

The g -tensor of aromatic ions

by D. J. M. FASSAERT and E. DE BOER

Department of Physical Chemistry, University of Nijmegen, Nijmegen,
The Netherlands

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The theory of Stone on the calculation of g -tensors of aromatic positive and negative ions implies that for even-alternant molecules, made up of six-membered rings, the difference between the in-plane g -tensor components is equal in magnitude, but opposite in sign for both ions. To verify this prediction careful linewidth studies were performed on the E.S.R. spectra of the positive and negative ions of anthracene, tetracene and perylene in dilute solutions and at low temperature. The spectra were analysed with the aid of the theories of Freed and Fraenkel and of Kivelson and Schreurs. In agreement with Stone's predictions, in all three cases a change in sign on going from the positive to the negative ion was observed. However, quantitative discrepancies exist between the theoretical g -values and the observed ones. This may be caused by the approximations inherent in Stone's theory or by the assumptions, such as isotropic rotational motion, in our analysis of the linewidths. It is shown that only large anisotropies in tumbling motion of the ion could seriously affect the experimental results.

1. INTRODUCTION

In 1964 Stone developed a theory of the g -tensor of aromatic ions [1]. For several condensed aromatic systems he calculated the numerical values of the g -tensor components. One of the striking features of his results was that for even-alternant hydrocarbon ions the difference between the in-plane g -tensor components is equal in magnitude but opposite in sign for both ions, as a consequence of the so called 'pairing' relation. This relation states that the Hückel or self consistent field molecular orbital of the odd electron in the positive ion can be derived from that in the negative ion simply by changing the sign of some molecular orbital coefficients (i.e. those belonging to the unstarred carbon atoms).

To check Stone's conclusions directly one should perform E.S.R. experiments on single crystals of aromatic ions. The difficulty is that these single crystals are not easily formed. Till now we were able to produce single crystals of only a few negative ions [2]. However, there is also an indirect way for obtaining information on the g -tensor. McConnell [3] was the first to show that the relaxation effect of the anisotropic g -tensor interaction causes the linewidths of hyperfine components in E.S.R. spectra of radicals in solution to depend on the value of the g -tensor components. In principle therefore, linewidth studies should furnish information on the g -tensor. In order to verify Stone's predictions we decided to investigate alternant aromatic systems for which positive as well as negative ions could be made. Stone [1] already reported some preliminary results of our study; here we give a more detailed account of it.

We have studied the E.S.R. spectra of the positive and negative ions of anthracene, tetracene and perylene. For the analysis of the linewidths we used the

linewidth theory of Freed and Fraenkel [4] as well as the theory of Kivelson and Schreurs [5]. For the presentation of our results we have chosen the Freed and Fraenkel theory, particularly because in the meantime a linewidth study of Segal, Reymond and Fraenkel [6] has appeared, using the same theory and dealing with the negative ion of anthracene and the positive and negative ion of tetracene, also studied by us. This gives us an opportunity to compare our results on these ions with theirs. In appendix B we give a brief account of our linewidth analysis based on the theory of Kivelson and Schreurs.

2. EXPERIMENTAL PROCEDURES

The negative ions of anthracene, tetracene and perylene were prepared by standard procedures [7]. As solvents tetrahydrofuran and 1,2-dimethoxyethane were used, with sodium as reducing agent. The positive ions were obtained by reaction with 96 per cent sulphuric acid.

The E.S.R. spectra were measured with a Varian V 4502 X-band spectrometer, equipped with a variable temperature control and a fieldial. The magnetic field was measured with an AEG gaussmeter and the frequency was monitored with a Hewlett Packard 5245 L frequency counter.

For each radical ion several spectra were taken under slow scanning conditions (about 500 mOe/min). Inasmuch as the peak-to-peak amplitude of the first derivative of the absorption curve can be measured more accurately than the derivative linewidths, only amplitude measurements were carried out. The amplitude measurements were only performed on spectra recorded under optimum conditions as regards concentration and temperature; they were chosen as low as possible to avoid broadening of the linewidths and additional splitting by the sodium cations. Amplitude measurements were only performed on hyperfine lines characterized by only one quantum number unequal to zero and well separated from other hyperfine lines, so that overlap corrections could be avoided.

3. THEORY OF LINEWIDTH VARIATION

3.1. *The spectral density $j^{(DG)}(0)$*

The relaxation matrix theory of linewidths in E.S.R. has been developed by Freed and Fraenkel [4]. From their theory it follows that the combined effect of the anisotropic electron dipole-nuclear dipole and g -tensor interactions gives rise to a linear dependence of the linewidth on the nuclear magnetic quantum number. For hyperfine lines, originating from a set of equivalent nuclei and characterized by only one quantum number M unequal to zero (called the principal hyperfine lines), the following equation for T_2^{-1} holds:

$$T_2^{-1} = KM^2 + LM + C, \quad (1)$$

where K , L and C are parameters. Information on the g -tensor is hidden in the parameters L and C . Since other relaxation processes contribute to C , the parameter L will be utilized for the determination of the g -value components.

Experimentally L is obtained by subtracting the linewidths of principal hyperfine lines, characterized by the same absolute value of the magnetic quantum number, from each other.

The theoretical expression for L is given by [4, 8]

$$L = \frac{1}{8} j^{(DG)}(0) B_0, \quad (2)$$

where B_0 is the external magnetic field and $j^{(DG)}(0)$ is the spectral density function, due to the cross term between the time dependent anisotropic dipole and g -tensor interactions. This equation has been derived for the case that $\omega^2 \tau_R^2 \gg 1$, where ω is the angular resonance frequency of the electron and τ_R the correlation time for molecular tumbling. Segal, Reymond and Fraenkel [6] have shown that this assumption is justified under our experimental conditions.

For a magnetic nucleus in the i th equivalent group $j^{(DG)}(0)$ is given by [4, 8]

$$j^{(DG)}(0) = \frac{\pi |\beta_e|}{5\hbar} \zeta_i \tau_R \{ D_i^{(0)} g^{(0)} + [D_i^{(+2)} + D_i^{(-2)}] g^{(2)} \}, \quad (3)$$

where

$$\zeta_i = \frac{1}{2\pi} |\gamma_e| \gamma_i \hbar,$$

$$D_i^{(m)} = \sqrt{\left(\frac{6\pi}{5}\right)} \langle \psi | r^{-3} Y_{2m}(\theta, \phi) | \psi \rangle,$$

$$g^{(0)} = \frac{1}{\sqrt{6}} [2g_3 - (g_1 + g_2)],$$

$$g^{(2)} = \frac{1}{2} (g_1 - g_2),$$

g_1, g_2, g_3 are the principal components of the molecular g -tensor, the dipolar coefficients $D_i^{(m)}$ are the expectation values over the electronic wave function in the principal coordinate system of the g -tensor, and the $Y_{2m}(\theta, \phi)$ are the spherical harmonics of order two; the other symbols have their usual meaning.

Equation (3) is based on the assumption that the molecular tumbling motions are isotropic. The influence of anisotropic rotation on our results is considered in appendix A.

Since $D_i^{(+2)} = (D_i^{(-2)})^*$ and writing, as is usually done, $\zeta_i D_i^{(m)} = \bar{D}_i^{(m)}$, equation (3) can be rewritten as

$$j^{(DG)}(0) = \frac{\pi |\beta_e|}{5\hbar} \tau_R [\bar{D}_i^{(0)} g^{(0)} + 2R \bar{D}_i^{(2)} g^{(2)}], \quad (4)$$

where $R \bar{D}_i^{(2)}$ means the real part of $\bar{D}_i^{(2)}$ (the $\bar{D}_i^{(m)}$ are expressed in frequency units, Hz). For planar aromatic radicals g_3 , the component of the g -tensor perpendicular to the aromatic plane, may be set equal to g_e [1, 9], the free electron g -value 2.002319. In doing this the quantity $g^{(0)}$ reduces to

$$g^{(0)} = \sqrt{\left(\frac{3}{2}\right)} (g_e - g_{\text{iso}}), \quad (5)$$

where g_{iso} is the isotropic g -value. For the ions of interest the g_{iso} are known [10, 6], (see table 1). Since the dipolar coefficients $D_i^{(m)}$ can be computed (*vide infra*), $j^{(DG)}(0)$ can be calculated as a function of $g^{(2)} = \frac{1}{2}(g_1 - g_2)$, in which g_1 and g_2 are the in-plane components of the g -tensor. A numerical value for $(g_1 - g_2)$ can be obtained by setting the ratio of two spectral density functions, belonging to different

Ion	g_{iso}
Anthracene ⁺	2·002565
Anthracene ⁻	2·002709
Tetracene ⁺	2·002598
Tetracene ⁻	2·002682
Perylene ⁺	2·002578
Perylene ⁻	2·002667

Table 1. Isotropic g -values†.

† Taken from ref. [6, 10].

sets of equivalent nuclei equal to the ratio of the corresponding experimental L values.

3.2. The dipolar coefficients $D_i^{(m)}$

The radical anions under investigation are planar aromatic systems. Therefore the wave function of the unpaired electron can be described with sufficient accuracy by a linear combination of $2p\pi$ -atomic orbitals ϕ_k on each of the atoms k in the π -electron system

$$\psi = \sum_k C_k \phi_k. \quad (6)$$

The spin density on atom $k = \rho_k = |C_k|^2$.

Recently Owen and Vincow [11] showed that contributions to $D_i^{(m)}$ arising from overlap terms between the orbitals ϕ_k are negligibly small. Hence $D_i^{(m)}$ may be written as

$$D_i^{(m)} = \sum_k \rho_k D_{ki}^{(m)}, \quad (7)$$

where the $D_{ki}^{(m)}$ are the dipolar contributions to $D_i^{(m)}$ arising from an electron in a $2p\pi$ -orbital on atom k .

Explicit expressions for the dipolar coefficients are given by Freed and Fraenkel [4, 8]. The numerical values are evaluated by using the quantities given by McConnell and Strathdee [12]. The spin densities ρ_k are obtained from an S.C.F. calculation, improved by a first-order configurational interaction procedure.

4. CALCULATION OF L FROM THE SPECTRA

As has been pointed out, calculations on linewidths are only carried out on principal hyperfine lines, for which equation (1) is valid. The parameter L^i for the equivalent set of nuclei i can then be determined from hyperfine components, characterized by the same absolute value of the magnetic quantum number. When ΔH is the full linewidth at half height of the absorption curve, L^i is given by

$$L^i = \frac{\Delta H_{j^i} - \Delta H_{-j^i}}{4|M_j|}, \quad (8)$$

where j refers to the magnetic quantum number M_j .

For a lorentzian line the following relation holds:

$$(\Delta H_{j^i})^2 = \alpha \frac{D_{ij}}{I_j^i}, \quad (9)$$

where D_{ij} is the degree of the degeneracy of the hyperfine component considered, I_j^i the peak-to-peak amplitude and α a proportionality constant, depending only on the concentration of the radical ions.

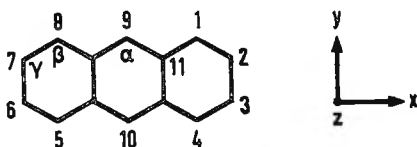
Using this, equation (8) transforms into

$$L^i = \frac{\alpha^{1/2} D_{ij}^{1/2} [(I_{-j}^i)^{1/2} - (I_j^i)^{1/2}]}{4 |M_j| \{I_j^i \cdot I_{-j}^i\}^{1/2}}. \quad (10)$$

In the evaluation of our experimental results we use only ratios of different L^i , so that the proportionality factor α cancels.

5. RESULTS AND DISCUSSION

5.1. Anthracene cation



In the anthracene molecule three groups of equivalent protons can be distinguished, denoted in the structure diagram by α , β and γ . The best resolved E.S.R. spectra are measured in the temperature range from -14°C to $+22^\circ\text{C}$. From the spectra it could be concluded that L^α and L^β are negative and L^γ positive. For the determination of the sign, all hyperfine splitting constants (h.f.s.c.) have been taken negative [13]. Owing to the overlap of the principal α hyperfine lines only the ratio of L^β to L^γ could be determined

$$\frac{L^\beta}{L^\gamma} = -0.669 \pm 0.072. \quad (11)$$

For the spin densities we calculated:

$$\rho_9 = +0.266, \quad \rho_1 = +0.114, \quad \rho_2 = +0.031 \quad \text{and} \quad \rho_{11} = -0.028.$$

With the aid of these spin densities and using equations (4) and (5) the spectral densities $j_i^{(DG)}(0)$ ($i = \alpha, \beta$ or γ) have been calculated (the superscript *DG* will be dropped further).

$$j_\alpha(0) = 453.3 - 534.4(g_1 - g_2) \times 10^4, \quad (12 a)$$

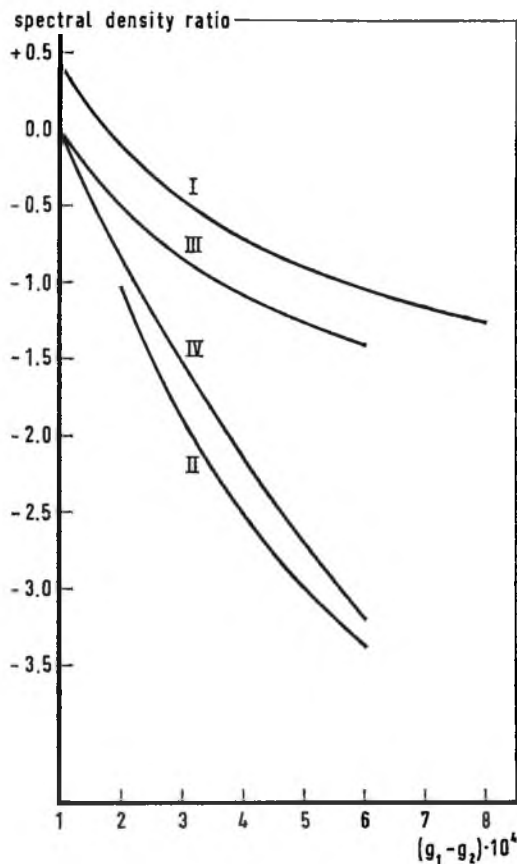
$$j_\beta(0) = 363.6 - 206.5(g_1 - g_2) \times 10^4, \quad (12 b)$$

$$j_\gamma(0) = 268.9 + 93.8(g_1 - g_2) \times 10^4. \quad (12 c)$$

In the expressions (12) and also in the next expressions for $j_i(0)$ we have omitted the constant factor $\pi |\beta_e| \tau_R / 5\hbar$, occurring in equation (4).

From the measured signs of the different L^i and equations (12) it can be concluded that $(g_1 - g_2) > 1.8 \times 10^{-4}$, whereas from $L^\beta / L^\gamma = j_\beta / j_\gamma$ follows that $(g_1 - g_2) = (g_x - g_y) = (3.8 \pm 0.3) \times 10^{-4}$.

To check how critical the ratio j_β / j_γ depends on the value of $(g_1 - g_2)$, we have calculated this ratio for various values of $(g_1 - g_2)$. The results are plotted in the figure. Due to the sharp variation of j_β / j_γ with $(g_1 - g_2)$ the numerical value of $(g_1 - g_2)$ may be considered to be fairly reliable.



Spectral density ratio versus $(g_1 - g_2) \times 10^4$:

- I for the β and γ protons of the anthracene cation
- II for the α and γ protons of the tetracene cation
- III for the α and γ protons of the perylene cation
- IV for the α and β protons of the perylene cation.

5.2. Anthracene anion

The E.S.R. spectra of the negative ion of anthracene dissolved in tetrahydrofuran were studied in the temperature range from -125°C to $+20^\circ\text{C}$. It was noticed that a slight change in the values of the h.f.s.c.'s occurred in the temperature range studied. At -125°C the h.f.s.c.'s for the α , β and γ protons were 5.42, 2.88 and 1.55 oersted respectively; at $+20^\circ\text{C}$ they were, in the same sequence, 5.56, 2.80 and 1.58 oersted. Due to these changes in h.f.s.c.'s only at temperatures lower than -80°C were the principal β and γ hyperfine lines sufficiently separated from neighbouring lines to warrant reliable amplitude measurements. It appeared that L^β is positive and $L^\gamma \ll L^\beta$. Measurements at -80°C yielded a negative sign for L^γ ; however, at temperatures lower than -112°C a positive sign was found. Since L^γ is so small, the uncertainty in the ratio L^β/L^γ is so large that it cannot be used in evaluating $(g_1 - g_2)$. To get an idea about its magnitude, it is better to consider the spectral density functions.

We found for them

$$j_{\alpha}(0) = 718.9 - 534.4(g_1 - g_2) \times 10^4, \quad (13 a)$$

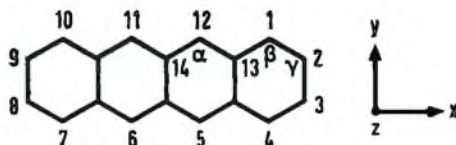
$$j_{\beta}(0) = 576.6 - 206.5(g_1 - g_2) \times 10^4, \quad (13 b)$$

$$j_{\gamma}(0) = 425.5 + 93.8(g_1 - g_2) \times 10^4. \quad (13 c)$$

To make L^{γ} small, $(g_1 - g_2)$ should be of the order of -4×10^{-4} . This agrees with the positive value of L^{β} and confirms Stone's prediction that $(g_1 - g_2)$ changes sign on going from the positive to the negative ion.

The negative ion of anthracene has also been studied by Segal *et al.* [6] in three different systems: i.e. with Na^+ in 1,2-dimethoxyethane, with K^+ in tetraglyme and in N,N -dimethylformamide in which anions of anthracene were generated electrolytically. They found also that L^{β} is positive and $L^{\gamma} \ll L^{\beta}$ (these authors used a different notation, $L^{\beta} = B_1'$ and $L^{\gamma} = B_2'$).

5.3. Tetracene cation



The protons in tetracene can be classified in three groups of four equivalent protons each, in the structure diagram indicated as α , β and γ protons. E.S.R. spectra have been measured from -20°C to $+75^{\circ}\text{C}$. From the spectra it could be deduced unambiguously that L^{α} and L^{β} have the negative sign, whereas L^{γ} has the positive sign, taking again the signs of all h.f.s.c.'s negative. Quantitative amplitude measurements could only be performed on the principal hyperfine lines of the α and γ protons with quantum number $|M_j| = 1$, because the other principal lines overlapped too much with other lines for carrying out reliable amplitude measurements.

It was found that

$$L^{\alpha}/L^{\gamma} = -2.44 \pm 0.27. \quad (14)$$

In 1962 Hyde and Brown [14] made an E.S.R. study of the tetracene positive ion. Their most accurate results are the measurements carried out at 0°C and $+26^{\circ}\text{C}$. From the results reported in table III and V of their publication one can derive an average value for L^{α}/L^{γ} of -2.34 in good agreement with our result. Segal *et al.* [6] reported for L^{α}/L^{γ} ($= B_3'/B_2'$) at room temperature a value of -2.21 ± 0.22 .

For the spin densities we found: $\rho_{12} = +0.202$, $\rho_{13} = -0.013$, $\rho_1 = +0.061$, $\rho_2 = +0.019$ and $\rho_{14} = -0.040$. Using this the spectral densities are calculated to be

$$j_{\alpha}(0) = 451.4 - 387.3(g_1 - g_2) \times 10^4, \quad (15 a)$$

$$j_{\beta}(0) = 298.8 - 96.3(g_1 - g_2) \times 10^4, \quad (15 b)$$

$$j_{\gamma}(0) = 195.2 + 60.0(g_1 - g_2) \times 10^4. \quad (15 c)$$

In view of the measured signs of L^i , consistent results are only obtained if $(g_1 - g_2) > 3.1 \times 10^{-4}$. From equation (14) follows that $(g_1 - g_2) = (g_x - g_y) = (3.9 \pm 0.4) \times 10^{-4}$. The figure shows that the ratio j_α/j_γ varies strongly with the value of $(g_1 - g_2)$, rendering the above results more reliable.

5.4. Tetracene anion

Several spectra were measured at -95°C in 1,2-dimethoxyethane. The signs of L^α and L^β were found to be positive, the sign of L^γ could not be determined, but its absolute value must be small, since even at -95°C the amplitudes of the principal γ -lines with the same $|M_j|$ were almost equal. These results are in agreement with the results of Segal, Reymond and Fraenkel [6] using the same solvent and alkali ion, where L^γ was also found to be very small. Quantitative measurements on the amplitudes were impossible, because all the principal lines were strongly overlapped. For the spectral densities we found

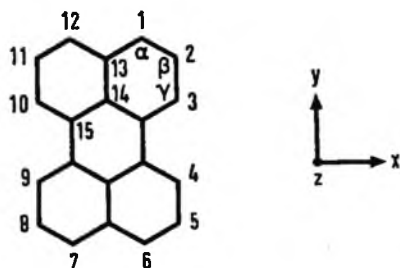
$$j_\alpha(0) = 587.3 - 387.3(g_1 - g_2) \times 10^4, \quad (16 a)$$

$$j_\beta(0) = 388.7 - 96.3(g_1 - g_2) \times 10^4, \quad (16 b)$$

$$j_\gamma(0) = 253.9 + 60.0(g_1 - g_2) \times 10^4. \quad (16 c)$$

Since $j_\gamma(0)$ must be almost zero, one may infer that $(g_1 - g_2) \approx -4 \times 10^{-4}$.

5.5. Perylene cation



The protons in perylene can be divided into three classes of four equivalent protons, indicated in the structure diagram as α , β and γ .

E.S.R. spectra were measured in the temperature range from -7°C to $+96^\circ\text{C}$. From the spectra it became evident that L^α is negative and L^β and L^γ positive, taking the h.f.s.c. of the α and γ protons negative and the h.f.s.c. of the β protons positive. The latter corresponds to a negative spin density on the adjacent carbon atom, as is proved experimentally [15] and also is in agreement with the calculated spin densities (*vide infra*). Amplitude measurements have been carried out on all principal hyperfine lines, characterized by the quantum number $|M_j| = 1$.

The following results were obtained:

$$\frac{L^\alpha}{L^\gamma} = -1.20 \pm 0.45, \quad \frac{L^\alpha}{L^\beta} = -1.50 \pm 0.32. \quad (17)$$

The spin densities in the perylene cation are $\rho_1 = +0.138$, $\rho_2 = -0.011$, $\rho_3 = +0.096$, $\rho_{13} = -0.030$, $\rho_{14} = -0.014$ and $\rho_{15} = +0.048$.

For the spectral densities we found

$$j_{\alpha}(0) = 276.4 - 281.8(g_1 - g_2) \times 10^4, \quad (18 a)$$

$$j_{\beta}(0) = 302.0 + 23.34(g_1 - g_2) \times 10^4, \quad (18 b)$$

$$j_{\gamma}(0) = 341.8 + 110.1(g_1 - g_2) \times 10^4. \quad (18 c)$$

Equations (18 *a*) and (18 *b*) confirm the positive sign of the β h.f.s.c., since for no value of $(g_1 - g_2)$ can j_{α} and j_{β} become negative simultaneously. From equation (17) it follows that $(g_1 - g_2) = 4.6 \times 10^{-4}$, and $(g_1 - g_2) = 3.0 \times 10^{-4}$, respectively. In the figure is shown how the ratios of the spectral densities are changing as a function of $(g_1 - g_2)$. From this and the inaccuracies in the experimental values of L^{α}/L^{γ} and L^{α}/L^{β} (equation (17)), one may draw the conclusion that $(g_1 - g_2) = (g_x - g_y)$ lies between 3×10^{-4} and 3.5×10^{-4} .

5.6. Perylene anion

E.S.R. spectra of the negative ion of perylene were measured in 1,2-dimethoxyethane at temperatures between $+20^{\circ}\text{C}$ and -95°C . At no temperature were the principal hyperfine lines not overlapped with other lines. This is caused by the fact that the h.f.s.c. of the α protons is almost equal to the sum of the h.f.s.c.'s of the β and γ protons. No quantitative amplitude measurements were carried out. From the spectra at -95°C , where the linewidth variations became most pronounced, it could be concluded that L^{α} is large and positive, $L^{\beta} < L^{\alpha}$ and also positive, whereas L^{γ} is small, while its sign could not be determined. The spectral densities are

$$j_{\alpha}(0) = 371.4 - 281.8(g_1 - g_2) \times 10^4, \quad (19 a)$$

$$j_{\beta}(0) = 405.7 + 23.34(g_1 - g_2) \times 10^4, \quad (19 b)$$

$$j_{\gamma}(0) = 459.2 + 110.1(g_1 - g_2) \times 10^4. \quad (19 c)$$

If $(g_1 - g_2) \approx (-3 \text{ to } -4) \times 10^{-4}$, good agreement exists with the signs and the orders of magnitude of the L^i .

6. CONCLUSION

In table 2 the results of our measurements are summarized, together with the theoretical results of Stone [1]. It appears that Stone's prediction that $(g_1 - g_2)$ is positive for cations and negative for anions is fulfilled in all three cases. Quantitatively there exist discrepancies between the experimental and the theoretical results, e.g. the predicted decrease in $(g_1 - g_2)$ going from anthracene $^{\pm}$ to tetracene $^{\pm}$ is not reflected in the observed values. This becomes even more evident if we consider the results obtained on the naphthalene anion by Segal, Reymond and Fraenkel [6] and confirmed by us. It was found that $(g_1 - g_2)$ is almost zero, whereas Stone predicted -9×10^{-4} . This may be caused by approximations introduced in Stone's theory as well as by simplifications made in the derivation of the formulas of the spectral density $j^{(DG)}(0)$. One of the simplifications is that isotropic rotation has been assumed. In appendix A it is shown that, unless large anisotropies are involved, this will not affect the outcome of our results very much. Fluctuations of the h.f.s.c.'s by ion pairing phenomena does not affect our results either, since as shown by Segal, Reymond and Fraenkel [6] they only influence the parameters K and C in equation (1) and not L .

Ion	$(g_1 - g_2) \times 10^4$		
	Experimental		Stone
	(a)	(b)	
Anthracene ⁺	+3.8	+2.9	+7
Anthracene ⁻	~ -4	~ -3.5	-7
Tetracene ⁺	+3.9	+3.0	+5
Tetracene ⁻	~ -4	~ -3.5	-5
Perylene ⁺	+3.1	+2.4	+10
Perylene ⁻	-3 to -4	-3 to -4	-10

(a) based on $g_3 = g_e$.

(b) based on $g_3 - g_e = 6 \times 10^{-5}$.

Table 2. Comparison between the experimental values of $(g_1 - g_2)$ and the theoretical values obtained by Stone.

Moreover the experimental conditions are chosen such that the effects of ion pairing are minimized.

Segal, Reymond and Fraenkel [6] showed that the ratio of the linewidth parameters are rather insensitive to the choice of spin densities. This can also be seen by comparing the spectral densities for anthracene⁻ calculated by us with theirs. The results of Segal are based on experimental spin densities, ours on theoretical ones. The differences between the two sets of j_s are small and have no significant effect on the calculated numerical values of $(g_1 - g_2)$.

In the analysis of our data we have used the free electron value for g_3 , like Segal, Reymond and Fraenkel. Stone calculated for $(g_3 - g_e)$ a value of 6×10^{-5} . Assuming this we recalculated $(g_1 - g_2)$; the results are listed in table 2. It appears that the absolute value of $(g_1 - g_2)$ is influenced, without affecting our conclusions.

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APPENDIX A

Anisotropic rotational motion

When anisotropic rotational motion is included Freed [16] has shown that equation (4) has to be replaced by

$$j^{(DG)}(0) = \frac{\pi |\beta_e|}{5\hbar} \zeta_i \tau_R \sum_{m, m'} D_i^{(m)} g^{(m')} \lambda_{mm'} \quad (m, m' = 0, \pm 2). \quad (\text{A } 1)$$

The coefficients $\lambda_{mm'}$, defined by equations (2.14) and (3.6) of [16], are functions of the principal values R_1, R_2, R_3 of the molecular diffusion tensor R .

For two cases, i.e. the positive ions of anthracene and tetracene, we determined the $\lambda_{mm'}$ for various ratios of $R_1 : R_2 : R_3$, substituted them into equation (A 1) and then calculated the ratios of the spectral density functions. Setting the latter equal to the observed ratio of the corresponding L 's, one obtains the corresponding values of $(g_1 - g_2)$: they are listed in table 3.

$R_1 : R_2 : R_3$	$(g_1 - g_2) \times 10^4$	
	Anthracene ⁺	Tetracene ⁺
1 : 1 : 1	3.8	3.9
3 : 2 : 1	3.1	3.2
2 : 1 : 1	4.3	4.4
5 : 1 : 1	4.9	5.0
1 : 10 : 5	0.8	0.7
1 : 10 : 10	2.0	1.9
10 : 10 : 1	1.5	1.5
20 : 1 : 1	5.3	5.4

Table 3. Influence of anisotropic rotation on $(g_1 - g_2)$ for the anthracene cation and the tetracene cation.

It is evident that a rather large anisotropy is required to influence $(g_1 - g_2)$ considerably and that the sign of $(g_1 - g_2)$ remains positive. Since the species which are tumbling are most likely solvated ions, large anisotropies are not very likely.

APPENDIX B

The theory of Kivelson and Schreurs

The linewidth variations studied in this paper can also be treated with the theory of Kivelson and Schreurs [5]. These authors considered each hyperfine line as a single lorentzian-shaped line and calculated the relaxation times T_1 and T_2 , using time-dependent perturbation theory. In the more general theory of Freed and Fraenkel [4] a degenerate hyperfine line is a superposition of hyperfine components with different widths.

However, if the linewidth variations among the different components are small the composite line is to a good approximation a lorentzian line with an average width.

In our case we are dealing with small linewidth variations compared to the average width, so that the formulas of Freed and Fraenkel pertaining to this situation can be applied. However, if small variations among the different hyperfine components exist, the theory of Kivelson and Schreurs [5] is also applicable and should give the same results. According to their theory T_2^{-1} for a set of principal hyperfine lines belonging to a set of equivalent nuclei i , is given by

$$T_2^{-1} = (K' + \frac{4}{3}K_0')M^2 + (L' + \frac{4}{3}L_0')M + C, \quad (\text{B } 1)$$

where

$$\frac{K_0'}{K'} = \frac{L_0'}{L'} = 1 + \omega^2 \tau_R^2 \quad (\omega \text{ is the angular resonance frequency}).$$

The parameter L' , determining the linear term in M , is (in standard notation)

$$L' = \frac{\tau_R}{1 + \omega^2 \tau_R^2} \frac{g_e \beta_e^2 g_N \beta_N B_0}{5 \hbar^2} \{ \sqrt{\frac{3}{2}} (g_1 - g_2) (c_i + c_i^*) + (2g_3 - g_1 - g_2) a_i \},$$

where the coefficients a_i and c_i are related to the dipolar coefficients $D_i^{(m)}$ (see [17]).

For $\omega^2\tau_R^2 \gg 1$, holding under our experimental circumstances (see [6]), we calculated for the ions under investigation the ratios of the various ($L' + \frac{1}{3}L_0'$). Setting this equal to the ratio of the observed L 's, we obtained in the usual manner ($g_1 - g_2$). Within a few per cent the same numerical values were found as before.

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