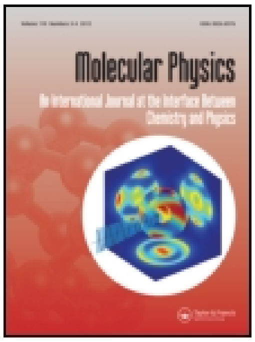

Molecular Physics

An International Journal at the Interface Between Chemistry and Physics

ISSN: 0026-8976 (Print) 1362-3028 (Online) Journal homepage: http://www.tandfonline.com/loi/tmph20

ENDOR study of pentaphenylcyclopentadienyl radicals in solution. Lifting of orbital degeneracy by methyl substitution

K. Möbius , H. Van Willigen & A.H. Maki

To cite this article: K. Möbius , H. Van Willigen & A.H. Maki (1971) ENDOR study of pentaphenylcyclopentadienyl radicals in solution. Lifting of orbital degeneracy by methyl substitution, Molecular Physics, 20:2, 289-304, DOI: 10.1080/00268977100100271

To link to this article: http://dx.doi.org/10.1080/00268977100100271

MOLECULAR PHYSICS, 1971, VOL. 20, NO. 2, 289–304

ENDOR study of pentaphenylcyclopentadienyl radicals in solution. Lifting of orbital degeneracy by methyl substitution

by K. MÖBIUS†, H. VAN WILLIGEN‡, and A. H. MAKI
Department of Chemistry, University of California, Riverside, California 92502

(*Received* 29 *June* 1970)

An electron-nuclear-double-resonance (ENDOR) study has been made of pentaphenylcyclopentadienyl (PPCPD) and a series of *para*-methylated PPCPD radicals in liquid solution. The hyperfine splitting (hfs) constants in PPCPD and pentamethyl PPCPD (MPPCPD) do not show a significant π–σ spin delocalization effect. This indicates that the phenyl substituents are twisted less than 60° out of the plane of the five-membered ring. A MO calculation based on σ–π separability using the McLachlan approximation gives good agreement between experimental and theoretical hfs constants for a twist angle of 40°. The ring proton hfs constants in PPCPD and MPPCPD are practically identical, indicating a negligible effect of the methyl groups on the spin density distribution. Moreover, the hfs constants in both radicals are not affected noticeably by temperature variations. The ring proton splittings in the partially methylated PPCPD radicals, on the other hand, vary widely and show a marked temperature dependence. The same is true for the methyl proton splittings in these compounds.

This remarkable difference between the PPCPD and the MPPCPD radicals on the one hand and the partially *para*-substituted radicals on the other can be explained satisfactorily by considering the effect of partial methylation on the orbital ground states of the radicals. It is assumed that partial methyl substitution lifts the orbital degeneracy in the PPCPD radical giving rise to a symmetric (or antisymmetric) orbital ground state with an antisymmetric (or symmetric) thermally accessible excited state. The values of the methyl hfs constants are used to determine the symmetry of the orbital ground states in the partially methylated compounds. The temperature dependence of these couplings is used to derive the values of the energy gaps between the symmetric and antisymmetric states. The experimental data are in good agreement with the results of simple HMO calculations in which the effect of the methyl substituents is treated as purely inductive.

1. INTRODUCTION

Recently there has been a renewed interest in radicals with twisted phenyl substituents because of the possibility of studying π–σ electron delocalization by means of its effect on electronic g values [1, 2] and hyperfine splittings (hfs) [3–5]. The theoretically predicted anomalies in the g values indeed have been observed for a number of aromatic hydrocarbon radicals having phenyl substituents which are twisted considerably out of the plane of the molecule (for instance, the radical ions of 9,10-diphenylanthracene) [1, 2]. However, an unambiguous analysis of the complex ESR spectra was not possible. The predicted anomalies in the relative

---

† Present address: II. Physikalische Institut, Freie Universität, Berlin 33, Germany.

‡ Present address: Department of Chemistry, University of Massachusetts, Boston, Massachusetts 02116.

magnitudes of the hfs of the *ortho*, *meta*, and *para* protons in the phenyl substituents, therefore, could not be verified experimentally.

By applying the electron-nuclear-double-resonance (ENDOR) technique the number of spectral lines is reduced considerably, making it a powerful tool for determining hyperfine interactions in radicals which give rise to very complex E.S.R. spectra [6–17]. ENDOR, when applied to these non-planar radicals in solution, thus should facilitate the study of hfs anomalies arising from π–σ delocalization.

In this paper we report an ENDOR and E.S.R. study of the pentaphenylcyclopentadienyl (PPCPD) radical shown in figure 1 and a series of *para* methyl substituted PPCPD radicals. The steric requirements of the phenyl groups suggest that the hfs constants of these radicals might show the effect of π–σ delocalization due to non-planarity. In fact, the results of an earlier attempt to analyse the complex hfs pattern in the E.S.R. spectrum of PPCPD [18] and the reported g factor of this radical [19] indicate that the radical is non-planar.

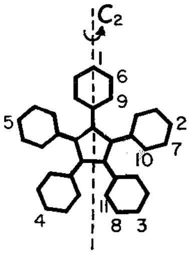

Figure 1. Numbering scheme in pentaphenylcyclopentadienyl (PPCPD).

While our initial interest in the PPCPD and *para*-methylated PPCPD radicals was concerned with an attempt to derive information regarding the π–σ delocalization effects on the spin density distribution, the emphasis later shifted to a study of the effects of the methyl substituents on the spin density distribution, which proved to be much more pronounced.

In general, the effect of a methyl substituent on the spin density distribution in a free radical is very small. However, as has been shown in E.S.R. and N.M.R. studies of the benzene, toluene and xylene anion radicals [20–22], the effect can be significant if the orbital ground state of the parent free radical is two-fold degenerate and methyl substitution, by lowering the symmetry, removes the degeneracy.

A Hückel MO calculation for the PPCPD and penta-*para*-methyl-PPCPD (MPPCPD) radicals, both having D_5 symmetry, shows that the orbital of the unpaired electron is two-fold degenerate [23, 24]. As in the benzene anion, the spin density distribution is an average over the two orbitals. In the mono-, di-, tri-, and tetra-*para*-methyl substituted radicals, however, the two-fold degeneracy is lifted. The hfs constants, therefore, reflect either the spin density distribution in one of the orbitals or a weighted average of the distributions in both orbitals, depending on whether the energy gap is large compared with kT or of the same order of magnitude, respectively.

A study of this methyl substitution effect with E.S.R. alone was found to be impossible due to the large number of hfs constants. In fact, it is even questionable whether the E.S.R. spectrum of MPPCPD containing only three hfs constants could be interpreted unambiguously without the help of ENDOR. We find that even the ENDOR spectra of the partially *para*-methylated-PPCPD radicals are rather complicated; theoretically nine different splitting constants are possible, and up to eight could be resolved in one spectrum. The analysis of these spectra is, however, greatly facilitated by the difference in temperature behaviour of the ENDOR linewidths and intensities of methyl and ring protons caused by the large difference in anisotropy of their hyperfine tensors [11]. Thus, we have been able to make a detailed study of the effect of methyl substitution on the electronic state of the PPCPD radical and to relate the experimental data to the results of simple MO calculations.

2. Experimental section

Besides PPCPD (1) and MPPCPD (8) the following set of *p*-methyl substituted pentaphenylcyclopentadienyl radicals has been studied: 1-CH_3—(2); 2,5-CH_3—(3); 3,4-CH_3—(4); 1,2,5-CH_3—(5); 1,3,4-CH_3—(6); 2,3,4,5,-CH_3—(7) (cf. figure 1 for the numbering of the C atoms). The compounds were a generous gift from Dr. H. Kurreck, Freie Universität Berlin. The radicals were prepared by treating carefully degassed solutions of the monobromides with silver amalgam. Quartz tubes with an o.d. of 10 mm were used as sample tubes in the ENDOR and E.S.R. experiments.

ENDOR spectra were recorded with the high-power spectrometer described previously [13]. E.S.R. spectra were taken with a Varian V4502 spectrometer with 9 in. magnet, variable temperature accessory, and wide stack cavity. Radical concentrations for ENDOR and E.S.R. work were of the order 10^{-3} *M* and 10^{-4} *M*, respectively.

The solvents used were octane (m.p. −57°c), pentane (m.p. −130°c), and isopentane (m.p. −160°c). Using radical solutions in octane and pentane the relative intensities of the ENDOR lines remained the same upon cooling. In general, maximum intensities were obtained just above the melting points of these solvents, while the intensities decreased rapidly with increasing temperature. In isopentane ENDOR signals could be observed over a wide temperature range (between −50° and −180°c); the relative intensities of the lines, however, were strongly affected by temperature variations (see next section).

In order to verify the assignment of the coupling constants of PPCPD and MPPCPD derived from ENDOR spectra, E.S.R. spectra were calculated on an IBM 7040 computer using the modified SESRS programme [25] and compared with the experimental E.S.R. spectra.

3. Results and discussion

3.1. *Radicals with D_5 symmetry*

PPCPD

The room temperature E.S.R. spectrum of a dilute solution of PPCPD is only partly resolved [18, 19]. We found that the resolution could be improved considerably by cooling a solution of PPCPD in pentane down to about −80°c, whereby the linewidth is reduced from 150 mG (room temperature) to 50 mG. The temperature variation does not affect the hfs constants. The resolution could be improved further by setting the phase angle of the reference signal to the 100 kHz lock-in amplifier off zero degrees. The effect of this procedure on the apparent width and intensity of narrow hfs lines has been discussed in the literature [26]. It yields a somewhat distorted lineshape so that a perfect agreement between

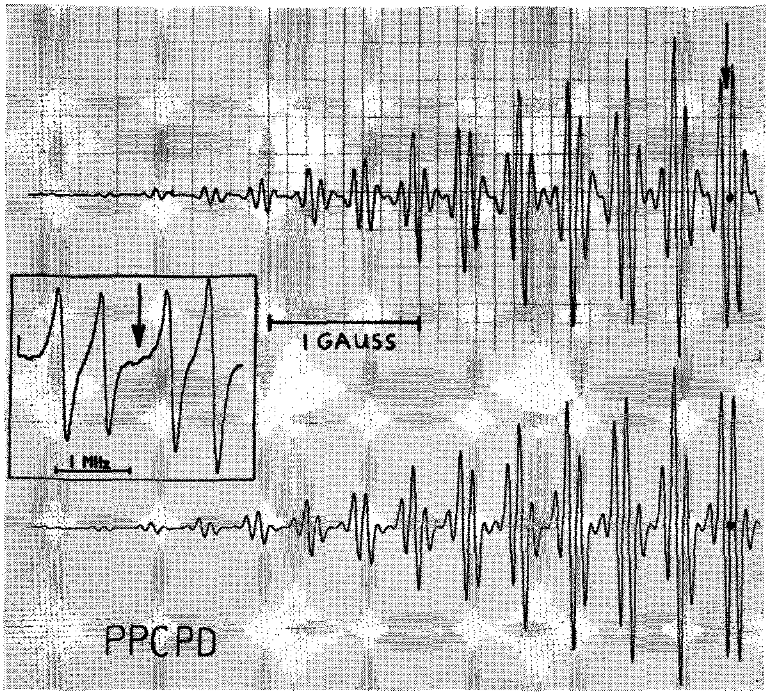

Figure 2. Comparison between experimental and calculated E.S.R. spectra of PPCPD. The lineshape employed in the calculation is Gaussian with peak-to-peak linewidth of 40 mG. (Phase angle off zero degrees, see text.) Inserted is the ENDOR spectrum. The centres of the spectra are marked by an arrow.

experimental and computed spectra cannot be expected. The E.S.R. spectrum of PPCPD obtained under conditions of maximum resolution is shown in figure 2.

The ENDOR spectrum of PPCPD in pentane also is included in figure 2. The *ortho*, *meta* and *para* protons give rise to only two ENDOR lines on either side of the free proton Larmor frequency, with a linewidth of 100 kHz. There is no indication of a third coupling, so that two hfs constants must be equal within the limits of the ENDOR resolution which according to a conservative estimate is about 5 mG. This result is different from that observed in the case of triphenylmethyl radicals [11, 14], where all three couplings are clearly resolved. Although, in general, the relative intensities of ENDOR lines are not proportional to the numbers of equivalent protons responsible for the enhancement, this proportionality holds fairly well if the couplings are similar in magnitude. The observed intensity ratio in the ENDOR display, therefore, suggests the following assignment $|a_m| < |a_o| = |a_p|$. The measured splitting constants are listed in table 1. The observed ratio $|a_p|/|a_m| = 2{\cdot}3$ is very close to that found in triphenylmethyl [11, 13].

Recent INDO calculations of Pople and Beveridge [3] on delocalization of π-spin density into the σ system of twisted phenyl substituents suggest an alternative assignment. These authors calculated the proton hfs for the benzyl radical as a function of the angle θ between the CH_2 plane and the plane of the phenyl ring. They found that the *ortho*- and *para*- proton splittings decrease much more drastically with increasing twist angle than the *meta*-splitting does. By interpolating their data it is predicted that for $\theta = 60°$, $|a_o| \simeq |a_m| \simeq 2|a_p|$. In a

	Position	Twist angle 0°	20°	40°	60°	80°	Exp.‡
PPCPD	Ortho	−1·03	−0·95	−0·73	−0·40	−0·05	0·707
	Meta	0·36	0·34	0·28	0·17	0·04	0·314
	Para	−1·09	−1·04	−0·82	−0·50	−0·07	0·707
MPPCPD	Ortho			−0·64	−0·33	−0·04	0·700
	Meta			0·20	0·12	0·03	0·303
	Methyl			0·87	0·52	0·07	0·775

† Using $a = Q\rho$ with $Q = -27$ G for aromatic protons and $+29{\cdot}3$ G for methyl protons. Spin densities ρ for different twist angles were calculated according to McLachlan ($\lambda = 1{\cdot}15$) [28] with the resonance integral of the twisted bond interpreted as $\beta/\beta_0 = \cos\theta$. The methyl groups have been considered according to a modified Coulson–Crawford model [36].

‡ Only the absolute values of the hfs constants could be measured.

Table 1. Calculated† and experimental hfs constants (in gauss).

very crude approach one would expect that in PPCPD the proton splittings would be about one-fifth of the benzyl splittings. The observed PPCPD splitting constants are very close to one-fifth of the calculated benzyl splitting constants for $\theta \simeq 60°$ [benzyl (60°): $a_0 = a_m = 3{\cdot}15$ G, $a_p = 1{\cdot}60$ G; PPCPD: 0·71 G and 0·31 G]. A *meta* splitting larger than the *ortho*- and *para*-splittings has recently been observed for the benzoyl radical [5], in which the unpaired electron occupies a σ-orbital.

The assignment $|a_p| < |a_o| = |a_m|$ must be rejected, however, as this interpretation cannot account for the recorded E.S.R. spectrum and the intensity ratio of the ENDOR lines. Figure 2, on the other hand, shows that a good agreement between calculated and recorded E.S.R. spectra is obtained with the 'conventional' ($|a_m| < |a_o| = |a_p|$) assignment (the slight discrepancies are attributed to the instrumental phase effect [26] mentioned above). This interpretation is further supported by the ENDOR spectrum of MPPCPD, where the methyl splitting could be assigned unambiguously (*vide infra*).

We conclude, therefore, that the twist angle in PPCPD is rather small and certainly less than 60°. For relatively small twist angles, conventional MO theory based on the σ–π separability will be appropriate to describe the spin density distribution. In fact, from a hyperconjugative model of twisted phenyl rings [2], we estimated that the amount of π-spin density which is delocalized into the σ system of the phenyl rings in PPCPD is smaller than 4 per cent for twist angles less than 60° [27]. Accordingly, we have calculated the spin density distribution for different twist angles using the SCF–MO approximation of McLachlan [28]. The theoretical hfs constants calculated with the McConnell relation [29]

$$a_r^{\mathrm{H}} = Q_{\mathrm{H}} \rho_r^{\mathrm{H}} \tag{1}$$

with $Q_{\mathrm{H}} = -27$ G [30], and where ρ_r^{H} are the calculated π-spin densities, are compared with the experimental values in table 1. The McLachlan method was preferred over the simple Hückel method because it is well known [31] that HMO spin densities are generally rather inaccurate for non-alternant radicals. The comparison in table 1 indicates that the twist angle of the phenyl rings is about 40° for PPCPD.

Molecular Physics 1971.20:289-304.

MPPCPD

A solution of MPPCPD in pentane also gives a rather well resolved E.S.R. spectrum at $-80°C$ as is shown in figure 3. The three splitting constants in MPPCPD could be derived from the ENDOR spectrum also reproduced in figure 3 and are summarized in table 1. The assignment of the couplings was derived from the temperature dependence of the relative ENDOR line intensities, which will be discussed in some detail further on, and is consistent with the E.S.R. results as is illustrated by the almost perfect agreement between calculated and experimental spectra in figure 3. The E.S.R. spectrum shown was recorded with a phase angle of zero degrees in order to avoid line-shape distortion.

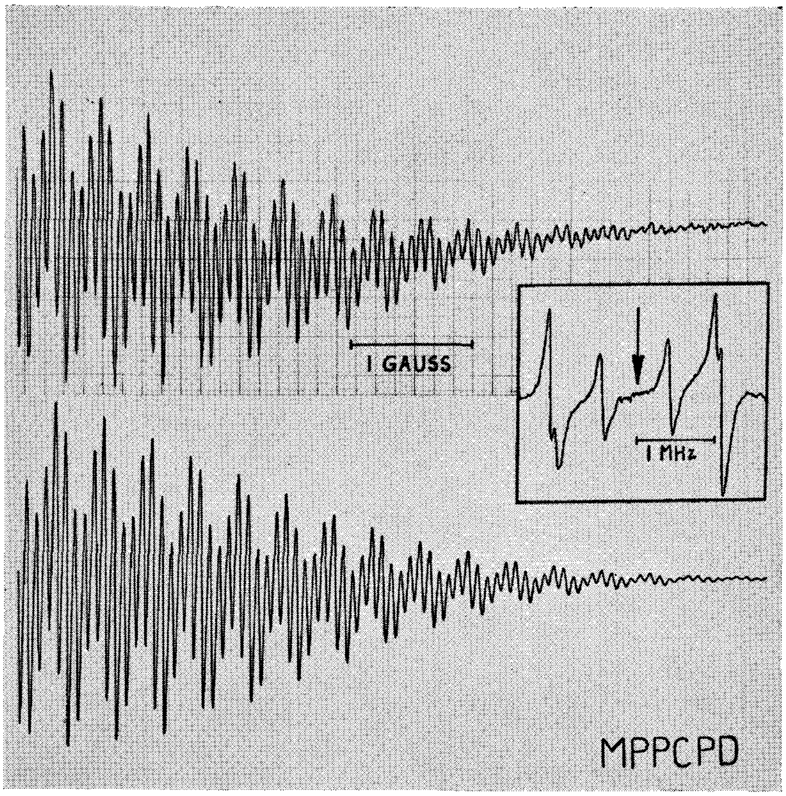

Figure 3. Comparison between experimental and calculated E.S.R. spectra of MPPCPD. The lineshape employed in the calculation is Lorentzian with peak-to-peak linewidth of 60 mG. (Phase angle zero degrees, see text.) Inserted is the ENDOR spectrum.

A comparison of the experimental splitting constants of PPCPD and MPPCPD shows that the effect of the *para*-methyl substituents on the *ortho* and *meta*-splittings is very small, whereas the methyl splitting is about 10 per cent larger than the para splitting in PPCPD. This is in accordance with the observations in substituted triphenylmethyl radicals [11, 14].

For a freely rotating methyl group there exists a simple relation between the methyl splitting constant and the π-spin density at the neighbouring aromatic carbon atom (ρ_α^π) [32, 33]

$$a^{\mathrm{CH}_3} = Q_{\mathrm{CH}_3}\rho_\alpha^\pi, \tag{2}$$

where $Q_{\mathrm{CH}_3} = 29{\cdot}3$ G [34, 35] if the delocalization of spin density into the pseudo-π-orbitals of the methyl group is taken into account in the calculation of ρ_α^π. This delocalization reduces the spin density ρ_r^π by about 8 per cent, where ρ_r^π is the spin density at the carbon r *before* the methyl group is attached to this position [34, 35]. In the calculation of the hfs constants of MPPCPD, which are listed in table 1, the methyl groups have been considered according to a modified Coulson and Crawford model [36]. Also for MPPCPD the comparison between experimental and calculated splittings indicates a twist angle of about 40°.

Our data in table 1 suggest that we can describe the hfs constants in MPPCPD equally well by using the ρ_r^π values of PPCPD and reducing instead the Q_{CH_3} value by 8 per cent to $+27$ G. This conclusion is of importance for the interpretation of the ENDOR data of the remaining methyl-substituted radicals.

3.2. *Radicals with C_2 symmetry*

Description of the E.S.R. and ENDOR spectra

The radicals with reduced symmetry due to incomplete methyl substitution exhibit very complex E.S.R. spectra. Whereas compound 2 at -90°C exhibits a moderately well-resolved spectrum with a characteristic intensity pattern, compound 7 at this temperature merely shows a broad envelope with some additional structure. No attempt has been made to calculate the E.S.R. spectra of these compounds on the basis of the ENDOR results mainly because of the drastic changes found in the patterns upon temperature variation. These changes obviously are due to temperature-dependent hfs coupling constants and are not observed in the E.S.R. spectra of the PPCPD and MPPCPD radicals. Figure 4 depicts the ENDOR

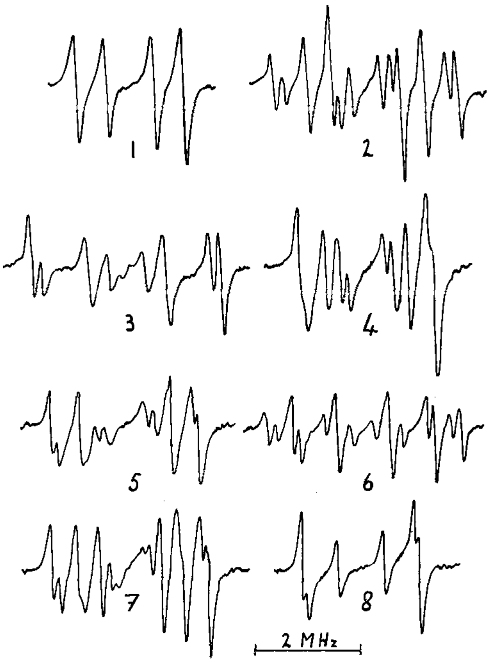

Figure 4. ENDOR spectra of compounds 1 to 8 in isopentane at about -90°C. The linewidth is about 70 kHz, the FM deviation is only 20 kHz to reduce modulation broadening effects.

spectra of all the radicals studied here. Temperature and FM index of the r.f. field were chosen for maximum resolution rather than maximum signal intensity.

The main problem in ENDOR is the assignment of coupling constants. This is because the intensity-determining relaxation mechanisms depend partially on the magnitudes of the hyperfine couplings [37]. As a result, the ENDOR line intensities are only a rough indication of the number of protons involved. In case of different classes of protons, however, with pronounced differences in the anisotropy of their hyperfine interactions, assignments can be facilitated by the different temperature dependences of the ENDOR line widths and intensities of these protons [11]. Such a difference exists, for instance, for ring and methyl protons. Whereas the anisotropy of ring protons amounts to about 50 per cent of the isotropic coupling [38], the anisotropy of a rotating methyl group is only of the order of 10 per cent of the isotropic coupling [39]. As a result, when cooling the sample and thereby increasing the viscosity of the solvent, the E.S.R. and ENDOR lines of ring protons broaden at higher temperatures than the methyl proton lines because of the incomplete averaging of the anisotropic hyperfine interactions. This effect is clearly demonstrated in figure 5 for the radicals MPPCPD and 6 in isopentane, where with decreasing temperature the relative line intensities change drastically in favour of the methyl lines. This temperature dependence enabled us to assign the methyl proton peaks for all radicals unambiguously.

Such an effect could not be observed when using octane or pentane as solvents. This is reasonable in view of the relatively small viscosities of these solvents at their freezing points; 3·6 cP and 2·2 cP, respectively [40]. Unfortunately, we could only find viscosity data for 0° and 15°c for isopentane [40]. At these two temperatures the viscosities of pentane and isopentane are the same, however. In order to estimate the order of magnitude of η near the freezing point of isopentane it was

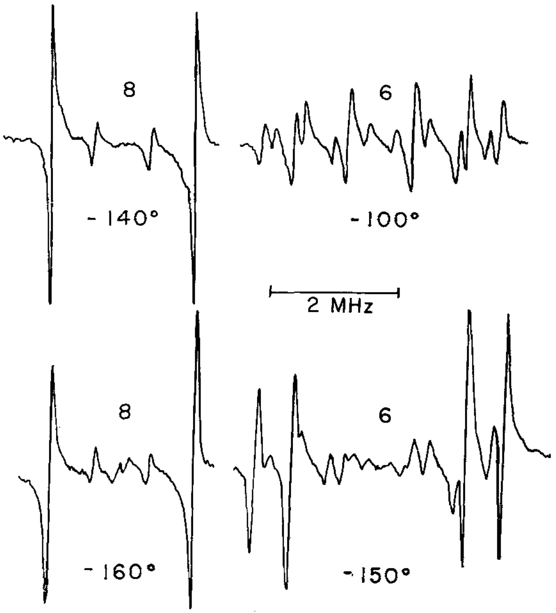

Figure 5. ENDOR spectra of MPPCPD (8) and 1,3,4-CH_3-PPCPD (6) in isopentane at different temperatures. Note also the additional doublet which appears at −160°c around the free proton Larmor frequency of 8, which we attribute to matrix ENDOR (see text).

assumed that the solvents have similar viscosities also in the temperature range of −100° to −130°C. The viscosity data of pentane in this region [40] closely follow the expression $\ln \eta = -A + B/T (A, B > 0)$. Extrapolating to −160°C (the melting point of isopentane) then yields a value of 65 cP. This order of magnitude for η seems quite reasonable in view of the observation that isopentane, in contrast with octane and pentane, readily supercools to form a glass. Thus, while the rotational tumbling rates in octane and pentane remain high compared with the anisotropy of the ring proton hyperfine interactions, this is no longer the case in isopentane at low temperatures because its viscosity is more than an order of magnitude greater.

In general, we observed an increase in ENDOR enhancement in the sequence octane, pentane, isopentane. This supports theoretical conclusions [37 a] that for most free radicals the optimum enhancement is determined by the magnitude of the dynamic electron–nuclear dipolar interaction. Lattice-induced nuclear transition rates due to this mechanism are proportional to η/T, which can be made larger in this sequence of solvents.

In glassy isopentane solutions we could observe strong methyl ENDOR lines down to −170°C, indicating that the methyl groups were still rotating. In addition the glassy solution spectra always showed matrix ENDOR lines in the centre [11] (see figure 5). In contrast to earlier observations [11] the matrix ENDOR always consisted of a doublet with a splitting of the order of 150 kHz. Qualitatively, the matrix ENDOR doublet can be interpreted as being due to the classical electron–nuclear dipolar interaction between the unpaired electron and the protons of the first solvation shell. This can give rise to two strong peaks with a separation of $B\langle r^{-3}\rangle$ G and two small shoulders with twice this splitting [41], where B is about 28 G and r is the distance vector between electron spin and nuclear spin. Identifying the matrix ENDOR doublet as the two strong peaks one derives for the expectation value $\langle r^{-3}\rangle \approx 2 \times 10^{-3}$ Å^{-3}. This admittedly crude estimate gives $\langle r^{-3}\rangle^{-1/3} \approx 8$ Å. It should be emphasized that little meaning can be attached to this number, as the electron spin is highly delocalized.

Discussion of the lifting of orbital degeneracy

The methyl hfs constants in the compounds 2 to 7 vary widely and, in addition, they all show a distinct temperature variation as has been illustrated in figure 6. In contrast, the methyl splitting in MPPCPD does not show a variation with temperature. The variation in methyl couplings from compound to compound and the temperature effects can be explained qualitatively if one assumes that the incomplete *para*-methyl substitution lifts the orbital degeneracy of the electronic ground state of the PPCPD radical and that the splitting of the degenerate state is of the order of kT so that thermal mixing plays a role.

As pointed out in the introduction, the hfs constants in the toluene and xylene anion radicals could be interpreted by assuming that the methyl substituents lift the orbital degeneracy of the electronic state of the benzene anion. It was reasoned [20, 42] that since the methyl group is an electron repelling substituent the lowest state must be the one with the smallest π-charge density at the ring carbon atom to which the methyl is attached. In the case of toluene this is the state in which the unpaired electron is in the antisymmetric (a.s.) first antibonding π orbital. As the π MO's are not affected significantly by methyl substitution, the hfs constants are predicted to reflect the spin density distribution in this a.s. orbital of benzene.

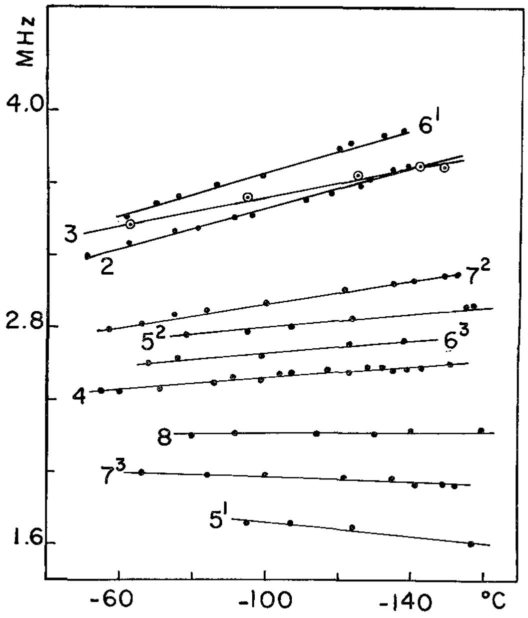

Figure 6. Methyl coupling constants (see figure 1 for the numbering scheme) of compounds 2 through 8 in isopentane as a function of temperature. The large number refers to the compound, while the superscript refers to the position. The fractional temperature coefficient reaches values of $6 \times 10^{-3}/°\mathrm{C}$.

We have applied similar arguments to interpret the methyl hfs constants in compounds 2 through 7. In PPCPD and MPPCPD the unpaired electron can sit in either one of the two degenerate π orbitals, which are chosen to be symmetric and antisymmetric with respect to the two-fold symmetry axis retained in the partially methylated compounds (cf figure 1). The spin density distribution is an average of the distributions in these orbitals. Upon partial methyl substitution the state with the lowest total π-electron charge density

$$\left(\sum_{r} q_r\right)$$

at the methyl substituent-carrying carbon atoms r will be energetically most favourable. In table 2 we have given the π-electron charge densities and spin densities at the three distinct *para*-positions (under C_2 symmetry) for the symmetric (sym.) (unpaired electron in the sym. π-MO) and antisymmetric (electron in the a.s. π-MO) states. The spin densities were calculated with the McLachlan method for a twist angle of 40°. The charge densities are obtained from a HMO calculation (twist angle 40°) for reasons which will be discussed later. A comparison of the sums of the charge densities at the methylated positions in compounds 2 to 7 between a.s. and sym. states suggests the assignment of the ground states given in table 3. This assignment agrees very well with the magnitude of the measured methyl hfs constants relative to the methyl splitting in MPPCPD. In 2, for instance, which has a sym. ground state, table 2 shows a high spin density at the methylated *para*-position for this state so that the methyl coupling constant must be larger than in MPPCPD as is indeed observed. In 5, predicted to have an a.s. ground state, table 2 predicts a large splitting for the methyl protons at positions 2

para-position	q_r (sym.)	q_r (a.s.)	ρ_r (sym.)	ρ_r (a.s.)
1	0·963	1·016	0·059	−0·005
2,5	1·011	0·968	0·002	0·055
3,4	0·981	0·998	0·041	0·021

† q_r and ρ_r calculated in the HMO and McLachlan approximations, respectively.

‡ Refer to figure 1.

§ The averaged values over the sym. and a.s. states should reflect the five-fold symmetry of PPCPD. This is not fulfilled for the spin densities listed because the McLachlan correction of the Coulomb integrals introduces only C_2 symmetry.

Table 2. π-electron charge densities† q_r and spin densities† ρ_r for the sym. and a.s. states at the three distinct *para*-positions‡ under C_2 symmetry§. The twist angle assumed is 40°.

and 5 (cf. figure 1) and a small splitting for position 1. This is again confirmed by the ENDOR results, which allowed an unambiguous assignment of the two methyl splittings on the basis of the relative intensities of the methyl peaks. Table 2 shows that the spin densities at position 3 for the sym. and a.s. states do not differ as much as at positions 1 and 2. One expects, therefore, that the corresponding methyl couplings will differ less from the MPPCPD value. Figure 6 confirms this expectation for compounds 6 and 7.

The observed temperature variation of the methyl couplings further justifies our interpretation on the basis of a lifting of the degeneracy. A calculation of the energy gap between sym. and a.s. states in the p-xylene anion shows [22] that this gap is much larger than kT so that there is effectively no thermal population of the upper state. Consequently, one expects and observes no temperature dependence of the hfs constants. In the PPCPD radicals the differences between the charge density sums in the sym. and a.s. states are much smaller than in *p*-xylene, however. On the basis of simple electrostatic arguments one may conclude, therefore, that the energy gap induced by the methyl substitution will be much less than in the *p*-xylene anion, and thus it is feasible that the excited state becomes thermally accessible. If that is the case, one predicts that as the temperature is raised the spin densities, which are now a statistical average of the densities in the symmetric and antisymmetric states, will converge on the PPCPD values. All the methyl couplings in compounds 2 to 7 thus are expected to converge on the MPPCPD value as the temperature increases. Figure 6 shows that this is indeed observed experimentally.

The temperature effect can be used to obtain values for the energy gaps between the sym. and a.s. states. When the ground state is a.s. the measured splitting constant a_m is given by

$$a_m = \frac{a_a + a_s \exp(-\Delta E/kT)}{1 + \exp(-\Delta E/kT)}, \tag{3}$$

where a_a and a_s stand for the values of the coupling constant in the a.s. and sym. state, respectively, and ΔE is the energy gap. A similar formula for the case that the ground state is sym. is obtained by interchanging the subscripts. The limiting values a_a and a_s, unfortunately, could not be determined experimentally. They were derived from a calculation of the spin density distribution in the two states, which undoubtedly introduces some error in the evaluation of ΔE. Since methyl substituents produce only minor perturbations of the π-orbital wavefunctions (see our conclusion in the previous section) we have based our calculation of the gaps on the spin density distribution in the sym. and a.s. states of PPCPD given by the McLachlan method for a twist angle of 40° (see table 2). The limiting values a_a and a_s were deduced using the expression $a = Q\rho$, where $Q = 27$ G (see previous section).

The energy gaps ΔE were obtained from plots of

$$\ln \{(a_m - a_a)/(a_s - a_m)\} \text{ versus } 1/T,$$

two representative examples of which are depicted in figure 7. In all cases the temperature dependence could be interpreted satisfactorily using expression (3). The energy gaps derived in this way have been summarized in table 3. The values obtained are of a reasonable order of magnitude considering that the energy gap for the toluene anion was calculated [22] to be 384 cm^{-1}.

Compound	Substitut. positions r	$\Sigma\, \Delta q_r$ r	Ground state symmetry	ΔE_{calc} (cm^{-1})†	ΔE_{exp} (cm^{-1})
2	1	0·053	sym.	61	115
3	2,5	−0·086	a.s.	99	101
4	3,4	0·033	sym.	38	89
5	1,2,5	−0·033	a.s.	38	25
6	1,3,4	0·086	sym.	99	136
7	2,3,4,5	−0·053	a.s.	61	58

† The calculation was performed according to equation (5) with the charge densities listed above and $h = -0{\cdot}06$, $\beta_0 = -2{\cdot}37$ ev.

Table 3. Ground state assignment and energy gaps between the sym. and a.s. states.

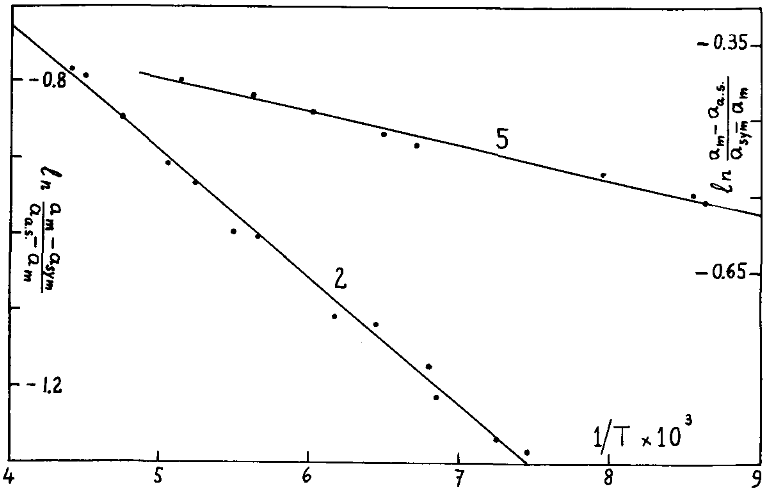

Figure 7. Arrhenius plots for the compounds 2 and 5. The straight lines represent least-squares fits.

In an attempt to rationalize the ΔE_{exp} data we also estimated the gaps using HMO calculations. In an admittedly crude approximation one can calculate the effect of methyl substitution on the π-electron energy treating it as a purely inductive effect. In the HMO method the change in total π-electron energy of a state in first order is given by [23]

$$\delta E_\pi = \sum_r q_r \Delta\alpha_r = h\beta_0 \sum_r q_r, \tag{4}$$

where q_r is the electron charge density at the ring carbon atom r carrying a methyl group and $\Delta\alpha_r$ represents the change in the Coulomb integral due to methyl substitution at this position. The energy gap between the sym. and a.s. states then is given by

$$\Delta E = \delta E_{\pi\mathrm{s}} - \delta E_{\pi\mathrm{a.s.}} = h\beta_0 \sum_r \Delta q_r, \tag{5}$$

where Δq_r is the difference in electron charge densities at r between the two states. Inductive parameters $\Delta\alpha_r$ of the order of $-0{\cdot}1\beta_0$, where β_0 is the resonance integral, have been used in the literature [23]. In our estimate of the ΔE's we have tried to improve our crude model somewhat by adjusting h to a value which would give the energy gap of 384 cm^{-1} obtained by a SCF–CI calculation for the toluene anion [22] (Δq_r for benzene is $\frac{1}{3}$).

Taking β_0 as $-2{\cdot}37$ ev, h is found to be $-0{\cdot}06$. It should be noted that the SCF–CI calculation of the energy gap in p-xylene anion yielded [22] a value of 868 cm^{-1} offering some support for our assumption in (4) and (5) that the inductive effect of methyl groups on ΔE is roughly additive.

Table 3 shows that the energy gaps calculated on the basis of this simple inductive model are of the correct order of magnitude. The fact that the calculated energy gaps of 2 and 7, 3 and 6, as well as 4 and 5 are identical is, of course, implicit in our model. Since the Δq_r values in MPPCPD turned out to be the same as in PPCPD, removal of one CH_3 group from the completely methylated PPCPD induces the same gap as addition of one group to PPCPD in our model, while the ordering of the states is reversed. This ' pairing property ' is not shown in the experimentally determined ΔE's. This is not surprising in view of the highly approximative nature of our calculation of the gaps. If one considers the effect of an improvement of the HMO π-electron energy calculation by, for instance, a configuration interaction method, one may expect that the energy corrections for the sym. and a.s. states will be different in which case the pairing is lost. The fact that the experimental ΔE's for all three pairs of radicals are larger in the species with sym. ground states suggests that this CI energy correction in fact is slightly larger for the sym. states.

Finally, something should be said about the ring proton hfs constants. The splittings all show a temperature variation similar to those found for the methyl groups, as expected on the basis of the interpretation given above. However, as the ENDOR lines of the ring protons cannot be readily assigned *a priori*, contrary to the methyl peaks, and also cannot be studied over such a wide temperature range, the temperature variations cannot be used to derive information regarding the energy gaps. On the other hand, it turned out that these ENDOR peaks could be assigned satisfactorily by using:

I. The predicted splittings at a given temperature using the McLachlan spin densities in the sym. and a.s. states of PPCPD and the experimentally determined energy gaps between the two states.

II. The predicted temperature dependence of the splittings.

III. The results for PPCPD which suggest that the *ortho* and *para* splittings in a non-methylated phenyl ring are not resolved, while the *meta* splitting is slightly less than half the *ortho* and *para* splittings.

IV. The results for MPPCPD which suggest that the *ortho*-splitting in a *para*-methylated ring is slightly smaller than the methyl splitting and slightly more than twice the *meta*-splitting in this ring.

The assignment of the splitting constants in the six compounds at about −90°c, which is consistent with these considerations and the observed relative intensities of the ENDOR lines, is given in table 4.

Compound	2	3	4	5	6	7
Position‡	Hyperfine splitting constants					
1	1·22§	0·24	0·89	0·61§‖	1·29§	0·41
6	0·46	0·07	0·36	0·27‖	0·51	0·18
9	1·08	0·24	0·89	0·61	1·17	0·41
2	0·46	1·25§	0·55	1·00§	0·36‖	1·02§
7	0·20	0·51	0·24	0·38	0·14	0·41
10	0·46	1·12	0·55	0·90	0·36	0·93
3	0·78	0·51	0·89§	0·61	0·94§	0·70§
8	0·35	0·24	0·36	0·27	0·36	0·27
11	0·78	0·51	0·80	0·61	0·85	0·64

† See text.

‡ Refer to figure 1.

§ Methyl proton hfs.

‖ ENDOR peak partly resolved in two peaks at lower temperatures.

Table 4. Values (in gauss) and assignments† of the experimentally determined hyperfine splitting constants at temperatures about −90°c.

As we could not verify this assignment with a comparison of experimental and calculated E.S.R. spectra we cannot claim that it is completely unambiguous. It may be feasible to measure the splitting constants and associated temperature variations more precisely with N.M.R.

In conclusion, the magnitudes as well as the temperature variations of all the hfs constants in the partially methylated systems can be explained very satisfactorily assuming lifting of the orbital degeneracy associated with thermal averaging. While other processes, such as radical–solvent interactions [43], can give rise to temperature-dependent splitting constants it is not likely that they play a significant role here in view of the consistency between experimental results and the theoretical interpretation. Moreover, recent measurements [43] of temperature coefficients of hfs constants suggest that radical–solvent interaction effects are negligibly small in our radical solutions, since the solute is only slightly polar and the solvent is nonpolar.

The authors wish to thank Dr. H. Kurreck, Freie Universität Berlin, for supplying us with all the compounds. We also are grateful to Dr. M. Plato, AEG-Forschungsinstitut, Frankfurt, for performing part of the computer calculations. K. M. is grateful to the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship. This work received support from a National Science Foundation grant, for which we are grateful.

REFERENCES

[1] MÖBIUS, K., and PLATO, M., 1969, *Z. Naturf.* A, **24,** 1078.

[2] PLATO, M., and MÖBIUS, K., 1969, *Z. Naturf.* A, **24,** 1083.

[3] POPLE, J. A., and BEVERIDGE, D. L., 1968, *J. chem. Phys.*, **49,** 4725.

[4] HUTCHISON, C. A., and KOHLER, B. E., 1969, *J. chem. Phys.*, **51,** 3327.

[5] KRUSIC, P. J., and RETTIG, T. A., 1970, *J. Am. chem. Soc.*, **92,** 722.

[6] FEHER, G., 1956, *Phys. Rev.*, **103,** 834.

[7] HYDE, J. S., and MAKI, A. H., 1964, *J. chem. Phys.*, **40,** 3117.

[8] HYDE, J. S., 1965, *J. chem. Phys.*, **43,** 1806.

[9] HYDE, J. S., 1967, *J. phys. Chem.*, **71,** 68.

[10] HYDE, J. S., BRESLOW, R., and DE BOER, C., 1966, *J. Am. chem. Soc.*, **88,** 4763.

[11] HYDE, J. S., RIST, G. H., and ERIKSSON, L. E. G., 1968, *J. phys. Chem.*, **72,** 4269.

[12] KISPERT, L. D., HYDE, J. S., DE BOER, C., LAFOLLETTE, D., and BRESLOW, R., 1968, *J. phys. Chem.*, **72,** 4276.

[13] MAKI, A. H., ALLENDOERFER, R. D., DANNER, J. C., and KEYS, R. T., 1968, *J. Am. chem. Soc.*, **90,** 4225.

[14] ALLENDOERFER, R. D., and MAKI, A. H., 1969, *J. Am. chem. Soc.*, **91,** 1088.

[15] BRAUER, H. D., STIEGER, H., HYDE, J. S., KISPERT, L. D., and LUCKHURST, G. R., 1969, *Molec. Phys.*, **17,** 457.

[16] DAS, M. R., CONNOR, H. D., LENIART, D. S., and FREED, J. H., 1970, *J. Am. chem. Soc.*, **92,** 2258.

[17] HYDE, J. S., 1967, *Magnetic Resonance in Biological Systems*, edited by A. Ehrenberg, B. G. Malmström, and T. Vänngård (Pergamon Press), p. 63.

[18] REITZ, D. C., 1961, *J. chem. Phys.*, **34,** 701.

[19] MÖBIUS, K., 1965, *Z. Naturf.* A, **20,** 1117.

[20] BOLTON, J. R., and CARRINGTON, A., 1961, *Molec. Phys.*, **4,** 497.

[21] LAWLER, R. L., BOLTON, J. R., FRAENKEL, G. K., and BROWN, T. H., 1964, *J. Am. chem. Soc.*, **86,** 520.

[22] DE BOER, E., and COLPA, J. P., 1967, *J. phys. Chem.*, **71,** 21.

[23] STREITWIESER, A., 1961, *Molecular Orbital Theory* (John Wiley & Sons).

[24] STREITWIESER, A., and BRAUMAN, J. I., 1965, *Supplemental Tables of Molecular Orbital Calculations*, Vol. II (Pergamon Press), p. 1205.

[25] STONE, E. W., and MAKI, A. H., 1963, *J. chem. Phys.*, **38,** 1999.

[26] PLATO, M., 1968, *Wiss. Ber. AEG—Telefunken*, **41,** 81.

[27] Equation (19) in reference [2].

[28] MCLACHLAN, A. D., 1960, *Molec. Phys.*, **3,** 233.

[29] MCCONNELL, H. M., 1956, *J. chem. Phys.*, **24,** 632.

[30] BOLTON, J. R., and FRAENKEL, G. K., 1964, *J. chem. Phys.*, **40,** 3307.

[31] MÖBIUS, K., and PLATO, M., 1967, *Z. Naturf.* A, **22,** 929.

[32] MCLACHLAN, A. D., 1958, *Molec. Phys.*, **1,** 233.

[33] HELLER, C., and MCCONNELL, H. M., 1960, *J. chem. Phys.*, **32,** 1535.

[34] FESSENDEN, R. W., and SCHULER, R. H., 1963, *J. chem. Phys.*, **39,** 2147.

[35] FISCHER, H., 1965, *Z. Naturf.* A, **20,** 428.

[36] BOLTON, J. R., CARRINGTON, A., and MCLACHLAN, A. D., 1962, *Molec. Phys.*, **5,** 31.

[37] (*a*) FREED, J. H., 1967, *J. phys. Chem.*, **71,** 38. (*b*) ALLENDOERFER, R., and MAKI, A. H., 1970, *J. Mag. Resonance*, **3,** 396.

[38] MCCONNELL, H. M., HELLER, C., COLE, T., and FESSENDEN, R. W., 1960, *J. Am. chem. Soc.*, **82,** 766.

[39] MORTON, J. R., and HORSFIELD, A., 1961, *J. chem. Phys.*, **35,** 1142.

[40] Landolt–Börnstein, 1969, *Zahlenwerte und Funktionen*, Vol. II (Springer-Verlag), p. 92.
[41] Ingram, D. J. E., 1958, *Free Radicals* (Butterworth's), p. 181.
[42] Carrington, A., and McLachlan, A. D., 1967, *Introduction to Magnetic Resonance* (Harper & Row), p. 88.
[43] Reddoch, A. H., Dodson, C. L., and Paskovich, D. H., 1970, *J. chem. Phys.*, **52**, 2318.