Tetrahedron, 1964, Vol. 20, pp. 1489 to 1493. Pergamon Press Ltd. Printed in Northern Ireland

INTERACTION OF ELECTRON ACCEPTORS WITH BASES—XI[1]

OUTER CHARGE-TRANSFER COMPLEXES OF DINITRONAPHTHALENES WITH N,N,N',N'-TETRAMETHYL-*p*-PHENYLENEDIAMINE

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(*Received* 8 *February* 1964)

Abstract—The stability constants of complexes of each of the ten dinitronaphthalenes with N,N,N'N'-tetramethyl-*p*-phenylenediamine in cyclohexane have been measured by a spectroscopic method. The relative stabilities can be satisfactorily explained by assuming that nitro groups in β-positions have higher electronegativities than those in α-positions.

No SYSTEMATIC study appears to have been made of the "outer" charge-transfer complexes which polynitronaphthalenes should form in their rôle as electron acceptors with electron donor molecules. It has been shown[2] that for dinitrobenzenes with alkylanilines as the donor molecule the relative stability of the complex is: 1,2- < 1,3- < 1,4-. This was interpreted in terms of the $-$I and $-$M effect of the nitro group in the acceptor molecule. In the case of the 1,3-isomer the $-$M effect of the two groups is not concerted and this might therefore be expected to be the weakest acceptor of the three. The spatially more extensive delocalization in the 1,4-isomer leads to the expectation that this would be more effective than the 1,2-isomer. Steric interference of the two nitro groups in this latter isomer however makes this in fact the weakest acceptor of all three isomers. It is presumed that a major contribution to this weakness is the loss of $-$M delocalization through the non-planarity of the nitro groups with the ring. Some vindication of this idea is that with the corresponding dicyanobenzenes the order of stability of the complexes[1] (with the donor N,N,N',N'-tetramethyl-*p*-phenylenediamine, henceforth described as TMPD) is in the order 1,3- < 1,2- < 1,4-. In this case the linear nitrile substituents allow for a planar configuration even in the vicinal substituted compound.

In di-substituted naphthalenes the lower symmetry of the parent molecule gives rise to the possibility of other structural differences, absent in the case of benzene derivatives, which might affect the relative complexing ability.

RESULTS AND DISCUSSION

Mixtures of a dinitronaphthalene (A) and a common electron donor, TMPD (D) in solution show an optical absorption in excess of the sum of both components alone in solution. This absorption is characteristic of the complex as a whole. It may appear as a resolved band with a discrete maximum. The equilibrium constant (K) for the interaction:

$$A + D \leftrightharpoons (AD)_{CT} \qquad (1)$$

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[1] Part X: R. Foster and T. J. Thomson, *Trans. Faraday Soc.* **59**, 2287 (1963).

[2] B. Dale, R. Foster and D. LL. Hammick, *J. Chem. Soc.* 807 (1954).

where $(AD)_{CT}$ is the charge-transfer complex, $K = [(AD)_{CT}]/[A][D]$ l. mole^{-1} and $\Delta G = -RT \ln K$ has been determined in each case from spectrophotometric measurements of this absorption. The method presently used has been described previously by Foster *et al.*[3] TMPD was chosen as the donor since it is known[4] to be a very effective electron donor in charge-transfer complexes, giving high values of K; the transitions in the donor molecule itself being at high energies relative to other donor molecules which might give comparable K values and comparable positions of the charge-transfer band. Obviously the more separated the intermolecular transition is from transitions in the components, the easier it is to use this latter absorption as a measure of the concentration of the complex. Cyclohexane was used as the solvent in order to minimize solvent–solute interaction. Previous work[5,6] has shown that, apart from the perfluorohydrocarbons,[7] the association constants are higher in the paraffins than in other aprotic solvents. Unfortunately the dinitronaphthalenes were found to be only sparingly soluble in cyclohexane, though more soluble in cyclohexane containing TMPD. In practice this has restricted measurements to those at, or above, room temperature. At elevated temperatures however, values of K were too small to be sufficiently reliable for the evaluation of ΔH and ΔS of the equilibrium (1). Mulliken and Orgel[8] have pointed out that in such evaluations of K, and incidently ϵ (the molar extinction coefficient of $(AD)_{CT}$), no cognisance is made of contact charge-transfer,[8] consequently these values of K and ϵ should be termed "apparent". The results of the determinations are summarized in Table 1.

Mulliken[9] has described the ground state ψ_N of charge-transfer complexes in terms of: (i) a no-bond function $\psi(A, D)$ which includes such van der Waals interactions as localized dipole–dipole, dipole-induced dipole, quadrupole, dispersion and suchlike forces, and: (ii) a dative structure $\psi(A^- - D^+)$ in which one electron has been transferred from the donor to the acceptor molecule. For weakly interacting systems, the contribution of this latter function will be small in the ground state, i.e. $b \ll a$ in Eq. 2:

$$\psi_N = a\psi(A, D) + b\psi(A^- - D^+) \tag{2}$$

It is the transition to the excited state ψ_E, in which the main structure is the dative function $\psi(A^- - D^+)$, which gives rise to the intermolecular charge-transfer absorption, viz:

$$\psi_E = a^*\psi(A^- - D^+) - b^*\psi(A, D) \tag{3}$$

where

$$a^* \gg b^*$$

For some series of complexes where the donor molecule is varied, there is a linear relationship between ΔG and the frequency of the maximum of the charge-transfer band (ν_{max}), for example the three sets of complexes of a series of methylated benzenes

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[3] R. Foster, D. LL. Hammick and A. A. Wardley, *J. Chem. Soc.* 3817 (1953).

[4] See for example: G. Briegleb, *Elektronen-Donator-Acceptor-Komplexe* pp. 37, 82, 149. Springer-Verlag, Berlin (1961).

[5] R. Foster and D. LL. Hammick, *J. Chem. Soc.* 2685 (1954).

[6] C. C. Thompson and P. A. D. de Maine, *J. Amer. Chem. Soc.* **85**, 3096 (1963).

[7] D. F. Evans, *J. Chem. Phys.* **23**, 1429 (1955).

[8] L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.* **79**, 4839 (1957).

[9] R. S. Mulliken, *J. Amer. Chem. Soc.* **72**, 605 (1950); **74**, 811 (1952); *J. Phys. Chem.* **56**, 801 (1952).

with chloranil,[10] with 1,3,5-trinitrobenzene,[11] and with iodine.[12] In the present work, although there is a tendency for the more stable complexes to have charge-transfer bands at lower energies, the correlation is small. Where linear relationships of this type do exist, it is a fortuitous result determined by the relative magnitude of several energy terms. The causes of such proportionality, in particular between $\nu_{\max}$ and the ionization potential of the donor for a set of complexes between a given acceptor and a series of donors, has been remarked upon by many workers, in particular by Mulliken.[13]

TABLE 1. EQUILIBRIUM CONSTANTS (K), FREE ENERGIES OF FORMATION ($-\Delta G$), MOLAR EXTINCTION COEFFICIENTS (ϵ) AND POSITIONS OF THE MAXIMA OF THE INTERMOLECULAR CHARGE-TRANSFER BANDS FOR THE SERIES OF COMPLEXES OF TMPD WITH DINITRONAPHTHALENES (AND 1,3-DINITROBENZENE) IN CYCLOHEXANE AT 22°

Dinitronaphthalene isomer	λ^a (mμ)	ϵ^a	K (l.mole^{-1})	$-\Delta G$ (cals/mole^{-1})	$\lambda_{\max}$ (mμ)	$\epsilon_{\max}$
2,7-	528	93_5	$4{\cdot}3_2$	860	528	930
	528	92_3	$4{\cdot}3_2$			
2,6-	570	50_1	$3{\cdot}2_4$	690	567	520
	570	51_6	$3{\cdot}2_1$			
1,3-	530	57_2	$3{\cdot}1_2$	660	530	560
	530	54_5	$3{\cdot}0_9$			
1,7-	491	43_5	$2{\cdot}5_0$	540	493	440
	491	43_8	$2{\cdot}5_4$			
1,6-	485	63_3	$2{\cdot}2_4$	460	485	620
	485	61_4	$2{\cdot}1_7$			
2,3-	435	46_9	$2{\cdot}2_0$			
	435	49_6	$1{\cdot}9_7$	400	Sh 417–443	
	435	48_9	$2{\cdot}0_1$			
1,4-	535	32_7	$1{\cdot}8_1$	350	535	320
	535	31_7	$1{\cdot}8_3$			
1,2-	500	37_7	$1{\cdot}2_8$	160	Sh 474–506	
	500	38_0	$1{\cdot}3_3$			
1,5-	470	56_3	$1{\cdot}1_2$	60	460	550
	480	57_3	$1{\cdot}0_9$			
1,8-	430	64_3	$1{\cdot}0_8$			
	460	59_9	$1{\cdot}1_0$	50	430	630
	460	60_7	$1{\cdot}0_8$			
	500	47_1	$1{\cdot}1_0$			
1,3-Dinitrobenzene	490	73_8	$2{\cdot}5_4$	550	496	760
	496	76_2	$2{\cdot}5_8$			

[a] Wavelength at which determination was made.

Lack of information about the single-electron reduction potentials does not allow

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[10] R. Foster, D. LL. Hammick and B. N. Parsons, *J. Chem. Soc.* 555 (1956).

[11] G. Briegleb and J. Czekalla, *Z. Elektrochem.* **59**, 184 (1955).

[12] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.* **77**, 2164 (1955).

[13] C. Reid and R. S. Mulliken, *J. Amer. Chem. Soc.* **76**, 3869 (1954); R. S. Mulliken, *Proc. International Conference on Coordination Compounds* p. 371. Amsterdam (1955); R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.* **13**, 109 (1962).

any comparison to be made of this measure of electron affinity of the acceptor molecule[14] with $\nu_{\max}$ or ΔG.

Although the coefficient b in Eq. (2) is likely to be small for outer complexes,[1,11] the fraction of the total energy may be significant because of the large bond energy associated with $\psi(A^- - D^+)$ compared with $\psi(A, D)$. If this is the case, one might be able to relate ΔG with the electronic structure of the acceptor molecule for a series of complexes with a common donor. In the present set of complexes, such a correlation appears to be possible in terms of two effects:

(a) that β-nitro groups in naphthalene have a higher electronegativity than those in α-positions. Hodgson and Ward[15] have made a similar suggestion to explain the electrophilic substitution of dinitronaphthalenes.

(b) Steric interference of planarity. This may arise either from *vic*-substituted dinitro groups or, in the case of α-nitro groups, through repulsion with the *peri*-hydrogen [this latter may be a partial explanation of the difference in electronegativity of α- and β-nitro groups discussed under (a)]. In either case a decrease in electronegativity by a diminution of the —M effect of the nitro group will decrease the electron accepting properties of the molecule.

Thus the dinitronaphthalenes may be divided into three groups:

(a) *Dinitronaphthalenes with two β-nitro groups.* This set contains the acceptors which form the strongest complexes. The 2,3-isomer is exceptional but the lower value of $|\Delta G|$ may be explained under heading (b) above, namely the decrease in acceptor strength through the large steric hindrance of the *vic* nitro groups

isomer	2,7-	2,6-	2,3-
order of $\lvert\Delta G\rvert$	1	2	6

(b) *Dinitronaphthalenes with one β-nitro group.* These represent the group of intermediate strength acceptors save the 1,2-isomer where again the *vic*-substituted nitro groups make this isomer relatively ineffective.

isomer	1,3-	1,7-	1,6-	1,2-
order of $\lvert\Delta G\rvert$	3	4	5	8

(c) *Dinitronaphthalenes with no β-nitro groups.* These represent as a group the weakest acceptors, and the 1,8-isomer with two nitro groups *peri* to one another is the least effective isomer.

isomer	1,4-	1,5-	1,8-
Order of $\lvert\Delta G\rvert$	7	9	10

Concerted conjugation, similar to that referred to above in the discussion of the relative stabilities of the dicyano- and dinitro-benzene complexes, does not appear to be effective. It would lead to the expectation that: 1,2-; 1,4-; 1,5-; 1,7-; 2,3- and 2,6-isomers which are conjugated would in the absence of steric effects be stronger acceptors than the remaining isomers. Only the 2,6- and 2,7-isomers are free of both *peri*-hydrogen-nitro and *vic*-dinitro steric interference. The 2,6-isomer which is conjugated in fact forms a *weaker* complex than the unconjugated 2,7-isomer.

[14] M. E. Peover, *Nature, Lond.* **191**, 702 (1961); *Trans. Faraday Soc.* **58**, 1656, 2370 (1962).

[15] H. H. Hodgson and E. R. Ward, *J. Soc. Dyers and Colourists* **63**, 141 (1947).

Comparison of the complexes 1,3-dinitronaphthalene—TMPD with 1,3-dinitrobenzene—TMPD (Table 1), indicates that the former is the stronger acceptor irrespective as to whether ΔG or ν_{max} is taken as the measure.

There appears to be no correlation of the molar extinction coefficients of the various dinitronaphthalene complexes with either ν_{max} or ΔG.

EXPERIMENTAL

Analytical. Since the dinitronaphthalenes are only slightly soluble in cyclohexane the set of solutions required for a determination[8] was made up from two basic solutions, one containing TMPD alone in cyclohexane, the other containing the dinitronaphthalene dissolved in a solution of TMPD in cyclohexane. This dilution technique has been described previously.[16] The optical densities of the solutions were measured at 22° in either 1 cm or 4 cm silica cuvettes using either an Optica CF4 or a Unicam SP 600 spectrophotometer. There was close agreement of K and ϵ when the same system was studied using either the two different instruments, or the two different path-lengths.

TABLE 2. PURIFICATION AND M.PS OF THE DINITRONAPHTHALENES

Isomer	Recrystallizing solvent	m.p.	lit. m.p.[a]
1,2-	× 2 Ethanol	161·5–162°	161–2°
1,3-	× 2 Ethanol	148°	148°
1,4-	× 1 Ethanol	134°	134°
1,5-	× 2 Acetone	218°	219°
1,6-	× 2 Ethanol	166°	166·5°
1,7-	× 2 Cyclohexane	157–8°	156°
1,8-	× 1 Ethanol	172°	172°
2,3-	× 2 Methanol	175°	174·5–175°
2,6-	× 2 Chloroform	280°	279°
2,7-	× 1 Ethanol	233°	234°

[a] All lit. m.ps quoted from N. Donaldson, *The Chemistry and Technology of Naphthalene Compounds* Arnold, London (1958).

Materials. B.D.H. *cyclohexane* "Special for Spectroscopy" was used without further treatment *Tetramethyl-*p*-phenylenediamine* was obtained as free base from the dihydrochloride, and redistilled thrice *in vacuo*, m.p. 51°. 1,3-*Dinitrobenzene* was recrystallized twice from carbon tetrachloride, m.p. 91°. *Dinitronaphthalenes* isomers (8) were given by Dr. E. R. Ward. The remaining two were prepared by the nitration of acetylated 2-naphthylamine, which gave the 1-, 6- and 8-nitro-2-acetoxyaminonaphthalenes. From the latter two isomers, 2,6- and 1,7-dinitronaphthalene were prepared by Sandmeyer reactions.[17] The various isomers were purified by recrystallization as indicated in Table 2.

Acknowledgements—The authors wish to thank Dr. E. R. Ward of Leicester College of Technology and Commerce for his generous gift of nitronaphthalenes. This work was carried out during the tenure (by P. H. E.) of a Strathmore-Cobb Scholarship.

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[16] R. Foster, *J. Chem. Soc.* 1075 (1960).

[17] H. H. Hodgson, A. P. Mahadevan and E. R. Ward, *Org. Synth.* **28**, 52 (1948).