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**INFRARED SPECTROSCOPIC ANALYSIS
OF POLYMORPHISM IN DIPHENYL CARBAZIDE**

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Infrared (IR) analysis is used here to investigate the changes in N-N, N-H, and C=O bonds of thermally treated diphenyl carbazole (DPC) during the variation from room temperature up to 160 °C. Polymorphism in the DPC compound has been studied by detecting the changes in some IR spectroscopic parameters (e.g., mode shift, band contour) during the elevation of temperature. Beside IR spectroscopy, also differential scanning calorimetry, X-ray diffraction, NMR, and atomic mass spectra were used as supplementary identification techniques. All of the vibrations of DPC were found to be due to the ionic fundamentals 3311 cm⁻¹, 3097 cm⁻¹, 3052 cm⁻¹, 1677 cm⁻¹, 1602 cm⁻¹, 1492 cm⁻¹, 1306 cm⁻¹, 1252 cm⁻¹, 887 cm⁻¹ and 755 cm⁻¹. The results revealed for the first time that the thermally treated DPC traverse four different phase transformations at 50, 90, 125, and 140 °C. The crystal structure was found to be amorphous, monoclinic, tetragonal,

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orthorhombic and amorphous in the temperature range of 30–160 °C. The X-ray diffraction patterns support the results obtained by IR.

Introduction

Diphenyl carbazide (DPC; $C_{13}H_{14}N_4O$) is one of the important organic compounds mainly used as an artificial donor material. Also, it is frequently utilised in analytical chemistry as a sensitive reagent for some metal ions, especially Hg^{2+} , Cd^{2+} and CrO_4^{2-} [1], when the latter can be determined in the form of the complex with DPC in real samples with the aid of calorimetry [2], colorimetry [3–7], or electrochemical stripping analysis [8]. The DPC molecule has an orthorhombic structure with space group pnma, characterised by the lattice parameters of $a = 5.7171\text{ \AA}$, $b = 8.4121\text{ \AA}$, and $c = 25.6982\text{ \AA}$. The two phenyl hydrazide groups are located on either side of a crystallographic symmetry plane, passing along the bond direction of the carbonyl group [9].

The present work is considered as an extension of our previous work on DPC, in which differential thermal analysis (DTA), differential scanning calorimetry (DSC), and some electrical measurements were carried out [10,11]. The previous work on DPC compound has shown the presence of an exothermic phase transformation at a temperature of about 90 °C. Nowadays and after more than twelve years, instrumental resolution, sensitivity and accuracy have been widely improved. Besides that, most of the techniques have been computerized. Thus, it is very interesting and promising to perform thermal scanned programs for studying the effect of heat treatment on the spectroscopic properties of the heat treated DPC. Then, the molecule of DPC can be subjected to an infrared (IR) spectroscopic analysis under conditions similar to that performed previously in thermal and electrical study [11]. The nature of the temperature dependence of the vibrating groups is of great interest, as its role is fundamental to explain many of the physical properties of this complex organic compound.

Herein, we report on the important IR changes accompanying new polymorphic transformations in the DPC molecule during the controlled heat treatment of the samples. Also, a thermal histogram will be suggested for describing what happened in DPC during the transformation to several polymorphic states. Beside the IR analysis itself, X-ray diffraction (XR), nuclear magnetic resonance (NMR) and mass spectrometry (MS) are also used as complementary identification techniques. The present study aims to reveal that there is not only one, but several phase transformations in DPC during the heat treatment from ambient conditions up to a temperature of 160 °C.

Experimental

Chemicals and Reagents

Diphenyl carbazide (DPC) used for analysis was in powdered form and of ultra-pure grade (obtained from the British Drug House, Lab. Chem. Division; UK). KBr used for FTIR and the solvent DMSO for NMR measurements; both being purchased from Sigma-Aldrich.

Instrumental Techniques

IR spectra were recorded using the FT-IR spectrometer (model “Satellite 2000”, Perkin Elmer), when the respective experimental procedure has already been reported [12]. The samples used were prepared in the form of discs 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 within the wave-number region of 4000-400 cm⁻¹ and run by means of a computer-controlled system.

NMR analysis was performed in dimethyl sulphoxide (DMSO) selected as the solvent of choice [12] and the spectra recorded using a commercial instrument by Varian (model “Gemim 20”, operating at 200 MHz). Finally, the mass spectra (MS) of heat-treated DPC were obtained using a quadrupole mass spectrometer (GC-MS type, model “QP 1000 EX”; Shimadzu, Japan). The ions were formed in the electron impact (EI) mode at 70 eV and with a temperature of the ions of about 250 °C. The work took place in vacuum, and depending on the vapour pressure of the sample, the operational pressure was in the order of 10⁻⁴ Torr.

Results and Discussion

Survey and Commentary of the Experiments Performed

In previous investigations, the DPC compound was studied in amorphous form, including its characterization via the electrical and thermal properties when the latter gave rather inconclusive results. In the present study, however, the powdered form of DPC yielded the thermograms that have clearly indicated that there are apparent phase changes at 50, 90, and 140 °C — see Fig. 1.

Also, obvious sudden changes have been observed in electrical properties (dielectric constant, d.c. resistivity, pyroelectric current, etc.) at 125 °C. Thus, according to both techniques, probable polymorphs at 50, 90, 125, and 140 °C in DPC can be expected. IR spectroscopic analysis could be used here to confirm the

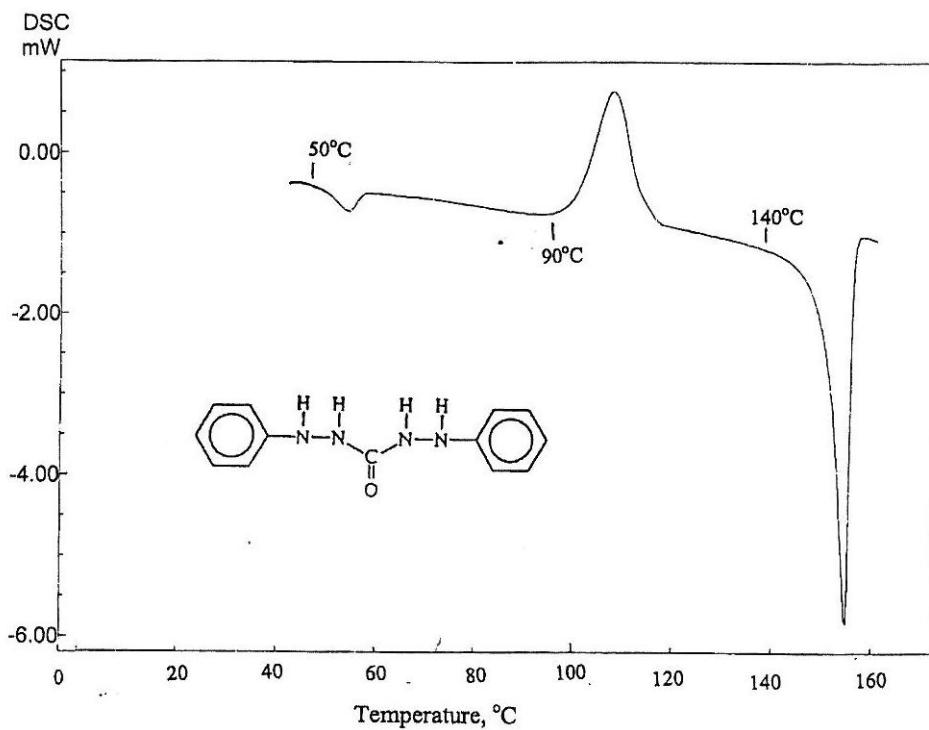


Fig. 1 Differential scanning calorimetric curve obtained by analysing the compound of interest (diphenyl carbazide, DPC; $C_{13}H_{14}N_4O$)

polymorphism in thermally treated DPC. The spectral change accompanying the polymorphic transitions are obtained from 400 cm^{-1} up to 4000 cm^{-1} for original samples of DPC and thermally treated (previously melted DPC) from room temperature ($R.T \approx 30\text{ }^{\circ}\text{C}$) up to $160\text{ }^{\circ}\text{C}$ melting point (m.p. of DPC). IR analysis used here covered this temperature range.

Figure 2 shows the IR spectra of DPC samples at room temperature (before heat treatment Fig. 2A), and after melting and cooling to room temperature, Fig. 2 B. One can easily observe a slight change in the mode frequencies between spectra A and B.

Also, there is a remarkable variation in the transmittance. This may be due to a change in the crystal structure after melting. According to our previous work on DPC [10-13], the crystal structure of the R.T. phase of DPC (before heat treatment) is orthorhombic while that after heat treatment is amorphous. The normal modes of vibrations of these two phases are due to the ionic fundamentals and given in Table I. The bands obtained are due to ionic fundamentals of N–H, C–H, N–N, and C=O.

In fact, however, there is also an alternate interpretation that can be summarized as follows

- 3359 – Stretching N–H vibration (in the case of secondary amides there is only 1 band and it is impossible to have symmetric and asymmetric bands, which is

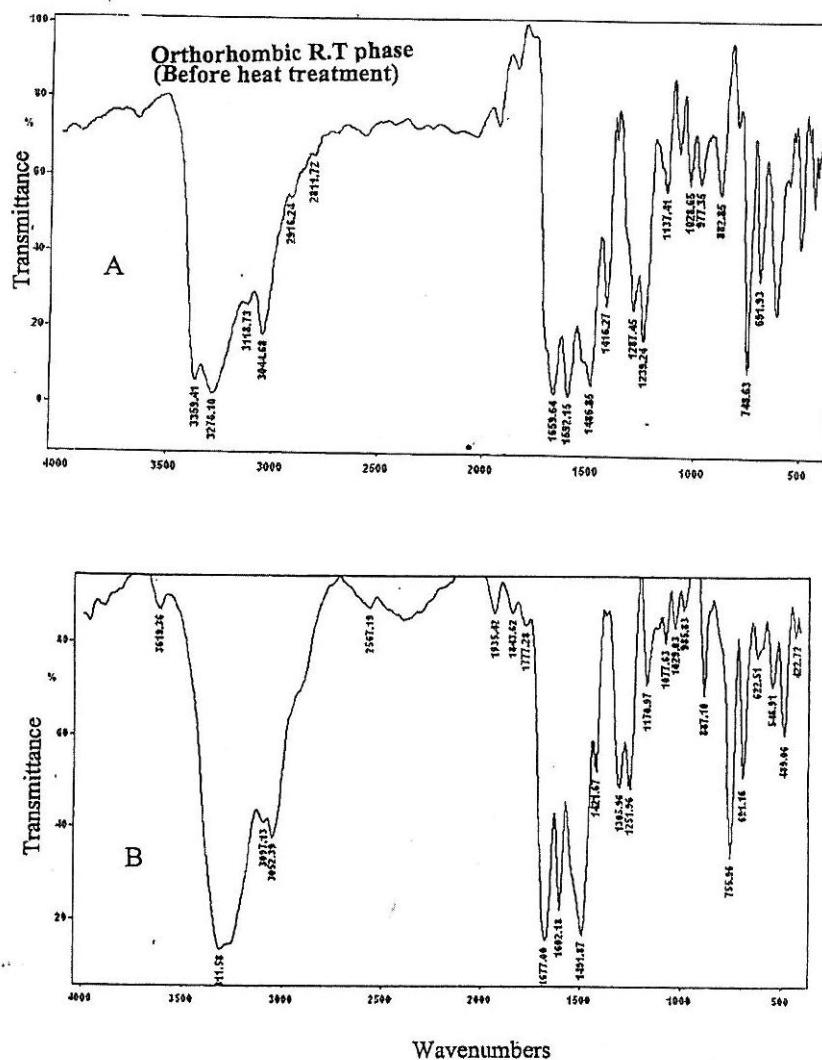


Fig. 2 IR spectroscopy of DPC; a) before heat treatment (on top) and b) after cooling down to room temperature (below)

possible only for primary amides).

- 3118 – Band belonging to the group of aromatic C–H stretching bands together with the band at 3044 cm^{-1} .
- 3044 – Correctly interpreted as aromatic C–H stretching.
- 1659 – Band called Amide I. It is combination band of stretching C=O and bending N–H vibrations.
- 1592 – Band called Amide II. It is combination band of stretching C–N and bending N–H vibrations.
- 1486 – Band belonging to the aromatic C=C stretching system of bands.
- 1287 – Band called Amide I. It is combination band of stretching C=O, bending N–H and stretching C–N vibrations.
- 748 – Out of plane C–H bending indicating the monosubstituted benzene. Moreover, this mono-substitution is showed by two bands (748 and 691 cm^{-1})

as one can see in Fig. 2).

- Finally, it is impossible to assign bands 1239 and 882 cm⁻¹ to any characteristic groups because of the fact that these bands are typical for the finger print region of FTIR spectrum, i.e. these bands are joined with the vibration of the DPC molecule.

Table I Ionic fundamental vibrations of the DPC compound before and after melting

Normal vibrations of DPC due to ionic fundamentals	Orthorhombic DPC (at R.T.)	Amorphous DPC (at R.T.)
Asymmetric stretching of N–H	3359	3311
Symmetric stretching of N–H	3118	3097
Bending or deformation mode of N–H	1659	1677
Aromatic C–H stretching	3044	3052
Out of plane C–H bending	882	887
N–N stretching symmetric vibrations	1592	1602
N–N astretching symmetric vibrations	1486	1492
C–H stretching vibrations	1287	1306
C=O stretching vibrations	1239	1252
Monosubstituted benzene	748	756

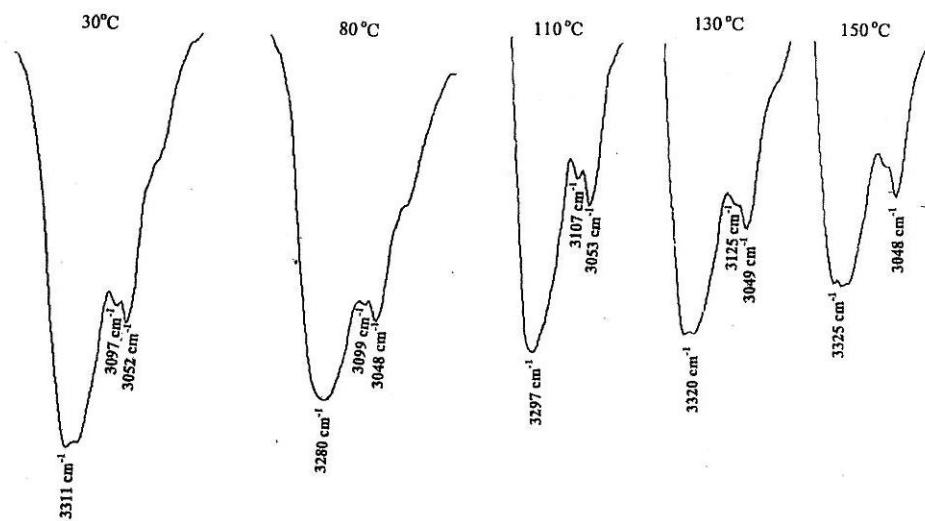


Fig. 3 Detailed IR contour variation of asymmetric and symmetric stretching of N–H and aromatic C–H bonds in consequence of polymorphism in the molecule of DPC

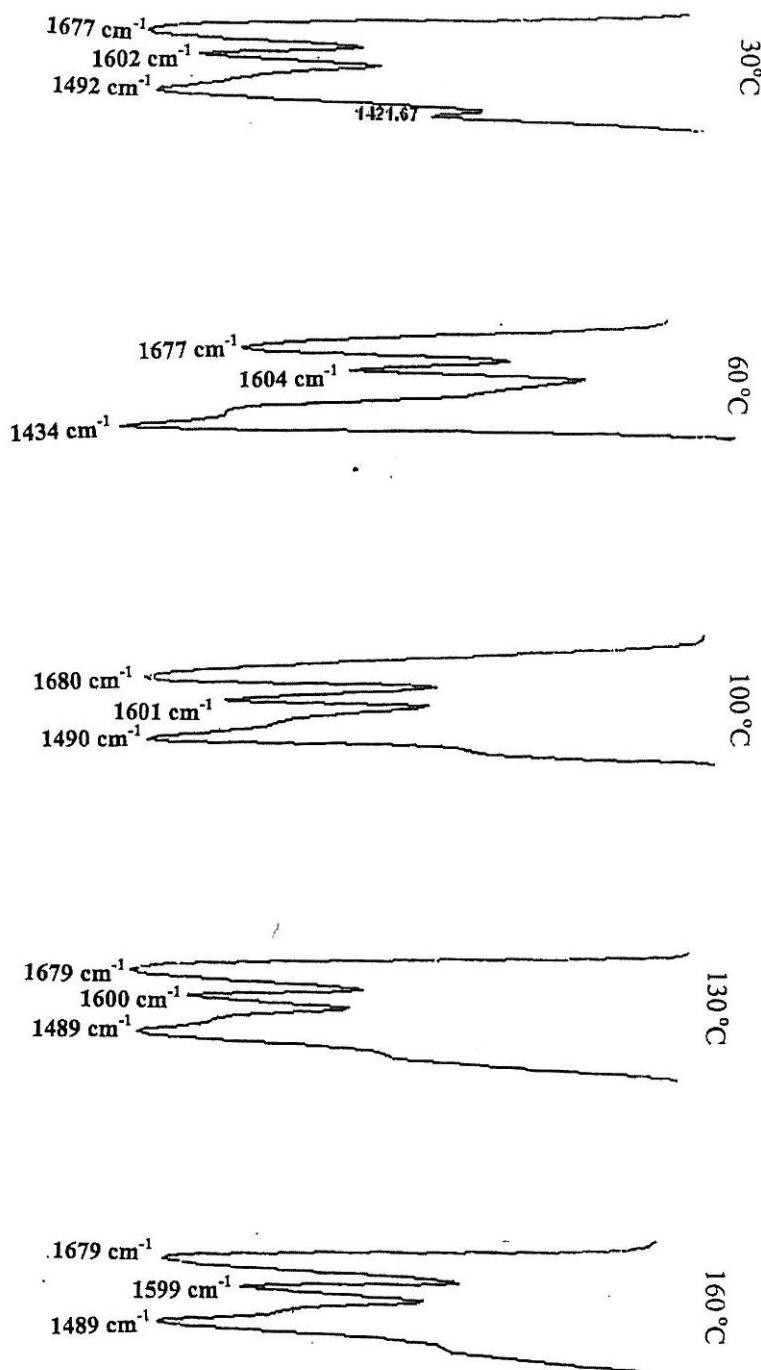


Fig. 4 Detailed IR contour variation of bending mode of N–H, asymmetric and symmetric stretching vibrations of N–N during the polymorphism in DPC

In order to support one of these hypotheses, it should be necessary to re-evaluate or even re-measure some data again. In this respect, the authors remain open for further discussion; nevertheless, the following text will be consistent with the first interpretation presented by means of Tables I and II.

The nature of temperature dependence of vibrating groups is of great

interest since its role is fundamental in explaining many of the physical properties of this organic compound. The spectrum shown in Fig. 2 A, indicates that the strongest bands are at 3359 cm^{-1} and 3276 cm^{-1} . In the amorphous phase Fig. 2 B, the strongest band is that at 3311 cm^{-1} . It is due to the asymmetric stretching of N–H, while the mode 3097 cm^{-1} indicates the symmetric stretching of N–H. The aromatic C–H stretching mode appears here at 3044 and 3052 cm^{-1} for both orthorhombic and amorphous phases respectively. The variation of the band contours of the three modes 3311 , 3097 and 3052 cm^{-1} at temperatures 30 , 80 , 110 , 130 and $150\text{ }^{\circ}\text{C}$ are those corresponding to different phase states of DPC. As

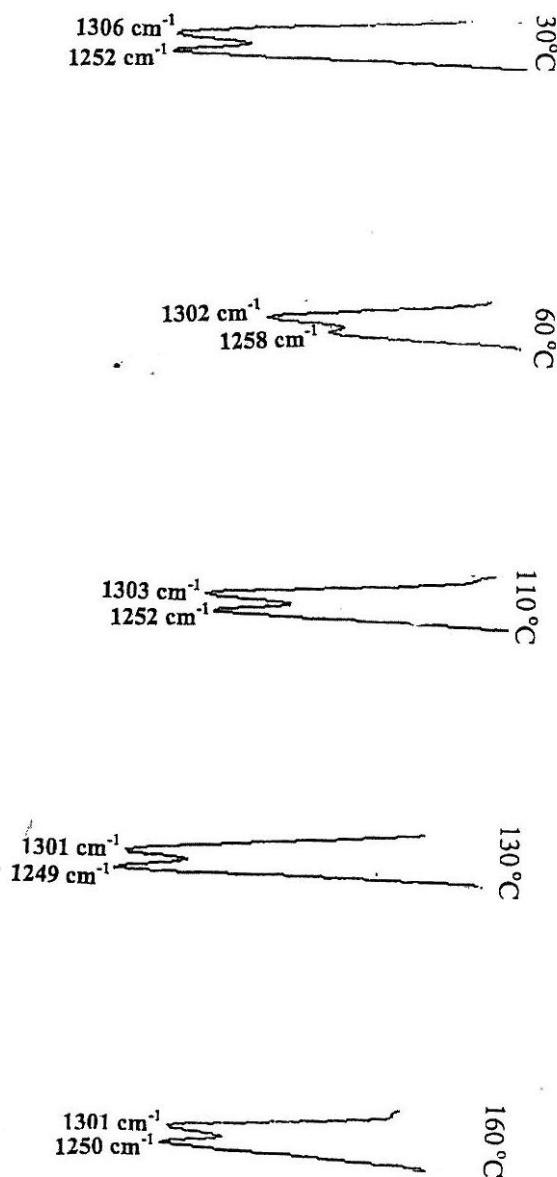


Fig. 5 Detailed IR contour variation of C–H stretching vibrations and C=O stretching vibration during the polymorphism in DPC

shown in Fig. 3, the frequency and shape changes of these modes at the different temperatures are very good indication of the polymorphic changes in DPC during heating.

Also, it is well known that the distinct shape of a transmittance band for particular molecule relates to the number of ions that undergo the various energy transitions. Thus, the most intense absorbance line is that which represents the largest number of ions undergoing a particular transition and the band envelope as a whole is an indication of the total number of ions involved. As the temperature of ions increases the band contour will change.

Figure 4 shows detailed variation of the band contours of bending mode of N–H, symmetric and asymmetric stretching vibrations of N–N as DPC temperature increased from 30 °C to 160 °C. The change in mode frequency here is very little, but the change of the mode shape is very clear. The band contours also change systematically during the temperature elevation and accompany the successive phase variation in DPC. Figure 5 shows the band contour variation of C–H stretching vibrations and C=O stretching vibration during polymorphic change. Clearly, the mode shift is very little, but the change in band shape is obvious.

Figure 6 shows the variation of the bond contour of the out-of-plane C–H bending mode during the elevation of temperature between 30 °C and 160 °C. Here the change in band shape is very clear. The out-of-plane C–H bending mode is a very sharp one. Its peak height changes alternatively during phase changes. This indicates that the C–H group may be responsible for phase change, i.e., the oriented motion of this group in space is responsible for phase transition in DPC.

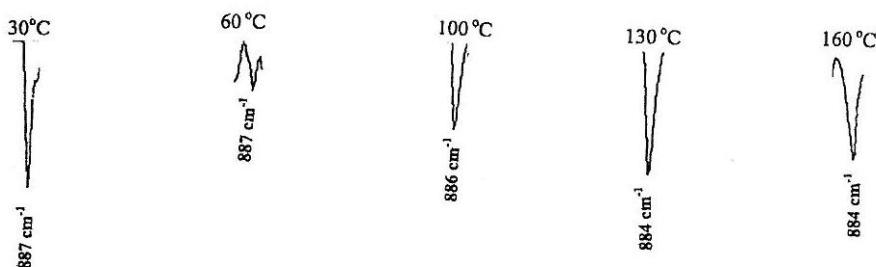


Fig. 6 Detailed IR contour variation of the out-of-plane C–H bending vibration during the polymorphism in DPC

Figure 7 shows the variation of the band contour of mono-substituted benzene during a temperature variation from 30 °C up to 160 °C. The change in mode frequency and band shape for this band is very limited. The effect of heating on ten modes of vibrations of DPC is summarized in Table II.

This effect is clearly notified in the first two stretching modes of (asymmetric and symmetric) vibrations of N–H. In the other modes of vibrations,

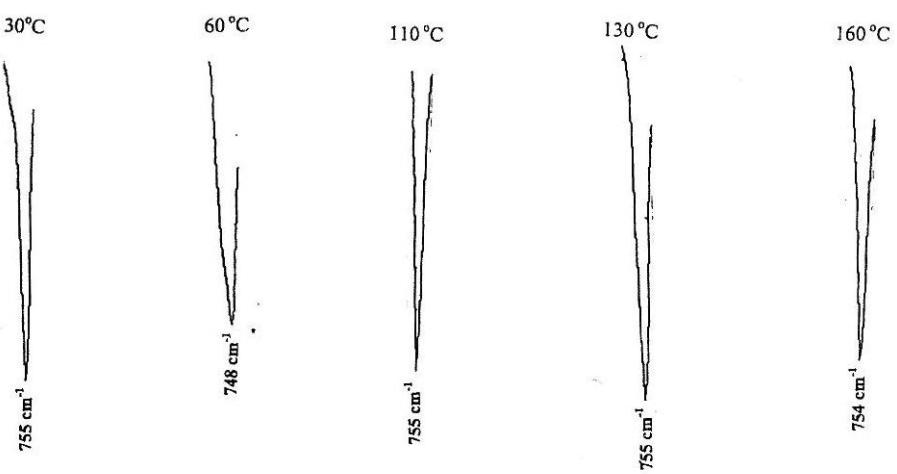


Fig. 7 Detailed IR contour variation of monosubstituted benzene moiety during the polymorphism in DPC

Table II Normal mode vibrations during polymorphic changes in thermally treated DPC

Phase number	R.T. Phase	Thermally treated				Untreated DPC
		IV	III	II	I	
Crystal structure	1	2	3	4	1	4
Temperature, °C	30	80	110	130	150	R.T.
Asymmetric stretching of N–H	3311	3280	3297	3320	3325	3359
Symmetric stretching of N–H	3097	3099	3107	3125	3150	3118
Bending or deformation mode of N–H	3052	3048	3053	3049	3048	3044
Aromatic C–H stretching	1677	1676	1679	1679	1679	1659
Out of plane C–H bending	1602	1600	1601	1600	1599	1592
N–N stretching symmetric vibrations	1492	1488	1489	1489	1489	1486
N–N astretching symmetric vibrations	1306	1300	1302	1301	1299	1287
C–H stretching vibrations	1252	1248	1251	1249	1248	1239
C=O stretching vibrations	887	885	886	884	884	882
Mono-substituted benzene	755	753	755	755	754	748

1 – amorphous; 2 – monoclinic; 3 – tetragonal; 4 – orthorhombic

the effect of heating seems to be little. Such behaviour of N–H group indicates that N–H group may be responsible for the polymorphism in DPC. This means that the oriented motion of N–H in space may control the phase state of DPC. Now, an important question arises after these five polymorphic transitions: what is the molecular formula of the final compound? Is it still DPC or this reagent has changed into a new organic compound? In order to put answer such a question,

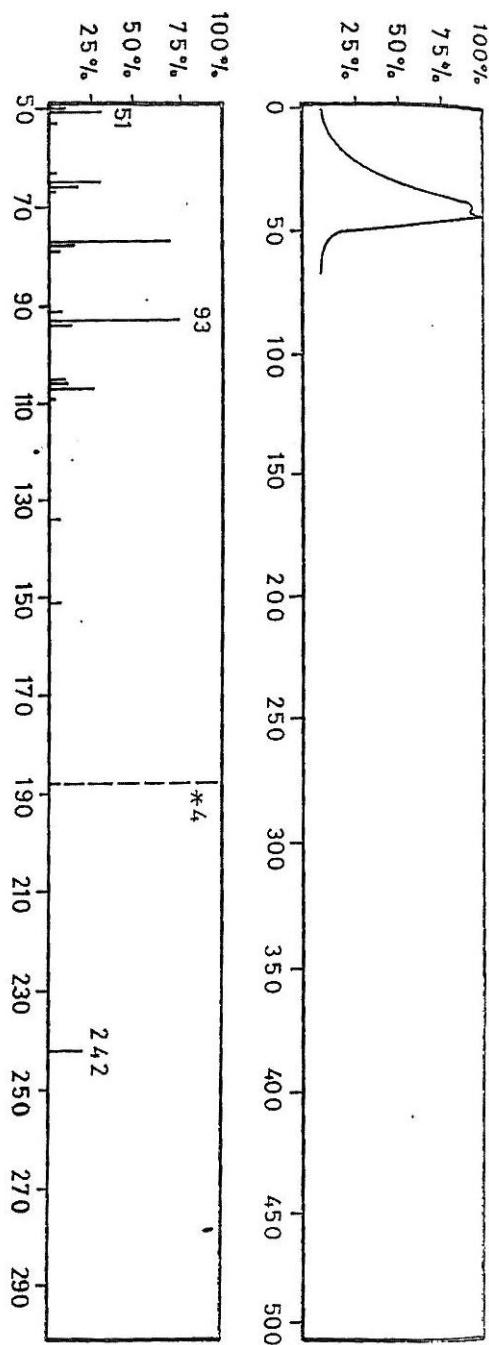


Fig. 8 MS spectra of re-heated DPC (analysed at 70eV)

NMR and mass spectra of DPC were obtained by electron impact at 70 eV. Based on the results of the microchemical analysis, Table III could be assembled and Figs 8 and 9 drawn.

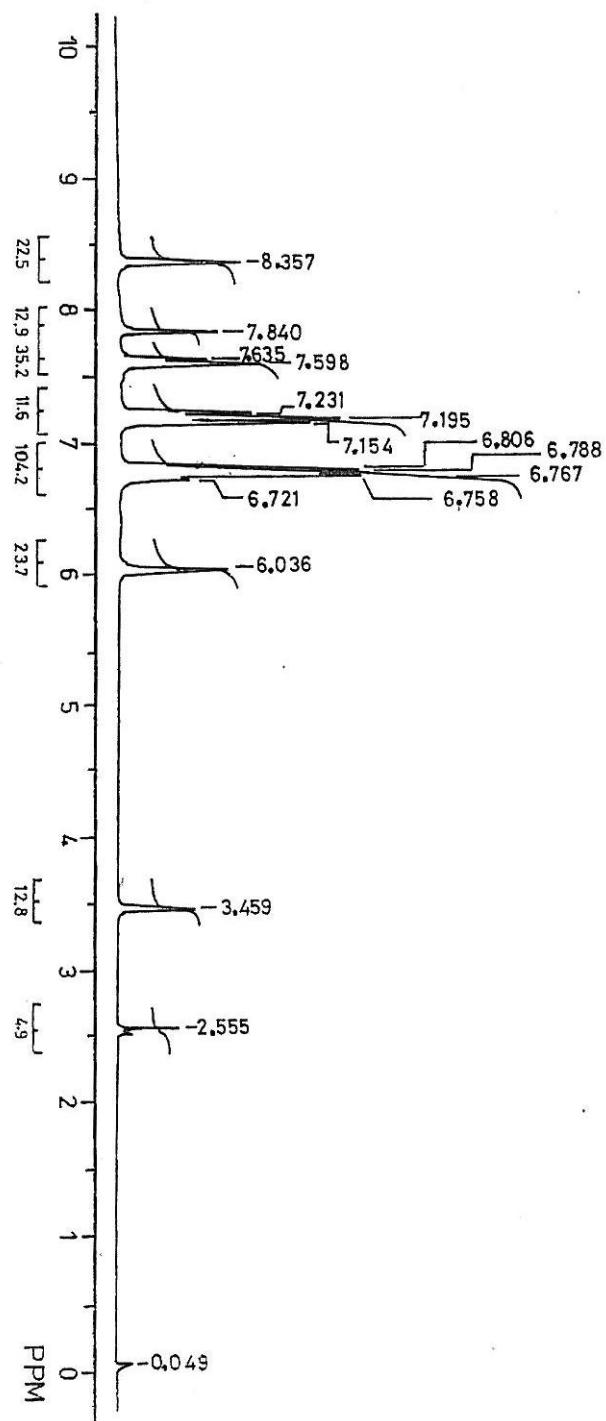


Fig. 9 NMR spectra of re-heated DPC

Table III The relative abundance for the mass spectra of DPC by electron impact (at 70eV)

Mass	Int, %						
50	10.3	51	32.0	52	11.3	53	6.6
54	2.2	55	0.8	56	0.4	57	1.0
59	0.1	60	2.3	61	1.6	62	3.1
63	6.1	64	6.1	65	31.8	66	17.4
67	1.2	69	0.4	70	0.7	71	0.2
73	0.7	74	2.1	75	0.2	76	1.8
77	70.1	78	15.5	79	5.1	80	4.4
81	1.4	82	0.6	83	0.7	84	0.5
85	0.1	87	1.0	88	0.2	90	1.1
91	8.4	92	32.7	93	100.0	94	13.3
95	1.5	97	1.2	105	9.7	106	11.3
107	27.9	108	35.0	109	2.7	110	0.5
111	0.6	117	0.4	120	0.7	121	0.4
133	0.8	134	5.9	135	1.0	149	0.8
150	2.6	151	8.5	152	6.5	153	0.4
167	0.8	169	1.5	240	1.0	242	4.8
243	1.5						

The general molecular formula of the compound under investigation can be given as $C_{13}H_{14}N_4O$. This means that after all polymorphic transitions, DPC at 50, 90, 125, and 140 °C still has the same molecular weight of 242 g mol^{-1} , which is the same as that of the original unheated DPC. But it belongs to another phase modification and a new crystal structure. It seems that under the present experimental conditions the formation of this new crystal structures is an end of the thermodynamic phase transformation of the original DPC subjected to heat treatment processes, as shown in Fig. 10, illustrating the effect of heat and re-heat treatment of DPC and the resulting polymorphic phase changes.

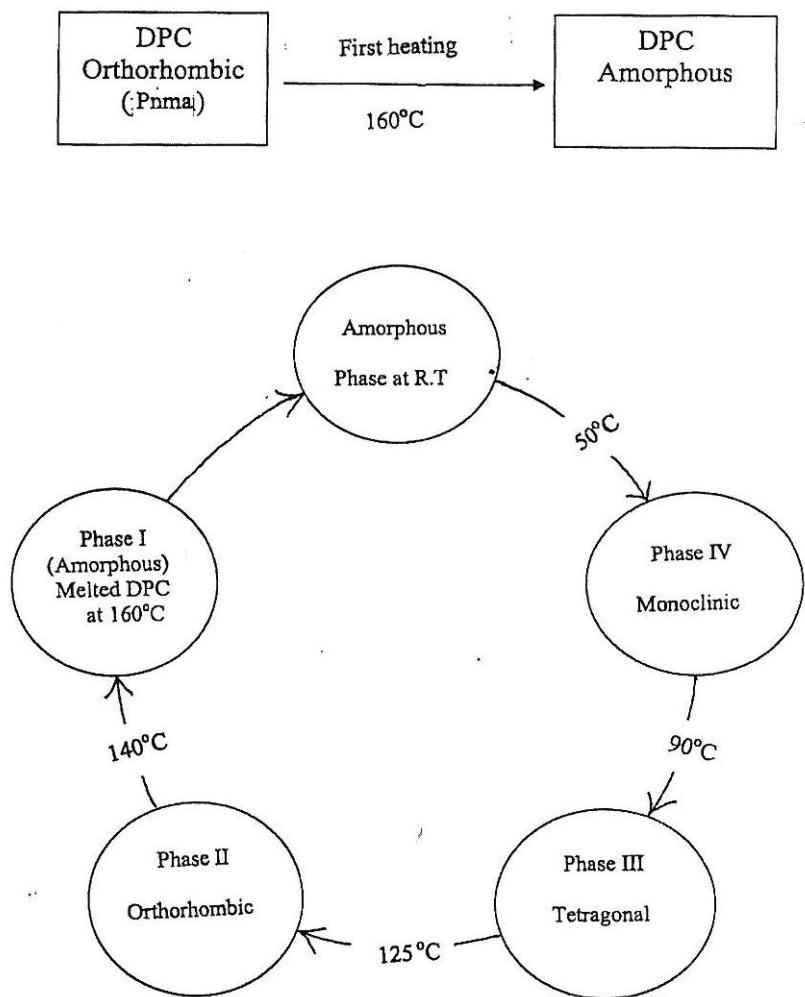


Fig. 10 Effect of heating and re-heating treatment upon the polymorphism of DPC; A scheme

Interpretation of the Results and Discussion on the Principal Observations

Polymorphic transitions in organic compounds are of particular interest especially for pharmaceuticals and light sensitive compounds. However, polymorphism [14] is the property exhibited by certain substances changing, at certain temperature, their crystal symmetry class or structure. This is accompanied by changes in physical characteristics [15]. In the framework of phenomenological theory, one can describe the anomalies in thermodynamic quantities and also, determine the nature of the changes that occur in the spectrum of the elementary excitations of the crystal of DPC in the neighbourhood of the phase transitions. The order parameter is related to the change that occurs in the positions of the atoms in the

crystal lattice during phase transition. The changes in the vibrational (phonon) spectrum of the crystal in the neighbourhoods of the critical point of such phase transition are experimentally the most noticeable. A change in structure occurs in displace – type phase transition as a result of the displacement of the ions (atoms) in the crystal lattice.

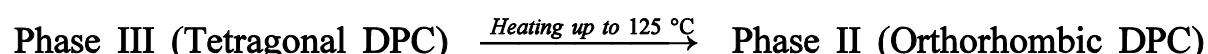
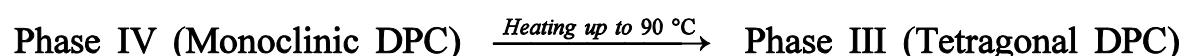
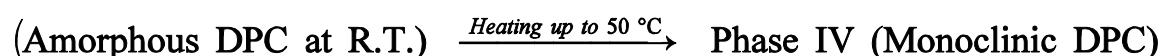
Here the IR spectra of thermally treated diphenyl carbazide are due to lattice vibrations of the individual ions and internal vibrations of molecules. Since the vibrations occur through the lattice and are not connected with a single unit cell, these vibrations are often observed as broad peaks which represent a composite band of several vibrations. In fact, the stability of DPC and its critical properties depend on the extent of changes which occur in the hydrogen bonding of the amino ions (N–H) to the carbonyl (C=O) ions.

In a polyatomic molecule like DPC, each atom has three degrees of freedom in three directions which are perpendicular to one another. Consequently, a polyatomic molecule like that requires three times as many degrees of freedom as the number of its atoms. In the case of DPC and according to the character of vibration, the normal modes of vibrations of DPC can be divided into two principal groups; stretching vibration and bending vibration. In the first type the atoms move essentially along the bond axis, so that the bond length increases or decreases periodically, i.e., at regular intervals.

In the second type, there occurs a change in bond angles between bonds with a common atom or there occurs the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another. The first type appears at high frequencies while the second type appears at lower frequencies. In fact, in a polyatomic molecule like DPC, the same bond can perform stretching and bending vibrations simultaneously.

Conclusion

It can be stated that, according to De Ranter *et al.* [9], the DPC studied possesses an orthorhombic structure at room temperature. After melting (at ≈ 160 °C), it then transforms to the amorphous structure. Now, re-heat treatment of amorphous DPC causes a set of phase transformations according to the following scheme



Phase II (Orthorhombic DPC) $\xrightarrow{\text{Heating up to } 140 \text{ }^{\circ}\text{C}}$ Phase I (Amorphous DPC)

Thus, the effect of heat treatment on DPC is a full circle — it starts in the amorphous state and ends with amorphous state. The successive re-heat treatment of DPC for several times, repeat the same phase transition cycle and always ends with amorphous state whatever the number of heating cycles passed. To check behaviour like that, an X-ray diffraction pattern for DPC has been performed, which is shown in Fig. 11, depicting the state after the first heat treatment cycle (A) and after the second cycle (B).

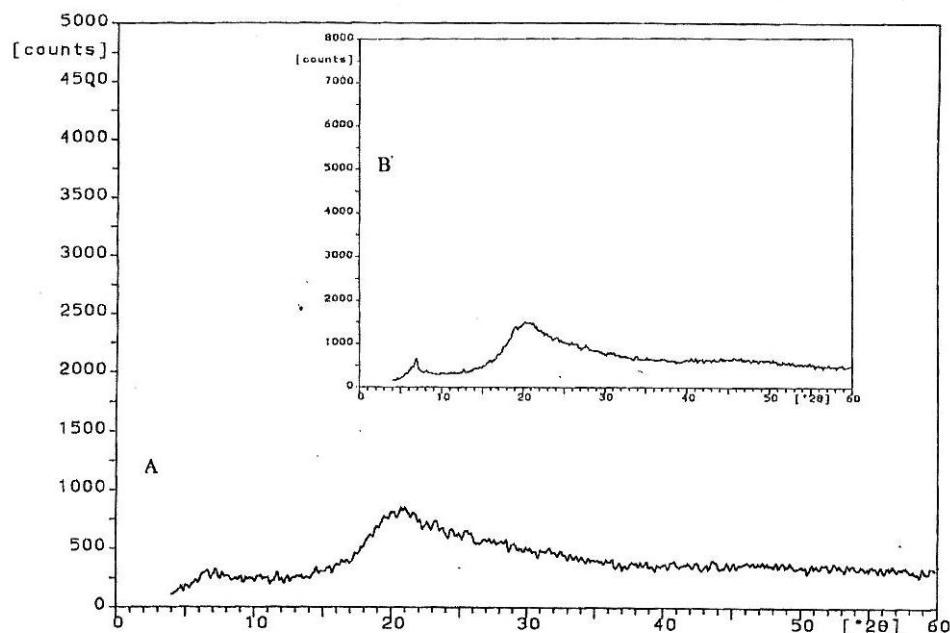


Fig. 11 X-ray diffraction patterns for DPC samples after A) first and B) second run of heating

Both of these two X-ray diffraction pattern indicate amorphous structure for the starting phase and final phase whatever the number of heating cycles passed. Such behaviour has already been depicted above — in Fig. 10.

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