at the corresponding temperatures and the results are given in fig. 9

The study of the heating effect on the physical properties of amorphous DPC samples can provide better understanding of the nature of transition in this organic compound. The associated changes in the interaction potential of the atoms or molecules during the transformation process play an important role in this transition. Near the phase transition point, the probability of reorientations or vibrations of the molecules is considerably changed with increasing temperature. But at the transition point itself, the nature of this motion changes qualitatively, and in turn lead to a change in the characteristic structure of the sample [18, 19].

In fact, the data presented here for the variation of different electric parameters as a function of temperature, showed two completely different regions before and after the phase transition points. This means that there are two independent mechanisms which are operative in the two phase regions. The energy activating values control the electric conduction mechanisms in these four different phases are 0.22, 0.3, 0.16 and 0.47 eV. The largest value corresponds to the highest temperature phase. With respect to the transition at 323 K, this phase changes from amorphous structure to monoclinic structure. It may be due to the variation in hydrogen bonding of N-H to the carbonyl group $C=O$. This leads to a twisted intramolecular charge transfer (TICT) in the temperature region of such phase transition (323 K) [13-15].

During the transition at (363 K), the crystal structure changes from monoclinic to tetragonal structure. This phase transition is probably due to a change in N-H, which is involved a change in the hydrogen bonding of amino ions (N-H) to the carbonyl group ($C=O$). However, it is possible to attribute this transition to a weakening of the N-H hydrogen bonding during the increasing of temperature. Also, here the thermal energy required for this phase transformation is sufficient to stimulate the reorientational molecular motion to another equivalent position which resulting in the observed structural phase transition [16].

As the sample temperature exceeds 373 K, another phase transition takes place at 395K in which the structure is changed from tetragonal to orthorhombic structure. This phase transformation is accompanied by a small thermal activated energy for conduction process. It may be explained as a large change in the intermolecular hydrogen bonding with $-CO$ as well as $-N-H$ groups [17]. These changes can be greatly affect the charge distribution so as to affect the transition process (populated locally excited states) and also may be assigned to a TICT state which is generated via twisting in the higher excited state [13-15].

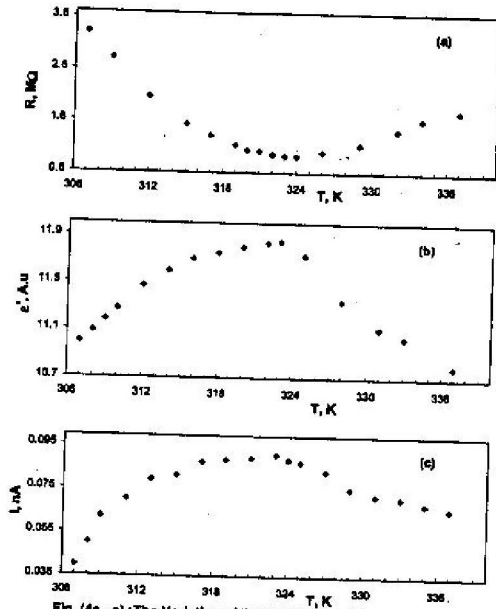


Fig. (4a - c) : The Variation of the electrical resistance (a), the dielectric constant (b) and the pyroelectric current (c) with temperature for amorphous DPC samples during the heating transformations.

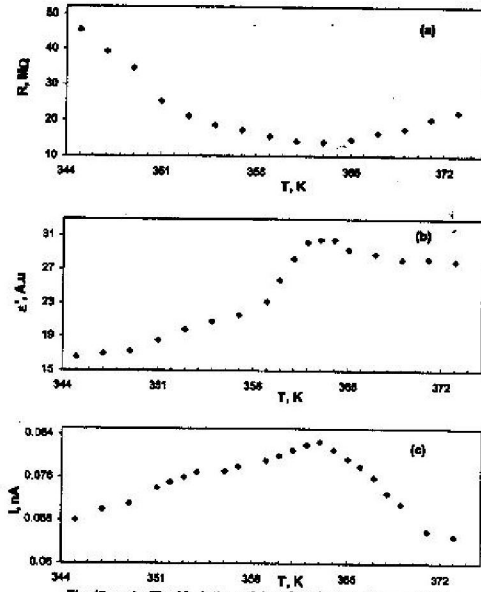


Fig. (5a - c) : The Variation of the electrical resistance (a), the dielectric constant (b) and the pyroelectric current (c) with temperature for amorphous DPC samples during the heating transformations.

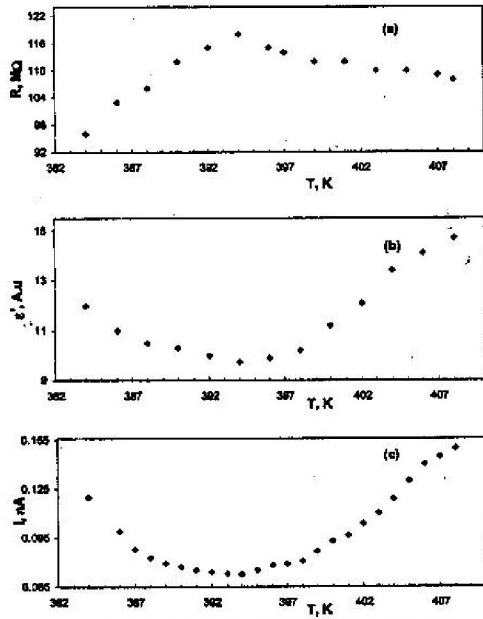


Fig. (6a - c) : The Variation of the electrical resistance (a), the dielectric constant (b) and the pyroelectric current (c) with temperature for amorphous DPC samples during the heating transformations.

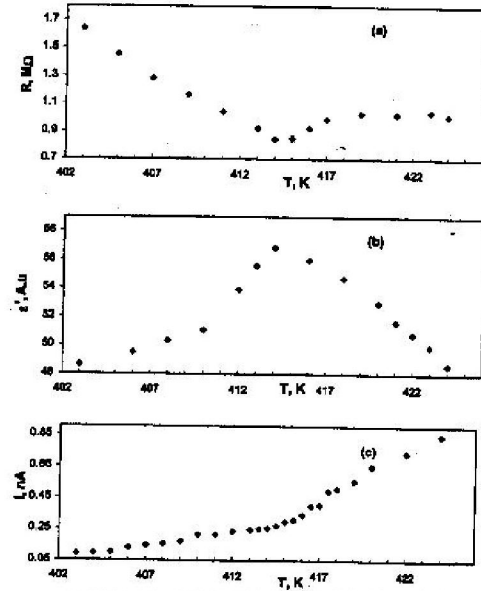


Fig. (7a - c) : The Variation of the electrical resistance (a), the dielectric constant (b) and the pyroelectric current (c) with temperature for amorphous DPC samples during the heating transformations.

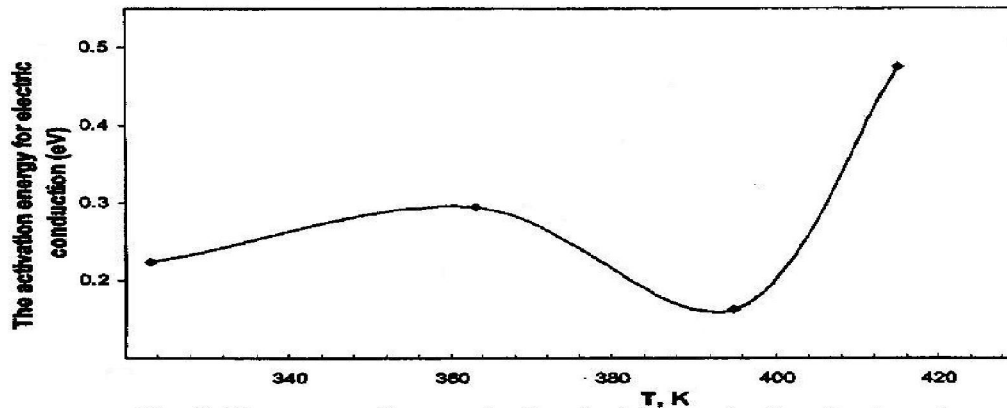


Fig. 8. The energy diagram for the electric conduction mechanism during the transformation in the amorphous DPC samples with temperature.

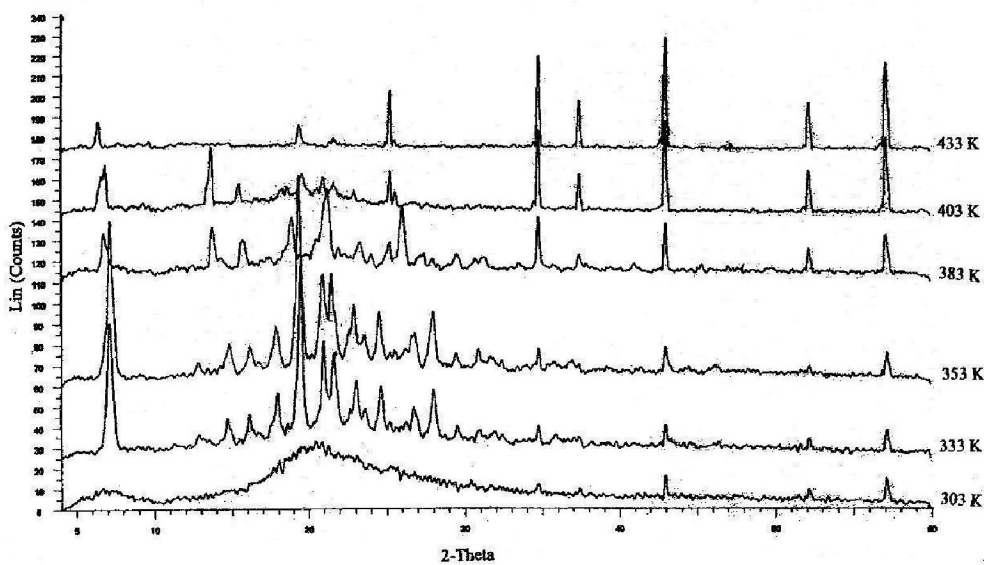


Fig. 9 X-ray diffraction patterns for the polymorphism of amorphous DPC at different temperatures (303, 333, 353, 383, 403, 433 K).

The increase in the thermal activated energy for conduction process during the phase transition (415K), may be related to the existence of a high ordering transformation which is characterized by sudden changes in the atomic arrangements at higher temperature (Thermoplastic phenomena) [20]. This phase transition changes from orthorhombic to amorphous structure. Also this phase transformation may be related to the variation of the hydrogen bond in N-H group.

The electrical resistivity of a dielectric material depends on the presence of locally excited states due to the activation of the thermal energy, which act as a source of ions in the dielectric material. Here, the conduction mechanism is complex, because it depends on the physical and chemical properties of the dielectric materials. In fact, DPC is considered as an artificial electron donor, so that the presence of electrons causes the conduction in it to be electronic process where it is easy for formation of electronic excited states. The rate of formation of (EES) depends on the change of temperature inside the material and the crystal structure transformation from state to another. The conduction mechanism which occurs in the amorphous DPC material within the temperature range from room temperature (303 K) up to the melting point (435 K) is mainly related to the electronic conduction process.

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