76. Chlorine Hyperfine Splittings and Spin Density Distributions of Phenoxy Radicals. An ESR. and Quantum Chemical Study

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Summary

ESR. spectra of the chlorine substituted phenoxy radicals listed in Table 1, which were produced by photo-oxidation of the parent phenols in aprotic solvents, are reported. In most cases the chlorine splittings could be resolved and analysed in detail. Experimental data as well as quantum chemical calculations were used for assignment of all measured chlorine couplings and determination of their relative signs.

Spin density distributions and polarization parameters for chlorine are discussed and compared with the results from current semiempirical molecular orbital theories.

Chlorine couplings associated with the larger splittings are found positive in sign, whereas signs of small couplings appear difficult to establish. Limitations in the applicability of *McConnell* or *Karplus-Fraenkel* type relations to chlorine substituted aromatic radicals will be discussed and related to peculiar properties of the spin density matrix of such systems.

1. Introduction. – The number of reported coupling constants for chlorine substituents in radicals is at present rather limited [1]. In the case of aromatic radicals in particular this has to be traced back to a number of factors, *e.g.* small hyperfine splittings, overlapping of spectra of isotopic modifications, nuclear quadrupole effects and chemical instability. As a consequence of these difficulties the theory which should explain the chlorine splittings is much less developed than the theory for corresponding fluorinated aromatic radicals [1] [2]. In this work ESR. spectra of a series of chlorine substituted phenoxy radicals were investigated with the aim to obtain sufficient experimental data for an unambiguous assignment of observed hyperfine splittings, in particular for the chlorine substituent. This in turn should provide a basis for testing spin density values as obtained from different MO theories and, eventually, lead to a determination of polarization constants for the chlorine substituent in an aromatic radical.

2. Experimental Part. - Chemicals purchased from *Fluka* were used in the purest commercially available form without further purification. Typically 1.0×10^{-3}M solutions of the parent phenols in carbon tetrachloride circulating in a flow system were photolysed directly in the microwave cavity of an X-band spectrometer. To one series of solutions, di-*t*-butyl peroxide was added as reaction initiator. In most cases it was found that solutions with and without di-*t*-butyl peroxide gave the same ESR. spectra. Therefore two photochemical equations (I) and (II) may be postulated:

$$\text{AR–OH} \xrightarrow{h\nu} \text{Ar–O}\cdot + \text{H}\cdot \qquad \text{(I)}$$

or, respectively

$$(t\text{-But–O})_2 \xrightarrow{h\nu} t\text{-But–O}\cdot$$

$$t\text{-But–O}\cdot + \text{Ar–OH} \longrightarrow t\text{-But–OH} + \text{Ar–O}\cdot \qquad \text{(II)}$$

Since more intense signals were obtained by method II, it was used for determination of the coupling parameters, the optimum peroxide concentration being about 10^{-1}M. UV. light supplied by a 500 W mercury lamp (*Osram* HBO 500) was focussed onto the window of the ESR M 231 *Varian* cavity by a quartz lens system. The magnetic field at the site of the sample was calibrated with the ESR. signal of the stable radical 4-hydroxy-2,2,2′,2′-tetramethyl-piperidineoxide, whose magnetic parameters in CCl_4 solution at room temperature are $g_{iso} = 2.0053 \pm 0.0001$ and $a^N = 14.74 \pm 0.02$ Gauss. In a number of cases the field was measured by means by a proton resonance magnetometer.

3. Results and Analysis. - The steady state ESR. signals of two monochlorophenoxy radicals are shown in Fig. 1. The quality of the spectra of the monochlorophenoxyls is comparable to or better than that obtained by oxidation of phenols in aqueous solutions [3] [4]. An increase in the number of chlorine substituents leads to more complicated spectra with lower resolution and signal-to-noise ratio, as exemplified by Fig. 2.

Since natural chlorine occurs as a mixture of two isotopes with a ratio $p(^{35}Cl)/p(^{37}Cl)$ of about 3:1, the chlorine substituted radicals are a mixture of isotopic molecules, whose relative concentrations may be computed in each specific case from the above ratio. In some cases ESR. lines from isotopically different radicals are resolved.

The procedure used for analysis of spectra may be summarized as follows: (i) the isotropic spin hamiltonian for each isotopic modification of a radical is formulated as the sum of the electron *Zeeman* and the hyperfine terms:

$$\hat{H} = \mu_e g_{iso} H_0 \hat{S}_z + \hat{S}_z \sum_{l=1}^{L} a(H)_l \hat{I}_{z,l} + \hat{S}_z \sum_{m=1}^{M} a(^{35}Cl)_m \hat{I}_{z,m} + \hat{S}_z \sum_{n=1}^{N} a(^{37}Cl)_n \hat{I}_{z,n} \qquad (1)$$

where L, M, N are the total number of ^1H, ^{35}Cl, ^{37}Cl nuclei in the molecule, respectively; (ii) the first order ESR. spectrum is computed from eq. (1) using estimates for the spectral quantities $a(H)_l$, $a(^{35}Cl)_m$, $a(^{37}Cl)_n$, g_{iso} and $\Delta H_{1/2}$ (linewidth parameter).

The spectra of all relevant isotopic modifications, weighted according to their relative concentration, are then summed yielding a simulated spectrum; (iii) if an acceptable resemblance has been obtained in step (ii) the digitized experimental spectrum is fitted to hamiltonian (1), where the estimates from step (ii) are used as starting values. Provided the fitting process converges, the resulting values will be

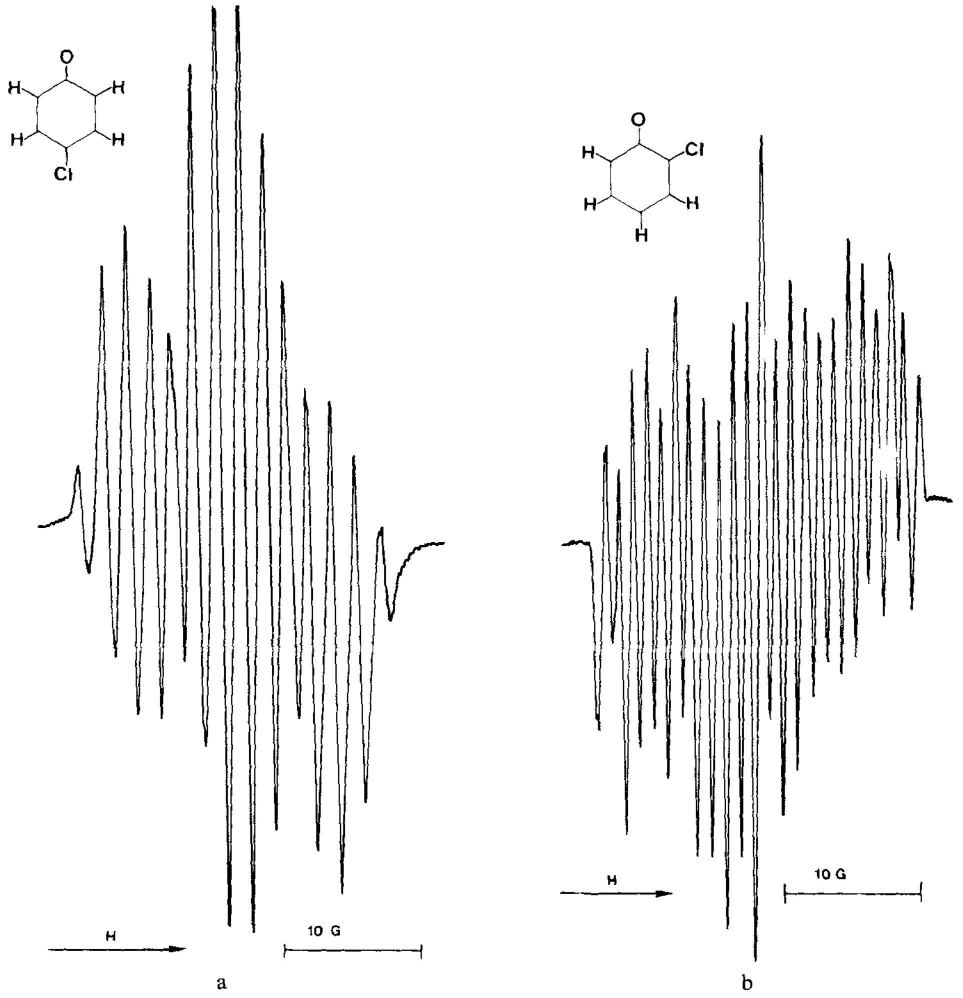

Fig. 1. *ESR. Spectra of Monochloro-phenoxyls* (10^{-3} mol/l solution in CCl_4 photolysed at room temperature)
a) 2-Chloro-phenoxyl
b) 4-Chloro-phenoxyl

accepted as the experimental data. These are listed in Table 1. A typical example for the step by step approach is shown in Fig. 3, where the experimental spectrum of 2,6-dichlorophenoxyl and the synthesized spectrum of all components are shown. In the synthesis a lorentzian line shape function with constant line width for all transitions was assumed. From Fig. 2 it is obvious that this assumption does not hold for all radicals (*cf.* sect. 4).

4. Discussion. – By systematic variation of substituents and the use of symmetry arguments all the observed coupling constants may be assigned without previous calculation of spin densities. The same method of assignment has been successfully

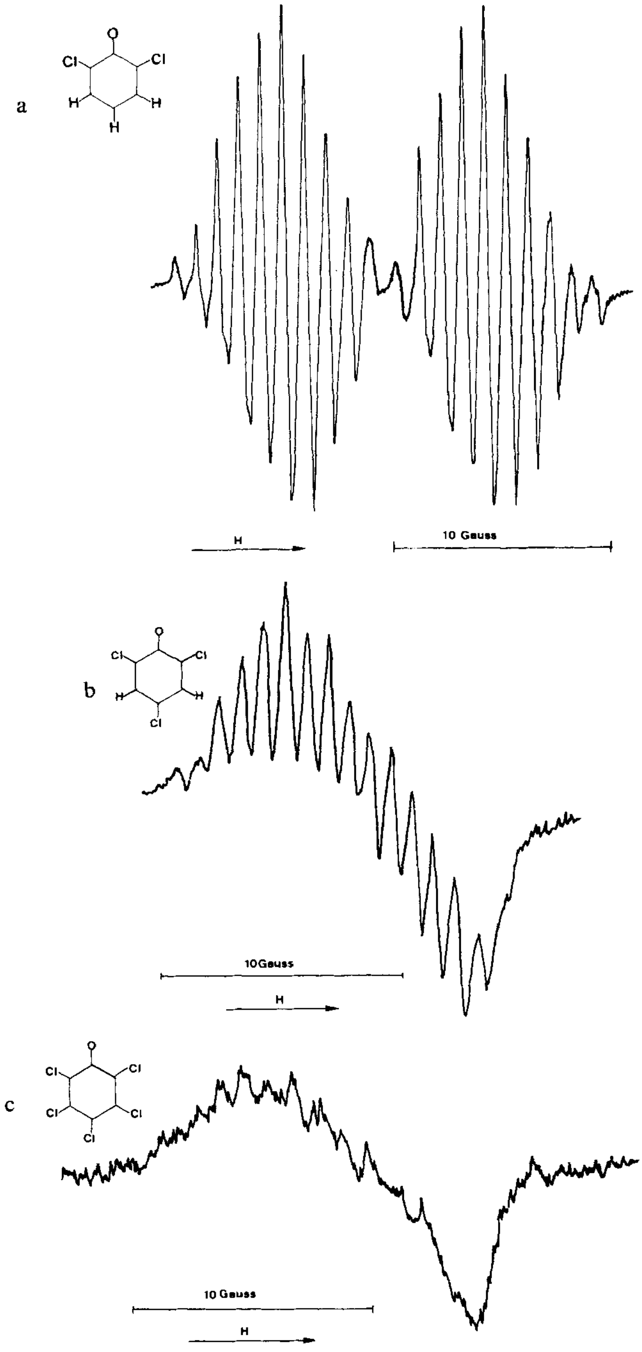

Fig. 2. *ESR. Spectra of Polychloro-phenoxyls* (10^{-3} mol/l solution in CCl_4 photolysed at room temperature)
a) 2,6-Dichloro-phenoxyl, b) 2,4,6-Trichloro-phenoxyl, c) 2,3,4,5,6-Pentachloro-phenoxyl.

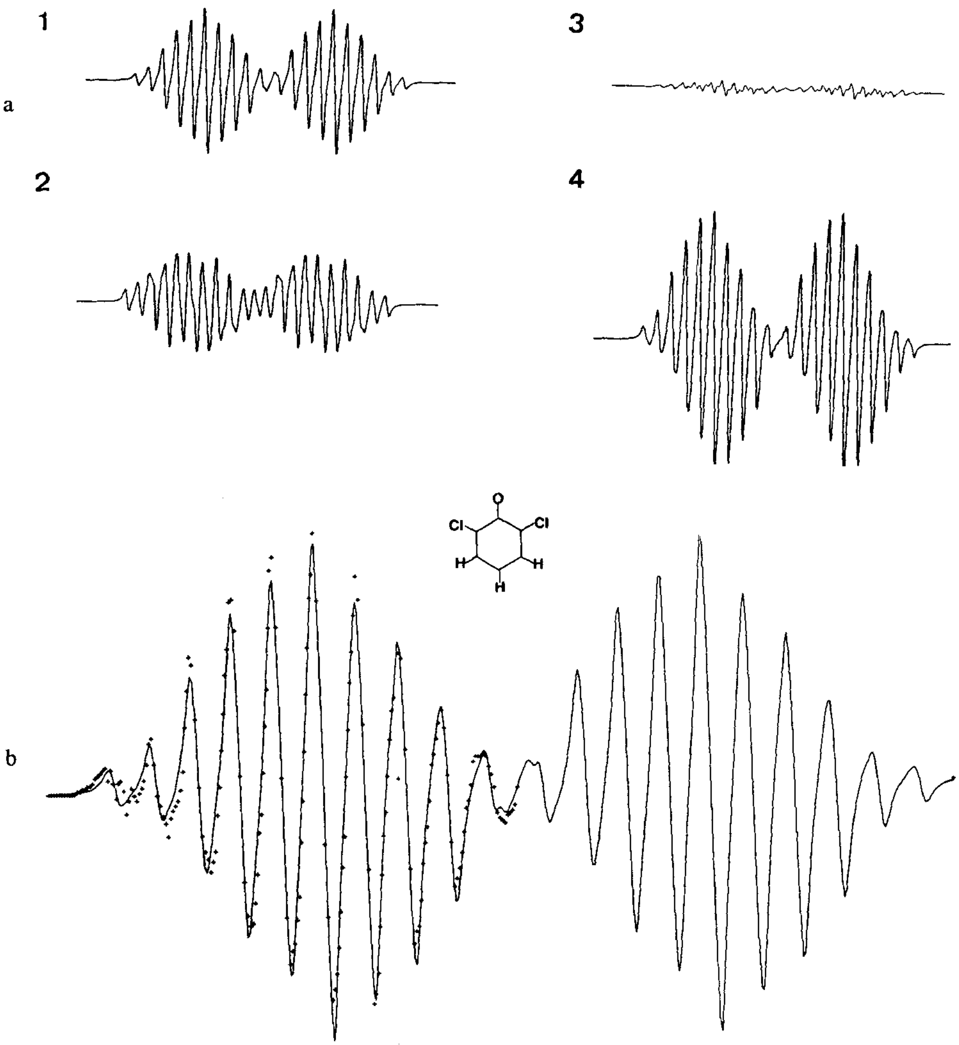

Fig. 3. *Synthesis of ESR. Spectra by Lineshape Analysis*
a) Superposition of spectra of isotopic modifications
1) 2,6-[^{35}Cl]-phenoxyl 3) 2,6-[^{37}Cl]-phenoxyl
2) 2-[^{35}Cl]-6-[^{37}Cl]-phenoxyl 4) superposition of 1), 2) and 3).

b) Least square fit of experimental ESR. spectrum of natural isotopic mixture of 2,6-dichloro-phenoxyl
solid line: synthetic spectrum
+ : experimental points
lorentzian line shape

applied by *Dixon et al.* [4] in the interpretation of a large number of substituted phenoxyls. A number of remarks follow directly from inspection of Table 1.

Firstly, it appears that the large coupling constants a^H at the different ring positions are only slightly affected by chlorine substituents at other ring positions

Table 1. *Hyperfine splittings and* g-*values for chlorine substituted phenoxy-radicals*

Radical	g-Value	Position[a]	Proton hyperfine splitting [Gauss]		Chlorine hyperfine splitting[d] [Gauss]	
			$\lvert a^{H}_{exp.}\rvert$	$a^{H}_{calc.}$[b]	$\lvert a^{Cl}_{exp.}\rvert$	$a^{Cl}_{calc.}$[c]
phenoxyl	2.0053	2,6	7.01	$-$ 7.00		
		3,5	2.05	1.67		
		4	10.13	$-$10.06		
2-chloro-phenoxyl	2.0062	2			1.1	1.1
		3	2.09	2.56		
		4	9.36	$-$ 9.59		
		5	1.92	0.68		
		6	6.38	$-$ 5.84		
3-chloro-phenoxyl	2.0062	2	6.35	$-$ 5.60		
		3			$\approx$ 0.4	0.5[e]
		4	10.25	$-$10.49		
		5	2.28	2.07		
		6	7.50	$-$ 7.90		
4-chloro-phenoxyl	2.0063	2,6	6.56	$-$ 6.49		
		3,5	1.99	1.08		
		4			1.7	1.8
2,6-di-chloro-phenoxyl	2.0065	2,6			1.0	0.8
		3,5	2.04	1.83		
		4	9.34	$-$ 9.35		
3,5-di-chloro-phenoxyl	2.0063	2,6	7.08	$-$ 6.56		
		3,5			$\approx$ 0.4	0.4[e]
		4	10.85	$-$10.52		
2,4,6-tri-chloro-phenoxyl	2.0076	2,6			$\approx$ 0.9	0.7
		3,5	$\approx$ 2.5	2.10		
		4			$\approx$ 1.9	1.7

[a] Numbering of substitutional sites according to Fig. 4.

[b] Calculation based on *McLachlan's* formula for spin densities (*cf.* Table 3, Fit II).

[c] Calculation based on PPP charge densities (*cf.* Table 4, and eq. (6)).

[d] Chlorine splittings refer always to the ^{35}Cl isotope.

[e] Sign of a^{Cl} not established.

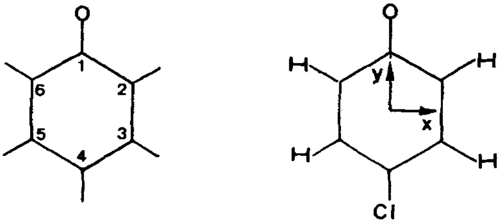

Fig. 4. *Numbering of substitutional sites and molecular coordinate system for phenoxyls*
The local coordinate system for Cl at the 4 position is assumed parallel to the molecular coordinate system

(for instance, at the *para* position, $a^H = -10.13$ Gauss for phenoxyl and $a^H = -10.85$ Gauss for 3,5-dichloro-phenoxyl).

Secondly, the chlorine couplings a^{Cl} are not very sensitive to the degree of chlorination. This indicates that chlorine-chlorine interactions are weak, at least in the ground state.

Finally we note that the ratio $a^H : a^{Cl}$ for couplings at the same position is approximately constant. Combining our data with those from the corresponding fluorinated phenoxy type radicals [2] one obtains the following crude rule for the hyperfine coupling at all positions:

$$a^F : a^H : a^{Cl} \approx 15 : 5 : 1$$

The single crystal study of *Kohin* of CHClCOOH [5] and the line width study of *Hudson* of $CH_3CClCOOH$ [6] established that the isotropic part of a^{Cl} is positive for this type of radical.

The positive sign was later confirmed for other aliphatic radicals by further investigations [7]. For chlorinated aromatic radicals, however, no conclusive determination of the sign of the chlorine hyperfine coupling has been reported so far, except in the case of the pentachloro-cyclopentadienyl radical C_5Cl_5, for which the complete hyperfine tensor A^{Cl} has been determined. The latter investigation yielded a positive sign for a^{Cl}_{iso} [9].

From Fig. 2 it is apparent that the high field lines are preferentially broadened in the ESR. spectrum of 2,4,6-trichloro-phenoxyl, and this effect is likewise pronounced for the pentachloro-phenoxy radical C_6Cl_5O. Using the same arguments as in [6], one comes to the conclusion that the product a^{Cl} times ϱ^{Cl} is positive, and since ϱ^{Cl}, at the positions where it is sufficiently large, is almost certainly positive, the associated isotropic coupling constant for Cl may be expected to be positive too. This prediction seems to hold for the larger chlorine splittings, whereas for the smaller ones, *e.g. meta*-splittings, no such prediction seems to be possible. In this case the magnitude and sign of ϱ^{Cl} require closer inspection and will be analyzed later on.

In analogy to equations which have been introduced for a^F the following equations may be used to describe the relation between a^{Cl} and the π-spin densities in the $>$C–Cl fragment [1] [2]:

$$a^{Cl} = Q^{Cl}_{CC}\,\varrho^{\pi}_{C} + Q^{Cl}_{ClCl}\,\varrho^{\pi}_{Cl} + Q^{Cl}_{CCl}\,\varrho^{\pi}_{CCl} \tag{2}$$

$$a^{Cl} = Q^{Cl}_{CC}\,\varrho^{\pi}_{C} + Q^{Cl}_{ClCl}\,\varrho^{\pi}_{Cl} \tag{2'}$$

$$a^{Cl} = Q^{Cl}_{CC}\,\varrho^{\pi}_{C} \tag{2''}$$

where the ϱ's denote π-spin densities and the Q's polarisation parameters.

There have been a number of attempts to determine the polarisation factors in eq. (2). The values proposed in the literature scatter very widely. *Allen & Vanneste* [3] base their reasoning on eq. (2″) and suggest $Q^{Cl}_{CC} = 4.6 \pm 0.6$ Gauss for phenoxy type radicals. By calculating a negligible spin density on chlorine and making use of the same eq. (2″) *Broze & Luz* obtain values for Q^{Cl}_{CC} ranging from 1.5 to about 7.0 Gauss, depending on the radical considered.

From a regression analysis on a limited set of species, *Graf & Günthard* obtained the values $Q^{Cl}_{CC} = -5.0 \pm 0.8$ Gauss and $Q^{Cl}_{ClCl} = +54.0 \pm 4$ Gauss by using eq. (2′) [8].

The values for the Q constants are very sensitive both to the values of spin densities and the experimental coupling parameters [2].

Formulae of type (2) have been found suitable only for planar π-radicals. In any type of radical the isotropic hyperfine splitting on chlorine will be to a good approximation proportional to the unpaired electron density in the chlorine 3s orbital, $\varrho_{Cl}(3s)$, therefore:

$$a^{Cl} = k\,\varrho_{Cl}(3s)\,,$$

$$k = (4/3)\,\pi\,g\,\beta\,\gamma_{Cl}\,\hbar\,\langle\hat{S}_z\rangle^{-1}\,|\Phi^{Cl}_{(3s)}(\vec{r}^{\,Cl})|^2\,, \tag{3}$$

where k is a constant for each type of nucleus [10].

Eq. (3) has been used in predicting a^{Cl} for small radicals by *Hudson et al.* [11], who extended the original INDO program in order to include second row elements [12]. Although parameter optimization has been necessary in this approach there is little doubt that it is basically more appropriate than eq. (2).

In the case of the aromatic radical C_5Cl_5 CNINDO calculations allowed a satisfactory analysis of the chlorine hyperfine interaction [9].

4.1. *Quantum Chemical Analysis of Coupling Parameters.* Table 2 gives a collection of spin and charge densities resulting from the three quantum chemical approaches used in this work in order to support the assignment of spectra.

Table 2. *π-Spin or π-charge densities for 4-chloro-phenoxyl from different approximations*

Center [a]	Hückel I [b]	McLachlan I [b]	Hückel II [b]	McLachlan II [b]	PPP [c]	CNDO [d]	INDO [e]
C(1)	0.171	0.180	0.172	0.181	0.255	−0.128	−0.144
C(2)	0.168	0.218	0.165	0.214	0.107	0.133	0.151
C(3)	0.029	−0.045	0.031	−0.040	0.063	−0.077	−0.094
C(4)	0.261	0.319	0.261	0.311 0.315	0.281	0.114	0.136
O	0.152	0.152	0.166	0.214	0.74	0.881	0.887
Cl	0.022	0.001	0.021	0.007	0.047	0.010	0.008

[a] Numbering of π-centers according to Fig. 4.
[b] *Cf.* Table 3.
[c] Charge densities obtained with parameters Table 4, see text.
[d] Spin densities according to CNDO/2 method, original parametrization.
[e] INDO spin densities, parametrization for chlorine according to (11).

4.1.1. McLachlan's *Method.* The original formula (*cf.* [14]) expressing the spin density on an atom r within the framework of the *Hückel* approximation

$$\varrho_r = c^2_{or} - \lambda \sum_s \pi_{rs}\,\varrho^2_{os} \tag{4}$$

was used. The *McLachlan* parameter λ was given the standard value of 1.2.

Since *McConnell*'s relation between a_H and spin densities ϱ^{π}_C is well established, it appears natural to use the same values ϱ^{π}_C as a starting point for estimates of chlorine spin densities in eq. (2).

In order to obtain these estimates two fits were carried out. In fit I a simultaneous linear and nonlinear adjustment of all parameters was made, whereas for fit II α_{Cl} (h_{Cl}) and β_{Cl} (k_{Cl}) values proposed by *Streitwieser* were inserted [15]. In Table 3 sets of parameters resulting from the two fits are collected; Table 2 gives the resulting π-densities. The following comments may be made:

Table 3. McLachlan *Approach*: Optimized hetero atom and polarization parameters used for calculation of π-densities

	Q^H_{CH}	h_O	k_{CO}	h_{Cl}	k_{CCl}	λ
Fit I	−30.95	2.16	1.48	1.61	0.27	1.2
Fit II	−30.95	2.16	1.48	2.00	0.40	1.2

- set I leads to a very good prediction of proton splittings a^H for all radicals, the standard deviation being about 0.16 Gauss. For the π-densities on chlorine fit I leads to very small values. They do not exceed +0.001 even at the positions with larger chlorine splittings, *e.g.* the *para* position in 4-chlorophenoxyl. If negligible chlorine densities are to be used in eqs. (2), then these obviously reduce to (2″), unless one accepts polarisation parameters Q^{Cl}_{ClCl}, Q^{Cl}_{CCl} of the order of 1000 Gauss, which seems quite unlikely. Similar conclusions have been drawn in other work, *e.g.* by *Broze et al.* [16] and *Falle et al.* [17]. For the phenoxy radicals studied in this work, fit I leads to a value of 5.0 ± 5 Gauss for the polarization parameter Q^{Cl}_{CC}.
- fit II leads to a larger standard deviation (0.39 Gauss). In contrast to fit I, appreciable π-densities on chlorine are now obtained, which deviate less from those obtained by other methods. In Table 1 the proton couplings obtained from fit II are listed.

4.1.2. *PPP-method.* SCF calculations based on the PPP approximation were carried out for all measured phenoxy radicals. For the parametrization of C and O, the scheme proposed in [18] was applied. Parameters for Cl donating two electrons to the π-system are less certain. An estimate may be obtained according to a suggestion by *Pariser* [19] and the method outlined by *Hinze & Jaffe* [20]. The set of parameters finally used is shown in Table 4, and lies close to the set proposed by *Schug* in his paper on optimum parametrization in π-electron theory [21]. In order to avoid additional parametrization by λ, change densities (c^2_{or}) rather than spin densities were computed. As a consequence, the obtained values can approximate correctly only positions at which the actual spin densities are positive and large. Inspection of Table 2 reveals the following features for the PPP charge densities:

Table 4. *PPP Approach*: Molecular Parameters for Chlorinated Phenoxyls

	γ_{XX} (eV)	β_{CX} (eV)	IP_X (eV)	R_{CX} (Å)
X=C	11.13	−2.5	−11.16	1.40
X=O	18.60	−3.0	−33.90	1.36
X=Cl	11.40	−1.0	−23.80	1.70

– for phenoxyl, for which experimentally the sequence $|a^{H}_{para}| > |a^{H}_{ortho}| > |a^{H}_{meta}|$ has been found, the parametrization given in Table 4 leads to the same sequence for ($2p_z$) densities. The *McLachlan* approach (parametrization Table 3) also yields this sequence. However, PPP SCF calculations including configuration interaction carried out by *Hincliffe* [22] predict $|a^{H}_{para}| < |a^{H}_{ortho}|$. The same discrepancy is found in the INDO approach (*cf.* sect. 4.1.3.).

The chlorine spin densities are critically dependent on the interelectronic repulsion integral γ_{ClCl}. There is a fairly large spin density on the chlorine substituent (*e.g.* 0.05 at *para* and 0.02 at the *ortho* position). An approximate ratio $\varrho^{\pi}_{Cl}/\varrho^{\pi}_{C} \approx 1/6$ is observed at these positions. Chlorine substituents exert an influence over the whole ring. In 3-chlorophenoxyl chlorine induces spin densities of 0.076 and 0.106 at sites 2 and 6, respectively. Results from PPP calculations suggest therefore that a relation of the type eq. (2') should be used. As noted above, there exists an approximate proportionality between ϱ^{π}_{Cl} and ϱ^{π}_{C} in a $\rangle$ C–Cl fragment so that it becomes difficult to determine independently Q^{Cl}_{CC} and Q^{Cl}_{ClCl} from a regression analysis. As a consequence one is directed to relations of type (5) proposed by *Möbius et al.* [13]:

$$a^{Cl} = \bar{Q}^{Cl}_{Cl}\,\varrho^{Cl}_{\pi} = \bar{Q}^{Cl}_{CC}\,\varrho^{C}_{\pi} \qquad (5)$$

where, *e.g.* $\bar{Q}^{Cl}_{CC} = Q^{Cl}_{CC} + \mu\, Q^{Cl}_{ClCl}$ and $\mu \approx 1/6$.

One dimensional regression analysis of the data shown in Table 1 yields the results:

$$\bar{Q}^{Cl}_{ClCl} = 39.0 \pm 3.0 \text{ Gauss} \quad \text{and} \qquad (6)$$

$$\bar{Q}^{Cl}_{CC} = 6.5 \pm 0.5 \text{ Gauss}$$

Chlorine hyperfine couplings calculated according to eq. (6) are collected in Table 1. They show fairly good agreement with the experimental data. The values of the polarisation parameters themselves lie close to those proposed by *Möbius et al.* ($|Q^{Cl}_{CC}| = 4.7$ Gauss and $|Q^{Cl}_{ClCl}| = 29.0$ Gauss) on the basis of empirically determined spin densities [13].

4.1.3. *CNDO/INDO-Approach.* It has been noticed on several occasions that CNINDO spin densities for phenoxy type radicals are burdened with large systematical errors and are critically dependent on molecular parameters, *e.g.* on bond lengths [1] [4]. In particular the *ortho* spin densities are predicted larger than the *para* spin densities, in obvious contrast to what is found experimentally. Nevertheless, the over all spin density distribution is probably reproduced more accurately by CNDO/INDO than by π-electron methods.

For the phenoxy radicals studied in this work the calculated 3*s*-spin densities on chlorine turned out to be systematically too small with the parametrization of [9]. Table 5 gives a value of +0.002 for $\varrho_{Cl}(3s)$ in *p*-chloro-phenoxyl, which corresponds to a coupling constant a^{Cl} of about 0.6 Gauss when a scaling factor of 3000 Gauss is used. This value has to be compared with an experimental value of 1.7 Gauss. Since the $\varrho_{Cl}(3s)$ densities originate as a small difference between two large numbers, they are obviously very difficult to calculate. Closer inspection of the CNDO/INDO spin

Table 5. *Spin densities in the $>$C–Cl fragment of 4-chloro-phenoxyl*

spin density[c]	CNDO[a]	INDO[a][b]
$\varrho_{\mathrm{C}}(2\mathrm{p}_z)$	0.1137	0.1361
$\varrho_{\mathrm{C}}(2\mathrm{s})$	–	0.0083
$\varrho_{\mathrm{Cl}}(3\mathrm{p}_z)$	0.0094	0.0078
$\varrho_{\mathrm{Cl}}(3\mathrm{s})$	–	0.0002
$\varrho_{\mathrm{CCl}}(2\mathrm{p}_z\text{–}3\mathrm{p}_z)$	−0.0337	−0.0336
$\varrho_{\mathrm{Cl}}(3\mathrm{d}_{yz})$	0.0103	–
$-\sqrt{\varrho_{\mathrm{C}}(2\mathrm{p}_z)\,\varrho_{\mathrm{Cl}}(3\mathrm{p}_z)}$	−0.0327	−0.0326

[a] All densities before annihilation.
[b] Parametrization for chlorine according to *Hudson* [11].
[c] Numbering and coordinate systems according to Fig. 4.

density matrix elements of the $>$C–Cl fragment (*e.g.* 4-chloro-phenoxyl, *cf.* Table 5) reveals that the approximative relationship

$$-\varrho_{\mathrm{CCl}}(2\,\mathrm{p}_z^{\mathrm{C}} - 3\,\mathrm{p}_z^{\mathrm{Cl}}) = \sqrt{\varrho_{\mathrm{C}}(2\,\mathrm{p}_z)\,\varrho_{\mathrm{Cl}}(3\,\mathrm{p}_z)} \qquad (7)$$

holds fairly well in close analogy to what has been found for fluorine by *Schastnev* [2]. This fact should be taken into account if one tries to determine all three polarization constants in eq. (2). On the other hand a relation of type eq. (2) is suggested by CNDO/INDO spin density data.

There still remains the problem of the relative signs of the small Cl hyperfine couplings, *e.g.* Cl substituted in the *meta* position. Both by experimental and quantum chemical arguments the larger a^{Cl} are positive for substitution sites in which a^{H} is negative. If $a^{\mathrm{H}} > 0$ for a particular site, the corresponding a^{Cl} is small and use of eqs. of type (2) as well as predictions seem questionable.

In the application of the CNINDO approach to 4-chlorophenoxyl a $3d_{yz}$ orbital of correct symmetry centered at the chlorine nucleus may be included. Then, as shown by Table 5 one finds a $3d$ spin density $\varrho_{\mathrm{Cl}}(3d_{yz})$ of the same order of magnitude as $\varrho_{\mathrm{Cl}}(3p_z)$.

5. Conclusions. – The experimental and semiempirical quantum chemical data presented above suggest a number of conclusions concerning the reliability of relations of the type (2), (3) and (5).

1) The assumption of positive signs for large couplings a^{Cl} is supported by the fact that the line width of radicals with large $|a^{\mathrm{Cl}}|$ increases with increasing field. This phenomenon has been predicted by *Pooley & Whiffen* [23].

At present the reliable determination of the sign of small couplings a^{Cl} from ESR. solution spectra does not appear to be possible. In the light of the present work the assignment of a positive sign to the global (^{35}Cl/^{37}Cl) chlorine coupling constant of 75 mGauss in a complex heteroaromatic chlorine substituted radical which was recently carried out by *Kennedy et al.* does not seem to be completely reliable. The same critisism applies to chlorine spin densities derived from small $|a^{\mathrm{Cl}}|$'s [24].

Chlorine substituted aromatic radicals appear generally to exhibit isotropic couplings small in comparison to dipolar coupling. This, however, does not imply that Cl couplings are generally small or zero, as has been claimed in a recent paper by *Corvaja et al.* [25].

2) Qualitative prediction of a^{Cl} by INDO type calculations for large radicals seems far less successful than for small aliphatic radicals [11]. One of the reasons for the large discrepancy between experimental and INDO values goes back to a very pronounced dependence of spin densities on structural parameters [4]. Ad hoc adjustment of INDO parameters for improvenemt of predicted a^{Cl} values appears possible though not satisfactory.

3) π-Electron methods appear to allow more accurate predictions of sign and magnitude of chlorine coupling constants in aromatic radicals. In literature there exists no agreement on polarization constants for chlorine in *McConnell* or *Karplus-Fraenkel* type relation. As is shown in Table 2 π-spin densities from semiempirical π electron approaches deviate widely from each other and from CNDO/INDO values.

4) It should be pointed out that according to CNDO calculations (*cf.* Table 5), contributions to spin density from chlorine 3*d* orbitals are not negligible. This implies that equations of type (2) and (5), which rest on π-electron approaches, should be modified. A deeper insight into the nature of chlorine couplings might result from *ab initio* calculations on small chlorine substituted radicals. Also further reliable measurements of full chlorine coupling tensors appear quite desirable.

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