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Electron Paramagnetic Resonance, ENDOR and TRIPLE Resonance Study of Methyl-substituted Benzoquinol Radical Cations

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EPR and ENDOR spectra have been recorded for hydroquinone, methylhydroquinone, 2,3-dimethylhydroquinone, 2,5-dimethylhydroquinone, 2,6-dimethylhydroquinone, 2,3,5-trimethylhydroquinone and tetramethylhydroquinone radical cations. The radicals were generated by Ce^{4+} or Zr^{4+} oxidation in FSO_3H or FSO_3H and CH_3NO_2 solution. The radical cations were stable in strongly acidic media, where they existed in double-protonated form. The splittings of hydroxyl protons were assigned by deuteriation and other coupling constants by the additivity relationship. The *cis–trans* isomerism of the double-protonated cation radicals showed up clearly in EPR and ENDOR spectra of four of the radicals.

Bolton and Carrington reported the EPR spectrum of the *p*-benzoquinone radical cation some 30 years ago.[1] They also showed that semiquinones are stable in strongly acidic media, where they exist as double-protonated cations.[2] A few years later Forbes and Sullivan found that aluminium chloride–nitromethane is more satisfactory than concentrated sulfuric acid for producing radical cations.[3] Subsequently, this solvent system was used successfully in studies of the *cis–trans* isomerism of hydroquinone radical cation.[4,5] Wan and co-workers generated benzoquinone radical cation by irradiation of 1,4-benzoquinone in trifluoroacetic acid with a mercury lamp,[6] and Channdra and Symons investigated benzoquinone cation in Freon at 77 K, producing the radical by ^{60}Co γ-radiation.[7] Liu *et al.* investigated the radical cations of 1,4-benzoquinone and methyl-, 2,5-dimethyl- and 2,6-dimethyl-1,4-benzoquinone produced by *in situ* UV photolysis in trifluoroacetic acid.[8]

Earlier, in 1962, Bolton and Carrington reported a marked linewidth alternation effect, dependent on temperature and solvent, in the EPR spectrum of duroquinone radical cation.[9,10] Their experiment was one of the first to demonstrate the phenomenon of linewidth alternation. Sullivan estimated the potential barrier to rotation about the carbon–oxygen bond for the hydroquinone and duroquinol cation radicals[11] and measured the temperature-dependent splitting constants of 2,5-dimethylhydroquinone.[12]

The EPR spectra of 1,4-benzoquinone radical cations are often the sum spectra of the isomers but at least in one case, tetramethylhydroquinone, even the isomer ratio could be estimated.[13] As we will show in this paper, ENDOR allows the two isomers to be measured separately.

We undertook a systematic investigation of the radical cations of methyl-substituted hydroquinones, recording ENDOR as well as the EPR spectra, carrying out deuteriation experiments and applying the additivity relationship in order to assign as many coupling constants as possible. Considerable effort went into finding good solvent oxidation systems for ENDOR measurements and establishing the standard chemical conditions needed for the application of the additivity relationship to the EPR results.

Experimental

Materials

Hydroquinone (photopur) from Merck, 1,4-benzoquinone (98%), tetramethyl-1,4-benzoquinone (97%), methyl-1,4-benzoquinone (98%), 2,3-dimethyl-1,4-hydroquinone (99%), 2,6-dimethyl-1,4-benzoquinone (99%) and 2,3,5-trimethylhydroquinone from Aldrich and 2,5-dimethyl-1,4-benzoquinone from Kodak were used without further purification. Other chemicals were FSO_3H (techn.) and CH_3NO_2 (purum) from Fluka and $Ce(SO_4)_2 \cdot 4H_2O$ (pro analysi), CF_3CO_2D (Uvasol) and $ZrCl_4$ (zur Synthese) from Merck.

Equipment

EPR spectra were measured, as described earlier,[14] on a Bruker ESP-300 and Varian E-9 spectrometers, and ENDOR and TRIPLE spectra on a Bruker ER 200D-SRC spectrometer. UV illumination was provided by an Airam HGU 300 W mercury lamp and a Philips HP 3133 460 W lamp.

Sample Preparation

A cuvette system with two side tubes, one for the metal salt and the other for nitromethane was used. The nitromethane was stored under P_2O_5 and distilled in vacuum over FSO_3H in the cuvette containing the sample capillary. The side tube and cuvette were cut off and sealed by flame in high vacuum. The ratio of FSO_3H to nitromethane was 1 : 1. According to a thermogram kindly supplied by Dr. Ilkka Pitkänen, $Ce(SO_4)_2 \cdot 4H_2O$ contains 4.5 mol water, which evaporates upon heating to 623 K. A cuvette system equipped with vacuum stopcocks, and nitrogen gas flow, was used to find the optimum conditions, after which samples were prepared by a high-vacuum technique as described elsewhere.[14] The deuteriated radical cations were generated in deuteriated acids where they existed in double-deuteriated form.

Results

Hydroquinone

Two isomers were resolved in the EPR spectrum of the radical cation generated from hydroquinone in FSO_3H with $Ce(SO_4)_2$. When the radical cation was produced in a mixture of FSO_3H and CH_3NO_2 with $Ce(SO_4)_2$, the isomers were also resolved in the ENDOR spectrum (Fig. 1). The spectra were the same whether the starting material was hydroquinone or benzoquinone. With FSO_3H as solvent, ENDOR spectra could be scanned in the temperature range 203–233 K. With CH_3NO_2 added to the system, the optimum ENDOR temperature was *ca.* 226 K. This temperature was also optimum for detecting both isomers by

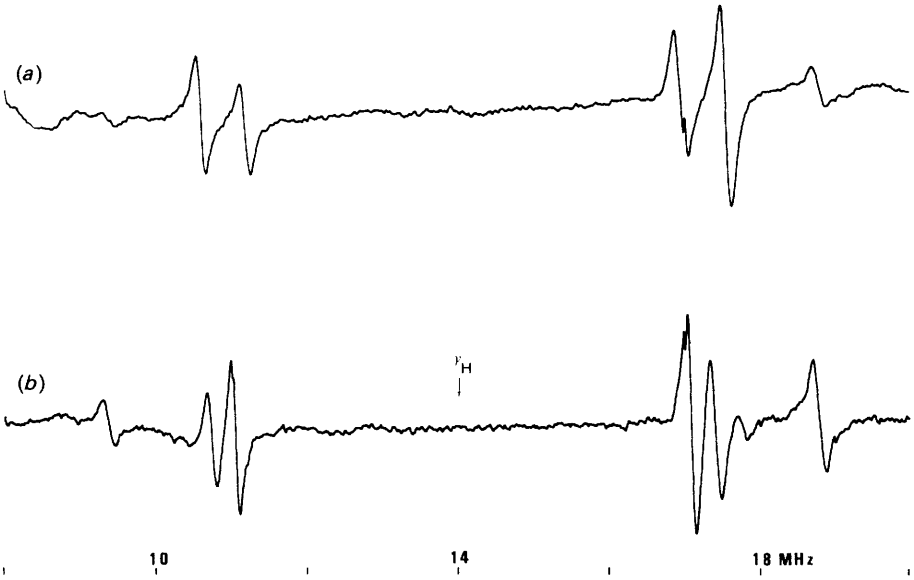

Fig. 1 ENDOR spectra of (*a*) *trans* and (*b*) *cis* isomers of the radical cation generated from 1,4-benzoquinone with $Ce(SO_4)_2$ in a mixture of FSO_3H and CH_3NO_2 (1 : 1) at 226 K

ENDOR. The relative intensity of the ENDOR lines was different for the two isomers, while the coupling constant of the OH protons was the same. According to the general TRIPLE spectrum the signs of the coupling constants are the same. The coupling constants detected by ENDOR (see Table 1) were in good agreement with the EPR values reported by Barabas *et al.*[4]

The deuteriated radical cation was produced in a mixture of D_2SO_4, CH_3NO_2 and $Ce(SO_4)_2$. The ratio $^{D}a_{OD} : {}^{H}a_{OH}$ was 0.154.

Methylhydroquinone

Fig. 2(*a*) shows the EPR spectrum of the methylhydroquinone radical cation produced in FSO_3H with $Ce(SO_4)_2$. The spectrum is a superposition of isomers. Fig. 2(*b*) shows the ENDOR spectrum and Table 1 the coupling constants, which are different from those reported earlier.[8] The best temperature for ENDOR was 233 K. We were not able to detect the relative signs of the coupling constants by TRIPLE.

When the deuteriated radical cation was generated in a mixture of D_2SO_4, CH_3NO_2 and $Ce(SO_4)_2$, the EPR spectrum was not resolved. When it was generated in CF_3CO_2D with $ZrCl_4$, however, the well resolved EPR spectrum of deuteriated radical cation shown in Fig. 2(*c*) was recorded.

2,3-Dimethylhydroquinone

A well resolved EPR spectrum was recorded from 2,3-dimethylhydroquinone in a mixture of FSO_3H–CH_3NO_2 and $Ce(SO_4)_2$. Only one isomer was detected. The intensity of the ENDOR lines for OH protons increased with temperature. According to the TRIPLE spectrum the sign of the CH_3 protons is opposite to the sign of the ring protons.

The EPR spectrum of the deuteriated radical cation generated in a mixture of D_2SO_4, CH_3NO_2, CH_2Cl_2 and $Ce(SO_4)_2$ was well resolved (Fig. 3). The ENDOR spectrum gave a proton coupling constant, 0.180 mT, only for the methyl protons. According to the EPR spectrum there are also 0.039 and 0.051 mT deuterium quintets.

2,5-Dimethylhydroquinone

The radical cation was generated by $Ce(SO_4)_2$ in a mixture of FSO_3H and CH_2Cl_2. Both the EPR and ENDOR spectra were well resolved, but only one isomer was detected. The intensity of the ENDOR lines for OH protons decreased with decreasing temperature and, according to the TRIPLE spectrum, the methyl protons have different sign to the other protons. The radical cation was also produced using D_2SO_4 and CH_3NO_2 as solvent system. The coupling constants obtained from the ENDOR spectrum (Table 1) are in good agreement with the EPR values reported by Sullivan and Brette.[12]

2,6-Dimethylhydroquinone

The radical cation was generated by $Ce(SO_4)_2$ or $ZrCl_4$ in a 1 : 1 mixture of FSO_3H and CH_3NO_2. The best ENDOR spectrum was detected with $ZrCl_4$, and the optimum temperature was 222 K. According to the ENDOR spectrum, there are six coupling constants (Table 1), and two isomers were distinguished on the basis of simulation. The EPR spectrum is shown in Fig. 4(*a*) and the ENDOR spectrum in Fig. 4(*b*).

The deuteriated radical cation was generated by $Ce(SO_4)_2$ in the solvent system D_2SO_4–CH_3NO_2 and the coupling constants obtained from the EPR spectrum are collected in Table 1. We were unable to record an ENDOR spectrum of the deuteriated radical cation.

2,3,5-Trimethylhydroquinone

The radical cation was produced in a mixture of FSO_3H and $Ce(SO_4)_2$ and the deuteriated cation was generated in CF_3CO_2D and $ZrCl_4$. Both spectra are shown in Fig. 5 and

Table 1 Hyperfine coupling constants (accuracy ±0.005 mT) obtained from the experimental EPR and ENDOR spectra of the radical cations generated from variously substituted hydroquinones in strongly acidic media

			hyperfine coupling constants/mT					
compound	isomer		1 (OH)	2	3	4 (OH)	5	6
hydroquinone		obs.	0.337 (9.440)	0.206 (5.778)	0.249 (6.971)	0.337	0.206	0.249
	trans	obs.[a]	0.3294	0.2055	0.2465	0.3294	0.2055	0.2465
		obs.	0.337 (9.449)	0.239 (6.694)	0.239	0.337	0.215 (6.042)	0.215
	cis	obs.[a]	0.3294	0.2356	0.2356	0.3294	0.2147	0.2147
		calc.[b]		0.203	0.203		0.203	0.203
		deuteriated	0.055	0.210	0.250	0.055	0.210	0.250
2,3-dimethylhydroquinone		obs.	0.316 (8.856)	0.180 (5.032)	0.180	0.316	0.257 (7.216)	0.257
		obs.[c]		0.183	0.183		0.258	0.258
		calc.[b]		0.192	0.192		0.249	0.249
		deuteriated	0.051	0.180 (5.057)	0.180	0.051	0.039	0.039
2,5-dimethylhydroquinone		obs.	0.306 (8.573)	0.371 (10.390)	0.092 (2.586)	0.306	0.371	0.092
		obs.[d]	0.3032	0.3679	0.0957	0.3032	0.3679	0.0957
		calc.[b]		0.375	0.113		0.375	0.113
		deuteriated	0.049	0.370	0.095	0.049	0.370	0.095
tetramethylhydroquinone		obs.	0.263	0.258 (7.240)	0.151 (4.236)	0.263	0.258	0.151
	trans	obs.[e]	0.273	0.2483	0.1571	0.273	0.2483	0.1571
		obs.	0.263	0.216 (6.066)	0.216	0.263	0.190 (5.332)	0.190
	cis.	obs.[e]	0.273	0.2151	0.2151	0.273	0.1903	0.1903
		calc.[b]		0.208	0.208		0.208	0.208
methylhydroquinone	I	obs.	0.340 (9.580)	0.254 (7.095)	0.130	0.323	0.295	0.207 (5.720)
	II	obs.	0.321	0.306 (8.592)	0.119 (3.387)	0.475	0.172 (4.785)	0.168
		calc.[b]		0.280	0.127		0.263	0.189
		deuteriated	0.050	0.300	0.110	0.055	0.190	0.190
2,6-dimethylhydroquinone	I	obs.	0.304 (8.554)	0.248 (7.026)	0.220 (6.568)	0.311	0.183	0.172 (4.829)
	II	obs.	0.311	0.209 (5.755)	0.209	0.304	0.172	0.220 (6.110)
		obs.[c]		0.218	0.199		0.199	0.218
		calc.[b]		0.201	0.187		0.187	0.201
		deuteriated	0.050	0.252 (7.053)	0.220 (6.161)	0.050	0.185 (5.723)	0.180 (4.950)
2,3,5-trimethylhydroquinone	I	obs.	0.330	0.321 (8.486)	0.097 (2.712)	0.245 (7.029)	0.321 (8.486)	0.195 (5.916)
	II	obs.	0.334	0.285 (7.992)	0.130 (3.608)	0.260	0.255	0.180 (4.884)
		calc.[b]		0.287	0.113		0.295	0.173
		deuteriated	0.050	0.292 (8.201)	0.110 (3.085)	0.040	0.292	0.200 (5.707)

Values in parentheses are measured in MHz. [a] Ref. 4. [b] Additivity method, ref. 18. [c] Ref. 5. [d] Ref. 12. [e] Ref. 13.

the coupling constants are listed in Table 1. Two isomers were detected.

Tetramethylhydroquinone

The radical cation was produced in the same way as that of 2,6-dimethylhydroquinone and the ENDOR spectrum showed four coupling constants, as listed in Table 1. The spectra of the two isomers were well resolved and differed in intensity. OH protons were not detected in the ENDOR spectrum, only methyl protons. The coupling constants for both cation and deuteriated radical cations are in agreement with the EPR values reported by Sullivan. According to Ondercin and Sullivan, the *cis–trans* isomer ratio is 70 : 30 in favour of the *trans* form.

Discussion

Highly resolved EPR and ENDOR spectra were scanned with $Ce(SO_4)_2$ and the FSO_3H and CH_3NO_2 solvent mixture. In some cases $ZrCl_4$ gave better results than $Ce(SO_4)_2$, but the TRIPLE spectra were not then always well resolved. Once optimal conditions were established it was possible to distinguish the *cis–trans* isomers of two of the radicals by ENDOR, as was done by EPR for tetramethylhydroquinone radical cation many years ago.[13] The existence of a non-overlapping hyperfine component is essential if individual isomers are to be distinguished by ENDOR.

Once more it was demonstrated that the same radical cation is generated from hydroquinone as from benzoquinone in strong acidic medium. Use of a deuteriated solvent system allowed us to identify the OH protons by EPR and ENDOR, except for 2,3-dimethylhydroquinone where the ring protons at position 5,6 were deuteriated as well. The deuterons at positions 5,6 give rise to the quintet 0.039 mT, and the OD quintet is 0.051 mT. The assignment was arrived at on the basis of the temperature dependence of the ENDOR lines corresponding to the 0.316 mT coupling and of the corresponding magnetogyric ratio.

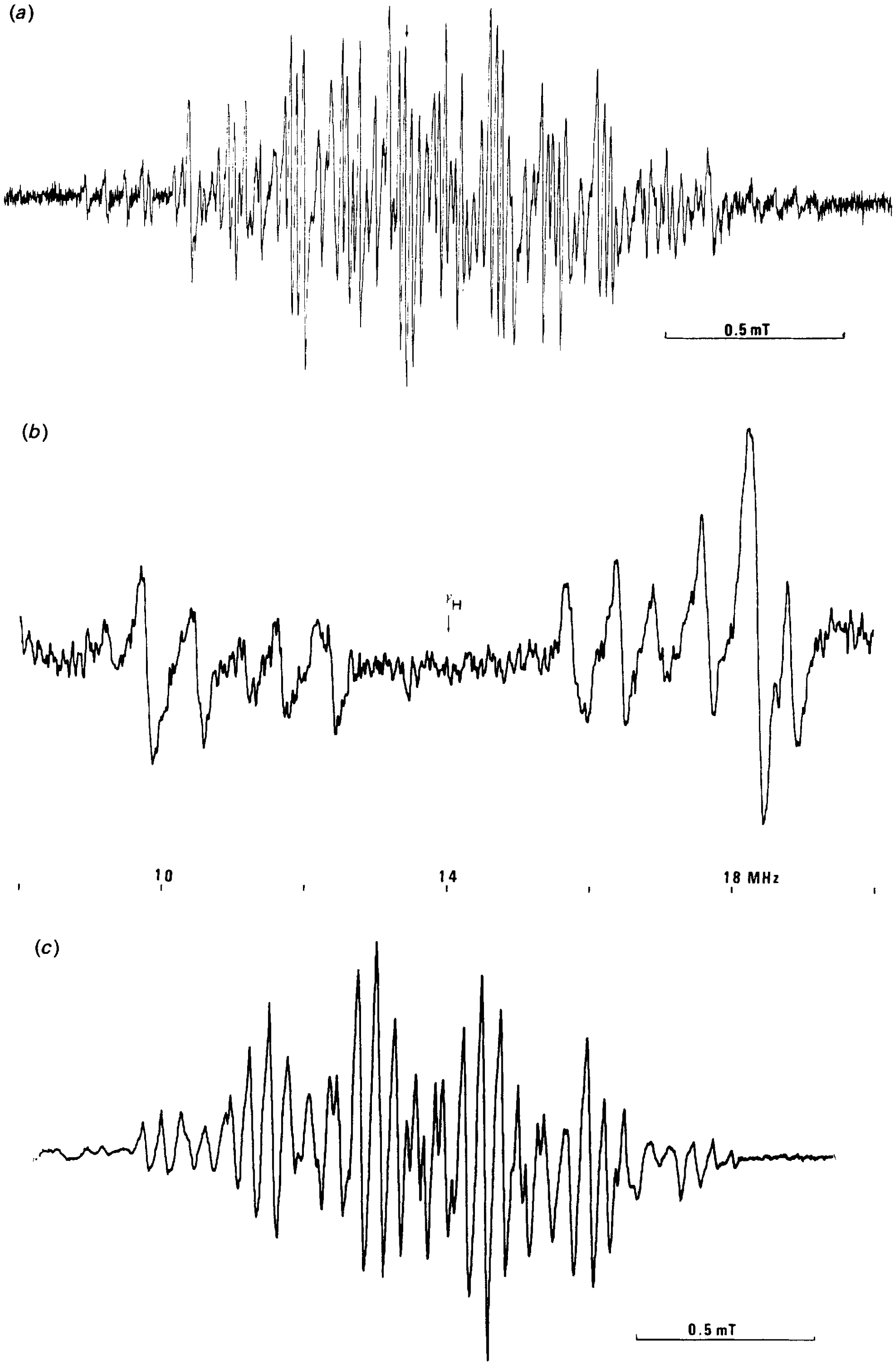

Fig. 2 (*a*) EPR and (*b*) ENDOR spectra of the radical cation generated from methylhydroquinone with $Ce(SO_4)_2$ in FSO_3H at 233 K. (*c*) EPR spectrum of the deuteriated radical cation in the mixture of CF_3CO_2D and $ZrCl_4$ at 263 K. (The arrow indicates the field setting for the ENDOR experiment)

The intensity of the ENDOR lines for OH protons is very temperature dependent in the case of 2,5-dimethylhydroquinone. The ratio ${}^{D}a_{OD} : {}^{H}a_{OH}$ is 0.16, and higher than the ratio of magnetogyric ratios 0.153. Similarly high values have been measured for anthraquinone radicals.[15]

The EPR spectra of 2,3-dimethylhydroquinone and 2,5-dimethylhydroquinone cation radicals did not indicate rotational isomerism over the temperature range studied.

In the case of 2,6-dimethylhydroquinone it is clear from the EPR spectrum of the deuteriated cation, which shows the deuterium quintet, that the coupling constants of the OH protons are almost the same. The EPR spectrum is a superposition of the isomers and, according to the simulated spectrum, all hyperfine lines of the two isomers overlap. The ENDOR spectrum is also a sum spectrum and so isomers could not be distinguished by ENDOR. Nor was it possible, therefore, to detect the relative signs of the coupling constants by TRIPLE. The deuteriation and the temperature dependence of the lines corresponding to the coupling 0.303 mT allow assignment of the OH proton coupling constants.

The hydroxyl group is rotating about the carbon–oxygen bond and, theoretically, there are many possible conformers

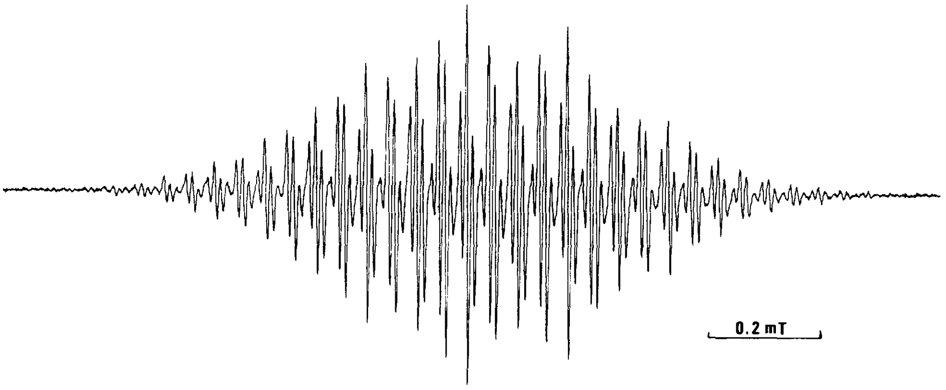

Fig. 3 EPR spectrum of the radical cation derived from 2,3-dimethylhydroquinone with $Ce(SO_4)_2$ in a mixture of D_2SO_4, CH_3NO_2 and CH_2Cl_2 at 243 K

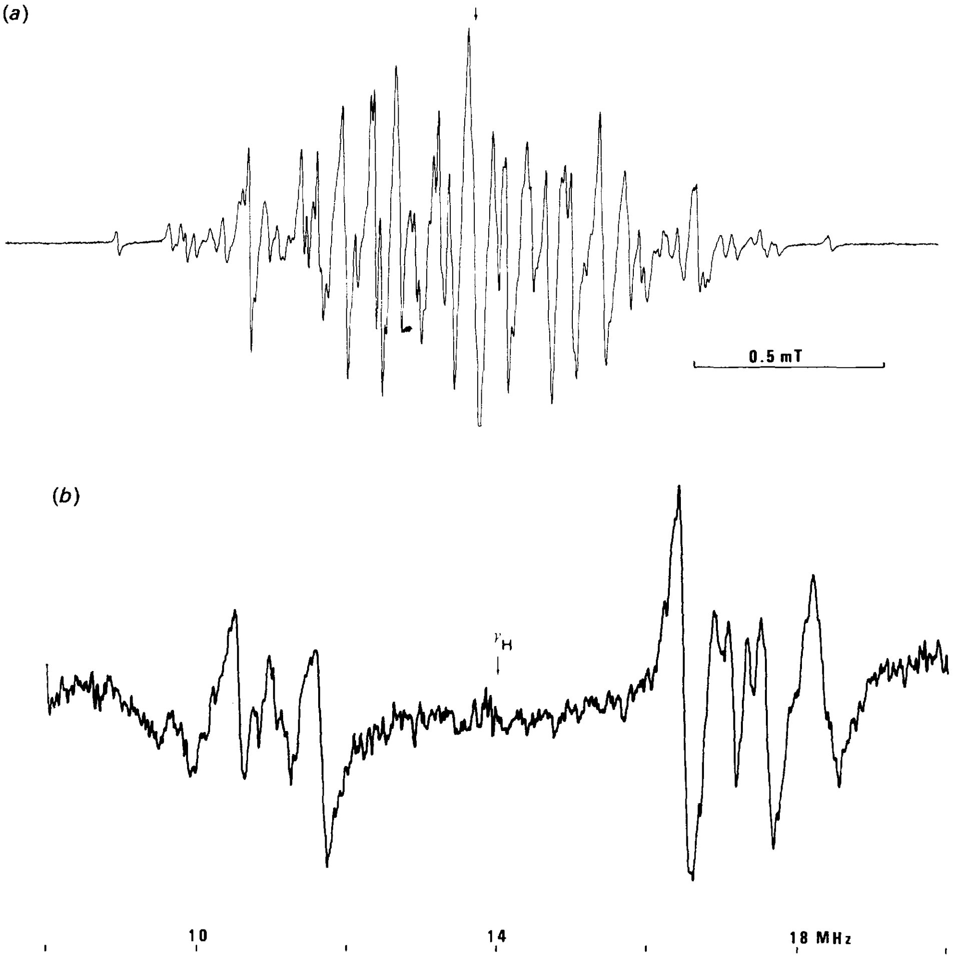

Fig. 4 (*a*) EPR and (*b*) ENDOR spectra of the radical cation derived from 2,6-dimethylhyroquinone with $ZrCl_4$ in a mixture of FSO_3H and CH_3NO_2 (1 : 1) at 233 K. (The arrow indicates the field setting for the ENDOR experiment)

for methyl-, 2,6-dimethyl- and 2,3,5-trimethylhydroquinone. Our observation of two conformers indicates a fairly deep potential well, and the rate of rotation (oscillations) is slow on the timescale of an EPR experiment, so the conformers exist long enough to give a spectrum. The lifetime of a particular conformation must be large compared with $1/\Delta\omega$, where $\Delta\omega$ is the frequency separation between corresponding lines of the separate isomers.[16]

The barrier to rotation about the carbon–oxygen bond can be determined by studying the temperature dependence of the hydroxyl proton coupling constant. In the case of the 2,5-dihydroxyhydroquinone cation, no isomers were observed, and the position of potential-energy minimum is where the hydroxyl group lies in the plane of the ring.[17] To give the correct stuctures for methyl-, 2,6-dimethyl- and 2,3,5-trimethylhydroquinone cation conformers would require *ab*

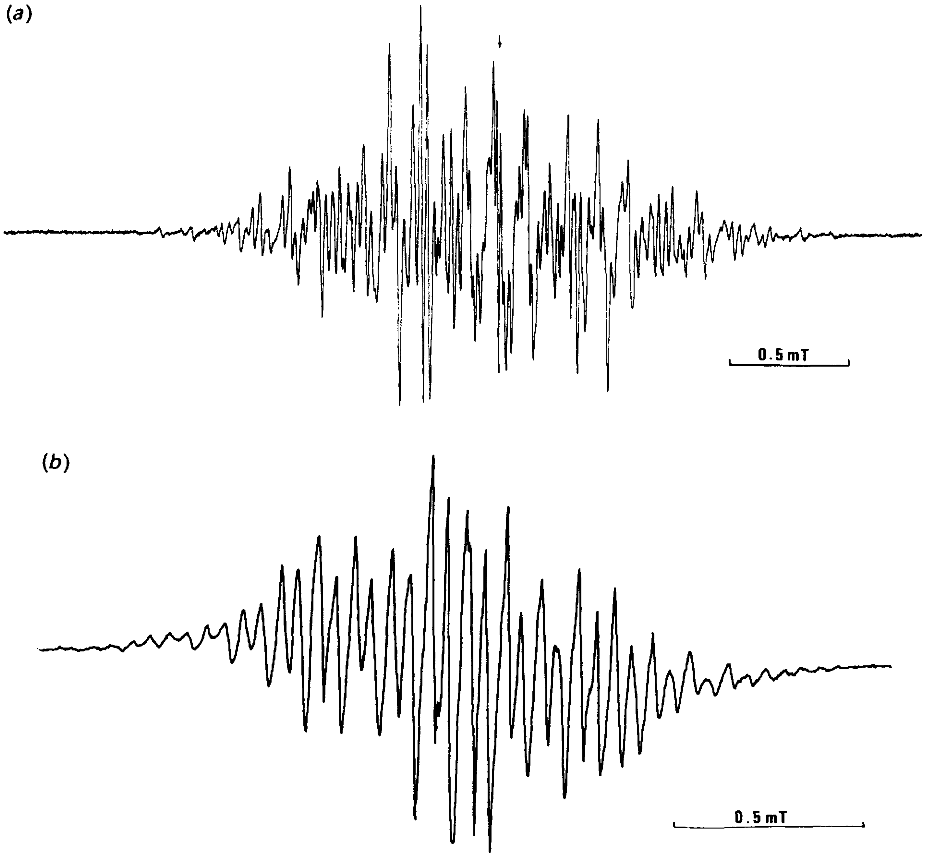

Fig. 5 EPR spectra of 2,3,5-trimethylhydroquinone radical cations generated in (*a*) FSO_3H and $Ce(SO_4)_2$ and (*b*) CF_3CO_2D and $ZrCl_4$ at 243 K. (The arrow indicates the field setting for the ENDOR experiment)

initio calculations optimizing the geometry and the temperature dependence of the hydroxyl group interaction.

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