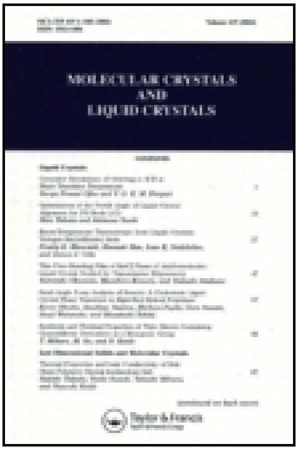

Molecular Crystals and Liquid Crystals

Molecular Interaction between Naphthalene and 2,4-Dinitrophenol in Solid State

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Version of record first published: 22 Sep 2010

To cite this article: N. B. Singh, A. Srivastava, N. P. Singh & Ashutosh Gupta (2007): Molecular Interaction between Naphthalene and 2,4-Dinitrophenol in Solid State, Molecular Crystals and Liquid Crystals, 474:1, 43-54

To link to this article: http://dx.doi.org/10.1080/15421400701693484

Mol. Cryst. Liq. Cryst., Vol. 474, pp. 43–54, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701693484

Molecular Interaction between Naphthalene and 2,4-Dinitrophenol in Solid State

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Kinetics of the solid-state reaction between naphthalene and 2,4-dinitrophenol have been studied at different temperatures (30–50°C), and it was found that naphthalene diffuses toward 2,4-dinitrophenol. When naphthalene enters into the crystal lattice of 2,4-dinitrophenol, a 1:1 addition compound is formed with an orthorhombic crystal lattice, and the unit cell volume is much higher than the sum of the unit cell volumes of the components. As a result of this, cracks are formed and the reaction goes to completion. Computer calculations have shown that charge-transfer interaction occurs between the two components during the reaction.

Keywords: 2,4-Dinitrophenol; interaction; kinetics; naphthalene; solid state reactions

INTRODUCTION

Organic solid-state reactions are important both from a synthetic and mechanistic point of view. During recent years, a large number of such reactions have been studied [1]. Reaction products and the mechanism of reactions depend very much on the nature of interactions. Naphthalene is a planar and symmetrical molecule with zero dipole moment, whereas 2,4-dinitrophenol is unsymmetrical and dipolar. During a solid-state reaction, a very weak interaction would be

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expected between the two components. Weak interactions control the reaction kinetics in the solid state. For this reason, kinetics of the solid-state reaction between naphthalene and 2,4-dinitrophenol has been investigated, and the mechanism is discussed in this article.

EXPERIMENTAL

2,4-Dinitrophenol was purified by repeated crystallization from hot water. The purified sample melts at 114°C. Naphthalene was purified by distillation under reduced pressure. The melting point of the pure sample of naphthalene was 80°C.

Preparation of Reaction Product

From Solution

Solutions of 2,4-dinitrophenol and naphthalene in benzene were mixed in a 1:1 molar ratio. A light-brown-coloured reaction product precipitated, which was dried and stored in a desiccator. The reaction product melts at 94°C.

By Solid-State Reaction

Solid powder of 2,4-dinitrophenol and naphthalene in equimolar amounts were ground together in an agate mortar with pestle. The entire mass was then kept in an incubator at 50°C for a week with occasional grinding. The reaction product melts at 94°C.

Kinetic Studies of Reaction between Naphthalene and 2,4-Dinitrophenol in Solid State

Capillary Technique

The solid-state reaction between naphthalene and 2,4-dinitrophenol was studied by the capillary technique [2]. A glass capillary sealed at one end was half-filled with 2,4-dinitrophenol (particle size $<$ 350 mesh). For uniform packing of 2,4-dinitrophenol, each capillary was tapped for 5 min. The surface was made smooth by a thin glass rod. The remaining half of the capillary was filled with naphthalene (particle size $<$ 350 mesh). At the junction of the two reactants, the reaction started with a color change (light brown). The kinetics was followed by measuring the thickness of the product layer at different intervals of time with the help of a traveling microscope. The experiment was performed at 30, 35, 40, and 50°C.

Attempts were made to study the kinetics by creating air gaps of different lengths between the components at 60°C. The reaction started at the surface of 2,4-dinitrophenol, but only a thin layer of the product was formed, the thickness of which did not show measurable change, and hence kinetic studies could not be made.

Gravimetric Technique

The gravimetric study was performed in a way described earlier [3]. A known amount of 2,4-dinitrophenol was taken in a separate glass tube fitted with a B_{19} female joint and was connected with another tube fitted with B_{19} male joint containing naphthalene. The assembly was kept in an incubator maintained at constant temperature. The vapors of naphthalene started reacting with solid 2,4-dinitrophenol, forming light-brown-colored product. The kinetics was studied by measuring the change in weight of the tube containing 2,4-dinitrophenol at different intervals of time. The experiments were carried out at different temperatures.

Microscopic and Microphotographic Studies

A small amount of 2,4-dinitrophenol was placed on a glass slide at 116°C and allowed to melt. The cover slip was glided over the melt and allowed to undercool. Nucleation started from one side, and care was taken to have unidirectional freezing. The microphotograph was taken with the help of camera attached to the microscope at a suitable magnification. In a small glass beaker, solid naphthalene was heated at 60°C so that the beaker was full of vapor. The slide of 2,4-dinitrophenol was kept on the top of the beaker. 2,4-Dinitrophenol reacted with the vapors of naphthalene, and the change in microstructure was photographed as a function of time.

Study of Phase Diagram

Phase-diagram studies were made by the thaw melt method [4].

Powder X-ray Diffraction Studies

Powder X-ray diffraction (XRD) pattern of the reaction product obtained from the solid-state reaction was recorded at Regional Sophisticated Instrumentation Center (RSIC), Nagpur, using CuK_α radiation.

UV-Visible Spectra

UV-visible spectra of the components and the mixture in 1:1 molar ratio were recorded in methanol.

Electronic Structure Calculations

Gaussian 03 [5] program suite was used for the electronic structure calculations. Geometries of the complex under investigation were fully optimized at the RHF level of theory using a 6-31G (d,p) basis set. The interaction energy (ΔE) was computed using the supermolecule approach,

$$\Delta E = E_{AB} - E_A - E_B,$$

where E is the energy of a molecule in a particular geometry.

The electrostatic potential maps were generated for an isosurface of electron density for individual molecules as well as for the complex using Gauss View [6]. The blue color denotes regions of strong positive potential, and the red color denotes the regions of strong negative potential. The other colors, namely green and yellow, represent intermediate values of electrostatic potential. Because there are a large number of geometries under consideration for different molecules and complexes, the scales are not shown in each case.

RESULTS AND DISCUSSION

The reaction product obtained from solution and solid-state reactions have the same melting point (94°C), and the elemental analysis shows that naphthalene reacts with 2,4-dinitrophenol in a 1:1 molar ratio. The phase diagram studies (Fig. 1) show the formation of a 1:1

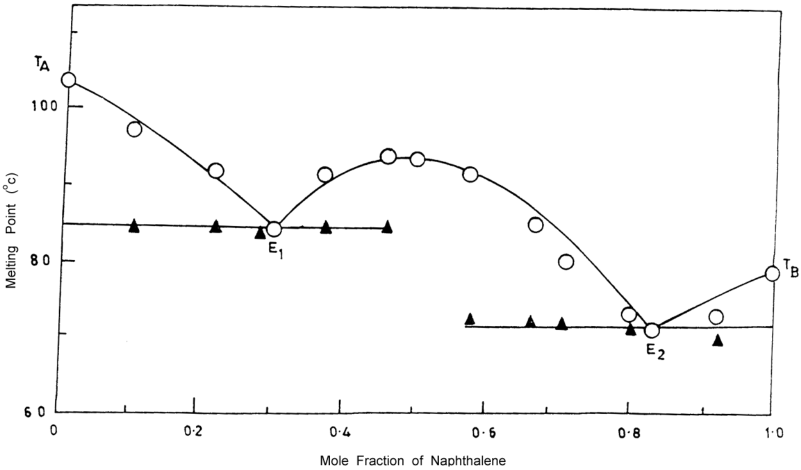

FIGURE 1 Solid–liquid equilibrium data of 2,4-dinitrophenol–naphthalene system.

addition compound. Because the maxima is flat, it appears that the addition compound is stable in the solid state and dissociated in the solution or molten state.

When solid powders of the two reactants (naphthalene and 2,4-dinitrophenol) were kept in contact in a glass capillary, a light-brown-colored reaction product was formed at the surface of 2,4-dinitrophenol, the thickness of which increased with time. It was inferred that naphthalene molecules diffused toward 2,4-dinitrophenol. The kinetics was studied by measuring the thickness of the product layer (ξ) as a function of time. The kinetic data obeyed Eq. (1):

$$\xi = k_1 t^n \tag{1}$$

where ξ is the thickness of the product layer at any time t, k_1 is the apparent rate constant, and n is another constant. When log ξ is plotted against log t, straight lines are obtained (Fig. 2), indicating the validity of Eq. (1). From the intercepts and the slope of the lines, the values of k_1 and n were calculated and are given in Table 1. Equation (1) is empirical in nature, and the value of n does not have much theoretical background.

When log k_1 was plotted against 1/T, a straight line was obtained showing the validity of the Arrhenius equation. The energy of activation was found to be 26.4 kJ/mol. The diffusion of naphthalene molecules toward 2,4-dinitrophenol may take place via vapor phase, grain boundary, defects, or bulk and surface migration. Because the energy of activation is very low, the contributions of grain boundary, defects, and bulk diffusion might be very small. The process of diffusion might take place via vapor phase and surface migration. The heat of sublimation of naphthalene is 63 kJ/mol, which is much higher than the energy of activation. Therefore, the diffusion is not a vapor-phase-dominated process. Further, when the two reactants were separated by air gaps of different length, the reaction started at the surface of 2,4-dinitrophenol, but the increase in the thickness of the product layer was very small. This clearly shows that the diffusion is not taking place exclusively via the vapor phase. Because the energy of activation for the solid-state reaction is much less than the heat of sublimation of naphthalene, it appears that diffusion occurs through some easier method. Because the gliding of organic molecules [7] over the surface of glass is not uncommon, it may also glide over the surface of 2,4-dinitrophenol. Thus diffusion may also occur via surface migration. In the capillary method, kinetics is studied only by seeing the color change at the surface. Therefore, the inference in favor of surface migration is more probable. Further, when k_1 was plotted against r (r = radius of particles), a straight line is obtained indicating

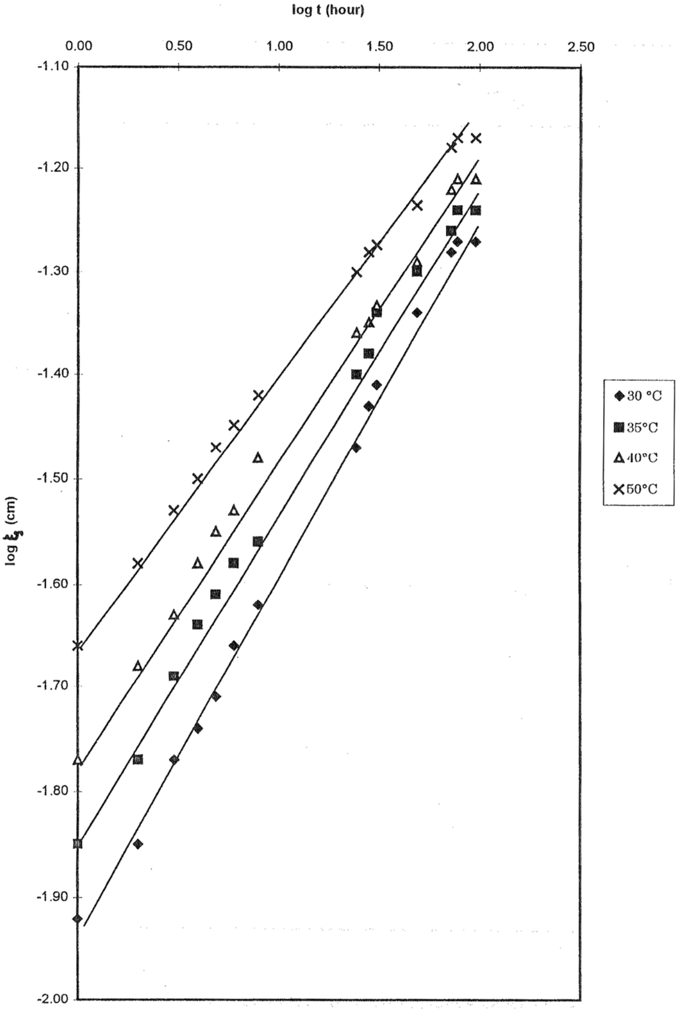

FIGURE 2 Verification of Eq. (1).

that as the particle size increased, the rate of surface migrations is increased. The values are given in Table 2. This supports the idea that naphthalene might be diffusing toward 2,4-dinitrophenol via surface migration. The surface migration is slow because the 2,4-dinitrophenol molecule is neither planar nor symmetrical. It has a very high value of dipole moment ($\mu_{\text{cis}} = 3.09\,\text{D}$, $\mu_{\text{trans}} = 5.51\,\text{D}$) [8], and as a result it hinders the surface migration of naphthalene molecules over the surface of 2,4-dinitrophenol.

TABLE 1 Kinetic Parameter of Eq. (1)

Temperature (°C)	k_1 (cm/h)	n
30	0.012 ± 0.001	0.33 ± 0.02
35	0.014 ± 0.001	0.32 ± 0.01
40	0.017 ± 0.002	0.29 ± 0.01
50	0.022 ± 0.002	0.28 ± 0.01

When the kinetics of the reaction between naphthalene (vapors) and 2,4-dinitrophenol (solid) were studied gravimetrically, the kinetic data obeyed Eq. (2):

$$\Delta W = k_2 t, \tag{2}$$

where ΔW is the increase in weight at any time t and k_2 is rate constant. The reactions at 60 and 70°C go to completion after 936 and 816 h respectively, and show that the reaction between naphthalene and 2,4-dinitrophenol occurs in a 1:1 molar ratio. When ΔW was plotted against t, straight lines are obtained, showing the validity of Eq. (2). The energy of activation for the reaction determined by this technique was found to be 35 kJ/mol. This value is nearly one and half times higher than the value obtained by the capillary technique. Because the reaction goes to completion, it appears that the reaction product is porous or cracks and voids are formed in the product layer as a result of volume changes.

The XRD lines for the 1:1 addition compound formed between naphthalene and 2,4-dinitrophenol were indexed for an orthorhombic system. The lattice parameters and unit cell volumes are given in Table 3. When naphthalene molecules enter into the crystal lattice of 2,4-dinitrophenol, the following possibilities may occur:

(i) When there is no interaction between the components, the unit cell volume of the addition compound will be sum of the unit cell volumes of the components.

TABLE 2 Effect of Particle Size on the Rate Constant

Particle-size (mesh)	r (cm)	k_1 (cm/h)
140–200	0.0424	0.39
200–240	0.0374	0.34
240–300	0.0346	0.32
300–350	0.0300	0.29

TABLE 3 Crystal Data

Compound	Crystal data	Reference
Naphthalene	Monoclinic, a = 8.010 Å, b = 5.884 Å, c = 8.536 Å z = 2, V = 402.31 $Å^3$	9
2,4-Dinitrophenol	Orthorhombic, a = 6.122 Å, b = 23.290 Å, c = 5.189 Å z = 4, V = 739.85 $Å^3$	9
Naphthalene–2,4-dinitrophenol	Orthorhombic, a = 23.042 Å, b = 11.968 Å, c = 6.762 Å z = 6, V = 1864.73 $Å^3$	

(ii) When there is some sort of interaction between the reacting components, the unit cell volume of the addition compound may be higher or lower than the sum of the unit cell volumes of the components.

One can write it as

$$U_{diff} = U_{N:DNP} - (U_N + U_{DNP}), \tag{3}$$

where U_{diff}, $U_{N:DNP}$, U_N, and U_{DNP} are the difference of the unit cell volumes, unit cell volumes of naphthalene–2,4-dinitrophenol addition compound, naphthalene, and 2,4-dinitrophenol respectively. On putting the numerical values in Eq. (3), one gets the value

$$U_{diff} = 1864.73\,\text{Å}^3 - (402.31\,\text{Å}^3 + 739.85\,\text{Å}^3) = 722.57\,\text{Å}^3$$

There is an increase in the unit cell volume as a result of interaction between the two components. As a result of this, there is a possibility of formation of cracks and voids during the course of the reaction.

The reaction product is a fine crystalline material having different morphology than those of the reactants. It appears that in the crystal structure of 2,4-dinitrophenol, there are appropriate cavities where the naphthalene molecule can enter easily, resulting in the separation of reaction product. For completion of the reaction, naphthalene molecules must enter into the crystal lattice of 2,4-dinitrophenol, which is possible only when the diffusion occurs through defects, and as such it will involve higher activation energy.

Further, the microstructure of 2,4-dinitrophenol is shown in Fig. 3a. When this was exposed to vapors of naphthalene at 60°C for 10 min, the microstructure changed (Fig. 3b). It appears that naphthalene vapors react rapidly on the surface of 2,4-dinitrophenol, forming a very thin layer of reaction product, which cracks. When the slide with 2,4-dinitrophenol is exposed to the vapors of naphthalene for 1 h, the

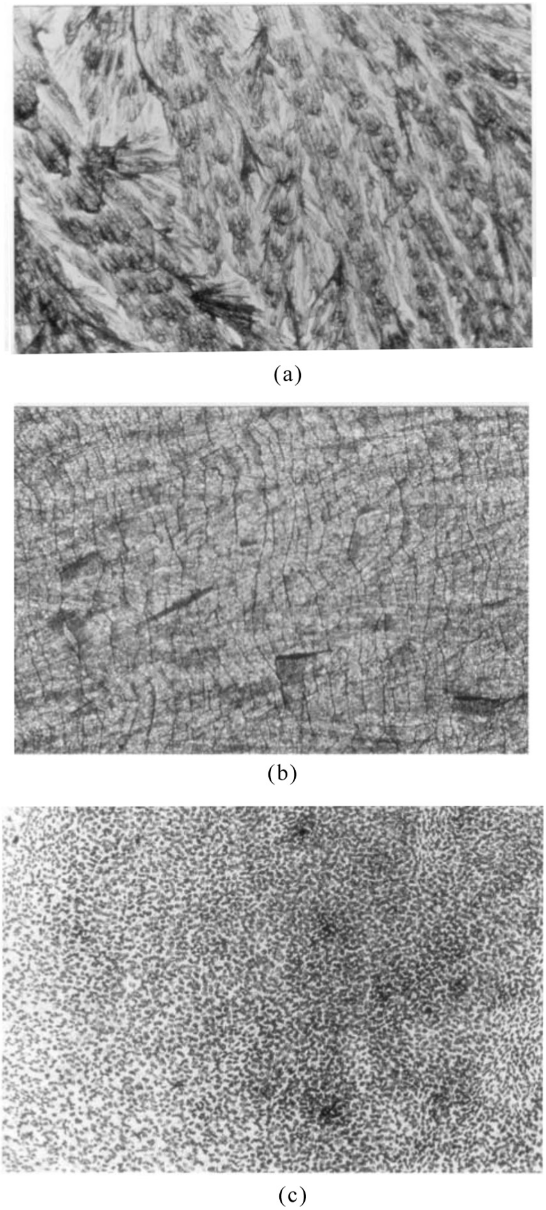

FIGURE 3 (a) Microstructure of 2,4-dinitrophenol, ×150. (b) Microstructure of 2,4-dinitrophenol exposed to the vapors of naphthalene for 10 min at 60°C, ×150. (c) Microstructure of 2,4-dinitrophenol exposed to the vapors of naphthalene for 1 h at 60°C, ×150.

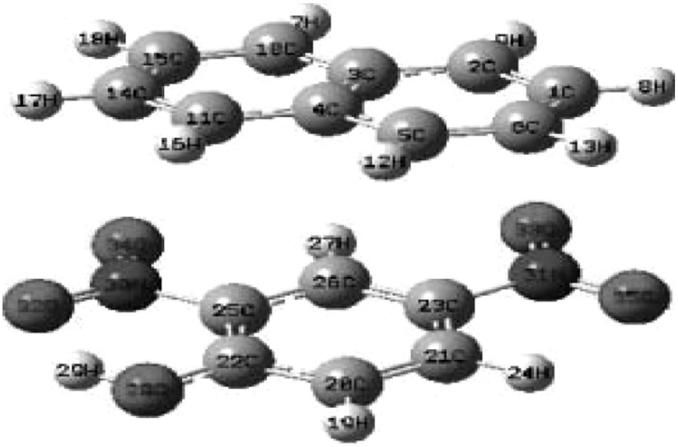

FIGURE 4 Optimized geometry of the complex formed between naphthalene and 2,4-dinitrophenol.

microstructure changed completely and the reaction product appeared in the form of small particles having a rod-type morphology (Fig. 3c). This indicates the possibility of structural change during the solid-state reaction.

The optimized geometry of the complex formed between naphthalene and 2,4-dinitrophenol is shown in Fig. 4, which clearly shows that there is an alternate stacking of the two molecules but that the two planes containing naphthalene and 2,4-dinitrophenol respectively are not parallel to each other. There is a possibility of van der Waals or charge-transfer interaction between the two molecules.

Molecular electrostatic potential surface (MESP) of naphthalene, 2,4-dinitrophenol, and the complex naphthalene–2,4-dinitrophenol were generated (Figs. 5–7). On comparing the top view of

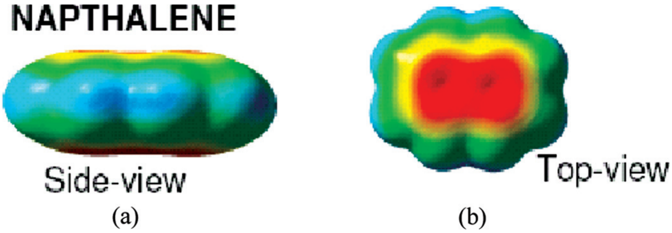

FIGURE 5 Molecular electrostatic potential surface (MESP) of naphthalene. (See COLOR PLATE I)

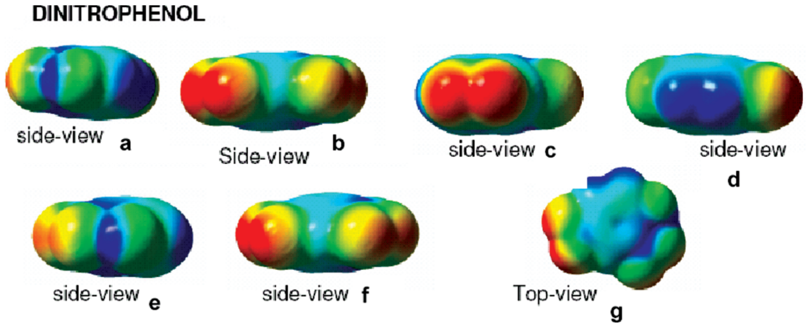

FIGURE 6 Molecular electrostatic potential surface (MESP) of 2,4-dinitrophenol. (See COLOR PLATE II)

naphthalene–2,4-dinitrophenol complex MESP (in which naphthalene is seen from above, (Fig. 7b) with naphthalene top view MESP (Fig. 5b), the color change is noticeable. In Fig. 7b, the color is yellow above the ring, implying lack of electron density, whereas in Fig. 7b, the color is dark red above the ring, which implies that electron density is high. It should be noted that when electron density is high then it is shown by red color, and if there is less electron density, it is shown by blue color. Such observation implies that electron density is getting transferred from naphthalene moiety to 2,4-dinitrophenol, showing the formation of the charge-transfer complex. The same conclusion can be obtained if Figs. 7f and 6g are compared.

In Fig. 7f, the naphthalene–2,4-dinitrophenol complex is seen such that the plane of 2,4-dinitrophenol lies above. The color of the MESP is less blue with a few areas of green color. Such color pattern is not present in Fig. 6g (isolated 2,4-dinitrophenol). Some areas of green color in Fig. 7f imply that electron density has increased because of transfer of electrons from naphthalene to 2,4-dinitrophenol. Thus it

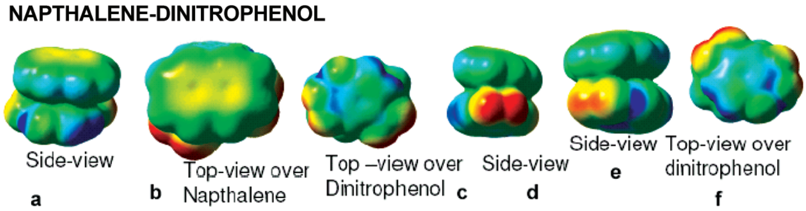

FIGURE 7 Molecular electrostatic potential surface (MESP) of complex naphthalene–2,4-dinitrophenol. (See COLOR PLATE III)

can be seen that electron-charge transfer complex has formed between naphthalene and 2,4-dinitrophenol. The calculated interaction energy for charge-transfer complex is $-2.80\,\text{kcal/mol}$ [RHF/6-31G(d,p) for optimized geometry]. This shows the possibility of charge-transfer interaction between the two components in the addition complex.

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