Studies on Nitroaromatic Compounds. Part IV.[1] Electron Acceptor Properties of Polynitronaphthalene-1,8-dicarboxylic Anhydrides in Complex Formation

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The charge-transfer complex formation of polynitronaphthalene-1,8-dicarboxylic anhydrides with a number of aromatic hydrocarbons has been investigated. The electron affinities of the nitronaphthalenecarboxylic anhydrides have been estimated from the charge-transfer transition energy in the complexes. Thermodynamic and other data has been obtained for the complex formed between pyrene and 3,6-dinitronaphthalene-1,8-dicarboxylic anhydride.

ANHYDRIDE and nitro-groupings are electron-withdrawing entities and when bonded to atoms in a π-electron system cause an electron deficiency in the π-system. The electron acceptor properties of 3-nitronaphthalenedicarboxylic anhydride have been reported [2,3] but apart from this work the combined effects of anhydride and nitro-groups on the charge density in the naphthalenic π-electron system has not been studied. Results now obtained on the electron acceptor properties of 2,5-dinitronaphthalenedicarboxylic anhydride, 3,6-dinitronaphthalenedicarboxylic anhydride, 4,5-dinitronaphthalenedicarboxylic anhydride and 2,4,5-trinitronaphthalenedicarboxylic anhydride are reported herein.

TABLE 1

The charge-transfer maxima ($\lambda_{max.}$, nm) [a] and the energy of charge-transfer (E_{CT}, J mol^{-1} × 10^5) for a series of donor–acceptor complexes in the solid state and in chloroform solution

Donor \ Acceptor		Solid state				Solution		
		3,6- [b]	4,5-	2,4,5-	TNB [c]	2,5-	3,6-	TNB
Naphthalene	$\lambda_{max.}$	— [d]	445	460	400	420	—	370
	E_{CT}		2·69	2·60	2·99	2·85		3·23
Phenanthrene	$\lambda_{max.}$	—	450	470	410	420	—	370
	E_{CT}		2·66	2·54	2·92	2·85		3·23
Chrysene	$\lambda_{max.}$	450	+ [e]	+	450	460	460	420
	E_{CT}	2·66			2·66	2·60	2·60	2·85
1,2,5,6-Dibenzanthracene	$\lambda_{max.}$	470	+	+	450	500	490	430
	E_{CT}	2·54			2·66	2·39	2·44	2·78
1,2-Benzanthracene	$\lambda_{max.}$	470	+	+	460	520	510	440
	E_{CT}	2·54			2·60	2·30	2·34	2·72
Pyrene	$\lambda_{max.}$	490	550	570	475	520	510	445
	E_{CT}	2·44	2·17	2·10	2·52	2·30	2·34	2·69
Anthracene	$\lambda_{max.}$	500	560	600	490	525	525	460
	E_{CT}	2·39	2·14	1·99	2·44	2·28	2·28	2·60
3,4-Benzopyrene	$\lambda_{max.}$	550	610	640	520	570	570	475
	E_{CT}	2·17	1·96	1·87	2·30	2·10	2·10	2·52
Perylene	$\lambda_{max.}$	570	620	670	530	600	600	480
	E_{CT}	2·10	1·93	1·78	2·26	1·99	1·99	2·49

[a] Estimated accuracy is ±5 nm. [b] 3,6-Dinitronaphthalenedicarboxylic anhydride. [c] 1,3,5-Trinitrobenzene. [d] Peak minimum could not be observed. [e] Complex not formed.

RESULTS AND DISCUSSION

The wavelengths of the absorption maxima for the charge-transfer complexes formed between polynitronaphthalene-1,8-dicarboxylic anhydrides and aromatic hydrocarbons in the solid state and in chloroform solution are given in Table 1. The values for the corresponding complexes formed with 1,3,5-trinitrobenzene are included in the Table for comparison. These values are in good agreement with previously reported values.[4-7]

An interesting feature of the results given in Table 1 is that whereas the wavelength values for the complexes formed with 1,3,5-trinitrobenzene increase in going from solution to the solid state the values for the complexes formed with 3,6-dinitronaphthalenedicarboxylic anhydride decrease. It is to be noted that the intermolecular separation of the components in a charge-transfer complex can alter on changing phase and that this can contribute to a change in the energy

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of the charge-transfer transition.[8-12] It is thus feasible that the difference in the energy changes for the charge-transfer transition in the 1,3,5-trinitrobenzene and 3,6-dinitronaphthalenedicarboxylic anhydride complexes on changing phase is related to a difference in the relative separations of the components in the two types of complex. A complex can only be formed if the donor and acceptor species approach sufficiently close to each other and in this respect it is significant that solid state complexes could not be prepared between chrysene, 1,2,5,6-dibenzanthracene, and 1,2-benzanthracene as donors and 4,5-dinitronaphthalenedicarboxylic anhydride and 2,4,5-trinitronaphthalenedicarboxylic anhydride as acceptors. These particular acceptors have nitro-groups in the *peri*-positions of the naphthalene ring and because of mutual interaction between the nitro-groups they will be twisted out of the plane of the ring. Consequently the approach of the donor to the acceptor will be sterically hindered and in the case of large donor molecules the interaction may be sufficient to prevent the components taking up positions which would give stable complexes.

The electron affinities of the nitronaphthalenedicarboxylic anhydrides studied herein were calculated from the data of Table 1 using the methods of Briegleb.[13] The mean of the electron affinity values show an increasing trend in the order 3,6-dinitronaphthalenedicarboxylic anhydride ($0{\cdot}94 \times 10^5$ J mol^{-1}), 2,5-dinitronaphthalenedicarboxylic anhydride ($1{\cdot}05 \times 10^5$ J mol^{-1}), 4,5-dinitronaphthalenedicarboxylic anhydride ($1{\cdot}13 \times 10^5$ J mol^{-1}), and 2,4,5-trinitronaphthalenedicarboxylic anhydride ($1{\cdot}31 \times 10^5$ J mol^{-1}). This order can be rationalised if the effects of nitro-group substitution are additive and if substitution of a nitro-group into the positions *ortho*, *meta*, or *para* to the anhydride group has differing effects on the charge density in the π-electron system, *meta*-substitution having the least effect and *para*-substitution the greatest effect.

Electron-acceptor properties can also be evaluated from measurements of the association constants for complex formation and from measurements of the enthalpies of formation of complexes. This approach to the determination of electron acceptor ability was limited in the present study to 3,6-dinitronaphthalenedicarboxylic anhydride because of the low solubility of the other nitronaphthalenedicarboxylic anhydrides. The thermodynamic parameters evaluated for the pyrene-3,6-dinitronaphthalenedicarboxylic anhydride are given in Table 2.

The values for the enthalpy of formation of the pyrene-3,6-dinitronaphthalenedicarboxylic anhydride complex and for the oscillator strength and transition dipole moment of the charge-transfer transition are comparable to values reported for other π,π complexes.[15,16] The π,π complexing power of 3,6-dinitronaphthalenedicarboxylic anhydride will be similar to that of the 2,5-, 4,5-, and 2,4,5-nitronaphthalenedicarboxylic anhydrides and comparison of their electron affinities with other reported values [13] shows that the π,π-complexing ability of the polynitro-1,8-naphthalenedicarboxylic anhydrides is similar to that of the 2,4,7-trinitro-9-fluorenone.

TABLE 2

Association constant (K_c^{AD}), enthalpy of formation (ΔH), oscillator strength (f), and transition dipole moment (μ^2) for the 3,6-dinitronaphthalenedicarboxylic anhydride–pyrene in chloroform solution

Temp. (°C)	(K_c^{AD}) [a] (cm^3 mol^{-1})	($-\Delta H$) [b] (J mol^{-1} $\times 10^4$)	(f) [c]	(μ^2) [c] (D)
2·9	9·56 ± 0·25	3·1 ± 0·2	0·14	19·04
27·5	3·27 ± 0·10			
41·0	1·73 ± 0·07			

[a] Calculated using the method given in ref. 14. [b] Calculated from the plot of log K_c^{AD} *versus* reciprocal of temperature. [c] Calculated from the equations given in ref. 15.

EXPERIMENTAL

3,6-Dinitronaphthalenedicarboxylic anhydride and 4,5-dinitronaphthalenedicarboxylic anhydride were prepared by literature methods.[17] 2,5-Dinitronaphthalenedicarboxylic anhydride and 2,4,5-trinitronaphthalenedicarboxylic anhydride were prepared by methods to be reported elsewhere.[18]

The solid complexes were prepared by mixing a solution of the nitronaphthalenedicarboxylic anhydride in hot acetic anhydride with a solution of an equimolar quantity of the donor in hot chloroform. The mixture was allowed to cool and the solid which precipitated was filtered off, washed with light petroleum (b.p. 40—60°), and dried at room temperature *in vacuo*. Elemental analysis confirmed that in each case the stoicheiometry of the complex was 1 : 1. The visible absorption spectra of the solid complexes were recorded on a Unicam SP 800 spectrophotometer fitted with a diffuse-reflectance attachment.

Complexes were prepared in solution by mixing chloroform solutions of equimolar concentration in donor and acceptor. The visible absorption spectra of the complexes were recorded on a Unicam SP 800 spectrophotometer using 40 mm cells and with a solution of the acceptor in the reference beam of the same concentration as in the sample beam.

The measurements for the determination of the association constants were taken on a Unicam SP 500 spectrophotometer fitted with a thermostat system accurate to within ±0·1°. Stock solutions of pyrene and 3,6-dinitronaphthalenedicarboxylic anhydride in chloroform were prepared just prior to use. Solutions were made up for

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measurement by mixing appropriate volumes of the stock solutions so that the concentration of 3,6-dinitronaphthalenedicarboxylic anhydride was kept constant at each temperature ($2{\cdot}20 \times 10^{-4}$M at 2·9°, $2{\cdot}5 \times 10^{-4}$M at 27·5°, and $3{\cdot}19 \times 10^{-4}$M at 41·0°) and the concentration of pyrene was varied over the range $0{\cdot}5 \times 10^{-1}$—$2{\cdot}7 \times 10^{-1}$M. A solution of 3,6-dinitronaphthalenedicarboxylic anhydride of the same concentration as in the solution under study was used as the reference. Each optical density measurement was repeated three times and the average value was taken.

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