Stabilities of Electron Donor–Acceptor Complexes of Aromatic Hydrocarbons with 1-(2,4,6-Trinitrophenyl)propan-2-one in Solution from Nuclear Magnetic Resonance Shift Measurements

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The change in the chemical shifts of the three singlets in the ^1H n.m.r. spectrum of 1-(2,4,6-trinitrophenyl)propan-2-one (picrylacetone) (A) as a function of the concentration of various added aromatic hydrocarbons, acting as electron donors (D), has been measured under the conditions $[D] \gg [A]$. The results are more consistent with an association in which bimolecular complexes (DA) and termolecular complexes (D_2A) are formed than with a recently proposed model which involves the formation of complexes with only a 1 : 1 stoicheiometry together with 'additional unspecific shielding' (AUS) of both complexed and uncomplexed acceptor by the donor molecules.

Determinations of association constants for the interaction of electron donors (D) with electron acceptors (A) to form electron donor–acceptor (EDA) complexes from concentration-dependent n.m.r. chemical shifts have several important advantages over the longer established spectrophotometric methods.[1]

(i) Chemical shifts are generally insensitive to small concentrations of impurities. By contrast, spectrophotometric methods cannot generally be used with confidence if there is significant absorption by extraneous species at the wavelength of measurement. Such species sometimes enter the system as impurities in the donor and acceptor samples. In many cases they are formed by some slow chemical reaction of the D and A in solution.

(ii) Ideally, with the spectrophotometric method, the absorbances of a series of solutions are measured at the wavelength(s) corresponding to the maximum absorption coefficient(s) for the intermolecular charge-transfer band(s) ($\lambda_{max.}$), and for which the absorbance owing to free A and D (and solvent) is zero. In practice, there are very few systems where this set of conditions is even approached. Sometimes, by making measurements at longer wavelengths than $\lambda_{max.}$, the fractional contribution of free A and D to the total absorbance can be reduced and allowance made, though not always satisfactorily. In the usual n.m.r. determinations,[2] it is line positions not line intensities that are required. Because of the narrowness of n.m.r. lines there is less chance of the lines we wish to observe, usually of the acceptor, being masked by absorptions due to the donor or solvent compared with the corresponding situation in u.v.–visible spectroscopy. Nevertheless, problems do sometimes arise in n.m.r. spectra because of the high intensities of absorptions due to the donor in solutions where $[D] \gg [A]$ or to absorptions by the solvent, effects sometimes exacerbated by spinning side-bands.

(iii) Often more than one n.m.r. probe in an acceptor can be used, thus providing multiple sets of experimental data from which independent evaluations of equilibrium parameters can be calculated. It may be argued that, in optical experiments, multiple sets of data may be derived from measurements of absorbance at several wavelengths.[3] However, where such measurements are made, they are generally obtained from the same charge-transfer band and therefore lack the degree of independence which is obtained in the n.m.r. experiment. (There are a few cases [4] where two or more charge-transfer bands do allow a more satisfactory wavelength range of absorbances to be used.)

N.m.r. Shift Method

In the simplest model of an EDA interaction it is supposed that a 1 : 1 complex (DA) is in equilibrium with its components and that an equilibrium constant equation (1) may be written.

$$K = [DA]/[D][A] \qquad (1)$$

There is good independent evidence that the rates of formation and dissociation of the complex are fast.[5] In the n.m.r. experiment a single set of signals is observed for a given set of chemical-shift-equivalent nuclei in the A species, irrespective of whether the particular A molecules are complexed or not. For a given system, if Δ is the difference in shift between a signal in A in the absence of D and in the presence of an added amount of D equivalent to a concentration $[D]_0$, then it may be shown [2] that for $[D]_0 \gg [A]_0$ [the subscript zeros indicating the total (free plus complexed) concentration of the species] to a good approximation equation (2) is valid, where Δ_0 is the

$$\Delta/[D]_0 = -K\Delta + K\Delta_0 \qquad (2)$$

shift of the measured signal in the pure complex in solution, relative to that in uncomplexed A. Equation (2) is the analogue of an expression used to derive K from optical data (Scatchard[6] equation) and will be referred to as such. The Scatchard plot of $\Delta/[D]_0$ *versus* Δ should be linear and the gradient of the line, equal to $-K$, should be independent of the particular nucleus measured. In practice several anomalies have been noted. These include: (a) non-linear Scatchard plots; [7] (b) apparently linear plots in which the gradient is dependent on the particular nucleus measured; [8] (c) disagreement between K-values obtained from n.m.r. data compared with those from optical data.[9]

Recently, Stamm *et al.*[10] have argued that it is incorrect to take Δ as the measure of the shift for the signal in the equilibrium mixture relative to that in solutions where $[D]_0 = 0$. Their argument is that Δ and Δ_0 are measured from a signal due to A alone in the pure solvent whereas they should be referred to A in a hypothetical solution containing the appropriate concentration $[D]_0$ but in which there was no specific complex formation. This suggestion derives from observations of line positions of single solutes in isotropic solvents (usually carbon tetrachloride) compared with those in anisotropic solvents (usually benzene). The shift difference 'aromatic solvent induced shift' (ASIS) has been ascribed to non-complexing collisions by molecules of the anisotropic solvent.[11] Stamm has argued that this effect will operate in solutions containing D and A molecules and will be extra to the 1 : 1 association described above. Stamm has called this effect 'additional unspecific shielding (AUS).' For solutions under present consideration the effective anisotropic 'solvent' would be the mixture of D and the diluting solvent. Such an effect would in many ways be the n.m.r. analogue of 'contact charge-transfer' absorption.[12,13]

If it is assumed AUS is linearly proportional to $[D]_0$ both for shifts in A (proportionality constant a_1) and in DA (proportionality constant a_2) then for a 1 : 1 association with $[D]_0 \gg [A]_0$ a modified Scatchard equation may be written as equation (3). For a curved Scatchard plot, a value of a_2

$$\frac{\Delta}{[D]_0} = -K(\Delta - a_2[D]_0) + K(\Delta_o + \frac{a_1}{K}) \qquad (3)$$

generally may be selected to linearise the plot. Stamm and his co-workers have argued that if the measured nucleus is near the centre of the A molecule, the probability of collision will be less and a_2 will be smaller than for a nucleus nearer the periphery of the molecule. As a consequence any estimate of K which ignores AUS will be less in error for the more centralised probes.

An earlier interpretation of the curvature of the Scatchard plots had been made [7,14] by postulating that in solutions where $[D]_0 \gg [A]_0$, the stoicheiometry of the product is not restricted to 1 : 1 but that some termolecular association, D_2A, also occurred, equation (4). For such a system the relationship corresponding to equation (2) is [14] as given in equation (5) where $\Delta_0(1)$ and $\Delta_0(2)$ are the shifts of DA and D_2A, respectively, relative to A.

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

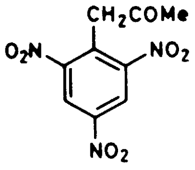
$$\Delta/[D]_0 = -K_1(1 + [D]_0K_2)\Delta + K_1\Delta_0(1) + K_1K_2[D]_0\Delta_0(2) \qquad (5)$$

In this paper we have analysed the ^1H chemical-shift dependence of the aromatic, methylene and methyl protons of picrylacetone (1) [as the electron acceptor (A)] as a function of added aromatic hydrocarbon [as the electron donor (D)] in a series of solutions with $[D]_0 \gg [A]_0$ on the basis of each of the three alternative assumptions: (a) 1 : 1 association with no AUS (equation 2); (b) 1 : 1 association with AUS (equation 3); and (c) 1 : 1 and 2 : 1 complex formation (DA and D_2A) (equation 5).

Overlap of the near u.v.-visible absorption bands of picrylacetone with the intermolecular charge-transfer bands of the various EDA complexes and problems in achieving sufficiently high reproducibility of absorbance measurements at the level required for solutions of picrylacetone alone within the required wavelength region prevented an independent study of these systems by spectrophotometry. It should be noted that the requirements for experiments on the basis of (b) or (c) are more demanding than for an experiment based on (a) for which an equation such as that described by Ketelaar *et al.*[15] might be applied to allow for the absorption of uncomplexed A at the wavelength of measurement of absorbance within the charge-transfer band.

Experimental

Picrylacetone [1-(2,4,6-trinitrophenyl)propan-2-one] was prepared from ethyl 3-hydroxy-2-(2,4,6-trinitrophenyl)but-2-enoate [16] (originally described as the corresponding keto tautomer [17]). It was recrystallised thrice from ethanol, m.p. 89 °C (lit.,[17] m.p. 89 °C). Benzene was B.D.H. spectroscopic grade, b.p. 80 °C; naphthalene was B.D.H. the pure for molecular weight determination grade, m.p. 80.5 °C; phen-

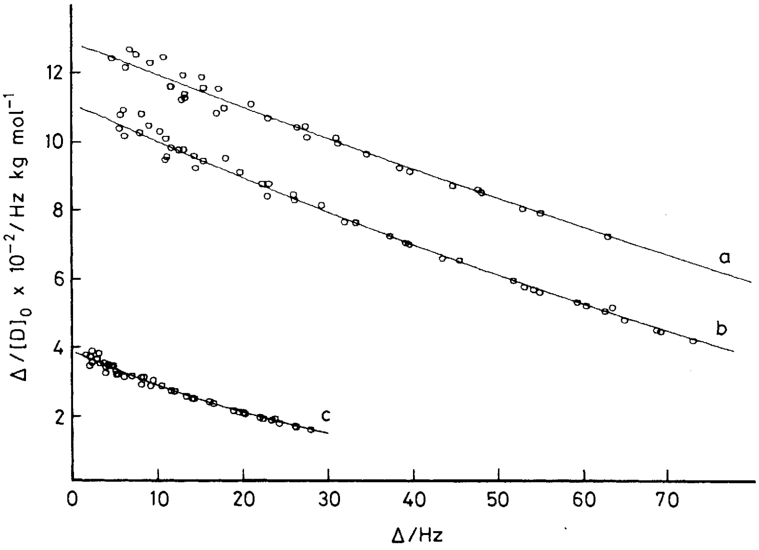


(1)

Table 1. Concentration ranges, saturation fraction (s) ranges [a] and number of solutions measured (N) for the various donor–picrylacetone systems

Donor	Solvent	Probe	s-Range	Range of [D] [b]/ mol kg^{-1}	N
Benzene	CCl_4	Ar	0.23—0.66	0.3—1.5	30
		CH_2	0.23—0.66	0.3—1.5	30
			0.23—0.94	0.3—7.1	36
		Me	0.23—0.66	0.3—1.5	30
			0.23—0.94	0.3—7.1	36
Naphthalene	CCl_4	Ar	0.14—0.67	0.03—0.30	42
		CH_2	0.14—0.77	0.03—0.43	46
		Me	0.14—0.75	0.03—0.43	45
Phenanthrene	CCl_4	Ar	0.08—0.76	0.01—0.59	33
		CH_2	0.08—0.75	0.01—0.59	53
		Me	0.07—0.85	0.01—0.59	53
Pyrene	CCl_4	Ar	0.18—0.61	0.01—0.06	32
		CH_2	0.18—0.81	0.01—0.17	44
		Me	0.17—0.84	0.01—0.17	45
	$CDCl_3$	Ar	0.23—0.69	0.01—0.18	34
		CH_2	0.23—0.72	0.01—0.20	39
		Me	0.23—0.72	0.01—0.20	39

[a] Saturation fraction is the fraction of A complexed. In this Table the values are calculated on the assumption that DA and D_2A complexes are formed. [b] Concentrations in mol kg^{-1} of solution.



Scatchard plots relating to the shifts of: a, aromatic protons; b, methylene protons; c, methyl protons in picrylacetone with various concentrations $[D]_0$ of pyrene in carbon tetrachloride

Table 2. 1 : 1 Association constants (K_1) and $\Delta_0(1)$ values for various electron donor–picrylacetone complexes at 33.5 °C using the ^1H probes Ar, CH_2, and Me of the acceptor with: (i) assumption (a), equation (2); (ii) assumption (b), equation (3), and for the latter the a_2 values

			Equation (2) [assumption (a)]		Equation (3) [assumption (b)]		
Donor	Solvent	Probe	K_1/kg mol^{-1}	Δ_0 (p.p.m.)	K_1/kg mol^{-1}	Δ_0 (p.p.m.)	a_2 (p.p.m.)
Benzene	CCl_4	Ar	0.49 ± 0.006 [a]	1.23 ± 0.01 [a]	0.54 ± 0.006 [a]	1.09 ± 0.01 [a]	0.02 [a]
		CH_2	0.41 ± 0.003	1.04 ± 0.01	0.40 ± 0.002	1.08 ± 0.01	−0.002
		Me	0.30 ± 0.002	0.92 ± 0.01	0.31 ± 0.002	0.89 ± 0.01	0.002
Naphthalene	CCl_4	Ar	2.0 ± 0.02	1.53 ± 0.04	2.3 ± 0.02	1.25 ± 0.03	0.21
		CH_2	1.9 ± 0.03	1.07 ± 0.05	2.4 ± 0.04	0.81 ± 0.03	0.19
		Me	1.4 ± 0.06	0.67 ± 0.05	2.3 ± 0.1	0.31 ± 0.03	0.22
Phenanthrene	CCl_4	Ar	5.3 ± 0.1	1.55 ± 0.25	6.5 ± 0.01	1.19 ± 0.1	0.64
		CH_2	5.3 ± 0.1	1.33 ± 0.2	6.2 ± 0.05	1.12 ± 0.06	0.28
		Me	4.4 ± 0.1	0.55 ± 0.2	6.8 ± 0.1	0.33 ± 0.03	0.29
Pyrene	CCl_4	Ar	9.6 ± 0.3	1.53 ± 0.08	12.2 ± 0.4	1.07 ± 0.06	1.77
		CH_2	10.0 ± 0.2	1.25 ± 0.06	12.3 ± 0.2	0.95 ± 0.04	0.95
		Me	8.5 ± 0.2	0.50 ± 0.15	12.4 ± 0.3	0.31 ± 0.10	0.59
	$CDCl_3$	Ar	3.6 ± 0.1	1.63 ± 0.03	5.4 ± 0.2	0.88 ± 0.02	1.22
		CH_2	3.7 ± 0.1	1.33 ± 0.02	5.3 ± 0.1	0.80 ± 0.01	0.83
		Me	3.0 ± 0.1	0.57 ± 0.02	3.7 ± 0.1	0.41 ± 0.01	2.07

[a] Errors calculated at 95% confidence level.

anthrene was recrystallised thrice from ethanol, m.p. 101 °C, ^1H n.m.r. indicated that if there remained any anthracene impurity it was less than 1%; pyrene was recrystallised twice from ethanol, m.p. 150 °C; carbon tetrachloride (B.D.H. spectroscopic grade) and deuteriochloroform (Aldrich), were used without further purification.

N.m.r. line positions were measured at 33.5 °C on a Bruker HX90/2 spectrometer internally referenced from 2% tetramethylsilane (Me_4Si). Previous work [18] had established the justification for using this internal reference for such systems. For each solution the average of five measurements was taken. Agreement was always within ±0.1 Hz. Although all the experimental measurements were made in Hz, and are so listed in the Supplementary Publication, values of $\Delta_0(1)$ and $\Delta_0(2)$ have been expressed in p.p.m. in the paper.

All solutions were made up by weight and concentrations expressed in mol kg^{-1} of solution. The dimensions of K_1 and K_2 are in reciprocal concentration units. The acceptor concentration for the main series of experiments was 3×10^{-3} mol kg^{-1}. Some determinations were repeated with $[A]_0 = 5 \times 10^{-3}$ mol kg^{-1} and $[A]_0 = 1.5 \times 10^{-3}$ mol kg^{-1}. The results were independent of these changes in $[A]_0$. Donor concentrations were in the ranges indicated in Table 1.

Detailed experimental data are listed in Supplementary Publication No. SUP 23687 (17 pp.).*

In all cases Scatchard plots of $\Delta/[D]_0$ *versus* Δ are curved,

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* For details of the Supplementary Publication Scheme see Instructions to Authors, *J. Chem. Soc., Perkin Trans. 2*, 1983, Issue 1.

Table 3. Association constants K_1 and K_2 and shifts $\Delta_0(1)$ and $\Delta_0(2)$ for various electron donor–picrylacetone complexes at 33.5 °C using the ^1H probes Ar, CH_2, and Me of the acceptor [based on equation (5), assumption (c)]

Solvent	Donor	Donor concentration [a] (mol kg^{-1})	Probe	K_1/kg mol^{-1}	K_2/kg mol^{-1}	$\Delta_0(1)$ [b]	$\Delta_0(2)$ [b]
CCl_4	Benzene	0.3—1.0	Ar	1.0 ± 0.1 [c]	0.2 ± 0.05 [d]	0.61 ± 0.03 [c]	1.38 ± 0.22 [d]
			CH_2	1.0 ± 0.1	0.2 ± 0.05	0.43 ± 0.03	1.18 ± 0.28
			Me	1.0 ± 0.1	0.2 ± 0.05	0.27 ± 0.03	0.92 ± 0.16
CCl_4	Benzene	0.3—7.1	Ar [e]	—	—	—	—
			CH_2	0.93 ± 0.1	0.25 ± 0.05	0.46 ± 0.03	1.02 ± 0.28
			Me	1.0 ± 0.1	0.2 ± 0.05	0.28 ± 0.03	1.07 ± 0.28
CCl_4	Naphthalene	0.03—0.30	Ar	5.2 ± 0.3	1.0 ± 0.1	0.60 ± 0.02	1.71 ± 0.22
		0.03—0.43	CH_2	5.3 ± 0.4	1.0 ± 0.15	0.40 ± 0.02	1.21 ± 0.16
		0.03—0.43	Me	5.5 ± 0.8	0.5 ± 0.2	0.18 ± 0.03	1.05 ± 0.22
CCl_4	Phenanthrene	0.01—0.59	Ar	8.6 ± 0.2	1.3 ± 0.2	0.95 ± 0.02	2.00 ± 0.08
			CH_2	8.5 ± 0.1	1.2 ± 0.2	0.84 ± 0.02	1.61 ± 0.10
			Me	7.7 ± 0.7	0.4 ± 0.3	0.33 ± 0.02	1.22 ± 0.33
CCl_4	Pyrene	0.01—0.06	Ar	20.5 ± 1	4.2 ± 1.0	0.70 ± 0.02	1.79 ± 0.04
		0.01—0.17	CH_2	21.4 ± 1	3.8 ± 0.5	0.58 ± 0.01	1.51 ± 0.04
		0.01—0.17	Me	20.4 ± 1	2.8 ± 0.5	0.21 ± 0.02	0.70 ± 0.10
$CDCl_3$	Pyrene	0.01—0.18	Ar	7.9 ± 0.5	1.0 ± 0.4	0.73 ± 0.02	2.78 ± 0.24
		0.01—0.2	CH_2	7.8 ± 0.5	1.1 ± 0.4	0.64 ± 0.02	1.87 ± 0.18
		0.01—0.2	Me	8.1 ± 0.5	1.2 ± 0.4	0.21 ± 0.02	0.77 ± 0.18

[a] In mol kg^{-1} of solution. [b] In p.p.m. [c] Errors at 95% confidence level. [d] Errors at 95% confidence level with allowance for range of values of K_1, $\Delta_0(1)$. [e] Could not be measured because of overlap of signal with that of benzene.

e.g. the Figure. In the application of assumption (a) a linear least-squares program was used to calculate K_1 and $\Delta_0(1)$. This was refined by an iterative procedure to replace $[D]_0$ by [D] in the Scatchard plot. In assumption (b) the program SCAUS devised by Stamm and his co-workers was used. This program has built in the transformation from $[D]_0$ to [D]. In assumption (c) a program MINDS was used. This involves a sub-routine held on ICL Library files. Again a procedure was included so that concentrations of donor were expressed as [D]. That is, in all three procedures, the $[D]_0$ terms in equations (2), (3), and (5) are replaced by the equilibrium concentrations [D]. A further sub-routine devised by Dr. R. A. Brown was used to evaluate the errors at given confidence levels in the evaluation of parameters by the application of equation (5).

Results and Discussion

(a) *Assumption of Simple* 1 : 1 *Association.*—Application of equation (2), with the refinement $[D]_0 \longrightarrow [D]$, yields values of K_1 and $\Delta_0(1)$ listed in Table 2. The results show for each system a dependence of the value of K_1 on the particular ^1H probe. The relative effect is greatest for the benzene interaction. This dependence, and the related non-linearity of the Scatchard plot, underlines the insufficiency of this model.

(b) *Assumption of* 1 : 1 *Association with AUS.*—Application of equation (2) through Stamm's program yields values of K_1 $\Delta_0(1)$ and a_2 listed in Table 2. There is generally good agreement between the K_1 values obtained from the three ^1H probes for each of the systems studied with the exception of benzene. Here the poor agreement under condition (a) is exacerbated by the application of equation (3).

The present results show a second inconsistency with the AUS model. For a series of complexes of aromatic hydrocarbon donors with the same electron acceptor in the same solvent we might reasonably expect to see the same sequence of a_2 values for the series of ^1H probes irrespective of the particular donor. Incidentally, if the dominant configuration of D relative to A in the complex involves the interaction of the aromatic π* LUMO of (1), then the AUS argument should lead to the order Me > CH_2 > Ar for the a_2 values for a given complex. In no case is this observed. In fact, it is more likely that complexing involves a wide range of D–A configurations. If such is the case the overall effect, which must involve details of the dynamics of formation and dissociation, could not be predicted simply. It should also be noted that the set of $\Delta_0(1)$ values of the benzene complexes for the three probes which, in this analysis have nearly equal values, is not consistent with the sets of values derived for the other DA systems (Table 2).

(c) *Assumption of* 1 : 1 *and* 2 : 1 *Association.*—Application of equation (5) with the refinement $[D]_0 \longrightarrow [D]$ yields the values in Table 3. Here there is good agreement between the K_1 values from the three probes for each of the systems, including the benzene interaction. Furthermore the Δ_0 values for the three ^1H probes are in the expected order Ar > CH_2 > Me for aromatic π–aromatic π* interaction between D and A.

The values of the parameters K_2 and $\Delta_0(2)$ appear to be generally acceptable. However, it should be emphasised that these derive from what is essentially a second-order perturbation of the simple 1 : 1 association. In terms of the Scatchard plot [equation (5)] the computation requires an evaluation of the intercept with the abscissa to determine $\Delta_0(2)$.[6,13] We prefer to maintain relatively dilute solution conditions. Furthermore, in the case of donors of increasing size, solubility provides a practical upper limit to $[D]_0$ and consequently on Δ. It therefore follows that the precision with which we can evaluate $\Delta_0(2)$ must be less than that for $\Delta_0(1)$. Also, since the gradient of the Scatchard plot as represented by equation (5) at the high saturation limit[6] is $-K_2[1 - \Delta_0(1)/\Delta_0(2)]^{-1}$, it must also follow that the precision with which K_2 can be evaluated must be significantly less than that for K_1. An additional factor which may, in part, account for the less consistent values of K_2 for some of the systems as evaluated by the methyl probe is that the magnitudes of these shifts are significantly smaller than those of the Ar or CH_2 protons, leading again to lower precision which will more prominently reflect in the evaluation of K_2 and $\Delta_0(2)$ than of K_1 and $\Delta_0(1)$.

In the case of the benzene interactions where there is no solubility constraint, a second series of solutions was measured in which the range of $[D]_0$ was greatly increased. The results (Table 3) show that, at least for this system, the analysis is not seriously dependent on the $[D]_0$ range. It must be recognised, however, that such systems introduce the additional factor of a large change in the bulk solvent within the series of solutions used to evaluate the four parameters K_1, K_2, $\Delta_0(1)$, and $\Delta_0(2)$, which weakens the argument for the analysis.

Whilst model (c) is more consistent than model (b) with the present observations, the results cannot be taken to demonstrate that an AUS effect does not exist, but rather that any such effect is too small to be significant when the degree of complexation is of the order manifested in the present systems as opposed to very weak interactions where K_1 might be <0.3 kg mol^{-1} (0.2 dm^3 mol^{-1}), although any such quantitative definition of a very weak interaction is arbitrary.[13]

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