Table IV. Optimized Geometry for $LiCH_3$ (Distances in au)

	Model potential	FSGO (frozen 1s core)	Ab initio[a]
$R_{C\text{-}Li}$	3.482	3.613	3.819
$R_{C\text{-}H}$	2.195	2.188	2.058
∠H-C-H, deg	96.66	96.34	105.8

which tends to preserve the proper valence energy. Thus the $2a_{1g}$ and $2a_{2u}$ orbitals, which sample this part of the potential most heavily, give improved orbital energies.

Finally, in Table IV we present the results of calculations on $LiCH_3$ where for Li we have used the model potential developed earlier (ref 2a). This tests the model when two different (C, Li) potentials interact. It is seen that the agreement of C-Li bond distance is not as good as some of the previous results but is still acceptable.

Conclusion

The model potential developed in ref 2a has been shown to work quite well when used in an FSGO scheme for some organic compounds. The improvement over attempted calculations, employing more structured and more sophisticated potentials, is particularly noteworthy and seems to justify previous conclusions about the need to balance the extent of detailed structure in the description of core and valence regions. As a next step the present method may be extended to larger atoms where greater savings over the all-electron FSGO calculations would be realized. In addition, it seems one might consider optimizing a similar model to give closer agreement with experimental rather than FSGO results. Both of these possibilities are being investigated.

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ESR, NMR, and ENDOR Studies of Partially Deuterated Phenyl Substituted Anthracenes. π–σ Delocalization

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Abstract: From the negative and positive radical ions of partially deuterated phenyl substituted anthracenes ESR and ENDOR-in-solution spectra have been recorded, which suggest that pure π-MO theories fail to describe the spin distribution in highly twisted aromatic radical ions. The observed sequence of the phenyl proton coupling constants $|a_H^{meta}| = |a_H^{para}| < |a_H^{ortho}|$ points to the necessity of *π–σ mixing* to interpret the observed data. Deuterium ENDOR resonances in solution have been detected for the first time. Sign determinations of the hfs couplings were performed using the new electron-nuclear-nuclear TRIPLE resonance technique. The synthesis of the various deuterated phenyl substituted anthracenes is described. Unambiguous assignments of the deuterated positions were performed using mass spectroscopy, ^1H and ^{13}C NMR including noise- and off-resonance-decoupling techniques, respectively.

Simple π-MO calculations have proved to be successful in describing the π-electronic structure of planar aromatic hydrocarbons. For the description of hyperfine splittings (hfs) and electronic *g* factors excited molecular states with σ symmetry have to be taken into account, but in most cases only gross assumptions about the distribution and energies of the σ electrons seem to be required. Previously, Stone had shown that a linear correlation between experimentally determined *g* factors and the energy of the half-filled MO of planar aromatic radicals is expected, assuming a large energy gap between the π and σ electrons.[1] Results from photoelectron spectroscopy for a variety of aromatic molecules contradict this assumption, indicating the absence of such a large energy gap.[2] In molecules with lowered symmetry such as sterically overcrowded phenyl substituted aromatic compounds, separation of π and σ electrons for symmetry reasons is no longer valid. Indeed, experimental *g* factors of nonplanar phenyl substituted aromatic radical ions, e.g., the ions of rubrene, 9,10-diphenylanthracene (**1**), and 9-phenylanthracene (**5**), do not fit Stone's correlation. Labeling of the compounds refers to Figure 1.

Recently an attempt was made to account for this by mixing the π-type MO's of the unpaired electron with σ MO's of the phenyl substituent.[3] This *phenyl hyperconjugation model* is similar to the description of the conventional methyl hyperconjugation.[4] The *g*-factor anomalies cannot be rationalized by this model owing to the neglect of large spin-orbit matrix elements resulting from π–σ mixing.[3b] The unpaired electron

Compound	Deuterated Positions
1	–
2	4'
3	2', 4', 6'
4	2', 3', 4', 5', 6'
5	–
6	2', 4', 6'
7	1, 8
8	3, 6

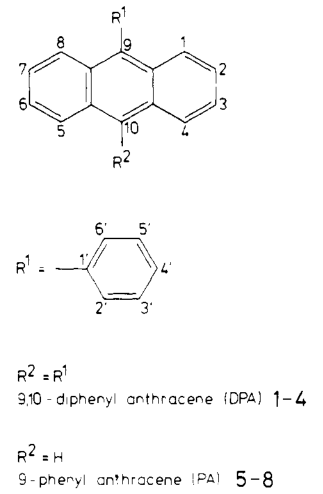

Figure 1. Numbering scheme of the compounds.

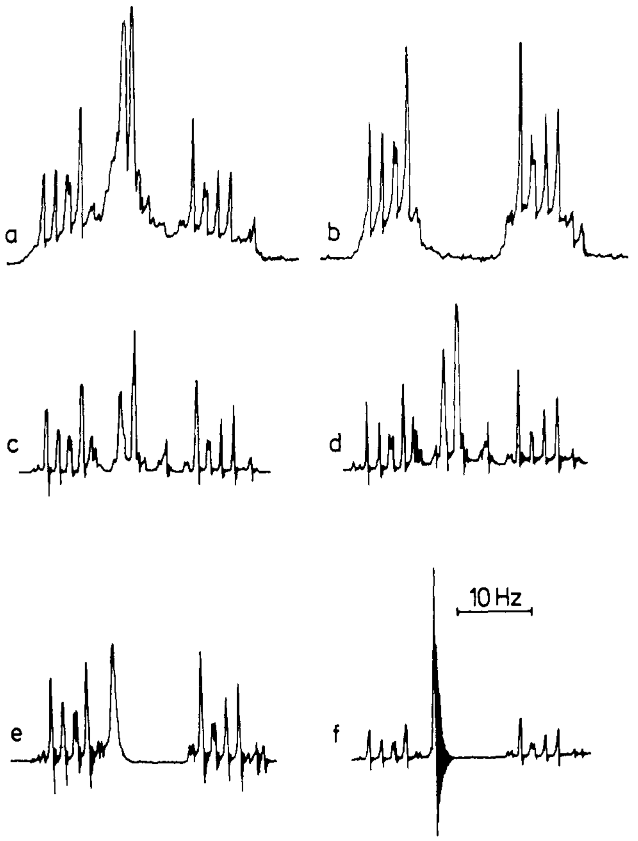

Figure 2. ^1H NMR spectra (100 MHz) of 9,10-diphenylanthracene (**1**) and its deuterated analogues (**2–4**) in $CDCl_3$: (a) **1**, (b) **4**, (c) **2**, (d) **2** with {D} noise decoupling, (e) **3**, (f) **3** with {D} noise decoupling.

distribution in the phenyl substituent, however, is in qualitative agreement with all-valence electron INDO calculations using the twisted benzyl radical as a model compound.[5] In contrast to the predictions of pure π-MO theories these calculations yield a large hyperfine coupling constant for the meta protons in the phenyl ring even for a twist angle (referred to the plane of the CH_2 fragment) of 90°. Furthermore, the result of a recent ENDOR (electron nuclear double resonance) study of the negative and positive radical ions of rubrene[6] supports the phenyl hyperconjugation model. In contrast to the conventional ordering the following sequence was found to be valid

$$|a_H^{\text{meta}}| > |a_H^{\text{para}}|, |a_H^{\text{ortho}}|$$

Unfortunately, the phenyl hyperconjugation model overestimates this π–σ mixing. Further improvement calls for more experimental data from molecules with similar geometry, but due to poor resolution of the ESR spectra of the radical ions of **1** and **5** the hitherto existing interpretations are ambiguous.[3,7] Therefore, in the present paper an ENDOR and electron-nuclear-nuclear TRIPLE resonance study on the radical ions of these compounds is reported. Assignments of the hfs couplings in both cases called for specifically deuterated compounds. Hence, an unambiguous knowledge of the deuterium positions is of importance, requiring comprehensive NMR studies.

Results

Preparation of Compounds and Mass Spectrometry. The partially deuterated phenyl substituted anthracenes were prepared by treating the corresponding phenyllithium with anthraquinone and anthrone respectively and subsequent reduction of the parent carbinols.[8] Bromobenzene-d_1 (to give **2**) was obtained by the reaction of *p*-bromophenylmagnesium bromide with D_2O. Bromobenzene-d_3 (to give **3** and **6**) was prepared from aniline by H/D exchange using D_2O, followed by a Sandmeyer reaction. Bromobenzene-d_5 (to give **4**) is commercially available. **7** and **8** were prepared from the corresponding dibromo derivatives by reduction with $LiAlD_4$.

The deuterium contents and isotopic distribution, i.e., H and D, in the anthracene compounds were determined by mass spectrometry. Using a conventional high energy electron beam (70 eV) only the diphenylanthracenes give rise to a characteristic fragmentation. The starting fragmentation of M^+ gives $(M - \text{benzene})^+$ yielding $(M - 78)^+$ for **1**, $(M - 79)^+$ for **2**, $(M - 81)^+$ for **3**, and $(M - 83)^+$ for **4**, respectively; evidently in this scission the deuterons are exclusively in the benzene fragment. It is to be noted that the degree of deuteration cannot be deduced from the mass spectrum, e.g., the $(M - 1)^+$ peak may arise from loss of one hydrogen atom from M^+ and it may be caused by a molecular ion of a molecule with one additional proton instead of D. Thus, the mass spectrometric deuterium analysis of the compounds has been performed at low voltages (<30 eV) where the ejection of hydrogen is no longer observed. Hence this method serves well to determine the overall deuterium contents and the results are as follows. **2**, 96.5%; **3**, 99.1%; **4**, 99.3%; **6**, 98.2%; **7**, 86.5%; **8**, 94.0%. There is no scrambling of D from the phenyl rings into the anthracene fragment in **2–4**, but it should be pointed out that mass spectrometry fails in the unequivocal determination of the specific labeled molecular position.

^1H NMR Measurements of DPA. The ^1H NMR spectrum of DPA **1** (Figure 2a) exhibits a AA'BB' spin system[9] δ_A = 7.66 ppm, δ_B = 7.30 ppm, $J_{AA'}$ = 0.8 Hz, J_{AB} = 9.0 Hz, $J_{AB'}$ = 1.5 Hz, $J_{BB'}$ = 6.7 Hz) for the protons of the anthracene fragment and a complex five-spin system for the two equivalent phenyl substituents. Comparing the spectra in Figures 2a and 2b the unperturbed well-resolved AA'BB' spin system is found only in the case of DPA **4**. Thus, within experimental error the total isotopic purity of the compound is assured. Since all other deuterated substances were prepared in a similar manner H/D scrambling effects between phenyl ring positions and the anthracene moiety can generally be excluded. The ^1H NMR spectrum of DPA **2** (Figure 2c) shows a less complex pattern of the phenyl ring protons as compared with **1** (Figure 2a). Due to unresolved H–D couplings the deuterium noise decoupling technique has to be used for an unambiguous extraction of the basic spin system (AA'BB'X), see Figure 2d. Since this spectrum can only be simulated with the typical parameters of para disubstituted benzene derivatives (δ_A = 7.59 ppm, δ_B = 7.49 ppm, J_{AB} = 8.5 Hz, $J_{AB'}$ = 0.5 Hz, $J_{AA'}$ = 2.5 Hz, $J_{BB'}$ = 2.3 Hz), the deuterons are in the para positions 4'. The protons H-3' and H-5' resonate at a lower field, with respect to H-2'

Table I. Carbon Chemical Shifts (in ppm downfield from TMS) and Coupling Constants (in Hz) of **1–4**[a]

C-atom multiple	**1**	**2**	**3**	**4**
$C_{1'}$ quart	139.09, m	139.06, d,t, $J_{C-1'/H-3'} = 7.8$, $J_{C-1'/H-2'} = 1.0$	138.90, t, $J_{C-1'/H-3'} = 7.8$	138.88, s
C_9 quart	137.09, m	137.06, t, $J_{C-9/H-1} = 3.9$	137.02, t, $J_{C-9/H-1} = 3.9$	137.05, t, $J_{C-9/H-1} = 3.9$
$C_{2'}$ tert	131.34, $^1J = 158.4$, d,d, $J_{C-2'/H-4'} = 7.5$, $J_{C-2'/H-6'} = 5.0$	131.26, $^1J = 158.4$, d, $J_{C-2'/H-6'} = 5.0$		
C_{4a} quart	129.87, m	129.85, m	129.87, m	129.87, m
$C_{3'}$ tert	128.39, $^1J = 160.8$	128.22, $^1J = 159.9$, $J_{C-3'/H-5'} = 7.8$, $\nu_{1/2} = 3$ Hz	128.11, $^1J = 159.4$, $J_{C-3'/H-5'} = 7.8$, $\nu_{1/2} = 1$ Hz	
$C_{4'}$ tert	127.47, m			
C_1 tert	126.90, $^1J = 163.5$, m	126.89, $^1J = 163.5$, m	126.90, $^1J = 163.5$, m	126.90, $^1J = 163.5$, m
C_2 tert	124.94, $^1J = 161.5$, d,d, $J_{C-1/H-3} = 8.8$, $J_{C-1/H-2} = 1.5$	124.93, $^1J = 161.5$, d,d, $J_{C-1/H-3} = 8.8$, $J_{C-1/H-2} = 1.5$	124.92, $^1J = 161.5$, d,d, $J_{C-1/H-3} = 8.8$, $J_{C-1/H-2} = 1.5$	124.94, $^1J = 161.5$, d,d, $J_{C-1/H-3} = 8.8$, $J_{C-1/H-2} = 1.5$

[a] quart = quaternary, tert = tertiary, s = singlet, d = doublet, t = triplet, m = multiplet. Numbering of positions refers to Figure 1.

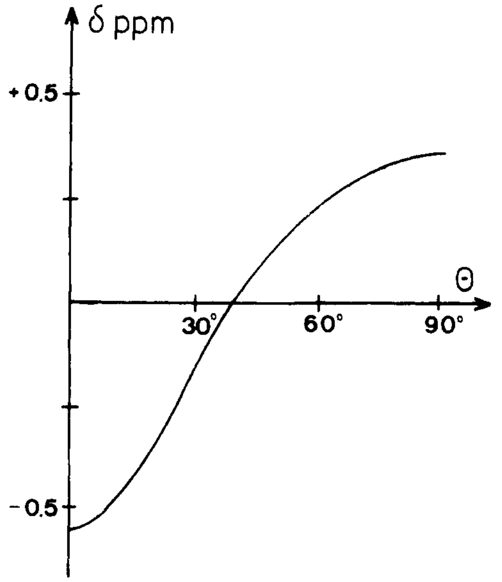

Figure 3. Theoretical relation between the twist angle of the phenyl substituents in **1** and the relative chemical shift of the proton H-1.

and H-6′, and are significantly broadened by H–D coupling. This result is consistent with the spectrum of **3** (Figures 2e and 2f) which exhibits a singlet for the protons H-3′ and H-5′ at 7.59 ppm.

The twist angle of the phenyl substituents in the diamagnetic species can be deduced from the ^1H NMR data. Provided that the electron density at H-1 and H-2 is not affected by the phenyl substituents, the significant high field shift (0.25 ppm and 0.05 compared with the corresponding resonances in anthracene, respectively) can only be caused by the anisotropy of the aromatic ring current in the phenyl rings. The theoretical dependence of the dihedral angle vs. the relative chemical shift of proton H-1 is shown in Figure 3. For this calculation the ring current data of Haigh and Mallion[10] and the x-ray analysis of anthracene[11] and diphenyl[12] were used. On this basis a twist angle of 62° is determined, which is in excellent agreement with the value previously obtained from UV data.[7i] This value reflects the more pronounced steric hindrance as compared with the less overcrowded diphenyl (42°, neutron diffraction) in the gaseous phase.[13]

^{13}C NMR Measurements of DPA. The carbon chemical shifts were measured in order to confirm the foregoing assumption, that the charge distribution in the anthracene moiety is not much altered by the phenyl substitution. Changes in the electron distribution should easily be deduced from carbon chemical shifts since they remain unaffected by any ring current anisotropies[14] and since these shifts are significantly more sensitive to changes in electron density than proton chemical shifts ($\Delta\delta_C$ = 160 ppm/electron, $\Delta\delta_H$ = 10)[15]. Using the published assignment of the carbon signals of **1**[16] carbon C-1 shows a low field shift of 3 ppm as compared with anthracene.[17]

From this fact a significant change in the electron distribution cannot be excluded. Since the interpretation of the CMR spectrum of **1** was only obtained by comparison with ^{13}C data of some model compounds, we felt a reinvestigation to be necessary. Therefore the ^{13}C spectra of the deuterated derivatives **2–4** were recorded.

The proton noise decoupled (natural abundance) ^{13}C NMR spectrum of **1** shows up eight singlets between 126 and 140 ppm, but only carbon C-4′ could be identified due to its lower intensity. An assignment of the remaining carbons of the phenyl substituents was achieved by comparing the noise decoupled CMR spectra of **1** with those of the deuterated compounds **2–4**. Carbon atoms C-1 and C-2 were distinguished by applying the $^{13}C\{^1H\}$ off-resonance technique.[18] Obviously the carbon resonating at 126.9 ppm is directly attached to proton H-1 at 7.66 ppm, i.e., one deals with C-1. Additionally the proton coupled spectra of **1–4** display for C-2 a distinct doublet of doublets while C-1 exhibits a crude doublet of triplets. For the assigned carbons the patterns are identical with those of anthracene.[19] The assignment of the quaternary carbons C-1′, C-9, and C-4a was achieved by comparing the proton coupled spectra of the compounds **2–4** (Table I) using the well-established coupling constants of benzene ($^2J_{CH}$ = 1.0 Hz, $^3J_{CH}$ = 7.4 Hz, $^4J_{CH}$ = 1.1 Hz[20]). The complete assignments and the results of all ^{13}C NMR measurements are collected in Table I. From these data the magnitudes of the ortho high field deuterium isotopic shifts can be determined to be in the order of 0.1 ppm; these are consistent with those of other polycyclic aromatic hydrocarbons.[21]

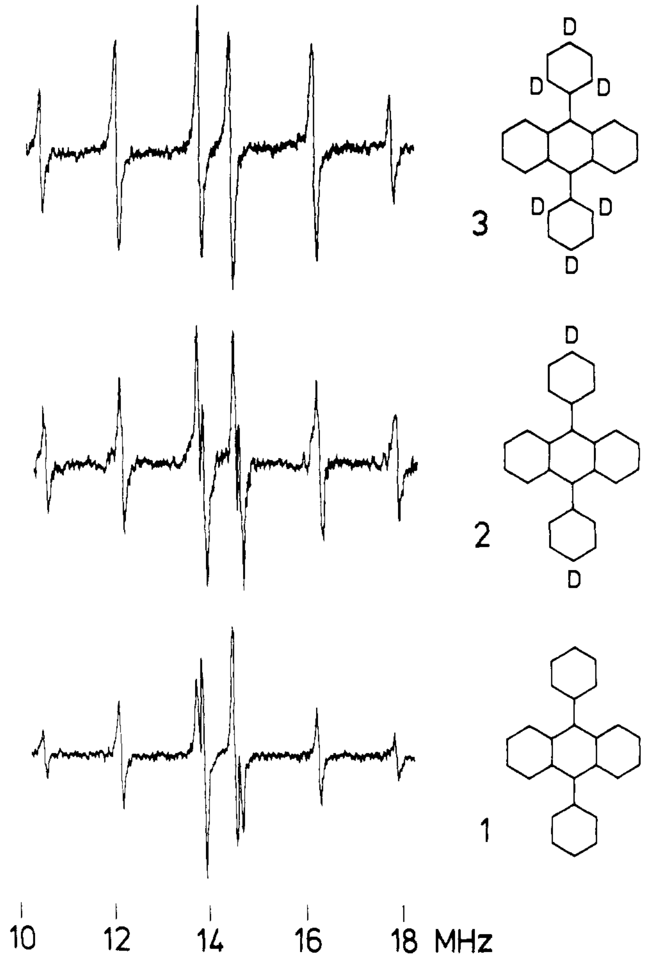

Figure 4. ENDOR spectra of the anion radicals of compounds **1**–**3** at 200 K (DME/K).

Using the revised assignment of **1** (Table I) the carbon chemical shifts of the respective C-1, C-2, and C-4a are only slightly different (≈1 ppm) in **1** and anthracene. This confirms the basic assumption used for the calculation of the twist angle, i.e., the phenyl substituents do not affect the charge distribution in the anthracene moiety.

ESR and ENDOR Measurements. The radical anions of **1**–**8** were prepared by standard methods[22] including reduction with potassium in dimethoxyethane (DME). The radical solutions showed a slight green/blue color and the radical concentration was in the order of 5×10^{-4} mol/L. By dissolving PA in concentrated sulfuric acid[23] the radical cations were produced showing a brownish color. The DPA's were oxidized by an excessive amount of aluminum trichloride in nitromethane (NM).[24] Short time UV irradiation increased the radical concentration by an order of magnitude. The color of the radical solutions was deep blue. The mechanism of the photochemical reaction is not yet known. ESR and ENDOR spectra from radical cations produced in concentrated sulfuric acid showed smaller line widths; however, the cation generation with $AlCl_3$ in nitromethane has proved to be appropriate to achieve high radical concentrations and thus a better signal-to-noise ratio. The broader lines in this system may be due to some paramagnetic impurities in the $AlCl_3$ used, shortening the electron spin relaxation time.

Five sets of proton hfs coupling constants are expected for the radical anion of **1** due to molecular symmetry, but only four could be extracted from the ENDOR spectrum (Figure 4). By comparison with the spectra of the radical anions of **2** and **3** an unambiguous assignment of all five couplings is possible.

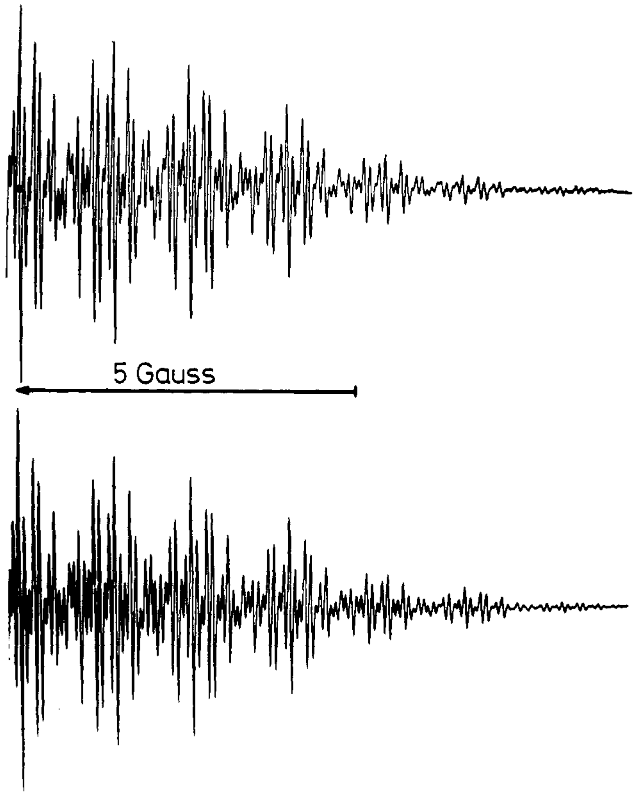

Figure 5. Experimental (top) and simulated ESR spectra of the anion of **1** (DME/K).

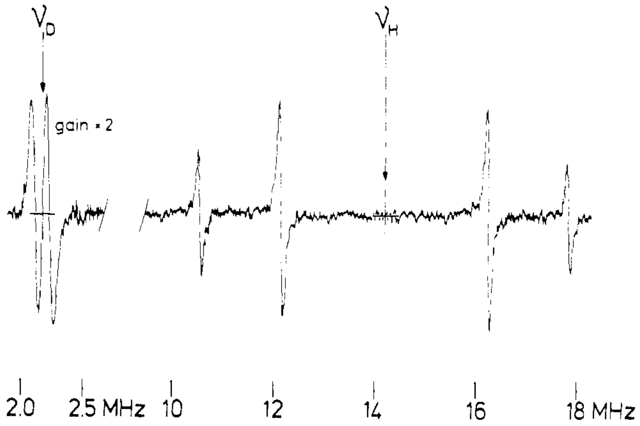

Figure 6. Deuterium- and proton-ENDOR spectrum of the anion of **4** at 200 K (DME/K). Note change in spectrometer gain.

Multiplicities of the hfs couplings were achieved by simulating the ESR spectrum of the anion of **1** using the ENDOR couplings. Excellent agreement with the experimental ESR spectrum was obtained (Figure 5). The fit procedure yielded hyperfine couplings being identical with the starting ENDOR values within ±25 kHz.

Deuterium ENDOR lines cannot be observed in the proton ENDOR frequency range due to the smaller gyromagnetic ratio $\gamma_D = \gamma_H/6.5$. The deuterium ENDOR resonances show up as two lines symmetrically spaced around 2.2 MHz, i.e., the free deuterium frequency, see Figure 6. This is the first detection of deuterium ENDOR in solution. Although the observed superimposed deuterium line widths of radical anion **4** of approximately 20 kHz are significantly smaller than the unsaturated proton line width of about 40 kHz, the expected two line pairs could not be resolved, because the deuterium hfs couplings are also reduced by γ_D/γ_H.[25]

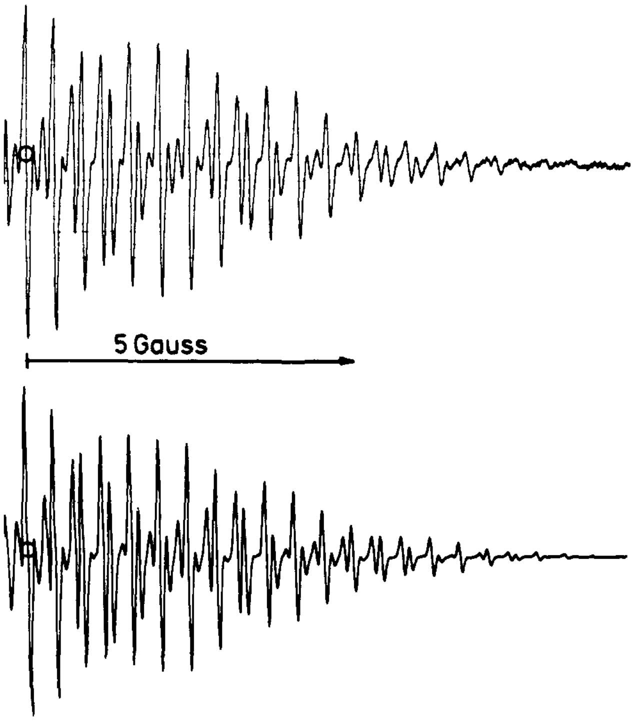

Figure 7. Experimental (top) and simulated ESR spectra of the cation of **1** at 300 K (H_2SO_4).

The assignment and multiplicities of the hfs data of the cation of **1** were obtained in the same way. For comparison the ESR spectrum of the cation of **1** and the simulated spectrum using the ENDOR results is shown in Figure 7. The hyperfine couplings obtained for the radical ions of DPA are collected in Table II.

The assignment of the hfs data for the protons of the phenyl substituents in the DPA anion is different from that previously obtained for the rubrene anion.[6] Therefore, to assure the assignment for the radical ions of PA where ESR and ENDOR investigations yielded the complete set and multiplicities of the proton hfs couplings,[26] different specifically deuterated PA compounds were synthesized; they are also collected in Figure 1. From these compounds using ENDOR and TRIPLE techniques (vide infra) the unambiguous assignments of the couplings including their signs were obtained for the PA anion, see Table II. In the DPA and PA radicals an influence of deuteration on the remaining proton couplings could not be observed within experimental error.

The cation of PA could only be prepared in sufficient concentration using concentrated sulfuric acid. Assignment of the proton couplings of the anthracene fragment using the partially deuterated PA's **7** and **8** failed, because a fast quantitative electrophilic D/H exchange was observed in the anthracene moiety during radical formation; always the spectrum of the cation of **5** was obtained even from **7** and **8.**

Sign Determination of Hfs Coupling Constants with TRIPLE Resonance. The new electron–nuclear–nuclear TRIPLE resonance technique has been described elsewhere,[27] therefore only some remarks, necessary for the present study, will be made. In TRIPLE resonance, which is an extension of the ENDOR experiment, one additionally "pumps" an arbitrarily chosen NMR transition of a nucleus in the radical under investigation with a second highly saturating unmodulated rf field. When sweeping the first NMR frequency and observing the ESR absorption one obtains an ENDOR like spectrum with a characteristic different line intensity pattern as compared to the normal ENDOR spectrum.

By relaxation considerations concerning a spin system, containing one electron coupled to different sets A, B, . . . of nuclei, it was shown to hold generally that the TRIPLE lines from nuclei in set B which are on the

$$\begin{array}{c|c} \text{same} & \text{other} \\ \hline \text{same} & \text{other} \end{array}$$

side as the pumped NMR transitions of the nuclei in set A in the spectrum show an intensity

$$\begin{array}{c|c} \text{decrease} & \text{decrease} \\ \hline \text{increase} & \text{increase} \end{array}$$

as compared to the corresponding lines in the ENDOR spectrum if the hfs couplings a_A and a_B of the nuclei in set A and set B have an

$$\begin{array}{c|c} \text{equal} & \text{unequal} \\ \hline \text{unequal} & \text{equal} \end{array}$$

sign. This statement holds for the assumption sign (γ_A) = sign (γ_B) which is fulfilled if one only deals with one kind of nuclei, e.g., protons. The terminus "same side of the spectrum" refers to the situation where two NMR transitions are both higher or lower in frequency than the corresponding free nuclear frequency and vice versa.

To illustrate the TRIPLE effect let us pump the high frequency ENDOR transition of nuclei A. The corresponding low frequency ENDOR line always will increase and if the ENDOR lines of nuclei B show the same behavior while pumping on A, i.e., decrease of the high frequency and increase of the low frequency line, the couplings of A and B have the same sign. If pumping yields an inverse behavior of the line intensities of B, the signs of a_A and a_B are unequal.

The proton ENDOR and TRIPLE spectra of the cation of **3** which contains only meta protons in the phenyl substituents are shown in Figure 8. In this case the 18 MHz NMR transition was pumped (the peculiar shape and the inversed phase of this line will not be discussed in the present paper). From the remaining high frequency lines it becomes obvious that the 14.3 MHz transition is enhanced while the line at 15.8 MHz is deenhanced as compared to the intensities in the normal ENDOR spectrum. With respect to the previous statements the two large hfs couplings belonging to the anthracene fragment have equal sign, opposite to the sign of the meta phenyl protons. From the corresponding spectra of the cations (**1, 2**) the signs of the ortho and para couplings were estimated to be

Table II. Hfsc of the Radical Ions of DPA and PA from ENDOR

Positions[a]	H hfsc, MHz Anion	H hfsc, MHz Cation
DPA		
1,4,5,8	−7.29	−7.49
2,3,6,7	−4.08	−3.53
2′,2″,6′,6″	−0.86	−1.235
3′,3″,5′,5″	+0.65	+1.235
4′,4″	−0.65	−1.235
PA		
1,8	−7.10	−8.02[b]
2,7	−4.74	−3.12[b]
3,6	−3.62	−4.10[b]
4,5	−7.88	−7.52[b]
10	−15.46	−18.35
2′,6′	−0.95	−1.365
3′,5′	+0.74	+1.365
4′	−0.74	−1.365

[a] The numbering of positions refers to Figure 1. Experimental error ±25 kHz. [b] These values could not be experimentally assigned. Earlier calculations (EXTH[26]) yielded the above assignment.

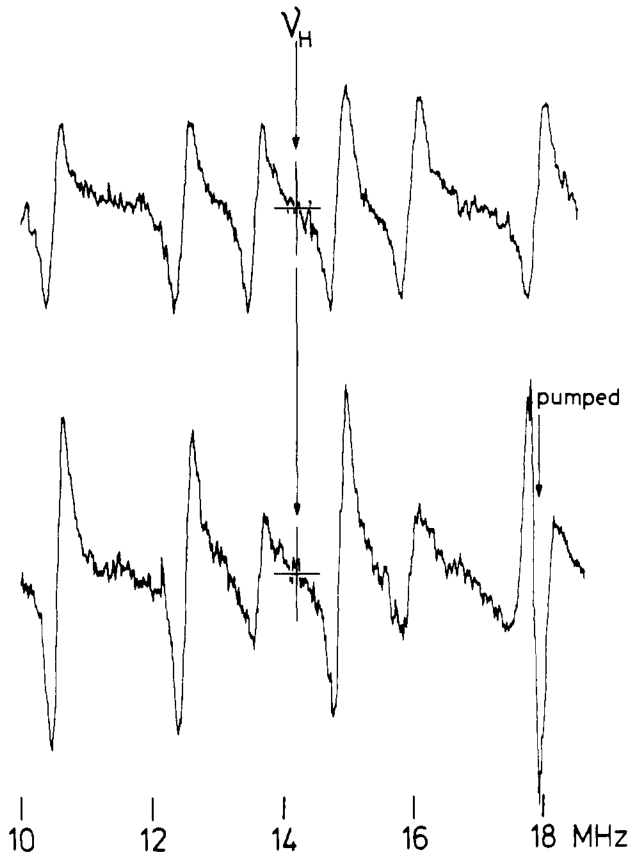

Figure 8. Proton-ENDOR (top) and TRIPLE spectra of the radical cation of **3**.

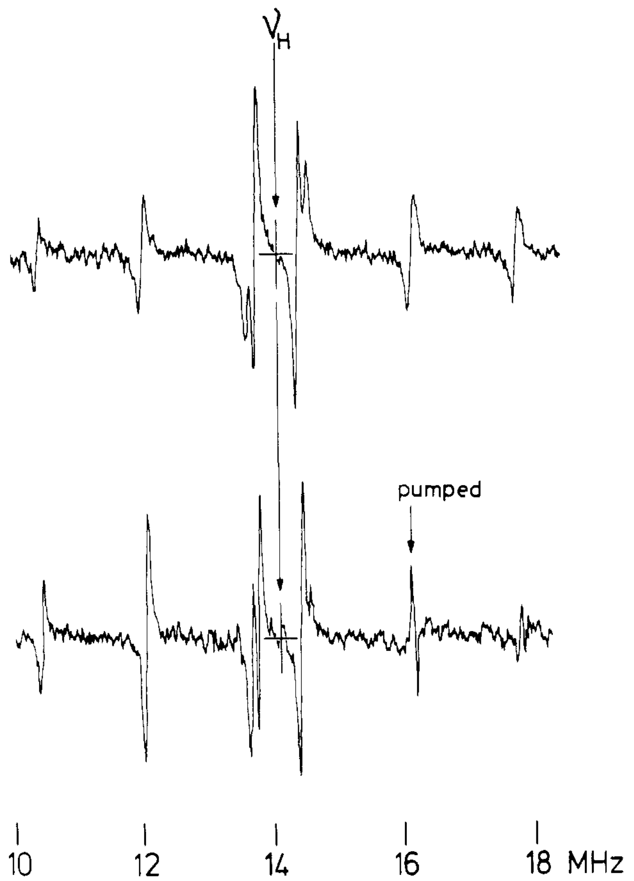

Figure 9. Proton-ENDOR (top) and TRIPLE spectra of the radical anion of **1**.

both equal and opposite to the sign of a_H^{meta}. The same result was obtained for the hfs couplings of the radical anions derived from DPA and PA. The TRIPLE and ENDOR spectra of the anion of **1** are shown in Figure 9.

It is straightforward to deduce absolute signs of hfs couplings from NMR contact shift measurements on highly concentrated radical solutions.[28] However, this method is often hampered by solubility and stability problems of the radicals and is therefore restricted in its application. Thus no successful NMR measurements are known for cation radicals in the literature. TRIPLE resonance is much more sensitive and therefore applicable to highly diluted samples with concentrations of approximately 10^{-4} mol/L. Only relative signs are obtained by this method. Therefore NMR and TRIPLE are complementary methods in this respect.

The spin distribution in the anthracene moiety is only slightly influenced by the phenyl substituents. From NMR contact shift measurements of unsubstituted anthracene radical anions[29] one can safely assume the signs of the corresponding proton hfs couplings in the DPA anion to be negative. Due to the pairing theorem[30] the same signs are expected for the cation radicals. Thus, the signs of the hfs couplings in the meta phenyl positions of both ions are positive. This is in agreement with the results found for the rubrene anion radical.[6]

Discussion

From the results in Table II it becomes obvious that the hfs coupling constants of the phenyl protons for DPA are comparable with the respective values measured for the PA radicals. The experimental data indicate that the hyperfine couplings for the meta protons are not negligible in comparison with a_H^{ortho} and a_H^{para}. Thus, earlier interpretations solely made on the basis of pure π-MO models, resulting in

$$|a_H^{para}| > |a_H^{ortho}| \gg |a_H^{meta}| \qquad (1)$$

are superceded.[3a,7] The ordering

$$|a_H^{ortho}| > |a_H^{para}| = |a_H^{meta}| \qquad (2)$$

observed for the PA and DPA anion radicals, however, is different from the sequence of the phenyl proton couplings previously established for the anion of rubrene:[6]

$$|a_H^{meta}| > |a_H^{para}| = |a_H^{ortho}| \qquad (3)$$

For the positive ion radicals of PA, DPA, and rubrene the absolute values of the phenyl proton couplings were found to be equal within the ENDOR line width. Hitherto only positive signs for the meta protons in phenyl substituted hydrocarbon radicals are measured. This fact agrees with π-electron theories when taking polarization effects within the π system[31] into account. But previously Allendoerfer pointed out that an unrealistically large π-π-polarization parameter λ is required in order to fit the experimental data derived from nonplanar molecules, which are similar to the orderings (2) and (3) of PA, DPA, and rubrene, respectively.[32]

However, sign and magnitude of a_H^{meta} can readily be understood by considering a hyperconjugative delocalization of the unpaired electron into the hydrogen 1s orbitals of the meta protons in the phenyl σ system.[33] The predictions of this hyperconjugation model are as follows: the unpaired electron population ρ(H 1s) of the meta hydrogen orbital is proportional to the π-orbital spin population ρ(C 2p$_z$) of the carbon atom where the phenyl ring is attached and to the twist angle θ between the planes of the parent molecular fragment and the phenyl substituent.[33] Using the hyperfine splitting of a free hydrogen atom, a_H^{free} = 1420 MHz, the following correlation is found to be valid:

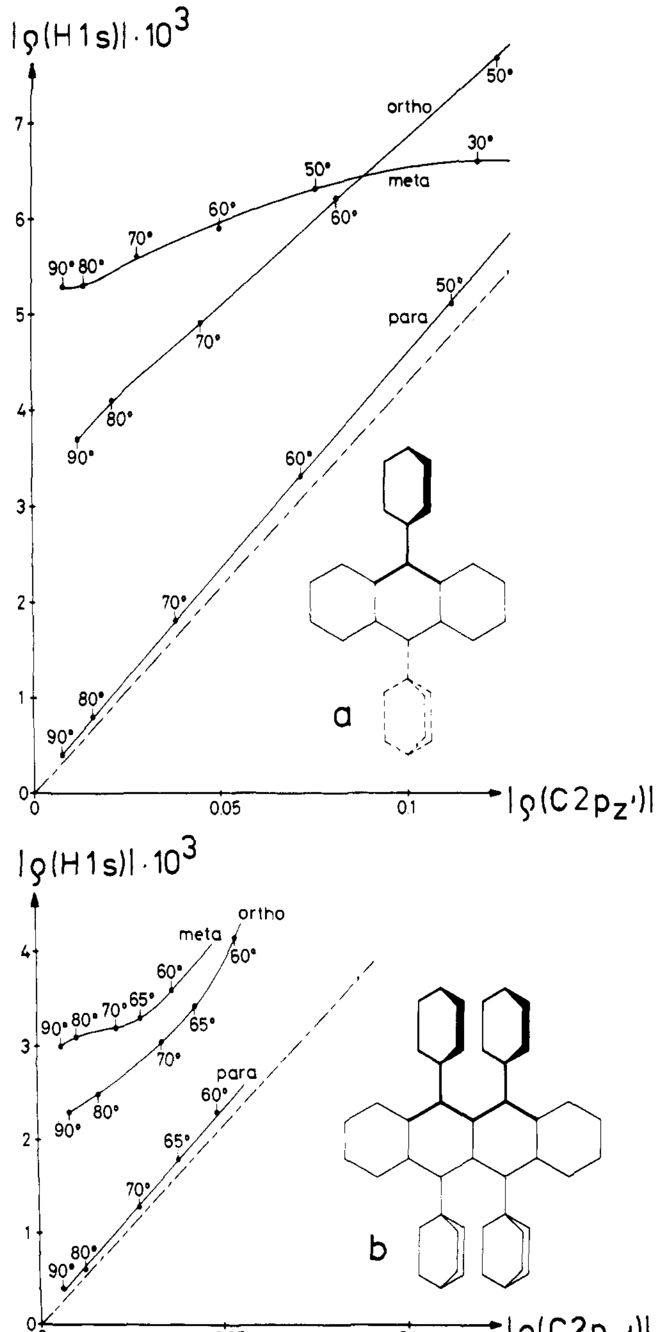

Figure 10. All-valence electron calculation in the INDO approximation on the model compounds benzyl (a) and 1,3-diphenylpropenyl (DPP) (b). Depicted is the spin population in the H 1s orbital as a function of the adjacent C $2p_{z'}$ orbital population for different twist angles. The primed coordinates are defined with respect to the plane of the phenyl substituents. The dotted line represents the linear correlation for planar hydrocarbons.[37,39]

$$a_H^{\text{meta}} = k\ 1420\ \text{MHz}\ \langle \sin^2\theta\rangle \rho(\text{C}\ 2p_z) \qquad (4)$$

The proportionality factor $k = 6,7 \times 10^{-3}$ is derived from a second order perturbation calculation when mixing the σ orbitals of the phenyl fragment with a single C $2p_z$ orbital of a free carbon atom using the standard bond length of 1.39 Å. The prediction from eq 4 agrees well with results of an all-valence electron calculation in the CNDO approximation[34] for the twisted neutral benzyl radical, yielding the proportionality to $\langle \sin^2\theta\rangle$, and for $\theta = (\pi/2)$, $k_{\text{CNDO}} = 5.3 \times 10^{-3}$. Furthermore the spin density of the ortho hydrogen atoms due to π-σ mixing was found to remain negligibly small as is predicted by the hyperconjugation model. For negative and positive ion radicals the constant k is expected to be different due to changes in the energy of the half-filled π MO. This is supported by the observation that an increase by a factor of about 2 is found by going from $a_H^{\text{meta}}(-)$ to $a_H^{\text{meta}}(+)$ in the corresponding ions under investigation.

A similar ratio is observed for the protons of a methyl group attached to planar aromatic radical ions.[4a] For such systems the spin density at the methyl protons is solely described by hyperconjugative π-σ mixing.[4] In methyl hyperconjugation only one σ-type group orbital has to be considered. Fast rotation of the methyl fragment results in averaged values for θ, $0 \leq \theta \leq 2\pi$. Thus, two different k values are obtained, belonging to the positive and negative radical ion, respectively. The product $k(a_H^{\text{free}})$ is then fitted to the experimentally observed proton hyperfine couplings. Obviously the description of phenyl hyperconjugation is more complex. From 11 σ-type phenyl MO's with proper symmetry at least two MO's have to be considered, a close lying bonding and antibonding MO. Moreover there are individual twist angles θ for different radicals. For the neutral DPA molecule, NMR measurements provided a mean phenyl twist angle of approximately 62°, vide supra. This value is consistent, with the geometry of DPA and PA derived from molecular models. We expect that the phenyl twist angles in the radical ions are the same as in the neutral PA and DPA molecules since they are caused mainly by the steric hindrance of the ortho phenyl and the anthracene peri protons, see Figure 10.

Experimental data concerning the molecular geometry in solution are not known for rubrene,[35] but even larger twist angles are expected for this molecule due to additional repulsion between the phenyl substituents in peri position. This is consistent with a previously calculated twist angle of $\theta = 90 \pm 15°$.[3] The hyperfine couplings of the ortho and para protons should not be affected by π-σ mixing; this is obvious from symmetry reasons for the latter. These couplings should decrease with increase of twist angle θ due to their proportionality to $\cos^2\theta$. For the para protons this prediction is supported by a calculation of the benzyl model system within the INDO approximation,[33] where one-center contributions of the π-σ polarization are also taken into account (see Figure 10a). Thus, the difference in the sequences (2) and (3) for PA, DPA, and rubrene could be interpreted in terms of the differences in the twist angles of these systems.

The foregoing considerations neglect the "through space" interaction of the neighbored phenyl substituents in rubrene, which may also influence the spin distribution in the substituents. Therefore, an INDO all-valence electron calculation has been performed and the neutral 1,3-diphenylpropenyl radical (DPP) was chosen as a model system. As can be seen from Figure 10b the phenyl substituents in DPP picture the geometrical situation of the rubrene molecular fragment. For rubrene all valence electron calculations are still not accessible. In DPP as well as in rubrene the ortho respectively the meta protons are no longer symmetry equivalent, which was not observed in the experiments.[6] This can be explained by the results of previous ENDOR studies on phenyl substituted radicals of low symmetry.[36] In such systems the phenyl rings are involved in thermally activated jump processes with fairly low hindrance potentials. For rubrene the calculated potential barrier is even lower; thus, being in the fast jump limit over the accessible temperature range, only averaged hfs couplings are observed.[3b] Hence, the unpaired electron populations for DPP are averaged for the values θ and $(\pi$-$\theta)$. In Figures 10a and 10b the mean values represent the dependence of the spin population of the C $2p_{z'}$ orbitals of the adjacent carbon atom on mean values of $\langle\theta\rangle$. The correlation $\rho(\text{H 1s}) = 4.29 \times 10^{-2}\rho(\text{C } 2p_{z'})$ obtained from INDO calculations for a variety of planar hydrocarbon radicals is also shown.[37] This linear relationship is used to correlate experimentally determined proton hfs constants with π spin densities obtained from π-MO theories. The correlation is valid for the para protons in DPP and benzyl (see Figures 10a and 10b) independent of the twist angles as is expected from symmetry arguments. The ortho and meta proton couplings do not fit this correlation, the H 1s population always being too large, thus reflecting strong π–σ mixing. A similar dependence is found for the systems investigated and at a mean twist angle of about 65° a_H^{meta} exceeds the other hfs couplings in the phenyl rings. Hence, in the spin density distribution in the substituents of DPP, being only little affected by additional phenyl–phenyl interaction, the experimental determined sequence (3) for rubrene is a consequence of the larger twist angle $\langle\theta\rangle = 90 \pm 15°$. Considering the ordering (2) for PA and DPA a twisting of $\langle\theta\rangle \leq 65°$ can be deduced. At this stage the lack of more accurate data for $\langle\theta\rangle$ does not allow a more quantitative analysis of the hyperconjugation model.

It should be pointed out that other possible conformations of the rubrene molecule have to be taken into account, e.g., involving changes of hybridization, i.e., the angle of the anthracene phenyl bond. This kind of deformation has been observed in crystalline 1,4,5,8-tetraphenylnaphthalene, presumably being similar in geometry with respect to the phenyl substituents.[38] ENDOR studies on the radical ions of this compound are still in progress.

In order to increase the phenyl twist angle $\langle\theta\rangle$ in PA and DPA we intend to substitute the ortho positions of the phenyl rings with bulky groups and determine the dependence of the hfs couplings on the twist angle using ENDOR in solution.

Conclusions

Combining all the magnetic resonance techniques ESR, NMR, ENDOR, and TRIPLE and resolving ambiguities by the use of specifically deuterated compounds we conclude that the phenyl hyperconjugation model serves well for interpreting unusual spin distributions in highly twisted π radicals. It must be pointed out, however, that this model of π–σ mixing as well as the more advanced all-valence electron calculations overestimate the effect on the hyperfine spectra of the radicals of PA, DPA, and rubrene.[40]

Experimental Section

The mass spectra were recorded on a CH 5-DF Varian-MAT spectrometer. The ^{1}H NMR spectra were recorded on a Varian XL 100. For the determination of the proton chemical shifts tetramethylsilane was used as internal standard. The compounds were dissolved in $CDCl_3$ and carefully degassed. The ^{13}C FT NMR spectra were recorded on a Varian CFT 20 spectrometer operating at 20 MHz. Sample tubes 10 mm in diameter and undegassed samples with $CDCl_3$ as solvent were employed. The D resonance of the solvent was used as lock signal.

To registrate the ESR spectra a commercial AEG X-20 spectrometer was used. ENDOR and TRIPLE spectra were recorded on a broad band spectrometer built up in the Institut für Molekülphysik, Freie Universität Berlin, which has already been described[27a] and on a commercial AEG ENDOR accessory, respectively (ENDOR spectra only). Dimethoxyethane (DME) and nitromethane (NM) were purified by distillation, carefully degassed by the freeze-pump-thaw technique, and stored over sodium/potassium alloy (DME) and over calcium hydride (NM), respectively. The line width of the anion radicals in ESR (42 mG) was limited by the sidebands of the 125 kHz field modulation. The temperature of the samples was optimized to give maximum resolution of the spectra and varied from 180 to 220 K for DME and NM and 300 to 330 K for sulfuric acid.

1,8-Dibromo-9,10-dihydro-9-oxoanthracene. 1,8-Dibromoanthraquinone (3.7 g, 0.01 mol) was dissolved in 150 mL of hot concentrated H_2SO_4. After cooling 0.6 g (0.02 mol) of Al powder was added within 0.5 h. The mixture was stirred and the temperature was kept at 30 °C. The color changed from orange to black and green and finally was bright yellow. After 3 h the reaction was complete and the mixture was poured on ice. The precipitate was dried, dissolved in $CHCl_3$, and treated with charcoal. After chromatography on SiO_2 in benzene 1.9 g (54%) of the pure product was obtained, mp 204 °C. Anal. Calcd: C, 47.90; H, 2.01; Br, 45.53. Found: C, 47.91; H, 2.36; Br, 44.97.

3,6-Dibromo-9,10-dihydro-9-oxoanthracene. 2,7-Dibromoanthraquinone (3.7 g, 0.01 mol) was reduced in the same way as described above. From NMR measurements using the shift reagent $Eu(fod)_3$ the reduction product was determined to be 3,6-dibromo-9,10-dihydro-9-oxoanthracene; yield 71%, mp 212 °C. Anal. Calcd: C, 47.90; H, 2.01; Br, 45.53. Found: C, 47.44; H, 1.78; Br, 44.96.

1,8-Dibromo-9-phenylanthracene and 3,6-Dibromo-9-phenylanthracene. A solution of phenylmagnesium bromide was prepared from 1.8 g (0.011 mol) of bromobenzene and 0.27 g (0.011 mol) of Mg in a mixture of 50 ml of ether and 50 ml of benzene. 1,8- and 3,6-dibromoanthrone (1.8 g, 0.005 mol), respectively, were added in small portions. The mixture was stirred for 1 h at room temperature and for 0.5 h at 80 °C. After hydrolysis with diluted D_2SO_4 and separation of the organic layer, chromatography on SiO_2 in $CHCl_3$ yielded 0.8 g (38%) of the 1,8-derivative, mp 177 °C, and 1.13 g (63%) of the 3,6-compound, mp 173 °C. Anal. Calcd: C, 58.29; H, 2.93; Br, 38.78. Found: 1,8-dibromo-PA: C, 58.14; H, 3.24; Br, 38.61. 3,6-dibromo-PA: C, 58.03; H, 3.15; Br, 38.75.

9-Phenylanthracene-*1,8-d₂* (7) and 9-Phenylanthracene-*3,6-d₂* (8). THF (tetrahydrofuran) (100 mL) and 10 mL of benzene were refluxed for 1 h with 1 g of $LiAlD_4$; 500 mg (1.2 mmol) of the corresponding dibromo compound was added. The temperature was kept at 60 °C and three portions of 0.5 g $LiAlD_4$ were added after 2, 6, and 12 h. Excessive $LiAlD_4$ was decomposed by D_2O. The solvent was evaporated and the residue was chromatographed on SiO_2 in $CHCl_3$ and recrystallized from ligroin/toluene (4:1). **7** yielded 280 mg (90%), mp 154 °C; **8** yielded 300 mg (96%), mp 156 °C.

9-Phenyl-*2′,4′,6′-d₃*-anthracene (6). A solution of phenyllithium in 50 ml of ether was prepared from 3.2 g (0.02 mol) bromobenzene-d_3 and 0.3 g (0.043 mol) of lithium. To this solution a total amount of 1.94 g (0.01 mol) of anthrone was added in small portions. Toluene (100 mL) was added and refluxed for 2 h. After hydrolysis with dilute HCl, the mixture was steam distilled to remove biphenyl. The residue was chromatographed on SiO_2 in toluene, yielded 1.8 g (70%), mp 153 °C.

9,10-Diphenylanthracenes (1–4). All the diphenylanthracenes (**1–4**) were prepared in the following manner: Bromobenzene (0.1 mol) in 50 mL of ether was slowly added to 50 mL of ether containing 1.5 g (0.22 mol) of lithium. To this solution of phenyllithium 9.3 g (0.045 mol) of anthraquinone was added in small portions producing a thick orange mixture. After refluxing for 30 min, 30 mL of D_2O was added. The solvent was removed and the remaining solid was extracted with ethyl acetate. The obtained 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracenes were purified by recrystallization from toluene. The yield was about 78% in all cases. Six grams (~0.016 mol) of each parent diol were dissolved in 100 mL of hot acetic acid. HI (5 mL, 67%) was added and the mixture was boiled for 1 min. After cooling the precipitate was collected and washed with cold ethanol. The products were recrystallized from ligroin/$CHCl_3$ (3:1) and sublimed for further purification, yielding 94%, mp 249 ± 1 °C.

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Effect of Carbon–Halogen Bonds on Nuclear Magnetic Resonance Chemical Shifts. 2. Proton and Carbon Nuclear Magnetic Resonance Spectra of Cyclobutyl Halides[1,2]

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Abstract: As part of a study of the effect of carbon–halogen bonds on NMR chemical shifts, the proton and carbon NMR spectra of the cyclobutyl halides have been determined. The proton spectra have been completely analyzed. The coupling constants were found to be essentially invariant on going from one halide to the next, indicating that all had the same geometry. In several cases, for both the proton and ^{13}C spectra, the replacement of a hydrogen by a halogen led to an upfield shift rather than the more usual downfield shift. The changes in proton chemical shift from one halide to the next are linearly related to the changes in carbon chemical shifts, suggesting that similar mechanisms are operative for both.

Although proton and carbon chemical shifts have been studied for many years, origins of the shifts are still not well understood.[4] Simple formulations which include the magnetic anisotropy and field effect of a substituent in a classical fashion are not adequate to explain the magnitude of the effects.[5] In order to clarify the problem, it appears necessary to have data for a large number of protons and carbons having different geometrical relationships to the bond causing the chemical shift. This would map the geometrical component of the shifts and would permit one to analyze the factors involved in creating them. We are examining the NMR spectra of a series of halides which have well-defined geometries. Halides were chosen since the carbon–halogen bond is cylindrically symmetrical, thus simplifying the analysis of the problem. Also, since the dipole moments of the several C–X bonds are similar,[6] the contribution of the field effect to the difference in chemical shift from one halide to the next should be minimal.

The proton NMR spectra of the cyclopropyl halides[2,7] as well as the ^{13}C NMR spectra have been reported.[8] We have presented a complete analysis of the seven-spin system, cyclobutanol.[9] We now report the proton NMR spectra of the cyclobutyl halides, along with the ^{13}C NMR spectra. Subsequently, we shall present the spectra of some bicyclo[2.1.1]hexyl halides and norbornyl halides.

Whereas cyclobutane is conformationally mobile with a very low barrier to inversion,[10] the cyclobutyl halides exist predominantly in one conformation. The structures of cyclobutyl chloride[11] and bromide[12] have been determined by microwave spectroscopy, and both were found to be puckered in the same fashion as cyclobutane itself. Unlike the cyclohexyl halides