*J. Org. Chem.* 1988, *53*, 1267–1273 1267

# Inert Carbon Free Radicals. 9. The First Perchlorinated Triarylmethyl and Fluorenyl Radicals with a Heteroaromatic Ring, and Related Compounds

L. Juliá,* M. Ballester,* J. Riera,* J. Castañer, J. L. Ortin, and C. Onrubia

*Departamento de Materiales Orgánicos Halogenados, Centro de Investigación y Desarrollo (CSIC), Jorge Girona Salgado 18-26, 08034 Barcelona, Spain*

*Received December 9, 1986*

Perchlorodiphenyl(4-pyridyl)methyl (**13**), perchlorodiphenyl(2-pyridyl)methyl (**14**), and perchloro-9-(4-pyridyl)fluorenyl (**15**) radicals, the first inert carbon free radicals with a heteroaromatic ring, have been synthesized from $\alpha H$-tetradecachlorodiphenyl(4-pyridyl)methane (**3**), $\alpha H$-tetradecachlorodiphenyl(2-pyridyl)methane (**7**), and 9*H*-dodecachloro-9-(4-pyridyl)fluorene (**12**), respectively. The thermal and chemical stabilities of these radicals have been studied. The thermolysis of radical **13** gives a mixture of radical **15** and perchloro-3-aza-9-phenylfluorenyl radical (**16**). The oxidative hydrolysis of radicals **13** and **15** with oleum yields perchloro-4-(phenyl(4-pyridyl)methylene)cyclohexa-2,5-dienone (**17**) and perchloro-9-(4-pyridyl)fluoren-3-one (**18**), respectively. While the oxidation of radical **14** with concentrated $HNO_3$ affords perchloro-2-(diphenylmethylene)pyridin-5(2*H*)-one (**19**), with concentrated $H_2SO_4$ it gives a mixture of perchloro-9-phenylindeno[2,1-*b*]pyridin-3-one (**22**) and perchloro-10-phenylpyrido[1,2-*a*]indole (**9**), a cyclization product that is also obtained in the thermolysis of radical **14** or $\alpha$H compound **7**. The ESR, IR, and UV–vis spectra of the radicals and other compounds here synthesized are reported and studied. The variation of the magnetic susceptibility of those radicals with temperature has been measured, giving purities nearly 100%.

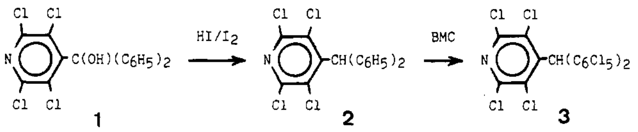
For several years, we have been engaged in the synthesis and study of the so-called "inert carbon free radicals" (IFR).[1] Typical of these radicals are perchlorotriphenylmethyl (PTM)[1a] and perchloro-9-phenylfluorenyl (PPF).[1e] Such radicals owe their exceptional chemical inertness and thermal stability to steric shielding of their molecular backbone—particularly the trivalent carbon where the highest spin density resides—by the bulky chlorine substituents. Replacement of *p*-chlorine atoms in PTM by chemically active substituents affords radicals which usually react at the substituents without impairment of the radical character.[1b–d,h]

Most significant work has been done with nitroxide (aminyloxide) radicals as spin labels.[2] The ESR spectra of the spin-labeled substrates display well-resolved 1:1:1 triplets due to coupling with $^{14}N$ nuclear spin which, as intended, are sensitive to structural changes in the substrate. Work on spin-labeling with functionalized IFRs has been published.[1d] However, they display in the ESR either a single line or unsatisfactory resolved multiplets. Consequently, it was decided to explore the synthesis and, eventually, to investigate the properties and applications of a new subclass of free radicals with a perchloropyridyl ring attached to the trivalent carbon.

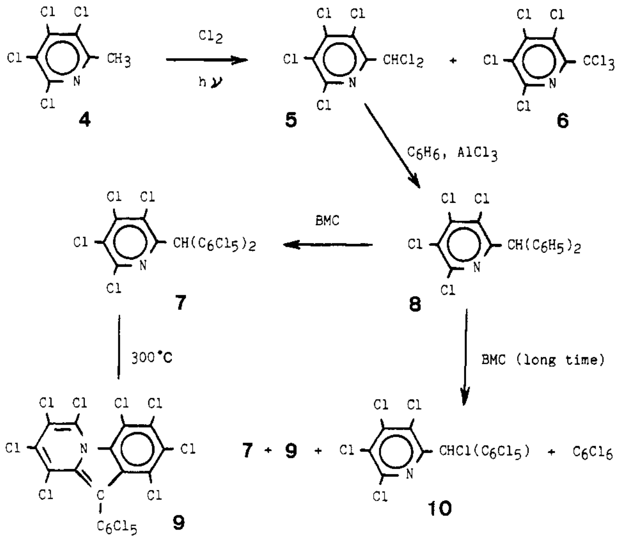
## Results and Discussion

**Synthesis of Precursors. 1. $\alpha H$-Tetradecachlorodiphenyl(4-pyridyl)methane (3).** Diphenyl(tetrachloro-4-pyridyl)methanol[3] (**1**) is reduced with $HI/I_2$ in refluxing aqueous hexane affording diphenyl(tetrachloro-4-pyridyl)methane (**2**), which is chlorinated with reagent BMC ($SO_2Cl_2$, $AlCl_3$, $S_2Cl_2$)[4] to methane **3** (Scheme I).

**Scheme I**



**Scheme II**



**2. $\alpha H$-Tetradecachlorodiphenyl(2-pyridyl)methane (7).** The photochlorination of 3,4,5,6-tetrachloro-2-methylpyridine[5] (**4**) yields a mixture of tetrachloro-2-(trichloromethyl)pyridine (**6**) and tetrachloro-2-(dichloromethyl)pyridine (**5**). The Friedel–Crafts condensation of the latter with benzene gives diphenyl(tetrachloro-2-pyridyl)methane (**8**), which is finally perchlorinated with reagent BMC[4] to methane **7**. The latter reaction, with

---

(1) (a) Ballester, M.; Riera, J.; Castañer, J.; Badia, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215. (b) Ballester, M.; Castañer, J.; Riera, J.; Ibáñez, A.; Pujadas, J. *J. Org. Chem.* **1982**, *47*, 259. (c) Ballester, M.; Riera, J.; Castañer, J.; Rodriguez, A.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1982**, *47*, 4498. (d) Ballester, M.; Riera, J.; Castañer, J.; Rovira, C.; Veciana, J.; Onrubia, C. *J. Org. Chem.* **1983**, *48*, 3716. (e) Ballester, M.; Castañer, J. *Riera*, J.; Pujadas, J.; Armet, O.; Onrubia, C.; Rio, J. A. *J. Org. Chem.* **1984**, *49*, 770. (f) Ballester, M.; Castañer, J.; Riera, J.; Pujadas, J. *J. Org. Chem.* **1984**, *49*, 2884. (g) Ballester, M.; Veciana, J.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *J. Org. Chem.* **1986**, *51*, 2472.

(2) Nelsen, S. F. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 550.

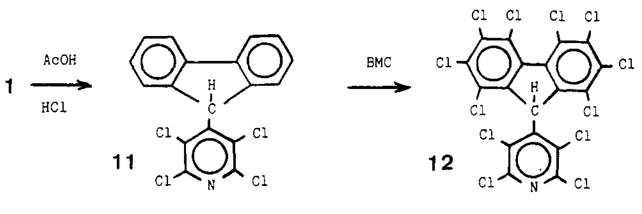
(3) Edmondson, A. E.; Jukes, A. E.; Gilman, H. J. *J. Organomet. Chem.* **1970**, *25*, 273.

(4) Ballester, M.; Molinet, C.; Castañer, J. *J. Am. Chem. Soc.* **1960**, *82*, 4254. Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; p 1131.

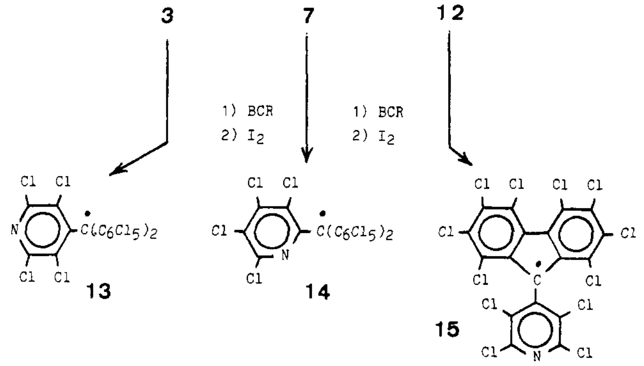
(5) Binss, F.; Suschitzky, H. *J. Chem. Soc. C* **1971**, 1226.

0022-3263/88/1953-1267$01.50/0 © 1988 American Chemical Society

**Scheme III**



**Scheme IV**



increasing reaction times (hours), affords lower yields of 7, along with rather small amounts of perchloro-10-phenylpyrido[1,2-*a*]indole (9), *αH*-decachlorophenyl(2-pyridyl)methane (10), and perchlorobenzene. Indole 9 can be obtained in high yield by heating methane 7 at 300 °C (Scheme II). Its formation is assumed to occur by nucleophilic attack of the nitrogen atom on one ortho carbon of the pentachlorophenyl rings, followed by HCl elimination. Similar cyclizations, such as that of 2-benzylpyridine to pyrido[1,2-*a*]indole by heating at 650 °C, are already known.[6]

**3. 9*H*-Dodecachloro-9-(4-pyridyl)fluorene (12).** Walton et al.[7] reported that (pentafluorophenyl)diphenylmethanol in refluxing formic acid gives the expected triphenylmethane together with a major proportion of 9-(pentafluorophenyl)fluorene. Both products are presumably formed through (pentafluorophenyl)diphenylcarbenium ion, which undergoes simultaneously both a hydride transfer from formate ion to the former and an intramolecular electrophilic cyclization to the latter. Consequently, it was decided to test the cyclization of methanol 1 to 9-(tetrachloro-4-pyridyl)fluorene (11), under carbenium ion formation conditions but in the absence of formic acid, i.e., a mixture of acetic acid and concentrated aqueous HCl. Accordingly, fluorene 11 was obtained as the sole product and in a high yield. Aromatic perchlorination of 11 with reagent BMC[4] affords the desired fluorene 12 (Scheme III).

**Synthesis of the Radicals.** Triarylmethanes 3 and 7, as well as fluorene 12, are converted into the radicals perchlorodiphenyl(4-pyridyl)methyl[8] (13), perchlorodiphenyl(2-pyridyl)methyl (14), and perchloro-9-(4-pyridyl)fluorenyl[8] (15), respectively, by the conventional two-step process used for the radicals of the PTM series,[1a] i.e., treatment of the substrates with reagent BCR[10] (NaOH–$Me_2SO$–ethyl ether) to give red solutions of the corresponding carbanions, and oxidation of these anions to the radicals with $I_2$ (Scheme IV).

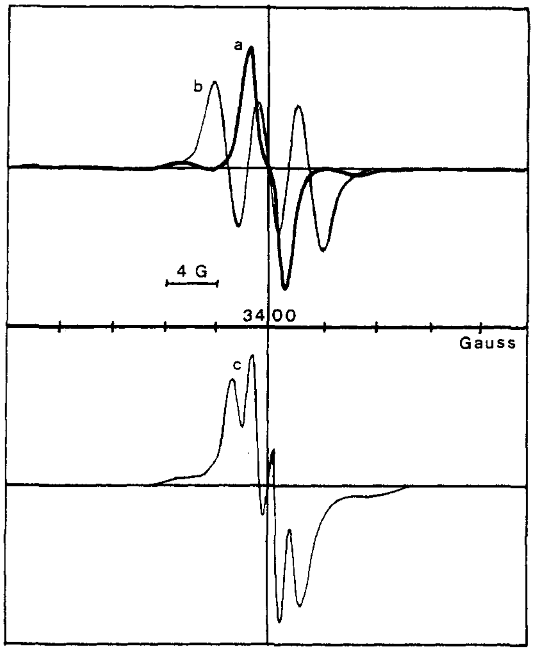


**Figure 1.** ESR spectra of (a) radical 13 in dioxane, (b) radical 14 in dioxane, and (c) radical 13 in $H_2SO_4$.

**Table I. Chemical Stabilities of the Radicals at Room Temperature**

| radical | reagent | solvent | rctn time, days | recovery,[a] % |
|---|---|---|---|---|
| 13 | $O_2$ (air) | $C_6H_{12}$ | 4 | 100 |
| 14 | | | | 100 |
| 15 | | | | 100 |
| 13 | hydroquinone | $CCl_4$ | 5 | 96 |
| 14 | | | | 100 |
| 15 | | | | 88 |
| 13 | $Cl_2$ | $CCl_4$ | 2.7 | 100 |
| 14 | | | 3 | 98 |
| 15 | | | 2.7 | 52 |
| 13 | $Br_2$ | $CCl_4$ | 3 | 93 |
| 14 | | | | 88 |
| 15 | | | | 73 |
| 13 | concd $H_2SO_4$ | - | 2 | 99 |
| 14 | | | | 0[b] |
| 15 | | | | 65 |
| 13 | concd $HNO_3$ | - | 2 | 92 |
| 14 | | | | 0[b] |
| 15 | | | | 90 |

[a] The recovered radicals have been identified by IR spectrum. The recoveries have been ascertained by combining weight and absorptivity of bands at 560, 574, and 625 nm for radicals 13, 14, and 15, respectively. Taking into account the size of the samples (~0.05 g), a loss of at least 1–5% should be allowed for product isolation and handling. [b] The absence of radical 14 in the residue has been ascertained by ESR spectroscopy and TLC analysis.

**Table II. Recoveries[a] (%) of the Radicals after 1 h of Heating in the Air**

| radical | 200 °C | 250 °C | 300 °C |
|---|---|---|---|
| 13 | 100 | 100 | traces |
| 14 | 100 | 0[b] | |
| 15 | 100 | 99 | 76 |

[a] See footnote *a* in Table I. [b] See footnote *b* in Table I.

**Chemical and Thermal Stabilities of the Radicals.** The chemical stabilities of the radicals 13–15 toward a variety of chemical agents have been tested (Table I). In most cases, their stabilities are similar to those of radicals

---

[6] Soldatenkov, A. T.; Bogdali, M. V.; Radzham, P. K.; Brindkha, O. S.; Edogiaverie, S. L.; Fomichev, A. A.; Prostakov, N. S. *Zh. Org. Khim.* **1983**, *19*(6), 1326.

[7] Andrews, A. F.; Mackie, R. K.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1980**, 96.

[8] A short notice on it has been advanced.[9]

[9] Juliá, L.; Riera, J.; Castañer, J. *An. Quim., Ser. C* **1985**, *81*, 188.

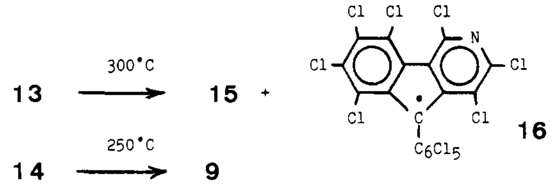
[10] Ballester, M.; Olivella, S. In *Polychloroaromatic Compounds*; Suschitzky, H., Ed.; Plenum: London, 1974; p 127.

Table III. ESR Spectral Data of the Radicals

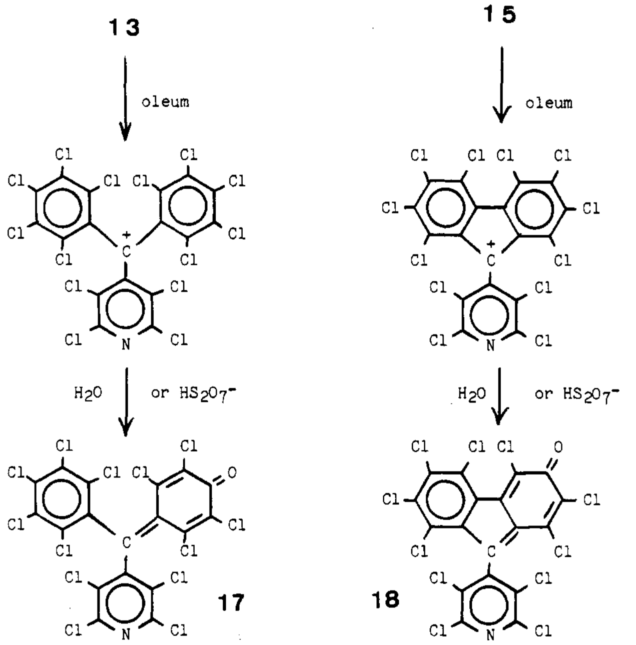
| | | | | | splittings (gauss) | | | |
|---|---|---|---|---|---|---|---|---|
| radical | solvent | $g$ value | no. of lines | line width (gauss) | N | H | $\alpha$-$^{13}$C | arom $^{13}$C |
| 13 | dioxane | 2.0028 | 1[a] | 1.21[b] | 0.96[b] | | 29.6 | 12.9, 10.4 |
| | $H_2SO_4$ | 2.0023 | 4[a] | 1.14[b] | 1.36[b] | 1.43[b] | 29.5 | 11.8, 9.5 |
| 14 | dioxane | 2.0032 | 3[a] | 1.21[b] | 3.21 | | 27.8 | 12.4, 10.0 |
| 15 | dioxane | 2.0037 | 1 | 4.00 | | | 18.7[b] | |
| 16 | dioxane | 2.0038 | 1 | 4.78 | | | 19.3[c] | |

[a] Distorted lines. [b] Found by computer simulation. [c] Shoulder of the main line.

Scheme V



Scheme VI



PTM[1a] and PPF.[1e] In contrast with these radicals, **14** reacts readily with concentrated $H_2SO_4$ or concentrated $HNO_3$, and **15** is significantly altered by concentrated $H_2SO_4$, $Cl_2$, and $Br_2$. It is pointed out that radicals **14** and **15** are less sterically shielded than radical **13** and the PTMs. It has also been found that radical **13** protonates on the nitrogen atom in concentrated $H_2SO_4$ without impairment of the radical character (see ESR spectrum in Figure 1 and Table III). Accordingly, when its solutions in $H_2SO_4$ are poured into abundant water, the radical is quantitatively recovered.

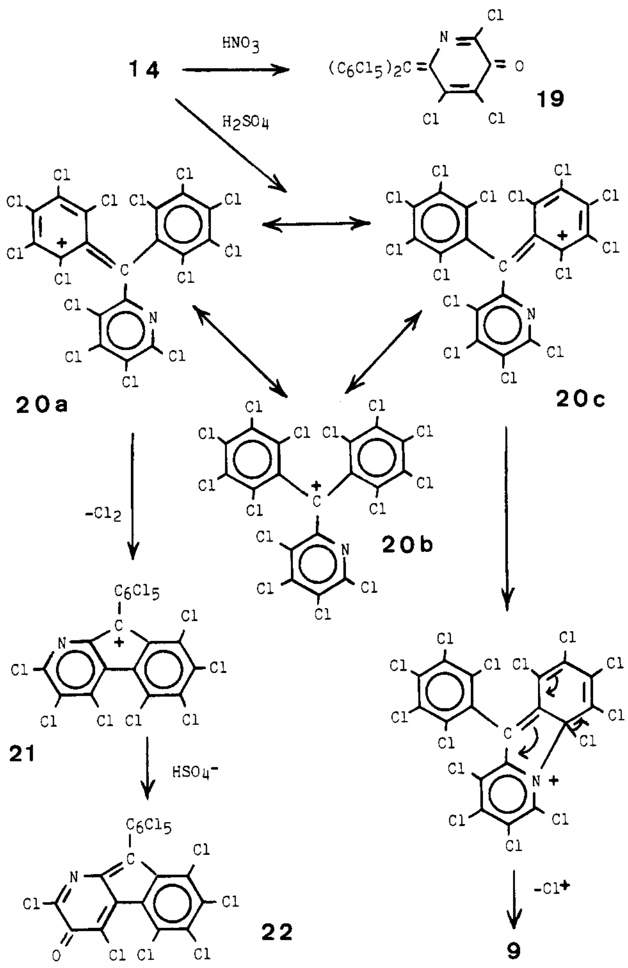
Some thermal stabilities in air of radicals **13–15** are shown in Table II (radical PTM melts with decomposition around 305 °C,[1a] and radical PPF decomposes around 350 °C[1e]). The thermal decomposition of radical **13** under argon gives a complex mixture from which small proportions of fluorenyl radical **15** and perchloro-3-aza-9-phenylfluorenyl radical (perchloro-5-phenyl-5*H*-indeno[1,2-*c*]pyridin-5-yl radical) (**16**) can be isolated (Scheme V). In this connection it is mentioned that the thermolysis of radical PTM is one of the most convenient syntheses of radical PPF.[1e] The structure of radical **16** has been ascertained on the basis of the following. (a) Its UV–vis spectrum is almost coincident with that of radical PPF (see UV–vis spectra section). (b) Its ESR spectrum is also very similar to that of PPF (see ESR spectra section). (c) Its mass spectrum presents a molecular peak group corresponding to $C_{18}Cl_{12}N$ with a 12 Cl peak distribution, and peak groupings corresponding to 2 Cl, 4 Cl, and 6 Cl losses; the peak group corresponding to the loss of $C_6Cl_5$ from the $M^+$ peak is also present. The thermal decomposition of radical **14** yields indole **9**, as it occurs with the corresponding triarylmethane **7** (Scheme V).

**Oxidation of the Radicals.** (a) The oxidation of radicals **13** and **15**, both with a tetrachloro-4-pyridyl ring, using oleum at room temperature takes place smoothly, giving perchloro-4-(phenyl(4-pyridyl)methylene)cyclohexa-2,5-dienone (**17**) and perchloro-9-(4-pyridyl)fluoren-3-one (**18**), respectively. The mechanism of these oxidations is assumed to be similar to those postulated for the oxidations of radicals PTM[1c] and PPF,[1e] respectively, where the first step is the formation of the corresponding carbenium ions, followed by a nucleophilic attack of $H_2O$ (or $HS_2O_7^-$) in a least shielded para position of the molecule (Scheme VI).

(b) The reaction of radical **14** with concentrated $H_2SO_4$, at room temperature, gives a mixture of perchloro-10-phenylpyrido[1,2-*a*]indole (**9**) and the product of hydrolysis perchloro-9-phenylindeno[2,1-*b*]pyridin-3-one (perchloro-1-aza-9-phenylfluoren-3-one) (**22**). This is a quite remarkable behavior since the PTM radicals usually remain unaltered under such a treatment. It is emphasized that although a carbenium ion cyclization from methanol **1** to fluorene **11** takes place, nevertheless both the conversions of radicals **13** or **14** into their carbenium ions as well as the cyclization of the latter are regarded as unfavorable processes, since first, cold concentrated $H_2SO_4$ is too weak an oxidant to convert a perchlorinated free radical into the corresponding carbenium ion (oleum is adequate), the second, the cyclization of a perchlorinated carbenium ion involves an electrophilic attack on a pentachlorophenyl ring, another electrophilic species. According, radical **13** does not cyclize, not even with oleum.

The conversions of radical **14** to indole **9** and ketone **22** in cold concentrated $H_2SO_4$ are consequently ascribed to a moderate weakening of the shield protecting its central trivalent carbon, here constituted by five ortho chlorines instead of the usual six, thus allowing the formation of carbenium ion **20** through an electron transfer from that carbon atom to the $H_2SO_4$. The cyclization of carbenium ion **20** to **21** is probably an electrophilic, four-center reaction where biphenyl bond formation is concerted with molecular-chlorine elimination, as it might be in the thermolysis of PTM radicals to PPFs.[1e] Such a process would avoid the intermediacy of energy-rich nonaromatic structures and benefit from the Cl–Cl bond-formation energy. The resulting carbenium ion **21** would hydrolyze to ketone **22**, as usual (Scheme VII). It is assumed that cyclization of carbenium ion **20** to indole **9** occurs through a nucleophilic attack by the nitrogen on a pentachlorophenyl ring, giving a transient pyridinium ion, which would finally undergo a chlorine cation elimination by the chlo-

**Scheme VII**



ride ion—formed in the hydrolysis of ketone **22**—and/or maybe other nucleophilic species present (Scheme VII).

(c) The reaction of radical **14** with concentrated $HNO_3$, at room temperature, gives a high yield of perchloro-2-(diphenylmethylene)pyridin-5(2*H*)-one (**19**) (Scheme VII). This reaction is quite analogous to that with perchloro-2-phenyldiphenylmethyl radical (PODM) as substrate, yielding perchloro-4-(2-biphenylylmethylene)cyclohexa-2,5-dienone.[1f] Notice, however, that in the present case neither attack on a pentachlorophenyl group by $HNO_3$ nor cyclization occurs. Consequently, a carbenium ion mechanism is quite unlikely. As proposed in the oxidation of PODM,[1f] $NO_2^{\bullet}$ radical might be the attacking species.

The structures given for ketones **17** and **18** are based on their UV–vis (Figure 1 of supplementary material) and IR spectra, which are very similar to those of perchlorofuchsone[1c] and perchloro-9-phenylfluoren-3-one,[1e] respectively (see Table I of supplementary material). As far as the structure of ketone **19** is concerned, while its UV–vis spectrum (Figure 1 of supplementary material) is very similar to that of perchlorofuchsone,[1c] suggesting a chromophore of the fuchsone type, its IR spectrum is significantly different (see Table I of supplementary material), with a C=O stretching band at higher values (1688 vs 1660 $cm^{-1}$). This indicates that the nitrogen atom is located in the quinomethane ring, in agreement with the fact that the $^{\bullet}NO_2$ radical, postulated in the oxidation mechanism, attacks preferentially the 4-position of the 2-pyridine ring, since this carbon atom is the less hindered point of the ring having the higher spin density (less twisted; see ESR spectra section). Finally, the structure of ketone **22** has been ascertained on the basis of the following. (a) Its elemental analysis, corresponding to $C_{18}Cl_{11}NO$, indicates that it is a cyclized ketone. (b) The high value of its C=O stretching band in the IR spectrum, as compared with that of perchloro-9-phenyl-3-fluorenone[1e] (1697 vs 1652 $cm^{-1}$; Table I of supplementary material), indicates that the nitrogen atom is located in the quinomethane ring, as in the case of ketone **19**. (c) Its UV–vis spectrum (Table I and Figure 1 of supplementary material) is consistent with the high conjugation expected for the planar 1-azafluoren-3-one structure. In fact, it shows a bathochromic shift of the conjugation band (located ~530 nm) with respect to that of the fluorenic ketones **18** and perchloro-9-phenyl-3-fluorenone[1e] (located ~460 nm), in agreement with the presence of a N atom in the 3-fluorenone system.

**Electron Spin Resonance Spectra.** The spin densities in perchlorotriphenylmethyl (PTM) radical have been calculated by means of MaLachlan's configuration interaction approach, and the relevant calculated coupling constants with the $^{13}C$'s compared with the experimental values.[11] It was concluded, as expected, that PTM radical is a propeller-like molecule with a high ($\theta \simeq 60°$) "blade" or twist angle, and that the spin densities on its three bridgehead, six ortho, and three para carbon atoms are comparable, being less than one-tenth that of the $\alpha$-carbon. However, only the spin couplings with the $\alpha$ ($a_c \simeq 30$ G), the bridgehead ($\simeq 11$ G), and the ortho ($\simeq 12.5$ G) $^{13}C$'s (natural abundance) are significant enough to appear as separate satellite lines. It is concluded, therefore, that the spin interaction with the para $^{13}C$'s is significantly smaller. To account for this unexpected observation, it was assumed that a hyperconjugative mechanism is operative and predominates, so enhancing the spin density of the ortho $^{13}C$'s; i.e., a direct overlap between the $\alpha$-carbon 2p orbital and the ortho carbon 2s orbitals. Such an overlap is effective because of the propeller-like molecular shape, caused by the repulsions among the ortho chlorines. Thus that 2p orbital forms an angle equal to $\theta$ with the hexagonal pentachlorophenyl ring axis. This has been confirmed in other twisted triphenylmethyl radicals.[12]

In this connection it is pointed out that the ESR spectra of two perchloro radicals containing nitrogen have previously been described. These are perchlorodiphenylaminyl[13] and perchlorodiphenylnitroxide,[14] and their spectra consist in well-resolved triplets due to spin interaction with the $^{14}N$ nucleus. Their hyperfine coupling constants $a_N$ are about 8 G, and their spin densities reside, as expected, mostly on the nitrogen.

While the ESR spectrum of radical **14** consists in a triplet, $a_N = 3.21$ G (Figure 1b), in radical **13** the triplet has collapsed down to a blunted absorption line (Figure 1a), its $a_N = 0.96$ G being estimated by computer simulation. As in the couplings with the ortho $^{13}C$ (12.5 G), the much higher spin coupling with the $^{14}N$ in radical **14** is attributed to hyperconjugation involving the $^{14}N$ 2s orbital. The ESR data for radicals here described are given in Table III. The fact that spin coupling with the $\alpha$-$^{13}C$ in radical **14** is smaller (27.8 G) than that in PTM radicals ($\approx 30$ G), and radical **13** as well (29.6 G), suggests a twist angle $\theta$ for the tetrachloropyridyl ring of radical **14** smaller than that for the pentachlorophenyls, thus enhancing spin delocalization from the $\alpha$-carbon to the pyridyl ring, particularly on its $^{14}N$. Nevertheless, since in the PTMs

---

(11) Falle, H. R.; Luckhurst, G. R.; Horsfield, A.; Ballester, M. *J. Chem. Phys.* **1969**, *50*, 258.

(12) Schreiner, K.; Berndt, A.; Baer, F. *Mol. Phys.* **1973**, *26*, 929.

(13) Ballester, M.; Castañer, J.; Olivella, S. *Tetrahedron Lett.* **1974**, 615.

(14) Ballester, M.; Riera, J.; Onrubia, C. *Tetrahedron Lett.* **1976**, 945.

hyperconjugation seems to override p–π conjugation, the higher $a_N$ value for radical **14** (vs radical **13**) can hardly be due to an increase in p–π conjugation, which consequently would result in a decreased hyperconjugation.

Radical **13** protonates in $H_2SO_4$:

$$\underset{(13)}{(C_6Cl_5)_2\dot{C}C_5Cl_4N} \xrightarrow{H^+} (C_6Cl_5)_2\dot{C}C_5Cl_4NH^+$$

On account of the presence of $^1H$ bonded to the nitrogen, its ESR spectrum consists of an ill-resolved multiplet, like that of carbon radical 4-aminotetradecachlorotriphenylmethyl.[1c] It has been ascertained by computer simulation that its hyperfine coupling constant with $^{14}N$ (1.36 G) is higher than in nonprotonated radical **13** (0.96 G). Nitrogen 2s spin-density calculations predict this effect in a simple model pair: the 4-pyridylmethyl radical and its protonated form. Accordingly, the spin density for the latter is higher (–0.011 vs –0.009). In this connection it is mentioned that an increase in the $^{14}N$ coupling constant has been observed going from $^{\bullet}NR_2$ to $^{\bullet}NR_3^+$. This has tentatively been accounted for by simply assuming that the electron spin density on the $^{14}N$ of the radical cation is larger because spin polarization through the nitrogen lone pair of electrons is more effective when the latter is shared with $R^+$,[15] a rationalization that might not be applicable to a complex system such as radical **13**.

Like the radicals of the perchloro-9-phenylfluorenyl (PPF) series,[1e] the spectrum of radicals **15** and **16** consists of a single line with a pair of weak satellite lines (shoulder in radical **16**) due to $\alpha$-$^{13}C$ splitting. In the PTMs, the unresolved lines traced to couplings with ring $^{35}Cl$ and $^{37}Cl$, low magnetic moment nuclei, contribute substantially to line width (~1.5 G). In radicals **15** and **16**, the higher spin delocalization from the 9-carbon to the close-to-planar fluorene system increases ring couplings significantly, causing further line-width broadening (~4.5 G).

**Ultraviolet–Visible Spectra.** While the spectra of triarylmethyl radicals **13** and **14** (Figure 2 of supplementary material), with radical band D at 560 nm and 574 nm, respectively, are very similar to those of PTM radicals (PTM: 562 nm),[1a] the spectra of fluorenyl radicals **15** and **16** (Figure 2 of supplementary material), with radical bands at 539, 575, 625 nm and 535, 576, 627 nm, respectively, are almost coincident with those of PPF radicals (PPF: 530, 573, 622 nm).[1e] The small bathochromic shift observed (14 nm) in radical **14** with respect to radical **13** can be accounted for by the presence of a 2-pyridyl ring in the former; the absence of an *o*-chlorine allows a greater coplanarity of this ring and, consequently, a greater resonance. This agrees with the higher nitrogen hcc value in radical **14** as compared with that of radical **13** (see ESR spectra section).

**Magnetic Susceptibility.** The specific magnetic susceptibilities of the radicals **13**–**16** (Table II of supplementary material) have been measured from 77 °K (liquid $N_2$) to room temperature. Least-squares correlation of their Curie–Weiss plot gives often low, unacceptable values for the specific diamagnetic susceptibility ($\chi_{dia}$), indicating an abnormal magnetic behavior. However, assuming the Weiss constant ($\theta$) equal to 0 °K and adopting the modified Pascal's data[1c] to calculate $\chi_{dia}$, the application of the Curie–Weiss equation to each radical at the temperatures studied gives close Bohr magneton ($\mu_B$) values, which, when averaged, afford the radical purities listed in Table II of the supplementary material, all near 100%.

## Experimental Section

**General Methods.** The IR, UV–vis, and ESR spectra were recorded with Perkin-Elmer 682, Beckman Acta M-VI, and Varian E-109E spectrometers, respectively. The magnetic susceptibilities were measured in helium with a Varian 4-in. magnet with constant-force caps and a Cahn RG electrobalance.

The handling of radicals in solution was performed in the dark. Since the locations of the IR peaks of perchloroorganic compounds differ markedly from those of their nonchlorinated counterparts, they are included in this section.

**Diphenyl(tetrachloro-4-pyridyl)methane (2).** A mixture of diphenyl(tetrachloro-4-pyridyl)methanol[3] (1) (5.42 g), aqueous 57% HI (15 mL), and hexane (200 mL) was refluxed for 4 h, cooled, and treated with water. The organic layer was washed with aqueous $NaHCO_3$ and with water, dried, and evaporated to give **2** (5.21 g; 100%): mp 143.5–146.0 °C; IR (KBr) 3080 (w), 3050 (w), 3020 (w), 2905 (w), 1600 (m), 1515 (m), 1490 (s), 1445 (m), 1378 (w), 1340 (s), 1312 (s), 1285 (s), 1270 (s), 1225 (m), 1202 (m), 1095 (m), 1075 (m), 1030 (m), 942 (m), 827 (m), 753 (m), 732 (s), 707 (s), 695 (s) $cm^{-1}$; UV ($C_6H_{12}$) 232 (sh) nm, 260 (sh), 268 (sh), 292, 297 ($\epsilon$ 18 000, 3200, 2900, 4700, 4600); $^1H$ NMR ($CCl_4$) $\tau$ 2.6–3.0 (m, 10, arom H), 3.57 (s, 1, $\alpha$-H). Anal. Calcd for $C_{18}H_{11}Cl_4N$: C, 56.4; H, 2.9; N, 3.6. Found: C, 56.6; H, 3.3; N, 3.8.

***αH*-Tetradecachlorodiphenyl(4-pyridyl)methane (3).** A solution of compound **2** (0.500 g) and $S_2Cl_2$ (0.334 g) in $SO_2Cl_2$ (25 mL) was added slowly to a refluxing solution of anhydrous $AlCl_3$ (1.01 g) in $SO_2Cl_2$ (25 mL). After a few minutes, a solution of $S_2Cl_2$ (1.61 g) in $SO_2Cl_2$ (25 mL) was added gradually while the resulting solution was concentrated gently to 10 mL and then refluxed for 7 h with the volume kept constant with small additions of $SO_2Cl_2$. After cooling, the $SO_2Cl_2$ was eliminated under vacuum and the residue was treated with water. Solid $NaHCO_3$ was added gradually until no more gas evolution took place. The resulting mixture was heated on a steam bath for 30 min, cooled, and strongly acidified with aqueous 12 N HCl. The resulting solid was filtered, dried, digested with pentane, and recrystallized ($CHCl_3$–hexane), giving $\alpha$H compound **3** (0.717 g; 75%): mp 266.0–268.5 °C; IR (KBr) 2960 (w), 1525 (m), 1360 (s), 1295 (s), 1240 (m), 1197 (m), 1105 (m), 812 (s), 692 (m), 667 (s) $cm^{-1}$; UV ($C_6H_{12}$) 219 nm, 240 (sh), 256 (sh), 286 (sh), 295, 303 ($\epsilon$ 133 500, 60 000, 20 000, 3800, 5690, 5670); $^1H$ NMR ($CDCl_3$) $\tau$ 3.02 (s, $\alpha$-H). Anal. Calcd for $C_{18}HCl_{14}N$: C, 29.7; H, 0.1; N, 1.9. Found: C, 30.1; H, 0.3; N, 2.2.

**Tetrachloro-2-(dichloromethyl)pyridine (5).** A slow stream of dry $Cl_2$ was passed (1 h) through a refluxing solution of 3,4,5,6-tetrachloro-2-methylpyridine[5] (4) (0.640 g) in purified $CCl_4$ (50 mL) during illumination with a 500-W incandescent lamp situated underneath the Pyrex container, thus providing for the heat. Evaporation of the solvent afforded an oily residue, which was submitted to column chromatography (silica gel; hexane), giving two main fractions. (a) Tetrachloro-2-(trichloromethyl)pyridine (6) (0.220 g; 24%): mp 62–63 °C (lit. mp 58–60 °C,[16] 67.0–67.5 °C,[17] and 58.7–60.3 °C[18]); IR (KBr) 1532 (w), 1502 (m), 1370 (w), 1348 (w), 1328 (s), 1300 (w), 1220 (m), 965 (m), 820 (s), 790 (s), 768 (s), 730 (s), 620 (s), 572 (m) $cm^{-1}$; UV ($C_6H_{12}$) 218 nm, 240 (sh), 276 (sh), 285, 294 ($\epsilon$ 37 600, 9200, 1950, 3210, 3130). Anal. Calcd for $C_6Cl_7N$: C, 21.6; Cl, 74.3; N, 4.2. Found: C, 21.8; Cl, 74.1; N, 4.1.

(b) Pyridine **5** (0.591 g; 71%):[18,19] mp 65–67 °C;[20] IR (KBr) 3060 (vw), 1525 (m), 1355 (s), 1290 (s), 1255 (m), 1220 (s), 1098 (m), 974 (s), 868 (m), 797 (s), 775 (s), 732 (s) $cm^{-1}$; UV ($C_6H_{12}$)

---

(15) Symons, M. C. R. *Chemical & Biochemical Aspects of the Electron Spin Resonance Spectroscopy*; Van Nostrand Reinhold: New York, 1978; p 50.

(16) Norton, F. H.; Taplin, W. H. U.S. Patent 3 256 167; *Chem. Abstr.* **1966**, *65*, 8882c.

(17) Shcheglov, Yu.; Sokolow, M. S.; Kasikhim, A. N.; Zhukov, N. P.; Boronin, Yu. B.; Kirmalova, M. L.; Litvinov, V. P. *Agrokhimiya* **1967**, 105; *Chem. Abstr.* **1968**, *68*, 21795*g*.

(18) Kosorotov, V. I.; Stul, B. Ya.; Dzhagatspayan, R. V. *Zh. Org. Khim.* **1980**, *16*, 2163.

(19) Seiber, J. N. U.S. Patent 3 687 827; *Chem. Abstr.* **1972**, *77*, 151980*k*.

(20) References 18 and 19 do not report the melting point.

214 nm, 236 (sh), 276 (sh), 286, 293 ($\epsilon$ 36 800, 7100, 2100, 3600, 3500); $^1$H NMR ($CCl_4$) $\tau$ 2.99 (s, $\alpha$-H). Anal. Calcd for $C_6HCl_6N$: C, 24.0; H, 0.3; N, 4.7. Found: C, 24.4; H, 0.4; N, 4.8.

**Diphenyl(tetrachloro-2-pyridyl)methane (8).** A solution of picoline **5** (1.052 g) in benzene (50 mL) was added slowly to a suspension of anhydrous $AlCl_3$ (1.9 g) in refluxing benzene (50 mL). The resulting mixture was refluxed with stirring for 26 h and evaporated to dryness. The residue was treated with aqueous diluted HCl and ethyl ether. The decanted ethereal layer was washed with aqueous $NaHCO_3$ and with water, dried, and evaporated. The oily residue was purified through silica gel (hexane) and recrystallized (same solvent) to give **8** (1.123 g; 83%): mp 136.5–137.5 °C; IR (KBr) 3080 (w), 3050 (w), 3020 (w), 1600 (w), 1532 (w), 1495 (s), 1450 (m), 1365 (s), 1352 (s), 1332 (w), 1312 (m), 1268 (m), 1200 (m), 1075 (m), 852 (m), 788 (s), 740 (s), 725 (m), 692 (s), 662 (m) cm$^{-1}$; UV ($C_6H_{12}$) 206 nm, 236 (sh), 270 (sh), 286, 291 ($\epsilon$ 56 000, 11 000, 2100, 4800, 4850); $^1$H NMR ($CCl_4$) $\tau$ 2.78 (s, 10, arom H), 4.03 (s, $\alpha$-H). Anal. Calcd for $C_{18}H_{11}Cl_4N$: C, 56.4; H, 2.9; N, 3.6. Found: C, 56.4; H, 3.0; N, 3.4.

***αH*-Tetradecachlorodiphenyl(2-pyridyl)methane (7).** 1. **3-h Reaction Time.** A solution of compound **8** (0.480 g) and $S_2Cl_2$ (2.300 g) in $SO_2Cl_2$ (25 mL) was added slowly to a refluxing solution of anhydrous $AlCl_3$ (1.00 g) in $SO_2Cl_2$ (10 mL) and allowed to concentrate up to 18 mL; then a solution of $S_2Cl_2$ (2.90 g) in $SO_2Cl_2$ (30 mL) was added slowly, and the resulting mixture was refluxed for 3 h and worked up as in the synthesis of $\alpha$H compound **3**. The crude product was purified through silica gel (hexane) and digested with pentane to give **7** (0.739 g; 81%): mp 299–300 °C; IR (KBr) 2922 (w), 1533 (w), 1508 (m), 1356 (s), 1332 (s), 1308 (m), 1282 (m), 1250 (m), 842 (m), 822 (s), 810 (m), 681 (m), 660 (m), 643 (m) cm$^{-1}$; UV ($C_6H_{12}$) 217 nm, 236 (sh), 288, 295 ($\epsilon$ 99 000, 50 000, 6060, 6250); $^1$H NMR ($CDCl_3$) $\tau$ 3.03 (s, $\alpha$-H). Anal. Calcd for $C_{18}HCl_{14}N$: C, 29.7; H, 0.1; Cl, 68.2; N, 1.9. Found: C, 29.8; H, 0.2; Cl, 68.3; N, 2.0.

2. **7-h Reaction Time.** The preceding reaction was repeated with 7 h of refluxing. Starting materials: compound **8** (0.482 g), $S_2Cl_2$ (2.284 g), $SO_2Cl_2$ (25 mL); $AlCl_3$ (1.00 g), $SO_2Cl_2$ (10 mL); $S_2Cl_2$ (2.90 g), $SO_2Cl_2$ (30 mL). The crude product (0.988 g), after chromatography (silica gel; hexane) and several crystallizations in the same solvent, yielded $\alpha$H compound **7** (0.277 g; 30%), hexachlorobenzene (0.033 g; 4%), indole **9** (0.034 g; 4%), and $\alpha$*H*-decachlorophenyl(2-pyridyl)methane (**10**), (0.110 g; 17%): mp 226.5–227.5 °C; IR (KBr) 2978 (w), 1534 (w), 1505 (m), 1360 (s), 1332 (s), 1302 (m), 1285 (w), 1252 (s), 1233 (m), 1083 (m), 937 (m), 812 (s), 798 (s), 773 (s), 720 (m), 684 (s), 648 (s), 620 (s), 557 (m), 514 (s) cm$^{-1}$; UV ($C_6H_{12}$) 214 nm, 287, 294 ($\epsilon$ 83 500, 5000, 5200). Anal. Calcd for $C_{12}HCl_{10}N$: C, 28.1; H, 0.2; Cl, 69.0; N, 2.7. Found: C, 28.1; H, 0.1; Cl, 69.0; N, 2.7.

**Perchloro-10-phenylpyrido[1,2-*a*]indole (9). 1. From Radical 14.** Radical **14** (0.050 g) was heated (250 °C; 1 h), and the resulting mass was purified by TLC (silica gel; hexane), giving indole **9** (0.033 g; 69%): yellow crystals, mp 302–303 °C; IR (KBr) 1590 (w), 1555 (w), 1509 (m), 1468 (w), 1400 (m), 1370 (m), 1340 (s), 1310 (m), 1263 (s), 1193 (s), 1100 (m), 851 (s), 819 (s), 783 (m), 750 (s), 718 (m), 687 (m), 643 (s), 622 (m), 582 (m), 578 (m), 497 (m) cm$^{-1}$; UV–vis ($C_6H_{12}$) 240 (sh) nm, 289, 320 (sh), 336 (sh), 356, 373, 427 ($\epsilon$ 34 000, 52 800, 5600, 3300, 3980, 4100, 5300); MS (all $^{35}$Cl), 685 ($C_{18}Cl_{13}N^+$). Anal. Calcd for $C_{18}Cl_{13}N$: C, 31.3; Cl, 66.5; N, 2.0. Found: C, 31.2; Cl, 66.5; N, 2.1.

2. **From $\alpha$H Compound 7.** Compound **7** (0.040 g) was heated (290–300 °C; 4 h) under argon, and the resulting mass was purified by TLC (silica gel; pentane), giving indole **9** (0.027 g; 71%).

**9-(Tetrachloro-4-pyridyl)fluorene (11).** 1. A solution of alcohol **1** (2.50 g) in anhydrous formic acid (25 mL) was refluxed for 15 min, cooled, and treated with water. The solid formed was filtered, washed with water, dried, and purified through silica gel (hexane), giving **11** (1.72 g; 72%): mp 171.5–174.0 °C; IR (KBr) 3050 (w), 3005 (w), 2905 (w), 1945 (w), 1905 (w), 1602 (w), 1577 (w), 1518 (s), 1470 (w), 1445 (s), 1390 (w), 1368 (w), 1333 (s), 1270 (s), 1223 (m), 1100 (m), 1088 (m), 950 (m), 871 (m), 844 (m), 765 (m), 740 (s), 728 (s), 692 (s), 628 (s), 518 (m) cm$^{-1}$; UV ($C_6H_{12}$) 213 nm, 223 (sh), 231, 236 (sh), 258 (sh), 267, 274 (sh), 291, 301 ($\epsilon$ 80 100, 35 000, 24 300, 19 500, 19 000, 21 300, 18 000, 10 300, 9100); $^1$H NMR ($CCl_4$) $\tau$ 2.14–3.0 (m, 8, arom H), 4.08 (s, 1, 9-H). Anal. Calcd for $C_{18}H_9Cl_4N$: C, 56.7; H, 2.4; N, 3.7. Found: C, 56.8; H, 2.3; N, 3.7.

2. A mixture of alcohol **1** (1.00 g), acetic acid (15 mL), and aqueous 12 N HCl (1.2 mL) was refluxed for 1 h, cooled, and treated with water. The precipitate was filtered, washed with water, and dried to give **11** (0.964 g; 100%), identified by melting point and IR spectrum.

**9*H*-Dodecachloro-9-(4-pyridyl)fluorene (12).** A solution of fluorene **11** (1.00 g) and $S_2Cl_2$ (0.334 g) in $SO_2Cl_2$ (50 mL) was added slowly to a refluxing solution of anhydrous $AlCl_3$ (0.521 g) in $SO_2Cl_2$ (50 mL), then concentrated to about 10 mL, and finally refluxed for 3 h with the volume kept constant with small additions of $SO_2Cl_2$. The resulting solution was treated as in the preceding chlorination, yielding finally fluorene **12** (1.41 g; 82%): mp 275 °C; IR (KBr) 2898 (w), 1512 (m), 1380 (m), 1322 (s), 1252 (m), 1228 (m), 1163 (m), 1091 (m), 985 (m), 900 (m), 847 (m), 820 (s), 693 (m), 643 (s) cm$^{-1}$; UV ($C_6H_{12}$) 208 nm, 234, 260 (sh), 272, 299, 302 (sh) ($\epsilon$ 49 300, 57 800, 16 000, 12 200, 28 700, 28 200); $^1$H NMR ($CDCl_3$) $\tau$ 3.90 (s, 9 H). Anal. Calcd for $C_{18}HCl_{12}N$: C, 32.9; H, 0.1; N, 2.1. Found: C, 33.1; H, 0.1; N, 2.2.

**Perchlorodiphenyl(4-pyridyl)methyl Radical (13).** A mixture of $\alpha$H compound **3** (0.761 g), powdered NaOH (0.80 g), ethyl ether (100 mL), and $Me_2SO$ (30 mL) was shaken for 6 days in the dark, a deep red color being formed. The NaOH was filtered off, and the filtrate was poured into a solution of $I_2$ (2.5 g) in ethyl ether (70 mL). The resulting solution was left undisturbed for 23 h, then washed with aqueous $NaHSO_3$ (to destroy $I_2$) and with water (to eliminate $Me_2SO$), dried, and evaporated. The resulting solid was purified through silica gel ($CCl_4$) and recrystallized (hexane) to give radical **13** (0.469 g; 62%): bright-red crystals, mp 275–277 °C dec; IR (KBr) 1500 (m), 1350 (w), 1330 (s), 1300 (s), 1250 (s), 1012 (m), 878 (m), 817 (m), 710 (m), 653 (m) cm$^{-1}$; UV–vis ($C_6H_{12}$) 220 nm, 275 (sh), 292, 335 (sh), 365 (sh), 380, 410 (sh), 515, 560 ($\epsilon$ 84 000, 8000, 8300, 6250, 16 000, 25 500, 2100, 1560, 1410); ESR, Table III and Figure 1; magnetic susceptibility, Table II of supplementary material. Anal. Calcd for $C_{18}Cl_{14}N$: C, 29.8; N, 1.9. Found: C, 29.9; N, 2.2.

**Perchlorodiphenyl(2-pyridyl)methyl Radical (14).** This synthesis was performed as in that of radical **13**. Starting materials: $\alpha$H compound **7** (0.350 g); NaOH (0.40 g); ethyl ether (50 mL); $Me_2SO$ (15 mL); reaction time, 24 h; $I_2$ (1.0 g); reaction time, 3 h. The crude product was purified through silica gel (hexane), yielding radical **14** (0.308 g; 88%): garnet crystals, mp 245 °C dec; IR (KBr) 1515 (w), 1450 (m), 1334 (s), 1309 (s), 1282 (m), 1260 (m), 1200 (m), 1082 (m), 842 (m), 821 (m), 789 (m), 747 (m), 712 (m), 668 (m), 648 (m) cm$^{-1}$; UV–vis ($C_6H_{12}$) 218 nm, 245 (sh), 277, 290 (sh), 335 (sh), 368 (sh), 381, 425 (sh), 505 (sh), 527, 574 ($\epsilon$ 85 000, 29 000, 7100, 6700, 10 800, 23 500, 25 600, 2500, 1390, 1400, 1700); ESR, Table III and Figure 1; magnetic susceptibility, Table II of supplementary material. Anal. Calcd for $C_{18}Cl_{14}N$: C, 29.8; Cl, 68.7; N, 1.9. Found: C, 29.8; Cl, 68.3; N, 1.9.

**Perchloro-9-(4-pyridyl)fluorenyl Radical (15).** A mixture of fluorene **12** (0.501 g), powdered NaOH (0.52 g), ethyl ether (100 mL), and $Me_2SO$ (30 mL) was treated as in the synthesis of radical **13**, yielding radical **15** (0.320 g; 64%): dark-green crystals, mp ~250 °C dec; IR (KBr) 1532 (m), 1482 (w), 1433 (w), 1375 (s), 1343 (w), 1315 (s), 1298 (s), 1256 (s), 1185 (m), 1092 (s), 1035 (m), 883 (s), 849 (m), 750 (m), 694 (m), 651 (m) cm$^{-1}$; UV–vis ($C_6H_{12}$) 210 nm, 233, 270 (sh), 294, 320 (sh), 350 (sh), 373, 388, 410, 460, 497, 539, 575, 625 ($\epsilon$ 59 200, 37 100, 25 800, 53 200, 13 000, 5400, 7860, 8480, 5760, 1920, 1520, 960, 3420, 8500); ESR, Table III; magnetic susceptibility, Table II of supplemental material. Anal. Calcd for $C_{18}Cl_{12}N$: C, 32.9, N, 2.1. Found: C, 33.3; N, 2.2.

**Thermolysis of Perchlorodiphenyl(4-pyridyl)methyl Radical (13).** Radical **13** (0.150 g) was heated (295–300 °C; 1 h) under argon in a flask connected to a small column containing Cu turnings to eliminate the $Cl_2$ formed. The resulting complex mixture was submitted to TLC (silica gel; hexane–$CHCl_3$) giving the following. (a) Perchloro-3-aza-9-phenylfluorenyl radical (**16**) (0.015 g; 11%): dark green crystals, mp around 245 °C; IR (KBr) 1520 (w), 1497 (m), 1382 (s), 1360 (w), 1352 (s), 1339 (s), 1298 (m), 1283 (m), 1250 (s), 1188 (m), 1080 (s), 1011 (m), 838 (m), 802 (m), 760 (m), 702 (m), 662 (m), 632 (s), 509 (s) cm$^{-1}$; UV–vis ($C_6H_{12}$) 220 nm, 240 (sh), 272 (sh), 281, 303, 338, 348 (sh), 362, 386 (sh), 420 (sh), 464, 501, 535, 576, 627 ($\epsilon$ 62 000, 35 800, 34 500, 37 500, 22 600, 6400, 6800, 8430, 4500, 1810, 843, 497, 1360, 4135, 9560); ESR, Table III; magnetic susceptibility, Table II of supplementary material; MS (all $^{35}$Cl), 650 ($C_{18}Cl_{12}N^+$; $M^+$), 580 ($M^+ - 2$ Cl), 510

($M^+$ – 4 Cl), 440 ($M^+$ – 6 Cl), 403 ($M^+$ – $C_6Cl_5$). (b) A complex mixture (0.045 g) containing some fluorenyl radical **15** (IR spectrum).

**Perchloro-4-(phenyl(4-pyridyl)methylene)cyclohexa-2,5-dienone (17).** A mixture of radical **13** (0.414 g) and 30% oleum (20 mL) was stirred (23 h) at room temperature and in the dark. The resulting mixture was poured into ice–water and extracted with ether–$CHCl_3$. The resulting solution was dried and evaporated to a residue, which by chromatography through silica gel ($CCl_4$) yielded starting radical **13** (0.160 g; 39%) and dienone **17** (0.221 g; 55%): orange crystals, mp 288–290 °C; IR (KBr) 1652 (s), 1551 (m), 1508 (s), 1470 (m), 1350 (m), 1330 (s), 1305 (s), 1252 (m), 1218 (m), 1195 (m), 1127 (s), 1008 (s), 852 (m), 765 (m), 750 (s), 730 (s), 718 (m), 670 (s), 647 (m), 628 (m), 521 (m), 502 (m) $cm^{-1}$; UV-vis ($CHCl_3$), Table I of supplementary material. Anal. Calcd for $C_{18}Cl_{13}NO$: C, 30.6; Cl, 65.2; N, 2.0. Found: C, 30.9; Cl, 65.2; N, 2.2.

**Perchloro-9-(4-pyridyl)fluoren-3-one (18).** A mixture of radical **15** (0.060 g) and 30% oleum (10 mL) was treated as in the preceding reaction, yielding fluorenone **18** (0.042 g; 72%): red crystals, mp over 350 °C; IR (KBr) 1652 (s), 1572 (m), 1520 (s), 1392 (m), 1370 (m), 1360 (m), 1318 (s), 1303 (m), 1210 (m), 1182 (m), 1157 (m), 1120 (m), 1030 (m), 1013 (s), 960 (m), 921 (m), 853 (m), 820 (m), 780 (m), 761 (m), 730 (m), 683 (m), 645 (m), 503 (m) $cm^{-1}$; UV-vis ($CHCl_3$), Table I of supplementary material. Anal. Calcd for $C_{18}Cl_{11}NO$: C, 34.0; Cl, 61.3; N, 2.2. Found: C, 34.0; Cl, 61.2; N, 2.2.

**Perchloro-9-phenylindeno[2,1-*b*]pyridin-3-one (22).** A mixture of radical **14** (0.100 g) and concentrated $H_2SO_4$ (10 mL) was stirred (2 days) at room temperature and in the dark. The resulting mixture was treated as in the preceding reaction, and the residue yielded, by column chromatography (silica gel), indole **9** (elution with hexane) (0.046 g; 48%) and ketone **22** (elution with $CHCl_3$) (0.025 g; 28%): red crystals, mp over 325 °C; IR (KBr) 1697 (s), 1642 (s), 1593 (m), 1522 (m), 1348 (s), 1298 (m), 1152 (m), 1090 (m), 1034 (m), 953 (m), 823 (m), 747 (m) $cm^{-1}$; UV-vis ($CHCl_3$), Table I of supplementary material. Anal. Calcd for $C_{18}Cl_{11}NO$: C, 34.0; Cl, 61.3; N, 2.2. Found: C, 33.8; Cl, 61.1; N, 2.1.

**Perchloro-2-(diphenylmethylene)pyridin-5(2*H*)-one (19).** A mixture of radical **14** (0.081 g) and concentrated $HNO_3$ (10 mL) was stirred (2 days) at room temperature and in the dark. The resulting mixture was poured into ice–water and extracted with $CCl_4$. The organic extract was washed with water, dried, and evaporated to give a residue, which by TLC (silica gel; $CCl_4$–hexane) gave dienone **19** (0.075 g; 95%): orange crystals, mp 246–248 °C; IR (KBr) 1688 (s), 1593 (m), 1538 (m), 1346 (m), 1332 (s), 1310 (m), 1260 (m), 1102 (s), 1022 (m), 821 (m), 790 (m), 776 (m), 759 (m), 680 (m), 658 (m), 650 (m), 547 (m) $cm^{-1}$; UV-vis ($CHCl_3$), Table I of supplementary material. Anal. Calcd for $C_{18}Cl_{13}NO$: C, 30.6; Cl, 65.2; N, 2.0. Found: C, 30.7; Cl, 65.2; N, 2.0.

**Acknowledgment.** We thank Dr. J. Rivera for the mass spectra and Dr. J. Olivella for spin-density calculations on protonated and nonprotonated 4-pyridylmethyl radical.

**Supplementary Material Available:** UV spectra and magnetic susceptibility data of radicals **13–16** and UV spectra of ketones **17–19** and **22** (4 pages). Ordering information is given on any current masthead page.

---

# Semiempirical Calculations of Carbenes with Aromatic Substituents: A Comparison of Theory with Experiment

Yu-Zhuo Li and Gary B. Schuster*

*Department of Chemistry, University of Illinois, Roger Adams Laboratory, Urbana, Illinois 61801*

*Received June 25, 1987*

MINDO/3, MNDO, and AM1 calculations were carried out on a set of 20 singlet and triplet carbenes with aromatic substituents. The computational results were compared with experimental determinations of the structure, energy, and reactivity for those cases where these parameters have been determined. The three semiempirical methods yield comparable results; each gives essentially the same geometry and consistently predicts the energy difference between the triplet and singlet states ($\Delta H_{st}$) of aryl-substituted carbenes contained in five- or six-membered rings. The calculations give values of $\Delta H_{st}$ that are approximately linearly related to the experimental estimates of the energy gap. The trend in $\Delta H_{st}$ is related to electronic properties of the substituent and the bond angle at the carbene–carbon. The predicted values of $\Delta H_{st}$ from the MINDO/3 method are uniformly closer to the experimental values than are those of MNDO or AM1. The electrophilic reactivity of these singlet carbenes is found to be related to their calculated LUMO energies.

One objective of chemical research is to relate systematically and reliably the structure of a substance to its chemical and physical properties. Attaining this objective requires the careful interplay of experiment with theory. It seems unlikely that a more striking example of this interplay than methylene ($CH_2$:, the simplest carbene) will be found. The long history of this pursuit has recently been described by Schaefer and Shavitt.[1] There were two contentious issues; the bond angle of triplet ground-state methylene and the energy gap ($\Delta H_{st}$) between the triplet and the lowest singlet state of this molecule. Presently theory and experiment[2] are in agreement; the triplet is bent (134°) and 8.5 kcal/mol below the singlet state. After throughtful consideration of methylene and other cases, Schaefer ends his review with the conclusion that quantum chemistry is coming of age as a full partner with experiment.

Research on carbenes entered a new phase in 1976 when Closs and Rabinow reported the detection and characterization of diphenylmethylene (DPM) by flash photolysis of diphenyldiazomethane in solution.[3] Their kinetic

---

[1] (a) Schaefer, H. F., III. *Science (Washington, D.C.)* **1986**, *231*, 1100. (b) Shavitt, I. *Tetrahedron* **1985**, *41*, 1531.

[2] Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1048.

[3] Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

0022-3263/88/1953-1273$01.50/0