Steric Hindrance to Termolecular Complex Formation in an Electron-donor–acceptor Complex of 2,7-Dinitro-1,6-methano[10]annulene

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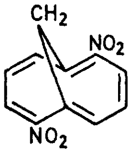
N.m.r. shift measurements of carbon tetrachloride solutions containing 2,7-dinitro-1,6-methano[10]annulene as an electron acceptor in the presence of large excesses of *NNN'N'*-tetramethyl-*p*-phenylenediamine as an electron donor indicate that complexes with only 1 :1 stoicheiometry are formed, whereas if the electron acceptor is *p*-dinitrobenzene, 1 :1 and 2 :1 complexes are formed. This difference can be accounted for in that *p*-dinitrobenzene is able to accommodate one donor molecule above and another below the acceptor molecular plane, whereas the annulene ring has one side which effectively sterically hinders the approach of a donor molecule.

THE formation of complexes between electron donors (D) and electron acceptors (A) in solution has been the subject of many studies.[1,2] Generally it is assumed that the stoicheiometry of the complexes is 1 : 1. Measurements are usually made on such systems under the concentration condition $[D]_0 \gg [A]_0$ where the subscript zero is a notation for the total (free plus complexed) concentration of the given species. The possible formation of higher-order complexes under these conditions has been considered occasionally, for example by McConnell and his co-workers.[3] More recently, particularly from spectrophotometric and n.m.r. shift measurements, evidence of 1 : 1 and 2 : 1 complexing has been obtained for a number of π-electron-donor–π^*-electron-acceptor systems for which the corresponding association constants K_1 and K_2 [equations (i)] have been

$$K_1 = [DA]/[D][A] \text{ and } K_2 = [D_2A]/[DA][D] \quad \text{(i)}$$

evaluated.[4-6] In the interaction of tetracyanoethylene with hexamethylbenzene the ground-state dipole moments of the 1 : 1 and 2 : 1 complexes have been estimated.[7] The fact that the latter is, within the admittedly large experimental error, zero, suggests that such termolecular complexes have a symmetrical structure of the form D · · · A · · · D, rather than A · · · D · · · D.



(1)

If this structure is correct then an electron acceptor which has on one side some built-in structural steric hindrance to the approach of a donor molecule should be able to form only 1 : 1 complexes, even in solutions containing large excesses of donor. Such an acceptor is 2,7-dinitro-1,6-methano[10]annulene (1). Its behaviour with the strong electron donor *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) in carbon tetrachloride solution is compared here with that of the ' two-sided ' electron acceptor *p*-dinitrobenzene.

EXPERIMENTAL

2,7-Dinitro-1,6-methano[10]annulene was prepared from 1,6-methano[10]annulene[8] by nitration with copper(II) nitrate in acetic anhydride.[9] Spectroscopic grade carbon tetrachloride was used. Other compounds were purified by standard techniques.

The method of determining K_1 and K_2 and chemical shifts of nuclei in the 1 : 1 and 2 : 1 complexes relative to shifts in the uncomplexed acceptor [$\Delta_0(1)$ and $\Delta_0(2)$, respectively] is outlined in the next section, and has been described fully elsewhere.[5] The errors were estimated by a sub-routine devised by Dr. R. A. Brown.[10] In the case of the annulene complex the n.m.r. line measured was the singlet due to the methano protons. For the *p*-dinitrobenzene interaction the signal arising from the four equivalent ring protons was used. Measurements were made with a Bruker HX/90 spectrometer operating at 90.00 MHz. All shifts were measured by a frequency meter. The average of four readings was taken for each solution; agreement was always found to be within ± 0.1 Hz. All solutions were made up by weight and all concentrations are expressed in mol kg^{-1} of solution. The donor concentrations were in the range 0.02—0.4 mol kg^{-1} and the acceptor concentration *ca.* 10^{-3} mol kg^{-1}. The annulene–TMPD system was measured at -20 °C and the *p*-dinitrobenzene–TMPD system at $+15$ °C.

p-Dinitrobenzene was chosen as the particular ' two-sided ' electron-acceptor as it had: (*a*) an ' apparent association constant ' (see below) with TMPD which was similar in magnitude to the association for the complex of the annulene (1) with TMPD; (*b*) the simplest of proton n.m.r. spectra. Initially, it was intended to use the obvious structural analogue of the annulene (1), namely 1,5-dinitronaphthalene, as the second acceptor. These

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[1] G. Briegleb, ' Elektronen-Donator-Acceptor-Komplexe,' Springer-Verlag, Berlin, 1961.

[2] R. Foster, ' Organic Charge-transfer Complexes,' Academic Press, London and New York, 1969.

[3] J. Landauer and H. M. McConnell, *J. Amer. Chem. Soc.*, 1952, **74**, 1221; D. M. G. Lawrey and H. M. McConnell, *ibid.*, pp. 6, 175.

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

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

[6] S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, 1957, **79**, 76; P. J. Trotter and D. A. Yphantis, *J. Phys. Chem.*, 1970, **74**, 1399; M. I. Foreman, J. Gorton, and R. Foster, *Trans. Faraday Soc.*, 1970, **66**, 2120; Y. E. Ho and C. C. Thompson, *J.C.S. Chem. Comm.*, 1973, 609; A. A. S. Bright, J. A. Chudek, and R. Foster, *J.C.S. Perkin II*, 1975, 1256.

[7] R. Foster and N. Kulevsky, *J.C.S. Faraday I*, 1973, 1427.

[8] E. Vogel, W. Klug, and A. Brever, *Org. Synth.*, 1974, **54**, 11.

[9] E. Vogel and W. A. Böll, *Angew. Chem.*, 1964, **76**, 784.

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

attempts were frustrated by the low solubility of this acceptor and also the broadness and the number of lines in the proton n.m.r. spectra. The spectrum of the acceptor does not have to be a singlet, but the more complex the spectra the lower will be the overall sensitivity in terms of observing a signal above the noise at a given acceptor concentration. The combination of adverse factors led to an unacceptably high error in the experimental measurements of the line positions.

All essential experimental data are listed in Supplementary Publication No. SUP 22005 (3 pp.).*

RESULTS AND DISCUSSION

The method of evaluating the association constant(s) is based on that described by Foster and Fyfe.[11] If there is only 1 : 1 association, then under the condition $[D]_0 \gg [A]_0$ equation (ii) applies, where K_1 is defined in

$$\Delta/[D]_0 = -K_1\Delta + K_1\Delta_0(1) \qquad \text{(ii)}$$

equations (i) and Δ is the line position of the measured nucleus in the acceptor in a solution containing a concentration $[D_0]$ of donor relative to the line position of the same nucleus of the acceptor in a solution containing no donor.

In the absence of 2 : 1 complexing, a plot of $\Delta/[D]_0$ *vs.* Δ should be linear, with gradient equal to $-K_1$.

On the other hand, if the termolecular complex D_2A is also present, instead of equation (ii), the relationship between $\Delta/[D]_0$ and Δ is [4,5] (iii) and a plot of $\Delta/[D]_0$ *vs.* Δ

$$\Delta/[D]_0 = -K_1\Delta(1 + K_2[D]_0) + K_1\Delta_0(1) + K_1K_2\Delta_0(2)[D]_0 \qquad \text{(iii)}$$

will be curved. If this plot can be determined over a sufficiently wide range of $[D]_0$ then K_1, K_2, $\Delta_0(1)$, and $\Delta_0(2)$ may be evaluated.

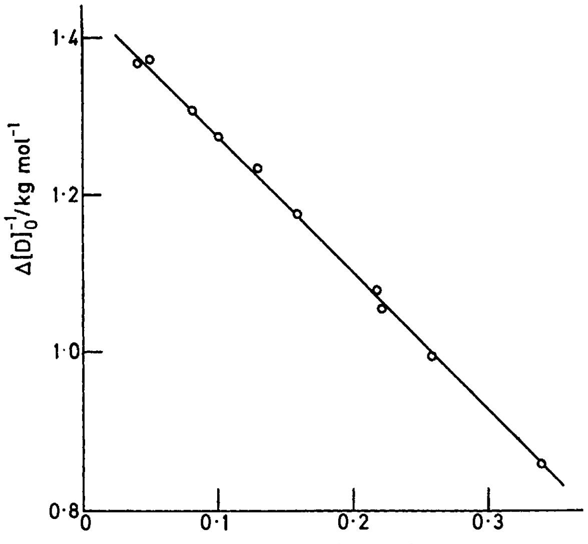

FIGURE 1 Plot of $\Delta/[D]_0$ *vs.* Δ for a series of solutions of the annulene (1) in the presence of various concentrations of TMPD (= D)

Measurements on the annulene–TMPD system over the range of $[D]_0$ permitted by the condition $[D]_0 \gg [A]_0$ and the solubility of TMPD yielded a plot of $\Delta/[D]_0$ *versus* Δ showing no trend towards curvature (Figure 1). The measurements were made at −20 °C in order to increase the chance of detecting curvature had it been present. The primary reason is that the larger the degree of complex formation, the less the relative experimental error. We would not expect K_1/K_2 to change significantly over the limited range of temperature we can use in that for other π-donor–π*-electron acceptor systems we have studied the values of $\Delta H^\ominus$ for the 1 : 1 and 2 : 1 complexes are similar.

Corresponding measurements on the *p*-dinitrobenzene–TMPD system yielded a curved plot (Figure 2). Measurements were made at +15 °C in order to make the line joining the two extreme experimental points (−2.2 mol kg^{-1}) comparable with the gradient of the line in Figure 1 (−1.8 mol kg^{-1}). The saturation fraction (*s*) as defined by Deranleau [4] for the annulene system, *viz.* 0.05—0.41, is similar to that for the *p*-dinitrobenzene system, namely 0.04—0.49, when the latter is based on a comparable linear treatment of the Scatchard plot.

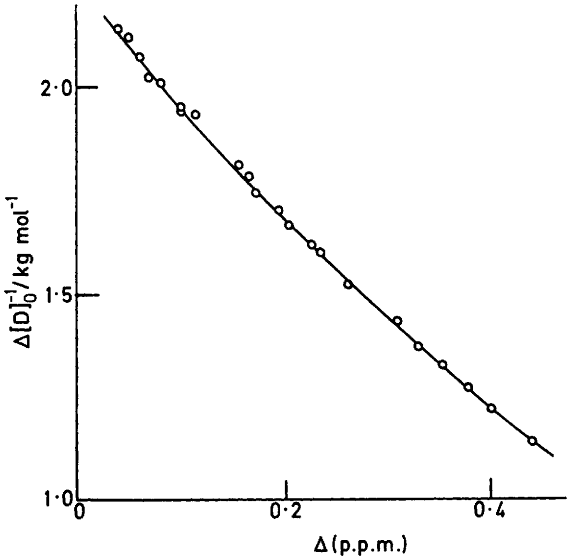

FIGURE 2 Plot of $\Delta/[D]_0$ *vs.* Δ for a series of solutions of *p*-dinitrobenzene in the presence of various concentrations of TMPD (= D)

The linearity of the plot in Figure 1 and the curvature of the plot in Figure 2 are consistent with the suggestion that TMPD can only form a 1 : 1 complex with the ' one-sided ' annulene acceptor when under similar conditions this donor can form a 2 : 1 as well as a 1 : 1 complex with the ' two-sided ' acceptor *p*-dinitrobenzene.

The values of the various parameters for the two systems are given in the Table. From measurements of K_1 for the annulene complex at five temperatures between −20 and +33.3 °C, $\Delta H^\ominus = -5.6 \pm 1.6$ kJ mol^{-1},

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* See Notice to Authors No. 7, *J.C.S. Perkin II*, 1976, Index issue.

[11] R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, 1965, **61**, 1626.

$\Delta S^{\ominus} = -17 \pm 5$ J K^{-1} (referred to standard state of 1 mol kg^{-1}; errors at 95% confidence level).

For the annulene acceptor, the line position of the methylene protons moves *down*field and that of the ring protons moves *up*field as the donor TMPD is added. A similar effect is observed when hexamethylbenzene is the donor. By contrast, the line position of the ring protons of *p*-dinitrobenzene moves *up*field as the donor is added. We had earlier suggested that the ^1H chemical shift changes which occur when this type of complex is formed could be the result of a perturbation in the ring current of the acceptor.[12] Thus, in all aromatic acceptors in which the proton probe is in the plane of the ring (*i.e.* in the zone deshielded by the ring current) the line moves upfield when donor is added; that is, the proton becomes less deshielded. By contrast, the bridge-methylene protons used as the n.m.r. probe in the annulene are in the ' shielding cone ' of the ring current. Reduction of the ring current on complex formation would reduce the shielding and lead to a downfield shift as is observed.

Values of parameters for acceptor–TMPD complexes in carbon tetrachloride [a]

Acceptor	Temp. (°C)	$\frac{K_1}{\text{kg mol}^{-1}}$	$\frac{K_2}{\text{kg mol}^{-1}}$	$\Delta_0(1)$ [b]	$\Delta_0(2)$ [b]
Annulene (1)	−20	1.78 ±0.12		0.82 ±0.06	
p-DNB [c]	+15	5.96 ±0.08	0.92 ±0.02	0.377 ±0.004	1.17 ±0.02

[a] Errors expressed at 99.9% confidence level. [b] Change in ^1H chemical shift (p.p.m.). [c] *p*-Dinitrobenzene.

Curvature of the Scatchard plot is dependent not only on the magnitudes of K_1 and K_2, but also on $\Delta_0(1)/\Delta_0(2)$. It is therefore impossible to state absolutely an upper limit to K_2 for the TMPD–annulene complex which might have gone unobserved. However, synthetic data indicate that we would have at least detected the result of termolecular complexing in this system of the ratios if K_1/K_2 for the annulene and *p*-dinitrobenzene complexes had been the same as had been $\Delta_0(1)/\Delta_0(2)$, whilst the actual value of K_1 for the annulene complex had remained at 1.8 kg mol^{-1}.

Experimental evidence, reported recently, suggests that in dilute solutions involving π-donor–π*-acceptor interactions of this type, activity effects are probably small.[13]

The present results, therefore, although not providing an irrefutable argument that ' normal ' π-donor–π*-acceptor can form $D \cdots A \cdot : \cdot D$ type termolecular complexes in solution, nevertheless support this suggestion.

Attempts to demonstrate a similar behaviour by unsubstituted 1,6-methano[10]annulene with π*-acceptors in solutions in which $[A]_0 \gg [D]_0$ were thwarted by solubility limitations.

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