¹³C, ¹⁹F, and ¹H ENDOR Investigations of Substituent Effects on Lifting of Orbital Degeneracy in Cyclopentadienyl Radicals. Syntheses

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Abstract: A variety of substituted, partially deuterated, and ¹³C-labeled pentaphenylcyclopentadienyl radicals ("Ziegler's radicals") have been synthesized. It is shown from ¹³C, ¹⁹F, and ¹H ENDOR experiments that monosubstitution removes the orbital degeneracy of the HOMO's in the cyclopentadienyls. These studies demonstrate that ENDOR is a very sensitive tool to probe the electron-donating and -withdrawing influence of substituents on the spin density distributions and its temperature dependence. Analyses of the spectra in combination with HMO McLachlan calculations allow determination of the thermal equilibrium between the two different species having the unpaired electron in the symmetric or antisymmetric MO, respectively.

In previous years open-shell monocyclic π electron radicals exhibiting degenerate HOMO's have been studied by means of ESR spectroscopy and, to the best of our knowledge, only once by ENDOR spectroscopy.¹ Besides cyclobutadiene, the cyclopentadienyl system turned out to be one of the most interesting systems in this respect. Looking at the paramagnetic properties of the latter, triplet spin states could unambiguously be established, e.g., of pentaphenyl-,^{2,3} pentachloro-,⁴ and even of unsubstituted cyclopentadienyl cation.5 Concerning the cyclopentadienyl radical, removing of the orbital degeneracy and the dependence of the energy gap between these orbitals on the substituents have been investigated by ESR⁶⁻⁹ and ENDOR spectroscopy.¹ Since the carbocyclic ring has no "magnetic nuclei"-neglecting natural abundance ¹³C—all experimental data obtained from the hyperfine interaction actually were "second hand", i.e., referring to hyperfine splitting constants (hfsc's) belonging to the substituents, e.g., of phenyl rings.¹ Only in some cases could ¹³C ESR satellite signals of unlabeled cyclopentadienyl radicals be detected.8-10

Recently it has been demonstrated that ENDOR is not restricted to protons but can be extended to nuclei other than protons, e.g., ¹³C.¹¹ Thus, we felt encouraged to perform ¹³C ENDOR studies of the substituent effects on the orbital degeneracy of the cyclopentadienyl radical. A prerequisite of this investigation was the synthesis of differently ¹³C labeled and substituted precursors of these radicals, i.e., the cyclopentadienyl halides. In fact, natural abundance ¹³C ENDOR spectroscopy turned out to be restricted to very specific species exhibiting unusually small anisotropic ^{13}C hyperfine interactions.12

In this investigation we report on an extensive ¹³C ENDOR study of electron-withdrawing and -donating substituent effects on the magnetic properties of the five-membered carbocyclic ring using ¹³C labeled "Ziegler radical" type systems.

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			position
radical	R	¹³ C	C ₆ D ₅
1	Н	1	
1b	D	1	1, 2, 3, 4, 5
2a	CH ₃	1	
2b	CH ₃	3, 4	
2c	CH ₃	2, 4	
3a	CF ₃	1	
3b	CF ₃		2, 3, 4, 5
3c	CF ₃	3, 4	
3d	CF_3	2, 4	
4 a	F	1	
4b	F		2, 3, 4, 5
5a	C6H	1	
6a	OČH ₃	1	
6 b	OCH ₃		2, 3, 4, 5

Table I. Numbering Scheme of Compounds

Experimental Section

Preparation of Compounds. The starting material to obtain the ¹³Clabeled compounds was ¹³CO₂ (from Ba¹³CO₃), which was allowed to react with the respective organometallic material. As can be seen from Figure 1 the respectively labeled tetraphenylcyclopentadienones (tetracyclones) first had to be synthesized.

Reaction of the tetracyclones with the respective Grignard reagent or organolithium compound yielded the para-substituted pentaphenylcyclopentadienols (carbinols), which were converted to the cyclopentadienyl bromides by reaction with HBr. It has to be pointed out that substitution of OH⁻ by Br⁻ occurs via an S_N1 mechanism, resulting in a mixture of isomers as regards the position of the bromo substituent.³ Reaction of the bromides, however, with Ag yields identical cyclopentadienyl radicals caused by the delocalization of the unpaired electron.

Tetracyclone- $1^{-13}C$ was obtained via phenylacetic- $1^{-13}C$ acid,¹³ acid chloride, ethyl ester which was reacted with benzyl cyanide to give 1cyano-1,3-diphenylacetone-2-13C. Hydrolysis with H₂SO₄ yielded 1,3diphenylacetone- $2^{-13}C^{14}$ Condensation of the latter with benzil produced the tetracyclone.3,15

Tetracyclone-3,4-¹³ C_2 was obtained from benzoic-1-¹³C acid¹⁶ reduction to give benzyl-I- ^{13}C alcohol, 16 which was oxidized to benzaldehyde-1- ^{13}C , 17 and subsequent benzoin condensation¹⁸ followed by oxidation to give benzil-1,2- $^{13}C_2$.¹⁹ Condensation with diphenylacetone yielded the tetracyclone.3,15

Tetracyclone-2,4⁻¹³ C_2 was synthesized by base-catalyzed condensation of 1,3-diphenylpropenone-3-¹³ C^{20} (obtained from benzaldehyde-1-¹³C and

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Figure 1. Synthesis of the ¹³C labeled tetracyclones and pentaphenylcyclopentadienyl radicals.

acetophenone) and desoxybenzoin- $l^{-13}C^{21}$ (obtained via Friedel-Crafts reaction of benzene and phenylacetic- $l^{-13}C$ acid chloride) to give 1,2,3,5-tetraphenylpentane-1,5-dione- $l,3^{-13}C_2^{-22}$ Reaction with Na resulted in ring closure to yield tetraphenylcyclopentadiene- $l,3^{-13}C_2^{-23,24}$ which was oxidized with p-(dimethylamino)nitrosobenzene to the tetracyclone.^{23,24}

(*p*-(Trifluoromethyl)phenyl)tetraphenylcyclopentadienol. To a solution of 50 mg of tetracyclone (0.13 mmol) in 20 mL of benzene was added, at room temperature, a Grignard solution of 0.06 g of Mg and 0.59 g of *p*-(trifluoromethyl)phenyl bromide, until the violet color was completely removed. After the mixture was refluxed for 30 min, hydrolyzed with diluted HCl, and extracted by ether, the crude product was purified chromatographically (silica gel/benzene) and recrystallized from heptane: yield 70%; mp 206-208 °C. Anal. Calcd for $C_{36}H_{25}OF_{3}$: C, 81.49; H, 4.74. Found: C, 81.22; H, 4.64. The other carbinols were obtained as described earlier.^{3,24,25}

Pentaphenylcyclopentadienyl Bromides.^{3,24} The carbinols were dissolved in benzene and treated with gaseous HBr for 45 min. The water formed was removed azeotropically. The solution, saturated at 0 °C with HBr, was allowed to stand at room temperature for 24 h; then the benzene was removed. This mixture of substituted pentaphenylcyclopentadienyl bromides (vide supra) was used without further purification.

Preparation of Samples. The free cyclopentadienyl radicals 1-6 (see Table I) were prepared on a high-vacuum line in the ESR/ENDOR sample tube by reaction of the cyclopentadienyl bromides with Ag using isopentane as solvent. The sample tube allowed distillation of the solvent

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Figure 2. Top: ¹H ENDOR (left) and ¹H TRIPLE (right) spectra of the pentaphenylcyclopentadienyl radical **1a**. Center: ¹³C ENDOR spectrum; only the high-frequency ¹³C ENDOR line at $\nu = 7.01$ MHz could be detected. Bottom: ESR spectra of the perdeuterated radical **1b** in isotropic (--) and nematic (---) phase of liquid crystal LICRI 4.

under vacuum conditions for concentrating or diluting.

Instrumentation. ESR spectra were recorded on a Bruker ER 220 D ESR spectrometer. The ENDOR and TRIPLE instrumentation basically consists of a Bruker 220 D ESR spectrometer equipped with a Bruker ENDOR cavity (ER 200 ENB) and NMR facilities described elsewhere.²⁶ ENDOR spectra were accumulated by using a Nicolet Signal Averager 1174 employing 1K data points; typically, 32 sweeps were taken, 30 s per scan. For ¹H, rf fields in the range 0.5–0.7 mT in the rotating frame and modulation amplitudes of ±15 to ±30 kHz were used; for ¹³C 1.2 mT and ±200 kHz were used. The temperature was varied with a Bruker B-VT 1000 temperature control unit, constant to ±1 K and checked by means of a thermocouple.

Results

ESR and ENDOR Spectra. The theory of the electron nuclear double resonance (ENDOR) and electron nuclear nuclear triple resonance (TRIPLE) experiments are now well understood and described in several review articles²⁷ and monographs.²⁸ According to the ENDOR resonance condition

$v_{\text{ENDOR}} = |v_{\text{N}} \pm aM_{\text{S}}|$

in the case of a doublet radical, i.e., $M_{\rm S} = \pm^{1}/_{2}$, each set of equivalent nuclei gives rise to one ENDOR line pair. If |a/2| <

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Table II.	Hyperfine	Coupling	Constants (MH	(z) ^a of th	ne Substituted	Pentaphenylcy	yclopentadienyl	Radicals at 200 H	K
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¹³ C hfsc's, a_i^{Cb}				¹ H hfsc's, a_i^{Hc}					an X c,d	
R	1 *	2 ^h	3 ^h	74	8 ^h	13, 15 ^h	14 ^h	19, 21 ^h	20 ^k	- ⁶ 9 ^h
OCH ₃	+27.41			-3.92	+1.43 ^e	-0.73	+0.31	-2.21	+1.01	+0.67 ^e (H)
CH ₃	+16.16	-1.21 ^f	+9.25	-2.89	+1.29	-1.29	+0.56	-2.10	+0.90	+3.17 (H)
C ₆ H ₅	+14.88			-2.80	+1.32	-1.33	+0.53	-2.09	+0.92	-0.53 ^g (H)
F	+9.08			-2.13	+0.87	-1.77^{e}	+0.87	-2.05°	+0.87	+5.38 (F)
н	+6.36	+6.36	+6.36	-1.96	+0.87	-1.96	+0.87	-1.96	+0.87	-1.96 (H)
CF3	-5.18	+15.61	+2.80	-1.04	+0.42	-2.58	+1.12	-1.74	+0.74	+1.29 (F)

^a Estimated errors are ± 0.03 MHz. ^bSigns of hfsc's from liquid crystal studies; see text. ^cSigns of hfsc's from general TRIPLE experiments. ^d Hfsc's of the nuclei X, in the substituent group R. ^eAmbiguous assignments. ^fDetermination of signs from the temperature dependence of the hfsc's; see text. ^gHfsc's of the ortho and para protons of the phenyl group R. ^hPosition numbers.

 $\nu_{\rm N}$, then these lines are centered around the free nuclear frequency $\nu_{\rm N}$ and spaced by the hyperfine coupling constant *a*. Given the condition $|a/2| > \nu_{\rm N}$, the ENDOR lines are centered around a/2 and spaced by $2\nu_{\rm N}$. Looking at the non-proton ENDOR experiments, specifically ¹⁹F and ¹³C ENDOR, usually higher microwave and radiofrequency power levels and higher temperatures are required as compared to ¹H ENDOR. This can be understood by taking account of the larger hyperfine anisotropy of these nuclei and of the smaller magnetogyric ratio of the ¹³C nucleus. A detailed outline of the experimental non-proton ENDOR conditions is given in ref 11.

Pentaphenylcyclopentadienyl (1a). Figure 2 depicts the EN-DOR spectrum of the parent compound, ¹³C labeled at one central ring position (90%). Two different ¹H hfsc's ($|a^{H}_{ortho}| = |a^{H}_{para}|$ > $|a^{H}_{meta}|$) could be deduced from the ENDOR spectrum, the values being in accordance with the data given in a previous paper;¹ see Table II. Concerning ¹³C ENDOR, only the high-frequency signal could be detected. Since the free ¹³C frequency can be calculated from the known free ¹H frequency, the ¹³C hfsc is unambiguously accessible even from one ENDOR component. This hfsc ($a^{C} = 6.36$ MHz) is comparable in magnitude to that of unsubstituted cyclopentadienyl radical ($a^{C} = 7.46$ MHz).⁹ Thus, it can be concluded that phenyl substitution does not affect the planarity of the five-membered ring, since deviations from planarity should result in increased ¹³C hfsc's.²⁹

Whereas the optimum ¹H ENDOR response occurs in the temperature range 160–200 K—using isopentane as solvent—that of ¹³C requires higher temperatures (220–260 K) and, in addition, higher rf power levels. Moreover, the ¹³C ENDOR lines are significantly broader (line width \approx 400 kHz) than the ¹H ENDOR lines (\approx 100 kHz).

The parent compound 1a shows no significant temperature dependence of the hfsc's, e.g., $da_C/dT = 2.8 \text{ kHz/K}$.

Relative signs of the ¹H hfsc's could be determined by performing general TRIPLE experiments. On the other hand, the ¹³C ENDOR line intensity was not affected in the TRIPLE investigation; thus, the sign of this hfsc had to be determined by liquid crystal ESR measurements of the perdeuterated radical **1b** using LICRI 4 as solvent. (The high viscosity of this solvent did not allow detection of ¹³C ENDOR lines.) Taking account of the fact that the hyperfine shift Δa_i^C —obtained when cooling from the isotropic to the nematic phase—is essentially dependent on the spin density $\rho_i^{\pi,30,31}$ from $|a_i^C(iso)| > |a_i^C(nem)|$ it can be concluded that the sign of the ¹³C hfsc must be positive (Figure 2). It should be pointed out that the signs of the ¹H hfsc's could not be deduced from these liquid crystal studies because twisting of the phenyl substituents prevented a proper ordering in the host crystals.³¹

(*p*-(Trifluoromethyl)phenyl)tetraphenylcyclopentadienyl (3a-3d). In monosubstituted pentaphenylcyclopentadienyl radicals from symmetry three different sets of carbon atoms in the central ring are expected, referring to positions 1, 2 = 5, 3 = 4. Therefore,



Figure 3. Temperature dependence of the ¹H and ¹⁹F hfsc's, a_i , of the radical 3 (R = CF₃). The numbers in parentheses refer to the molecular positions of the nuclei observed.

differently ¹³C-labeled radicals have been studied. In addition, the partially deuterated compound **3b** has been examined for assignments of the hfsc's to molecular positions.

Whereas the ESR spectra exhibit only a single broad line, well-resolved ENDOR spectra could be recorded including ¹H, ¹⁹F, and ¹³C ENDOR resonances. The most important feature of these spectra is the strong temperature dependence of all hfsc's being clearly in contrast to the behavior of the unsubstituted D_{5h} symmetric system; see Figure 3. In Figure 4 (top) the ENDOR spectra of 3b at two different temperatures are reproduced. Apart from the ¹H ENDOR lines of the two sets of protons belonging to the substituted phenyl ring the ¹⁹F ENDOR lines show up centered around the free ¹⁹F frequency and spaced by the isotropic hfsc a_{CF_3} ^F (because $\gamma_H \neq \gamma_F$ the ENDOR spectrum is not symmetric). It is noteworthy that the ¹⁹F nuclei show a different relaxation behavior as compared to that of the perimeter protons; see Figure 4 (top). On cooling, the ENDOR lines of the latter decrease in intensity whereas those of the ¹⁹F nuclei exhibit the most intense ENDOR lines at 120 K. Obviously, the CF₃ group is still freely rotating in the glassy matrix of the isopentane solvent. From general TRIPLE measurements of 3a and 3b, a positive sign for the ¹⁹F hfsc could be deduced; see Figure 4 (bottom). As to the ¹³C hfsc's, different values are indeed obtained for the different positions. Unfortunately, (relative) sign determination by general TRIPLE measurements failed in the case of ¹³C. The positive sign of the hfsc belonging to position 2 is known from liquid crystal measurements; vide supra. From the temperature dependence of the hfsc's (cf. Figure 5), the negative sign of the hfsc of position

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Figure 4. ¹H and ¹⁹F ENDOR spectrum (top) at different temperatures and TRIPLE spectrum (bottom) of the partially deuterated radical 3b $(\mathbf{R} = \mathbf{CF}_3).$

1 and positive sign of that of position 2 could be evaluated; vide infra.

(p-Fluorophenyl)tetraphenylcyclopentadienyl (4a and 4b). The ¹H ENDOR spectrum of 4a is comparable to that of 1a except for small additional splittings of the signals. The temperature dependence of the hfsc's is not very pronounced; thus, it can be concluded that an α -fluorine nucleus only exhibits small substituent effects, in the present case very weak electron-donating properties. Again for an unambiguous assignment of the ¹H hfsc's to molecular positions the partially deuterated radical 4b has been studied. On account of the larger hyperfine anisotropy the temperature dependence of the fluorine ENDOR line intensities is to be contrasted with that of the CF₃ group and is comparable with the relaxation properties of the ${}^{13}C$ nucleus. As can be seen from Figure 6 at about 160 K only ¹H ENDOR lines show up. At elevated temperatures, 180 K, the ¹⁹F ENDOR lines can be detected, and at 240 K the high-frequency ¹³C ENDOR line appears in the spectrum. Higher rf power levels are required for an optimum ENDOR response of the latter.

The positive sign of the ¹⁹F hfsc could be determined by general TRIPLE resonance. Because an α proton at the substituted position is known to have a negative hfsc, direct overlap of fluorine p orbitals with the π system has to be assumed.

Methyl-, Phenyl-, and Methoxy-Substituted Pentaphenylcyclopentadienyls. The dominant feature of the ENDOR spectra of these substituted systems is the large positive ¹³C hfsc of position 1 and its strong temperature dependence. Whereas the substituent effects of methyl and phenyl are comparable in magnitude, the electron-donating influence of the methoxy group is much more pronounced, resulting in a very large ¹³C hfsc of position 1 at 200 K of $a_1^{C} = +27.41$ MHz; see Table II. Judging from the ¹H hfsc's of the partially deuterated radical 6b the substituted phenyl ring bears the largest spin population as compared to the unsubstituted rings. According to theory (vide infra), all hfsc's of the methyl-, phenyl-, and methoxy-substituted radicals exhibit a quite different behavior as compared with that of the molecule with the electron-withdrawing substituent CF₃.



Figure 5. Temperature dependence of the ${}^{13}C$ hfsc's, a_i , of the substituted pentaphenylcyclopentadienyl radicals. The numbers in parentheses refer to the ¹³C-labeled molecular positions.

Discussion

Assuming D_{5h} symmetry HMO predicts doubly degenerate HOMO's for the pentaphenylcyclopentadienyl radical, i.e., $\psi_{\rm S}$ (symmetric) and ψ_A (antisymmetric); see Figure 7. Thus, the molecules can be expected to oscillate between the two different populations, and the spin density at any central carbon should be 1/5. Perturbation of the fivefold symmetry by introduction of substituents results in removing of the degeneracy. Provided the energy difference of the orbitals $\psi_{\rm S}$ and $\psi_{\rm A}$ is in the range of kT, the experimentally found hfsc's are the weighted averages of the hfsc's $a_{S,i}^{0}$ and $a_{A,i}^{0}$ referring to the situation where the unpaired electron is only found in ψ_S and ψ_A , respectively. By introduction of the relative probabilities, $p_{\rm S}$ and $p_{\rm A}$, of finding the electron in the respective orbital the following equations are valid:^{1,6,32}

$$a_i = p_{\mathrm{S}} a_{\mathrm{S},i}^{\circ} + p_{\mathrm{A}} a_{\mathrm{A},i}^{\circ} \tag{1}$$

$$p_{\rm S}/p_{\rm A} = \exp(\Delta E/RT)$$
 (2)

The energy difference $\Delta E = E_{\rm S} - E_{\rm A}$ between the two orbitals can be evaluated from the temperature dependence of the hfsc's provided the values of $a_{S,i}^{\circ}$ and $a_{A,i}^{\circ}$ are known from theoretical calculations; see eq 3. So far we have only considered the "static

$$\ln \frac{a_i - a_{A,i}^{\circ}}{a_{S,i}^{\circ} - a_i} = \frac{\Delta E}{RT}$$
(3)

case"; i.e., the electronic wave functions have been regarded as independent of the nuclear coordinates. As could be shown, however, e.g., by Hobey,³³ close-lying but nondegenerate electronic states may be strongly coupled vibronically ("pseudo-Jahn-Teller effect"). Vibronic coupling causes an additional mixing of the two states $\psi_{\rm S}$ and $\psi_{\rm A}$. Thus, thermal admixture no longer occurs between purely electronic states but rather has to be described in terms of mixing of vibronic ground and excited states. A smaller vibronic energy difference is expected as compared to the purely

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Figure 6. ENDOR spectra of the radicals 4b (left) and 4a (right) at different temperatures. For experimental conditions see instrumentation.



Figure 7. Hückel molecular orbital diagram for the cyclopentadienyl system (top) and removing of degeneracy of the molecular orbitals $\psi_{\rm S}$ and ψ_A by electron-donating and electron-withdrawing substituents (bottom).

electronic energy difference.33,34

The extent of vibrational interaction depends on the magnitude of the energy separation of the electronic levels and hence on the type of substituent introduced. 32,33 For an accurate quantitative interpretation sophisticated calculations using vibronic wave functions and energy splittings have to be performed. Extensive

calculations are known for some substituted cyclic hydrocarbon radicals, such as $C_6H_6^{-,34-37}$ $C_7H_7^{-,32}$ and $C_8H_8^{-,38,39}$

In the case of the toluene anion radical it could be shown that the vibronic ground state contains about 12% of the excited electronic state, whereas the excited vibronic state contains about 30% of the electronic ground state.³⁴ Similar results could be obtained by Jones, Wood, et al.35 (vibronic and initial electronic energy differences 2.69 and 3.95 kJ/mol, respectively). In the studies of a weakly disturbed system, i.e., the isotopic effect on deuteriobenzene anion radicals, an energy separation of 0.24 kJ/mol could be evaluated.^{37,40} It could be shown that about 18% of the excited (ground) electronic state is admixed to the vibronic ground (excited) state.37

In the present paper we have not performed a vibronic calculation because this is beyond the scope of this investigation. The energy separations of the different pentaphenylcyclopentadienyl radicals are in the same ranges as in the examples given above. Since in our calculations the limited accuracy of the energy differences is mainly caused by the considerable errors of the different a_i° values used (vide infra), we expect that vibrational contributions are within these errors, thus giving us justification to confine ourselves to the purely electronic states.

When the results of the differently substituted compounds are compared qualitatively, it is seen that (strongly) electron-donating substituents (CH₃, OCH₃, phenyl) cause a large ¹³C hfsc in position 1, whereas introduction of electron-withdrawing substituents (CF₃) results in large ¹³C hfsc's of positions 2, 5. α -Fluorine substitution does not affect the central ring ¹³C hfsc's

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Table III. Population Probabilities p_{s}^{a} at 200 K and Energy Gaps ΔE^{b} (kJ/mol) between ψ_{s} and ψ_{A} of the Substituted Pentaphenylcyclopentadienyl Radicals

R	$p_{\rm S} \; (T = 200 \; {\rm K})$	method a ^d	method b ^e	method of	
OCH ₃	0.85	3.07 (1)	2.01 (1)	4.14 (7)	
CH ₃	0.67	0.80 (1)	0.64 (1)	0.96 (7)	
-		0.94 (2)	0.70 (2)		
		0.64 (3)	0.55 (3)		
Ph	0.66	0.77 (1)	0.61 (1)	0.71 (7)	
F	0.53	0.16 (1)	0.13 (1)	0.29 (7)	
Н	0.50	0.00	0.00	0.00	
CF ₃	0.33	-1.09 (1)	-0.81 (1)	-0.88 (7)	
-		-0.93 (2)	-0.75(2)		
		-1.82 (3)	-1.13 (3)		

^a For determination see text. At the given values, the standard deviations between calculated and measured hfsc's are less than 0.25 MHz. ^b Standard deviations obtained from the least-square fit are less than 5%. ^c The numbers in parentheses refer to the molecular positions of the nuclei. ${}^{d}\Delta E$ values are estimated from the temperature dependence of the ¹³C hfsc's by using the Q values of this work; see text. ${}^{e}\Delta E$ values were estimated from the temperature dependence of the ¹³C hfsc's by using the Q values of ref 49; see text. $f\Delta E$ values were estimated from the temperature dependence of the ¹H hfsc's in position 7 with $Q_{CH}^{H} = -84$ MHz.^{6,8}

markedly. Apparently at increased temperatures all hfsc's of the radicals under study converge on the values of the unsubstituted "Ziegler radical" (Figures 3 and 5). This can be understood because the difference of the population probabilities of the two MO's becomes smaller when the temperature is increased.

HMO McLachlan Calculations. HMO McLachlan calculations were performed by using $\lambda = 1.2^{41}$ and heteroatom parameters taken from the literature.⁴² In order to account for the CF₃ group the hyperconjugative model, which often has successfully been used for methyl groups, was applied. The twist angle of the phenyl substituents was assumed to be $\rho = 37^{\circ}$ according to a previous ENDOR study of Möbius et al. $(k = k_0 \cos \rho)$.¹ The resonance integral parameters of both forms, ψ_A and ψ_S , were set to be k = 1. We have neglected the dependence of the resonance integrals of the bond orders, as described in the literature.^{43,44} because in our case it does not affect the results within the errors obtained.

One of the most important results of the calculations in the context of this study is the fact that the spin populations of the π orbitals $\psi_{\rm S}$ and $\psi_{\rm A}$ essentially remain unaffected by the substituents (maximum spin density deviations ~ 0.04). Hence it can safely be assumed that the changes of the hfsc's observed in these experiments are mainly caused by changes of the population probabilities. This assumption is confirmed by the finding that fivefold substitution-retaining the fivefold symmetry-results in hfsc's that are identical with those of the unsubstituted system.¹ Assignments of the hfsc's to molecular positions could be achieved in two ways. Firstly, partial deuteration was applied in some cases; vide supra. Secondly, correlation diagrams were used for the MO's $\psi_{\rm S}$ and $\psi_{\rm A}$. A representative example is given in Figure 8a for radical 3 showing the calculated ¹H hfsc's vs. the population probabilities $p_{\rm S}$ of MO $\psi_{\rm S}$.

A Q_{CH}^{H} parameter of -84 MHz was used in the McConnell relation, directly obtained from the ¹H hfsc of unsubstituted cyclopentadienyl radical.^{6,8} Since p_S should increase with increasing temperatures, the hfsc's can be assigned to molecular positions by comparison of the calculated data (Figure 8a) with the respective, experimentally found, temperature dependencies of the hfsc's (Figure 3). So, in the range of $p_{\rm S} \approx 0.3$ excellent agreement is found between theory and experiments in regard to sign, magnitude, and temperature dependence of the hfsc's. It is particularly noteworthy that this also holds for the ¹⁹F hfsc using $Q_{CCF_3}^{F} = +108 \text{ MHz}^{45}$ Very similar correlation diagrams could be obtained for the other electron-donating substituents except for the increasing p_A when the temperature is increased.

The effect of substitution can be deduced from the population probabilities at one temperature, e.g., 200 K (this temperature was chosen because under this condition ¹H as well as ¹³C EN-DOR signals could be recorded). The $p_{\rm S}$ values collected in Table III were determined by minimizing the mean square deviations of calculated and measured hfsc's. The results indicate that $p_{\rm S}$ (T = 200 K) increases with the electron-donating properties of the substituent, e.g., $p_S = 0.33$ (CF₃) and 0.85 (OCH₃).

¹³C ENDOR Experiments. The Karplus-Fraenkel treatment of ¹³C hfsc's⁴⁶

$$a_i^{\rm C} = Q_{\rm C}{}^{\rm C}\rho_i + \sum_{j \neq i} Q_{\rm CC}{}^{\rm C}\rho_j \tag{4}$$

is very often less satisfactory than the respective McConnell relation applied for protons. In fact, the agreement between theory and experiment is dependent on the Q values selected, and quite different Q values have been used in the literature.⁴⁶⁻⁴⁸ For instance, when the parameters determined by Karplus and Fraenkel are applied, extreme values $a_{S,i}^{\circ}$ and $a_{A,i}^{\circ}$ are obtained, part of which are even smaller than the hfsc's measured. According to a recent study⁹ of alkyl-substituted cyclopentadienyl radicals, acceptable values could be obtained if the Yonezawa-Kawamura-Kato treatment⁴⁹ was applied

$$a_i^{\rm C} = Q_{\rm C}{}^{\rm C}\rho_i + \sum_{j \neq i} Q_{\rm CC}{}^{\rm C}\rho_j + \sum_{j \neq i} R_{\rm CC}\rho_{ij}$$
(5)

and the values $Q_{\rm C}^{\rm C}$ = +129 MHz, $Q_{\rm CC}^{\rm C}$ = -48.5 MHz, and $R_{\rm CC}$ = +5.47 MHz were used.

It has to be pointed out, however, that these parameters were determined for CC₂H fragments whereas the phenyl-substituted radicals of this study have CC3 fragments. But, as shown by Strom et al.,⁴⁸ deviations, if any, should be within experimental error of the determined Q parameters. Another promising way to interpret the experimental data was to find out individual Qparameters for the paramagnetic species under study. In this procedure $p_{\rm S}$ and $p_{\rm A}$ were calculated from the ¹H hfsc's, allowing determination of the spin densities at 200 K (weighted spin densities of the pure MO's ψ_A and ψ_S). From eq 4—using the measured hfsc's of Table II— $Q_C^C = +112 \pm 5$ MHz and $Q_{CC}^C = -32 \pm 3$ MHz were obtained. These values seem to be reasonable and compare well with the values given by Bolton et al.⁴⁷ for the CC₂H fragment (Q_{C}^{C} = +107 MHz, Q_{CC}^{C} = -29.7 MHz) and by Strom et al.⁴⁸ (Q_{C}^{C} = +108 MHz, Q_{CC}^{C} = -32.5 MHz). They are in between the Karplus-Fraenkel data and those of

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Figure 8. Calculated hfsc's (HMO-McLachlan), a_i , of the radical 3 (R = CF₃) as a function of the population probability p_S (Figure 8a, top left, for protons; Figure 8c, bottom left, for ¹³C) and dependence of the experimental hfsc's of the para-substituted pentaphenylcyclopentadienyl radicals (200 K) on the σ_p^+ values (Figure 8b, top right, for protons; Figure 8d, bottom right, for ¹³C). The numbers in parentheses refer to the molecular positions of the nuclei.

Yonezawa, Kawamuro, and Kata. The standard deviations of experimental and calculated hfsc's amount to 1.3 MHz; the correlation coefficient is 0.99.

Using these Q parameters one can calculate the ¹³C hfsc's $a_{S,i}^{\circ}$ and $a_{A,i}^{\circ}$, i.e., the hfsc's for the situation where the radicals are

in the pure S or A forms, respectively. It turned out that within 10% the same a_i° values were found for all cyclopentadienyls studied. As a representative example Figure 8c shows the correlation diagram for compound 3. As in the case of the protons, again the dependence of the calculated ¹³C hfsc's on p_S is analogous



Figure 9. Plots of $|\ln ((a_i - a_{A,i}^\circ)/(a_{S,i}^\circ - a_i))|$ vs. 1/T for the determination of the energy gaps ΔE of the substituted pentaphenylcyclopentadienyl radicals by method a; see text and eq 3. The numbers in parentheses refer to the molecular positions of the ¹³C nuclei.

to the dependence of the experimental 13 C hfsc's (Figure 5) on temperature.

Energy Gap between the Two Configurations. The energy differences between ψ_A and ψ_S can be estimated in three ways: (a) by using the above given Q parameters of the ¹³C hfsc's, (b) by using the values reported by Yonezawa, Kawamuro, and Kata, and (c) by using the ¹H hfsc's and $Q_{CH}^{H} = -84$ MHz.^{6,8} Figure 9 depicts the dependencies according to eq 3 with the data taken from a. For comparison in Table III the results of all three methods, a, b, and c, are listed. It can be seen that significant deviations of the energy differences are obtained, in some cases exceeding more than 100%. Obviously these differences are essentially caused by errors of the $a_{S,i}^{\circ}$ and $a_{A,i}^{\circ}$ values. On the other hand, the errors of the energy differences obtained from a least-squares fit having correlation coefficients of about 0.91–0.99 are only in the range of 5%.

Regardless of these discrepancies it can be stated that any procedure qualitatively gives the same dependence of the energy differences on the substituents, viz., the energy of MO ψ_S is increased in the sequence $CF_3 < H < F < CH_3 \approx C_6H_5 < OCH_3$. It is noteworthy that the mesomeric electron-donating effect of the fluorine substituent dominates its electron-withdrawing inductive effect.

Hammett's σ - ρ **Relation.** In the studies of substituent effects the so-called linear free energy relationship has widely been used.⁵⁰

In order to obtain good agreement between experimental parameters and σ constants several groups of the latter are now in use. In the present study the best results were obtained by using the σ_p^+ values of Brown and Okamoto,⁵¹ indicating strong resonance interaction between substituent and reaction center. In Figure 8, parts b and d, the substituent effects are reproduced by correlation of hfsc's and σ_p^+ values. Actually satisfactory correlation coefficients of 0.99 for ¹³C hfsc's (position 1) and 0.93–0.98 for ¹H hfsc's were obtained. Only in the case of phenyl substitution (4) would a $\sigma_{\rm p}^{+}$ value similar to that of the methyl group be more appropriate to account for the experimental hfsc's. As can be seen from comparison of Figure 8, parts a and c, with Figure 8, b and d, the dependencies of the experimental hfsc's on the σ_{p}^{+} values are quite analogous to those of the calculated hfsc's of the population probabilities $p_{\rm S}$. In fact, a relation of the form $p_{\rm S}$ (T = 200 K) = $0.54 - 0.39\sigma_{\rm p}^{+}$ can be evaluated that gives an excellent fit of all experimental results, the correlation coefficient being 0.98. It is to be noted that this correlation additionally supports the assignments of the experimental hfsc's to molecular positions (vide supra).

Walter⁵² has divided free radicals into the two classes "O" (donor and acceptor substituents produce shifts of the observed properties in opposite directions) and "S" (the shifts are in the same direction). In order to determine whether a radical belongs to class "O" or "S", he suggested a valence bond method. This method seems to fail in the case of the tetraphenylpyrryl radical,⁴³ which may be considered as a strongly perturbated cyclopentadienyl system. Our work shows that the cyclopentadienyl system belongs to Walter's class "O", which is due to the fact that the energy of ψ_S as compared to ψ_A may be either decreased or increased by the substituent.

Conclusions

It has been shown by ¹³C, ¹⁹F, and ¹H ENDOR spectroscopy that monosubstitution of the pentaphenylcyclopentadienyl radical causes lifting of the HOMO's degeneracy. As a consequence, considerable spin density redistributions within the π systems and significant temperature dependencies of the hfsc's can be observed. The substituent effects can be treated quantitatively within the framework of Hammett's σ - ρ relation. In molecules with electron-withdrawing or electron-donating substituents the spin populations of the central ring are mainly determined by the antisymmetric MO ψ_A or by the symmetric MO ψ_S , respectively.

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