Inert Carbon Free Radicals. 11. Synthesis and Magnetic Behavior of (4,4′-Dicarboxytridecachlorotriphenyl)methyl Radical and Related Results

V. M. Domingo, J. Castañer,* and J. Riera*

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

A. Labarta

Departamento de Física de Estado Sólido, Facultad de Física, Universidad de Barcelona, Avda. Diagonal 647, 08028 Barcelona, Spain

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The syntheses of the title radical, its dimethyl ester, and 4*H*,4′*H*-(tridecachlorotriphenyl)methyl radical are described. Their ESR spectra and magnetic susceptibilities are reported and commented upon.

Introduction

Organic stable free radicals of the perchlorotriphenylmethyl (PTM) series are exceptionally stable, both chemically and thermally.[1] Usually, they follow the Curie–Weiss law with negative or near-zero values of the Weiss constant (θ).[1b–e] Positive values of θ are of great interest because they suggest ferromagnetic interactions and even the possibility of ferromagnetism at low temperatures.[2] Although intermolecular interactions have been found to be usually very small and at best antiferromagnetic, there are few examples in the literature of free radicals with ferromagnetic interactions.[3] In some of them, the magnetic behavior has been correlated with their X-ray structure in terms of McConnell's model.[4] Recently, a nitroxide radical in which the three-dimensional network has been obtained through hydrogen bondings has been published by Veciana et al.[5] Since the Weiss constant of (4-carboxytetradecachlorotriphenyl)methyl radical is positive (+0.9 K),[1b] and the presence of two carboxy groups in (4,4′-dicarboxytridecachlorotriphenyl)methyl radical (**16**) would increase the possibility of intermolecular hydrogen bondings, it was decided to synthesize radical **16** in order to obtain a two- or three-dimensional molecular framework where the ferromagnetic interactions might be present.

Results and Discussion

Synthesis of Precursors. The synthesis of αH-(nonadecachloro-4,4′-dimethyltriphenyl)methane (**4**),[6] a precursor of dicarboxy radical **16**, was attempted by two different methods: (a) The new trifluoromethylating reagent (CCl_3F–$AlCl_3$) for the synthesis of highly chlorinated trifluoromethylbenzenes[7] suggested the route **1** → **2** → **4** outlined in Scheme 1. Unfortunately, the trifluoromethylation of **1** to **2** with this reagent did not work; compound **1** was recovered in practically quantitative yield. Since it is known that the free-radical character increases the reaction rates in highly chlorinated triphenylmethyl radicals,[1d] the trifluoromethylation of 4*H*,4′*H*-(tridecachlorotriphenyl)methyl radical (**3**) to radical **5** with the same reagent was attempted for the purpose of converting **5** into dicarboxy radical **16**. However, this trifluoromethylation reaction did not work either, radical **3** being recovered in very high yield. Starting radical **3** was synthesized by treatment of triphenylmethane **1**[8] with tetrabutylammonium hydroxide, followed by oxidation of the resulting carbanion with *p*-chloranil (a one-pot reaction already used for the synthesis of other PTM radicals).[1e]

(b) In view of the above negative results, the more complex synthetic route shown in Scheme 2 for the synthesis of **4** was performed.[9] This route is analoguous to that developed for the synthesis of αH-(heptadecachloro-4-methyltriphenyl)methane (**9**).[1b]

The photochemical chlorination of (4,4′-dimethyltriphenyl)methane (**6**) with Cl_2 and white light gave α-chloro-(4,4′-bis(trichloromethyl)triphenyl)methane (**7**), which was selectively reduced with $LiAlH_4/AlCl_3$[12] to (4,4′-bis-(trichloromethyl)triphenyl)methane (**8**). Controlled aromatic perchlorination of **8** with reagent BMC (initial components: $AlCl_3$, S_2Cl_2 and SO_2Cl_2)[13] afforded a complex

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(3) (a) Kosaki, A.; Suga, H.; Seki, S.; Mukai, K.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1525. Mukai, K.; Sogabe, A. *J. Chem. Phys.* **1980**, *72*, 598. (b) Awaga, K.; Maruyama, Y. *J. Chem. Phys.* **1989**, *91*, 2743. (c) Benoit, A.; Flouquet, J.; Gillon, B.; Schweizer, J. *J. Magn. Magn. Mater.* **1983**, *31–3*, 1155. (d) Ciarelli, R.; Rassat, A.; Rey, P., *J. Chem. Soc., Chem. Commun.* **1992**, 1081. (d) Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. M. *Chem. Phys. Lett.* **1991**, *186*, 401. (e) Allemand, P. M.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1990**, *112*, 9391.

(4) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

(5) Hernàndez, E.; Mas, M.; Molins, E.; Rovira, C.; Veciana, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 882.

(6) For the sake of clarity, the nomenclature here used for highly chlorinated compounds is a most convenient extension of the IUPAC "indicated hydrogen" recommendations.

(7) (a) Riera, J.; Castañer, J.; Carilla, J.; Robert, A. *Tetrahedron Lett.* **1989**, *30*, 3825. (b) Castañer, J.; Riera, J.; Carilla, J.; Robert, A.; Molins, E.; Miravitlles, C. *J. Org. Chem.* **1991**, *56*, 103.

(8) Ballester, M.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *Synthesis* **1986**, *1*, 64.

(9) Fragmentary data about the synthesis of compound **4**,[10a,11] dicarboxylic acid **10**,[10a] and diesters **12**[10a] and **17**[10c] have already been reported.

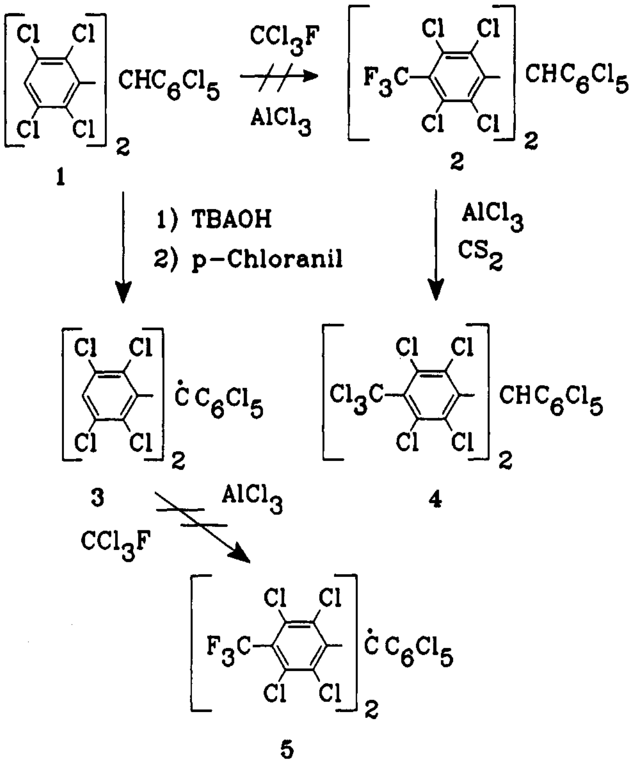
(10) Ballester, M.; Olivella, S. In *Polychloroaromatic Compounds*; Suschitzky, H., Ed.; Plenum: New York, 1974; (a) p 161; (b) p 160; (c) p 143.

(11) Ballester, M.; Castañer, J.; Riera, J.; *U.S. Clearinghouse Fed. Sci. Tech. Inform.* **1968**, AD 672319, Avail. CFSTI; *Chem. Abstr.* **1969**, *70*, 46980t.

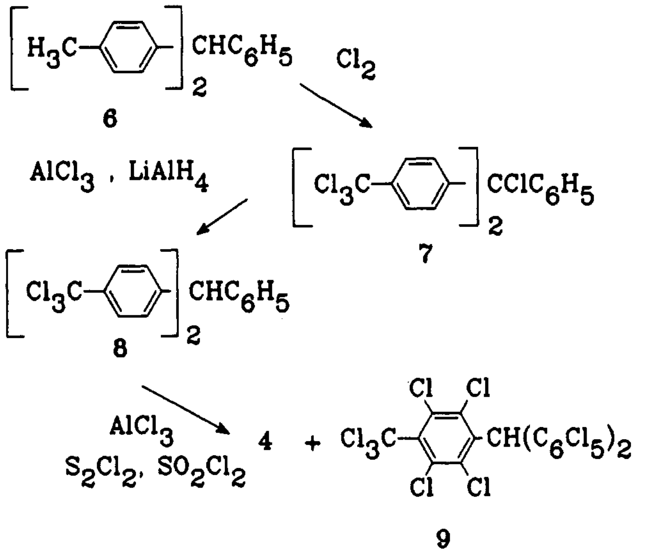
(12) In the absence of $AlCl_3$, partial reduction of the CCl_3 groups also takes place.

0022-3263/94/1959-2604$04.50/0

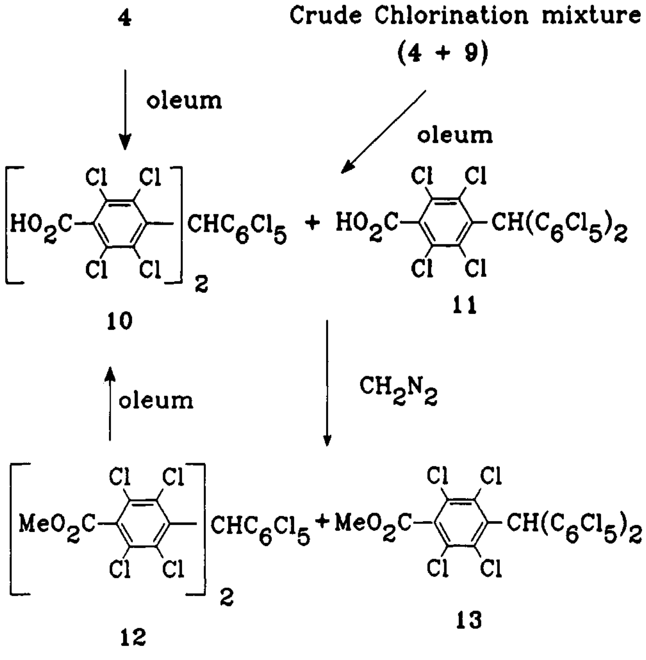
Scheme 1



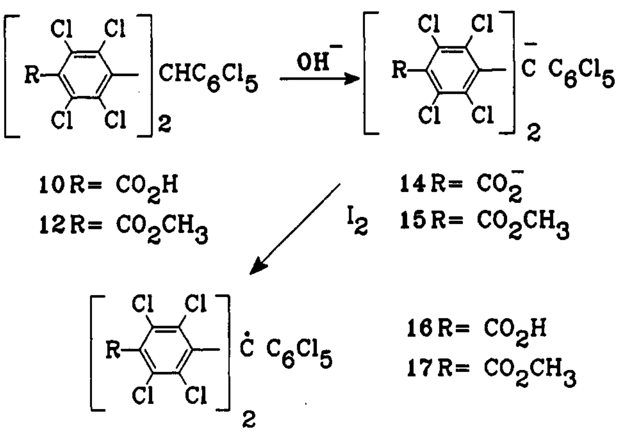
Scheme 2



Scheme 3



Scheme 4



mixture (see Experimental Section) from which bis(trichloromethyl) compound 4 (25%) along with mono(trichloromethyl) compound 9 (9.7%) and other chlorinated byproducts were isolated.

The hydrolysis of bis(trichloromethyl) compound 4 gave *αH*-(tridecachlorotriphenyl)methane-4,4′-dicarboxylic acid (10),[9] the immediate precursor of dicarboxy radical 16. However, since the overall yield of 10 starting from 8 was very low (21%) due to the cumbersome isolation of 4[14] from the chlorination mixture, it was decided to perform the hydrolysis of this mixture (after some purification) and then the separation of 10 either directly (30%) or through its methyl ester (33%) (Scheme 3).

Synthesis of Radicals 16 and 17. The synthesis of dicarboxy radical 16 from 10 through the formation of the corresponding trianion 14 and subsequent oxidation with I_2 (Scheme 4) presented "a priori" two major difficulties: (1) the formation of this trianion might be difficult and (2) the possibility of a competitive decarboxylative iodination of 14 could occur, since a similar process was observed in the synthesis of (4-carboxytetradecachlorotriphenyl)methyl radical by oxidation of the corresponding dianion with I_2.[1b] The first difficulty was overcome by using powdered NaOH and pure DMSO as solvent (instead of THF, alone or in admixture with DMSO). The second one was surmounted by using the theoretical amount (or a slight excess) of I_2 and short reaction times.

(4,4′-Bis(methoxycarbonyl)tridecachlorotriphenyl)methyl radical (17) was synthesized from the corresponding triarylmethane (12) by means of a one-pot reaction using tetrabutylammonium hydroxide–THF for the formation of carbanion 15 and I_2 as oxidant.

Isotropic ESR Spectra in Solution. Dicarboxy radical 16 and diester radical 17 show a single main line (line widths of 1.96 and 1.15 G, respectively). The *g* factors are identical (2.0026). Both radicals present one pair of α-^{13}C satellites (a = 31.75 and a = 30.1 G, respectively)

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

[14] The low solubility of compounds 4 and 9 in hexane (the eluent of the flash chromatography) as well as the similarity of their R_fs in this solvent make their separation very difficult. More polar solvents make both R_fs practically identical.

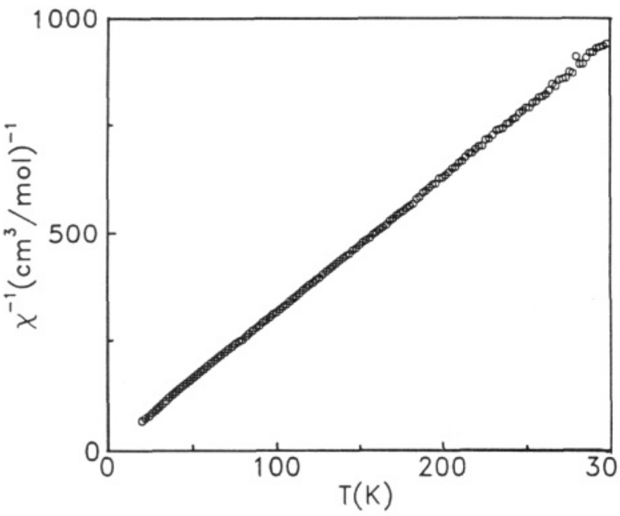

Figure 1. Thermal dependence of the molar paramagnetic susceptibility of radical **16**.

and aromatic ^{13}C satellites (one pair in the case of diacid **16** (a = 13.1 G) and two pairs in the case of diester **17** (a = 10.5 and 12.9 G)). Radical **3** shows three lines (1:2:1, line width = 1.0 G) due to the coupling with the two hydrogen atoms of the molecule (a_H = 1.9 G). The g factor is also 2.0026. The α-^{13}C splitting is 29.9 G, and the aromatic ^{13}C splittings are 9.9 and 12.6 G. In all these radicals the g values and the hyperfine couplings with the ^{13}C do not differ significantly from those of the PTM series,[1] as expected.

Magnetic Susceptibility of Dicarboxy Radical 16. The molar magnetic susceptibility (χ_M) of the title radical was measured in the interval 20–300 K. The experimental data were corrected ($\chi_M - \chi_{dia} = \chi'_M$) for the diamagnetic susceptibility of the molecule ($\chi_{dia} = -0.528.10^{-6}$ emu) which was theoretically estimated by using Pascal's systematics.[15] The thermal variation of $1/\chi'_M$ is shown in Figure 1. For the whole range of studied temperatures, the corrected experimental data follow the Curie–Weiss law. From these data, a molar Curie constant of 0.3170 ± 0.0004 cm^3 K mol^{-1}, which is in agreement with the existence of one radical center per molecule, and a Weiss constant of +0.4 ± 0.3 K, which may be associated to the existence of weak ferromagnetic interactions among the radical centers of neighboring molecules, were estimated. These results rule out the possibility of the presence of a two- or three-dimensional framework with strong ferromagnetic interactions.[16]

Experimental Section

General Methods. Perkin-Elmer 682, Perkin-Elmer Lambda Array 3840, Bruker WP 80 SY, and Varian E112E spectrometers were used for IR, UV–vis, ^1H NMR, and ESR spectroscopy, respectively. The routine magnetic susceptibilities were measured with a Varian 4-in. magnet with constant-force caps operating at 8 KOe, and a Cahn RG electrobalance. More precise data were collected with a Faraday balance magnetometer in the range 20–300 K, operating with a field strengh of 20 KOe. The data were corrected for the magnetization of the sample holder. Since the locations of the IR peaks of highly chlorinated compounds differ markedly from their nonchlorinated counterparts they are included in this section, although weak peaks in the region 1300–400 cm^{-1} are not given.

***αH,4H,4′H*-(Tridecachlorotriphenyl)methane (1).** This compound was prepared by Friedel–Crafts condensation between αH-heptachlorotoluene and 1,2,4,5-tetrachlorobenzene, using the method described by Ballester et al.[8]

***4H,4′H*-(Tridecachlorotriphenyl)methyl Radical (3).**[17] Tetrabutylammonium hydroxide (40% in water) (4 mL) was added to a solution of $\alpha H,4H,4'H$-(tridecachlorotriphenyl)methane (**1**) (3.21 g) in purified THF (1 L), and the resulting mixture was stirred at room temperature for 24 h. Then p-chloranil (2.0 g) was added, and the stirring was continued for 24 h. The resulting brown solution was concentrated (500 mL) and diluted with water (500 mL) to give a solid precipitate which was filtered, passed through silica gel (hexane), and recrystallized (from the same solvent) affording radical **3** (2.74 g, 85%) as dark-red crystals: mp 243–4 °C; IR (KBr) 3150 (w), 1535 (w), 1377 (s), 1350 (m), 1330 (s), 1323 (s), 1255 (s), 1245 (m), 1165 (s), 1010 (m), 860 (m), 732 (m), 700 (s), 660 (m), 628 (m), 495 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 285, 330 (sh), 360 (sh), 376, 480, 550 nm (ϵ 6090, 5820, 16 500, 29 500, 1010, 820); ESR (CCl_4) (see Results and Discussion). Magnetic susceptibility $\chi_{dia} = -0.525 \times 10^{-6}$ emu, $\theta = -7.8$ K, $\mu_{eff} = 1.73$ (spins/mol = 6.02×10^{23}), purity 100%. Anal. Calcd for $C_{19}H_2Cl_{13}$: C, 33.0; H, 0.3; Cl, 66.7. Found: C, 33.1; H, 0.3; Cl, 66.7.

Attempted Trifluoromethylation of *αH,4H,4′H*-(Tridecachlorotriphenyl)methane (1). A mixture of triphenylmethane **1** (1.12 g), anhydrous $AlCl_3$ (4.0 g), and CCl_3F (40 mL) was stirred at room temperature in a pressure vessel for 8 h (the internal pressure rises to 1.5 atm). Then the mixture was cooled to −10 °C (to eliminate overpressure), $AlCl_3$ (4.0 g) was added, and the stirring was continued at room temperature for 24 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness giving a residue of slightly impure **1** (1.038 g) identified by its IR spectrum.

Attempted Trifluoromethylation of *4H,4′H*-(Tridecachlorotriphenyl)methyl Radical (3). This radical was treated as **1** (preceding attempt) but in the dark. Starting materials: **3** (2.74 g), $AlCl_3$ (5.2 g + 5.2 g), and CCl_3F (100 mL). The residue obtained was slightly impure radical **3** (2.65 g), identified by its IR spectrum.

(4,4′-Dimethyltriphenyl)methane (6). This compound was prepared by condensation between benzaldehyde and toluene by means of concentrated H_2SO_4 using the method of Kliegel.[18]

***α*-Chloro(4,4′-bis(trichloromethyl)triphenyl)methane (7).** A slow stream of dry Cl_2 was passed (6 h) through a gently refluxing solution of triphenylmethane **6** (48.9 g) in purified CCl_4 (1.6 L) while it was illuminated with an incandescent lamp (500 W) situated underneath the Pyrex container, thus providing the heat. The end point of the chlorination was monitorized by ^1H NMR spectroscopy. Elimination of the solvent afforded a yellow resin (115.8 g) which by recrystallization from hexane gave **7** (74.7 g, 81%): mp 135–6 °C; IR (KBr) 3060 (w), 1935 (w), 1485 (m), 1445 (s), 1400 (s), 1200 (s), 1180 (s), 1020 (m), 865 (s), 795 (s), 755 (s), 740 (s), 700 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} 237 nm (ϵ 25 120); ^1H NMR (CCl_4) δ 7.85 (d, 4, J = 9 Hz, o-CCl_3), 7.30 (d, 4, J = 9 Hz, m-CCl_3), 7.25 (m, 5, ArH). Anal. Calcd for $C_{21}H_{13}Cl_7$: C, 49.1; H, 2.5; Cl, 48.3. Found: C, 49.2; H, 2.6; Cl, 48.3.

(4,4′-Bis(trichloromethyl)triphenyl)methane (8). α-Chloro compound **7** (15.0 g, 29 mmol) was added to a solution of $LiAlH_4$ (0.99 g, 26 mmol) and anhydrous $AlCl_3$ (7.2 g, 54 mmol) in anhydrous ethyl ether (1.3 L), and the mixture was refluxed (5 h) under argon. The end point was monitored by ^1H NMR spectroscopy. After cooling, ice–water was added slowly. Evaporation of the solvent gave a yellow resin (15.2 g) which was passed through silica gel (hexane) and recrystallized (from the same solvent) to give **8**, (12.1 g, 86%); mp 121–3 °C; IR (KBr) 3060 (w), 3010 (w), 2870 (w), 1600 (m), 1500 (m), 1490 (s), 1445 (s), 1410 (s), 1190 (s), 1175 (s), 1020 (m), 880 (s), 870 (s), 860 (s), 845 (s), 815 (s), 785 (s), 755 (s), 730 (s), 710 (s), 530 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 235 nm (ϵ 25 600); ^1H NMR (CCl_4) δ 7.85 (d, 4, J = 9 Hz, o-CCl_3), 7.18 (d, 4, J = 9 Hz, m-CCl_3), 7.25 (m, 5, ArH), 5.60 (s, 1, CH). Anal. Calcd for $C_{21}H_{14}Cl_6$: C, 52.6; H, 2.9; Cl, 44.4 Found: C, 52.6; H, 2.9; Cl, 44.2.

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[15] Hellwege, K., Hellwege A., Eds. *Landolt-Börnstein II. Diamagnetic Susceptibility*; Springer-Verlag: Berlin, 1977; Vol. 16, p 1.

[16] Unfortunately, no crystals suitable for X-ray analysis could be obtained.

[17] The synthesis of this radical and the handling of its solutions were performed in the dark.

[18] Kliegel, A. *Chem. Ber.* **1904**, *37*, 92.

***αH*-(Nonadecachloro-4,4′-dimethyltriphenyl)methane (4).** A solution of bis(trichloromethyl) compound 8 (5.20 g) and S_2Cl_2 (2.58 g) in SO_2Cl_2 (100 mL) was added slowly to a refluxing solution of anhydrous $AlCl_3$ (1.53 g) in SO_2Cl_2 (325 mL). The resulting dark red solution was concentrated (2 h) to about 40 mL and then refluxed for 5 h (occasionally small amounts of SO_2Cl_2 were added to keep the volume constant). Water was added to the mass, and then solid $NaHCO_3$ was added gradually to the mixture until no more gas evolution took place. The resulting mixture was heated on a steam bath, cooled, and acidified with aqueous HCl. The insoluble material was collected, washed with water, and dried to give a solid (11.8 g) (chlorination mixture) which was digested with refluxing ether yielding a residue (6.60 g) that was worked up as follows: An aliquot of this residue (2.00 g) was subjected to flash chromatography (silica gel, hexane) yielding: (a) hexachlorobenzene (0.005 g), identified by its IR spectrum; (b) perchlorotoluene (0.003 g), identified by its IR spectrum;[19] (c) *αH*-(pentadecachloro-4,4′-dimethyldiphenyl)methane[10b,11] (0.011 g), identified by its IR spectrum;[20] (d) *αH*-(heptadecachloro-4-methyltriphenyl)methane (**9**) (0.269 g, 9.7%), identified by its IR spectrum;[1b] (e) an unresolved mixture of **9** and **4** (0.485 g), identified by TLC and IR spectrum; and (f) *αH*-(nonadecachloro-4,4′-dimethyltriphenyl)methane (**4**) (0.758 g, 25%): mp 234 °C dec (from hexane): IR (KBr) 2920 (w), 1525 (w), 1355 (m), 1320 (s), 1280 (s), 1125 (s), 1010 (m), 885 (m), 810 (s), 765 (s), 700 (s), 680 (m), 650 (s), 610 (m), 520 (m), 510 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 219, 307 (sh), 321 nm (ϵ 77 600, 2545, 3650); ^1H NMR (CCl_4) δ 7.06 (s). Anal. Calcd for $C_{21}HCl_{19}$: C, 27.2; H, 0.1; Cl, 72.7. Found: C, 27.2; H, 0.2; Cl, 72.4.

Dimethyl *αH*-(Tridecachlorotriphenyl)methane-4,4′-dicarboxylate (12). An aliquot (2.00 g) of the fraction (6.60 g) (see the preceding reaction) was passed through silica gel (hexane), and the eluate was evaporated to dryness. Then 30% oleum (500 mL) was added to the residue, and the mixture was stirred at 100 °C for 3.5 h. The dark brown solution obtained was poured slowly onto cracked ice, and the white precipitate formed was extracted with ether. The ethereal solution was extracted with aqueous $NaHCO_3$, and the aqueous extract, containing a solid in suspension, was centrifuged. The resulting aqueous solution was acidified with aqueous HCl and extracted with ether, and the ethereal extract was treated with CH_2N_2. Evaporation of the volatile parts of the resulting solution gave a residue (1.68 g) which was subjected to flash chromatography (silica gel, CCl_4) yielding: (a) methyl *αH*-(tetradecachlorotriphenyl)methane-4-carboxylate (**13**) (0.041 g), identified by its IR spectrum;[1b] and (b) dimethyl *αH*-(tridecachlorotriphenyl)methane-4,4′-dicarboxylate (**12**) (1.64 g, 46%), mp 210–2 °C; IR (KBr) 2950 (w), 1750 (s), 1550 (w), 1430 (m), 1370 (m), 1340 (m), 1325 (m), 1295 (m), 1260 (s), 1220 (s), 1200 (m), 1170 (m), 1115 (m), 960 (m), 845 (m), 835 (m), 805 (m), 785 (m), 760 (m), 745 (m), 725 (m), 675 (m), 650 (m), 610 (m), 570 (m), 520 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 222, 244 (sh), 283 (sh), 293, 301 nm (ϵ 105 300, 44 130, 2140, 2790, 2980); ^1H NMR (CCl_4) δ 4.01 (6, CH_3), 7.00 (1, CH). Anal. Calcd for $C_{23}H_7Cl_{13}O_4$: C, 34.1; H, 0.9; Cl, 57.1. Found: C, 34.1; H, 0.8; Cl, 56.9. The centrifuged solid was treated with aqueous HCl and extracted with ether, and the resulting ethereal solution was treated with CH_2N_2. Evaporation of the resulting solution gave a residue (0.260 g) which was purified through silica gel in CCl_4 giving ester **13** (0.240 g), identified by its mp and IR spectrum. The overall yield in **13** was 8.2%.

***αH*-(Tridecachlorotriphenyl)methane-4,4′-dicarboxylic Acid (10). (1) By Hydrolysis of Compound 4.** A mixture of **4** (0.750 g) and 30% oleum (125 mL) was stirred at 100 °C for 4 h. The resulting dark brown solution was poured slowly onto cracked-ice, and the white precipitate formed was extracted with ether. The ethereal solution was extracted with aqueous $NaHCO_3$, the aqueous extract was acidified with aqueous HCl, and the precipitate formed was extracted with ether. Evaporation of the solvent gave a solid (0.582 g) which by recrystallization from ether–hexane afforded dicarboxylic acid **10** (0.533 g, 84%); mp 318–9 °C; IR (KBr) 3550–2800 (m), 1750 (s), 1735 (s), 1550 (w), 1370 (s), 1330 (s), 1300 (s), 1210 (m), 1180 (s), 1120 (m), 810 (m), 715 (m), 690 (m), 610 (m), 530 (m) cm^{-1}; UV (MeOH) λ_{max} 220, 253 (sh), 288 (sh), 300 nm (ϵ 100 200, 30 980, 2470, 1560); ^1H NMR (C_3D_6O) δ 7.16 (s, 1, CH), 6.81 (s, 2, CO_2H). Anal. Calcd for $C_{21}H_3Cl_{13}O_4$: C, 32.3; H, 0.4; Cl, 59.1. Found: C, 32.5; H, 0.4; Cl, 59.4.

(2) By Hydrolysis of Diester 12. A mixture of diester **12** (0.343 g) and 30% oleum (60 mL) was stirred at 115 °C for 4 h. The resulting dark brown solution was treated as in the preceding hydrolysis yielding dicarboxylic acid **10** (0.234 g, 71%), identified by its mp and IR spectrum.

(3) By Hydrolysis of the Chlorination Mixture of 8. An aliquot (2.00 g) of the fraction (6.60 g) (see the above synthesis of **4**) was treated with oleum as in the synthesis of diester **12**. The solution obtained was poured slowly onto cracked ice, and the mixture was extracted with ether. The ethereal solution was extracted with aqueous $NaHCO_3$, and the aqueous extract, containing a solid in suspension, was centrifuged. The resulting aqueous solution was acidified with aqueous HCl and extracted with ether. The organic extract was then evaporated yielding a solid (1.10 g) which was digested with CH_2Cl_2 and recrystallized from ether–hexane to give dicarboxylic acid **10** (0.77 g, 30%)[21] identified by its IR spectrum. The mother liquors, evaporated to dryness, gave a residue (0.27 g) which was identified (TLC) as a mixture of diacid **10** and monoacid **11** (0.27 g). The centrifuged solid was treated with aqueous HCl and extracted with ether. Evaporation of the resulting ethereal solution gave **11** (0.23 g, 9%),[21] identified by its mp and IR spectrum.[1b]

(Tridecachloro-4,4′-dicarboxytriphenyl)methyl Radical (16).[17] A mixture of diacid **10** (0.150 g, 0.192 mmol), powdered NaOH (0.5 g), and purified DMSO (15 mL) was shaken under argon for 24 h. The red mixture obtained was filtered through a sintered glass funnel over I_2 (0.048 g, 0.190 mmol), and the resulting solution was left undisturbed under argon for 20 min. Then the solution was diluted with aqueous $NaHSO_3$, and the precipitate formed (0.145 g) was filtered and dissolved in aqueous $NaHCO_3$. The resulting aqueous solution was filtered, acidified with aqueous HCl and extracted with ether. The organic layer was evaporated, and the residue recrystallized from ether to give radical **16** (0.136 g, 90%), dark red crystals: mp 295–8 °C dec; IR (KBr) 3500–2900 (m), 1750 (s), 1730 (s), 1530 (w), 1320 (s), 1200 (m), 720 (m), 695 (m), 610 (m) cm^{-1}; UV (MeOH) λ_{max} 288, 340 (sh), 364 (sh), 381, 499, 560 nm (ϵ 5400, 6600, 17 340, 32 750, 1130, 1100); ESR (CCl_4) (see Results and Discussion); magnetic susceptibility: (1) routine data (8 KOe, 77–300 K, 11 points) $\chi_{dia} = -0.500 \times 10^{-6}$ emu, $\theta = +0.9$ K, $\mu_{eff} = 1.64$ (spins/mol = 5.41×10^{23}), purity 90%; (2) more precise data (20 KOe, 20–300 K, 200 points) $\chi_{dia} = -0.528 \times 10^{-6}$ emu (Pascal's systematics[15]), $\theta = +0.4 \pm 0.3$ K; $\mu_{eff} = 1.592 \pm 0.001$ μB (spins/mol = 5.08×10^{23}), purity 84.5%. Anal. Calcd for $C_{21}H_2Cl_{13}O_4$: C, 32.3; H, 0.2; Cl, 59.1. Found: C, 32.4; H, 0.5; Cl, 59.2.

(Tridecachloro-4,4′-bis(methoxycarbonyl)triphenyl)methyl Radical (17).[10,17] Tetrabutylammonium hydroxide (40% in water) (0.10 mL) was added to a solution of diester **12** (0.105 g) in purified THF (15 mL), and the resulting red solution was stirred at room temperature under argon for 6 h. Then I_2 (0.070 g) was added, and the stirring was continued for 1 h. The solution obtained was poured into water–$NaHSO_3$, and the solid precipitate (0.098 g) was filtered and recrystallized from CCl_4–heptane to give radical **17** (0.091 g, 87%) as dark red crystals: mp 239–41 °C dec (lit.[10c] mp 238–9 °C); IR (KBr) 2900 (w), 1745 (s), 1430 (m), 1340 (m), 1320 (s), 1220 (s), 1130 (m), 950 (m), 710 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 289, 332 (sh), 361 (sh), 380, 485, 556 nm (ϵ 6200, 5350, 15 120, 29 380, 1120, 910); ESR (CCl_4), (see Results and Discussion); magnetic susceptibility $\chi_{dia} = -0.427 \times 10^{-6}$ emu, $\theta = +0.8$ K, $\mu_{eff} = 1.73$ (spins/mol = 5.984×10^{23}), purity 99%. Anal. Calcd for $C_{23}H_6Cl_{13}O_4$: C, 34.2; H, 0.7; Cl, 57.1. Found: C, 34.2; H, 0.9; Cl, 57.1.

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(20) Unpublished data. IR spectral data collection of the Departamento de Materiales Orgánicos Halogenados, Centro de Investigación y Desarrollo (CSIC): IR (KBr) 2970 (w), 1525 (w), 1365 (m), 1320 (s), 1285 (m), 1250 (s), 1125 (s), 950 (m), 855 (m), 815 (m), 775 (s), 720 (m), 700 (m), 672 (s), 650 (s), 520 (m), 513 (m) cm^{-1}.

(21) Yield calculated starting from bis(trichloromethyl) compound 7.