Conformational Behaviour of Isomeric Bithienyls. An *Ab Initio* Study

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The conformational behaviour of isomeric bithienyls has been analysed by means of *ab initio* STO-3G computations optimizing the most significant geometrical parameters. The torsional potentials of bithienyls are very similar to those of the corresponding bifuranyls and are characterized by minima at planar conformations and maxima at perpendicular conformations. The energy difference between *cis*- and *trans*-conformers is very low except in the case of the 2,2′-isomer. Inclusion of the *d* orbitals on sulphur atoms does not alter the general trends, but significantly increases the energy barrier of the 2,2′-isomer.

The conformational behaviour of heteroaromatic systems formed by two rings linked together by essentially single bonds has been the subject of several experimental[1–15] and semi-empirical quantum mechanical[15–26] investigations in view of the considerable interest of some compounds of this class in many fields of physical and chemical technology.[27,28] However, it is quite a difficult task to generate full rotational potential functions from experimental data since only conformations in the vicinity of the potential minima are appreciably populated; information regarding the remainder of the potential function is necessarily indirect. On the other hand complete potential functions $V(\psi)$ may be readily generated theoretically by carrying out calculations for an appropriate number of rotational angles, ψ, but semi-empirical methods of the NDO type (no matter which parametrization is used) are often unrealistic in this connection, due to a strong preference for conformations in which the two rings are in perpendicular planes.[15,22] Since other all-valence methods also show significant shortcomings,[25,26] in recent times systematic *ab initio* studies have started to appear,[15,29–36] especially in view of the fact that conformational problems of this type can be easily studied at the Hartree–Fock level and even employing minimal basis sets. Our previous studies on azabiphenyls have shown that molecules with the same local environment of the inter-ring carbon atoms (*i.e.* the same *ortho* groups) have very similar equilibrium conformations, irrespective of their composition, and that replacement of *ortho*-CH groups by nitrogen atoms alleviates some of the steric hindrance that arises as the two rings become coplanar. As a natural extension to this analysis we have now turned our attention to systems resulting from the connection of two five-membered rings. Bifuranyls and bithienyls provide a good choice in this connection since the different isomers show several combinations of CH groups and heteroatoms in the local environment of inter-ring carbon atoms (C_{ir}). The 2,2′-isomers are characterized by one short H • • • H contact and the interaction between the lone pairs on the heteroatoms in the *cis*-conformation, whereas in the *trans*-conformation they are replaced by two (lone pair) • • • H interactions. On the other hand, two short H • • • H contacts are operative in both the *cis*- and *trans*-structures of the 3,3′-isomers. Finally the 2,3′-isomers display one H • • • H and one (lone pair) • • • H short contact in both the *cis*- and *trans*-arrangements.

Bifuranyls have been studied recently by Orti *et al.*[34] and bithienyls are the subject of the present paper. We have approached the conformational problem, as in the case of azabiphenyls, by quantum mechanical calculations at the *ab initio* level using a minimal STO-3G basis set.[37] However, the computed dipole moment of thiophene is severely underestimated by this basis set (0.09 D *versus* an experimental value of 0.54 D[38]) and this is essentially due to the strong positive π-charge on sulphur, the σ-contribution being vanishing small. Previous studies[39,40] have shown that inclusion of *d* orbitals on sulphur is mandatory for obtaining a good dipole moment since these orbitals account for a sensibly negative σ-charge on sulphur, able to counterbalance the positive π-charge, which is essentially basis-set independent. In order better to analyse this point we have recomputed the electronic structure of thiophene employing the STO-3G* basis set, in which a manifold of five *d*-type functions, consisting of one second-order Gaussian each, is added to the minimal STO-3G basis set for second-row atoms only.[41] The computed dipole moment becomes 0.63 D, in good agreement with the experimental value and, especially, with extended basis set results[40] as is also the case for the charge distribution. On these grounds we have also performed some computations on bithienyls with this basis set.

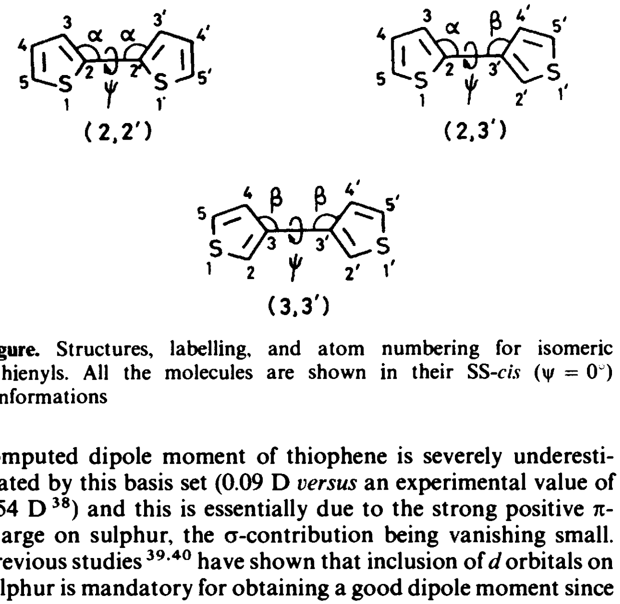

Figure. Structures, labelling, and atom numbering for isomeric bithienyls. All the molecules are shown in their SS-*cis* (ψ = 0°) conformations

Calculations

As a first step the torsional potentials of isomeric bithienyls (see Figure) were computed by the internal STO-3G basis set[37] of the GAUSSIAN/80 package[42] using the microwave structure of the thiophene ring,[43] and an inter-ring distance of 1.48 Å along the direction of the inter-ring bonds. The torsional angle ψ (that is the angle between the planes of the two rings) was spanned in steps of 30°. The thiophene–thiophene bond distance and the angles between this bond and the assumed rigid ring structures (see Figure) were then optimized at each value of ψ using the analytical gradient procedure implemented

Table 1. Conformational energies with respect to planar SS-*cis* forms (ΔE) and potential constants (V_i) for isomeric bithienyls. All the data are in kJ mol^{-1}

	STO-3G			STO-36^{opt}			STO-3G^{opt}/STO-3G*		
Parameter	(2,2′)	(2,3′)	(3,3′)	(2,2′)	(2,3′)	(3,3′)	(2,2′)	(2,3′)	(3,3′)
$\Delta E(90°)^a$	13.6	19.0	21.2	12.1 (15.3)	14.8 (17.8)	11.0 (13.6)	25.1	13.4	15.7
$\Delta E(180°)^a$	−4.4	0.4	−0.4	−5.0 (−3.4)	0.8 (0.7)	−1.3 (−0.6)	−3.7	−0.3	−1.0
P_{cis}	14%	54%	46%	12%	58%	37%	19%	48%	41%
V_1	−2.3	0.4	−0.6	−3.8	0.3	−0.9	−3.7	−0.4	−0.5
V_2	16.0	18.9	21.7	14.7	14.2	12.0	26.9	13.7	15.7
V_3	−2.0			−1.2			0.02		
V_4	−1.7	−2.0	−2.3	−1.5	−1.8	−3.4	−7.7	−2.3	−5.0

^{a} The values in parentheses for STO-3G^{opt} data are those reported in ref. 12 for the corresponding bifuranyls.

in the GAUSSIAN/80 package.[44] For the sake of consistency we have used in this case the STO-3G-optimized geometry of thiophene.[30] This procedure should be quite reliable since within the rather large experimental error the intramolecular geometrical parameters of bithienyls are the same as those of thiophene,[2,37] but important (conformation-dependent) modifications often occur in the environment of the twisting bond. Further ψ values were considered in some cases for a better definition of equilibrium conformations. The above partially optimized structures (hereafter referred to as STO-3G^{opt} ones) were finally used for fixed-geometry computations by the STO-3G* basis set.[41]

Table 2. Geometric (see text and Figure for the definition and units) and electronic (dipole moments, μ/D, and total energies in a.u.) parameters for isomeric bithienyls. Energies are reported as $|E| - 1\,089$ a.u. When two entries are given for the same quantity *a* refers to STO-3G^{opt} results and *b* to STO-3G* ones

Isomer	Parameter		$\psi = 0°$	$\psi = 90°$	$\psi = 180°$
(2,2′)	R		1.488	1.496	1.484
	α		127.2	127.3	127.7
	μ	*a*	0.08	0.09	0.0
		b	0.99	0.77	0.0
	$2P_{ir}$	*a*	0.268		0.265
		b	0.265		0.265
	Energy*	*a*	0.055 11	0.050 52	0.057 01 (0)
		b	0.143 48	0.133 93	0.144 89 (0)
(2,3′)	R		1.491	1.500	1.491
	α		127.7	127.4	127.7
	β		124.6	123.4	123.4
	μ	*a*	0.35	0.34	0.38
		b	1.14	1.07	0.90
	$2P_{ir}$	*a*	0.255		0.255
		b	0.255		0.256
	Energy*	*a*	0.055 18	0.049 82	0.054 91 (5.5)
		b	0.144 88	0.139 78	0.144 97 (−0.2)
(3,3′)	R		1.498	1.505	1.497
	β		123.9	124.1	124.1
	μ	*a*	0.03	0.04	0.0
		b	0.55	0.42	0.0
	$2P_{ir}$	*a*	0.242		0.244
		b	0.244		0.244
	Energy*	*a*	0.053 03	0.048 79	0.053 51 (9.1)
		b	0.144 77	0.139 22	0.145 13 (−0.6)

* In parentheses energy differences are with respect to (2,2′) in kJ mol^{-1}.

Results and Discussion

The constitution, atom numbering, and labelling of isomeric bithienyls are shown in the Figure. The curves obtained at the STO-3G level using rigid geometries show that energy maxima correspond to perpendicular conformations ($\psi = 90°$) and energy minima to broad regions in the neighbour of planar SS-*cis* ($\psi = 0°$) and SS-*trans* ($\psi = 180°$) conformations. Energy variations as low as 1 kJ mol^{-1} are involved for torsions of up to 30° around $\psi = 0$ and 180°, but no evidence is found of smooth minima occurring at values of ψ *ca.* 30°, as reported in some experimental studies.[1,5,8,10] Partial optimization of the geometry, extension of the basis set, and computation of points at $\psi = 10$ and 170° for the different isomers confirm that energy minima occur at planar conformations in all cases.

The SS-*trans*-conformers are more stable than the *cis*-ones for the (2,2′- and 3,3′-isomers) by 4.4 and 0.4 kJ mol^{-1}. This corresponds, at 300 K, to populations (P_{cis}) of 14 and 46%, respectively for the *cis*-conformers. In the case of the 2,3′-isomer the SS-*cis*-conformer is favoured over the SS-*trans*-one by 0.4 kJ mol^{-1}, which corresponds to a P_{cis} of 54% at 300 K. These results indicate that only in the case of the 2,2′-isomer is one of the two planar conformations (SS-*trans*) noticeably more populated.

Partially optimized geometries of planar and perpendicular conformers are reported in Table 2. It can be appreciated that both bond length (0.01 Å) and bond angle (1°) variations are very small. The results of Table 1 show that geometry optimization has only minor effects on the relative stabilities of SS-*cis*- and SS-*trans*-conformers, but generally reduces energy barriers. In fact geometry optimization affects the perpendicular more than the planar conformers (especially concerning the inter-ring distance), producing the relative stabilization of the former. On the other hand the optimized geometries of SS-*cis*- and SS-*trans*-conformers are very similar, so that the difference in *cis–trans* stabilities is not significantly affected. It is finally noteworthy that the conformational behaviour of bithienyls is essentially identical to that of the corresponding bifuranyls (see Table 1), but for a general decrease of the barrier heights between the *cis*- and *trans*-conformers.

Addition of the *d* orbitals on sulphur does not alter the general trends, but gives some quantitative differences. In particular the energy barriers are generally increased, whereas the *cis–trans* energy differences remain essentially unaffected. Of course the largest modification is obtained for the 2,2′-isomer due to the vicinal disposition of the sulphur atoms (see Table 1).

From a general point of view we can make the following observations.

(i) Theoretical computations indicate that all isomeric bifuranyls and bithienyls have planar equilibrium conformations. No experimental data are available for bifuranyls, but electron diffraction[1,18] and n.m.r.[5,6,8] data tend to favour slightly non-planar equilibrium conformations for 2,2′- and 3,3′-bithienyl in the gas and oriented phases. In the solid phase all the isomeric bithienyls are planar according to *X*-ray diffraction,[2] but this finding is not surprising since several cases are well known (*e.g.* biphenyl) in which twisted molecules are flattened by the effect of the crystalline field.

(ii) The dipole moments computed at the STO-3G* level are in good agreement with experimental values (0.77, 1.05, and 0.75 D for 2,2′-, 2,3′-, and 3,3′-bithienyl, respectively[45]), but do not allow a solution of the conformational problem, apart from the indication of a large preference of the *cis*- over the *trans*-conformer for the 2,2′-isomer.

(iii) The barrier heights between the *cis*- and *trans*-forms is largest for 2,2′-bithienyl and the value obtained at the STO-3G* level is in remarkable agreement with that estimated from n.m.r. data[5] (21 ± 8 kJ mol^{-1}). This trend is clearly diagnostic of a larger reluctance of the 2,2′-isomer to lose π-conjugation between the two rings. Support for this point of view might be found in the marked hypsochromic displacement observed in the u.v. spectra of the bithienyls when compared with the 2,2′-isomer.[46]

(iv) With the exception of the 2,2′-isomer, the energy difference between the *cis*- and *trans*-conformers is found to be relatively small and in some instances even negligible. This means that the relative importance of the steric factors (mentioned in the Introduction) operative in the *cis*- and *trans*-conformations, respectively, is comparable. The different behaviour of the 2,2′-isomers suggest that in this case the non-bonded interactions between the lone pairs of the heteroatoms (*cis*-conformations) are more repulsive than the non-bonded repulsions between one lone-pair and one hydrogen atom (*trans*-conformation). According to electron diffraction findings for 3,3′-bithienyl[18] the *trans*-conformer is more stable than the *cis* by *ca.* 1.3 kJ mol^{-1}, in good agreement with our STO-3G$^{\text{opt}}$ and STO-3G* computations.

As mentioned in the Introduction, the most important advantage of theoretical computations is the analysis of the whole torsional potential. This potential is a complicated function and, in order to facilitate its interpretation, it is desirable to break it down into simpler components. A method that has been successfully used to this end is to expand the potential function $V(\psi)$ [expressed as the total energy $E(\psi)$ minus the energy $E(0°)$ of the planar *cis*-conformation] as a Fourier series (1). In all cases considered here the potential is

$$V(\psi) = 1/2\sum_j V_j[1-\cos(j\psi)] + 1/2\sum_k V_k\sin(k\psi) \quad (1)$$

symmetric about $\psi = 0°$ so that the sine terms disappear. As far as the truncation of the cosine series is concerned, the spacing of 30° adopted in our computations allows the determination of up to six potential constants. A complete fitting of the 2,3′- and 3,3′-isomers results in V_3, V_5, and V_6 of the order of 0.1 kJ mol^{-1}, so that these terms can be neglected. The resulting least-squares fitting of the quantum mechanical results gives in all cases energy values within 0.1 kJ mol^{-1} and angles within 0.5° for the complete series. In the case of the 2,2′-isomer the V_5 and V_6 terms are again negligible, but, at the STO-3G level, the V_3 term is quite important. Addition of *d* orbitals on sulphur reduces the V_3 term to a negligible value. In conclusion three terms are sufficient for an accurate description of the torsional potential of bithienyls, but the best fitting is obtained including the V_4 term in place of the V_3 term used in previous studies on similar molecules.[31]

A deeper analysis of the results of Table 1 can be performed remembering that the torsional potential of bithienyls arises from the variations (as a function of ψ) of the interactions between the π systems of the two rings (the so-called conjugation energy), which tend to keep the molecules planar, and the interactions between non-bonded atoms belonging to different rings (of steric and electrostatic origin), which may be generally alleviated by deviation from planarity.[47] The conjugative contribution $E_C(\psi)$ to the torsional potential can be written as in equation (2) where K is proportional to the square

$$\Delta E_C(\psi) = E_C(\psi) - E_C(0°) = K[\cos^2\psi - 1] = -K/2[1-\cos2\psi] \quad (2)$$

of the π-density matrix element P_{ir} for the inter-ring π bond.[47,48] As a consequence conjugative interactions only contribute to the V_2 term in the Fourier expansion (1), whereas steric and electrostatic interactions (which are functions of the interatomic distances between non-bonded atoms) contribute to all terms. The results of Table 1 show that the V_2 term is by far the dominant one and this confirms that the conformational behaviour of systems composed of two five-membered rings, contrary to those composed of six-membered rings, is always dominated by conjugative interactions. In the former case, in fact, non-bonded atoms belonging to different rings are separated by quite larger distances. However, if only the loss of conjugation energy determined the energy barrier between planar forms the expected order of these barriers would be (on the grounds of the bond orders of Table 2) (2,2′) > (2,3′) > (3,3′). In fact the barrier heights for (2,3′) and (3,3′) are reversed and this is due to the fact that, as we have already shown for azabiphenyls, H ··· H repulsions are much larger than (lone pair) ··· H ones.

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