Molecular Complex Formation between Bridgehead Amines and Quinones

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Formation of 1 : 1 complexes occurs between the bridgehead amines triethylenediamine, quinuclidine, and quinuclidin-3-ol and 1,4-quinones. Values of the equilibrium constant (Kc_1), molar absorptivity (ε_1), standard enthalpy, and entropy changes were obtained from optical data for the stronger complexes whilst only the product $Kc_1\varepsilon_1$ could be determined for the weaker complexes. Formation of 2 : 1 complexes was observed for solutions containing chloranil and an excess of triethylenediamine. CNDO/2 calculations show that complex formation should occur at four equivalent positions corresponding to the mid-point between C(1) and C(2). The non-bridgehead amines piperidine and triethylamine do not form complexes in solution under the same conditions.

Molecular complex formation between aliphatic amines and π-acceptors such as trinitrobenzene,[1,2] hexafluorobenzene,[3] cyclic aromatic anhydrides,[4] and benzonitrile [5] is well known. It is surprising that although quinones are strong electron acceptors, studies of their interaction with aliphatic amines in solution have so far failed to provide evidence for complex formation.[6] In this paper we present evidence for just such an interaction between bridgehead amines and 1,4-quinones.

Experimental

Materials.—Benzoquinone (cyclohexa-2,5-diene-1,4-dione) was recrystallised from hexane, m.p. 111 °C. Duroquinone (tetramethylcyclohexa-2,5-diene-1,4-dione) was of general purpose reagent grade. Fluoranil (tetrafluorocyclohexa-2,5-diene-1,4-dione) was recrystallised from chloroform. The solid sublimed at 173 °C. Chloranil (tetrachlorocyclohexa-2,5-diene-1,4-dione) was recrystallised from acetone, m.p. 297 °C with some sublimation and decomposition. Bromanil (tetrabromocyclohexa-2,5-diene-1,4-dione) was recrystallised from chloroform, m.p. 300 °C with sublimation. Dichlone (2,3-dichloronaphthalenedione) was recrystallised from chloroform, m.p. 195 °C. Triethylenediamine (1,4-diazabicyclo-[2.2.2]octane) was a general purpose reagent obtained from B.D.H. Ltd. It analysed at 99.5% by titration with hydrochloric acid and gave a single spot on t.l.c. Quinuclidine (1-azabicyclo[2.2.2]octane) was obtained as the free base or prepared from the hydrochloride by extraction into cyclohexane from a strongly basic solution. In either case it was recrystallised from cyclohexane. Quinuclidin-3-ol (1-azabicyclo[2.2.2]octan-3-ol) was recrystallised from ethyl acetate. Cyclohexane and ethyl acetate were of analytical reagent grade. An equivolume mixture of the two solvents was used for the determination of stoicheiometry and equilibrium constants and was dried over molecular sieve 3A. All quinone solutions were protected from light.

Measurements of Stoicheiometry and Equilibria.—Fixed wavelength measurements at 20 °C were carried out with a Pye-Unicam SP500 series 2 spectrometer. A Pye-Unicam SP8-200 spectrometer with a thermostatted cell-holder was used for measurements above 20 °C. Cells of various path lengths were used in the measurement of equilibrium constants to cover the maximum possible concentration range.

Calculations.—The following geometries were used for MO calculations, using the numbering in Figure 1. The quinone geometries were based on a diffraction study for benzoquinone:[7] (a) ammonia, N–H 0.103 nm, $H\hat{N}H$ 107.3°; (b) benzoquinone, C(1)–C(2) 0.150, C(2)–C(3) 0.132, O(1)–C(1) 0.123, C(2)–H 0.110 nm, $C(1)\hat{C}(2)C(3)$ 116°, $H\hat{C}(2)C(3)$ 119°; (c) fluoranil, geometry as for benzoquinone, C–F 0.141 nm.

Results and Discussion

Visible Spectra.—A new band in the visible spectrum is observed immediately on mixing solutions of bridgehead amines and quinones. This band, which is broad and featureless, is well separated from the quinone spectrum only for the complexes of triethylenediamine with halogenated quinones. The frequencies of these bands are plotted against the frequencies of the π-acceptor *NN*-dimethylaniline with the same quinones in Figure 2 and against the electron affinity of the quinone [8] in Figure 3. The speed of reaction, the shapes of the absorption bands, and the regular (though not linear) relationships observed for Figures 2 and 3 are characteristic of charge-transfer bands. It is concluded that molecular complex formation occurs.

The frequencies for triethylenediamine are much lower than those of the monobasic amines. This is also observed for the iodine complexes [9] and is attributed to overlap destabilising the lone pairs,[9,10] which is confirmed by a red shift in the $n \longrightarrow \sigma^*$ transition.[11]

Stoicheiometry.—The stoicheiometry was determined by Job's method in an equivolume mixture of cyclohexane and ethyl acetate. This solvent mixture gave the best compromise between solubility of the halogenated quinones and stability of the charge-transfer absorption. The number of absorbing species was determined from absorbance measurements at two wavelengths.[12] The results are shown in Table 1. In every case 1 : 1 complex formation with a single absorbing species was found.

Solutions containing triethylenediamine and chloranil in ratios 1 : 1 to 520 : 1 were prepared and the spectra were analysed by the Bigauss computer program [13,14] which resolves spectra into Gaussian bands. Weak sub-bands were resolved, although at varying wavelengths and intensities. None could be assigned to a 2 : 1 complex, which is expected

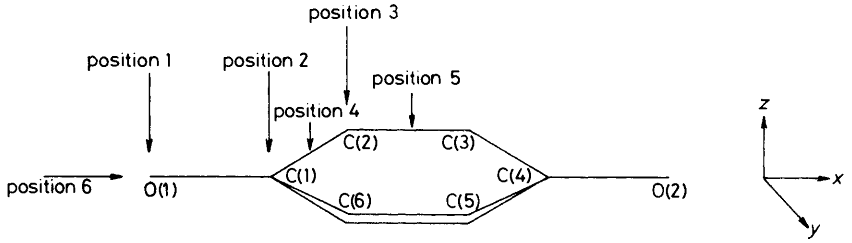

Figure 1. Benzoquinone molecules showing the possible complexing sites

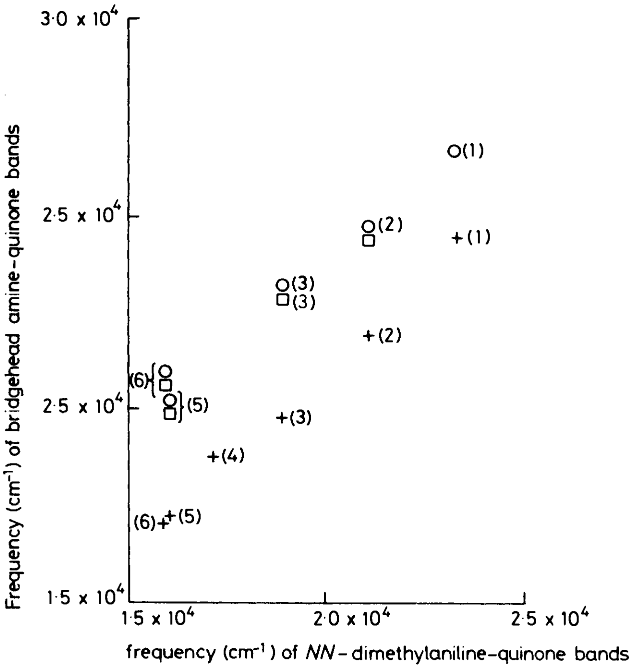

Figure 2. Charge-transfer absorption band frequencies of quinone–amine complexes for the bridgehead amine triethylenediamine, +; quinuclidine, ○; and quinuclidin-3-ol, □, plotted against the corresponding frequencies of *NN*-dimethylaniline complexes with the same quinones: duroquinone (1), benzoquinone (2), dichlone (3), fluoranil (4), bromanil (5), and chloranil (6)

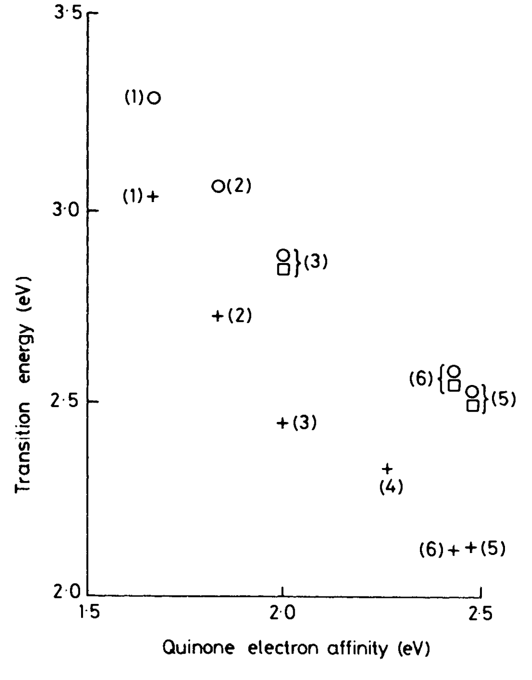

Figure 3. Energies of the charge-transfer bands of complexes of quinones with the amines triethylenediamine, +; quinuclidine, ○; and quinuclidin-3-ol, □, plotted against the electron affinities of the quinones: duroquinone (1), benzoquinone (2), dichlone (3), fluoranil (4), bromanil (5), and chloranil (6)

Table 1. Stoicheiometry of amine–quinone complex formation in an equivolume mixture of cyclohexane and ethyl acetate

Donor	Acceptor	Stoicheiometry by Job's method	Number of absorbing species
Triethylenediamine	Chloranil	1 : 1	1
	Bromanil	1 : 1	1
	Dichlone	1 : 1	1
	Benzoquinone	1 : 1	1 [a]
Quinuclidine	Chloranil	1 : 1	1
	Bromanil	1 : 1	1 [a]
	Dichlone	1 : 1	1
Quinuclidin-3-ol	Dichlone	1 : 1	1

[a] Absorbance unstable giving a variable ratio.

to absorb close to the 1 : 1 maximum.[15] The oscillator strength of the 1 : 1 complex, calculated from the integrated intensity of the main band, was 0.03 at 25 °C. This is much lower than the value found for the strong iodine complex (0.32).[9]

Measurements of Equilibria.—Three methods were used to calculate the equilibrium constant for 1 : 1 complex formation (Kc_1) and molar absorbtivity (ε_1). Method 1 was the graphical procedure of Foster and Matheson [16] using equimolar solutions of amines and quinones. This did not give sufficiently precise results for weaker complexes, and in method 2 the product $Kc_1\varepsilon_1$ was determined by the approximate equation (1)

$$Kc_1\varepsilon_1 = \frac{\text{Abs}}{([D_0]-[DA])([A_0]-[DA])} \simeq \frac{\text{Abs}}{[D_0][A_0]} \qquad (1)$$

where Abs is the absorbance due to the complex, with a path length of 1 cm, $[D_0]$ is the initial concentration of donor, $[A_0]$ is the initial concentration of acceptor, and [DA] is the concentration of complex at equilibrium. It is assumed that [DA] is much less than $[D_0]$ or $[A_0]$ which is true for the weaker complexes when either component is not in a large excess. This procedure gives slightly low values of $Kc_1\varepsilon_1$. The upper limit of the systematic error was determined for the strong complexes of triethylenediamine and quinuclidine with chloranil

Table 2. Measurements of equilibria for amine–quinone complexes. Conditions: temperature 20 °C, solvent an equivolume mixture of cyclohexane and ethyl acetate

Amine	Quinone	Kc_1/dm^3 mol^{-1} Mean	Kc_1/dm^3 mol^{-1} Standard error	ε_1/cm^{-1} dm^3 mol^{-1} Mean	ε_1/cm^{-1} dm^3 mol^{-1} Standard error	$Kc_1\varepsilon_1$ Mean	Standard error	Method
Triethylenediamine	Chloranil	16.3	1.2	1 093	57	17 520	201	1
	Chloranil	5.13	0.17	3 522	90	18 000	249	3
	Bromanil					17 420	900	1
	Dichlone	1.13	0.08	2 618	125	2 933	81	3
	Benzoquinone					321	8.6	2
Quinuclidine	Chloranil	6.4	0.7	1 440	141	9 222	134	1
	Bromanil					11 570	97	2
	Dichlone					1 080	54	2
Quinuclidin-3-ol	Dichlone					2 440	135	2

Table 3. Kc_2 and ε_2 for the triethylenediamine–chloranil complex determined from Scatchard data. Conditions: temperature 20 °C, solvent an equivolume mixture of cyclohexane and ethyl acetate

Ratio of amine to quinone D_0/A_0 Minimum	Maximum	Kc_2	ε_2
78	373	3.76	3 308
84	405	3.05	4 000
197	608	4.06	3 292
202	646	4.27	3 357

Table 4. Standard enthalpy (ΔH°) and entropy (ΔS°) changes on complexing triethylenediamine and quinuclidine with chloranil in an equivolume mixture of cyclohexane and ethyl acetate

Donor	Acceptor	ΔH°/ kJ mol^{-1}	ΔS°/ J K^{-1} mol^{-1}
Triethylenediamine	Chloranil	-18.0 ± 2.5	-37.7 ± 8.8
Quinuclidine	Chloranil	-15.4 ± 1.7	-38.1 ± 5.0

to be *ca.* 17%. Method 3 was that of Scatchard [17,18] using a large excess of the amine.

In most cases the measurements were made at a wavelength higher than the charge-transfer maximum to minimise the contribution from the quinone and a second experiment was carried out to compare ε at the wavelength of the measurement and at the maximum. The exception was the triethylenediamine–chloranil complex where there is no interference at the maximum. The results are shown in Table 2. The interactions omitted from Table 2 could not be studied because of chemical reactions, low solubility, or a low equilibrium constant.

In contrast to the behaviour of iodine,[9] chloranil forms stronger complexes with triethylenediamine than with quinuclidine.

As expected [8] $Kc_1\varepsilon_1$ increases with the electron affinity of the quinone. A difference was found between the results from Foster and Matheson's method 1 and the Scatchard method 3 for the triethylenediamine complex of chloranil, the Scatchard method giving a much lower value of Kc_1 and a higher value of ε_1. A similar but smaller difference for the hexamethylbenzene–fluoranil complex was attributed to the presence of 2 : 1 complexes in the Scatchard solutions.[15] In this work there was no spectroscopic evidence for 2 : 1 amine–quinone complexes even with a large excess of amine; however, this would not be detected if the spectrum was similar to that of the 1 : 1 complex. It is also possible for the two quinone molecules to complex a triethylenediamine molecule at both nitrogens, but this would be negligible at the concentrations of quinone used.

Foster [15] has reported a computerised iterative treatment of Scatchard data from systems containing both 1 : 1 and 2 : 1 complexes. A different approach was taken in the present work. The Scatchard equation modified to take account of 2 : 1 complex formation is (2) where Kc_2 and ε_2 are the equilibrium constant and molar absorptivity for the complex D_2A formed by the reaction $DA + D \longrightarrow D_2A$. If the values of Kc_1 and ε_1 determined by method 1 using equimolar solutions (where the concentration of D_2A is negligible) are substituted in the equation together with absorbance and concentration data from the Scatchard method, the result is a series of simultaneous equations of form (3).

$$\frac{\mathrm{Abs}}{[D_0][A_0]} = -\frac{\mathrm{Abs}}{[A_0]} \cdot Kc_1\,(1 + [D_0]Kc_2) + Kc_1\,(\varepsilon_1 + \varepsilon_2[D_0]Kc_2) \qquad (2)$$

$$Kc_2\varepsilon_2 - pKc_2 = q \qquad (3)$$

Each equation contains a different value of p and q. For each set of data this gives an overdetermined system in K_2 and ε_2 which can be solved by standard matrix algebra.[19] The results for the triethylenediamine–chloranil complex are given in Table 3. Kc_2 appears to increase with an increase in the ratio of amine to quinone. The ratio of Kc_1 to Kc_2 is similar to that found for π-donor–π-acceptor complexes such as hexamethylbenzene–fluoranil and 5-methoxyindole–trinitrobenzene.[15,20] The ratio of ε_2 to ε_1 is *ca.* 3. A similar ratio was reported for the hexamethylbenzene–trinitrobenzene complex although the results for other π–π complexes are nearer to 2,[15,20] the theoretical value for two similar but independent transitions.

Values of ΔH° and ΔS° were determined for the triethylenediamine and quinuclidine complexes of chloranil from the variation in $Kc\varepsilon$ with temperature using Foster and Matheson's method 1. The results are shown in Table 4. ΔS° is lower for the triethylenediamine–chloranil complex than for the triethylenediamine–phthalic anhydride complex (−59.0 J K^{-1} mol^{-1}) [4]. Possible reasons for this are discussed later.

Preparation of a Solid Complex.—A solid triethylenediamine–chloranil complex was prepared by evaporating a solution in cyclohexane–ethyl acetate and allowing the solid to crystallise from a small volume of solvent. The product was a blue-black 1 : 1 crystalline complex (confirmed by elemental analysis and titration of the amine). A solution exhibited the charge-transfer band which did not obey Beer's law on

Table 5. Energy changes calculated by CNDO/2 for complexing with ammonia at the van der Waals distance

Acceptor	Complexing site	Energy change (kJ mol^{-1})	Charge transferred to quinone	Population analysis, nitrogen–quinone atom
Benzoquinone	Oxygen (position 1)	−0.791	0.0001	−0.0002
	C(1) (position 2)	−1.895	0.0004	0.004
	Midpoint C(1)–C(2) (position 4)	−1.979	0.0003	
	C(2) (position 3)	−1.682	0.0001	0.0002
	Midpoint C(2)–C(3) (position 5)	−1.586	0	
	Oxygen, x axis (position 6)	+1.310	0	0.0001
Fluoranil	Oxygen (position 1)	−2.264	0.0002	−0.0002
	C(1) (position 2)	−3.874	0.0005	0.0005
	Midpoint C(1)–C(2) (position 4)	−4.050	0.0005	
	C(2) (position 3)	−3.410	0.0002	0.0003
	Midpoint C(2)–C(3) (position 5)	−3.431	0	
	Oxygen, x axis (position 6)	+0.381	0.0001	0.0001

dilution. The i.r. spectrum contained bands from the parent molecules, although there were some minor differences such as a decrease in the carbonyl frequencies from 1 695 and 1 685 cm^{-1} to 1 690 and 1 680 cm^{-1}. Attempts to produce crystals suitable for *X*-ray diffraction were unsuccessful.

Theoretical Studies.—The interaction of amines with quinones was explored using two model systems, ammonia–benzoquinone and ammonia–fluoranil. Symmetry arguments supported by Hückel calculations suggested that there were three complexing sites corresponding to energy minima, shown as positions 1—3 in Figure 1.

Using the Extended Hückel method,[21] no energy minimum on complex formation was predicted. A similar result has been reported for the benzene–tetracyanoethene complex.[22] The CNDO/2 method [23] gave an energy minimum at an unrealistically small intermolecular separation. When the separation was set to the van der Waals distance (0.335 nm for C–N, 0.29 nm for O–N), complex formation was predicted for positions 1—5 with in some cases a slight transfer of charge to the quinone. Complexing at position 6 (forbidden on symmetry grounds) did not correspond to an energy minimum at the van der Waals distance, although a minimum was obtained when the distance was decreased. The calculated population analyses are very small and in the case of complexation at oxygen predict an antibonding interaction for position 1 and a bonding interaction for position 6. This disagrees with the calculated energy changes. The results are shown in Table 5.

From the calculated energy changes there are four equivalent preferred complexing sites, at the midpoint of C(1)–C(2) on each quinone molecule. However, a stable complex is predicted for any approach of the amine lone pair perpendicular to the quinone molecule.

These predictions apply strictly only to the gas phase but should be approximately correct for solutions unless the quinone molecule is selectively solvated to hinder complexing in one or more positions. The presence of isomeric complexes may contribute to the lower value of ΔS° found for the chloranil complex of triethylenediamine (−37.7 J K^{-1} mol^{-1}) compared with the phthalic anhydride complex (−59.0 J K^{-1} mol^{-1}).

The energy change on adding a second ammonia molecule to benzoquinone at the van der Waals distance was calculated by the CNDO/2 method. Excluding those orientations in which there was steric hindrance between the two ammonia molecules, 2 : 1 complexes were predicted to be stable. The energy change for adding the second ammonia molecule was lower, which corresponds to $Kc_2 < Kc_1$. Although the site of complexing could not be determined experimentally, the CNDO/2 model reproduces qualitatively the observed features of amine–quinone complex formation when using a realistic molecular separation.

Studies of Non-bridgehead Amines.—Triethylamine and piperidine do not form complexes in solution under the conditions used for the bridgehead amines. These two amines can invert about nitrogen, which would be impossible if they were complexed and this may explain the lack of reactivity. An alternative explanation is that complex formation is prevented by steric hindrance from the alkyl groups. It is of interest that piperidine adsorbed onto chloranil from the vapour phase appeared to form a complex, giving a very broad and weak absorption band in the visible region. However, experimental difficulties did not permit precise location of the maximum. Complex formation has also been reported for triethylamine under similar conditions.[24]

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