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ESR, ^{1}H-, D-, ^{13}C-ENDOR AND TRIPLE RESONANCE STUDIES OF ALKYL SUBSTITUTED PHENALENYL RADICALS

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Abstract—A variety of alkyl substituted phenalenes, including deuterated and ^{13}C labeled compounds, was synthesized via an organometallic reaction. From the respective paramagnetic oxidation products, the phenalenyls, ESR spectra and proton, deuterium and ^{13}C ENDOR resonances could be obtained. From the electron-nuclear-nuclear-TRIPLE resonance experiments the signs of all hyperfine coupling constants could be determined. An interpretation of the spin density distributions on the basis of the hyperconjugation model is given. The results of HMO-McLachlan and INDO calculations are reported.

In the field of magnetic resonance spectroscopy on organic free radicals phenalenyl has proven to be one of the most suitable doublet state molecules. The results of the extensive studies on phenalenyls and on the diamagnetic precursors, the phenalenes, have been described in two review articles.[1] Very recent papers are dealing with the first general TRIPLE (electron-nuclear-nuclear) resonance experiments performed on phenalenyl as a model compound,[2] the hyperfine interaction of the Cl atom in chloro substituted phenalenyls,[3] and the detection of deuterium ENDOR and the determination of deuterium quadrupole couplings by means of ENDOR in liquid crystals on partially deuterated phenalenyl.[4] Moreover all the investigations on this system reveal that phenalenyl is readily accessible from a variety of precursors and that its stability remains nearly unaffected by alkyl or phenyl substitution. Therefore we felt alkyl phenalenyls to be the radicals of choice for studying

(1) The influence of alkyl substitution on the "aromatic" portion of the molecule such as loss of the threefold symmetry.

(2) The spin density distributions within the alkyl groups in order to clarify the mechanisms of spin density transfer into the side chains, e.g. hyperconjugation or spin polarization. In this respect it is of particular value that the relative signs of the experimental HFSC's (hyperfine splitting constants) are accessible by means of the TRIPLE resonance technique.

(3) Hindered rotations and equilibrium conformations of the alkyl substituents with respect to the plane of the phenalenyl moiety. Similar ESR investigations are well-known from transient alkyl radicals but for intensity reasons these species cannot be studied by means of ENDOR and TRIPLE. On the other hand, due to the much better resolution these multiple resonance techniques have proved to give more detailed information on hyperfine interactions than conventional ESR does.

(4) The validity and limitations of the quantum mechanical approaches for calculating the electron spin density distributions in alkyl substituents.

In the present communication we wish to report on the synthesis, ESR, ENDOR, and TRIPLE resonance spectroscopy of phenalenyls, and discuss the use of INDO calculations for the interpretation of the experimental HFSC's in some detail.

EXPERIMENTAL

Synthesis of compounds. For the present purpose all the phenalenyls were obtained from the respective alkyl substituted phenalenes via oxidation, *vide infra*. The phenalenes were prepared by the organometallic reaction of the respective Grignard component and phenalenone,[5] the latter being commercially available.

From proton[6] and ^{13}C NMR measurements it is obvious that the mono substituted phenalenes consist of a mixture of tautomers (see Fig. 1). It is noteworthy that these measurements revealed the presence of the fat-faced portion of the phenalenes, pictured in Fig. 1, in all isomers. Hence, the isomers V and VI could not be detected in our NMR studies. It may be assumed that the existence of V and VI is disfavored for steric reasons.

Phenalenes. An ethereal soln of the appropriate alkyl magnesium halide, prepared from 150 mmol of alkyl halide [MeI, Me-^{13}C iodide (90 atom-%), Me-d$_3$ iodide (99.5 atom-%), EtI, i-PrBr, tBuCl] and Mg (3.6 g) was treated with a benzoic soln of phenalenone (30 mmol) at room temp. Stirring for about 20 hr, aqueous work-up, and purification by column chromatography (silica gel/benzene) yielded the respective phenalenes **2a**–**7a**. The analytical data of the phenalenes are collected in Table 1.

Generation of the radicals. The phenalenyls were obtained by heating the solns of the phenalenes in toluene or in mineral oil (Shell Ondina) in the presence of atmospheric O_2 for about 10 min. Subsequently the solns were carefully degassed on a high vacuum line.

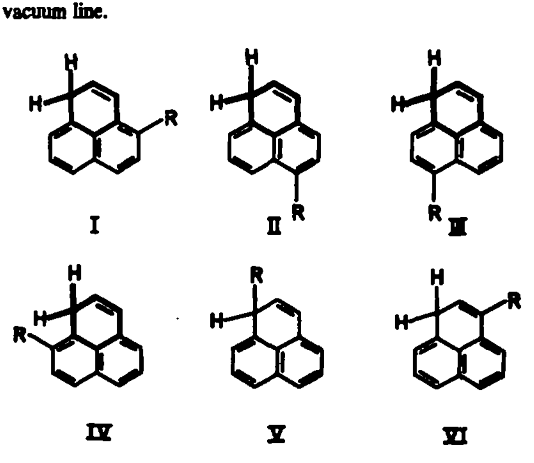

Fig. 1. Isomeric alkylphenalenes. Note that all substituted phenalenes **a** consist of a mixture of isomers I–IV, whereas the possible isomers V and VI proved to be absent, see text. For cipher code of phenalenes and phenalenyls see Table 1 and text.

Table 1. Yields, analytical and MS data of the phenalenes 2a–7a

Compound	Yield [%]	$C_{calc.}$ C_{found}	$H_{calc.}$ H_{found}	M^{+} m/e
Methylphenalene (2a)	12	93.46 93.51	6.67 6.67	179
Methyl-^{13}C-phenalene (3a)	15	---	---	181
Methyl-d_3-phenalene (4a)	14.8	---	---	183
Ethylphenalene (5a)	11.7	92.78 92.91	7.22 7.34	194
Isopropylphenalene (6a)	22.5	92.31 92.00	7.69 8.16	208
tert.-Butylphenalene (7a)	9	91.89 91.28	8.11 8.48	222

Instrumentation. The ESR spectra were recorded on an AEG-12X-ESR-spectrometer. The ENDOR and TRIPLE spectrometer consists basically of an AEG-20X-ESR spectrometer, the ENDOR accessory was built in this laboratory. A detailed description of our cw ENDOR spectrometer has been presented elsewhere.[7] Temp. variation was achieved with an AEG temp. control unit; the ESR splittings were measured with an AEG proton NMR gaussmeter and a hp frequency counter (5245L).

RESULTS

ESR spectra. Figure 2 depicts the ESR spectra of the phenalenyls taken at 240 K in toluene. In most of the cases the HFS spectra are clearly resolved and the HFSC's could be extracted. As can be seen from the spectra all magnetic nuclei including deuterium and ^{13}C in the labeled positions contribute to the line pattern, except the Me protons of the Et (5b) and tBu (7b) groups.

ENDOR spectra. A more accurate determination of the HFSC's was possible from the ENDOR spectra, given in Fig. 3 (for experimental details see Fig. caption). It is to be noted that under our experimental conditions even deuterium and ^{13}C resonances could be observed.

According to the ENDOR resonance condition

$$\nu_i = |\nu_N \pm a_i/2|$$

each set of equivalent protons and deuterons should give rise to one pair of lines equally spaced around the free proton (ν_H = 14.020 MHz) and the free deuterium (ν_D = 2.152 MHz) frequency, respectively, separated by the respective isotropic HFSC, whereas the ENDOR resonances of ^{13}C

$$\left|\frac{a(^{13}C)}{2}\right| > \nu_{^{13}C} = 3.525\,\text{MHz}$$

should occur around a(^{13}C)/2 separated by $2\nu_{^{13}C}$. Only the high frequency deuterium line at 3.407 MHz and the high frequency ^{13}C line at 8.843 MHz could be obtained, because no ENDOR lines below ≈ 3 MHz could be detected due to experimental drawbacks.

Due to the smaller magnetogyric ratio of deuterium a significant reduction of HFSC's is observed when replacing H by D. The ratio of the respective couplings should be represented by the quotient of the magnetogyric ratios of the two nuclei $\gamma_H/\gamma_D = 6.514$. This is approximately what is experimentally found (a_H/a_D = 6.642).

It is noteworthy that the maximum (high frequency) ^{13}C-ENDOR enhancement occurred at about the same experimental conditions as for the proton lines. Such a behaviour of ^{13}C-ENDOR resonances was also reported very recently for p-benzoyl-di-t-butyl-phenoxyl ^{13}C-labeled in the CO position.[8] The relaxation properties of ^{13}C in this radical were rationalized by assuming a very small HFS anisotropy of the ^{13}C-nucleus. The nuclear relaxation rates, which determine ENDOR amplitudes, line widths and optimum ENDOR response, depend quadratically on the HFS anisotropy. The small HFS anisotropy could be established by HMO–McLachlan and INDO calculations. Cross relaxation effects, usually obtained in the ^{13}C-ENDOR experiments, can be excluded in the phenalenyl radical (3b) because these effects are known to occur within the accessible temperature range if the anisotropies of the HFS are quite large.

Electron-nuclear-nuclear TRIPLE Resonance spectra. The relative signs of the HFSC's were accessible from general TRIPLE experiments.[10] Figure 4 represents the TRIPLE spectrum of 3b, the most interesting phenalenyl in this respect. Making use of the fact that the sign of the largest proton coupling of phenalenyl 1b is known to be negative from ESR studies in liquid crystals[11] the *absolute* signs of all proton (deuterium) and ^{13}C HFSC's are available. The experimental HFSC's from ESR and from ENDOR/TRIPLE are collected in Table 2.

Assignments of HFSC's to molecular positions. Particular care had to be taken of a proper assignment of all HFSC's to molecular positions. Using only ESR the assignments of the splittings might be ambiguous as can be seen from the analysis of the ESR spectrum of 2b: Two of the HFSC's are found to be ~ 16.9 MHz and ~ 17.5 MHz, referring to 4 and 3 equivalent protons, respectively. At first glance the latter coupling might be assigned to the Me protons. This has in fact been done in a recent ESR study on 2b,[5b] being in disagreement with our results. Obviously the splitting of 17.5 MHz belongs to 3 of the large perimeter proton HFSC's, whereas the 4 protons with the 16.9 MHz coupling are equivalent by chance (within experimental line width), 3 of them belonging to the Me group for the following reasons:

(i) Deuteration of the Me group decreases the intensity of the ENDOR lines belonging to the 16.9 MHz coupling.

(ii) From the TRIPLE experiment one finds positive sign for the 16.67 MHz coupling and negative signs for the other large HFSC's (see Fig. 4).

(iii) As is known from a previous ENDOR study on

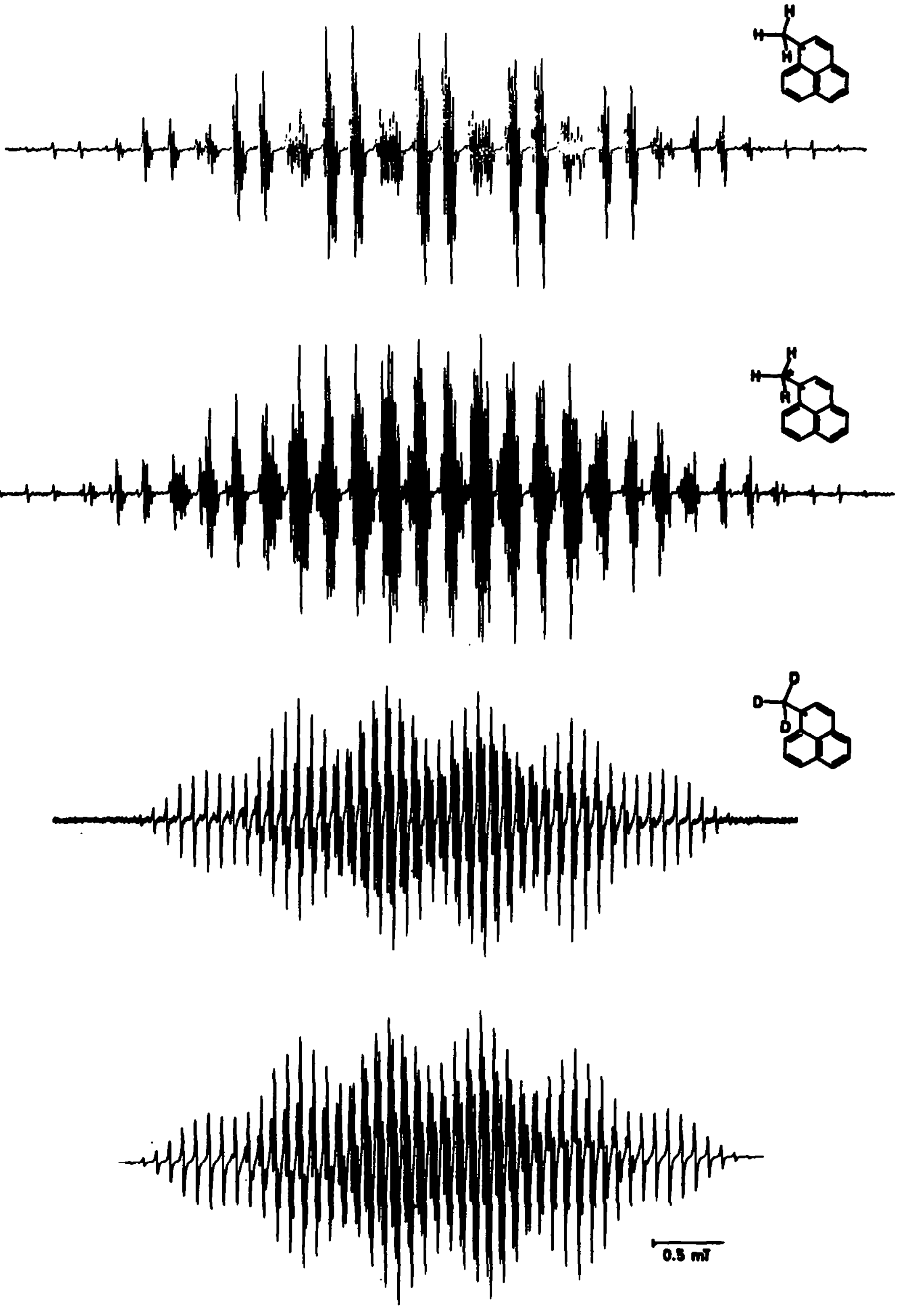

Fig. 2a.

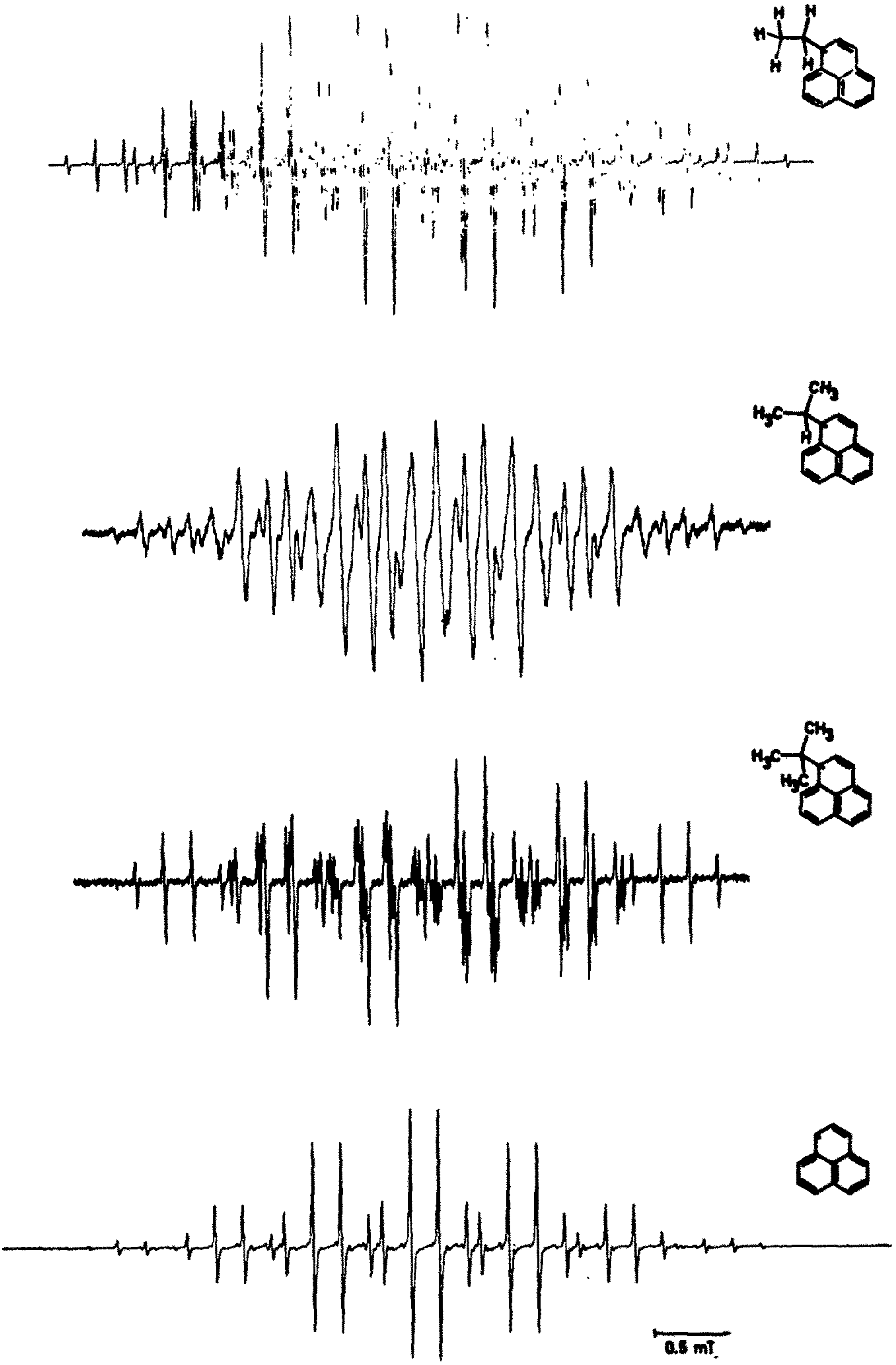

Fig. 2b.

Fig. 2. Experimental ESR spectra of the phenalenyls 1b–7b; solvent toluene, 240 K. In addition the computer-simulated ESR spectrum of 4b is shown for comparison (2a bottom).

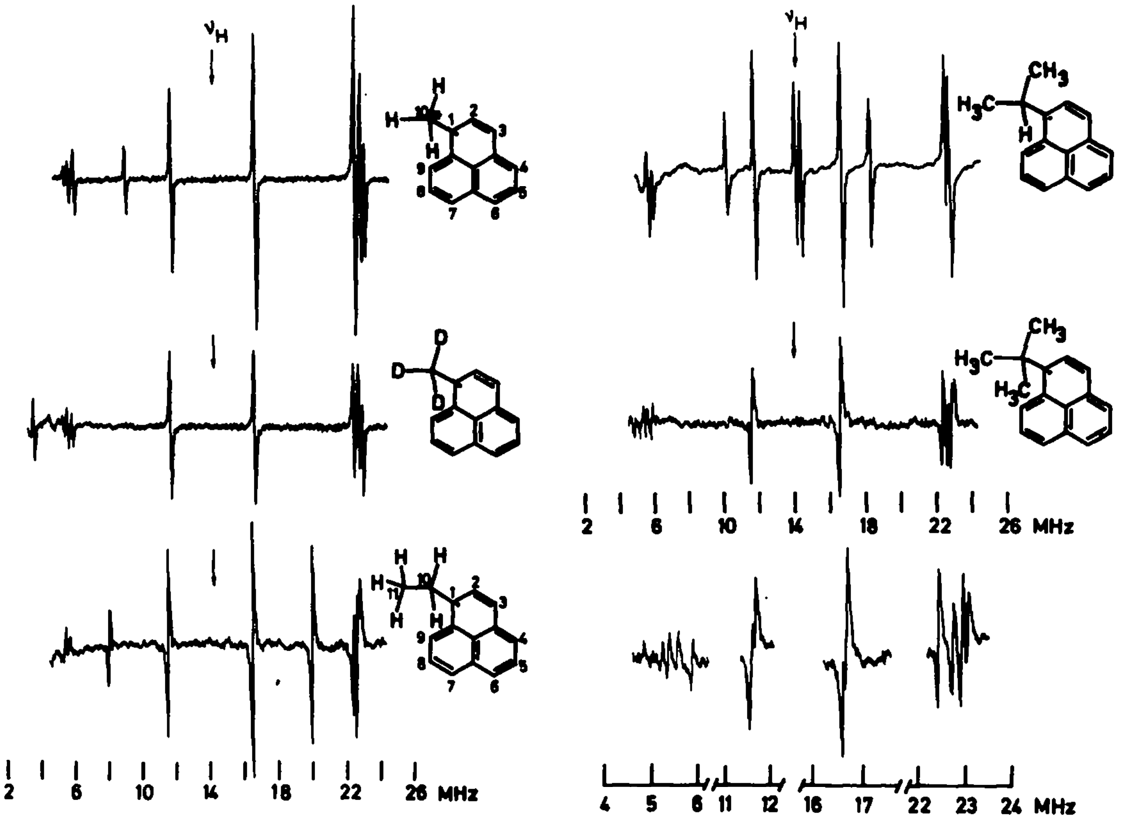

Fig. 3a. Fig. 3b.

Fig. 3. ENDOR spectra of the phenalenyls 3b–7b; solvent mineral oil, 290 K. The ENDOR spectrum of 7b is also represented under high resolution conditions (3b bottom, note the different frequency scale); $B_{NMR} = 0.4$ mT (rot. frame), 10 kHz-fm-modulation ±20 kHz amplitude.

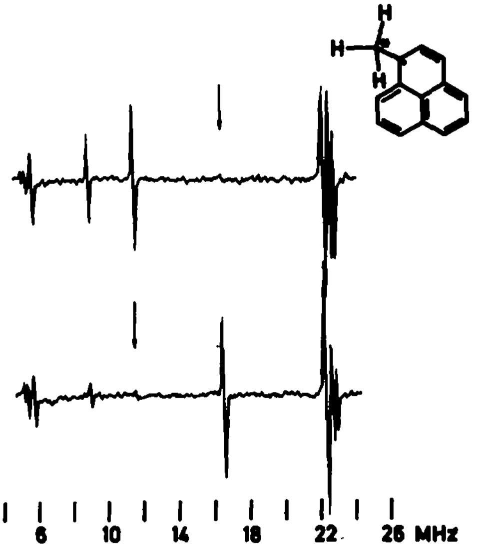

Fig. 4. General TRIPLE spectra of 3b; mineral oil, 270 K. The arrows indicate the pump frequencies; $B_{NMR}(\text{pump}) = 0.8$ mT, $B_{NMR}(\text{scan}) = 0.4$ mT (rot. frame), 10 kHz-fm-modulation ± 50 kHz amplitude.

Me substituted pentaphenylcyclopentadienyl radicals[12] the Me protons show a smaller HFS anisotropy than the perimeter protons resulting in a different relaxation behaviour. Actually, on cooling the sample the ENDOR lines of the Me protons experience a less pronounced decrease of intensity than the perimeter protons. This effect is demonstrated in Fig. 5, depicting part of the ENDOR spectrum of 2b at two different temperatures. Thus, additional evidence of the assignment of the methyl proton coupling is obtained.

Unambiguous assignments of all HFSC's to molecular positions were achieved by simulating the ESR spectra using the respective ENDOR couplings. Excellent agreement with the experimental ESR spectra was obtained, which is reflected in the experimental and calculated ESR spectra of 4b (Fig. 2a, bottom), serving as a typical representative. Actually, the fit procedure yielded hyperfine couplings being identical with the

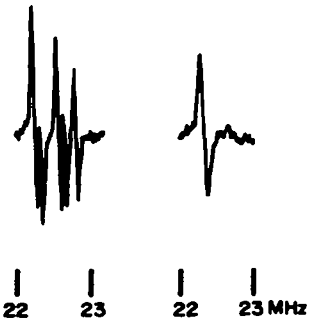

Fig. 5. Part of the ENDOR spectrum of 3b at 300 K and 260 K; for details see text.

Table 2. Isotropic HFSC's from ESR (toluene, 240 K) and from ENDOR (mineral oil, 290 K, high resolution conditions)

	ESR [MHz] Toluene, 240 K			ENDOR [MHz] Mineral oil, 290 K		
Radical	2.5.8.[a]	3.4.6.7.9.	Substituent	2.5.8.	3.4.6.7.9.	Substituent
2b	4.96(3H)	16.87(1H)	16.87(3H)	5.027	16.661	16.819
		17.52(3H)			17.381	
		18.05(1H)			17.553	
					17.905	
3b	4.96(3H)	16.82(1H)	16.87(3H)	+5.014	-17.381	+16.672
		17.52(3H)	10.65(^{13}C)		-17.541	-10.636(^{13}C)
		18.05(1H)			-17.906	
4b	4.99(3H)	16.79(1H)	2.66(3D)	4.999	16.803	2.510(D)
		17.40(3H)			17.407	
					17.558	
		17.94(1H)			17.925	
5b	4.96(3H)	17.40(4H)	11.80(2H)	5.049	16.921	12.047
					17.359	
					17.500	
		17.71			17.711	
6b	4.96(3H)	17.32(4H)	8.35(1H)	5.00	-17.03	+ 8.38
		17.43(1H)	0.39(6H)		-17.44	+ 0.31
					-17.49	
					-17.612	
7b[b]	4.89(1H)	16.56(1H)		4.952	16.632	
	5.01(2H)	17.19(1H)		5.140	17.278	
		17.63(2H)			17.660	
		17.85(1H)			17.934	

[a] For numbering of molecular positions see Figure 3.

[b] ESR couplings taken from a HFS fit procedure.

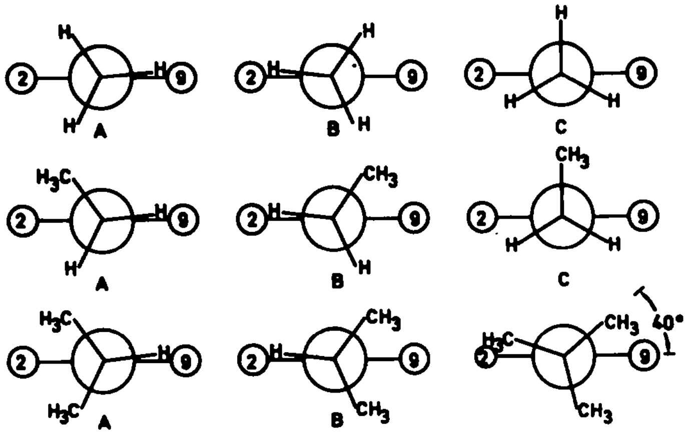

Fig. 6. Newman representations of the different conformations of alkyl substituents; for details see text.

starting ENDOR HFSC's within the ESR line width (~250 kHz).

The ENDOR spectra of the substituted phenalenyls show that the equivalence of the protons belonging to the largest splitting of the phenalenyl portion is slightly lifted whereas the smaller one remains unaffected by the substituents except that of **7b**. In the latter molecule additional splittings could be observed especially under high resolution conditions, see Fig. 3b (bottom). It stands to reason that these additional splittings of the phenalenyl protons could not be assigned to individual molecular positions and even the INDO results allow no specific ordering of these couplings (*vide infra*).

DISCUSSION

Hyperconjugation effects. As could already be shown in previous ESR investigations of 1-methyl phenalenyl (**2b**)[5b] the Me proton coupling is comparable in magnitude to the largest ring proton HFSC's. The significant delocalization of unpaired spin density into the σ-type alkyl substituents was observed in a variety of Me substituted ionic π-radicals and has generally been interpreted in terms of spin polarization and hyperconjugation effects.[13] But due to the lack of sign determination the hitherto existing interpretations might be ambiguous for the following: If hyperconjugation and homohyperconjugation are the dominant mechanisms of spin transfer rather than spin polarization effects both the σ-spin densities of β- and γ-protons and the π-spin population of the adjacent carbon center should have the same sign. Since the sign of the carbon π-spin population of the substituted position of phenalenyl is known to be positive[11], positive HFSC's are then expected for the β- and γ-alkyl protons. Actually, from our TRIPLE experiments we deduced positive signs for all β-protons in the Me (**2b**, **3b**), Et (**5b**) and i-Pr (**6b**) groups, and positive sign for the γ-protons of **6b**. Moreover the hyperconjugation model, dealing with orbital overlap, implies a strong conformational dependence of the β-proton couplings.[14] This is in accordance with our measurements since the β-proton HFSC's decrease significantly when substituting the Me protons successively by additional Me groups, see Table 2 [$a_H(\beta)$(MHz): **2b** = 16.87, **5b** = 11.80, **6b** = 8.35]. Obviously a strong steric hindrance is present in the phenalenyls **5b** and **6b**, e.g. a substantial peri interaction between the alkyl substituent and the proton at the 9 position (In the limit of very low barriers to rotation the β-proton HFSC's should remain nearly unaltered when replacing Me by Et or i-Pr). The observed substituent dependence of the splittings can be accounted for by a preference of selected conformations of the alkyl groups. Accepting the hyperconjugation model one might expect a significant temperature dependence of the β-proton HFSC's. This has in fact been the subject of several investigations.[a] In the present case only **5b** exhibits a temperature dependent β-proton coupling within the accessible temperature range, see Table 2. As is to be expected increasing the temperature yields an increase of the coupling. We intend to study this effect in more detail but it will not be discussed further in this context.

HMO-McLachlan calculations. Unsubstituted phenalenyl radical (**1b**) shows 2 isotropic proton HFSC's which could previously be rationalized in the HMO-McLachlan approximation.[16] We have repeated these calculations by using $\lambda = 1$, yielding spin densities of 0.219 and -0.060 for the pertinent positions.[17] The ratio of these values (-3.65) is in satisfactory agreement with the ratio of the HFSC's found in our experiments (-3.49). The Q_{CH}-parameters of the McConnell relation obtained from these data are -28.81 Gauss and -30.17 Gauss, respectively, being within the limits usually accepted for the Q_{CH}-values.

As is well-known the HMO-McLachlan approach is restricted to the sp^2-carbon centers and therefore is unable to give any information about the spin density distributions of the side chains of the radicals. However, the application of the hyperconjugative, the inductive or even the heteroatom model within the HMO-McLachlan frame[17] often allows an estimation of the effect of substitution on the π-system. But from our respective calculations of methyl phenalenyl (**2b**) no influence on the HFSC's of the perimeter protons could be obtained, being in contrast with the experimental findings. Obviously these models are too approximate to give perfect agreement between calculated and experimental data.

INDO calculations. The foregoing results prompted us to perform an INDO calculation on the substituted phenalenyls. For this reason a Fortran program has been developed on the basis of the QCPE programs 136 and 223 allowing CNDO and INDO calculations also for larger molecules, which are additionally shown in a diagram for geometric control. Calculations have been performed on the CDC CYBER 175 of "Wissenschaftliches Rechenzentrum Berlin". The data obtained from the INDO calculations are collected in Table 3 (For more details concerning geometric parameters, etc. see Table caption). As can be seen by comparing Tables 2 and 3 the agreement between all the HFSC's derived from the INDO treatment, and the experimental couplings is rather poor. This is not surprising in view of the unsatisfying results obtained for the perimeter proton couplings of the unsubstituted compound **1b** (a_1(INDO) = -20.89 MHz, a_1(ENDOR) = -17.68 MHz; a_2(INDO) = 11.71 MHz, a_2(ENDOR) = 5.07 MHz). On the other hand, our INDO calculations reveal some interesting aspects regarding the conformations of the alkyl substituents:

It is seen from the INDO treatment of **2b** that the conformation B (denoted in Fig. 6 top) of the methyl group gives minimum SCF energy and therefore may be considered the favored conformation. The methyl proton HFSC, taken as the mean value of the 3 couplings found in the INDO calculation of conformation B, and the ^{13}C-HFSC are in moderate agreement with the experimental data, see Tables 2 and 3.

In the ethyl phenalenyl radical (**5b**) the conformation C with the Me group perpendicular to the plane of the phenalenyl moiety (Fig. 6) seems to be the most stable one for energy reasons. Therefore, in Table 3 only the HFSC's of this conformation are collected. The satisfying agreement between INDO (mean value) and experimental β-proton HFSC's is in accordance with the proposed conformation C.

From the INDO investigations of the isopropyl substituted phenalenyl (**6b**) minimum energy was obtained for the conformations A and B (Fig. 6), both of them being comparable in energy and the angular dependence is not very pronounced up to a degree of rotation of the C-H-bond direction of 60° out of the molecular plane. The calculations proved the β-proton coupling to be smaller in magnitude as compared to those of **2b** and **5b**.

Considering the t-butyl phenalenyl (**7b**) it is seen that the conformation depicted in Fig. 6 (bottom right) is favored and no significant changes of the perimeter proton HFSC's are found in the INDO calculations.

To conclude the discussion of the INDO results it has to be pointed out that optimization of molecular geometries, such as changes in bond angles and/or bond lengths often yielded improvements of the calculated HFSC's of the phenalenyls. But we think it not reasonable to allow larger deviations from standard geometries.

CONCLUSIONS

The spin density distributions of a variety of alkyl substituted phenalenyls could unambiguously be determined by using ESR, ENDOR and TRIPLE resonance techniques. The experimental HFSC's of the substituents could be interpreted by means of hyperconjugation effects. More sophisticated quantum mechanical approaches, such as the INDO approximation, gave no satisfactory interpretation of the experimental HFSC's of the perimeter proton splittings. On the other hand, the

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[a] See Ref. 15.

Table 3. Isotropic HFSC's of **2b** and **5b** derived from INDO calculations[a]

	A(**2b**) -14.126 A.U. [MHz]	B(**2b**) -14.130 A.U. [MHz]	C(**2b**) -14.128 A.U. [MHz]	C(**5b**)[b] -15.315 A.U. [MHz]
a_2^H	11.80	11.80	11.80	11.77
a_3^H	-20.51	-20.74	-20.63	-20.57
a_4^H	-20.57	-20.63	-20.60	-20.57
a_5^H	11.57	11.60	11.57	11.57
a_6^H	-20.60	-20.63	-20.60	-20.60
a_7^H	-20.68	-20.51	-20.57	-20.57
a_8^H	11.63	11.55	11.60	11.57
a_9^H	-21.03	-20.63	-20.85	-20.85
a_{10}^C	- 9.81	- 9.86	- 9.84	-8.97
a_{11}^C	---			10.93
$a_{10(\beta_1)}^H$	1.77	30.21	11.46	10.31
$a_{10(\beta_2)}^H$	29.87	1.65	11.10	10.82
$a_{10(\beta_3)}^H$	29.87	30.21	39.26	
$a_{11(\gamma_1)}^H$				- 1.40
$a_{11(\gamma_2)}^H$				2.02
$a_{11(\gamma_3)}^H$				-1.21

[a] For the INDO calculationes standard bond lengths and standard bond angles were used ($C_{aromatic}-C_{aromatic}$: 1.395 Å, $C_{aromatic}-C_{aliphatic}$: 1.530 Å; $C_{aliphatic}-C_{aliphatic}$: 1.540 Å; $C_{aromatic}-H$: 1.08 Å; $C_{aliphatic}-H$: 1.01 Å; sp^2: 120°; sp^3: 109.5°).

[b] Conformation A(**5b**): -15.192 A.U.; B(**5b**): -15.248 A.U.

INDO method proved to be suitable in the elucidation of the favored conformations of the alkyl substituents with respect to the plane of the phenalenyl portion.

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