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Incorporation of Stable Organic Radicals of the Tris(2,4,6-trichlorophenyl)methyl Radical Series to Pyrrole Units as Models for Semiconducting Polymers with High Spin Multiplicity. 1. [2,6-Dichloro-4-[2,5-bis(5-methyl-2-thienyl)-1-pyrrolyl]phenyl]bis(2,4,6-trichlorophenyl)methyl Radical as a Precursor of a Disjoint Heterospin Diradical with a Triplet or a Nearly Degenerate Singlet−Triplet Ground State

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The condensation reactions between (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical and acetylacetone or 1,4-bis(5-methyl-2-thienyl)-1,4-butanedione yield [2,6-dichloro-4-(2,5-dimethyl-1-pyrrolyl)phenyl]bis(2,4,6-trichlorophenyl)methyl radical (**3**$^\bullet$) and [2,6-dichloro-4-[2,5-bis-(5-methyl-2-thienyl)-1-pyrrolyl]phenyl]bis(2,4,6-trichlorophenyl)methyl radical (**4**$^\bullet$), respectively. EPR studies of both radicals **3**$^\bullet$ and **4**$^\bullet$ in CH_2Cl_2 solution suggest a weak electron delocalization with coupling constant values of 1.25 and 1.30 G, respectively, with the six aromatic hydrogens. Their electrochemical behavior was analyzed by cyclic voltammetry. Both radicals show reversible reduction processes at $E° = -0.69$ V and −0.61 V versus SSCE, respectively, and anodic peak potentials at $E_p{}^a = 1.10$ and 0.72 V, respectively, versus SSCE at a scan rate (ν) of 200 mV s^{-1}, being reversible for radical **4**$^\bullet$. X-ray analysis of radical **3**$^\bullet$ shows a high value (65°) of the dihedral angle between the 2,5-dimethylpyrrolidyl moiety and the phenyl ring. Smooth oxidation of radical **4**$^\bullet$ in CH_2Cl_2 containing trifluoroacetic acid gives an ionic diradical species with a weak electron interaction ($|D/hc| = 0.0047$ cm^{-1}). A Curie plot of the $\Delta m_s = \pm 2$ signal intensity versus the inverse of the absolute temperature in the range between 4 and 70 K suggests a triplet or a nearly degenerate singlet−triplet ground state.

Introduction

One of the main objectives in the field of magnetic materials is the preparation of new purely organic compounds with ferromagnetic properties.[1] One approach is the design of organic structures that could accommodate both localized and delocalized electron spins. The localized spins must be strategically situated in these systems to show spin ordering through the conduction electrons.

A number of reports on novel organic spin systems based on electron-transfer complexes have recently appeared.[2] In these particular systems, the electron-transfer salts that support radical substituents are potential candidates to achieve ferromagnetic coupling between the "static" and "dynamic" unpaired electrons. Consequently, high-spin multiplicity must be achieved between the two unpaired electrons at the molecular level, one situated in the substituent and the other generated on the donor or acceptor units. An examination of the intramolecular exchange interaction in the ion-diradical species generated by the redox reaction would be crucial in this respect.

In addition, two conditions must be satisfied before testing the potential ferromagnetism of these organic systems: (1) the localized radical moieties linked to the donor or acceptor units must be stable, and (2) the oxidation potentials of donors or the reduction potentials of acceptors should be lower than the corresponding potentials of radical moieties, to prevent the generation of closed-shell cationic or anionic species in the oxidative or reductive processes to ferromagnetic systems, respectively.[2d]

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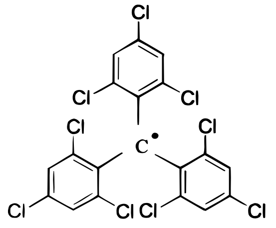
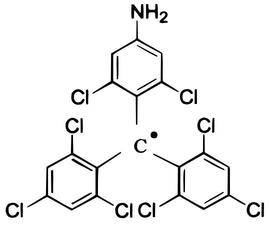
10.1021/jo000217b CCC: $19.00

Chart 1



1$^\bullet$



2$^\bullet$

In our efforts to apply the chemistry of the very stable C-centered free radicals derived from TTM (tris(2,4,6-trichlorophenyl)methyl radical,[3] **1**$^\bullet$) series,[4] we reported the synthesis of the amine radical **2**$^\bullet$[5] (Chart 1) as a potential intermediate in the synthesis of new magnets, taking advantage of the extensive chemical reactivity of the amine group.

As part of a program directed toward the synthesis of new molecular compounds with high multiplicity, our research deals with novel structures based on the incorporation of pyrroles and 2,5-bis(thienyl)pyrroles as substituents in the TTM radical. These molecules are composed of a stable localized spin, a trivalent carbon atom the stability of which is due to the presence of six chlorines in the ortho position, and an electron-rich substituent capable of locating conduction electrons by oxidative polymerization. In this way, new potentially ferromagnetic systems can be designed by replacing electron-transfer complexes by polymeric chains containing dynamic unpaired electrons.

Here we report on the synthesis of [2,6-dichloro-4-(2,5-dimethyl-1-pyrrolyl)phenyl]bis(2,4,6-trichlorophenyl)-methyl radical (**3**$^\bullet$) and [2,6-dichloro-4-[2,5-bis(5-methyl-2-thienyl)-1-pyrrolyl]phenyl]bis(2,4,6-trichlorophenyl)-methyl radical (**4**$^\bullet$) (Chart 2), characterized by electron paramagnetic resonance (EPR). The molecular structure of radical **3** was elucidated by X-ray analysis. The electrochemical behavior of **3**$^\bullet$ and **4**$^\bullet$ was analyzed by cyclic voltammetry (CV) and compared with that of 3,5-dichlorophenyl)-2,5-dimethylpyrrole (**5**) and 1-(3,5-dichlorophenyl)-2,5-bis(5-methyl-2-thienyl)pyrrole (**6**) (Chart 2). The most favorable conditions for the chemical oxidation of pyrroles **5** and **6** to their radical cations, detected by EPR, were tested and applied to the oxidation of radical **4**$^\bullet$ to the corresponding radical cation species. The nature of this diradical was studied by EPR at different temperatures and its multiplicity has been assigned.

Synthesis

Pyrroles **5** and **6** and triphenylmethyl radicals **3**$^\bullet$ and **4**$^\bullet$ were synthesized by well-known procedures. An equimolecular mixture of 3,5-dichloroaniline and acetylacetone in benzene, in the presence of montmorillonite K_{10} as a desiccator, gave an excellent yield of pyrrole **5**.[7] A different cyclization procedure was used to obtain triphenylmethyl radical **3**$^\bullet$ in a quantitative yield.[8] Thus, a mixture of amine radical **2**$^\bullet$ and 2 equiv of acetylacetone was refluxed in benzene, in a Dean−Stark apparatus in the presence of acetic acid as catalyst. Reduction of radical **3**$^\bullet$ with sodium hydroxide and dimethyl sulfoxide in diethyl ether and then neutralization of the anion with diluted aqueous hydrochloric acid gave the corresponding diamagnetic triphenylmethane **7**.

A more powerful procedure was used to synthesize the sterically crowded pyrrole **6** and the triphenylmethyl radical **4**$^\bullet$. It involved the use of titanium tetrachloride ($TiCl_4$) as a scavenger of water[9] and as a Lewis acid to enhance the electrophilicity of the carbonyl carbon atoms of the 1,4-diketone, 1,4-bis(5-methyl-2-thienyl)-1,4-butanedione[10] (**8**). Thus, the reaction of **8** and an excess of 3,5-dichloroaniline in benzene, in the presence of $TiCl_4$, gave a good yield of pyrrole **6**. Similarly, an equimolecular mixture of amine radical **2**$^\bullet$ and butanedione **8** with $TiCl_4$ in the presence of an excess of triethylamine gave a moderate yield of radical **4**$^\bullet$.

Both radicals **3**$^\bullet$ and **4**$^\bullet$ are dark red microcrystalline solids, very stable either in solid or in solution. Their electronic spectra in cyclohexane are as follows: λ/nm (ϵ/L mol^{-1} cm^{-1}); radical **3**$^\bullet$, 371 (20.000), 500 (sh) (730), 543 (830), and radical **4**$^\bullet$, 373 (35 600), 500 (740), 543 (860).

Molecular Structure of Radical 3$^\bullet$

An ORTEP drawing of the molecular structure of the triphenylmethyl radical **3**$^\bullet$ is shown in Figure 1, including the atom numbering scheme, and a selection of bond lengths and bond angles are summarized in Table 1. This radical species crystallizes from *n*-hexane in the monoclinic system, space group $P2_1/n$, with four molecules in the elemental cell. All the distances and angles for the central carbon atom C(1) with aromatic carbon atoms C(2), C(8) and C(14) are in good agreement with an sp^2 hybridization for C(1) (Table 1). Therefore, these four carbon atoms are located in a plane (plane 1) with a maximum deviation of 0.005 Å, except for C(1), for which the deviation is −0.016 Å.

The molecule is constituted by four more planes corresponding to the three benzene rings, C2,C3,C4,C5,-C6,C7 (plane 2), C14,C15,C16,C17,C18,C19 (plane 3), and C8,C9,C10,C11,C12,C13 (plane 4), and the dimethylpyrrolyl plane, N,C20,C21,C22,C23 (plane 5). Due to the presence of six chlorines ortho to C(1), the phenyl rings are twisted around their bonds to C(1); the dihedral angles between planes are as shown in Table 2. Therefore, the molecule adopts a propeller-like conformation. The high value (65°) of the dihedral angle between planes 4 and 5 deserves special mention. In this case, the torsion from planarity avoids the interaction between the methyl substituents in the pyrrole ring and the phenyl hydrogen atoms. It is also remarkable that the heterocyclic plane is quite planar, as revealed by the small maximum (−0.004 Å) for C22 deviation from the least-squares

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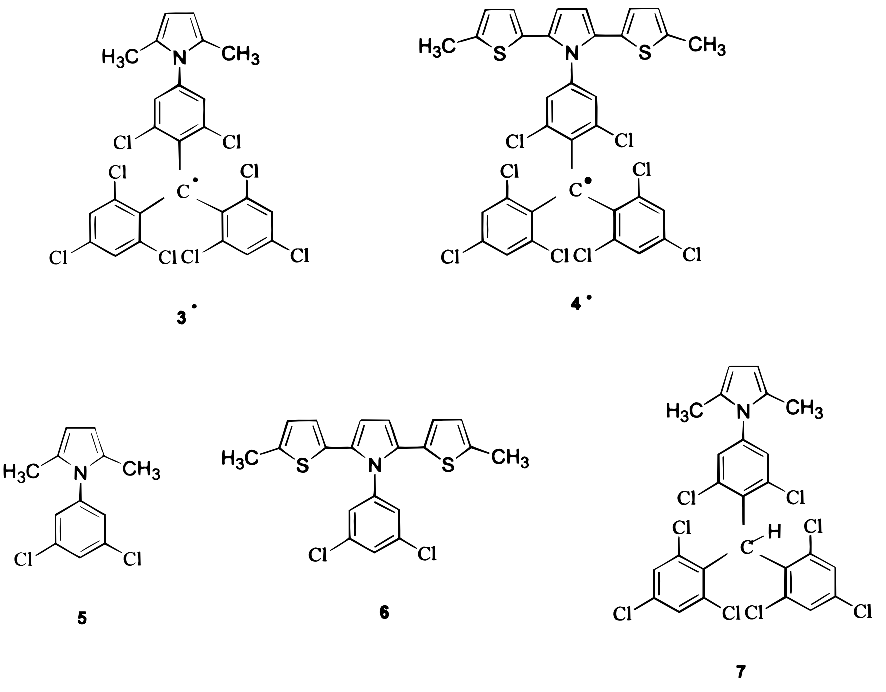
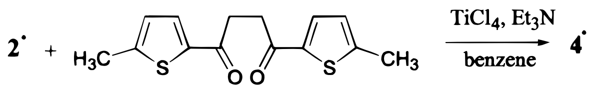
Chart 2



$3^{\bullet}$ $4^{\bullet}$ 5 6 7

Chart 3



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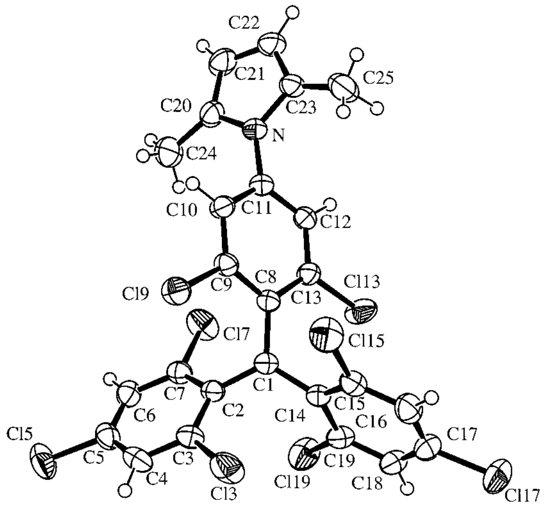

Figure 1. Perspective view of the structure with the atom numbering of radical $3^{\bullet}$.

Table 1. Selected Bond Lengths and Angles of Triphenylmethyl Radical $3^{\bullet}$

bond lengths (Å)		bond angles (deg)	
C1−C2	1.463(3)	C2−C1−C8	118.6(2)
C1−C8	1.471(3)	C8−C1−C14	118.2(2)
C1−C14	1.472(3)	C14−C1−C2	122.5(2)
C11−N	1.425(2)	C20−N−C23	109.7(2)
		C11−N−C20	123.5(2)

Table 2. Dihedral Angles (deg) between Planes in Triphenylmethyl Radical $3^{\bullet}$

P1−P2	42.20(9)
P1−P3	53.96(7)
P1−P4	50.34(7)
P4−P5	65.13(8)

plane, and the benzene planes are less planar, as shown by the large maxima (−0.022 for C2 in plane 2; 0.028 Å for C14 in plane 4; 0.040 Å for C8 in plane 3) for deviations from the least-squares planes attributed to steric effects.

Cyclic Voltammetry

Reduction Processes. Cyclic voltammograms for the reduction of triphenylmethyl radicals $3^{\bullet}$ and $4^{\bullet}$ ($\sim 10^{-3}$ M) in CH_2Cl_2 containing *n*-tetrabutylammonium perchlorate (TBAP) ($\sim 10^{-1}$ M) at 25 °C show a couple O_1/R_1 at $E° = -0.69$ and -0.61 V versus SSCE (sodium chloride saturated calomel electrode), respectively. They are displayed in Figure 2 together with a voltammogram of tris(2,4,6-trichlorophenyl)methyl radical (TTM), with a redox couple at $E° = -0.66$ V obtained in the same conditions. The R_1 peaks are related to the reduction of substrates to their anions, which are very stable in solution, and their O_1 peaks correspond to the oxidation of the reduced species. All reduction peaks have similar heights, and the $|I_p{}^a|/I_p{}^c$ ratio between the anodic and cathodic peak currents for both couples is close to 1. The height of these peaks increase linearly with the square root of the scan rates, as expected for diffusion-controlled processes.[11,12]

Oxidation Processes. (a) Cyclic voltammograms for the oxidation of triphenylmethyl radical $3^{\bullet}$, the diamagnetic parent compound **7**, and pyrrole **5** showed irreversible oxidation peaks in the same potential region, at $E_p{}^a = 1.10$ V for $3^{\bullet}$ and **7** and at $E_p{}^a = 1.13$ V for **5**, versus SSCE at a scan rate (ν) of 200 mV s^{-1}. In contrast, at ν values larger than 50 mV s^{-1}, TTM radical displayed a

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[12] *Organic Electrochemistry. An Introduction and a Guide*; Lund, H., Baizer, M. M., Ed.; Marcel Dekker: New York, 1991; Chapters 2, 3, and 7.

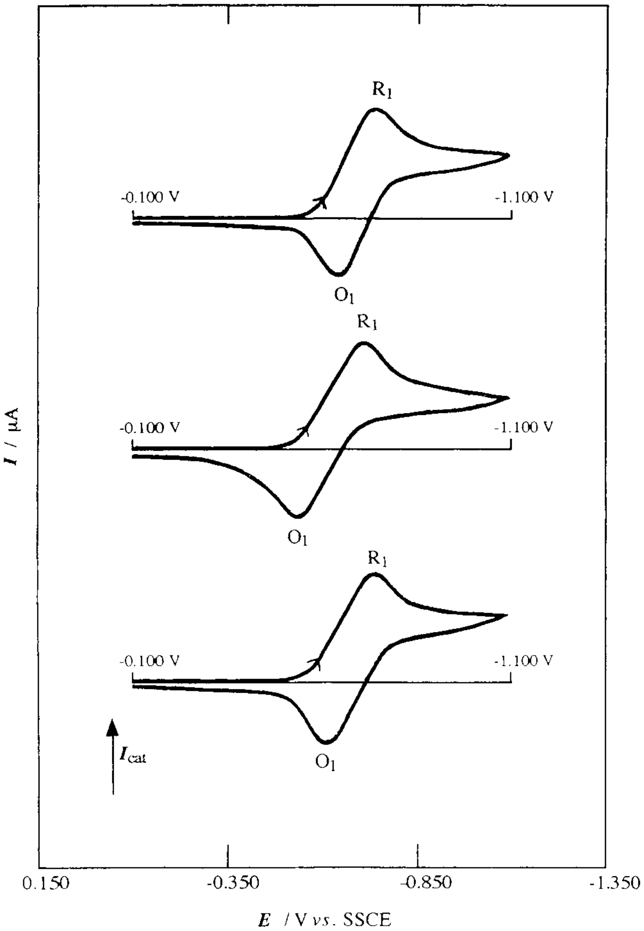

Figure 2. Cyclic voltammograms for the reduction of (a) a 1 mM solution of radical $3^{\bullet}$, (b) a mM solution of radical $4^{\bullet}$, and (c) a 1 mM solution of TTM radical in CH_2Cl_2 with 0.1 M of TBAP on Pt. Initial and final potentials −0.100 V. Reversal potential −1.100 V. Scan rate 200 mV s^{-1} at 25 °C.

reversible redox process with a standard potential $E°$ (O_2/R_2) = 1.20 V, the oxidation peak appearing at more positive potentials, $E_p{}^a = 1.26$ V at $v = 200$ mV s^{-1}. At $v \leq 25$ mV s^{-1} the R_2 peak was not observed. This redox process for TTM radical involves a one-electron transfer and is ascribed to the equilibrium reaction between TTM radical and its cation TTM^+. All these results suggest that the dimethylpyrrole moiety of radical $3^{\bullet}$ is oxidized in its O_2 peak instead of the trivalent carbon atom, as occurs in the O_2 peaks for pyrrole **5** and hydrocarbon **7**.

Comparison of the heights of the oxidation peaks of $3^{\bullet}$, **5**, and **7** with that of TTM radical indicates that the overall oxidation of the dimethylpyrrole moiety is complex, involving at least two electrons per molecule. These heights increase linearly with $v^{1/2}$, as expected for diffusion-controlled processes.[11,12]

According to all these findings and to kinetic results, it is plausible to propose that the dimethylpyrrole moiety of $3^{\bullet}$, **5**, and **7** is initially oxidized to its radical cation in a one-electron step and that this process is the rate-limiting step of the global oxidation. The electrogenerated cations, which are unstable in solution, decompose quickly to yield other stable intermediates, which undergo further oxidation.

(b) Cyclic voltammograms for the oxidation of triphenylmethyl radical $4^{\bullet}$ and bis(2-thienyl)pyrrole **6** showed different behavior. Both displayed two consecutive peaks in the same potential region. In both cases the first oxidation process, O_2, is associated with a reduction peak R_2. This can be seen in Figure 3, where the cyclic voltammograms for these compounds from 0.100 to 1.350 V at 200 mV s^{-1} are displayed. The reversibility of the first oxidation peak was confirmed by reversing the scan at 0.850 V. The O_2 peaks for $4^{\bullet}$ and **6** ($E_p{}^a$ = 0.72 and 0.73 V at 200 mV s^{-1}, respectively) have similar heights to the R_2 peak, indicating that they correspond to one-electron processes, and the $|I_p{}^a|/I_p{}^c$ ratio for their O_2/R_2 pairs is close to 1 at all v values tested. All these peaks are diffusion-controlled because their heights increase linearly with $v^{1/2}$. The ($E_p{}^c - E_p{}^a$) difference for both couples increased from 100 mV at 20 mV s^{-1} to 160 mV at 200 mV s^{-1}, as expected for a quasireversible one-electron charge-transfer process.[11,12] Their standard potentials are $E°$ (O_2/R_2) = 0.64 and 0.63 V for **6** and $4^{\bullet}$, respectively. These redox processes are ascribed to the equilibrium reactions between the neutral species and their cations:

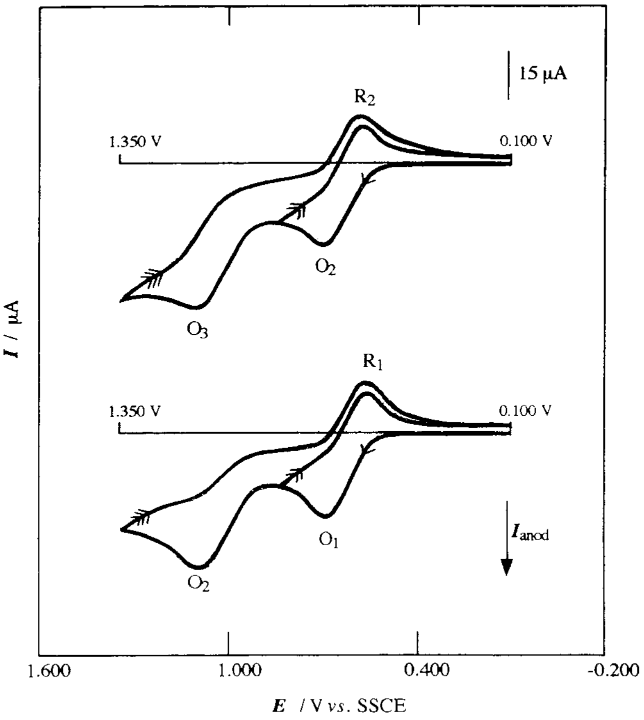

Figure 3. Cyclic voltammograms for the oxidation of (a) a 1 mM solution of radical $4^{\bullet}$ and (b) a 1 mM solution of pyrrole **6** in CH_2Cl_2 with 0.1 M of TBAP on Pt. Initial and final potentials 0.100 V. First reversal potential 0.850 V; second reversal potential 1.350 V. Scan rate 200 mV s^{-1} at 25 °C.

$$\mathbf{4}^{\bullet} \rightleftharpoons \mathbf{4}^{\overset{2\bullet}{\oplus}} + e^-$$

$$\mathbf{6} \rightleftharpoons \mathbf{6}^{\overset{+}{\bullet}} + e^-$$

As before, the close resemblance of the standard potentials of radical $4^{\bullet}$ and pyrrole **6** suggests that the oligomeric moiety of radical $4^{\bullet}$ is oxidized in its O_2 peak in a similar way to pyrrole **6**. The electrogenerated cations are stable in solution, and they are the electroactive species of the consecutive O_3 peaks at $E_p{}^a$ = 1.12 and 1.13 V for $4^{\bullet}$ and **6**, respectively. In these second oxidation peaks, one-electron processes controlled by diffusion are also involved, since their heights are similar

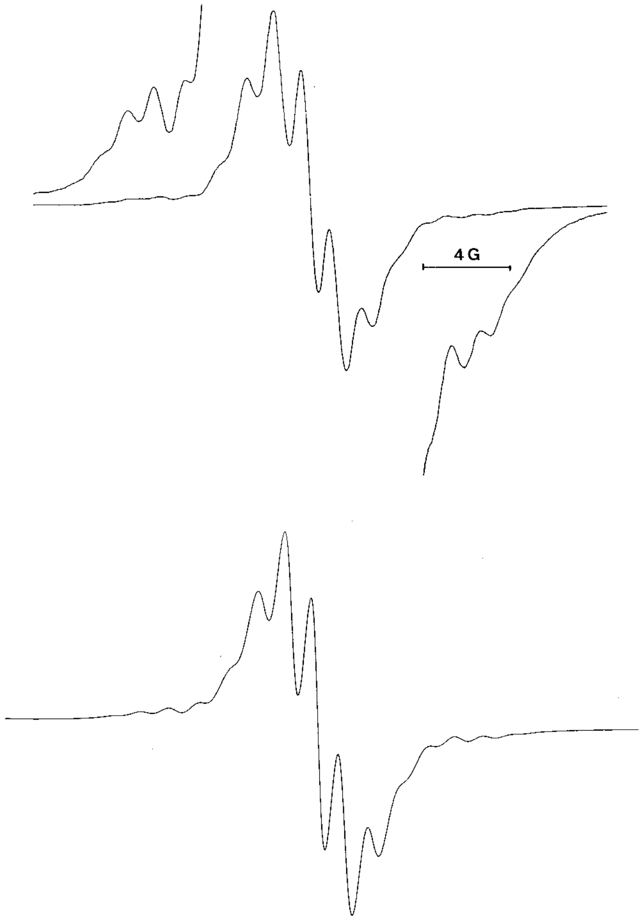

Figure 4. (a) EPR spectrum of a solution of radical **3**$^{\bullet}$ in CH_2Cl_2 at 163 K and amplification showing ^{13}C couplings. (b) Computer simulation with the values given in the text.

to those of the first reversible oxidation peaks. Consequently, the initial reaction for the second oxidation peaks corresponds to one-electron oxidation to give dications, which are reactive in the medium.

$$\mathbf{4}^{\overset{2\cdot}{\oplus}} \longrightarrow \mathbf{4}^{2+} + e^{-}$$

$$\mathbf{6}^{\overset{+}{\cdot}} \longrightarrow \mathbf{6}^{2+} + e^{-}$$

Electron Paramagnetic Resonance

X-Band electron paramagnetic resonance (EPR) spectra of triphenylmethyl radicals **3**$^{\bullet}$ and **4**$^{\bullet}$ were recorded in deoxygenated CH_2Cl_2 solutions at 163 and 183 K, respectively. Both spectra are similar to that of TTM radical, and that of radical **3**$^{\bullet}$ is displayed in Figure 4 with a computer simulation using the following EPR parameters: $a_{6H} = 1.25$ G and peak-to-peak line width $\Delta H_{pp} = 0.8$ G. Similar parameters were used to simulate the spectrum of **4**$^{\bullet}$: $a_{6H} = 1.30$ G and $\Delta H_{pp} = 1.0$ G. g values are close to that of the free electron, $g = 2.0032$ and $g = 2.0029$ for **3**$^{\bullet}$ and **4**$^{\bullet}$, respectively, and similar to that of the TTM radical ($g = 2.0032$),[3] indicating a small spin−orbit coupling. Therefore, both spectra consist of an overlapping septet of lines corresponding to weak coupling with the six aromatic protons in the meta position, which are magnetically equivalent despite the presence of the substituent in the para position. At higher values of the gain, the isotropic coupling with the ^{13}C nuclear spins of the α-carbon atom, the three bridgehead carbon atoms, and the six ortho-carbon atoms for each radical species appeared in the spectra on both sides of the main spectrum at 29.75 G, 13.25 and 10.15 G for **3**$^{\bullet}$, and 31.12 G, 13.25, and 10.15 G for **4**$^{\bullet}$.

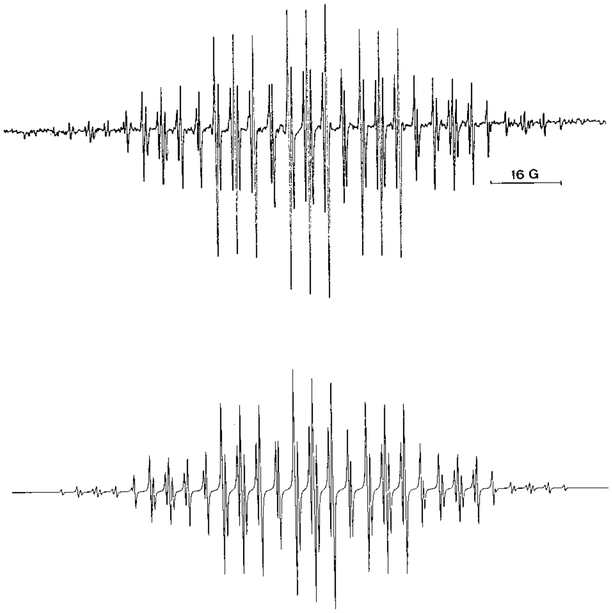

Figure 5. (a) EPR spectrum of an irradiated solution of 1-(3,5-dichlorophenyl)-2,5-dimethylpyrrole (**5**) in TFA in the presence of thallium(III) trifluoroacetate at 298 K, with a modulation amplitude, MA = 0.1. (b) Computer simulation using the values given in the text.

The EPR spectrum of the oxidized species **5**$^{\bullet+}$, generated by photolyzing a solution of **5** in trifluoroacetic acid (TFA) at room temperature in the presence of thallium(III) trifluoroacetate, is shown in Figure 5. A computer simulation of this spectrum was obtained by using the following hyperfine splitting (hfs) constants: $a(6H) = 16.6$ G, $a(1N) = 4.4$ G, and $a(2H) = 3.6$ G, with a line width of $\Delta H_{pp} = 0.2$ G. The g value is 2.0025. These values do not differ appreciably from the parameters of the spectra of radical cations from other related pyrroles reported in the literature.[13] The values of the coupling constants with the benzene hydrogens are not distinguished and are always ≤ 0.2 G.

Figure 6 shows an excellent and well-defined EPR spectrum of **6**$^{\bullet+}$, generated at room temperature by smooth oxidation of parent compound **6** in CH_2Cl_2 solution containing TFA (20%). A spectrum with similar resolution appeared when 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) was used as solvent.[14] This radical cation is quite stable in solution, and the intensities of the signals in the spectrum remained constant for more than 2 h. An accurate simulation (Figure 6) was obtained by using the following parameters: $a(6H, 2CH_3) = 5.12$ G, $a(3'H, 3''H) = 3.87$ G, $a(3H, 4H) = 2.30$ G, $a(1N) = 2.62$ G, $a(4'H, 4''H) = 0.19$ G, $\Delta H_{pp} = 0.1$ G, $g = 2.0023$. All these values have been assigned by reference to those of similar

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[14] This secondary alcohol has proved to be a good solvent to stabilize radical cation species in solution, see: Eberson, L.; Hartshorn, M. P.; Persson, O.; Radner, F. *J. Chem. Soc., Chem. Commun.* **1996**, 2105.

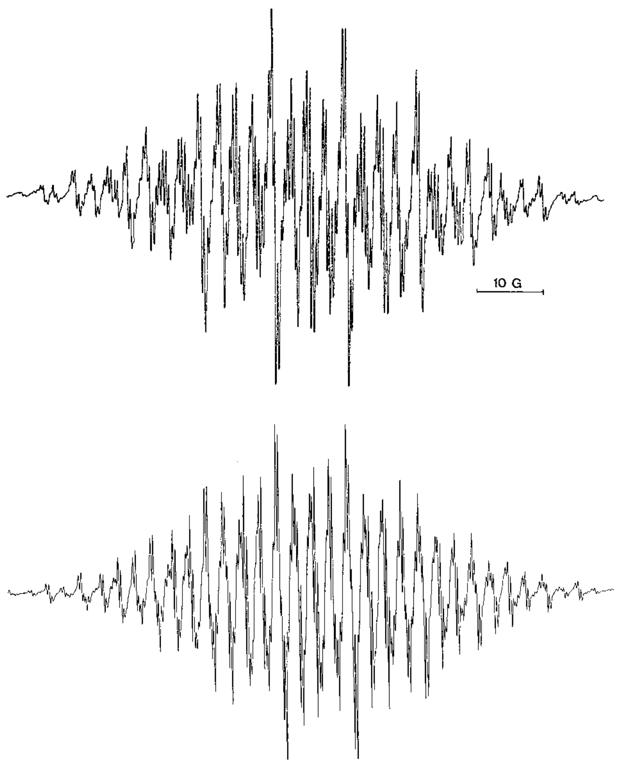
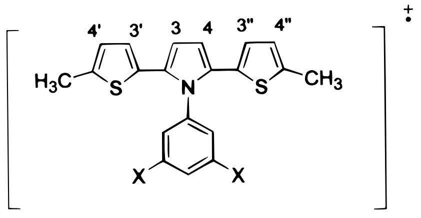


Figure 6. (a) EPR spectrum of 1-(3,5-dichlorophenyl)-2,5-bis-(5-methyl-2-thienyl)pyrrole (**6**) in CH_2Cl_2 solution containing TFA (20%) with MA = 0.1. (b) Computer simulation using the values given in the text..



6$^{+\bullet}$: X = Cl

9$^{+\bullet}$: X = H

oxidized species.[15] As expected, the spectrum of **6**$^{\bullet+}$ does not differ from the spectrum of radical cation **9**$^{\bullet+}$ (the spectral parameters of which are as follows: a(6H, $2CH_3$) = 5.17 G, a(3′H, 3″H) = 3.70 G, a(3H, 4H) = 2.31 G, a(1N) = 2.59 G, a(4′H, 4″H) = 0.25 G, ΔH_{pp} = 0.17 G, g = 2.0023),[16] suggesting small delocalization of the unpaired electron into the phenyl moiety. The very weak interactions with aromatic hydrogens only contribute to the line width of the signals.

Radical **4**$^{\bullet}$ was dissolved in CH_2Cl_2 containing TFA (25%) in the same conditions as those used to generate the radical cation **6**$^{\bullet+}$. Under these conditions and even in TFA as the sole solvent the radical nature of **4**$^{\bullet}$ did not change. This was established in experiments with TTM radical, a species of the same series, which was quantitatively recovered. The EPR spectrum obtained at room temperature consisted of a single broad line centered at $g = 2.0031$, with a peak-to-peak line width ΔH_{pp} = 3.75 G, which practically corresponded to the spectrum of neutral radical **4**$^{\bullet}$ in CH_2Cl_2 solution at room temperature.

In addition, smooth tails were apparent in the region around the central line of the spectrum. In a glassy solution (100 K), a typical spectrum of an axial-symmetric triplet state (Figure 7), described by the zero-field splitting parameter $|D/hc|$ = 0.0047 cm^{-1} (the principal values of the g tensor were $g_{zz} = 2.0036$, $g_{yy} = g_{xx} = 2.0029$) appeared superimposed with an intense central line corresponding to $S = {}^1/_2$ species. Further confirmation of the triplet state configuration of the species was provided by the observation of the $\Delta m_s = \pm 2$ region of a broad (ΔH_{pp} = 5.2 G) line centered at $g = 4.0025$. From parameter D, the average distance between the radical centers[17] was estimated to be 8.2 Å, being the distance between the trivalent carbon and the nitrogen of 5.699(2) Å, as confirmed by X-ray analysis. This fact suggests a strong delocalization of one electron into the thienyl rings, the other electron being mainly confined in the trivalent carbon atom where the spin density is maximal. A Curie plot of the $\Delta m_s = \pm 2$ signal intensity versus the inverse of the absolute temperature in the range between 4 and 70 K gave a straight line (correlation coefficient = 0.998), indicating a triplet ground state or nearly degenerate with a singlet state (Figure 8).

Discussion

Radicals **3**$^{\bullet}$ and **4**$^{\bullet}$ are examples of stable radical species the stability of which is conferred by the steric shielding of the six chlorines surrounding the trivalent carbon atom, leading to a propeller-like conformation with a significant inhibition of the conjugation of the unpaired electron into the phenyl rings.[18] Both radicals were synthesized by direct condensation of amino radical **2**$^{\bullet}$ with the corresponding 1,4-diketone. While **3**$^{\bullet}$ was prepared in good yield, radical **4**$^{\bullet}$ was obtained in moderate yield due most probably to the steric hindrance shown by diketone **8** when condensing with **2**$^{\bullet}$. Electrochemical analysis of radical **4**$^{\bullet}$ demonstrated its amphoteric character, consisting in the presence of reversible one-electron reduction and oxidation processes in the cyclic voltammograms leading to anionic and cationic species, respectively. Radical **3**$^{\bullet}$ has similar reductive redox behavior, but its anodic process is irreversible. Furthermore, the similarity of the cathodic potential of TTM radical to those of radicals **3**$^{\bullet}$ and **4**$^{\bullet}$ indicates that these reductions take place in the trivalent carbon of both radicals, yielding stable anions. In addition, the similarity of the anodic potentials of radical **3**$^{\bullet}$ to those of hydrocarbon **7** and pyrrole **5**, and of the radical **4**$^{\bullet}$ to that of pyrrole **6** suggests that oxidation in **3**$^{\bullet}$ and **4**$^{\bullet}$ takes place in the heterocyclic moieties. On the other hand, the difference between the anodic behavior of **3**$^{\bullet}$ and **4**$^{\bullet}$, an irreversible process for **3**$^{\bullet}$ and reversible for **4**$^{\bullet}$, is similar to the difference shown in pyrroles **5** and **6**, which is ascribed

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[15] Alemán, C.; Domingo, V. M.; Fajarí, Ll.; Juliá, L.; Karpfen, A. *J. Org. Chem.* **1998**, *63*, 1041.

[16] **9** as a new compound was synthesized by the same method as compound **3**$^{\bullet}$ (see Experimental Section), but using aniline and 1,4-bis(5-methyl)-2-thienyl-1,4-butanedione: yield 75%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44−7.25 (complex signals, 5H), 6.43 (dq, 2H, J = 3.6 Hz, J' = 1 Hz), 6.44 (s, 2H), 6.23 (d, 2H, J = 3.6 Hz), 2.34 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.3, 132.7, 130.0, 129.8, 129.0, 128.8, 125.1, 124.0, 109.2, 15.0.

[17] Reitz, D. C.; Weissman, S. I. *J. Chem. Phys.* **1960**, *33*, 700. Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

[18] This is a general property of the stable radicals derived from TTM radical; see for instance refs 3 and 4.

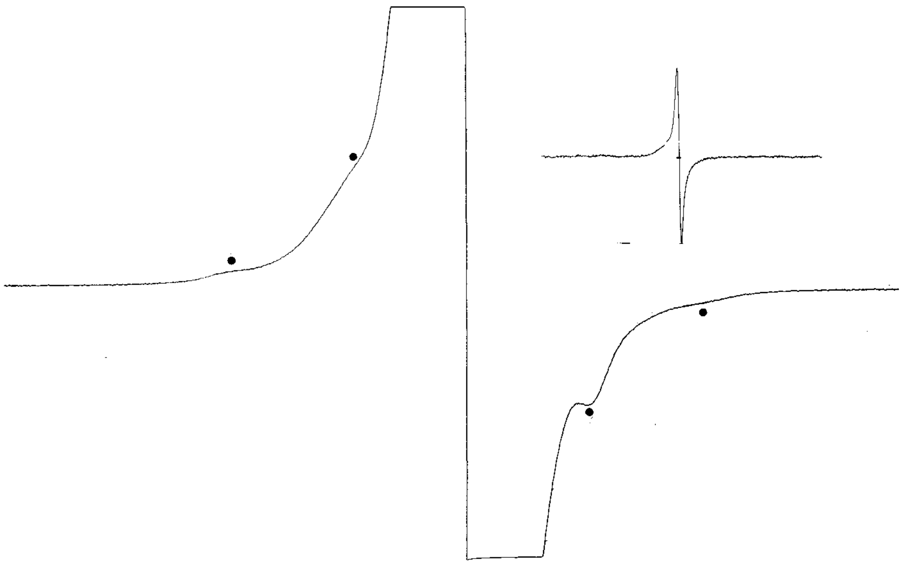


Figure 7. EPR spectrum of radical **4**$^\bullet$ in CH_2Cl_2 containing TFA acid (25%) at 100 K with peaks showing the $\Delta m_s = \pm 1$ transition of $\mathbf{4}^{2\bullet,+}$. Insert shows the signal corresponding to $\Delta m_s = \pm 2$ forbidden transition at 4 K.

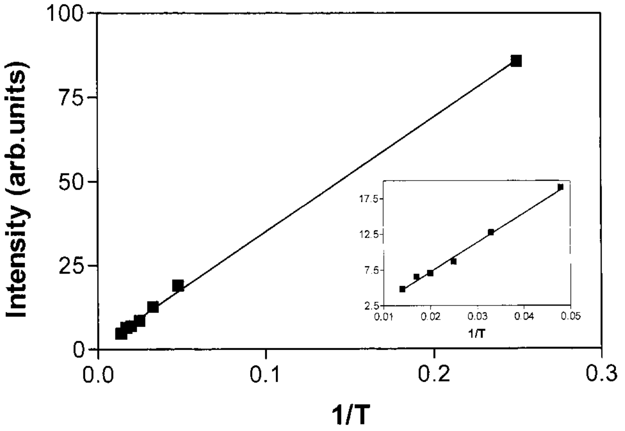
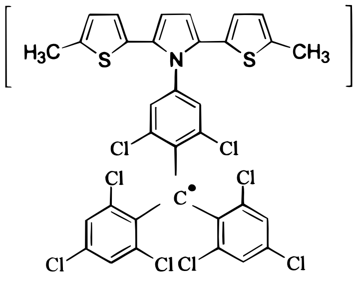


Figure 8. Temperature dependences of the $\Delta m_s = \pm 2$ EPR signal intensities for $\mathbf{4}^{2\bullet,+}$ in CH_2Cl_2 containing TFA acid (25%) from 4 to 70 K.

to the greater stability of the radical cation $\mathbf{6}^{\bullet+}$ than $\mathbf{5}^{\bullet+}$. Consequently, the triphenylmethyl and the heterocyclic moieties of radicals **3**$^\bullet$ and **4**$^\bullet$ behave independently to each other, because the steric hindrance to planar conformation between the two moieties prevents effective electronic conjugation between them. These results are consistent with the twisted angle between both moieties in **3**$^\bullet$, as determined by X-ray analysis.

EPR spectra of radicals **3**$^\bullet$ and **4**$^\bullet$, and those of radical cations $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$ explain the spin multiplicity of the diradical generated by smoothly oxidation of radical **4**$^\bullet$. The splitting values of aromatic hydrogens in the spectra of **3**$^\bullet$ and **4**$^\bullet$ ($a_{6H} = 1.25$ and 1.30 G, respectively) indicate a weak spin delocalization onto the phenyl rings, confirming that the spin density mainly resides in the trivalent carbon atom, as reported for other radicals of the same TTM series. On the other hand, the negligible splittings of phenyl protons in the corresponding spectra of $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$ also demonstrate a very small distribution of the electronic spin in the N-phenyl ring. Both results are ascribed to steric hindrance to planar geometry. The nature of the oxidized species from radical **4**$^\bullet$ corresponds to a true ionic diradical $\mathbf{4}^{2\bullet,+}$, and not to a diamagnetic quinonoidal structure, with one electron mainly localized in the trivalent carbon atom and the other one situated in the heterocyclic system, with a weak electron interaction ($|D/hc| = 0.0047\ cm^{-1}$) between them. X-ray analysis of radical **3** suggests that the quinonoidal structure in these species is not energetically supported due to the high torsion angles between the phenylene plane and the planes of the sp^2 carbon atom and the heterocyclic system. The ground state of this new charged species $\mathbf{4}^{2\bullet,+}$ has been shown to be a triplet or a nearly degenerate singlet−triplet state by the thermal variation of the intensity of the $\Delta m_s = \pm 2$ transition.



$\mathbf{4}^{\overset{2\bullet}{\oplus}}$

Conclusions

Smooth oxidation of radical **4**$^\bullet$ with TFA gives a persistent ionic diradical species by electron transfer from the heterocyclic system. The nature of this species is an excepcional case of a highly twisted *p*-phenylene diradical in which the exchange coupling interaction between the unpaired electrons is so strongly affected by the geometry of the molecule that they even invert the energetic preference, so that the ground state is a triplet or a nearly degenerate singlet−triplet state. This contradicts the predictions based on the para-connectivity between the two magnetic moieties.[19] Consequently, the nature of this ground state cannot be classified as a closed-shell quinonoidal structure but rather as a diradical structure. An

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(19) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. Lahti, P. M.; Ichimura, A. S. *J. Org. Chem.* **1991**, *56*, 3030.

example of violation of the topology rule concerning disjoint *p*-phenylene-bridged homospin diradicals in which the triplet is the ground state has recently been reported.[20] However, as far as we know, this is the first example of violation in *p*-phenylene-bridged heterospin diradicals.

Experimental Section

General Procedures. Melting points were obtained by using a "Reichert" Köfler microscope and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ solutions on spectrometers operating at 200 and 300 MHz for ^{1}H and 50 and 75 MHz for ^{13}C, respectively. Solvents were dried by standard methods and distilled prior to use. Photosensitive radicals were handled in the dark. (4-Amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical[5] and 1,4-bis(5-methyl)-2-thienyl-1,4-butanedione[10] were prepared according to literature procedures.

EPR Experiments. EPR spectra were recorded with a spectrometer working in the X band, and using a temperature controller, with the facility for photolysis of the samples in the cavity by light from a 500 W high-pressure Hg lamp. A continuous-flow liquid helium cryostat and a temperature-controller system was used to obtain EPR spectra at lower temperatures (down to 4 K). Computer simulations were carried out by the public domain WINSIM.[21] Diluted solutions of the heterocycles ($\approx 10^{-3}$ M) in the appropriate solvents with or without thallium(III) trifluoroacetate, were degassed by passing a stream of dry argon through the solution to remove oxygen before being inserted into the cavity of the spectrometer. Samples of stable radicals were prepared in the appropriate solvent ($\approx 10^{-3}$ M) and degassed by three freeze−pump−thaw cycles before being inserted into the EPR cavity.

Electrochemical Measurements. The cyclic−voltammetric measurements were carried out in a jacketed three-electrode cell under an argon atmosphere. The working electrode was a platinum sphere with an area of 0.093 cm^2 and the counter electrode was a Pt wire. The reference electrode was an SSCE (sodium chloride saturated calomel electrode) connected to the cell through a salt bridge containing a 0.1 M TBAP−CH_2Cl_2 solution. Cyclic voltammograms were recorded with standard equipment consisting of a potentiostatic system connected to a *X*−*Y* recorder. Scan rates ranging between 20 and 200 mV s^{-1} were studied. The volume of all test solutions was 25 cm^3. The temperature was kept at 25 °C.

***N*-(3,5-Dichlorophenyl)-2,5-dimethylpyrrole (5).** A mixture of acetonylacetone (1.0 g; 8.5 mmol), 3,5-dichloroaniline (1.43 g; 8.6 mmol), montmorillonite (3.16 g) and dry benzene (2 mL) was stirred at room temperature (30 h), and then diluted with CH_2Cl_2 (25 mL). The mixture was filtered and the solution was evaporated, giving a residue which was chromatographed in hexane through silica gel to pyrrole **5** (1.47 g; 78%): mp 80−2 °C (from hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41 (t, 1H, $J = 1.8$ Hz), 7.14 (d, 2H, $J = 1.8$ Hz), 5.90 (s, 2H), 2.05 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$)141.0, 135.2, 128.6, 128.0, 127.0, 106.7, 13.0. Anal. Calcd for $C_{12}H_{11}Cl_2N$: C, 60.0; H, 4.6; Cl, 29.6; N, 5.8. Found: C, 59.9; H, 4.6; Cl, 29.6; N, 5.8.

Bis(2,4,6-trichlorophenyl)[2,6-dichloro-4-(2,5-dimethyl-1-pyrrolidyl)phenyl]methyl radical ($3^{\bullet}$). (a) Synthesis. A solution of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (0.39 g; 0.7 mmol), acetonylacetone (0.17 g; 1.5 mmol), and acetic acid (4.5 mL) in dry benzene (30 mL) was refluxed (24 h) in a flask equipped with a Dean−Stark trap under argon and in the dark. The crude was poured into a saturated aqueous solution of $NaHCO_3$ and the mixture was extracted with chloroform. The organic solution was washed with water, dried over anhydrous Na_2SO_4 and evaporated at reduced pressure, yielding a residue which was chromatographed (silica gel, CCl_4) to give radical $\mathbf{3}^{\bullet}$ (0.45 g; 99%): red solid mp 210 °C dec (from hexane); IR (KBr) 3060 (w), 2930 (w), 1580 (s), 1550 (s), 1525 (s), 1515 (s), 1445 (m), 1380 (s), 1370 (s), 1180 (s), 1130 (m), 860 (s), 810 (s), 800 (s), 760 (s) cm^{-1}; UV−vis (cyclohexane) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) 543 (830), 500 (sh) (730), 371 (20 000). Anal. Calcd for $C_{25}H_{14}Cl_8N$: C, 49.1; H, 2.3; Cl, 46.4; N, 2.3. Found: C, 49.3; H, 2.3; Cl, 46.2; N, 2.3.

(b) X-ray Analysis. Crystal Data. Molecular formula $C_{25}H_{14}Cl_8N$. Molecular weight 611.97. Monoclinic $P2_1/n$, No. 14. Cell dimensions: $a = 13328(1)$ Å, $b = 14.753(1)$ Å, $c = 14.178(1)$ Å, $\alpha = 90.00°$, $\beta = 115.664(8)°$, $\gamma = 90.00°$, $V = 2512.8(3)$ Å^3, $Z = 4$, $F(000) = 1228$, $D_c = 1.618$ g/cm^3, $\mu = 0.914$ mm^{-1}, crystal dimensions 0.28 × 0.22 × 0.03 mm. **Data Collection.** The diffractometer was an Enraf Nonius CAD4 with a graphite monochromated MoKα radiation, $\lambda = 0.71069$ Å. Cell parameters were determined from refinement of 25 reflections using the CAD4 Express software[22] 7605 reflections were measured with $2.11 \le \theta \le 30.42°$ and index ranges $-17 \le h \le 18$, $0 \le k \le 21$, $-20 \le l \le 0$ in $\omega/2\theta$ mode, $0.58 + 0.46 \tan(\theta)$ scanwidth and maximum final scan time of 60 s. Three standard reflections were measured every 3600 s to check for the intensity variation and 3 more standards were measured every 50 reflections to check the crystal orientation. Intensity decay was 1.26% and was corrected. Absorption correction was made using 9 ψ scans, $T_{max} = 99.61\%$ and $T_{min} = 63.91\%$. **Resolution and Refinement.** The structure was solved by direct methods using the SumF-TF[23] and refined on F^2 with 7605 unique reflections and 341 parameters. Final R factors: $R = 3.84\%$ for $F^2 > 4\sigma(F^2)$ and $wR^2 = 11.10\%$, GoF = 1.024 for all data, where $R = \Sigma\, ||F_o| - |F_c||/\Sigma|F_o|$, $\omega R^2 = [\Sigma\omega(F_o{}^2 - F_c{}^2)^2]^{1/2}$, $\omega = 1/[\Sigma\delta(F_o{}^2)^2 + (0.0529P)^2 + 0.0246P]$, $P = [\max(F_o{}^2,0) + 2F_c{}^2]/3$, $\mathrm{GoF} = [(\Sigma\omega(F_o{}^2 - F_c{}^2))'(n - p)]^{1/2}$, ($n$, 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 0.443 and −0.508 e Å^{-3}, respectively. A SHELXL-93 program[24] was used for refinement and plots were made with PLUTON programs.[25]

Bis(2,4,6-trichlorophenyl)[2,6-dichloro-4-(2,5-dimethyl-1-pyrrolidyl)phenyl]methane (7). A mixture of bis(2,4,6-trichlorophenyl)[2,6-dichloro-4-(2,5-dimethyl-1-pyrrolidyl)phenyl]-methyl radical (0.20 g; 0.32 mmol), powdered sodium hydroxide (0.2 g), ethyl ether (41 mL), and DMSO (9 mL) was shaken in the dark (6 days). The resulting crude was poured into diluted aqueous hydrochloric acid and the ethereal layer separated. The organic solution was washed with aqueous $NaHCO_3$ and with water, then dried and evaporated to dryness, giving a residue which was chromatographed (silica gel, CCl_4) to give **7** (0.14 g; 68%): mp 225−8 °C (from hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.78 (s, 1H), 5.80 (s, 2H), 2.05 (s, 6H); 1H NMR (200 MHz, deuterated-acetone) δ 7.64 (d, 2H, $J = 2.4$ Hz), 7.47 (d, 2H, $J = 2.4$ Hz), 7.46 (d, 1H, $J = 2$ Hz), 7.27 (d, 1H, $J = 2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 137.9, 137.8, 137.6, 137.1, 137.0, 136.7, 134.5, 133.9, 133.7, 130.1, 129.9, 129.8, 128.5, 128.4, 128.1, 106.6, 49.9, 12.9; IR (KBr) 3050 (w), 2910 (w), 1585 (s), 1565 (s), 1535 (s), 1515 (m), 1455 (s), 1375 (s), 1365 (s), 1185 (m), 1165 (m), 1135 (m), 1120 (m), 1070 (m), 1015 (m), 895 (m), 875 (m), 855 (s), 835 (m), 800 (s), 755 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{15}Cl_8N$: C, 49.0; H, 2.5; N, 2.3. Found: C, 49.2; H, 2.7; N, 2.2%.

2,5-Bis(5-methyl-2-thienyl)-1-(3,5-dichlorophenyl)pyrrole (6). To a solution of 3,5-dichloroaniline (0.73 g; 4.49 mmol)

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(20) Okada, K.; Imakura, T.; Oda, M.; Murai, H. *J. Am. Chem. Soc.* **1996**, *118*, 3047.

(21) WINSIM program provided by D. Dulog, Public EPR Software Tools, National Institute of Environmental Health Sciences, Bethesda MD 1996.

(22) CAD4-Express operating software, V. 5.1, Enraf-Nonius, Delft Instruments X-ray diffraction, Deft, The Netherlands, 1992.

(23) Rius, J. *Acta Crystallogr., Sect. A* **1993**, *49*, 406.

(24) SHELXL-93, *A program for refinement of crystal structures*; Sheldrick, G. M., Ed.; Göttingen University: Germany, 1993.

(25) PLUTON, *program for display and analysis of crystal and molecular structures*; Spek, A., Ed.; Utrecht University: The Netherlands, 1993.

and 1,4-bis(5-methyl-2-thienyl)-1,4-butanedione (0.22 g; 0.9 mmol) in dry benzene (25 mL) was added titanium tetrachloride (0.5 mL; 4.6 mmol), via syringe, and the resulting mixture was stirred (3 h) at room temperature under an argon atmosphere and then at reflux (1 h, 45 min). The crude was poured into a water/ice slurry and the mixture was washed with aqueous ammonia and extracted with ethyl ether. The organic solution was dried and evaporated to dryness, giving a residue which was purified by chromatography (silica gel, CCl_4) to give pyrrole **6** (0.14 g; 44%): mp 165−7 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44 (t, 1H, $J = 1.8$ Hz), 7.21 (d, 2H, $J = 1.8$ Hz), 6.51 (d, 2H, $J = 3.6$ Hz), 6.42 (s, 2H), 6.34 (d, 2H, $J = 3.6$ Hz), 2.39 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 139.2, 134.9, 131.7, 129.9, 129.1, 128.6, 125.3, 124.8, 110.0, 15.1. Anal. Calcd. for $C_{20}H_{15}Cl_2NS_2$: C, 59.4; H, 3.7; N, 3.4; S, 15.8. Found: C, 59.6; H, 3.8; N, 3.3; S, 15.7.

Bis(2,4,6-trichlorophenyl)[2,6-dichloro-4-[2,5-bis(5-methyl-2-thienyl)-1-pyrrolidyl]phenyl]methyl Radical ($4^\bullet$). To a solution of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical (0.45 g; 0.85 mmol) and 1,4-bis(5-methyl-2-thienyl)-1,4-butanedione (0.25 g; 0.85 mmol) in dry benzene (25 mL) were added dry triethylamine (0.5 mL; 3.93 mmol) and titanium tetrachloride (0.5 mL; 4.55 mmol), via syringe, and the resulting mixture was stirred (6 h) at room temperature under an argon atmosphere in the dark. The crude was poured into water/ice, $CHCl_3$ was added and the mixture was washed with a saturated solution of aqueous ammonia. The organic layer was dried and evaporated to dryness, giving a residue which was purified by chromatography (silica gel, CCl_4) to give radical $\mathbf{4}^\bullet$ (0.16 g; 23%): red solid; mp 254−6 °C dec; IR (KBr) 3080 (w), 2915 (w), 1580 (m), 1550 (s), 1525 (s), 1450 (m), 1380 (s), 1370 (s), 1180 (m), 1135 (m), 860 (s), 800 (s), 765 (s) cm^{-1}; UV−vis (cyclohexane) λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 543 (860), 500 (740), 373 (35.600). Anal. Calcd for $C_{33}H_{18}Cl_8NS_2$: C, 51.0; H, 2.3; N, 1.8; S, 8.2. Found: C, 50.7; H, 1.8; N, 2.1; S, 8.1.

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Supporting Information Available: Tables with the listing of fractional atomic coordinates and equivalent isotropic displacement parameters, hydrogen coordinates, anisotropic displacement parameters, bond lengths, bond angles, and least-squares planes (X, Y, Z in crystal coordinates) and deviations from them of the molecular structure of $\mathbf{4}^\bullet$. This material is available free of charge via the Internet at http://pubs.acs.org.

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