STRUCTURE AND DYNAMICS OF THE LOWEST TRIPLET STATE IN p-BENZOQUINONE.
IV. THE EFFECT OF MILD SUBSTITUTION ON THE PROTON ENDOR SPECTRA

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The effect of mild (deuterium and methyl) substitution on the proton ENDOR spectra in the lowest \( n\pi^* \) triplet state of \( p \)-benzoquinone is reported and analyzed. The conclusion is that, as recently suggested by Merienne-Lafore and Trommsdorff, \( p \)-benzoquinone in its lowest triplet state is best described as a dimer.

1. Introduction

In the past couple of years several papers on the optical [1-3] and magnetic resonance spectroscopy [4] of the lowest triplet state in \( p \)-benzoquinone (PBQ) have appeared. Well established now is the fact that the lowest \( n\pi^* \) triplet state (\( B_{1g} \)) in PBQ is strongly vibronically coupled to a nearby (340 cm\(^{-1}\)) \( A_{1u} \ n\pi^* \) triplet state. The effect of this coupling manifests itself most dramatically in the extreme sensitivity of the optical and magnetic resonance spectra towards isotopic substitution [5-7]. Our understanding of this isotope effect, even on a qualitative level, however, is still marginal. This motivated us to a further study of the effect of mild (deuterium and methyl) substitution on the proton ENDOR spectra of PBQ.

In this final report on proton ENDOR spectra of PBQ we are specifically concerned with PBQ-\( h_4 \), PBQ-\( dh_3 \) and PBQ-CH\(_3 \) (toluquinone, TOL). Additional (incomplete) data of 2,6 PBQ-\( dh_2 \), PBQ-\( dh_3 \) and mono deutero (ring) toluquinone are also reported and used to support assignments made. Analysis of the data shows that mono deutero- and methyl-substitution in PBQ leaves the \( C_{2v} \) symmetry (approximately) of the unsubstituted half of the molecule virtually intact. This finding lends support to the hypothesis, recently forwarded by Merienne-Lafore and Trommsdorff [8] that PBQ may be considered as a dimer for its lowest \( n\pi^* \) (singlet and triplet) states.

2. Experimental details

All isotopically mixed crystals used were grown from the Bridgman furnace with a guest concentration of about 1 mole \%. Ringdeuterated toluquinone-\( d_3 \) was obtained by an (acid) exchange of the corresponding hydroquinone followed by an oxidation with chromic acid as described by Charney and Becker [9]. PBQ-\( dh_3 \) was found as an “impurity” in pure PBQ-\( dh_4 \) and TOL-\( dh_2 \) as a by-product in the formation of TOL-\( dh_3 \). The other materials were obtained as described previously [5].

The setup used to detect the excited state magnetic resonance signals (EPR and ENDOR) has also been described [5,6] and we emphasize that all results reported here were obtained at about 2 K.

The \( g \) and \( D \) tensors of the species studied and given in table 1 were determined through angular dependent measurements of the magnetic field value at which the optically detected \( \Delta M_s = \pm 1 \) EPR transitions occurred. “Half field” (\( \Delta M_s = \pm 2 \)), LAC and CR magnetic field values were also used to improve the accuracy of the tensor elements. In all cases we found that the \( g \) and \( D \) tensors coincide. In addition, for toluquinone we find that the \( g \) and \( D \) tensors coincide with a molecular axes system whereby the \( z \) axis is the oxygen–oxygen axis, the \( y \) “in plane” axis parallel to the cleavage plane [10] and the \( x \) axis perpendicular to both. For \( p \)-benzoquinone we find instead, that while the \( z \) axis of the \( g \) and \( D \) tensors coincides with the oxygen–oxygen direction...
they is rotated some -5 degrees from the molecular plane. A recent low-temperature crystal structure determination of p-benzoquinone shows that the molecular plane is tilted 3.2° away from the cleavage (201) plane. The proton ENDOR data taken at the $\Delta M_s = -1$ transition were used to determine the hyperfine tensors. CRENDOR data were also obtained and used for additional (sign) information.

In a primary fitting procedure only three hyperfine elements were least-square fitted. For ENDOR the first order frequency equation [5] was used and for CRENDOR the full $6 \times 6$ Hamiltonian matrix ($S = 1, I = \frac{1}{2}$) was diagonalised [6]. At least three (nearly) perpendicular rotation planes were used in the total fit of all six hyperfine elements. The signs of the rotation angles, which determine the sign of the nondiagonal hyperfine elements, were obtained from the ENDOR data of the two translational inequivalent molecules (for the $A_{xy}$ and $A_{xz}$ elements) or by the angular dependence of the EPR for both these two molecules. As in toluquinone the x-axes of the two translational inequivalent molecules coincide, our ENDOR data were not accurate enough to discriminate between two (very similar) solutions of the hyperfine tensors. In all calculations we have further assumed the hyperfine tensor to be symmetric and ignored the nuclear dipole–dipole interactions.

3. Results

Fig. 1 shows an example of an ENDOR spectrum obtained for PBQ-$d_3$ in PBQ-$d_4$ at 2 K. Note that the spectrum contains only four lines of alternating intensity (approximately $1 : 2 : 1 : 2$). The same was
For PBQ-CH$_3$ in ring deuterated PBQ-CH$_3$ six proton ENDOR lines were observed for all crystal orientations. A typical example of an ENDOR spectrum is shown in fig. 2. The triplet of lines (near 23 MHz) is assigned to the methyl-protons, while the other lines must be due to ring-protons.

Figs. 3, 4 and 5 give an impression of the fit obtained between the experimental points and the curves calculated by the computer from the spin-hamiltonian (eq. 4 of ref. [5]) with the hyperfine interactions included.

The final hyperfine tensors obtained for all ring protons in perproto, mono-deutero and methyl p-benzoquinone are gathered in the appendix. First note that the final results given here for PBQ-$\text{d}_4$ are somewhat different from the ones reported previously [5]. This is due to the fact that in the original fit a wrong choice was made in the sign of one of the off-diagonal hyperfine tensor elements.

Note also that for PBQ-CH$_3$ we are left with two solutions for the hyperfine coupling tensors. Fortunately, the difference between the two solutions is small and of no importance in the context of the present paper. The hyperfine coupling tensors of the methyl protons have also been determined but they will be reported and discussed in a forthcoming paper.
Fig. 5. Computer fits of the proton ENDOR frequencies of TOL-d3 as guest in TOL-d3 crystal. See also text to fig. 3. The three lowest lines show the angle dependences of the methyl protons. Note that the two aromatic protons of TOL-dh3 give about the same angle dependences as the protons of TOL-dh3 marked with ◦ and x (numbers 11 and 10, respectively) measured from −10° until +25°. The proton with number 12 (+) is lacking in TOL-dh3.

[14]. Finally, we have summarized in table 2 the round off principal values of the hyperfine coupling constants in a form more suitable for discussion. Note that in the case of PBQ-h4 and PBQ-dh3 the average is given of the nearly equivalent proton hyperfine coupling constants.

4. Discussion

The main problem of this paper is to assign the different hyperfine interaction tensors to specific protons.

In the parent compound, PBQ-h4 this is a trivial problem. The molecule is at a center of inversion and protons positioned para with respect to one another are equivalent. The protons ortho to one another are not related by a space group symmetry element and may therefore be different. The slightly different proton hyperfine coupling tensors observed are therefore ascribed to protons being ortho to another and the difference is caused by the crystal field.

The assignment in the case of PBQ-dh3 and PBQ-CH3 is less trivial and will be given in the following sections. In fig. 6 the axes and atom numbering in p-benzoquinone is given whereby the substituent is attached to, unless stated otherwise, carbon atom 2.

4.1. Proton ENDOR assignment in mono deuterop-benzoquinone

As stated before, in the proton ENDOR spectrum of PBQ-dh3 in PBQ-d4 we observe four transitions, of which two have (roughly) double the intensity of the other ones. This observation surprised us, as six separate transitions were expected. The above observation however can, in principle, be explained in three

<table>
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<tr>
<th></th>
<th>Axx</th>
<th>Ay</th>
<th>Az</th>
<th>φ</th>
<th>Aiso</th>
<th>Notes</th>
</tr>
</thead>
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<tr>
<td>PBQ-h4</td>
<td>−3.06</td>
<td>4.66</td>
<td>−1.60</td>
<td>±15°</td>
<td>9.60</td>
<td>inversion symmetry</td>
</tr>
<tr>
<td>PBQ-dh3</td>
<td>−3.34</td>
<td>4.63</td>
<td>−1.29</td>
<td>±13°</td>
<td>8.92</td>
<td>protons 9 and 12 (int. ∼ 1)</td>
</tr>
<tr>
<td></td>
<td>−2.91</td>
<td>4.85</td>
<td>−1.94</td>
<td>±19°</td>
<td>9.76</td>
<td>protons 10 and 11 (int. ∼ 2)</td>
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<tr>
<td>TOL-h3</td>
<td>−1.70</td>
<td>2.51</td>
<td>−0.81</td>
<td>5°</td>
<td>5.10</td>
<td>methyl protons A = 1/3 (A1 + A2 + A3)</td>
</tr>
<tr>
<td></td>
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<td>−3.85</td>
<td>−28°</td>
<td>8.65</td>
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</tr>
<tr>
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<td>25°</td>
<td>8.80</td>
<td>aromatic proton 11</td>
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<tr>
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<td>−0.59</td>
<td>4°</td>
<td>5.85</td>
<td>aromatic proton 12</td>
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</table>
absolute difference in hyperfine coupling of protons 10 and 11 is presumably only caused by the crystal field.

The assignments of the different hyperfine coupling tensors to the different protons can now be made, using only the predicted angle of rotation \[ \alpha \] of the in-plane hyperfine tensor axes. The assignment made is also included in table 2.

Note that the molecule on isotopic substitution retains approximate C\textsubscript{2v} symmetry at the unsubstituted half.

4.2. Proton ENDOR assignments in toluquinone

As table 2 shows in toluquinone, two of the aromatic protons have quite similar hyperfine interaction constants while the third proton exhibits a rather different hyperfine splitting. Again, in principle, there are three possible assignments for the third (exceptional) proton. However in view of the assignment made in mono-deutero p-benzoquinone we assign the third proton to position 12. The other assignments are then easily made and included in table 2.

The following additional measurements on a ring-deuterated isotope of toluquinone support our assignment. In isotopically mixed crystals of toluquinone we have also measured proton ENDOR spectra of a mono ring substituted deutero isotope of toluquinone. In this isotope, as given in fig. 5, the exceptional proton evidently was replaced by deuterium. Moreover, measurement of the fine-structure constants of this isotopic impurity revealed this isotope to have a significantly larger fine structure parameter \( D \) than toluquinone itself. As we have found that the fine-structure parameter \( D \) of PBQ-2,6\textsubscript{d2}h\textsubscript{2} exceeds that of PBQ-\textsubscript{d}h\textsubscript{3} (as shown in table 1), this finding is only consistent with the assumed deuterium substitution in position 12. Additional support for the assignments made may be derived from the resulting relationship between the fine-structure parameter \( D \) and the angle of rotation (in the molecular plane) \( \alpha \) of the proton hyperfine tensor. In fig. 7 we have displayed all data available on isotopes of p-benzoquinone and note that there is a very consistent relationship between \( \alpha \) and \( D \).

Also note that the methyl perturbation nicely fits into this picture.
J.H. Lichtenbelt, D.A. Wiersma/ENDOR of p-benzoquinone
dorf [8], that p-benzoquinone in its lowest nπ* singlet and triplet states may be considered as a dimer, is correct.

The isotope effect on the fine structure and hyperfine structure constants in p-benzoquinone then basically derives from two effects. The first one is that "isotopic" (deuterium, methyl) substitution changes the zero-order excitation energy of the substituted fragment. The second one is that isotopic substitution in general will also affect the vibronic mixing between the monomer excited nπ* states.

It seems worthwhile then to comment here on our observation [7] that isotopic substitution of oxygen-16 by oxygen-17 or -18 hardly affects the fine-structure parameter D in PBQ. In view of our present understanding of the isotopic effect we can only interpret this as evidence for the fact that the oxygen atom is at rest in the modes that vibronically mix the near degenerate nπ* triplet states.

Finally our EPR and proton ENDOR measurements show that there is a very distinct correlation between the increase in $D$, $g_{zz}$ (Table 1) and the change of the hyperfine tensor elements (Table 2) on isotopic substitution. In mono deutero p-benzoquinone we see from the hyperfine data in Table 2 that the absolute value of $A_{xx}$ becomes larger at the substituted site of the molecule.

Results of previously reported [7] calculations of the proton anisotropic hyperfine elements show that the increase of $|A_{xx}|$, in a substituted "dimer", can be explained by assuming a slight "localization" of the nπ* excitation, on the oxygen of the substituted fragment. This idea is also confirmed by semi-empirical calculations of the Derbyshire type [13].

The importance of charge transfer in the nπ* excitation is not assessed by the experiments presented.

Acknowledgement

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Appendix

Experimental proton hyperfine tensor elements (in MHz) of the lowest nπ* triplet state of
p-benzoquinone and toluquinone, given in the molecular axes system. The relation between the molecular and crystal axes system is given in fig. 6. In parentheses are given the errors by the ENDOR experiments.

**PBQ-\(h_4\):**
- proton 10 and 12:
  - 6.664(20)
  - -0.757(42) 13.732(34)
  - 0.165(12) -1.797(7) 8.536(5)
- proton 9 and 11:
  - 6.814(17)
  - 1.389(33) 13.477(28)
  - 0.108(11) 1.555(5) 8.416(4)

**PBQ-\(d^3h_3\) (with the excitation “localized” on the 9–12 side)**
- proton 9:
  - 5.705(41)
  - -0.885(80) 13.211(65)
  - -0.258(18) 1.194(11) 7.894(5)
- proton 10:
  - 6.884(24)
  - -0.396(67) 14.045(46)
  - 0.059(10) -2.126(8) 8.515(4)
- proton 11:
  - 6.956(32)
  - -0.783(96) 13.724(72)
  - -0.338(24) 1.924(13) 8.461(6)
- proton 12:
  - 5.601(30)
  - -0.381(115) 13.181(63)
  - -0.023(20) -1.384(9) 7.981(5)

**TOL-\(d^2h_2\)**
- One measurement in the molecular plane gave us the following elements:
  - proton 10:
    - 12.24(26)
    - -4.15(2) 6.89(2)
  - proton 11:
    - 12.09(39)
    - 3.40(7) 6.90(2)

**References**