Studies of the Charge-transfer Complexes of 1,4-Naphthoquinone Acceptors

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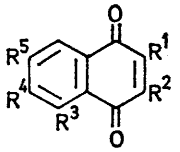
The naphthoquinone acceptors form stable charge-transfer complexes in solutions of aprotic solvents with aromatic hydrocarbons as donors. From the charge-transfer transition energies of the complexes as well as from the polarographic half-wave reduction potentials of the acceptors relative electron affinities of the acceptors are determined. In addition, the association constant, molar extinction coefficients, oscillator strengths, and enthalpies of formation of the complexes were obtained from charge-transfer spectral studies with hexamethylbenzene as donor. The average electron affinities of 2,3-dichloro- (0·90 eV), 2,3-dichloro-5-nitro- (1·18 eV), 2,3,5,6-tetrachloro-7-nitro- (1·30 eV), 2,3-dicyano- (1·53 eV), 2,3-dicyano-5-nitro- (1·68 eV), and 2,3-dicyano-5,6-dichloro-7-nitro-1,4-naphthoquinone (1·75 eV) obtained from the charge-transfer spectral studies clearly show the cumulative effects of electron-withdrawing substituents on the naphthoquinone π-system. The π-acid character of 1,4-naphthoquinone acceptors are also correlated with the calculated molecular orbital energies and with the experimental polarographic half-wave reduction potential.

New and unique electron acceptors can be developed by combining the structural features of two or more electron acceptors in one molecular framework. In previous work, this concept was utilized by combining the structural characteristics of tetracyanoethylene with that of 1,2,3-indanetrione [1] and by the introduction of the dicyanomethylene moiety into a 1,4-naphthoquinone π-system.[2] In both cases, a considerable enhancement of the electron affinity of the new acceptors relative to the parent acceptors, 1,2,3-indanetrione and 1,4-naphthoquinone, was achieved.

It seemed worth while to study the effects of electron-withdrawing groups such as chloro-, nitro-, and cyano-substituents on the 1,4-naphthoquinone π-system. It is expected that with selective control over the nature, number, location, and electronegativity of the substituents a new series of electron acceptors with predictable properties could be developed.[3]



(I)

a; $R^1 = R^2 = R^3 = R^4 = R^5 = H$
b; $R^1 = Cl, R^2 = R^3 = R^4 = R^5 = H$
c; $R^1 = R^2 = Cl, R^3 = R^4 = R^5 = H$
d; $R^1 = R^2 = Cl, R^3 = NO_2, R^4 = R^5 = H$
e; $R^1 = R^2 = CN, R^3 = R^4 = R^5 = H$
f; $R^1 = R^2 = CN, R^3 = NO_2, R^4 = R^5 = H$
g; $R^1 = R^2 = R^3 = R^4 = Cl, R^5 = NO_2$
h; $R^1 = R^2 = CN, R^3 = R^4 = Cl, R^5 = NO_2$

This report presents a comparative study of the charge-transfer complexes and electron affinity of selected 2,3-dicyano- and 2,3-dichloro-1,4-naphthoquinone derivatives. Further, a possible correlation of the calculated molecular orbital energies of 1,4-naphthoquinone acceptors with the experimental polarographic half-wave reduction potentials ($E_{0\cdot5}$) has been investigated as a test of the acceptor property.

The preparation and properties of the naphthoquinone acceptors (I) are detailed in the Experimental section.[4-8]

Electron Affinity of 1,4-*Naphthoquinones*.—These were determined from the charge-transfer transition energies (E_π) of the π-complexes with aromatic hydrocarbon donors. The relative electron affinities (E_A) of the new acceptors have been evaluated from the charge-transfer transition energies (E_π') of a standard acceptor of known electron affinity E_A' against the same series of donors according to equation (1).[9] Table 1 lists the average electron affinities of the 1,4-naphthoquinone acceptors based on chloranil as standard acceptor ($E_A' = 1\cdot37$ eV).

$$E_A + E_\pi = E_A' + E_\pi' \qquad (1)$$

Polarographic Results.—The determination of one-electron reversible half-wave reduction potentials ($E_{0\cdot5}$) of acceptors in aprotic solvents provides an alternative method for the evaluation of electron affinities.[10] The relation between polarographic half-wave reduction potential and electron affinity is given [11] by equation (2)

$$E_{0\cdot5} = E_A - \Delta F_{\text{solv.}} - \phi_{\text{Hg}} - E_{\text{Hg}:\text{Hg}^{2+}} \qquad (2)$$

for a standard calomel electrode, where ϕ_{Hg} is the work function of mercury (4·5 eV), $E_{\text{Hg}:\text{Hg}^{2+}}$ is the absolute value of the calomel electrode (0·53 eV), and $-\Delta F_{\text{solv.}}$ is the difference in the solvation energy between neutral molecule and ion which is largely dependent on the solvation of the anion. Although $\Delta F_{\text{solv.}}$ may vary from compound to compound it is usually assumed constant for a closely related series. An average value of $-3\cdot66$ eV is used for many electron acceptors,[12]

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[1] (*a*) S. Chatterjee, *J. Chem. Soc.* (*B*), 1969, 725; (*b*) S. Chatterjee, Abstract of papers: 5th Caribbean Chem. Conf., Barbados, January, 1969, P12.

[2] S. Chatterjee, *J. Chem. Soc.* (*B*), 1967, 1170.

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in which case equation (2) reduced to the simple form of equation (3). Electron affinities determined from equation (3) generally agree rather well with the values determined by other methods.[1,13]

$$E_A = E_{0{\cdot}5} + 1{\cdot}41 \qquad (3)$$

The naphthoquinone acceptors were reduced polarographically at the dropping mercury electrode in acetonitrile solution in the presence of tetra-n-propylammonium perchlorate as ion carrier. The half-wave potentials became progressively anodic as the nature and number of negative substituents increased in the 1,4-naphthoquinone π-system. A plot of the experimental half-wave reduction potentials ($E_{0{\cdot}5}$) of 1,4-naphthoquinones listed in Table 2 against the average values of E_A determined from the charge-transfer spectral studies (Table 1) gave the straight line $E_A = 0{\cdot}884E_{0{\cdot}5} + 1{\cdot}33$. In light of the divergent structural characteristics of the 1,4-naphthoquinones, the agreements of this correlation with equation (3) is satisfactory. It also suggests that the average value of $\Delta F_{\text{solv.}}$ assumed in equation (2) is reasonable.

TABLE 1

Charge-transfer transition energy (E_π eV) and average electron affinity (E_A) of hydrocarbon complexes of 1,4-naphthoquinone acceptors (I)

Donor	(Ia)	(Ib)	(Ic)	(Id)	(Ie)	(If)	(Ig)	(Ih)	E_π'/eV Chloranil
Hexamethylbenzene	3·14	2·92	2·78	2·55	2·28	2·14	2·48	2·08	2·39
Pentamethylbenzene				2·58	2·40	2·23	2·67	2·20	2·48
Anthracene	2·82	2·55	2·39	2·17	1·74	1·66	2·06	1·61	1·93
Pyrene	2·73	2·61	2·28	2·23	1·82	1·67	2·10	1·66	2·00
Coronene		2·64	2·53	2·27	1·88	1·69	2·14	1·66	2·09
Perylene		2·27	2·14	1·89	1·54	1·65	1·74	1·65	1·63
Phenanthrene	3·12				2·34	2·15	2·66	2·21	2·63
1,2-Benzanthracene	2·85		2·53	2·25	2·67	1·67	1·82	1·65	2·11
1,2-Benzpyrene	2·85		2·58	2·29	1·90	1·74	2·17	1·72	2·10
3,4-Benzpyrene	2·64		2·25	1·97	1·69	1·66	1·86	1·63	1·75
Fluorene				2·58	2·27	2·10	2·53	2·10	2·45
Chrysene	3·22			2·43	2·27	1·90	2·29	1·86	2·29
Naphthalene					2·36	2·16		2·15	2·59
E_A [equation (1)]	0·57	0·78	0·90	1·18	1·53	1·68	1·30	1·75	1·37

TABLE 2

Polarography of 1,4-naphthoquinone acceptors (solvent acetonitrile; supporting electrolyte tetra-n-propylammonium perchlorate)

Acceptor	$E_{0{\cdot}5}$ *vs* SCE	$E_{3/4} - E_{1/4}$	I [a]	E_A [b]	ε_i [c]	$-E_{0{\cdot}5}$ (calc.)
(Ia) 1,4-Naphthoquinone	−0·69	60	3·37	0·72	0·4840	0·71
(Ib) 2-chloro-	−0·58	60	3·26	0·83	0·3445	0·47
(Ic) 2,3-Dichloro-	−0·43	70	3·03	0·98	0·356	0·50
(Id) 2,3-Dichloro-5-nitro-	−0·225	65	2·95	1·18	0·1400	0·27
(Ig) 2,3,5,6-Tetrachloro-7-nitro-	−0·20	58	2·0	1·21	0·1960	0·234
(Ie) 2,3-Dicyano-	+0·05	100	2·93	1·41	0·0657	0·013
(If) 2,3-Dicyano-5-nitro-	+0·30	70	3·17	1·71	0·2358 [d]	
(Ih) 5,6-Dichloro-2,3-dicyano-7-nitro-	+0·70	80	2·97	2·10	0·0953 [d]	

[a] Equation (5). [b] Equation (3). [c] Energy of first normally unoccupied MO in units of β. [d] Not included in least-squares fit.

Information on the molecular energy levels can also be obtained from the reversible polarographic half-wave potentials[14] by means of the relationship between the energy of the normally unoccupied orbital (ε_i) of an organic molecule to its electron affinity.[15] If the calculated energies in units of β are plotted against the polarographic half-wave potentials for a series of closely related compounds, a straight line ($E_{0{\cdot}5} = \varepsilon_i +$ constant) is expected whose slope yields an apparent value of β. In view of the varied nature of the heteroatom substitution in the 1,4-naphthoquinone acceptors it seemed worth while to examine whether the above correlation is found for the naphthoquinone π-system.

The orbital energies of 1,4-naphthoquinones were calculated by molecular orbital techniques by use of a Hückel programme.[16] For the 1,4-naphthoquinones, several resonance integrals (β) and coulomb integrals (α) are required. The empirical parameters associated with these integrals are defined by the relations $\alpha_X = \alpha_O + h_X\beta_O$ and $\beta_{OX} = k_{OX}\beta_O$, where α_O and β_O are the coulomb and resonance integrals respectively, α_X, the coulomb integral for heteroatom X, β_{OX} the resonance integral for the C–X bond, and h_X and k_{OX} are empirical parameters.

In these calculations the empirical parameters shown in Table 4 were used. These were suggested by Frankel,[17] Fukui,[18] and Brown [19] and their co-workers

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for the coulomb and resonance integral parameters associated with the carbonyl, nitro-, cyano-, and chloro-functions in the molecule. Within the naphthoquinone π-system, these values offered the best correlation with the experimental $E_{0\cdot5}$ data.

The calculated π-electronic energies of the 1,4-naphthoquinone acceptors are listed in Table 2. It is evident that energies and experimental half-wave potentials follow the same relative order for most of the naphthoquinones. However, deviations are observed for the energies of (If) and (Ih). A least-squares fit of the data resulted in the following equation: $E_{0\cdot5} = 0\cdot0974 - 1\cdot68x$ where x is the energy in units of β. Half-wave potentials calculated from this equation are also presented in Table 2.

EXPERIMENTAL

I.r. spectra were taken with a Perkin-Elmer Infracord 137B spectrometer with potassium bromide pellets. U.v. and visible spectra were measured with a Cary model 14 spectrophotometer.

Table 3

Association constant (K_c), extinction coefficient ($E_c^{max.}$), bonding enthalpy ($-\Delta H$), oscillator strength (f), and transition dipole moment (μ_{EN}), for the hexamethylbenzene complexes of (I) in dichloromethane solution at 25 °C

1,4-Naphthoquinone	$\tilde{\nu}_{CT}^{max.}$/cm^{-1}	$\tilde{\nu}_{0\cdot5}$/cm^{-1}	$E_c^{max.}$/l mol^{-1} cm^{-1}	10^2f	μ_{EN}/D	K_c/l mol^{-1}	K_x [a]	$-\Delta H$/kcal mol^{-1}	$\Delta F°$/kcal mol^{-1}	$-\Delta S°$/cal mol^{-1} K^{-1}
(If) 2,3-Dicyano-5-nitro-	17,241	7627	5100	16·8	4·9	49·96	914·76	8·82	2·31	21·82
(Ie) 2,3-Dicyano-	18,520	5376	4380	10·16	4·75	23·74	444·65	8·06	1·88	20·75
(Id) 2,3-Dichloro-5-nitro-	20,619	5792	565	1·40	1·65	7·93	148·50	7·83	1·22	20·18
(Ic) 2,3-Dichloro-	22,472	5839	526	1·32	1·60	6·27	117·40	4·75	1·08	12·30
(Ig) 2,3,5,6-Tetrachloro-7-nitro-	20,000	5445	1531	3·6	2·73	4·28	80·16	3·76	0·86	9·73
(Ih) 5,6-Dichloro-2,3-dicyano-7-nitro-	16,949	5207	5032	11·3	4·89	48·80	893·32	8·80	2·30	21·80

[a] $K_x = K_c\ (1000d/M)$; d = density, M = molecular weight of solvent.

Charge-transfer spectral measurements were performed in purified dichloromethane solution with equal-volume mixtures of 0·01M-acceptors and 0·02M-donor. Saturated solutions of known concentrations were also used whenever the donor solubility was less.

Preparation of 1,4-*Naphthoquinones* (I).—2,3-*Dicyano*-1,4-*naphthoquinone* (Ie). To a suspension of 2-chloro-1,4-naphthoquinone (Ib) (8·0 g, m.p. 110—111 °C) in methanol (75 ml) a solution of sodium cyanide (6·0 g) in water (25 ml) was added slowly with stirring. The temperature was kept below 40 °C during the addition. After ½ h of stirring at room temperature, the dark red reaction mixture was acidified with ice-cold hydrochloric acid. The solid precipitate was filtered off and washed with cold water, and had m.p. >300 °C (7·2 g, 83·0%); $\lambda_{max.}$ (KBr) 4·45 µm (–CN).

The above solid (2·0 g) was dissolved in glacial acetic acid (10 ml) and oxidized with concentrated nitric acid (1 ml) on a steam-bath. The mixture was poured on ice and the precipitated yellow *solid* was filtered off, air-dried, and crystallized from dichloromethane, and had m.p. 270—271 °C (yield, 1·3 g, 60%) (Found: C, 69·0; H, 1·95; N, 13·2. $C_{12}H_4N_2O_2$ requires C, 69·35; H, 1·9; N, 13·5%); $\lambda_{max.}$ (CH_2Cl_2) 245 (ε 27,900), 250 (29,900), 260 (16,900), 332 (3900), and 345 (shoulder) (3500) nm; $\lambda_{max.}$ (KBr): 4·45 µm (short) (C≡N). I.r. spectrum for KBr pellets was identical with that of the sample prepared from the reaction of sodium cyanide with 2,3-dichloro-1,4-naphthoquinone (Ic).[7]

5,6-*Dichloro*-2,3-*dicyano*-7-*nitro*-1,4-*naphthoquinone* (Ih). To a solution of 2,3,5,6-tetrachloro-7-nitro-1,4-naphthoquinone (1·0 g, m.p. 188 °C) in methanol (50 ml) and acetonitrile (50 ml) at 5 °C and under nitrogen, a solution of sodium cyanide (1·0 g) in water (5 ml) was added slowly for 5 min with stirring. The temperature of the mixture was kept below 15 °C during and for 20 min after the addition of cyanide solution. The dark red mixture was acidified with cold dilute hydrochloric acid and extracted with benzene. The solid residue obtained after the evaporation of benzene was dissolved in glacial acetic acid and warmed on a steam-bath for a few minutes after the addition of concentrated nitric acid (1·5 ml). The reaction mixture was then poured on crushed ice and the precipitated solid was extracted with dichloromethane. The solid residue obtained after the evaporation of the solvent at room temperature was crystallized from methylcyclohexane–dichloromethane and the *naphthoquinone* then had m.p. 175—178 °C (decomp.) (940 mg, 86%) (Found: C, 44·55; H, 0·3; N, 13·05; Cl, 22·0. $C_{12}HCl_2N_3O_4$ requires C, 44·7; H, 0·3; N, 13·05; Cl, 22·05%); $\lambda_{max.}$ (CH_2Cl_2) 223 (ε 37,350), 275 (12,670), and 389 nm (3330); $\lambda_{max.}$ (KBr) 4·5 and 5·95 µm.

The following were prepared as in the reference cited: 2,3-dichloro-5-nitro-1,4-naphthoquinone (Id),[4] m.p. 165—166 °C (lit.,[4] 174—175 °C) (Found: C, 44·2; H, 1·2; N, 5·2; Cl, 25·9. Calc. for $C_{10}H_3Cl_2NO_4$: C, 44·15; H, 1·1; N, 5·15; Cl, 26·1%); $\lambda_{max.}$ (CH_2Cl_2) 248 (ε 13,330), 254 (14,800), 274 (13,300), and 337 nm (3200); 2,3-dicyano-5-nitro-1,4-naphthoquinone (If),[8] m.p. 201—203 °C (decomp.) [lit.,[8] 203 °C (decomp.)] (Found: C, 57·05; H, 1·45; N, 16·4. Calc. for $C_{12}H_3N_3O_4$: C, 57·0; H, 1·2; N, 16·6%), $\lambda_{max.}$ (CH_2Cl_2) 220 (ε 19,400), 281 (11,640), 271 (13,164), and 365 nm (2100); and 2,3,5,6-tetrachloro-7-nitro-1,4-naphthoquinone (Ig),[5] m.p. 185—187 °C (Found: C, 35·6; H, 0·3; N, 4·0; Cl, 41·9. Calc. for $C_{10}HCl_4NO_4$: C, 35·2; H, 0·3; N, 4·1; Cl, 41·6%), $\lambda_{max.}$ (CH_2Cl_2) 235 (ε 22,850), 265 (14,820), 275 (13,760), 285 (13,460), and 335 nm (4700).

1,4-Naphthoquinone (m.p. 121—124 °C), 2-chloro-1,4-naphthoquinone (m.p. 110—111 °C), and 2,3-dichloro-1,4-naphthoquinone (m.p. 195—197 °C) were commercial and were purified by high-vacuum sublimation and crystallization from benzene.

Determination of K_c, E_c, *and* ΔH.—The association constants (K_c) were determined with a Cary model 14 spectrophotometer fitted with a constant-temperature cell compartment. The spectrophotometric relation of Benesi and Hildebrand [20] in the form of equation (4) gave values

$$1/\text{O.D.} = 1/K_cE_cA_0 \,.\, 1/D_0 + 1/E_cA_0 \qquad (4)$$

of K_c and E_c. Here, O.D. is the optical density of a solution which contained the complex in a 1 cm cell, and A_0 and D_0 indicate the initial concentrations of acceptor and donor. For this series of measurements the initial donor concentration was maintained in excess of a fixed acceptor concentration. The association constant for hexamethylbenzene complexes were determined for at least three temperatures. The bonding enthalpies ($-\Delta H$) of these complexes were obtained by the usual procedure.[21] The experimental values for K_c, E_c, and ΔH are in Table 3.[22] *

The oscillator strength (f) and transition moment (μ_{EN}) for the hexamethylbenzene complexes of (I) were calculated from formulae [2, 21] from the experimental $\tilde{\nu}_{CT}^{\text{max.}}$ and $E_c^{\text{max.}}$ values in Table 3.

TABLE 4

Molecular orbital parameters

Substituent	Atom X	h_X	Bond C–X	k_{CX}
Nitrile (C–N) [a]	N	1·0	C–N	0·80
Nitro (NO_2) [b]	N	2·0	N–O	1·65
	O	1·4	C–N	1·20
Carbonyl (C=O) [c]	O	1·20	C–O	1·55
Chlorine	Cl	−0·015 [d] 2·00 [e]	C–Cl	0·90

[a] Ref. 17. [b, c] P. H. Reiger and G. K. Frankel, *J. Chem. Phys.*, 1962, **37**, 2795, 2811. [d] Ref. 19. [e] Ref. 18.

Polarography.—This was performed with a Sergent model 21 polarograph and a Sergent IR compensator model A and a dropping mercury electrode. Polarographic reductions of the 1,4-naphthoquinones were performed in anhydrous acetonitrile solution with tetra-n-propylammonium perchlorate as ion carrier against standard S.C.E. The limiting current constant (I) was evaluated from equation (5). Here, i_d is the diffusion

$$I = i_d/m^{2/3} \,.\, t^{1/6} \,.\, C \qquad (5)$$

current in μA.; m, the mass of mercury flowing in mg s^{-1}; C, the concentration (mM), and t, drop time in seconds. The number of electrons associated with each wave was determined by the use of Thom's relationship,[23] $E_{3/4} - E_{1/4} = 59$ mV for one-electron reduction (Table 2).

DISCUSSION

The comparison of the π-acid properties of 1,4-naphthoquinone acceptors (Tables 1—3) show that considerable enhancement is provided by the introduction of 2,3-dicyano- and 5- and 7-nitro-groups in the 1,4-naphthoquinone system. The key role played in this enhancement by the conjugation between cyano- and nitro-moieties with the naphthoquinone π-system within the same molecular framework is manifested by the comparison among the data presented for the 2,3-dichloro-, 2,3-dichloro-5-nitro-, and 2,3,5,6-tetrachloro-7-nitro-derivatives.

The electron affinities of naphthoquinone acceptors obtained from charge-transfer spectra (Table 1) show expected trends and also agree well with the E_A values obtained from the polarographic reduction studies. The relative values of K_c, E_c, f, and the thermodynamic constants calculated for the hexamethylbenzene complexes (Table 3) also reflect the trend expected on the basis of the relative electron affinities of the acceptors.

In general, the calculated orbital energies (ε_i) of the 1,4-naphthoquinone acceptors correlate well with the polarographic half-wave potential ($E_{0\cdot 5}$). However, considerable deviation is observed as the $E_{0\cdot 5}$ values tend toward high positive potentials. In the light of the number of heteroatoms in the 1,4-naphthoquinone π-system, the value of $\beta = 1\cdot 67$ eV obtained from the least-squares fit of $E_{0\cdot 5}$ against ε_i is acceptable and is reasonably close to the reported value of $\beta = 2\cdot 37$ eV for hydrocarbons.[24] However, it is felt that optimization of the values of the empirical parameters h_X and k_{CX} should provide better correlation and a better value of β.

In conclusion, our experimental data support the original theory and demonstrate the feasibility of using selective substitution to a known π-acid system namely 1,4-naphthoquinone ($E_A = 0\cdot 69$ eV) in order to develop new acceptors with predictable π-acid character.

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* Our experimentally determined association constants (K_c) and molar extinction coefficients (E_c) for the 1,4-naphthoquinone complexes should be considered as 'apparent' values. For this series of measurements a 1 : 1 complex formation between the donor hexamethylbenzene (concn. 0·1M—0·01M) with the acceptor (concn. 10^{-3}M) was assumed in each case.

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