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Lichtenbelt, Jan H.; Fremeyer, Jan G.F.M.; Veenliet, Hendrik; Wiersma, Douwe A.

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STRUCTURE AND DYNAMICS OF THE LOWEST TRIPLET STATE IN *p*-BENZOQUINONE

II. An optically detected EPR and proton ENDOR study

Jan H. LICHTENBELT, Jan G.F.M. FREMEYER, Hendrik VEENVLIET and Douwe A. WIERSMA

Laboratory for Physical Chemistry, University of Groningen, Groningen, The Netherlands

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Optically detected high field EPR and proton ENDOR experiments on the zero-point (*g*-inversion) level of the lowest triplet state in *p*-benzoquinone-*h*₄ as guest in *p*-benzoquinone-*d*₄ are reported. The results are used to obtain the parameters of the molecular spin hamiltonian and the following results are obtained at 1.8 K: The fine-structure principal values are $X = -798.2 \pm 0.6$ MHz, $Y = -569.1 \pm 0.6$ MHz, and $Z = 1367.3 \pm 0.6$ MHz; while the molecular *g*-values are found to be $g_{xx} = 2.0045 \pm 0.0005$, $g_{yy} = 2.0035 \pm 0.0005$, and $g_{zz} = 2.00994 \pm 0.00008$.

The principal *z* axes of both the fine-structure and *g*-tensor are found to coincide with the carbonyl bond direction of the *p*-benzoquinone ground state structure.

The orientation of the *x* and *y* axes of the fine-structure and proton hyperfine-structure tensor however indicates that the molecule in the excited state is distorted into a centrosymmetric chair-form, which also implies that the symmetry of this state is only *A*_g. The $\frac{1}{2}$ trace of the proton hyperfine interaction tensor is found to be 9.6 MHz and from this we calculate that 1.8% of the unpaired *n*-electron density is at each proton.

We further report the effect of mono deuteration on the fine-structure and *g*-tensor principal values and these data are used to calculate the fine-structure parameter *Z* of the *u*-inversion level (20 cm⁻¹ above the zero-point level) in the triplet state of *p*-benzoquinone-*h*₄. This method yields $Z = 5.8$ GHz which is to be compared with the value 6 ± 1.3 GHz obtained from the temperature dependence of the corresponding fine-structure parameter of the zero-point level.

Finally, a new effect — the observation of radio-frequency induced changes in the phosphorescence cross relaxation signal — is reported and used to identify the electron spin state, in which the (ENDOR) proton spin flips take place.

1. Introduction

The spectroscopic interesting properties of aromatic diketones mainly stem from the near degeneracy of the lowest $n\pi^*$ excitations in these molecules. As a result of this near degeneracy, vibronic coupling strongly mixes these electronic excitations and the potential energy surface of the lower state may then acquire a double minimum potential (DMP) well along a vibronic coupling mode [1,2].

The pseudo Jahn–Teller character of the lowest excited triplet state in the prototype aromatic diketone *p*-benzoquinone was recently demonstrated through a series of experiments [3,4] of which the observed large isotope effects on the fine-structure parameter *D* [5] was most intriguing. In *p*-benzoquinone (PBQ ($L = z$, $M = y$)) vibronic coupling between the *B*_{1g} and *A*_u $n\pi^*$ triplet states is so strong that the potential energy surface of the lowest (*B*_{1g}) triplet state indeed

contains a DMP well along a *b*_{1u} type nuclear motion.

Much of our effort in the past was devoted to an optical study aimed at further identification of the lowest inversion levels in the DMP well of the lowest triplet state in PBQ and in part I of the series [6] we reported results of an isotope effect study on the absorption, emission and ODMR spectra of the lowest triplet state. Next to a detailed optical study, we are also engaged in an EPR and ENDOR study of the lowest triplet state in PBQ of several isotopic species such as: PBQ-*h*₄, -*d**h*₃, -2,6-*d*₂*h*₂, -*d*₃*h*, ¹³C and ¹⁷O using PBQ-*d*₄ as a host crystal. In the present paper we are primarily concerned with the results of an EPR and proton ENDOR study of the zero-point (*g*-inversion) level of the lowest triplet state in PBQ-*h*₄ as guest in PBQ-*d*₄ at 1.8 K.

The preliminary results of EPR experiments at 4.2 K on the *u*-inversion level of the DMP well in PBQ-*h*₄ will also be presented and discussed.

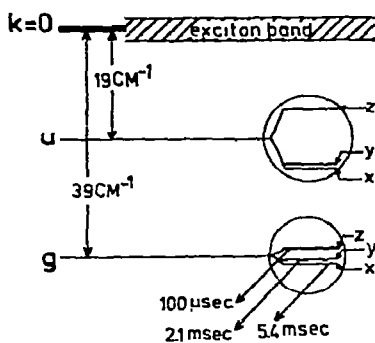


Fig. 1. Location of the inversion levels in the lowest triplet state of *p*-benzoquinone- h_4 with respect to the lowest triplet exciton band of *p*-benzoquinone- d_4 . The data in this figure have been taken from ref. [6]. It should be further noted that the zero field splitting of the inversion levels has been expanded (about 120 times) and that the ordering of the x and y spin sublevels in the u -inversion level is unknown.

Finally we demonstrate the usage of a new phenomenon: the observation of r.f. induced changes in the cross relaxation effect, which is used to determine the absolute sign of the proton hyperfine coupling constants in the lowest $n\pi^*$ triplet state of PBQ- h_4 .

2. EPR measurements

Fig. 1 schematically shows the energy level diagram of the PBQ- h_4 molecular trap inside the PBQ- d_4 host crystal. The zero-point (g -inversion) level of the PBQ- h_4 trap is 39 cm^{-1} and the u -inversion (vibronic) level is only 19 cm^{-1} below the host triplet exciton band [6]. In part I we have shown that the dynamics of this system is very much temperature dependent, however de-

tailed knowledge of the communication process among the inversion levels is lacking at present. In case of Boltzmann equilibrium among the inversion levels at all temperatures, only at very low temperature, e.g., 1.8 K, the g -inversion level, for its magnetic properties, may be considered isolated [consult also eq. (2)]. At, e.g., 4.2 K however, EPR and ENDOR measurements on the g -inversion level indirectly probe magnetic properties of the u -inversion level and vice versa.

In a recent communication [5] we reported the fine-structure parameters and g -tensor principal values of the zero-point level of the lowest $n\pi^*$ triplet state of PBQ- h_4 and PBQ- dh_3 as guest in a PBQ- d_4 host crystal at 1.8 K. In the meantime we have been able to considerably improve the accuracy of these data, especially the g -tensor principal values, by using much more accurate magnetic field measurements than in the previous report. The parameters in table 1 were calculated from angular dependent EPR measurements at 1.8 K performed in orthogonal crystal planes, whereby the resonance field positions of both inequivalent molecules in the unit cell were accurately determined. They were further adjusted such that the magnetic resonance data of the symmetry related molecules in the unit cell [7] were simultaneously optimal fitted to the following well known spin hamiltonian:

$$H = |\beta_e| (S_x g_{xx} H_x + S_y g_{yy} H_y + S_z g_{zz} H_z) - h(XS_x^2 + YS_y^2 + ZS_z^2). \quad (1)$$

Herein are g_{xx} , g_{yy} and g_{zz} the principal values of the g -tensor of the triplet spin system, X , Y and Z the principal values of the fine-structure tensor with zero trace, S_x , S_y and S_z components of the spin angular

Table 1

Fine-structure parameters and g -tensor principal values in the lowest triplet state of PBQ- h_4 and PBQ- dh_3 as guest (1 mol%) in PBQ- d_4 at 1.8 K as obtained from high field EPR measurements. The numbers in parentheses are obtained from zero-field ODMR experiments [6]

	PBQ- h_4		PBQ- dh_3
X (MHz)	-798.2 ± 0.6	(-797.3 ± 0.8)	-915.5 ± 0.6
Y (MHz)	-569.1 ± 0.6	(-569.3 ± 0.8)	-705.5 ± 0.6
Z (MHz)	1367.3 ± 0.6	(1366.6 ± 0.8)	1621.0 ± 0.6
g_{xx}	2.0045 ± 0.0005		2.0045 ± 0.0005
g_{yy}	2.0035 ± 0.0005		2.0038 ± 0.0005
g_{zz}	2.00994 ± 0.00008		2.01038 ± 0.00008

momentum in the molecular axes system and $|\beta_e|/h$ a constant which in this paper is taken from ref. [8]. ($|\beta_e|/h = 1.3996109$ GHz/kG.)

We have further assumed in the treatment of our data that the principal axes system of the fine-structure- and g -tensor coincide. Our experiments indeed show this to be the case for the z axes, but positive evidence that this is also the case for the x and y axes could not be produced.

This is primarily due to the fact that the splitting between the X and Y spin substates is very small, which makes the fitting procedure rather insensitive to a small rotation around the z -axis of the g -tensor versus the fine-structure tensor.

It is gratifying to see in table 1, that the fine-structure parameters obtained in this manner very nicely agree with the refined ODMR data obtained in zero field.

We would like to point out that, although the spread in the reported g_{zz} values is rather large, the absolute difference in these parameters for PBQ- h_4 and PBQ- dh_3 can be determined quite accurately as all EPR measurements were made on crystals that simultaneously contained these species. The observed isotope effect on the g - and fine-structure tensor reported here are unprecedented and it is interesting to note that g_{zz} and $|D|$ both significantly increase on mono deuteration.

In part I of these series we have shown that this can be explained as a change in spin-orbit contribution to these parameters. When we compare the g -tensor principal values of PBQ- h_4 with those of benzophenone- h_{10} [9] we note that g_{zz} is of similar magnitude in both compounds, while g_{xx} and g_{yy} in benzophenone- h_{10} both are smaller than the free electron g -value, but in PBQ- h_4 they are both larger. This most likely illustrates the fact that g_{zz} values in $\pi\pi^*$ triplet states of aromatic carbonyls are mainly determined by spin-orbit coupling with the nearest higher $\pi\pi^*$ triplet state of the correct symmetry [10]. The g_{xx} and g_{yy} values however probably result from many such interfering spin-orbit coupling terms and a simple interpretation of these parameters therefore seems impossible.

Our EPR results for PBQ- h_4 further show that the z -axis of the fine-structure tensor in the zero-point level coincides with the oxygen-oxygen (L) direction of the PBQ- h_4 ground state structure [7]. The $x(N)$ and $y(M)$ axes of this tensor however deviate slightly

($5 \pm 2^\circ$) from the ground state molecular axes system. We conclude that the lowest triplet state in PBQ- h_4 is no longer planar and this is confirmed by the proton ENDOR experiments (*vide infra*).

Fig. 2 shows a typical tracing of the optically detected EPR spectrum of PBQ- h_4 in a PBQ- d_4 host crystal at 1.8 K for the magnetic field parallel to the z -axis of one of the two molecules (α) in the unit cell. The figure also shows the cross relaxation (CR) and level anti-cross (LAC) signals observed in this crystal. The CR signal at 362 ± 1 gauss* is due to cross relaxation between an unknown doublet ($S = \frac{1}{2}$) and a PBQ- h_4 (α) excited triplet species. We will show in section 5 that the CR signal can be used to probe hyperfine interactions in the triplet excited state of PBQ- h_4 . The LAC signal observed at 726 ± 2 gauss* (minimum line-width observed 60 MHz) is due to LAC between the Z and Y spin substates of the α -species and its position is in good agreement with the one calculated (727.7 gauss) from the parameters in table 1.

Sofar the experiments discussed here refer to the isolated zero-point level of the lowest triplet state of PBQ- h_4 in a PBQ- d_4 host crystal at 1.8 K. When the temperature is raised to 4.2 K and assuming Boltzmann equilibrium among the inversion levels we expect to measure a change in D_g (the fine-structure parameter of the zero-point (g -inversion) level) according to the following expression:

$$D_g(T) = Z^{-1} [D_g(0) + D_u(0) e^{-\Delta E/kT}], \quad (2)$$

wherein $D_g(0)$ and $D_u(0)$ are the fine-structure parameters of the g - and u -level under isolated conditions, ΔE the gap between the inversion levels (20 cm^{-1}) and Z^{-1} the partition function of the system. We can write Z^{-1} to a very good approximation as $(1 + e^{-\Delta E/kT})^{-1}$. Eq. (2) shows that for identical $D_g(0)$ and $D_u(0)$ we expect $D_g(T)$ to be temperature independent. We have measured $|D_g(T)|$ at 4.2 K and found an average increase of 8 ± 2 MHz versus the value measured at 1.8 K.

From eq. (2) we then calculate the fine-structure parameter D of the vibronic (u -inversion) level and find $D_u(0) = -9 \pm 2$ GHz. There are two other pieces of information that support such a large value of the

* The accuracy of our field measurements below 750 gauss is low due to the fact that our AEG probes do not cover this area.

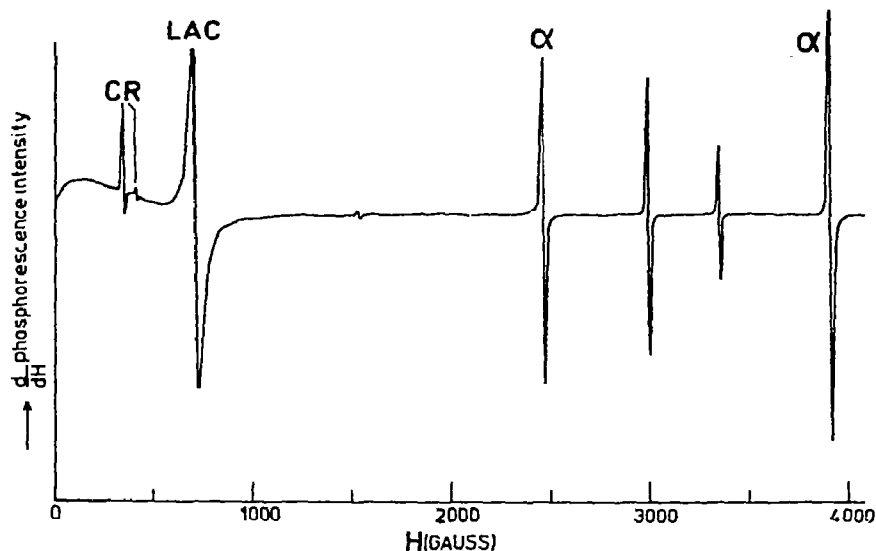


Fig. 2. Optically detected EPR spectrum of the lowest triplet state in *p*-benzoquinone- h_4 as guest in *p*-benzoquinone- d_4 at 1.8 K. The signals are taken for the magnetic field parallel to the z -axis of one of the molecules (α) in the unit cell. The signal denoted by LAC is due to level anticrossing between the z and y spin sublevels of the α -species and the signals denoted by CR are due to cross relaxation between a triplet species (the most intense one α) and a doublet spin system. Note that the CR and LAC signals are persistent in the absence of a microwave field.

fine-structure parameter D in the u -inversion level of the lowest triplet state in $PBQ-h_4$.

First, from integrated oscillator strength intensity measurements on the inversion levels in pure $PBQ-h_4$ and $PBQ-dh_3$ crystals [6] one concludes that, in a two-state model, the zero-point level of the lowest triplet state in $PBQ-dh_3$ (compared to $PBQ-h_4$) should be described as

$$|g'\rangle = 0.97 |g\rangle + 0.24 |u\rangle. \quad (3)$$

Herein is $|g\rangle$ the wave function of the zero-point and $|u\rangle$ the wave function of the u -inversion level in $PBQ-h_4$. From eq. (3) and the magnetic resonance data of table 1 we calculate the fine-structure parameter D of the u -inversion level to be -8.7 ± 1.0 GHz.

Secondly, direct polarized Zeeman absorption experiments on pure $PBQ-d_4$ crystals [4] show the fine-structure parameter D of the u -inversion level in this molecule to be -10 ± 3 GHz.

These results stimulated us to search for EPR signals that could be attributed to microwave transitions in the spin system of the u -inversion level. And indeed in a 1 mol% $PBQ-h_4$ in $PBQ-d_4$ isotopic mixed crystal at 4.2 K intense EPR, CR and LAC signals (the latter at

3635 gauss for $H||z$ of one of the PBQ -molecules in the unit cell) were observed that must be due to a triplet species with $D = -10.2 \pm 0.1$ GHz.

We are however, at this point, not able to exclude the possibility of other transients (like photochemically produced carbenes) to be responsible for the signals observed at 4.2 K. This is a point of further investigation in our laboratory.

We have further in mind to probe the fine-structure parameters of the u -inversion level indirectly by an electric field effect study on the ODMR spectra of the g -inversion level at 1.8 K.

3. EPR hyperfine structure

In only the best $PBQ-h_4$ in $PBQ-d_4$ host mixed crystals that were grown, we have been able to observe at 1.8 K hyperfine structure for the magnetic field approximately parallel to the short (y) molecular axis. A five line pattern, with a splitting of ~ 14 MHz and intensity distribution characteristic to four equivalent protons, was observed. Along other magnetic field directions, under the same conditions, no such

well resolved splittings were obtained. This indicates that the hyperfine interaction constants along the *x* (A_{xx}) and *z* (A_{zz}) molecular axes apparently are smaller than the one along the *y* (A_{yy}) molecular axis. Usually the optically detected EPR lines were 30–45 MHz wide and it soon became clear that the EPR hyperfine structure would not yield us the hyperfine interaction constants nor principal axes system to an accuracy we wanted. We therefore decided to try to obtain these data from optical detected ENDOR measurements. *p*-Benzoquinone seemed quite a good candidate for optical detection of ENDOR transitions, since the phosphorescence lifetime is very short ($\tau_z = 100 \mu\text{s}$) and the optically detected EPR signals quite often showed a signal to noise ratio of 500 or even better. Fig. 3 shows an optically detected ENDOR spectrum of PBQ- h_4 in a PBQ- d_4 mixed crystal at 1.8 K for a magnetic field parallel to the long (*z*) molecular axis of one of the molecules in the unit cell.

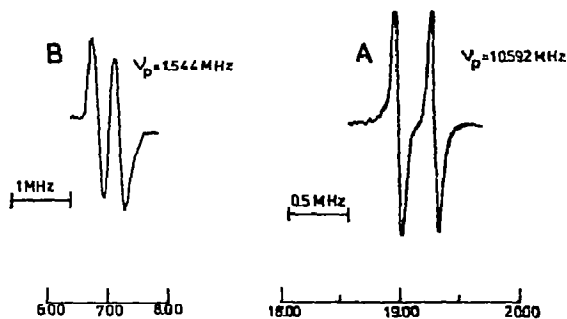


Fig. 3. Optically detected ENDOR(A) and CRENDOR(B) transitions in the lowest triplet state of *p*-benzoquinone- h_4 as guest in *p*-benzoquinone- d_4 at 1.8 K. The magnetic field in both cases is oriented along the long molecular (*z*) axis of one of the inequivalent PBQ molecules in the unit cell. The ENDOR signals are observed on the low field ($0| \rightarrow -1$) EPR transition, and the CRENDOR signals on the cross relaxation ($0| \rightarrow -1$) transition.

4. Proton ENDOR measurements

The basic principles underlying the electron nuclear double resonance (ENDOR) technique are well established [11]. Nuclear spinflips, induced by a tuned r.f. source are used to (de)saturate a partly saturated EPR transition. We are thus interested in a calculation of the nuclear spin energy levels in a triplet state electron spin system. These energy levels are determined by the following well-known spin hamiltonian:

$$\begin{aligned}
 H = & \underbrace{|\beta_e| S \cdot g_e \cdot H_0}_{H_1} - \underbrace{h(XS_x^2 + YS_y^2 + ZS_z^2)}_{H_2} \\
 & - \underbrace{|\beta_n| g_n H_0 \cdot \sum_k I_k}_{H_3} + \underbrace{S \cdot \sum_k A_k \cdot I_k}_{H_4}, \quad (4)
 \end{aligned}$$

where $S = 1$; $I_k = \frac{1}{2}$, for protons and k sums over all nuclei.

Hutchison and Pearson [12] have shown that, to a very good approximation, the nuclear eigenvalues may be calculated from a first-order perturbation treatment of H . In this approximation, the exact eigenfunctions of $H_1 + H_2$ are used to calculate the diagonal contributions of $H_3 + H_4$ to the energy of the compound electron–nuclear spin state. A calculation of the off-

diagonal elements of $H_3 + H_4$ for the case of PBQ- h_4 shows that the maximum error in the nuclear eigenvalues is expected to be $(A_{yy})^2/\nu_{\text{EPR}} \approx 20 \text{ kHz}$. It does not seem unreasonable then to neglect these second order contributions as the narrowest ENDOR lines observed had a linewidth of 50 kHz. Using the above outlined procedure one calculates for the ENDOR shift of the k th proton [12]:

$$\begin{aligned}
 \Delta\nu_k = & h^{-1} \{ (\langle S_x \rangle A_{xx}^k + \langle S_y \rangle A_{xy}^k + \langle S_z \rangle A_{xz}^k - l h \nu_p)^2 \\
 & + (\langle S_x \rangle A_{yx}^k + \langle S_y \rangle A_{yy}^k + \langle S_z \rangle A_{yz}^k - m h \nu_p)^2 \\
 & + (\langle S_x \rangle A_{zx}^k + \langle S_y \rangle A_{zy}^k + \langle S_z \rangle A_{zz}^k - n h \nu_p)^2 \}^{1/2} - \nu_p, \quad (5)
 \end{aligned}$$

in which l , m and n are the direction cosines of H_0 in the molecular axes system. A_{ij}^k are the elements of the hyperfine tensor of the k th proton in the molecular axes system. The A_{ij}^k tensor is only symmetric for an isotropic g_e tensor. In PBQ- h_4 this is not the case but the largest difference between A_{ij}^k and A_{ji}^k ($i \neq j$) is only expected to be $(1 - g_{yy}/g_{zz}) \times 100\% = 0.3\%$. In our present treatment of the ENDOR data we have ignored these differences and taken the A_{ij}^k tensor to be symmetric. The expectation values of $\langle S_x \rangle$, $\langle S_y \rangle$ and $\langle S_z \rangle$ were calculated by computer, using the parameters of table 1.

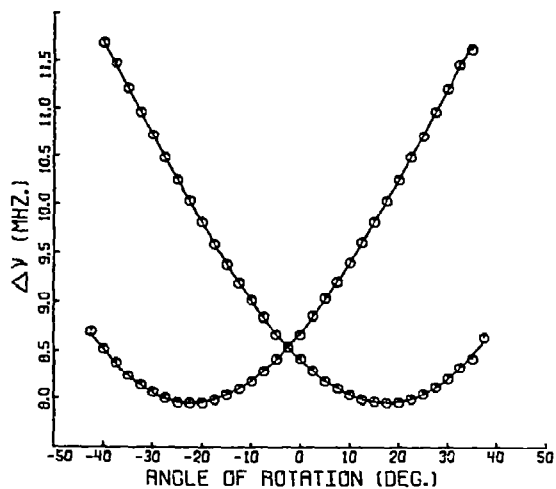


Fig. 4. Experimental proton ENDOR data (circles) and computer fitted curves for the lowest triplet state in *p*-benzoquinone- h_4 at 1.8 K. The magnetic field is rotated in the (201) cleavage plane (nearly yz molecular plane) and at zero degrees is parallel to the long molecular (z) axis. $\Delta\nu$ represents the difference between the measured proton ENDOR frequency and the free proton frequency at the EPR transition studied.

In the case of *PBQ-h₄*, with the magnetic field in the neighbourhood of the y -axis, we were only able to observe ENDOR transitions occurring in the $|0\rangle$ elec-

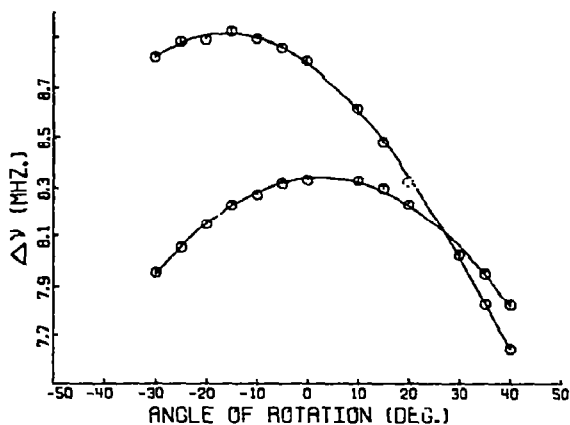


Fig. 5. Experimental proton ENDOR data (circles) and computer fitted curves for the lowest triplet state in *p*-benzoquinone- h_4 at 1.8 K. The magnetic field is rotated in the (nearly) xz molecular plane and at zero degrees is parallel to the long molecular (z) axis. See also the caption of fig. 4.

Table 2

Hyperfine tensors (in MHz) of the two inequivalent protons in the lowest triplet state of *PBQ-h₄* as guest in *PBQ-d₄* at 1.8 K. The tensors are assumed to be symmetric and described in the molecular ground state principal axes system [7].

The principal values (A^P) together with the direction cosines of the principal axes system are also given.

The numbers in parentheses represent standard deviations (in MHz) of the computer fittings of the ENDOR data

$A_1 =$	$\begin{pmatrix} 6.5 & (0.2) \\ 0.8 & (0.3) \\ -0.21 & (0.02) \end{pmatrix}$	$\begin{pmatrix} 13.6 & (0.2) \\ -1.87 & (0.01) \end{pmatrix}$	$\begin{pmatrix} 8.6 & (0.1) \end{pmatrix}$
A_1^P	6.4 (0.3)	14.3 (0.2)	8.0 (0.2)
L	0.005	-0.312	0.950
M	-0.105	0.945	0.311
N	0.994	0.101	0.028
$A_2 =$	$\begin{pmatrix} 6.7 & (0.2) \\ -0.5 & (0.3) \\ -0.11 & (0.02) \end{pmatrix}$	$\begin{pmatrix} 13.7 & (0.2) \\ 1.50 & (0.01) \end{pmatrix}$	$\begin{pmatrix} 8.4 & (0.1) \end{pmatrix}$
A_2^P	6.7 (0.2)	14.1 (0.2)	8.0 (0.1)
L	0.003	0.252	0.968
M	0.071	0.965	-0.252
N	0.997	-0.069	0.015

tron spin state (strong field approximation). For magnetic fields in the neighbourhood of the z -axis, ENDOR transitions occurring in the $| -1 \rangle$ electron spin state were most intense. This feature is probably due to the fact that T_z is the most radiative level in *PBQ-h₄* and that ENDOR transitions are dominant in those electron spin states for which longitudinal relaxation is slowest. We have also been able to measure ENDOR transitions on the " $\Delta m = 2$ " (half field) EPR signal and again only ENDOR transitions that could be correlated with the $| -1 \rangle$ electron spin state were observed. The ENDOR data obtained were in a self-consistent manner, least-squares fitted to expression (5) with ν_p being the free proton frequency measured during each ENDOR scan. The plane of rotation was in each experiment determined by fitting the observed EPR magnetic field data to a spin hamiltonian $[(H_1 + H_2)$ of eq. (4)] using the parameters of table 1. Figs. 4 and 5 show some of the experimental ENDOR data and the computer fitted curves for the zero-point level of *PBQ-h₄* as trap in *PBQ-d₄* at 1.8 K. Table 2 contains all the hyperfine coupling data that were obtained from the present proton ENDOR study.

There are two important structural features of the

PBQ- h_4 molecule in its zero-point level of the lowest triplet state that are immediately obvious from this proton ENDOR study.

First, fig. 3 already shows that for $H\parallel z$ of one of the molecules in the unit cell there are 2 proton ENDOR signals, instead of 1 expected for a D_{2h} symmetric molecule.

Secondly, fig. 5 and table 2 clearly show that the z -axis is not an ENDOR shift stationary point for rotation in the nearly xz molecular plane, which means that the PBQ-molecule in its lowest triplet state is not lower planar.

The conclusion from the proton ENDOR study thus is that the PBQ- h_4 molecule in its lowest excited triplet state only preserves site inversion symmetry. X-ray examination of the *p*-benzoquinone crystal at room temperature further showed [7] that the molecule in the ground state is planar. The non-planarity of the molecule in the excited state thus seems a purely molecular property similar to the reported non-planarity of the lowest triplet $n\pi^*$ state of formaldehyde [13].

The minor inequivalence of the ortho-ring protons is probably due to hydrogen bonding effects which have shown to be very important in PBQ crystals [6]. The proton ENDOR experiments further show that the x -axes of the proton hyperfine structure tensors are counter rotated some 5 degrees and this strongly suggests a chair-form structure of the molecule in the lowest triplet state.

The magnitude of the out-of-plane distortion is not extractable from the present proton ENDOR experiments. The analysis of the phosphorescence spectrum of PBQ- h_4 in PBQ- d_4 [5] (no progressions in out-of-plane modes!) however indicates the out-of-plane distortion to be minor. We hope to probe the distortion more directly by measuring ^{13}C -ENDOR on ring-substituted ^{13}C -PBQ- h_4 isotopes. Preliminary ^{13}C -ENDOR experiments on one of the ^{13}C -PBQ- h_4 isotopes indeed show that we can certainly complete such a study.

Next to the structural information of the PBQ- h_4 molecule in its lowest excited triplet state that is obtained from the proton ENDOR study, we are also able to discuss some qualitative features of the spin-density distribution in this state. From table 2 we calculate the isotropic proton hyperfine interaction constant (h.i.c.) to be +9.6 MHz. Venkataraman et al. [14]

have measured the corresponding hyperfine constant of the PBQ- h_4 negative ion and found it to be -6.7 MHz. If correlation effects between the unpaired electrons are assumed to be small, which was shown to be the case for the naphthalene lowest excited triplet state [15], we can calculate from the above data the unpaired n -electron density at the protons in the zero-point level of the lowest triplet state in PBQ- h_4 . Assuming for calculation purposes a planar structure for the PBQ- h_4 molecule in its lowest triplet state and its reduced form (negative ion), the isotropic proton h.i.c. for the lowest triplet state can be expressed by the following McConnell type relation:

$$a_{\text{H}} = \frac{1}{2} (a_{\text{H}}^{\text{(-)}} + \rho_{\text{H}}^{\text{n}} Q_0), \quad (6)$$

wherein $a_{\text{H}}^{\text{(-)}}$ is the isotropic h.i.c. for the negative ion and $\rho_{\text{H}}^{\text{n}}$ is the unpaired n -electron spin density at the proton and Q_0 a constant that is 1420.4 MHz [16].

With eq. (6) and the hyperfine data quoted (vide retro) we calculate $\rho_{\text{H}}^{\text{n}}$ is 1.8×10^{-2} . The proton ENDOR measurements thus provide in this case direct evidence for the suggested delocalization of the unpaired n -electron density throughout the molecular frame [17]. The anisotropic part of the proton hyperfine interaction in the lowest triplet state of PBQ- h_4 is determined by the total spin-density distribution in this state. A manifestation hereof is the observed $15 \pm 2^\circ$ rotation of the largest principal value of the hyperfine-interaction tensor versus the C-H ground state bond direction [18]. We are now pursuing ^{13}C - and ^{17}O -ENDOR measurements to completely solve the spin-density distribution in the zero-point level of the lowest triplet of PBQ- h_4 . We are also engaged in a proton ENDOR study of the lowest triplet state in PBQ- dh_3 , $-2,6-d_2h_2$, $-d_3h$ and $-\text{CH}_3$ in the hope of obtaining a better insight in the cause and consequences of the non-Born-Oppenheimer effects that we observe in the lowest $n\pi^*$ triplet state of PBQ.

In a following paper we will report the results of all these ENDOR experiments and compare the results with theoretical calculations of the spin density distribution in the lowest triplet state of PBQ.

5. Cross relaxation nuclear double resonance (CRENDOR)

An important advantage of ENDOR experiments

over EPR hyperfine measurements is that, knowing the electron spin state wherein the nuclear transitions occur one can determine directly the absolute sign of the hyperfine coupling constants. In PBQ- h_4 we observe strong ENDOR transitions on the EPR low field ($|0\rangle \leftrightarrow |-1\rangle$) line and weak ENDOR transitions on the high field ($|+1\rangle \leftrightarrow |0\rangle$) line. However, both set of transitions are found on the same side of the free proton ENDOR signal and thus occur in the same electron spin state. Although one would guess from intensity considerations that the ENDOR transitions observed were due to nuclear spin flips in the $|-1\rangle$ state (strong field approximation), definite proof for this assumption was lacking.

We have however obtained such proof from the observation of r.f. induced changes in the cross relaxation signal, where the electron spin state, in which the nuclear spin flips were induced, was known.

For a magnetic field parallel to the z -axis of one of the PBQ- h_4 molecules in the unit cell, at a field value that corresponds to $\sim \frac{1}{2} D$ the energy gap between the $|0\rangle$ and $|+1\rangle$ electron spin levels (high field approximation) is identical to the Zeeman splitting in a doublet spin system. At this point cross relaxation [19] (population exchange) between the triplet excited molecule and this doublet spin system can occur which is observed as an increase in the phosphorescence intensity from the PBQ-molecule monitored (see fig. 2). As cross relaxation is a nuclear spin conserving process, the transitions in the triplet and radical spin system thus take place between electron spin states of the same nuclear spin configuration. If for some reason (e.g., temperature) the population of the nuclear spin states is different, r.f. induced nuclear spin flips will change the population of the cross relaxing electron-nuclear spin state and thus modulate the cross relaxation signal intensity. The results of such an experiment are also shown in fig. 3 and as we know now that these nuclear spin flips must occur in the $|+1\rangle$ electron spin state the results are unambiguous. This CRENDOR experiment thus shows that the ENDOR transitions that we observe (see also fig. 3) indeed occur in the $|-1\rangle$ electron spin state as was guessed. An angular dependent CRENDOR study can be made in the case of PBQ- h_4 and the results obtained are in very good agreement with those predicted on basis of the results of our ENDOR experiments.

This new CRENDOR technique may thus be help-

ful in obtaining additional information regarding hyperfine interactions in excited states. We expect such r.f. induced nuclear spin flips also to be observable in the doublet spin system.

6. Experimental

The *p*-benzoquinone isotopic mixed crystals were grown from a Bridgeman furnace and cleaved or cut with a sharp razor blade in the desired direction.

Optical detection of EPR and ENDOR was accomplished as follows: The PBQ crystal was mounted against a rotatable quartz light pipe inside a quartz cold finger tip glass dewar of the type used by Hornig et al. [20], and excited with a 1000 watt Xenon lamp through the bottom of the cavity. The excitation light was filtered by the Corning filters 4-72 and 7-54 and the total phosphorescence output was detected through a Corning filter 3-71 by a Philips 150 UVP photomultiplier. Field measurements were made using an AEG proton flux meter, while EPR frequency measurements were made with an HP 340B transfer oscillator, a 30 MHz Dymec transfer oscillator synchronizer and an HP 5245 L electronic counter. Measurements below 750 gauss were not possible due to lack of a probe in this area. The ENDOR set up used, basically consisted out of a Varian-E9 EPR spectrometer and a HP 8601 A (100 kHz–110 MHz) sweep generator. The output of the HP 8601 A was amplified by an IFI M 5000 wide band amplifier (max. output 10 watt) and fed into the ENDOR coil that was in series with a 50 Ω terminating resistor.

The ENDOR coil mounted inside the dewar consisted out of three windings in the center of which was the sample. Optimum ENDOR signals were obtained through 1 kHz FM modulation of the r.f. source while using a microwave power of 2–10 mW. At 4.2 K optical detection of EPR signals of the g -inversion level was just possible, but all the ENDOR experiments on the g -inversion level reported here were performed at ~ 1.8 K.

7. Summary and conclusions

This paper contains the results of EPR and proton ENDOR experiments on the lowest inversion levels

of the *p*-benzoquinone- h_4 triplet state in an isotopic mixed crystal.

An interesting conclusion of the present study is that the molecule in its lowest excited state is non-planar, much like what would be expected if *p*-benzoquinone would be considered as a formaldehyde dimer.

Our experiments further show that the deuteration effects observed on the fine-structure and *g*-tensor principal values are due to the widely different values that these parameters attain in both inversion levels.

The proton ENDOR experiments have also shown the expected delocalization of the n -electron density throughout the molecular frame to occur.

Finally we expect the reported CRENDOR effects occasionally to be a useful tool in the study of hyperfine interactions in excited states.

We consider the results reported here a first step towards our goal of a better understanding of the pseudo Jahn-Teller effects that occur in the lowest triplet state of *p*-benzoquinone. In a forthcoming paper (part III of this series) we will present additional results of proton, carbon-13 and oxygen-17 ENDOR experiments on isotopic species of *p*-benzoquinone.

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