

STUDIES OF INTER- AND INTRAMOLECULAR DONOR-ACCEPTOR INTERACTIONS—VIII

THE ACCEPTOR PROPERTIES OF METHYL 2,4,6-TRINITROBENZOATE

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Abstract—It is shown that the electron acceptor properties of methyl 2,4,6-trinitrobenzoate are fully comparable with those of 1,3,5-trinitrobenzene as judged from the position of the charge transfer absorption bands and the thermodynamic parameters for intermolecular complexes with various aromatic π -donors.

INTRODUCTION

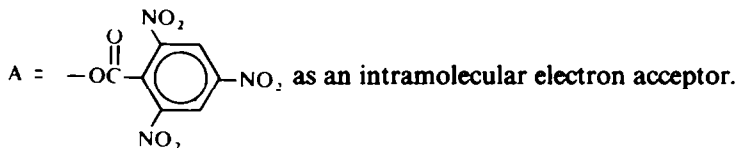
IN PREVIOUS papers¹⁻⁶ we have shown that intramolecular Charge Transfer (CT) interaction can occur in systems:



in which D is a *neutral* electron donor (e.g. an aromatic group) and A is a *positively charged* electron acceptor (e.g. a substituted pyridinium ion). There are indications⁸⁻¹² in the UV spectra of certain systems that such interaction also occurs when A is a *neutral* acceptor. In contrast with our results for the charged systems, the *intramolecular* CT transition in all uncharged systems so far investigated appears to be very weak and strongly overlapped by the absorptions of the separate chromophores.

Recently however, we described some systems which show discrete intramolecular CT transitions, resulting from interaction between a neutral donor and a neutral acceptor.⁷

We are now testing the possibility to use



For this group reasonable acceptor properties are expected in analogy with 1,3,5-trinitrobenzene.¹³⁻¹⁵ To obtain more insight in the acceptor properties of the 2,4,6-trinitrobenzoate group we studied the intermolecular CT interaction between some donors and methyl 2,4,6-trinitrobenzoate (TNMB).

RESULTS

The "strength" of an electron acceptor can be judged from two criteria:

- (i) The CT transition energy in complexes with electron donors, which is directly correlated with the electron affinity of the electron acceptor.
- (ii) The formation constant of its complexes with electron donors. As has been shown both criteria are not necessarily correlated.^{15,16}

CT absorption bands resulting from interaction of TNMB with some electron donors

TABLE 1. CT ABSORPTION BANDS RESULTING FROM THE INTERACTION BETWEEN SOME π -DONORS WITH METHYL-2,4,6-TRINITROBENZOATE (TNMB) AND WITH CHLORANIL MEASURED IN CHCl_3 AT 25°.

Donor	I_D (eV)	TNMB			Chloranil		
		λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	$h\nu$ (eV)	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	$h\nu$ (eV)
Benzene	9.24 ^a	—	—	—	—	—	—
1,4-dimethoxybenzene	7.64 ^b	—	—	—	—	—	—
1,2,4-trimethoxybenzene	7.49 ^b	439.5 ± 1	22.75	2.82	594.5 ± 1	16.82	2.09
1,2,4,5-tetramethoxybenzene	7.25 ^b	476	21.01	2.60	654.5	15.28	1.89
Naphthalene	8.16 ^a	—	—	—	—	—	—
Anthracene	7.43 ^a	475	21.05	2.61	639.5	15.64	1.94
Pyrene	7.72 ^a	465	21.51	2.67	618	16.18	2.01
3,4-benzopyrene	7.37 ^a	504	19.84	2.46	694	14.41	1.79

^a from Ref 18

^b from Ref 6

In Table 1 the long-wavelength absorption maxima observed in chloroform solutions containing TNMB and electron donors are compiled.

The energy of a CT transition ($h\nu_{\text{CT}}$) is given by:

$$h\nu_{\text{CT}} = I_D - E_A + C + W$$

in which:

I_D = ionization potential of the donor

E_A = electron affinity of the acceptor

C = Coulomb-term

W = term containing resonance and solvation effects.

If the interaction between an acceptor and a series of "structurally related" donors is studied, a linear relation between $h\nu_{\text{CT}}$ and I_D is normally found.¹⁷

The structure relationship between the donors tabulated in Table 1 is very poor as shown (*cf* Fig 1) by the lack of any simple correlation between I_D and $h\nu_{\text{CT}}$ in their complexes with TNMB.

The variations in C and W , which are apparently responsible for the absence of a linear correlation in Fig 1 can partially be eliminated by comparing the CT transition energies of two different electron acceptors with the same series of donors. This is shown in Fig 2 for TNMB and chloranil (*cf* Table 1).

The linear correlation found supports the CT character of the transitions observed.

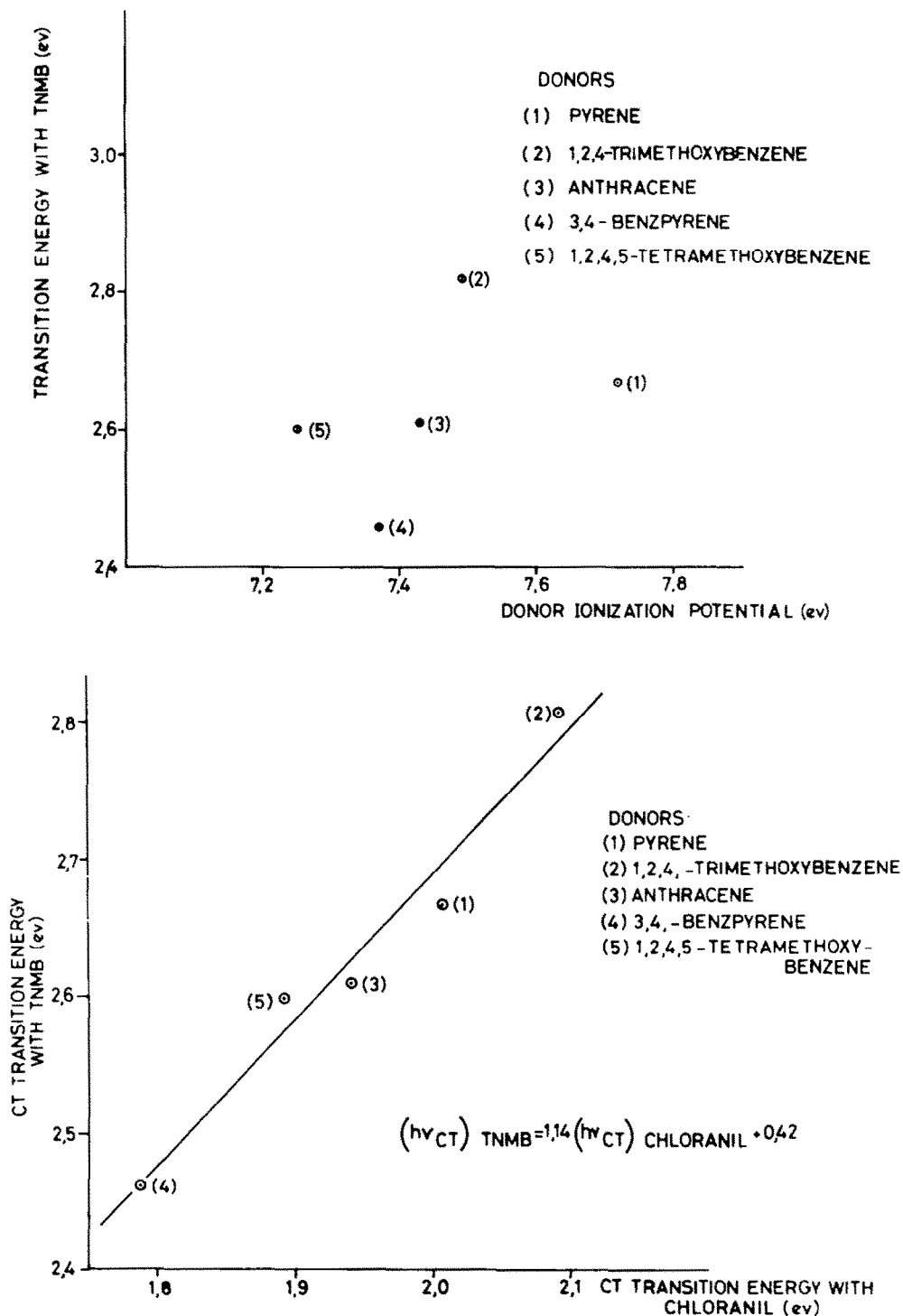


FIG 2

TABLE 2. PHYSICAL PARAMETERS FOR SOME CT COMPLEXES AS DETERMINED BY UV AND NMR ON A MOLARITY SCALE IN CHCl_3 AT 25°.

Complex	UV		NMR		
	λ^* (nm)	ϵ (l. mol ⁻¹ . cm ⁻¹)	K^{25} (l. mol ⁻¹)	Δ_0 (Hz at 100 MHz)	K^{25} (l. mol ⁻¹)
Benzene + TNMB	—	—	—	Ar-H	-27 ± 13
1,4-dimethoxybenzene	440	963 ± 30	0.4 ± 0.04	Ar-H	-28 ± 3
+ TNMB	460	761	0.4		0.6 ± 0.3
	480	525	0.5		0.8 ± 0.1
	500	312	0.5		
	520	162	0.6		
Naphthalene	440	461 ± 10	1.0 ± 0.1	Ar-H	-230 ± 3
+ TNMB	450	298	1.0		0.8 ± 0.02
	460	163	1.1	Ar-COO-CH ₃	0.1 ± 0.04
	470	80	1.3		
Anthracene	460	1042 ± 100	3.2 ± 0.5	Ar-H	-246 ± 25
+ TNMB	470	1131	3.0		2.3 ± 0.4
	475	1200	2.8	Ar-COO-CH ₃	-11 ± 16
	480	1131	3.0		2.7 ± 7.1
	490	1042	3.2		
Pyrene	450	865 ± 10	3.1 ± 0.1	Ar-H	-262 ± 12
+ TNMB	460	793	3.5		3.3 ± 0.04
	465	797	3.5	Ar-COO-CH ₃	-43 ± 3
	470	783	3.6		1.2 ± 0.1
	480	733	3.7		
Pyrene	420	1156 ± 20	1.6 ± 0.1	Ar-H	-265 ± 55
+ 2,4,6-trinitrotoluene	440	912	1.8		1.7 ± 0.6
	450	796	1.8	Ar-CH ₃	-193 ± 3
	460	670	1.8		1.6 ± 0.05
	480	376	2.1		

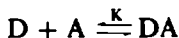
* λ_{max} has been underlined.

From the known E_A of chloranil (1.37 eV^{18}) and from the average difference in $h\nu_{CT}$ for chloranil and TNMB complexes with the donors from Table 1 (0.68 eV), we can estimate the E_A of TNMB to be $1.37 - 0.68 \approx 0.7 \text{ eV}$ under the assumption that the differences in $h\nu_{CT}$ between chloranil and TNMB complexes are only caused by differences in electron affinity. This E_A equals the E_A of 1,3,5-trinitrobenzene (0.7 eV^{18}) as estimated by the same method.

Formation constants for complexes of TNMB with some electron donors

Various methods have been employed for the measurement of the CT complex formation constant.¹⁹⁻²² Most commonly complex formation is detected from variations in the UV or the NMR spectra. Large discrepancies between the results from these two methods have been observed.²³ Whenever possible both methods should be used in combination and only mutually consistent values for the formation constants can be regarded as significant.

The spectrophotometric method (UV method)¹⁵

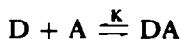


In this method it is assumed that the intensity of the observed intermolecular CT transition is proportional to the concentration of the complex DA.

By studying the influence of variation in the concentrations of D and A on the intensity of the CT band, both K and ϵ (= molecular extinction coefficient of DA) can be found at any wavelength. Frequently a graphical evaluation by the method of Benesi, Hildebrand and Scott^{15, 19} is applied.

This method however requires the use of a large excess of one of the components (in most cases the electron donor for solubility reasons). In our case we used a computer analysis of the measurements in which K and ϵ are found by an iterative procedure (Experimental) under the assumption of a 1:1 complex. In Table 2 the results obtained by this method are compiled. Wavelength dependence of K is found in some cases. This has been observed before^{16, 24, 25} and has as yet not been explained satisfactorily. The obvious explanation²⁴ involving formation of higher order complexes is insufficient in many cases.^{16, 23} However, changes in position and width of the CT absorption band induced by variation of the medium upon changes in concentration may account for this phenomenon.² (This implies that the complex does not follow Beer's law).

The NMR method²⁶



The fast equilibrium set up between D and A makes that the measured chemical shift (δ) of some magnetic nucleus in D or A is a weighted average of the chemical shifts for this nucleus in the free and complexed form. For instance if a magnetic nucleus in A is observed:

$$\delta = \delta_A \cdot p_A + \delta_{DA} \cdot p_{DA}$$

δ_A = chemical shift of the magnetic nucleus in free A, δ_{DA} = chemical shift of the magnetic nucleus in pure DA, p_A and p_{DA} are the fractions of free and complexed A

TABLE 3. THERMODYNAMIC PARAMETERS FOR SOME OF THE COMPLEXES FROM TABLE 2 AS ESTIMATED FROM THE CHEMICAL SHIFT OF THE AROMATIC PROTONS ON A MOLE-FRACTION SCALE (CF. EXPERIMENTAL PART).

Complex	K_x^{25}	Δ_0^* (Hz at 100 MHz)	ΔG^{25} (kcal. mol ⁻¹)	ΔH (kcal. mol ⁻¹)	ΔS (cal. mol ⁻¹ . deg. °)
1,4-dimethoxybenzene + TNMB	10.0 ± 1.2	-27 ± 1	-1.36	-1.75	-1.3
Naphthalene + TNMB	11.2 ± 0.1 (17.0)†	-211 ± 0.3	-1.43	-2.95	-5.1
Anthracene + TNMB	31.3 ± 5.9 (39.8)†	-221 ± 7	-2.04	-3.20	-3.9
Pyrene + TNMB	39.0 ± 0.3	-268 ± 0.3	-2.17	-3.10	-3.1
Pyrene + 2,4,6-trinitrotoluene	24.3 ± 5.9	-233 ± 10	-1.90	-3.07	-3.9

* Somewhat different values are found on a molarity scale (cf. Table 2 and exp. part).

† Value for corresponding complex of 1,3,5-trinitrobenzene, as determined spectrophotometrically.¹⁵

respectively. As in the UV method two parameters e.g. K and Δ_0 ($\Delta_0 = \delta_{DA} - \delta_A$) can be estimated from the variation of Δ ($\Delta = \delta - \delta_A$) upon variation of the concentrations (Experimental). It has been stated²⁶ that K can be determined more reliably by this method than by the UV method, since complications caused by deviations from Beer's law are excluded.

Another complication however arises since inconsistent values of K are found from measurements involving different magnetic nuclei within the same complex as will be shown below; this phenomenon has been observed before.²⁷

In Table 2 the results obtained by this method for complexes between TNMB and some donors are compiled.

K and Δ_0 were determined from the chemical shifts of the aromatic protons of TNMB and of its methoxyl protons.

DISCUSSION

At first sight it may seem somewhat surprising that the carbomethoxy group does not make TNMB a better acceptor than TNB. Apparently the electron attracting properties of the carbomethoxy group in TNMB are offset by steric hindrance between this group and the *ortho*-nitro groups, so that it cannot exert its full -M effect, by lack of coplanarity with the ring. Reasonable agreement (cf. Table 2) between K -values measured with UV and NMR are obtained when (i) concentrations are in the same range, (ii) NMR signals with relatively large Δ_0 values are considered. (Δ_0 is the chemical shift difference between corresponding nuclei in free and complexed acceptor molecules).

This last condition implies that reference protons should be close to the center of complex formation (e.g. on the aromatic nucleus) while methoxyl signals in TNMB lead to erroneous results (Table 2).

On the other hand reasonable values for K are obtained from the shift of the Me signals in complexes between 2,4,6-trinitrotoluene and pyrene (Table 2). The Δ_0 -values in all these complexes suggest structures with parallel planes of donor and acceptor and approximate centro-symmetry.

EXPERIMENTAL

TNMB was prepared by reaction of MeI with the Ag salt of trinitrobenzoic acid²⁸ (m.p. 158–160°). Trinitrotoluene and all donors used were of the purest grade commercially available.

To the chloroform (Merck-UVASOL) 2% TMS and 1% cyclohexane were added as NMR references. In all concentration ranges the chemical shift difference between TMS and cyclohexane was found to be constant.

For determination of equilibrium constants, a series of solutions were made with an acceptor concentration of $5 \cdot 10^{-3}$ M and donor concentration varying from $5 \cdot 10^{-3}$ M to approximately 1 M.

The same samples of solns were used for the UV and NMR measurements. UV spectra were recorded on a Cary Model 14 recording spectrophotometer at 25° in cells of 1 cm pathlength. NMR spectra were recorded on a Varian HA100 spectrometer at 25° and 50°. Under the assumption of a 1:1 complex the UV absorption (E) in the region of the CT absorption band equals

$$\epsilon_{DA}[DA]$$

when the separate donor and acceptor do not absorb in the spectral region studied.

Thus

$$E = \epsilon_{DA}[DA] = \epsilon_{DA} \cdot K \cdot [D][A] = \\ = \epsilon_{DA} \cdot K([D_0] - [DA])([A_0] - [DA])$$

K = equilibrium constant for complex formation. $[D_0]$ and $[A_0]$ are the stoichiometric concentrations of D and A.

The degree to which the NMR signal of a nucleus in A is shifted upon complex formation is given by

$$\Delta = \Delta_0 \frac{[DA]}{[A_0]}$$

or

$$\Delta[A_0] = \Delta_0 \cdot K[D][A] = \\ = \Delta_0 \cdot K([D_0] - [DA])([A_0] - [DA])$$

A computer program was used to determine from the measured UV absorptions and NMR shifts the parameters ϵ_{DA} , K and Δ_0 by iterative procedure.^{16, 29}

For determination of the thermodynamic parameters the NMR data at 25° and 50° were treated on a mole fraction scale (Table 3).

A slight dependence of Δ_0 on the concentration scale is observed (Tables 2 and 3).

This has been noted before and can be attributed to the non-ideal character of the solns.²⁶

ΔH and ΔS were calculated from the variation of the chemical shift (Δ) in a given soln when the temp was raised from 25° to 50°.

Under the assumption that Δ_0 is temp independent the following expressions hold:

$$\Delta G = -RT \ln K_x = -RT \left[\ln \frac{\Delta_0 \Delta}{\Delta_0 - \Delta} \ln (\Delta_0 [D_0] - \Delta [A_0]) \right]$$

ΔH can then be calculated, if ΔS is assumed to be temp independent, from the observed chemical shifts (Δ) in a given soln at two temps with

$$\Delta H = - \frac{T_1 T_2}{T_2 - T_1} R \left[\ln \frac{\Delta_0 [D_0] - \Delta^{T_2} [A_0]}{\Delta_0 [D_0] - \Delta^{T_1} [A_0]} + \ln \frac{\Delta^{T_1} (\Delta_0 - \Delta^{T_2})}{\Delta^{T_2} (\Delta_0 - \Delta^{T_1})} \right]$$

In this expression the term containing $[D_0]$ and $[A_0]$ usually can be neglected.

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