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Intrinsic Flexing Abilities of Molecular Muscles Based on Tetrakis(2,3-thienylene): A Quantum Mechanical Study

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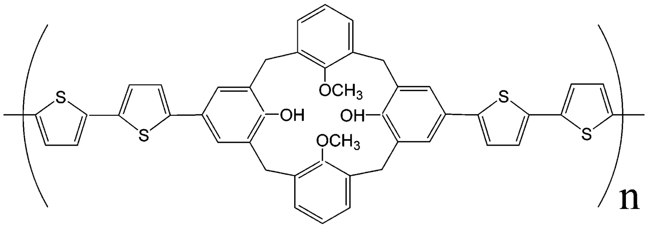
The conformational and energetic properties of tetrakis(2,3-thienylene), which is the building block of a single-molecule electroactive mechanical actuator, and some substituted derivatives have been characterized using quantum mechanical calculations. More specifically, calculations have been used to investigate the actuation range and the ability to be oxidized of tetrakis(2,3-thienylene), its homodimer, and some derivatives containing charged substituents. The actuation range of tetrakis(2,3-thienylene) upon oxidation to the 1+ state was found to be about 6%, while oxidation to the 2+ state with triplet and singlet spin multiplicities produces dimensional changes of 5% and 11%, respectively. Interestingly, the singlet dicationic state was predicted to be significantly more stable than the triplet one. Similar changes in the molecular length were obtained for the dimer of tetrakis(2,3-thienylene) upon oxidation, in this case the actuation range of the dication being about 11% for the two spin multiplicities. However, it was found that the actuation range increases to about 14% and 19% when the 3+ and 4+ states are considered for the dimer. Finally, incorporation of substituents on the tetrakis(2,3-thienylene) unit led to stabilization of the charged states, even though no relevant improvement in the range of actuation was detected.

Introduction

The development of efficient "molecular" actuators able to transform chemical, electrical, or electromagnetic energy into mechanical work has become an important field within the nanotechnology context. In these materials the mechanical actuation is a property intrinsic to individual polymer chains rather than a bulk phenomenon. Among all potential mechanical actuators, those fabricated from conducting organic polymers, i.e., redox-active polymers, have received special attention from researchers.[1−4] Although frequently the actuation of these materials is a bulk property based on the diffusion of small molecules through the supporting matrixes promoting macroscopic changes of volume,[5] some single-molecule actuators based on conducting polymers have been successfully engineered by enhancing the conformational flexibility of the individual molecules. Thus, the main characteristic of molecular actuators is related to their actuation response upon external stimuli, which consists of individual conformational changes, i.e., controlled variations of the molecular length.

Quantum mechanical methods can be successfully used to describe and understand the molecular mechanism of actuators based on conducting polymers. For instance, recent theoretical studies allowed explanation of the conformational variations that take place upon the electronic structure changes of poly(calix[4]arene bis(bithiophene)),[6,7] which is a single-molecule electromechanical actuator constituted by quarterthiophene oligomers (bis(bithiophene units)) and calix[4]arene scaffolds (25,27-dihydroxy-26,28-dimethoxycalix[4]arene) (Scheme 1).[8,9] We found that the contraction−expansion movements of poly(calix[4]arene bis(bithiophene)) are mainly promoted by the deprotonation of the two hydroxyl groups of the calix[4]arene scaffold rather than by the oxidation of the quarterthiophene segments.[6] Thus, the strong repulsive interaction between the deprotonated oxygen atoms produces a drastic reduction of the molecular length, calix[4]arene scaffolds being considered as very active elements in the actuation mechanism of poly(calix[4]arene bis(bithiophene)) due to their conformational flexibility.

SCHEME 1: Chemical Repeating Unit of Poly(calix[4]arene bis(bithiophene))



Poly(tetrakis(2,3-thienylene)) is a recently developed molecular actuator with a linear polythiophene backbone, whose expansion−contraction mechanism is based on the reversible redox-induced flexing of cyclooctatetraene (Scheme 2).[10−13] The S−C−C−S dihedral angles (ϕ) reflect the dimensional change of the system, $\phi = 0°$ indicating a completely planar structure. The values of ϕ measured by X-ray crystallography for the tetrakis(2,3-thienylene) were 47.6° and 46.2°, indicating that in the neutral state this is not a planar system. It should be noted that the distances between the α-carbons of opposite thiophene rings (d), i.e., a···c and b···d in Scheme 2, decrease when the dihedral angles ϕ increase. Thus, the redox-induced conformational change of tetrakis(2,3-thienylene) is similar to the tub-

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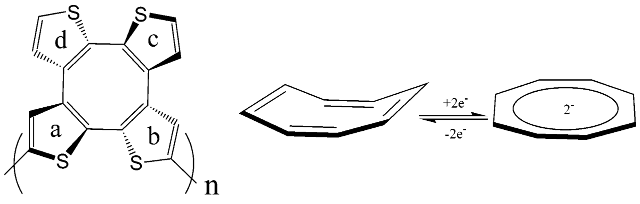
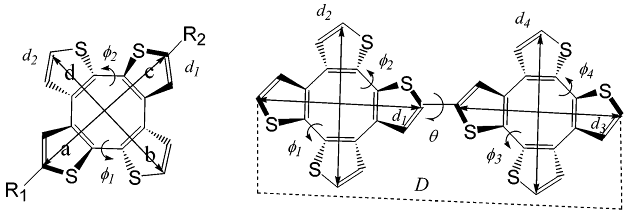
SCHEME 2: Chemical Repeating Unit of Poly(tetrakis(2,3-thienylene)) (Left) and Reversible Redox-Induced Tub-to-Planar Conformational Change in Cyclooctatetraene (Right)[a]



[a] The thiophene rings of the tetra(2,3-thienylene) unit have been labeled as a−d.

SCHEME 3: Compounds Investigated in This Work



1: R_1=R_2= H
2: R_1=R_2= OH
3: R_1=R_2= O^-
4: R_1= O^- and R_2= NH_3^+

1-d

to-planar change in cyclooctatetraene, the latter also being displayed in Scheme 2. Cyclooctatetraene is a nonplanar 8π macrocycle that transforms into an aromatic $4n + 2$ system upon oxidation or reduction by two electrons, the planar arrangement gaining aromatic stabilization in these charged states.[14] However, in practice, the tub-to-planar conformational change in cyclooctatetraene occurs upon oxidation or reduction to any state, 2+, 1+, 1−, and 2−.

Electrochemical studies on a tetrakis(2,3-thienylene) model molecule with butyl side groups attached to the α-carbon atoms of the thiophene rings c and d revealed a reversible oxidation toward a 1+ state, even though further oxidation to a 2+ state was not observed.[12,13] Quantum mechanical calculations at the B3LYP/6-31G(d) level predicted an increase in the distance *d* of 5.7% when the tetrakis(2,3-thienylene) is oxidized from the neutral state to the radical cation.[13] This change is within the range typically exhibited by bulk electromechanical actuators based on electroactive polymers, i.e., ∼10%.[1] On the other hand, cyclic voltammetry studies showed that the homodimer of tetrakis(2,3-thienylene), i.e., Scheme 2 (left) with $n = 2$, undergoes 1+ and 2+ oxidation states, the latter being a consequence of two distinct one-electron oxidations (1+ per monomeric unit).[12] The variation of *d* predicted from B3LYP/6-31G(d) calculations when this dimer oxidizes to 1+ and 2+ is 3.5% and 5.9%, respectively.

In this work we have used ab initio and density functional theory (DFT) quantum mechanical methods to investigate different aspects of the actuation mechanism of tetrakis(2,3-thienylene) units. First, we have examined how the oxidation of tetrakis(2,3-thienylene) (compound **1** in Scheme 3) affects both the conformation and the energy of the system. After this, calculations were performed on the homodimer of tetrakis(2,3-thienylene) (compound **1-d** in Scheme 3) to study how the molecular size affects the actuation mechanism. Next, to increase the range of actuation of the tetrakis(2,3-thienylene) unit and to facilitate its oxidation to a 2+ state, different substituents were attached to the α-position of rings a and c. More specifically, we have investigated the effects produced by the incorporation of (a) two hydroxyl groups, both the protonated (acid pH) and fully deprotonated (basic pH) forms being considered (compounds **2** and **3**, respectively, in Scheme 3), and (b) one hydroxyl and one amino group, the zwitterionic form of the molecule being the only one considered (compound **4** in Scheme 3), i.e., the deprotonated hydroxyl group and the positively charged ammonium group. We are aware that the substitution pattern of compounds **2**−**4** precludes the formation of poly(tetrakis(2,3-thienylene)) with a linear polythiophene backbone such as that displayed in Scheme 2. However, it should be noted that poly(tetrakis(2,3-thienylene))s can also be obtained considering other points of backbone connectivity, for instance, the β-positions of all the rings or the α-positions of rings b and d. Furthermore, we are interested in how the repulsive or attractive interactions between the substituents affect the range of actuation of tetrakis(2,3-thienylene), the effect of these interactions in the flexing capabilities of the system being maximum when the substituents are attached to the α-positions of rings a and c or, equivalently, of rings b and d.

Methods

All the ab initio and DFT quantum mechanical calculations were performed using the Gaussian 03 computer program.[14] Geometry optimizations for compounds **1**−**4** were carried out at the HF/6-31G(d)[15] and B3LYP/6-31G(d)[16,17] levels. Furthermore, additional geometry optimizations were performed for selected charged states of compound **1** at the MP2/6-31G(d) level, single-point energy calculations being carried out at the MP2/6-31+G(d,p)[18] and MP2/6-311++G(d,p) levels using the MP2/6-31G(d) geometries. Four different electronic states were considered in all cases: (i) the reduced neutral state, (ii) the cationic 1+ state, (iii) the dicationic 2+ state with triplet spin multiplicity (two separated 1+ charges), which has been labeled as 2(1+), and (iv) the dicationic 2+ state with singlet spin multiplicity, which has been labeled as 1(2+). Calculations on the 1+, 2(1+), and 1(2+) states were performed considering the unrestricted quantum chemical formalism (UHF, UB3LYP, and UMP2). In all cases the minimum energy conformations were derived from full geometry optimizations, no constraint being applied to force symmetry restrictions.

The energies reported for all the charged states have been calculated relative to that of the neutral state. These relative energies are accurate estimations of ionization potentials (IPs) because they were computed using the quantum mechanical energies of the fully relaxed neutral and ionized species. Accordingly, the relative energies of the 1+ and 2+ oxidized states include the energy required to extract one or two electrons, respectively, and the relaxation energy of the charged molecule.

Results and Discussion

Actuating Unit (1). The conformational parameters *φ* and *d* calculated for the neutral and oxidized states are listed in Table 1, while the molecular energies relative to that of the neutral state are displayed in Table 2. The evolution of the molecular conformation upon oxidation is schematically displayed in Figure 1. In general, there is excellent agreement between the conformations predicted at the (U)HF and (U)B3LYP levels. Furthermore, although geometry optimizations were performed without imposing any constraint, the conformations obtained for the different states of **1** are symmetric, i.e., $\phi_1 = \phi_2$ and $d_1 = d_2$. On the other hand, as expected the parameters listed in Table 1 for **1** and $\mathbf{1}^{1+}$ are very similar to those recently reported by Marsella et al.[12]

TABLE 1: Conformational Parameters[a] (Scheme 3) Calculated at the HF/6-31G(d) and B3LYP/6-31G(d) Levels for the Different States of Compound 1

	HF/6-31G(d)			B3LYP/6-31G(d)		
state	d_1, d_2	ϕ_1, ϕ_2	Δd_1, Δd_2	d_1, d_2	ϕ_1, ϕ_2	Δd_1, Δd_2
0	6.680	52.9		6.883	49.1	
1+	7.040	38.6	+5.4	7.298	34.0	+6.0
2(1+)	7.014	32.4	+5.0	7.247	33.0	+5.3
1(2+)	7.438	24.2	+11.3	7.494	25.8	+10.8

[a] Distances (d) in angstroms and dihedral angles (ϕ) in degrees. Δd (%) values are calculated with respect to the neutral state. The symmetry relations $\phi_1 = \phi_2$ and $d_1 = d_2$ are satisfied.

TABLE 2: Energies (kcal/mol) of the Different Charged States Relative to That of the Neutral State

	HF/6-31G(d)[a]				B3LYP/6-31G(d)[b]				
state	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1-d**
1+	144.3	142.2	−50.0	105.1	153.6	144.9	−22.7	103.7	140.1
2(1+)	374.2	344.8	−33.8	282.7	402.9	379.5	36.2	314.7	342.4
1(2+)	393.0	376.9	41.1	289.7	395.9	375.2	43.5	339.7	343.8

[a] Energies of the neutral states at the HF/6-31G(d) level: compound **1**, $E = -2200.552807$ au; compound **2**, $E = -2350.245927$ au; compound **3**, $E = -2349.070608$ au; compound **4**, $E = -2330.307019$ au. [b] Energies of the neutral states at the B3LYP/ 6-31G(d) level: compound **1**, $E = -2207.243279$ au; compound **2**, $E = -2357.658411$ au; compound **3**, $E = -2356.507713$ au; compound **4**, $E = -2337.705542$ au; compound **1-d**, $E = -4412.299128$ au.

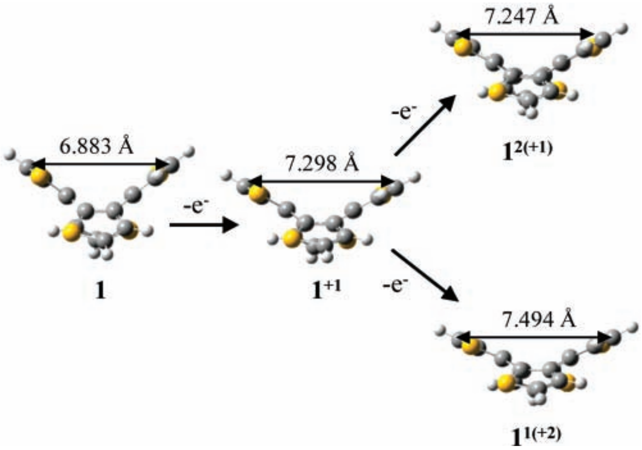


Figure 1. Evolution of the molecular conformation of **1** upon oxidation. The distances d provided by (U)B3LYP/6-31G(d) calculations are displayed.

Regarding the relative energies listed in Table 2, it should be noted that the results predicted for $\mathbf{1^{1+}}$ and $\mathbf{1^{1(2+)}}$ at the HF and B3LYP levels are in good agreement (Table 2). However, the two computational schemes differ considerably when the triplet dicationic state, $\mathbf{1^{2(1+)}}$, is considered. Thus, at the UHF/6-31G(d) level $\mathbf{1^{2(1+)}}$ is 18.8 kcal/mol more stable than $\mathbf{1^{1(2+)}}$, while the latter is more stable than the former by 7.0 kcal/mol at the UB3LYP/6-31G(d) level. To investigate the influence of the computational method on the relative stability of $\mathbf{1^{2(1+)}}$ and $\mathbf{1^{1(2+)}}$, the two species were reoptimized at the UMP2/6-31G(d) level, single-point energy calculations at the UMP2/6-31+G(d,p) and UMP2/ 6-311++G(d,p) levels also being performed. The results, which were consistent with those obtained at the UB3LYP/6-31G(d) level, are displayed in Table 3 indicating that $\mathbf{1^{1(2+)}}$ is the most stable dicationic state. On the other hand, it should be mentioned that conformational parameters obtained at the UMP2/6-31G(d) level for $\mathbf{1^{1(2+)}}$ ($\phi_1 = \phi_2 = 26.2°$ and $d_1 = d_2 = 7.391$ Å) and $\mathbf{1^{2(1+)}}$ ($\phi_1 = \phi_2 = 36.1°$ and $d_1 = d_2 = 7.172$ Å) are fully consistent with those displayed in Table 1.

TABLE 3: Relative Energies (kcal/mol) between $\mathbf{1^{2(1+)}}$ and $\mathbf{1^{1(2+)}}$ Calculated at Different Computational Levels

	$\mathbf{1^{2(1+)}}$	$\mathbf{1^{1(2+)}}$
UHF/6-31G(d)//UHF/6-31G(d)	−18.8	0.0[a]
UB3LYP/6-31G(d)//UB3LYP/6-31G(d)	7.0	0.0[b]
UMP2/6-31G(d)//UMP2/6-31G(d)	26.6	0.0[c]
UMP2/6-31+G(d,p)//UMP2/6-31G(d)	28.0	0.0[d]
UMP2/6-311++G(d,p)//UMP2/6-31G(d)	28.7	0.0[e]

[a] $E = -2199.926523$ au. [b] $E = -2206.612369$ au. [c] $E = -2202.496739$ au. [d] $E = -2202.592899$ au. [e] $E = -2202.883863$ au.

The overall results obtained for **1** are consistent with available experimental data, which are only qualitative. As mentioned above, only the 1+ oxidation state has been detected by cyclic voltammetry for tetra(2,3-thienylene) monomers. The results displayed in Table 2 indicate that the relative energy of the dication is about 2.6 times higher than the first IP, suggesting that oxidation to a 2+ state in either the singlet or triplet spin state is a very unfavorable process. On the other hand, it should be noted that, as evidenced in Figure 1, the variation of d predicted for $\mathbf{1^{1(2+)}}$ is about 2 times greater than that obtained for $\mathbf{1^{1+}}$ (Table 1). This dimensional change, which reflects the range of actuation, is expressed by Δd (percent change) in Table 1. As can be seen, Δd is about 6% and 11% for $\mathbf{1^{1+}}$ and $\mathbf{1^{1(2+)}}$, respectively. Accordingly, taking into account that $\mathbf{1^{1(2+)}}$ is the most stable dicationic state, it would be very desirable to reduce its relative energy in the tetrakis(2,3-thienylene) unit to improve the efficiency of the electromechanical actuator.

Dimerization of the Actuating Unit (1-d). The results obtained at the (U)B3LYP/6-31G(d) level for **1-d** are displayed in Tables 2 and 4, while those derived from (U)HF/6-31G(d) calculations are available upon request from the authors. Obviously, the number of conformational parameters required to describe **1-d** is considerably larger than that used for **1**. The new parameters, which are shown in Scheme 3, are the following: (i) d_3, d_4, ϕ_3, and ϕ_4, which correspond to the distances and dihedral angles associated with the second actuating unit, (ii) the interunit dihedral angle θ, which is defined by the sequence S−C−C−S and describes the relative conformation between the two actuating units, and (iii) the distance D, which provides the molecular length of the whole dimer. On the other hand, the ranges of actuation of the individual units and the complete molecule are expressed by Δd_i and ΔD, respectively. The molecular shape of **1-d** is illustrated in Figure 2, which shows the conformation provided by the B3LYP/6-31G(d) method for the neutral state.

Comparison of the distances d and dihedrals ϕ listed in Table 4 with those of Table 1 indicates that dimerization does not produce significant conformational changes in the neutral, 1+, and 2(1+) states of the individual actuating units. This is reflected by the actuation ranges Δd of **1** and **1-d**, which are very similar for these two charged states. However, inspection of the results obtained for the dicationic 1(2+) state reveals that dimerization drastically reduces the dimensional change of the actuating units, this reduction being about 5%. Thus, the actuating units are less planar in $\mathbf{1\text{-}d^{1(2+)}}$ than in $\mathbf{1^{1(2+)}}$. On the other hand, the molecular length of the dimer, D, changes with the oxidation state, the following order being obtained: $\mathbf{1\text{-}d} < \mathbf{1\text{-}d^{1+}} < \mathbf{1\text{-}d^{2(1+)}} \approx \mathbf{1\text{-}d^{1(2+)}}$. Accordingly, upon the introduction of the second positive charge, the molecular actuation range increases from 5.6% to more than 11%, the influence of the spin multiplicity in the dimensional change of the dicationic state being very small in this case. It should be noted that the value of D is influenced not only by d_1 and d_3 but also by the dihedral angle θ. These results suggest that the efficiency of

TABLE 4: Conformational Parameters[a] (Scheme 3) Calculated at the B3LYP/6-31G(d) Level for the Different States of 1-d

state	d_1, d_3	d_2, d_4	ϕ_1, ϕ_4	ϕ_2, ϕ_3	θ	Δd_1, Δd_3	Δd_2, Δd_4	D	ΔD
0	6.928	6.896	48.7	48.6	164.2			12.762	
1+	7.137	7.099	38.4	43.3	171.8	+3.3	+2.9	13.474	+5.6
2(1+)	7.312	7.266	35.5	33.7	165.6	+5.5	+5.4	14.183	+11.1
1(2+)	7.341	7.271	31.2	36.4	172.1	+6.0	+5.4	14.220	+11.3
3+	7.422	7.331	30.8	30.6	169.7	+7.1	+6.3	14.610	+14.5
2(2+)	7.544	7.441	27.9	25.6	163.9	+8.9	+7.9	15.145	+18.7
3+, 1+	7.434	7.282	30.3	30.5	169.0	+7.3	+5.6	14.691	+15.1

[a] Distances (d and D) in angstroms, dihedral angles (θ and ϕ) in degrees, and ΔD in percent. Δd (%) values are calculated with respect to the neutral state. The symmetry relations $\phi_1 = \phi_4$, $\phi_2 = \phi_3$, $d_1 = d_3$, and $d_2 = d_4$ are satisfied.

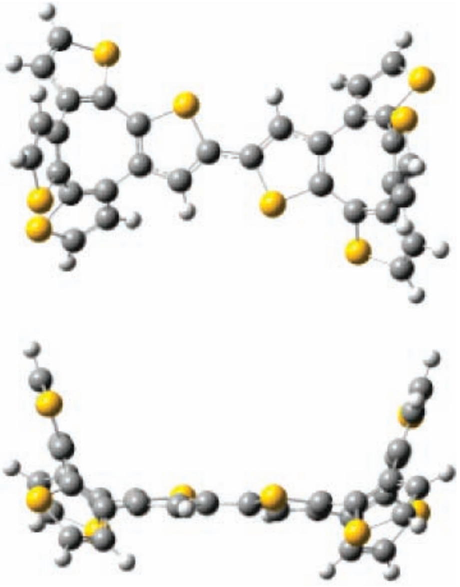


Figure 2. Equatorial (top) and axial (bottom) views of the molecular conformation provided by B3LYP/6-31G(d) calculations for **1-d**.

the actuator depends not only on the tetrakis(2,3-thienylene) unit but also on the chain length.

The relative energies displayed in Table 2 indicate that the IPs decrease when the second monomer is incorporated. Thus, the relative energies of both the cationic and dicationic states are smaller for **1-d** than for **1**. Furthermore, comparison between **1-d$^{1(2+)}$** and **1-d$^{2(1+)}$** reveals that the two 2+ oxidation states are energetically closer, the former being slightly favored. These results, which represent a significant change with respect to **1**, agree from a qualitative point of view with available experimental data. Thus, electrochemical measurements evidenced that the distribution of the dication on **1-d** is consistent with 1+ per tetrakis(2,3-thienylene) unit.[12]

As was mentioned above, the inter-ring dihedral angle affects the molecular length of the dimer. To ascertain the influence of the conformation on the molecular actuation range, the internal rotation of **1-d**, **1-d^{1+}**, **1-d$^{1(2+)}$**, and **1-d$^{2(1+)}$** was investigated by scanning the dihedral angle θ in steps of 30°. Figure 3a represents the rotational profile of the four species, energies being relative to the minimum of each species (see Table 4). As expected, the lowest energy arrangement corresponds in all cases to the *anti* arrangement, whereas the *syn* conformation is a local minimum with a relative energy of about 1 kcal/mol. The barrier at $\theta = 90°$ is 3.3 kcal/mol for the neutral state, this value being 2 times larger than that calculated for 2,2′-bithiophene.[19] The barrier of the 1+, 2(1+), and 1(2+) states increases to 10.3, 4.7, and 14.4 kcal/mol, respectively, indicating that the contribution of quinoid canonical forms is higher for **1-d^{1+}** and **1-d$^{2(1+)}$**. Figure 3b displays the variation of ΔD, which has been evaluated with respect to the distance D of the lowest energy conformation of **1-d** (12.762 Å in Table 4), with θ for the four investigated species. As can be seen, the folded conformations, which are less stable than the planar ones, provide the larger actuation ranges in all cases. For example, for $\theta = 90°$ the value of ΔD predicted for **1-d**, **1-d^{1+}**, **1-d$^{1(2+)}$**, and **1-d$^{2(1+)}$** corresponds to 9.0%, 15.7%, 19.2%, and 20.1%, respectively. Unfortunately, the folded conformations are significantly destabilized with respect to the *anti* minimum (see Figure 3a), precluding such a degree of efficiency for the charged states. On the other hand, in a recent study we found that the influence of the organic and polar solvents on the conformational preferences of 2,2′-bithiophene, i.e., molecular geometries and relative energies of the minima, is relatively small.[19a] Accordingly, the actuation range is not expected to change significantly in solution.

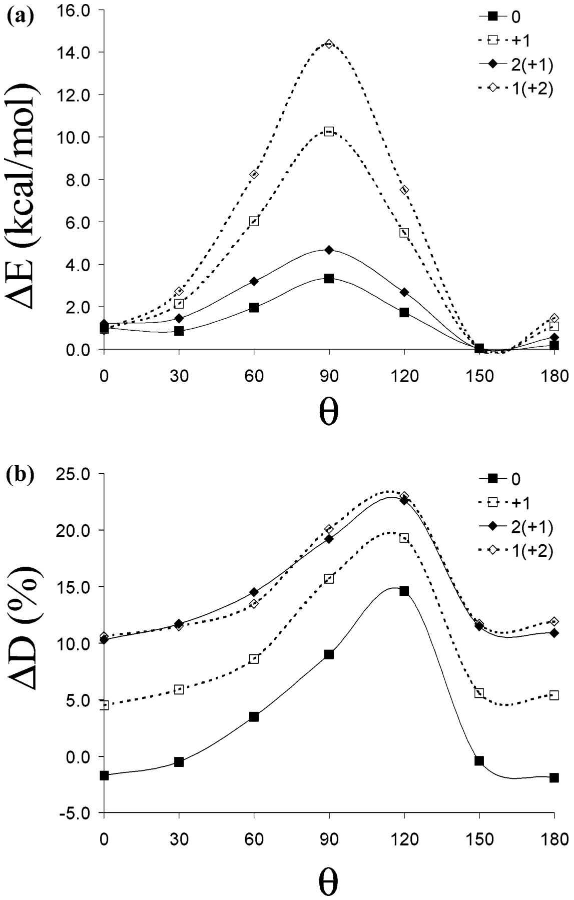


Figure 3. For the four examined species: (a) rotational profile and (b) variation of the distance D calculated with respect to the lowest energy conformation of **1-d**.

On the other hand, to ascertain whether the actuation range of **1-d** increases with the number of positive charges, additional calculations were performed considering the 3+ and 4+ charged states. A doublet spin multiplicity was considered for the 3+

TABLE 5: Conformational Parameters[a] **(Scheme 3) Calculated at the HF/6-31G(d) and B3LYP/6-31G(d) Levels for the Different States of 2**

	HF/6-31G(d)			B3LYP/6-31G(d)		
state	d_1, d_2	ϕ_1, ϕ_2	Δd_1, Δd_2	d_1, d_2	ϕ_1, ϕ_2	Δd_1, Δd_2
0	6.684	53.0		6.884	49.2	
	6.690			6.923		
1+	7.250	32.0	+8.5	7.267	34.1	+5.6
	7.259		+8.5	7.311		+5.6
2(1+)	7.207	34.8	+7.8	7.169	34.7	+4.1
	7.176		+7.3	7.230		+4.4
1(2+)	7.378	25.2	+10.3	7.444	26.1	+8.1
	7.420		+10.9	7.509		+8.5

[a] Distances (d) in angstroms and dihedral angles (ϕ) in degrees. Δd (%) values are calculated with respect to the neutral state. The symmetry relation $\phi_1 = \phi_2$ is satisfied.

state (**1-d**$^{3+}$), while both the singlet and triplet spin multiplicities were considered for the 4+ state (**1-d**$^{2(2+)}$ and **1-d**$^{3+,1+}$, respectively). In all cases the minimum energy conformations were derived from full geometry optimizations at the UB3LYP/6-31G(d) level, the *anti* arrangement being used as the starting geometry. Interestingly, **1-d**$^{2(2+)}$ was found to be favored with respect to **1-d**$^{3+,1+}$ by 3.6 kcal/mol. Analysis of the structural parameters of these additional species, which are included in Table 4, indicates that the actuation range increases with the charge. Thus, the actuation range predicted for **1-d**$^{3+}$ and **1-d**$^{2(2+)}$ is 1.4% and 18.7%, respectively.

Introduction of Protonated (2) and Deprotonated (3) Hydroxyl Groups in the Actuating Unit. To favor the formation and stabilization of dicationic species in tetrakis(2,3-thienylene), especially that with a 1(2+) state, and to alter the strength of the intramolecular interactions, hydroxyl groups were introduced at the α-positions of rings a and c (compound **2** in Scheme 3). The conformational parameters d and ϕ calculated for **2**, **2**$^{1+}$, **2**$^{2(1+)}$, and **2**$^{1(2+)}$ are listed in Table 5. As can be seen, the incorporation of hydroxyl groups in two rings introduces some conformational changes with respect to compound **1**. Thus, in this case the symmetry relationship between d_1 and d_2 is not detected, showing that the ability of the hydroxyl group to interact with other parts of the molecule, for example, the sulfur atoms, induces some differences in these parameters. Conversely, all the calculated species show that $\phi_1 = \phi_2$. On the other hand, the Δd values displayed in Table 5 indicate that the dimensional changes of **2** do not show significant differences with respect to those calculated for **1**, indicating that the hydroxyl groups are not able to alter the amplitude of intrinsic actuation in isolated tetrakis(2,3-thienylene) units.

Inspection of the relative energies displayed in Table 2, which were calculated with respect to the neutral state, reveals that the incorporation of hydroxyl groups only produces a slight stabilization of the 1+ state with respect to compound **1**, i.e., 2.1 and 8.7 kcal/mol at the UHF and UB3LYP levels, respectively. However, it is worth noting that the dicationic states of **2** undergo a significant stabilization with respect to those of **1**. Thus, the stability of the 2(1+) and 1(2+) states increases by 23.4 and 20.7 kcal/mol, respectively, at the UB3LYP level after the incorporation of the hydroxyl groups. Furthermore, again the UHF method seems to overestimate the stability of the 2(1+) state with respect to the 1(2+) state, which probably leads to prediction of an erroneous relative energy order. However, as was found above (see Table 3), the UB3LYP method is expected to provide a satisfactory qualitative description of the relative stability between **2**$^{2(1+)}$ and **2**$^{1(2+)}$, even though the relative energy of the former species is probably underestimated by this method yet.

TABLE 6: Conformational Parameters[a] **(Scheme 3) Calculated at the HF/6-31G(d) and B3LYP/6-31G(d) Levels for the Different States of 3**

	HF/6-31G(d)			B3LYP/6-31G(d)		
state	d_1, d_2	ϕ_1	Δd_1, Δd_2	d_1, d_2	ϕ_1	Δd_1, Δd_2
0	6.773	44.6		7.010	39.3	
	7.302			7.523		
1+	7.070	37.4	+4.4	7.147	34.0	+1.9
	7.323		+0.3	7.540		+0.2
2(1+)	7.092	38.0	+4.7	6.968	40.8	−0.6
	7.214		−1.2	7.197		−4.3
1(2+)	7.174	25.5	+5.9	7.234	28.2	+3.2
	7.446		+2.0	7.568		+0.6

[a] Distances (d) in angstroms and dihedral angles (ϕ) in degrees. Δd (%) values are calculated with respect to the neutral state. The symmetry relation $\phi_1 = \phi_2$ is satisfied.

In a recent study[6] we found that the actuation mechanism of poly(calix[4]arene bis(bithiophene)) is mainly due to the strong electrostatic repulsion between the deprotonated oxygen atoms of the two hydroxyl groups attached to the calix[4]arene scaffolds, this interaction being responsible for the drastic contraction of the material. Accordingly, we decided to investigate whether the deprotonation of the two hydroxyl groups of **2** would increase the dimensional change. Energetic and structural results calculated for compound **3**, which corresponds to the fully deprotonated form of **2** (Scheme 3), are displayed in Tables 2 and 6, respectively. It should be emphasized that, although the net charge of the 1+ and 2+ states of **3** is 1− and 0, respectively, due to deprotonation of the hydroxyl groups, they should be considered as equivalent to the 1+ and 2+ states of **2** since in both cases the oxidation state was obtained through an oxidation process.

Inspection of Table 6 reveals that upon deprotonation the difference between d_1 and d_2 increases to even ∼0.5 Å. This must be attributed to both the repulsive interaction between the deprotonated oxygen atoms and the electronic delocalization between each deprotonated oxygen atom and the corresponding thiophene ring. Thus, the electronic structure of the substituted thiophene rings (a and c) is completely different from that of rings b and d, which enhances the difference between d_1 and d_2. Furthermore, the dihedral angle symmetry relationship $\phi_1 = \phi_2$ is retained in all cases, the maximum difference being 0.1°. This conformational behavior is fully consistent with that described above for **2**.

It is worth noting that the actuation ranges predicted for the positively charged states of compound **3** are considerably smaller than those predicted for the charged states of **1** and **2**, indicating that the effect of the electrostatic repulsion between the two charged oxygen atoms is opposite that in poly(calix[4]arene bis(bithiophene)). This must be mainly attributed to the steric interactions between neighboring β-thienyl hydrogens, which prohibit tetrakis(2,3-thienylene) from adopting a planar conformation. Thus, although this arrangement is expected to alleviate the repulsive interaction between the charged oxygen atoms, steric hindrance of adjacent thiophene rings produces a relatively inflexible folded conformation. Additional calculations have been performed on the partially deprotonated compound ($R_1 = OH$ and $R_2 = O^-$ in Scheme 3). These results (available upon request from the authors), which are consistent with dimensional changes of about 5−6%, indicate that the range of actuation is not amplified by the full or partial deprotonation of the hydroxyl groups.

On the other hand, the relative energies displayed in Table 2 indicate that the 1+ oxidation state is more stable than the

TABLE 7: Conformational Parameters[a] (Scheme 3) Calculated at the HF/6-31G(d) and B3LYP/6-31G(d) Levels for the Different States of 4

	HF/6-31G(d)			B3LYP/6-31G(d)		
state	d_1, d_2	ϕ_1, ϕ_2	Δd_1, Δd_2	d_1, d_2	ϕ_1	Δd_1, Δd_2
0	6.751	44.1		7.039	35.1	
	6.622	59.0		7.010	58.9	
1+	6.620	38.6	−1.9	6.898	42.8	−2.0
	6.519	51.3	−1.5	6.922	50.2	−1.2
2(1+)	6.925	50.4	+2.5	7.205	43.2	+2.3
	6.845	31.2	+3.4	7.076	30.2	+0.9
1(2+)	6.881	44.8	+1.9	7.259	35.2	+3.1
	6.811	49.3	+2.8	7.182	37.9	+2.4

[a] Distances (d) in Å and dihedral angles (ϕ) in degrees. Δd (%) values are calculated with respect to the neutral state.

neutral state at both the UHF and UB3LYP levels of theory. Furthermore, the latter method reveals that the energies of the two dicationic states are relatively close to that of the neutral state. Both UHF/6-31G(d) and UB3LYP/6-31G(d) calculations show that $\mathbf{3}^{\mathbf{2(1+)}}$ is more stable than $\mathbf{3}^{\mathbf{1(2+)}}$, even though as occurred previously for **1** and **2** the stability of the 2(1+) state is probably overestimated by the former method.

Introduction of Attractive Electrostatic Interactions (4). As the incorporation of substituents with charges of identical sign was not able to improve the actuation range of tetrakis(2,3-thienylene) due to the low stability of the planar conformation, we tried to increase the dimensional change of the actuation unit by enhancing the flexing degree of the tub conformation. For this purpose, we incorporated substituents with opposite charge at the α-position of rings a and c (compound **4** in Scheme 3). Thus, strong attractive electrostatic interactions are expected through the zwitterion structure of this compound. The conformational parameters of **4**, $\mathbf{4}^{\mathbf{1+}}$, $\mathbf{4}^{\mathbf{2(1+)}}$, and $\mathbf{4}^{\mathbf{1(2+)}}$ after geometry optimization are displayed in Table 7, while the energies relative to the neutral state are included in Table 2.

As can be seen, the incorporation of $-O^-$ and $-NH_3^+$ groups produces a stabilization of the three charged states. Thus, at the UB3LYP/6-31+G(d,p) level the first IP is about 50 kcal/mol smaller for **4** than for **1**, while the energy of the dicationic states decreases by about 56−88 kcal/mol depending on the spin multiplicity. On the other hand, it is worth noting that the 2(1+) state is energetically favored with respect to the 1(2+) state at both the UHF and UB3LYP levels of theory, even though the former method underestimates such stabilization by 18.0 kcal/mol with respect to the latter one. This is consistent with the results obtained for **3**, which is also a compound with charged substituents. Thus, the overall results listed in Table 2 indicate that the 1(2+) state is energetically favored with respect to the 2(1+) state in compounds with uncharged sustituents, while the incorporation of charged substituents exchanges the relative stability of these dicationic states.

Inspection of the Δd_1 and Δd_2 values displayed in Table 7 reveals that the incorporation of two functional groups with charges of opposite sign does not induce any relevant change in the molecular length of the actuation unit. Accordingly, upon oxidation there is a small contraction (about 2%) followed by a small expansion (about 3%). It is worth noting that the actuation ranges for the two dicationic states are very similar, independent of the spin multiplicity. Thus, the considerable dimensional change observed for the 1(2+) state of **1** and **2** is not detected in **4**. On the other hand, it should be noted that the charged substituents introduced in **4** are expected to affect the packing of the molecular actuator chains. Thus, a network of strong electrostatic interactions between the actuating units of different molecular chains probably would be formed. These interactions would help to form self-assembled structures as is frequently observed in systems containing groups with charges of opposite sign.[20]

Conclusions

The range of actuation and the ability to be oxidized of the tetrakis(2,3-thienylene) unit, which is the building block of poly(tetrakis(2,3-thienylene)), have been examined using quantum mechanical calculations. The results obtained for $\mathbf{1}^{\mathbf{1+}}$ are consistent with the qualitative observations of Marsella and coworkers,[12] even though the largest dimensional change (∼11%) was obtained for $\mathbf{1}^{\mathbf{1(2+)}}$. Accordingly, to improve the efficiency of the actuator, the stabilization of the dicationic state with singlet spin multiplicity, which has not been experimentally detected yet, is highly desirable. Interestingly, $\mathbf{1}^{\mathbf{1(2+)}}$ was found to be significantly more stable than the dication with triplet spin multiplicity, the actuation range predicted for the latter being similar to that found for $\mathbf{1}^{\mathbf{1+}}$. In contrast, the triplet spin multiplicity was found to be slightly favored for the dication of **1-d**, which was consistent with reported electrochemical results,[12] i.e., 1+ per tetrakis(2,3-thienylene) unit. The variation of the molecular length upon oxidation predicted for **1-d** was similar to that obtained for **1**, even though the local change of the two actuating units contained in the former was smaller than that of the latter. Furthermore, the actuation range calculated for the dication of **1-d** was about 11%, independent of the spin multiplicity. Additional calculations on **1-d** considering the 3+ and 4+ states indicate that the actuation range increases with the charge.

The results obtained for **2** and **3** indicate that the incorporation of hydroxyl groups on rings a and c of tetrakis(2,3-thienylene) stabilizes the positively charged states. This stabilization is particularly important when the two hydroxyl groups are deprotonated. Furthermore, deprotonation produces a change in the relative stability of the two dicationic forms calculated for **2** and **3**, the 1(2+) and 2(1+) states being the most stable for the former and the latter, respectively. Nevertheless, the dimensional change of **1** was not enlarged by the incorporation of hydroxyl groups, either protonated or deprotonated, indicating that the driving forces found in the actuation mechanism of poly(calix[4]arene bis(bithiophene))[6] cannot be successfully applied to poly(tetrakis(2,3-thienylene)). This is a consequence of the strong repulsive interactions detected in the planar conformation of tetrakis(2,3-thienylene). Finally, the formation of a zwitterion through the incorporation of substituents with charges of opposite sign does not lead to amplification of the dimensional change of the actuating unit, even though a significant stabilization of the 1+ and 2+ charged states was detected. Interestingly, for **4** the triplet spin multiplicity was the most stable dication, which is in agreement with the results obtained for **3**. This feature indicates that the electronic distribution of the 2+ state depends on the charged/uncharged nature of the substituents attached to the tetrakis(2,3-thienylene) unit.

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