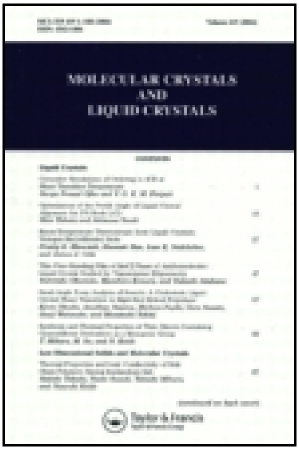

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Chemistry of Binary Organic Eutectics and Molecular Complexes: Phenanthrenem. Nitrobenzoic Acid System

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Chemistry of Binary Organic Eutectics and Molecular Complexes: Phenanthrene-m.Nitrobenzoic Acid System

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Phase diagram, linear velocity of crystallization, thermochemistry, microstructure, electrical conductivity, X-ray diffraction and spectral behaviour of phenanthrene-m.nitrobenzoic acid system have been studied. The results obtained in the present investigation have been discussed in the light of recent advancement in the area of organic eutectics and molecular complexes.

1. INTRODUCTION

The modern age of science demands materials with specific properties. Direct observation of the freezing interfaces of transparent organic systems$^{1-5}$ has been the most useful technique for unravelling the mysteries of solidification, which in turn, control the properties of materials. Because of their potential use in the modern civilization, the metal eutectics and the intermetallic compounds^{6} constitute an interesting area of investigation in metallurgy and materials science. However, due to low transformation temperature, ease in purification, transparency, minimized convection effects and wider choice of materials, organic systems are more suitable for detailed investigation of the parameters which control the mechanism of solidification. In addition, the experimental techniques used for organic systems are simpler and more convenient as compared to those adopted in metallic systems. The above-mentioned inherent physical properties of the organic compounds and the simplicity of their experimentation have prompted a number of research groups$^{1-8}$ to work on some physicochemical aspects of organic eutectics and molecular complexes. As such, in the present article phenanthrene (Ph)-m.nitrobenzoic acid (NBA) system which is an organic analogue of nonmetal-nonmetal system has been undertaken and its phase diagram, linear velocity of crystallization, thermochemistry, microstructure, electrical conductivity, X-ray diffraction and spectral behaviour have been studied.

2. EXPERIMENTAL

2.1 Materials and Purification

Phenanthrene (Thomas Backer & Co., Bombay) was purified by fractional crystallization with ethanol. m.Nitrobenzoic acid (Aldrich, West Germany) was purified by recrystallization from 1 percent hydrochloric acid. The purity of each compound was checked by determining its melting point which was found to be in good agreement with the literature values.

2.2 Phase Diagram

The phase diagram of Ph-NBA system was determined[9-10] by the thaw-melt method.

2.3 Linear Velocity of Crystallization

The linear velocity of crystallization of the pure components, the eutectics and the addition compound at different undercoolings was determined by the capillary[11,12] method.

2.4 Heat of Fusion

The values of heat of fusion of the pure components, the eutectics and the addition compound were determined[13,14] by the DTA method using Stanton Redcroft STA-780 Series Unit.

2.5 Microstructure

To record[15,16] microstructure, a small amount of sample was placed on a glass slide maintained at a temperature slightly above the melting point of the compound. It was then subjected to unidirectional solidification, and optical photomicrographs were recorded using a camera attached with Leitz Laborlux D, Optical Microscope.

2.6 X-Ray Diffraction

X-ray diffraction patterns of pure components, the eutectics and the addition compound were recorded[17,18] on a computerized X-ray diffraction unit, PW 1710 model using Cu—K_α radiation.

2.7 Electrical Conductivity

To measure[19] electrical conductivity of the parent components, the eutectics and the addition compound, the pellets (in the range of 0.8 to 1.7 mm thickness) were prepared using a uniform pressure of 15 tons/cm^2 in a metallic die. The electrical conductivity was measured at 28°C using a digital multimeter (MIC 6000Z). To improve the contact quality, the surface of the pellet was coated with the silver using a vacuum chamber (Hindivac, Vacuum pumping system model-VS-4). The electrical conductivity (E.C.) was calculated using relation.

$$\text{E.C.} = \frac{1}{aR}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

where 1, a and R are width, cross section area and resistance of the pellet, respectively.

2.8 Spectral Studies

Infrared spectra of pure components and addition compound were recorded[20] in the nujol mull in the region of 4000–625 cm^{-1} on a Perkin-Elmer 783 Infrared Spectrometer. Proton NMR spectra of pure components and addition compound were recorded[21] on Jeol, FX 90 Q Fourier Transform NMR spectrometer using $CDCl_3$ as a solvent. Nujol was used as solvent to measure λ_{max} in the UV spectrum of the pure components and the addition compound using a Shimadzu, UV-160A, UV-Visible Recording Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Phase Diagram

The phase diagram of Ph—NBA system, given in Figure 1 in the form of a temperature-composition curve, shows the formation of a 1:2 molecular complex (C) surrounded by two eutectics E_1 and E_2. The melting temperatures of the complex, E_1 and E_2 are 129.5, 94.5 and 125°C, respectively, and the corresponding compositions are 0.665, 0.085 and 0.800 mole fraction of m.nitrobenzoic acid. On addition of NBA in Ph the melting point of the mixture decreases and attains the minimum at E_1 (the first eutectic of the system). With continued addition of the acid, the melting point again rises and attains the maximum at C where the com-

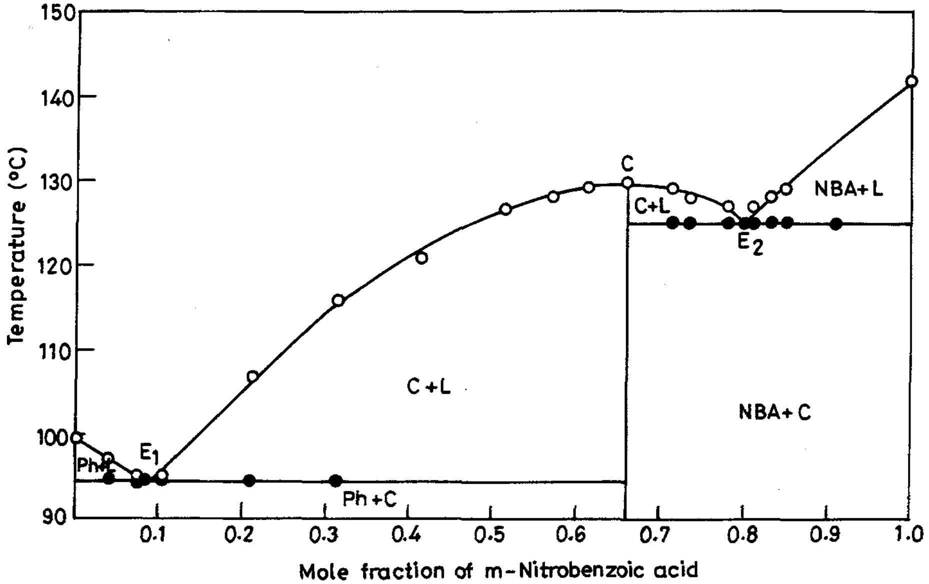

FIGURE 1 Phase diagram of phenanthrene-m.nitrobenzoic acid system. ○ Melting temperature, ● Thaw temperature.

position of solid and liquid phases are identical. This is the congruent melting point of the compound formed in the system. A further increase in the concentration of NBA causes a decrease in the melting point till the minimum at E_2 (the second eutectic of the system) is attained. A flatness of the curve near the melting point of the molecular complex suggests that the addition compound is dissociated[22] in the molten state. At this point the equilibrium reaction[23] can be written as

$$A + B \rightleftharpoons AB(\text{liquid}) \rightarrow AB(\text{solid})$$

when the solid addition compound melts, the components still remain in the associated form as shown above.

3.2 Growth kinetics

According to Hillig and Turnbull,[24] the linear velocity of crystallization (v) is related to undercooling (ΔT) by the expression

$$v = u(\Delta T)^n \tag{1}$$

where u and n are constants depending on the solidification behaviour of materials involved. Equation (1) can be arranged to give

$$\log v = \log u + n \log (\Delta T) \tag{2}$$

Thus, the value of u and n can be evaluated from the plots of log u versus log ΔT for different materials. The linear plots are given in Figure 2 and the values of u and n are reported in Table I. It is evident from the table that the values of u for the eutectics and addition compound are close to two. This suggests a square relationship between the growth velocity and the undercooling. Two theories[25] have been advanced for the growth mechanism which predict that $n = 2$. While one theory is based on the conduction of heat from the tip of the crystal to the surrounding liquid, the other is based on the screw dislocation mechanism of growth.

It is well known that the value of u gives a measure of rate of solidification. Accordingly, it can be inferred from Table I that the solidification rate of the addition compound is lowered than those of the pure components. Studies[26] on crystal morphology of the addition compound indicate that they crystallize as a definite chemical entity. However, during crystallization, the two components from the melt have to enter the crystal lattice, simultaneously, in such a way that the composition of the metal conforms to the respective molar ratios of the two components. Due to this, the linear velocity of crystallization of the addition compound may be expected to be of the order of the growth velocity of the species crystallizing with a lower rate. From the value of u (given in Table I) it can be inferred that the crystallization rate of E_1 is higher than that of the components (Ph and the addition compound) and in the case of E_2 it lies between the end members, namely, NBA and the addition compound. These results can be explained on the basis of the mechanism proposed by Winegard *et al.*[27] According to them, the eutectic

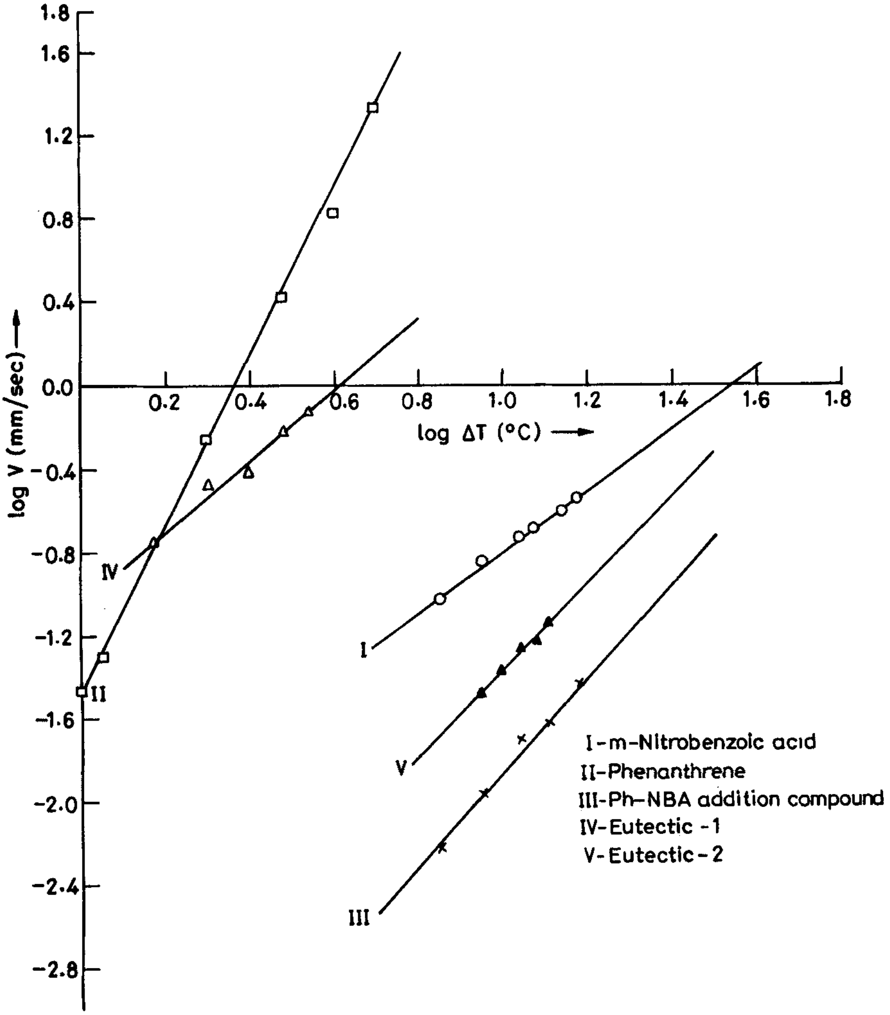

FIGURE 2 Linear velocity of crystallization at various degree of undercoolings for Ph-NBA system.

solidification begins with the formation of the nucleus of one of the phases. This would grow until the surrounding liquid becomes rich in the other component and a stage is reached when the second component starts nucleating. Now, there are two possibilities. First, two initial crystals may grow side by side. This explains the cases in which the rates of solidification of eutectic is not lower than those of the parent components. The second possibility is that there may be alternate nucleation of the two components. This explains the solidification phenomena in the cases where the crystallization velocity of eutectics is lower than that of either component. The solidification of E_1 and E_2 may be accounted by side by side growth of two phases. For both the eutectics the addition compound behaves as one of the components. In the case of E_1 the solidification starts with the nucleation of the addition compound and the two phases grow side by side. On the other hand in the case

TABLE I

Value of u and n

System	u (mm sec^{-1} deg^{-1})	n
Ph-NBA		
Ph	3.39×10^{-2}	4.0
NBA	5.50×10^{-3}	1.5
$Eutectic_1$	9.12×10^{-2}	1.7
$Eutectic_2$	3.63×10^{-4}	2.1
1:2 Addition compound	7.86×10^{-5}	2.3

TABLE II

Heat of fusion, enthalpy of mixing, roughness parameter and interfacial energy

System	Heat of fusion (kJ/mol)		Enthalpy of mixing (kJ/mol)	Roughness parameter $(\Delta s_f/R)$	Interfacial energy (erg/cm^2)
	Experi-mental	Calculated by the mixture law			
Ph	18.12			5.86	22.06
NBA	21.73			6.30	36.57
$Eutectic_1$	14.12	18.51	-4.36	4.62	23.26
$Eutectic_2$	17.46	21.44	-3.98	5.28	33.67
Addition compound	21.25	34.64	-13.39	6.35	31.73

of E_2, the solidification starts with the nucleation of NBA followed by nucleation of the addition compound and the two phases grow side by side.

3.3 Thermochemistry

The experimental values of heat of fusion of pure components, the eutectics and the addition compound are given in Table II. For the purpose of comparison, the values of the heats of fusion of the eutectics calculated by mixture law[28] and that of the addition compound computed by the graphical method[29] are also given in the same table. An appreciable difference between the calculated and experimental values of the enthalpy of fusion suggests[30] that there is sufficient interaction between the components forming the eutectics and the addition compound. Heat of mixing (ΔH_m) which is the difference between an experimental and a calculated value of heat of fusion is given by

$$\Delta H_m = (\Delta_f h)_{exp} - \Sigma(x_i \Delta_f h_i^0) \qquad (3)$$

where $(\Delta_f h)_{exp}$ is the heat of fusion of the eutectic, determined experimentally, x_i and $\Delta_f h_i^0$ are the mole fraction and the heat of fusion of the component i, respectively. It is evident from the values of heat of fusion given in Table II that in all the cases the heat of mixing is negative. Thermochemical studies[31] suggest that the structure of the eutectic melt depends on the sign and magnitude of the enthalpy of mixing. Accordingly, three types of structures are suggested; quasieutectic for $\Delta H_m > 0$, clustering of molecules for $\Delta H_m < 0$ and molecular solution for $\Delta H_m = 0$. The negative values of ΔH_m suggest clustering of molecules in the eutectic melt. The highly negative magnitude of enthalpy of mixing in the case of the addition compound, suggests that these results are quite different from those of the simple eutectic systems where merely ordering of the parent phases in the melts has been suggested. It seems there is considerable enhancement in the interaction due to the presence of a 1:2 molecular complex in the eutectic melt.

The excess thermodynamic function which is defined as the difference between the thermodynamic function of mixing for a real system and the corresponding value for an ideal system at the same temperature and pressure, was calculated to throw light on the deviation from the ideal behaviour. As such, the excess free energy (g^E), the excess enthalpy (h^E) and the excess entropy (s^E) were calculated using the following equation[28]

$$g^E = RT(x_1 \ln\gamma_1^l + x_2 \ln\gamma_2^l) \tag{4}$$

$$s^E = -R\left(x_1 \ln\gamma_1^l + x_2 \ln\gamma_2^l + x_1 T \frac{\delta \ln\gamma_1^l}{\delta T} + x_2 T \frac{\delta \ln\gamma_2^l}{\delta T}\right) \tag{5}$$

$$h^E = -RT^2\left(x_1 \frac{\delta \ln\gamma_1^l}{\delta T} + x_2 \frac{\delta \ln\gamma_2^l}{\delta T}\right) \tag{6}$$

where x_i^l and γ_i^l are the mole fraction and activity coefficient of the component i in the liquid phase, respectively. The activity coefficient of any component (γ_i^l) in the liquid phase was calculated using the equation

$$-\ln x_i^l \gamma_i^l = \frac{\Delta_f h_i^o}{R}\left(\frac{1}{T} - \frac{1}{T_i^o}\right) \tag{7}$$

where $\Delta_f h_i^o$ is the heat of fusion of the component i at melting temperature T_i^o, R is the gas constant and T is the melting point of the eutectic. This equation is derived from considering the general condition of phase equilibrium for the two phases and assuming that heat of fusion is independent of temperature and the two phases are miscible in the liquid phase only. The variation of activity coefficient with temperature was calculated by differentiating equation (7) and taking the slope of the liquidus line near the eutectic point. The values of excess functions are given in Table III. The positive value[32] of g^E suggests that there is strong attractive interaction between like molecules in comparison to that between unlike

TABLE III

Excess thermodynamic functions of eutectics

System	g^E (J/mol^{-1})	h^E (kJ/mol^{-1})	s^E ($Jmol^{-1}K^{-1}$)
Eutectic$_1$	476.6	29.9	79.9
Eutectic$_2$	690.5	4.5	9.5

molecules. The value of h^E and s^E correspond to the excess free energy and are the measures of excess enthalpy of mixing and entropy of mixing, respectively.

It is well known that solidification involves two discrete steps: (i) the formation of tiny stable particle (nucleation) and (ii) the increase in size of these stable particles (growth). While the former step depends on the surface energy and the free energy of a material the latter step depends on the roughness of the solid-liquid interface. According to Chadwick[33] the critical size of the nucleus r* is related to the undercooling (ΔT) by the following relationship:

$$r^* = \frac{2\sigma T_m}{L\Delta T} \tag{8}$$

where σ is the interfacial energy (Table II) and T_m and L are the melting temperature and the enthalpy of fusion of the compound per unit volume, respectively. The interfacial energy required to calculate the critical size of the nucleus from equation (8) was estimated using an empirical equation proposed by Glicksman *et al.*[34] The critical size of the nucleus for the components and the eutectics was calculated at different undercoolings and the values are reported in Table IV. It can be concluded from the data in the table that the size of the critical nucleus decreases with increasing undercooling values.

3.4 X-ray Diffraction

There are conflicting ideas[35,36] about the nature of eutectics. According to one, the binary eutectics are a mechanical mixture of the two components. Another group believes that there is a merging of electron levels at the molecular level. In view of this, some preliminary investigations on X-ray diffraction of the pure components, the eutectics and the addition compounds were carried out and the results are reported in Tables V and VI. It is evident that in the case of E_1 (Table V) the strong reflections of Ph and the addition compound are either absent or show a decrease in intensity in the eutectic E_1. Similarly, in the case of E_2, strong reflections, in general, either show a decrease in intensity or are absent in the eutectic E_2. Thus, the recorded results reveal that for a particular d value there is a marked difference in the relative intensities of the components. Accordingly, for a particular d value, the relative intensity of reflections of Ph and the addition

TABLE IV

Radius of critical nucleus at different undercooling

	Critical radius × 10^6 (cm)				
Material	Ph	NBA	Eutectic$_1$	Eutectic$_2$	Addition compound
Undercoolings (ΔT)					
1.0	16.47				
1.5			13.99		
2.0	8.24		10.49		
2.5			8.39		
3.0	5.49		6.99		
3.5			5.99		
4.0	4.12				
5.0	3.29				
7.0		2.23			2.22
9.0		1.74		2.08	1.73
10.0				1.87	
11.0		1.42		1.70	1.41
12.0		1.30		1.56	
13.0				1.46	1.91
14.0		1.12			1.11
15.0		1.04			1.04

compound varies in E_1. A similar conclusion can be drawn from the data on X-ray diffraction for E_2 reported in Table VI.

If a eutectic is a mechanical mixture of two components, the X-ray patterns of the two components should be exactly superimposed on the eutectic composite. From the X-ray diffraction patterns of the pure components, the eutectics and the addition compound, it is clear that there is a marked difference in the interplanar distances and the relative intensities of the composite material and the individual components. Thus, the X-ray patterns of the pure components cannot be exactly superimposed on the corresponding eutectic composite meaning thereby that the eutectic is not a purely mechanical mixture of two components but also there is orientation of some planes in the composite.

3.5 Microstructure

It is well known that the microstructure of a material plays a very significant role in deciding its mechanical, electrical, magnetic and optical properties. The growth morphology developed by a eutectic system, during solidification, depends on the growth characteristics of the individual constituent phases, on the basis of which phases solidify with either faceted or non-faceted interfaces. This behaviour is related to the nature of solid-liquid interface and can be predicted from the value of entropy of fusion. According to Hunt and Jackson[37] the type of growth from an eutectic melt depends upon a factor α, defined as

$$\alpha = \xi \frac{\Delta_f h}{RT} = \frac{\Delta s_f}{R} \qquad (9)$$

TABLE V

'd' values and relative intensity (RI) of Ph, E_1 and addition compound of Ph-NBA system

Phenanthrene		Eutectic$_1$		1:2 Addition compound	
d (A°)	RI	d (A°)	RI	d (A°)	RI
9.54	100				
		9.10	100	9.05	2
		7.19	4	7.19	37
		6.02	4	6.01	54
5.88	3				
5.0	92			5.03	29
		4.89	27	4.87	9
4.75	15				
		4.62	12		
4.58	34			4.53	4
		4.49	12		
4.40	7	4.30	5		
4.27	16			4.23	5
4.19	14	4.19	9		
4.06	54	4.01	23	4.0	8
3.61	9	3.70	2	3.69	6
3.47	22	3.43	10	3.49	5
3.39	54	3.35	27	3.33	100
3.14	5	3.10	3		
				3.02	17
2.95	4	2.93	2	2.94	4
		2.73	2	2.64	7
2.58	5	2.53	4		
2.54	8	2.45	2	2.45	2
2.36	6	2.35	2	2.35	4
2.07	5	2.18	2	2.16	3
1.95	4	1.99	2	1.97	4
1.82	3	1.80	1	1.80	4

where ξ is a crystallographic factor depending upon the geometry of the molecules and has the value less than or equal to one. $\Delta s_f/R$ which is also known as the Jackson's roughness parameter, is the entropy of fusion in dimensionless unit and R is the gas constant. When α is greater than two, the phases exhibit a faceted growth. On the other hand when it is less than two, it results non-faceted growth. The values of α for the pure components, the eutectics and the addition compound are reported in Table II. These values suggest faceted growth of E_1, E_2 and the addition compounds. The typical microstructures of E_1, E_2 and the molecular complex are given in Figures 3, 4 and 5, respectively. While E_1 shows an irregular

TABLE VI

'd' values and relative intensity (RI) of NBA, E_2 and addition compound of Ph-NBA system

m.Nitrobenzoic acid		Eutectic$_2$		1:2 addition compound	
d(A°)	RI	d(A°)	RI	d(A°)	RI
		14.12	4		
		12.59	4		
				9.05	2
		7.8	9		
		7.2	47	7.2	37
6.55	37				
		6.42	12		
		6.12	35		
		6.03	63	6.01	54
		5.05	33	5.03	29
4.97	7				
		4.88	19	4.87	9
4.79	6	4.70	7		
		4.54	7	4.53	4
4.49	17	4.42	7		
		4.24	8	4.23	5
4.16	7	4.10	9		
4.04	6	4.0	18	4.0	8
3.86	100	3.82	27		
3.60	5	3.69	18	3.69	6
		3.51	14		
		3.45	14	3.49	5
3.39	13	3.33	100	3.32	100
3.25	39	3.23	16	3.23	5
2.97	18	3.02	29	3.01	17
		2.94	11	2.94	3
2.87	12	2.85	8	2.89	3
2.67	11	2.65	10	2.64	4

growth, the E_2 exhibits a radial irregular growth. The microstructure of the addition compound given in Figure 5 shows a radial growth from the nucleation centre.

3.6 Electrical Conductivity

The electrical conductivity of Ph and NBA are 12.8×10^{-9} and 15.8×10^{-9} ohm^{-1} cm^{-1} respectively whereas the electrical conductivity of addition compoound, E_1 and E_2 are found to be 9.0×10^{-9}, 9.9×10^{-9} and 5.9×10^{-9} ohm^{-1} cm^{-1} respectively. From these values it is very clear that there is a slight change in the value of the electrical conductivity of addition compound or eutectics as compared

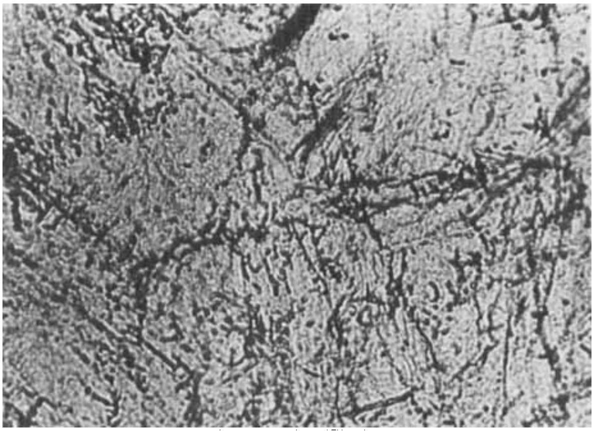

FIGURE 3 Microstructure of directionally solidified Ph-NBA eutectic$_1$ containing 0.085 mole fraction of NBA × 1100.

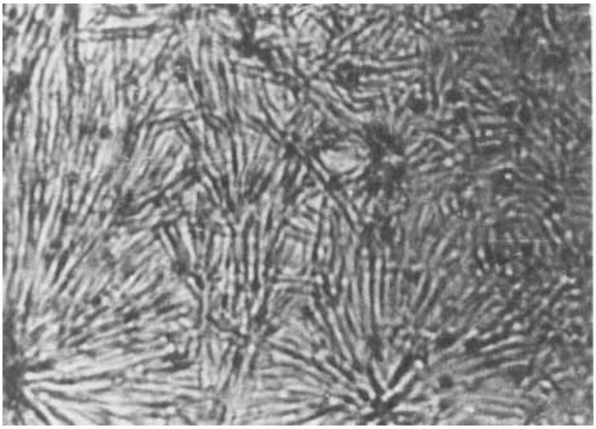

FIGURE 4 Microstructure of directionally solidified Ph-NBA eutectic$_2$ containing 0.800 mole fraction of NBA × 1100.

to that of end components and it can be inferred that the release of electron from the molecule of one component to the molecule of another component does not conduct electricity in the eutectics and in the addition compound of the system.

3.7 Spectral Studies

The UV spectrum of Ph in nujol gives an absorption peak at 378 nm and that of NBA gives an absorption maximum at 336 nm. The addition compound was found to give an absorption maximum at 349 nm. This may be due to formation of a charge-transfer molecular complex between Ph and NBA. In order to assess the nature of bonding between the two components IR and NMR studies were also carried out on the system under investigation. The infrared spectrum of NBA gives a strong peak at 1500 cm^{-1} due to —N═O stretching vibration. The addition

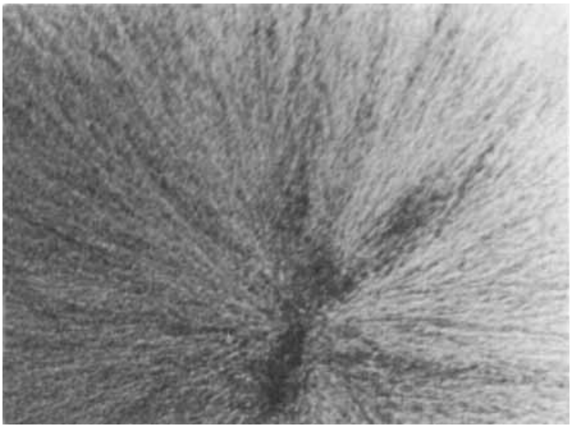

FIGURE 5 Microstructure of directionally solidified Ph-NBA 1:2 molecular complex containing 0.665 mole fraction of NBA × 1100.

compound gives a strong peak at 1485 cm^{-1}. The proton NMR spectrum of NBA gives a signal of $\delta_{11.01}$ due to carboxylic proton. On the other hand, the addition compound shows a proton signal of carboxylic group at $\delta_{11.91}$. The downfield shifting[38,39] of the proton signal in the NMR and low wave number shifting of the —N=O stretching in the compound may be due to the inter-molecular hydrogen bonding between two components forming the molecular complex.

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