ISOTROPIC AND ANISOTROPIC CHLORINE HYPERFINE COUPLING OF DICHLORO-DICYANO BENZOQUINONE ANION RADICAL*

Carlo CORVAJA, Luigi PASIMENI and Marina BRUSTOLON Institute of Physical Chemistry, University of Padova, Italy

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The ESR spectrum of 2,3-dichloro-5,6-dicyano benzoquinone anion has been recorded in the isotropic and in the nematic phase of liquid crystal solvents. In the isotropic phase it shows splitting only by two ¹⁴N nuclei, while in the nematic phase at high orientation degree, the pattern is that expected for hyperfine coupling with two chlorine nuclei. The orientation of the free radical in the nematic solvent is inferred from the variation of the ¹⁴N splitting.

The chlorine anisotropic coupling is used to get the unpaired electron spin density on the chlorine π orbital and the isotropic coupling is discussed in terms of a relationship analogous to that proposed by Karplus and Fraenkel for ¹³C.

1. Introduction

Hyperfine splitting by chlorine nuclei is rarely observed in the ESR spectra of chlorine substituted radical anions, even if the chlorine atom is substituted in a position of high spin density. Thus for chlorosemiquinones chlorine splittings has been resolved in very few cases [1].

The reason of this behaviour is not clear, since little information is available on the mechanism of spin transfer to the chlorine nucleus. The lack of hyperfine structure has been also attributed to rapid quadrupole relaxation caused by the molecular tumbling motion, which should collapse the hyperfine levels; broadening effects attributable to quadrupole relaxation to support this assumption have been reported [1].

In the course of an investigation on the radical anion of 2,3-dichloro-5,6-dicyano benzoquinone (DDQ) we were puzzled by the remarkably narrow ESR lines, which do not show splitting by the chlorine nuclei. In order to investigate the anisotropic part of the hyperfine coupling, we have extended the study of DDQ in the nematic phase of a liquid crystal where a chlorine splitting was indeed observed. A complete understanding of the spin distribution in DDQ is also interesting because the DDQ salts are among the very few systems which exhibit the triplet exciton behaviour [2].

2. Experimental

Brown crystals of DDQ tetramethyl ammonium salt were prepared by the reaction under vacuum of DDQ with an equimolar amount of tetramethyl ammonium iodide in acetone [2]. A few milligrams of the salt were dissolved in acetone dimethoxyethane (DME) mixture, or in the appropriate solvent; the solution was carefully degassed by the pumping and freezing technique. The 2,3-dicyano-1,4-benzoquinone (DCQ) anion was prepared by oxidation of the corresponding dianion in DME with iodine. Potassium *t*butoxide was added to the solution of the hydroquinone to form the dianion.

The ESR spectra were recorded with a JEOL-PE-3X spectrometer equipped with variable temperature accessories; the temperature was controlled by a thermocouple. The magnetic field was calibrated by an NMR gaussmeter (Harwey Well G 202) whose frequency was monitored by a Hewlett Packard 5245-L counter. g factors were measured by reference with the signal of a water solution of Fremy's salt

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(g = 2.005665). Some of the spectra have been recorded with a 15 kHz modulation unit to allow for careful linewidth analysis.

3. Results

The ESR spectrum of the DDQ anion in acetone-DME mixture consists of five lines due to the hyperfine coupling of the unpaired electron with two equivalent ¹⁴N nuclei. Satellites due to ¹³C occurring in the natural isotopic mixture in three different positions in the molecule were observed. The spectrum, with the ¹³C satellites, is reported in fig. 1. With 15 kHz modulation, a linewidth of 80 mG was measured. The spectrum was registered also at low temperature. The ¹³C lines broaden, the widening affecting less the external multiplet.

The same spectrum was obtained for DDQ anion dissolved in the isotropic phase of butyl p-(pethoxyphenoxycarbonyl)-phenyl carbonate (BPC) and of p-azoxyanisole (PAA). When the temperature is lowered to the nematic phase of BPC one observes a decrease in the ¹⁴N splitting due to the addition of anisotropic contributions of opposite sign to the isotropic coupling. Upon further cooling the spectrum collapses into a single broad line. In PAA a single broad



Fig. 1. ESR spectrum of DDQ in DME-acetone mixture. The wings of the spectrum are recorded with an amplification 100 times that for the central part to display the ¹³C satellite lines.



Fig. 2. Experimental (top) and computer simulated ESR spectrum of DDQ in the nematic phase of PAA at 118°C.

line is observed just below the isotropic--nematic transition temperature; on further cooling the line is split in a complex structure which is well reproduced by assuming a coupling by two equivalent chlorine nuclei. The experimental spectrum and its computer simulation taking into account the natural isotopic distribution of 35 Cl and 37 Cl are shown in fig. 2. The agreement is good even if not perfect. The discre-





	Experimental					Calculated b)					
۹.	a _N	a _H	$a_{\rm C}^1$	a ² C	a ³ C	a _N	a _H	a ^{CN} C	aCO CO	^a C ^H	^a C ^{−CŃ}
DQ C)	0.57		4.58	4.11	2.80	0.456		-3.82	-3.23		0.83
CQ d)	0.61	1.05	4.83	3.89	_	0.456	-1.58	-3.82	-3.23	-1.07	0.83

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a) The values are given in gauss. b) McLachlan spin densities and standard Q parameters [4,5] were used. c) Experimental hyperfine splitting constants from spectra in DME/acetone mixture. d) Experimental hyperfine splitting constant from spectra in DME.

pancies are probably due to different linewidths of the different hyperfine components, which we did not take into account in the calculations.

The 35 Cl hyperfine splitting constant one gets from the simulation is $a_{Cl} = 0.279$ gauss.

In the nematic phase we were unable to detect the ^{13}C satellites structure.

On passing from the isotropic to the nematic phase of PAA we observe also a variation in the g factor from 2.00519 to 2.00566 (at 126°C).

The ESR spectrum of the DCQ anion (fig. 3) which was recorded for comparison consists of 15 lines arising from the hyperfine splitting by two equivalent nitrogen nuclei and two equivalent protons. Only two sets of $1^{3}C$ satellites were detected.

The hyperfine splitting constants of the two radicals in isotropic solutions are reported in table 1.

4. Discussion

Table 1

4.1. ¹³C hyperfine splitting constants

A discussion of the ¹³C hyperfine splittings is useful to get an insight into the spin distribution of the DDQ anion which will be used to investigate the relation of the chlorine hyperfine coupling with the spin density.

A McLachlan calculation [3] of the spin density distribution in the DDQ and DCQ anions was performed. With these values the ¹³C hyperfine constants of table 1 are calculated according to the Karplus and Fraenkel equation (4):

$$a_{\mathbf{C}} = \left(S + \sum_{\mathbf{X}} Q_{\mathbf{C}\mathbf{X}}^{\mathbf{C}}\right) \rho_{\mathbf{C}}^{\pi} + \sum_{\mathbf{X}} Q_{\mathbf{X}\mathbf{C}}^{\mathbf{C}} \rho_{\mathbf{X}}^{\pi}.$$
 (1)

The Q's were taken from the literature [5]. The

agreement with the experiment is not very good; however, we did not try to improve the calculations because of the rather large number of parameters involved. The results qualitatively show that for both radicals the largest splitting should be attributed to 13 C in the CN position; an assignment which is supported by the fact that the lines of the external satellite multiplet are the narrowest at low temperature, as reported above.

In fact the modulation of the anisotropic ${}^{13}C$ hyperfine splitting constant is expected to be less effective for this ${}^{13}C$ because of the very small "local" spin density or the CN carbons [6]. Probably the smallest splitting (2.80 G), which is not detected in the spectrum of DCQ is due to ${}^{13}C$ bonded to the chlorine atom. The lack of literature data for Qparameters involving the C--Cl bond prevents any reliable calculation.

It is interesting to note that the chlorine substitution has only little effect on the spin distribution, as reflected by the very small (~5%) variation of the ¹³C and ¹⁴N splitting constants. This result is in agreement with previous observations [1]. It is therefore reasonable to assume that the spin density on the carbon atom to which a chlorine atom is bonded is the same as in the DCQ anion. For the latter we obtain $\rho_{\rm C}^{\pi} \approx 0.047$ from the proton splitting through the McConnell equation, with a Q value of -23 G.

4.2. Orientation of the DDQ radical anion in the nematic phase

The hyperfine splitting constant of a nucleus of a partially oriented radical is given by [7]

$$a = a_{iso} + \mathcal{D}_{0,0}^{(2)} A_{zz} + (\mathcal{D}_{0,2}^{(2)} + \mathcal{D}_{0,-2}^{(2)}) (A_{xx} - A_{yy}), (2)$$

where the $\mathcal{D}_{0,\mu}^{(2)}(\mu=0,\pm 2)$ are the second rank sphetical tensor components of the orientation matrix, and the A_{ii} are the principal values of the anisotropic hyperfine tensor. When the latter has axial symmetry $(A_{xx} = A_{yy})$ the third term vanishes and eq. (2) reduces to:

$$a = a_{iso} + \mathcal{D}_{0,0}^{(2)} A_{zz} . \tag{3}$$

Completely analogous relationships hold for the g factor.

The nitrogen hyperfine tensor of a cyano group is axially symmetric because the most important contribution to the anisotropic tensor comes from the "local" spin density on the nitrogen p_z orbital. "Non-local" contributions are small because of the small spin density on the nitrilic carbon. We use therefore in this case eq. (3).

The values of the nitrogen tensor components of the DDQ anion are not known; however they can be obtained with rather good confidence by comparison with other cyano substituted radicals as tetracyano ethylene (TCNE) (8), tetracyano quinodimethane (TCNQ) and 3,4-bis(dicyanomethylene)cyclobutane-1, 2-dione (BDCB) [9] for which the tensor components were measured in rigid glass matrix. In these systems there is a rough proportionality between isotropic and anisotropic hyperfine constants, the latter being about three times larger. If we assume that the same occurs for DDQ, from the isotropic constant of 0.56 G we get $A_{zz_{ex}} = 1.70$ G, which substituted into eq. (3) gives $\mathcal{D}_{0,0}^{(2)}$. The values we obtain are -0.16 for BPC and -0.3 for PAA. The g factor of DDQ is not expected to be axially symmetric so that its variation in going to the nematic phase should be accounted for by eq. (2). However if the orientation matrix is axially symmetric, the term $(\mathcal{D}_{0,2}^{(2)} + \mathcal{D}_{0,-2}^{(2)})$ is equal to zero, which should be approximately the case because of the shape of the radical.

Therefore an equation analogous to (3) can be used.

On passing from the isotropic to the nematic phase of PAA (126°C) we observe a variation of the g factor from 2.00519 to 2.00566. The increase is consistent with a g_z component lower than g_x and g_y as it should be the case for π electron systems. Using eq. (3) with $\mathcal{D}_{0,0}^{(2)} = -0.3$ one gets $g_z = 2.0036$.

4.3. Quadrupole relaxation

Before discussing in detail the chlorine hyperfine

coupling it is important to make sure whether the splitting we observe in the nematic phase is due only to dipolar interaction, or if it contains a contribution from the isotropic coupling. The latter would be the case if the lack of splitting in the isotropic phase was due to the averaging out of the structure by rapid quadrupole relaxation. In a free radical containing a single nucleus with a nuclear spin I > 1 and a quadrupole coupling tensor Q, the quadrupole contribution to the width of a hyperfine component is given by [10,11]:

$$(1/\dot{T}_2)_Q = 4 \left(f_1(I,M) \sum_m |F_Q^{(m)}|^2 j_{1m} + f_2(I,M) \sum_m |F_Q^{(m)}|^2 j_{2m} \right),$$
(4)

where

$$f_1(I, M) = I(I+1)(1+4M^2) - 5M^2 - 4M^4$$

$$f_2(I, M) = I(I+1)[I(I+1) - 2M^2 - 2] + 5M^2 + M^4$$

and $F_Q^{(m)}(m=0, \pm 2)$ are the spherical components of the quadrupolar tensor Q.

 j_{1m} and j_{2m} are the Fourier transforms of the correlation functions of the Wigner rotation matrices:

$$j_{qm} = \frac{1}{2} \int \langle \mathcal{D}^{(2)}_{-qm}(t) \mathcal{D}^{(2)}_{-qm}(t+\tau) \rangle e^{i\omega\tau} d\tau .$$

With the usual assumption of an exponential decay of the correlation function, j_{qm} will depend on the average values of the Wigner rotation matrices over the Euler angles describing the orientation of the free radical. Therefore the spectral densities are in principle different for an isotropic and a nematic phase.

When I = 3/2 as it is the case for ³⁵Cl

$$f_1(I,M) = f_2(I,M)$$

and

$$f_{1,2}(3/2,\pm 3/2) = f_{1,2}(3/2,\pm 1/2) = 6$$

so that the linewidth contribution is the same for all components and eq. (4) reduces to:

$$(1/T_2)_Q = 24 \left(\sum_m |F_Q^{(m)}|^2 (j_{1m} + j_{2m}) \right).$$
 (5)

The quadrupole coupling constant of 35 Cl in DDQ has been determined to be 76.7 MHz [12].

If this value is introduced in eq. (5) for the case of

an isotropic tumbling motion in an isotropic liquid (for which case $j_{1m} = j_{2m} = 1/30$) one obtains $(1/T_2)_Q$ = 0.006 MHz. The result does not change considerably if one assumes an anisotropic diffusion tensor, accounting for a molecular shape different from the spherical one.

Since in order to have a complete averaging of the hyperfine structure due to a hyperfine splitting constant a by the quadrupolar relaxation process the condition should be fulfilled

$$(1/T_2)_O \geq a ,$$

we conclude that the single line we observe in the isotropic phase is not a collapsed quartet and that the isotropic ^{3S}Cl coupling is very small or zero, and therefore the chlorine hyperfine splitting constant we measure there is only due to dipolar interaction.

The above analysis was made for a free radical containing a single Cl nucleus; when more are present some complications may arise when they are equivalent because the relaxation matrix is no longer diagonal. However, the behaviour is expected to remain qualitatively the same.

4.4. The chlorine hyperfine coupling

The isotropic hyperfine coupling of a chlorine nucleus is accounted for by an equation similar to that proposed by Karplus and Fraenkel for ^{13}C

$$a_{\rm CI} = Q \,\rho_{\rm CI}^{\pi} + Q_{\rm CCI}^{\rm C1} \,\rho_{\rm C}^{\pi} \,. \tag{6}$$

Some authors have neglected the first term of this equation because of the smallness of ρ_{Cl}^{π} as calculated by the McLachlan procedure [13]. However, according to our following analysis it seems that the value of ρ_{Cl}^{π} one obtains with McLachlan calculations is too small and that it is not correct to neglect this term.

It is possible to get a more reliable value for ρ_{Cl}^{π} from the anisotropic experimental splitting in the nematic phase.

From the ESR spectra of the CICHCOOH radical trapped in a single crystal, Kohin [15] has shown that the largest contribution to the anisotropic coupling of the Cl nucleus arises from the spin density on the chlorine $3p_z$ orbital.

The contribution to the anisotropic coupling from the spin density on the chlorine atom ρ_{Cl}^{π} has axial symmetry with a calculated principal value in the z

direction
$$A_{zz}^{Cl} = 100\rho_{Cl}^{\pi}$$
 [16]. Since
 $\alpha_{Cl} = \mathcal{O}_{0,0}^{(2)} A_{zz}^{Cl}$, (7)

from the observed splitting in the nematic phase of PAA and with $\mathcal{D}_{0,0}^{(2)} = -0.3$, one gest a spin density $\rho_{Cl}^{\pi} = 0.009$ which is more than four times larger than that calculated by the McLachlan procedure.

Wc conclude that, the chiorine hyperfine splitting constant for being zero, the two terms in eq. (6) must be equal and opposite in sign.

By using the experimental values of the ρ 's we can obtain the ratio Q/Q' that results to be -5.

From this ratio we can guess the relative magnitudes of the different terms contributing to Q.

The values of Q stems from the sum of three terms:

$$Q = S + Q_{\text{CIC}}^{\text{CI}}(\sigma) + 2Q_{\text{CIC}}^{\text{CI}}(1p), \qquad (8)$$

in which the first one represents the polarization by the unpaired spin density in the chlorine π orbital on the inner core s orbitals of chlorine and the other ones that of the C-Cl bond and of the chlorine lone pair orbitals respectively.

We can estimate S from the isotropic hyperfine coupling of chlorine atoms in their ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ states, as measured by molecular beam experiments [17,18].

It is possible to show that for an atom with nuclear spin $I \neq 0$, with an unpaired electron in an *n*p orbital, the hyperfine splitting constant due to the polarization of the s shells electrons is given by

$$A(n^{2}P) = \frac{1}{2}(5a_{3/2} - a_{1/2}), \qquad (9)$$

where $a_{3/2}$ and $a_{1/2}$ are the hyperfine splittings in the ${}^{2}P_{3/2}$ and ${}^{2}P_{1/2}$ states.

From the data in the literature [17,18] one gets

$$A^{Cl}(3^{2}P) = -5.9 G$$

This value is actually slightly different from S, since inner core s orbitals are different in unbonded and bonded atoms, and it takes into account also valence shell 3s orbital polarization.

Nevertheless, the actual difference from S should be quite small, and we conclude therefore that Sshould not be bigger than a few gauss.

Following the theory for the ¹³C hyperfine splitting, one can guess the approximate magnitudes of chlorine $Q_{CIC}^{CI}(\sigma)$ and Q_{CCI}^{CI} .

Provided that the hybridization parameters are about

Since their values are expected to be very close [20], we can conclude that (i) they should be of the same order of ^{13}C parameters [4], and (ii) they should be very similar.

In order to have Q a few times larger than $Q_{CC1}^{Cl}(\sigma)$, $Q_{CIC}^{Cl}(lp)$ must therefore give a contribution of the same order of $Q_{CCC}^{Cl}(\sigma)$.

It is worth to observe that the relation

$$Q_{\rm CC1}^{\rm Cl}\rho_{\rm C}=-Q\rho_{\rm C1}$$

is probably more or less satisfied for all π organic radicals containing chlorine atoms bonded to π -carbon atoms, since the spin density ratio $\rho_{Cl}^{\pi}/\rho_{C}^{\pi}$ is probably almost constant.

This fact might explain the very small or zero values of the chlorine hyperfine splitting constant generally found in this kind of radicals.

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