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# (2,6-Dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl Radical. Synthesis, Magnetic Behaviour and Crystal Structure

**José Carilla,[a] Lluís Fajarí,[a] and Luis Juliá*[a]**

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

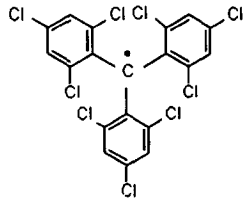
**Joan Sañé,[b] Jordi Rius,[b]**

[b]Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, 08193 Bellaterra, Spain.

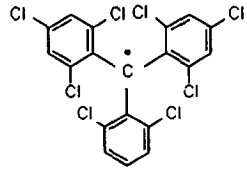
***Abstract:*** (2,6-Dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (**2**) has been prepared through a reaction sequence of five stages obtaining four new intermediate compounds **1-4**. Assignment of the structures of these compounds have been completely ascertained by means of their $^1$H NMR spectra. The new persistent radical **2** has been characterized by EPR spectra and magnetic susceptibility measurements. The X-ray structural analysis of **2** shows that it adopts a propeller-like conformation with the phenyl rings twisted around their bonds to trivalent carbon. Magnetic susceptibility of **2** is characteristic of a paramagnet with a weak antiferromagnetic interaction at low temperatures (Weiss constant, $\Theta$ = -1.8 K). Copyright © 1996 Elsevier Science Ltd

Polychlorotriphenylmethyl radicals are among the most persistent carbon centered free radicals, being assigned as inert free radicals (IFR).[1,2] This persistence is mainly due to steric hindrance of the substituents around the trivalent carbon. All these radicals are completely disassociated either in solid or in solution, and have been characterized by electron paramagnetic resonance (EPR), and some of them even by X-ray diffraction.

At present, our efforts are directed to prepare this kind of polychloroorganic radicals with a minimum content of chlorine, leaving only those indispensable chlorine atoms to stabilize the molecule. In this way, the preparation and stability of tris(2,4,6-trichlorophenyl)methyl (TTM) radical (**1**) and other non-perchloroaromatic radicals were reported by our laboratory some years ago,[2a] and it was ascertained the essential role in the steric hindrance of the *ortho*-chlorines sorrounding the trivalent carbon. More recently, other radicals of the TTM series, prepared by substitution of one *para*-chlorine by other functional groups, have been reported by us.[3] Now, we present the synthesis, stability, crystal structure determination, electronic and EPR spectra of (2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (**2**), a new radical of the TTM series with one free *para*-position.



1

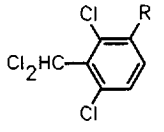


2

## RESULTS

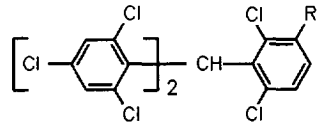
*Synthesis*

We have not been able to obtain (2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methane (**7**) by direct Friedel-Crafts condensation between $\alpha,\alpha$,2,6-tetrachlorotoluene (**3**) and 1,3,5-trichlorobenzene in the presence of $AlCl_3$ as a catalyst. In fact, infusible solids, most probably high oligomers of the auto-condensation of **3**, have been always obtained. The strategy carried out to overcome these difficulties consisted in deactivating the alkylating agent **3** with an electron-withdrawing substituent which could be easily removed in a last stage of the reaction sequence. So, nitration of **3** with nitronium tetrafluoroborate yielded the substituent in a *meta*-position to give $\alpha,\alpha$,2,6-tetrachloro-3-nitrotoluene (**4**), which was characterized by $^1H$ NMR spectrum. **4** afforded (2,6-dichloro-3-nitrophenyl)bis(2,4,6-trichlorophenyl)methane (**5**) in excellent yield in the condensation conditions above formulated. Easy reduction of the nitro group in **5** with $SnCl_2$ in ethanol yielded (3-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methane (**6**). Removal of the amino group through the corresponding diazonium salt, by treating methane **6** with isoamyl nitrite in DMF and then with acid, gave (2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methane (**7**). Radical **2** was prepared from **7** with tetra-*n*-butylammonium hydroxide in THF to generate the anion followed by oxidation with *p*-chloranil. This organic radical **2** was characterized by elemental analysis and spectroscopy. It is stable in air without decomposition. Its stability in solution and in the dark was accomplished by its electronic spectrum. There was no appreciable differences in the absorbance [$\lambda$ nm($\epsilon$): 261(4500), 369(26 000), 486(490), 532(490)] in cyclohexane after one week.



**3** R = H

**4** R = $NO_2$



**5** R = $NO_2$

**6** R = $NH_2$

**7** R = H

*Nuclear Magnetic Resonance*

In aromatic compounds, a dichloromethyl substituent flanked by two *ortho*-chlorines shows a restriction to the free rotation, and a low-strain conformation of the molecule is obtained when the two α-chlorines are located above and below the ring and the hydrogen lies on it.[4] It has been reported that the barrier to rotation of dichloromethyl in 1,3,5-trichloro-2-(dichloromethyl)benzene is 14.9 kcal mol-1.[5]

The *meta* position of the $NO_2$ group in **4** has been ascertained by $^1H$ NMR spectroscopy.In **4**, due to the asymmetry of the molecule, two distinct low-strain conformations with the methyl hydrogen lying on the plane of the molecule are expected: one with the methyl hydrogen proximal to the $NO_2$ group and one with the hydrogen distal to the $NO_2$ group. Therefore, the $^1H$ NMR spectrum of **4** is expected to feature resonances corresponding to both conformers; the two overlapped doublets arising at the lowest field in the aromatic region (δ, 7.76 and 7.70; J, 8.7 Hz) will correspond to the hydrogen *ortho* to the $NO_2$ group, one for each conformer. These signals are doublets because of the coupling with the vicinal-hydrogen. The rest of the spectrum consists of a multiplet (δ, 7.49-7.59) corresponding to the other two hydrogens of the molecule in both conformations.

The structure of the triphenylmethanes **5** and **6** has also been confirmed by a thoroughly analysis of the $^1H$ NMR spectra of both of them. As it has been reported by Mislow *et al.*,[6] symmetrically substituted triarylmethanes with restricted rotation of the phenyl rings around the methine carbon, due to per-substitution in *ortho*-positions have a propeller ($C_3$) conformation in the ground state with the rings twisted on the same sense with respect to the plane defined by the three carbon atoms attached to the central carbon, and may exist in two enantiomeric forms. In this way, *meta*-hydrogens are magnetically non-equivalents and show different chemical shifts. This should be the case for triphenylmethane **7** which shows a singlet at δ 6.74 corresponding to the methine hydrogen and a multiplet at δ 7.11-7.36 corresponding to seven aromatic hydrogens which can not be assigned on account of the complexity of the spectrum.

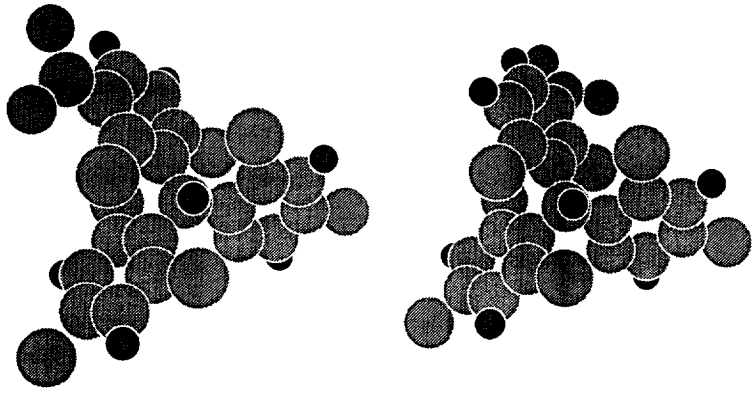


**Figure 1.** Space-filling representation of the structure of the conformers of **5**.

But, as far as methanes **5** and **6** are concerned, an additional feature appears in their NMR analysis

which contributes to make more difficult the assignments of their spectra. This is due to the asymmetry of the third phenyl as a consequence of the *meta*-nitro or *meta*-amino groups. On account of the substitution of a hydrogen by a nitronium ion in *meta*, two low-strain conformations of the molecules are expected for **5** and, consequently, for **6** which are not in equilibrium due to the high activation energy between them. A space-filling representation of the structure of both conformers for **5** are displayed in Figure 1.

In short, it is expected for **5** and **6** the presence of two stable conformers with a pair of enantiomers for each one. So, a rational assignment of the spectrum of **5** (Figure 2) is as follows: two doublets at δ 7.66 and 7.60 corresponding to the *ortho*-hydrogen to the $NO_2$ group in both conformers which are coupled, J = 8.6 Hz, to the vicinal-hydrogen which appears at δ 7.36 and 7.48, respectively. The two *meta*-hydrogens of the other two phenyls have chemical shifts different between them in the same conformation and different for the same hydrogen in the two conformers. In this way, four different doublets appear at δ 7.39, 7.38, 7.26 and 7.25 with a coupling constant for a *meta*-interaction of J = 2.4 Hz. Finally, two very close singlets at δ 6.80 and 6.79 correspond to the methine hydrogen in both conformers. A similar analysis for **6** leads to the following assignment: two coincident doublets at δ 6.69 for the *ortho*-hydrogen to the $NH_2$ group coupled, J = 8.6 Hz, to the vicinal-hydrogen at δ 7.12 and 6.98, for the two conformers. Next, four different doublets at δ 7.36, 7.35, 7.23 and 7.22 with J = 2.0 Hz attributed to the *meta*-hydrogens in the other two phenyls and two singlets at δ 6.70 and 6.68 for the methine hydrogen.

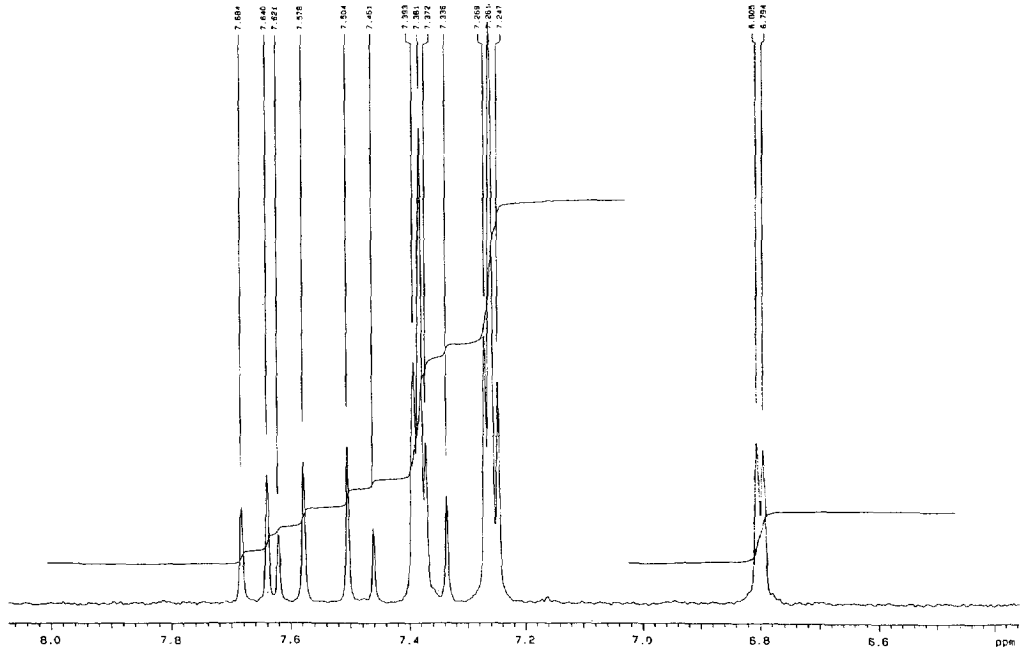



**Figure 2.** $^1H$ NMR spectrum (200 MHz) of **5** ($CDCl_3$).

*Electron Spin Resonance*

X-Band epr spectrum of radical **2** was recorded in solid as a single crystal sample at r.t. and in deoxygenated $CH_2Cl_2$ solution at 173 K.

Small single crystal was mounted in a quartz tube with crystal axes aligned along the tube axis and single dependence-orientation signal was measured by rotating the crystal with a goniometer about the axis every 10°. For the three orientations of the crystal, the maximum and minimum g-values were chosen. These values along with the corresponding peak-to-peak linewidth ($\Delta H_{pp}$) in parenthesis are: $g_1$ = 2.0047 (1.25 G), $g_2$ = 2.0031 (1.30 G) and $g_3$ = 2.0025 (1.0 G). The small shifts of these values from that of free spin, 2.0023, are typical of an organic $\pi$-radical. Furthermore, the lowest value will correspond to the closest component of the g-tensor aligned with the methyl-carbon $2p_z$-orbital which contains the unpaired electron.[7]

The spectrum of **2** in $CH_2Cl_2$ solution, centered at $g_{iso}$ = 2.0031, consists of seven lines corresponding to an overlapped ($\Delta H_{pp}$= 0.62 G) doublet of septets, as ascertained by simulation, due to the coupling of the electronic spin with a *para*-hydrogen ($a_H$= 2.1 G) and six equivalent *meta*-hydrogens ($a_{6H}$= 1.24 G) (Figure 3). At higher gain resolution, the hyperfine splitting of the free electron with $^{13}C$ atoms appears at $a_\alpha$= 29.3 G and $a_{arom}$= 13.2 G and 10.7 G. All these values are similar to those encountered for radical **1** in similar conditions ($a_{6H}$= 1.24 G; $a_\alpha$= 30.0 G; $a_{arom}$= 12.9 G and 10.5 G)[2a].

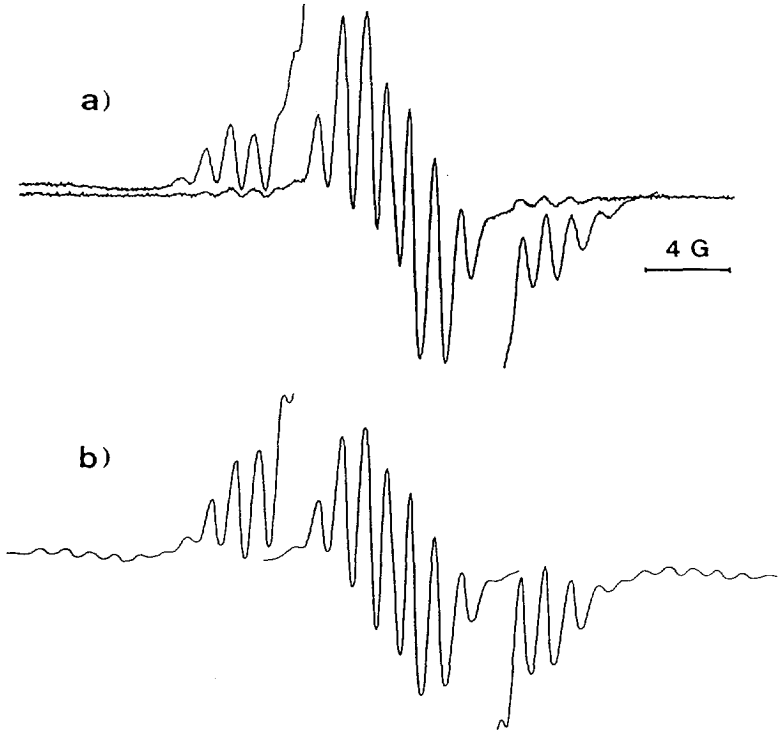



**Figure 3.** (a) EPR spectrum of radical **2**, and amplification showing $^{13}C$ couplings. (b) Computer simulation.

*Magnetic Susceptibility*

The specific magnetic susceptibility of the radical **2** has been measured from 77 K to 299 K. The experimental data were corrected for the diamagnetic susceptibility of the molecule ($\chi_{dia}$ = -0.516·10$^{-6}$ cm$^3$·g$^{-1}$) which was theoretically estimated by using Pascal's systematics.[8] Least squares correlation of the resulting Curie-Weiss plot gave the Bohr magnetons ($\mu_B$ = 1.7318) and the Weiss constant ($\Theta$ = -1.8 K). From $\mu_B$-value, the radical purity has been calculated to be ~100%. The low and negative value of $\Theta$ corresponds to a weak anti-ferromagnetic interaction between molecules at low temperature.

*Molecular and Crystal Structure of 2*

Radical **2** crystallizes from hexane (triclinic system, P-1 space group). A perspective view of the structure with the atom numbering is displayed in Figure 4. The bond distances and angles are reported in Table 1. All the distances and angles for the central carbon atom C(1) with aromatic carbons (2), (8) and (14) are in good agreement with a sp$^2$ hybridization for the methyl carbon, the unpaired electron being localized in a pure *p* orbital. Because of the presence of six chlorine atoms *ortho* to C(1), the phenyl rings are twisted around their bonds to C(1) with torsion angles C(8)-C(1)-C(14)-C(15): 47.2(6), C(8)-C(1)-C(2)-C(7): 49.5(6)and C(2)-C(1)-C(8)-C(9): 50.9(6), and the molecule adopts a propeller-like conformation with an approximate 3-fold symmetry, $D_3$.

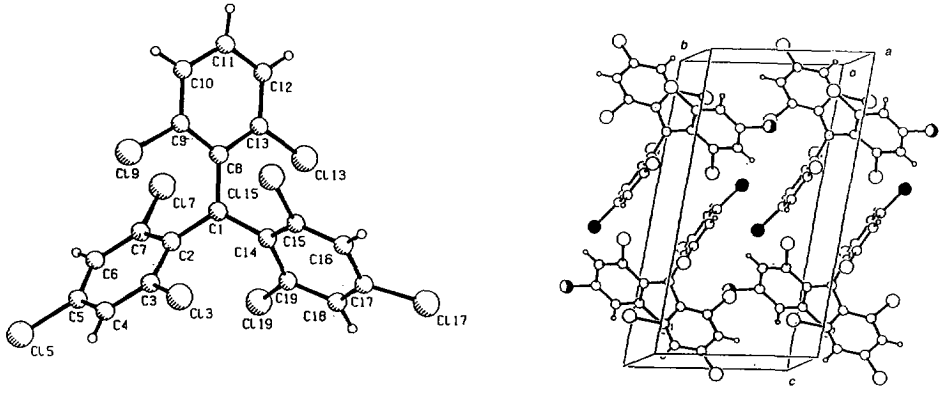



**Figure 4.** **(a)** The molecular structure of radical **2** with the X-ray atom numbering. **(b)** Perspective view of the unit cell illustrating the molecular packing. The disordered chlorine atoms are labelled as follows: ○ Cl(17), ● Cl(11) and ◑ Cl(5).

There are two symmetry-related disordered molecules in the unit cell (Figure 4) and the molecular packing is compatible with the three different orientations of the molecule around the ternary axis, thus leading to a partial disorder. The refined occupation parameters of the H and Cl atoms are given in Table 2.

Table 2 shows that the two orientations with the H(11) or H(17) positions occupied are the most probable (~44.9%, both), the remaining one being the less probable (~10.3%).

**Table 1.** Selected Bond Lengths [Å] and Angles [deg] for **2**

| Bond | [Å] | Angle | [deg] | Angle | [deg] |
|---|---|---|---|---|---|
| Cl(3)-C(3) | 1.735(4) | C(2)-C(1)-C(8) | 120.8(3) | C(8)-C(13)-Cl(13) | 120.2(3) |
| Cl(5)-C(5) | 1.719(4) | C(2)-C(1)-C(14) | 120.6(3) | C(19)-C(14)-C(15) | 115.1(3) |
| Cl(7)-C(7) | 1.729(4) | C(8)-C(1)-C(14) | 118.6(3) | C(19)-C(14)-C(1) | 122.8(3) |
| Cl(9)-C(9) | 1.737(4) | C(3)-C(2)-C(7) | 114.1(3) | C(15)-C(14)-C(1) | 122.0(3) |
| Cl(11)-C(11) | 1.701(5) | C(3)-C(2)-C(1) | 123.1(3) | C(16)-C(15)-C(14) | 123.3(4) |
| Cl(13)-C(13) | 1.738(4) | C(7)-C(2)-C(1) | 122.8(3) | C(16)-C(15)-Cl(15) | 116.2(3) |
| Cl(15)-C(15) | 1.738(4) | C(4)-C(3)-C(2) | 123.3(3) | C(14)-C(15)-Cl(15) | 120.4(3) |
| Cl(17)-C(17) | 1.703(5) | C(4)-C(3)-Cl(3) | 116.3(3) | C(15)-C(16)-C(17) | 118.2(4) |
| Cl(19)-C(19) | 1.738(3) | C(2)-C(3)-Cl(3) | 120.4(3) | C(18)-C(17)-C(16) | 121.1(4) |
| C(1)-C(2) | 1.464(4) | C(5)-C(4)-C(3) | 119.0(4) | C(18)-C(17)-Cl(17) | 119.7(4) |
| C(1)-C(8) | 1.467(5) | C(4)-C(5)-C(6) | 121.5(3) | C(16)-C(17)-Cl(17) | 118.7(3) |
| C(1)-C(14) | 1.479(5) | C(4)-C(5)-Cl(5) | 119.3(3) | C(17)-C(18)-C(19) | 118.8(4) |
| C(2)-C(3) | 1.402(5) | C(6)-C(5)-Cl(5) | 119.2(3) | C(18)-C(19)-C(14) | 123.3(3) |
| C(2)-C(7) | 1.409(5) | C(5)-C(6)-C(7) | 118.5(4) | C(18)-C(19)-Cl(19) | 116.1(3) |
| C(3)-C(4) | 1.387(5) | C(6)-C(7)-C(2) | 123.6(3) | C(14)-C(19)-Cl(19) | 120.3(3) |
| C(4)-C(5) | 1.361(6) | C(6)-C(7)-Cl(7) | 116.1(3) | | |
| C(5)-C(6) | 1.372(6) | C(2)-C(7)-Cl(7) | 120.2(3) | | |
| C(6)-C(7) | 1.383(5) | C(9)-C(8)-C(13) | 115.0(3) | | |
| C(8)-C(9) | 1.392(5) | C(9)-C(8)-C(1) | 122.9(3) | | |
| C(8)-C(13) | 1.394(5) | C(13)-C(8)-C(1) | 122.0(3) | | |
| C(9)-C(10) | 1.375(6) | C(10)-C(9)-C(8) | 123.3(3) | | |
| C(10)-C(11) | 1.357(6) | C(10)-C(9)-Cl(9) | 116.0(3) | | |
| C(11)-C(12) | 1.385(6) | C(8)-C(9)-Cl(9) | 120.6(3) | | |
| C(12)-C(13) | 1.370(6) | C(11)-C(10)-C(9) | 118.7(4) | | |
| C(14)-C(19) | 1.386(5) | C(10)-C(11)-C(12) | 121.4(4) | | |
| C(14)-C(15) | 1.389(5) | C(10)-C(11)-Cl(11) | 119.7(4) | | |
| C(15)-C(16) | 1.373(6) | C(12)-C(11)-Cl(11) | 118.4(3) | | |
| C(16)-C(17) | 1.378(6) | C(13)-C(12)-C(11) | 118.0(4) | | |
| C(17)-C(18) | 1.361(6) | C(12)-C(13)-C(8) | 123.5(4) | | |
| C(18)-C(19) | 1.371(6) | C(12)-C(13)-Cl(13) | 116.2(3) | | |

**Table 2.** Refined occupation parameters of the Cl and H atoms

| | | | |
|---|---|---|---|
| Cl(5) | 0.897(2) | H(5) | 0.103(2) |
| Cl(11) | 0.551(4) | H(11) | 0.449(4) |
| Cl(17) | 0.552(4) | H(17) | 0.448(4) |

The phenyl rings C(8) to C(13) and C(14) to C(19) deviate significantly from planarity ($\chi^2$ = 58.05 and 69.27, respectively). The average derivations of the Cl atoms from the mean L.S. plane is 0.132 Å, the greatest deviation (~0.32 Å) being for Cl(5) and Cl(11) atoms.

## DISCUSSION

While stabilization of a radical is largely due to delocalization of the unpaired electron, persistence is attributed to steric factors.[9] So, phenyl groups exhibit a high stabilization effect in the triphenylmethyl radicals, but the persistence of the polychlorophenylmethyl radicals is mainly due to steric hindrance caused by the *ortho*-chlorines, which disturbs the delocalization of the unpaired electron into the aromatic ring by twisting the phenyls out of the nodal plane and, as a consequence, reduces the spin density, particularly in *para*-position, being largely confined into the methyl carbon. In the molecular structure of **2**, the phenyl twist angles, as indicated more above, are all large and very similar in value to each other, indicating that the conjugation is considerably diminished and that the stable conformation corresponds closely to an idealized $D_3$ with negligeble variations in the conjugation in each phenyl. This is also reflected in the equivalence of the three $C_{methyl}$-$C_{aryl}$ bond lengths and also confirmed by the markedly low value of the splitting of the unpaired electron with the *para*-hydrogen, and the equivalence of the splitting values with all *meta*-hydrogens, in spite of the different *para*-substitution in one of them.

Furthermore, the twist angles are not influenced by the absence of one chlorine in *para*-position. This is inferred by comparing the molecular structure of **2** and **1** as well as the EPR spectra of both radicals. So, elimination of one chlorine in *para* does not cause any decrease in the steric hindrance, and, consequently, radical **2** is as persistent as radical **1**.

## EXPERIMENTAL

### *General Methods*

Melting points are uncorrected. $AlCl_3$ and other reagents were used as provided by commercial sources. Column cromatography separation and purification were accomplished on SDS silica gel of 60-200 μm. The IR spectra were recorded with a Perkin-Elmer model 683 spectrometer, and the UV-vis spectra with a Perkin-Elmer Lambda Array 3840 spectrometer coupled with a Perkin-Elmer 7300 computer. $^1$H NMR

spectra were determined at 200 and 300 MHz with Varian Gemini 200HC and XL-300 spectrometer, respectively. EPR spectra were recorded with a Varian E-109 spectrometer working in the X band and using a Varian E-257 temperature-controller. The EPR computer simulation was performed with a Hewlett-Packard 9835-B computer, using a modified version of the software package from Varian E-935 data Acquisition System. Magnetic susceptibilities were measured with a Varian 4-in magnet with constant-force caps operating at 8 kOe, and a Mettler microbalance.

*α,α,2,6-Tetrachloro-3-nitrotoluene (4).* A solution of α,α,2,6-tetrachlorotoluene (4.087 g; 17.8 mmol) and nitronium tetrafluoroborate (2.928 g; 22.0 mmol) in sulfolane (80 mL) was warmed (85 °C) and stirred in an anhydrous atmosphere for 1.5 h, and then poured over cracked ice. The resulting mixture was extracted with ether and the organic layer, washed with water dried and evaporated, gave a residue which was distilled (150-160 °C; 0.5 mm Hg) to afford α,α,2,6-tetrachloro-3-nitrotoluene (4.652 g; 95%): IR (NaCl neat) 3140 (w), 3080 (m), 3040 (m), 2880 (w), 1580 (s), 1570 (s), 1535 (s), 1440 (s), 1395 (m), 1350 (s), 1310 (w), 1240 (m), 1220 (m), 1200 (w), 1175 (m), 1140 (w), 1100 (s), 940 (s), 830 (s), 790 (m), 775 (s), 750 (w), 720 (w), 700 (s), 640 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 7.76 (1H, d, $J_{1,2}$ 8.7Hz), 7.70 (1H', d, $J_{1,2}$= 8.7Hz), 7.59-7.49 (2H, m). Anal. Calcd. for $C_7H_3Cl_4NO_2$: C, 30.6; H, 1.1; Cl, 51.6; N, 5.1. Found: C, 30.6; H, 1.1; Cl, 51.8; N, 5.0.

*(2,6-Dichloro-3-nitrophenyl)bis(2,4,6-trichlorophenyl)methane (5).* A mixture of toluene 4 (0.987 g; 3.59 mmol), 1,3,5-trichlorobenzene (6.57 g; 217.6 mmol) and $AlCl_3$ (0.600 g) was heated at 120 °C for 4.5 h, and then poured over craked ice. The resulting mixture was extracted with chloroform. The organic layer, washed with water dried and evaporated, gave a residue which recrystallized from *n*-pentane afforded **5** (1.772 g; 87%), m.p. 170-4 °C: IR (KBr) 3060 (w), 2910 (vw), 1565 (s), 1555 (s), 1530 (s), 1420 (m), 1360 (s), 1340 (s), 1235 (w), 1180 (w), 1160 (w), 1125 (w), 1080 (vw), 940 (w), 880 (m), 840 (s), 810 (s), 805 (m), 790 (s), 765 (w), 750 (w), 730 (w) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 7.66 (1H, d, J = 8.6 Hz), 7.60 (1H, d, J = 8.6 Hz), 7.48 (1H, d, J = 8.6 Hz), 7.36 (1H, d, J = 8.6 Hz), 7.39 (1H, d, J = 2.4 Hz), 7.38 (1H, d, J = 2.4 Hz), 7.26 (1H, d, J = 2.4 Hz), 7.25 (1H, d, J = 2.4 Hz), 6.80 (1H, s), 6.79 (1H, s). Anal. Calcd. for $C_{19}H_7Cl_8NO_2$: C, 40.4; H, 1.3; Cl, 50.2; N, 2.5. Found: C, 40.3; H, 1.2; Cl, 49.9; N, 2.4.

*(3-Amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methane (6).* A solution of **5** (0.290 g; 0.51 mmol), $SnCl_2$ x $2H_2O$ (0.352 g; 1.51 mmol), concentrated hydrochloric acid (0.5 mL) and ethanol (16 mL) was refluxed for 5.5 h, and then evaporated. The residue was extracted with ether and the solution, washed with saturated aqueous $NaHCO_3$ and water, dried and evaporated, gave a residue which recrystallized from hexane afforded **6** (0.176 g; 64%), m.p. 197-9 °C: IR (KBr) 3460 (w), 3370 (w), 3070 (w), 2910 (vw), 1610 (s), 1575 (s), 1540 (s), 1465 (s), 1450 (s), 1435 (m), 1370 (s), 1335 (w), 1310 (w), 1260 (w), 1240 (w), 1200 (w), 1185 (w), 1175 (w), 1160 (w), 1150 (m), 1140 (m), 1075 (w), 895 (s), 850 (s), 835 (m), 800 (s),

780 (m), 770 (m), 740 (w) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 7.36 (1H, d, J = 2.0 Hz), 7.35 (1H, d, J = 2.0 Hz), 7.23 (1H, d, J = 2.0 Hz), 7.22 (1H, d, J =2.0 Hz), 7.12 (1H, d, J = 8.6 Hz), 6.98 (1H, d, J = 8.6 Hz), 6.69 (2H, d, J = 8.6 Hz), 6.70 (1H, s), 6.68 (1H, s). Anal. Calcd. for $C_{19}H_9Cl_8N$: C, 42.7; H, 1.7; Cl, 53.0; N, 2.6. Found: C, 42.6; H, 1.7; Cl, 53.0; N, 2.6.

*(2,6-Dichlorophenyl)bis(2,4,6-trichlorophenyl)methane (7).* A solution of **6** (0.343 g; 0.641 mmol) in DMF (2 mL) was dropwise added to a stirred solution of isoamyl nitrite (0.108 g; 0.922 mmol) in DMF (1 mL) at 65 °C, and the resulting solution was kept at this temperature for a further 20 min. The reaction mixture was poured over aqueous hydrochloric acid (20%) (11 mL) and the mixture was extracted with ether. The organic layer, washed with water dried and evaporated, gave a residue which was chromatographed (silica gel, hexane) to afford **7** (0.194 g; 58%), m.p. 215-6 °C: IR (KBr) 3070 (w), 2910 (vw), 1570 (s), 1540 (s), 1440 (s), 1420 (s), 1370 (s), 1335 (m), 1240 (m), 1200 (m), 1190 (m), 1170 (s), 1155 (w), 1140 (m), 1125 (m), 1090 (w), 1075 (w), 890 (s), 850 (s), 830 (s), 800 (s), 780 (s), 765 (s), 750 (s), 720 (w), 700 (w), 670 (m), 655 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 7.11-7.36 (7H, m), 6.74 (1H, s). Anal. Calcd. for $C_{19}H_8Cl_8$: C, 43.9; H, 1.6; Cl, 54.6. Found: C,43.9; H, 1.5; Cl, 54.7.

*(2,6-Dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl Radical (2). 1) Synthesis.* An aqueous solution of tetra-*n*-butylammonium hydroxide (0.220 g; 40%) was added to a solution of **7** (0.132 g; 0.255 mmol) in THF (5 mL), and the resulting mixture was stirred at r.t. under an argon atmosphere for 24 h. Then, chloranil (0.139 g; 0.565 mmol) was added and the stirring was continued (24 h). The reaction mixture was filtered, and the solution was evaporated to give a residue which was chromatographed on column (silica gel, $CCl_4$) to afford **2** (0101 g; 77%), m.p. 237-8 °C: IR (KBr) 3070 (w), 1545 (s), 1515 (s), 1420 (s), 1365 (s), 1280 (m), 1275 (m), 1230 (w), 1190 (s), 1175 (s), 1130 (s), 1120 (m), 1075 (m), 950 (w), 915 (m), 890 (m), 850 (s), 820 (s), 800 (s), 785 (s), 765 (s), 715 (m), 700 (w), 665 (m) $cm^{-1}$. Magnetic susceptibility, temp. Curie: Θ = -1.1 K, $\mu_{eff}$= 1.724 (spins/mol = 6.01 x $10^{23}$), purity 99%. Anal. Calcd. for $C_{19}H_7Cl_8$: C, 44.0; H, 1.4; Cl, 54.7. Found: C, 43.9; H, 1.3; Cl, 54.8.

*2) X-ray analysis. a) Crystal data.* Molecular formula: $C_{19}H_7Cl_8$, molecular weight 518.85. Triclinic, space group P-1, No. 2. Cell dimensions: a = 8.189(3), b = 8.182(2), c = 16.096(8) Å, α = 77.15(3), β = 77.00(3), γ = 87.67(3) °, V = 1024.5(7) $Å^3$, Z = 2, F(000) = 514, Dc = 1.682 $g/cm^3$, μ = 1.102 $mm^{-1}$, crystal specimen prismatic 0.41 x 0.41 x 0.32 mm, red colored. *b) Data collection.* The diffractometer was an Enraf Nonius CAD4 with a graphite monochromated MoKα radiation, λ = 0.7103 Å. Cell parameters were determined from refinement of 25 reflections using the CAD4 Express software.[10] 7536 reflections were measured with $3.63 \leq \Theta \leq 30.41°$ and index ranges $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-22 \leq l \leq 0$ in ω/1.7 Θ scan mode, 0.7 + 0.49 tan(Θ) scanwidth and maximun final scan time of 60 s. 3 standard reflections were measured every 3600 s to check for the intensity variation and 3 more standards were measured every 50

reflections to check the crystal orientation. Intensity decay was 0.71% and was corrected. Absortion correction was made using 8 psi-scans, $T_{max}$= 99.85% and $T_{min}$= 93.39%. *c) Solution and refinement.* The structure is pseudo monoclinic C. Careful inspection of the results indicated that it was triclinic. The structure was solved using the extended tangent formula[11] and refined with 6192 unique reflections with 163 parameters and 1 restraint. Final R factors ($I > 2\sigma(I)$): R= 6.02%, $\omega R^2$ = 15.55%, Goof = 1.119, where $R = \sum \| Fc| - |Fc \| / - \sum |Fo|$, $\omega R^2 = [\sum \omega(Fo^2-Fc^2)^2 / \sum \omega(Fo^2)2]^{1/2}$, $\omega = 1/[\sum \delta(Fo^2)^2 + (0.554P)^2 + 0.92P]$, $P = [Max(Fo^2,0) + 2Fc^2]/3$, $Goof = [(\sum \omega(Fo^2 - Fc^2)) / (n-p)]^{1/2}$ (n = number of reflections, p = number of parameters). Final shifts/esd were less than 0.001 in the last cycle, and the maximum and minimum residual electron density in the final Fourier difference were 0.45 and -0.41 eÅ$^{-3}$. A SHELXL-93 program[12] was used for refinement, and plots were made with PLUTON[13] and ZORTEP[13] programs.

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