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CHEMISTRY OF ORGANIC EUTECTICS AND 1:1 ADDITION COMPOUND: *p*-PHENYLENEDIAMINE–CATECHOL SYSTEM

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ABSTRACT

The phase diagram of the *p*-phenylenediamine–catechol system, determined by the thaw–melt method, shows the formation of a 1:1 molecular compound and two eutectics. The linear velocities of crystallization of the pure components, the eutectics and the addition compound, determined by measuring the rate of movement of the growth front in a capillary, suggest that crystallization data obey the Hillig–Turnbull equation

$$v = u(\Delta T)^n$$

where u and n are constants and ΔT is the undercooling. Experimental values of the heats of fusion and the entropy of fusion and calculated excess thermodynamic functions were considered and the results were explained on the basis of cluster formation in the eutectic melt. X-ray diffraction data of the pure components, the eutectics and the addition compound infer that these eutectics are not simply a mechanical mixture of the two components; preferential ordering of atomic planes occurs during their formation. The IR studies carried out on this system suggest intermolecular hydrogen bonding between the two components which form the molecular compound.

INTRODUCTION

The chemistry of eutectics [1–5] has been actively investigated in recent years due to the unusual physical properties of eutectics which are not normally shown by the parent components. Metallic [6,7] eutectics and intermetallic compounds constitute an interesting area of present investigation in metallurgy and materials science. However, the various studies carried out on these systems are inadequate and incomplete as the high transformation temperatures, opacity and difficulties involved in purification present serious problems. Apart from these problems, large differences in density between the two components forming the metal eutectics causes density driven convection effects, which in turn affect their solidification. Owing to the low transformation temperatures, ease of purification, transparency, lack of convection and wider choice of materials, organic systems [8–13] are more suitable and are therefore used as model systems for

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detailed investigation of the parameters which control solidification. Futhermore the experimental techniques, required for their investigation are simpler and more convenient compared with those adopted in metallic systems.

Most of the organic systems studied in the past have been simple eutectic types. However, there are other types of phase diagram in which two components form a molecular compound [14] with a congruent melting point. The formation of such molecular compounds has been established on the basis of phase diagrams which exhibit a characteristic maximum surrounded by two eutectics corresponding to the stoichiometry of the molecular compound formed. Generally, the growth morphology of the eutectics depends on the growth characteristics of the individual constituent phases. The constituent phases can solidify either with faceted or with non-faceted interfaces. This behaviour is related to the nature of the solid–liquid interface and can be predicted for pure materials from their entropy of fusion data. Hogan et al. [15] have established a unique crystallographic orientation relationship between the constituent phases and their mating planes. Gruzleski and Winegard [6] have observed perfect lamellar grains in Sn–Cd eutectics, but in a number of other systems, the eutectic grains do not exhibit a fixed crystal orientation with respect to external lines of force. Bassi and Sharma [17] have studied the IR spectra of the naphthalene–benzoic acid eutectic system and infer that a specific orientation exists between the constituents.

In order to investigate the mechanism and nature of interactions, the *p*-phenylenediamine(PPD)–catechol(CT) system was studied and its phase diagram, linear velocity of crystallization and heat of fusion were determined. The structures of the eutectics and the molecular compound were also examined using IR and X-ray methods.

EXPERIMENTAL

Materials and purification

p-Phenylenediamine (High Purity Chemicals, India) and pyrocatechol (BDH) were purified by repeated distillation under vacuum and were stored in coloured bottles to avoid exposure to light. Their purity was confirmed by determining their melting points which were in good agreement with literature values.

Phase diagram study

The phase diagram of the *p*-phenylenediamine–catechol system was determined [18,19] by the thaw–melt method. Various mixtures of *p*-

phenylenediamine–catechol covering the complete range of composition were prepared. The appropriate amounts of the two components were placed in long-necked test tubes which were then sealed before melting. The mixtures were subjected to a number of cycles of melting followed by chilling in ice to achieve homogeneity. They were further homogenized by grinding in a mortar, care being taken to avoid moisture or any other contamination. The melting and thaw temperatures were determined using a Toshniwal melting point apparatus.

Linear velocity of crystallization

The linear velocities of crystallization of the pure components, the eutectics and the addition compound were determined by measuring the rate of movement of the growth front in a capillary. The experimental details have been reported previously [20,21].

Heats of fusion

The heats of fusion of the pure components, the eutectics and the 1 : 1 addition compound were determined [22] from their DTA patterns obtained using a Stanton Redcroft STA-780 series unit. All the runs were carried out with a heating rate of 2° C min^{-1}, a chart speed of 10 mm min^{-1} and a chart sensitivity of 200 μV $(20 \text{ mV})^{-1}$. Samples of 5–10 mg were used for each estimation. Using phenanthrene as a standard substance, the heats of fusion of the unknown compounds were determined with the following equation

$$\Delta H = \Delta H_s \times \frac{W_s}{W} \times \frac{A}{A_s} \tag{1}$$

where ΔH is the heat of transition of the unknown sample and ΔH_s is the heat of fusion of the standard substance. W and A are weight and peak area, respectively.

IR studies

The IR spectra of the pure components, the eutectics and the adduct were recorded [23] in nujol mull in the region 4000–600 cm^{-1} on a Perkin–Elmer 783 IR spectrophotometer.

X-ray diffraction studies

X-ray diffraction patterns of the pure components, the eutectics and the 1 : 1 addition compound were recorded on a computerized X-ray diffraction unit, PW 1710 model, using Cu $K\alpha$ radiation.

RESULTS AND DISCUSSION

Phase diagram

The phase diagram of the *p*-phenylenediamine–catechol sytem, given in Fig. 1, shows the formation of one 1 : 1 addition compound with a congruent melting point surrounded by two eutectics E_1 and E_2 containing 0.321 and 0.873 mole fractions of catechol, respectively. The melting temperatures of the molecular complex and the eutectics E_1 and E_2 are 110.0, 100.5 and 92.5 ° C, respectively. For each eutectic, the addition compound serves as one of the components. The maximum in this system is broad, indicating [14] that the addition compound is dissociated in the molten state. From the phase diagram it can also be inferred that the addition compound can exist as a solid compound in equilibrium with a liquid of the same composition. From the first eutectic point E_1, on addition of the second component, the melting point again rises and attains a maximum at C, where the compositions of the liquid and solid phases are identical. The existence of a eutectic point on either side of the maximum provides information about the large stability of the molecular complex formed.

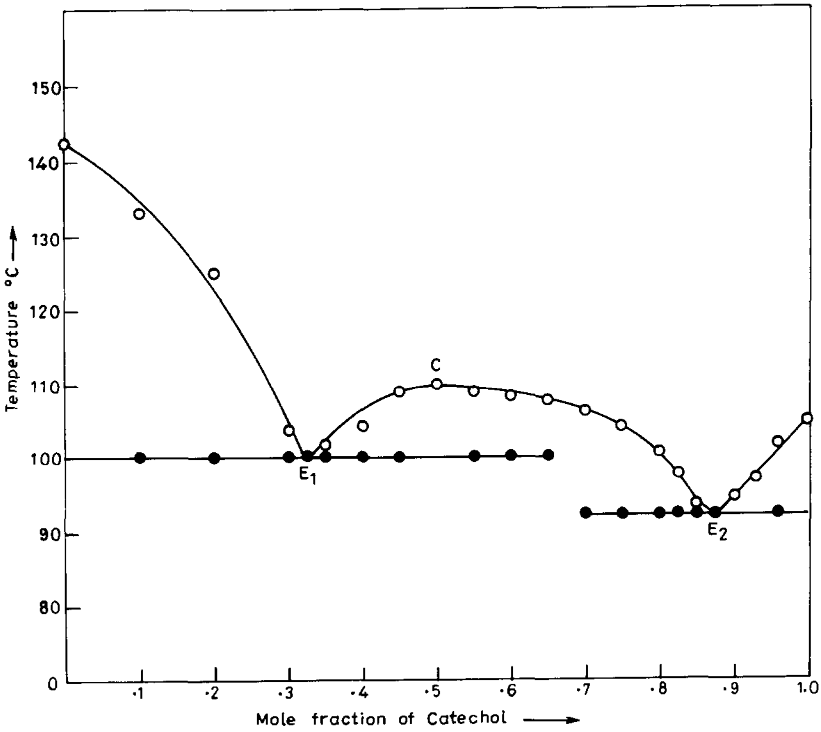


Fig. 1. Phase diagram of the *p*-phenylenediamine–catechol system: o, melting temperature; ●, thaw temperature.

Crystallization kinetics

The linear velocities of crystallization v of the pure components, the eutectics and the 1 : 1 addition compound, determined by measuring the growth rates of the moving front at different undercoolings ΔT, are given in Fig. 2 in the form of log v vs. log ΔT. The linear relationship between growth velocity and undercooling suggests that the crystallization data obey the Hillig–Turnbull [24] relation

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

where u and n are constants depending on the behaviour of solidification of the system under investigation. The experimental values of these constants are given in Table 1. The values of n, which are close to 2, suggest a square relationship between the linear growth velocity and the undercooling. The deviations in the value of n from 2, observed in some cases, may be due to the difference [20] between the bath temperature and the temperature of the growing interface.

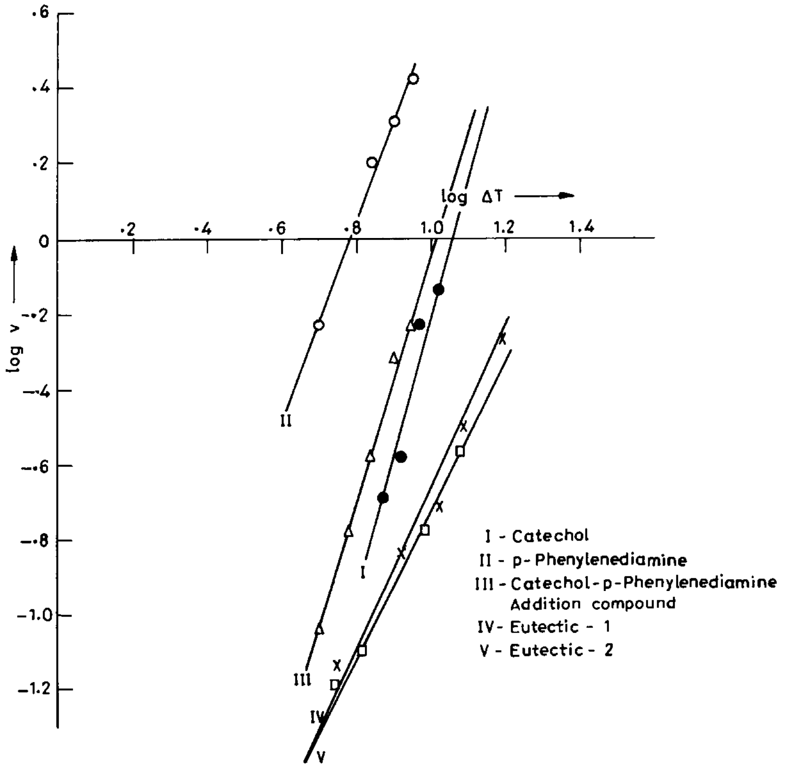


Fig. 2. Linear velocities of crystallization of the pure components, the eutectics and the addition compound at different undercoolings.

TABLE 1

Values of *u* and *n*

Compound	*u* (mm s^{-1} K^{-1})	*n*
p-Phenylenediamine	0.01023	2.60
Catechol	0.0001698	3.30
1 : 1 addition compound	0.0008921	3.20
Eutectic 1	0.00138	2.10
Eutectic 2	0.002042	2.00

From the values of *u*, given in Table 1, it can be inferred that the addition compound of *p*-phenylenediamine with catechol crystallizes at a rate higher than that of catechol and lower than that of *p*-phenylenediamine. Studies on the crystal morphology of the addition compound indicate that it crystallizes 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 melt corresponds to a 1 : 1 molar ratio of the two components. Owing to this, the velocity of crystallization of the addition compound may be expected to be of the same order as the velocity of the species crystallizing at the slower rate.

It is evident from the values of *u* that the crystallization velocities of both eutectics E_1 and E_2 are lower than *p*-phenylenediamine but higher than catechol and the 1 : 1 addition compound. The first eutectic E_1, which has a low molar concentration of catechol, solidifies more slowly than the second eutectic E_2 with a high molar concentration of catechol. These results may be explained on the basis of the mechanism proposed by Winegard et al. [25]. According to them, in a binary system, the eutectic solidification begins with the formation of a nucleus of one of the phases. This will grow until the surrounding liquid becomes rich in the other component and a stage is reached when the second component also starts nucleating. Then there are two possibilities. Firstly, the two initial crystals may grow side by side. This explains the case in which the rates of solidification of the eutectics are 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 case where the crystallization velocities of the eutectics are lower than those of the parent components. Thus, the solidification of the eutectics E_1 and E_2 takes place by side by side growth of the two phases. For eutectic E_1 crystallization starts with the nucleation of *p*-phenylenediamine and the 1 : 1 addition compound and these phases grow side by side. The nucleation of the 1 : 1 addition compound and catechol and their subsequent side by side growth occurs in eutectic E_2.

Thermochemistry

The experimental results of the heats of fusion of the parent components, the eutectics and the addition compound are given in Table 2. If the eutectics were a simple mixture of the two components involving no heat of mixing or any type of association in the melt, the heat of fusion would simply be given by the law of mixtures [26]

$$(\Delta_f h)_e = x_1 \Delta_f h_1 + x_2 \Delta_f h_2 \tag{3}$$

where x_1 and x_2 are the mole fractions and $\Delta_f h_1$ and $\Delta_f h_2$ are the heats of fusion of the parent components 1 and 2, respectively. The heats of fusion, calculated from the law of mixtures are also given in Table 2. It is evident from the table that the value of the heats of fusion calculated using eqn. (3) are higher than the experimental values. This difference can be attributed to the formation of clusters in the eutectic melt. It can be imagined that during cluster formation, heat will be liberated, which may lower the actual values of the heat of fusion. Cluster formation will be favoured if the molecules can associate by certain weak intermolecular forces. In eutectic systems where one or both components contain the hydroxyl group, there will be a tendency to form hydrogen bonds and, as a result, cluster formation will be favoured. This is one of the reasons why the experimental values of the heats of fusion are much lower than those calculated using eqn. (3).

The heat of mixing ΔH_m, which is the difference between the experimental and calculated values of the heat of fusion, can be calculated by

$$\Delta H_m = (\Delta_f h)_{exp} - \Sigma x_i \Delta_f h_i \tag{4}$$

where $(\Delta_f h)_{exp}$ is the heat of fusion of the eutectic determined experimentally and x_i and $\Delta_f h_i$ are the mole fraction and the heat of fusion of the end

TABLE 2

Heat of fusion and entropy of fusion

Material	Heat of fusion (kJ mol^{-1})	Entropy of fusion (kJ mol^{-1} K^{-1} $\times 10^2$)	Roughness parameter ($\Delta S_f/R$)
p-Phenylenediamine	24.86	5.98	7.22
Catechol	22.74	6.02	7.28
Eutectic 1 (experimental)	20.51	5.49	6.63
Eutectic 1 (law of mixtures)	24.18	6.47	–
Eutectic 2 (experimental)	20.70	5.66	6.84
Eutectic 2 (law of mixtures)	23.01	6.29	–
1 : 1 addition compound	18.68	4.88	5.89

components, respectively. In the present system, for both eutectics E_1 and E_2, the values of the heat of mixing are highly negative. Thermochemical studies suggest that the structure of the eutectic melt depends on the sign and magnitude of the enthalpy of mixing. Three types of structures [27] are suggested: quasi-eutectic for $\Delta H_m > 0$, clustering of molecules for $\Delta H_m < 0$ and molecular solution for $\Delta H_m = 0$. The highly negative values of ΔH_m for the eutectics E_1 and E_2 of the PPD–CT system suggest clustering of molecules in the eutectic melt and substantiate the conclusion drawn earlier.

In order to determine the nature of the interactions between the components forming the eutectics, some thermodynamic functions, such as the excess free energy g^E, the excess enthalpy of mixing h^E, and the excess entropy of mixing s^E, were calculated using the following equations

$$g^E = RT\left(x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l\right) \tag{5}$$

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

$$s^E = -R\left(x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l + x_1 T \frac{\delta \ln \gamma_1^l}{\delta T} + x_2 T \frac{\delta \ln \gamma_2^l}{\delta T}\right) \tag{7}$$

The details of the calculation of the excess thermodynamic functions have been reported previously [26]. Values of the excess functions are given in Table 3. The positive values of the excess free energy are a measure of the departure of the system from ideal behaviour and suggest interaction among the components forming the eutectic melt. The negative values of h^E and s^E correspond to the excess free energy and are a measure of the excess enthalpy of mixing and the excess entropy of mixing, respectively.

The entropies of fusion ΔS of *p*-phenylenediamine, catechol, the eutectics and the addition compound were calculated using the following relation

$$\Delta S = \frac{\Delta_f h}{T} \tag{8}$$

where $\Delta_f h$ is the heat of fusion and T is the fusion temperature; they are given in Table 2. In all cases the ΔS values are positive, indicating an increase in randomness during melting. According to Jackson and Hunt [1]

TABLE 3

Excess thermodynamic functions for eutectic 1 and eutectic 2

Excess functions	Eutectic 1 (J mol^{-1})	Eutectic 2 (J mol^{-1})
g^E	138.6	137.1
h^E	−13167.9	−3760.4
s^E	−35.6 [a]	−10.7 [a]

[a] J mol^{-1} K^{-1}.

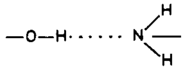
the type of growth from a eutectic melt depends on a factor α, defined by the equation

$$\alpha = \xi \frac{\Delta S_f}{R} \tag{9}$$

where ξ is a crystallographic factor depending on the geometry of the molecules and has values of less than or equal to unity. $\Delta S_f/R$, which is also known as Jackson's roughness parameter (dimensionless), is the entropy of fusion divided by the gas constant R. When $\alpha < 2$, non-faceted growth occurs; when $\alpha > 2$ faceted growth occurs. *p*-Phenylenediamine, catechol, eutectic E_1, eutectic E_2 and the adduct have $\Delta S_f/R$ values of 7.22, 7.28, 6.63, 6.84 and 5.89, respectively, which indicate that they will exhibit faceted growth. The observations made under the microscope confirm this conclusion.

IR studies

The IR spectrum of pure *p*-phenylenediamine shows a band at 3380 cm^{-1}. That of pure catechol has characteristic bands at 3060, 3340 and 3460 cm^{-1}. The peak at 3460 cm^{-1} is due to intramolecular hydrogen bonding. The addition compound has bands at 3380 and 3320 cm^{-1}. The new band at 3320 cm^{-1} may be due to the formation of an intermolecular hydrogen bond [28] of the type indicated below



From the IR spectral studies of the parent components and the addition compound it is concluded that the formation of the 1 : 1 addition compound is due to intermolecular hydrogen bonding between the components; alternate stacking of the molecules occurs in the three-dimensional lattice of the addition compound.

X-ray diffraction studies

The experimental results of some preliminary investigations of the X-ray diffraction of the pure components, the eutectics and the addition compound are reported in Tables 4–6. It is well known that *p*-phenylenediamine and catechol belong to the monoclinic system. It is evident from the *d* spacings of the eutectics E_1 and E_2 that both belong to the same crystal system and have similar lattices. The cell parameters of the pure components, the eutectics and the addition compound are given in Table 6. It is evident from Tables 4 and 5 that the number of reflections of the addition compound is comparable with the number of reflections of the pure compo-

TABLE 4

X-ray diffraction results

p-Phenylenediamine		Eutectic 1		1 : 1 Addition compound	
d(Å)	Relative intensity	*d*(Å)	Relative intensity	*d*(Å)	Relative intensity
–	—	16.05	vw	–	–
11.60	vw	–	–	–	–
–	–	10.39	w	10.39	w
–	–	–	–	9.30	vw
–	–	7.37	vw	–	–
–	–	6.73	vw	6.80	vw
–	–	6.10	vs	6.10	vvs
5.74	vvs	5.80	s	–	–
–	–	–	–	4.86	vw
4.75	vs	4.73	w	4.73	vw
4.42	vs	4.43	vs	4.43	vs
–	–	4.37	vs	–	–
4.18	s	4.18	s	4.19	s
4.02	vs	4.04	w	3.98	w
3.87	vs	3.86	vw	–	–
3.78	s	3.78	vw	3.74	s
3.65	vw	3.70	vw	–	–
–	–	3.59	vw	3.59	vw
3.48	vs	3.50	vw	–	–
3.37	w	3.42	vw	3.42	s
3.31	w	3.30	vvs	3.30	vs
3.27	vs	–	–	–	–
–	–	–	–	3.13	vw
3.08	vs	3.05	s	3.05	s
3.01	w	–	–	–	–
2.88	w	2.90	w	2.93	w
2.81	vw	2.81	vw	2.84	vw
2.74	vw	2.75	vw	–	–
2.68	w	2.65	w	2.65	w
2.54	w	2.53	w	2.53	vw
2.43	w	2.43	w	2.43	w
–	–	2.36	vw	–	–
–	–	2.31	vw	–	–
2.21	vw	–	–	2.19	w
–	–	2.12	vw	2.12	vw
–	–	2.09	vw	2.09	vw
–	–	2.00	w	2.00	w
1.95	w	1.95	vw	1.93	vw
1.88	vw	1.88	vw	1.89	vw
–	–	–	–	1.87	vw
1.82	w	–	–	1.80	vw
1.78	vw	–	–	–	–
–	–	–	–	1.74	vw
1.70	w	–	–	1.70	vw
1.65	vw	–	–	–	–

The classification of the relative intensities of the lines is based on the following criteria: vvs = 90–100; vs = 50–90; s = 25–50; w = 10–25; vw = below 10.

TABLE 5

X-ray diffraction results

Catechol		Eutectic 2		1 : 1 Addition compound	
d(Å)	Relative intensity	d(Å)	Relative intensity	d(Å)	Relative intensity
–	–	14.13	vw	–	–
–	–	13.08	vw	–	–
–	–	10.71	vw	10.39	w
–	–	–	–	9.30	vw
8.86	s	8.84	vs	–	–
–	–	6.80	vw	6.80	vw
–	–	6.10	s	6.10	vvs
5.45	w	5.50	w	–	–
4.79	vs	4.84	vs	4.86	vw
4.70	vw	–	–	4.73	vw
4.43	vw	4.43	s	4.43	vs
–	–	4.28	s	–	–
–	–	4.18	vw	4.19	s
3.84	w	3.86	s	–	–
3.72	w	3.73	s	3.74	s
–	–	–	–	3.59	vw
3.45	vvs	3.46	vvs	3.42	s
–	–	3.30	w	3.30	vs
–	–	–	–	3.13	vw
3.00	w	3.00	vw	3.05	s
2.92	vw	2.96	vs	2.93	w
2.84	vw	–	–	2.84	vw
2.76	vw	2.74	vw	–	–
2.72	vw	–	–	–	–
2.66	w	2.67	s	2.65	w
2.64	vw	–	–	–	–
–	–	–	–	2.53	vw
2.44	vw	2.44	w	2.43	w
2.40	vw	–	–	–	–
2.34	vw	2.34	w	–	–
2.32	vw	2.29	vw	–	–
–	–	–	–	2.19	w
–	–	–	–	2.12	vw
2.08	vw	2.08	w	2.09	vw
–	–	2.03	w	2.00	w
–	–	1.97	vw	1.93	vw
–	–	–	–	1.89	vw
–	–	1.86	vw	1.87	vw
–	–	1.82	w	–	–
–	–	1.79	vw	1.80	vw
–	–	1.76	vw	1.74	vw
–	–	–	–	1.70	vw

The classification of the relative intensities of the lines is based on the following criteria: vvs = 90–100; vs = 50–90; s = 25–50; w = 10–25; vw = below 10.

TABLE 6

Lattice parameters of the pure components, the eutectics and the addition compound

Material	a(Å)	b(Å)	c(Å)	β(deg)
p-Phenylenediamine	8.29	5.93	24.92	112.97
Catechol	17.46	10.74	5.48	94.25
Eutectic 1	10.37	7.37	6.10	52.00
Eutectic 2	14.58	10.72	8.84	57.95
Addition compound	10.26	6.10	4.86	72.00

nents and the eutectics. This suggests that the addition compound also belongs to the monoclinic system. It is also clear from Tables 4 and 5 that the intensities of the reflections diminish with decreasing d values and some reflections in the eutectics have stronger intensities than similar lines in the pure components and the addition compound. Moreover, some lines are absent in the eutectics. The first eutectic (E_1) occurs at a higher molar concentration of PPD; the second eutectic (E_2) occurs at a higher molar concentration of CT; the complex is formed at an equimolar concentration. It can be observed from the X-ray diffraction patterns of the pure components, the eutectics and the complex that for a particular d value there are marked differences in the relative intensities. This may be explained by a structural consideration of the compounds under investigation. It is evident from Table 4 that for a given d value the intensity of eutectic E_1 is closer to that of the addition compound than to the other component PPD. This suggests that the structural character of the addition compound dominates in the eutectic E_1. The absence of such a similarity for the eutectic E_2 (Table 5) infers that E_2 has a mixed structural character with no domination of either component.

The first eutectic (E_1) formed between PPD and the addition compound has some reflections with stronger intensities, i.e. at d values of 6.10, 5.80, 4.43, 4.37, 4.18, 3.30 and 3.05 Å, whereas some reflections of PPD and the molecular complex are missing. In the case of the second eutectic (E_2) formed between CT and the molecular compound a similar trend is observed. In this eutectic the reflections corresponding to d values of 8.84, 6.10, 4.84, 4.43, 4.28, 3.86, 3.73, 3.46, 2.96 and 2.67 Å have stronger intensities. These experimental results infer [19] that the eutectics are not simply mechanical mixtures of the two components; orientation of some atomic planes occurs and a preferential ordering takes place during their formation. These findings are supported by microscopic and spectral studies carried out on this system.

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