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Electron Paramagnetic Resonance, ENDOR and TRIPLE Resonance Studies on Substitution Reactions of 2-Methyl-1,4-benzoquinone and 2,3-Dimethoxy-5-methyl-1,4-benzoquinone in Alkaline Methanol

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Substitution of 2-methyl-1,4-benzoquinone with methanol takes place in alkaline methanol, giving rise to methoxy-substituted methyl-1,4-benzoquinone radical anions. The relative signs and absolute values of the hyperfine coupling constants (hfcs) of the various mono-, di- and tri-substituted methoxymethyl-1,4-benzoquinones have been measured by EPR, ENDOR and TRIPLE resonance spectroscopy. The hfcs of OCH_3 and CH_3 protons had the same positive sign, except in the 3,5-dimethoxy-2-methyl-1,4-benzoquinone radical anion. The ENDOR signals of the methoxy protons could be distinguished from the methyl proton signals by using perdeuterated methanol as solvent. Partial optimizations of the geometry of the radicals were performed by using the unrestricted MNDO method. In the most stable conformers the methoxyl groups had twisted out of the aromatic plane. INDO calculations were performed by using optimized structures, and the hfcs were compared with those obtained using standard bond lengths and angles. The hfcs of the ring protons were assigned by McLachlan calculations and support of the assignment was provided by the additivity relationship method. The general TRIPLE technique allowed identification of the methyl, methoxy and ring protons of the different methoxy-substituted methyl-1,4-benzoquinone radical anions.

Substituted 1,4-benzoquinone radicals have been widely studied by EPR spectroscopy.[1] Recently two general reviews[2–3] of the physical and chemical analysis of quinones were published. According to one of these,[2] *ca.* 22 000 papers dealing with one or more aspects of the spectroscopy or chemical determination of quinones have appeared since 1973. Less well studied by EPR and ENDOR spectroscopies are the reactions of 1,4-benzoquinones with solvent. In alkaline alcoholic solutions 1,4-benzoquinones undergo chemical reactions, *e.g.* hydroxylations and alkoxylation processes,[4–7] in which radicals appear as secondary and further radical stages, causing considerable difficulties in the assignment and interpretation of hfcs. EPR has also been used to study the exchange reactions of alkoxyl groups of 1,4-benzoquinones induced by the alkoxyl groups of alkaline alcoholic solvents.[7–9] Das *et al.*[10] were the first to measure the ENDOR spectra of quinones of biological interest in ethanolic solution. Leniart *et al.*[11] developed an experimental test of the ENDOR theory for free radicals in solution using various quinone radical anions dissolved in ethanol and dimethoxyethane. ENDOR spectroscopy has also been used to analyse the radical anions produced in alkoxylation reactions and to determine the hfcs of methoxy-, ethoxy- and propoxy-substituted 1,4-benzoquinones in solution.[12–14] To the best of our knowledge, TRIPLE resonance spectroscopy has been carried out for methoxy-substituted 1,4-benzoquinones only once.[15] It is important to remember this extremely sensitive substitution reaction in alkaline alcoholic systems, especially in biochemical studies. When the resolution of the spectra is not optimum, results need to be analysed with great care.

Experimental

Materials

2-Methyl-1,4-benzoquinone (98%) from Aldrich and 2,3-dimethoxy-5-methyl-1,4-benzoquinone (purum) from Fluka were used without further purification. CH_3OH (99.8%), CD_3OD (99%), NaOD (40% in D_2O, degree of deuteration $\geqslant$99.5%), KOH (pro analysi) and NH_3 (99.99%, gas) were from Merck.

Equipment

EPR spectra were recorded on a Varian E-9 spectrometer equipped with a microwave counter TR 5211 (Takeda-Riken Industry Co.) and Varian E 500 gaussmeter and interfaced with an Apple II microcomputer, and on a Bruker ESP380 spectrometer equipped with a pulse bridge PB 1010 with CW option. ENDOR and TRIPLE resonance spectra were recorded on a Bruker ER 200 D-SRC spectrometer equipped with Varian E-12 magnets, a Varian field frequency lock E-272B and self-built ENDOR coils. g-Values were measured using a microcomputerized EPR system[16] with an accuracy of $\pm 0.000\,005$. Gas chromatography/mass spectrometry were used in analysing the reaction products. The electron-impact mass spectra were recorded by Mirja Lahtiperä on a Finnigan MAT 212 spectrometer interfaced with a Varian Series 3700 gas chromatograph.

Sample Preparation

A small amount of parent 1,4-benzoquinone was added in a capillary tube to a measured mixture of methanol and KOH and samples were prepared by a high-vacuum technique or under a nitrogen atmosphere. The concentration of KOH in the samples was varied from 0.01 to 2.30 mol dm^{-3}. Sample preparation also took place in a special cuvette system (kindly supplied by Dr. Mikko Vuolle) equipped with two vacuum stopcocks, where NH_3 gas was bubbled through the solution until the desired radical was obtained.

Results

2-Methyl-1,4-benzoquinone

We propose a qualitative reaction mechanism (scheme) for the substitution reaction of 2-methyl-1,4-benzoquinone. The ENDOR spectrum [Fig. 1(*a*)] of the 2-methyl-1,4-benzoquinone radical anion was measured in a mixture of methanol and KOH (0.01 mol dm^{-3}). The general TRIPLE spectrum [Fig. 1(*b*)] showed opposite signs for the hfcs of the methyl and ring protons. In accordance with general practice, we assume a negative sign for the ring protons. The special

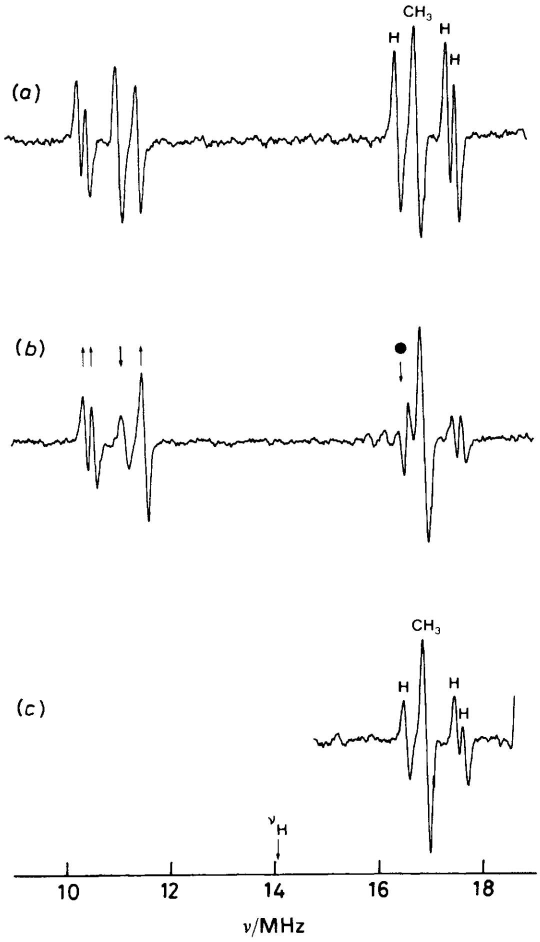


Fig. 1 (*a*) ENDOR, (*b*) general TRIPLE and (*c*) special TRIPLE spectra of the 2-methyl-1,4-benzoquinone radical anion prepared from 2-methyl-1,4-benzoquinone in a mixture of methanol and KOH (0.01 mol dm^{-3}) at 233 K (method 1 in the scheme). Pumping frequency is marked ● and changes in the intensities of low-frequency peaks are illustrated by arrows

TRIPLE technique works well in this case, as the recorded spectrum [Fig. (1*c*)] shows. Signals represent 1, 3, 1 and 1 equivalent protons in each group, as expected.

The hfcs of 2-methyl-1,4-benzoquinone radical anion were measured in different alkaline solutions to show the extent to which the hfcs depend on the chosen system (Table 1). The ENDOR spectrum measured in 0.01 mol dm^{-3} KOH in methanol showed four nicely resolved hfcs [Fig. 1(*a*)]. When the methanol was made alkaline with gaseous ammonia (method 2 in the scheme) the two largest hfcs of the ring protons became equivalent [see exp (2) in Table 1]. In liquid ammonia (method 4 in the scheme) the absolute value of the smallest hfc of the ring proton became equivalent with the hfc of the methyl protons [see exp (4) in Table 1]. Owing to accidental degeneracy of hfcs the corresponding EPR spectra were different and the multiplicities were confirmed by simulations.

2-Methoxy-5-methyl-1,4-benzoquinone

Reaction of 2-methyl-1,4-benzoquinone with alkaline methanol (method 1 in the scheme: KOH in CH_3OH) gave the radical anion of 2-methoxy-5-methyl-1,4-benzoquinone. Fig. 2(*a*) shows the ENDOR and Fig. 2(*b*) the general TRIPLE spectrum of the radical anion. The signs of the hfcs of methyl and methoxy protons are positive and opposite to those obtained for the hfcs of the ring protons, as one can deduce from the general TRIPLE spectrum [Fig. 2(*b*)].

Table 1 Experimental and calculated hfcs (in G) of the methoxy-substituted methyl-1,4-benzoquinone radical anions

method	2	3	5	6
2-methyl-1,4-benzoquinone				
exp (1)	2.03	−1.77	−2.57	−2.46
exp (2)	2.05	−1.77	−2.54	−2.54
exp (3)	2.09	−1.73	−2.57	−2.44
exp (4)	1.90	−1.90	−2.70	−2.46
exp (7)	2.05	−1.76	−2.56	−2.49
McLachlan	2.10	−2.07	−2.59	−2.37
INDO (st)[a]	2.10	−1.99	−1.79	−1.50
A[b]	2.01	−1.74	−2.58	−2.43
INDO (a)[c]	1.57	−1.56	−1.29	−1.00
2-methoxy-5-methyl-1,4-benzoquinone				
exp (1)	0.85	−0.60	3.43	−1.41
exp (2)	0.76	−0.76	3.42	−1.44
exp (3)	0.84	−0.64	3.49	−1.37
exp (5)	—	−0.62	3.29	−1.51
exp (6)	—	−0.69	3.47	−1.41
exp (7)	—	−0.67	3.47	−1.40
McLachlan	−0.78	−0.44	2.76	−1.79
INDO (st)	0.95	−0.81	4.47	−0.96
A	1.07	−0.66	3.09	−1.42
INDO (b)	0.09	−0.29	2.92	−1.13
INDO (c)	0.12	−0.13	2.63	−1.35
INDO (d)	−0.05	−0.56	2.15	−1.29
2-methoxy-6-methyl-1,4-benzoquinone				
exp (1)	0.82	−0.69	−2.82	1.70
exp (2)	0.78	−0.78	−2.88	1.69
exp (3)	0.83	−0.72	−2.91	1.63
exp (7)	—	−0.67	−2.91	1.65
McLachlan	0.48	−0.61	−3.04	2.11
INDO (st)	−0.02	−0.69	−2.69	1.72
A	0.86	−0.83	−3.04	1.72
3,5-dimethoxy-2-methyl-1,4-benzoquinone				
exp (1)	1.07	−0.04	0.90	−0.54
McLachlan	2.80	1.28	1.89	−1.57
INDO (st)	1.96	−0.39	−0.08	−1.08
A	1.49	0.63	0.60	−1.88
INDO (i)	1.26	−0.08	−0.07	−0.86
INDO (j)	1.28	−0.08	−0.07	−0.88
2,3-dimethoxy-5-methyl-1,4-benzoquinone				
exp (1)	0.05	0.05	2.42	−2.02
exp (4)	0.00	0.00	2.24	−2.24
exp (5)	0.05	0.05	2.42	−2.07
McLachlan	1.35	1.40	2.64	−2.83
INDO (st)	0.00	−0.05	2.90	−2.32
INDO (X)[d]	−0.16	0.05	2.49	−1.36
A	1.10	0.63	2.80	−2.64
INDO (e)	0.03	0.07	2.86	−1.53
INDO (f)	0.04	0.04	2.43	−1.80
INDO (g)	0.06	0.05	1.77	−1.54
INDO (h)	−0.15	−0.13	1.74	−1.55
2,3,6-trimethoxy-5-methyl-1,4-benzoquinone				
exp (1)	0.03	0.03	1.60	0.03
exp (5)	0.06	0.06	1.77	0.06
McLachlan	1.06	1.12	1.71	0.72
A	—	—	1.20	—
INDO (st)	−0.06	−0.02	0.84	0.01
INDO (k)	−0.09	−0.05	0.89	−0.05

Numbers in exp ( ) indicate the method used in preparing the radical (see the scheme) and the letters in INDO ( ) indicate the corresponding structure in Fig. 5. [a] INDO (st) means the hfcs obtained by the INDO method[20] using standard bond lengths and angles.[22] [b] A means the hfcs calculated by the additivity relationship method both for methyl protons and ring protons. [c] INDO ( ) means the hfcs for the UMNDO partially optimized structures. [d] INDO (X) means the INDO calculation with X-ray values.[23]

The reaction of 2-methyl-1,4-benzoquinone with alkaline CD_3OD (method 5 in the scheme: 40% NaOD–D_2O in CD_3OD) gave the corresponding deuterated radical anion, 2-($^2H_3$)methoxy-5-methyl-1,4-benzoquinone, where the OCH_3 group is replaced by an OCD_3 group. Fig. 2(*c*) shows

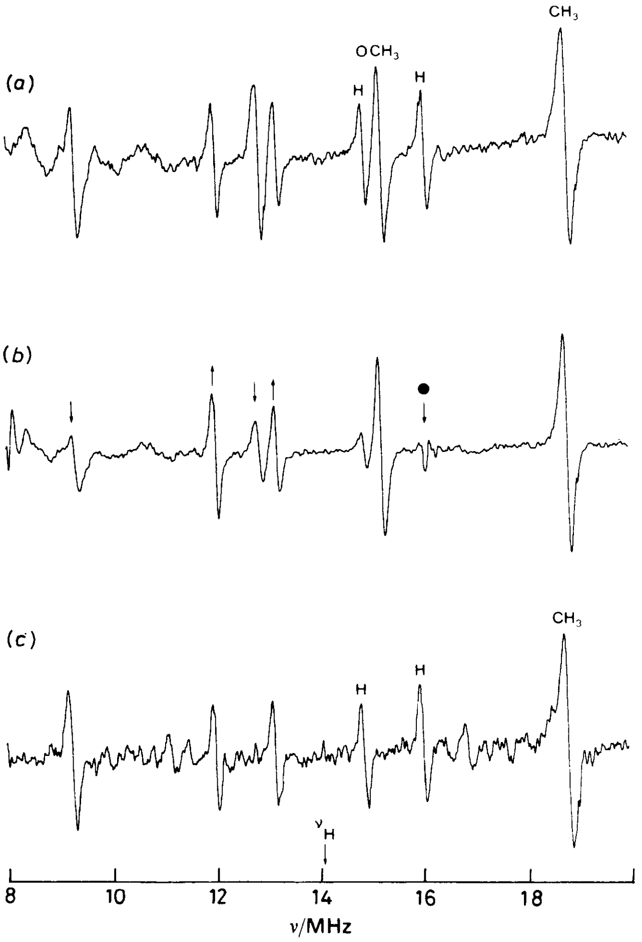


Fig. 2 (*a*) ENDOR and (*b*) general TRIPLE spectra of the 2-methoxy-5-methyl-1,4-benzoquinone radical anion prepared from 2-methyl-1,4-benzoquinone in a mixture of methanol and KOH (0.69 mol dm^{-3}) at 233 K (method 1 in the scheme). Pumping frequency is marked ● and changes in the intensities of low-frequency peaks are illustrated by arrows. (*c*) ENDOR spectrum of [2-$^2H_3$]methoxy-5-methyl-1,4-benzoquinone radical anion prepared from 2-methyl-1,4-benzoquinone in a mixture of CD_3OD and 40% $NaOD–D_2O$ at 238 K (method 5 in the scheme)

its ENDOR spectrum, where one pair of the ENDOR signals is missing relative to Fig. 2(*a*). Because all other proton couplings remain the same as before, we can distinguish the signals of the methoxy protons from those of the methyl protons.

2-Methoxy-6-methyl-1,4-benzoquinone

Simultaneously with the radical anion of 2-methoxy-5-methyl-1,4-benzoquinone, its isomer 2-methoxy-6-methyl-1,4-benzoquinone was formed. It was formed in very small amounts, however (only a few per cent of the first; estimated from the EPR sum spectrum, not shown), and it was also less stable. The hfcs of the 2-methoxy-6-methyl-1,4-benzoquinone radical anion were obtained by using a similar procedure to that described for the 2-methoxy-5-methyl-1,4-benzoquinone radical anion. The signs and values of the hfcs of both isomers are presented in Table 1.

2-Methoxy-3-methyl-1,4-benzoquinone

We were not able to find the radical anion of 2-methoxy-3-methyl-1,4-benzoquinone. This is in accord with Pedersen's[6] failure to find the 2-hydroxy-3-methyl-1,4-benzoquinone radical anion among the products of hydroxylation reactions, although he measured two analogous hydroxy radicals: 2-hydroxy-5-methyl-1,4-benzoquinone and 2-hydroxy-6-methyl-1,4-benzoquinone.

3,5-Dimethoxy-2-methyl-1,4-benzoquinone

In Scheme 1 we assume that 2-methoxy-5-methyl-1,4- benzoquinone radical anion reacts further to form the 3,5-dimethoxy-2-methyl-1,4-benzoquinone radical anion. A very small hfc of 0.04 G is found for methoxy protons in position 3 of the disubstituted radical. According to the general TRIPLE experiments the two smallest couplings have the same sign, which is opposite to that of the two largest couplings (see Table 1). The hfc of 0.04 G is so small that it is hidden in the EPR linewidth. Simulation of the EPR spectrum verified the multiplicities of one ring proton, three methyl protons and three methoxy protons. Deuterated solvent was therefore used for the identification of this radical product.

The reaction of methyl-1,4-benzoquinone with alkaline CD_3OD (method 5 in Scheme 1: 40% $NaOD–D_2O$ in CD_3OD) gave the corresponding deuterated radical anion of [3,5-$^2H_6$]dimethoxy-2-methyl-1,4-benzoquinone, where the two OCH_3 groups are replaced by two OCD_3 groups. The two methoxyl groups can thereby be distinguished from the methyl group by ENDOR.

2,3-Dimethoxy-5-methyl-1,4-benzoquinone

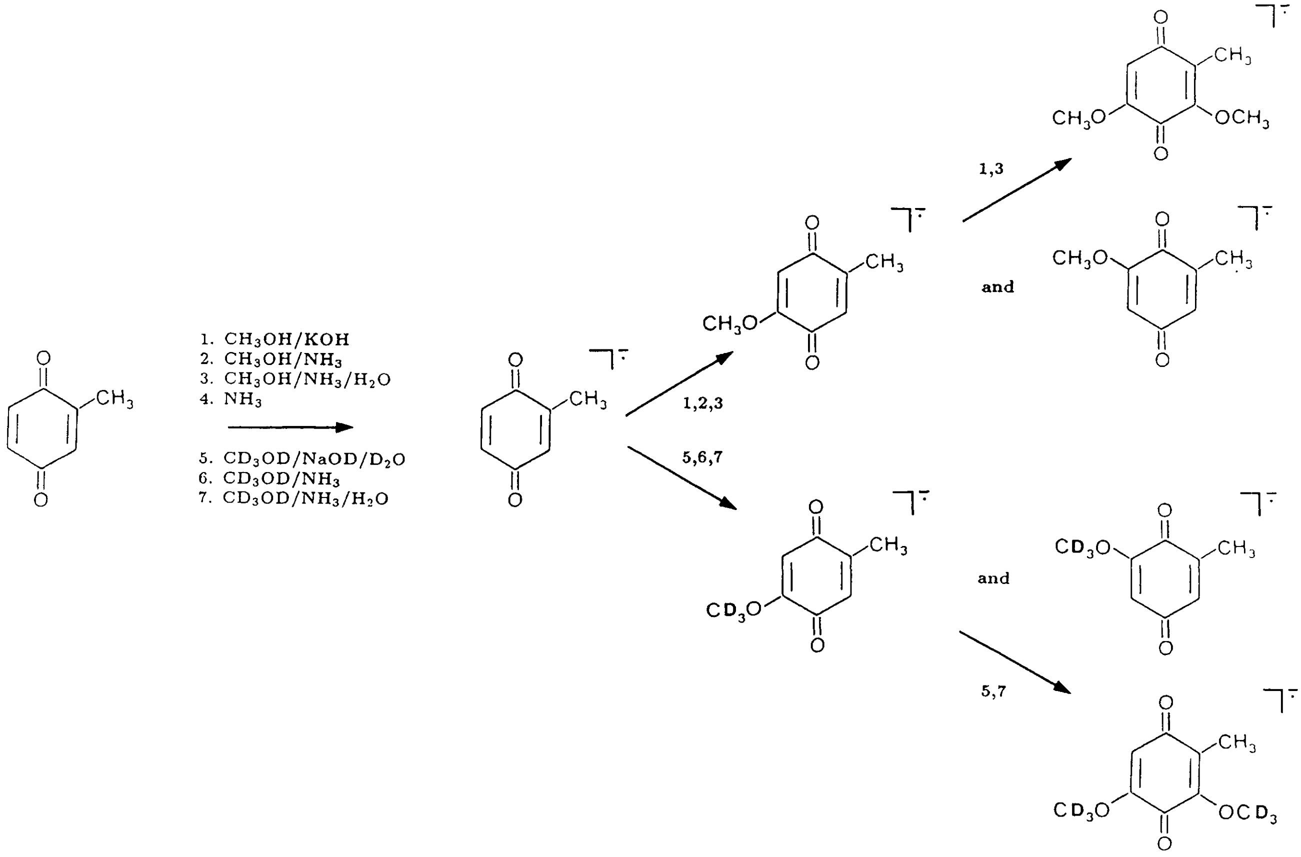
We emphasize that it was not possible to obtain the 2,3-dimethoxy-5-methyl-1,4-benzoquinone radical anion using 2-methyl-1,4-benzoquinone as starting material. The radical anion was prepared from 2,3-dimethoxy-5-methyl-1,4-benzoquinone in a mixture of methanol and KOH (0.05 mol dm^{-3}). This is the first time that the hfcs of the two adjacent methoxyl groups have been measured without EPR linewidth analysis.[7] Gascoyne and Szent-Györgyi[17] suggested that the missing proton hfcs of the neighbouring methoxyl groups can be explained by steric interactions between those groups. This is discussed in the Calculation and Discussion sections below. The intensity of the methoxy proton signals in the ENDOR spectra (not shown) increases with temperature, but the value of the hfc is smaller than the EPR linewidth in all spectra in the measured temperature region. The ENDOR spectrum [Fig. 3(*a*)] shows three well resolved couplings, and the signs of the hfcs of methyl and methoxy protons are positive [Fig. 3(*c*)] and the sign of the hfc of the single ring proton is negative.

2,3,6-Trimethoxy-5-methyl-1,4-benzoquinone

The EPR spectrum (not shown) of 2,3,6-trimethoxy-5-methyl-1,4-benzoquinone radical anion consists of a quartet, indicating only the presence of methyl protons. This radical was prepared from 2,3-dimethoxy-5-methyl-1,4-benzoquinone in a mixture of methanol and KOH (0.05 mol dm^{-3}). The ENDOR spectrum [Fig. 3(*b*)] again reveals signals from methoxy protons and, according to the general TRIPLE spectrum [Fig. 3(*d*)], the signs of the hfcs are the same.

Calculations

Semiempirical molecular orbital calculations were performed using the MNDO[18] option of the GAUSSIAN 90[19] program, the INDO option of the CNINDO[20] program and the McLachlan[21] method. Partial optimization of the radical geometries was performed by unrestricted MNDO (UMNDO) and the hfcs were calculated by INDO using, in



Scheme 1

addition to optimized bond lengths and angles, standard[22] and X-ray values.[23] Fig. 4(*a*) shows the bond-length parameters used in the optimization of the radical states of methoxy substituted methyl-1,4-benzoquinone anion radicals. X-Ray values of bond angles of the quinodic ring given for 2,3-dimethoxy-5-methyl-1,4-benzoquinone,[23] were used for all other methoxy-substituted radicals as presented in Fig. 4(*b*).

The optimized structures are shown in Fig. 5 and the optimized parameters are collected in Table 2. Fig. 5 shows two planar conformers (*b*) and (*c*) and one out-of-plane conformer (*d*) of the 2-methoxy-5-methyl-1,4-benzoquinone radical anion. According to UMNDO calculations the methoxyl group is twisted 80° out of the plane. The smallest barrier to the rotation of the methoxyl group (Fig. 6) is 16.2 kJ mol^{-1} [(*c*) – (*d*)] and clearly confirms that the out-of-plane conformer is preferred over the planar ones.

Fig. 5 shows two in-plane and two out-of-plane conformers for 2,3-dimethoxy-5-methyl-benzoquinone anion radicals. The planar structures (*e*) and (*f*) have almost equal energies, $\Delta E = 2.0$ kJ mol^{-1}, but the two out-of-plane conformers (*g*) and (*h*), the *cis* and *trans* conformers, respectively differ by $\Delta E = 9.0$ kJ mol^{-1}. The *trans* conformer (*h*) is considerably more stable than the most stable in-plane conformer (*f*), the energy difference being $\Delta E = 67.5$ kJ mol^{-1}. The *trans* conformer (*i*) of the 3,5-dimethoxy-2-methyl-1,4-benzoquinone radical anion was as stable as the *cis* conformer, $\Delta E = 0.8$ kJ mol^{-1}. One of the possible *trans* conformers of 3,5,6-trimethoxy-2-methyl-1,4-benzoquinone radical anions is shown in Fig. 5(*k*).

Theoretical and experimental hfcs of substituted 1,4-benzoquinone radical anions are collected in Table 1 together with the results obtained by the additivity calculations first described by Venkataraman *et al.*[24] Several authors have used this additivity principle in the assignment of coupling constants, with good success.[1,15,17,25–33] Replacement of ring protons with a single methoxyl group was assumed to have such a small effect on the spin density of the radical that it could be handled by first-order perturbation theory. In this work we applied the additivity relationship method in two different ways. Normal additivity optimization was done for methyl protons, and these values are shown in Table 1. For ring protons we used a method that has not been described earlier, but for which Venkataraman *et al.*[24] suggested the idea. First, the hfcs for ring protons of all methyl-1,4-benzoquinones were collected.[1] Then, with best knowledge of the assignment (there are several unambiguously assigned symmetrical compounds), and calculating the changes that the methyl group induces in *ortho*, *para* and *meta* positions, additivity parameters of +0.68, −0.16 and −0.01 G, respectively, and 4.40 G for the CH_3 group were obtained. After this the hfcs of methoxy-1,4-benzoquinones,[17] similarly substituted to the methyl compounds case were considered and additivity parameters of 1.77, −1.28 and 0.32 G, respectively, and 3.17 G for the OCH_3 group were calculated. When the methyl group (the former values) is replaced by the methoxyl group (the latter values), the changes in the additivity parameters are thus 1.09, −1.12, 0.33 G, respectively, and −1.23 G for the OCH_3 group. To calculate the values for mixed substitutions we used as reference a methyl-substituted compound with known experimental hfcs, which was then converted to the compound of interest by changing one or two of the methyl groups, one at a time, to methoxyl groups. The values for the ring protons are collected in Table 1.

In McLachlan's method we used parameters $k(C_{ar}{-}C_{sp^3}) = 0.9$, $k(C_{sp^3}{\equiv}H_3) = 2.5$, $h(C_{sp^3}) = -0.1$ and $h(H_3) = -0.5$, as given by Wilson.[34] The parameters $k(C{=}O) = 1.5$ and $h({=}O) = 1.5$ were chosen for the quinone oxygen. In the case of the methoxyl parameters we gave the same value for both single carbon–oxygen resonance inte-

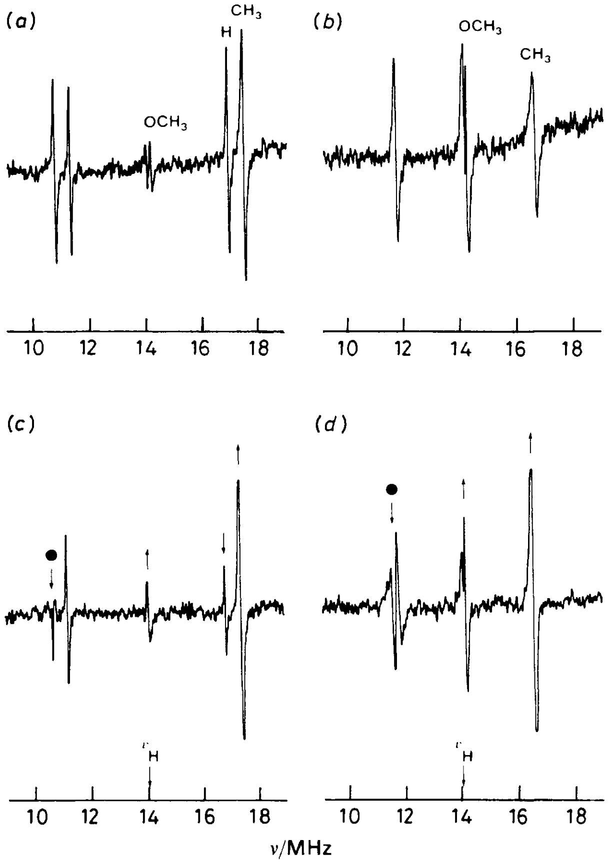


Fig. 3 (*a*) ENDOR and (*c*) general TRIPLE spectra of the 2,3-dimethoxy-5-methyl-1,4-benzoquinone radical anion and (*b*) ENDOR and (*d*) general TRIPLE spectra of the 2,3,6-trimethoxy-5-methyl-1,4-benzoquinone radical anion. Both radicals were prepared from 2,3-dimethoxy-5- methyl-1,4-benzoquinone in a mixture of methanol and KOH (0.05 mol dm^{-3}) at 223 K. Pumping frequency is marked ● and changes in the intensities of high-frequency peaks are illustrated by arrows

grals: $k(C_{ar}—O) = k(C_{sp^3}—O) = 0.75$. This was half of the value chosen for the double bond. We accepted a hyperconjugation model for the methoxy group and used Sullivan's[35] parameters $k(C_{sp^3}{\equiv}H_3) = 2.5$, $h(C_{sp^3}) = -0.1$ and $h(H_3) = -0.5$.

McLachlan's value of -24.2 G was chosen for the McConnell[36,37] Q-value with sp^2-hybridized carbon spin density. The McConnell-type relationship $a_H = Q'\rho(CH_3)$ was used for proton hfcs in methoxyl groups. The Q' value was assumed to be -586 G ($\approx 24.2 \times 24.2$) and $\rho(CH_3)$ was the σ-spin density at the sp^3 carbon.

Discussion

In solutions ranging from slightly to saturated alkaline (0.01–2.3 mol dm^{-3}), 2-methyl-1,4-benzoquinone and 2,3-dimethoxy- 5-methyl-1,4-benzoquinone form substitution products in the radical state. The reactions depended on temperature and alkali concentration (KOH or NH_3 gas). The formation rate of these secondary and other radicals increased with increasing alkali concentration of the solvent. Below an alkali concentration of 0.01 mol dm^{-3}, the products of methoxylation reaction were not detected. The critical temperature at which the methoxylation reaction starts or stops is *ca.* 233 K.

The hfcs depended strongly on the chosen solvent and alkali concentration in such a way that even accidental degeneracy of hfcs took place. The more polar the solvent system was the better resolved the hfcs were; see, *e.g.* the 2-methyl-1,4-benzoquinone radical anion. The quinone oxygens are the basic sites of the radicals and their interaction with the solvent or counter-ions can explain the differences in hfcs. The differences in hfcs are at maximum when the solvent can form hydrogen bonds to the quinone oxygen atoms, perturbing the electron distribution so that it can be detected as changes in hfcs. This was checked for the 2-methyl-1,4-benzoquinone radical anion by adding a few drops of water to a mixture of $CH_3OH–NH_3$, and the degeneracy of two hfcs of

Table 2 Optimized parameters obtained by UMNDO calculations for different methoxy-substituted methyl-1,4-benzoquinone radical anions

parameter	$k^{\bullet -}$	$i^{\bullet -}$	$h^{\bullet -}$	$g^{\bullet -}$	$f^{\bullet -}$	$e^{\bullet -}$	$d^{\bullet -}$	$c^{\bullet -}$	$b^{\bullet -}$	$a^{\bullet -}$
RCC (1)	1.4730	1.4743	1.4775	1.4795	1.4990	1.5006	1.4798	1.4932	1.4916	1.4779
RCC (2)	1.4144	1.4032	1.4115	1.4102	1.4281	1.4187	1.4005	1.3972	1.4033	1.3808
RCC (3)	1.4955	1.4893	1.4852	1.4869	1.4955	1.4995	1.4806	1.4837	1.4821	1.4686
RCC (4)	1.4813	1.4840	1.4788	1.4786	1.4592	1.4668	1.4796	1.4771	1.4776	1.4627
RCC (5)	1.3865	1.3835	1.3746	1.3748	1.3955	1.3950	1.3741	1.3766	1.3829	1.3797
RCC (6)	1.5179	1.5180	1.5139	1.5139	1.5109	1.5107	1.5136	1.5126	1.5121	1.5171
RCH (1)	1.1081	1.1082	1.1086	1.1086	1.1091	1.1090	1.1088	1.1088	1.1090	1.1088
RCH (2)	1.1162	1.1165	1.1164	1.1165	1.1143	1.1143	1.1166	1.1156	1.1145	1.0892
RCH (3)	1.1162	1.0886	1.1164	1.1165	1.1145	1.1142	1.0891	1.0873	1.0889	1.0894
RCH (4)	1.1165	1.1166	1.0942	1.0942	1.0937	1.0932	1.0945	1.0948	1.0943	1.0909
RCO (1)	1.2607	1.2626	1.2603	1.2600	1.2542	1.2616	1.2634	1.2615	1.2667	1.2600
RCO (2)	1.2501	1.2519	1.2531	1.2530	1.2572	1.2490	1.2541	1.2540	1.2509	1.2604
RCO (3)	1.3678	1.3700	1.3689	1.3691	1.3592	1.3624	1.3711	1.3612	1.3636	
RCO (4)	1.4077	1.4061	1.4070	1.4057	1.4002	1.4007	1.4002	1.4055	1.4010	
RCO (5)	1.3688	1.3790	1.3705	1.3708	1.3638	1.3599				
RCO (6)	1.4074	1.4057	1.4071	1.4058	1.3993	1.3982				
RCO (7)	1.3777									
RCO (8)	1.4061									
α	120.06	120.04	122.42	122.43	123.10	122.94	122.47	122.58	122.67	122.02
β	119.72	120.45	119.70	118.56	127.05	125.96	121.23	114.39	128.45	118.95
γ	119.57	119.45	119.52	120.46	132.28	132.37	119.76	126.40	131.27	
δ	121.33	121.84	121.19	122.30	113.25	130.47	121.71	123.36	122.00	120.93
ε	119.65		119.54	120.46	132.19	133.83				
π	116.03	116.28	116.43	116.42	116.06	116.46	116.73	116.62	116.79	117.82
ω	120.26	120.14								
E/E_h	−0.3197	−0.2554	−0.2615	−0.2580	−0.2357	−0.2350	−0.1973	−0.1914	−0.1882	−0.1336

Letters in the headings of columns refer to the structures presented in Fig. 5. R in Å and E in E_h.

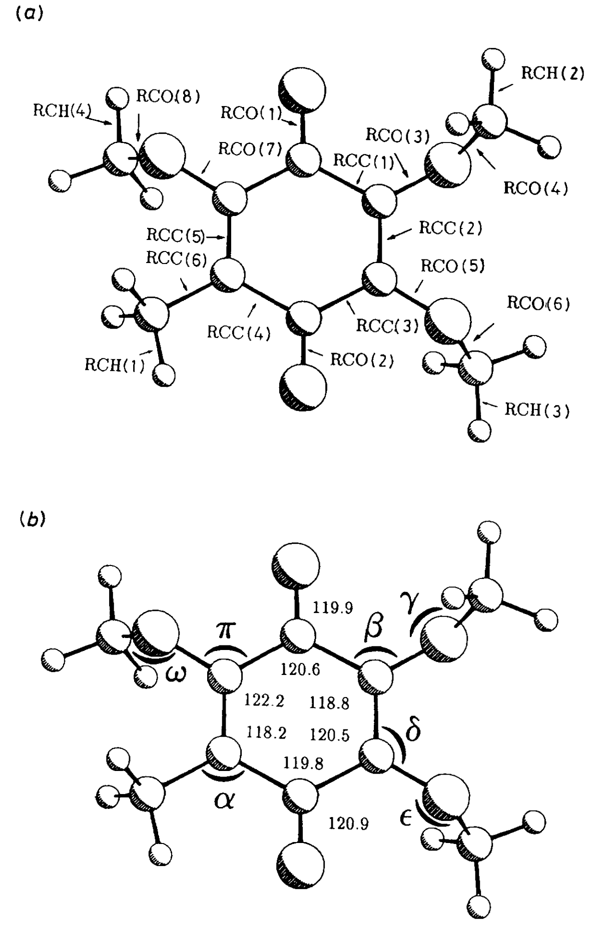


Fig. 4 Parameters used in the partial optimization of the radical states of the methoxy substituted methyl-1,4-benzoquinone radical anions by UMNDO method. (*a*) Bond lengths and (*b*) bond angles (fixed values have been taken from the X-ray results[23])

the ring protons was found to be removed. The same effect was found for other studied radical anions (see Table 1.

The *g*-value of 2-methyl-1,4-benzoquinone was 2.004 534, but the *g*-values measured under the same conditions (CH_3OH–KOH) for 2-methoxy-5-methyl-1,4-benzoquinone, 2,3-dimethoxy-5-methyl-1,4-benzoquinone and 2,3,6-trimethoxy-5-methyl-1,4-benzoquinone were 2.004 496, 2.004 598 and 2.004 643, respectively. Spin densities on the oxygen atoms (both the quinone and the methoxy oxygens) particularly contribute to the *g*-values, as the increasing values suggest. Because oxygen atoms in the methoxyl groups can form hydrogen bonds with the solvent, the identification of quinone radicals on the basis of *g*-values alone is unreliable.

Additivity calculations performed for the ring protons and for the methyl protons were in good agreement with experimental values in the case of the monomethoxy-substituted radicals (see Table 1), but the agreement was less good for the di- and tri-substituted radicals. The hfcs obtained by INDO for 2-methyl-1,4-benzoquinone disagree with the values of McLachlan and additivity calculations. Comparison of the INDO and experimental hfcs shows (see Table 1) that the different conformers cannot be distinguished and that the values are not good enough to allow an absolute assignment of hfcs. INDO calculations done with the partially optimized geometry suggest very small hfcs of −0.05 G for the methoxy protons of the 2-methoxy-5-methyl-1,4-benzoquinone radical anion, whereas the experimental value is 0.85 G. Experimental hfcs and multiplicities used in simulations suggest a hyperconjugation mechanism and free rotation of methyl protons in the methoxyl group of monosubstituted methyl-1,4-benzoquinone radicals. It is difficult to estimate how much the solvation of the radicals can decrease the preference for the out-of-plane conformer. Reynolds[38] recently investigated the conformers of the hydrated benzoquinones and their reduced forms in gas phase and solution in order to determine the most stable form in solution and thereby calculate

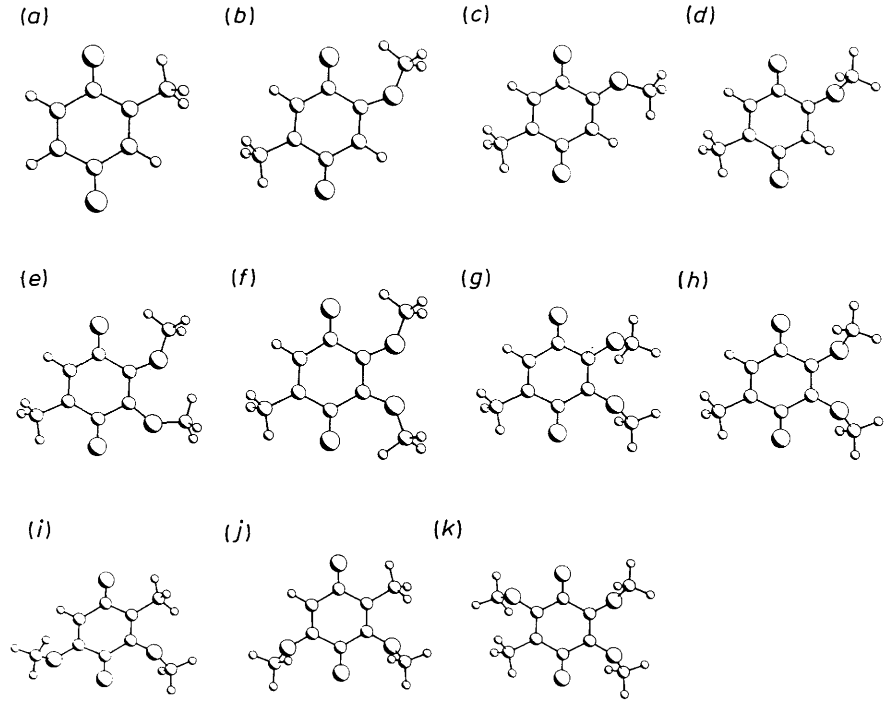


Fig. 5 Partially optimized structures (UMNDO) of the radical anions of (*a*) 2-methyl-1,4-benzoquinone; (*b*), (*c*) and (*d*) 2-methoxy-5-methyl-1,4-benzoquinone; (*e*), (*f*), (*g*) and (*h*) 2,3-dimethoxy-5-methyl-1,4-benzoquinone; (*i*) and (*j*) 3,5-dimethoxy-2-methyl-1,4-benzoquinone and (*k*) 2,3,6-trimethozy-5-methyl-1,4-benzoquinone

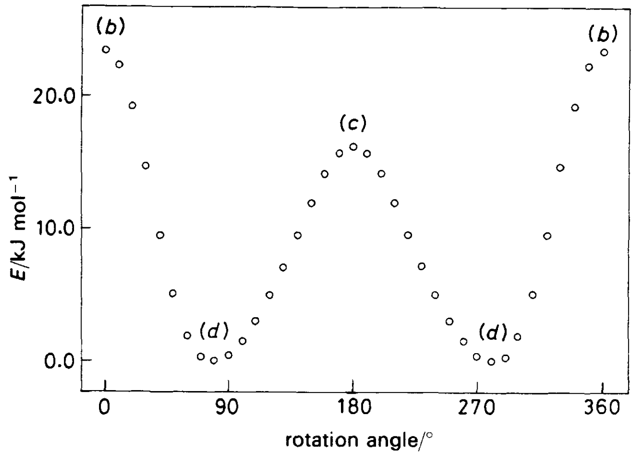


Fig. 6 Calculated potential-energy curve for the rotation of methoxy group in the 2-methoxy-5-methyl-1,4-benzoquinone radical anion. Partial optimization was done for each structure during rotation by UMNDO. The letters inset show the most important conformers

the electrode potential. Reynolds's[38] *ab initio* calculations showed that in the gas phase those conformers with an intramolecular hydrogen bond were always the most stable in the gas phase. Moreover, these same conformers always had a more positive hydration energy than those with potential to form intermolecular hydrogen bonds with the solvent. According to Reynolds[38] the most stable conformer in solution is determined by the combination of both effects and the corresponding enthalpy, entropy and zero-point energies.

Ladik *et al.*[39] performed *ab initio* unrestricted Hartree–Fock calculations for various methoxy-substituted 1,4-benzoquinone radical anions, but they could not explain the breakdown of the additivity principle, especially in the case of adjacent methoxyl groups. According to their calculations the in-plane conformer of the 2,3-dimethy-1,4-benzoquinone radical anion should be more stable than the out-of-plane conformer. This is a surprising result in view of that obtained for 2,3-dimethoxy-5-methyl-1,4-benzoquinone radical anion by the UMNDO method, where the out-of-plane conformer [Fig. 5(*h*)] was 67.5 kJ mol^{-1} more stable than the planar one. O'Shea and Fox[40] performed AM1 calculations for various 2-(methoxy-methyl)-1,4-benzoquinone radical anions and found that the sidechain was twisted out of plane.

Our opinion is that to obtain reliable structures one should perform complete optimizations with much better basis sets (double ζ + polarization functions) in *ab initio* calculations. However, we believe that, qualitatively, our results indicate a preference for the out-of-plane conformers.

We were able to measure small hfcs (not previously detected) for the methoxy protons in the 2,3-dimethoxy-5-methyl-1,4-benzoquinone radical anion. The calculated (INDO) hfcs of *ca.* 0.05 G were the same for the adjacent methoxy groups, in good agreement with the experimental results. However, we cannot say if the ENDOR signals come from one or two methoxyl groups. In the case of 3,5-dimethoxy-2-methyl-1,4-benzoquinone, the hfcs of both methoxyl groups were identified. It can be assumed, in conformity with the X-ray results,[23] that in sterically crowded radicals the structure of quinones is strongly distorted (see Table 2) and the methoxyl groups are twisted out of the aromatic plane causing a breakdown of hyperconjugation. It may even by that one methoxyl group is planar and the other has twisted out of plane.

The use of EPR spectroscopy as an analytical tool requires well resolved spectra, which must be simulated to guarantee the identification. In the case of radical mixtures this is not always possible. ENDOR and TRIPLE spectroscopies proved to be extremely effective methods in the analysis of radical mixtures of methoxy substituted 2-methyl-1,4-benzoquinones. Highly resolved ENDOR spectra were obtained even for secondary radical concentrations of only a few per cent of primary radical concentrations. Determination of the signs of the hfcs by general TRIPLE technique helped to distinguish the ring protons from methoxy and methyl protons, and the special TRIPLE technique also worked well. Without doubt these methods can be applied to the analytical problems of much more complicated chemical and biological systems.

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