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Abstract: The synthesis of *trans*-perchlorovinylenebis($\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-1,3-xylylene) (1), an exceptionally stable organic carbon tetraradical, which is isolated as a deep red solid, stable in air up to 200 °C, is reported. The electronic spectrum of 1 is presented and commented on. The cyclic voltammogram of 1, exhibiting two consecutive redox couples with standard potentials of -0.175 and -0.480 V vs SCE, is discussed in view of the exhaustive controlled-potential electrolysis of the tetraradical into the corresponding tetraanion. Magnetic susceptibility measurements from 4.2 to 300 K show that a pair of triplets is the ground state of the tetraradical, being $2J = 240 \pm 10 \text{ cm}^{-1}$ (0.69 kcal/mol), the triplet-singlet energy gap. At low temperatures, a weak antiferromagnetic interaction was observed (negative and low value of Weiss constant $\theta = -1.1 \pm 0.1$ K). From an EPR analysis in frozen 2-methyltetrahydrofuran over the range 4-129 K, the presence of two diastereoisomeric forms of the molecule is tentatively suggested. Accordingly, from the two symmetric and outer pairs of peaks of $\Delta m_s = \pm 1$ transition in the spectrum, two different |D/hc| values, 0.010 and 0.013 cm⁻¹, are calculated that are in good agreement with those reported for perchloro-*m*-xylylene. Supporting the presence of the two forms of 1, the $\Delta m_s = \pm 2$ transition exhibits two overlapping lines. The intensity of this transition rises continuously from 129 to 4 K, also supporting that the ground state is a pair of triplets.

Considerable attention has recently been focused on organic materials with novel optical, electronic, and magnetic properties. Conjugated hydrocarbons belonging to no classical Kekulé structures and possessing half-filled nonbonding molecular orbitals (NBMOs) are optimum candidates for these materials, the great limitation being their lack of stability. Some of them have been recently detected by ESR spectroscopy at very low temperatures and identified as structures with high spin states.²

The most stable carbon free radicals described to date belong to the so-called PTM (perchlorotriphenylmethyl) series. Their exceptionally high chemical and thermal stability are mainly attributed to steric shielding by the chlorine attached to their molecular carbon backbone.³

In our efforts to prepare stable high-spin organic molecules with characteristic magnetic properties, we report the synthesis and characterization of the first carbon tetraradical of the PTM series, *trans*-perchlorovinilenebis-5- $(\alpha, \alpha, \alpha', \alpha')$ -tetraphenyl-1,3-xylylene) (1), for which no classical Kekulé structure can be written.

Experimental Section

General Procedures. Perkin-Elmer 682, Perkin-Elmer Lambda-Array 3840, and Bruker WP80SY spectrometers were used for IR, UV-vis, and ¹H NMR spectroscopy, respectively. Solvents were dried and purified before use. THF was freshly distilled from sodium benzophenone ketyl. The handling of tetraradical 1 in solution was performed in the dark.

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(f) Ballester, M.; Pascual, I.; Riera, J.; Castañer, J. J. Org. Chem. 1991, 50, 217. (g) Ballester, M.; Pascual, I. J. Org. Chem. 1991, 56, 841. (h) Juliá, L.; Riera, J.; Teixidô, R. J. Chem. Soc., Perkin Trans. 1 1991, in press. Electrochemical Measurements. All electrochemical experiments were conducted in a three-electrode cell under an argon atmosphere. The working electrode employed in cyclic voltammetry was a platinum sphere with an area of 0.0704 cm^2 . The working cathode used in controlledpotential electrolysis was a platinum foil of 3×4 cm. A Pt wire in a 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) solution in CH₂Cl₂ was used as the counter electrode, being separated from the cathodic compartment by a porous sintered glass frit. The reference electrode was a SCE (NaCl-saturated solution) that was connected to the cell by a salt bridge containing a 0.1 M TBAP-CH₂Cl₂ solution. The temperature of test solutions and of SCE was kept at 25.0 ± 0.1 °C.

The instrument employed for cyclic voltammetric measurements was standard equipment consisting of an Amel 551 potentiostat, a PAR 175 universal programmer, and a Philips PM 8043 X-Y recorder. Controlled-potential electrolyses and coulometric measurements were performed with an Amel 555A potentiostat equipped with an Amel 721 current integrator.

The volume of test solutions was 25 cm³. CH₂Cl₂ was used as solvent. The concentration of TBAP as supporting electrolyte was 0.1 M in all cases. Cyclic voltammograms of 0.5, 1.0, and 2.0 mM tetraradical 1 solutions were recorded in the scan rate range 0.01–0.2 V s⁻¹. Several exhaustive controlled-potential electrolyses of 2×10^{-5} mol of 1 were carried out at potentials corresponding to its overall reduction process. The number of electrons transferred per reacting molecule (*n* value) was obtained coulometrically by considering the background corrections, which were determined by electrolyzing 25 cm³ of 0.1 M TBAP–CH₂Cl₂ solution under the same experimental conditions.

Magnetic Measurements. Molar magnetic susceptibilities (χ_M) were measured in the temperature range 4.2-300 K with a SHE SQUID magnetometer operating in a field strength of 20 kOe. The data $(\chi'_M = \chi_M - \chi_{dia})$ were corrected for the magnetization of the sample holder and for the diamagnetic susceptibility of the molecule, which was experimentally determined from compound 5 $(\chi_{dia} = -1.13 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1})$.

EPR Experiments. A Varian Associates E-112 spectrometer working in the X band fit with an Oxford Instruments CF-900 continuous-flow liquid helium cryostat was used to obtain EPR spectra at low temperatures. Samples of 1 were prepared by adding 2.5 mg to 1 mL of 2methyltetrahydrofuran (MTHF) (used as supplied). The solutions were placed in quartz EPR tubes and degassed by three freeze-pump-thaw cycles before being inserted into the EPR cavity.

trans-Dichlorovinylenebis (2,4,6-trichlorobenzene) (3). Iron pentacarbonyl (10.4 g, 53.1 mmol) was slowly added to a stirred solution of 2 (5.51 g, 18.4 mmol) in benzene (27 mL), and the mixture was then refluxed (45 min). After cooling to room temperature, the mass was evaporated and the residue was digested with diluted aqueous HCl acid and extracted with CHCl₃. The organic solution, washed with water, dried (Na₂SO₄), and evaporated, gave a residue that was purified by column chromatography (silica gel, hexane) and successive recrystalli-

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zations in hexane to yield 3^4 as a white crystalline solid (2.52 g, 60%): mp 222 °C; IR (KBr, cm⁻¹) 3060, 1720, 1575, 1545, 1445, 1435, 1390, 1370, 1240, 1185, 1140, 1080, 890, 860, 820, 810, 760, 695, 575, 445; ¹H NMR (CDCl₃) δ 7.47 (s, 4 H); UV (cyclohexane) λ_{max} 288 (sh), 255 (sh), 240 nm (e 630, 6340, 19 900 dm³ mol⁻¹ cm⁻¹). Anal. Calcd for C14H4Cl8: C, 36.9; H, 0.9; Cl, 62.2. Found: C, 36.9; H, 0.5; Cl, 62.4. The mother liquors were combined, the resulting solution was evaporated, and the residue was recrystallized from n-pentane to give cis-dichlorovinylenebis(2,4,6-trichlorobenzene) (0.884 g, 21%): mp 152-3 °C; IR (KBr, cm⁻¹) 3060, 1720, 1570, 1540, 1445, 1420, 1390, 1240, 1200, 1190, 1150, 1145, 1090, 1080, 965, 890, 875, 860, 845, 820, 805, 690, 585, 520, 515, 470, 435; ¹H NMR (CDCl₃) δ 7.26 (s, 4 H); UV (cyclohexane) λ_{max} 304 (sh), 270, 241 (sh) nm (e 330, 7830, 16 300 dm³ mol⁻¹ cm⁻¹). Anal. Calcd for C14H4Cl8: C, 36.9; H, 0.9; Cl, 62.2. Found: C, 36.7; H, 0.9; Cl, 62.3.

trans - Dichlorovinylenebis[2,4,6-trichloro-3,5-bis(dichloromethyl)benzene] (4). Powdered anhydrous AlCl₃ (0.60 g, 4.5 mmol) was added to a solution of 3 (0.500 g, 1.1 mmol) in CHCl₃ (25 mL), and the resulting mixture was stirred at reflux (24 h). After cooling to room temperature, the mixture was poured into cold diluted aqueous HCl acid and extracted with CHCl₃. The organic solution, washed with water, dried (Na₂SO₄), and evaporated, gave a residue that was purified by column chromatography (silica gel, CCl₄) to yield 4 (0.612 g, 71%): mp 347 °C dec; IR (KBr, cm⁻¹) 3040, 1545, 1400, 1370, 1265, 1220, 1045, 1005, 840, 785, 760, 735, 710, 660, 625, 500, 470, 455; ¹H NMR (CD-Cl₃) δ 7.65 (s, 4 H); UV (CHCl₃) λ_{max} 301 (sh), 292 nm (ε 624, 928 dm³ mol⁻¹ cm⁻¹). Anal. Calcd for $C_{18}H_4Cl_{16}$: C, 27.4; H, 0.5; Cl, 72.0. Found: C, 27.3; H, 0.5; Cl, 72.5.

trans - Dichlorovinylenebis[2,4,6-trichloro-3,5-bis[(pentachlorophenyl)methyljbenzene] (5). Powdered anhydrous AlCl₃ (4.0 g, 30.0 mmol) was added to a mixture of 4 (1.0 g, 1.27 mmol) and pentachlorobenzene (5.0 g, 20 mmol), and the reacting mass was stirred at 140-50 °C (5 h 45 min). After cooling to room temperature, the crude was treated with diluted aqueous HCl acid, and the precipitate was washed with water and dried. The excess of pentachlorobenzene was sublimated off, and the residue was purified by column chromatography (silica gel) eluting successively with hexane, CCl4, and CHCl1. From the eluted fractions in CCl₄ and CHCl₃, 5 was obtained (2.1 g, 95%): mp 320 °C; IR (KBr, cm⁻¹) 2920, 1540, 1370 (br), 1345, 1310, 1300, 1245, 1210, 1195, 1120, 1045, 840, 810, 800, 720, 690, 680, 645, 535, 485, 465; ¹H NMR δ 6.98 (br s, 4 H); UV (cyclohexane) λ_{max} 303, 297.5, 292, 283 (sh), 251 (sh) nm (e 4340, 2680, 2940, 2220, 126 500 dm³ mol⁻¹ cm⁻¹). Anal. Calcd for C₆₆H₄Cl₄₈: C, 31.7; H, 0.2; Cl, 68.1. Found: C, 31.7; H, 0.3; Cl, 68.2.

trans - Perchlorovinylenebis-5- $(\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-1,3-xylylene) (1). Aqueous tetra-n-butylammonium hydroxide (40%) (0.127 g, 0.196 mmol) was added to a solution of 5 (0.060 g, 0.024 mmol) in THF (12 mL), and the resulting red solution was left at room temperature (20 h). Then, tetrachlorobenzoquinone (0.058 g, 0.235 mmol) was added, and the solution was left in the dark (2 h) and evaporated, and the residue was purified by column chromatography (silica gel, CCl₄). The red fraction obtained was evaporated, and the residue digested in refluxing hexane gave 1 as a brilliant deep red crystalline solid (0.031 g, 52%): mp 320 °C; IR (KBr, cm⁻¹) 1505, 1340, 1310, 1260, 1230, 840, 820, 805, 740, 710 (br), 655, 645, 540, 505; UV-vis (CHCl₃) λ_{max} 562, 495, 388, 373 (sh), 278 (sh) nm (e 4670, 4950, 105 200, 75 200, 24 700 dm³ mol⁻¹ cm⁻¹). Anal. Calcd for C₆₆Cl₄₈: C, 31.8; H, 0.0; Cl, 68.2. Found: C, 31.8; H, 0.3; Cl, 68.1.

Results and Discussion

trans-Vinylene 1 was prepared as follows: 2,4,6-Trichloro-1-(trichloromethyl)benzene $(2)^6$ with Fe(CO)₅ in benzene was converted into trans-stilbene 3; similar to the preparation of highly chlorinated aryl methanes,⁷ a Friedel-Crafts alkylation reaction on 3 with CHCl₃ by means of AlCl₃ afforded 4, which by condensation with a great excess of pentachlorobenzene in the presence of the same inorganic chloride gave the overcrowded stilbene 5; treatment of this with tetra-n-butylammonium hydroxide in THF, followed by oxidation of the resulting tetracarbanion with pchloranil,⁸ afforded tetraradical 1, isolated as infusible deep red



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(8) This is a general procedure to obtain highly chlorinated carbon free radicals; see ref 3b.



Figure 1. Cyclic voltammogram of a 0.5 mM tetraradical 1 solution in CH₂Cl₂ containing 0.1 M TBAP as supporting electrolyte: scan rate 0.1 V s⁻¹ and temperature 25.0 °C, starting potential 0.500 V and reversal potential -1.000 V (potential values vs SCE (NaCl-saturated solution).

crystals, stable in air up to 200 °C without decomposition. 1 does not react with oxygen in solution in the dark. Its electronic absorption spectrum displays the characteristic bands of the radical character of the molecule [λ (ϵ , dm³ mol⁻¹ cm⁻¹), 388 (105 200), 495 (4950), 562 (4670) nm]. Their molar absorptivities indicate the presence of four radical centers since they are around twice those for perchloro-m-xylylene (PMX) [387 (62600), 513 (2750), 563 (2680) nm],⁹ which in turn are around twice those for perchlorotriphenylmethyl (PTM) radical [382 (37 200), 510 (1190), 562 (1200) nm].10







Figure 2. Thermal variation of μ_{eff} (μ_B) for compound 1. The solid line was calculated with eq 2 and the values of the parameters as discussed in the text. In the inset, the dependence of the isothermal magnetization vs the magnetic field strength at 5 and 20 K is shown; the solid lines represent the field variation predicted by eq 3 with the values of the parameters fitted with eq 2.

As can be seen in Figure 1, cyclic voltammograms of 1 exhibit two consecutive redox couples, O_1/R_1 and O_2/R_2 , which behave as quasi-reversible systems. Their respective standard potentials (E°) were found to be -0.175 and -0.480 V vs SCE. The presence of these two redox pairs is indicative of the existence of an intermediate in the reduction process of 1. Several exhaustive controlled-potential electrolyses of 1 at -0.800 V vs SCE (a potential value corresponding to its overall reduction process) always lead to a coulometric n value of 4. Accordingly, by acidifying the electrolyzed solution with 2 M aqueous HCl, compound 5 (proceeding from tetraanion 14-) was identified as the final reaction product. These electrochemical findings allow one to ascribe the O_1/R_1 couple to the equilibrium

$$1 + 2e^- \Rightarrow 1^{2-}$$

the O_2/R_2 pair to the system

$$1^{2-} + 2e^{-} = 1^{4-}$$

It is assumed that the formation of 1^{2-} from 1 takes place by the reduction of one triarylmethyl radical in each xylylenyl substituent. Unfortunately, this intermediate dianion-diradical 12can not be obtained from bulk electrolysis of 1, because the reduction of 1 and 1²⁻ takes place in similar potential regions, as can be easily deduced from the partial overlapping of the consecutive cathodic peaks R_1 and R_2 of 1 (see Figure 1).

By considering that the molecule 1 could be treated as two pairs of radical centers, each of them modeled by two spins of value $\frac{1}{2}$ coupled by the interaction energy (J), the thermal dependence of the molar paramagnetic susceptibility (χ'_{M}) can be written as a modified Bleaney-Bowers equation:11

$$\chi'_{\rm M} = F \frac{4Ng^2 \mu_{\rm B}^2}{k_{\rm B}(T - \Theta)} \frac{1}{3 + \exp(-2J/k_{\rm B}T)}$$
(1)

where F is an empirical factor introduced to correct the reduction in the magnetic susceptibility of the sample due to the presence of mono-, di-, and triradical impurities, the factor 4 accounts for the fact that four radical centers are present in the molecule, and the Curie–Weiss constant Θ is associated to the existence of weak magnetic interactions between the pairs of radical centers. As $\chi'_{\rm M} = N\mu_{\rm eff}^2/3k_{\rm B}T$, the thermal variation of the molar effective magnetic moment is

$$\mu_{\rm eff}(\mu_{\rm B}) = 4 \left[\frac{FT}{T - \Theta} \frac{3}{3 + \exp(-2J/k_{\rm B}T)} \right]^{1/2}$$
(2)



Figure 3. ESR spectrum of 1: (a) in MTHF solution at room temperature, (b) $\Delta m_s = \pm 1$ transitions in MTHF glass at 60 K, (c) $\Delta m_s = \pm 2$ transition in MTHF glass at 76 K.

where g has been taken equal to 2 and the term $3/(3 + \exp(2J/k_{\rm B}T$ reproduces the thermal variation of the magnetization of a pair of radical centers due to the population of the excited singlet state, being 2J, the triplet-singlet energy gap.

The free parameters Θ , 2J, and F were determined by fitting experimental data to eq 2 (Figure 2), resulting in the following values: $\theta = -1.1 \pm 0.1$ K, $2J = 240 \pm 10$ cm⁻¹, and F = 0.916 \pm 0.001. The rather abrupt decrease in μ_{eff} below 45 K is related to the negative value of Θ , which indicates a weak antiferromagnetic interaction between pairs of radicals. Since μ_{eff} is nearly constant and equal to the value of 3.8 μ_B in the interval 45-105 K, it is considered that 1 is a molecule with a pair of triplets (theoretical value, $4.0\mu_B$). In this interval, the effect of the an-

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tiferromagnetic interaction is negligible, and the temperature is low enough for the singlet states not to be significantly populated. Above 105 K, μ_{eff} decreases steadily on increasing the temperature up to 300 K due to the thermal population of the singlet states. The existence of some kind of weak inter- or/and intramolecular antiferromagnetic interactions is supported by a slight deviation of the magnetization at low temperatures (5 K) (see inset in Figure 2) from the expected behavior (eq 3) for a pair of independent triplet states separated from the excited singlet states by the energy gap 2J:

$$M(T,H) = \frac{2FN_{\rm A}}{A} \frac{\sum m_i e^{-E_i/k_{\rm B}T}}{\sum e^{-E_i/k_{\rm B}T}}$$

i.e.

$$M(T,H) = 2F \frac{N_A \mu_B g}{A} \frac{-e^{-2\mu_B H/k_B T} + e^{2\mu_B H/k_B T}}{e^{-2\mu_B H/k_B T} + e^{2\mu_B H/k_B T} + e^{-2J/k_B T} + 1}$$
(3)

where m_i and E_i are the magnetization and energy of each state, respectively, N_A is the Avogadro's number, A is the molecular weight, 2 is a factor due to the fact that two pairs of radical centers are present in the molecule, and H is the magnitude of the applied magnetic field. Equation 3 represents the mean value of the magnetization per mass unit taking into account the thermal population of the triplet and singlet states of each pair of radical centers.

The $\Delta m_s = \pm 1$ region of the EPR spectrum of the sample obtained of 1 in frozen MTHF over the range 4-129 K shows a complex pattern with several lines (Figure 3), and some of these might be due to the presence of two diastereoisomeric forms of the molecule because of the restricted rotation of pentachlorophenyl groups.¹² Supporting the presence of these species, the

 $\Delta m_s = \pm 2$ region of the spectrum (Figure 3) exhibits two overlapping lines, one of which can be saturated by increasing the microwave power. From the two symmetric and outermost pairs of peaks with $\Delta m_s = \pm 1$, the zero splitting parameters |D/hc| for these high-spin species are predicted to be 0.010 and 0.013 cm⁻¹. Such small values are in satisfactory agreement with those reported for *m*-xylylene $(0.011 \text{ cm}^{-1})^{13}$ and the two diastereoisomers of perchloro-*m*-xylylene $(0.0156 \text{ and } 0.0080 \text{ cm}^{-1}).^{14}$ The center peak of the spectrum is assigned to doublet impurities. Accordingly to this, the EPR spectrum of 1 in MTHF solution at room temperature seems to be a superposition of a sharp line and a broad line. The former, which has the characteristics (g = 2.0033; ΔH_{pp} = 3.87 G) of the highly chlorinated triphenylmethyl radicals,³ is attributed to the impurities.

Since it has been calculated that the triplet-singlet energy gap value is quite high (0.69 kcal/mol) and the signal intensity of the $\Delta m_s = \pm 2$ transition rises continuously when the temperature is lowered from 129 to 4 K, it is concluded that the ground state of 1 is a pair of triplets.

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Registry No. 1, 135773-36-3; 2, 14379-95-4; 3, 135773-37-4; 4, 135773-38-5; 5, 135773-39-6; cis-dichlorovinylenebis(2,4,6-trichlorobenzene), 135773-40-9; pentachlorobenzene, 608-93-5.

Surface Raman Scattering of Self-Assembled Monolayers Formed from 1-Alkanethiols: Behavior of Films at Au and Comparison to Films at Ag

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Abstract: Surface Raman scattering is used to study self-assembled monolayers formed from a series of 1-alkanethiols, $CH_3(CH_2)_nSH$, where n = 3-5, 7, 8, 11, and 17, at mechanically polished and electrochemically roughened Au surfaces. Defect structure in these films is investigated by use of the relative intensities of peaks due to trans and gauche conformations in the ν (C-S) and ν (C-C) frequency regions. Surface selection rules for Raman spectroscopy are used to estimate orientation of the alkanethiol layers at Au. The orientation proposed on the basis of the Raman spectral data is consistent with those previously reported on the basis of other measurements at Au surfaces. This orientation is compared to that previously determined for these films at Ag. Alkanethiols at Ag are found to have a chain tilt from the surface normal less than the 30° previously reported for Au. The C-S bond is found to be perpendicular to the Ag surface while it is largely parallel to the surface at Au. Differences in the spectra of short-chain alkanethiols from smooth and rough surfaces are attributed to disordering of the film at the roughened Au surface which occurs predominantly near the S end of the molecule on rough Au surfaces.

Introduction

The spontaneous self-assembly of 1-alkanethiols at Au surfaces has been studied with many analytical methods including IR spectroscopy,¹ ellipsometry,² XPS,³ electron diffraction,⁴ contact angle measurements,⁵ and electrochemistry.⁶ In general, the conclusions from these studies are that highly ordered, defect-free monolayer films spontaneously form at Au surfaces.

IR spectroscopy has been commonly used to characterize the packing and orientation of these films.^{2,3} IR results suggest that

self-assembled monolayer films are densely packed in a crystalline arrangement, with the alkane chain in an all-trans conformation.³ Comparisons of the frequencies in the ν (C-H) region between adsorbed and solid alkanethiols have been used to deduce con-

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⁽¹²⁾ Two diastereoisomers differing only in the propeller helicity of triarylmethyl groups have been recently isolated for the structurally related perchloro-m-xylylene.14

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