# A Computational Study of Neutral and Charged Pyrroles. Functionalization of 1-Phenylpyrrole and 2,5-Dimethyl-1-phenylpyrrole with Electron Donating Methylsulfanyl Groups

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We present a detailed computational study of the geometric structure and torsional potential of 1-phenylpyrrole, 2,5-dimethyl-1-phenylpyrrole, 3,4-bis(methylsulfanyl)-1-phenylpyrrole, and 3,4-bis(methylsulfanyl)-2,5-dimethyl-1-phenylpyrrole. Both the neutral molecule and the corresponding radical cation are investigated for each compound. Calculations of the neutral species and radical cations are performed at the RHF/6-31G(d) and UHF/6-31G(d) levels, respectively. Our study has two major aims: (i) to assess and evaluate the effects of the bulky methyl substituents at 2,5 positions and (ii) to investigate the effects exerted by the electron-donating methylsulfanyl groups. The analysis of the results has revealed that both the methyl and methylsulfanyl substituents induce unusual structural properties, particularly in the radical cations.

## Introduction

In the field of molecular-based magnetic materials, heterocycles as spin-carrier components connected through ferromagnetic couplers have been of great interest. One strategy to design molecules with high-spin multiplicity is the orthogonal alignment between spin carriers and ferromagnetic couplers,[1,2] resulting stable triplets in a para-connectivity, against the topology rule. Some authors have reported the additional influence of the electronic nature of the heteroatoms to the violation of the topology rule.[2]

Our attention in this topic has been focused to prepare molecules based on pyrroles coupled through phenyl rings to neutral stable free radicals centered at the carbon atom. In this context, recently, we have reported a stable ferromagnetic interaction in the doped [2,6-dichloro-4-[2,5-bis(5-methyl-2-thienyl)-1-pyrrolyl]phenyl]bis(2,4,6-trichlorophenyl)-methyl radical (**1**).[3] The stability of this diradical cation species is conferred by the presence of two thienyl rings in the 2,5 pyrrolic positions to stabilize the corresponding radical cation moiety, and by the use of a carbon free radical derived from tris(2,4,6-trichlorophenyl)methyl (TTM) radical attached in the 1-pyrrolic position, whose stability is due to the steric shielding provided by the six chlorines around the trivalent carbon.

For the purpose to stabilize further the pyrrole radical cation moiety of these molecules, we tried to block the reactive $\beta$ positions in the model 2,5-dimethyl-1-phenylpyrrol (**2**), by inserting electron-donor substituents, and study their electronic properties. Consequently, very recently we have reported the synthesis of two 3,4-bis(alkylsulfanyl)-2,5-dimethyl-1-phenylpyrrol and their electrochemical and electronic properties compared with those of **2**.[4] Cyclic voltammograms of these new compounds revealed a higher stability of the respective radical cations, showing anodic peaks at similar potential values but now completely reversibles. EPR spectroscopy also confirms the high stability of the monocharged species, and shows important variations in the electron spin distribution in SOMOs.

With the aim to improve our knowledge of these pyrroles, now we report theoretical calculations on **2** and 3,4-bis(methylsulfanyl)-2,5-dimethyl-1-phenylpyrrole (**3**), either in neutral or charged species, by using ab initio quantum mechanical methods. Furthermore, the study has been extended to 1-phenylpyrrole (**4**) and 3,4-bis(methylsulfanyl)-1-phenylpyrrole (**5**), in which the steric effects induced by the methyl substituents in 2 and 5 positions are not present.

## Methods

Neutral systems were investigated at the ab initio RHF level of theory. The reliability of the RHF method to study the torsional potential of bicyclic compounds was recently proved by comparison with ab initio post-RHF and density functional theory levels.[5] Investigation of radical cations was performed at the UHF level. This computational method was successfully used to investigate both the molecular geometry and conformational behavior of charged 2,2′-bithiophene and 2,2′,5′,2′′-terthiophene.[5f] The standard 6-31G(d) (d functions on S and C atoms) basis set[6] was used in both RHF and UHF calculations.

Equilibrium structures of neutral and charged compounds were obtained by geometry optimization without any constraint. Minimum energy structures were characterized as such by calculating and diagonalizing the Hessian matrix and ensuring that they do not have a negative value. The rotational profiles of **2**, **3**, **4**, and **5** were computed spanning the torsional angle between the planes of the two rings, which was denoted $\theta$, in steps of 30°. A flexible rotor approximation was used in all cases, the molecular geometry of each point of the rotational profile being optimized at a fixed $\theta$ value.

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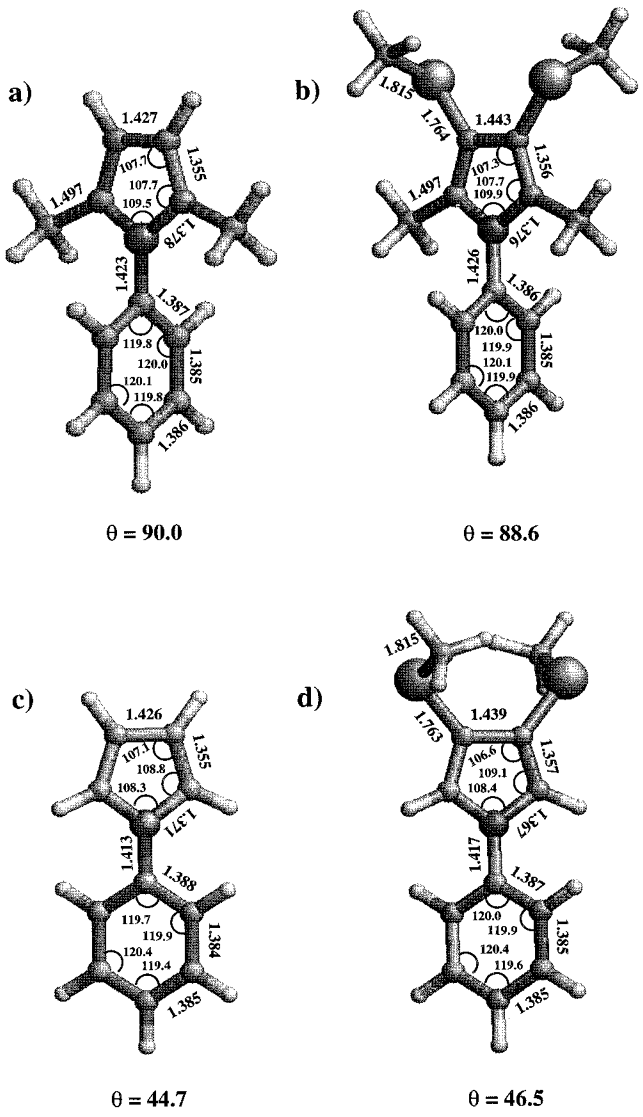


**Figure 1.** Lowest energy conformation of **2** (a), **3** (b), **4** (c), and **5** (d). Optimized bond lengths and angles are displayed.

Ionization potentials (IP) were computed as the difference between the energies of radical cations and its corresponding neutral species. In all cases the energies of the minimum energy conformations were used.

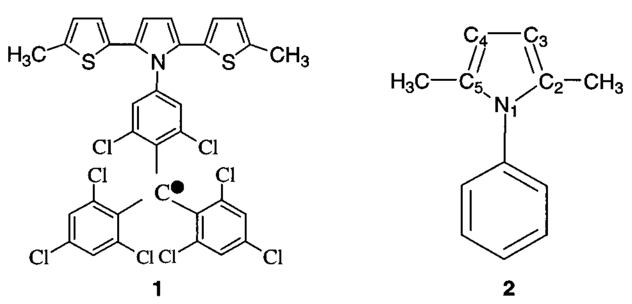
All the calculations were carried out with the Gaussian-98 computer program.[7]

## Results and Discussion

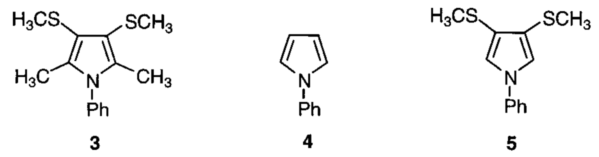
**Equilibrium Geometries of Neutral Compounds.** Figure 1 shows the optimized molecular geometries and the most relevant parameters for the minimum energy conformations of the four neutral compounds. As it is expected, the equilibrium parameters of both the pyrrole and the benzene rings present a relation of molecular symmetry in all cases. Thus, for the pyrrole ring the equilibrium distances N1−C2 and C2−C3 and angles <N1−C2−C3 and <C2−C3−C4 are almost identical to the equilibrium parameters N1−C5, C5−C4, <N1−C5−C4, and <C5−C4−C3, respectively. The same type of molecular symmetry is observed for the benzene ring. To clarify the illustration, identical parameters have been not included in Figure 1.

The minimum energy conformation of **2** corresponds to the gauche−gauche one, which is located at $\theta = 90.0°$. A very different conformational behavior is obtained for **4**. Thus, the most stable conformation of the latter is the syn-gauche one, which appears at a torsional angle $\theta$ of 44.7°. These results indicate that a large twisting between the two rings is induced by the methyl substituents in 2,5 positions. Furthermore, from Figure 1 one can also observe that the conjugation effect, which is completely lost in the perpendicular arrangement of **2**, causes an increase of the inter-ring bond length, i.e., 0.010 Å. A similar behavior has been observed in bithiophenes substituted at positions 3,3.[5b,8]

**SCHEME 1**



**SCHEME 2**



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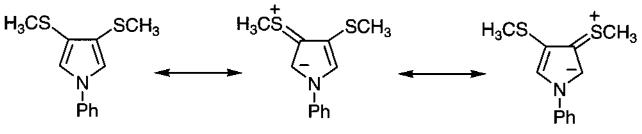


The minimum energy conformations of **3** and **5** correspond to the gauche−gauche ($\theta = 88.6°$) and syn-gauche ($\theta = 46.5°$) ones, respectively. The differences between **3** and **5**, which are probably induced again by the variation of the conjugation effect with the torsional angle, follow the trends previously described for the compounds without methylsulfanyl groups.

On the other hand, comparison between corresponding bond lengths of the pyrrole ring in the four compounds under study reveals some significant differences, mainly involving the C3−C4 and N1−C2 bonds. Thus, C3−C4 is larger in **3** and **5** than in **2** and **4**, and N1−C2 is shorter in **3** and **5** than in **2** and **4**. The most significant lengthening corresponds to the C3−C4 bond, being of 0.013 Å in the two cases. This deformation can be attributed to the repulsive interactions between the electron lone pairs of the sulfur atoms. On the other hand, a mesomeric effect induced by the methylsulfanyl substituents should be expected in both **3** and **5.** This electronic effect, which is illustrated in Scheme 3 for **5**, should produce a decrease in the double bond character of C2−C3 and C4−C5. However, the length of these bonds is almost identical for the four compounds under study. Furthermore, the length of the $S-CH_3$ bonds corresponds in all cases to that typically observed in S−C single bonds.[9] Accordingly, no significant mesomeric effect was found in the compounds with two methylsulfanyl substituents, even although this is a group with electron-donor properties. Thus, it seems that the mesomeric effects, which are usually found in rings with only one methylsulfanyl substituent,[9] are compensated and canceled by the two close electron-donor groups of **3** and **5**.

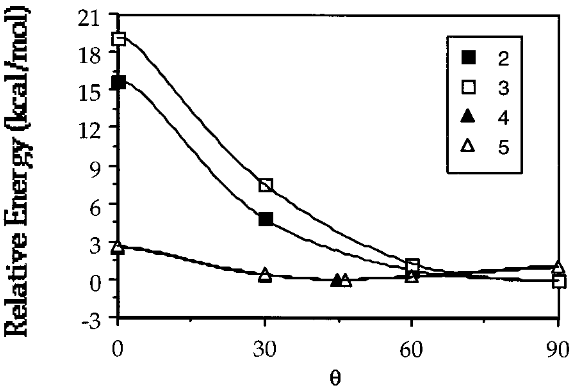


**Figure 2.** Rotational barriers for **2**, **3**, **4**, and **5** as obtained from ab initio HF/6-31G(d) calculations.

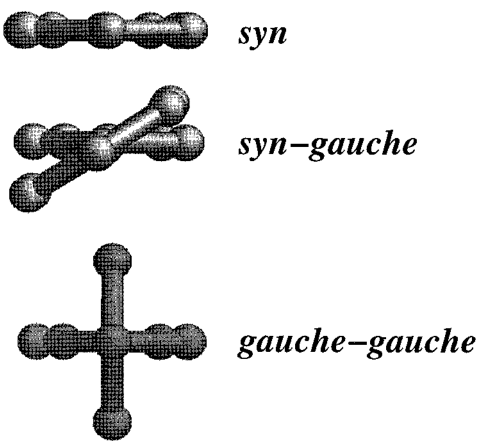


**Figure 3.** Schematic picture of the syn, syn–gauche, and gauche–gauche conformations for 1-phenylpyrrole derivatives. Conformations are displayed looking down the rotated bond from one ring to the other.

**Torsional Potentials and Conformational Analysis of Neutral Compounds.** Figure 2 displays the torsional potentials of the four neutral compounds. Figure 3 presents a schematic picture of the relative orientation between the two rings for the most significant conformations of the investigated compounds: syn ($\theta = 0°$), syn-gauche ($\theta = 45°$), and gauche–gauche ($\theta = 90°$).

The most stable conformation of both **2** and **3** is the gauche–gauche, the syn conformation ($\theta = 0°$) being less favored by 15.7 and 19.2 kcal/mol, respectively. The reason of these conformational preferences has to be found in the repulsive interactions originated by the methyl groups. These interactions are minimized when the angle $\theta$ increases to 90.0°. On the other hand, it is worth noting that the planar arrangement is 3.5 kcal/mol less favored for **3** than for **2**. The substituents in 3,4 positions seem to be responsible for this energetic difference. Thus, the conformational properties of **3** are the result of a delicate balance among three types of repulsive interactions: (i) the interactions between the methylsulfanyl substituents and the adjacent methyl groups; (ii) the interactions between the electron lone pairs of the two sulfur atoms; and (iii) the interactions between the methyl substituents and the phenyl ring.

The conformational preferences of **4** and **5** are completely different from those of **2** and **3**. Thus, the lowest energy conformation for the former compounds corresponds to the syn-gauche, which is localized at $\theta = 44.7°$ and $\theta = 46.5°$, respectively. This twisted conformation is found to be more stable than the syn structure by about 2.4–2.6 kcal/mol. The low stability of the planar conformation is due to the absence of $\pi$-electron conjugation along the molecular frame. Indeed, the syn conformation is about 1.3–1.6 kcal/mol less stable than the gauche–gauche one, in which the two rings adopt a perpendicular arrangement.

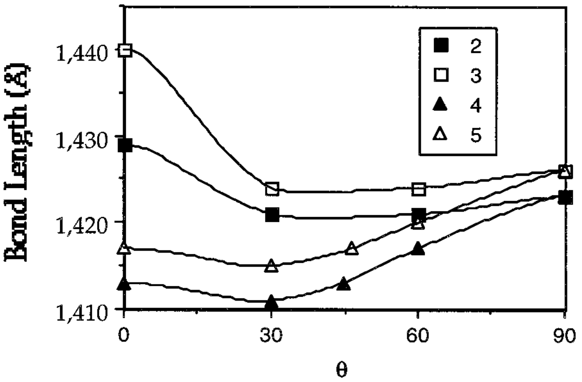


**Figure 4.** Evolution of the inter-ring bond length for **2**, **3**, **4**, and **5** as a function of the torsional angle between the rings.

It should be mentioned that the most stable orientation of the methylsulfanyl groups has been considered in the conformational analysis of both **3** and **5**. The orientation of these substituents in the structure displayed in Figure 1 corresponds to the anti-gauche arrangement (the dihedral angles C2–C3–S–C and C5–C4–S–C range from 104.0° to 105.6°), which is the lowest energy one. Thus, other arrangements of the methylsulfanyl groups, like syn, perpendicular and anti, are more energetic. Accordingly, the torsional potentials of **3** and **5** (Figure 2) were computed considering an anti-gauche orientation for the methylsulfanyl substituents.

The dependence of the inter-ring bond length and the torsional angle $\theta$ is displayed in Figure 4. For **2** and **3** the largest distances correspond to $\theta = 0°$, i.e., the syn conformation, where the steric clashes are maximized. On the other hand, for **4** and **5** the shortest distance is found at the syn-gauche minimum, whereas the largest one appears at the gauche–gauche conformation. The inter-ring bond elongates by only 0.006, 0.014, 0.009, and 0.010 Å for **2**, **3**, **4**, and **5**, respectively. These small values indicate that in all cases the inter-ring bond has an almost negligible double bond character.

**Equilibrium Geometries of Charged Compounds.** The most relevant geometrical parameters for the minimum energy structures of $\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$ are displayed in Figure 5. A comparison of the main geometrical parameters predicted for the radical cations with those obtained for the neutral compounds (Figure 1) reveals significant changes.

For **2**, the bond lengths of the pyrrole ring are very sensitive to ionization effects. Thus, the main trends observed in this ring can be summarized as follows: (i) the distance N1–C2 adopts similar values in both the neutral and charged species, the difference between them being only 0.019 Å; (ii) the distance C2–C3 is 0.074 Å larger in the radical cation than in the neutral compound; and (iii) the distance C3–C4 is 0.073 Å shorter in the radical cation than in the neutral compound. On the other hand, notice that the inter-ring distance elongates by 0.022 Å with respect to the neutral compounds indicating a reduction in the strength of this bond. However, for both **2** and $\mathbf{2}^{\bullet+}$ the inter-ring distance is consistent with a single bond character. Furthermore, the dihedral angle $\theta$ for the minimum energy conformation of $\mathbf{2}^{\bullet+}$ is 90.0°, which precludes the existence of a double bond between the two rings.

Regarding $\mathbf{4}^{\bullet+}$, the geometric parameters undergoing the most significant changes with respect to the corresponding neutral

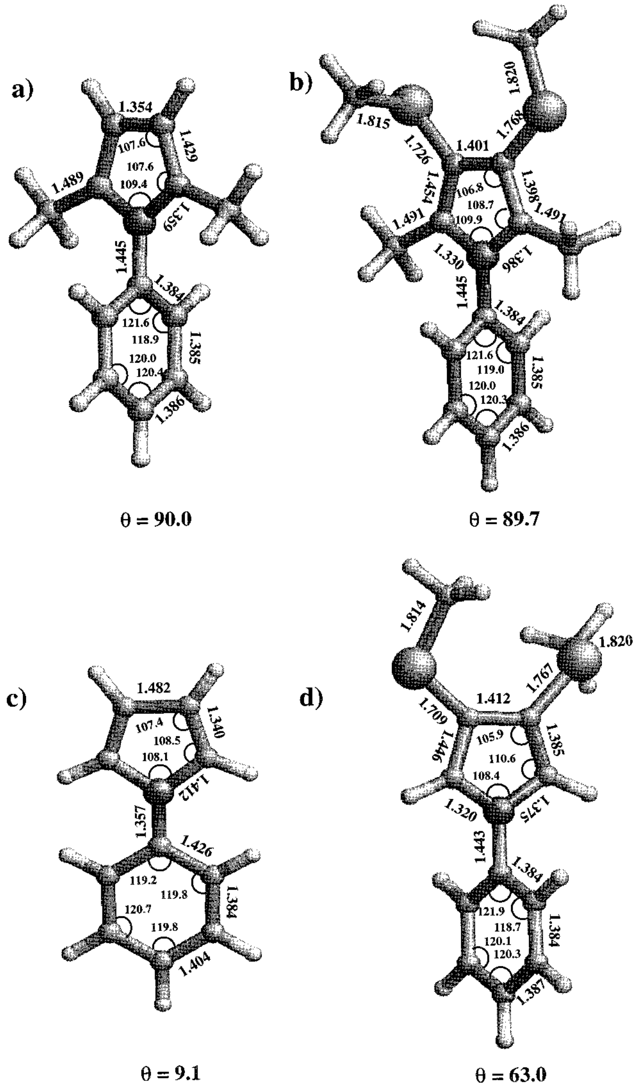


**Figure 5.** Lowest energy conformation of $\mathbf{2}^{\bullet+}$ (a), $\mathbf{3}^{\bullet+}$ (b), $\mathbf{4}^{\bullet+}$ (c), and $\mathbf{5}^{\bullet+}$ (d). Optimized bond lengths and angles are displayed.

compound are the inter-ring bond (C−N1), N1−C2, and C3−C4. The inter-ring bond length shortens by 0.056 Å for $\mathbf{4}^{\bullet+}$. Thus, the $\pi$ conjugation between the two rings is evidenced in the radical cation by the double bond character of the inter-ring distance. This conjugation allows the explanation of the significant changes found in the C−C bonds of the phenyl ring with respect to all the other compounds studied in this work. The consequence of this behavior is the increase of the molecular planarity, which is consistent with the syn conformation ($\theta$ = 9.1°) displayed by the minimum energy structure. On the other hand, the N1−C2 and C3−C4 bonds lengthen by 0.041 and 0.056 Å, respectively, which indicate an increment in their single bond character.

Both $\mathbf{3}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ present similar geometrical trends in their minimum energy conformations. It is worth noting that the molecular symmetry is lost in the pyrrole ring after geometry optimization. Thus, the N1−C2 and C2−C3 bond lengths are different from the N1−C5 and C4−C5 ones, respectively. A loss of symmetry is also detected in bond angles. However, the difference in such parameters is not significant and, therefore, they have not been included in Figure 5. It should be mentioned that the asymmetries displayed in bond lengths have not been attributed to an inaccuracy of the computational method because they are very large. However, they could be slightly overestimated by the UHF wave function. Thus, multiconfigurational methods, which are computationally prohibitive for large systems such as those of the present work, are more suitable than the UHF one to describe the ground state of open shell systems.

**TABLE 1: Computer Atomic Spin Densities ($\rho$) and Experimentally Determined Hyperfine Splitting Constants[a] (hfs; in Gauss) for $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$**

| radical species | no. | C2, C5 | N | C3, C4 | $\Sigma_i C_i{}^b$ |
|---|---|---|---|---|---|
| $\mathbf{2}^{\bullet+}$ | r | 0.657 | 0.291 | 0.015 | 0.129 |
| | hfs | 16.60 | 4.40 | 3.60 | |
| $\mathbf{3}^{\bullet+}$ | r | 0.598 | 0.228 | 0.312 | 0.108 |
| | hfs | 9.4 | 1.62 | | |

[a] From ref 4. [b] $\Sigma_i C_i$ is the sum of the $\rho$ on the six carbon atoms of the phenyl ring.

The most relevant changes found in $\mathbf{3}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ with respect to the neutral species can be summarized as follows: (i) the distance N1−C5 shortens by about 0.04−0.05 Å; (ii) the distance C4−C5 lengthens by almost 0.10 Å whereas the distance C2−C3 only increases by about 0.03−0.04 Å; (iii) the distance C3−C4 shortens by about 0.03−0.04 Å; and (iv) the inter-ring bond length increases by about 0.03 Å. The latter indicates that the strength of the bond between the two rings decreases upon the removal of one electron. This is consistent with the torsional angle $\theta$ of the minimum energy conformation of $\mathbf{5}^{\bullet+}$, which is 16.5° larger than that of **5**. On the other hand, while the bond the sulfur atom of one methylsulfanyl group and the carbon atom of the ring does not significantly change on going from the neutral compound to the charged species, the other one is shorter in the radical cation than in the neutral compound. Thus, the C4−S bond length is markedly shorter in the radical cations (1.726 and 1.709 Å for $\mathbf{3}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$, respectively) than in the neutral compounds (1.763 and 1.764 Å for **3** and **5**, respectively). These values indicate that the mesomeric effect usually associated to the methylsulfanyl groups only appears after ionization, and not simultaneously in both methylsulfanyl groups.

The total atomic spin densities ($\rho$) were computed for the minimum energy conformations of $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$. The $\rho$ on the heavy atoms contained in the pyrrole ring are listed in Table 1. As it can be seen, the spin density mainly resides in the 2,5 positions. These results are in good agreement with experimental data[4] obtained for the same compounds. Thus, highly resolved EPR spectra indicated a large coupling constant value at the 2,5 positions and small one at the 3,4 position. The experimentally determined hyperfine splitting (hfs) constants have been included in Table 1 for the sake of comparison. On the other hand, the values of $\rho$ on the carbon atoms contained in the phenyl ring are very small, indicating that the unpaired electron is confined in the pyrrole ring. These electron confinement characteristics of $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ were experimentally detected by EPR spectroscopy.[4] Table 1 shows the parameter $\Sigma_i C_i$, which corresponds to the sum of the $\rho$ on the six carbon atoms of the phenyl ring.

**Rotational Barriers of Charged Compounds.** The torsional potential and the variation as a function of the torsional angle $\theta$ of inter-ring bond length computed for the four radical cations are displayed in Figures 6 and 7, respectively.

The rotational profiles of $\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$ are very similar to those of the corresponding neutral species (Figure 2). For $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$, the syn conformation is predicted to be 18.7 and 21.2 kcal/mol higher in energy than the gauche−gauche minimum, respectively. These high energy barriers are due to strong steric interactions that take place for the planar confor-

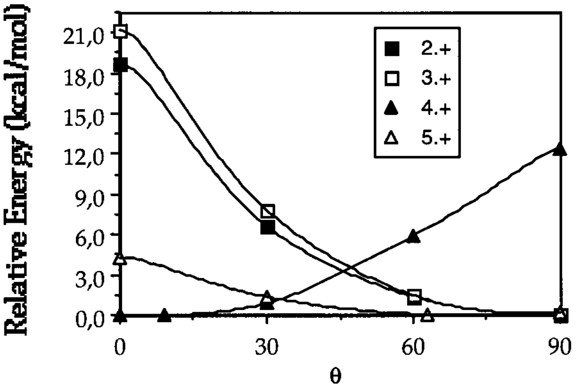


**Figure 6.** Rotational barriers for $2^{\bullet+}$, $3^{\bullet+}$, $4^{\bullet+}$, and $5^{\bullet+}$ as obtained from ab initio UHF/6-31G(d) calculations.

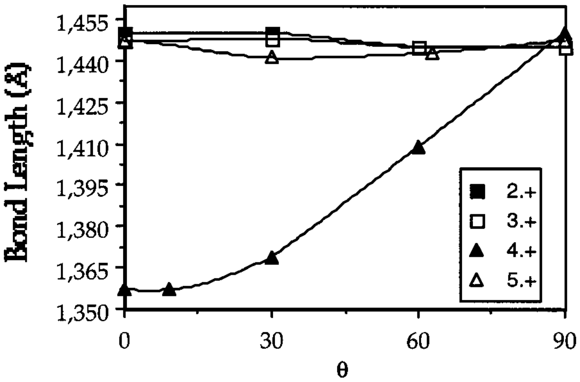


**Figure 7.** Evolution of the inter-ring bond length for $2^{\bullet+}$, $3^{\bullet+}$, $4^{\bullet+}$, and $5^{\bullet+}$ as a function of the torsional angle between the rings.

mation. For $5^{\bullet+}$, the *syn-gauche* minimum is separated from the syn and gauche−gauche conformers by barriers of 4.3 and 0.2 kcal/mol, respectively. The variation with the torsional angle $\theta$ of the inter-ring bond distance (Figure 7) is in all cases very small. Thus, this bond elongates by only 0.005, 0.003, and 0.006 Å for $2^{\bullet+}$, $3^{\bullet+}$, and $5^{\bullet+}$, respectively.

Inspection to the conformational preferences of the methylsulfanyl groups in $3^{\bullet+}$ and $5^{\bullet+}$ reveals some differences with respect to those obtained for the corresponding neutral compounds. In the radical cations these substituents display anti and gauche−gauche orientations with respect to the pyrrole ring. Thus, for $3^{\bullet+}$ the dihedral angles C2−C3−S−C and C5−C4−S−C are 167.6° and 90.9°, respectively, whereas for $5^{\bullet+}$ they are 174.0° and 90.2°.

The minimum energy conformation of $4^{\bullet+}$ is the syn arrangement ($\theta = 9.1°$). The energy barrier, which corresponds to the gauche−gauche conformation, is 12.4 kcal/mol. The remarkable differences between the rotational profiles of **4** and $4^{\bullet+}$ must be attributed to the double bond character of the inter-ring bond in the latter. This is evident when the bond lengths between the rings are compared (1.413 and 1.357 Å for **4** and $4^{\bullet+}$, respectively). On the other hand, Figure 7 indicates that the variation of the inter-ring bond length with the torsional angle $\theta$ is considerable for $4^{\bullet+}$. Thus, such distance elongates by 0.093 Å when the syn conformation goes toward the gauche−gauche conformation. It is worth noting that for the latter conformation the inter-ring bond length is 1.450 Å, which is even larger than the distance obtained for the minimum energy conformation of the neutral species The elongation of the inter-ring bond in $4^{\bullet+}$ is due to the complete loss of the double bond character during the rotation.

**TABLE 2: Estimated Ionization Potentials (IP; in eV) and Experimentally Determined Oxidation Potentials[a] ($E°$; in V) for the Compounds under Study**

| | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| IP | 5.6 | 5.8 | 6.3 | 6.2 |
| $E^{o}$ | 1.02 | 1.03 | - | |

[a] From ref 8.

**Ionization Potentials.** The IP indicates whether a given acceptor (p-type donant) is capable of ionizing the compound. The estimated IPs are displayed in Table 2, where the oxidation potentials measured by cyclic voltammetry in $CH_2Cl_2$ solution have been also included for comparison.[4]

An analysis of these results suggests that the presence of methyl substituents in the 2,5 positions increase the oxidative ability of these compounds. The IPs are lower for **2** and **3** than for **4** and **5** by about 0.5−0.7 eV. Moreover, the effects of the methylsulfanyl substituents are almost negligible with respect to the pronounced influence of the methyl substituents. Thus, the IPs of **2** and **3** differ by only 0.2 eV and an even smaller difference is obtained for **4** and **5**. The small influence of these electron donating substituents is supported by the measured oxidation potentials. So, a difference of approximately 0.01 V is displayed between the values of the oxidation potentials for **2** and **3**.

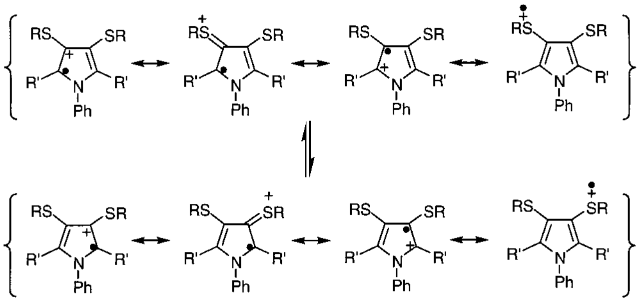
## Conclusions

The minimum energy conformations and the barriers to internal rotation about the bond between the planes of the two rings have been computed for **2**, **3**, **4**, and **5** and their corresponding radical cations using ab initio quantum mechanical calculations. The conformational preferences of **2** were very similar to those of **3**. The minimum energy conformation corresponds to the gauche−gauche perpendicular structure and the energy maximum to the syn planar structure. The former conformation lies 15.7 and 19.2 kcal/mol below the latter for **2** and **3**, respectively. The shape of the torsional potential for the radical cations $2^{\bullet+}$ and $3^{\bullet+}$ is very similar to that of the neutral species. The barriers between the minimum and maximum energy conformations, which are located at the same positions, are 18.7 and 21.2 kcal/mol for $2^{\bullet+}$ and $3^{\bullet+}$, respectively. Despite this similarity it should be emphasized that the molecular geometries of the four compounds are very different among them. However, their conformational preferences are mainly governed by the repulsive steric interactions between the phenyl ring and the methyl groups at 2,5 positions.

On the other hand, **4** and **5** present almost identical torsional profiles. For the two compounds, the minimum energy conformation corresponds to the syn-gauche and the energy barriers associated to the syn and gauche−gauche conformations are very low, i.e., about 2.5 and 1.0 kcal/mol, respectively. Conversely, the conformational preferences of $4^{\bullet+}$ and $5^{\bullet+}$ are very different. Thus, $5^{\bullet+}$ presents a preference for the syn−gauche conformation whereas the minimum energy conformation of $4^{\bullet+}$ corresponds to the syn planar structure. This is because the double bond character of the inter-ring bond in latter radical cation.

The loss of symmetry in the stable conformations of $3^{\bullet+}$ and $5^{\bullet+}$ showed in different bond lengths and angles between equivalent atoms in the neutral compounds can be accounted for by the inability to show simultaneously the mesomeric effect in both sulfanyl groups due to steric hindrance. This is confirmed by the different values in the dihedral angles C2−C3−S−C (167.6°) and C5−C4−S−C (90.9°). However, as two confor-

**SCHEME 4**



mations are equally probable, the real situation is an equilibrium between stable conformations as showed in Scheme 4. In both conformations, only those canonical structures in which participate the electronic pair on sulfur atoms are displayed.

The spin densities predicted for the minimum energy conformations of the radical cations are in good agreement with EPR measurements.[4] Both theoretical spin densities and experimental data point out the electron confinement characteristics of **2**$^{•+}$ and **3**$^{•+}$, which are explained by their conformational preferences. Thus, $\pi$ conjugation between the pyrrole and phenyl rings is not allowed by the steric interactions originated by the substituents at 2,5 positions. A different behavior is predicted for **4**, **5** and their corresponding radical cations. The preferences of **4** and **4**$^{•+}$ for the syn−gauche and syn conformations, respectively, clearly indicate that ionization increases the $\pi$ conjugation in this compound. The large similarities between the conformational preferences of **4** and **5** suggest that no mesomeric effect is induced by the methylsulfanyl groups in the latter compound. However, such effect appears in **5**$^{•+}$ inducing a preference for the syn−gauche conformation rather than for the planar structure. Accordingly, the behavior of **5**$^{•+}$, in terms of electron confinement and $\pi$ conjugation, is intermediate with respect to those displayed by the other radical cations investigated in this work.

## References and Notes

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