Phase Diagram and Association Constants of a Molecular Complex in the 1,3,5-Trinitrobenzene–Benzene Binary System

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The phase diagram of the binary system of the electron acceptor (A) 1,3,5-trinitrobenzene with the electron donor (D) benzene has been determined by differential scanning calorimetry. A termolecular, congruently melting complex AD_2 was found. Association constants of the complex in the molten state have been obtained from the analysis of the liquidus line of the complex in terms of concurrence of complexing and non-complexing interactions. The proton chemical shifts of 1,3,5-trinitrobenzene and benzene have been measured as a function of the concentration over the whole composition range of the A–D binary system in the molten state. The data were analysed by a multiparametric curve-fitting method. Fitting was performed for simple AD and AD_2 and double AD + AD_2 equilibrium models, each with and without non-complexing interactions. No reasonable fit could be obtained for the ideal association models. The inclusion of non-complexing interactions allowed the data to be fitted by either the simple AD or the double AD + AD_2 equilbrium model. The results are compared with those obtained from analysis of the phase diagram data.

In a previous paper[1] on the phase diagrams of binary systems formed by electron acceptor (A) 1,3,5-trinitrobenzene (TNB) and electron donor (D) aromatic hydrocarbons it was found that the association of TNB with naphthalene, anthracene, and carbazole forms nearly ideal double simple-eutectic-type phase diagrams with a 1:1 complex as a component of the eutectic mixtures. The appearance of two different eutectic lines in the composition range 0.5—1.0 mole fraction TNB corresponding to two modifications of TNB was a common peculiarity for the systems under consideration. A further feature in common was agreement between experimental liquidus lines of the complexes and those calculated by the Vieland equation for a completely dissociated complex in the liquid phase. This latter fact was in disagreement with the observation that the melted complexes are coloured. A reasonable way out of this dilemma was to assume that the liquidus lines of complexes were apparently ideal, *i.e.*, the product of the activity coefficients related to complexing ('chemical') and non-complexing ('physical') interactions was taken to be unity. The activity coefficients related to non-complexing effects were estimated by applying the regular solutions theory[2] and the association constants were then evaluated from the 'chemical' activity coefficients. Many years ago Hammick *et al.*[3] published fragmentary data on the liquidus line position in the binary system of TNB with benzene (BEN). They reported the existence of an AD_2 complex in this system. However, neither the composition nor the temperature of the eutectics were specified. Thus, revision of the phase diagram of the TNB–BEN system and evaluation of association constants by described procedures[1b] seemed interesting.

It seemed worthwhile to determine the equilibrium constants for complex formation in the systems under discussion by an independent method. Significant experimental difficulties arose from the fact that the measurements had to be performed at elevated temperatures (at least above the m.p.s of complexes) and, in order to avoid degradation of the material during melting, under conditions protected from atmospheric moisture and oxygen. In these respects, the n.m.r. chemical shift method seemed to be most convenient.

In the paper we report the results for the TNB–BEN system. The results for the TNB–naphthalene system will be given elsewhere.

Experimental and Computational

Materials.—TNB was purified as described previously.[1a] Benzene was distilled immediately before use through a Vigreux column in a system protected from atmospheric oxygen and moisture. Ethylene glycol (p.a. grade) was stored over 3 Å molecular sieves and was used without further purification.

Calorimetric Measurements.—The phase diagram was studied using a Perkin-Elmer DSC-1B differential scanning calorimeter. Mixtures were prepared by weighing appropriate amounts of components into aluminium sample pans. The pans were then sealed using the volatile sample press supplied with the calorimeter. Sample masses were in the range 5—10 mg and the overall mole fractions were known to ± 0.0002. A sample was heated until molten and then rapidly cooled below the m.p. This procedure was repeated several times for each binary sample. The measurements were carried out on samples stored at room temperature for 2—3 months. The $TNB\cdot(BEN)_2$ complex was grown by slowly cooling a solution containing 20 mol% TNB in benzene in a sealed glass ampoule. The line positions on the phase diagram were determined from thermograms recorded at four heating rates: 4, 2, 1, and 0.5 K min^{-1} by using the procedures described previously.[4] The standard error in temperature and enthalpy measurements was ± 0.3 K and ± 400 kJ mol^{-1}, respectively.

N.m.r. Measurements.—Samples for n.m.r. measurements were prepared by weighing appropriate amounts of the components into a thin-walled capillary of *ca.* 2 mm outer diameter (o.d.). The capillary charge was frozen by dipping into liquid nitrogen and then the capillary was sealed under vacuum (*ca.* 10^{-1} Torr). The exact content of benzene was established by weighing after sealing (assuming non-volatility of TNB). The capillary charge was then homogenized by melting and shaking.

Etheylene glycol was placed in 5 mm o.d. n.m.r. tube coaxial with the sample capillary. ^1H N.m.r. spectra were recorded on a Tesla BS 497 spectrometer operating at 100 MHz and equipped with a variable-temperature probe. Proton resonance signals for benzene and TNB were measured relative to that of the CH_2 group in ethylene glycol as external reference.

Measurements at one temperature over the whole concentration range for the TNB–BEN system were not possible since the m.p. of TNB is higher than the b.p. of benzene. The sample was heated just above its m.p. and the signal recordings were then performed for several temperatures in the range exceeding the sample m.p. up to *ca.* 40°. In some cases it was possible to carry out measurements on super-cooled liquid samples. The n.m.r. line positions were plotted against the temperature and extrapolated to 346.9 K, *i.e.*, to the m.p. of the TNB·(BEN)$_2$ complex. Chemical shifts were referred to Me_4Si. The observed chemical shifts, δ^i_{obs}, were corrected for two effects: (1) for the external reference, and (2) for the shift due to the concentration dependence of the magnetic susceptibility of the samples. The latter had to be taken into account because the measured chemical shifts in binary mixtures resulted both from intermolecular interactions and from the differences in the volume magnetic susceptibilities of the pure component and the binary mixture.

The corrected chemical shifts, δ^i_{corr}, were calculated using relationship (1) where χ^r_v, χ^s_v, and χ^i_v are the volume magnetic

$$\delta^i_{corr} = \delta^i_{obs} + \frac{2\pi}{3}(\chi^r_v - \chi^s_v) + \frac{2\pi}{3}(\chi^i_v - \chi^s_v) \quad i = \mathrm{A,D} \quad (1)$$

susceptibility of the reference, the sample, and the pure liquid component, respectively. The volume susceptibilities were calculated using the following values of molar susceptibilities χ_M: χ_M(BEN) -55.64×10^{-6}, χ_M(TNB) -73.61×10^{-6}, and χ_N(ethylene glycol) -38.78×10^{-6} (all derived by the increment method from the data in ref. 5) and the following values of molar volume V V(BEN) 95.20, V(TNB) 133.00, and V(ethylene glycol) 59.15 (all in cm^3, at 346.9 K, calculated according to Bondi[6]).

The reproducibility of the n.m.r. line positions was within ±0.5 Hz, but the extrapolation and correction procedures introduced an additional uncertainty. The total error in the chemical shifts was estimated at ±0.02 p.p.m.

The corrected chemical shifts may be attributed to intermolecular interactions and, therefore, they can be used in the association constant calculations.

Calculation of Association Constants from Chemical Shift Measurements.—The stoicheiometry of the crystalline complex in the TNB–BEN system, as evidenced by the phase diagram, is AD$_2$. After melting, a double equilibrium, in which complexes AD and AD$_2$ are formed, seems to be most probable but a simple 1:1 or 1:2 equilibrium cannot be excluded *a priori.*

Some authors argued that in order to determine the association constants, it is necessary to take into account the additional non-complexing A–D collisions between acceptor and donor molecules[7] while higher order complexes were postulated as a sufficient explanation of equlibria in solution.[8]

With regard to the above, it seemed best to analyse the concentration dependences of the proton chemical shift for acceptor (δ^A_{corr}) and donor (δ^D_{corr}) on the basis of each of six models assuming three different stoicheiometries (1:1, 1:2, and 1:1 + 1:2) each of them with and without taking into account non-complexing interactions.

To relate the n.m.r. measurements to the equilibrium, the generalized equation (2)[9] was utilized where δ is the measured

$$\delta = \sum_i P_i\delta_i \quad (2)$$

chemical shift of a given nucleus, P_i is the relative population of the nucleus in the *i*th environment, and δ_i is the chemical shift of the nucleus in the *i*th neat environment.

The proton chemical shifts of acceptor and donor in the A–D binary mixtures for the six models postulated can be described by equations (3)—(8) collected in Table 1 along with the specification of unknown quantities as the fitting parameters of the corresponding equation.

The association constants can be combined with equations (3)—(8) by the relationships between the initial and equilibrium concentrations of the component.

A 1:1 association of acceptor and donor molecules, A + D = AD ($K_1 = {}^x\mathrm{AD}/x_Ax_D$), leads to relationship (9) between the $x_{o,D}$, initial, and the x_D, equilibrium, mole fraction of donor [equation (9)]. For a 1:2 association model, A + 2D = AD$_2$

$$x_D^2K_1x_{o,D} + x_D(1 + K_1 - 2K_1x_{o,D}) - x_{o,D} = 0 \quad (9)$$

($K_2 = {}^x\mathrm{AD}_2/x_Ax_D^2$), equation (10) can be written. If a double

$$x_D^3(2K_2x_{o,D} - K_2) + x_D^2(2K_2 - 3K_2x_{o,D}) + x_D - x_{o,D} = 0 \quad (10)$$

equilibrium is postulated in which complexes AD and AD$_2$ coexist, A + D = AD ($K_1 = {}^x\mathrm{AD}/x_Ax_D$) and A + 2D = AD$_2$

Table 1. Equations for the chemical shifts of acceptor and donor (δ^i) in the A–D liquid binary system for various models of complex formation

Model[a]	Complex	Equation for chemical shift[b]	Fitting parameters
I	1:1	$\delta^i = \frac{1}{n_{o,i}}[n_i\delta_i + n_{AD}\delta^i_{AD}]$ (3)	K_1,δ^i_{AD}
	1:2	$\delta^i = \frac{1}{n_{o,i}}[n_i\delta_i + Nn_{AD_2}\delta^i_{AD_2}]$ (4)	$K_2,\delta^i_{AD_2}$
	1:1 + 1:2	$\delta^i = \frac{1}{n_{o,i}}[n_i\delta_i + n_{AD}\delta^i_{AD} + Nn_{AD_2}\delta^i_{AD_2}]$ (5)	$K_1,K_2,\delta^i_{AD},\delta^i_{AD_2}$
II	1:1	$\delta^i = \frac{1}{n_{o,i}}[(n_i - n^i_{A-D})\delta_i + n_{AD}\delta^i_{AD} + n^i_{A-D}\delta^i_{A-D}]$ (6)	$K_1,\delta^i_{AD},\delta^i_{A-D}$
	1:2	$\delta^i = \frac{1}{n_{o,i}}[(n_i - n^i_{A-D})\delta_i + Nn_{AD_2}\delta^i_{AD_2} + n^i_{A-D}\delta^i_{A-D}]$ (7)	$K_2,\delta^i_{AD_2},\delta^i_{A-D}$
	1:1 + 1:2	$\delta^i = \frac{1}{n_{o,i}}[(n_i - n^i_{A-D})\delta_i + n_{AD}\delta^i_{AD} + Nn_{AD_2}\delta^i_{AD_2} + n^i_{A-D}\delta^i_{A-D}]$ (8)	$K_1,K_2,\delta^i_{AD},\delta^i_{AD_2},\delta^i_{A-D}$

[a] II,I denotes models with and without taking into account non-complexing interactions, respectively. [b] Subscript i denotes acceptor (A) or donor (D); $N = 1$ if i = A and $N = 2$ if i = D; δ_i is the chemical shift of pure liquid component; δ^i_{AD}, $\delta^i_{AD_2}$, and δ^i_{A-D} are the chemical shift of pure hypothetical complex of the form AD, AD$_2$, and A–D, respectively. See text for details of notation.

($K_2 = {}^{x}AD_2/x_Ax_D^2$), it can be shown that the relationship between the initial and equilibrium donor concentrations is given by equation (11) where $\beta = x_{o,D}/x_{o,A}$; $x_{o,A}$ and $x_{o,D}$ are

$$x_D^3K_2(\beta - 1) + x_D^2[\beta(K_1 - K_2) + 2K_2] + x_D[K_1(1 - \beta) + \beta + 1] - \beta = 0 \quad (11)$$

the initial (free + complexed) mole fraction of acceptor and donor, respectively. The numbers of moles of particular species at equilibrium (n_A, n_D, n_{AD}, and n_{AD_2}) can be easily obtained by solving equations (9)—(11) for assumed K values.

Non-complexing A–D interactions are taken into account in equations (6)—(8). This is implemented through n_{A-D}, moles of non-complexing associations ('contact pairs' or 'collision complexes'). In equation (6)—(8) this quantity is subtracted from the mole number of the acceptor (or donor) and an additional last term is inserted.

For the sake of continuity between our previous paper [1b] and the present one, the n_{A-D} value was estimated by applying the regular solutions theory [2] which provides an equation for evaluating γ_p, the activity coefficient related to non-complexing ('physical') interactions. According to us the mole number of non-complexing associations may be related to the physical activity coefficient by equation (12). The physical activity

$$n^i_{A-D} = n_i(\gamma_{p,i} - 1) \quad (12)$$

coefficients were calculated as described in ref. 1*b* using the following solubility parameters, 22.0 × 10³ and 18.4 × 10³ for TBN and benzene, respectively (all in $J^{1/2}\ m^{-3/2}$), and for molar volumes as given above.

The parameters varied to obtain the fit were: the association constants K_1 and K_2, and the chemical shifts δ^i_{AD}, $\delta^i_{AD_2}$, and δ^i_{A-D}. A least-squares fit between theory and experiment was performed by using a subroutine for minimization based on the Powell method.[10]

Two criteria for verification of the hypothetical model equations were employed: one was that the calculated chemical shifts are within the uncertainty in the experimental points and the other in that the values of K in calculations performed separately for the acceptor and donor data set are consistent.

The precision with which K values can be evaluated is limited by the scatter of the experimental points in δ^i_{corr} *versus* $x_{o,D}$ plots and the present data were not sufficient to determine K more accurately than *ca.* 10—30% (depending on the model used).

Results and Discussion

Phase Diagram.—The phase diagram of the TNB–BEN system is shown in Figure 1 together with the calculated liquidus lines. The liquidus lines of the parent components were calculated using the Schröder–van Laar equation (13) and the

$$-RT\ln x_{o,i} = \Delta H_{f,i} - T\Delta S_{f,i} \quad i = A,D \quad (13)$$

liquidus line of the complex was calculated using the Vieland equation (14) adopted for a 1:2 addition compound where $x_{o,A}$

$$-RT\ln\frac{x_{o,A}x^2_{o,D}}{x_{A,AD_2}x^2_{D,AD_2}} = \Delta H_{f,AD_2} - T\Delta S_{f,AD_2} \quad (14)$$

and $x_{o,D}$ are the mole fractions of acceptor and donor at temperature T in the binary liquid along the liquidus line; $x_{A,AD_2} = 0.3333$ and $x_{D,AD_2} = 0.6667$; $\Delta H_{f,i}$ and $\Delta S_{f,i}$ are the enthalpy and entropy of fusion of the pure component, respectively; $\Delta H_{f,AD_2}$ and $\Delta S_{f,AD_2}$ are the enthalpy and entropy of fusion of the complex, respectively.

Table 2. Temperature (T_f) and enthalpies (ΔH_f) of fusion for the components and complex, eutectic temperatures (T_e) and compositions (x_e) (in mole fraction of TNB) in the TNB–BEN system

	Fusion		Eutectic	
Compound–eutectic	T_f/K	ΔH_f/kJ mol⁻¹	T_e/K	x_e
TBN I (stable)	398.4	15.0		
TBN II (metastable)	380.3	14.8		
BEN	278.6	9.8		
Complex: TBN·(BEN)$_2$	346.9	28.9		
Eut.: BEN + Complex			274.9	0.02
Eut.: Complex + TNB I			344.4	0.50
Eut.: Complex + TNB II			341.4	0.58

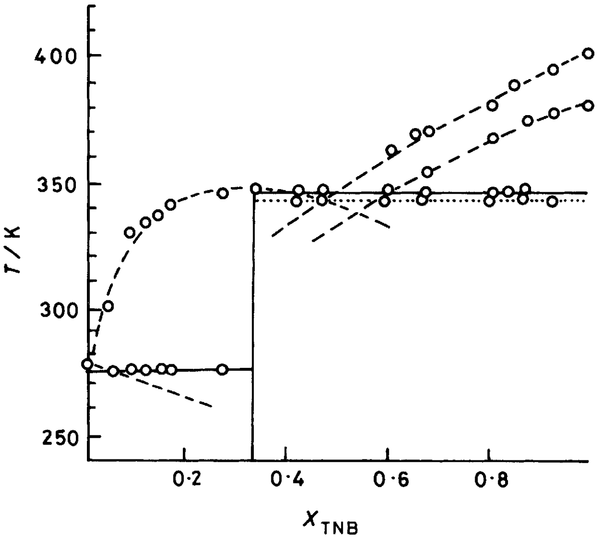

Figure 1. The 1,3,5-trinitrobenzene–benzene phase diagram. ——, · · · ·, Experimental lines; – – – –, lines calculated from equations (13) and (14)

A termolecular, congruently melting complex AD$_2$ was found in the TNB–BEN system, consist with the results reported by Hammick *et al.*[3] The complex forms simple eutectics with the parent components. Every sample in the composition range 0.3333—1.0 mole fraction of TNB exhibited two eutectic temperatures and two final temperatures of fusion. Higher temperatures corresponded to samples stored at room temperature for 2—3 months while the lower temperatures were observed for freshly frozen ones. A similar situation was observed for three systems earlier reported.[1] As a possible explanation of this fact it was suggested that a stable and metastable modification of TNB may exist as a component of the complex–TNB eutectic mixtures.

The experimental calorimetric data for the TNB–BEN system are given in Table 2.

The calculated liquidus lines, both for the complex and for the parent components, are in agreement with experimental error with the measured ones. The agreement between experimental and calculated lines for the complex might indicate complete dissociation of the complex upon melting. However, for TNB–BEN solvent systems a 1:1 complex was found.[11]

For this reason we decided to calculate the equilibrium constant of complex formation using the method described previously.[1b] This method assumes the liquidus line of a complex to be apparently ideal and thus equation (14) may be

$$-RT\ln\frac{x_{o,A}\gamma_{p,A}\gamma_{c,A}x^{2}_{o,D}[\gamma_{p,D}\gamma_{c,D}]^{2}}{x_{A,AD_2}x^{2}_{D,AD_2}} = \Delta H_{f,AD_2} - T\Delta S_{f,AD_2} \quad (15)$$

rewritten in the form (15) with the product of the activity coefficients being unity [equation (16) where γ_p and γ_c are the

$$\gamma_{p,A}\gamma_{c,A}\gamma^{2}_{p,D}\gamma^{2}_{c,D} = 1 \quad (16)$$

activity coefficients of particular species corresponding to non-complexing ('physical') and complexing ('chemical') interactions in the acceptor–donor binary system, respectively]. Equation (16) is obeyed for all compositions along the whole liquidus line of a complex and hence the activity coefficients in the denominator of equation (15) can be omitted. This method can be extended to cover the cases of binary systems with a strong addition compound where the experimental liquidus line of a complex does not fulfil the Vieland equation. However, in such cases, the product of the activity coefficients is less than unity and the activity coefficients in the denominator of equation (15) must be specified.

The coefficients concerning physical interactions, γ_p, were calculated as described above. The activity coefficients related to complexing, γ_c, are defined by equation (17). For the

$$\gamma_{c,i} = x_i/x_{o,i} \quad i = A,D \quad (17)$$

calculations of association constant by this method, the complex composition need to be known *a priori*. Until now the stoicheiometry of the complex in the TNB–BEN system in the molten state has not been determined. The composition of the complex in the solid state implies a 1:2 equilibrium after melting. On the other hand, in earlier investigations[11] no deviations from 1:1 association were reported. For these reasons, calculations were made for both 1:1 and 1:2 simple equlibria.

The values of the association constants K_1 and K_2 as calculated from a combination of equations (16)—(17)—(9) and (16)—(17)—(10), were: K_1 0.68 ± 0.05 and K 0.86 ± 0.05, respectively (at 346.9 K). Uncertainties were estimated by applying the formula for the propagation of errors with values for the errors in x and T as given above. The question arises: which of the two complex stoicheiometries is correct? To test the possibilities, an additional investigation of the n.m.r. chemical shifts was carried out on the same system.

Association Constants from Chemical Shift Measurements.—The corrected proton chemical shifts of benzene and TNB as functions of the concentration in the TNB–BEN system are shown in Figure 2 along with the calculated curves. The pattern of the chemical shift observed both for benzene and TNB protons shows a continuous displacement towards higher field with increasing mole fraction of the other component. When attempts were made to fit the experimental chemical shifts using the models given in equations (3)—(5) (*i.e.*, without the non-complexing interactions), no satisfactory convergence could be obtained except the data set for benzene which could be fitted by the 1:1 + 1:2 model. Since no quantitative fit could be obtained with the acceptor data set, this could indicate that the conclusions drawn from the analysis of data set for only one component might be mistaken.

If the non-complexing interactions were taken into account both data sets could be fitted either by a 1:1 or by a 1:1 + 1:2 equilibrium model. The consequence of applying equation (7), was similar to that observed for equation (5), namely, the data set for one component was not capable of being fitted whereas the other set did fit this model quite well. It should be noted that analysis of the n.m.r. data allows one to exclude the possibility of a simple 1:2 equilibrium in the TNB–BEN binary system in molten state. The results of the calculations for model equations are collected in Table 3.

At first sight, the results seem to be in conflict with expectation that only one equlibrium model should be an accurate representation of the phenomena involved. However, the inconsistency is not serious if we realize that the result for the

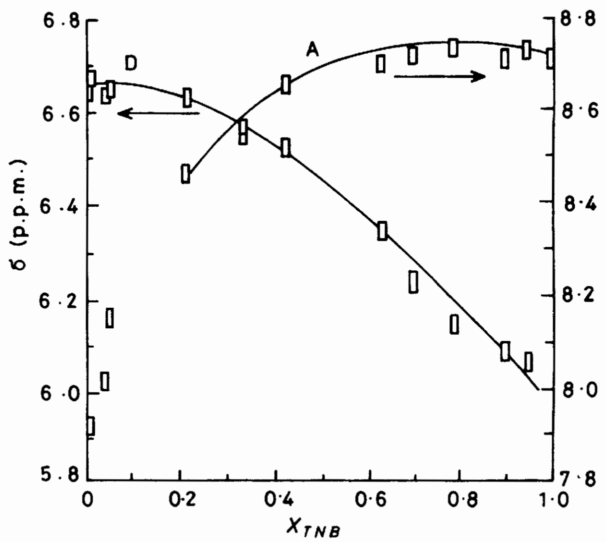

Figure 2. The proton chemical shift of benzene (D) and 1,3,5-trinitrobenzene (A) as a function of concentration in benzene–1,3,5-trinitrobenzene binary system at 346.9 K. The full curves represent lines calculated from equation (6) with following parameter values: K_1 0.6, δ^{A}_{AD} 9.35, δ^{A}_{A-D} 6.91, δ^{D}_{AD} 7.53, and δ^{D}_{A-D} 3.74

Table 3. Parameters obtained from the fit data of ^{1}H chemical shift measurements in benzene–1,3,5-trinitrobenzene binary system at 346.9 K to model equations

		Association constants		Chemical shifts of pure complexes[b]		
Model equation	Fit[a] (p.p.m.)	K_1	K_2	δ_{AD} (p.p.m.)	δ_{AD_2} (p.p.m.)	δ_{A-D} (p.p.m.)
(5; i = D)	0.020	0.9 ± 0.1	0.5 ± 0.2	5.24 ± 0.06	8.13 ± 0.68	
(6; i = A)	0.029	0.6 ± 0.2		9.35 ± 0.03		6.91 ± 0.20
(6; i = D)	0.025	0.6 ± 0.2		7.53 ± 0.26		3.74 ± 0.42
(7; i = A)	0.019		0.5 ± 0.1		11.73 ± 0.42	5.60 ± 0.36
(8; i = A)	0.028	0.8 ± 0.1	0.15 ± 0.05	9.31 ± 0.02	10.60 ± 0.23	6.15 ± 0.22
(8; i = D)	0.023	0.8 ± 0.1	0.15 ± 0.05	6.43 ± 0.34	8.80 ± 0.30	4.78 ± 0.56

[a] Standard deviation of chemical shift value residuals. [b] Uncertainties are standard error with allowance for ranges of K_1 and K_2 values.

1:1 + 1:2 model indicates that the 1:1 association is dominant ($K_2 < K_1$). It must also be recognized that in the case of the 1:1 + 1:2 model, the five parameters are adjusted by comparison with those in the 1:1 model which weakens the argument for the former arrangement. Further, in earlier studies of equilibria in TNB–BEN–solvent systems by n.m.r.,[11a] optical,[11b] and calorimetric [11c] methods, no deviations from the assumed 1:1 association were noted. This led us to believe that the 1:1 equilibrium model is better than a double equilibrium. There is agreement between the value of K_1 obtained from analysis of the liquidus line of complex (K_1 0.68 ± 0.05) and that estimated from n.m.r. measurements (K_1 0.6 ± 0.2). This result provides support for the description of the acceptor–donor binary systems in terms of complexing ('chemical') and non-complexing ('physical') interactions between the acceptor and donor molecules.

Accordingly, one may expect that in the liquid state, the benzene and TNB molecules form a TNB•BEN complex as a result of the charge-transfer (CT) interactions and a TNB–BEN collision complex due to non-complexing interactions.

It is reasonable to ask whether the numerical values of the chemical shifts for the neat complexes, δ^i_{AD} and δ^i_{A-D}, as obtained in the minimization procedure, have a physical meaning. We found the relative shift Δ^i_{AD}, for the TNB•BEN charge-transfer complex ($\Delta^i_{AD} = \delta^i_{AD} - \delta_i$), to be positive both for acceptor and donor protons. It is worth noticing that the same sign for the relative shift for TNB protons was reported by Chudek *et al.* in their studies [12] of weak molecular complexes. The chemical shifts for the CT complex correspond to the signals from protons at lower field than that observed in the parent components. Contrary to the CT complex shifts, the relative shifts for the TNB–BEN collision complex are found to be negative which corresponds to an increase in proton shielding in the complex. There are two effects which may be expected to contribute to the values of the chemical shift of protons in AD and A–D complexes: (i) variation of the electron charge density distribution, leading to different shieldings of the protons in the pure component and in the complex and (ii) a shielding cone effect on account of the difference in the mutual orientation of molecules in the liquid components in relation to the binary mixture. The first effect should be more pronounced in AD charge-transfer complexes because for A–D collision complexes no considerable variation in the charge density distribution is expected.

If these two effects are superimposed, as in the AD complexes, it is difficult to estimate qualitatively the resultant effect and quantitative calculations are needed. The results of such calculations for TNB•BEN complex will be given elsewhere. It appears that the shielding cone effect is satisfactory to explain the positions of proton resonance signals in the A–D collision complex. It is more likely that non-complexing interactions may be considered as an essentially infinite array of possible A–D orientations except for the configuration favourable to charge-transfer. This latter, by analogy with CT complexes of TNB in the solid state, can be expected to be the face-to-face arrangement of the molecules with the TNB shifted off centre so that one carbon of the TNB ring lies above the centre of the benzene molecule.[13] The fact that both calculated values of δ^A_{A-D} and δ^D_{A-D} show an upfield shift suggests that the resultant effect of all possible A–D orientations is determined by the configuration in which both molecules experience an enhanced shielding cone effect by comparison with the same effect in their parent liquids. This direction of the shift may be expected if it is assumed that mixing of benzene with TNB involves a decrease in the mean molecule separation. Unfortunately, relevant experimental data are not available.

Conclusions.—The experimental results for the concentration dependences of the proton chemical shift fo TNB and benzene in TNB–BEN binary system are not interpretable in terms of an ideal simple 1:1 and 1:2 or double 1:1 + 1:2 equilibrium. Apart from specific chemical complexing, non-complexing physical interactions must be assumed to account for the measured chemical shifts. When non-complexing intereactions are taken into account, the experimental data can be fitted using either the 1:1 or 1:1 + 1:2 equilibrium model. The numerical results obtained for the equilibrium constants show that 1:1 association is dominant.

From the present study the conclusion can be drawn that the stoicheiometry of the complex in the solid state does not wholly determine the stoicheiometry in the liquid phase. The stoicheiometry of the crystalline complex in benzene–TNB system is AD_2 but the decomposition of this complex upon fusion is probably complete and in the liquid phase there is an equilibrium between the AD associations and their components.

For two models out of six studied, we found that the data set for one component was not capable of fitting a given model, whereas the data for the other component did fit the same model quite well. Hence, we may conclude that an estimate of the association constants by analysis of the n.m.r. data for only one component, a common practice in most determinations, can easily lead to an erroneous interpretation.

Agreement between the K_1 values derived from analysis of the liquidus line of a complex and from chemical shift measurements is satisfactory. A simple model involving the concurrence of complexing and non-complexing interactions in the acceptor–donor binary systems is thus successful in demonstrating the consistency of the data derived from calorimetry and n.m.r. techniques.

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