

Anisotropy and Asymmetry of the Diamagnetic Susceptibility of the Carbonium Ion of Anthracene

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Abstract: The anisotropy ($\Delta\chi$) and asymmetry ($\delta\chi$) of the diamagnetic susceptibility of anthracene- d_{10} and its carbonium ion have been determined from quadrupolar ^2H line splittings in high-field NMR spectra. The results show that $\Delta\chi$ of ion and molecule are the same within experimental error. The influence of localized charges on the quadrupole coupling of the deuterons is discussed; in the olefinic part of the central ring of the ion this coupling differs drastically from the one in the molecule.

An important property of a molecule is its magnetic susceptibility, a second rank tensor commonly denoted by the symbol $\bar{\chi}$. In the principal frame of reference (x, y, z) of a molecule, χ is diagonal and can be characterized by its trace $1/3 \sum \chi_{\alpha\alpha}$ ($\alpha = x, y, z$), its anisotropy $\Delta\chi = \chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$, and its asymmetry $\delta\chi = \chi_{xx} - \chi_{yy}$. For diamagnetic molecules, the susceptibility is a well-studied property; a number of reviews are given in ref 1. On the other hand, magnetic susceptibilities of ions, e.g., carbonium and carbanions, have rarely been studied. The reason for this deficiency is obvious: the ions are usually generated in strongly acidic or basic media, often at low concentration. The principal experimental method, the Cotton-Mouton effect, measures a bulk property from which the contribution of the ions cannot easily be extracted. A recently developed NMR technique^{2,3} to study χ has the inherent advantage that the solutes (e.g., ions, neutral molecules) and the solvent give separate spectral resonances, facilitating the ions to be studied per se. Another important advantage is that both anisotropy and asymmetry of χ are open to investigation; in the Cotton-Mouton effect, the contribution of $\delta\chi$ is difficult to assess, unless it is zero by symmetry. NMR investigations on a large number of aromatic molecules have recently been reviewed.³ Up to now only one ion has been investigated, the fluorenyl carbanion.⁴ In this paper we report the determination of the anisotropy and asymmetry of the diamagnetic susceptibility of anthracene and its carbonium ion from deuterium NMR measurements at 14.09 T (^1H frequency 600 MHz).

Theory

Both the NMR method^{2,3} and the Cotton-Mouton effect¹ rely on the partial alignment of molecules by a magnetic field. In NMR the alignment, generated by the magnetic field of the spectrometer, is small (for diamagnetic molecules $\approx 10^5$ times smaller than in liquid crystals) but well measurable. As a consequence, anisotropic nuclear interactions (e.g., quadrupolar or dipolar couplings) may become visible in the NMR spectrum. For instance, in the ^2H spectrum of a deuterated molecule the resonance lines are split into doublets, the splittings of deuteron i being related to $\Delta\chi$ and $\delta\chi$ by the formula^{2,3}

$$\Delta\nu_i \text{ (Hz)} = \frac{B^2}{10kT} \left(\frac{eQ}{h} \right) \left\{ \Delta\chi V_{zz}^i + \frac{1}{2} \delta\chi (V_{xx}^i - V_{yy}^i) \right\} \quad (1)$$

in which

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$$V_{\alpha\alpha} = eq \left[\frac{1}{2} \cos^2 \delta_{z''\alpha} - \frac{1}{2} \right] + \frac{1}{2} \eta [\cos^2 \delta_{z''\alpha} - \cos^2 \delta_{y''\alpha}] \quad (2)$$

B is the magnetic induction in gauss; eQ is the nuclear quadrupole moment, and $V_{\alpha\alpha}$ ($\alpha = x, y, z$) denotes the electric field gradient at the site of the nucleus. Equation 2 relates $V_{\alpha\alpha}$ to the major local field gradient $eq (= V_{z''z''})$ at a certain deuteron. The molecular frame (x, y, z) as well as the local frame (x'', y'', z'') are defined in Figure 1; for each deuteron z'' is taken along its C-D bond. The asymmetry parameter $\eta = (V_{x''x''} - V_{y''y''})/V_{z''z''}$. The angles $\delta_{z''\alpha}$, $\delta_{y''\alpha}$, and $\delta_{x''\alpha}$ can be calculated from the figure, assuming regular hexagons for the rings. It should be noted that in the derivation of the formulas rigid molecules are assumed. Furthermore, χ denotes an effective susceptibility as intermolecular interactions may play a role.

To calculate $\Delta\chi$ and $\delta\chi$, the quadrupole coupling constant (e^2qQ/h) and the asymmetry parameter η of the deuterons have to be known. For aromatic molecules (e^2qQ/h) = 186 \pm 6 KHz and η is in the range 4-6%.⁵ However, in ions these values might be different. Unfortunately, no (e^2qQ/h) values for aromatic ions are known to our knowledge. In our study of fluorenyl carbanion,⁴ relaxation times were exploited to check the quadrupolar coupling constants, leading to the conclusion that (e^2qQ/h) does not change noticeably for the deuterons in the outer aromatic rings. This fitted well with the expected values calculated by means of a simple point charge approximation, where each additional electron in the $2p_z$ orbital on the carbon atom leads to a change of -49 kHz in the quadrupole coupling constant and +0.835 in the asymmetry parameter.⁶ Using an analogous approach for the increase in (e^2qQ/h) and η in case of electron deficiencies, one can estimate the constants from charge densities. MacLean and Mackor⁷ estimated the delocalization of the positive charge over the anthracenium rings and found the following electron densities: C(1), 0.968; C(2,4), 0.917; C(3), 0.957; and C(10), 0.724. Taking 186 kHz and 0.05 for respectively (e^2qQ/h) and η in the molecule, where the electron density is 1.00, the following values for the quadrupole coupling constants (in kHz) and the asymmetry parameters in the ion can be calculated: 187.6 and 0.077 for D(1), 190.1, and 0.119 for D(2,4), 188.1 and 0.086 for D(3), and 199.5 and 0.280 for D(10). The changes in the quadrupole coupling constant of D(1 to 4) are within 2-3% of the molecular value. Going from the molecule to the cation, the number of π electrons in the rings decreases from 14 to 12, which would be expected to give a decrease of approximately 14% in $\Delta\chi$. This should be easily detectable if the same (e^2qQ/h) is taken for D(1-8) in the

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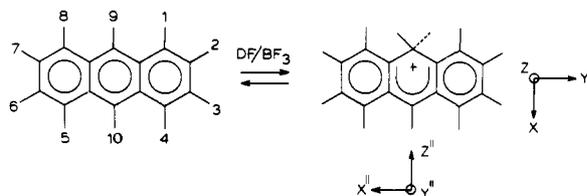


Figure 1. Definition of axes and numbering of nuclei of anthracene- d_{10} and its carbonium ion.

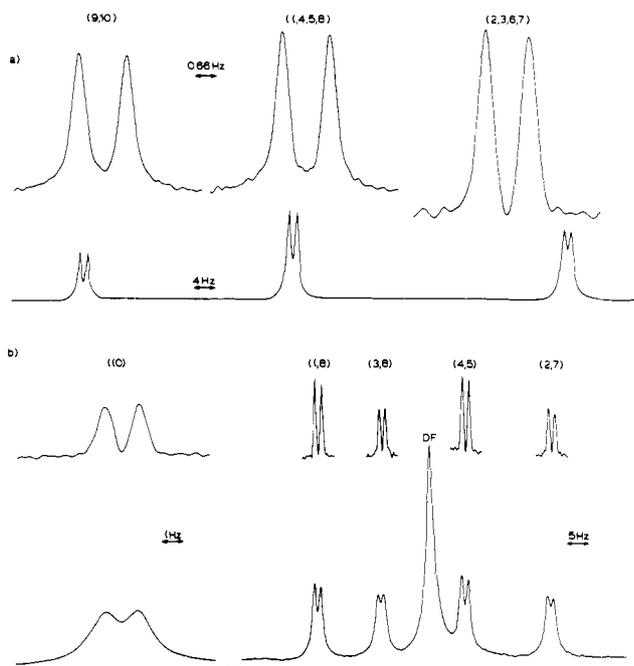


Figure 2. Normal and resolution enhanced ^2H spectra (14.09 T, 296 K) of (a) anthracene- d_{10} in ether and (b) anthracene carbonium ion in DF/BF_3 (D(10)) and in HF/BF_3 (D(1-8)).

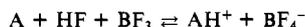
molecule and the ion. From the splitting of the deuteron in position 10 some conclusions can then be drawn about the change in (e^2qQ/h) and/or η under influence of the decreased charge density in the carbon $2p_z$ orbital of C(10).

Experimental Section

The carbonium ion of anthracene was prepared by saturation of an anthracene- d_{10} /HF(DF) solution with BF_3 . The color of the solution was clear reddish brown. An air-free Teflon/stainless steel flow system of conventional type was used. To obtain ^2H quadrupolar splittings for all deuterons in the cation, two separate solutions had to be made. From the mixture anthracene- d_{10} in DF/BF_3 only the splittings of deuterons 9 and 10 are obtainable, since the other resonances disappear under the intense DF peak. However, the splittings of these deuterons can be obtained from the protonated complex, prepared from anthracene- d_{10} in HF/BF_3 . Here, the 9,10 deuterons exchange immediately, but for the others this takes about 8 h (at room temperature). Directly after the preparation of the cation the Teflon sample tube was placed in a standard NMR tube and its NMR spectrum subsequently recorded. To eliminate the couplings of exchanged protons to the ring deuterons, proton decoupling was applied. Measuring and locking on deuterium could be accomplished with the rapid scan correlation console, designed by Dadok. As a locking agent some acetone- d_6 was also present in solution. The ion concentration in both tubes was about 1 mol %. In order to have a reference for $\Delta\chi$ and $\delta\chi$ of the molecule, a third tube containing 0.5 mol % of anthracene- d_{10} in ether was measured with normal ^2H FTNMR and proton locking.

All spectra were recorded on the 14.09-T spectrometer (^2H frequency 92.19 MHz) at Carnegie-Mellon University, Pittsburgh.

Proton (deuterium) exchange did not broaden the ^2H resonances too much (Figure 2b); as expected from the literature⁸ the equilibrium



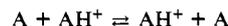
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Table I. ^2H NMR Splittings, $\Delta\nu$ (in Hz),^a and Calculated $\Delta\chi$ and $\delta\chi$ (in emu)^b at 14.09 T and 296 K for Anthracene and Its Carbonium Ion

	anthracene	anthracenium	
$\Delta\nu(1,4,5,8)$	1.47	$\Delta\nu(1,8)$	1.47
		$\Delta\nu(4,5)$	1.47
$\Delta\nu(2,3,6,7)$	1.36	$\Delta\nu(2,7)$	1.37
		$\Delta\nu(3,6)$	1.41
$\Delta\nu(9,10)$	1.51	$\Delta\nu(9)$	c
		$\Delta\nu(10)$	2.00
$\Delta\chi$	-2.94×10^{-28}	$\Delta\chi^d$	-2.98×10^{-28}
		$\Delta\chi^e$	-2.80×10^{-28}
$\delta\chi$	0.11×10^{-28}	$\delta\chi^d$	0.08×10^{-28}
		$\delta\chi^e$	0.08×10^{-28}

^a Experimental error 2-4%. ^b From splittings of deuterons 1 to 8. ^c Not measurable. ^d Using quadrupolar couplings of deuterons in the molecule. ^e Using quadrupolar couplings adjusted for charge density changes.

is shifted virtually completely to the right, eliminating exchange reactions like



Chemicals. All compounds except DF were of commercial origin and used without purification; DF was prepared from the reaction of D_2SO_4 with CaF_2 . Anthracene- d_{10} and D_2SO_4 were purchased from Merck Sharp and Dohme; HF and BF_3 were from Matheson. Teflon NMR tubing was obtained from Wilmad.

Results and Discussion

The 14.09-T ^2H NMR spectra of anthracene- d_{10} and its carbonium ion are given in parts a and b of Figure 2, respectively. For anthracene three split lines are found; the formation of the ion decreases the molecular symmetry, and the number of lines doubles. The CD_2 group in the ion does not show a splitting as a consequence of the unfavorable angle of the C-D bonds with the molecular z axis; the resonance of D(9) is at high field and is not shown in Figure 2.

The deuterium line splittings for both compounds are given in Table I, together with $\Delta\chi$ and $\delta\chi$ calculated from the splittings of deuterons 1 to 8, using a quadrupole coupling constant (from now on abbreviated as qcc) of 186 kHz and an asymmetry parameter η of 5%. $\Delta\chi$ of the molecule is in good agreement with the literature value of -3.03×10^{-28} emu;¹ it is slightly smaller than the previous NMR value³ on account of inclusion of η , which was neglected so far.

As is obvious from the table, $\Delta\chi$ does not change within experimental error when going from the molecule to the cation. This result was not anticipated: as explained in the theoretical section, the rupture of the central ring current is expected to decrease $|\Delta\chi|$ by about 14%.

In an attempt to reconcile the experimental data with a decreased $|\Delta\chi|$, one could suppose that qcc and η in the ion need to be modified on account of the excess positive charge, which is distributed over the conjugated system according to the charge densities mentioned in the theory section. In this respect, investigation of the splittings of deuterons 1, 4, 5, 8, and 10, whose C-D bonds are all parallel, is of interest. In anthracene these nuclei all give the same splitting within experimental error, indicating a leveled out charge density distribution and therefore equal qcc's and η 's. In the ion $\text{D}(1,8) = \text{D}(4,5) = 1.47$ Hz and $\text{D}(10) = 2.00$ Hz; the calculated excess charges are $\text{C}(1,8) = 0.032$, $\text{C}(4,5) = 0.083$, and $\text{C}(10) = 0.276$. Apparently, on positions (1,8) and (4,5) the qcc's and η 's are equal, indicating a more even charge distribution over the outer ring than the calculated one. Therefore, we take an average charge density for the carbon atoms in the outer ring for the coming calculations. The large excess charge in the central ring is clearly reflected in the splitting of D(10), and it can be concluded that qcc and η of D(10) are significantly changed.

In order to investigate the influence of these modified qcc's and η 's, we recalculate $\Delta\chi$ and $\delta\chi$ from the average qcc and η of the deuterons in the outer rings to see whether they reproduce the splitting of D(10). The averages are $\text{qcc}(1-8) = 189$ kHz and

$\eta(1-8) = 0.010$, giving $\Delta\chi = -2.80 \times 10^{-28}$ emu and $\delta\chi = 0.08 \times 10^{-28}$ emu; for D(10), using $qcc(10) = 199.5$ kHz and the experimental splitting, one finds $\eta(10) = 0.43$, which is larger than the theoretically estimated value of 0.28.

The calculated $\Delta\chi$ and $\delta\chi$ are equal to the ones in anthracene within a few percent. A $\Delta\chi$ value, reduced by 14%, would require $\eta(1-8) = 0.23$ and $\eta(10) = 0.60$ if the above qcc values are used; these values seem too extreme to be correct.

Two points should be stressed which both support the reliability of these calculations: first, in the analogous study of the fluorenyl carbanion,⁴ the charge density differences between molecule and ion are comparable, but no alteration of the asymmetry parameter of the outer ring deuterons was necessary to account for the expected change in $\Delta\chi$; second, the line widths of D(1-8) in molecule and ion are about the same, as is expected if the qcc's, η 's, and rotational correlation times are not changed noticeably. (In the same temperature range the viscosities of ether and HF are the same within a few percent.⁹) The larger qcc of D(10)

relative to that of D(1-8) is also reflected in its larger line width.

In the foregoing we have neglected the counterion BF_4^- , which in principle could affect the quadrupolar coupling in the deuterons of the cation; however, HF is strongly polar and ion-pair formation will be negligible.

So, the final conclusion is that going from the molecule to the ion, $\Delta\chi$ maximally changes by 4-5%, i.e., much less than expected.

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Registry No. D₂, 7782-39-0; anthracene-*d*₁₀, 1719-06-8; anthracene-*d*₁₁ carbonium ion, 95589-70-1.

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Magnetic Properties of Manganese in the Photosynthetic O₂-Evolving Complex

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Abstract: We report the continuous power saturation and temperature dependence of three EPR signals which are generated by low-temperature illumination of dark-adapted Photosystem II (PSII) membranes and are associated with the S₂ state of the O₂-evolving complex of photosynthesis. PSII membranes which are dark-adapted for 4 h at 0 °C and illuminated at 200 K for 2 min exhibit a S₂ state EPR signal which saturates easily ($P_{1/2} = 3.7$ mW at 6.0 K) and has an intensity maximum at 6.9 K under nonsaturating conditions. The S₂ state EPR signal obtained from 6-min dark-incubated samples illuminated at 160 K exhibits no intensity maximum in the 4.0-16.0 K range under nonsaturating conditions and saturates at higher microwave powers ($P_{1/2} = 37.1$ mW at 6.0 K). Finally, a third signal produced by 170 K illumination of 6-min dark-adapted membranes shows an intensity maximum at 5.9 K under nonsaturating conditions and is not saturated with our current experimental setup ($P_{1/2} > 156$ mW at 6.0 K). We conclude that each EPR spectrum originates from a thermally excited state of one of three distinct configurations of the manganese complex which is believed to make up the active site. The temperature dependence data are fitted to a model in which two paramagnetic sites are ferromagnetically exchange coupled. All three sets of data can be accounted for by varying the magnitude of the superexchange coupling constant.

It is currently accepted that the four-electron photooxidation of H₂O to O₂ catalyzed by the O₂-evolving center (OEC) of Photosystem II (PSII) occurs stepwise with the generation of five intermediate oxidation states known as S_{*i*} (*i* = 0 to 4) states.¹ Both the S₀ and S₁ states are stable in short-term dark-incubated chloroplasts or PSII membranes, where they are present in a 1:3 proportion, due to rapid back-reaction from the S₂ and S₃ states to the S₁ state.² The S₄ state is relatively unstable and quickly releases O₂, cycling the system back to the S₀ state.^{1,2}

Since this S state scheme was first proposed, many attempts have been made to probe these photoactive intermediates spectroscopically.³ Electron paramagnetic resonance (EPR) has been a helpful tool in the elucidation of this problem. Dismukes and Siderer⁴ showed that irradiation of spinach chloroplasts with one

saturating laser flash quickly followed by freezing at 77 K produced a multiline EPR signal centered at $g = 2.0$. Later, Brudvig et al.⁵ showed that an identical EPR signal could be obtained by continuously illuminating dark-adapted chloroplasts at 200 K, and then trapping at 77 K. The properties derived from this multiline EPR signal⁵ agreed well with the properties of the S₂ state measured by thermoluminescence,⁶ fluorescence,⁷ and O₂ evolution⁸ studies.

Efforts to account for the molecular species giving rise to the multiline EPR signal have pointed toward a manganese complex as a likely model. The involvement of manganese in O₂ evolution is well-known,³ and computer simulations using antiferromagnetically exchange coupled mixed-valence manganese dimers as

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