IR Study of the Low Temperature phase Transition in Amorphous Diphenyl Carbazide $C_{13}H_{14}N_4O$

F. El-Kabbany, S. Taha* and M. Hafez

Physics Dept., Faculty of Science, Cairo University.
* Physics Dept., Faculty of Science, Fayoum University.
profdrsthassan@yahoo.com

Abstract: The low temperature dependence of IR spectra of amorphous diphenyl carbazide $C_{13}H_{14}N_4O$ has been investigated below zero temperature. The data is reported here between room temperature and down to -70°C and the IR spectra are recorded in the frequency range 400-4000 cm^{-1}. This study is an extension of a recent one, which detected the presence of polymorphic character of this complex compound by IR, DSC and DTA at 50°C, 90°C, 120 ^{o}C and 140 ^{o}C. It includes measurements and interpretation of the IR spectral band shape, frequencies of modes and band shifts as a function of temperature. Eleven different fundamental modes have been investigated explicitly. Special attention is paid to the most sensitive modes which reflect the low temperature phase transition process in detail. These modes are 3328 cm^{-1}, 1677 cm^{-1}, 1602 cm^{-1}, 1251 cm^{-1}, 750 cm^{-1} and 494 cm^{-1} in which the variations strongly support the low temperature phase transition in DPC at -47°C. This phase transition does not show structural change but just a transformation from amorphous state to amorphous state as detected by x-ray analysis. The phase transition here is suggested to be of displacive type. A low temperature phase transition has been detected here for the first time in diphenyl carbazide at - 47°C. [Journal of American Science. 2011;7(1):147-155]. (ISSN: 1545-1003).

Keywords: Low temperature IR spectra; Diphenyl carbazide.

1. Introduction

Diphenyl carbazide (DPC) $C_{13}H_{14}N_4O$ is a complex organic compound frequently used in analytical chemistry. It is also used as a sensitive reagent for metal ions (mercury and cadmium). It has many applications, especially in the field of biophysics and microbiology. DPC is used in differential regulation of high light tolerance in mutant and wild-type Anacystis cells [1-3]. The crystal structure of DPC has been determined by De Ranter [4] and found to be orthorhombic at room temperature with space group pbnm with a = 5.7171 A^o, b = 8.4121 A^o and c = 25.6982 A^o. The melting point of DPC is 162°C after that, it transforms to amorphous structure.

IR spectroscopy has been widely used to identify the presence and relative population of phase transformations in solids [5-8]. Recently, IR spectroscopy was used to measure and identify new structure formation accompanying phase transformation [9-14].

The vast majority of IR spectroscopy deals with the determination of IR fingerprint of a polymorphic modification. In the present work we wish to employ the IR technique to obtain physical information somewhat beyond the mere identification of a particular crystal modification.

Previous work on DPC showed the presence of several phase transitions above room temperature and up to its melting point. In the present work, a low temperature investigation of the IR characteristic mode changes in DPC was discussed in details.

This study aims to detect a probable low temperature phase transition below zero degrees centigrade down to -70°C. In fact there is absolutely no previous study for this compound in this low temperature range.

2. Experimental

Diphenyl Carbazide powder (ultra pure) was obtained from the British Drug House (BDH), Laboratory Chemical Division, England. IR spectra were recorded using the FT-IR type Perkin Elmer recorded on satellite 2000 spectrometer and the experimental technique employed has been reported [15]. The samples used were in the form of discs prepared by mixing 20 mg of DPC with one gram of KBr in a cylindrical die of 10 mm diameter. The die was then evacuated to ensure dryness and the sample was pressed. The spectra were recorded in the region of 400- 4000 cm^{-1} by a computerized system attached to a monitor and a printer.

3. Results

A specimen of DPC is analyzed at first at low temperature by differential scanning calorimetry

DSC. Fig. 1 shows the differential scanning calorimetry (DSC) thermogram and its derivative with time of pure DPC compound. The DPC sample is cooled at first in the DSC cell down to -70°C by using liquid nitrogen. After that, the DPC sample is slowly heated with a heating rate of 5°C/min. The DSC thermogram in fig. 1 illustrates at first very little variation, then, sudden drop at - 47°C. This is clearly indicates a probable low temperature phase transformation of DPC at - 47°C. The derivative of DSC indicate a peak at – 36°C, i.e, the transformation to the next state has been completed at this temperature. So, there is no doubt, that there is a low temperature phase transition in DPC near to - 50°C. Now, we are going to follow up what happened in such transition by studying the IR vibrating modes at selected set of low temperatures -70°C, - 40°C, - 30°C, - 20°C, - 10°C and room temperature.

　　　Fig. 2 shows the IR spectra of a crystalline sample (orthorhombic) of DPC at room temperature (30°C). Eleven different ionic modes are shown in this figure. It showed no band which could be attribute to any mode other than those due to the ionic fundamentals of N-H, C-H, N-N, C=O, C-H and C-C groups. A quick glance at the spectrum shows that the strongest bands are at 3359 cm^{-1}, 3276 cm^{-1}, 3045 cm^{-1} (sharp), 1659 cm^{-1}, 1592 cm^{-1} (sharp), 1487 cm^{-1}, 1287 cm^{-1}, 1239 cm^{-1} (sharp), 882 cm^{-1} (sharp), 748 cm^{-1} (sharp) and 515 cm^{-1} (sharp). The broad band contains the three important modes 3359 cm-1 (asymmetric stretching of N-H), 3276 cm^{-1} (symmetric stretching of N-H) and 3045 cm^{-1} (sharp) (aromatic C-H stretching). The next modes at 1659 cm^{-1}, 1592 cm^{-1} (sharp) and 1486 cm^{-1} indicate the bending or deformation of N-H, N-N stretching symmetric vibration and N-N stretching asymmetric vibration respectively. The next two bands of the spectra at 1287 cm^{-1} and 1239 cm^{-1} (sharp) indicate the C-H stretching and C=O stretching vibrations. The sharp band at 882 cm^{-1} indicates the out of plane C-H bending. Also, the sharp bands at 748 cm^{-1} and 515 cm^{-1} are due to monosubstituted benzene and N-H oscillation respectively. All of these modes of vibrations of crystalline DPC at room temperature are tabulated in table (1). Crystalline diphenyl carbazide (DPC) can be melted at 162°C. Melted DPC transforms to amorphous structure at room temperature. Amorphous sample of DPC is subjected to IR and the obtained spectra are shown in fig. 3. The numerical values of the fundamental modes of vibration are given in table (1). One can easily observe a clear mode shift in the fundamental modes of vibrations as DPC transforms from crystalline (orthorhombic) structure to amorphous one. The mode shift corresponds to each ionic vibration of DPC is given

in table (2). It is clear that the asymmetric stretching of N-H recorded the maximum mode shift (= - 48 cm^{-1}) when DPC changes to amorphous structure. One can deduce that the stretching of N-H is very sensitive to any structure change of DPC.
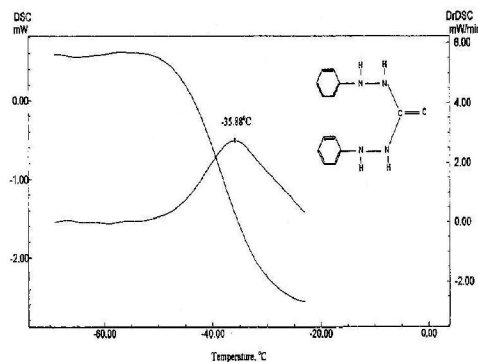

Fig.1 Low temperature DSC thermogram and its first derivative for amorphous DPC sample.
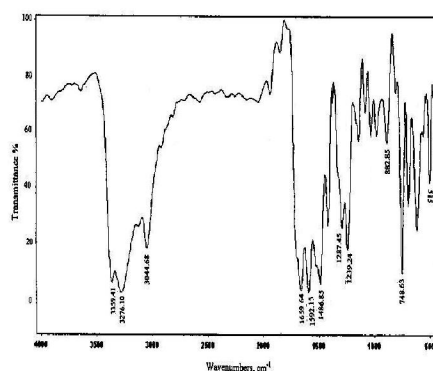

Fig.2 IR spectra of orthorhombic DPC at room temperature.

　　　Now, amorphous DPC is studied by IR at low temperatures. A set of selected low temperatures -70°C, - 40°C, - 30°C, - 20°C, - 10°C are chosen and the spectra at these temperatures are shown in figs. 4, 5, 6, 7 & 8. Clear mode shift can be easily noticed in symmetric stretching of N-H, bending mode of N-H, N-N stretching symmetric vibrations, C-H stretching vibration, monosubstituted benzene and N-H oscillation. As an example for such mode shift is given in table (3) in which the temperature changed from - 70°C to - 30°C. Such mode shift is probably due to a low temperature phase transition at - 47°C as previously detected by thermal analysis. Also, in these figs. 4, 5, 6, 7 & 8, the band contour (band shape) is widely varied and loses its sharpness. This means that, more cooling of DPC cause more broadening of bands. Also, noisy band contour often appears for lower temperature below zero. The main

objective of the present work is to study the temperature dependence of the IR analysis of DPC below zero temperature. For a detailed investigation three important spectral regions, fig.9 will be studied at three different temperatures.

The variation of band contours during cooling below zero temperature is shown in fig. 9, for the principle ionic modes of vibrations of amorphous DPC. The band shapes in this fig.9 is completely different above - 70°C (i.e, at - 30°C & 30°C). As the sample temperature approach the room temperature (30°C) the noisy character in the vibrating mode disappeared. Also, the broadening of bands becomes little. In fact, such character accompanied the low temperature phase transition in amorphous DPC.

4. Discussions

The study of the low temperature phase transition in DPC by IR technique is based on the fact that after the absorption of IR radiation, DPC molecule vibrates at many rates of vibrations and forms close-packed absorption bands. Different bands observed in the present investigation are correspond to various functional groups and bonds found in DPC molecules.

The IR spectra of DPC in its solid state arise from some vibrations of the individual ions and internal vibrations of molecules. Since the vibrations occur throughout the lattice and are not concerned with a single unit cell, these vibrations are often observed as broad peaks which represent a composite band of several vibrations. The mass of ions here plays an important role in determination of the frequency of absorption. However, a regular change in frequency is observed during the variation of temperature. For those lattices containing covalent molecules, the vibrations likely to be observed in the IR spectrum arise from two sources:

i) Molecular lattice vibrations which would occur at very low frequencies due to the mass of molecule.

ii) Internal vibrations of the molecules.

Within this second class there are stretching and bending vibrations which involve heavy atoms and hindered rotation of ligands attached to cental atom.

Changing the temperature of cation or anion shifts the strongest absorption. This behavior appears to be characterizing the lattice vibrations in complex compounds. According to DSC and the present IR analysis, a low temperature phase transition at - 47°C take place in amorphous DPC. An x-ray structure analysis is carried out for DPC before and after the phase transition point. The obtained results are given in fig. 10.

Table (1) Infrared spectra of DPC at a set of low temperatures and room temperature.

| Modes of vibrations of DPC	-70 ^{o}C	- 40°C	- 30°C	- 20°C	- 10°C	Orthorhombic DPC at R.T	Amorphous DPC at R.T
Asymmetric stretching of N-H	3339	3328	3328	3319	3319	3359	3311
Symmetric stretching of N-H	3276	3275	3275	3269	3260	3276	3255
Aromatic C-H stretching	—	3049	3049	3052	3052	3044	3052
Bending or deformation mode of N-H	1685	1677	1677	1666	1666	1659	1677
N-N stretching symmetric vibrations	1592	1602	1602	1600	1600	1592	1602
N-N stretching asymmetric vibrations	1492	1493	1493	1490	1490	1486	1492
C-H stretching vibrations	1248	1251	1251	1247	1247	1287	1306
C=O stretching vibrations	1174	1174	1174	1169	1169	1239	1252
Out of plane C-H bending	883	887	887	882	882	882	887
Monosubstituted benzene	737	750	750	749	749	748	755
N-H oscillation	507	494	494	466	466	515	489
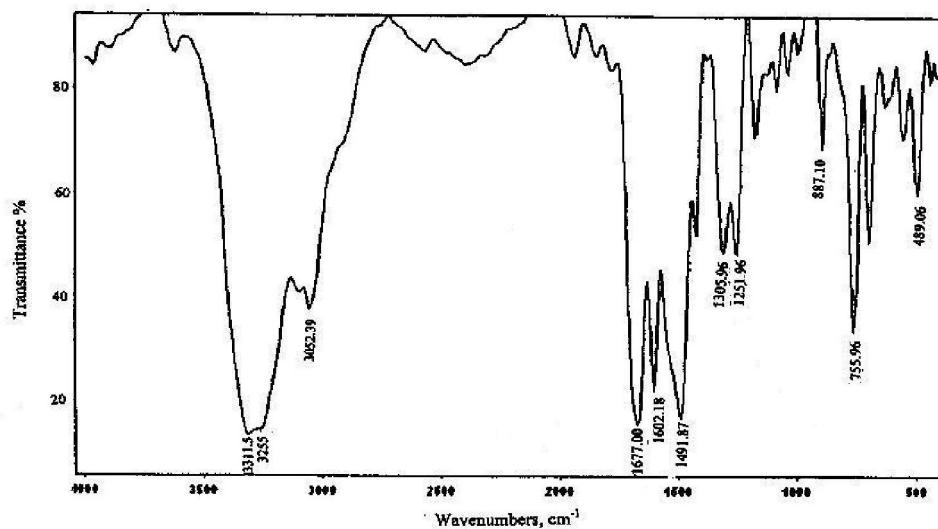
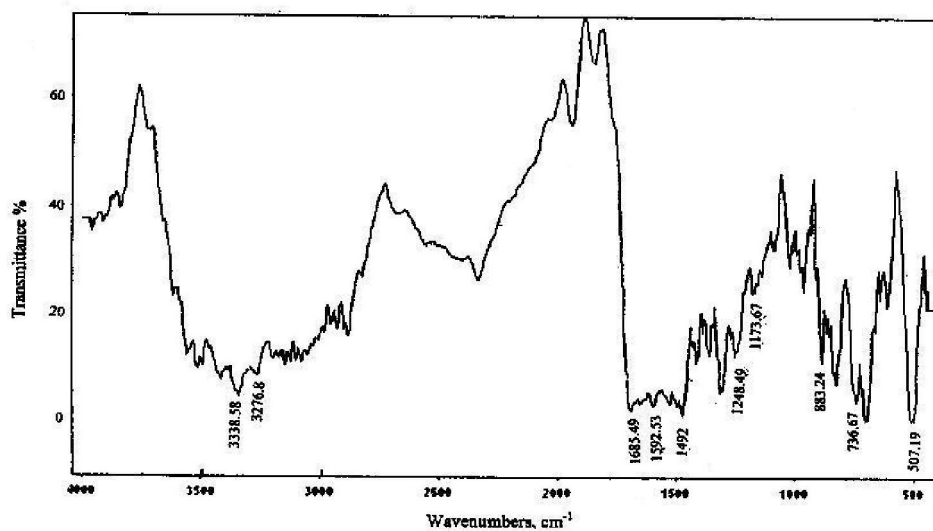Fig.3 IR spectra of amorphous DPC at room temperature.
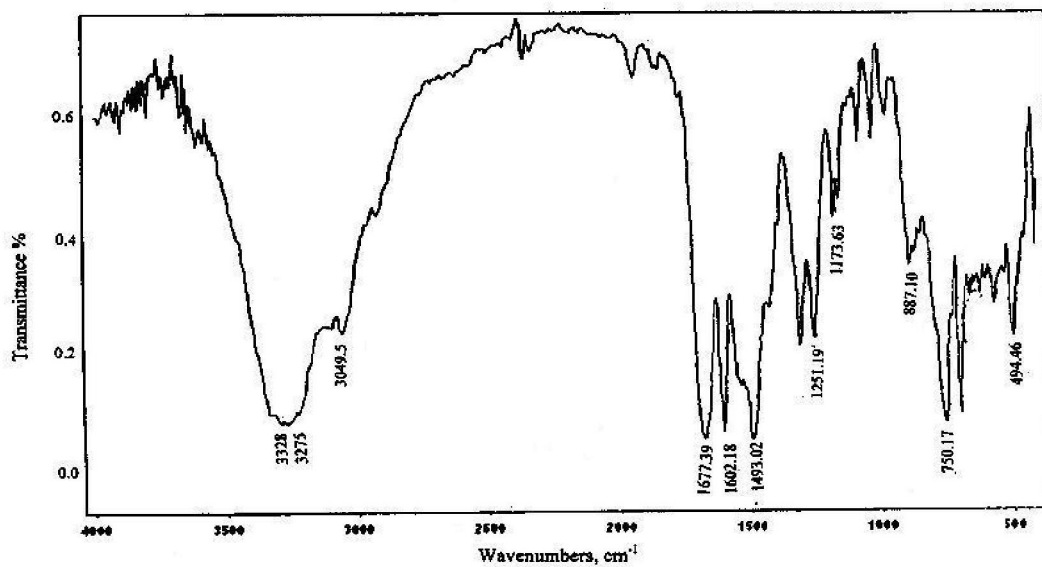

Fig.4 IR spectra of amorphous DPC at -70°C.

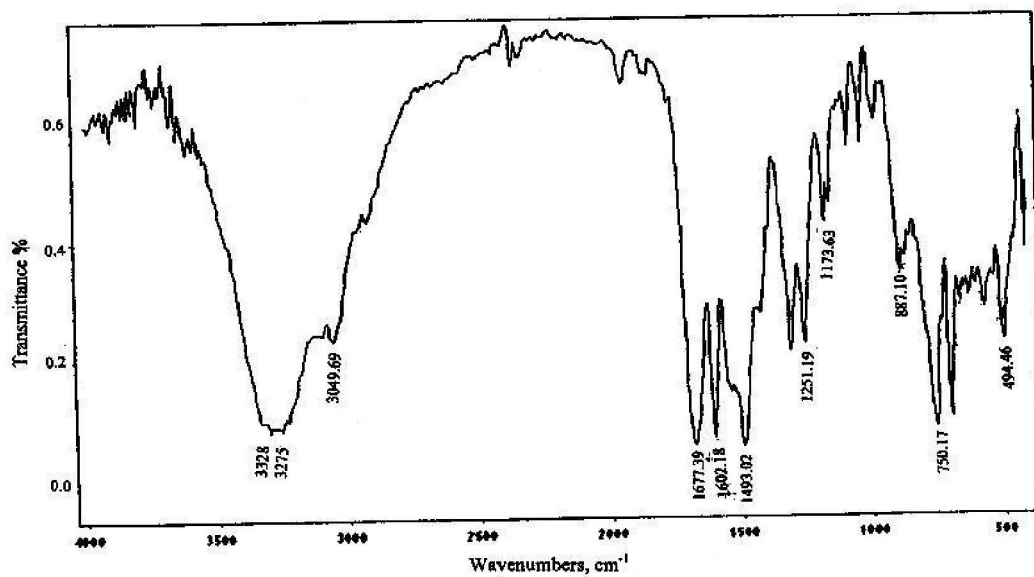Fig.5 IR spectra of amorphous DPC at -40°C.

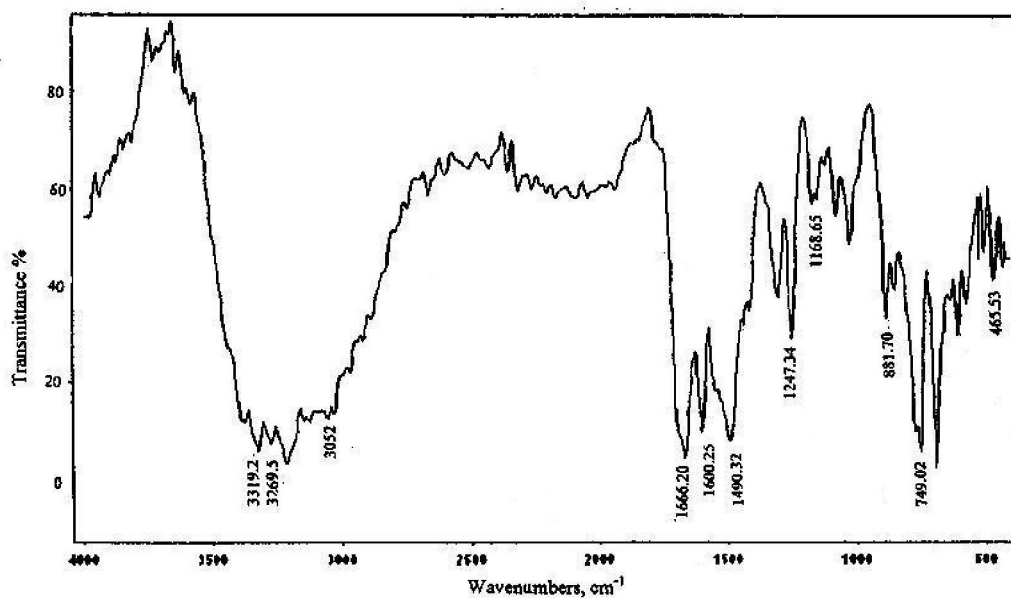Fig.6 IR spectra of amorphous DPC at -30°C.
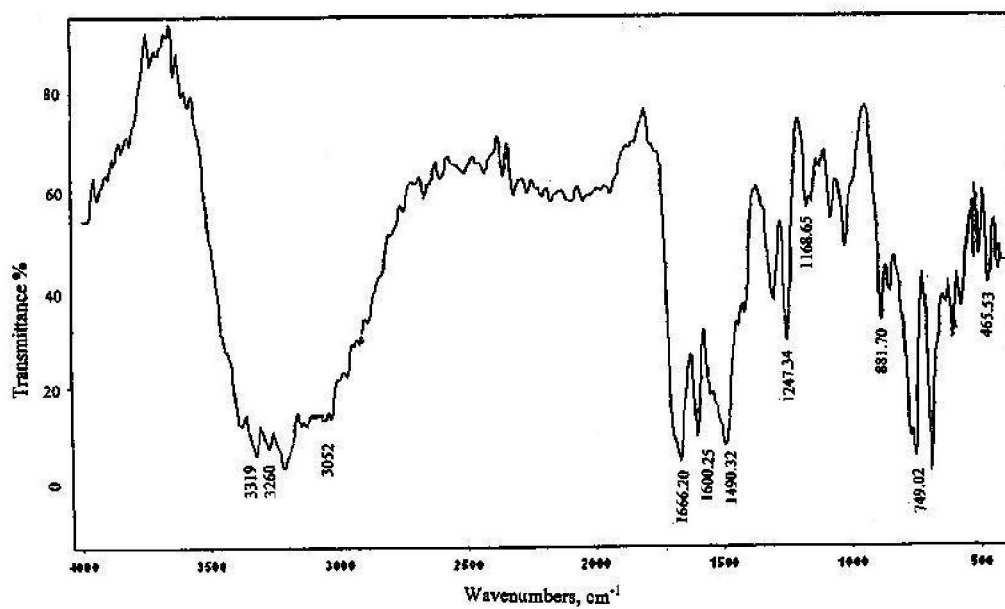
Fig.7 IR spectra of amorphous DPC at -20°C.

Fig.8 IR spectra of amorphous DPC at -10°C.

Table (2) Mode shifts as DPC changes from crystalline structure to amorphous structure.

Modes of vibrations of DPC	Mode shift, Δv (cm^{-1})
Asymmetric stretching of N-H	- 48
Symmetric stretching of N-H	- 21
Aromatic C-H stretching	+ 8
Bending or deformation mode of N-H	+ 18
N-N stretching symmetric vibrations	+ 10
N-N stretching asymmetric vibrations	+ 6
C-H stretching vibrations	+ 19
C=O stretching vibrations	+ 13
Out of plane C-H bending	+ 5
Monosubstituted benzene	+ 7
N-H oscillation	+ 26

Table (3) Fundamental mode shift during low temperature phase transition

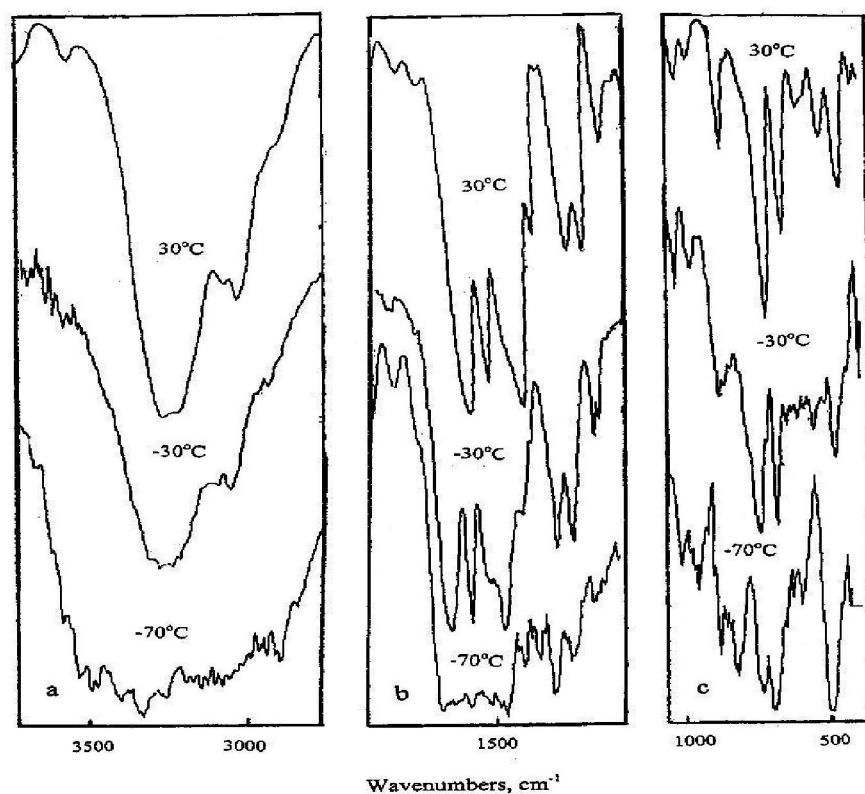| Fundamental mode	-70°C	- 30°C	Mode shift, Δv
Asymmetric stretching of N-H	3339cm^{-1}	3328cm^{-1}	- 11 cm^{-1}
Bending or deformation mode of N-H	1685 cm^{-1}	1677 cm^{-1}	- 8 cm^{-1}
N-N stretching symmetric vibrations	1592 cm^{-1}	1602 cm^{-1}	+ 10 cm^{-1}
C-H stretching vibrations	1248 cm^{-1}	1251 cm^{-1}	+ 3 cm^{-1}
Monosubstituted benzene	737 cm^{-1}	750 cm^{-1}	+ 13 cm^{-1}
N-H oscillation	507 cm^{-1}	489 cm^{-1}	- 18 cm^{-1}

Fig.9 Variation of band shapes at a set of selected temperatures (-70°C,
-30°C, 30°C) for DPC modes:-
a)Asymmetric stretching of N-H.
b)Bending or deformation mode of N-H, N-N stretching
symmetric vibrations and C-H stretching vibrations.
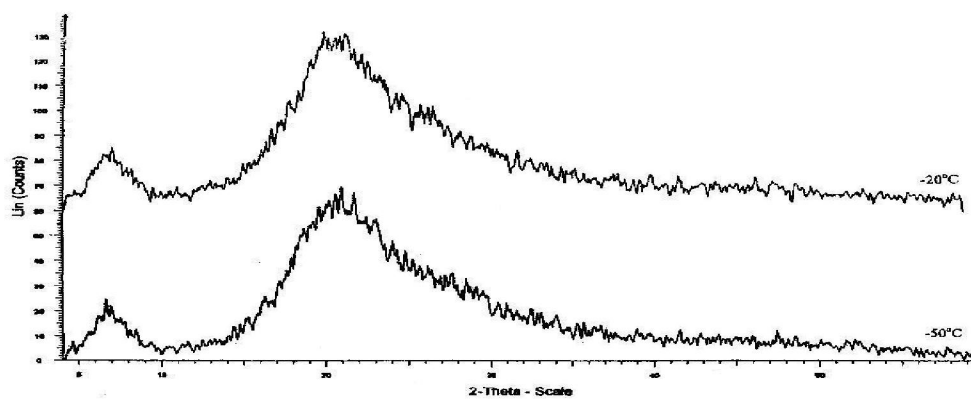c)Monosubstituted benzene and N-H oscillaton.

Fig.10 X-ray diffraction patterns of DPC at -20°C and -50°C.

The X-ray analysis strongly indicates that the crystal structure is amorphous before and after the phase transition process. This means that this low temperature phase transition in DPC involves no crystal structure changes. So, this type of phase transition is displacive type. According to Burger's [16, 17], in displacive transition, the initial lattice is deformed to a final lattice without breaking all bonds that link the particles within the crystal. The transition is considered displacive if a resemblance is found between the structures of the phases. It is asserted that these transitions must occur rapidly.

In order to explain the anomalous behavior shown in fig.9, it is proposed that N, H, C and O ions are oriented in a disordered fashion among the positions with nearly equal energies and symmetry. The rate of reorientation among these positions increases with temperature due to thermal agitation. The observed splitting in different band modes indicates a remarkable lowering in the site symmetry of the different ions. Also, both of the observed change in wave number and splitting in certain characteristic peaks can be linked to an overall change in the local molecular environment of vibrational dipole moments. It is hypothesized here that varying temperature will also have some effect on molecular order and thus on the IR spectrum of DPC.

In the present study, DPC complex compound contains large number of atoms, and thus many modes of vibrations will exist. When a complex with mixed ligands is formed, there is always a decrease in symmetry. This reduction in symmetry causes an increase in the number of IR bands of the complex compound [18].

Corresponding Author:
*Corresponding author. Prof. S. Taha
  E-mail: profdrsthassan@yahoo.com
  Tel: +202 35676753

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