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Trichloro-2,6-pyridylene, a Good Ferromagnetic Coupling Unit between Two Persistent Carbon Radical Centers

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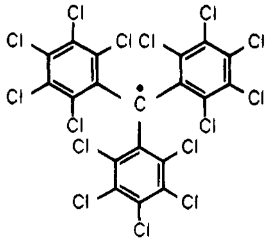
The synthesis, characterization, and physical properties of perchloro-2,6-bis(diphenylmethyl)-pyridine-α,α′-ylene biradical (**1**) and α*H*-tricosachloro-2,6-bis(diphenylmethyl)pyridine-α′-yl radical (**2**) which present exceptionally high stabilities are reported. The synthesis of **1** and **2** have been accomplished using different strategies in order to get them separately, although **1** always contains **2** as an impurity. **1** is a molecule constituted by two trivalent carbon atoms linked by a trichloro-*m*-pyridylene spacer which has proved to be a good ferromagnetic coupling unit. Magnetic susceptibility measurements from 4.2 to 300 K show that the ground state of **1** is the triplet being $2J = 358 \pm 14$ cm^{-1} (1.03 kcal/mol), the triplet−singlet energy gap. At low temperatures, an antiferromagnetic interaction between intermolecular spines was observed (Curie temperature, $\theta_1 = -2.02 \pm 0.10$ K). The EPR spectrum of **1** in frozen 2-methyltetrahydrofuran (133 K) in the $\Delta m_s = \pm 1$ region affords three symmetric pairs of lines corresponding to a triplet species without axial symmetry with zfs parameters $|D/hc| = 0.0081$ cm^{-1} and $|E/hc| = 0.00075$ cm^{-1}. The $\Delta m_s = \pm 2$ transition follows the Curie law over the range 10.0−62.0 K, supporting the highest multiplicity of the molecule in the ground state. The cyclic voltammogram of **1** exhibits a redox couple ($E^\circ = 0.18$ V *vs* SCE) which is attributed to the reduction of this biradical to the stable radical anion **12** ($\mathbf{1}^-$), and a second irreversible peak ($E_p{}^c = -0.25$ V *vs* SCE) which is ascribed to the formation of the unstable dianion **13** ($\mathbf{1}^{2-}$). The electronic spectrum of **1** is presented and discussed.

Introduction

One of the important issues for organic molecules to be good candidates for magnetic materials is stability; however, the recent advances in the preparation of ferromagnetic materials have been seriously limited by the unavailability of free radicals with sufficient stabilities.[2,3]

The perchlorophenyl groups have an enormous effect on the stability of polyarylmethyl radicals by sterically protecting the radical center of the molecule, i.e., the trivalent carbon atom where the highest spin density resides.[4] This protection is ascribed to shielding by the chlorines surrounding the trivalent methyl carbons. Therefore, the most stable carbon free radicals described to date belong to the so-called PTM (perchlorotriphenylmethyl) series.[4,5] Replacement of *p*-chlorine atoms in PTM by chemically active substituents affords radicals which usually react at the substituents without impairment of the radical character.[4] All these organic radicals, named as inert free radicals (IFR's), have been synthesized and isolated as brilliant-colored crystals, are completely disassociated even in solid form, and possess half-lives up to the order of years in solution at room temperature, in the dark and in contact with air.



PTM radical

Taking advantadge of the IFR's stability, the synthesis of biradicals, one triradical, and one tetraradical, all them containing PTM units and isolated as stable solids, have been recently published.[6] In these polyradicals, the *m*-phenylene fragment has proved to be a good ferromagnetic coupling unit between the paramagnetic centers, as in other reported cases.[7]

In view of the central role played by the structural spacer linking paramagnetic centers in enforcing a ferro or antiferromagnetic coupling between them, it was

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[5] (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,** *56,* 841. (h) Juliá, L.; Riera, J.; Teixidó, R. *J. Chem. Soc., Perkin Trans. 1* **1991,** 1101.

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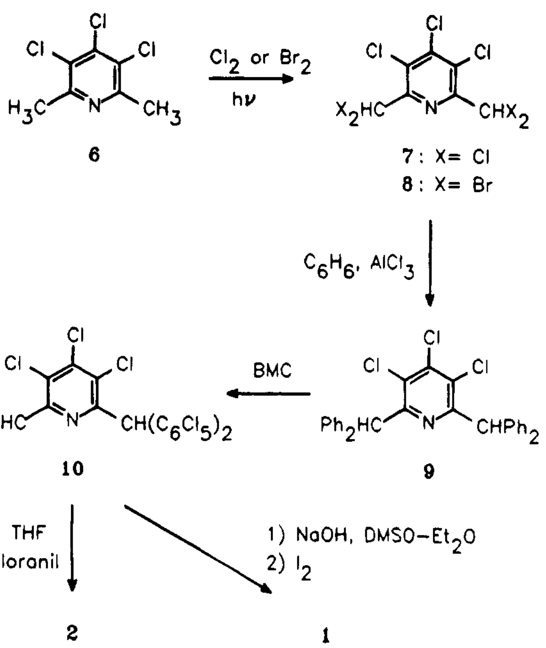
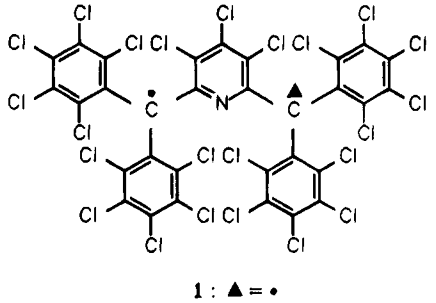
Scheme 1



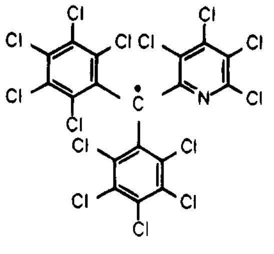
considered interesting to expand the series of synthesized biradicals with different spacers, stables enough to experimentally check their magnetic properties.

We now present the synthesis and characterization of perchloro-2,6-bis(diphenylmethyl)pyridine-α,α′-ylene (**1**), a very stable biradical isolated as a red solid, whose radical centers are connected by a trichloro-2,6-pyridylene spacer. In the course of the studies on the synthesis of **1**, α*H*-tricosachloro-2,6-bis(diphenylmethyl)-pyridine-α′-yl radical (**2**), has also been obtained.



1 : ▲ = •
2 : ▲ = H

In the context of our investigations on IFR's with a heteroaromatic ring, it is mentioned that some of us have reported the synthesis of a new subclass of free radicals of the PTM series by incorporating a perchloropyridyl ring instead of a perchlorophenyl ring into the structural backbone of the molecule. These new radicals, perchlorodiphenyl(2-pyridyl)methyl (**3**) and perchlorodiphenyl-(4-pyridyl)methyl (**4**),[5c] are highly stable both in the solid form and in solution.



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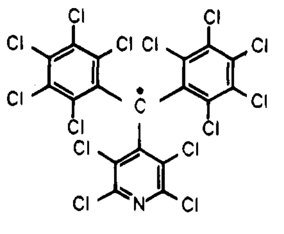

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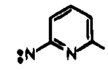
Some theoretical results concerning the 2,6-pyridylene spacer predict it to be a good ferromagnetic coupling unit in 2,6-pyridinedinitrene (**5**) with a quintet as the ground state being the triplet with the lowest high excited state.[7f] Now, our experimental results on biradical **1** are consistent with the computational predictions on this spacer, particularly as a good ferromagnetic coupling unit between two carbon centered radicals. Although, as far as **1** is concerned, torsion of the pyridine ring relative to the planes of the three sp^2 bonds of each trivalent carbon atom, due to the presence of chlorines, greatly reduces exchange coupling.



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Results and Discussion

Syntheses. The synthesis of 3,4,5-trichloro-2,6-bis-[bis(pentachlorophenyl)methyl]pyridine (**10**), precursor of biradical **1** and monoradical **2** was performed as outlined in Scheme 1. The 3,4,5-trichloro-2,6-dimethylpyridine (**6**) was prepared as described in the literature from pentachloropyridine *N*-oxide.[8] The photochlorination with Cl_2 or the photobromination with Br_2 of pyridine **6** gave intermediates 3,4,5-trichloro-2,6-bis(dichloromethyl)pyridine (**7**) or 3,4,5-trichloro-2,6-bis(dibromomethyl)pyridine (**8**), respectively, which were separated from the complex mixtures resulting from the different degrees of photohalogenation of **6**. An $AlCl_3$-promoted Friedel–Crafts alkylation of benzene by bis(dihalomethyl)pyridines **7** or **8** afforded 3,4,5-trichloro-2,6-bis(diphenylmethyl)pyridine (**9**) in excellent yield. Extended nuclear chlorination of **9** with reagent BMC[9,10] (initial components: SO_2Cl_2, S_2Cl_2, and $AlCl_3$), using a great excess of reactants, gave a moderate yield of pyridine **10**. All attempts carried out to synthesize pyridine **10** by the Friedel–Crafts condensation between pentachlorobenzene and bis(dihalomethyl)pyridines **7** or **8**, to avoid the chlorination of phenyl rings, were unsuccessful.[11]

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(7) *m*-Phenylene spacer as a ferromagnetic coupling unit has been extensively studied: (a) Kothe, G.; Denkel, K.-H.; Sümmermann, W. *Angew. Chem., Int. Ed. Engl.* **1970,** *9,* 906. (b) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983,** *105,* 628. (c) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985,** *107,* 5409. (d) Haider, K.; Platz, M. S. *J. Am. Chem. Soc.* **1988,** *110,* 2318. (e) Rajca, A. *J. Am. Chem. Soc.* **1990,** *112,* 5890. (f) Lahti, P. M.; Ichimura, A. S. *J. Org. Chem.* **1991,** *56,* 3030. (g) Rajca, A.; Utamapanya, S.; Xu, J. *J. Am. Chem. Soc.* **1991,** *113,* 9235. (h) Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992,** *114,* 9952. (i) Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 180. (j) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993,** *115,* 847.

(8) Binns, F.; Suschitzky, H. *J. Chem. Soc., Chem. Commun.* **1970,** 750. Binns, F.; Suschitzky, H. *J. Chem. Soc. (C)* **1971,** 1223.

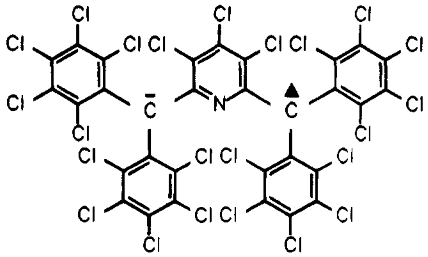
(9) Ballester, M.; Molinet, C.; Castañer, J. *J. Am. Chem. Soc.* **1960,** *82,* 4254. Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis;* Wiley: New York, 1967; p 1131.

(10) It has been proved that shorter reaction times of chlorination yield crudes of reaction whose ^1H NMR spectra displayed multiplets corresponding to nonsubstituted aromatic hydrogens. The difficulty to perchlorinate the aromatic rings can be explained by steric hindrance.

(11) It is worthwhile to mention that some of us have published some Friedel–Crafts condensations between polychlorobenzenes and highly chlorinated alkylating agents by means of $AlCl_3$ leading to highly overcrowded arylmethanes. See: Ballester, M.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *Synthesis* **1986,** 64. Span. Patent 541,891, 1985. Span. Patent 541,892, 1985. Riera, J.; Castañer, J.; Armet, O.; Rovira, C. *An. Quim.* **1986,** *82,* 268. García, R.; Riera, J.; Carilla, J.; Juliá, L.; Molins, E.; Miravitlles, C. *J. Org.Chem.* **1992,** *57,* 5712.

As a general rule, highly chlorinated triarylmethanes are converted into highly stable free radicals by a two-step process which consists of the treatment of the substrate with a base to give red solutions of the corresponding carbanions followed by oxidation to the radicals with I_2 or *p*-chloranil. Accordingly, the synthesis of biradical **1** and monoradical **2** were performed as outlined in Scheme 1. Treatment of pyridine **10** with basic reagent BCR[12] (powdered NaOH, DMSO–ethyl ether) and then oxidation of the resulting red solution with I_2 gave biradical **1** with some impurities of monoradical **2** as indicated below in the magnetic susceptibility section, isolated as infusible deep red crystals stable in air up to 220 °C, containing presumably about 1.4% of hexane (elemental analysis).[13] If the basic reagent consisted of a tetrahydrofuran solution of 4 equiv of tetra-*n*-butylammonium hydroxide (TBAH), and the resulting deep red solution was then oxidized with *p*-chloranil, monoradical **2** was isolated as infusible red crystals, stable in air up to 310 °C. Solutions of either biradical **1** or monoradical **2** do not react with oxygen in the dark. The structure of biradical **1** was determined by infrared, electronic, and epr spectra, and reversion to its precursor **10**.[14] Monoradical **2** was characterized by infrared, epr, and electronic spectra and elemental analysis.

Therefore, it is possible to prepare separately biradical **1** and monoradical **2**, although the former contains **2** as an impurity. The key step in this two-step process leading to the synthesis of **1** or **2** resides in the basic treatment of pyridine **10**. The second deprotonation reaction leading from monocarbanion **12** to dicarbanion **13** is much slower than the first one due to the Coulombic repulsion between the two negative charges and, as a consequence, takes some time to be accomplished. Besides, DMSO–ether is an appropiate solvent to stabilize dicarbanion **13** which, after 24 h of treating pyridine **10** with NaOH, is in great proportion in the medium, and the action of I_2 is to oxidize it to **1**. If THF is the solvent, as dicarbanion **13** is unstable in the medium it decomposes as soon as it is obtained, and the reaction can be stopped in a short time after mixing pyridine **10** and TBAH, when a great proportion of monocarbanion **12** is present, and the action of *p*-chloranil is then to oxidize it to **2** which can be conveniently separated from the impurities.



11 : ▲ = H
12 : ▲ = •
13 : ▲ = −

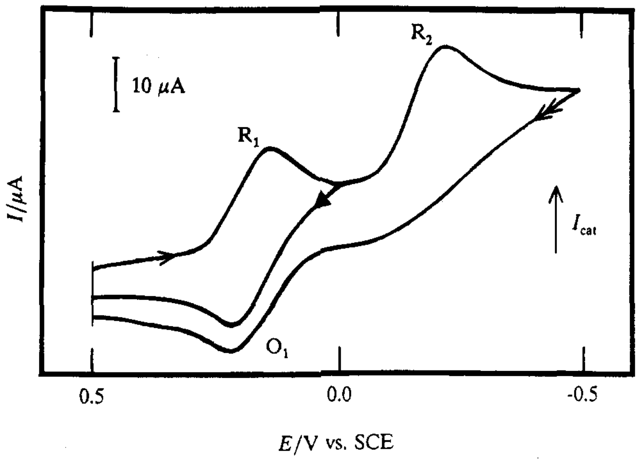


Figure 1. Cyclic voltammogram for the reduction of **1** (c = 1.0 mM) in DMF containing 0.1 M TBAP, at a Pt electrode, at a scan rate of 50 mV s^{-1} and at 25.0 °C. Starting potential: (—>—) 0.5 V. Reversal potentials: (—◄—) 0 V and (—>>—) −0.5 V.

Radical absorption bands in the electronic spectrum of monoradical **2** [λ (ϵ dm^3 mol^{-1} cm^{-1}), 378 (22 500), 570 (1590) nm] are similar to those of radical **3** [381 (25 600), 574 (1700) nm].[5c] The electronic spectrum of biradical **1** also displays the radical bands at [374 (41 180), 547 (3080) nm], with molar absorptivities about twice those of monoradical **2** in accordance with the similar structure of the radical moieties of **1** and **2**. Thus, the trichloro-2,6-pyridylene spacer between the two trivalent carbons in **1** does not contribute to any extension of the conjugation of the unpaired electrons, being the two half-filled nonbonding molecular orbitals (NBMOs) of the biradical **1** of the same nature as that of monoradical **2**. The moderate hypsochromic shift (23 nm) of the band at 547 nm of biradical **1** with respect to the corresponding band at 570 nm of monoradical **2** can be accounted for by assuming that the delocalization of the unpaired electrons of **1** into the heteroaromatic ring is disfavored because of the Coulombic repulsions between the electron charges of them.

Cyclic Voltammetry (CV). Cyclic voltammograms for the reduction of biradical **1** in 0.1 M tetrabutylammonium perchlorate (TBAP)–dimethylformamide (DMF) exhibited two consecutive reduction peaks R_1 and R_2 on the cathodic portion of the curve. These reduction peaks can be observed in Figure 1, which also shows the presence of one oxidation peak O_1 when the scan was reversed once it reached the cathodic peak potential (E_p^c = 0.15 V) of peak R_1, this indicating that both peaks yield a redox couple. All peaks showed practically equal height at a given v (scan rate) value and were diffusion-controlled since a linear variation of the height of each peak with the square root of the scan rate was always found.[15]

The standard potential (E°) of the O_1/R_1 couple was 0.18 V *vs* SCE and the difference between its anodic and cathodic peak potentials ($E_p^a - E_p^c$) was found to be *ca.* 60 mV in all scan rates tested, as expected for a reversible one-electron system.[15] The O_1/R_1 couple can then be ascribed to the following equilibrium between the biradical **1** and its radical anion **12** (1^-):

$$1 + e^- \rightleftharpoons 1^-$$

The radical anion 1^- electrogenerated in peak R_1, is stable in solution, being further reduced in peak R_2 (E_p^c

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

[13] A thermogravimetric analysis of **1** showed the impossibility in eliminating the solvent without decomposition of the sample.

[14] Treatment of IFR's with ascorbic acid has shown to be a good method to revert to their α*H*-precursors (Ballester, M.; Riera, J.; Castañer, J.; Casulleras, M. *Tetrahedron Lett.* **1978**, 643). Thus, reduction of **1** with ascorbic acid in THF–water yielded pyridine **10**.

[15] Galus, Z. *Fundamentals of Electrochemical Analysis;* Horwood: Chichester, 1976; Chapt. 7.

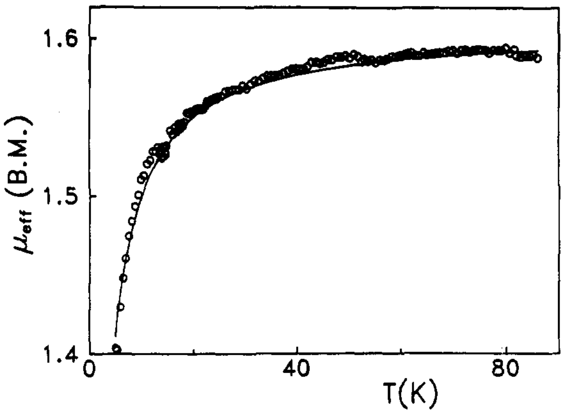


Figure 2. Thermal variation of μ_{eff} (μ_B) for monoradical **2**. The solid line was calculated with eq 1 and the values of the parameter are discussed in the text.

= −0.25 V). For this irreversible peak, the difference between the half-peak and cathodic peak potentials ($E_{p/2}^c - E_p^c$) was found to be between 85 mV and 95 mV, whereas E_p^c showed a linear variation with log v with a slope close to 60 mV per decade. All these parameters are in agreement with the theoretically established values for an irreversible one-electron change reaction with a transfer coefficient (α) *ca.* 0.5 (theoretical values[15] at 25.0 °C: $E_{p/2}^c - E_p^c = 48/\alpha$ mV, slope of E_p^c *vs* −log v plot = 29.6/α mV per decade). It can then be established that reduction of $\mathbf{1}^-$ in peak R_2 is initiated by an irreversible one-electron step (the rate determining) leading to the formation of the dianion **13** ($\mathbf{1}^{2-}$).

$$\mathbf{1}^- + e^- \rightarrow \mathbf{1}^{2-}$$

Since the height of peak R_2 is similar to that of monoelectronic peak R_1, it seems plausible to consider that in peak R_2 only the above one-electron process leading to $\mathbf{1}^{2-}$ takes place as an electrochemical reaction. The irreversibility of peak R_2 can then be explained by assuming that the initially electrogenerated dianion $\mathbf{1}^{2-}$ is unstable in the reaction medium and undergoes a fast decomposition, involving either a protonation reaction by the tetrabutylammonium cation of the background electrolyte,[16] or, most probably, an intramolecular cyclization reaction involving the nitrogen of the pyridine ring and a phenyl ring. As mentioned, the instability of electrogenerated dianion $\mathbf{1}^{2-}$ can be accounted for by the strong intramolecular Coulombic repulsions between close negative charges and the lack of solvent effects in their stabilization.

By CV, a reversible one-electron redox couple with $E°$ = 0.03 V *vs* SCE was also found for a saturated solution of monoradical **2** in 0.1 M TBAP−DMF. This couple can be ascribed to the following equilibrium between the substrate and its anion **11** ($\mathbf{2}^-$).

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

The more positive $E°$ value for the reversible reduction of **1** than of **2**, indicating that the former is more easily reducible than the latter, may be attributed to the cross-conjugation between negative and radical centers of $\mathbf{1}^-$ with the following canonical structures in resonance:

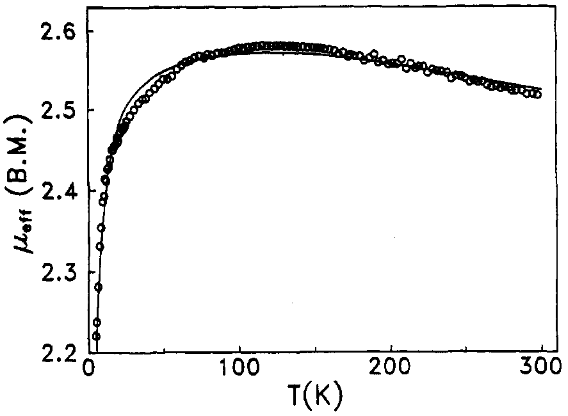
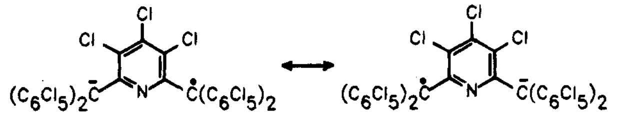


Figure 3. Thermal variation of μ_{eff} (μ_B) for biradical **1**. The solid line was calculated with eq 2 and the values of the parameters are discussed in the text.



It is worthwhile to say that biradical **1** is more easily reducible than other reported perchlorinated polyradicals without pyridine ring. Thus, the first redox potential in CV of *trans*-perchlorovinylenebis(α,α,α′,α′-tetraphenyl-1,3-xylylene) is $E°$ = −0.175 V,[6c] and those for 2,4,6-trichloro-α,α,α′,α′,α″,α″-hexakis(pentachlorophenyl)mesitylene and 2,4,6-trichloro-α,α,α′,α′,α″,α″-hexakis(pentachlorophenyl)mesitylene triradical are $E°$ = −0.22 V[6d] and $E°$ = −0.19 V,[6d] respectively.

Magnetic Susceptibility (MS). The molar paramagnetic susceptibility (χ_2) of monoradical **2** was measured in the temperature range 4.2−85 K and the thermal dependence of the molar effective magnetic moment in Bohr magnetons (μ_B) is:

$$\mu_{eff}(\mu_B) = \sqrt{F_2 g^2 \frac{1}{2}\left(\frac{1}{2} + 1\right)\frac{T}{T - \theta_2}} = \sqrt{3\frac{F_2 T}{T - \theta_2}} \qquad (1)$$

where F_2 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 has been taken equal to 2, and the Curie temperature θ_2 is associated to the existence of intermolecular interactions. The parameters F_2 and θ_2 were determined by fitting experimental data in eq 1 (Figure 2), resulting in the following values: $F_2 = 0.86 \pm 0.01$ and $\theta_2 = -1.48 \pm 0.10$ K. The value of θ_2 indicates a weak intermolecular antiferromagnetic interaction.

The molar paramagnetic susceptibility (χ_1) of biradical **1** was measured in the temperature range 4.2−300 K, and the thermal variation of the molar effective magnetic moment in Bohr magnetons shown in Figure 3 is given by:

$$\mu_{eff}(\mu_B) = \sqrt{3k_B/N\mu_\beta^2}\sqrt{\chi_1 T} = 2.828\sqrt{\chi_1 T}$$

where N is the Avogadro's number and k_B the Boltzmann constant. By considering that the only radical impurity of the biradical sample is monoradical **2**,[17] the thermal dependence of μ_{eff} can be accommodated by the following

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[16] Lund, H.; Baizer, M. M. *Organic Electrochemistry. An Introduction and a Guide;* Marcel Dekker: New York, 1991; Chapt. 7.

[17] The presence of hexane as impurity of biradical **1**, presumably about 1.4%, does not influence significantly in the values of μ_{eff}.

expression:

$$\mu_{\mathrm{eff}}(\mu_{\mathrm{B}}) = 2.828\sqrt{F_1\chi_1{}^{\mathrm{theor}}T + (1 - F_1)\chi_2{}^{\mathrm{theor}}T} = 2.828\sqrt{T\left[\frac{F_1}{T - \theta_1}\frac{3}{3 + \exp(-2J/k_{\mathrm{B}}T)} + (1 - F_1)\frac{0.3751}{T - \theta_2}\right]} \tag{2}$$

where F_1 is an empirical factor introduced to correct the reduction in the magnetic susceptibility of the sample due to the presence of monoradical **2** as an impurity, Curie temperatures θ_1 and θ_2 are associated to the intermolecular interactions (for θ_2 the resulting value of eq 1 was used), and the term $3/[3 + \exp(-2J/k_{\mathrm{B}}T)]$ reproduces the thermal variation of the susceptibility of **1** due to the population of the excited singlet state, the triplet being the ground state of the molecule and $2J$ the triplet–singlet energy gap.[18]

The free parameters θ_1, J, and F_1 were determined by fitting experimental data to eq 2, resulting in the following values: $\theta_1 = -2.02 \pm 0.10$ K, $J = 258 \pm 20$ K $= 179 \pm 14$ cm^{-1}, and $F_1 = 0.75 \pm 0.01$. Accordingly with these values, the rather abrupt decrease observed in μ_{eff} for biradical **1** (Figure 3) at low temperature is associated with an intermolecular antiferromagnetic interaction (negative value of θ_1). In the interval 75–160 K, where μ_{eff} is nearly constant ($\mu_{\mathrm{eff}} \approx 2.58\ \mu_{\mathrm{B}}$), both Curie temperatures θ_2 and θ_1 are much lower than the temperature and, therefore, the effect of the intermolecular interaction is negligible.

The observed disagreement between experimental values and the theoretical curve of the thermal variation of μ_{eff} for biradical **1**, mainly in the interval of low temperatures, as depicted in Figure 3, can be attributed to the fact that the theoretical pattern used to describe the intermolecular interactions (Curie–Weiss law) does not take into account the real topology of these interactions into the crystalline structure of the sample. The existence of any kind of ordered stack (parallel or perpendicular pairs) in the molecules of the biradical **1** associated with antiferromagnetic interactions between radical centers of neighboring molecules might explain the slower increase of μ_{eff}, in the range 17–62 K, as the experimental results indicate. This might also induce (a) a decrease in the maximum value of μ_{eff} (2.58 μ_{B}) (the normal value for a species with a ground triplet state is 2.83 μ_{B}), if those antiferromagnetic interactions are not completely excluded before the excited singlet state starts to be populated at around 125 K and (b) an artificial reduction in the empirical purity (factor F_1).

Electron Paramagnetic Resonance (EPR). The isotropic EPR spectrum of monoradical **2** was recorded at room temperature in tetrachloroethylene solution. A characteristic feature of this spectrum is that it consists of a 1:1:1 triplet which arises through coupling of an unpaired electron with a nitrogen nucleus. g-Factor (2.0036), ^{14}N hyperfine splitting (3.25 G), and line width (1.91 G, peak to peak) are very similar to those of radical **3** in the same solvent ($g = 2.0035$, $a_{\mathrm{N}} = 3.25$ G, line width $= 1.97$ G).[5c] As in the case of radical **3**, the coupling with nitrogen is mainly attributed to hyperconjugation involving direct overlap between the N 2s orbital and the 2p$_z$ orbital of the α carbon.

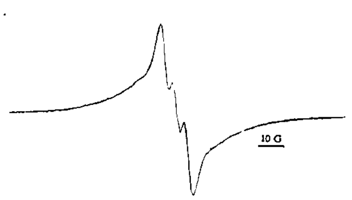

Figure 4. Isotropic EPR spectrum of biradical **1** at 233 K in MTHF.

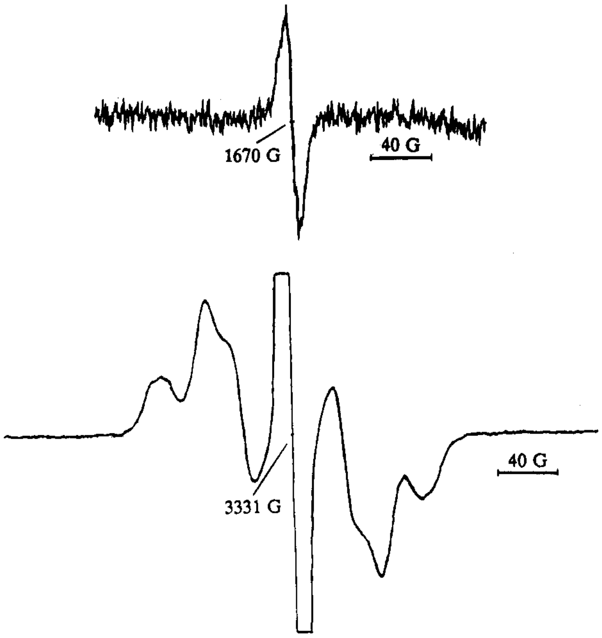

Figure 5. EPR spectrum of **1**; $\Delta m_s = \pm 1$ transitions in MTHF glass at 133 K. Insert shows the signal corresponding to $\Delta m_s = \pm 2$ forbidden transition.

With a much higher gain, pairs of symmetrical satellite triplets appear in the spectrum of **2** on account of ^{13}C splittings. The corresponding α-^{13}C = 28.9 G and arom ^{13}C = 12.25 G, both of them also similar to those of radical **3** (α-^{13}C = 28.4 G and arom ^{13}C = 13.0 and 11.3 G).[5c] The similitude between the EPR parameters of radicals **2** and **3** supports the structure given for the former.

The EPR spectrum of a sample of biradical **1** at 233 K in fluid solution of 2-methyltetrahydrofuran (MTHF) (Figure 4) appears to be an overlap of two types of spectra: a broad line with a peak-to-peak width of ≈15G, due to the electron–electron dipolar interactions, assigned to the triplet, and a set of three narrower lines which probably are due to the presence of monoradical **2** as an impurity.

The spectrum of biradical **1** in a 10^{-3} M MTHF rigid glass showed in the $\Delta m_s = \pm 1$ region the fine structure (three pairs of lines corresponding to the three canonical orientations) typical of a randomly oriented ensemble of immobilized triplet species without axial symmetry (Figure 5) and described by zero-field splitting (zfs) parameters $|D/hc| = 0.0081$ cm^{-1} and $|E/hc| \approx 0.00075$ cm^{-1}. The intense line at 3330 G arises from impurities of monoradical **2**. Supporting the presence of a triplet species, the half-field region of the spectrum exibits at ≈1670 G a single line corresponding to the $\Delta m_s = \pm 2$ forbidden transition (Figure 5). The variation of the signal intensity of this line with the reciprocal of the temperature between 10.0 and 62.0 K follows the Curie law, $I = C/T$, indicating that the triplet is the ground

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[18] Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, Heidelberg, 1986; p 75.

state of biradical **1** and confirming the results obtained by susceptibility measurements.

Experimental Section

General Procedures. Melting points were obtained by using a Köfler microscope "Reichert" and are uncorrected. The UV and IR spectra were recorded with Beckman Acta M-VI and Perkin-Elmer 682 spectrometers, respectively. ^{1}H NMR spectra were recorded with a Bruker WP805Y spectrometer and were obtained using $CDCl_3$ as solvent (unless otherwise indicated) and tetramethylsilane as internal reference. EI mass spectra were obtained on a TS-250 (VG, Manchester, UK) spectrometer. Pentachloropyridine 1-oxide,[19] 3,4,5-trichloro-2,6-dimethylpyridine 1-oxide,[8] and 3,4,5-trichloro-2,6-dimethylpyridine (**6**)[8] were prepared according to published procedures.

Magnetic Measurements. Molar magnetic susceptibilities (χ_M) were measured with a SQUID magnetometer in the temperature range 4.2−300 K for biradical **1** operating in a field strength of 30 kOe, and in the temperature range 4.2−85 K for monoradical **2** in a field strength of 50 kOe. The data ($\chi'_M = \chi_M - \chi_{dia} - \chi_{holder}$) for both **1** and **2** were corrected for the magnetization of the sample holder and for the diamagnetic susceptibility of the molecule, which was experimentally determined from pyridine **10** ($\chi_{dia} = -0.61\ 10^{-3}$ cm^3 mol^{-1}).

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 SCE (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 25.0 ± 0.1 °C. In all experiments, the cell was maintained in the darkness to avoid the photochemical decomposition of substrates in solution.

CV measurements were performed with a 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 s^{-1}. Solutions of substrates had a volume of 25 cm^3 and were prepared with DMF containing 0.1 M TBAP as supporting electrolyte.

Biradical **1** showed a good solubility in DMF and a substrate concentration (c) of 1.0 mM was tested by CV. Monoradical **2** showed a rather limited solubility in DMF, and a saturated solution in this medium was studied by CV. Note that **2** was found to be practically insoluble in the most common organic solvents such as DMSO, CH_2Cl_2, and THF, thus preventing the use of these media for its electrochemical study.

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 to obtain spectra at temperatures as low as 130 K. A Bruker ESP 300 spectrometers with a Bruker ER 4112 HV continous-flow liquid helium cryostat and an Oxford Instruments temperature-controller system was used to obtain EPR spectra at lower temperatures (4 K). Samples of biradical **1** and monoradical **2** were prepared in 2-methyltetrahydrofuran (MTHF) (∼10^{-3} M) placed in quartz EPR tubes and degassed by three freeze-pump-thaw cycles before being inserted into the EPR cavity. Handling of radicals in solution was performed in the dark.

Chlorination of 3,4,5-Trichloro-2,6-dimethylpyridine (6). A slow stream of dry Cl_2 was passed (35 min) through a refluxing solution of pyridine **6** (2.00 g) in CCl_4 (160 mL) illuminated with a 500 W incandescent lamp situated underneath the Pyrex container, thus providing a source of heat as well as light. Then a stream of N_2 was passed to eliminate the Cl_2, and evaporation of the solvent afforded a residue, which was flash chromatographed (silica gel, hexane) to give (i) **perchloro-2,6-dimethylpyridine** (0.06 g, 1.5%): mp 110−112 °C (from hexane); IR (KBr, cm^{-1}) 1500, 1365, 1345, 1275, 1250, 1230, 1095, 1010, 910, 840, 810, 780, 720, 595, 580, 545; UV (cyclohexane) λ_{max} 219, 236 (sh), 242 (sh), 267, 277, 286 nm (ϵ 41 295, 10 520, 9425, 1430, 1580, 1100 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for C_7NCl_9: C, 20.2; N, 3.4; Cl, 76.5. Found: C, 20.3; N, 3.3; Cl, 76.8. (ii) **3,4,5-Trichloro-2-(dichloromethyl)-6-(trichloromethyl)pyridine** (0.60 g, 17%), mp 90.5−94.5 °C (from hexane); IR (KBr, cm^{-1}) 1515, 1360, 1285, 1250, 1220, 1210, 1090, 1010, 905, 830, 780, 750, 715, 600, 590, 550, 470; ^{1}H NMR δ 7.11 (s); UV (cyclohexane) λ_{max} 216, 235 (sh), 268 (sh), 277, 286 nm (ϵ 42 590, 10 495, 1610, 2085, 1735 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for C_7HNCl_8: C, 22.0; H, 0.3; N, 3.7; Cl, 74.1. Found: C, 22.1; H, 0.2; N, 3.5; Cl, 74.4. (iii) **3,4,5-Trichloro-2,6-bis(dichloromethyl)pyridine (7)** (1.34 g, 41%): mp 57−60 °C (from hexane); IR (KBr, cm^{-1}) 1525, 1380, 1295, 1280, 1260, 1230, 1210, 1090, 1010, 785, 710, 690, 660, 630, 590, 570, 480; ^{1}H NMR δ 7.09 (s); UV (cyclohexane) λ_{max} 215, 235 (sh), 271 (sh), 279, 288 nm (ϵ 43 670, 10 620, 1820, 2620, 2445 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_7H_2NCl_7$: C, 24.1; H, 0.6; N, 4.0; Cl, 71.3. Found: C, 24.3; H, 0.5; N, 3.9; Cl, 71.5. (iv) **3,4,5-Trichloro-2-(chloromethyl)-6-(dichloromethyl)pyridine** (0.56 g, 19%): mp 56−60 °C (from hexane); IR (KBr, cm^{-1}) 3010, 1530, 1440, 1390, 1380, 1305, 1270, 1215, 1090, 1015, 930, 880, 790, 770, 710, 680, 620, 590, 500, 475, 440; ^{1}H NMR δ 7.10 (s, $CHCl_2$), 4.81 (s, CH_2Cl); UV (cyclohexane) λ_{max} 214, 233 (sh), 271 (sh), 281, 289 nm (ϵ 42 590, 10 320, 1805, 2830, 2690 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_7H_3Cl_6N$: C, 26.8; H, 0.9; N, 4.5; Cl, 67.8. Found: C, 27.0; H, 0.9; N, 4.2; Cl, 67.9.

Bromination of 3,4,5-Trichloro-2,6-dimethylpyridine (6). A refluxing solution of pyridine **6** (2.10 g) and bromine (12.78 g) in CCl_4 (50 mL) under an anhydrous atmosphere was illuminated with a 500 W incandescent lamp (34 h) situated underneath the Pyrex container, thus providing a source of heat as well as light. Then, more bromine (11.9 g) was added and the reaction was continued under the same conditions (17 h). Evaporation of the solvent gave a residue which was repeatedly treated with CCl_4 and evaporated to dryness until elimination of the excess bromine. The residue was flash chromatographed (silica gel, hexane) to afford (i) **3,4,5-trichloro-2,6-bis(tribromomethyl)pyridine** (0.20 g, 3%): mp 177−178 °C (from hexane); IR (KBr, cm^{-1}) 1540, 1492, 1362, 1345, 1335, 1320, 1250, 1235−1225, 1088, 995, 785, 760, 735, 720, 690, 660, 595, 562, 528, 490; UV (cyclohexane) λ_{max} 225, 252 (sh), 284, 294 (sh) nm (ϵ 36 350, 11 090, 3150, 2260 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_7NBr_6Cl_3$: C, 12.3; N, 2.0. Found: C, 12.2; N, 2.0. (ii) **3,4,5-Trichloro-2-(dibromomethyl)-6-(tribromomethyl)pyridine** (0.85 g, 14%): mp 103−105 °C (from hexane); IR (KBr, cm^{-1}) 3030, 1540, 1505, 1360, 1340, 1275, 1240, 1195, 1135, 1085, 1000, 815, 775, 760, 750, 725, 680, 645, 585, 570, 550, 535, 490, 435; ^{1}H NMR δ 7.06 (s); UV (cyclohexane) λ_{max} 223, 250 (sh), 287, 296 (sh) nm (ϵ 35 235, 10 835, 3315, 2690 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_7HNBr_5Cl_3$: C, 13.9; H, 0.2; N, 2.3. Found: C, 13.8; H, 0.3; N, 2.8. (iii) **3,4,5-Trichloro-2,6-bis-(dibromomethyl)pyridine** (**8**) (1.29 g, 25%): mp 100.0−101.5 °C (from hexane); IR (KBr, cm^{-1}) 3030, 1510, 1380, 1365, 1340, 1300, 1290, 1205, 1145, 1075, 1060, 1015, 880, 765, 745, 725, 685, 660, 645, 575, 550, 525, 490; ^{1}H NMR δ 7.05 (s); UV (cyclohexane) λ_{max} 222, 246 (sh), 288, 296 (sh) nm (ϵ 36 240, 11 190, 3475, 3290 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_7H_2NBr_4Cl_3$: C, 16.0; H, 0.4; N, 2.7. Found: C, 16.0; H, 0.3; N, 2.8.

Attempted Condensation of 3,4,5-Trichloro-2,6-bis(dichloromethyl)pyridine (7) with Pentachlorobenzene. A stirring mixture of pyridine **7** (0.10 g, 0.3 mmol), pentachlorobenzene (1.14 g, 4.6 mmol), and $AlCl_3$ (0.59 g, 7.12 mmol) was heated (140−150 °C) (5.7 h) in a stainless steel pressure vessel. The resulting mixture was poured on ice/diluted hydrochloric acid and extracted with $CHCl_3$. The organic layer, washed with water, dried with anhydrous sodium sulfate, and evaporated, gave starting material **7** and pentachlorobenzene (TLC, IR).

3,4,5-Trichloro-2,6-bis(diphenylmethyl)pyridine (9). (1) From Pyridine 7. A solution of pyridine **7** (0.30 g, 0.9 mmol) in benzene (25 mL) was added (20 min) into a magnetically stirred and refluxed suspension of $AlCl_3$ (0.92 g, 6.9 mmol) in benzene (25 mL) under an anhydrous atmosphere. The

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(19) Chivers, G. E.; H. Suschitzky *J. Chem. Soc. (C)* **1971**, 2867.

mixture was then refluxed for a further 26 h. Evaporation of the solvent gave a residue which was treated with ice/diluted hydrochloric acid and extracted with ether. The organic layer, washed with $NaHCO_3$ aqueous solution and then with water and dried with anhydrous Na_2SO_4 and evaporated, gave a residue, which was chromatographed on column (silica gel, hexane) to afford **9** (0.39 g, 87%): mp 146−147.5 °C (from hexane); IR (KBr, cm^{-1}) 3100, 3070, 3030, 1605, 1520, 1495, 1455, 1450, 1375, 1080, 1030, 1010, 910, 840, 810, 770, 740, 730, 710, 690, 635, 620, 590, 565, 550, 500; ^{1}H NMR (CCl_4) δ 7.22−6.88 (m, 20 H), 5.95 (s, 2 H); UV (cyclohexane) λ_{max} 204 (sh), 235 (sh), 259 (sh), 266, 283, 289 nm (ϵ 68 310, 14 600, 3290, 3170, 4800, 4935 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_{13}H_{22}NCl_3$: C, 72.3; H, 4.3; N, 2.7; Cl, 20.7. Found: C, 72.3; H,4.4; N, 2.9; Cl, 20.8.

(2) From Pyridine 8. The reaction was carried out according to the preceding procedure. Starting materials: **8** (0.87 g, 1.65 mmol), benzene (82 mL), $AlCl_3$ (1.95 g, 14.6 mmol), benzene (82 mL). Addition time: 60 min. Reaction time: 26 h. The residue was purified as above to give **9** (0.70 g, 83%).

3,4,5-Trichloro-2,6-bis[bis(pentachlorophenyl)methyl]pyridine (10). A solution of pyridine **9** (0.38 g) and S_2Cl_2 (3.65 g) in SO_2Cl_2 (19 mL) was slowly added (28 min) to a boiling and stirred suspension of $AlCl_3$ (1.61 g) in SO_2Cl_2 (7.5 mL). The reflux was continued until the volume was concentrated (~5 mL) (31 min). More S_2Cl_2 (4.62 g) in SO_2Cl_2 (23 mL) was added and then the reflux was continued (5 h) with occasional small additions of SO_2Cl_2 to keep the volume constant (~5 mL). Successive additions of $AlCl_3$ and S_2Cl_2 at different times were then carried out. Additions: (1) $AlCl_3$ (1.60 g), S_2Cl_2 (3.68 g), and the reflux was continued (13 h); (2) $AlCl_3$ (0.50 g), S_2Cl_2 (1.00 g), reflux (8 h); (3) $AlCl_3$ (0.51 g), S_2Cl_2 (1.01 g), reflux (8 h); (4) $AlCl_3$ (1.58 g), S_2Cl_2 (8.27 g), reflux (7.75 h). Subsequent additions of SO_2Cl_2 were performed to keep the volume constant (5 mL). The reaction was monitored by IR of the residues, collected from aliquots, until disappearance of the band at 1410 cm^{-1}.

Most of the SO_2Cl_2 was then evaporated under reduced pressure at 40−50 °C, the rest was poured over cracked ice, and solid $NaHCO_3$ was added until gas evolution ceased. The mixture was then heated (50−60 °C, 30 min), and, when cold, strongly acidified with concd aqueous HCl and extracted with $CHCl_3$. The organic layer was washed with water, and the residue was chromatographed on a column (silica gel, $CHCl_3$) giving, after digestion with ether, **10** (0.33 g, 37%): mp > 310 °C; IR (KBr, cm^{-1}) 2930, 1525, 1520, 1370, 1340, 1295, 1285, 1240, 1210, 1195, 1110, 1075, 1045, 860, 825, 810, 795, 755, 745, 710, 685, 675, 650, 635, 600, 525, 505; ^{1}H NMR δ 6.82; UV ($CHCl_3$) λ_{max} 282, 290 nm (ϵ 7815, 8200 dm^3 mol^{-1} cm^{-1}); MS 1193 ($C_{31}H_2N^{35}Cl_{23}$, M$^+$), 1158 (M$^+$ − Cl), 1123 (M$^+$ − 2Cl), 1088 (M$^+$ − 3Cl), 1053 (M$^+$ − 4Cl), 1018 (M$^+$ − 5Cl). Anal. Calcd for $C_{31}H_2NCl_{23}$: C, 30.9; H, 0.2; N, 1.2; Cl, 67.7. Found: C, 30.7; H, 0.2; N, 1.1; Cl, 67.9.

***αH*-Tricosachloro-2,6-bis[bis(pentachlorophenyl)methyl]pyridine-α′-yl Radical (2).** An aqueous solution of tetrabutylammonium hydroxide (1.64 M, 0.61 mL) was added to a mixture of pyridine **10** (0.30 g) and THF (60 mL), and the resulting mixture was stirred at room temperature under an argon atmosphere for 3.5 h. Then, chloranil (0.28 g) was added and the stirring was continued (2 h). The reaction mixture was filtered, and the solution was evaporated to give a residue which was chromatographed on column (silica gel, hexane), giving after digestion with $CHCl_3$−hexane, monoradical **2** (0.10 g, 34%): red crystals mp > 310 °C; IR (KBr, cm^{-1}) 2925, 1520, 1475, 1355, 1335, 1310, 1295, 1265, 1200, 1115, 1085, 1070, 870, 825, 815, 800, 745, 725, 705, 690, 675, 660, 645, 640, 625; UV-visible ($CHCl_3$) λ_{max} 378, 475 (sh), 570 nm (ϵ 22 500, 1590, 1590 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_{31}HNCl_{23}$: C, 31.0; H, 0.1; N, 1.2; Cl, 67.8. Found: C, 31.0; H, 0.2; N, 1.2; Cl, 67.7.

Perchloro-2,6-bis(diphenylmethyl)pyridine-α,α′-ylene Biradical (1). A mixture of pyridine **10** (0.26 g), powdered NaOH (1.64 g), ethyl ether (40 mL), and DMSO (9 mL) was shaken under an argon atmosphere for 24 h. The mixture was filtered onto I_2 (1.49 g), and the resulting solution was allowed to stand for a while (3 h) and then washed with aqueous $NaHSO_3$ (to destroy I_2) and with water (to eliminate DMSO). During this process some precipitate appeared. The mixture obtained was then evaporated to give a residue (0.18 g) which was flash chromatographed (silica gel, hexane) to give **1** (0.12 g, 46%): deep red crystals 220 °C dec; IR (KBr, cm^{-1}) 1515, 1445, 1335, 1305, 1265, 1205, 1225, 1075, 865, 815, 805, 740, 700, 685, 665, 640, 620, 500, 490; UV-visible ($CHCl_3$) λ_{max} 374, 500 (sh), 547 nm (ϵ 41 180, 3260, 3080 dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_{31}NCl_{23}\cdot 0.2C_6H_{14}$: C, 31.7; H, 0.2; N, 1.1; Cl, 66.9. Found: C, 32.1; H, 0.4; N, 1.1; Cl, 67.2.

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