Pergamon

Tetrahedron Vol. 51, No. 26, pp. 7301-7312, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00353-3

Inert Carbon Free Radicals. 13. New Free Radicals of PTM (Perchlorotriphenylmethyl) series with *meta* Functionalization.

Salomé López,[a] José Carilla,[a] Lluís Fajarí,[a] and Luis Julià.[*a]

[a] Departament de Materials Orgànics Halogenats, Centre d'Investigació i Desenvolupament (CSIC). Jordi Girona 18-26, 08034 Barcelona, Spain.

Enrique Brillas,[b]

[b] Departament de Química Física, Universitat de Barcelona, Avgda Diagonal 647, 08028 Barcelona, Spain.

Amilcar Labarta[c]

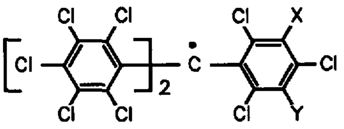
[c] Departament de Física Fonamental, Universitat de Barcelona, Avgda Diagonal 647, 08028 Barcelona, Spain.

Abstract: The synthesis of new organic free radicals of the PTM (perchlorotriphenylmethyl) series with different substituents in the 3- and 5-positions of one phenyl ring and their α-H precursors are described. All these radicals are stable red solids with high melting points. Their electron spin resonance spectra in solution and their magnetic susceptibilities in solid are reported and commented upon. Electrochemical behavior of radical **5** by means of cyclic voltammetry is also presented.

The syntheses and study of molecular magnets are subjects of increasing interest.[1] But there are some great difficulties in trying to build magnets from odd-electron organic molecules. Most of them are highly unstable and tend to dimerize or to decompose. Their stability, a requirement for their potential application, is a function of the conjugative delocalization of the unpaired electron through a π system and/or steric protection of the radical center which makes it inaccessible to neighboring molecules.

The most stable carbon free radicals described so far belong to the so-called PTM (perchlorotriphenylmethyl) series.[2,3] Their stability is mainly attributed to steric shielding of their molecular carbon backbone by the chlorine substituents. Functionalized PTM radicals have been obtained by substitution of *para*-chlorines by chemically active groups. These radicals react at the functional group without impairment of the radical character.

At present, we are concerned with the synthesis of new persistent radicals and polyradicals as a program directed to the development of new organic ferromagnets.[4] Now, we report the preparation and electron spin resonance (ESR) of new radicals of the series of PTM, radicals **1-5**, which represent the first highly chlorinated triphenylmethyl radicals with substituents others than chlorine in *meta*-position. These radicals have proved to be very stable either in solid or in liquid solutions in the dark, and their purities have been ascertained by magnetic susceptibility measurements.



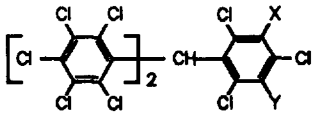
1 X = H, Y = NO_2
2 X = Y = NO_2
3 X = Y = CO_2H
4 X = Y = CO_2Me
5 X = Y = COCl
6 X = Y = H

Among these new radicals, the radical **5**, with chlorocarboxy substituents, is very attractive due to its potential of forming biradicals and triradicals by condensation with other persistent radicals, bearing either amino or alcohol functions, through amide or ester. In this context, the intramolecular electron spin-spin interaction between two triplet nitrene units linked through a benzanilide chromophore has been reported recently, concluding that the amide bond is effective as an exchange coupler.[5] Similarly, an efficient electron dipole-dipole interaction has been shown in perchlorobistriphenylmethyl diradicals of the PTM series linked together by inserting a CO-O-CO function between them.[6]

RESULTS AND DISCUSSION

Syntheses of Precursors

Bis(pentachlorophenyl)(2,4,6-trichlorophenyl)methane **7**[7] treated with fuming nitric acid gave triarylmethane **8** by electrophilic substitution of the hydrogen. If the nitrating agent was fuming nitric acid - oleum (30%), a mixture of triarylmethanes **8** and **9** was obtained. An $AlCl_3$-promoted Friedel-Crafts alkylation of triphenylmethane **7** by an excess of chloroform afforded bis(pentachlorophenyl)[2,4,6-trichloro-3,5-(dichloromethyl)phenyl]methane (**10**) in excellent yield. Hydrolysis of **10** with oleum (30%) and then with water yielded the dialdehyde **11** which was oxidized to the diacid **12** by means of CrO_3. Methylation of **12** with an ethereal solution of CH_2N_2 gave the dimethyl ester **13**.



7 X = Y = H
8 X = H, Y = NO_2
9 X = Y = NO_2
10 X = Y = $CHCl_2$
11 X = Y = CHO
12 X = Y = CO_2H
13 X = Y = CO_2Me

Syntheses of Radicals

Radicals 1-4 were prepared from the corresponding αH-precursors 8, 9, 12 and 13, respectively, by the two-step process used for other highly chlorinated triphenylmethyl radicals, *i.e.* neutralization of the substrates with tetra-*n*-butylammonium hydroxide in THF, followed by electron transfer reaction of the carbanions to *p*-chloranil. Radical **5** was obtained directly by treatment of the dicarboxy radical **3** with $SOCl_2$ without disturbing the radical character of the molecule. All these new radicals, isolated as fusible deep red crystals, were characterized by elemental analysis and spectroscopy. They are stable in air without decomposition and do not react with oxygen in solution and in the dark.

Electron Spin Resonance (ESR)

X-Band ESR spectra of radical **1** was recorded in deoxygenated CH_2Cl_2 solution at 173 K and those corresponding to radicals **2-5** in desoxygenated tetrachloroethylene solution at room temperature. Although the ESR spectrum of bis(pentachlorophenyl)(2,4,6-trichlorophenyl)methyl radical (**6**) has been reported in $CFCl_3$ at 163 K,[3b] now it is recorded under the same conditions of solvent and temperature as radical **1** so as to compare their characteristic ESR values with each other. Spectral data of the radicals **1-6** are listed in Table 1.

The spectrum of radical **1** is displayed in Figure 1 together with its computer simulation. It consists of an overlapped doublet which is assigned to the coupling of the free electron with the aromatic proton in *meta*. At higher gain conditions, spin coupling with the ^{13}C nuclei (^{13}C natural abundance, 1.1%) is observed. In the figure only those pairs due to the bridgehead and the *ortho* carbons can be observed. On the other hand, radicals **2-5** display single and broad lines.

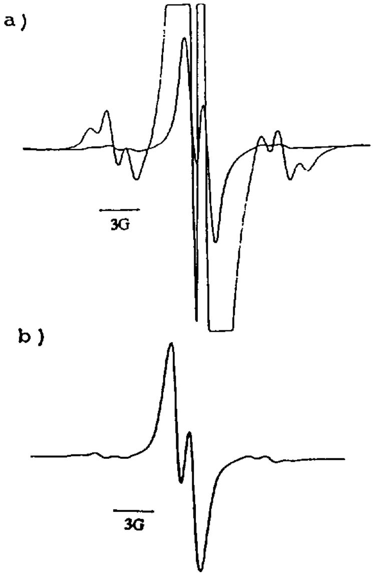


Figure 1. (a) ESR spectrum of radical **1** in CH_2Cl_2 at -100 °C and (b) its computer simulation.

Table 1. ESR Spectral data of the radicals **1-6**.

radical	g value	ΔH_{pp}***	splitting (G)		
			H	α-^{13}C	arom-^{13}C
1*	2.0033	0.90	1.24	30.0	13.2; 10.9
2**	2.0034	1.34		30.2	12.0; 11.0
3**	2.0032	1.02		30.2	12.9; 10.7
4**	2.0034	1.05		30.5	13.0; 11.5
5**	2.0034	1.05		30.4	12.8; 11.9
6*	2.0031	0.69	1.26	30.0	13.3; 10.7

* The spectra of radicals **1** and **6** were recorded in CH_2Cl_2 solution at 173 K; the coupling constants found by computer simulation.

** The spectra of radicals **2-5** were recorded in $Cl_2C{=}CCl_2$ at r.t.

*** Peak-to-peak first derivative line width.

The α and aromatic ^{13}C coupling constant values for all the radicals are very similar to each other and to those for PTM radical.[3a] This fact suggests that the stable conformation of these radicals and PTM radical in solution are practically identical, being governed only by the steric effects of the six *ortho*-chlorines of the molecule. Furthermore, the very similar values for the coupling constants of hydrogen in radicals **6** and **1** are a consequence of the very weak electronic effect of the nitro substituent in *meta*, not enough to influence appreciably in the ring spin density. This is accounted for by steric inhibition of the resonance between nitro group and aromatic ring due to the presence of two *ortho*-chlorines. If the spectrum of **1** is recorded at room temperature, a single and broad line without hyperfine splitting is displayed. This fact is a consequence of an increasing of the linewidth with temperature due, most probably, to a shortening of the spin-lattice relaxation time or to a decrease of intermolecular electron spin-electron spin exchange.

Cyclic voltammetry (CV)

Cyclic voltammetry is a reliable experimental method for the determination of redox potentials in highly chlorinated triphenylmethyl radicals. A striking feature of this class of organic materials is that they undergo reversible, one-electron redox behaviour, which is accounted for by the stability of both oxidized, the neutral radical, an the reduced, the anion, species. CV data for radical **2**, as a representative example of the radicals described in this paper, are now reported and compared with those for PTM radical.

Cyclic voltammograms for the reduction of radical **2** in 0.1 M tetrabutylammonium perchlorate (TBAP) - dimethylformamide (DMF) exhibited one cathodic peak R with a peak potential E^c_p = 0.36 V *vs.* SSCE (a SCE with NaCl-aqueous satured solution). When the potential was reversed at values more cathodic than 0.36 V, one anodic peak O with a peak potential E^a_p = 0.42 V was also recorded, as can be observed in Figure 2. This indicates that peaks R and O yield a redox couple. Both peaks were diffusion-controlled, since their peak currents (I^a_p anodic peak current for peak O, I^c_p cathodic peak current for peak R) showed a linear variation with square root of the scan rate.[8]

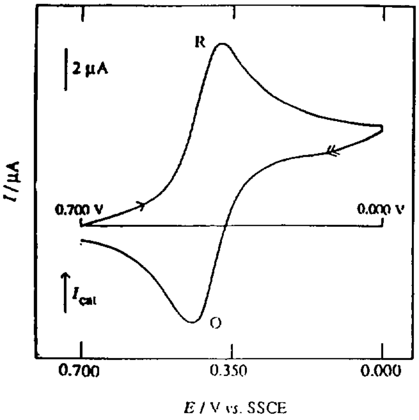


Figure 2. Cyclic voltammogram for the reduction of 0.5 mM of radical **2** in DMF containing 0.1 M TBAP, at a Pt electrode, at 100 mV s^{-1} and at 25.0 °C. Initial potential 0.700 V and reversal potential 0 V.

The $|I^a_p/I^c_p|$ ratio for the O/R couple was found to be close to 1 at all scan rates tested. Peak potentials for both peaks were independent of the scan rate and their difference (E^a_p - E^c_p) was 60 mV. The standard potential (E^0) was found to be 0.39 V *vs.* SSCE. All these findings agree with the theoretical behaviour expected for a reversible one-electron charge transfer reaction[8] and hence, the O/R can be ascribed to the following equilibrium reaction between the radical **2** an its anion $\mathbf{2}^-$:

$$\mathbf{2} + e^- \rightleftharpoons \mathbf{2}^-$$

The presence of this reversible O/R couple is indicative of a strong stability of both species, **2** and $\mathbf{2}^-$, in solution.

A parallel CV study for PTM radical revealed that it also displayed a reversible one-electron redox couple with $E^0 = 0.07$ V *vs.* SSCE in 0.1 M TBAP-DMF, respectively. This couples can then be associated with the reversible conversion of substrates into their anions.

Since E^0 value for radical **2** is more positive than that of PTM radical, it can be established that the former is more easily reducible than the latter, as a consequence of the higher electron-withdrawing power of nitro than chlorine.

Magnetic susceptibility

Although suitable crystals for an X-ray analysis of the carboxy radical **3** to know the relative orientation of the molecules in the lattice were not obtained, the molar magnetic susceptibility (χ_M) of the microcrystalline solid has been studied in some detail using a SQUID magnetometer operating with a field strength of 20 KOe in the interval 4.2-300 K. The presence of two carboxy groups in this radical opens the possibility of intermolecular magnetic interactions between the spins of neighboring molecules due to an organized packing of the molecules within the crystal through hydrogen bonding.[9] Recently, the existence of very weak intermolecular ferromagnetic coupling in an isomeric radical of the PTM series with the possibility of hydrogen bonding, the (4,4'-dicarboxytridecachlorotriphenyl)methyl radical,[10] has been reported. The experimental data were corrected for the diamagnetic susceptibility of the molecule ($\chi_{dia} = -388.01 \times 10^{-6}$ cm^3/mol) which was theoretically estimated by using Pascal's constants.[11]

$$\chi'_M = \chi_M - \chi_{dia}$$

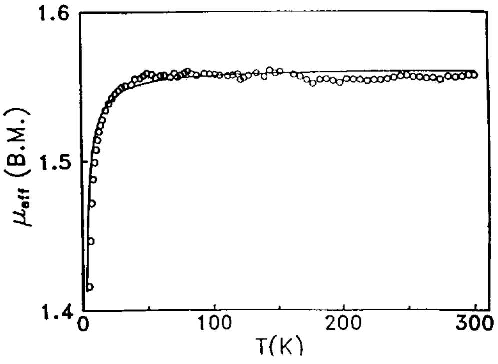


Figure 3. Thermal variation of μ_{eff} (B.M.) for radical **3**. The solid line was calculated with eq 1 and the values of the parameters are discussed in the text.

Figure 3 shows the temperature T dependence of the molar effective magnetic moment in Bohr magnetons [μ_{eff}(B.M.) = 2.828(χ'_MT)$^{1/2}$]. The values of μ_{eff} can be fitted to the semiempirical expression

$$\mu_{eff}(\text{B.M.}) = [F \cdot g_e^2 \cdot 1/2(1/2 + 1) \cdot T/T-\theta]^{1/2} = [3 \cdot F \cdot T/T-\theta]^{1/2} \quad (1)$$

where F = 0.813 is an empirical factor introduced to correct the reduction in the magnetic susceptibility of the sample due to the presence of diamagnetic impurities, the gyromagnetic factor $g = 2$, and the Weiss constant θ = -0.62 K. In this case, the negative value of θ is associated to the existence of weak intermolecular antiferromagnetic interactions.

The specific magnetic susceptibilities of radicals **1**, **2**, **4**, and **5** have been measured from 77 K to room temperature with a Faraday balance magnetometer operating at 8 KOe. All these values were also corrected for the specific diamagnetic susceptibilities calculated independently from modified Pascal's data.[11] Least-squares correlation of the resulting Curie-Weiss plot gave the Bohr magnetons (μ_B) and the Weiss constants (θ) reported in Table 2. From μ_B-values the radical purities have been also calculated.

Table 2. Magnetic properties of radicals **1**, **2**, **4**, and **5**.

radical	M_B	$10^6\chi_a$,^{a}emn	θ,K	purity,%
1	1.70	- 0.536	- 3	96
2	1.61	- 0.524	- 8	87
4	1.74	- 0.554	- 4	100
5	1.68	- 0.545	-4.5	95

[a] Values calculated independently from modified Pascal's data.[11]

EXPERIMENTAL

General Methods

Melting points were obtained by using a Köfler microscope "Reichert" and are uncorrected. The UV spectra were recorded with a Perkin-Elmer Lambda Array 3840 spectrometer coupled with a Perkin-Elmer 7300 computer. IR spectra were recorded with a Perkin-Elmer 682 spectrometer.

ESR Experiments

ESR spectra were recorded with a Varian E-109 spectrometer working in the X band, and the ESR simulations were carried out with a Hewlett-Packard 9835-B computer using a modified version of the software package of a Varian E-935 Data Adquisition System. Handling of radicals in solution was performed in the dark. For the recording of the ESR spectra, the solution of the radicals in the ESR tubes was carefully degassed by the freeze-pump-thaw technique.

Electrochemical Measurements

The cyclic voltammetric experiments were carried out in a three-electrode cell under an argon atmosphere. A platinum sphere with an area of 0.093 cm^2 was used as the working electrode and a Pt wire as the counter electrode. The reference electrode was a SSCE (a SCE with NaCl-saturated aqueous solution) connected to the cell through a salt bridge containing a 0.1 M of TBAP-DMF solution. The temperature of test solutions and of SSCE was kept at 25.0 ± 0.1 °C. In all experiments the cell was maintained in the darkness to avoid the photochemical decomposition of substractes in solution.

Solutions of radicals PTM and **2** (10^{-3} M) in DMF containing TBAP (0.1 M) as background electrolyte were studied by CV. The volume of all solutions were 25 cm^3.

CV measurements were performed with a standard equipment consisting of a PAR 175 universal programmer, an Amel 551 potentiostat, and a Phillips 8043 X-Y recorder. Cyclic voltammograms of all solutions were recorded in the scan rate (v) ranging between 20 and 200 mV s^{-1}.

Magnetic susceptibilities

The magnetic susceptibilities for radicals **1**, **2**, **4** and **5** were measured with a Varian 4-in. magnet with constant-force caps operating at 8 KOe, and a Cahn RG electrobalance. The magnetic susceptibilities for radical **3** were measured with a SQUID magnetometer in the temperature range 4.2-300 K operating in a field strengh of 40 KOe. The data were corrected for the magnetization of the sample holder.

Bis(pentachlorophenyl)(2,4,6-trichloro-3-nitrophenyl)methane (**8**), *and bis(pentachlorophenyl)(2,4,6-trichloro-3,5-dinitrophenyl)methane* (**9**). (a) *With oleum (30%) and fuming nitric acid.* To a mixture of **7** (0.516 g) and oleum (30%) (5 mL), fuming nitric acid (d=1.5 g·mL^{-1}) (6.5 mL) was added dropwise and the resulting mixture was stirred (120 °C) for a time (30 h). The resulting mixture was poured into ice-water, and the precipitate was filtered, washed with water, and dried. The solid obtained was flash chromatographed [silica gel; CCl_4-hexane (60:40)] to give (i) starting material **7** (0.280 g, 54%) identified by its melting point and IR sprectrum; (ii) **8** (0.052 g, 9%), m.p. 262-3 °C (Found: C, 31.2; H, 0.4; N, 1.9; Cl, 62.7. $C_{19}H_2Cl_{13}NO_2$ requires C, 31.0; H, 0.3; N, 1.9; Cl, 62.5%); $\lambda_{max}(C_6H_{12})$ 220, 238 sh, 254sh, 294 and 303 nm (ε 98 000, 55 060, 20 850, 620, 600); ν_{max}(KBr) 3080, 2930, 1570, 1550, 1375, 1350, 1335, 1300, 1290, 1235, 1185, 1110, 1005, 970, 890, 855, 835, 795, 770, 705, 680, 665 and 640 cm^{-1}; (iii) **9** (0.067 g, 11.5%); m.p. 330-1 ^{0}C; (Found: C, 29.2; H, 0.2; N, 3.4; Cl, 58.7. $C_{19}HCl_{13}N_2O_4$ requires C, 29.2; H, 0.1; N, 3.6; Cl, 58.9%); $\lambda_{max}(C_6H_{12})$ 219, 294 and 305 nm (ε 104 575, 1600, 1600); ν_{max}(KBr) 2925, 1555, 1355, 1335, 1300, 1235, 1205, 1185, 1110, 1005, 940, 815, 805, 765, 710, 685, 670, 650, 640, 620 and 600 cm^{-1}.

(b) *With fuming nitric acid*. A mixture of **7** (0.510 g) and fuming nitric acid (d=1.5 g mL^{-1}) (6.5 mL) was stirred (100 °C) for a time (22 h). The resulting mixture was treated as before and the solid obtained was flash cromatographed [silica gel; CCl_4-hexane (60:40)] to give (i) starting material **7** (0.115 g, 23%) identified by its melting point and IR sprectrum; (ii) methane **8** (0.181 g, 33%); m.p. 260-1 °C, identified by its melting point and IR spectrum.

Bis(pentachlorophenyl)[2,4,6-trichloro-3,5-(dichloromethyl)phenyl]methane (**10**). A mixture of triphenylmethane **7** (1.11 g), anhydrous $AlCl_3$ (2.19 g) and anhydrous $CHCl_3$ (49 mL) was refluxed for 20 h. The solution was poured into an excess of ice-water and extracted with more $CHCl_3$. The extract was evaporated to dryness and the residue in hexane was passed through silica gel, to yield **10** (1.22 g, 89%), m.p. 256-8 °C (recrystallized from ethanol-hexane, 6:1) (Found: C, 29.5; H, 0.4; Cl, 70.1. $C_{21}H_3Cl_{17}$ requires C, 29.4; H, 0.4; Cl, 70.3%); $\lambda_{max}(C_6H_{12})$ 228, 255sh, 295 and 304 nm (ε 110 290, 38 250, 3300, 3120); ν_{max}(KBr) 3050, 2930, 1540, 1370, 1350, 1325, 1310, 1285, 1225, 1110, 1025, 1005, 805, 795, 775, 730, 715, 710, 685, 665, 645, 635, 625, 610 and 605 cm^{-1}.

5-[Bis(pentachlorophenyl)methyl]-2,4,6-trichlorobenzene-1,3--dicarboxyaldehyde (**11**). A mixture of **10** (0.9 g) and 30% oleum (20 mL) was stirred (5 h) at 95 °C. The final solution was poured into an excess of ice-water and the resulting mixture was extracted with $CHCl_3$. The extract was evaporated to dryness, and the residue in hexane: $CHCl_3$ (1:1) was passed through silica gel to give **11** (0.752 g, 87%), m.p. 260-4 °C; (Found: C, 34.0; H, 0.6; Cl, 61.6. $C_{21}H_3Cl_{13}O_2$ requires C, 33.7; H, 0.5; Cl, 61.6%); $\lambda_{max}(C_6H_{12})$ 208, 238sh, 294 and 304 nm 323sh (ε 16 580, 80.600, 4310, 4760, 2630); ν_{max}(KBr) 2940, 2910, 2850, 1705, 1530, 1365, 1350, 1330, 1290, 1230, 1180, 1110, 1010, 985, 955, 890, 800, 705, 680, 665 and 640 cm^{-1}.

5-[Bis(pentachlorophenyl)methyl]-2,4,6-trichlorobenzene-1,3-dicarboxylic Acid (**12**). A solution of CrO_3 (0.732 g) in water (43 mL) was added dropwise at room temperature to another solution of **11** (0.70 g) in acetone (136 mL) and sulfuric acid (5 mL). The final green solution was left for 4 h and then poured into an excess of ice-water. The mixture was extracted with $CHCl_3$ and the organic solution was treated with a saturated aqueous $NaHCO_3$ solution. The aqueous solution acidified with an excess of hydrochloric acid was extracted with $CHCl_3$, and the organic solution evaporated to dryness gave the dicarboxylic acid **12** (0.62 g, 85%), m.p. 233-45 °C; (Found: C, 32.3; H, 0.5; Cl, 59.2. $C_{21}H_3Cl_{13}O_4$ requires C, 32.3; H, 0.4; Cl, 59.1%); $\lambda_{max}(C_6H_{12})$ 241, 255sh, 282, 293 and 303 nm (ε 53 570, 27 860, 3210, 3150, 2120); ν_{max}(KBr) 3680-2800, 1730, 1555, 1365, 1340, 1305, 1235, 1200, 1115, 920, 805, 715, 690, 675, 645, 625 and 605 cm^{-1}.

Dimethyl 5-[bis(pentachlorophenyl)methyl]-2,4,6-trichlorobenzene-1,3-dicarboxylate (**13**).- An excess of CH_2N_2 in diethyl ether was added dropwise to a solution of acid **12** (0.20 g) in diethyl ether (21 mL), and the final solution was evaporated to dryness to give a residue (0.19 g) which by recrystallization from hexane afforded **13** (0.11 g, 52%), m.p. 200-4 °C (Found: C, 34.1; H, 0.9; Cl, 56.8. $C_{23}H_7Cl_{13}O_4$ requires C, 34.2; H, 0.9; Cl, 57.0%); λ_{max}(C_6H_{12}) 221, 237sh, 251sh and 293 (ε 31 181, 67 094, 31 181, 1211); ν_{max}(KBr) 2920, 1740, 1550, 1445, 1425, 1365, 1350, 1335, 1310, 1300, 1290, 1220, 1195, 1170, 1160, 1110, 980, 930, 875, 810, 795, 760, 705, 675, 665 and 635 cm^{-1}.

Bis(pentachlorophenyl)(2,4,6-trichloro-3-nitrophenyl)methyl radical (**1**). An aqueous solution of tetra-*n*-butylammonium hydroxide (1.5 M, 0.39 mL) was added to a solution of **8** (0.30 g, 0.4 mmol) and THF (45 mL) and the resulting solution was left in the dark at room temperature under an argon atmosphere for 24 h. Then *p*-chloranil (0.41 g) was added and left for an additional time (2 h). The reaction mixture was dried at low pressure and the residue treated with CCl_4 at reflux. The organic solution was filtered and dried at low pressure to give a new residue which was flash cromatographed [silica gel; CCl_4-hexane (3:2)] giving after recryistallitation from hexane, radical **1** (0.155, 52%); m.p. 255-8 °C; (Found: C, 31.0; H, 0.2; Cl, 62.6; N, 1.9. $C_{19}HCl_{13}NO_2$ requires C, 31.0; H, 0.1; Cl, 62.6; N, 1.9%); λ_{max}(C_6H_{12}) 219, 283sh, 362sh, 382, 511, 562 nm (ε 87 180, 5655, 17 050, 34 410, 1040, 1020); ν_{max}(KBr) 3070, 1550, 1520, 1415, 1330, 1305, 1255, 1235, 1175, 1125, 1115, 1015, 900, 865, 835, 810, 790, 750, 735, 725, 705, 685, 660 and 625 cm^{-1}.

Bis(pentachlorophenyl)(2,4,6-trichloro-3,5-dinitrophenyl)methyl radical (**2**). The reaction was carried out according to the preceeding procedure. Starting materials: aqueous solution of tetra-*n*-butylammonium hydroxide (1.5 M, 0.17 mL), methane **9** (0.065 g, 0.08 mmol), THF (10 mL). Reaction time: 18 h. *p*-Chloranil (0.073g). Reaction time: 2 h. The reaction mixture was worked up as before, and the residue purified as above to give radical **2** (0.024 g, 37%); m.p. 289-90 °C (Found C, 29.4; Cl, 58.9; N, 3.5. $C_{19}Cl_{13}N_2O_4$ requires C, 29.2; Cl, 59.0; N, 3.6%); λ_{max}(C_6H_{12}) 218, 286sh, 369sh, 384, 515 and 570 nm (ε 94 220, 4530, 1450, 25360, 940, 1010); ν_{max}(KBr) 1540, 1330, 1300, 1255, 935, 820, 775, 745, 715,705, 680, 645 and 615 cm^{-1}.

(3,5-Dicarboxy-2,4,6-trichlorophenyl)bis(pentachlorophenyl)methyl Radical (**3**).- The reaction was carried out according to the synthesis of radical **1**. Starting materials: aqueous solution of tetra-*n*-butylammonium hydroxide (1.5 M, 1.1 mL), **12** (0.24 g, 0.3 mmol), THF (35 mL). Reaction time: 18 h. *p*-Chloranil (0.073 g, 0.3 mmol). Reaction time: 2 h. The reaction mixture was dried at low pressure and the residue treated with $CHCl_3$ and the organic solution with saturated aqueous $NaHCO_3$. The aqueous solution, acidified with an excess of aqueous HCl acid and extracted with $CHCl_3$, gave radical **3** (0.06 g, 25%), m.p. 271-3 °C (Found C, 32.4; H, 0.6. $C_{21}H_2Cl_{13}O_4$ requires C, 32.4; H, 0.3%); λ_{max}(C_6H_{12}) 282sh, 365sh, 382, 506 and 559 nm (ε 5410, 13 330, 28 700, 1010, 995); ν_{max}(KBr) 3700-2300, 1730, 1540, 1515, 1335, 1310, 1260, 1240, 1110, 920, 810, 715, 710, 660, 645 and 620 cm^{-1}.

Bis(pentachlorophenyl)[2,4,6-trichloro-3,5-bis(chlorocarbonyl)phenyl]methyl Radical (**5**).- A solution of radical **3** (0.17 g) in $SOCl_2$ (15 mL) was refluxed (24 h) and then the solvent evaporated off. The residue was passed in hexane through silica gel and then recrystallized from hexane to yield radical **5** (0.07 g, 38%), m.p. 260-3 °C; (Found: C, 31.0; Cl, 65.1. $C_{21}Cl_{15}O_2$ requires C, 30.9; Cl, 65.2%); $\lambda_{max}(C_6H_{12})$ 222, 282sh, 366sh, 383, 514 and 567 nm (ε 86 220, 5910, 19 130, 36 480, 1120, 1155); ν_{max}(KBr) 1770, 1520, 1495, 1360, 1340, 1320, 1300, 1245, 1200, 1120, 1060, 1015, 995, 895, 815, 800, 795, 780, 730, 705, 695, 675, 645, 635 and 615 cm^{-1}.

Bis(pentachlorophenyl)[2,4,6-trichloro-3,5-bis(methoxycarbonyl)phenyl]methyl Radical (**4**).- The reaction was carried out in a similar manner to the synthesis of radical **1**. Starting materials: compound **13** (0.2 g); THF (28 mL); tetra-*n*-butylammonium hydroxide (1.5 M, 0.15 mL). Reaction time: 2 h. *p*-Chloranil (0.07 g, 0.3 mmol). Reaction time: 2 h. The reaction mixture was evaporated to dryness, and the residue in CCl_4-$CHCl_3$ (70:30) was passed through silica gel to give radical **4** (0.09 g, 48%), m.p. 188-92 °C; (Found: C, 34.2; H, 0.7; Cl, 56.9. $C_{23}H_6Cl_{13}O_4$ requires C, 34.2; H, 0.8; Cl, 57.1%); $\lambda_{max}(C_6H_{12})$ 218, 280sh, 382, 505 and 558 nm (ε 99 610, 5150, 34 310, 920, 910); ν_{max}(KBr) 2940, 1745, 1735, 1535, 1525, 1510, 1445, 1430, 1350, 1325, 1300, 1250, 1210, 1170, 1165, 1105, 1040, 980, 935, 880, 805, 800, 715, 705, 680, 650 and 610 cm^{-1}.

ACKNOWLEDGMENTS

This work was supported by DGICYT of MEC (Spain) through project PB92-0031. The authors express their gratitude to Mrs. Avencia Diez from the ESR service of Centre d'Investigació i Desenvolupament (CSIC) in Barcelona.

REFERENCES

1. Mataga, N. *Theoret. Chim. Acta* **1968**, *10*, 372. Ouchinnikov, A. A. *Theoret. Chim. Acta*, **1978**, *47*, 297. Itoh, K. *Pure Appl. Chem.*, **1978**, *50*, 1251. Iwamura, H. *Pure Appl. Chem.*, **1986**, *58*, 187. J. Miller, S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.*, **1988**, *88*, 201. Iwamura, H. *Adv. Phys. Org. Chem.*, **1990**, *26*, 179. Miller, J. S.; Epstein, A.J. *Angew. Chem., Int. Ed. Engl.*, **1994**, *33*, 385.
2. Ballester, M. *Acc. Chem. Res.*, **1985**, *18*, 380. Ballester, M. *Adv. Phys. Org. Chem.*, **1989**, *25*, 267 and references cited therein.
3. a) Ballester, M.; Riera, J.; Castañer, J.; Badia, C.; Monsó, J. M. *J. Am. Chem. Soc.*, **1971**, *93*, 2215. b) Armet, O.; Veciana, J.; Rovira, C.; Riera, J.; Castañer, J.; Molins, E.; Rius, J.; Miravitlles, C.; Olivella, S.; Brichfeus J. *J. Phys. Chem.*, **1987**, *91*, 5608. c) Juliá, L.; Ballester, M.; Riera, J.; Castañer, J.; Ortin, J. L.; Onrubia, C. *J. Org. Chem.*, **1988**, *53*, 1267. d) Ballester, M.; Riera, J.; Castañer, J.; Carreras, C.; Ubierna, J. J.; Badia, C.; Miravitlles, C.; Molins. E. *J. Org. Chem.*, **1989**, *54*, 4611. e) Ballester, M.; Pascual, I.; Torres, J. *J. Org. Chem.*, **1990**, *55*, 3035. f) Ballester, M.; Pascual, I.; Riera, J.; Castañer, J. *J. Org. Chem.*, **1991**, *56*, 217. g) Ballester, M.; Pascual, I. *J. Org. Chem.*, **1991**, 841.

h) Juliá, L.; Riera, J.; Teixidó, R. *J. Chem. Soc., Perkin Trans. 1*, **1991**, 1101.

4. Carilla, J.; Juliá, L.; Riera, J.; Brillas, E.; Garrido, J. A.; Labarta, A.; Alcalá, R. *J. Am. Chem. Soc.*, **1991**, *113*, 8281. Chaler, R.; Carilla, J.; Brillas, E.; Labarta, A.; Fajarí, Ll.; Riera, J.; Juliá, L. *J. Org. Chem.*, **1994**, *59*, 4107. Carilla, J.; Fajarí, Ll.; Juliá, L.; Riera, J.; Viadel, Ll. *Tetrahedron Lett.* **1994**, *35*, 6529.
5. Ichimura, A. S.; Ochiai, K.; Koga, N.; Iwamura, H. *J. Org. Chem.*, **1994**, *59*, 1970.
6. Ballester, M.; Pascual, I.; Carreras, C.; Vidal-Gancedo, J. *J. Am. Chem. Soc.*, **1994**, *116*, 4205.
7. Ballester, M.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *Synthesis*, 1986, 64.
8. Galus, Z. *Fundamentals of Electrochemical Analysis*. Horwood Chichester, 1976; chapt. 7.
9. Etter, M. C. *Acc. Chem. Res.*, **1990**, *23*, 120.
10. Domingo, V. M.; Castañer, J.; Riera, J.; Labarta, A. *J. Org. Chem.*, **1994**, *59*, 2604.
11. Foex, G.; Gorter, C.; Smith, L. J. *Constants Selectionées. Diamagnetisme et Paramagnetisme, Relaxation Paramagnetique*. Masson et Cie: Paris, 1957; pp 222-225.

(*Received in UK* 31 *March* 1995; *revised* 28 *April* 1995; *accepted* 5 *May* 1995)