Bi- and Ter-molecular Electron Donor–Acceptor Complex Formation between Hexamethylbenzene and 1,3,5-Trinitrobenzene, and also between *NNN′N′*-Tetramethyl-*p*-phenylenediamine and 1,3,5-Trinitrobenzene in Solution

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The dependence of the line position in the ^{1}H n.m.r. spectra of dilute solutions of the electron acceptor (A) 1,3,5-trinitrobenzene on the concentration of excess of the electron donor (D) hexamethylbenzene in various paraffinic solvents has been interpreted in terms of equilibria involving the complex species DA and D_2A. The equilibrium quotients have been evaluated on several concentration scales.

The same interpretation provides a satisfactory explanation for similar observations involving the interaction of *NNN′N′*-tetramethyl-*p*-phenylenediamine with 1,3,5-trinitrobenzene. The results are in accord with those obtained from optical measurements.

Activity coefficient effects in themselves appear to be too small to provide an alternative explanation of the observed behaviour.

EXPERIMENTS designed to evaluate association constants (K) for complexes between electron donors (D) and electron acceptors (A) have not always proved satisfactory. One assumption, basic to the majority of determinations, is that the complexing can be described in terms of a 1 : 1 stoicheiometry, thus:

$$D + A \rightleftharpoons DA \qquad (1)$$

for which an equilibrium quotient may be defined as:

$$K_1 = [DA]/[D][A] \qquad (2)$$

The concentration condition $[D]_0 \gg [A]_0$ is often used (the subscript zeros indicate the total, free and complexed, concentration of the particular species). However, as far back as 1952, McConnell and his co-workers [1] suggested that it might not be sufficient to consider only the equilibrium (1), in that under this concentration condition a second equilibrium may be significant, namely:

$$DA + D \rightleftharpoons D_2A \qquad (3)$$

for which a second equilibrium quotient K_2 may be defined as:

$$K_2 = [D_2A]/[DA][D] \qquad (4)$$

Recently,[2] it has been shown that the concentration dependencies of the optical absorbance of the complexed species and of the line position of a magnetic resonance of a nucleus in the acceptor species for certain electron donor–acceptor systems could be accounted for in terms of the equilibria (1) and (3) in solutions where $[D]_0 \gg [A]_0$. These conclusions were based on calculations of K_1 and K_2 obtained from non-linear Scatchard [3] plots.[4]

Since then, the results of an n.m.r. study of the association of benzene with caffeine has been published by Hanna and Rose.[5] Their results cannot be interpreted simply in terms of an ideal 1 : 1 association: their explanation is that the stoicheiometry is 1 : 1 but one of the solute species fails to behave ideally.

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[1] J. Landauer and H. McConnell, *J. Amer. Chem. Soc.*, 1952, **74**, 1221; D. M. G. Lawrey and H. McConnell, *ibid.*, p. 6175.

[2] B. Dodson, R. Foster, A. A. S. Bright, M. I. Foreman, and J. Gorton, *J. Chem. Soc.* (*B*), 1971, 1283.

[3] G. Scatchard, *Ann. New York Acad. Sci.*, 1949, **51**, 660.

[4] D. A. Deranleau, *J. Amer. Chem. Soc.*, 1969, **91**, 4050.

[5] M. W. Hanna and D. G. Rose, *J. Amer. Chem. Soc.*, 1972, **94**, 2601.

Further, Andriessen and his co-workers[6] report no deviations from linearity for Scatchard plots in an n.m.r. study of a number of π-donor–π^*-acceptor systems. However, in most of the cases the complexes are very weak and, generally, deviations from linearity of Scatchard plots are less readily observable the less the overall interaction. The only system they studied which was identical with one for which we had reported[2] a non-linear Scatchard plot is hexamethylbenzene–fluoranil in carbon tetrachloride. Although the degree of complex formation was significant, for experimental reasons they had to use an external reference, with a consequent lowering in the accuracy of their shift measurements (±1 Hz). This could account for the apparent linearity. We have repeated our experiment, originally carried out on a 60 MHz spectrometer, using a 90 MHz instrument, and have obtained results which agree closely with those reported earlier.

In order to see whether activity effects could provide a plausible explanation of the behaviour of the type of system we have been studying, we have made n.m.r. shift measurements on hexamethylbenzene (HMB)–1,3,5-trinitrobenzene (TNB) in three different paraffinic solvents, keeping effectively dilute solution conditions.

We have also looked at a more strongly interacting system, namely *NNN′N′*-tetramethyl-*p*-phenylenediamine (TMPD)–1,3,5-trinitrobenzene, again under dilute solution conditions, using both n.m.r. and spectrophotometric methods to see if its behaviour is consistent with our postulate.

EXPERIMENTAL

TNB and HMB were recrystallised to constant m.p. TMPD was thrice distilled *in vacuo*. Hexadecane was fractionated and its purity checked by g.l.c. Other solvents were ' spectroscopic ' grade.

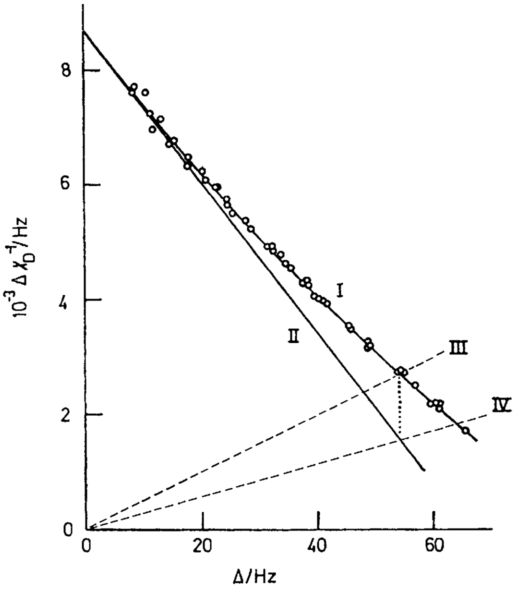
All solutions were made up by weight. In the HMB–TNB series, the volumes of the solutions were also measured at 20 °C and appropriate corrections made for thermal expansion in order to calculate the concentrations on the molar scale. The donor concentrations were in the range *ca.* 0.01 to *ca.* 0.4M. Concentrations of TNB were *ca.* 5×10^{-4}M for optical, and *ca.* 3×10^{-3}M for n.m.r. measurements.

All n.m.r. line positions were measured at 33.5 °C on a Bruker HX90/2 instrument, internally referenced from the solvents in hydrocarbon solutions and from tetramethylsilane in the carbon tetrachloride solutions. For each solution an average of five determinations was taken: agreement was always found to be within ±0.1 Hz. The line position for the ^{1}H resonance in the acceptor in a solution containing a concentration $[D]_0$ of donor, relative to the line position for the same resonance when $[D]_0 = 0$, termed Δ, was obtained for each of a series of up to 50 solutions.

Optical measurements were made on solutions in a 1 cm water-jacketted cuvette using an Optica CF4 manually-operated spectrophotometer. The same cuvette was used for all measurements. No cuvette was placed in the reference beam. Separate measurements of the cuvette filled with solvent and with solutions of donor alone and acceptor alone enabled the absorption of the complexed species to be estimated arithmetically. The absorbance scale was checked using sodium chromate solutions.

All essential experimental data are listed in Supplementary Publication No. SUP 21825 (9 pp.).*

In all the cases studied the Scatchard plot of $\Delta/[D]_0$ *vs.* Δ is curved. A typical plot is shown in the Figure. From the experimental values of Δ and $[D]_0$, K_1 and K_2 were computed by using a program (MINDS) involving a minimisation subroutine held on ICL library files. Two other parameters are obtained from the computation: in the n.m.r. determinations these are $\Delta_0(1)$ and $\Delta_0(2)$, the chemical shifts of the measured nuclei in the complexes DA and D_2A respectively, relative to the shift of the same nucleus in uncomplexed A. In the optical determinations the corresponding parameters are ε_1 and ε_2, the decadic molar absorption coefficients of DA and D_2A, respectively, at the wavelength of measurement. A further sub-routine was devised by Dr. R. A. Brown to enable errors in all four parameters to be evaluated at a given confidence level.[7]



Experimental points ○ and plot (curve I) for Δ *vs.* Δ/X_D (Scatchard plot) for hexamethylbenzene–1,3,5-trinitrobenzene in cyclohexane at 33.3 °C (X_D = mole fraction of donor). The line II is the computed tangent to I at $X_D = 0$. The line III is that corresponding to $X_D = 0.02$. The line IV is that corresponding to $X_D = 0.035$

RESULTS AND DISCUSSION

Hexamethylbenzene–1,3,5-*Trinitrobenzene*.—The values of K_1, K_2, and $\Delta_0(1)$ and $\Delta_0(2)$ for this interaction in cyclohexane in terms of each of the four concentration scales (moles per kg of solution, molal, molar, and mole fraction) are given in Table 1. The concentrations of donor were kept sufficiently low so that effectively dilute-solution conditions were maintained, whilst at

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* See Notice to Authors No. 7, *J.C.S. Perkin II*, 1975, Index issue.

[6] H. J. M. Andriessen, W. H. Laarhoven, and R. J. F. Nivard, *J.C.S. Perkin II*, 1972, 861.

[7] R. A. Brown, personal communication.

the same time the concentration range was sufficiently large so that the ratio of complexed A to uncomplexed A varied widely, thus providing sufficient information for the evaluation of the parameters.

In the limit of ideal dilute solutions, the relationships (5)—(7) should hold for the equilibrium quotient of a given equilibrium, where d is density (kg l^{-1}) and v

$$K(\text{mol per kg solution}) = K(\text{molal}) \qquad (5)$$

$$K(\text{molal}) = d_s K(\text{molar}) \qquad (6)$$

$$K(\text{mole fraction}) = v_s K(\text{molar}) \qquad (7)$$

molecular volume (l): the subscript s refers to the property of the solvent. The results in Table 1 show that these relationships are held to a reasonable degree, particularly when account is taken of the problems in computing the set of four parameters. Such calculations are of a different order of magnitude compared with the more normal problem experimentalists set themselves, namely the two-parameter problem based on the assumption that only equilibriation described by equation (1) occurs.[8]

TABLE 1

HMB–TNB interactions measured at 33.5 °C [a]

Solvent	Concn. scale	K_1 [b]	K_2 [b]	$\Delta_0(1)$ [c,d]	$\Delta_0(2)$ [c,e]
Hexane	mol kg^{-1} (K_r)	16.0 ± 0.3	3.1 ± 0.1	0.40	0.97
	molal (K_m)	16.3 ± 0.3	3.2 ± 0.1	0.39	0.94
	mole fraction (K_x)	179 ± 3	35 ± 1	0.41	0.96
	molar (K_c)	26.2 ± 0.6	4.9 ± 0.1	0.38	0.97
Cyclohexane	mol kg^{-1}	19.3 ± 0.5	3.6 ± 0.1	0.42	0.98
	molal	19.6 ± 0.5	3.7 ± 0.1	0.41	0.96
	mole fraction	231 ± 5	43 ± 1	0.42	0.97
	molar	26.9 ± 1	5.1 ± 0.1	0.42	0.97
Hexadecane	mol kg^{-1}	18.7 ± 0.5	3.4 ± 0.1	0.37	0.99
	molal	19.0 ± 0.5	3.5 ± 0.1	0.37	0.97
	mole fraction	82 ± 2	15 ± 0.5	0.37	1.00
	molar	24.9 ± 0.5	4.5 ± 0.1	0.37	0.99
Carbon tetrachloride [f]	molar	9.5 ± 0.3	2.0 ± 0.1	0.41	1.11

Hexane	$\left(\frac{K_m}{K_c}\right)_1 = 0.63 \pm 0.02$ kg l^{-1} $\left(\frac{K_m}{K_c}\right)_2 = 0.65 \pm 0.04$ kg l^{-1}	$d_s = 0.66$ kg l^{-1}	$\left(\frac{K_c}{K_x}\right)_1 = 0.14 \pm 0.01$ l $\left(\frac{K_c}{K_x}\right)_2 = 0.14 \pm 0.01$ l	$v_s = 0.13$ l
Cyclohexane	$\left(\frac{K_m}{K_c}\right)_1 = 0.73 \pm 0.05$ kg l^{-1} $\left(\frac{K_m}{K_c}\right)_2 = 0.74 \pm 0.02$ kg l^{-1}	$d_s = 0.78$ kg l^{-1}	$\left(\frac{K_c}{K_x}\right)_1 = 0.12 \pm 0.005$ l $\left(\frac{K_c}{K_x}\right)_2 = 0.12 \pm 0.005$ l	$v_s = 0.11$ l
Hexadecane	$\left(\frac{K_m}{K_c}\right)_1 = 0.76 \pm 0.04$ kg l^{-1} $\left(\frac{K_m}{K_c}\right)_2 = 0.78 \pm 0.04$ kg l^{-1}	$d_s = 0.77$ kg l^{-1}	$\left(\frac{K_c}{K_x}\right)_1 = 0.30 \pm 0.02$ l $\left(\frac{K_c}{K_x}\right)_2 = 0.30 \pm 0.02$ l	$v_s = 0.29$ l

[a] Errors at 99.9% confidence level. [b] In the reciprocal of the appropriate concentration scale units. [c] In p.p.m. measured at 90.00 MHz. [d] Error ±0.005 p.p.m. [e] Error ±0.01 p.p.m. [f] From ref. 2, modified by more recent data.

If the equilibrium quotients are small, say less than *ca.* 1 l mol^{-1}, then a not very obvious anomaly arises in the application of Scatchard,[3] Benesi/Hildebrand,[9] or related equations, namely that the value of the second parameter measured (in this case, Δ_0; in the case of spectrophotometric determinations, the decadic molar absorption coefficient of the complex at the wavelength of measurement) is apparently dependent on the concentration scale chosen to express the equilibrium quotient. This effect was first observed, and explained, by Scott[10] twenty years ago. More recently Trotter and Hanna[11] have made further useful contributions concerning this anomaly, which is essentially due to the fact that, at best, a solution can only be ideal on one concentration scale. For these very weak interactions the simple relationships such as equations (6) and (7) cannot be used. Instead, the more precise relationships, equations (8) and (9), respectively, have to be employed, where M = molecular weight, and the subscript D refers to the property of the donor. Here there is obviously no proportionality between the various K's.

$$K(\text{molal}) = \left(d_s - \frac{[\text{D}]_0 M_\text{D} d_s}{1\,000 d_\text{D}}\right) K(\text{molar}) \qquad (8)$$

$$K(\text{mole fraction}) = \left(v_s - \frac{[\text{D}]_0 M_\text{D} d_s}{M_s d_\text{D}} + [\text{D}]_0\right) K(\text{molar}) \qquad (9)$$

The values of Δ_0 for a given system in the present set of experiments are independent of the concentration scale chosen to express the equilibrium quotients in Table 1. Consequently, if there are deviations from

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[8] See, for example: (*a*) R. S. Mulliken and W. B. Person, 'Molecular Complexes, A Lecture and Reprint Volume,' Wiley–Interscience, New York, 1969; (*b*) R. Foster, 'Organic Charge-Transfer Complexes,' Academic Press, London and New York, 1969, ch. 6.

[9] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

[10] R. L. Scott, 'Proceedings of Internal Conference on Coordination Compounds,' Amsterdam, 1955, p. 265; *Rec. Trav. chim.*, 1956, **75**, 787.

[11] P. J. Trotter and M. W. Hanna, *J. Amer. Chem. Soc.*, 1966, **88**, 3724.

ideality then the deviations on one concentration scale are linearly proportional to those on another.

The values of Δ_0 obtained are also consistent with the model proposed, in that $\Delta_0(1)$ and $\Delta_0(2)$ for the HMB–TNB system are independent of the particular solvent used, despite the large differences in molecular volume. The same independence of solvent is observed in the other electron donor–acceptor system studied (see below).

In general terms, the non-ideal behaviour of one or more species in the equilibrium (1) may be expressed as equation (10), where K_{therm} is the true thermodynamic

$$K_{\text{therm}} = \frac{(\text{DA})}{(\text{D})(\text{A})} \frac{\gamma_{\text{DA}}}{\gamma_{\text{D}}\,\gamma_{\text{A}}} \qquad (10)$$

equilibrium constant and γ_{DA}, γ_{A}, and γ_{D} are the activity coefficients of DA, A, and D, respectively, all for a given concentration scale. For the Scatchard plot to be non-linear, the quotient of activity coefficients $\gamma_{\text{AD}}/\gamma_{\text{A}}\gamma_{\text{D}}$ must be dependent on $[\text{D}]_0$. We can readily estimate either the value we should need to assume for this quotient at a given concentration of $[\text{D}]_0$ (or contrariwise, the activity coefficient we should need to apply to D at a given value of $[\text{D}]_0$) in order to make the Scatchard plot linear. For the system under study, at a mole fraction $X_{\text{D}} = 0.02$, this would require $\gamma_{\text{DA}}/\gamma_{\text{D}}\gamma_{\text{A}} \approx 0.6$ (or equivalently, if the whole non-ideality is in D, then $\gamma_{\text{D}} \approx 1.7$; see Figure). Although no experimental activity coefficients for hexamethylbenzene are available, values for benzene in carbon tetrachloride can be calculated from vapour pressure measurements made by Scatchard and his co-workers.[12] For example, for a solution containing 0.1 mole fraction of benzene at room temperature, $\gamma_{\text{D}} = 0.98$. The corresponding values for hexamethylbenzene in paraffinic solvents will not be vastly dissimilar; our result therefore represents an effect two orders of magnitude smaller than that required to explain the curvature of the $\Delta/[\text{D}]_0$ *vs.* Δ plot. The present study also contrasts with the observations by Hanna and Rose [5] on the benzene–caffeine system referred to above. However, in that experiment, very high concentrations of donor (up to 0.54 mole fraction) were used. There the non-ideal behaviour of benzene, discussed by the authors, is undoubtedly significant.

*NNN'N'-Tetramethyl-*p*-phenylenediamine*–1,3,5-*Trinitrobenzene*.—The interaction between TMPD and TNB was chosen as the second example since it had been the source of several studies (in which it was generally assumed that the stoicheiometry was simply 1 : 1) which had indicated that TMPD was a significantly stronger donor than HMB. Since the technical problem of evaluating the parameters is very dependent on the magnitude of the change of the measured property as the concentration of the donor is altered, this system was attractive.

The Scatchard plots, based on the n.m.r. line positions of the ^{1}H resonance of TNB, have pronounced curvature. The parameters calculated from measurements of solutions in carbon tetrachloride and in cyclohexane are summarised in Table 2. As in the case of the HMB–TNB interactions, the values of both $\Delta_0(1)$ and $\Delta_0(2)$ for this second system are independent of the solvent.

TABLE 2

TMPD–TNB interactions measured at 33.5 °C [a]

Solvent	Method	K_1/kg mol^{-1}	K_2/kg mol^{-1}	$\Delta_0(1)$ [b]	$\Delta_0(2)$ [b]	ε_1 [c]/l mol^{-1} cm^{-1}	ε_2 [c]/l mol^{-1} cm^{-1}
CCl_4	N.m.r.	31.5 ± 1	3.8 ± 0.2	0.49 ± 0.02	1.02 ± 0.02		
C_6H_{12}	N.m.r.	52.8 ± 4	4.8 ± 0.4	0.44 ± 0.02	0.90 ± 0.02		
C_6H_{12}	Optical	52.5 ± 8	3.9 ± 0.8			940 ± 70	1 650 ± 8

[a] Errors at 99.9% confidence level. [b] In p.p.m. measured at 90.00 MHz. [c] Decadic molar absorption coefficient of the complex measured at 633 nm.

In the original study [2] of termolecular complex formation in solution by HMB–TNB, it was shown that there was agreement between the values of K_1 and of K_2 obtained from measurements of absorbance in the region of the optical intermolecular charge-transfer band(s) and those obtained from the n.m.r. measurements. We thought it desirable to check whether the TMPD–TNB system shows similar agreement. The results of the optical determination are, in fact, in accord with those of the n.m.r. experiment (Table 2).

General.—It appears that termolecular complex formation provides a major contribution to the explanation of the behaviour of these particular D–A solutions, and is probably important in other, similar, systems. A consequence of such behaviour, already pointed out,[2,13,14] is that many published values of association constants of D–A systems, calculated on the basis that only 1 : 1 association occurs, may be in considerable error.

It is not suggested that there are no activity coefficient effects. Indeed, the fact that the values of K_1 and K_2 for the HMB–TNB system in carbon tetrachloride are smaller than the corresponding values in cyclohexane (Table 1), and likewise in the TMPD–TNB system (Table 2), is a form of non-ideality. In earlier work involving 'apparent' values of K (derived from calculations which assumed the existence of complexes with only 1 : 1 stoicheiometry), a similar solvent behaviour had been noted.[15] In part, this may be due to competition of the solvent with one or other (or both) donor and acceptor for the other solute.[13,15] The present results suggest that, if this is occurring in the carbon

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[12] G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Amer. Chem. Soc.*, 1940, **62**, 712.

[13] Y. E. Ho and C. C. Thompson, *J.C.S. Chem. Comm.*, 1973, 609.

[14] A. A. S. Bright, J. A. Chudek, and R. Foster, *J.C.S. Perkin II*, 1975, 1256.

[15] Ref. 8*b*, p. 127.

tetrachloride solutions relative to the comparatively inert paraffinic solutions, it is not the whole explanation. Theory leads to the relation (11)[15] for the simple case

$$K_{\text{true}} = K_{\text{observed}} (1 + K_{\text{SA}}[\text{S}])(1 + K_{\text{SD}}[\text{S}]) \qquad (11)$$

of a 1 : 1 association of solvent with both the donor (equilibrium constant K_{SD}) and the acceptor (equilibrium constant K_{SA}); [S] is the concentration of the solvent in the appropriate units. The fact that for the TMPD–TNB system, the ratio of the K_1 value in cyclohexane to that in carbon tetrachloride is not equal to the ratio of the corresponding K_2 values (likewise for the HMB–TNB system) suggests that competition by the solvent is not the only factor which determines the solvent-dependence of K.

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