

# On the melting temperatures of 3,6-diamino-9*H*-carbazole and 3,6-dinitro-9*H*-carbazole

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## Abstract

This article records the diversely reported melting temperatures of 3,6-diamino-9*H*-carbazole (DAC) and 3,6-dinitro-9*H*-carbazole (DNC), and reports a reinvestigation on their melting phenomena, and associated specific observations. A rationalization of these reports has been attempted on the basis of IR spectroscopic, X-ray diffraction, thermal response, solubility behavior, and differential scanning calorimetric data on DAC and DNC. The data indicate that an exothermic inter-molecular deaminative self-condensation involving  $>N_9-H$  and  $-NH_2$  sets in prior to melting of DAC, which obscures the actual melting process. An extrapolated onset melting temperature of  $241.0^\circ C$  and a peak temperature of  $296.5^\circ C$  at zero heating rate have been assigned for DAC from DSC measurements. A possible structure of the polymeric self-condensation product is also presented. For DNC, a peak melting temperature of  $296.5 \pm 1.8^\circ C$ , but no onset melting temperature could be assigned.

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## 1. Introduction

3,6-Dinitro-9*H*-carbazole (DNC) and 3,6-diamino-9*H*-carbazole (DAC) are precursors to a large number of small molecular derivatives and polymers. Reactions of DNC and DAC with assorted substrates and reagents are well documented in published literature [1,2]. Chen and Natansohn [3] have recently synthesized and characterized some polyimides based on DAC. DAC can also be used for newer step-grown polymers of polyamides, polyureas and polyurethanes. Report on the synthesis of DNC and DAC dates back to 1910 when Ziersch [4] first synthesized 3,6-dinitrocarbazole and 3,6-diaminocarbazole by the conventional methods of nitration followed by reduction of the nitro group to amine functionality. Later, Eikhman et al. [5], Schotte et al. [6], Amemiya et al. [7] Oda et al. [8], Grotta et al. [9] and recently Chen and Natansohn [3] synthesized and characterized DNC

and DAC. All these researchers report melting points of both DNC and DAC, which are widely different from each other. While Chen and Natansohn [3] report a melting point of  $240^\circ$  for DNC, Eikhman, Schotte, Amemiya, Oda, and Grotta reported melting points of  $\sim 360$ ,  $365\text{--}367$ ,  $357$ ,  $320$ , and  $386\text{--}387^\circ C$ , respectively. The variously reported melting points of DAC are  $>320^\circ$  by Ziersch,  $281^\circ$  by Eikhman,  $320\text{--}322^\circ$  by Grotta, and  $255^\circ C$  by Natansohn. There are only a few commercial sources [10,11] of DNC and DAC, who are conspicuously silent about melting points of the two compounds in their product specifications. The Chemical Abstracts Service (CAS) does mention a normal boiling point of DAC at  $526.9 \pm 30^\circ C$  as predicted by Advanced Chemistry Development (ACD) software, but no melting point. It, however, records a melting temperature of  $>360^\circ C$ , as reported by Katritzky and Marson [12], and a normal boiling point of  $537.2 \pm 30^\circ C$  for DNC from ACD software. It is clear from these diverse reports that a lot of ambiguity prevail on the true melting temperatures of DNC and DAC till date. It also appears that there might be some inherent technical

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difficulties in the measurement of their melting points, or the compounds themselves could be structurally and chemically not amenable to crystalline melting. Varying levels of isomeric impurities in the precursor dinitrocarbazole could as well be the cause of these diverse melting temperatures of DAC.

These diversely reported melting temperatures of DNC and DAC were the major impediments in establishing the purity and the very chemical identities of the two compounds. Only after a long and thorough investigation could we arrive at a rationalization of these diverse reports. This article is primarily aimed at a rationalization of the anomalous reports on the melting temperatures of DAC and DNC from their IR spectrophotometric and differential scanning calorimetric responses.

## 2. Experimental

3,6-Dinitrocarbazole and 3,6-diaminocarbazole have been prepared by the methods both of Chen and Natansohn [3] and of Grotta et al. [9]. Products from both the synthetic methods were almost identical in physical appearance and analysis. Method of Natansohn appears to be much superior to that of Grotta in respect of yield. Purity and chemical identity of DAC have been established from analytical data.

### 2.1. Materials and measurements

Carbazole as the starting material was obtained from Aldrich Chemicals. Reagents and chemicals, concentrated  $\text{H}_2\text{SO}_4$ , concentrated  $\text{HNO}_3$ , acetic anhydride, acetic acid, copper(II) nitrate, hemipentahydrate, and other agents were obtained from E-Merck, India, as guaranteed reagents, and used directly without purification.

Brucker, 200 MHz multiprobe NMR spectrometer; Perkin-Elmer, Model 883 IR spectrophotometer; Shimadzu, UV-3100, UV-vis spectrophotometer; Philips, 1760 X-ray diffractometer; Perkin-Elmer, Model 2400 (series II), CHNS/O elemental analyzer were used for characterization of materials.

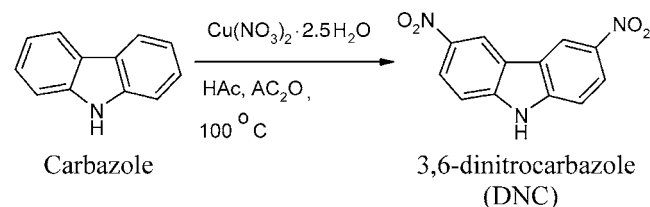
DSC measurements were carried out on a Shimadzu DT-40, heat-flux type unit in an argon atmosphere. Operating conditions were: sample size-3 mg (finely powdered); aluminum crucibles, 5 mm  $\varnothing$   $\times$  3 mm, crimped.

### 2.2. Synthesis

#### 2.2.1. 3,6-Dinitrocarbazole (DNC)

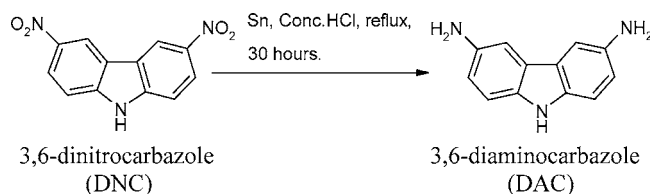
A homogeneous mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (7.0 g, 30 mmol), acetic acid (20 mL), and acetic anhydride (30 mL) was prepared at room temperature. To this solution were added carbazole (4.15 g,  $\sim$ 25 mmol) in small portions over 10 min. Temperature was maintained at 15–20 °C during addition of carbazole. The temperature was allowed to rise to room temperature (27 °C) over a period of 30 min and then to

90–100 °C. Reaction was continued with stirring for a period of 30 min at this temperature. The mixture was diluted with additional 10 mL of acetic acid, and poured into 250 mL of distilled water with constant stirring. The precipitate was collected by filtration, and washed five times each with about 100 mL of distilled water. The wet residue was dissolved in a cold solution of 20 g of KOH, 250 mL of ethanol, and 250 mL of water. The red solution was stirred for 30 min, and filtered. The filtrate was then acidified with concentrated hydrochloric acid, and allowed to settle for 30 min. A fluffy yellow precipitate was collected by filtration, washed several times with cold water, and dried in vacuum at 100 °C. Yield: 5.55 g, 85%.



#### 2.2.2. 3,6-Diaminocarbazole (DAC)

2.5 g ( $\sim$ 10.0 mmol) of the dinitro compound (DNC) were placed into a round-bottom flask together with 20 g ( $\sim$ 100 mmol) of Sn (metal), 60 mL of acetic acid, and 15 mL of concentrated hydrochloric acid. The mixture was refluxed for 30 h under a blanket of nitrogen. The resulting solution was cooled, and poured into an aqueous solution of 12.5 g of NaOH in 500 mL of water. The precipitate was filtered, washed free of alkali with water, and dried in vacuum at about 60 °C for 24 h. The product was purified by extraction with THF, evaporation of THF under vacuum, and subsequent recrystallization from ethanol in a nitrogen atmosphere. Yield: 1.50 g, 78%.



## 3. Results and discussion

### 3.1. Characterization

#### 3.1.1. Elemental analysis

Calculated for DNC ( $\text{C}_{12}\text{H}_7\text{N}_3\text{O}_4$ ): C, 56.03; H, 2.72; N, 16.34. Found: C, 56.08; H, 2.74; N, 16.11.

Calculated for DAC ( $\text{C}_{12}\text{H}_{11}\text{N}_3$ ): C, 73.10; H, 5.58; N, 21.32. Found: C, 65.76; H, 4.15; N, 17.50. Wide discrepancy in the analysis of DAC is a clear indication that the combustion is incomplete, possibly due to the formation of high molecular weight condensation products. This aspect has been discussed in some later sections.

### 3.1.2. IR absorptions

For DNC (KBr pellet): (3421, 3345), 3091, (2922, 2848), 1618, 1583, 1517, 1339, 1307, 1238, 1098, 752, 721  $\text{cm}^{-1}$ , as against 3395, 3082, 1634, 1612, 1579, 1517, 1307, 1102, 752, 718  $\text{cm}^{-1}$ .

For DAC (KBr pellet): 3396, 3285, 3193, 1625, 1578, 1497, 1330, 1221, 1168, 863, 798, 712  $\text{cm}^{-1}$ , as against 3388, 3286, 3188, 1632, 1577, 1503, 1331, 1222, 1168, 868, 807, 712  $\text{cm}^{-1}$  reported by Chen and Natansohn [3].

### 3.1.3. $^1\text{H}$ NMR

For DNC (200 MHz, acetone- $d_6$ ):  $\delta$  11.95 (s, br, 1H, H<sub>9</sub>); 9.22 (d, 2H, H<sub>4,5</sub>,  $J=2.25$  Hz); 8.35 (dd, 2H, H<sub>2,7</sub>,  $J=2.2$  Hz,  $J=8.9$  Hz); 7.80 (d, 2H, H<sub>1,8</sub>,  $J=9.0$  Hz), as against (400 MHz, DMSO- $d_6$ )  $\delta$  11.10 (s, br, 1H, NH), 9.34 (d, 2H, H<sub>4,5</sub>,  $J=2.3$  Hz), 8.40 (dd, 2H, H<sub>2,7</sub>,  $J=2.3$  Hz,  $J=8.9$  Hz), 7.78 (d, 2H, H<sub>1,8</sub>,  $J=8.9$  Hz).

For DAC (200 MHz, acetone- $d_6$ ):  $\delta$  9.65 (s, 1H, H<sub>9</sub>), 6.62 (s, 2H, H<sub>4,5</sub>), 6.59 (d, 2H, H<sub>1,8</sub>), 6.20 (dd, 2H, H<sub>2,7</sub>), 4.12 (s, br, 4H, 2NH<sub>2</sub>), as against (400 MHz, DMSO- $d_6$ )  $\delta$  10.09 (s, 1H, H<sub>9</sub>), 7.06 (d, 4H, H<sub>1,4,5,8</sub>), 6.66 (dd, 2H, H<sub>2,7</sub>) and 4.54 (s, br, 4H, 2NH<sub>2</sub>) reported by Chen and Natansohn [3].

### 3.1.4. $^{13}\text{C}$ NMR

For DAC (200 MHz, acetone- $d_6$ ):  $\delta$  130.49, 123.94, 113.18, 105.02, 101.18, and 94.08.

### 3.1.5. UV–vis

$\lambda_{\text{max}}$ : 238, 322 and 371 nm in acetonitrile, as against reported [3] values of 326 and 380 nm in THF.

## 3.2. Melting behavior of DAC

### 3.2.1. Thermal response

Chen and Natansohn [3] report melting of DAC at 255 °C with decomposition from DSC measurement in air. There is no information, however, as to how melting temperature of DAC had been determined by Ziersch, Eikhman, Amemiya, or Grotta. Possibly they adopted the conventional method of heating the sample in a sealed glass capillary tube. Melting with decomposition as reported by Natansohn is particularly noteworthy. Grotta et al. [9] report melting of DAC at 320–322 °C. Softening at 316 °C preceded the melting. This visually observed softening might well correlate the decomposition observed by Natansohn, although the two temperatures are widely different. In our observation, DAC did not suffer any visible change up to about 200 °C when subjected to heating in a sealed glass capillary tube. Beyond 200 °C, however, the powder DAC column started breaking, but without separation of a liquid phase even up to 300 °C. The melting temperature of 255 °C, as reported by Natansohn, appears to be in doubt on two counts. *First*, it is customary to carry out DSC measurements in an inert atmosphere using nitrogen or argon as the purging gas. Aromatic amines are known to undergo discoloration due to aerial oxidation. Thus, the use of air as a carrier gas might have changed the

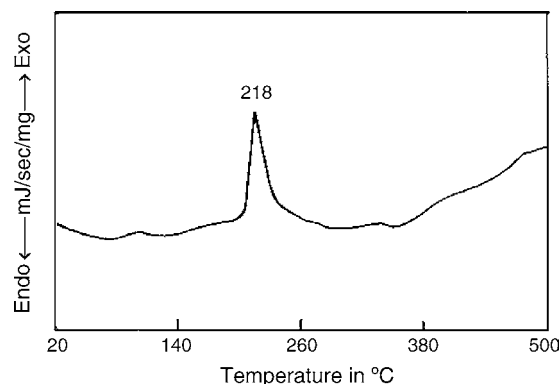


Fig. 1. DSC trace of DAC in argon at a heating rate of 15 °C/min. Sample size: 3 mg.

very characteristics or chemical identity of the analyte. *Second*, we observed a distinct but weakly exothermic change with a peak temperature of 218 °C in the DSC thermogram of DAC (Fig. 1), at a heating rate of 15 °C/min and using argon as the inert medium. This exothermic change cannot be entertained as one due to melting, since all fusion processes are endothermic. The only plausible explanation of this observation is that DAC might have undergone some physical or chemical change(s) other than melting. In the following sections, we provide additional evidences in support of our contention.

### 3.2.2. Solubility in organic solvents

DAC is freely soluble in THF, acetonitrile, acetone, chloroform, and dichloroethane, as also in concentrated H<sub>2</sub>SO<sub>4</sub>. When heated at 210–220 °C, it readily formed loose lumps. Also, its solubility in these solvents drastically reduced. As such, DAC dissolves in concentrated H<sub>2</sub>SO<sub>4</sub> with blue coloration. But DAC heated at 220 °C for half an hour in a vacuum-sealed tube, is insoluble, and coloration (blue or any other) in concentrated H<sub>2</sub>SO<sub>4</sub> was not visible.

### 3.2.3. IR spectra

IR spectra of DAC before and after heating at 220 °C are shown in Figs. 2 and 3, respectively. The carbazole  $>\text{N}_9\text{-H}$ , and  $-\text{NH}_2$  at 3- and 6-positions show clear absorptions at 3396 (singlet) and 3296, 3196  $\text{cm}^{-1}$  (doublet), respectively (Fig. 2). After heating in a sealed tube at 220 °C for 4 h, the spectrum remains essentially the same except some marginal shift in the absorption peaks at 3388, 3300 and 3200  $\text{cm}^{-1}$  (Fig. 3). But the intensity of  $-\text{NH}_2$  absorption relative to  $>\text{N}_9\text{-H}$  increased drastically, indicating that  $\text{N}_9\text{-H}$  protons have been relatively more depleted through some chemical interaction, presumably a condensation with  $-\text{NH}_2$  groups at 3- and 6-positions, with liberation of  $\text{NH}_3$ . This might have been responsible for breaking the powder column of DAC during its heating in a sealed glass capillary tube. Possibility of such an interaction cannot be ruled out on the ground that  $>\text{N}_9\text{-H}$  proton is acidic ( $\text{pK}_a$ ,  $5.25 \pm 0.30$ ) [13], and can involve itself in condensation with  $-\text{NH}_2$

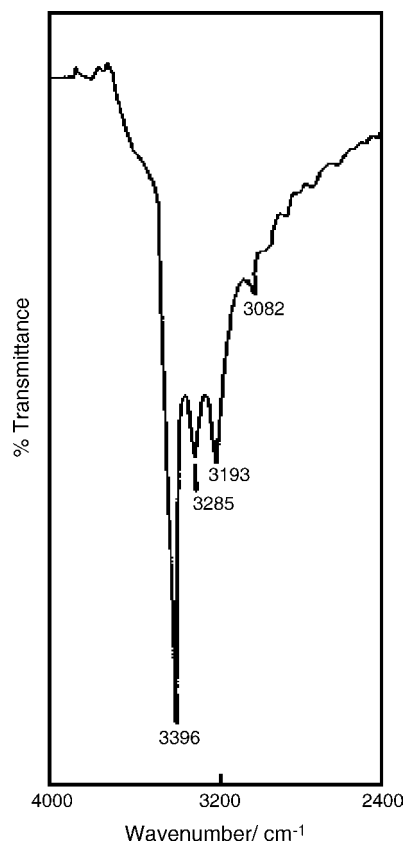


Fig. 2. IR spectrum of DAC (as synthesized) in the range, 2400–4000  $\text{cm}^{-1}$ .

groups, aided by elevated temperature. The weakly exothermic peak in the DSC trace of DAC is, therefore, due to its deaminative self-condensation. This observation, however, goes contrary to the generally observed endothermic nature of condensation reactions. A rough estimate of  $\Delta H_{593}^{\circ} = -17 \text{ kcal mol}^{-1}$  for self-condensation of DAC, calculated from dissociation enthalpies [14] of  $\text{>N-H}$  ( $85 \pm 2$ ) and  $\text{H}_2\text{N-H}$  ( $103 \pm 2 \text{ kcal mol}^{-1}$ ), however, goes much in favor of our contention. The structure of the polymeric self-condensation product may be represented as shown in Fig. 4.

### 3.2.4. X-ray diffraction pattern

Crystallization (exothermic) of DAC could be one of the possible events that might have led to the observed exotherm at  $218^{\circ}\text{C}$  in the DSC trace of DAC. Figs. 5 and 6 represent the X-ray diffraction pattern of DAC before and after sealed tube heating at  $220^{\circ}\text{C}$ . A comparison of the diffractograms clearly shows that DAC, as synthesized, is crystalline in nature, and there is no apparent change (increase or decrease) in its degree of crystallinity after heat treatment. Basic stacking pattern of the flat carbazole units is largely retained in its crystalline states, resulting in only some minor differences to be detected in the diffraction pattern of the heat-treated DAC.

### 3.2.5. DSC response of DAC

Discussion made earlier clearly indicates that the true melting temperature of DAC cannot be ascertained by con-

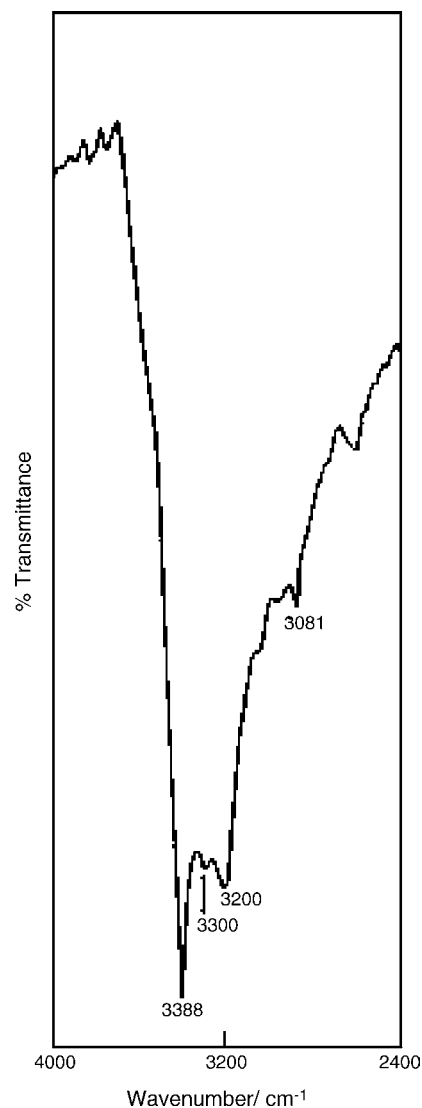


Fig. 3. IR Spectrum of DAC in the range 2400–4000  $\text{cm}^{-1}$  after heating in a vacuum-sealed tube at  $220^{\circ}\text{C}$  for 4 h.

ventional methods of measurements. Differential thermal analytical techniques, DSC in particular, have been successfully employed to determine transition temperatures of materials. Suitable adjustment of operating conditions of DSC analysis has been reported to help identify the temperature of particular transitions that are suppressed or obscured by thermal effects of some physical/chemical events just preceding the transition of interest. This has been well demonstrated in the determination of crystalline melting point of polyacrylonitrile [15]. By carrying out DSC measurements at heating rates of  $40^{\circ}\text{C}/\text{min}$  and above, it was possible to isolate and identify crystalline melting of polyacrylonitrile from its intramolecular polymerization-cyclization, which just preceded the crystalline melting. This technique was applied with DAC. The DSC traces at heating rates of 25, 40, and  $50^{\circ}\text{C}/\text{min}$  are shown, respectively, in Fig. 7(a–c). Below  $260^{\circ}\text{C}$ , DAC shows an endothermic change, more prominent at heating rates of 40 and  $50^{\circ}\text{C}/\text{min}$ , in the temperature

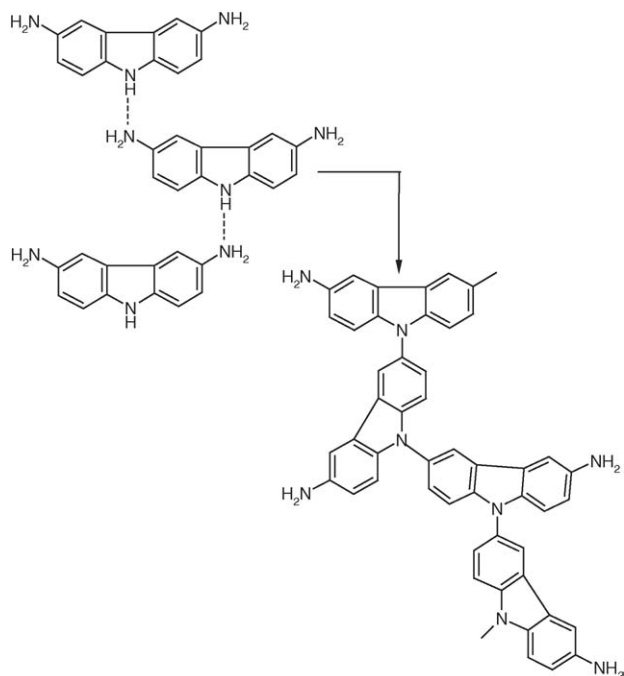


Fig. 4. Probable structure of the polymeric self-condensation product of DAC.

range 60–100 °C. These may be assigned to desorption of adventitious moisture. The exothermic hump around 120 °C at all heating rates possibly signifies the end of the desorption processes, beyond which the desiccated DAC shows its normal thermal response. There are distinct endothermic peaks at 297.3, 298.6, and 300.2 °C, at increasing heating rates of 25, 40, and 50 °C/min. These endotherms are in sharp contrast to only one exotherm at ~218 °C observed in the DSC trace of DAC obtained at a heating rate of 15 °C/min (Fig. 1). These endotherms may be assigned to crystalline melting of DAC. The corresponding peak melting temperatures are only the apparent melting points, i.e., without correction for the effect of heating rate. The total heat effect that can be cal-

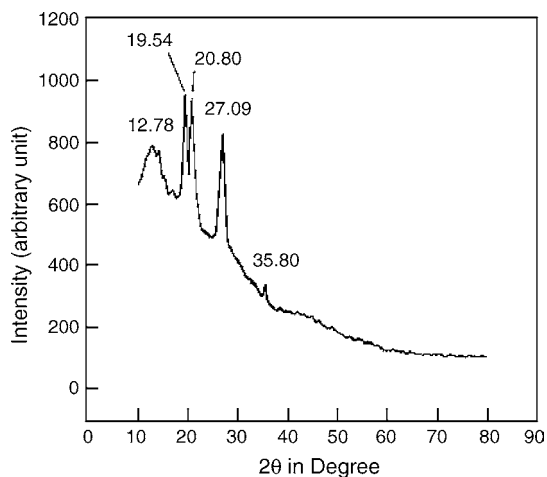


Fig. 5. X-ray diffraction pattern of DAC.

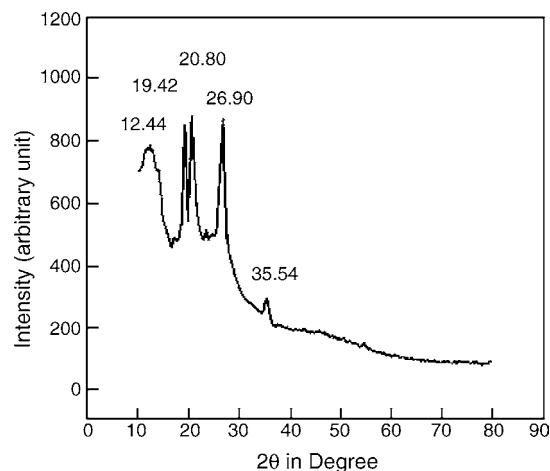


Fig. 6. X-ray diffraction pattern of DAC after heat treatment at 220 °C for 4 h.

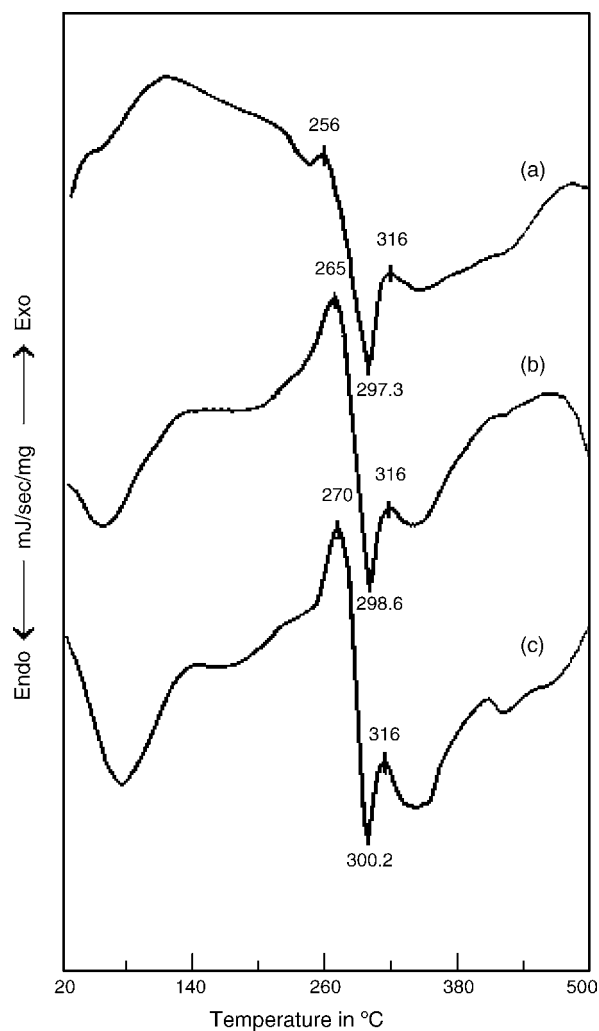


Fig. 7. DSC traces of DAC in argon at heating rates of (a) 25 °C/min; (b) 40 °C/min; (c) 50 °C/min. Sample size: 3 mg.



culated from the area under the endothermic peak, does not, however, represent the enthalpy of melting. It rather gives a measure of the sum total of the positive enthalpy change of melting and the negative enthalpy change of deaminative condensation.

The rationale behind adoption of this technique is as follows. At a lower rate of heating, the analyte gets more time to attain a temperature at which the actual melting process starts. During this longer span of heating, the process of self-condensation of DAC may be almost complete, leaving behind a little or no uncondensed DAC to undergo crystalline melting. As a consequence, only an exothermic peak due to self-condensation, and no endothermic peak for melting, could be observed. At higher rates of heating, however, a sizeable fraction of uncondensed DAC will be available for melting. This fraction of uncondensed DAC will also increase as the rate of heating is increased. At a hypothetical infinitely fast rate of heating, almost the whole of DAC would be available for melting, followed simultaneously by deaminative condensation. The peak melting temperature so recorded could have been accepted as the true melting point. But there are two possible sources of error in this improvised thermal analytical technique. The *first one* is the depression of freezing point due to a possible dissolution of the self-condensation product in uncondensed DAC. But such a possibility does not appear to be significant on the ground that the self-condensation product of DAC being polymeric in nature will have little or no solubility in uncondensed DAC, although it cannot be ignored altogether. Also, we do not have any known mechanism to quantitatively assess its contribution to the recorded peak melting temperatures. The *second one* is the heat transfer limitation to and within the sample at different heating rates. An increase in mass of analyte sample or in heating rate generally shifts the peak melting temperatures to higher values. In the present investigation, sample size has been kept constant at 3 mg. The observed small but recognizable shifts to higher values with increasing heating rates clearly indicate an influence of heat transfer limitations on peak melting temperatures, but only at a low level.

The extrapolated onset temperature of melting endotherms ( $T_e$ ), which is reportedly least influenced by heating rates, is generally recommended as the melting point of a material. Using  $T_e$  is acceptable only in cases of events that are well separated from other preceding events. But in the present system, deaminative polycondensation precedes and overlaps with the concerned event (i.e., melting). As a result, the onset temperature of melting cannot be precisely determined. What, however, could be determined precisely, is the temperature where the polycondensation exotherm intersects the melting endotherm. The apparent onset temperatures of melting endotherms in Fig. 7 (the foot of the peaks at 256, 265, and 270 °C at heating rates of 25, 40, and 50 °C/min, respectively), in fact, represent the temperatures where the polycondensation exotherms intersect the melting endotherms, but not the true onset temperatures. Wide variation of these starting temperatures is a clear evidence of the influence of

the preceding exothermic polycondensation. In contrast, the peak melting temperatures of DAC are fairly close to each other with only a minor influence of heat transfer limitations to and within the sample at different heating rates.

### 3.2.6. Computation of melting temperature of DAC

Because of the possible sources of error that have been discussed in the earlier section, the observed onset temperatures of melting endotherms are not quite suitable for computation of melting point of DAC. These temperatures vary in a very weakly exponential manner (almost linear with heating rate), and a linearly extrapolated (to zero heating rate) onset melting temperature of  $241.0 \pm 0$  °C may be assigned to DAC. Peak melting temperatures of DAC are found to increase exponentially with heating rates, and the corresponding extrapolated peak melting temperature at zero heating rate is  $296.47 \pm 0$  °C.

It is further to be noted in Fig. 7(a–c), that all these endothermic changes surprisingly span up to the same maximum temperature of  $\sim 316$  °C. This temperature has been obtained as the one corresponding to the digital maximums of heat flow signals in the vicinity of the endotherm ends. The temperature has a striking resemblance to “*equilibrium melting temperature*” of a crystalline polymer that signifies the melting point of a material that is three-dimensionally grown to an infinite size, and devoid of any crystal imperfection or defects, and is also the highest recordable melting point of a crystalline polymer. It is open to deliberation as to whether this analogy is acceptable or not, or if it is purely an accidental result since the end temperature of a thermal event,  $T_f$  is very strongly dependent on sample size and heating rate. But the fact is that DAC in its solid-state can exist as hydrogen-bonded chain involving acidic  $>N_9H$  and  $-NH_2$  at 3- and 6-positions ( $-H_2N \cdots HN_9<$ ), in a regular crystalline arrangement. This also lends credence to the thermally induced deaminative polycondensation of DAC, which is a characteristic of amine hydrochloride salts.

### 3.3. Melting temperature of DNC

DSC traces of DNC at heating rates of 15, 25, 40, and 50 °C/min in argon atmosphere are shown in Fig. 8(a–d), respectively. No difference in the general features of thermal response of DNC due to change in heating rate, can be observed in the thermograms. This clearly indicates the absence of any intra- or intermolecular chemical changes occurring in DNC during or preceding its melting.

There is only one distinct but weakly endothermic change in each of these DSC thermograms, which can be assigned to the melting of DNC. The values of these peak melting temperatures are, 297.0, 297.2, 298.6, and 299.7 °C, respectively, at heating rates of 15, 25, 40, and 50 °C/min. The thermograms are almost featureless below these melting temperatures. The peak melting temperature of DNC is seen to increase exponentially with heating rate with an extrapolated (to zero heating rate) value of  $296.5 \pm 1.8$  °C. This value,

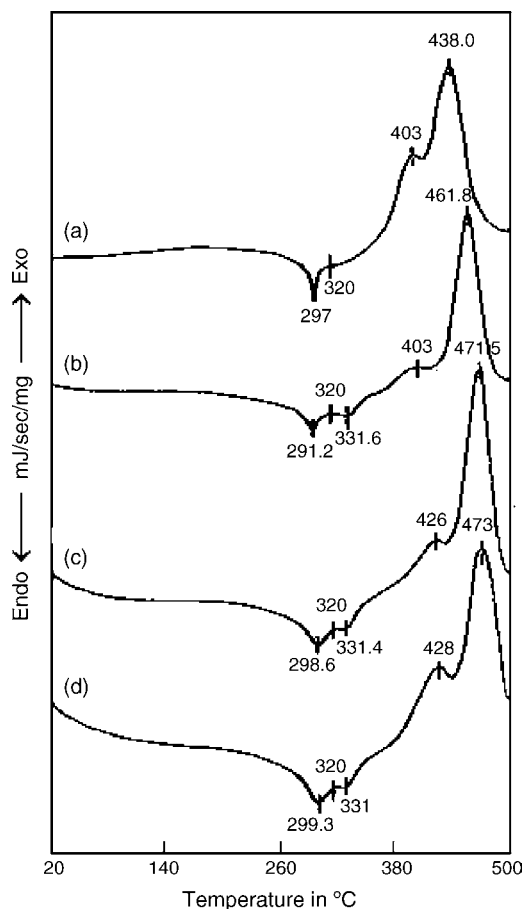


Fig. 8. DSC traces of DNC in argon at heating rates of (a) 15 °C/min; (b) 25 °C/min; (c) 40 °C/min; (d) 50 °C/min. Sample size: 3 mg.

however, differs widely from a melting temperature greater than 360 °C reported by Katritzky and Marson [12].

Although the melting endotherms are distinct with their peak temperatures, determination of the corresponding extrapolated onset temperatures is highly subjective, because of a very shallow and continuous endothermic drift of the DSC traces up to the melting peaks. For example, a set of extrapolated onset-melting temperatures ( $T_e$ ) of 274.6, 266.9, 263.0, and 261.1 °C is obtained from manual draw of tangents at heating rates of 15, 25, 40, and 50 °C/min, respectively. These temperatures, unlike those in the case of DAC, are in an exponentially decreasing order with increasing heating rates. Also, an extrapolation of these data on a first order exponential decay curve gave an onset melting temperature of  $303.5 \pm 8.9$  °C at zero heating rate. This value is higher than the observed peak melting temperatures, and therefore totally unacceptable. We, therefore, fail to report the extrapolated onset melting temperature of DNC at zero heating rate.

The exothermic peaks in the range 439–472 °C are assignable to a highly exothermic (nearly explosive) decom-

position of DNC, characteristic of polynitrated aromatic compounds.

Also to be noted further from the thermograms is the same maximum temperature of  $\sim 320$  °C that the endotherms span at all the four heating rates. This observation is exactly the same as in the case of DAC. Similar to DAC, DNC is also capable of forming relatively stronger H-bonds,  $-\text{ONO}\cdots\text{HN}_9<$  leading to a chain structure in its solid state.

#### 4. Conclusion

Diversely reported melting temperatures of 3,6-dinitro-9*H*-carbazole and 3,6-diamino-9*H*-carbazole have origins in their characteristic thermal responses. DAC is susceptible to an exothermic deaminative polycondensation involving  $>\text{N}_9\text{H}$  and  $-\text{NH}_2$  functionalities prior to its melting. This obscures the endothermic melting in the DSC trace of DAC at a low heating rate of 15 °C/min. The recorded peak melting temperatures of DAC at higher heating rates, on the other hand, are limited by heat transfer to and within the samples. It has been possible to detect the actual melting process by DSC analyses at variable heating rates. The extrapolated (to zero heating rate) onset- and peak-melting temperatures of  $241.0 \pm 0$  and  $296.5 \pm 0$  °C, respectively, have been computed for DAC from DSC analyses. For DNC, the extrapolated peak melting temperature is  $296.5 \pm 1.8$  °C. The onset melting temperature, however, could not be determined.

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