Electronic Effects on β-Substitution in 2,5-Dimethyl-1-phenylpyrrole by Alkylsulfanyl Groups: EPR Evidence of the Asymmetry in the Radical Cation of β-Disubstituted Derivatives

Victor M. Domingo,[†] Enric Brillas,[‡] Xavier Torrelles,[§] Jordi Rius,[§] and Luis Juliá*,[†]

Departament de Química Orgànica Biològica, Institut d'Investigacions Químiques i Ambientals de Barcelona (CSIC), Jordi Girona, 18−26, 08034 Barcelona, Spain, Departament de Química Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain, and Institut de Ciència de Materials (CSIC), Campus de la UAB, Bellaterra, 08193 Barcelona, Spain

ljbmoh@cid.csic.es

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Introduction

Short-chain oligomers are suitable models to study the electronic properties in conducting polymers.[1,2] One particular aspect of interest is the generation, analysis, and stability of their oxidized species, radical cations, since at low doping levels, these charged defects play an important role in the conductivity of the polymers.[3] Radical cations of pyrroles have been generated by oxidation, and their electron paramagnetic resonance (EPR) spectra have been registered with difficulty due to their low stability.[4] Alcoxy and mercapto substituents prolong the lifetime of these radical cations as well as increase the solubility of the neutral species. In this context, we have recently reported the EPR spectra of the first radical cations derived from 2,5-dimethyl-1-phenylpyrroles with two alkylsulfanyl groups in β-position.[5] These spectra display strong multiplets with high resolution. Here, we report a comparative study of 2,5-dimethyl-1-phenylpyrroles with one and two isopropylsulfanyl groups in β-position to know the influence of the steric hindrance in the electron-donating properties of sulfur atoms when two bulky mercapto groups are present in the molecule.

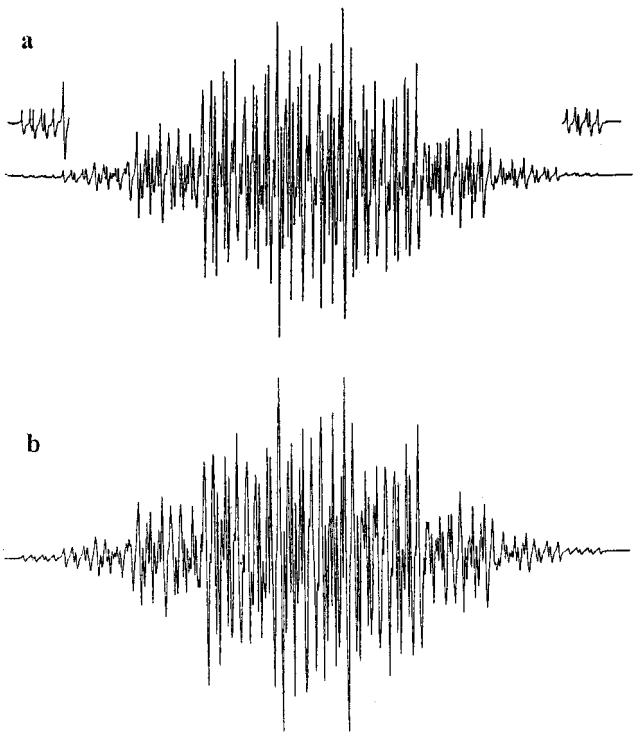

Figure 1. (a) EPR spectrum of $\mathbf{3}^{\bullet+}$ in CH_2Cl_2−TFA acid (∼10:1) at 253 K. (b) Computer simulation using the values given in the text.

Results and Discussion

Well-known methodology[6] has been used to prepare 2,5-dimethyl-3-methylsulfanyl-1-phenylpyrrole (**3**) and 3,4-bis(isopropylsulfanyl)-2,5-dimethyl-1-phenylpyrrole (**6**). Bromination[7] of 2,5-dimethyl-1-phenylpyrrole (**1**) with *N*-bromosuccinimide in THF yielded pyrroles **2** or **4**, depending on the molar ratio. Pyrrole **3** was prepared in good yield by treatment of **2** with *n*-BuLi and then with dimethyl sulfide and, similarly, pyrrole **6** was synthesized step by step, through pyrrole **5**, using diisopropyl disulfide as electrophile (Scheme 1).

A well-resolved but not persistent EPR spectrum was obtained when degassed solutions of **3** (10^{-1} M) in CH_2Cl_2 were treated with an excess of thallium(III) trifluoroacetate in trifluoroacetic (TFA) acid at 253 K (g = 2.0054). This spectrum assigned to $\mathbf{3}^{\bullet+}$ is shown in Figure 1 along with a well-fitted simulation[8] (ΔH_{pp} = 0.2 G) using the following splitting values: a(3H) = 10.0 G, a(3H) = 8.95 G, a(3H) = 5.62 G, a(N) = 1.55 G and a(1H) = 1.12 G.

Similarly, pyrrole **6** displayed an intense, more persistent, and well-resolved spectrum at 233 K (g = 2.0056), assigned to its radical cation $\mathbf{6}^{\bullet+}$ and simulated[8] (ΔH_{pp} = 0.26 G) using the following coupling values: a(6H) = 9.12 G, a(2H) = 2.38 G, a(N) = 1.62 G, and a(12H) = 0.12 G. The spectrum shows a symmetrical distribution of the

[†] Institut d'Investigacions Químiques i Ambientals de Barcelona (CSIC).
[‡] Universitat de Barcelona.
[§] Institut de Ciència de Materials (CSIC).

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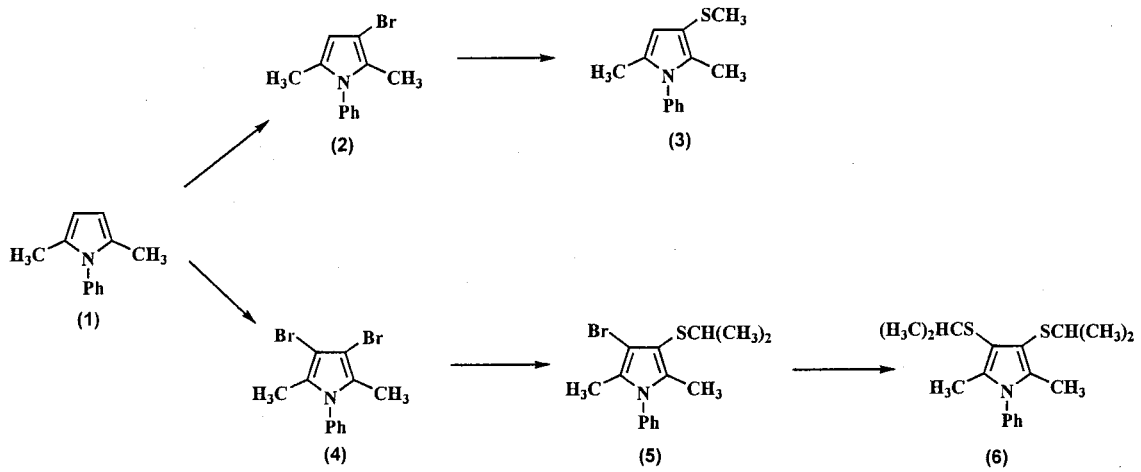
Scheme 1



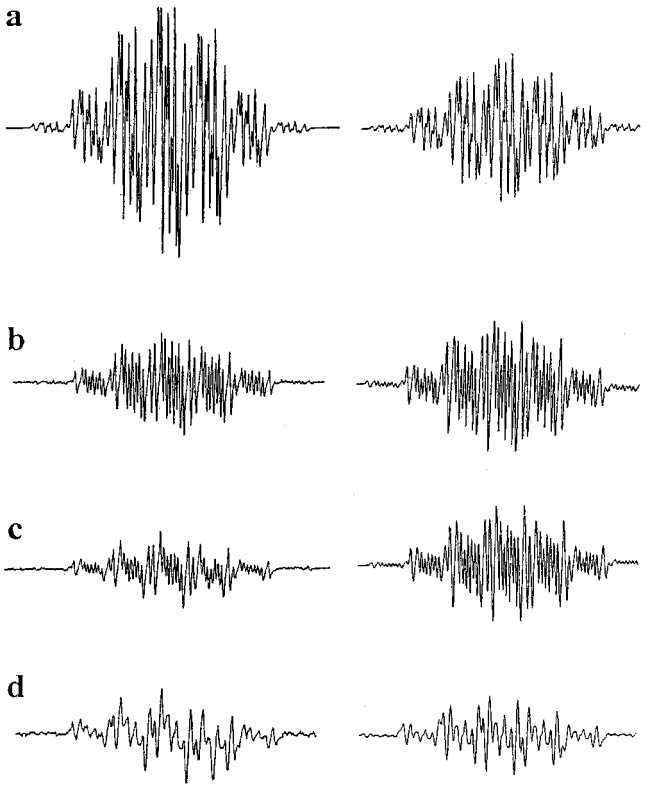


Figure 2. Evolution of the experimental EPR spectra of $\mathbf{6}^{\bullet+}$ (left column) and their simulation (right column) with temperature: (a) at 233 K (conformation **A**, 100%); (b) at 193 K (**A**:**B**; 74:26); (c) at 183 K (**A**:**B**; 66:34); (d) at 173 K (**A**:**B**; 44:55).

spin density, but small changes in the relative amplitudes of the peaks with temperature predicts the appearance of a new species which increases when lowering the temperature. A series of spectra at different temperatures with their simulations combining two radical species with different relative weights is shown in Figure 2. This series of changes in the spectra with temperature are completely reversibles and suggests the existence of an equilibrium between two different conformations of the same radical cation species. One of them corresponds to the symmetrical conformation above indicated, and the second one, which is more visible at 173 K, is well-fitted by using the following coupling values: a(6H) = 9.3 G, a(1H) = 5.12 G, a(N) = 1.62 G, and a(6H) = 0.2 G. This

Table 1. Values of Anodic Peak Potentials (E_a) (v = 50 MV s^{-1}) and Redox Potentials ($E°$) in CH_2Cl_2 with Bu_4NClO_4 as Electrolyte

	$E_a/E°$(V)
R = R' = H[†]	1.0/---
R = R' = SCH_3[†]	1.01/0.95
R = R' = SBu[†]	0.98/0.90
R = R' = $SCH(CH_3)_2$	1.02/0.96
R = H, R' = SCH_3	0.88/0.74

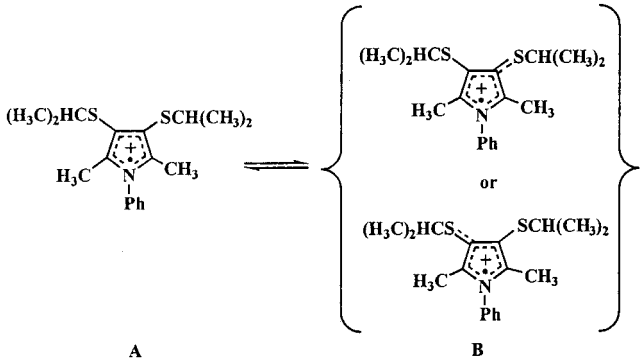
[†] Reference 5.

second species shows an asymmetrical distribution of the spin density, and it is more similar to the spectrum displayed by oxidation of the monosubstituted pyrrole **3**. It is not possible to observe any variation in g values for both conformations by the simulation program. An additional reversible change in the spectrum of $\mathbf{6}^{\bullet+}$ is denoted by a drastic decrease in the intensity of the multiplet when decreasing temperature which might be associated with the formation of singlet dimeric species.

Cyclic voltammetry (CV) at a platinum disk electrode in anhydrous CH_2Cl_2 solutions (10^{-3} M) of **3** and **6** in the presence of Bu_4NClO_4 (0.1 M) and at room temperature gave in each case one reversible couple of oxidation with standard potentials as shown in Table 1, which corresponds in each case to the equilibria $\mathbf{3} \rightleftharpoons \mathbf{3}^{\bullet+} + 1e$ and $\mathbf{6} \rightleftharpoons \mathbf{6}^{\bullet+} + 1e$.

Values for anodic peak potentials (E_a) of pyrroles **1**, **3**, and **6**, and other 3,4-dialkylsulfanylpyrroles reported in the literature are shown in the Table 1. The similarity of the E_a values of **1** and all 3,4-dialkylsulfanyl-2,5-dimethyl-1-phenylpyrroles at room temperature denotes a parallelism in their electronic structure and, therefore, the absence of mesomeric effect of the sulfur atoms. This fact is a consequence of the nonplanar orientation of the alkylsulfanyl substituents with respect to pyrrole ring, corroborated by X-ray diffraction analysis of a single crystal of pyrrole **6** (Figure S1, see Supporting Information available). The dihedral angles C(2)−C(1)−S(2)−C(14) and C(3)−C(4)−S(1)−C(11) are 80.5° and 80.6°, respectively, and the values of the bond distances S(1)−C(4) (1.74 Å) and S(2)−C(1) (1.74 Å) are those expected for a single C(sp^2)−S bond.[9] This peculiar feature was

Scheme 2



predicted before by theoretical calculations at the UHF/6-31G(d) level carried out on 3,4-bis(methylsulfanyl)-1-phenylpyrrole and 3,4-bis(methylsulfanyl)-2,5-dimethyl-1-phenylpyrrole[10] and were attributed to the repulsive interactions between the electron lone pairs of the sulfur atoms. This is not the case when substitution takes place only in one β-position. So, the value of E_a in the cyclic voltammogram of **3** is lower which suggests the effectiveness of the mesomeric effect of sulfur.

The electron donor properties of the β-substituent extending the π conjugation of the ring over the sulfur atom is also denoted in the EPR spectrum of its radical cation $\mathbf{3}^{\bullet+}$, where high values of the coupling constant with the three methylsulfanyl hydrogens and a very low value with the hydrogen in C3 are found. The stability of $\mathbf{3}^{\bullet+}$ is substantiated by the reversibility of the equilibrium $\mathbf{3} \rightleftharpoons \mathbf{3}^{\bullet+} + 1e$ in the electrochemical process, and it is mainly due to the mesomeric effect of sulfur.[11]

The main structural feature of **6** is the presence of an equilibrium between two different radical cation conformations **A** and **B** as denoted by the EPR of its radical cation $\mathbf{6}^{\bullet+}$. The asymmetry of the less energetic conformation and the values of the coupling constants in the EPR spectrum suggest a different torsion angle around the C(ring)−S bond in both alkylsulfanyl substituents. The high splitting value with one of the methynic hydrogens and its similitude with that of the methyl hydrogens in $\mathbf{3}^{\bullet+}$ would then be consistent with the effectiveness of the mesomeric effect in one sulfur atom at the expense of the effect in the other sulfur. The geometrical asymmetry of this conformation **B** in $\mathbf{6}^{\bullet+}$ has been predicted by ab initio quantum mechanical calculations,[10] where the dihedral angles C(2)−C(1)−S(2)−C(14) and C(3)−C(4)−S(1)−C(11) were estimated to be of 174.0° and 90.2°, respectively. Accordingly, both conformations in equilibrium can be formulated as depicted in the Scheme 2; this equilibrium is right-shifted at low temperatures.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ solutions on Varian Gemini XL200 spectrometer operating at 200 MHz for ^{1}H and 50 MHz for ^{13}C, respectively. EPR spectra of solutions of **3** and **6** in CH_2Cl_2 were degassed by passing a stream of dry argon through the solution and recorded with a Varian E−109 spectrometer working in the X band (microwave power 0.5 mW). 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 performed with standard equipment consisting of a PAR 175 universal programmer and an Amel 551 potentiostat connected to a Philips 8043 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.

2,5-Dimethyl-3-methylsulfanyl-1-phenylpyrrole (3). A stirred solution of **2**[7] (1.0 g; 4.00 mmol) in anhydrous THF (25 mL) under an argon atmosphere was cooled to −78 °C. A 2.5 M solution of n-BuLi in hexane (1.8 mL; 4.50 mmol) was added dropwise, and the solution was further stirred at −78 °C for 35 min. Then, dimethyl sulfide (0.45 g; 4.80 mmol) was added dropwise and stirred at −78 °C for 1 h. The reaction solution was poured into water, and the resulting mixture was extracted with diethyl ether. The organic solution was dried over anhydrous Na_2SO_4, and the solvent was evaporated at reduced pressure. The residue was purified by chromatography on silica gel ($CHCl_3$) to afford **3** as a white solid (0.691 g; 79%) mp 70−2 °C (from pentane); ^{1}H NMR (200 MHz, $CDCl_3$) δ, 2.00 (s, 3H), 2.07 (s, 3H), 2.30 (s, 3H), 6.03 (s, 1H), 7.5−7.1 (multiplet, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ, 11.17, 12.78, 20.56, 110.02, 110.26, 127.92, 128.12, 128.56, 129.16, 131.16, 138.78. Anal. Calcd. for $C_{13}H_{15}NS$: C, 71.9; H, 6.9; N, 6.4; S, 14.7. Found: C, 71.9; H, 7.0; N, 6.3; S, 14.6.

3-Bromo-2,5-dimethyl-4-methylsulfanyl-1-phenylpyrrole (5). A solution of **4**[1] (1.00 g; 3.04 mmol) in anhydrous THF (20 mL) was stirred and cooled to −78 °C under argon while a solution 2.5 M of n-BuLi in hexane (1.4 mL; 3.5 mmol) was slowly added via syringe. After the mixture was stirred for 35 min at −78 °C, diisopropyl disulfide (0.53 g; 3.5 mmol) was added. The entire mixture was stirred at −78 °C for 1 h. The reaction solution was poured into water, and the resulting mixture was extracted with diethyl ether. The organic solution was washed twice with a 2 M KOH solution and then with water. Upon drying with anhydrous Na_2SO_4, the solvent was removed under reduced pressure, yielding **2** as an oil (crude yield: 0.675 g; 68%); ^{1}H NMR (200 MHz, $CDCl_3$) δ, 1.24 (d, J = 6.6 Hz, 6H), 2.02 (s, 3H), 2.11 (s, 3H), 3.11 (hep, J = 6.6 Hz, 1H), 7.5−7.1 (multiplet., 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ, 12.04, 12.18, 23.05, 39.46, 103.00, 108.99, 126.50, 128.02, 128.39, 129.35, 134.01, 138.55.

3,4-Bis(isopropylsulfanyl)-2,5-dimethyl-1-phenylpyrrole (6). A stirred solution of crude **5** (0.5 g; 1.54 mmol) in anhydrous THF (20 mL) under an argon atmosphere was cooled to −78 °C. A 2.5 M solution of n-BuLi in hexane (0.7 mL; 1.75 mmol) was added, and the solution was further stirred at −78 °C for 35 min. Then diisopropyl disulfide (0.7 g; 4.62 mmol) was added dropwise and stirred at −78 °C for 1 h. The reaction was allowed to warm to room temperature and then was heated at 80 °C overnight. The solution was poured into water, and the resulting mixture was extracted with diethyl ether. The organic solution was washed twice with a 2 M KOH solution and then with water and dried over anhydrous Na_2SO_4, and the solvent was evaporated at reduced pressure. The residue was purified by chromatography on silica gel eluting first with hexane and then with 1:1 $CHCl_3/CCl_4$. The second fraction was evaporated to afford **3** (0.315 g; 64%) as a colorless solid mp 51−3 °C (from pentane); ^{1}H NMR (200 MHz, $CDCl_3$) δ, 1.22 (d, J = 6.6 Hz, 12H), 2.10 (s, 6H), 3.21 (hep, J = 6.6 Hz, 2H), 7.5−7.1 (c.s., 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ, 12.07, 23.13, 39.45, 113.17, 128.02, 128.14, 129.24, 133.90, 138.95. Anal. Calcd for $C_{18}H_{25}NS_2$: C, 67.6; H, 7.9; N, 4.3; S, 20.0. Found: C, 67.5; H, 8.0; N, 4.4; S, 20.0.

(9) Another considerable torsion from planarity in the molecular structure of **6** was found between the planes of pyrrole and benzene rings (83.8°) to avoid steric interactions between methyls and hydrogens, the C(5)−N bond distance (1.43 Å) being consistent with a single bond character between these atoms.

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(11) Radical cations from dialkylsulphanyl derivatives also show redox couples, contrary to the behavior of pyrrole **1**. The stability of these species is mainly due to persubstitution of ring positions.

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Supporting Information Available: Ortep drawing (Figure S1) and structural data for the X-ray analysis (positional and thermal parameters; bond distances and angles) of compound **6**. This material is available free of charge via the Internet at http://pubs.acs.org

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