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CALORIMETRIC STUDIES OF BINARY SYSTEMS OF 1,3,5-TRINITROBENZENE WITH NAPHTHALENE, ANTHRACENE AND CARBAZOLE. I. PHASE TRANSITIONS AND HEAT CAPACITIES OF THE PURE COMPONENTS AND CHARGE-TRANSFER COMPLEXES

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ABSTRACT

The enthalpies and temperatures of fusion and solid—solid transitions and the heat capacity curves for naphthalene (NAP), anthracene, carbazole, 1,3,5-trinitrobenzene (TNB) and charge-transfer complexes of TNB with these donors have been determined by using a Perkin-Elmer DSC-1B scanning calorimeter in the temperature range 180 K to just below the melting point.

Three modifications of TNB, one stable and two metastable, with melting points 398.4, 380.3 and 383.0 K, have been observed. Two phase transitions in the NAP—TNB complex, at 220 and 424.5 K, have been revealed. The probable nature of the phase transitions is discussed.

The quantity ΔC_p, where $\Delta C_p = C_p$ (complex) — C_p (donor) — C_p (TNB), is negative at higher temperatures, being equal to zero or positive at 180 K. This result is interpreted as an indication of a decrease in the complex stability in the solid state with decreasing temperature.

INTRODUCTION

The most striking effect observed in binary mixtures of 1,3,5-trinitrobenzene (TNB) with some aromatic hydrocarbons is the formation of crystalline, coloured solid compounds, usually of equimolar composition, named CT complexes. Melting of these molecular compounds gives the coloured melts, indicating the existence of complexes also in the fused state. The physical and chemical properties of these compounds have received considerable attention [1].

An earlier study on electrical conductivity [2] indicated that minute deviations from a stoichiometric ratio of complex could generate remarkable changes of some physical properties. Therefore a detailed recognition of phase relations in these systems seems to be a precondition of further examinations. The stability of the complex both in the solid and fused state is also an interesting question.

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For these reasons we carried out the calorimetric studies on a series of binary systems of TNB with three donors: naphthalene (NAP), anthracene (ANT) and carbazole (CAR). The melting point diagrams for these systems, as reported many years ago [3—5], evidenced the 1 : 1 complex formation in all three systems.

The results of measurements of the thermodynamic properties such as the heat capacity, enthalpy of fusion, enthalpy of the solid—solid transition of pure components and complexes, a detailed discussion of the probable nature of the observed transitions, as well as the problem of complex stability in the solid state, are presented in Part I of this work. Part II reports the revision of the phase diagrams of binary systems of TNB with three selected donors. An attempt to estimate the stability of the complex in the fused state has also been made.

EXPERIMENTAL

Initial purification was carried out by recrystallization as follows: naphthalene from benzene, anthracene from toluene, carbazole and 1,3,5-trinitrobenzene from methanol. All the compounds were subsequently purified by vacuum sublimation and zone-refining; approximately 100 zone passes were made.

Special care had to be taken to ensure the exact stoichiometric ratio of the molecular complexes: all the complexes were prepared by weighing stoichiometric amounts of the components into a glass tube, followed by further zone-refining. The exact compositions of the eutectic mixtures were obtained in the same way.

The thermograms and heat capacity measurements were made using a Perkin-Elmer DSC-1B scanning calorimeter, the masses of samples being 10—20 mg for the heat capacity measurements and 5—10 mg for the DSC traces.

The thermograms were recorded at four heating rates: 4, 2, 1 and 0.5 K min^{-1}. The temperatures of the onset and the end of a transition peak were plotted against the square root of scan rate and extrapolated to zero heating rate. This procedure resulted from the working principle of the calorimeter [6] and will be discussed in detail elsewhere.

The temperatures and enthalpies collected in Table 1 represent the arithmetic means of at least five determinations for different samples and the standard deviations amount to ± 0.3 K and ± 400 J mole^{-1}, respectively.

The heat capacity measurements from 180 K to a few degrees below the melting point were made on two samples of each compound (two runs were made for each sample) at heating (or cooling) rates of 2 and 4 K min^{-1}. The samples for heat capacity measurements were either in the form of pressed pellets or as single-crystalline boules. The plots of heat capacity vs. temperature are derived from the results of at least four runs. The standard deviation of C_p measurements amounted to ± 2.5 J K^{-1} mole^{-1}. A comparison of our C_p measurements for anthracene with the data reported by Goursot et al. [7] indicated that there is quite good agreement between the results ob-

TABLE 1

Temperatures and enthalpies of fusion and transitions of components and complexes in the binary systems of 1,3,5-trinitrobenzene (TNB) with naphthalene (NAP), anthracene (ANT) and carbazole (CAR)

Compound	Fusion		Transition		Ref.
	T_f (K)	ΔH_f (kJ mole^{-1})	T_t (K)	ΔH_t (kJ mole^{-1})	
NAP	353.3	19.0			This work
	353.45	18.991			20
ANT	490.6	29.0			This work
	488.97	29.39			7
	490.0	27.97			21
CAR	521.2	27.2			This work
	519.3	26.92	420	0.274	21
TNB I	398.4	15.0			This work
	394.2	22.61			15
	396.7				8
TNB II	380.3	14.8	Approx. 370	1.9	This work
	379.2				8
TNB III	383.0	13.2			This work
	382.2				8
1 : 1 NAP—TNB	430.8	31.9	Approx. 220	1.7	This work
			424.5	1.6	This work
	424.2		422.2		12
1 : 1 ANT—TNB	438.6	40.4			This work
	438.7	39.77			15
	415.2				16
1 : 1 CAR—TNB	477.5	43.7			This work

tained by us and those from adiabatic calorimetry. In the low temperature range this difference was equal to zero and amounted to about 10 J K^{-1} mole^{-1} just below the melting point.

RESULTS AND DISCUSSION

Thermograms of the components and complexes

No anomalies on the thermograms of naphthalene, anthracene and carbazole were observed on heating from 180 K to just below the melting point.

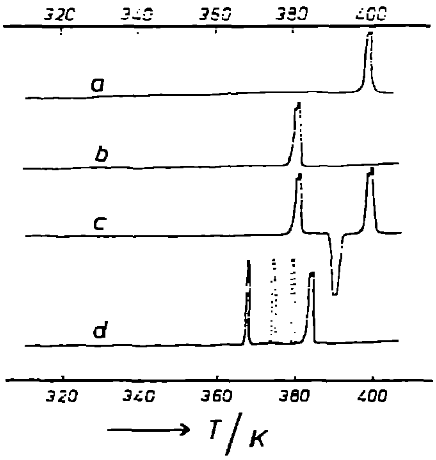
Kofler and Brandstätter [8] have reported the existence of five modifications of 1,3,5-trinitrobenzene. Our investigations, however, indicate that only three forms of TNB can be obtained: one stable and two metastable. Figure 1 shows the thermograms of TNB samples over the temperature range 310—410 K. No irregularities were observed on the thermograms from 180 to 310 K.

Most frequently "a" and "b" thermograms were observed. Thermogram "a" corresponds to the stable polymorph of TNB, whereas "b" refers to the metastable modification, and occasionally we observed the behaviour as shown on the "c" thermogram, i.e. on one heating run the same sample fused at approximately 380 K, froze and melted again at about 398 K. Such thermal behaviour of TNB was also observed microscopically.

Among the 40 thermograms of nine different samples of TNB we found only four thermograms of "d" type, where the solid—solid phase transition occurred before melting. This transition was strictly isothermal but its temperature was irreproducible (dashed lines in Fig. 1d).

Based on our data we have proposed the schematic diagram illustrating the stability of each form of TNB (Fig. 2). Thermodynamically stable modification I (m.p. 398.4 K) can be obtained directly from the melt, vapour and from some solvents: acetone, chloroform, tetrahydrofurane. Crystallization of TNB from benzene and CCl_4 gave the addition compounds: TNB + solvent, with melting points 347.5 and 332.0 K, respectively.

Metastable modification II of TNB (m.p. 380.3 K) may be easily obtained



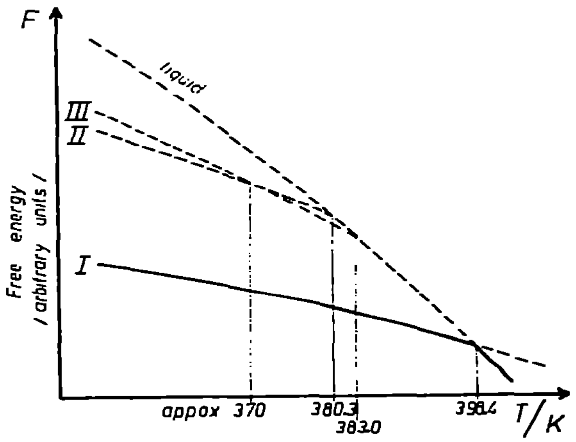


Fig. 1. Selected thermograms of 1,3,5-trinitrobenzene samples recorded at a heating rate of 2 K min^{-1}. See the text for explanations.

Fig. 2. Schematic stability diagram of the polymorphic forms of 1,3,5-trinitrobenzene.

on rapid cooling of the melt, especially if the melt has been heated at approximately 450 K for several hours. Modification II is stable for several months under ambient conditions.

At present, we are unable to give a reliable formula for initiating the transposition of modification II to III (m.p. 383.0 K). The investigation of this transition is difficult, since both forms are metastable and accidental agents can provoke the transposition.

The 1,3,5-trinitrobenzene molecule in the gas phase is non-planar and the deviations of all three NO_2-groups from the benzene ring plane amount to 20.8° [9]. In the crystalline state, these bendings are smaller but the TNB molecules are also non-planar [10]. It seems that three forms of the TNB molecule can exist. If all three NO_2-groups are bent on the same side of the ring plane two forms, left and right, are possible. A third molecule form can be realized if two NO_2-groups are bent on the same side, the third on the opposite one. The latter form would be optically inactive.

In our opinion the three modifications of TNB can be related both to different structures of the TNB molecule and to different structures of the crystalline lattice. This supposition will be verified by X-ray examination of TNB polymorphs.

Figure 3 shows typical thermograms of the NAP—TNB complex over the temperature range 180—440 K. Marked thermal anomalies with maxima at about 220, 424.5 and 430.8 K are evident, the latter being the melting transition.

The sharp exothermic phase transition at 220 K was observed only when the first cooling run was made. In the first heating cycle this peak disappeared and an endothermic shift of the baseline from 220 up to room temperature, with a maximum at about 280 K, was observed. After several runs both peaks (at 220 and 280 K) disappeared, both in the cooling and in the heating cycles. A broad maximum in this temperature range was observed. If the NAP—TNB complex sample was held over boiling nitrogen,

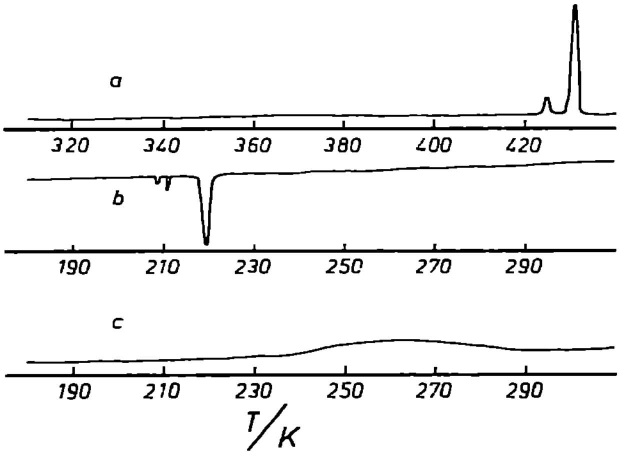


Fig. 3. Thermograms of the 1 : 1 naphthalene—TNB complex recorded at a heating (or cooling) rate of 2 K min^{-1}. a, heating from 310 to 410 K; b, cooling from 310 to 180 K (first run); c, heating from 180 to 310 K (for sample after several runs).

this transition could be observed visually as a sudden, mechanical disintegration of the sample, with a simultaneous disappearance of the yellow colour.

Two different explanations for these observations can be proposed: first, the NAP—TNB complex undergoes a certain structural phase transition; second, the NAP—TNB complex breaks up into two components in the solid phase when the temperature is decreased below 220 K. In our opinion, the second explanation is the more probable. The bending of the baseline on the DSC trace and also the changes in the heat capacity curve of the NAP—TNB complex on heating (see below) can be interpreted as a gradual formation of the complex, starting at 220 K up to room temperature. Identification of the transition at 220 K as the dissociation of the complex is also supported by our NMR measurements [11].

The phase transition just below the melting point of the NAP—TNB complex (at 424.5 K) has been reported by Kofler [12]. Our NMR data [11] indicate that a diffusional phase exists from 424.5 K to the melting point.

Phase transitions at 220 and 424.5 K were also observed in mixtures of TNB—NAP of composition $x = 0.5$, as shown in the phase diagram of the NAP—TNB system [13].

The thermal behaviour of the ANT—TNB complex is still in doubt despite the fact that it is one of the most thoroughly studied weak charge-transfer complexes. For example, several workers [12,14,15] agreed that the melting point of the ANT—TNB complex was 438 K. However, Boeyens and Herbstein [16] reported a melting point of 415 K.

In our calorimetric studies on the ANT—TNB complex from 180 K to the melting point, neither the thermograms nor the heat capacity curves displayed any phase transitions. However, Beckman et al. [17], by virtue of Raman and fluorescence spectra, suggest that the existence of a continuous, structural phase transition in the ANT—TNB crystals between 80 and 150 K is quite probable. In our opinion the colour change of the ANT—TNB crystal from orange to pale yellow on cooling to liquid nitrogen temperature [18] can also be considered as an indication of some phase transition.

Our electrical conductivity studies and charge-carrier mobility measurements [2,19] indicate that some samples of the ANT—TNB complex undergo a phase transition at about 350 K. This phase transition was observed in several samples but more frequently in the single-crystals grown from melt than in the pressed powder. The measurements of the spin-lattice relaxation time T_1 for the ANT—TNB complex from room temperature to the melting point [11] evidenced the existence of some molecular disorder which can be attributed to a rotational motion of the TNB molecules (jumping by 120° C), with some contribution from translational motions of TNB or anthracene molecules.

This observation may be explained if it is assumed that the thermal behaviour of the ANT—TNB complex is similar to that of TNB. Probably, in our calorimetric studies we dealt only with stable modification I (m.p. 438 K), whereas Boeyens and Herbstein [16] may have been working with metastable modification II (m.p. 415 K). In our electrical studies we observed both modifications I and II, the latter transformed into form III, with a melting point intermediate between 415 and 438 K. However, the existence of modification II and the phase transition in the ANT—TNB complex are not evidenced by our calorimetric studies and therefore the relevant data are not included in Table 1.

No phase transition in the CAR—TNB complex was observed over the entire temperature range studied. Some thermodynamic properties of the components and complexes in the binary systems of TNB with the studied donors are collected in Table 1.

Heat capacity of the components and complexes

The heat capacity results for 1,3,5-trinitrobenzene and the 1 : 1 NAP—TNB complex are shown in Fig. 4 together with the data reported by McCullough et al. [20] for naphthalene.

All three forms of TNB have been investigated in heat capacity measurements. The C_p values for modifications II and III are virtually identical. The decrease in heat capacity on going from metastable modifications II and III to stable polymorph I is unquestionable, despite the relatively poor accuracy of the C_p measurements. In Figs. 5 and 6 the heat capacity curves for TNB are plotted as smooth lines from a representative selection of the experimental results.

As described above, the NAP—TNB complex undergoes a phase transition at about 220 K but the marked peak in the thermogram was observed only in the first cooling cycle. This phase transition manifests itself by an increase in heat capacity. In the subsequent heating cycle, the heat capacity values were slightly higher than those obtained in the cooling run, and the equalization of the C_p values took place in the room temperature region.

Inspection of Figs. 5 and 6 shows that the heat capacity curves for the

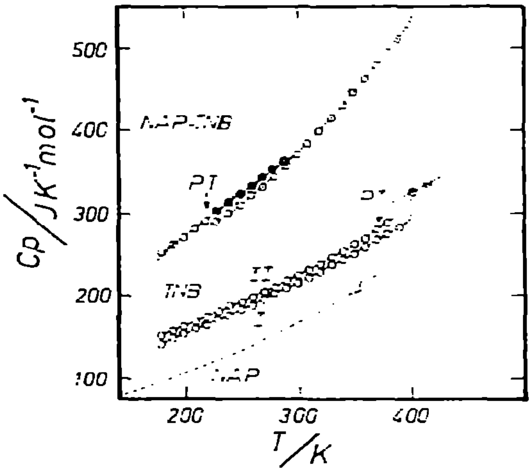
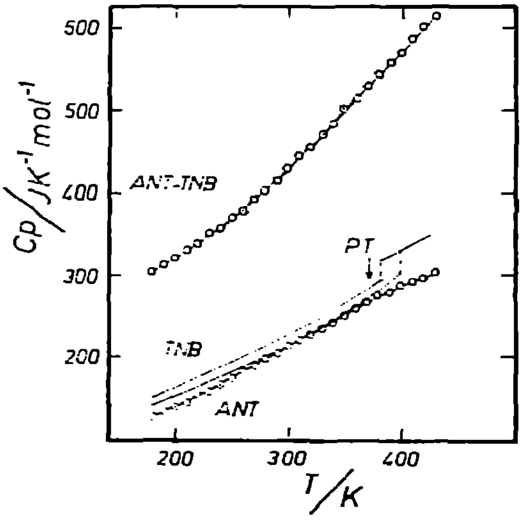


Fig. 4. The temperature dependence of the heat capacity C_p for naphthalene (NAP) (from data in ref. 20), 1,3,5-trinitrobenzene (TNB I and TNB II), and for the 1 : 1 NAP—TNB complex. For the NAP—TNB complex a hysteresis of the heat capacity curve was observed from 220 K to room temperature. ●, First heating run; ○, first cooling run. Dotted lines designate the quantities: C_p (TNB I) + C_p (NAP) and C_p (TNB II) + C_p (NAP).



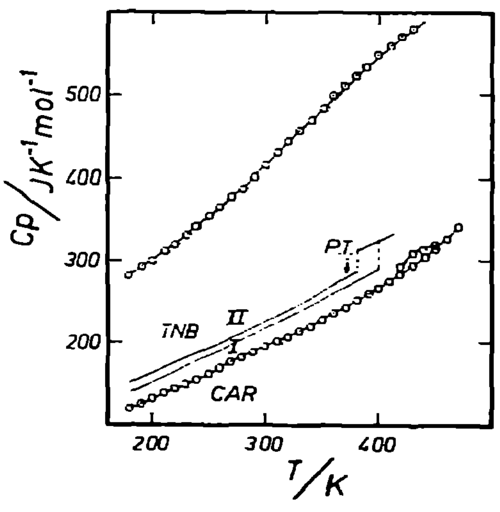


Fig. 5. The temperature dependence of the heat capacity C_p for anthracene (ANT), 1,3,5-trinitrobenzene (TNB) and the 1 : 1 ANT—TNB complex. Dotted lines designate the quantities: C_p (TNB I) + C_p (ANT) and C_p (TNB II) + Cp (ANT).

Fig. 6. The temperature dependence of the heat capacity C_p for carbazole (CAR), 1,3,5-trinitrobenzene (TNB) and the 1 : 1 CAR—TNB complex. Dotted lines designate the quantities: C_p (TNB I) + C_p (CAR) and C_p (TNB II) + C_p (CAR).

ANT—TNB and CAR—TNB complexes are of the normal sigmoid shape expected for compounds exhibiting no thermal anomalies.

The heat capacity curve for the carbazole reveals the small anomaly at about 420 K, which appeared in one out of four runs, depending upon the thermal history of the sample. We consider this anomaly as arising from the phase transition in carbazole, previously reported by Robinson and Scott [21].

The experimental C_p values for the compounds considered here were fitted to the polynomial

$$C_p = A + BT + CT^2$$

by the least squares method. The values of A, B and C are given in Table 2.

The quantities of ΣC_p, where $\Sigma C_p = C_p$ (TNB) + C_p (donor), are drawn in Figs. 4—6. The values of ΣC_p were calculated using the data of McCullough et al. [20] for naphthalene and our results obtained for other components under consideration. Two ΣC_p curves corresponding to the stable and metastable modifications of TNB are plotted.

It is interesting to compare the experimental heat capacity curve for the complex with the quantity ΣC_p. According to Clayton et al. [22], in a "normal" case the heat capacity values of the complex should be lower than the quantity ΣC_p at any temperature. The enhancement of attraction between donor and acceptor molecules in the complex places some restriction on the inter- and intra-oscillations of the molecules which involve the diminution of the C_p(complex) value with respect to that of ΣC_p.

In our measurements the difference between the heat capacity of the com-

TABLE 2

Values of A, B and C coefficients in the equation

$$C_p = A + BT + CT^2$$

for components and complexes in the binary systems of 1,3,5-trinitrobenzene (TNB) with naphthalene (NAP), anthracene (ANT) and carbazole (CAR)

Compound	Temp. range (K)	A ($\mathrm{J\ K^{-1}\ mole^{-1}}$)	B ($\mathrm{J\ K^{-2}\ mole^{-1}}$)	$C \times 10^4$ ($\mathrm{J\ K^{-3}\ mole^{-1}}$)
NAP	220—400	+52.00 [a]	+0.07083 [a]	+10.417 [a]
ANT	180—430	—14.20	+0.7973	—1.333
CAR	180—410	+54.87	+0.2328	+7.477
TNB I	180—400	+65.625	+0.2950	+6.875
TNB II	180—380	+96.625	+0.1184	+10.208
1 : 1 NAP—TNB	220—400	+194.67 [b]	—0.1697 [b]	+25.139 [b]
1 : 1 ANT—TNB	180—420	+208.25	+0.2083	+17.361
1 : 1 CAR—TNB	180—430	+123.54	+0.7308	+7.692

[a] From the data in ref. 20 extrapolated to 400 K.
[b] For the cooling run only.

plex and the sum of the heat capacities of components is negative at higher temperatures, being equal to zero or positive at temperatures about 180 K in all three cases. We believe that this result may be interpreted as evidence of a decrease in the complex stability in the solid state with decreasing temperature.

Values of the enthalpy of complex formation in the solid state are estimated in Part II this work [13]. Using these values as the $\Delta H_r(400)$ and ΔC_p values according to Table 2, $\Delta H_r(220)$ values have been calculated. The value of $\Delta H_r(220)$ for the NAP—TNB complex, estimated as +2.5 kJ mole^{-1}, is in reasonable agreement with +1.7 kJ mole^{-1}, the enthalpy of phase transition at 220 K (see Table 1). The observed phase transition in the NAP—TNB complex at 220 K is thus believed to be a break-up of the complex on cooling into two components. Complex formation takes place on the heating run and the rate of this process is limited by the diffusion parameters as a reaction in the solid state. The fact that the enthalpy of complex formation is an endothermal effect can be interpreted as an indication that this complex is stabilized by an entropy effect. However, a detailed discussion of the nature of the phase transition in the NAP—TNB complex at 220 K obviously needs the completion of X-ray measurements at low temperatures.

CONCLUSIONS

Three modifications of TNB, one stable and two metastable, have been observed. It is supposed that these modifications may be related both to the configurational isomers of the TNB molecule and to different structures of the crystalline lattice.

Two solid—solid phase transitions in the NAP—TNB complex, at 220 and 424.5 K, have been revealed. The latter is interpreted as a transition from the rotational to diffusional phase.

Presumably some weak charge-transfer complexes can break-up into the components in the solid state when the temperature is decreased. We believe that the phase transition at 220 K in the NAP—TNB complex is an example of this disintegration.

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