1 : 1, 2 : 1, and Apparent Association Constants for a Series of Electron Donor–Acceptor Complexes involving 1,3,5-Trinitrobenzene and Tetrafluoro-*p*-benzoquinone (Fluoranil)

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On the hypothesis that in certain solutions termolecular as well as bimolecular complexes are formed between π-donor and π*-acceptor molecules, the apparent, 1 : 1, and 2 : 1 association constants have been estimated for the series of donors: benzene, toluene, *p*-xylene, mesitylene, durene, pentamethylbenzene, and hexamethylbenzene with 1,3,5-trinitrobenzene in cyclohexane, and of the same series of donors with fluoranil in carbon tetrachloride. The results indicate that within these two groups of complexes of a set of structurally related donors and a common acceptor the apparent association constant is directly proportional to the 1 : 1 association constant (and also to the corresponding 2 : 1 association constant). This observation suggests that a number of published values of apparent association constants for such series of complexes are of use in making comparisons within the particular group, although the evidence given in the present paper suggests that such comparisons *between* groups might be misleading. The same comments apply to quantities which are dependent in their experimental estimation on an implicit or explicit knowledge of the concentration of the complex in solution (*e.g.* the molar absorption coefficient of the complex).

IN determinations of association constants for complexes between π-donors (D) and π*-acceptors (A), it has been noted that the model of a simple 1 : 1 association in which the quotient [AD]/[A][D] is a constant, does not always accommodate the experimental observations.[1] Thus Scatchard[2] plots of $A/(D)_0[A]_0$ against $A/[A]_0$ (where A is the absorbance due to the complexed species and the zero subscripts indicate the total, *i.e.* free and complexed, concentrations of the particular species) under the condition $[D]_0 \gg [A]_0$ are sometimes curved.[3] For 1 : 1 complex formation, in which the solute species behave ideally this plot should be linear. A similar effect is sometimes observed in the concentration dependence of the change in the line position (Δ) of the magnetic resonance of a nucleus in A on addition of D under the condition $[D]_0 \gg [A]_0$, the corresponding Scatchard plot being $\Delta/[D]_0$ against Δ.[3]

We[3] have recently accounted for the behaviour of a number of such systems by postulating that this anomalous behaviour is the result of the formation of small amounts of a termolecular complex AD_2 in addition to the 1 : 1 complex AD [reactions (1) and (2)]. The curvature of the Scatchard plots is often only apparent when a sufficient concentration range of D is used.[4] In many earlier determinations of association constant either this precaution was not taken or other plots, such as that due to Benesi and Hildebrand,[5] which are insensitive to departures from simple ideal 1 : 1 complex formation, were used. As a consequence, many published values of association constants for π-donor–π^*-acceptor interactions may be significantly in error and might reasonably be termed apparent ' association constants K_{app}. In the case of two series of such complexes we have evaluated and compared K_{app}, K_1, and K_2 on the basis of the hypothesis of the presence of termolecular complexes.

$$A + D \rightleftharpoons AD \quad K_1 = [AD]/[A][D] \qquad (1)$$

$$AD + D \rightleftharpoons AD_2 \quad K_2 = [AD_2]/[AD][D] \qquad (2)$$

We think that an explanation of the curvature in terms of a lack of ideality in a 1 : 1 association for which the true (thermodynamic) association constant is given by equation (3) is less likely in that the activity coefficient quotient $\gamma_{AD}/\gamma_A\gamma_D$ would need to change very considerably over a small concentration range of D, for example, by a factor of over two in the range $[D]_0 = 1$—8×10^{-2}M in the hexamethylbenzene–1,3,5-trinitrobenzene system in cyclohexane reported below. Furthermore, consistent values of K_1, on the basis of termolecular (AD_2) formation in solutions where $[D]_0 \gg [A]_0$, have been obtained for one system in four separate experiments, namely by spectrophotometry and by the n.m.r. shift method using the condition $[D]_0 \gg [A]_0$ and $[D]_0 = [A]_0$.[3]

$$K_t = \frac{[AD]}{[A][D]} \cdot \frac{\gamma_{AD}}{\gamma_A\gamma_D} \qquad (3)$$

EXPERIMENTAL

Chemicals were purified as described in previous papers.[3,6]

Chemical shift measurements of the ^{1}H n.m.r. resonance of 1,3,5-trinitrobenzene (*ca.* 10^{-3}M) in a series of solutions containing varying concentrations usually in the range (*ca.* 0.01—0.7M) of donor in cyclohexane. In terms of the apparent association constants these solutions contain a fraction of between *ca.* 0.04 and 0.7 of the species A (in this case 1,3,5-trinitrobenzene) in the complexed state. These fractions have been termed ' saturation fractions ' (s) by Deranleau.[4] The donors were benzene and the methylbenzenes indicated in the Tables. Similar measurements were made on the corresponding fluoranil systems in carbon tetrachloride. All measurements were made on a Bruker HX 90/2 spectrometer. In the case of ^{1}H measurements the field was locked on to, and the signals referenced from, the proton absorption of solvent cyclohexane. For the ^{19}F measurements, 2% tetramethylsilane was used as internal reference and field lock. For the 1,3,5-trinitrobenzene determinations the measurements were made at 35.0 ± 0.5° unless otherwise stated. In the case of the fluoranil complexes the measurements were made at 33.3 ± 0.1°. The built-in temperature control, with additional thermal insulation in the vicinity of the probe enabled a temperature control of ±0.1° for a given determination. This was checked before and after the run by means of a separate thermocouple placed in a dummy tube.

Apart from the association constant a second parameter may be calculated for each complex. This is the chemical shift of the measured nucleus in the pure complex compared with the shift of the same nucleus in the uncomplexed species: this is termed Δ_0.

Values of K_1, K_2, $\Delta_0(1)$, and $\Delta_0(2)$ were obtained from a series of measured values of Δ for solutions of donor concentrations $[D]_0$ by computation using a program (MINDS) involving a subroutine held on ICL library files.

K_{app} and the corresponding value of Δ_0, designated Δ_0 (app), were obtained from the tangents to the curves of the plots of $\Delta/[D]_0$ against Δ at the high concentration ends of the ranges measured.

The complete experimental data are available as Supplementary Publication No SUP 21428 (18 pp., 1 microfiche).*

RESULTS

1,3,5-Trinitrobenzene Complexes in Cyclohexane.—Figure 1 shows the plots of $\Delta/[D]_0$ against Δ for the various complexes. Apart from benzene and toluene, which, within experimental error, did not appear to deviate from linearity, all the donors gave plots which are obviously curved. For these latter systems application of the MINDS program gave values of K_1 and K_2 which were somewhat dependent on the starting guesses and which in any case yield values which did not vary monotonically with increasing methylation of the donor as might be expected. A corresponding randomness was noted in the values of the two other computed parameters, $\Delta_0(1)$ and $\Delta_0(2)$. By comparison, the product terms $K_1\Delta_0(1)$ and $K_2\Delta_0(2)$ increased in a regular fashion with increasing methylation of the donor. The computation was therefore simplified by arbitrarily fixing

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[1] *E.g.* R. Foster in ' Molecular Complexes,' ed. R. Foster, Elek Science, London; Crane Russak, New York, 1974, vol. 2, p. 107.

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

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

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

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

[6] N. M. D. Brown, R. Foster, and C. A. Fyfe, *J. Chem. Soc.* (*B*), 1967, 406.

a value of $\Delta_0(1)$ at 30 Hz for all the 1,3,5-trinitrobenzene 1 : 1 complexes, irrespective of the particular donor. The consequent computed values of K_1, K_2, and $\Delta_0(2)$ are given in Table 1.

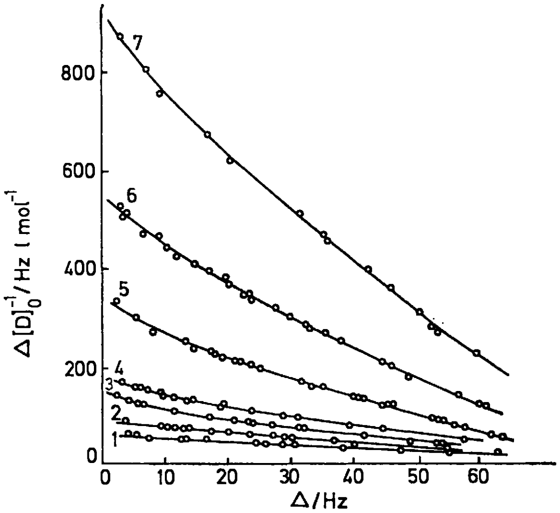

FIGURE 1 Plot of $\Delta/[D]_0$ against Δ from ^1H n.m.r. data for the complexes of (1) benzene; (2) toluene; (3) *p*-xylene; (4) mesitylene; (5) durene; (6) pentamethylbenzene; (7) hexamethylbenzene with 1,3,5-trinitrobenzene in cyclohexane at 35.0 ± 0.5°

Fluoranil Complexes in Carbon Tetrachloride.—Plots of $\Delta/[D]_0$ against Δ for all the systems studied gave curved plots, and all gave values for the four parameters K_1, K_2, $\Delta_0(1)$, and $\Delta_0(2)$ which were independent of the initial starting guess. These values are given in Table 2.

TABLE 1

Values of K_{app}, Δ_0 (app), saturation fraction (*s*), K_1, K_2, and $\Delta_0(2)$ for the association of 1,3,5-trinitrobenzene with various electron donors in cyclohexane at 35.0 ± 0.5° on the assumption that $\Delta_0(1)$ = 30 Hz, (=0.33 p.p.m.)

Donor	K_{app}/l mol^{-1}	Δ_0(app) [a]	*s*	K_1/l mol^{-1}	K_2/l mol^{-1}	$\Delta_0(2)$ [a]
Benzene	0.60	1.09	0.02—0.65	[b]	[b]	[b]
Toluene	1.1	0.88	0.04—0.66	[b]	[b]	[b]
p-Xylene	1.6	0.87	0.02—0.55	4.5	0.64	1.04
Mesitylene	2.2	0.83	0.03—0.72	5.6	1.1	0.89
Durene	3.5	0.88	0.03—0.80	10.5	1.9	0.91
Pentamethylbenzene	5.8	0.90	0.04—0.75	18.0	3.1	0.94
Hexamethylbenzene	10.1	0.91	0.07—0.72	29.7	5.8	0.93

[a] ^1H Signal of 1,3,5-trinitrobenzene measured in p.p.m. at 90.00 MHz. [b] Not possible to evaluate.

TABLE 2

Values of K_{app}, Δ_0 (app), saturation fraction (*s*), K_1, K_2 $\Delta_0(1)$, and $\Delta_0(2)$ for the association of fluoranil with various donors in carbon tetrachloride at 33.3 ± 0.1°

Donor	K_{app}/l mol^{-1}	Δ_0(app) [a]	*s*	K_1/l mol^{-1}	K_2/l mol^{-1}	$\Delta_0(1)$ [a]	$\Delta_0(2)$ [a]
Benzene	0.38	2.16	0.01—0.31	0.63	0.12	1.25	2.99
Toluene	0.56	2.56	0.01—0.43	1.1	0.25	1.29	2.89
p-Xylene	1.1	2.85	0.02—0.44	1.9	0.38	1.64	3.37
Mesitylene	1.6	3.17	0.02—0.47	3.0	0.44	1.76	3.97
Durene	2.9	3.78	0.04—0.80	5.5	0.75	2.30	4.22
Pentamethylbenzene	5.7	4.16	0.18—0.66	10.9	1.6	2.46	4.24
Hexamethylbenzene	10.8	4.49	0.16—0.75	20.4	2.9	2.66	4.58

[a] ^{19}F Signal of fluoranil in p.p.m. measured at 84.66 MHz.

DISCUSSION

The decision, described in the Results section, to assume that $\Delta_0(1)$ is independent of the particular donor in such a set of donors is not wholly indefensible. If it is accepted that Δ_0(app) is some measure of $\Delta_0(1)$ then the near constancy of Δ_0(app) with donor in Table 1 is of some consequence. This lack of sensitivity of Δ_0(app) on the donor in the case of 1,3,5-trinitrobenzenes had been noted previously.[6] It contrasts with the dependence of Δ_0(app) on the donor moiety for the fluoranil complexes (present work and ref. 6). The particular value of $\Delta_0(1)$ of 30 Hz has been taken as a rounded value from an earlier determination of 1,3,5-trinitrobenzene–hexamethylbenzene in carbon tetrachloride.[3] A plot of $K_1\Delta_0(1)$ against K_{app} [or of K_1 against K_{app} assuming $\Delta_0(1)$ 30 Hz, which in the circumstances, closely approximates to the former plot] is effectively a straight line passing through the origin such that $K_1 = (3.00 \pm 0.13)K_{app}$. This suggests that the earlier published K_{app} values for a series of complexes of a set of structurally related donors with a common acceptor species are directly proportional to K_1. Incidentally, a similar linear plot is obtained for K_2 against K_{app}, namely $K_2 = (0.59 \pm 0.03)\ K_{app}$.

However, it is the set of parameters obtained from the fluoranil complexes which leaves no doubt, at least for the series under investigation, that K_{app} is a linear measure of K_1 (Figure 2). A similar plot is obtained for K_2 against K_{app} (Figure 3). In these cases no assumptions are made in regard to any of the parameters and single-valued solutions are obtained from the computations. It may also be noted that $\Delta_0(1)$ and $\Delta_0(2)$ are both approximately proportional to Δ_0(app) throughout the fluoranil series of complexes.

Values of K_1 and K_{app} for a few other systems are available in the literature.[3,7] Some of these have been

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

plotted in Figure 2. It would appear that the linear relationship observed amongst a series of complexes of a set of related donors with a common acceptor cannot accommodate the values for *all* π-donor–π^*-acceptor interactions. A similar conclusion may be drawn concerning K_2 and K_{app} (see Figure 3). Alternatively, or in addition, the scatter of these latter points may reflect the inaccuracy of their determination.

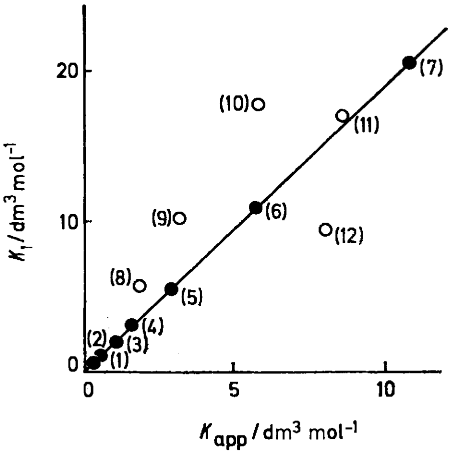

FIGURE 2 Plot of K_1 against K_{app} for the same series of donors as in Figure 1 with fluoranil in carbon tetrachloride at 33.3° (all plotted as ●). Corresponding points for other systems are marked ○ namely (8) hexamethylbenzene–2,4,6-trinitrobenzylidyne trifluoride in carbon tetrachloride; (9) hexamethylbenzene–1,3,5-trinitrobenzene in carbon tetrachloride; (10) pentamethylbenzene–1,3,5-trinitrobenzene in cyclohexane; (11) mesitylene–tetracyanoethylene in heptane; (12) *p*-xylene–tetracyanoethylene in heptane

For sometime it has been appreciated that to talk of the relative configuration of the two components in a 1 : 1 π-donor–π^*-acceptor complex in solution is to describe a time-averaged configuration or the most preferred of a wide range of configurations. Such a lack of a well defined structure may extend to the stoicheiometry whereby from time to time associations involving more than just one A and one D may be involved. Although such clustering might not be restricted to termolecular associations, *i.e.* AD_2 in solutions where $[D]_0 \gg [A]_0$, nevertheless it might be possible to represent such an effect as equivalent to the equilibria represented by equations (1) and (2).

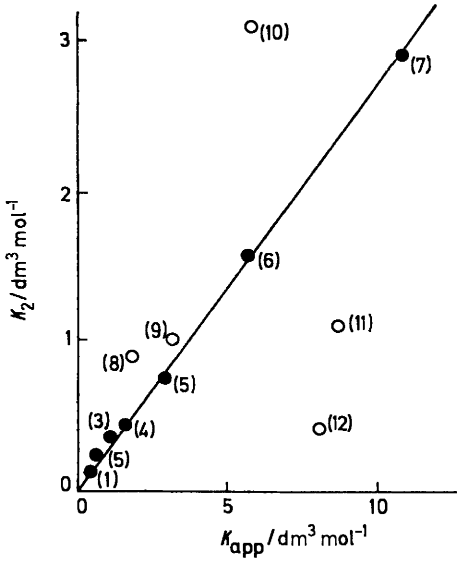

FIGURE 3 Plot of K_2 against K_{app} for the same series of donors as in Figure 1 with fluoranil in carbon tetrachloride at 33.3°. The identification of these points (●) and those corresponding to other systems (○) is the same as in Figure 2

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