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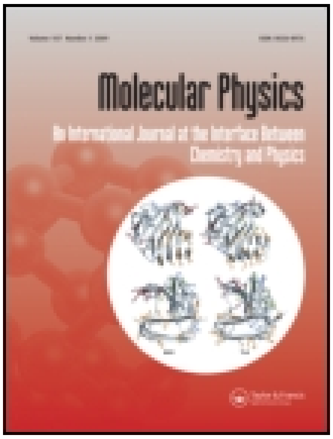

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The spin density distribution in some phenyl substituted imidazyl and pyrryl radicals

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ENDOR spectroscopy has been used to interpret the E.S.R. spectra of the 2,4,5-triphenylimidazyl, tetraphenylpyrryl, tetrakis (*p*-tolyl) pyrryl, tetrakis (*p*-anisyl) pyrryl radicals. Using the hyperfine coupling constants thus obtained in conjunction with a McLachlan-type HMO calculation the spin density distribution in these radicals is calculated. The configuration of the phenyl rings and the deviation of their bond lengths from hexagonal symmetry is inferred from the MO parameters required to fit the experimental couplings.

1. INTRODUCTION

Substituted pyrrole and imidazole molecules play an important role in many biological systems. In understanding the kinetics and mechanisms of their reactions, it would be useful to know the electronic structure of the pyrryl and imidazyl radicals often proposed as intermediates. These radicals are not stable enough in solution for detailed study by electron spin resonance but their phenyl substituted analogues are stable and have received considerable attention in the past. The tetraphenylpyrryl radical was first prepared by Kuhn and Kainer in 1953 [1] and its E.S.R. spectrum observed by Blinder *et al.* [2]. However, the spectrum was not well enough resolved to be analysed. Ueda [3] obtained a reasonably well resolved spectrum from the 2,4,5-triphenylimidazyl radical but was unable to give an unambiguous interpretation of it. Since the E.S.R. spectrum of neither radical was dominated by a large nitrogen hyperfine coupling, it was inferred that the odd electron was most likely not localized on nitrogen and the conclusion drawn that these radicals are best described as π radicals rather than σ radicals. By combining ENDOR spectroscopy with high resolution E.S.R., we have been able to interpret the E.S.R. spectra of the 2,4,5-triphenylimidazyl, tetraphenylpyrryl, tetrakis (*p*-tolyl) pyrryl and tetrakis (*p*-anisyl) pyrryl radicals. The nitrogen couplings are all small, in substantial agreement with the predictions of Hückel molecular orbital theory, so the original conclusion that these are best described as π radicals is substantiated. Careful adjustment of the molecular orbital parameters in our McLachlan type calculation [4] allow us also to infer the twist angle of several of the phenyl rings and to show that the bond lengths in these rings do not deviate substantially from hexagonal symmetry.

2. EXPERIMENTAL

The radicals were prepared by oxidizing 2,4,5-triphenylimidazole and the appropriate tetraphenylpyrrole with excess PbO_2. The pyrryl radicals are sufficiently stable that the unreacted PbO_2 and insoluble reaction products may be removed from the benzene solution of the radical by centrifuging the reaction mixture. The solutions are then degassed by the freeze-pump-thaw method. The pyrryl radicals prepared in this manner are stable for several days at room temperature. The 2,4,5-triphenylimidazyl radical can be prepared similarly but decays with a half life of a few hours [3]. Solutions left in contact with excess PbO_2 maintain a steady-state radical concentration indefinitely.

The E.S.R. and ENDOR spectra were recorded on a Varian V–4502 spectrometer modified to perform the high power CW ENDOR experiment as we have described previously [5].

3. RESULTS

Figure 1 shows the ENDOR spectrum of the 2,4,5-triphenylimidazyl radical taken at room temperature in toluene. The radical concentration is approximately 5×10^{-5} M. We were unable to obtain more concentrated solutions of the radical for the following reasons. In solution, the radical exists in equilibrium with its dimer [6] and is less than 10 per cent dissociated at room temperature. This, coupled with the limited solubility of the dimer (3×10^{-3} M in toluene), sets a limit on the maximum radical concentration at a given temperature. From measurements of the E.S.R. signal intensity as a function of temperature, we have calculated the enthalpy of dissociation of the dimer to be $6{\cdot}5 \pm 0{\cdot}5$ kcal/mole. The ENDOR spectrum shows six pairs of lines and the six proton hyperfine couplings thus obtained can readily be assigned to molecular positions by symmetry. On the basis of molecular orbital theory predictions, we expect each phenyl ring to have a spin density distribution similar to the benzyl radical, that is, $A_{\text{para}}{}^{\text{H}} > A_{\text{ortho}}{}^{\text{H}} \gg A_{\text{meta}}{}^{\text{H}}$. The six pairs of lines divide into two such sets of three with the proper coupling constant ratios and 1 : 2 : 2 intensity ratios. The more weakly coupled set is twice as intense as the stronger one so it is assigned to the two equivalent rings. These lines are slightly broader than those from the single ring which may indicate a small time-dependent variation in the couplings. As will be shown below these rings are twisted with respect to the plane of the imidazole ring and any variation in the twist angle would strongly effect the coupling constants. The coupling constants, converted to gauss, are given in table 1.

No effect of nitrogen hyperfine coupling is expected or observed in the ENDOR spectrum but the 1 : 2 : 3 : 2 : 1 pattern expected for two equivalent ^{14}N nuclei is easily seen in the E.S.R. spectrum with a hyperfine coupling of $0{\cdot}080 \pm 0{\cdot}005$ gauss. Figure 2 shows the experimental E.S.R. spectrum and one computed using the coupling constants given in table 1.

The resolution of the E.S.R. spectrum is strikingly solvent dependent. In benzene the nitrogen quintet is symmetrical and well resolved. The lines are best simulated with a 60 mG peak to peak gaussian-shaped line which probably indicates

Position	$A_{\text{ortho}}{}^{\text{H}}$	$A_{\text{meta}}{}^{\text{H}}$	$A_{\text{para}}{}^{\text{H}}$	A^{N}
Unique phenyl ring	2·285	0·780	2·660	—
Two equivalent rings	1·290	0·582	1·440	—
Two equivalent nitrogens	—	—	—	0·080

Table 1. The hyperfine coupling constants of the 2,4,5-triphenylimidazyl radical in gauss.

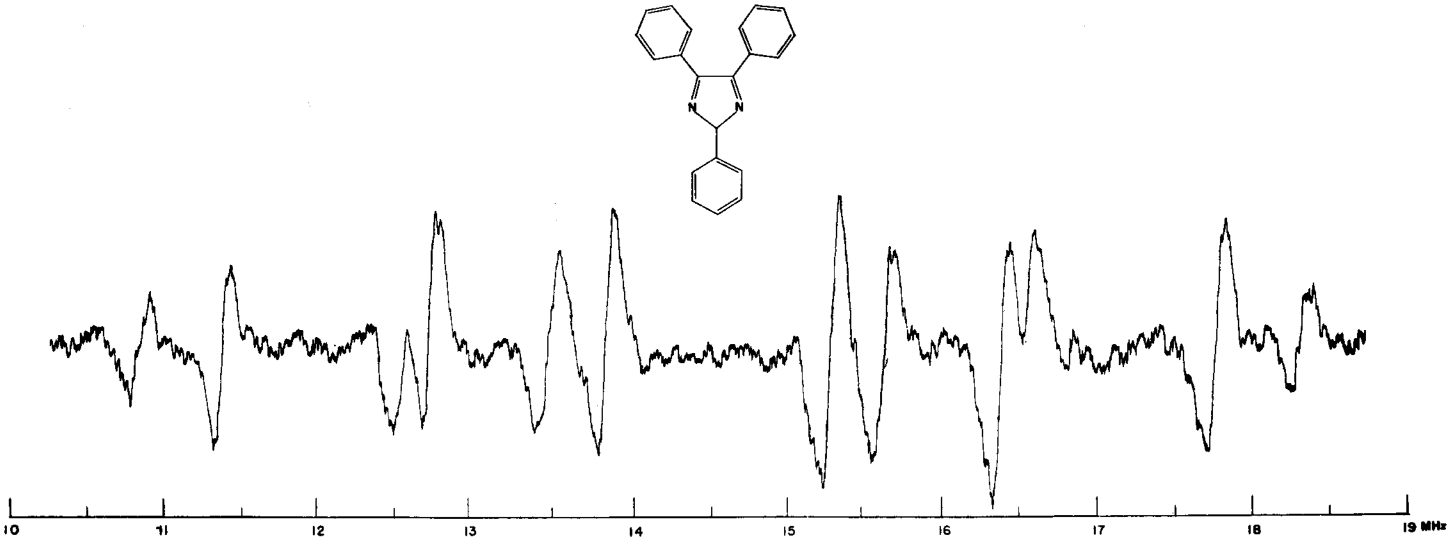

Figure 1. The ENDOR spectrum of the 2,4,5-triphenylimidazyl radical.

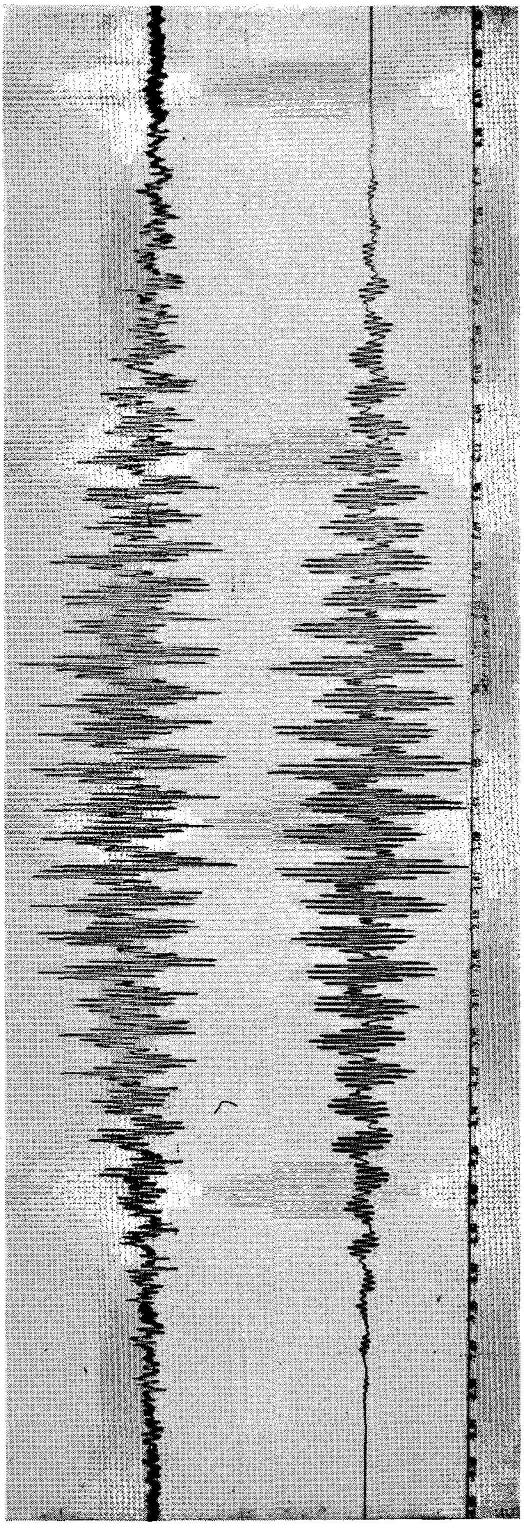

Figure 2. The experimental (upper) and computer simulated (lower) E.S.R. spectra of the 2,4,5-triphenylimidazyl radical.

that magnetic field inhomogeneity is limiting our linewidth. In xylene, on the other hand, the quintets are asymmetric and poorly resolved. Apparently, the molecule is so large that minor changes in solvent viscosity strongly affect the extent to which the hyperfine coupling anisotropies are averaged out.

The pyrryl radicals also form diamagnetic dimers in aromatic solvents but the solubilities and equilibrium constants are such that 10^{-3} M solutions of the radicals can be obtained. Room temperature ENDOR spectra for the tetraphenylpyrryl, tetrakis (*p*-tolyl) pyrryl and tetrakis (*p*-anisyl) pyrryl radicals dissolved in xylene are given in figure 3. The intensity of the spectra remain approximately constant between 25°C and −50°C because the increase in ENDOR intensity on cooling is just matched by the decrease in the E.S.R. signal due to radical dimerization. The ENDOR spectra are not sufficiently well resolved to obtain all the proton coupling constants directly but with the aid of the ENDOR coupling constants the E.S.R. spectrum of the tetraphenylpyrryl radical is readily interpreted. The three largest couplings in the ENDOR spectrum have the correct magnitude and intensity ratios to form a benzyl-like *ortho*, *meta*, *para* set of couplings from two equivalent rings. Hückel molecular orbital theory predicts much larger couplings for the two rings adjacent to the nitrogen so we have assigned these three couplings to these positions. There is no coupling in the E.S.R. spectrum corresponding to the strong 0·150 G central doublet in the ENDOR spectrum. However, the fine structure in the E.S.R. spectrum can be simulated by six equivalent 0·210 G couplings and four equivalent 0·085 G couplings which gives an average coupling close to the number

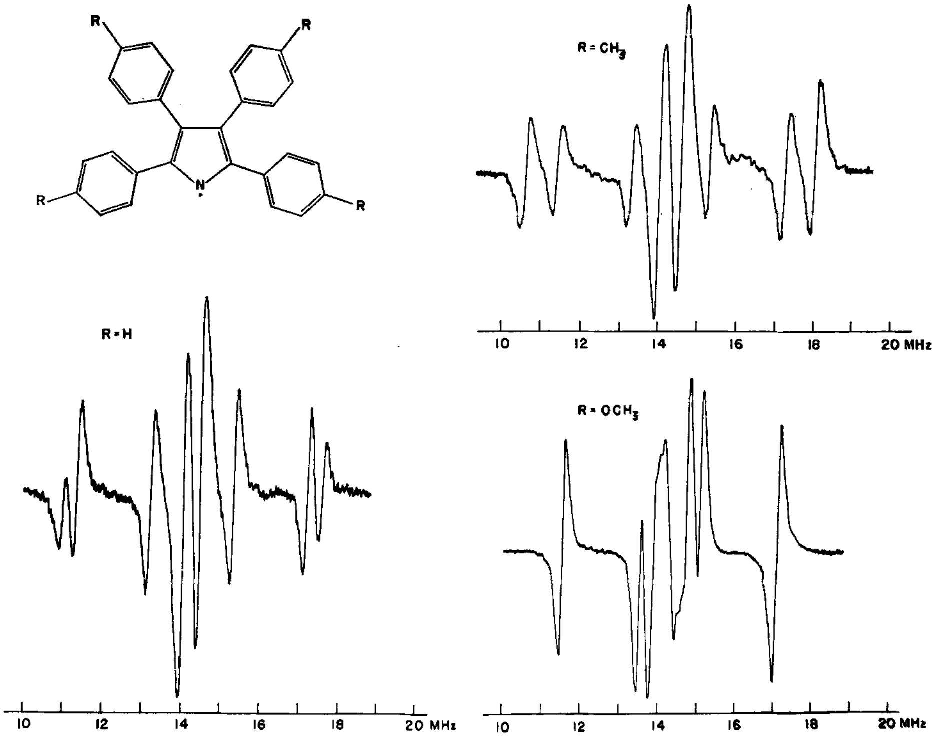

Figure 3. The ENDOR spectra of some substituted tetraphenylpyrryl radicals.

obtained by ENDOR. Again, assuming a benzyl-like spin density distribution, we assign the larger coupling to the *ortho* and *para* protons on the rings distant from the nitrogen and the remaining coupling to the *meta* protons. As with the imidazyl radical, once the proton couplings are assigned, the nitrogen hyperfine coupling is easily determined by simulating the entire E.S.R. spectrum. The coupling constants thus obtained are given in table 2.

Molecule	$A_{\text{ortho}}^{\text{H}}$	$A_{\text{meta}}^{\text{H}}$	$A_{\text{para}}^{\text{H}}$	$A_{\text{other}}^{\text{H}}$	A^{N}
Tetraphenylpyrryl	2·105	0·760	2·370	0·085, 0·210	1·905
Tetrakis (*p*-tolyl) pyrryl	2·075	0·715	2·645†	0·20‡	—
Tetrakis (*p*-anisyl) pyrryl	1·990	0·600	0·315§	0·100§	—

† Methyl proton coupling.

‡ Average coupling of all protons on distal ring.

§ The vicinal ring methoxy and all distal ring protons are not resolved but apparently fall into two groups with the couplings given. No assignment is implied by their position in the table.

Table 2. The hyperfine coupling constants of the tetraphenylpyrryl radicals in gauss.

The E.S.R. spectra of the tetrakis (*p*-tolyl) pyrryl and tetrakis (*p*-anisyl) pyrryl radicals are so complex (~ 10^5 lines predicted) and featureless that we are unable to distinguish between the various possible assignments for the small couplings and have thus been unable to determine the nitrogen splitting. The large couplings are assigned to molecular positions by analogy with the unsubstituted radical and are given in table 2.

4. Discussion

One of the principal reasons for undertaking this study was to obtain the spin density distribution in the imidazyl and pyrryl portions of the molecules studied. Since these rings have no protons, the odd electron density cannot be calculated directly from the hyperfine splitting constants, but must be obtained from a molecular orbital calculation. The accuracy of such calculation to be judged by how well it fits the proton hyperfine splitting of the phenyl substituents. Neutral radicals related to the benzyl radical are notoriously hard to calculate [7] and until recently even INDO calculations were unable to predict the correct *ortho* : *para* coupling constant ratio. The success of the current INDO calculations is achieved by allowing the bond lengths of the carbon–carbon bonds in the benzyl radical to deviate substantially from the normal average aromatic bond [8, 9]. Since the crystal structures of these radicals are not known it is necessary to obtain the required bond lengths by calculation. For the benzyl radical, these can be obtained by an iterative π-electron calculation using first-order bond fixation [8], but for the larger molecules in this study, it would be prohibitively expensive. In 1967, Schastnev and Zhidomirov [10] showed that essentially the same geometry calculated for the benzyl radical by Benson and Hudson [8] could be obtained from a McLachlan-type Hückel molecular orbital calculation [4]. By assuming relations between the resonance integral β_{rs} and the bond length and between the calculated π-bond order and bond length they were able to obtain a self-consistent set of resonance integrals, bond orders and bond lengths. Using this set of resonance integrals to predict the π-electron spin density gave much improved agreement with the experimental hyperfine splitting constants. In an effort to provide an accurate but feasible calculation of the π-electron spin density in our molecules, we have adopted a method similar to that just described [10], but which chooses the values for the resonance integrals in a much simpler way which we will illustrate first with the benzyl radical.

4.1. *Molecular orbital calculation*

If one assumes that all the carbon coulomb integrals in a simple Hückel molecular orbital calculation of the benzyl radical are equal, then the following relations between the π-electron spin densities and resonance integrals can be factored directly from the Hückel matrix with no approximations. The numbering scheme for the benzyl radical is given in figure 4:

$$\frac{\rho_4}{\rho_2}=\left(\frac{\beta_{23}}{\beta_{34}}\right)^2, \quad \frac{\rho_2}{\rho_7}=\frac{1}{4}\left(\frac{\beta_{17}}{\beta_{16}}\right)^2.$$

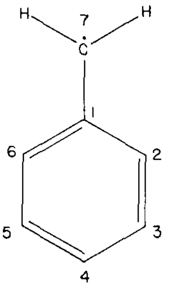

Figure 4. Numbering scheme for the benzyl radical.

Then, assuming a single McConnell relation is valid for all positions in the molecule, the resonance integral ratios can be calculated directly from the experimental hyperfine splitting constants. For simplicity, we have assumed the β_{34} and $\beta_{16}=1$, thus the coupling constant ratios give β_{23} and β_{17} directly. This choice does not effect the results of the HMO calculation of spin density, but leads to incorrect values for π-bond orders and bond lengths if they are used directly instead of as the ratios they now actually represent. Using these HMO obtained values of β_{17} and β_{23} as a starting point, we have varied β_{17}, β_{23}, λ, and Q in a McLachlan-type HMO calculation to fit the experimental hyperfine coupling constants of the benzyl radical [7] exactly. The final parameters used are given in table 3.

The value of Q obtained is well within the limits of the current best estimates for this parameter [11] and the value of λ is sufficiently close to the 1·0 originally used by McLachlan [4] that we feel justified in assuming the values of the β's obtained are meaningful and represent significant deviations of the carbon bond lengths from the average aromatic bond length normally assumed. Because of our initial assumption that $\beta_{16}=1$, the value for $\beta_{17}-1$ represents the combined deviations of these two parameters and is thus proportional to the difference in bond length R_{17}–R_{16} where R_{rs} is the length of the carbon r–carbon s bond in ångströms. In the limit of small deviations, the relation between β_{rs} and R_{rs} assumed by Schastnev and Zhidomirov [10] becomes $dR_{rs}/d\beta_{rs}=-\frac{1}{4}$. Using this relation, we can then calculate the bond

Radical	β_{17}	β_{23}	λ
Benzyl†	1·185	1·125	0·93
Trityl	0·850	1·075	1·45
Triphenylimidazyl			
Unique ring	1·165	0·990	1·27
Two equivalent rings	0·790	0·970	1·5
Tetraphenylpyrryl			
Vicinal rings	0·935	0·980	1·34
Distal rings	0·460	—	—

† $Q_{CH}{}^{H} = -26\cdot87$.

Table 3. Molecular orbital parameters required to match the experimental hyperfine couplings.

length differences predicted by McLachlan–HMO theory from E.S.R. data. For R_{17}–R_{16} we find $-0\cdot046$ Å and for R_{23}–R_{34}, $-0\cdot031$. These are to be compared to the values of $-0\cdot057$ and $-0\cdot014$ found by Benson and Hudson [8] and those of Shastnev and Zhidomerov [10], $-0\cdot039$ and $-0\cdot020$, using their SCMO method, since no crystal structure exists.

Encouraged by the apparent reasonableness of the results obtained, we have tested the method on one more radical, the trityl radical, where a crystal structure of the trityl cation does exist [12]. Because the extra electron in the radical is in a non-bonding orbital, the structure of the radical is expected to be similar to that of the carbonium ion [8]. There are only three hyperfine splittings in the trityl radical so the four-parameter fit described above cannot be made uniquely. We have, therefore, assumed $Q_{CH}{}^{H} = -26\cdot87$ throughout the rest of the calculations. Using β_{17}, β_{23} and λ as our variables, we can fit the experimental hyperfine couplings exactly and the final parameters are given in table 3. Computing the bond length differences as before, we obtain $R_{17}-R_{16} = 0\cdot038$ and $R_{23}-R_{34} = -0\cdot019$. The X-ray data [12] gives $R_{17}-R_{16} = 0\cdot046 \pm 0\cdot02$ and $R_{23}-R_{34} = -0\cdot008 \pm 0\cdot03$. The errors given are for the bond lengths themselves so the differences are perhaps more accurate than that. Thus, it appears the calculation described gives bond length differences well within experimental error and we will use it to estimate the geometries of the heterocyclic radicals in this work. The value of λ of 1·45 for the trityl radical calculation is well outside the usual range of 1·0 to 1·2 for this parameter and deserves some further comment. Since the *meta* carbon lies at a node in the π-molecular orbital containing the odd electron in the HMO approximation, the value of λ is directly proportional to the coupling constant observed for the meta proton. It appears the meta proton coupling in this radical is anomalously large, at least when compared with typical π-election calculations of its value and thus our large value of λ. Using their INDO method, Pople and Beveridge [13] have calculated the effect on the proton hyperfine couplings in the benzyl radical of twisting the phenyl ring with respect to the methylene group. Contrary to previous π-molecular orbital calculations, they predict an essentially constant, positive coupling constant for the *meta* proton while the negative *ortho* and *para* couplings decrease sharply in magnitude as the twist angle increases. The constancy of the *meta* coupling apparently arises because of delocalization of methylene π-electron density into the σ system of the phenyl ring as the twist angle increases [13]. This prediction that the magnitude of the *meta* coupling would exceed that of the *ortho* and *para* positions in severely twisted systems has been verified recently for the rubrene radical [14]. Thus, we believe our anomalously large value of λ is an artifact of our π electron only calculation and indicates that the assumption of complete σ–π separation is no longer strictly valid for aromatic systems twisted as little as the 30° typically calculated for the trityl radical [15].

4.2. *Configuration of the imidazyl and pyrryl radicals*

Table 3 also shows the MO parameters required to fit the experimental hyperfine couplings in the triphenylimidazyl and tetraphenylpyrryl radicals. By analogy with the results for the benzyl and trityl radicals we can infer the geometries of these radicals. The unique ring in the triphenylimidazyl radical has a value of β_{17}, which is, within the precision of this calculation, the same as that for the benzyl radical. This, coupled with the absence of any steric hindrance leads us to conclude that the phenyl and imidazyl rings are coplanar. For the two equivalent rings, on the other hand, we find $\beta_{17} = 0{\cdot}790$ which is similar to that found for the trityl radical. Thus, these rings are probably twisted with respect to the imidazyl ring by an amount similar to the 30° often calculated for the trityl radical [15]. The most striking feature of this calculation is that the experimental splittings cannot be fitted with a single value of λ. The larger value of λ required for the twisted rings is consistent with the difference found in λ for benzyl and trityl and confirms our hypothesis that for otherwise similar systems the appropriate value of λ is proportional to the ring twist and indicates the extent to which the odd electron is delocalized into the σ framework of the molecule.

The approximate geometry of the tetraphenylpyrryl radical can be calculated in a similar way. Models indicate that the two equivalent phenyl rings distant from the nitrogen must be sharply twisted ($>45°$) with respect to the pyrryl ring and this is confirmed by the small value of 0·46 for β_{17}. Assuming $\beta = \beta_0 \cos\theta$ gives a twist angle of 62°. This value is not expected to be very precise because the low value of β_{17} arises from a combination of twisting and stretching of this bond. The data are not sufficiently accurate to permit calculation of λ for these rings, but we expect it would be substantially greater than 1·5. The two equivalent rings adjacent to the nitrogen have an intermediate value of β_{17}, greater than the 0·850 value found for trityl, but less than the value of 1·185 found for benzyl, so they are probably slightly twisted (10°–20°) with respect to the pyrryl ring. Again assuming $\beta = \beta_0 \cos\theta$, the calculated twist angle is 20°.

4.3. *Heterocyclic ring spin densities*

After all the phenyl ring parameters have been optimized, within the limits of the McConnell relation, the McLachlan type–HMO calculation should give a reasonably accurate description of the odd electron density in the heterocyclic rings. Our calculated spin densities are shown in figure 5. The qualitative correctness of the distribution given is confirmed by the chemical reactivity of the various positions. Peroxide additions occur at the 2 position in tetraphenylpyrryl radical rather than 1 or 3 [16] and at the 4 position in 2,4,5-triphenylimidazyl rather than 1 or 2 [17] in agreement with the positions predicted to have the highest unpaired spin density. Great care must be exercised when applying the spin density distributions calculated above to biological systems such as porphyrins and histidines to ensure that the systems are in the same oxidation state. Our pyrrole ring is nearly fully conjugated

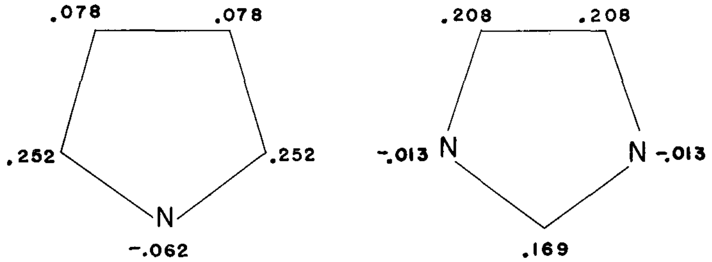

Figure 5. Unpaired spin densities on the heterocyclic rings in phenyl substituted imidazyl and pyrryl radicals.

to the phenyl π system at the 2,5 position but not at the 3,4 position and the imidazole ring is fully conjugated with the phenyl π system at the 2 position but only slightly so at the 4,5 position.

While the remarkably good fit to the proton hyperfine couplings by the π-electron MO calculation and the small values the nitrogen hyperfine couplings obtain make it clear that these molecules are best considered as fully delocalized π radicals rather than σ radicals with the odd electron localized on nitrogen, the McLachlan–HMO procedure used here should not be expected to give good values for the nitrogen π electron spin density. The pyrrole nitrogen lies at a node in HMO containing the odd electron and the imidazole–HMO nitrogen spin density is $< 0{\cdot}025$, so the magnitude of the spin densities calculated reflect almost directly the magnitude of the McLachlan correction with its uncertain value of λ and limited applicability to heteroatoms.

The nitrogen π-electron spin density can be calculated from the experimental nitrogen hyperfine coupling if the σ–π interaction parameters (Q's) and the adjacent carbon spin densities are known. The σ–π parameters calculated for heterocyclic nitrogen couplings vary substantially from one molecule to another and from one author to another [18] so this method is also necessarily approximate. A substantial part of the variation in predicted coupling constants between authors can be removed if the method used to calculate the spin densities in the unknown molecule is the same one used by the worker who originally determined the σ–π parameters quite independent of the absolute accuracy of this calculation. For example, we find the same predicted coupling constants from the equation

$$A^{\mathrm{N}} = Q_{\mathrm{N}}^{\mathrm{N}} \rho_{\mathrm{N}} + \sum_i Q_{\mathrm{C}}^{\mathrm{N}} \rho_{\mathrm{C}_i}$$

by using $Q_{\mathrm{N}}^{\mathrm{N}} = 29$ and $Q_{\mathrm{C}}^{\mathrm{N}} = -4{\cdot}3$ and pure HMO spin densities following Yonezawa *et al.* [18] or by using $Q_{\mathrm{N}}^{\mathrm{N}} = 23$ and $Q_{\mathrm{C}}^{\mathrm{N}} = -2{\cdot}0$ and our McLachlan–HMO spin densities following the calculations of Cottrell and Rieger [19]. Using the Cottrell and Rieger parameters, our McLachlan–HMO spin densities for the carbon atoms adjacent to the nitrogen, and the experimental coupling constants which are assumed to be negative; we calculate the nitrogen π-electron spin density in the tetraphenylpyrryl radical to be $-0{\cdot}039$, in reasonable agreement with the value given in figure 5. Similarly, we find a value of $+0{\cdot}029$ for each of the nitrogens in the 2,4,5-triphenylimidazyl radical which differs both in sign and magnitude from our M.O. calculation. On an absolute scale, this discrepancy is not significant but does serve to illustrate once again the unreliable nature of the HMO method for determining the signs and magnitudes of small spin densities.

4.4. *Substituent effects*

The data on the substituted tetraphenylpyrryl radicals give substantially the same geometry for these radicals as the unsubstituted one and we believe the small differences in *ortho* hyperfine couplings, for instance, can be interpreted solely on the basis of substituent effects on the spin density distribution.

Walter [20] has divided free radicals into two classes based on the direction of the substituent effect with respect to the sign of the Hammet σ value for the substituent. In Walter's class S all the substituent effects are in the same direction regardless of the sign of σ, and in class O the shifts correlate with the sign of σ. Walter has presented a correlation between the class of substituent effect and the possible Lewis structures which can be written for the free radical [20]. It is readily shown [21] that the structures for the phenyl rings in the tetraphenylpyrryl and triphenylimidazyl radicals are identical to those in the trityl radical, so we expected the substituent effects to be the same also. Table 4 shows that while the magnitude of the change in the *ortho* coupling is similar, the changes are in opposite directions for the trityl and tetraphenylpyrryl radicals.

Substituent	Trityl $A_{\mathrm{ortho}}{}^{\mathrm{H}}$	Pyrryl $A_{\mathrm{ortho}}{}^{\mathrm{H}}$
$-\mathrm{H}$	2·61†	2·11
$-\mathrm{CH_3}$	2·62‡	2·08
$-\mathrm{OCH_3}$	2·89§	1·99
$-\mathrm{Cl}$	2·64§	—
$-\mathrm{F}$	2·68‖	—

† Reference [15].
‡ Reference [22].
§ Reference [23].
‖ Reference [24].

Table 4. The effect of substituents on A^{H} ortho.

The trityl radical is in Walter's class S, that is, all substituents produce larger couplings at the ortho position than for the unsubstituted radical. This type of result is readily derived from HMO theory. Since the odd election is in a non-bonding orbital, substituents cause this orbital to become bonding or antibonding, depending on the sign of their Hammett σ value, but because of the orbital pairing theorem, any change in the eigenvalue for the orbital containing the unpaired electron changes the spin density the same direction. For the purposes of orbital symmetry, the tetraphenylpyrryl radical can be considered as a substituted cyclopentadiene radical where the orbital of the unpaired electron is strictly bonding. Thus, substituents may raise or lower the eigenvalue of the half-filled orbital, but it will remain bonding. Our calculations show that the value of the ortho coupling constant is directly proportional to the value of the coulomb integral α used for the *para* carbon atom. Negative values of α decrease the coupling and positive ones increase it. Since our substituents correspond to negative α's, HMO theory predicts the correct sign of the substituent effect, and we fully expect that if an electron withdrawing substituent were available, it would cause an increase in the *ortho* coupling constant, causing our radicals to fall into Walter's class O. In conclusion then, we believe that a more reliable division of radicals into classes S and O can be obtained from orbital symmetry considerations rather than by the valence bond method which appears to fail for the tetraphenylpyrryl radical, though this result currently lacks experimental confirmation.

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