The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/142126

Please be advised that this information was generated on 2019-04-07 and may be subject to change.
'H and 2D N.M.R. studies of the radical anions of biphenyl, fluorenone and phenanthrene

by G. W. CANTERS†, B. M. P. HENDRIKS, J. W. M. DE BOER
and E. DE BOER

Department of Physical Chemistry, University of Nijmegen,
The Netherlands

(Received 8 December 1972)

The proton N.M.R. spectra of biphenyl−, fluorenone− and phenanthrene− and the deuterium N.M.R. spectra of biphenyl-d10− and phenanthrene-d10− have been measured in ethereal solutions at room temperature. Sign and magnitude of the hyperfine splitting constants derived from the measured contact shifts are reported and compared with E.S.R. data and predictions from theory. From the measured proton and deuterium relaxation times values for the electron spin and the rotational correlation times have been obtained.

1. INTRODUCTION

In recent years N.M.R. techniques have been applied successfully to the study of radicals in solution [1]. Direction and magnitude of the contact shift give direct information about sign and magnitude of the Fermi contact interaction and thus about the distribution of the unpaired electron in the radical, while from the width of the N.M.R. signals important information about dynamic processes in solution can be obtained.

In practice the width of the signals is determined by the relatively large interactions of the nuclei with the unpaired electron. To obtain detectable signals these interactions have to be averaged out to a large extent by some time-dependent mechanism, for instance the electron spin relaxation process. A sufficient condition for sharp signals is that the electron spin correlation time \( \tau_e \) is short compared with the inverse of the interaction matrix elements expressed in frequency units.

In order to obtain sufficiently short \( \tau_e \)'s Kreilick used the liquid radical di-tertiarybutylnitroxide (DBNO) as a solvent [2]. Modulation of the Heisenberg exchange interaction between electrons on different radicals by random Brownian motion yielded \( \tau_e \)'s in the order of \( 10^{-11} \) s. Using in this way the solvent, as a 'spin relaxer' a number of neutral free radicals like the nitroxide and phenoxide radicals could be studied extensively by N.M.R. [2].

At the same time a slightly different technique was employed by others in the study of solutions of alkali radical ion pairs in ethereal solvents [3, 4]. Using sufficiently high radical concentrations (of the order of 1 M) again values of \( \tau_e \)

† Gorlaeus Laboratoria, Rijksuniversiteit, Leiden, The Netherlands.
of the order of $10^{-10} - 10^{-11}$ s could be obtained: the radical acts as its own spin relaxer. The two techniques are more or less complementary since it proved impossible up to now to prepare stable solutions of alkali radical ion pairs in DBNO. It appeared later on that the resolution in the proton N.M.R. spectra of radicals can be improved by employing deuterium N.M.R. [5] on the partly or completely deuterated radicals [6]. This opened up the possibility to measure the spectrum of a radical ion pair at relatively low concentrations by utilizing a high concentration of a second radical ion pair as a spin relaxer. If one species is deuterated and the other not the spectra of the two radicals do not interfere [7].

In the past proton or deuterium N.M.R. spectra have been measured of the radical ions of 1,3,5-triphenylbenzene [8], and naphthalene [7], while preliminary results were reported for biphenyl [3, 6]. Here we report on proton N.M.R. experiments on solutions of the Li and Na salts of biphenyl (Bp), fluorenone (Fl) and phenanthrene (Pht). Also deuterium N.M.R. experiments were performed on solutions of the radical anions of perdeutero-biphenyl and perdeutero-phenanthrene. It will be shown that the N.M.R. data essentially agree with results from E.S.R. measurements and with predictions from theory. A careful analysis is undertaken of the relaxation data measured on a sample containing a mixture of the anions of Bp–h10 and Bp–d10 after which the line-width data of the other systems are shortly discussed.

2. Theory

2.1. Contact shift

The contact shift in magnetic induction units, $\delta_c^0$, of a nucleus in a radical with electronic spin quantum number $S$ is given by [9]

$$\delta_c^0 = -\frac{\gamma_e}{\gamma_N} \frac{g \mu_B B_p}{3kT} S(S+1)$$

(1)

in which $B_p$ is the field at which resonance occurs and the other symbols have their usual meaning. $\delta_c^0$ is defined by

$$\delta_c^0 = B_p(1-\sigma_p) - B_0(1-\sigma_0) \approx (B_p - B_0) - B_0(\sigma_0 - \sigma_p),$$

(2)

where $B_0$ is the resonance field of the nucleus in the reference substance and $\sigma_p$ and $\sigma_0$ are the screening constants of the nucleus in the radical and the reference compound, respectively.

Equation (1) is valid provided $\tau_0 \ll (\gamma_e a)^{-1}$.

The present experiments were performed by gradually reducing a solution of the aromatic compound with an alkali metal. In partly reduced solutions electron transfer from reduced to neutral molecules usually is rapid enough to produce for a particular proton an average signal of which the shift, $\delta_c$, then is given by

$$\delta_c = f_p \delta_c^0$$

(3)
in which \( f_p \) is the fraction of the molecules reduced. From a plot of \( \delta \) versus \( f_p \), \( \delta^0 \) and subsequently the hyperfine splitting constant (hfsc), \( a \), can be determined. The spin density \( \rho \) at the adjacent carbon atom can be derived from \( a \), using the McConnell–Weissman relation [10]

\[
a = Q \cdot \rho
\]

in which \( Q \) is a constant \((-Q \approx 23-27 \text{ G} \dagger\)). Finally, it is pointed out that according to the equations (1) and (3) the ratio of the hfsc of two protons \( i \) and \( j \) can be found at any stage of the reduction from the measured contact shifts via

\[
a_i/a_j = \delta_{ij} / \delta_{ij}.
\]

In practice the contact shift \( \delta^{0} \) was measured by setting it equal to \((B_0 - B_p)\). According to equation (2) this introduces an error of \( B_0(\sigma_0 - \sigma_p) \) in \( \delta^0 \), which is shortly discussed here.

For the experiments references were used consisting of an unreduced solution of the hydrocarbon being studied. The term \((\sigma_0 - \sigma_p)\) is then determined by \([11, 12]\]

(a) the presence of cations in the reduced solution,
(b) the difference in solvation between reduced and unreduced species,
(c) the presence of an extra charge on the reduced molecule,
(d) the possible formation of ion pair clusters in the reduced solution.

The exact magnitude of these effects is difficult to establish but an estimate can be obtained from literature data.

(a + b). The electric fields produced by a cation in the vicinity of the radical and by the solvent dipoles in the solvent cage around the ion pair will affect the resonance positions of the nuclei in the radical, but in general the effect will be less than a few tenths of a p.p.m. [13].

(c) The excess charge in a reduced molecule will produce an increase in the shielding of the protons attached to it [11]. For a particular proton this increase is proportional to the excess charge present on the adjacent carbon atom. Schaefer and Schneider have shown that an excess charge of a full electron produces an increase in shielding of about 10 p.p.m. [11]. However, if the excess charge is produced by one unpaired electron, also an excess spin density is present on the C atom, which gives rise to a proton hfsc of \(-25 \text{ G}\) (see equation (4)). According to equation (1), at room temperature the proton N.M.R. signal would then be shifted to high field by an amount of 2000 p.p.m. Although particularly for C atoms bearing a small spin density, excess charge and total spin density are not necessarily equal it is clear that the excess charge will play in general a negligible role in determining the resonance positions of protons in radical ions. It will therefore be neglected throughout this paper.

(d) Finally, cluster formation of ion pairs is known to occur sometimes at concentrations \( \geq 10^{-2} \text{ M} \) [14, 15]. The resonance position of a proton in one

\[ G = 10^{-4} \text{ T}. \]
radical may then be influenced by the ring currents present in adjacent radicals. According to literature data the effect on the proton resonance positions will be smaller than 1 p.p.m. [16].

Disregarding the excess charge effect we conclude that for the experiments described here $|\sigma_0 - \sigma_p|$ will be less than 1 p.p.m. The error introduced in $\delta_0^0$ by the neglect of the term $B_0(\sigma_0 - \sigma_p)$ in equation (2) will therefore produce an error of less than 15 mG in the proton hfsc. Errors of this order of magnitude become important only for the determination of very small coupling constants. (The situation is different in the case of alkali N.M.R. experiments on alkali radical ion pairs, mainly because of the greater sensitivity of the shielding of the alkali nuclei towards the structure of the alkali ion solvation shell [17].)

2.2. Relaxation times

Relaxation times have been studied on completely reduced solutions only. Contributions to the relaxation times originate from intermolecular and intramolecular relaxation mechanisms. The contribution from the former interactions can be estimated from the width of the solvent peaks. The latter interactions, however, usually dominate and can be distinguished in the Fermi contact interaction, the anisotropic magnetic dipole interaction and the quadrupole interaction (for deuterium). Their contributions to the $T_1^{-1}$ of a proton or a deuteron in a doublet radical ($S = \frac{1}{2}$) are given by [18]

$$T_2^{-1}_{FC} = \frac{1}{4} \left( \frac{A}{\hbar} \right)^2 \left[ \tau_e + \frac{\tau_e}{1 + \omega_2^2 \tau_e^2} \right]$$

$$T_2^{-1}_D = \frac{1}{20} \left( \frac{B}{\hbar} \right)^2 \left[ 7\tau_d + \frac{13\tau_d}{1 + \omega_2^2 \tau_d^2} \right]$$

$$T_2^{-1}_Q = \frac{3}{8} \left( \frac{e^2Qq}{\hbar} \right)^2 \left[ 1 + \frac{\eta^2}{3} \right] \tau_e$$

respectively, while their contributions to the $T_1^{-1}$ of a proton are given by [18]

$$T_1^{-1}_{FC} = \frac{1}{2} \left( \frac{A}{\hbar} \right)^2 \frac{\tau_e}{1 + \omega_2^2 \tau_e^2}$$

$$T_1^{-1}_D = \frac{1}{10} \left( \frac{B}{\hbar} \right)^2 \left[ 3\tau_d + \frac{7\tau_d}{1 + \omega_2^2 \tau_d^2} \right]$$

$A$ and $B$ are defined by

$$A = \gamma J a$$

$$B = \left[ \frac{1}{8} \text{Trace} \left( \mathbf{T} \cdot \mathbf{T} \right) \right]^{1/2}$$

in which $\mathbf{T}$ is the tensor of the anisotropic dipolar interaction [8, 19]. $e^2Qq/\hbar$ is the quadrupole coupling constant (qcc) of the nucleus under consideration, $eQ$ being the quadrupole moment of the nucleus and $\varepsilon$ the electric field gradient at
the nucleus. \(\eta\) is the asymmetry parameter of the field gradient \((0 \leq \eta \leq 1)\). \(\tau_r\) is the rotational correlation time of the radical, the assumption of isotropic rotation being made, \(\tau_d\) is given by

\[
\tau_d^{-1} = \tau_e^{-1} + \tau_r^{-1},
\]

(9)

and \(\omega_e\) is defined by \(\omega_e = \gamma_e B_p\). The derivation of equation (7b) is similar to the derivation of equation (6b) [8].

3. Experimental

3.1. Apparatus

E.S.R. experiments were performed on a Varian 4502 X-band spectrometer. The N.M.R. apparatus has been described elsewhere [7]. Unless otherwise stated spectra were run at room temperature (approximately 30°C) and sample tubes were not spun.

3.2. Shift

Most of the proton spectra were measured as the derivative of the absorption spectrum. Deuterium N.M.R. spectra were recorded either as derivative spectra or directly as absorption spectra by operating in the side band mode. An example of a 2D N.M.R. absorption spectrum of a radical is shown in figure 1.

![Figure 1](image)

Figure 1. Deuterium N.M.R. spectrum of a solution of 1:1 M Na Bp-d10 in DME recorded at room temperature at 9.1 MHz in the sideband mode (modulation frequency 2 kHz). THF-d8 (see signals indicated by R) was added to the solution as an internal reference.

Resonance positions were measured by using the N.M.R. peaks of the solvent as an internal reference except for the 2D N.M.R. experiments on biphenyl-d10 where tetrahydrofuran-d8 was added to the solution as an internal reference, and except for the 2D N.M.R. experiments on phenanthrene-d10, where an external reference was employed (corrections for the difference in bulk susceptibility between sample and external reference have been taken into account). Since, in a reduced sample, the solvent peaks may be shifted somewhat by contact.
interactions with the radicals [20], a correction should be applied to $\Delta \sigma$ [21]. However, the correction usually amounts to less than 0.5 p.p.m. and has been neglected.

$f_0$ was found from the solvent shift [7].

3.3. Relaxation times

Values of $T_2^{-1}$ were obtained in most cases either by multiplying the half width at half height of the absorption signal by $\gamma_N$ or by multiplying the derivative peak-peak width $\Delta B$ by $\frac{1}{3}\sqrt{3}\gamma_N$. If the line shape is Lorentzian, values obtained in either way should be identical, as was indeed observed. Also occasionally the line shape was checked by fitting the experimental curve with a Lorentz curve over a total distance of 5–10 times the linewidth. Care was taken to avoid saturation during the linewidth measurements.

Corrections for broadening caused by finite modulation amplitude and non-zero modulation frequency were applied as described elsewhere [7, 17].

The magnitude of the correction for inhomogeneity broadening [22] was established by observing the width of the signal of the reference with and without sample spinning. Usually the inhomogeneity over the sample volume amounted to 1–2 mG.

The corrections for broadening by intermolecular interactions, mentioned in the previous section, usually amounted to 50–100 rads/s for the $^1$H measurements and 1.3–2.5 rads/s for the $^2$D measurements.

A more elaborate procedure to measure relaxation times consists of measuring $\Delta B$ as a function of the amplitude $B_1$ of the r.f. field. With $x=B_1/B_1^0$, in which $B_1^0$ is the value of $B_1$ at 0 dB, and $T_2'$ defined by $(T_2')^{-1}=\frac{1}{3}\sqrt{3}\gamma_N\Delta B$ it follows that for a Lorentzian lineshape [23]

$$\left(T_2'\right)^{-2}=T_2^{-2}+(\gamma_N B_1^0)^2 \frac{T_1}{T_2} x^2.$$  \hspace{1cm} (10)

By plotting $(T_2')^{-2}$ versus $x$, $T_2^{-2}$ and $(\gamma_N B_1^0)^2 T_1/T_2$ can be determined.

A second, less accurate, method to measure relaxation times is based on the relationship [23]

$$I=\alpha \frac{x}{(1+c x^2)^{3/2}},$$ \hspace{1cm} (11)

in which $I$ is the derivative signal height, $\alpha$ is a proportionality constant and $c=(\gamma_N B_1^0)^2 T_1 T_2$. When $I$ is measured as a function of $x$, $\alpha$ and $c$ can be found from a simple curve-fitting procedure. For qualitative purposes an estimated value of 100 mG was used for $B_1^0$ [24]. We note that if for two inequivalent protons values of both $(\gamma_N B_1^0)^2 T_1 T_2$ and $T_2$ have been determined the ratio of their $T_1$'s can be found independently of $B_1^0$.

3.4. Sample preparation

Samples were prepared on the vacuum line as described elsewhere [7]. Biphenyl (Bp) (BDH) and biphenyl-d10 (Bp-d10) (Merck, Sharp and Dohme) were crystallized from 96 per cent ethanol and sublimed in vacuo, fluorenone
(Fl) (UCB, 98 per cent) was crystallized from benzene and petroleum ether and
dried at 60–80°C, phenanthrene (Pht) (Fluka, puriss.) and phenanthrene–d10
(Pht–d10) (Merck, puriss.) were used directly from stock.

Purification of the solvents has been described elsewhere [7]. The abbrevi­
ations THF, MTHF, DME and Dg denote the solvents tetrahydrofuran, 2­
methyltetrahydrofuran, dimethoxyethane and diglyme (CH₃[OCH₂CH₂]₂OCH₃).

Concentrations weighed in usually amounted to about 1 M.

4. Results

4.1. Coupling constants

Examples of a proton N.M.R. spectrum of Fl— and proton and deuterium
spectra of Pht— are presented in figures 2, 3 (a) and 3 (b). N.M.R. spectra of
Bp— have been presented elsewhere [3, 6]. The ²D N.M.R. spectrum of Pht—
(figure 3 (b)) was measured on a 0·9 M solution of Na Pht in THF to which
Na Bp was added up to a concentration of 1·4 M as an additional spin relaxer.
In order to prevent dissociation of Na Bp into its neutral components [25]
spectra were run at 10°C instead of at room temperature. Comparison with
figure 3 (a) shows the increase in resolution: the single signal at high field in
the proton spectrum is now resolved into three peaks, of which the exact positions

could be determined by means of a computer simulation (see figure 3 (b)). In
the proton spectrum of Fl— (figure 2) one peak is missing probably again because
of lack of resolution. ²D N.M.R. experiments on partly deuterated fluorenone
could clarify this point.

Plots of δ₀ versus fₚ are presented in the figures 4 and 5 for Fl— and Pht—.
Plots for Bp— have been presented elsewhere [3, 6]. From the slopes the coupl­
ing constants have been calculated according to the equations (1) and (3),
except the hfsc of the (H₄, H₅) protons of Pht— and all the deuterium hfsc of
Pht–d10—, which were determined from the contact shift measured at the end of
the reduction. (The numbering of the C atoms is indicated in figure 6.) The
data are presented in the tables 1, 2 and 3. The theoretical values mentioned in
these tables were obtained by substituting the values of ρₗ calculated according to
the method of McLachlan [26] into equation (4) with Q = −25 G.
Figure 3.  (a) 60 MHz proton N.M.R. spectrum of a 1 M solution of Na Pht in THF recorded at room temperature. The unusual appearance of the solvent peak, denoted by S, is due to overmodulation.  (b) 9-1 MHz deuterium N.M.R. spectrum of a 0-9 M solution of Na Pht-d10 in THF recorded at 10°C. Na Bp-h10 (concentration 1-4 M) was added as a spin relaxer. The arrow indicates the position of the external reference, Pht-d10. The solid curve at high field is a computer simulation of the experimental spectrum.

Figure 4. Contact shifts of the protons of Fl versus the degree of reduction of solutions of the parent compound in THF at room temperature. For the reduction Na was employed.
$^1$H and $^2$D N.M.R. studies

Figure 5. Contact shifts versus the degree of reduction for some of the protons of Pht. For other conditions see legend of figure 4.

Figure 6. Structure of Fl and Pht with the numbering of the atoms as used in the text.

<table>
<thead>
<tr>
<th></th>
<th>Ortho</th>
<th>Meta</th>
<th>Para</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li Dg</td>
<td>$^1$H N.M.R.</td>
<td>$-2.7$</td>
<td>$+0.38$</td>
</tr>
<tr>
<td>Na DME $^1$H N.M.R.</td>
<td>$-2.6$</td>
<td>$+0.40$</td>
<td>$-5.0$</td>
</tr>
<tr>
<td>$^2$D N.M.R.</td>
<td>$-2.6$</td>
<td>$+0.36$</td>
<td>$-5.0$</td>
</tr>
<tr>
<td>E.S.R.</td>
<td>2.70</td>
<td>0.40</td>
<td>5.46</td>
</tr>
<tr>
<td>Na Dg $^1$H N.M.R.</td>
<td>$-2.5$</td>
<td>$+0.40$</td>
<td>$-5.2$</td>
</tr>
<tr>
<td>E.S.R.</td>
<td>2.62</td>
<td>0.39</td>
<td>5.30</td>
</tr>
<tr>
<td>Theory</td>
<td>$-2.54$</td>
<td>$+0.47$</td>
<td>$-5.10$</td>
</tr>
</tbody>
</table>

$\dagger$ Signal broadened beyond detection.
$\ddagger$ Deuterium hfsc multiplied by $\gamma_H/\gamma_D$.
§ Ref. [6].
|| Ref. [3].

Table 1. Theoretical and experimental values of the proton and deuterium coupling constants in gauss for the biphenyl$^-$ radical.
In solutions of Li F1 in THF an additional relatively sharp signal was observed at about the position of neutral F1. The signal doubled in intensity when MTHF was used instead of THF. This observation was matched by the appearance of a sharp signal with a virtually zero contact shift in the 7Li N.M.R. spectrum of the solution in addition to the broad and shifted 7Li N.M.R. signal of the paramagnetic species. The sharp 7Li signal also increased its intensity when MTHF was used as a solvent instead of THF.

<table>
<thead>
<tr>
<th></th>
<th>1,8</th>
<th>2,7</th>
<th>3,6</th>
<th>4,5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li THF</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>+0.65</td>
</tr>
<tr>
<td>3H N.M.R.</td>
<td>—</td>
<td></td>
<td></td>
<td>+0.65</td>
</tr>
<tr>
<td>E.S.R.</td>
<td>2.29</td>
<td>0.25</td>
<td>3.22</td>
<td>0.70</td>
</tr>
<tr>
<td>Na THF</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>+0.70</td>
</tr>
<tr>
<td>3H N.M.R.</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>+0.70</td>
</tr>
<tr>
<td>E.S.R.</td>
<td>2.09</td>
<td>0.12</td>
<td>3.18</td>
<td>0.67</td>
</tr>
<tr>
<td>Mg</td>
<td>2.62</td>
<td>0.42</td>
<td>3.33</td>
<td>—</td>
</tr>
<tr>
<td>E.S.R.†</td>
<td>2.62</td>
<td>0.42</td>
<td>3.33</td>
<td>—</td>
</tr>
<tr>
<td>Ca</td>
<td>2.53</td>
<td>0.35</td>
<td>3.25</td>
<td>0.73</td>
</tr>
<tr>
<td>E.S.R.†</td>
<td>2.53</td>
<td>0.35</td>
<td>3.25</td>
<td>0.73</td>
</tr>
<tr>
<td>Theory§</td>
<td>—</td>
<td>+0.08</td>
<td>—</td>
<td>+0.20</td>
</tr>
</tbody>
</table>

† Signal broadened beyond detection.
‡ Ref. [27].
§ Calculated spin densities at positions 9, 10, (4a, 4b) and (8a, 9a) are +0.41, +0.068, +0.102 and -0.008, respectively. See also: Takishita, T., and Hirota, N., 1971, J. Am. chem. Soc., 93, 6421.

Table 2. Theoretical and experimental values of the proton coupling constants in gauss for the fluorenone- radical. (Assignment of the hfsc is according to Dehl, R., and Fraenkel, G. K., 1963, J. Chem. Phys., 39, 1793).

<table>
<thead>
<tr>
<th></th>
<th>1,8</th>
<th>2,7</th>
<th>3,6</th>
<th>4,5</th>
<th>9,10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na THF</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3H N.M.R.</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>E.S.R.†</td>
<td>3.71</td>
<td>0.48</td>
<td>2.89</td>
<td>0.61</td>
<td>4.47</td>
</tr>
<tr>
<td>Na THF</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>*d N.M.R.†</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>E.S.R.§</td>
<td>3.83</td>
<td>0.90</td>
<td>3.05</td>
<td>1.00</td>
<td>4.85</td>
</tr>
<tr>
<td>Theory†</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

† Signal broadened beyond detection.
‡ Deuterium hfsc multiplied by $\gamma D/\gamma H$.
‖ Calculated spin densities as positions (4a, 4b) and (8a, 10a) are +0.022 and +0.006, respectively.

Table 3. Theoretical and experimental values of the proton and deuterium coupling constants in gauss for the phenanthrene- radical.

4.2. Relaxation times

Values of $T_2^{-1}$ measured in a solution of 0.9 M Na Bp–h10+0.6 M Na Bp–d10 in DME are presented in Table 4. Saturation measurements were performed on this sample for the ortho and meta protons. For the meta proton $\Delta B$ was measured as a function of the r.f. amplitude (see figure 7) while for the ortho
protons this was done for the derivative signal height. By applying equation (10) and equation (11) it was found that for the meta protons \((\gamma_N B_1)^2 T_1 T_2 = (1.18 \pm 0.03) \times 10^7 \) (rads/s) and for the ortho protons \((\gamma_N B_1)^2 T_1 T_2 = (3.2 \pm 1.6) \times 10^{-1}\).

### Table 4. Values of \(T_1^{-1}\) in rads/s for the protons and deuterons of biphenyl\(^-\) in a solution of 0.9 M Na Bp-h10 and 0.6 M Na Bp-d10 in DME at room temperature. Uncertainties represent three times the root mean square deviation.

<table>
<thead>
<tr>
<th></th>
<th>Ortho</th>
<th>Meta</th>
<th>Para</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_1^{-1})</td>
<td>Li Dg</td>
<td>3.1 \times 10^4 (1)</td>
<td>1.0 \times 10^4 (0.033)</td>
</tr>
<tr>
<td></td>
<td>Na DME†</td>
<td>1.1 \times 10^4 (1)</td>
<td>4.2 \times 10^3 (0.04)</td>
</tr>
<tr>
<td></td>
<td>Na Dg§</td>
<td>1.4 \times 10^4 (1)</td>
<td>7.0 \times 10^2 (0.05)</td>
</tr>
<tr>
<td>hfsc</td>
<td>—2.6 (1)</td>
<td>+0.39 (0.023)</td>
<td>—5.1 (3.85)</td>
</tr>
</tbody>
</table>

† Signal broadened beyond detection.
† Ref. [6]; concentration 1.6 M.
§ Ref. [3]; concentration 1.3 M.

### Table 5. \(T_2^{-1}\) in rads/s and N.M.R. hfsc in gauss for the protons of biphenyl\(^-\) in several alkali Bp solutions at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>1,8</th>
<th>2,7</th>
<th>3,6</th>
<th>4,5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_2^{-1})</td>
<td>Li THF†</td>
<td>—†</td>
<td>1.8 \times 10^8 (0.6)</td>
<td>—†</td>
</tr>
<tr>
<td></td>
<td>Na THF§</td>
<td>2.7 \times 10^4 (12)</td>
<td>1.2 \times 10^9 (0.5)</td>
<td>—†</td>
</tr>
<tr>
<td>hfsc</td>
<td>—2.6 (15)</td>
<td>+0.38 (0.31)</td>
<td>—†</td>
<td>+0.68 (1)</td>
</tr>
</tbody>
</table>

† Signal broadened beyond detection.
† Concentration 1.8 M.
§ Concentration 1.3 M.

Table 6. \(T_2^{-1}\) in rads/s and N.M.R. hfsc in gauss for the protons of fluorenone\(^-\) in several alkali Fl\(^-\) solutions at room temperature.

Linewidth data for the other systems are presented in the tables 5, 6 and 7. Values in parentheses represent the ratios of the linewidths, normalized with respect to the linewidth of an arbitrary proton. Also the N.M.R. hfsc are presented in the tables together with the ratios of their squares in parentheses.
Table 7. $T_2^{-1}$ in rads/s and N.M.R. hfsc in gauss for the protons and deuterons of phenanthrene in solutions of Na Pht–h10 or Na Pht–d10 in THF, respectively.

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^1\text{H N.M.R.}^\dagger$</td>
<td>$^2\text{H N.M.R.}^\dagger$</td>
<td>hfsc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_2^{-1}$</td>
<td>$5 \times 10^4$ (0.011)</td>
<td>$4.5 \times 10^4$ (1)</td>
<td>$3.3 \times 10^4$ (0.07)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{hfsc}$</td>
<td>$1.7 \times 10^3$ (1.8)</td>
<td>$2 \times 10^3$ (0.21)</td>
<td>$9.6 \times 10^2$ (1)</td>
<td>$2.8 \times 10^2$ (0.24)</td>
<td>$2.4 \times 10^2$ (2.5)</td>
</tr>
<tr>
<td>$\text{hfsc}$</td>
<td>$-3.5$ (1.8)</td>
<td>$+0.16$ (0.003)</td>
<td>$-2.8$ (1)</td>
<td>$-0.80$ (0.08)</td>
<td>$-4.4$ (2.5)</td>
</tr>
</tbody>
</table>

$^\dagger$ Signal broadened beyond detection.
$^\dagger$ Concentration 1.3 M.
$^\dagger$ Concentration 0.9 M; Na Bp (1.4 M) added as a spin relaxer; temperature: 10°C.

5. DISCUSSION

5.1. Coupling constants

Biphenyl

The data in table 1 demonstrate that for Bp the experimentally determined signs of the hfsc agree with the theoretical ones. Also E.S.R. and N.M.R. data agree within experimental error (r.m.s. deviation of N.M.R. hfsc is about 3 per cent). It is worth while to point out that, when at each stage of the reduction the ratios of the coupling constants are determined according to equation (5) and the average is taken, the values are almost an order of magnitude more accurate than the individual hfsc, e.g. for the system Na Bp–d10 in DME [6] $a_m/a_o = 0.140$ and $a_p/a_o = 1.97$ (r.m.s. deviations: 0.5 per cent) the suffices p,
Fluorenone

The data in table 2 show that for Li and Na Fl in THF there is disagreement between the E.S.R. and the N.M.R. hfsc: for the protons 1,8 and 2,7 the N.M.R. hfsc are larger than the corresponding E.S.R. values. On the other hand, the E.S.R. data of Ca and Mg Fl show much better agreement with the N.M.R. data of Li and Na Fl.

It is known that alkali fluorenone salts form dimers (II; see reaction scheme below) at concentrations ≥0.1 M [15]. Since Ca and Mg Fl are known to form ion triples in which the cation is sandwiched between two radicals the similarity of the hfsc probably originates from a similarity in ion pair structure.

The appearance of additional sharp signals exhibiting no contact shift in the proton as well as in the alkali N.M.R. spectra of solutions of the fluorenone salts indicates the existence of diamagnetic ion pair species (III; see reaction scheme below). This is in accordance with findings of Hirota et al. [15]. Our observation that the concentration of the diamagnetic species is solvent dependent also agrees with their results.

The formation of the different types of ion pairs can now be rationalized according to the following reaction scheme [15, 27]

\[
\begin{align*}
2 \quad &C=O^- Na^+ \rightleftharpoons \quad &\text{Na}^+ \quad \quad &C=O \quad \text{Na}^+ \\
\quad &C=O \
\end{align*}
\]

Since the paramagnetic (II) and diamagnetic (III) signals can be observed simultaneously a possible interconversion of the two species must be relatively slow at room temperature. For instance, the dissociation rate of III must be smaller than $10^4 \text{s}^{-1}$ as can be derived from the shift difference between the paramagnetic and diamagnetic signals.

Phenanthrene

Finally for phenanthrene the data in table 3 show that there is good agreement between the N.M.R. hfsc and the results of the E.S.R. measurements and the MO calculations, except for the positions 2,7 where the difference between N.M.R. and E.S.R. hfsc seems to fall outside the experimental error. A detailed explanation for this observation is lacking.

5.2. Relaxation times

Relaxation measurements on the system Na Bp-h10 + Na Bp-d10 in DME are discussed first. The data have been presented in table 4. Next the relaxation measurements on the other systems will be discussed.
According to the equations (6) and (7) for an analysis of the proton relaxation times a knowledge of the parameters $A$ and $B$ of each proton is required. Values of $A$ can be obtained directly from the experiment (see equation (8a)). According to equation (8b) for each proton the anisotropic magnetic dipolar tensor $\mathbf{T}$ must be calculated in order to obtain the appropriate value of $B$. The calculation of $\mathbf{T}$ was performed with the aid of a computer programme described elsewhere [8, 19]. The spin densities at the ortho, meta and para positions, which were needed for the calculation, were obtained by substituting in the McConnell–Weissman relation (equation (4)) the values of the hfsc while the spin densities on the two bridge carbon atoms were obtained from the normalization condition $\Sigma_{\rho_z} = 1$. $B$ was calculated for different values of $Q$ (see equation (4)) and for different values of the angle $\phi$ between the planes of the two rings of the Bp molecule. As an example values of $(B/h)^2$ for $Q = -25$ G and $\phi = 0$ are presented in table 8 together with values of $(A/h)^2$.

The data in table 8 show that with decreasing coupling constant the magnitude of $B$ relative to $A$ increases. The reason for this is that for a particular proton $A$ is only determined by the spin density on the adjacent carbon atom while $B$ is determined by the spin densities on all carbon atoms together. $A$ is therefore more sensitive to variations in the spin density on the adjacent carbon atom than $B$. The observed trend means that with decreasing hfsc the relative contribution of the anisotropic dipole interaction to the relaxation times will increase.

<table>
<thead>
<tr>
<th>Ortho</th>
<th>Meta</th>
<th>Para</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(A/h)^2$</td>
<td>2260</td>
<td>49.6</td>
</tr>
<tr>
<td>$(B/h)^2$</td>
<td>296</td>
<td>63.7</td>
</tr>
</tbody>
</table>

† Calculated with $\phi = 0$ and $Q = -25$ G.

Table 8. Values of the isotropic and anisotropic magnetic dipolar interaction constants for the protons of biphenyl$^-\text{in (mega-rads/s)}^2$.

The observed trend means that with decreasing hfsc the relative contribution of the anisotropic dipole interaction to the relaxation times will increase.
For the calculation of the correlation times we now use the values of $T_2^{-1}$ reported for $H_0$ and $H_m$ in table 4 together with the values of $A$ and $B$ mentioned above and apply the equations (6 a), (6 b) and (9). The results are reported in table 9. Also reported are the correlation times calculated from the linewidths not corrected for intermolecular and inhomogeneity broadening (uncorrected values: 509 rads/s for the meta proton and $11.7 \times 10^3$ rads/s for the ortho proton). The data in table 9 demonstrate that the correlation times calculated from the experiment are rather insensitive to the values used for $Q$ and $\phi$. However, $\tau_2$ appears to be very sensitive to the error in the metal proton linewidth. For instance, if the value of $T_2^{-1}$ of the meta proton is increased by 20 per cent, $\tau_2$ increases four to five-fold (see table 9). On the other hand $\tau_e$ is hardly affected by slight changes in the values of $T_2^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>$T_2^{-1} \ F_e\uparrow$</th>
<th>$T_2^{-1} \ D\uparrow$</th>
<th>$T_2^{-1} \ F_e+T_2^{-1} \ D\uparrow$</th>
<th>$T_2^{-1} \ exp\uparrow$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1H$ ortho</td>
<td>10.8 $\times 10^3$</td>
<td>8.11 $\times 10^3$</td>
<td>11.6 $\times 10^3$</td>
<td>11.6 $\times 10^3$</td>
</tr>
<tr>
<td>meta</td>
<td>2.36 $\times 10^3$</td>
<td>1.75 $\times 10^3$</td>
<td>4.11 $\times 10^3$</td>
<td>4.1 $\times 10^3$</td>
</tr>
<tr>
<td>para</td>
<td>4.40 $\times 10^4$</td>
<td>3.50 $\times 10^3$</td>
<td>4.75 $\times 10^4$</td>
<td>4.2 $\times 10^4$</td>
</tr>
<tr>
<td>$^2D$ ortho</td>
<td>254</td>
<td>19.1</td>
<td>273</td>
<td>269</td>
</tr>
<tr>
<td>meta</td>
<td>5.6</td>
<td>4.1</td>
<td>9.7</td>
<td>33</td>
</tr>
<tr>
<td>para</td>
<td>1037</td>
<td>82.5</td>
<td>1120</td>
<td>1038</td>
</tr>
<tr>
<td>$T_1^{-1} \ F_e\uparrow$</td>
<td></td>
<td>$T_1^{-1} \ D\uparrow$</td>
<td>$T_1^{-1} \ F_e+T_1^{-1} \ D\uparrow$</td>
<td>$T_1^{-1} \ exp\uparrow$</td>
</tr>
<tr>
<td>$^1H$ ortho</td>
<td>961</td>
<td>780</td>
<td>1741</td>
<td>1919</td>
</tr>
<tr>
<td>meta</td>
<td>21</td>
<td>168</td>
<td>189</td>
<td>296</td>
</tr>
</tbody>
</table>

† Values calculated with $\tau_e=18.2 \times 10^{-12}$ s, $\tau_d=4.1 \times 10^{-13}$ s and the values of $A$ and $B$ presented in table 8.
‡ Experimentally determined values of $T_2^{-1}$.
§ Experimental values obtained from ($\gamma N B_1^0)^2 T_1 T_2^{-1}=1.18 \times 10^1$ (rads/s)$^2$ for $H_{meta}$ and ($\gamma N B_1^0)^2 T_1 T_2=3.2 \times 10^{-1}$ for $H_{ortho}$ on the assumption $B_1^0=100$ mG [24]. These values have not been corrected for contributions from intermolecular interactions ($\approx 75$ rads/s).

Table 10. Contributions from the magnetic dipolar interactions to the $T_1^{-1}$ and $T_2^{-1}$ of the protons and deuterons of biphenyl in a solution of 0.9 M Na Bp–h10 + 0.6 M Na Bp–d10 in DME. Experimental values are presented in the last column. All values are given in rads/s.

With the calculated correlation times we can now calculate the contributions from the isotropic and the anisotropic dipolar interaction to the $T_2^{-1}$ and $T_1^{-1}$ of the various protons and deuterons in the biphenyl radicals. The results are presented in table 10. The values used for $\tau_e$ and $\tau_d$ are $18.2 \times 10^{-12}$ s and $4.1 \times 10^{-13}$ s (see table 8; $Q=-25$ G, $\phi=0$). The data in table 10 show that in general there is good agreement between theory and experiment. (For the $T_2^{-1}$ values of the ortho and the meta protons the agreement is artificial since the experimental values of $T_2^{-1}$ were used to calculate $\tau_e$ and $\tau_d$.) The data nicely demonstrate the increasing importance of $T_2^{-1}D$ when the coupling constant decreases: for the ortho and para protons $T_2^{-1}D$ accounts for only 7–9 per cent of the linewidth, while for the meta proton this increases to 40 per cent.
The situation is different for $T_{1}^{-1}$. There we see (table 10) that $T_{1}^{-1D}$ provides for 50 per cent of $T_{1}^{-1}$ in the case of the ortho proton, which contribution increases to even 85 per cent for the meta proton. It is therefore clear that $T_{2}^{-1}$ measurements are better suited for the determination of $\tau_{e}$ while $T_{1}^{-1}$ measurements can provide accurate estimates of $\tau_{d}$. If a correction of 75 rads/s for intermolecular contributions is subtracted from the experimental values of $T_{1}^{-1}$ reported in table 10 the agreement between calculated and experimental values of $T_{1}^{-1}$ is reasonable (see table 10), which must be considered somewhat fortuitous in view of the fact that the experimental values are based on an estimated value of $B_{1}^{0}$ [24].

More significantly is that the experimentally determined value of $6.5 \pm 3$ for the ratio of the $T_{1}^{-1}$'s of the ortho and the meta protons, which is independent of $B_{1}^{0}$ (see §2), agrees with the theoretical value of 6.9. (The latter value was calculated by adding an amount of 75 rads/s to the theoretical $T_{1}^{-1}$'s to account for contributions from intermolecular interactions to $T_{2}^{-1}$.)

Finally we consider the deuterium relaxation data of table 10. For the ortho and para positions the agreement between theory and experiment is satisfactory. For $D_{\text{meta}}$, however, there is a difference of 23 rads/s between theory and experiment. The discrepancy can be explained if we assume that there is a contribution from the quadrupolar relaxation of 23 rads/s to the linewidth, a contribution too small to be detectable for the ortho and para deuterons. The values of the qcc of deuterium atoms in aromatic compounds usually fall in the range of 180–200 kHz [28]. Although the presence of a Na$^{+}$ counterion may affect this value, a simple calculation shows that a Na$^{+}$ ion at the closest distance possible from a $^{4}$D nucleus (sum of van der Waals radii $= 2.2$ Å) contributes less than 10 kHz to the qcc. Similarly the effect of the extra charge on the Bp$^{-}$ ion will be small. Using a value of 200 kHz for the qcc and the value of 23 rads/s for $T_{2}^{-1Q}$ we find from equation (6$\epsilon$) depending on the value of $\eta$: $\tau_{r} = 2.9 \times 10^{-11}$ s ($\eta = 1$) or $\tau_{r} = 3.9 \times 10^{-11}$ s ($\eta = 0$). These values differ considerably from the value of $\tau_{r}$ calculated from the proton linewidths (table 9), which demonstrates once more the inaccuracy of the determination of $\tau_{r}$ from $T_{2}$ measurements on radicals. An additional check is provided by considering the width of the signals from the perdeutero-THF that was present in the solution as an internal standard. From $T_{2}^{-1Q} = 15.7$ rads/s ($\eta_{Q} = 1$) one finds $\tau_{r} = (2.6-3.5) \times 10^{-11}$ s, depending on the value of $\eta$. (For the calculation a value of 175 kHz was used for the qcc [28].) This value of $\tau_{r}$ is smaller than the $\tau_{r}$ values for Bp$^{-}$, which correspond with the smaller radius of the THF molecule with respect to that of biphenyl.

In conclusion it can be said that the value of $\tau_{r}$ derived from the proton linewidths is rather sensitive towards experimental error and that the values of $\tau_{r}$ calculated from $T_{2}^{-1Q}$ are probably more reliable. The calculations indicate that $\tau_{r}$ is of the same order of magnitude as $\tau_{e}$.

Other systems

As stated above, for protons with a large coupling constant the linewidth is almost completely determined by the Fermi contact interaction, while for protons with small coupling constants also the anisotropic dipolar interaction becomes important. Since $T_{2}^{-1PC}$ is always proportional to the square of the hfsc while for $T_{2}^{-1D}$ this only holds for protons with a large hfsc we expect the linewidth
to be proportional to $a^2$ when $a$ is large, while for small $a$ the linewidth will be larger than expected on the basis of an $a^2$ proportionality. This is borne out by the data in the tables 5, 6 and 7, where the ratios of the linewidths (in parentheses) can be compared with the ratios of the squares of the hfsc.

<table>
<thead>
<tr>
<th>Bp–h10</th>
<th>Li DME</th>
<th>$^1$H N.M.R.</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na DME</td>
<td>$^1$H N.M.R.</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Na Dg</td>
<td>$^1$H N.M.R.</td>
<td>3</td>
</tr>
<tr>
<td>F1</td>
<td>Li THF</td>
<td>$^1$H N.M.R.</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Na THF</td>
<td>$^1$H N.M.R.</td>
<td>6</td>
</tr>
<tr>
<td>Pht–h10</td>
<td>Na THF</td>
<td>$^4$H N.M.R.</td>
<td>8</td>
</tr>
<tr>
<td>–d10</td>
<td>Na THF</td>
<td>$^2$D N.M.R.†</td>
<td>6</td>
</tr>
</tbody>
</table>

† Measurements performed in the presence of 1-4 M Na Bp at 10°C.

Table 11. Values of $\tau_e$ in seconds for solutions of various alkali radical salts at room temperature.

The linewidth data for the deuterons 2,7 and 4,5 in Pht–d10− (table 7) demonstrate that these linewidths are mainly determined by quadrupolar relaxation. From these data it follows that $T_{2Q}^{-1} \approx 190$ rads/s, hence $\tau_e = 3.2 \times 10^{-10}$ s ($\eta = 0$). This value of $\tau_e$ is almost an order of magnitude larger than the $\tau_e$ observed in the solution of Na Bp in DME. The reason for this is probably that the high total concentration of alkali radical ion pairs in the sample (∼2.3 M) combined with the relatively low temperature at which the measurements were performed (10°C instead of 30°C) produces an unusually high viscosity in the sample resulting in a slowing down of the molecular tumbling rate.

A numerical analysis will further be restricted to the calculation of $\tau_e$. The simplest way to find $\tau_e$ is to consider the linewidth of a proton with a large coupling constant and to neglect the contribution from the anisotropic magnetic dipole interaction to the linewidth. The error introduced by this approximation over-estimates the value of $\tau_e$ by ca. 10 per cent. Values of $\tau_e$ calculated with the help of equation (6 a) from the data in the tables 5, 6 and 7 are presented in table 11. The data show that in solutions of alkali radical ion pairs at the final stage of the reduction $\tau_e$ may vary from $2 \times 10^{-11}$ s to $9 \times 10^{-11}$ s. Particularly what limits $\tau_e$ does not become clear from the experimental evidence.

The authors wish to thank Mr. A. A. K. Klaassen for his skilful assistance in carrying out the experiments. Part of the investigations has been carried out under the auspices of the Netherlands Foundation for Chemical Research (S.O.N.) and with the aid of the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

REFERENCES


