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(4-Amino-2,6-dichlorophenyl)-bis(2,4,6-trichlorophenyl)methyl Radical: A New Constituent of Organic Magnetic Materials

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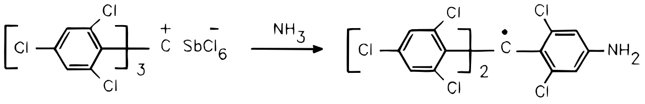
Introduction

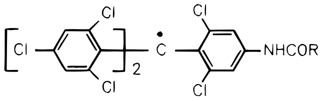
One rational approach to design magnetic organic materials, which has been conceptually proposed by Dougherty *et al.*[2] and systematically studied by many authors,[3] consists of dividing the high-spin material into two components: the spin-containing (SC) fragment, which provides the unpaired electron, and the ferromagnetic coupling (FC) unit, which connects radical centers ferromagnetically. In this context, intramolecular exchange interactions between two or more radical centers in π-conjugated systems involving different FC units have been analyzed. Very recently, the *amide* bond has shown to be a good FC unit in some isomeric benzanilides having a nitrene unit on each benzene ring.[4]

The chemistry of stable organic free radicals has been largely stimulated by the fact that these materials can be used as good SC fragments in the preparation of persistent ferromagnets.[5] Highly chlorinated triphenylmethyl radicals of perchlorotriphenylmethyl (PTM) series are the most stable carbon free radicals described to date.[6,7] On the other hand, the stability and properties of tris(2,4,6-trichlorophenyl)methyl radical (TTM), prepared and isolated in the solid state, are very similar to those of PTM, indicating that the absence of the *meta*-chlorines does not exert an important effect on the stability of the molecule.[7a]

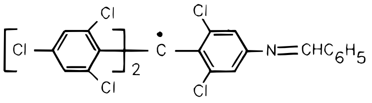
Recently, we have prepared the first functionalized radicals by substitution of one *para*-chlorine of the TTM by a functional group.[8] In this context, now we report the synthesis, electrochemical behavior, and electron spin resonance (EPR) of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (**2**), which is very attractive due to its potential of forming polyamide and polyimine bonds, constituents of the different FC units, to prepare polyradicals as magnetic materials. An X-ray analysis of the molecular and crystalline structure of **2** is also reported and commented in connection with its magnetic behavior. In the same way, three simple examples of condensation of radical **2** to obtain amide radicals, [4-[(*tert*-butylcarboxy)amino]-2,6-dichlorophenyl]bis(2,4,6-trichlorophenyl)methyl radical (**3**) and [4-[(phenylenecarboxy)amino]-2,6-dichlorophenyl]bis(2,4,6-trichlorophenyl)methyl radical (**4**), and an imine radical, [4-(benzylideneamino)-2,6-dichlorophenyl)]bis(2,4,6-trichlorophenyl)methyl radical (**5**) are reported to confirm the stability of the radical character of the molecule with the reactivity of the amino group.



1 **2**



3 R = $C(CH_3)_3$ **4** R = C_6H_5



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To prepare radical **2** we focused our attention on the reactivity of tris(2,4,6-trichlorophenyl)carbenium hexachloroantimoniate (**1**),[8] a stable dark blue microcrystalline salt that with an excess of ammonia in CH_2Cl_2 followed by treatment with $SnCl_2$ gave mainly radical **2** as a dark red microcrystalline solid. A secundary reaction product that arises most probably from the condensation of two molecules of salt **1** with ammonia, as is suggested by data from its elemental analysis (see the Experimental Section), is now being investigated. Acylation and benzoylation of amino radical **2** with trimethylacetyl chloride and benzoyl chloride in $CHCl_3$ and in the presence of triethylamine gave radicals **3** and **4**, respectively, and addition of **2** to benzaldehyde in absolute ethanol yielded radical **5**. These new radicals have been synthesized in excellent yields. Amino radical **2** is stable in air either in solution (UV−vis spectroscopy) or in solid form and shows good solvatochromic properties affecting the less energetic band in the UV−vis spectrum. This band, which is due to the radical character of the molecule,

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† Dedicated to Professor Fèlix Serratosa "in memoriam".

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Table 1. EPR Parameters for Radicals 2−5

			hfc constants (G)			
radical	g	ΔH_{pp} (G)	N	^{1}H	a-^{13}C	arom-^{13}C
2	2.0030	0.82	1.10	1.10	28.2	12.6, 10.5
3	2.0030	0.59		1.23	28.8	13.1, 10.5
4	2.0034	0.59		1.23	28.8	13.1, 10.6
5	2.0032	0.75	0.42	1.25	28.2	12.2: 10.2

shows a pronounced batochromic shift, losing its hyperfine structure, in going from aprotic (cyclohexane, λ_{max} 530 and 567 nm; $CHCl_3$, λ_{max} 535 and 574 nm) to protic solvents (ethanol, λ_{max} 601 nm), based on the different solvatation interactions concerning the amino group. Cyclic voltammograms for the reduction of radicals **2** and **5** in 0.1 M tetrabutylammonium perchlorate (TBAP) dimethylformamide (DMF) display a reversible, one-electron O/R couple at $E°$, −0.76 and −0.28 V vs SSCE (SCE with NaCl aqueous saturated solution), respectively. The presence of these redox couples is indicative of the stability of both species, neutral and anionic, in solution. Since $E°$ value for radical **5** is less negative than that of **2**, the former is more easily reducible than the latter, which is accounted for by the reduction of the electron-donating properties of the amino group by the formation of the aldimine.

X-band EPR spectra of radicals **2**−**5** were recorded in deoxygenated CH_2Cl_2 solution at 173 K, and spectral data are listed in Table 1. *g*-values are very closed to that of the free electron and similar to the TTM radical, indicating a small spin−orbit coupling. All the coupling constants have been found by computer simulation. The spectrum of radical **2**, displayed in Figure 1, consists of an overlapped and equally separated nonet of lines corresponding to the coupling with the six equivalent aromatic protons and the nitrogen. The small lines in both sides of the main spectrum correspond to the coupling of the free electron with the three bridgehead ^{13}C nuclei of the molecule. The spectrum of radical **3** is identical with that of radical **4**. Both spectra have been simulated without considering the interaction of the free electron with the nitrogen nucleus of the molecule, whose value must be too small to be observed.

Radical **2** crystallizes from hexane (monoclinic system, $P2_1/n$ space group). A perspective view of the structure with the atom numbering is displayed in Figure 2.[9] 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. C(1), C(2), C(8), and C(14) lie in a plane with *rmsd* lower than 0.005 Å. Due to 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), −48.7(9), C(2)−C(1)−C(8)−C(9), −44.4(9), and C(14)−C(1)−C(2)−C(3), −53.1(9), and the molecule adopts a propeller-like conformation with an approximate 3-fold symmetry D_3. There are four symmetry-related disordered molecules in the unit cell, 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 N and Cl atoms are given in Table 2.

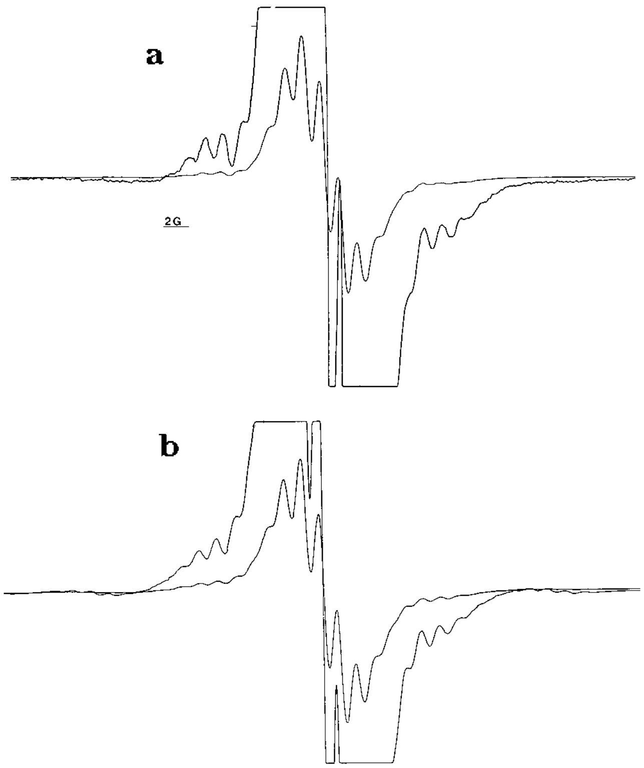

Figure 1. (a) EPR spectrum of a solution of radical **2** in CH_2Cl_2 at 173 K and amplification showing ^{13}C couplings. (b) Computer simulation.

Table 2 shows that the molecular orientation with the nitrogen in position 11 is the most probable (~52%), the remaining two being less probable (~24%). These results rule out the possibility of any strong hydrogen bonding between neighboring molecules. The N atoms of the disordered amine groups were geometrically fixed, d(C-N) = 1.40 Å, and the H atoms were not included.

The specific magnetic susceptibilities (χ) of the radical **2** were measured in the interval 4−290 K. Least-squares correlation of the resulting Curie−Weiss plot gave the Bohr magnetons ($\mu_B = 1.7067$), the specific diamagnetic susceptibility ($\chi_{dia} = -0.6004 \times 10^{-6}$ emu),[10] and the Weiss constant ($\Theta = -1.3$ K). From the μ_B-value the radical purity of **2** has been calculated to be 97%. So, radical **2** behaves as a good paramagnet species in the range of temperatures studied, except at very low temperatures, where the small and negative value of the Weiss constant may be associated to the existence of very weak antiferromagnetic interactions among the radical centers of neighboring molecules.

The absence of appreciable intermolecular magnetic phenomena is consistent with a remote separation between spin centers in the solid. So, an examination of the molecular structure shows that the unpaired electron is mainly localized in a pure *p*-orbital of the methyl carbon, due to the twisting of the phenyl rings, and the amino group does not exert any strong influence in the relative positions of the molecules in the crystalline lattice, being the intermolecular contacts of the van der Waals type.

The aim of this work has been to report the synthesis, properties, and stability of the amino radical **2**. Its

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(9) The authors have deposited atomic coordinates, bond lengths, bond angles, torsion angles, anisotropic displacement parameters, and observed and calculated structure factors for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(10) The value of χ_{dia} theoretically estimated by using Pascal's systematic[11] is -0.569×10^{-6} emu.

(11) Hellwege, K., Hellwege, A., Eds. *Landolt-Börnstein II. Diamagnetic Susceptibility*; Springer-Verlag: Berlin, 1977; Vol. 16, p 1.

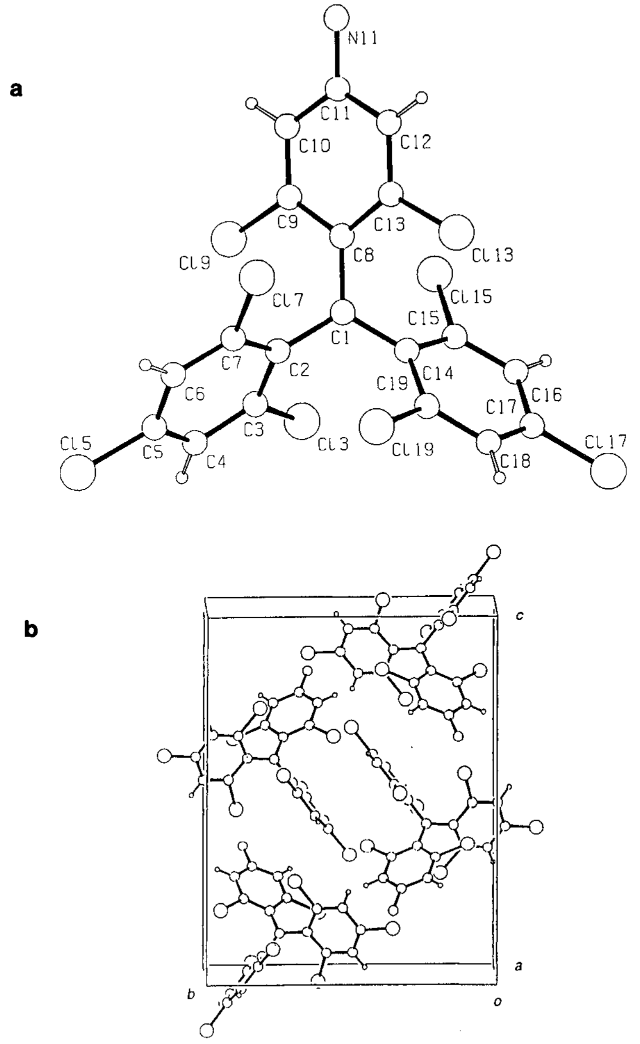

Figure 2. A perspective view of (a) the structure with the atom numbering of radical **2** and (b) the unit cell, illustrating the molecular packing.

Table 2. Refined Occupation Parameters of the N and Cl Atoms

Cl(5)	0.746(9)	N(5)	0.254(9)
Cl(11)	0.474(9)	N(11)	0.526(9)
Cl(17)	0.780(9)	N(17)	0.220(9)

magnetic behavior and its crystal and molecular structure indicates no appreciable intermolecular interactions. On the other hand, the preparation of radicals **3**−**5** has shown that the condensation reactions of the amino group with acid chlorides and aldehydes take place without impairment of the radical character. Further syntheses of polyradicals are now in progress.

Experimental Section

General Procedures. Melting points were obtained by using a Köfler microscope "Reichert" and are uncorrected. The UV−vis and IR spectra were recorded with Beckman Acta M-VI and Perkin-Elmer 682 spectrometers, respectively. CH_2Cl_2 and $CHCl_3$ were distilled over P_2O_5 before use. The handling of the radicals **2**−**5** was performed in the dark.

Magnetic Measurements. The routine magnetic susceptibilities of radicals **3**−**5** were measured with a Varian 4-in. magnet with constant-force caps operating at 8 KOe and a Cahn RG electrobalance. Measurements for radical **2** were collected in the range 4−290 K with a Manics DSM8 magnetometer equipped with a Helium continous flow cryostat and a DRUSCH EAF 16UE operating at 1.5 T. The data were corrected for the magnetization of the sample holder.

EPR Experiments. 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 the Varian E-935 data acquisition system. Samples of radicals were prepared in CH_2Cl_2 ($\sim10^{-3}$ M), placed in quartz EPR tubes, and degassed by three freeze−pump−thaw cycles before being inserted into the EPR cavity.

Electrochemical Measurements. The cyclic voltammetric (CV) 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 (NaCl-saturated aqueous solution) connected to the cell through a salt bridge containing a 0.1 M TBAP−DMF solution. The temperature of test solutions and of SCE was kept at 25 °C. In all experiments, the cell was maintained in the darkness to avoid the photochemical decomposition of radicals in solution. CV measurements were performed with standard equipment consisting of a PAR 175 universal programmer, an Amel 551 potentiostat, and a Philips 8043 X-Y recorder. Cyclic voltammograms of all solutions were recorded in the scan rate (v) range 20−200 $mV{\cdot}s^{-1}$. Solutions of substrates had a volume of 25mL and were prepared with DMF containing 0.1 M TBAP as supporting electrolyte.

(4-Amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl Radical (2). (a) Synthesis. Under an anhydrous atmosphere, ammonia gas was bubbled through a stirred blue solution of tris(2,4,6-trichlorophenyl)carbenium hexachloroantimoniate (2.12 g, 2.4 mmol) in CH_2Cl_2 (500 mL) until a rapid change to a reddish solution was observed. Then, argon was passed through the solution to eliminate the excess of ammonia. The resulting mixture was filtered off, and the filtrate was evaporated to give a reddish residue (1.54 g) that in THF (100 mL) was stirred with anhydrous $SnCl_2$ (0.56 g, 2.95 mmol) under argon (30 min).

The resulting green solution was evaporated, and the residue in ether was washed with a saturated $NaHCO_3$ aqueous solution and then with water, dried with anhydrous sodium sulfate and evaporated. The dark residue was flash chromatographed (silica gel, CCl_4:$CHCl_3$, 1:1) to afford (i) tris(2,4,6-trichlorophenyl)methyl radical (0.26 g, 9%), identified by IR, (ii) a green solid compound (0.14 g) (Anal. Calcd for $C_{38}H_{13}Cl_{16}N$: C, 43.4; H, 1.25; N, 1.3; Cl, 54.0. Found: C, 43.9; H, 1.4; N, 1.3; Cl, 53.9), and (iii) radical **2** (0.74 g, 58%): mp 250 °C dec (from hexane); IR (KBr) 3500 (w), 3400 (m), 3100 (w), 3070 (w), 1620 (s), 1590 (s), 1555 (m), 1525 (m), 1420 (m), 1385 (w), 1370 (m), 1305 (m), 1280 (m), 1240 (w), 1180 (m), 1135 (m), 1080 (w), 1060 (w), 920 (w), 850 (m), 835 (w), 820 (w), 800 (m), 785 (m), 715 (w) cm^{-1}; UV−vis (cychlohexane) λ_{max} (ϵ) 215 (38 100), 249 (6000 sh), 273 (12 300 sh), 360 (18 600 sh), 375 (27 700), 416 (6770 sh), 528 (2070), 566 (3450). Anal. Calcd for $C_{19}H_8Cl_8N$: C, 42.7; H, 1.5; N, 2.6; Cl, 53.2. Found: C, 42.9; H, 1.5; N, 2.6; Cl, 53.1.

(b) X-ray Analysis. Crystal Data: molecular formula $C_{19}H_8Cl_8N$; molecular weight 533.86; monoclinic $P2_1/n$, No. 14; cell dimensions, $a = 8.179(4)$ Å, $b = 14.064(3)$ Å, $c = 18.92(1)$ Å, $\beta = 102.18(3)°$, $V = 2127(2)$ Å^3, $Z = 4$, $F(000) = 1060$, $D_c = 1.667$ g/cm^3, $\mu = 1.066$ mm^{-1}, crystal specimen prismatic 0.87 × 0.23 × 0.003 mm. **Data Collection.** The diffractometer was an Enraf-Nonius CAD4 with graphite-monochromated Mo-Kα radiation, $\lambda = 0.7103$ Å. Cell parameters were determined from refinement of 25 reflections using the CAD4 Express software.[12] 3851 Reflections were measured with $1.82 \le \theta \le 24.97°$ and index ranges $-9 \le h \le 9$, $0 \le k \le 16$, $0 \le l \le 22$ in $w/1.7\ \theta$ scan mode, $0.7 + 0.49\tan(\theta)$ scanwidth, and maximum final scan time of 60 s. Three standard reflections were measured every 3600 s to check for the intensity variation, and three more standards were measured every 50 reflections to check the crystal orientation. Intensity decay was 0.1% and was corrected. Absorption correction was made using 8 ψ-scans, $T_{max} = 99.64\%$, and $T_{min} = 86.43\%$. **Resolution and Refinement.** The structure was solved using the extended tangent formula[13] and refined with

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(12) CAD4-Express Operating Software, V. 5.1, Enraf-Nonius, Delft Instruments X-Ray Diffraction, Deft, The Netherlands, 1992.

3735 unique reflections with 266 parameters and 1 restraint. The N atoms of the disordered amine groups were geometrically fixed (d(C−N) = 1.40 Å) but the H atoms were not included. Final R factors ($I > 2\sigma(I)$): $R = 6.97\%$, $\omega R2 = 16.59\%$, Goof = 1.102, where $\mathrm{R} = \sum||F_o| - |F_c||/\sum|F_o|$, $\omega R^2 = [\sum\omega(F_o{}^2 - F_c{}^2)^2/\sum\omega(F_o{}^2)^2]^{1/2}$, $\omega = 1/[\sum\delta(F_o{}^2)^2 + (0.554P)^2 + 0.92P]$, $P = [\max(F_o{}^2,0) + 2F_c{}^2]/3$, Goof = $[(\sum\omega(F_o{}^2 - F_c{}^2))/(n - p)]^{1/2}$ (n, number of reflections, and 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 0.44 and −0.45 e Å^{-3}, respectively. A SHELXL-93 program[14] was used for refinement, and plots were made with PLUTON programs.[15]

[4-[(*tert*-Butylcarboxy)amino]-2,6-dichlorophenyl]bis(2,4,6- trichlophenyl)methyl Radical (3). A solution of *tert*-butyl chloride (0.090 g, 0.63 mmol) in $CHCl_3$ (1 mL) was added dropwise to a stirred and cold (0 °C) solution of radical **2** (0.229 g, 0.43 mmol) and triethylamine (0.076 g, 0.75 mmol) in $CHCl_3$ (3 mL) under argon. The resulting mixture was stirred at 0 °C for a further 1 h and then at rt for 22 h. Evaporation of the solvent gave a residue that was placed in $CHCl_3$, washed with diluted aqueous hydrochloric acid and water, and dried with anhydrous sodium sulfate, and flash chromatographed (silica gel, $CHCl_3$) to afford radical **3** (0.225 g, 85%) mp 268−70 °C (from hexane−$CHCl_3$); IR (KBr) 3330 (m), 3120 (w), 3080 (w), 2950 (w), 2870 (w), 1670 (s), 1560 (s), 1550 (s), 1520 (m), 1470 (m), 1390 (w), 1365 (s), 1290 (m), 1250 (w), 1215 (m), 1185 (w), 1175 (m), 1160 (m), 1135 (m), 1070 (m), 1050 (w), 1020 (w), 915 (m), 875 (m), 865 (m), 850 (m), 815 (m), 810 (s), 800 (s), 785 (s), 715 (m) cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ) 215 (54 600), 248 (16 800 sh), 276 (5900 sh), 373 (24 700), 510 (1170), 554 (1430). Anal. Calcd for $C_{24}H_{16}Cl_8NO$: C, 46.6; H, 2.6; N, 2.3; Cl, 45.9. Found: C, 46.3; H, 2.5; N, 2.2; Cl, 46.0. Magnetic susceptibility χ_{dia} (Pascal) −0.566 × 10^{-6} emu, Θ −2.3 K, μ_B ∼1.73 (∼100% pure).

[4-[(Phenylenecarboxy)amino]-2,6-dichlorophenyl]bis(2,4,6- trichlorophenyl)methyl Radical (4). Benzoyl chloride (0.07 mL, 0.60 mmol) was added dropwise to a stirred and cold (0 °C) solution of radical **2** (0.25 g, 0.47 mmol) and triethylamine (0.076 g, 0.75 mmol) in $CHCl_3$ (3 mL) under argon. The resulting solution was stirred at 0 °C for a further 1 h and then at rt for 48 h. Evaporation of the solvent gave a residue that was worked up as before and flash chromatographed (silica gel, $CHCl_3$) to give (i) starting radical **2** (0.025 g, 10%), identified by IR, and (ii) radical **4** (0.215 g, 72%): mp 263−5 °C (from hexane−$CHCl_3$); IR (KBr) 3420 (w), 3240 (w), 3130 (w), 3060 (w), 1670 (m), 1650 (s), 1570 (s), 1555 (s), 1525 (m), 1500 (m), 1485 (m), 1375 (s), 1295 (s), 1250 (w), 1230 (w), 1190 (w), 1180 (m), 1135 (m), 1080 (w), 1020 (w), 950 (w), 920 (w), 895 (w), 850 (s), 820 (m), 800 (s), 790 (s), 715 (w), 700 (s), 685 (m), 6155 (w) cm^{-1}; UV−vis (cyclohexane) λ_{max} (ϵ) 213 (58 600), 251 (16 400), 278 (11 600 sh), 373 (30 400), 391 (23 700), 405 (17 000 sh), 515 (1360), 557 (1470). Anal. Calcd for $C_{26}H_{12}Cl_8NO$: C, 48.9; H, 1.9; N, 2.2. Found: C, 48.8; H, 1.8; N, 2.2. Magnetic susceptibility χ_{dia} (Pascal) − 0.568 × 10^{-6} emu, Θ −7.8 K, μ_B ∼1.73 (∼100% pure).

[4-(Benzylideneamino)-2,6-dichlorophenyl]bis(2,4,6-trichlorophenyl)methyl Radical (5). Benzaldehyde (0.1 mL, 0.98 mmol) was added dropwise to a solution of radical **2** (0.50 g, 0.94 mmol) in ethanol (30 mL), and the resulting solution was refluxed under argon for 32 h. Evaporation of the solvent gave a residue that was digested in *n*-pentane to afford radical **5** (0.55 g, 94%): mp 222−5 °C; IR (KBr) 3050 (w), 2940 (w), 2870 (w), 1620 (m), 1550 (s), 1520 (s), 1510 (s), 1445 (m), 1380 (m), 1360 (s), 1305 (w), 1280 (w), 1230 (w), 1185 (m), 1175 (s), 1160 (m), 1125 (m), 1070 (w), 1050 (w), 1015 (w), 965 (w), 945 (m), 915 (w), 900 (w), 875 (m), 850 (s), 840 (m), 815 (m), 795 (s), 785 (s), 745 (m), 715 (w) cm^{-1}; UV−vis (cychlohexane) λ_{max} (ϵ) 213 (68 800), 251 (22 100), 293 (10 600 sh), 373 (28 900), 408 (18 500), 444 (9600 sh), 524 (940 sh). Anal. Calcd for $C_{26}H_{12}Cl_8N$: C, 50.2; H, 1.9; N, 2.2; Cl, 45.6. Found: C, 50.4; H, 2.1; N, 2.2; Cl, 45.4. Magnetic susceptibility χ_{dia} (Curie−Weiss) −0.5425 × 10^{-6} emu, Θ −1.3 K, μ_B ∼1.74 (∼100% pure).

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