# A Molecular Orbital Study of the Barrier to Internal Rotation in 3,3'-Bithienyl and 2,2'-Bithienyl

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The Pariser-Parr-Pople approximation has been applied in an SCF study of the barrier to internal rotation of two isomers of bithienyl. For 3,3'-bithienyl, energy minima were found at about 30° and 150° from the planar form. For 2,2'-bithienyl, no distinct minima were found.

Bond distances and electronic transition energies were also calculated. The overall agreement between predicted and observed quantities was found to be satisfactory.

Presently, the molecules 2,2'-bithienyl and 3,3'-bithienyl have been investigated in both gaseous and crystalline phases. An electron diffraction study of the former molecule [1] gives as a result a non-planar model with an angle of twist of about 145° from the planar *syn* form although reservations were made as to the exact magnitude of this angle. A more recent investigation of gaseous 3,3'-bithienyl has been carried out at this institute.[2] This investigation has given as main results two energy minima, at about 30° and 150° from the planar form. An approximate evaluation of the relative amounts of the two isomers has given as results about 40 % of the *syn* form and 60 % of the *anti* form.

On the other hand, a recent X-ray investigation of both isomers [3] reports both molecules to be planar in the crystalline phase.

Also, previous theoretical studies of these molecules have been based on assumed planar structures.[4,5]

On this background, the present study is an attempt to calculate the barrier to internal rotation of these systems. The procedure followed has been outlined by Fischer-Hjalmars in her calculations of the rotational barriers in butadiene and biphenyl,[6] and in a similar study of benzaldehyde by Forsén and Skancke.[7]

The total energy of the molecules has been considered as the sum of three parts: $\pi$-electron energy, core energy, and van der Waals interactions. These three energy forms and the total energy have been calculated for a number of conformations. Bond distances and electronic transition energies have also been calculated for the different conformations.

## METHOD OF CALCULATION

The different conformations have been defined by the angle of twist, $\phi$, between the two thiophene planes. The angle $\phi$ has been given the following values, 0°, 30°, 45°, 60°, 90°, 120°, 135°, 150° and 180°. 0° has been defined as the planar *syn* form. The notation of atoms is given in Fig. 1. The assumed structural parameters within the thiophene ring are taken from a microwave investigation of thiophene by Bak *et al.*[8] and are listed in Table 2. The length of the $C_1 - C_6$ distance was assumed to be 1.46 Å.
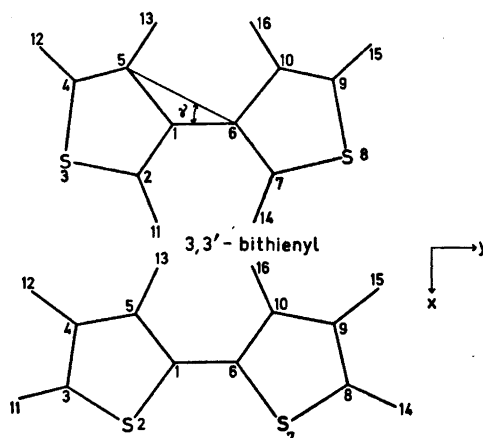


*Fig. 1.* Notation of atoms.

In the following the evaluation of the different types of energy will be treated separately.

*a) π-Electron energy.* The π-electron energy has been calculated by the well-known Pariser-Parr-Pople [9,10] approximation within the SCF theory. The applied parameters have been evaluated elsewhere.[11,12] The following brief presentation of the scheme is included in order to explain the definition of the applied parameters and does not pretend to be complete.

For the one-centre two-electron integrals for the carbon atom and the sulphur atom, values of 11.97 eV and 9.58 eV, respectively, were used. Arguments for this choice is given elsewhere.[12]

The two-centre two-electron integrals are divided into four different types, according to the following groups of internuclear distances:

1. Bond distances within one thiophene ring.
2. Distances between non-neighbours within one thiophene ring.
3. Angle-independent distances between atoms belonging to different rings, and
4. Remaining internuclear distances.

The two first types of integrals were treated like their counterparts in thiophene,[12] *i.e.*

$$\text{For 1)} \quad \gamma_{\mu\nu} = \gamma^\circ + \delta_{\mu\nu}{}^\gamma (R_{\mu\nu} - R^\circ) \tag{1}$$

$$\text{where} \quad \gamma_{CC}^\circ = 6.91 \text{ eV}, \ \gamma_{SC}^\circ = 7.28 \text{ eV}$$
$$\delta_{CC}{}^\gamma = \delta_{SC}{}^\gamma = -3.99 \text{ eV/Å}$$
$$R_{CC}^\circ = 1.397 \text{ Å}, \ R_{SC}^\circ = 1.714 \text{ Å}$$

and $R_{\mu\nu}$ is the distance in question.

For 2) the uniformly charged sphere approximation was used. The diameters of the tangent spheres were assumed to be 0.84 Å and 1.47 Å for sulphur and carbon, respectively; see Ref. 12.

For 3) the $2p\pi$ orbitals were decomposed into orbitals perpendicular and parallel to the plane of one thiophene ring. One of the atoms of this type was atom 1 or atom 6, and an angle $\gamma$ was defined as shown in Fig. 1. The general formula for these integrals is:

$$(\mu\mu|\nu\nu)_\phi = (\mu_x\mu_x|\nu_x\nu_x)\cos^2\phi + (\mu_x\mu_x|\nu_y\nu_y)\sin^2\phi \ \cos^2\gamma_{\mu\nu} + (\mu_x\mu_x|\nu_z\nu_z)\sin^2\phi \ \sin^2\gamma_{\mu\nu} \tag{2}$$

where atom $\nu$ is always atom 1 or 6. The sum on the right side of eqn. (2) may be derived using the charged sphere approximation for the term $(\mu_x\mu_x|\nu_x\nu_x)$. For the remaining integrals theoretical values scaled by a factor given by the ratio between the theoretical and the approximated value of $(\mu_x\mu_x|\nu_x\nu_x)$ were applied. However, at this stage a great simplification was introduced in the numerical calculations by the use of a generalized version of the charged sphere approximation. Details will be published elsewhere.[13] It is worth noticing that the final result gave only a slight deviation from the result of using the charged sphere approximation for parallel orbitals, *i.e.* the two-centre integrals were rather insensitive to the angle of twist.

For 4), the decomposition is more complex, since the internuclear distances depend on $\phi$, but also in this case the method mentioned above was successfully employed.

The diagonal elements of the core operator may be decomposed as

$$\alpha_\mu = W_\mu - \sum_{\nu \neq \mu} n_{\mu\nu}(\mu\mu|\nu\nu)_\phi \tag{3}$$

where $n_{\mu\nu}$ is an integer depending on the number of $\pi$-electrons contributed to the system by the different atoms. The one-electron integral $W_\mu$ is dependent on the surroundings to atom $\mu$ through the equation

$$W_\mu = W^\circ + \sum_{\nu=1}^{3} [\Delta W_\mu{}^\circ(\nu) + \delta_{\mu\nu}{}^W(R_{\mu\nu} - R^\circ)] \tag{4}$$

where $W^\circ$ is a constant for each atom, $\Delta W_\mu{}^\circ(\nu)$ is a constant correction term due to the replacement of hydrogen by a different atom $\nu$. The last term is a correction due to deviations from standard distances defined by eqn. (1). The numerical values employed were:

$$W_C^\circ = -9.84 \text{ eV}, \ W_S^+ = -20.20 \text{ eV}$$

$$\Delta W_C^\circ = 0.07 \text{ eV}, \ \Delta W_C^\circ(S) = -0.70 \text{ eV and}$$

$\delta_{CC}{}^W = \delta_{CS}{}^W = 9.22 \text{ eV/Å}$ as evaluated previously.[11,12] In these papers also the standard core resonance integral, $\beta^\circ$, has been evaluated, $\beta_{CC}^\circ = -2.42 \text{ eV}$ and $\beta_{CS}^\circ = -1.37 \text{ eV}$, and in cases of deviation from the standard distance this was accounted for by the relation

$$\beta_{\mu\nu} = \beta^\circ + \delta_{\mu\nu}{}^\beta \ (R_{\mu\nu} - R^\circ) \tag{5}$$

where

$$\delta_{CC}{}^\beta = \delta_{CS}{}^\beta = 3.05 \ \text{eV}/\text{Å}$$

As all bond distances were kept fixed and independent of the rotation, all $\beta$-values were also independent of $\phi$, whereas the $\alpha$'s varied with this angle.

b) *Core repulsion energy.* The repulsion between the positively charged core atoms was approximated by the sum of the two-centre two-electron integrals. Consequently, possible errors in the latter will hardly influence the sum $\varDelta E_\pi + \varDelta E_{core}$, the contribution to the rotational barrier from change in the total electronic energy.

c) *van der Waals interactions.* The contribution of van der Waals interactions has been estimated using an equation by Hill [14]

$$E/\varepsilon_{kl} = -2.25 \ \alpha^{-6} + 8.28 \times 10^5 \exp[-\alpha/0.0736] \tag{6}$$

where

$$\alpha = \frac{r}{r_k{}^* + r_l{}^*}$$

$r_k{}^*$ and $r_l{}^*$ are the van der Waals radii of the atoms k and l, and $r$ the distance between them. The parameter $\varepsilon_{kl}$ is specific to each atom pair, and is tabulated in the literature.[15]

## RESULTS AND DISCUSSION

The total potential curves for both molecules are shown in Fig. 2. The total energy of the molecules is obtained as the sum $E_{total} = E_\pi + E_{core} + E_{\text{van der Waals}}$. This sum was calculated for the whole series of angles. Finally, the potential curve was obtained by defining the potential as zero
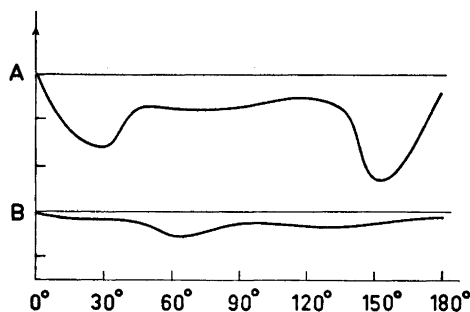


Fig. 2. Potential curves:
A, 3,3'-bithienyl;
B, 2,2'-bithienyl.

for 0°, *i.e.* $E(\phi) = E_{total}(\phi) - E_{total}(0°)$. The potential curve for 3,3'-bithienyl shows two significant minima, at about 30° and at about 150°. These minima are quite shallow, the barrier between them being only about 1 kcal/mol. In view of the uncertainties in the applied parameters, this molecule might have nearly free rotation around the central bond. However, comparing with

*Table 1.* Variation of the different energy terms as a function of the angle $\phi$. Energies in kcal/mol.

| Molecule | Energy $\phi$ | 0° | 30° | 45° | 60° | 90° | 120° | 135° | 150° | 180° |
|---|---|---|---|---|---|---|---|---|---|---|
| 3,3'-bithienyl | $E_\pi - E_\pi(0°)$ | 0.0(−10.549.29)[a] | 1.84 | 5.53 | 8.07 | 10.60 | 8.76 | 5.76 | 0.69 | 0.00 |
| | $E_{core} - E_{core}(0°)$ | 0.0(6883.42) | −3.23 | −5.99 | −8.53 | −11.06 | −8.99 | −6.22 | −2.77 | −0.46 |
| | $E_w - E_w(0°)^b$ | 0.0(69.99) | −0.20 | −0.26 | −0.27 | −0.27 | −0.28 | −0.26 | −0.21 | 0.00 |
| | $E_{total} - E_{total}(0°)$ | 0.0(−3595.88) | −1.59 | −0.72 | −0.73 | −0.73 | −0.51 | −0.72 | −2.29 | −0.46 |
| 2,2'-bithienyl | $E_\pi - E_\pi(0°)$ | 0.0(−10.691.85) | 4.75 | 9.59 | 13.31 | 21.54 | 22.16 | 21.40 | 20.57 | 19.19 |
| | $E_{core} - E_{core}(0°)$ | 0.0(7518.68) | −4.73 | −9.47 | −13.44 | −21.34 | −22.09 | −21.34 | −20.58 | −19.27 |
| | $E_w - E_w(0°)$ | 0.0(69.20) | −0.22 | −0.34 | −0.41 | −0.45 | −0.43 | −0.37 | −0.25 | −0.04 |
| | $E_{total} - E_{total}(0°)$ | 0.0(−3103.97) | −0.20 | −0.22 | −0.54 | −0.25 | −0.36 | −0.31 | −0.26 | −0.12 |

[a] Numbers in parentheses give the contribution from the different energy terms, and the total energy in the planar *syn* form.
[b] $E_w = E_{van der Waals}$.

experimental results,[2] it is interesting to note the excellent agreement between the results. The position of the two minima is confirmed by experiment, and the ratio of mixtures of the *syn* and *anti* forms (40 % and 60 %) found by electron diffraction is in good agreement with the potential curve presented in the figure.

For 2,2'-bithienyl, the agreement is not as good. From the present results, the molecule seems to have nearly free rotation around the central bond, the planar forms being somewhat less favourable than non-planar forms. The minimum at around 60° seems to be hardly significant as the barrier is less than 1 kcal/mol. The experimental results gave one minimum at about 145°.

In order to find the source of the minima at the potential curves, the contributions from the different energy terms have been studied separately. The results are listed in Table 1.

The van der Waals forces vary little with the angle of twist. When the contribution from each distance type was studied separately, hardly any variation with the angle of twist was observed, and the sum of these contributions was also nearly constant, the largest variation was 0.45 kcal/mol in 2,2'-bithienyl going from 0° to 90°.

The table also reveals the reasons for the energy minima of the potential curve of 3,3'-bithienyl. It is seen that going from 0° to 30° and from 180° to 150° there is a loss of core energy without a corresponding gain in $\pi$-electron energy. In addition there is a small loss in the van der Waals energy that makes the potentials somewhat deeper.

*Table 2.* Calculated bond distances (in Å units). Numbers in parentheses give the corresponding values for thiophene.

| Molecule | Dist | R |
|----------|------|---|
| 3,3'-Bithienyl | 1—2 | 1.370 (1.370) |
| | 2—3 | 1.709 (1.714) |
| | 3—4 | 1.713 (1.714) |
| | 4—5 | 1.362 (1.370) |
| | 1—5 | 1.437 (1.423) |
| | 1—6 | 1.466 (1.46)   assumed |
| 2,2'-Bithienyl | 1—2 | 1.716 (1.714) |
| | 2—3 | 1.717 (1.714) |
| | 3—4 | 1.363 (1.370) |
| | 4—5 | 1.433 (1.423) |
| | 1—5 | 1.371 (1.370) |
| | 1—6 | 1.458 (1.46)   assumed |

*Other molecular properties.* Table 2 presents the calculated bond distances compared to the bond distances of thiophene which have been used as a starting model in the iterative process. The bond distances were completely independent of the angle of twist, and it is seen that the geometry of the

*Table 3.* Calculated and observed electronic spectra (in eV). Numbers in parentheses give the calculated oscillator strengths.

| Molecule | 0° | 30° | 45° | 60° | 90° | 120° | 135° | 150° | 180° | Experimental $\Delta E$ | $\varepsilon \times 10^{-4}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3,3'-bi-thienyl | 4.78 (0.43) | 4.79 (0.45) | 4.79 (0.47) | 4.79 (0.48) | 4.79 (0.50) | 4.77 (0.52) | 4.76 (0.53) | 4.76 (0.53) | 4.75 (0.53) | 4.77[a] | 1.13 |
| | 4.95 (0.04) | 4.95 (0.04) | 4.95 (0.04) | 4.95 (0.03) | 4.95 (0.02) | 4.95 (0.01) | 4.95 (0.01) | 4.95 (0.00) | 4.95 (0.00) | | |
| | 5.10 (0.07) | 5.12 (0.09) | 5.14 (0.12) | 5.16 (0.16) | 5.20 (0.27) | 5.23 (0.39) | 5.25 (0.44) | 5.25 (0.47) | 5.26 (0.50) | 5.39[a] | 0.9—1.0 |
| | 5.55 (0.56) | 5.53 (0.53) | 5.51 (0.49) | 5.48 (0.44) | 5.42 (0.31) | 5.36 (0.16) | 5.33 (0.10) | 5.31 (0.04) | 5.30 (0.00) | | |
| | 6.31 (1.03) | 6.32 (1.03) | 6.33 (1.03) | 6.35 (1.02) | 6.37 (1.02) | 6.38 (1.02) | 6.38 (1.02) | 6.37 (1.02) | 6.38 (1.02) | 5.85[b] | — |
| 2,2'-bi-thienyl | 4.27 (0.95) | 4.29 (0.95) | 4.30 (0.95) | 4.32 (0.94) | 4.34 (0.94) | 4.33 (0.93) | 4.32 (0.93) | 4.30 (0.93) | 4.29 (0.92) | 4.12[a] | 1.30 |
| | 5.03 (0.01) | 5.04 (0.03) | 5.04 (0.06) | 5.04 (0.09) | 5.05 (0.15) | 5.06 (0.21) | 5.06 (0.23) | 5.06 (0.24) | 5.06 (0.25) | 5.04[a] | 0.60 |
| | 5.14 (0.20) | 5.13 (0.20) | 5.11 (0.19) | 5.09 (0.17) | 5.05 (0.13) | 5.00 (0.07) | 4.97 (0.04) | 4.96 (0.02) | 4.94 (0.00) | | |
| | 5.77 (0.17) | 5.76 (0.15) | 5.75 (0.13) | 5.73 (0.11) | 5.72 (0.07) | 5.73 (0.04) | 5.74 (0.02) | 5.75 (0.01) | 5.76 (0.00) | | |
| | 6.79 (0.00) | 6.81 (0.06) | 6.83 (0.13) | 6.86 (0.22) | 6.93 (0.43) | 6.99 (0.61) | 7.01 (0.67) | 7.03 (0.71) | 7.04 (0.74) | | |

Observed values: [a] Ref. 16; [b] Ref. 17.

thiophene ring seems to be well preserved in the bithienyls. The bond distances have been calculated from the formula [11,12]

$$R_{\mu\nu} = R_{\mu\nu}{}^\circ - 0.18 p_{\mu\nu} \quad \text{where}$$

$$R_{CC}{}^\circ = 1.517 \text{ Å}, \ R_{CS}{}^\circ = 1.773 \text{ Å}$$

and $p_{\mu\nu}$ is the mobile bond order between atoms $\mu$ and $\nu$.

The electronic transitions for the molecules have been calculated and the results compared to experimental values; see Table 3.

Wynberg and Bantjes [16] have reported the UV spectra of these molecules in ethanol solution.

For 3,3'-bithienyl, only two maxima are reported in the above mentioned paper, one at 4.77 eV, the other at 5.39 eV. The former definitely must correspond to the calculated value of 4.78 − 4.75 eV. The latter may be interpreted as the resultant of the two calculated values 5.10 − 5.26 eV and 5.55 − 5.30 eV. It is seen from the table that the first of these has intensities rapidly increasing with the angle $\phi$, while the intensities of the latter are decreasing. Wynberg and Kraak [17] have reported a UV spectrum in cyclohexane solution, and a pronounced maximum observed at 5.85 eV in this investigation may be assigned to the calculated value of 6.31 − 6.38 eV. The two different solvents used in the determination of the spectra must here be taken into account, especially as one solvent is polar, the other unpolar. In general, it is necessary to add a term in converting solution spectra to the equivalent of vapour spectra; in a former investigation this term was found to be somewhat less than 0.1 eV for ethanol used as a solvent.

For 2,2'-bithienyl, the first experimental transition at 4.12 eV is equivalent to the calculated transition of 4.27 − 4.29 eV. The transition found at 5.04 eV might well result from both the calculated transitions at 5.03 − 5.06 eV and 5.14 − 4.94 eV. The calculated transition of 5.77 − 5.76 eV does not have any counterpart in the experimental recording. As is shown in the table, the intensity of this transition decreases with the angle $\phi$, and for the planar *anti* form, this is a forbidden transition. Its absence in the experimental spectrum may be regarded as an indicator of the molecule being in *anti* form in ethanol solution. The transition of 6.79 − 7.04 eV is not confirmed experimentally, but is seems that the ethanol solution spectra were not recorded at that short wavelength.

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