

Electrochemical and Computational Interpretations of Hydrogen-bonding of Naphthoquinones with Methanol

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Summary: Cyclic Voltammetry technique was used to study the hydrogen bonding of MeOH with electroreduced naphthoquinones. The positive shift in both reduction waves of the compounds was investigated with the continuous increase in MeOH concentration. From the observed shifts, equilibrium constants and number of MeOH molecules bonded to anion and dianion of the naphthoquinone were calculated. The 'quinone-MeOH' interactions were resolved as hydrogen bonding. Following the calculations substituent and solvent effects were addressed. To support experimental results computational studies were also carried out. The theoretical results obtained from CNDO/CI method rationalized and logically explained the observed positive shift in the peaks. Three types of computations were made (i) Theoretical U.V spectral studies for the neutral, anion, dianion and their hydrogen bonded complexes. (ii) Geometries of neutral, anion, dianion and the corresponding hydrogen bonded complexes with MeOH. (iii) Charge transfer study so as to know about the transfer of charges during the formation of these complexes.

Introduction

Quinones and their one electron reduced forms occupy central part in electron transfer chemistry and biological energy conservation [1-4]. In photosynthesis quinones act as primary and secondary electron acceptors, both in plants and bacterial photosynthetic reaction centers [5-8]. In *Rhodospseudomonas viridis* reaction center, a fused ring quinone, Menaquinone, occupies the primary quinone-binding site Q_A . Menaquinone-1 or vitamin K_2 , is made up of a 1,4-naphthoquinone head group with a methyl substituent at the 2 position and an isoprenoid chain of varying length at the 3 position. Various forms of vitamin K are known to be critical in the blood-clotting cascade [9, 10] and in calcium homeostasis [11, 12]. Thus keeping in view the importance of quinones it is necessary to characterize their chemical behaviour in the environment analogous to *in vivo*. Here the effect of hydrogen bonding on the chemical function of quinones was investigated. Hydrogen bonding of quinones has been found to play an important role in controlling both intra and inter molecular structure in biological systems and biological function as an active site of quino-enzymes [13-16].

The electrochemical and spectrochemical investigations on redox quinone systems involving the equilibria of electron transfer coupled with hydrogen bonding give much more information concerning the effect of molecular structure and environment on these basic processes [14-16]. In the

reaction center of protein complex of photosynthetic bacteria and plant photosystem II there are two kinds of quinones termed as Q_a and Q_b . It is well recognized that Q_a and Q_b act in concert to enable efficient charge separation and are conferred by their interaction with protein environment [14].

A variety of spectroscopies have been applied to characterize quinones in quinonezymes and reaction center in photosynthesis [17, 18]. To understand the structure function relationships from the spectra observed in such studies, it is essential to characterize reduced quinones in view of hydrogen bonding. In recent years hydrogen bonding of 1,4-benzoquinone, radical anion and dianion have been studied for such reasons [19-22]. Similarly several electrochemical reports discussed the path way of such reactions [23-27]. In addition spectrochemical studies for 1,4-benzoquinones combined with ab-initio (molecular orbital) MO calculations have provided a clear description of molecular and electronic structures of the hydrogen-bonded complexes of dianion of 1,4-benzoquinone with methanol. The $n-\sigma$ type charge transfer (CT) has an important role in such hydrogen bonding. This suggests different functions and properties of biological quinone dianions are conferred by hydrogen bonding involving the CT interaction with their protein environment [28]. It is also necessary to understand as far as possible, the environmental factors which regulate the potential and reaction

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pathways of various species, both *in vitro* and in mitochondrial or photosynthetic membranes. Among these factors we are partially concerned in this paper with hydrogen bonding which has been implicated in biological functions of quinone systems [29, 30].

In the present work, structural and spectral properties of simple naphthoquinones, their anions, dianions and hydrogen-bonded complexes with MeOH were examined by electrochemical and molecular orbital (MO) calculations. CNDO/CI calculations were carried out to interpret the spectral characteristics of the electronic states of neutral, anion, dianion and their hydrogen bonded complexes with MeOH. Only one electron transition was taken into account for CI calculations. Optimized geometries were obtained by RHF/CNDO and UHF/CNDO for closed and open shell compounds respectively. The bond lengths and charge densities of free and interacted quinone molecules with MeOH were used to complement the experimental findings.

Results and Discussion

In dry neutral, aprotic solvent, naphthoquinones typically show two cathodic polarographic waves, (Fig. 1a) E_1 and E_2 separated by amount of about 0.7 V, which correspond to the formation of anion and dianion of naphthoquinones respectively. In these reductions first step is generally reversible and second is from reversible to quasi-reversible at customary scan speeds. It was observed that the cathodic peaks shift anodically if MeOH was added (Fig. 1b). This positive shift showed easier reduction of naphthoquinone compounds because of the emergence of hydrogen bonding of reduced species with MeOH. Positive shift is much more significant for the 2nd cathodic peak than for the 1st one. These findings imply that dianions form strong hydrogen bonded complex with MeOH compared to the neutral and anion molecules of naphthoquinones. When MeOH concentration increases second cathodic wave begins to merge with the first one in case of basic naphthoquinones such as 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone, but a smaller effect of MeOH addition has been found in case of less basic naphthoquinones such as 2,3-dichloro-1,4-naphthoquinone. This clearly shows that the hydrogen bonding accepting capability of less basic quinones is weaker than that of more basic quinones. Similar observation has been reported earlier for other quinones [23-29, 31]. Basic quinones have electron-donating substituents which increase the

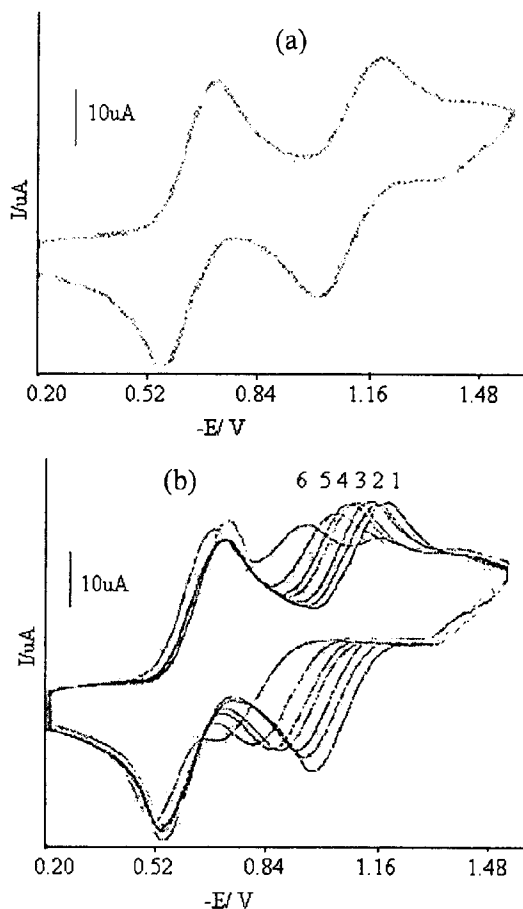


Fig. 1: (a) Representative cyclic voltammogram of 1mM 1,4-naphthoquinone in ACN + 0.1M TBAP at GC electrode vs. SCE. (b) Effect of added MeOH, Numbers 1 to 6 indicate the successive increments of MeOH in the concentration range of 0.05 to 1.3M.

electron density on carbonyl oxygen atoms whereas less basic quinones have electron-withdrawing substituents with reverse affect. Higher charge density on carbonyl oxygen of naphthoquinones favors strong hydrogen bonding with MeOH. This explains why shift in the 2nd cathodic peaks is much more for more basic quinones and results even in merging of the two cathodic peaks with the increase in the concentration of MeOH above certain limits.

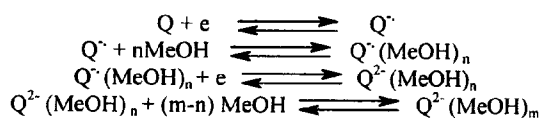
Solvent Effect

From plots of ΔE_p^c (separation between the two cathodic peaks) vs. the concentration of MeOH,

it is found that the separation between two cathodic peaks for each compound is affected by the nature of the solvent. In the beginning there was a large shift in the 2nd cathodic peak of naphthoquinones with the increase in the concentration of MeOH but later on it gets started smaller. In the case of DMSO ($\epsilon = 46.7$) all the compounds showed two well separated cathodic peaks over the given concentration range of MeOH, but in case of DMF ($\epsilon = 36.7$) and ACN ($\epsilon = 37.5$) the two cathodic waves merge with the increase of MeOH concentration. This can be envisaged from the dielectric constant (ϵ) values, the solvent polarity parameter. It was observed that hydrogen bonding ability decreases with the increase in polarity of the medium.

Quantitative Treatment of the System

In order to treat the situation quantitatively, formation of hydrogen-bonded complex is considered to be an equilibrium reaction. Hydrogen bonding equilibrium constant of neutral quinones is taken to be negligible compared to that with mono and dianions. Accordingly a scheme can be written as follows [29, 31]



Peover and Davis have noted the dependence of quinones reduction potential on the concentration and properties of cations and interpreted these reactions in term of cation-anion association equilibria [32]. By analogy with their treatment, following equation can be formulated.

$$E_{1/2} = E_{1/2}^0 + (RT/F) \ln (1 + K_{\text{eq}}^{(1)}[\text{MeOH}]^n) \quad (1)$$

where $E_{1/2}^0$ is the half wave potential in the absence of MeOH. If $K_{\text{eq}}^{(1)}[\text{MeOH}]^n \gg 1$ then a plot of $\Delta E_{1/2}$ ($= E_{1/2} - E_{1/2}^0$) vs $\log[\text{MeOH}]$ should give a straight

line. The straight lines are plotted in Fig. 2(a) the values of n and $K_{\text{eq}}^{(1)}$ estimated are given in Table-1. This procedure can be reasonably applied only to more strongly bonded basic quinones where we found larger shift in $E_{1/2}^{(1)}$. Values of n thus obtained are smaller for quinones of low basicity as in case of 2,3-dichloro-1,4-naphthoquinone (V) and larger for more basic quinones as in case of 2-methyl-1,4-naphthoquinone (II) and 1,4-naphthoquinone (I).

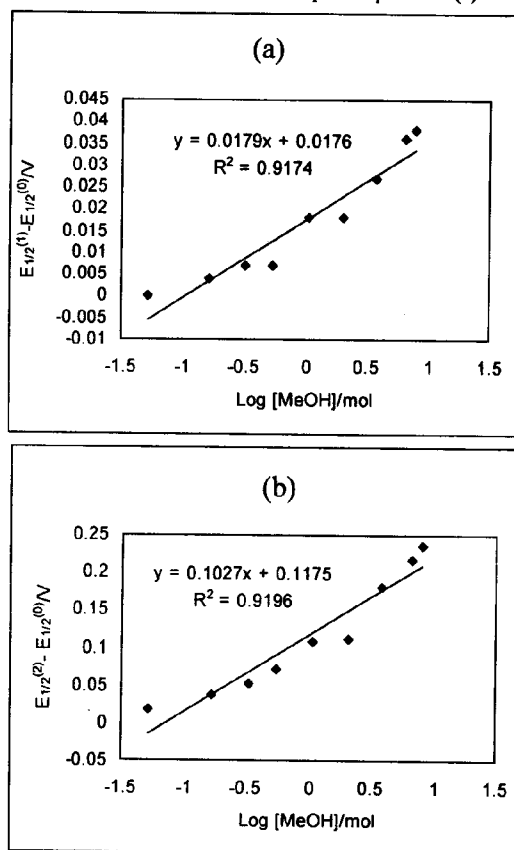


Fig. 2: (a) Plot of Log (MeOH) Vs $\Delta E_{1/2}^{(1)}$ (b) Plot of Log (MeOH) Vs $\Delta E_{1/2}^{(2)}$ for 1,4-naphthoquinone in ACN.

Table-1: Quantitative Parameters for hydrogen bonding of Naphthoquinones with MeOH.

Comp	n			K _{eq} ⁽¹⁾ /M ⁿ			m			K _{eq} ⁽²⁾ /M ^m		
	ACN	DMF	DMSO	ACN	DMF	DMSO	ACN	DMF	DMSO	ACN	DMF	DMSO
I	0.58	0.77	0.29	5.08	6.09	3.11	2.66	4.37	3.12	2.53x10 ³	8.49x10 ²	4.43x10 ²
II	0.54	0.60	0.28	2.91	3.10	3.03	2.39	4.13	3.29	4.56x10 ²	1.27x10 ³	1.67x10 ³
III	0.30	0.48	0.20	1.99	3.04	1.67	2.05	3.16	1.77	1.98x10 ²	3.38x10 ²	55.44
IV	0.56	1.01	0.06	3.06	5.94	1.23	1.97	3.16	1.55	1.24x10 ²	2.73x10 ³	65.18
V	0.28	0.06	c	1.75	1.16	c	2.12	2.91	1.97	3.08x10 ²	2.33x10 ²	73.34

n = number of MeOH molecules attached to anion radical. $K_{\text{eq}}^{(1)}$ = Association constant for anion-MeOH interaction.
 m = number of MeOH molecules attached to dianion. $K_{\text{eq}}^{(2)}$ = Association constant for dianion-MeOH interaction.
 C = due to small shift calculation was not possible.

The equilibrium constant for the first reduction step can be estimated from the intercept of the plot of equation 1. The values of $K_{eq}^{(1)}$ varies with the basicity of naphthoquinones. From the Table-1 it can be seen that $K_{eq}^{(1)}$ is largest for the unsubstituted compound-I (1,4-naphthoquinone) and smallest for dichloro-substituted compound-V (2,3-dichloro-1,4-naphthoquinone). Other compounds have intermediate values of $K_{eq}^{(1)}$ and n . Trend of this sort may be due to the inductive and steric effects of the substituents. Substituent present on the quinoid ring greatly affects $K_{eq}^{(1)}$ values. The substituent present may be donating or electron withdrawing, in the former case $K_{eq}^{(1)}$ value will be greater compared to the latter one. In case of compound-III (2-hydroxy-1,4-naphthoquinone), $K_{eq}^{(1)}$ and n values are smaller than that for compound-IV. The exceptional behaviour of compound-III has already been reported and discussed at length [25, 27]. Additionally this may probably be due to steric effect offered by substituents OH during the formation of hydrogen bonds of MeOH with naphthoquinones in compound-III, as in this compound substituent is on the same ring to which hydrogen bonding of MeOH occur. Similar interpretation can be made for the compounds I and II (2-methyl-1,4-naphthoquinone) also. In case of last compound (2, 3 dichloro 1,4- naphthoquinone) two substituents are present on the ring involved in the hydrogen bonding with MeOH, so the steric and inductive effects are very intense and result in the decrease of both values *i.e.* n and $K_{eq}^{(1)}$ for this compound.

The proposed inductive effect is in agreement with the Hammett substituent magnitudes. The values for the substituents present in the studied compounds are; $\sigma(\text{CH}_3) = -0.06$, $\sigma(\text{OH}) \text{ meta} = +0.02$, $\sigma(\text{OH}) \text{ para} = -0.22$, $\sigma(\text{Cl}) = 0.37$ [33].

Using the same analogy for hydrogen bonding equilibrium of second reduction step, we have [24]

$$\text{Exp}(f\Delta E_{1/2}) = (1 + K_{eq}^{(2)}[\text{MeOH}]^m) / (1 + K_{eq}^{(1)}[\text{MeOH}]^n) \quad (2)$$

where $f = F/RT$, m is the number of molecules of methanol hydrogen bonded to dianion of naphthoquinones and $K_{eq}^{(2)}$ is the corresponding equilibrium constant. For strong hydrogen bonding we may neglect 1 in the denominator and numerator and equation 2 becomes,

$$\Delta E_{1/2} = 1/f \ln (K_{eq}^{(2)} / K_{eq}^{(1)}) [\text{MeOH}]^{m-n} \quad (3)$$

Taking n from the first reduction step, values of m were estimated for all of the naphthoquinones. Having estimated m , n and $K_{eq}^{(1)}$ last equation then permit the evaluation of $K_{eq}^{(2)}$ (see Fig. 2b). The value of $K_{eq}^{(2)}$ should increase according to the basicity of quinones. From the Table-1 it is evident that the same trend was observed in case of second reduction of naphthoquinones as was for the first reduction. The only difference is that the values of m and $K_{eq}^{(2)}$ involved here are quite large than n and $K_{eq}^{(1)}$ respectively. It is reported [25, 27] that hydrogen bond strength increases with the increase in basic character of quinone. Dianion possesses more charge density than the anion therefore more basic; consequently interact more strongly to MeOH through hydrogen bonding than the anion. As the positive shift, in case of the second reduction peak, is more pronounced compared to the first one that is why, values of m and $K_{eq}^{(2)}$ are large. Here too, both steric and inductive effects are acting in the similar fashion as were in the first reduction.

Theoretical Studies

(a) Electronic Absorption Spectra of Naphthoquinones and their Hydrogen bonded Complexes with MeOH

Spectroelectrochemistry [28] provided the electronic spectra of dianions of benzoquinones in the absence and presence of various concentrations of MeOH. Additions of small amount of MeOH apparently cause a blue shift of the dianions band.

To treat the situation more quantitatively, CNDO/CI calculations were done. Table-2 lists the calculated data. The longest wavelength bands were taken to arise from the transition of HOMO to LUMO. From the optimized geometries data it was clear that anions and dianions of these compounds prefer to have a benzenoid form rather than quinoid form, which agrees with the optimized geometries given in the next section. The anion and dianion bands were regarded as benzenoid bands red shifted by the substituents. Fig. 3 shows the calculated MOs (molecular orbital) energies of HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) levels of neutral, anion, dianion and their hydrogen bonded complexes with MeOH, involved in the electronic transitions. The active MO of NQ^{2-} to the hydrogen bonding is localized on the carbonyl oxygen atoms, which is sufficiently activated to accept hydrogen with two-

Table-2: Calculated spectral data for naphthoquinones and their hydrogen bonded complexes with MeOH through Semi-empirical/CNDO method.

Compounds	λ/nm	f	$E_{(HOMO)}/eV$	$E_{(LUMO)}/eV$	$**\Delta E/eV$
NQ	139.69	2.813	-12.23	-0.380	11.850
NQ ⁻	251.15	0.254	-3.213	6.708	9.921
NQ ²⁻	244.37	0.365	3.395	12.645	9.250
NQ ⁻ -(MeOH) ₂	169.25	2.580	-11.774	-1.337	10.437
NQ ⁻ -(MeOH) ₂	229.38	0.387	-4.511	4.067	8.578
NQ ⁻ -(MeOH) ₄	220.36	0.445	-5.357	2.677	8.034
NQ ⁻ -(MeOH) ₆	207.81	0.447	-6.189	1.953	8.142
NQ ²⁻ -(MeOH) ₂	190.67	0.619	-0.255	10.171	10.426
NQ ²⁻ -(MeOH) ₄	182.73	0.685	-1.265	9.464	10.729
NQ ²⁻ -(MeOH) ₆	169.75	0.763	-2.278	9.107	11.385
MeNQ	143.39	2.776	-11.92	-0.337	11.583
MeNQ ⁻	252.00	0.262	-3.263	6.555	9.818
MeNQ ²⁻	237.00	0.598	3.154	12.250	9.096
MeNQ ⁻ -(MeOH) ₂	165.79	2.457	-11.687	-0.863	10.824
MeNQ ⁻ -(MeOH) ₂	228.53	0.376	-4.562	3.956	8.518
MeNQ ⁻ -(MeOH) ₄	218.47	0.422	-5.373	2.656	8.029
MeNQ ⁻ -(MeOH) ₆	210.23	0.407	-6.050	2.226	8.276
MeNQ ²⁻ -(MeOH) ₂	193.38	0.638	-0.260	10.023	10.283
MeNQ ²⁻ -(MeOH) ₄	185.40	0.687	-1.257	9.331	10.588
MeNQ ²⁻ -(MeOH) ₆	173.29	0.730	-2.193	9.005	11.198
2HyNQ	145.73	2.589	-11.94	-0.414	11.526
2HyNQ ⁻	255.86	0.240	-0.321	6.653	6.974
2HyNQ ²⁻	217.59	0.400	2.205	12.372	10.167
2HyNQ ⁻ -(MeOH) ₂	172.60	2.463	-11.611	-1.357	10.254
2HyNQ ⁻ -(MeOH) ₂	229.38	0.362	-4.508	4.216	8.724
2HyNQ ⁻ -(MeOH) ₄	219.19	0.409	-5.370	2.845	8.215
2HyNQ ⁻ -(MeOH) ₆	208.57	0.396	-6.031	2.270	8.301
2HyNQ ²⁻ -(MeOH) ₂	194.56	0.611	-0.191	10.122	10.313
2HyNQ ²⁻ -(MeOH) ₄	186.09	0.666	-1.194	9.414	10.608
2HyNQ ²⁻ -(MeOH) ₆	170.78	0.724	-2.221	9.138	11.359
5HyNQ	-	0	-11.747	-0.724	11.023
5HyNQ ⁻	194.33	0.445	-4.001	5.912	9.913
5HyNQ ²⁻	182.37	1.027	2.189	13.085	10.896
5HyNQ ⁻ -(MeOH) ₂	174.35	2.140	-12.073	-1.585	10.488
5HyNQ ⁻ -(MeOH) ₂	198.63	0.489	-4.977	4.100	9.077
5HyNQ ⁻ -(MeOH) ₄	199.55	0.519	-5.606	2.874	8.480
5HyNQ ⁻ -(MeOH) ₆	199.84	0.513	-6.143	2.109	8.252
5HyNQ ²⁻ -(MeOH) ₂	168.44	0.878	-0.551	10.752	11.303
5HyNQ ²⁻ -(MeOH) ₄	168.40	0.928	-1.413	9.906	11.319
5HyNQ ²⁻ -(MeOH) ₆	162.95	0.978	-2.189	9.472	11.661
CINQ	-	0	-12.35	-0.918	11.432
CINQ ⁻	242.23	0.280	-4.033	5.751	9.784
CINQ ²⁻	229.58	0.392	2.124	11.622	9.498
CINQ ⁻ -(MeOH) ₂	173.72	2.552	-11.970	-1.752	10.218
CINQ ⁻ -(MeOH) ₂	227.84	0.405	-5.089	3.589	8.678
CINQ ⁻ -(MeOH) ₄	218.80	0.462	-5.835	2.264	8.099
CINQ ⁻ -(MeOH) ₆	208.87	0.461	-6.447	1.832	8.279
CINQ ²⁻ -(MeOH) ₂	190.53	0.654	-0.745	9.679	10.424
CINQ ²⁻ -(MeOH) ₄	183.49	0.719	-1.690	8.975	10.665
CINQ ²⁻ -(MeOH) ₆	170.48	0.783	-2.611	8.681	11.292

* Oscillator strength

** $\Delta E = E_{(HOMO)} - E_{(LUMO)}$

NQ stands for 1,4-naphthoquinone, MeNQ for 2-methyl-1,4-naphthoquinone, 2HyNQ for 2-hydroxy-1,4-naphthoquinone, 5HyNQ for 5-hydroxy-1,4-naphthoquinone and CINQ for 2,3-dichloro-1,4-naphthoquinone.

electron reduction. It was found that activation of HOMO of NQ²⁻ as well as the lone pair orbitals were weakened by the hydrogen bonding of NQ²⁻ with MeOH, as illustrated in the figure. The blue shift of the NQ²⁻ spectra with MeOH addition is attributable

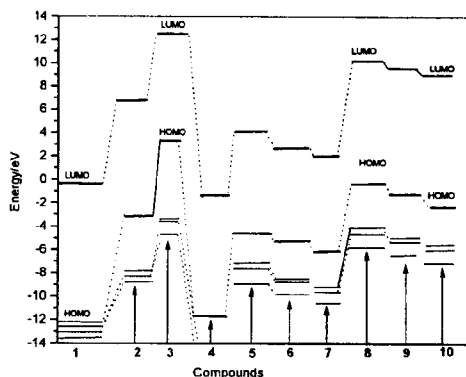


Fig. 3: Calculated energy level and illustrations of CNDO/CI MO related to the longest wavelength band. Numbers 1 to 10 on X-axis represents; NQ, NQ⁻, NQ²⁻, NQ⁻-(MeOH)₂, NQ⁻-(MeOH)₂, NQ⁻-(MeOH)₄, NQ⁻-(MeOH)₆, NQ²⁻-(MeOH)₂, NQ²⁻-(MeOH)₄ and NQ²⁻-(MeOH)₆ respectively.

to the remarkable stabilization of HOMO with hydrogen bond formation. From the theoretical data calculated and from the Fig. 3 same situation follows incase of the anions.

With the increase in the concentration of MeOH the blue shift that was expected from the experimental data was also supported from the theoretical calculations with the increase in number of molecules of MeOH bonded to these compounds, both in case of anions and dianions. All compounds given in the Table-2 followed the same typical behaviour as explained with the help of Fig. 3.

(b) Geometries of Neutral, Anion and Dianion of Naphthoquinones and their Hydrogen Bonded Complexes with MeOH

Geometries of all compounds and their hydrogen bonded complexes with MeOH were optimized. Fig. 4 reveals the optimized geometries of NQ system. The C=O bond distances are of typical double bond for neutral NQ and of a single for NQ²⁻, while those of NQ⁻ are in between. The C=O are elongated, but the C-C are contracted with the sequential reduction of NQ, indicating that quinoid forms change in to benzenoid ring. The structure of NQ²⁻ is therefore characterized by lengthening of the C=O and dissolution of bond alternation in the

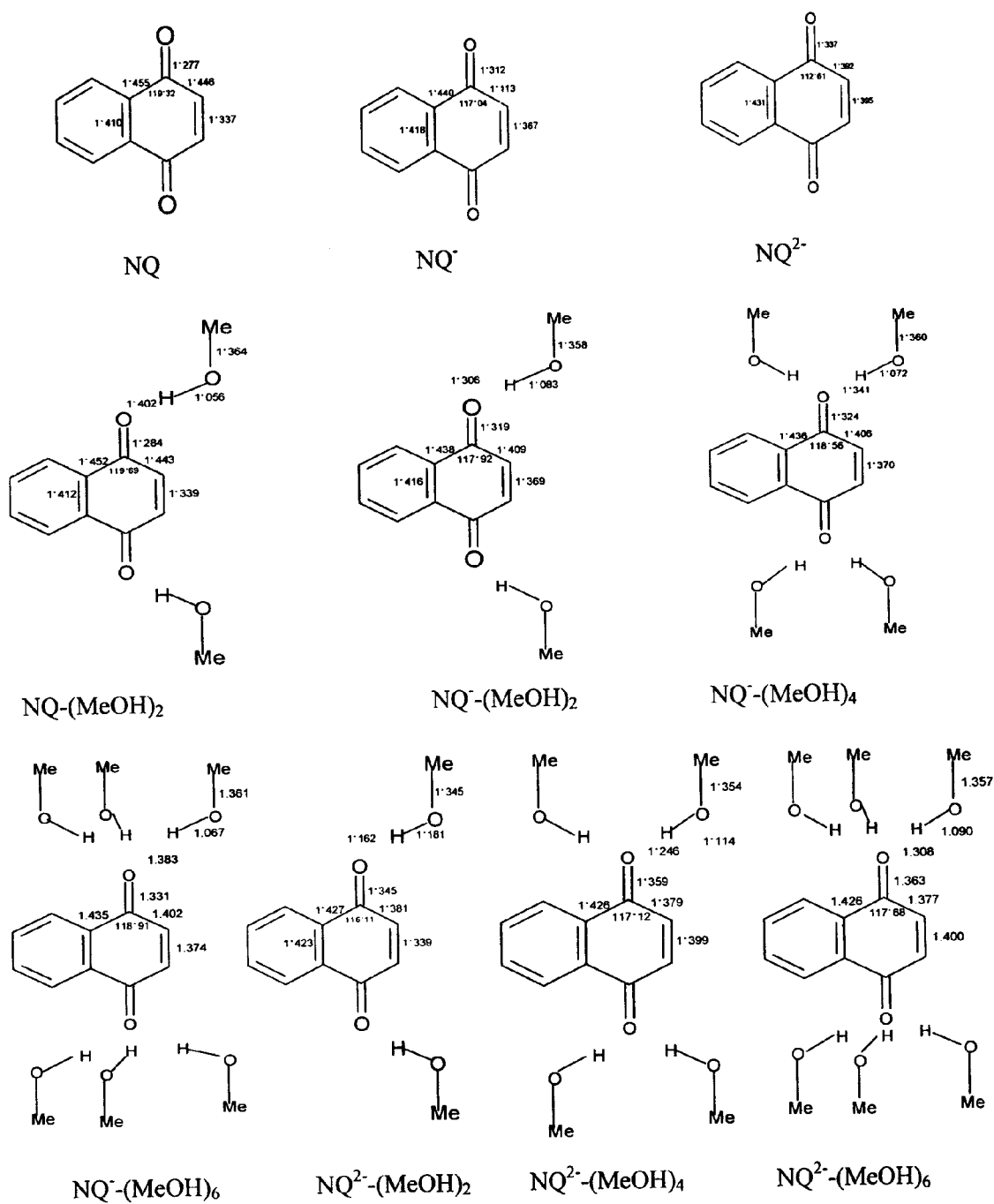


Fig. 4: Optimized Geometries of 1, 4-Naphtho-quinone and their hydrogen bonded complexes with MeOH. Calculated by RHF/CNDO or UHF/CNDO semiempirical methods. The bond lengths are in Å^o units.

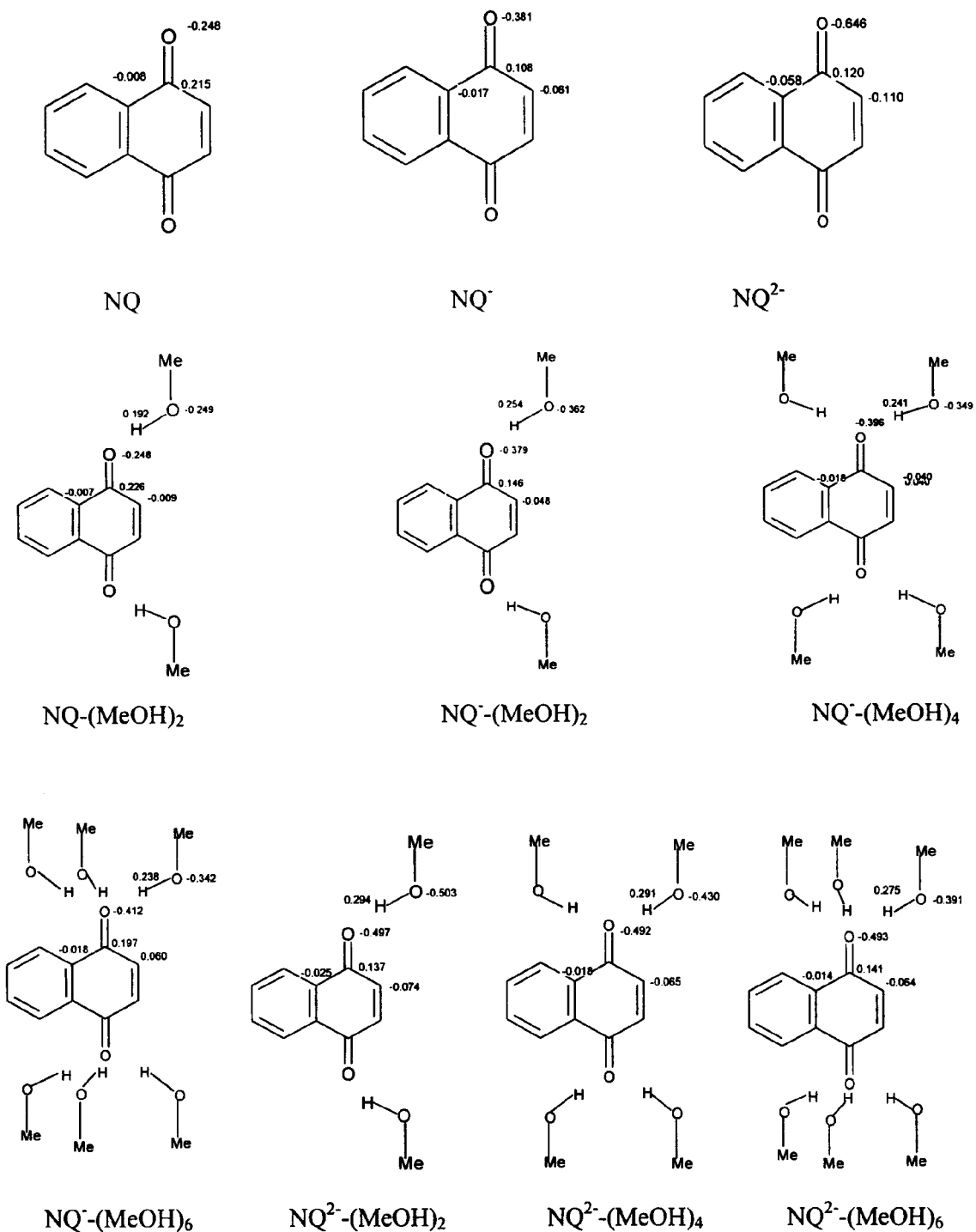


Fig. 5: Atomic Gross Charges of 1, 4-naphtho-quinone and their hydrogen bonded complexes with MeOH. Calculated by RHF/CNDO or UHF/CNDO semiempirical Methods.

quinoid structure. Other changes accompanied are the changes in internal angles of NQ. Internal angle of naphthoquinones changed in such a way that the quinoid ring was slightly elongated in the direction of carbonyl groups, while the other ring remained almost unaffected.

The hydrogen bond distance however significantly changed with the redox state of NQ. It was indicated that hydrogen bonds strengthen in going from NQ to NQ^- and NQ^{2-} . The hydrogen bond distance for 1:6 complexes is slightly longer than 1:4 complexes which are in turn longer than 1:2 complexes. This may be due to steric crowding of the 1:6 complexes. The *m* values in Table-1 support this argument. Similar trend was observed for other naphthoquinones from the optimized geometric data.

(c) n- σ Charge Transfer Interaction in the Hydrogen Bonds of Naphthoquinones with MeOH

It is well recognized that hydrogen bonds are substantially electrostatic in nature, and *n- σ* charge transfer interaction play an important role in their directionality and strength. *n* = 0, 1 and 2 for neutral, anion and dianion of quinone respectively for the carbonyl oxygen and the sigma (σ) corresponds to the hydrogen atom of hydroxyl moiety of alcohol. Indeed the formation energies of BQ^{2-} with MeOH are qualitatively explained by the charges on carbonyl oxygen atom. Upon reduction of neutral BQ to its anion and dianion, the charge transfer through the hydrogen bond is magnified and formation energies become large [23].

Fig. 5 shows the charges on different position of interest on NQ, NQ^- , NQ^{2-} and their 1:2, 1:4 and 1:6 hydrogen bonded complexes. The atomic charge is closely concerned in the π -electron distribution. As the charge transfer occurs from lone pair and HOMO orbitals of the carbonyl oxygen atoms to the MeOH, the charge transfer interaction significantly affects the MO energies and the electronic distribution of the π -electronic system of naphthoquinones as shown in the Fig. 3 and 5. The electronic transfer ability of naphthoquinone anions and dianions is therefore controlled by hydrogen bonding involving *n- σ* charge transfer interaction, because the π -HOMO of NQ^{2-} play an important role in the redox mediated electron transfer of NQ. Although the π -type charge transfer is negligible, a

considerable effect of hydrogen bonding on the function and properties of NQ^{2-} can be suggested. Similar results were obtained from the *n- σ* charge transfer complexes of the rest of naphthoquinones.

Experimental

Chemicals

Tetrabutyl ammonium perchlorate (99% TBAP), from Fluka Chemicals was used as supporting electrolyte without further purification. Dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and acetonitrile (ACN) of AR grade from BDH Chemicals Ltd. Poole England were used. All these solvents were further purified by the fractional distillation method. The present study was carried out on 1,4-naphthoquinone (I), 2-methyl-1,4-naphthoquinone (II), 2-hydroxy-1,4-naphthoquinone (III), 5-hydroxy-1,4-naphthoquinone (IV) and 2,3-dichloro-1,4-naphthoquinone (V) which were obtained from Fluka/Aldrich and were used without further purification.

Electrochemical Measurements

Cyclic Voltammetry was performed with three electrode system consisting of Glassy Carbon (GC) working electrode, a reference saturated calomel electrode (SCE) and a platinum counter electrode. Princeton Applied Research (PAR) electrochemical system 370 coupled with X-Y recorder was used as measuring instrument. All measurements were made at 25 ± 0.5 °C. The solutions were purged with purified N_2 gas to have oxygen free measurements.

MO Calculations

For MO calculation software used was HyperChem™ (Release 5.01 for Windows). For the hydrogen bonding studies of these compounds with MeOH geometries were optimized by semiempirical CNDO method only in the RHF or UHF frame work for closed and open shell compounds respectively. The results were used to interpret spectral characteristics and electronic states of these compounds and their complexes.

Conclusion

It was found that the reduced forms of naphthoquinones interact significantly with methanol.

The observed positive shift is ascribed to hydrogen bonding which depends upon the nature of quinone and on the added amount of methanol. It was noticed that for a given concentration of additive the hydrogen bonding depends upon the substituents attached to 1,4-naphthoquinone. These substituents not only determine the steric effect but also the basicity of the quinone. Higher the basicity stronger will be the quinone-methanol interaction and larger will be the K_{eq} values. From the data in three solvents it was found polarity of the solvent reduces the strength of hydrogen bonding. The theoretical UV-data indicated the blue shift behaviour with the increase in MeOH concentration thus supporting the experimental results. The optimized geometries of the complexes showed the preference of benzenoid form over the quinoid form. Moreover the n- σ charge transfer interaction studies also favoured the above mentioned interpretation.

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