

The Association Reactions of Ion Radicals with Neutral Molecules. VI. One-to-One and One-to-Two Complexes of Dianions with Hydroxylic Compounds

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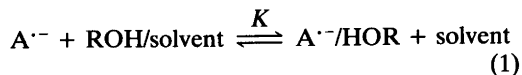
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Dianions of *p*-dinitrobenzene (*p*-DNB) and *p*-dibenzoylbenzene (*p*-DBB) form both A^{2-}/HOR and $A^{2-}/2HOR$ hydrogen-bonded complexes with water and methanol in DMF. Ranges of $0.1 M^{-1}$ to $1.3 M^{-1}$, $5 M^{-1}$ to $160 M^{-1}$, and $3 M^{-1}$ to $50 M^{-1}$ were observed at 273.2 K for $K_i/[DMF]$, $K_{ii}/[DMF]$ and $K_{iii}/[DMF]$, respectively. In general, for a particular hydrogen-bond donor/acceptor pair the relative values of $K_i:K_{ii}:K_{iii}$ are of the order of 1:(40–130):(10–40). The relatively small value of K_{ii}/K_{iii} (~ 3) is a consequence of the fact that the charges of the dianion are relatively distant and each can accommodate one H-bond. The fact that K_{ii} is invariably larger than K_{iii} shows that partial neutralization of one charge by hydrogen-bonding makes A^{2-}/HOR a weaker H-bond acceptor than A^{2-} .



Anion radicals derived from aromatic compounds form 1:1 hydrogen-bonded complexes with hydroxylic compounds.^{1–5} The equilibria are readily studied by reversible electrode potential measurements. In aprotic solvents, such as acetonitrile or *N,N*-dimethylformamide (DMF), the equilibria are described by eqn. (1):



in which ROH/solvent represents the hydroxylic compound hydrogen-bonded to the solvent.

Equilibrium constants, $K/[solvent]$, ranging from about 0.3 to $50 M^{-1}$ (273–293 K) have been reported for these reactions.^{1–5} The relatively low values of K reflect the fact that the hydroxylic compounds are rather tightly hydrogen-bonded to the solvent.^{6–7}

In this paper we report equilibrium constants for hydrogen-bond formation between the dianions of some difunctional aromatic compounds and water and methanol in DMF, and compare these with those for the corresponding anion radicals. As anticipated, we find that the equilibrium constants for the reactions of the dianions are much larger than those for the corresponding anion radicals. Furthermore, while the anion radicals do not appear to show much tendency to complex with a second molecule of the hydrogen-bond donor, the dianions do.

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Results and discussion

In order to study hydrogen-bonding of dianions of aromatic compounds by the effect of the equilibria on reversible potentials it is necessary that both the anion radicals and the dianions are stable under the conditions of the measurements. This places a severe limitation on the possible processes available for study. We selected two substrates which fulfil the necessary criteria, viz. *p*-dinitrobenzene (*p*-DNB) and *p*-dibenzoylbenzene (*p*-DBB). The consecutive reversible $1e^-$ reductions, first to the anion radical and then to the dianion are illustrated in Fig. 1 for *p*-DNB in DMF.

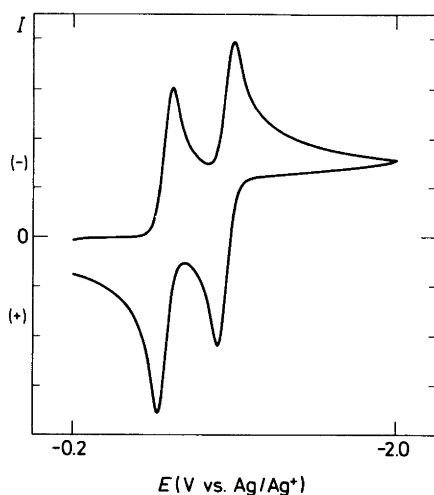
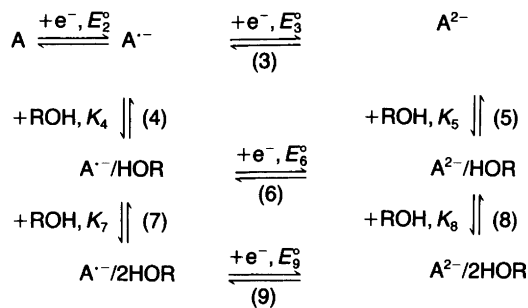


Fig. 1. Cyclic voltammogram at a Pt electrode ($d = 0.6$ mm) of 1.0 mM *p*-DNB in DMF (0.1 M Bu_4NBF_4 , 0.01 M Me_4NI) at 0.1 V s^{-1} ; $T = 273.2$ K.

Relationship between reversible electrode potentials and equilibrium constants for hydrogen-bonding. The formation of hydrogen-bonds to electrochemically formed dianions could follow several different pathways as outlined in Scheme 1.

In Scheme 1 and in the following, ROH represents the hydrogen-bonded species ROH/solvent, and the K 's (in M^{-1}) include the factor $[\text{solvent}]^{-1}$.

Previous papers in this series¹⁻⁵ have dealt with the determination of hydrogen-bonding equilibri-



Scheme 1.

um constants (K_4) for equilibria (4), using reversible electrode potential measurements and employing eqn. (10) first used by Peover and Davies,⁸ and in which:

$$\begin{aligned}
 \Delta E_2^{\text{rev}} &= E_2^{\text{rev}} - E_2^0 \\
 K_4 &= \{\exp[\Delta E_2^{\text{rev}}/(RT/F)] - 1\} / [\text{ROH}] \quad (10)
 \end{aligned}$$

A contribution to the reversible potentials (E_2^{rev}) deriving from equilibrium (7) would result in apparent equilibrium constants (K_{app}) which increase with increasing $[\text{ROH}]$ as expressed in eqn. (11) (which obviously reduces to eqn. (10) when $K_7 = 0$):

$$\begin{aligned}
 K_{\text{app}} &= K_4 + K_7 K_4 [\text{ROH}] \\
 &= \{\exp[\Delta E_2^{\text{rev}}/(RT/F)] - 1\} / [\text{ROH}] \quad (11)
 \end{aligned}$$

The observation of constant values of K_{app} over a range of $[\text{ROH}]$ was taken as evidence that hydrogen-bonding to a second molecule of ROH does not contribute significantly to the reversible potentials for the formation of acetophenone anion radicals in aprotic solvents,² and the same observation has been made for *p*-DNB and *p*-DBB in this study. Consequently, a reaction pathway including reactions (7) and (9) can be ruled out.

Two pathways leading to hydrogen-bonded dianions remain: (a) The second electron transfer occurs only via $\text{A}^{\cdot -}$ [reaction (3)] and A^{2-} forms complexes with one or two molecules of ROH [reactions (5) and (8)]. (b) The second electron transfer takes place only via the hydrogen-bonded anion radical $\text{A}^{\cdot -}/\text{HOR}$ [reactions (4) and (6)], and the hydrogen-bonded dianion

$$E_3^{\text{rev}} = E_3^{\circ} + RT/F \ln\{(1 + K_5[\text{ROH}] + K_5K_8[\text{ROH}]^2)/(1 + K_4[\text{ROH}])\} \quad (12)$$

$$E_6^{\text{rev}} = E_6^{\circ} + RT/F \ln\{(K_4 + K_4K_5[\text{ROH}] + K_4K_5K_8[\text{ROH}]^2)/(K_5 + K_4K_5[\text{ROH}])\} \quad (13)$$

may form a hydrogen-bond to an additional molecule of ROH via reaction (8). In case (a), the influence of equilibria (5) and (8) on the reversible potential, E_3^{rev} , is given by eqn. (12), taking into account also the influence of equilibrium (4) on the concentration of $A^{\cdot-}$. In case (b), the influence of equilibria (4) and (8) on the reversible potential E_6^{rev} is given by eqn. (13), which takes into account the influence of equilibrium (5) on the concentration of A^{2-}/HOR . E_3° can, like E_2° , be determined experimentally in the absence of ROH, whereas E_6° cannot. However, E_3° and E_6° are related through eqn. (14), express-

$$E_6^{\circ} - E_3^{\circ} = RT/F \ln(K_5/K_4) \quad (14)$$

ing that the reduction of $A^{\cdot-}/\text{HOR}$ takes place at a more positive potential than reduction of A^{2-} since the equilibrium constant for formation of a hydrogen-bond to the dianion, K_5 , is expected to be larger than the equilibrium constant for hydrogen-bond formation to the anion radical, K_4 . Substituting the expression for E_6° in eqn. (14) in (13) makes the right-hand side of eqn. (13) equal to that of eqn. (12), i.e. $E_6^{\text{rev}} = E_3^{\text{rev}}$. This shows that in the presence of ROH, the shift in reversible potential for the second electron transfer relative to E_3° depends on K_4 , K_5 and K_8 in the same way – namely as expressed in eqn. (12) – independently of the reaction pathway.

Rearrangement of eqn. (12) to eqn. (15) using $\Delta E_3^{\text{rev}} = E_3^{\text{rev}} - E_3^{\circ}$ shows that K_5 and K_8 can be determined from a plot of $f(\Delta E_3^{\text{rev}}, [\text{ROH}])$ against $[\text{ROH}]$.

The values of K_5 and K_8 may also be obtained from measurements of the changes in the difference in reversible potentials for the first and the second electron transfer:

$$\Delta \Delta E^{\text{rev}} = (E_2^{\text{rev}} - E_3^{\text{rev}}) - (E_2^{\circ} - E_3^{\circ})$$

$$K_5 + K_5K_8[\text{ROH}] = \{\exp[\Delta E_3^{\text{rev}}/(RT/F)](1 + K_4[\text{ROH}]) - 1\}/[\text{ROH}] = f(\Delta E_3^{\text{rev}}, [\text{ROH}]) \quad (15)$$

$$\Delta \Delta E^{\text{rev}} = RT/F \ln\{(1 + K_4[\text{ROH}])^2/(1 + K_5[\text{ROH}] + K_5K_8[\text{ROH}]^2)\} \quad (16)$$

$$K_5 + K_5K_8[\text{ROH}] = \{\exp[-\Delta \Delta E^{\text{rev}}/(RT/F)](1 + K_4[\text{ROH}])^2 - 1\}/[\text{ROH}] = g(\Delta \Delta E^{\text{rev}}, [\text{ROH}]) \quad (17)$$

where $E_2^{\circ} - E_3^{\circ}$ is the difference in reversible potentials in the absence of ROH. Combining eqns. (10) and (12) gives eqn. (16), similar to that presented earlier, but not used quantitatively, for the effect of Li^+ on the difference in reversible potentials for the first and second reduction of dinitrocompounds.¹¹ Rearrangement of eqn. (16) gives eqn. (17), which can be used analogously to eqn. (15) for determination of K_5 and K_8 .

Electrode potential measurements. The changes in peak potentials were assumed to reflect the changes in reversible potentials occurring upon changes in $[\text{ROH}]$. The peak potentials were measured at either a Pt ($d = 0.6$ mm), and Au (d

Table 1. Electrode peak potential data for the reduction of *p*-dibenzoylbenzene in DMF.^a

$[\text{H}_2\text{O}]/\text{M}$	$\Delta E_3^{\circ}/\text{mV}^b$	$\Delta \Delta E^{\circ}/\text{mV}^c$
0	—	—
0.0056	3.2	-3.0
0.0111	6.0	-5.6
0.0167	8.7	-8.1
0.0222	11.2	-10.4
0.0278	13.9	-12.9
0.0333	16.8	-15.5
0.0389	19.2	-17.5
0.0444	21.4	-19.6
0.0500	23.4	-21.7
0.0555	25.4	-23.7
0.0610	27.2	-25.3
0.0666	29.2	-27.2
0.0721	30.9	-29.0
0.0777	32.4	-30.3
0.0832	34.3	-32.4

^aIn solvent containing Bu_4NBF_4 (0.1 M) and Me_4NI (0.01 M). ^b $E_3^{\circ} - (E_3^{\circ})_{[\text{H}_2\text{O}]=0}$. ^c $(E_2^{\circ} - E_3^{\circ}) - (E_2^{\circ} - E_3^{\circ})_{[\text{H}_2\text{O}]=0}$.

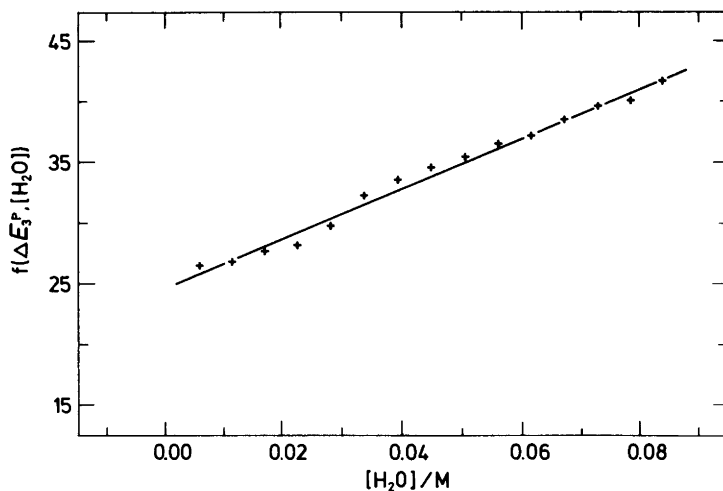


Fig. 2. Plot of $f(\Delta E_3^0, [H_2O]) = \{\exp[\Delta E_3^0/(RT/F)](1+K_4[H_2O]) - 1\} / [H_2O]$ vs. $[H_2O]$ for 1.0 mM *p*-dibenzoylbenzene in DMF (0.1 M Bu_4NBF_4 , 0.01 M Me_4NI) at $T = 273.2$ K.

Fig. 3. Plot of $g(\Delta\Delta E^P, [H_2O]) = \{\exp[-\Delta\Delta E^P/(RT/F)](1+K_4[ROH])^2 - 1\} / [H_2O]$ vs. $[H_2O]$ for 1.0 mM *p*-dibenzoylbenzene in DMF (0.1 M Bu_4NBF_4 , 0.01 M Me_4NI) at $T = 273.2$ K.

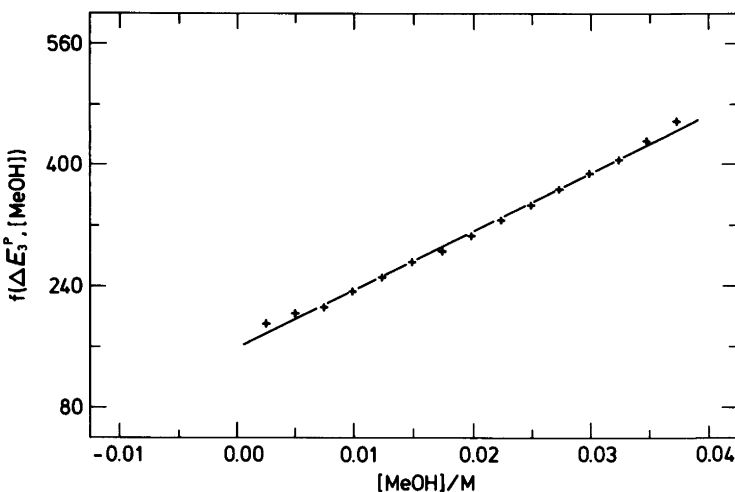
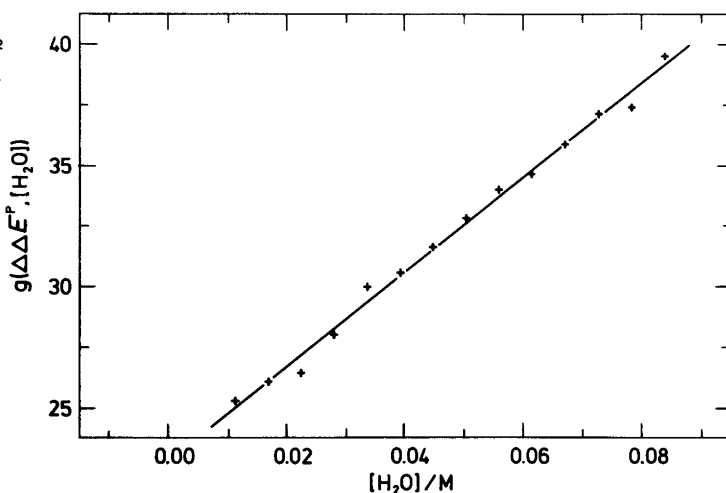


Fig. 4. Plot of $f(\Delta E_3^0, [MeOH]) = \{\exp[\Delta E_3^0/(RT/F)](1+K_4[MeOH]) - 1\} / [MeOH]$ vs. $[MeOH]$ for 1.0 mM *p*-dibenzoylbenzene in DMF (0.1 M Bu_4NBF_4 , 0.01 M Me_4NI) at $T = 273.2$ K.

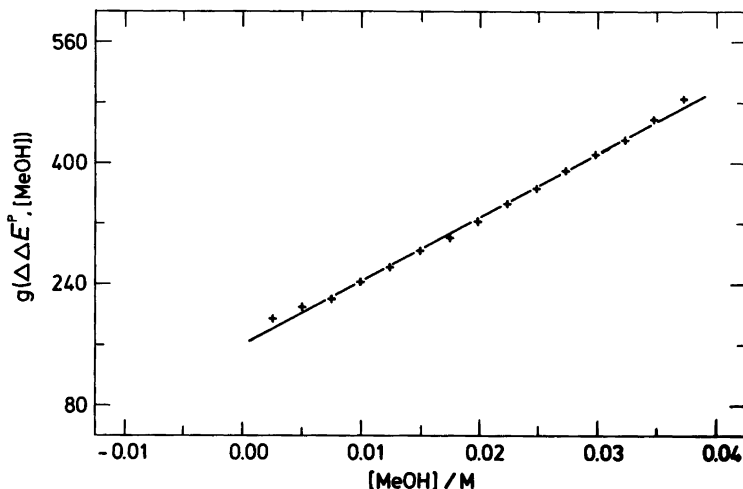


Fig. 5. Plot of $g(\Delta\Delta E_3^-, [\text{MeOH}]) = \{\exp[-\Delta\Delta E^p/(RT/F)](1+K_4[\text{MeOH}])^2-1\}/[\text{MeOH}]$ vs. $[\text{MeOH}]$ for 1.0 mM *p*-dibenzoylbenzene in DMF (0.1 M Bu_4NBF_4 , 0.01 M Me_4NI) at $T = 273.2$ K.

= 0.8 mm) or an Hg-plated Pt ($d = 0.8$ mm) electrode, using derivative linear sweep voltammetry.⁹ With a voltage sweep rate equal to 0.10 V s^{-1} and substrate concentrations equal to 1.0 mM, the peak potentials can be measured with a precision of about ± 0.1 mV.¹⁰ Measurements were first made on solutions of the substrate prepared from dry solvent and supporting electrolyte passed through a column of neutral alumina (Woelm neutral W200) under nitrogen immediately before use. The hydroxylic com-

pounds were then added and measurements were made after each new addition. A complete set of data for one particular experiment, viz. the reduction of *p*-DBB in the presence of water, is summarized in Table 1. Data for the reduction of both *p*-DNB and *p*-DBB are illustrated in Figs. 2–9.

Equilibrium constants for hydrogen-bonding. Equilibrium constants were obtained from plots of the data according to both eqns. (15) and (17),

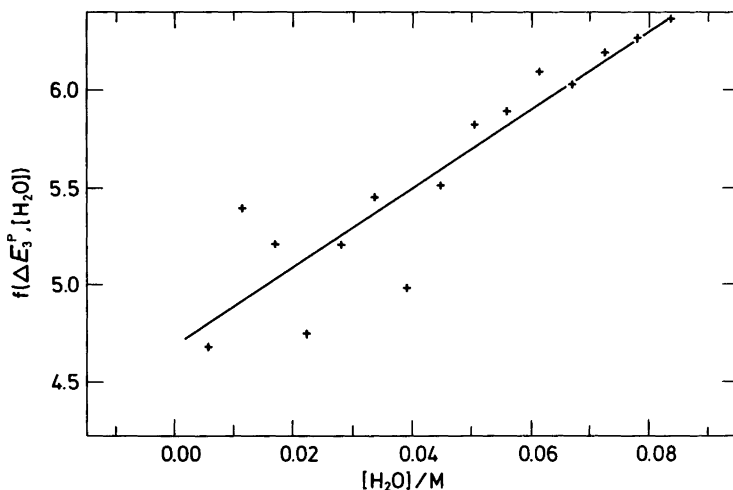


Fig. 6. As in Fig. 2. Substrate: 1.0 mM *p*-dinitrobenzene.

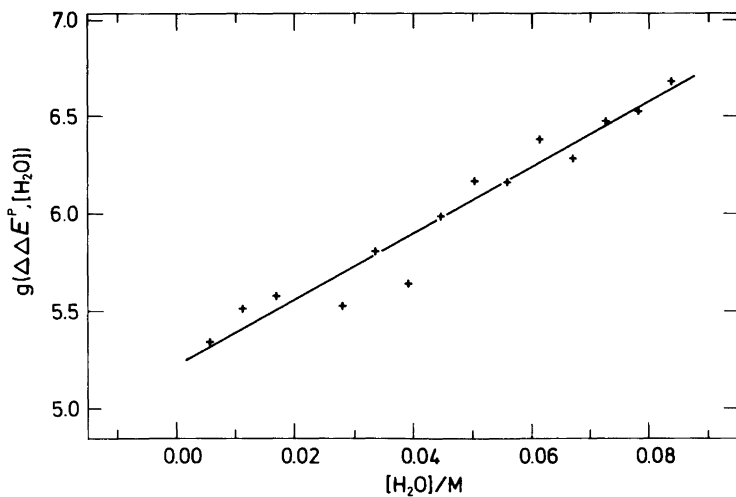


Fig. 7. As in Fig. 3. Substrate: 1.0 mM *p*-dinitrobenzene.

Fig. 8. As in Fig. 4. Substrate: 1.0 mM *p*-dinitrobenzene.

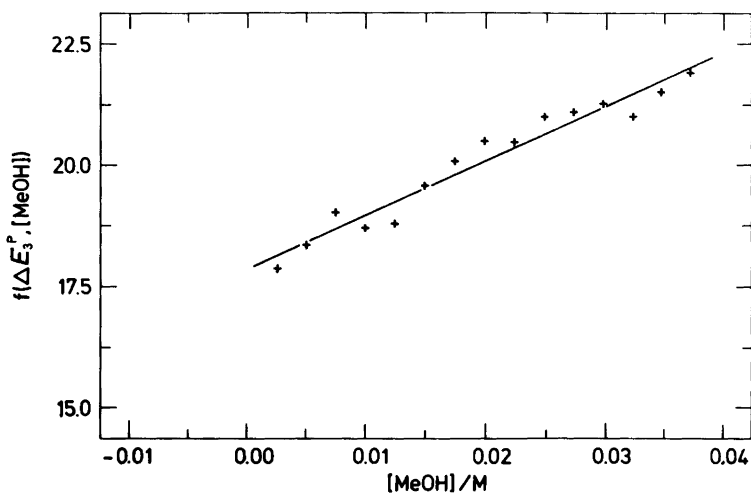


Fig. 9. As in Fig. 5. Substrate: 1.0 mM *p*-dinitrobenzene.

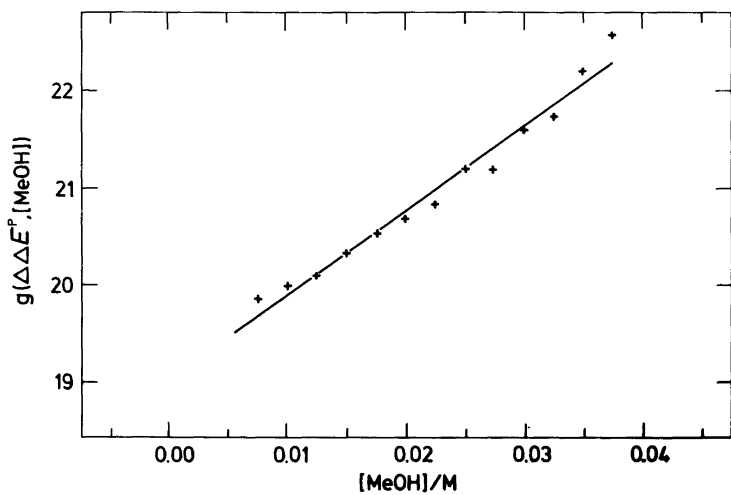


Table 2. Hydrogen-bonding equilibrium constants for reactions of dianions with water and methanol.^a

Substrate	K_4/M^{-1} ^b	Measurement	Fig.	ROH	K_5/M^{-1}	K_8/M^{-1}
<i>p</i> -DBB	0.84, 0.50 ^c	ΔE_3^p	2	HOH	25	8.4
<i>p</i> -DBB		$\Delta\Delta E^p$	3	HOH	23	8.6
<i>p</i> -DBB	1.25	ΔE_3^p	4	MeOH	160	49
<i>p</i> -DBB		$\Delta\Delta E^p$	5	MeOH	161	44
<i>p</i> -DNB	0.35, 0.11 ^c	ΔE_3^p	6	HOH	4.7	4.4
<i>p</i> -DNB		$\Delta\Delta E^p$	7	HOH	5.2	3.3
<i>p</i> -DNB	0.28	ΔE_3^p	8	MeOH	18	5.9
<i>p</i> -DNB		$\Delta\Delta E^p$	9	MeOH	19	4.6

^aMeasurements in DMF/Bu₄NBF₄ (0.1 M)/Me₄Ni(0.1 M) by derivative linear sweep voltammetry at 100 mV s⁻¹. All measurements were made at 0 °C. ^bEquilibrium constant for hydrogen-bonding reactions of the anion radicals reported in Ref. 5. ^cValues observed in this work.

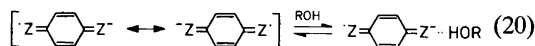
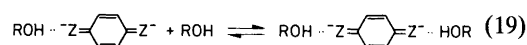
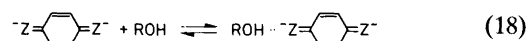
using the measured values of ΔE_3^p and $\Delta\Delta E^p$ for ΔE_3^{rev} and $\Delta\Delta E^{\text{rev}}$, respectively. Values of K_4 for ROH = H₂O were obtained from independent measurements of E_3^p in the concentration range 0–0.5 M and application of eqn. (10); for ROH = MeOH they were taken from previous work.⁵ The quantities on the right-hand sides of eqns. (15) and (17), $f(\Delta E_3^p, [\text{ROH}])$ and $g(\Delta\Delta E^p, [\text{ROH}])$, respectively, were plotted as the ordinate vs. [ROH] as the abscissa. The intercepts of the plots gave K_5 while the slopes of the linear regression lines gave values of K_5K_8 . The data were plotted according to eqn. (15) in Figs. 2, 4, 6 and 8, and according to eqn. (17) in Figs. 3, 5, 7 and 9. In general, the correlation for data sets obtained measuring $\Delta\Delta E^p$ is slightly better than for those obtained measuring ΔE_3^p . This could be related to the fact that small instabilities in the reference electrode are compensated for by the recording of potential differences, $E_3^p - E_3^p$, in the former type of measurements. The apparent curvature in the $\Delta\Delta E^p$ -data for the complexation of MeOH with the *p*-DNB dianion (Fig. 9) was considered insignificant, as no such trend was found for the corresponding ΔE_3^p -measurements (Fig. 8). The equilibrium constants resulting from the linear regression analyses are tabulated in Table 2.

In all cases the values for K_5 determined by the two types of measurements are in excellent agreement, while the values obtained for K_8 are more uncertain as could be expected due to their smaller magnitude.

Hydrogen-bonding equilibria of dianions. Three

of the four hydrogen-bond donor/acceptor pairs exhibit K_5/K_8 values of 3–5. The exception, i.e. *p*-DNB²⁻ + H₂O, shows an equilibrium constant ratio of about 1.5. The reason for this exception is not clear, but as evident from Figs. 4 and 5 this is the data set for which the poorest correlation was found.

The charge in both dianions can be considered to be strongly localized on the oxygen atoms of the functional groups. Thus, the equilibria can be approximated by eqns. (18) and (19), where Z represents the functional group (either NO₂ or PhCO). The charges in the corresponding anion radicals are considerably more dispersed since both functional groups are equally involved. It seems likely that hydrogen-bonding localizes the charge to a certain degree, so that the equilibria can be approximated by eqn. (20). A comparison of eqn. (19) with eqn. (20), and of the corresponding equilibrium constants, K_8 and K_4 , is revealing. Even when one of the charges in the mono-hydrogen-bonded dianion is essentially localized by the existing H-bond, hydrogen-bonding to the other site is still considerably more favorable than H-bonding to the anion radical, i.e. K_8/K_4 falls in the range of about 10 to 40.



Experimental

The cells, electrodes and instruments employed were as previously described.¹² The potential measurements were made by derivative linear sweep voltammetry (DLSV),⁹ and the peak potentials were determined from linear regression of a few points around the apparent zero-crossings. All measurements were carried out at 0.1 V s⁻¹ and $T = 273.2$ K.

p-Dinitrobenzene and *p*-dibenzoylbenzene were of reagent grade and were purified by conventional methods before use.

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