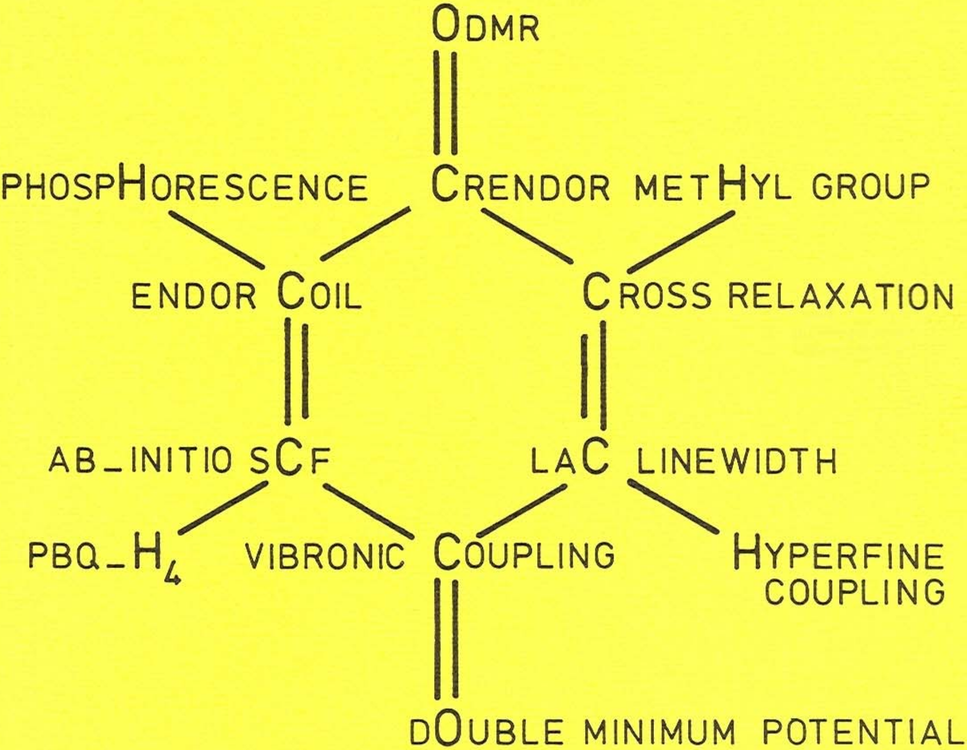
ODMR of PBQ

Optically Detected Magnetic Resonance of
para-benzoquinone in its lowest nπ* triplet state



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proefschrift

ter verkrijging van het doctoraat
in de wiskunde en natuurwetenschappen
aan de Rijksuniversiteit te Groningen
op gezag van de
Rector Magnificus Dr. L.J. Engels
in het openbaar te verdedigen op
vrijdag 13 mei 1983
des namiddags te 2.45 uur precies

door

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geboren te Utrecht

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CHAPTER 1 INTRODUCTION AND SUMMARY

Many interesting optical measurements [1-9] were made in the past two decennia on the aromatic diketone p-benzoquinone PBQ (fig. 1). By a symmetric and asymmetric combination of the two n-orbitals in PBQ there are two electronic nπ* states with B_{1g}- and A_u-symmetry (with D_{2h} symmetry for PBQ). Trommsdorff [2] was the first to propose that the lower nπ* (singlet) states in PBQ crystals, contrary to the accepted view at that time [3], were near-degenerate. There are nowadays two different interpretations of the observed close lying states of opposite parity.

The first one is proposed by Dunn and Francis [4] and more recently by Goodman and Brus [5]. They interpret the two states to be purely electronic without any interacting nuclear motion. The fact that the electronic levels are close ($\lesssim 20\ \mathrm{cm}^{-1}$) is caused by the localized nature of the nπ* excitations.

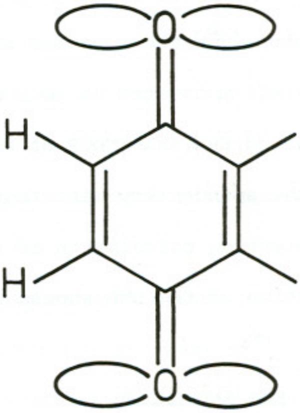

Fig. 1. *p-Benzoquinone*

The second interpretation was proposed by Hochstrasser et al. [6] and independently by Veenvliet and Wiersma [7]. They include a vibronic coupling between the two electronic B_{1g} and A_u nπ* (triplet) states. This coupling is so strong that the potential energy surface of the lowest B_{1g} state contains a double minimum potential (DMP) well along a b_{1u} type nuclear motion. Such a DMP can be shown to be formed under conditions where the electronic and nuclear motion are strongly correlated [8]. The g- and u-vibronic inversion states of the DMP of the lowest nπ* B_{1g} state have B_{1g}- and a little higher in energy ($\lesssim 20\ \mathrm{cm}^{-1}$),

A_u-symmetry.

Merienne-Lafore and Trommsdorff [9] performed a theoretical calculation which showed that for the description of the two nearly degenerate $n\pi^*$ B_{1g} and A_u states the molecule could approximately be considered as a dimer. Ter Horst et al. [10] confirmed this recently with a supersonic jet experiment.

In this vibronic picture a small symmetry disturbance, by e.g. asymmetric isotope substitution, will have a large influence on the DMP. It will be accompanied with a relative large change in the optical spectra [1-10] and the magnetic properties. The Optically Detected Magnetic Resonance (ODMR) spectra [7^b] shows indeed a large isotope dependence.

This all motivated us to a detailed magnetic resonance study, like optically detected EPR and ENDOR of PBQ in its lowest $n\pi^*$ triplet state, which gives us the spindensity distribution in this state. In combination with a theoretical calculation of the ab-initio molecular orbitals further identification of the DMP should be possible.

1.1. EPR AND ENDOR

Isotopic species of PBQ like: PBQ-h_4, -dh_3, -2,6 d_2h_2, -d_3h, -CH_3, -^{13}C and -^{17}O using PBQ-d_4 as a host crystal were used in the study of the zero-point (g-inversion) level of the lowest triplet state in PBQ at 1.8 K. Primarily the optically detected EPR and ENDOR of the protons and ^{13}C were performed. The EPR shows the zero field splitting- or fine structure parameter D to be very sensititve to deuterium and ^{13}C isotope substitution but *not* to ^{17}O- or ^{18}O-substitutions. Our interpretation of this isotope effect is that the oxygen atom is at rest in the b_{1u} mode that vibronically mixes the near degenerate $n\pi^*$ triplet states. This is in contrast with the assumptions of an asymmetric C=O b_{1u} vibronic mode proposed by other authors [7,10]. At 4.2 K a second, larger fine structure parameter D was determined from the EPR spectra. This could be from the other A_u inversion level. This was confirmed by optical experiments by Veenvliet and Wiersma [7] and lateron by rotary spin echo experiments by van 't Hof and Schmidt [11]. The crystal site has C_i inversion symmetry and the proton- and ^{13}C-ENDOR experiments showed that the $n\pi^*$ triplet state of PBQ-h_4 as guest in PBQ-d_4 has a *chairform* with the carbonyl group in the crystal cleavage plane. V. Bolhuis and Kiers [12] improved the earlier crystal structure measurements [13] at 77 K and showed the ground state structure to be a chair form too. Such a chair form was not found in the $n\pi^*$ singlet state as studied in a supersonic beam by Ter Horst et al. [10]. The ENDOR data of the isotope- and CH_3-substitutions in PBQ show that monosubstitution leaves the C_{2v} symmetry of the unsubstituted half of the molecule virutally intact. This favours the hypothesis of Merienne-Lafore and Trommsdorff [9] that PBQ may be considered as a dimer for its lowest $n\pi^*$ singlet and triplet states. The hyperfine data, in combination with ab-initio calculations, can be explained by assuming a slight "localization" of the $n\pi^*$ excitation on the oxygen at the substituted fragment.

1.2. HYPERFINE CALCULATIONS

The calculated ab-initio molecular orbitals [14] for the unpaired n- and π-orbitals yield hyperfine interaction constants that compare very nicely with the experimentally observed ones. These ab-initio results were further analyzed in terms of atomic contributions which give insight into the limitations of the semi-empirical analysis of the ENDOR data. Especially the different spin distribution of the n- and π-orbitals will lead to different atomic interaction constants for the anisotropic hyperfine interaction for e.g. oxygen and carbon of the carbonyl group in PBQ.

The semi-empirical calculation of the isotropic proton hyperfine data, however, fails completely. It lacks completely the large (extra) contribution of the neighbouring carbon 2s orbital.

The π-unpaired electron is almost equally divided among the carbonyl groups and the central ring system in contrast with the unpaired n-electron density which is largely confined (75%) to the oxygen atoms.

1.3. CRENDOR

A high degree of nuclear spin polarization can be achieved at a magnetic field where cross-relaxation occurs between a triplet excited PBQ molecule and a doublet spin system (which is photochemically induced). By a radio frequency this polarization can induce a phosphorescence change which we call Cross RElaxation Nuclear Double Resonance (CRENDOR).

In principle this, newly found, phenomenon gives the same information as the "high field" ENDOR experiments except that the CRENDOR is detected at lower magnetic fields and also possible from a different electronic state (e.g. $m_s = -1$ for ENDOR and $m_s = +1$ for CRENDOR).

For some crystal orientations detection of the ENDOR signal was not possible because of a too low signal to noise ratio but, by the larger polarization, CRENDOR detection was still possible. This made a better inter- and extrapolation possible of the hyperfine data at crystal orientations where neither ENDOR nor CRENDOR was possible.

1.4. LAC

The level-anti-crossing (LAC) of the lowest $n\pi^*$ triplet state of PBQ only shows a broad line. This is the result of a combination of a number of LAC's of the mixing of electronic-nuclear states through the hyperfine interaction and/or magnetig field misorientations.

A combination of a low frequency EPR (up to 100 MHz) and a prediction of the LAC signal, by an exact calculation with the known (hyper-)fine structure parameters, shows a disorder of 0.9° of the PBQ's of the molecular plane.

1.5. METHYL TUNNELING ROTATION

In experiments on toluquinone (TOL, which is a mono methyl substituted PBQ) a methyl tunneling rotation is seen in the ENDOR experiments. This phenomenon was previously extensively studied in doublet radicals with methyl groups by Clough et al. [15].

A tunneling frequency 3J of 2.9 GHz was derived from the TOL ENDOR spectra, corresponding to a torsional oscillator barrier of 2.77 kJ/mol, which shows that rotation of the methyl group at 1.8 K is strongly hindered.

A special optically detected triplet methylgroup tunneling phenomenon are the LAC side bands which are interpreted by a cross-relaxation between the lowest rotational $|A\rangle$ states with the higher $|E\rangle$ states (with local methyl C_3symmetry) of translationally equivalent molecules.

1.6. MAGNETIC RESONANCE THEORY AND EXPERIMENTAL

To complete this thesis an extended chapter on magnetic resonance theory is given. Exact equations for the triplet EPR-, LAC- and cross relaxation are derived. First order- and exact calculations of ENDOR- and CRENDOR transitions are given. And the 24th order spin hamiltonian matrix of the methyl group rotation in the tiplet system is derived. This hamiltonian is used for the second order perturbation energies from which the tunneling frequency 3J and the methyl group hyperfine data are derived.

In the experimental part, the NMR coil impedance matching conditions are theoretically derived for the frequency dependent ENDOR experiments. This leads to the conclusion, after all, that the best way to confirm ENDOR experiments is to use a few-winding-coil and a resistance in serie with an impedance equal to the impedance of the power amplifier. A new detail is that the length of the coaxial cables used *has to* be changed outside a special frequency range to avoid to much power reflections, and to optimize NMR field strength.

1.7. CONCLUSION

The optically detected EPR data of para-benzoquinone (PBQ) in its lowest $n\pi^*$ triplet state at 1.8 K showed the fine structure parameter D to be very sensitive to mild substitutions, but insensitive to ^{17}O- or ^{18}O-substitutions. This shows that the b_{1u} vibronic coupling mode, which mixes the near degenerate $n\pi^*$ triplet states is not the asymmetric carbonyl mode, but more likely one of the four other (mixed) b_{1u} modes.

The ENDOR data of PBQ showed that a mild substitution leaves the C_{2v} symmetry at the unsubstituted half of the molecule intact, which favours the dimer or Double Minimum Potential (DMP) model of PBQ.

Hyperfine constants calculated by ab-initio are comparable with the experimental ENDOR hyperfine constants and showed the π^*-unpaird electron to be spread over the molecule, while the unpaired n-electron is largely localized on the oxygen atoms.

The newly discoverd Cross RElaxation Double Resonance (CRENDOR) technique makes the inversion of an electronic into nuclear polarization possible, by a cross relaxation between a triplet and a doublet system. This electronic polarization enlarges the sensitivity of the optically detected nuclear transition. And this results in an improvement of the ENDOR data.

The low frequency EPR near the Level Anti Cross (LAC) signal exhibits a lineform which could be simulated by assuming a disorder of 0.9° in the tilt of the PBQ molecular planes.

The relatively strong dependence of the EPR and ENDOR spectra on mild substitutions favour the interpretation of the DMP of the lowest $n\pi^*$ B_{1g} triplet state of PBQ as guest in PBQ-d_4 at 1.8 K. The final conclusion is that the magnetic resonance data in the lowest $n\pi^*$ triplet state in PBQ favour the interpretation of this level as a vibronic strongly pertubated state.

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