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PHASE DIAGRAMS IN THE BINARY SYSTEMS OF 2,4,7-TRINITROFLUOREN-9-ONE WITH AROMATIC AND HETEROAROMATIC COMPOUNDS *

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ABSTRACT

Phase diagrams of the binary systems formed by 2,4,7-trinitrofluoren-9-one (TNF) and naphthalene (N), anthracene (AN), pyrene (P), fluorene (F), dibenzothiophene (DBT) or carbazole (C) have been elaborated by differential scanning calorimetry and hot-stage microscopy. Apart from known 1 : 1 charge transfer complexes, the existence of incongruently melting DA_2 compounds has been found in AN—TNF, P—TNF and C—TNF systems. Evidence of a solid—solid transition in the C · TNF complex is also given.

The literature data for the eutectic temperature and composition in AN—TNF and C—TNF systems have been verified and completed and the melting enthalpies of DBT, C, N · TNF, AN · $(TNF)_2$, P · $(TNF)_2$, F · TNF, DBT · TNF, C · TNF and C · $(TNF)_2$ are given.

INTRODUCTION

The majority of organic solids studied for their electrical conductivity are charge transfer (CT) complexes and there is a large number of publications dealing with the physical properties of these systems. The results, however, are sometimes contradictory. One of the possible reasons is the insufficient definition of experimental materials with regard to their chemical composition (stoichiometry and purity) as well as to their structural features (phase state and crystal perfection). The knowledge of chemical and physical features is of special importance as CT complexes are binary systems for which both stoichiometry and phase state may differ from those expected and thus require a thorough analysis before the conclusions can be drawn.

Unfortunately, knowledge of phase equilibria in binary organic systems has been far from complete hitherto. Their investigation has been greatly simplified by the introduction of differential scanning calorimetry (DSC) as a routine tool. At the same time new, easy and efficient methods of purification have been elaborated and applied in laboratories, especially column and gas chromatography and zone melting. Recently, increasing interest in the

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study of phase equilibria in CT systems has been aroused and new, more reliable data have been published.

Usually, 1 : 1 stoichiometry has been found, but the existence of CT complexes of different stoichiometry has been also observed. Stoichiometry and phase diagrams of systems with CT interactions have been discussed by Pigoń and Chojnacki [1].

The study of phase equilibria in the systems formed by 2,4,7-trinitrofluoren-9-one (TNF) and aromatic hydrocarbons seems to be especially interesting. TNF is frequently used in the identification and separation of aromatic hydrocarbons, particularly of isomeric pairs, due to its ability to form brightly coloured CT complexes of well-defined stoichiometry [2—7]. Moreover, TNF is widely used in electrophotography as an efficient photoconducting component [8]. In spite of this, published data on the phase equilibria of binary systems formed by TNF are scarce. Melting points of TNF CT complexes have been measured by some authors, especially by Orchin et al. [9,10]. The phase diagram of the binary system TNF—1,4-diphenylbutadiene, the only one known at the time the present work was started, has been given in ref. [10].

Laskowski et al. [11—13] published fragmentary data on the melting of eutectics and compounds formed in numerous TNF binary systems. However, neither the stoichiometry of the complexes nor the composition of the eutectics were scrutinized. Among the systems studied by the authors were those of naphthalene, anthracene and carbazole.

In 1975, Casellato et al. [14] published the results of their differential scanning calorimetry investigation of eleven CT complexes of TNF with aromatic hydrocarbons. They determined thermal stability of the complexes as well as the enthalpy and the entropy of melting.

In this work, phase diagrams of binary systems of TNF with several aromatic (naphtalene, anthracene, pyrene and fluorene) and heteroaromatic (dibenzothiophene and carbazole) donors have been studied.

EXPERIMENTAL

Materials

The use of carefully purified substances is a prerequisite for the determination of phase equilibria in binary systems. In this work, zone melting was used as a standard purification procedure and the purity of materials was checked by DSC.

TNF synthesized from fluoren-9-one [10,15] was crystallized from glacial acetic acid, then several times from ca. 50 wt.% nitric acid, washed with water and eventually dried under vacuum over phosphorus pentoxide for 2—4 weeks. Attempts at the purification of TNF by gradient sublimation [16] and by zone melting failed due to its low volatility and low thermal stability. The melting point (T_m) of the TNF batch used in this work was 449.0 K.

Naphthalene (commercial product, POCH) was crystallized from ethanol, sublimed and purified by zone melting (ca. 100 zone passes). T_m = 353.4 K.

Anthracene (pure, POCH) was purified by column chromatography, sublimation and zone melting (ca. 250 zone passes). T_m = 491.3 K.

Pyrene (pure, Fluka) was crystallized from benzene, sublimed and then purified by zone melting (ca. 300 zone passes). T_m = 425.4 K.

Fluorene (for gas chromatography, Serva) was purified by zone melting (ca. 100 zone passes). T_m = 389.0 K.

Dibenzothiophene (synthesized in our laboratory [17]) was steam distilled, sublimed and eventually purified by zone melting (ca. 100 zone passes). T_m = 372.4 K.

Carbazole (pure, Fluka) was crystallized from ethanol, sublimed and purified by zone melting (ca. 150 zone passes). T_m = 519.5 K.

Samples for DSC analysis (ca. 0.5 g each) were weighed with accuracy to 0.00005 g into glass ampoules. The ampoules were evacuated, filled with inert gas (N_2 or Ar, $p = 5 \times 10^4$ Pa) and sealed. The material was then melted and vigorously shaken. After rapid cooling, samples were annealed at 10—20 K below the eutectic melting point for 1—2 weeks and, eventually, slowly cooled to room temperature over 24 h to avoid the segregation of the components by sublimation. Material from the ampoules was ground in an agate mortar and used in DSC experiments. Samples containing volatile donor (naphthalene) were examined immediately after the ampoules were opened.

Apparatus and procedure

Thermal analyses were performed using a Perkin-Elmer DSC 1B apparatus. For microscopic observations, a Boetius hot-stage microscope was employed.

The DSC apparatus was calibrated according to the procedure given by the manufacturer [18], high-purity anthracene specially prepared in this laboratory being used as a standard substance. The use of anthracene as a standard for the DSC of organic systems has advantage over tin or indium, recommended by manufacturer, because similar thermal contact conditions are maintained in the calibration and in the experiments. The same measuring conditions (scanning rate 4 K min^{-1}, sensitivity range 4) were employed in the calibration and in all further experiments. Thus, a fairly good accuracy of temperature determination was attained without a cumbersome procedure of extrapolation to zero heating rate [19,20].

Melting and polymorphic transition temperatures of the pure compounds and CT complexes as well as eutectic and peritectic temperatures have been found by DSC. The positions of the liquidus lines in the diagram were determined by hot-stage microscopy. The samples were heated in sealed glass micro-tubes and the temperature of disappearance of the last crystals noted.

Thermograms were registered from 310 K up to temperature of melting of the whole material for both pure components and for numerous binary samples differing in composition by 5 mole % (mpc) or less. Six binary systems: naphthalene (N)—TNF, anthracene (AN)—TNF, pyrene (P)—TNF, fluorene (F)—TNF, dibenzothiophene (DBT)—TNF and carbazole (C)—TNF were examined. In all experiments, heating runs on virgin samples were recorded. Subsequent runs for the systems forming an incongruently melting

DA_2 complex gave erroneous results due to the appearance of undercooled metastable phases.

Samples (maximum 6 mg in weight) were hermetically sealed in aluminium pans.

The temperatures were determined as those at which the first deflection of the thermogram from the baseline was observed. The reproducibility of transition temperatures determined in independent experiments amounted to ±1 K. The enthalpy of transition was evaluated by planimetering of the peak areas [18] and reduced to 1 average-mole of a given mixture.

The composition of eutectics and terminal phases was evaluated by the Tammann triangle method [21].

RESULTS AND DISCUSSION

Thermal parameters of the pure components as determined in this work are given in Table 1 together with some data previously published.

The phase diagrams of the systems studied are shown in Figs 1—6. The phase transition in TNF, observed in virgin samples only, is omitted in the

TABLE 1

Thermodynamic data of the pure components

Component	Abbreviation	Melting point (K)	Heat of fusion (kJ $mole^{-1}$)	Transition temperature (K)	Heat of transition (kJ $mole^{-1}$)
Naphthalene	N	353.4	18.96		
		352.16 [a]	18.12 [a]		
		353.16 [b]	19.28 [b]		
Anthracene	AN	491.3	28.96		
		492.66 [a]	28.827 [a]		
		489.71 [b]	28.82 [b]		
		492.70 [c]			
Pyrene	P	425.4	17.28		
		424.46 [a]	17.112 [a]		
		423.16 [b]			
Fluorene	F	389.0	19.65		
		385.56 [a]	18.744 [a]		
		387.66 [b]			
Dibenzothiophene	DBT	372.4	22.35		
		372.86 [b]			
		372.16 [d]			
Carbazole	C	519.5	21.17		
		517.66 [b]			
		517.96 [e]			
2,4,7-trinitrofluoren-9-one	TNF	449.0	23.50	428.5	2.9 ± 1.0
		450.16 [f]	23.01 [f]	430.16 [f]	4.184 [f]
		448.36 [g]			

[a] Ref. 22. [b] Ref. 23. [c] Ref. 24. [d] Ref. 25. [e] Ref. 11. [f] Ref. 14. [g] Ref. 10. Remaining values, this work.

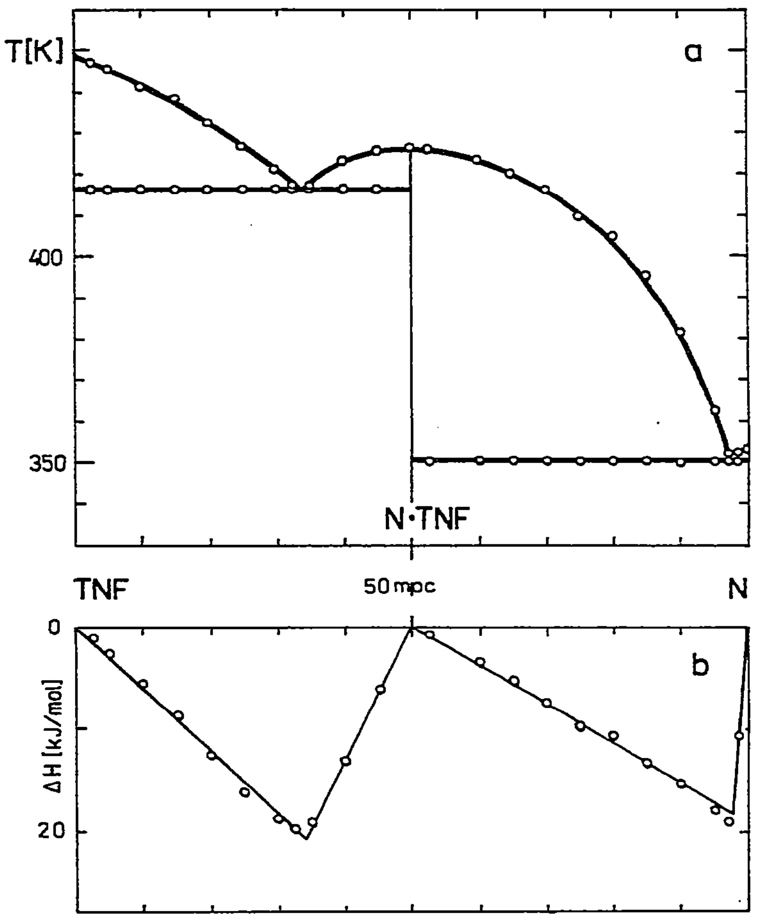


Fig. 1. (a) Phase diagram of the system naphtalene—TNF. o, Liquidus and eutectic lines. (b) Molar heat of eutectic melting vs. composition (for both eutectics).

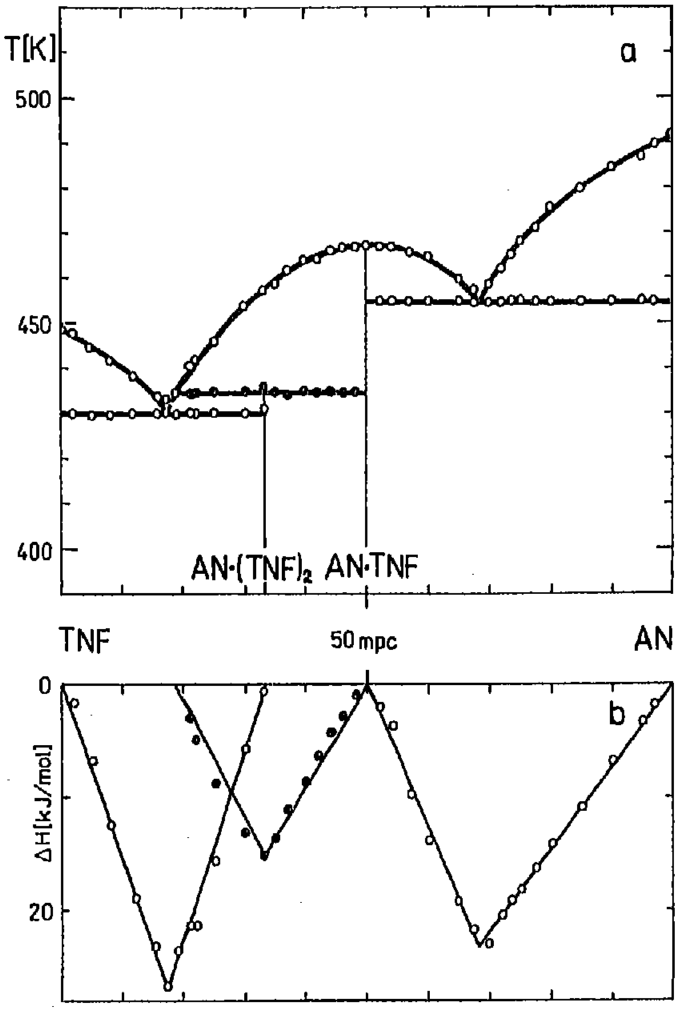
diagrams. It was not observed in annealed samples of either TNF or any binary mixtures containing TNF.

A consistency test is the comparison of the peak value of the eutectic melting enthalpy with the value calculated from the melting enthalpies of the components according to the formula

$$\Delta\mathcal{H}^0_{\mathrm{eut,calc}} = x_{\mathrm{DA}}\,\Delta\mathcal{H}^0_{\mathrm{DA}} + (1 - x_{\mathrm{DA}})\,\Delta\mathcal{H}^0_{\mathrm{X}}$$

where x_{DA} denotes the mole fraction of the complex in the eutectic melt. The differences did not exceed 8% and were mainly due to difficulty in the separation of overlapping peaks.

Characteristic features of the systems are summarized in Table 2. The data in Table 2 are in good agreement with those already published, the main differences being in the eutectic temperatures of the AN—TNF and C—TNF systems in this work and in ref. 11. In ref. 11, the eutectics were erroneously described as those of TNF and the 1 : 1 complex. In fact, the eutectics are formed by the 1 : 2 (DA_2) complex which melts incongruently at higher temperature. In the AN—TNF system, the temperatures of eutectic (430.0



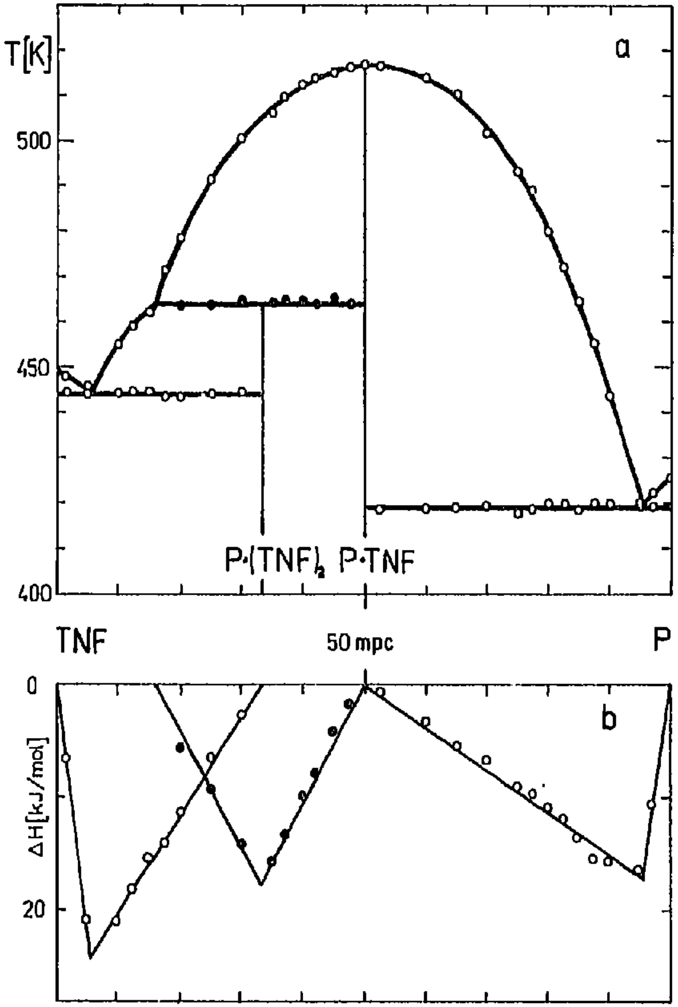


Fig. 2. (a) Phase diagram of the system anthracene—TNF. ○, Liquidus and eutectic lines; ●, peritectic line. (b) Molar heat of eutectic (for both eutectics) and peritectic melting vs. composition.

Fig. 3. (a) Phase diagram of the system pyrene—TNF. ○, Liquidus and eutectic lines; ●, peritectic line. (b) Molar heat of eutectic (for both eutectics) and peritectic melting vs. composition.

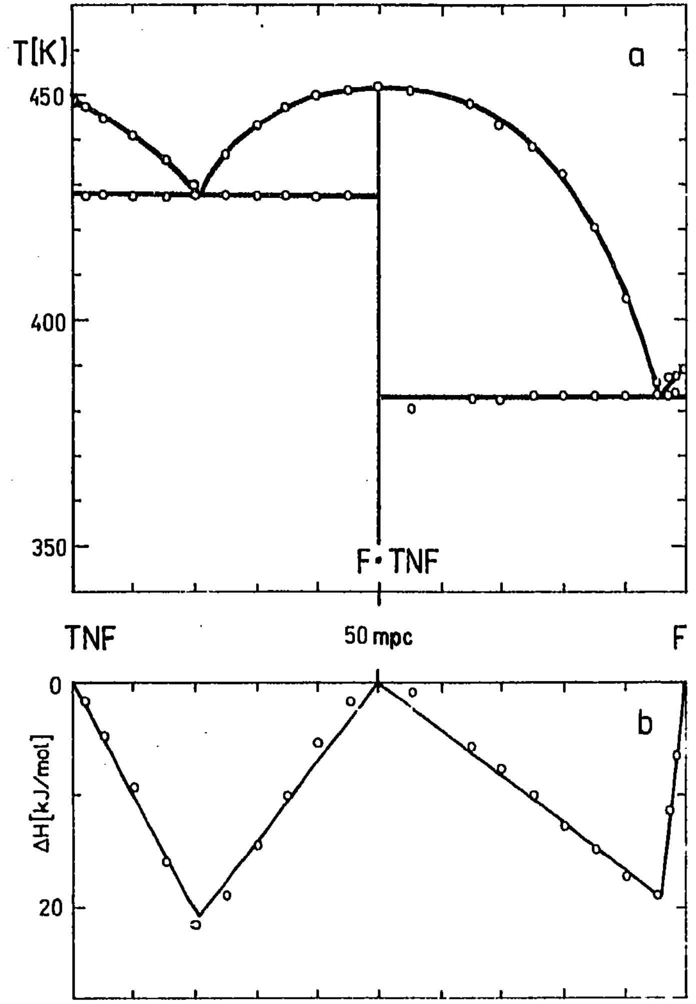


Fig. 4. (a) Phase diagram of the system fluorene—TNF. ○, Liquidus and eutectic lines. (b) Molar heat of eutectic melting vs. composition (for both eutectics).

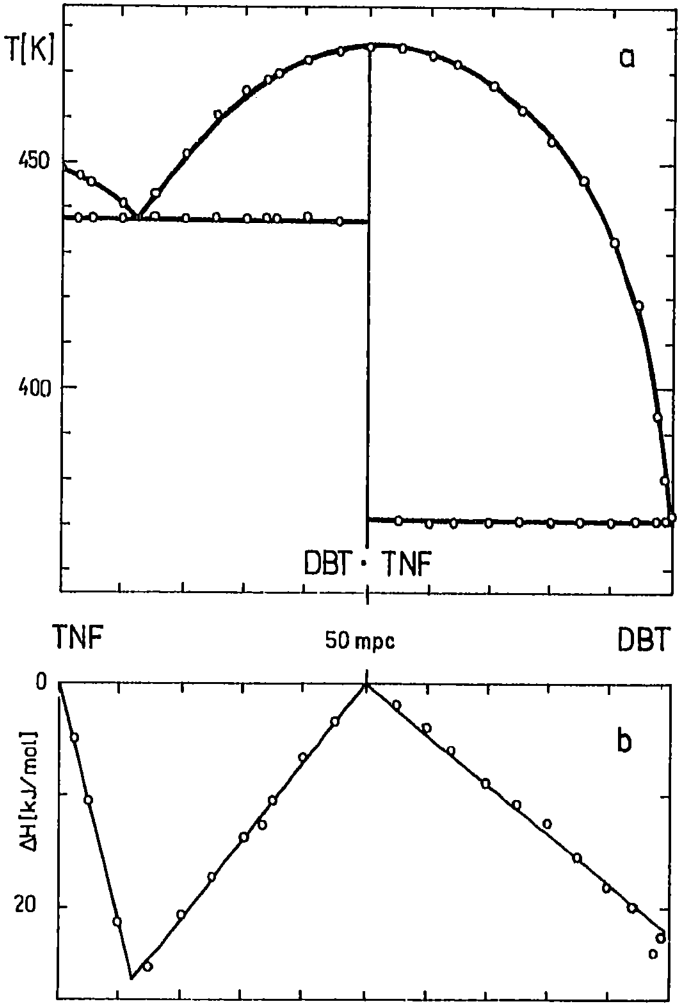
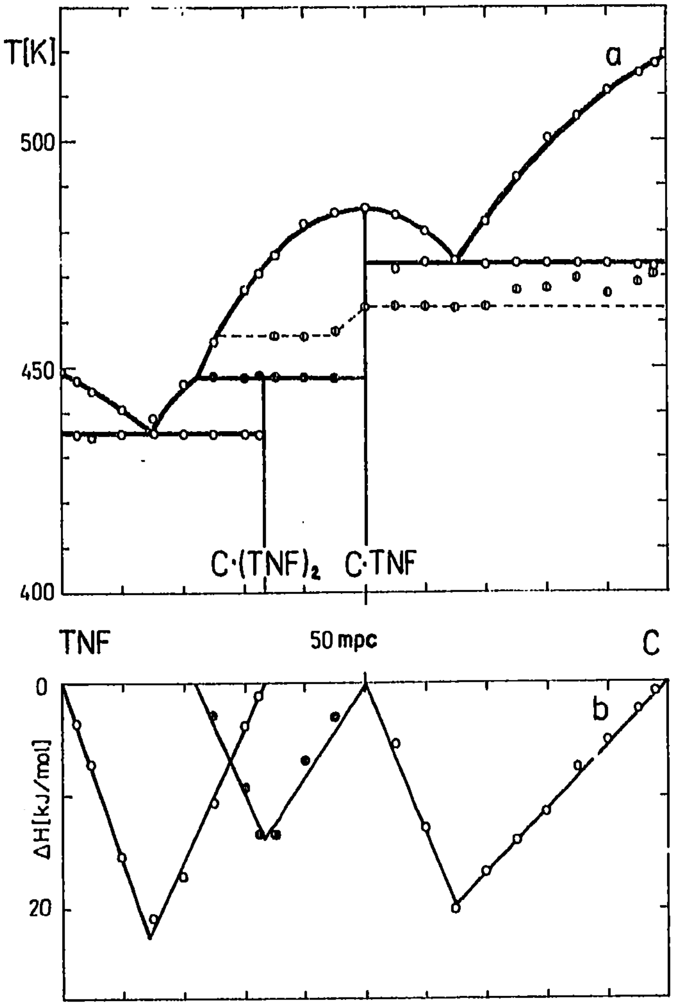


Fig. 5. (a) Phase diagram of the system dibenzothiophene—TNF, ○, Liquidus and eutectic lines. (b) Molar heat of eutectic melting vs. composition (for both eutectics).



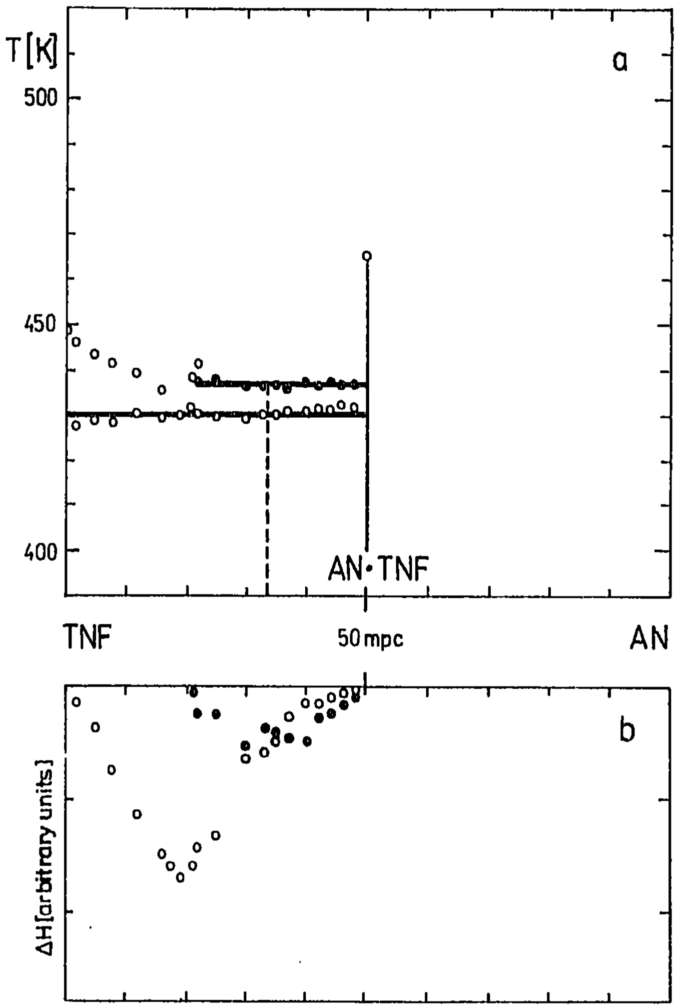


Fig. 6. (a) Phase diagram of the sytem carbazole—TNF. ○, Liquidus and eutectic lines; ●, peritectic line; ⦶, phase transition line. (b) Molar heat of eutectic (for both eutectics) and peritectic melting vs. composition.

Fig. 7. (a) Fragment of phase diagram of a non-equilibrium (metastable) system anthracene—TNF. ○, Liquidus and eutectic lines; ●, peritectic line. (b) Molar heat of eutectic and peritectic melting vs. composition.

TABLE 2

Characteristic data of the binary system TNF—aromatic hydrocarbon and TNF—heteroaromatic compound

System	Stoichiometry of compound D:A	Abbreviation of compound DA or DA_2	Melting point (decomposition) (K)	Heat of fusion (kJ $mole^{-1}$)	Eutectics	Composition at eutectic point (mpc of D)	Temperature of eutectic melting (K)	Colour
Naphthalene—TNF	1:1	N · TNF	426.4	37.76	A—D	34.0	416.6	Light-yellow
			426.86[a]				416.66[a]	
			424.36[b]					
					DA—D	97.5	350.6	
							351.16[a]	
Anthracene—TNF	1:1	AN · TNF	467.0	44.96	A—DA_2	17.5	430.0	Dark-red
			467.06[a]				432.36[a]	
			466.96[c]					
			466.46[d]	45.187[d]	DA—D	68.5	454.6	
							455.36[a]	
	1:2	AN · $(TNF)_2$	(434.4)	(44.40)				
Pyrene—TNF	1:1	P · TNF	516.5	43.55	A—DA_2	5.7	444.0	Dark-red
			515.16[c]					
			519.56[d]	43.932[d]	DA—D	95.5	419.0	
	1:2	P · $(TNF)_2$	(464.0)	(51.97)				
Fluorene—TNF	1:1	F · TNF	451.5	39.55	A—DA	21.0	427.5	Light-brown
			452.6[e]		DA—D	95.4	383.0	
Dibenzothiophene—TNF	1:1	DBT · TNF	476.1	58.69	A—DA	12.5	437.8	Orange
			483.16[f]		DA—D	>99.5	371.1	
Carbazole—TNF	1:1	C · TNF	485.0	38.20	A—DA_2	14.5	435.2	
			484.06[a]				434.46[a]	Dark-red
			446.56[c]					
			463.2[g]	14.70[g]	DA—D	65.1	473.0	
							471.96[a]	
	1:2	C · $(TNF)_2$	(447.8)	(43.09)				

[a] Ref. 11. [b] Ref. 10. [c] Ref. 9. [d] Ref. 14. [e] Ref. 26. [f] Ref. 25. [g] Phase transition in C · TNF 1:1 complex (this paper). Remaining values, this paper.

K) and peritectic (434.4 K) melting are fairly close one to the other and presumably have not been distinguished by the authors [11].

There is also a discrepancy between the melting point of the C · TNF 1 : 1 complex determined by us (485.0 K) and that given by Orchin and Woolfolk [9] (446.56 K). The latter is surprisingly close to the decomposition point of the C · $(TNF)_2$ complex (447.8 K) and one could suppose that the 1 : 2 complex was, in fact, precipitated from solution and studied in ref. 9.

A possible source of erroneous results is the lack of true thermodynamic equilibrium in the samples studied.

Examining unannealed samples (e.g. in a repeated run in DSC) in the TNF—AN · TNF system, we have obtained a phase diagram (Fig. 7) which lacks self-consistency.

For annealed samples, no eutectic arrest at 430.0 K has been observed in samples containing more than 33.3 mole% of anthracene (cf. Fig. 2), which indicates that the formation of the DA_2 complex from DA is a fairly slow reaction that is not completed during the cooling of the samples melted in DSC experiments. In an additional experiment, we detected the presence of the metastable phase even after annealing the samples at 420 K for more than 50 h. Similar behaviour has been found in other systems where 1 : 2 complexes are formed.

Annealing was also necessary to observe the phase transition in the C · TNF 1 : 1 complex. This transition, which occurs in the complex at 463.2 K and is accompanied by an enthalpy change of +14.7 kJ mole^{-1}, is absent in the unannealed samples, but partially recurs in those stored for several months at room temperature. Transition temperature depends on sample composition, being equal to 457.0, 463.2 and 467.0 K for samples containing 30—45, 50—70 and over 70 mole% of carbazole, respectively.

The thermodynamic discussion of the systems described will be given elsewhere [27].

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