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# Solvent free reactions

## Reactions of nitrophenols in 8-hydroxyquinoline–benzoic acid eutectic melt

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**Abstract** Reactions of nitrophenols have been studied in the eutectic melt of 8-hydroxyquinoline–benzoic acid, where it reacted with 8-hydroxyquinoline. The reactions were also carried out in solution. The reaction products obtained from both the methods were characterized by FT-IR, differential scanning calorimetry, X-ray diffraction technique and microstructural investigations. The reaction products obtained from eutectic melt were analyzed for C, H, N. The results showed that reaction products obtained from both the methods are same. An attempt has been made to propose the overall mechanism of the reaction in the eutectic melt.

**Keywords** Phase diagram · DSC studies · Thermochromic effect · Monoclinic crystal system

## Introduction

Presently materials are of immense importance in our daily life. In recent years, it has been observed that properties of materials are size dependent. Various methods have been developed to prepare materials needed for different purposes. It is found that certain metal oxides prepared through molten electrolytes such as nitrate and other melts [1–5] have lower particle size, higher surface area and as a result higher catalytic activity and reactivity. In the present time, increased environmental awareness demands the avoidance of hazardous compounds. Volatile organic compounds, particularly solvents, are major components of toxicity. Potential replacements for volatile organic compounds include use of ionic liquids, supercritical carbon dioxide and water or to perform the reactions in solvent free conditions [6–9]. Keeping in mind the ease of preparation and ecofriendly conditions, attempts have been made to prepare some compounds through organic eutectic melts in the absence of a solvent.

In this paper reactions of 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP) and 2,4,6-trinitrophenol (2,4,6-TNP) were carried out separately in 8-hydroxyquinoline (8-HQ)–benzoic acid (BA) eutectic melt (solvent free conditions). Reactions were also carried out in solution. The reaction products obtained from both the methods were characterized by using FT-IR spectroscopic, powder X-ray diffraction and differential scanning calorimetric techniques. Microstructural studies were also made.

## Materials and methods

8-Hydroxyquinoline (Sigma), 4-nitrophenol (Apex Chemicals) and 2,4-dinitrophenol (Loba Chem) were used without further purification. Benzoic acid (Ranbaxy) was purified by repeated recrystallization from hot water. 2,4,6-Trinitrophenol (S. D. Fine Chemicals) was purified by successive recrystallization from ethyl alcohol. The purities of the compounds were checked by determining their melting temperatures. The melting temperatures of the

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purified compounds were found in good agreement with their literature values [10].

Phase diagram of 8-HQ–BA system was studied by thaw melt method as described elsewhere [11]. Mixtures of different compositions were made by taking accurately weighed amounts of the two components in clean Pyrex glass tubes. The tubes were sealed in order to prevent the evaporation of the components. The tubes were then placed in a paraffin oil bath at temperatures slightly above the melting temperature of the components. After melting, the tubes were suddenly quenched in ice cold water. The process of melting and quenching were repeated several times in order to make the mixtures homogenous. The tubes were broken and the solidified masses were crushed into fine powders in an agate pestle mortar. The melting temperatures of different mixtures were determined with the help of a precision mercury thermometer which could read up to ±0.1 °C. The melting temperatures were plotted against the composition in order to obtain the phase diagram.

Known amounts of 4-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol were allowed to react separately with 8-hydroxyquinoline in molten 8-HQ–BA eutectic in 1:1 molar ratio. 1 g of the eutectic mixture was taken in a glass tube and melted in a liquid paraffin bath maintained at 70 °C. 0.6242 g of 4-NP was added to the eutectic melt and due care was taken to avoid the sticking of compound on the walls of the tube. Whole amount of 4-NP settled down at the bottom of the glass tube. Reaction started within a minute and temperature of the melt decreased by 5 °C. The melt was separated in two distinguished layers, i.e., upper layer was light orange and the bottom layer was dark orange in colour. After 2:30 min, the melt of the bottom layer started diffusing towards the upper layer with a rise in temperature of the melt ($\sim$2 °C). The particles of 4-NP, which was settled down at the bottom of the tube, started disappearing and the colour of the whole melt changed into dark orange after 14 min. The glass tube was taken out from the paraffin bath and kept at room temperature for 3–4 h but the melt remained highly viscous. It was then kept into refrigerator for 6 h where the whole mass got solidified into light yellow coloured mass. This was properly washed with hot water in order to remove the unreacted benzoic acid and dried at 30 °C in an oven. The percentage yield of the product was 82%.

The reaction 2,4-DNP was allowed to occur in a similar way as described above. 1 g of the eutectic mixture was taken in a glass tube and melted in a paraffin bath maintained at 70 °C. 0.8261 g of 2,4-DNP was added to the eutectic melt and due care was taken to avoid the sticking of compound on the walls of the tube. The particles of 2,4-DNP settled down at the bottom of the glass tube. Reaction started within a minute and cooling of about 4.8 °C was observed during the reaction. After 8 min, the particles of 2,4-DNP, disappeared and the colour of the whole melt was changed into dark orange. There was a slow rise in the temperature of the bath (about 1 °C per minute) and attained the reaction temperature after 5 min. The glass tube was kept at room temperature and the whole melt was solidified within 2–3 min. The yellow coloured product was properly washed with hot water in order to remove the unreacted benzoic acid and dried at 30 °C in an oven (m.p. 96.2 ± 0.0 °C). The percentage yield of the product was 86%.

The reaction of 2,4,6-TNP was also carried out in a similar manner as described above. 1 g of the eutectic mixture was taken in a glass tube and melted in a paraffin bath maintained at 70 °C. 1.0279 g of 2,4,6-TNP was added to the eutectic melt which settled down at the bottom of the glass tube. Reaction started within a minute and temperature of melt decreased by 1.6 °C and after 30 s, it attained the reaction temperature, i.e., 70 °C. The reacting compound, which got settled down at the bottom of the tube, started disappearing and the colour of the whole melt was changed into dark orange in 12 min. The dark orange coloured melt was kept at room temperature where a golden yellow coloured semi-solid product was obtained. The solidified mass was washed with hot water in order to remove the unreacted benzoic acid and dried at 30 °C in an oven. The percentage yield of the product was 72%.

Reaction of 8-HQ with 4-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol were also carried out separately in solution and reaction products were prepared. 8-HQ (0.1452 g) and 4-NP (0.1391 g) were dissolved separately in 15 mL of chloroform. Both the solutions were mixed and kept at room temperature for 6 h. The reaction started within half an hour and light yellow coloured reaction product was precipitated (m.p. 45.2 ± 0.1 °C). The percentage yield of the reaction product was 76%.

8-HQ (0.1452 g) and 2,4-DNP (0.1841 g) were dissolved in 15 mL of benzene separately. Both the solutions were warmed and mixed. After 24 h, yellow coloured crystals were obtained (m.p. 99.6 ± 0.0 °C). The percentage yield of the product was found to be 62%.

8-HQ (0.1452 g) and 2,4,6-TNP (0.2291 g) were dissolved in 15 mL of methyl alcohol separately and then mixed. The reaction started with the formation of golden yellow coloured reaction product and completed within 6 h. The reaction product decomposed on melting (200.0 ± 0.0 °C). The percentage yield of the reaction product was 62.6%.

Powder X-ray diffraction pattern of reaction products prepared by two different methods were recorded with a powder X-ray diffractometer using Cu $K_\alpha$ radiation.

The reaction products obtained from eutectic melt were analyzed for C, H and N by using Analytic gena elemental analyzer.

The FT-IR spectra of all the pure components and the reaction products were recorded on a Nicolet Impect 410 in the frequency range of 4000–450 $cm^{-1}$ by using KBr pellets. The uncertainty in the instrument was ±5 $cm^{-1}$.

DSC studies of reaction products prepared by different methods were carried out by using Differential Scanning Calorimeter (METTLER STAR SW 900) instruments. The powdered sample under investigation was taken in $Al_2O_3$ pan covered with $Al_2O_3$ lid and a blank pan was also taken as a reference. The two pans (sample + reference), kept simultaneously in identical conditions after base line correction were heated uniformly at a rate of 5 K $min^{-1}$ under continuous nitrogen gas purging. The purging flow rate 20/60 mL $min^{-1}$ was kept constant. The DSC curve was recorded from room temperature to 250 °C.

Small amount of fine powders of 8-HQ, BA and their reaction products prepared from both the methods were placed on separate glass slides. These glass slides were then placed in an oven maintained at a temperature slightly higher than the melting temperatures of the material under study. The specimen was allowed to melt completely at that temperature and then a glass coverslip was gently moved over the melt in one direction. The microphotographs of the crystallized fronts were recorded with the help of an optical microscope (Olympus Chi 20) at a magnification of 100×.

## Results and discussion

The phase diagram of 8-HQ–BA system is graphically represented in Fig. 1. The phase diagram curve indicates the formation of eutectic mixture at $x_2 = 0.3636$ (mole fraction of BA) which melts at 53.0 ± 0.0 °C.

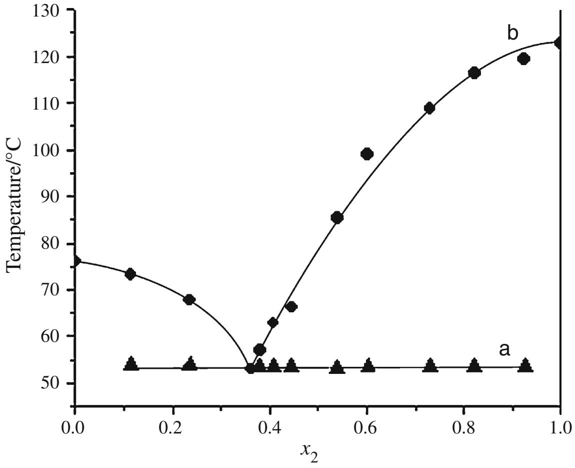

**Fig. 1** Phase diagram of 8-HQ–BA eutectic system *a* thaw melting temperature curve, *b* melting temperature curve

Eutectic mixtures melt at lower temperatures as compared to their components and hence molten state is obtained at a lower temperature. In molten state, reactant molecules come very close to each other due to high viscosity of the medium and stay for a longer time in contact to each other. Therefore, the reactions are expected to occur faster in comparison to reactions in solution and solid state. With this idea in mind when 4-NP was added to the eutectic melt, reaction between 8-HQ and 4-NP occurred with the formation of a light yellow viscous liquid which remained as liquid at room temperature but solidified when kept in a refrigerator for 6 h. It appears that in this case frictional forces between the molecules are very high and do not allow the liquid to freeze. However, since in the refrigerator the temperature is low, the frictional forces are seized and the liquid solidified. When 2,4-DNP was added to the eutectic melt, a yellow coloured solid reaction product was obtained within 2–3 min when kept at room temperature. On the other hand when 2,4,6-TNP was added to the eutectic melt, the light orange coloured eutectic melt changed into a dark orange colour within 1 min. Golden yellow coloured semi-solid material was obtained after keeping the melt at room temperature. This on crystallization gave crystalline solid. In each case, when nitrophenols were added to the eutectic melt, first cooling took place and then there were rise in temperature. The initial cooling might be due to decomposition of eutectic mixture into 8-HQ and BA. The liberated 8-HQ then reacted with nitrophenols with liberation of heat.

The reactions of nitrophenols and 8-HQ were also allowed to occur in solution. It was observed that similar reaction products as obtained through eutectic melt were obtained. The time of completion of the reactions, melting temperatures and percent yield of the reaction products from both the methods are given in Table 1. From the table, it is clear that time required for completion of each reaction is lower and the percentage yields are higher in the case of reactions through eutectic melt as compared to that through solution. The melting temperatures of the products obtained by two methods are almost same. Powder X-ray diffraction patterns are same. Sharp X-ray lines show that products are crystalline in nature. The overall results clearly show that the reactions carried out through eutectic melt are more efficient and the products obtained by two methods are same.

Elemental analyses of the reaction products are given in Table 2 and the results indicate that nitrophenols reacted with 8-HQ in 1:1 molar ratio. The reactions in the eutectic melt be written as

**Table 1** Values of melting temperature, reaction time and percentage yield of reaction products of 8-HQ and nitrophenols prepared in 8-HQ–BA eutectic melt and in solution

| Reaction product | In eutectic melt | | | In solution | | |
|---|---|---|---|---|---|---|
| | *T*/°C | Reaction time/min | % Yield | *T*/°C | Reaction time/h | % Yield |
| 8-HQ–4-NP | 43.8 ± 0.0 | 14 | 82 | 45.2 ± 0.1 | 6 | 76.0 |
| 8-HQ–2,4-DNP | 96.2 ± 0.0 | 08 | 86 | 99.6 ± 0.0 | 24 | 62.0 |
| 8-HQ–2,4,6-TNP | 197.2 ± 0.0 | 12 | 72 | 200.0 ± 0.0 | 6 | 62.6 |

**Table 2** Observed and theoretical values of C, H, N in the reaction products prepared in the eutectic melt

| Elements | 8-HQ–4-NP | | 8-HQ–2,4-DNP | | 8-HQ–2,4,6-TNP | |
|---|---|---|---|---|---|---|
| | Observed/% | Theoretical/% | Observed/% | Theoretical/% | Observed/% | Theoretical/% |
| C | 61.74 | 63.31 | 55.56 | 54.6 | 47.41 | 48.08 |
| H | 4.65 | 4.2 | 3.46 | 3.3 | 2.66 | 2.67 |
| N | 7.99 | 9.84 | 11.79 | 12.75 | 14.41 | 14.40 |

$$\text{8-HQ}-\text{BA(eutectic)} + \text{4-NP} \rightarrow \text{8-HQ} \cdot \text{4-NP} + \text{BA}$$

$$\text{8-HQ}-\text{BA(eutectic)} + \text{2,4-DNP} \rightarrow \text{8-HQ} \cdot \text{2,4-DNP} + \text{BA}$$

$$\text{8-HQ}-\text{BA (eutectic)} + \text{2,4,6-TNP} \rightarrow \text{8-HQ} \cdot \text{2,4,6-TNP} + \text{BA}$$

FT-IR spectral studies were made to know about the nature of interaction between the components in the reaction products. FT-IR spectra of 8-HQ, 4-NP and their reaction products prepared from solution and eutectic melt are shown in Fig. 2. FT-IR spectra of 8-HQ shows a broad peak at 3195 cm$^{-1}$ due to hydrogen bonded –OH group. 4-NP shows a stretching vibration frequency due to –OH group at 3329 cm$^{-1}$ (Fig. 2b). Asymmetric and symmetric stretching vibration frequencies due to –NO$_2$ group appeared at 1516 and 1345 cm$^{-1}$, respectively. The IR spectra of the reaction products prepared from the eutectic melt and solution are almost identical and are given in Fig. 2c and d, respectively. The characteristic peak positions of 8-HQ, 4-NP and their reaction products are given in Table 3. From Table 3, it is clear that the peak due to –OH group disappears from the spectra and that of –NO$_2$ group shifts towards lower wave numbers. This indicates the presence of hydrogen bonding between H-atom of –OH group of 8-HQ and O-atom of –NO$_2$ group of 4-NP.

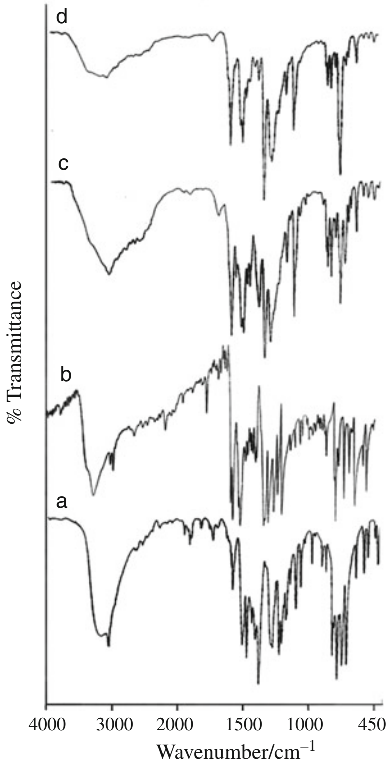

**Fig. 2** FT-IR spectra of *a* 8-HQ, *b* 4-NP, *c* reaction product prepared in 8-HQ–BA eutectic melt and *d* in solution state

The FT-IR spectra of 8-HQ, 2,4-DNP and their reaction products are shown in Fig. 3. The characteristic peak positions of 8-HQ, 4-NP and their reaction products are given in Table 3. The FT-IR spectrum of 2,4-DNP shows a broad peak at 3101 cm$^{-1}$. This could be attributed due to –OH group which is intramolecularly H-bonded with the –NO$_2$ group. The IR spectra of reaction products prepared from the eutectic melt and solution are almost similar (Fig. 3c, d). In the IR spectra of both the products (Table 3), the vibrational frequency of –OH group totally disappears and those of –NO$_2$ group shifts to lower frequencies. The shifts in the frequencies of –OH and –NO$_2$ groups indicate the presence of a weak hydrogen bond between H-atom of –OH group of 8-HQ and O-atom of –NO$_2$ group of 2,4-DNP.

**Table 3** FT-IR spectral bands of pure 8-HQ, 4-NP, 2,4-DNP, 2,4,6-TNP and their reaction products prepared in 8-HQ–BA eutectic melt and in solution state

| Stretching frequency | Wavenumber/cm$^{-1}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 8-HQ | 4-NP | | | 2,4-DNP | | | 2,4,6-TNP | | |
| | | Pure 4-NP | Reaction product in eutectic melt | Reaction product in solution state | Pure 2,4-DNP | Reaction product in eutectic melt | Reaction product in solution state | Pure 2,4,6-TNP | Reaction product in eutectic melt | Reaction product in solution state |
| $\nu_{\text{O–H}}$ | 3195 | 3329 | – | – | 3101 | – | – | 3100 | – | – |
| $\nu_{\text{N–O}}$ (asymmetric) | – | 1516 | 1498 | 1498 | 1540 | 1521 | 1520 | 1541 | 1521 | 1520 |
| $\nu_{\text{N–O}}$ (symmetric) | – | 1345 | 1330 | 1330 | 1340 | 1330 | 1329 | 1345 | 1330 | 1329 |

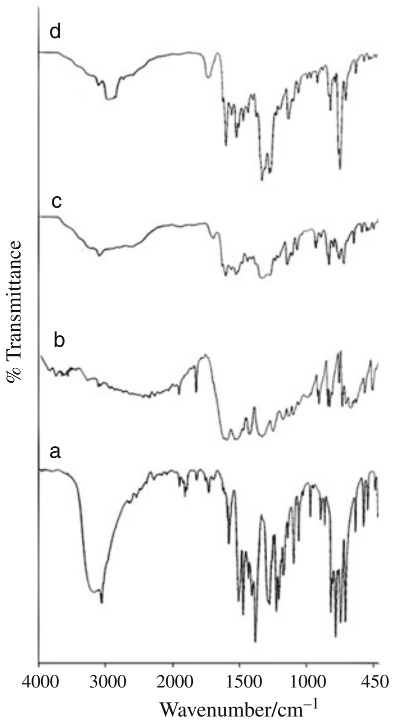

**Fig. 3** FT-IR spectra of *a* 8-HQ, *b* 2,4-DNP, *c* reaction product prepared in 8-HQ–BA eutectic melt and *d* in solution state

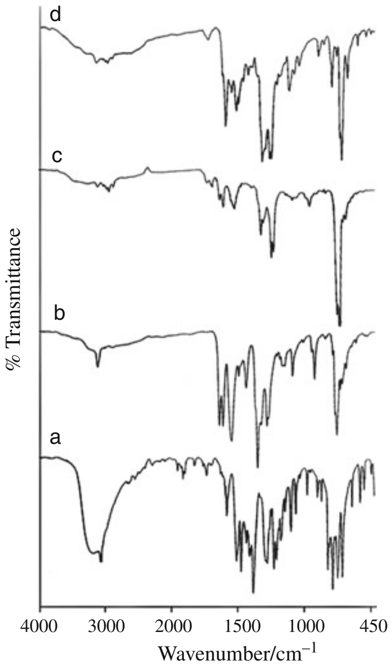

**Fig. 4** FT-IR spectra of *a* 8-HQ, *b* 2,4,6-TNP, *c* reaction product prepared in 8-HQ–BA eutectic melt and *d* in solution state

The FT-IR spectra of 2,4,6-TNP (Fig. 4b) shows a peak at 3100 cm$^{-1}$. The occurrence of this peak is due to stretching vibration of –OH group which is intramolecularly H-bonded with one of the –NO$_2$ groups. The IR spectra of reaction products obtained from the eutectic melt and solution are shown in Fig. 4c and d, respectively. The vibrational frequencies of pure components and reaction products are given in Table 3. The IR spectra of reaction products (Fig. 4c, d) suggest that both are the same and in these spectra the vibrational frequency of –OH group disappears and the vibrational frequencies of –NO$_2$ groups shift to lower values. These results clearly indicate the presence of hydrogen bonding between H-atom of –OH group of 8-HQ and O-atom of –NO$_2$ group of 2,4,6-TNP.

DSC studies of all the reaction products were made. The melting temperatures and heats of fusion values as determined by DSC curves are given in Table 4. The DSC curves of 8-HQ · 4-NP prepared through eutectic melt and solution are shown in Fig. 5. The endotherms at 43 °C (Fig. 5a) and 45.1 °C (Fig. 5b), respectively, correspond to the melting temperatures of the compounds prepared from the two methods. The corresponding heats of fusion values are $-112.64$ J g$^{-1}$ and $-106.78$ J g$^{-1}$. In the endotherms there are shoulders, which may be due to some contaminations. When the products were heated beyond their melting temperatures, the colour of the liquids changed. On cooling, the liquids regained the original colours. A broad endotherm between 220 and 240 in Fig. 5a and two broad endotherms between 220 and 240 °C in Fig. 5b correspond

**Table 4** Values of melting temperature (*T*) and heat of fusion ($\Delta H_{fus}$) of reaction products obtained from DSC studies

| Reaction product | Prepared in 8-HQ–BA eutectic melt | | Prepared in solution state | |
|---|---|---|---|---|
| | *T*/°C | $\Delta H_{fus}$/J $g^{-1}$ | *T*/°C | $\Delta H_{fus}$/J $g^{-1}$ |
| 8-HQ–4-NP | 43.0 | −112.64 | 45.1 | −106.78 |
| 8-HQ–2,4-DNP | 98.4 | −140.27 | 99.4 | −139.36 |
| 8-HQ–2,4,6-TNP | 198.2 | −145.67 | 200.4 | −141.49 |

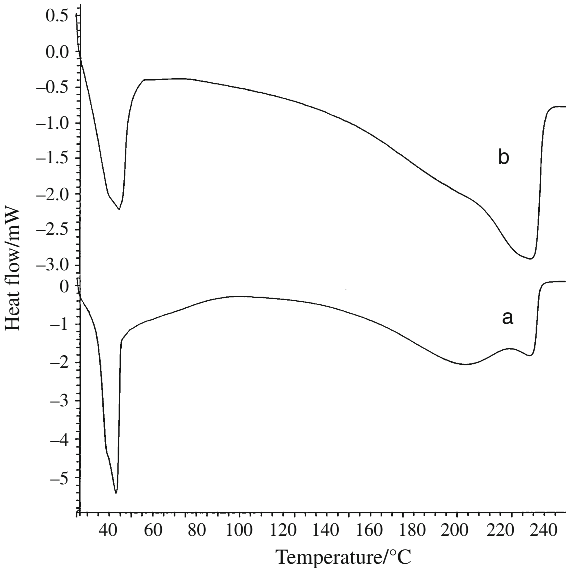

**Fig. 5** DSC curves of reaction products of 8-HQ and 4-NP prepared in *a* 8-HQ–BA eutectic melt and *b* in solution state

to this colour change and the phenomena is known as thermochromic effect [12].

DSC curves of the reaction product 8-HQ · 2,4-DNP prepared through eutectic melt and solution are shown in Fig. 6a and b, respectively. Endotherms at 98.4 °C (Fig. 6a) and at 99.4 °C (Fig. 6b) correspond to the melting temperatures of the reaction products prepared from the two methods. A small endotherm at 61.6 °C in Fig. 6b may be due to removal of solvent molecule. Some small endotherms in both the curves may be due to contaminations. The heats of fusion values of the reaction product as prepared through eutectic melt and solution are −140.27 and −139.36 J $g^{-1}$, respectively.

The DSC curves for the reaction product 8-HQ · 2,4,6-TNP prepared through eutectic melt and solution are shown in Fig. 7a and b. An endotherm at 198.2 °C appearing in Fig. 7a corresponds to the melting temperature of the reaction product prepared through eutectic melt and the heat of fusion value is found to be −145.67 J $g^{-1}$. In the DSC curve of the reaction product obtained from solution (Fig. 7b), a small endotherm at 98.3 °C is due to removal of contaminated solvent molecules, whereas a sharp endotherm at 200.4 °C corresponds to the melting

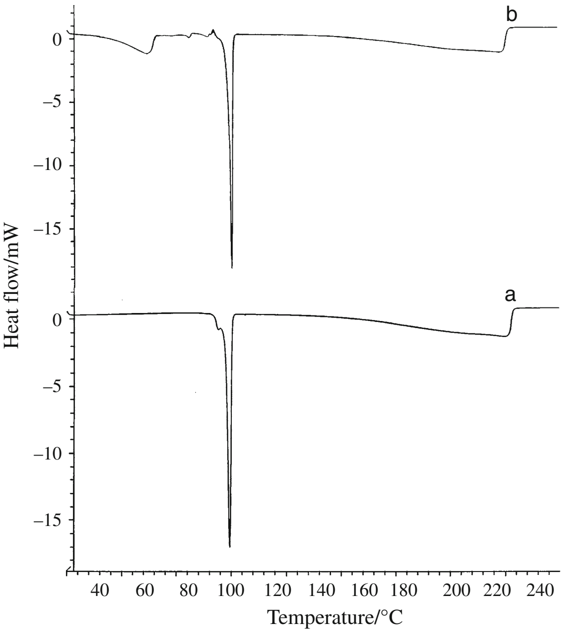

**Fig. 6** DSC curves of reaction product of 8-HQ and 2,4-DNP prepared in *a* 8-HQ–BA eutectic melt and *b* in solution state

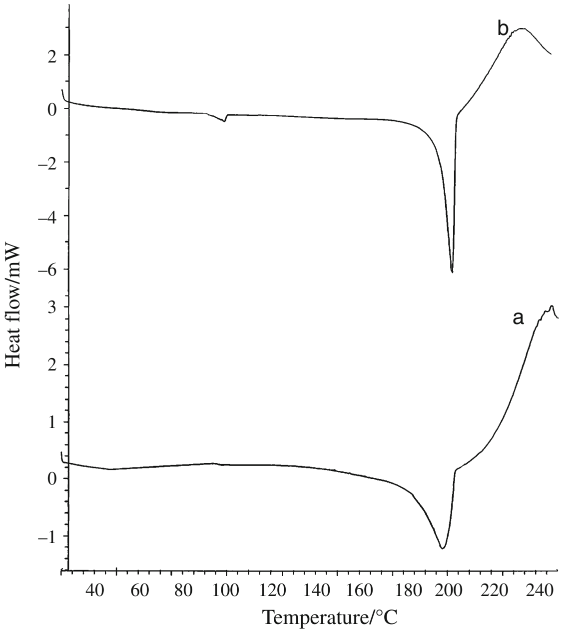

**Fig. 7** DSC curves of reaction product of 8-HQ and 2,4,6-TNP prepared in *a* 8-HQ–BA eutectic melt and *b* in solution state

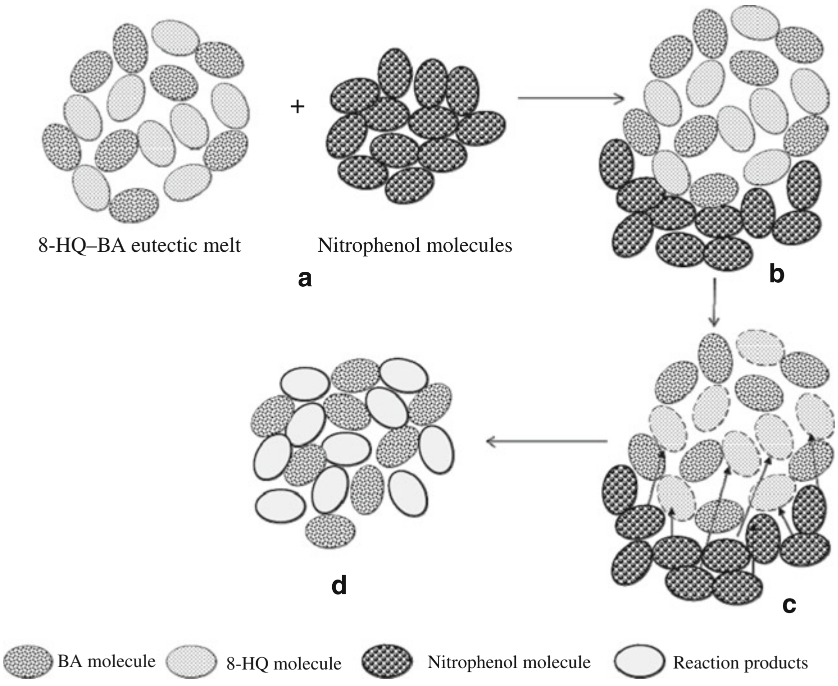

**Fig. 8** Proposed reaction model; *a* 8-HQ–BA eutectic in molten state in which nitrophenol molecules are being added. *b* Nitrophenols on addition settles down at the bottom of the reaction tube. *c* 8-HQ molecules are in perturbed state and nitrophenol molecules are penetrating in 8-HQ molecules and a reaction occurs between them. *d* Reaction products of 8-HQ and nitrophenols are formed and BA molecules remain unreacted

temperature. The heat of fusion value corresponding to this point is $-141.49$ J g$^{-1}$. The broadness of the endotherm in Fig. 7a indicates that probably the compound is less crystalline. DSC results clearly show that the reaction products obtained through eutectic melt and solution are identical.

To understand the mechanism of reactions of nitrophenols in 8-HQ–BA eutectic melt, a model has been proposed which is shown in Fig. 8. As proposed in Fig. 8b, when nitrophenol is added to the eutectic melt, it initially settled down in the reaction tube. In Fig. 8c it has been shown that nitrophenol molecules are approaching towards 8-HQ molecules. The BA does not take part in the reaction because both (nitrophenols and BA) when mixed separately do not react at all. In Fig. 8d, the formation of reaction products of nitrophenols and 8-HQ has been shown, whereas BA remained unreacted. For the completion of the reaction, the molecules of nitrophenols must enter into the crystal lattice of the 8-HQ. 8-HQ crystal is orthorhombic with lattice parameter $a = 29.18$, $b = 25.36$, $c = 3.91$ Å [13]. The cell volume of 8-HQ is 2893.42 Å$^3$. Crystal structure of $\alpha$-modification of 4-NP belongs to monoclinic with space group $P2_1/n$ and lattice parameters $a = 11.66$, $b = 8.78$, $c = 6.098$ Å and cell volume 624.28 Å$^3$ [14]. 2,4-DNP crystallized into orthorhombic space group $P2_12_12_1$. The lattice parameter are $a = 6.106(6)$, $b = 23.24(2)$, $c = 5.168(5)$ Å and the cell volume 733.36 Å$^3$ [15]. It is clear from the above data that cell volume of 8-HQ is higher than that of nitrophenols. Thus nitrophenol molecules can be accommodated in the lattice of 8-HQ. Therefore, this reaction may be considered as host–guest interaction in which 8-HQ molecule act as host and nitrophenols as guest molecule.

Microstructural studies are important because various physical properties of product material depend on their microstructures. It has been reported [16] that the formation of microstructures depend on various factors such as the nature and molecular structure of the components, concentration gradient, interface contact angles, diffusion, nucleation and crystallization characteristics of the two phases, chemical inhomogeneities and types of defects present in the growing nuclei. The microstructures of pure 8-HQ, pure BA and their eutectics are shown in Fig. 9. Microstructural pattern of pure 8-HQ has lamellar type structure with small lamellar spacing (Fig. 9a). The microstructure of BA seems to appear as irregular broken lamellar type (Fig. 9b) [17]. However, the growth pattern of the eutectic mixture seems to crystallize as densely populated thin fibrils (Fig. 9c). The microstructural patterns of pure 4-NP and the reaction products of 8-HQ and 4-NP as obtained from the 8-HQ–BA eutectic melt and from solution are presented in Fig. 10. The crystallization pattern of 4-NP appears like densely arranged stone aggregates (Fig. 10a). The microstructure of the reaction product as prepared by eutectic melt is quite different from the growth patterns of 4-NP and 8-HQ–BA eutectic. It appears as lamellar structure (Fig. 10b). Whereas, the product obtained from solution seems to crystallize as neat needle like long crystals in different directions (Fig. 10c). The microstructures of pure 2,4-DNP and the reaction

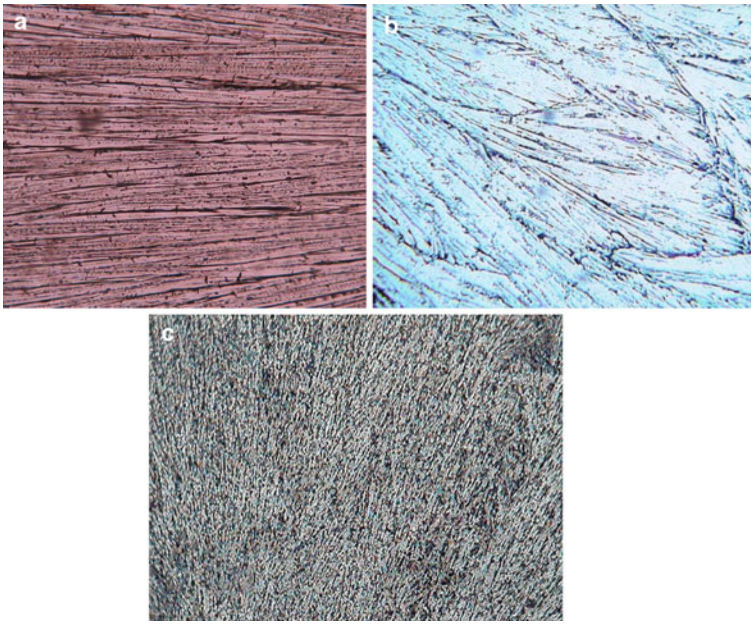

**Fig. 9** Microstructures of **a** pure 8-HQ, **b** pure BA and **c** 8-HQ–BA eutectic

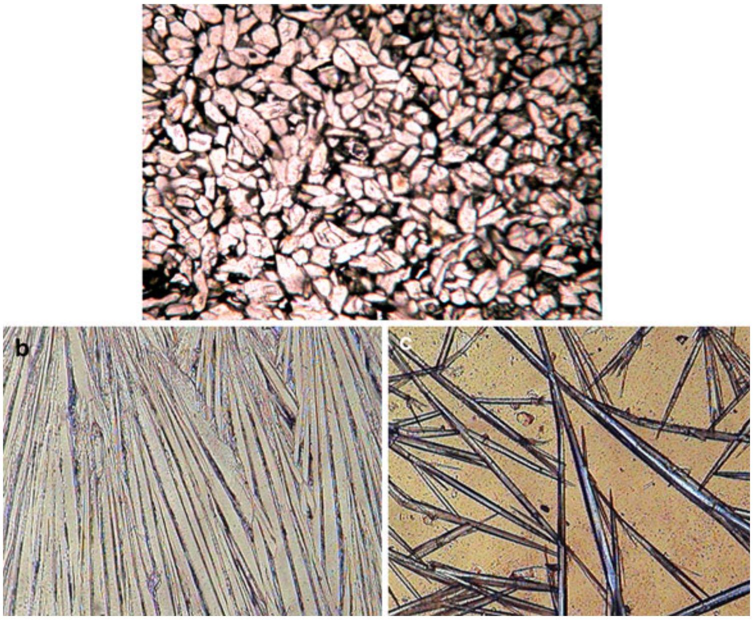

**Fig. 10** Microstructures of **a** pure 4-NP, **b** reaction product of 8-HQ and 4-NP prepared in the eutectic melt and **c** reaction product of 8-HQ and 4-NP prepared in solution state

products of 8-HQ and 2,4-DNP as obtained from eutectic melt and from solution are presented in Fig. 11. The microstructural pattern of 2,4-DNP appears like broken lamellar type structure with several black dots in between the lamellae (Fig. 11a). Growth pattern of the reaction product as obtained from eutectic melt is also different from the growth patterns of pure 2,4-DNP and 8-HQ–BA eutectic. In this case, it is seen as white coloured needle like crystals growing from one central point just like radially oriented lamellae (Fig. 11b, c). However, the product obtained from solution is fibrous in nature forming ovoid like structures (Fig. 11d, e). Well defined concentric rings are also formed which can be clearly seen in Fig. 11e. The reaction products of 8-HQ and 2,4,6-TNP obtained by both the methods decompose on melting. Thus, their microstructures could not be reported.

Microphotographic studies thus revealed that the microstructures of 8-HQ–BA eutectic, nitrophenols and reaction products are quiet different and the reaction products obtained via eutectic melt are more crystalline in nature.

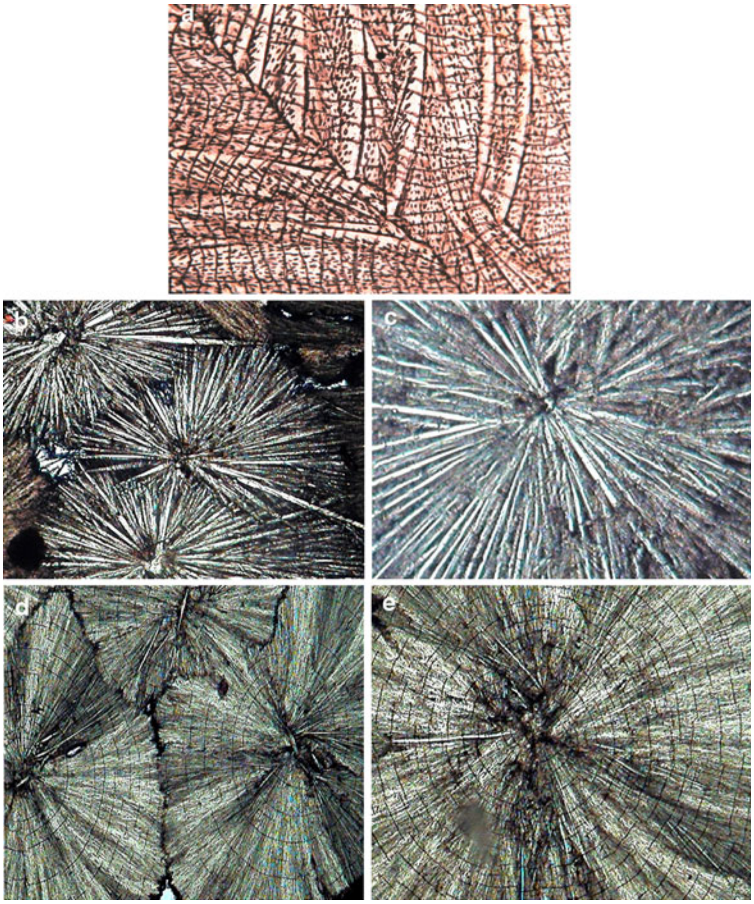

**Fig. 11** Microstructures of **a** pure 2,4-DNP, **b**, **c** reaction product of 8-HQ and 2,4-DNP prepared in the eutectic melt; **d**, **e** reaction product of 8-HQ and 2,4-DNP prepared in the solution state

## Conclusions

From the results, it is concluded that the reactions of nitrophenols with 8-hydroxyquinoline in molten eutectic are novel type of solvent free reactions. The components reacted in 1:1 molar ratio. The products obtained from two different methods are almost identical. In the eutectic melt the reactions occured faster with high yield as compared to that in solution. The reaction is completed much below the melting point of either of the reactants in the eutectic melt. Microstructural studies revealed that the products formed in the eutectic mixture are more crystalline in nature.

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