CHAIN FLEXIBILITY IN POLYHETEROAROMATIC POLYMERS
PART I. ELECTRONIC PROPERTIES, STRUCTURE AND VIBRATIONAL SPECTRA OF OLIGOMERS AS MODELS OF POLYPYRROLE AND POLYTHIOPHENE

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Abstract

The conformational properties of dimers and trimers of thiophene and pyrrole as obtained from experiments and quantum chemical calculations are discussed with the aim of analysing the validity and limitations of theoretical calculations. The roles played by intramolecular and intermolecular interactions are pointed out. New quantum chemical calculations are reported with full geometry optimization which includes torsional angles; their physical and spectroscopic relevance are discussed. A vibrational assignment is proposed for bithiophene.

1. Introduction

Great interest is presently being shown in the electrical conductivity of polypyrrole (PPy) and polythiophene (PTh) in their doped states and efforts have been made to relate the electrical conductivity of these materials with their molecular structure [1–3]. The attention of many workers has been initially focused on whether the five-membered rings in the pristine materials are coplanar or whether the whole molecule or sections of it consist of rings rotated about the inter-ring C–C bonds [4–6]. It has been well known for many years that coplanarity favours π-electron delocalization since the overlapping of the p\textsubscript{z} orbitals is maximum. Torsion about the C–C inter-ring bond (hereafter labelled θ) decreases the overlapping thus decreasing delocalization [7].

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The problem is of particular importance for the understanding of the structural and electrical properties of the new classes of alkyl derivatives of PTh which have recently been prepared and which are soluble in classical organic solvents [8–12]. Moreover these soluble materials can be doped even in solution [13].

We consider here the cases of the simplest oligomers of Py and Th, namely 2,2'-bipyrrrole (Py2), 2,2':5',2''-terpyrrrole (Py3), 2,2'-bithiophene (Th2) and 2,2':5',2''-terthiophene (Th3). Our aim is to obtain for the simplest systems numerical data and structural information for extrapolation to longer oligomers and polymers. We have carried out quantum mechanical calculations, compared our results with those obtained by other authors and collected some experimental data from electronic and vibrational spectroscopy which are interpreted with lattice dynamical calculations. In these studies the vibrational force field used is that obtained from the same quantum chemical calculations.

We think that the experimental data available on some of the oligomers studied in this work could already form a basis for the necessary extrapolation to longer oligomers or polymers. As discussed later in this paper only a few of these data can be compared with the innumerable quantum chemical calculations which were done before and after publication of the experimental results. Most of these calculations provide numbers for the minimum energy geometry and for the potential barrier separating states with different relative energies.

Since a great interest is being shown in the understanding of the chain flexibility in PTh and PPy and their derivatives we feel it is important to have a rough description of the whole potential energy as a function of the $\theta$ angle. The quantum chemical calculations we report in this paper are mainly concerned with the dependence of the total energy, ionization potential $I_p$, bandgap $E_g$ and normal vibrations on $\theta$.

2. Experimental structural data

2.1. Diffraction data

It has been known since 1958 that in the gas phase the Th2 molecule is twisted with $\theta=34^\circ$ as shown from gas-phase electron diffraction [14]. In the solid phase at $-140^\circ C$ the molecule is reported to be anti-coplanar with $\theta=0^\circ$ [15]. No diffraction data are available for Th3.

In the solid state Py2 and Py3 have been found to be anti-coplanar from X-ray diffraction studies [16].

2.2. Electronic spectra

We have recorded the UV–Vis spectra of Th2 and Th3 in the solid and solution states. Detailed analysis is reported elsewhere [17]. The observed absorption maxima are the following: Th2 solid 3.49 eV, solution 4.05 eV; Th3 solid 3.06 eV, solution 3.49 eV. The change in the HOMO–LUMO energy
gap of 0.5 eV indicates that the delocalization of the $p_z$ orbitals changes from a starting structure $\Sigma^o$ into a structure with a larger $E_g$, i.e. with less delocalization generated by the twisting of the Th rings yielding a distorted $\Sigma_g$ structure. The existence of structure $\Sigma^o$ with coplanar rings in the solid state is certain for Th2 and may be extrapolated to the case of solid Th3. The existence of $\Sigma_g$ structures in a solution of good solvents can be taken as proven by the electronic spectrum provided that molecular aggregation in solution can be shown not to take place.

High-resolution fluorescence excitation and emission spectra have been measured by Birnbaum and Kohler [18] for solid solutions of Th3 in n-decane at 4.5 K. The spectra are consistent with a coplanar structure in anti configuration.

The electronic spectrum of Py2 shows an absorption maximum at 280 nm in solution.

2.3. NMR spectra

Bucci et al. [19] have studied the conformation of bithiophene partially oriented in a nematic phase of a liquid crystalline solvent. The interpretation of the observed NMR spectra is consistent with the existence of two rotamers with the anti structure more stable than the syn by 0.2 kcal/mol and separated by a barrier of $5 \pm 2$ kcal/mol. The relative concentration of the two isomers is 64% anti to 36% syn.

3. Molecules 'in vacuo' and in the crystalline state

Before discussing the results of the theoretical calculations on these systems compared with the experimental data it should be pointed out that all the calculations so far presented by many authors consider a single isolated molecule 'in vacuo'. Intermolecular interactions have never been taken into account. The theoretical predictions of the properties of a molecule 'in vacuo' can be taken as a very close approximation to reality if (i) the experimental data used for comparison come from the system in the gas phase and (ii) the molecule is rigid and does not have any section which is conformationally flexible.

Case (ii) is of extreme importance since the conformation (and the properties) of the molecule in the gas phase may be different from those of the molecule in the solid crystalline state for flexible systems. This is precisely the case of the polyaromatic systems in which each aromatic ring is linked to its neighbour by a single C–C bond.

The textbook case which has already been discussed in detail is that of biphenyl in which we know from experiment that the two benzene rings are twisted with $\theta \approx 40^\circ$ in the gas phase [20] and become coplanar in the crystalline phase [21].

The physical situation of the polyaromatic systems where the rings form a chain being joined only by single C–C bonds can be qualitatively described
as sketched in Fig. 1 of ref. 22. The intramolecular potential of the molecule in the gas phase can be written as a contribution by two terms

\[ V_{\text{in vacuo}}(\theta) = V_{\text{steric}} + V_{\text{deloc}} \]  

(1)

The delocalization of the \( p_z \) electrons \( V_{\text{deloc}} \) would force the molecule to be coplanar \( (\theta=0^\circ) \) while steric repulsions, \( V_{\text{steric}} \), would favour a conformation in which the rings are orthogonal \( (\theta=90^\circ) \). The balancing of such competing forces yields a structure in the gas phase with \( 90^\circ > \theta > 0^\circ \). The barrier dividing the two minima cannot be too large for the kind of steric forces in these systems.

When the molecule is packed in an ordered lattice

\[ V_{\text{total}} = V_{\text{in vacuo}} + V_{\text{lattice}} \]  

(2)

where \( V_{\text{lattice}} \) represents the contribution by the intermolecular forces which are strong enough to squeeze the molecule into a coplanar structure \( (\theta=0^\circ) \). In such a new coplanar conformation the geometry of the molecule must relax with new bond lengths and bond angles.

It is well known that if the total energy of a polyconjugated aromatic system is plotted as a function of the effective conjugation coordinate \([23-25]\) (reminiscent of the dimerization coordinate \( u \) in polyacetylene) two minima are found as shown in Fig. 1. The deepest minimum A corresponds to the 'aromatic structure' and the second higher minimum B corresponds to the so-called 'quinoid structure'. In principle the larger the contribution by B the shorter is the inter-ring C–C bond (bond order \( >1 \)). But if the inter-ring C–C bond is stretched as a result of the potential \( V_{\text{total}} \) the contribution by B will decrease, i.e. the delocalization is affected by intermolecular interactions. This is precisely the case observed experimentally for the biphenyl molecule in the solid state (C–C bond length = 1.507 Å). This may also happen to the molecules studied in this work.

![Fig. 1. Qualitative sketch of the ground state energy of poly(C\(_4\)H\(_x\)X) (X=heteroatom) as a function of the effective conjugation coordinate.](image)
Since in normal conditions only the anti conformer crystallizes, $V_{\text{total}}$ has certainly a minimum at $\theta=0^\circ$ separated from any other minima probably by high barriers the height of which depends on $V_{\text{lattice}}$. Around $\theta=0^\circ$ the potential must be flat since it is obtained from the double minimum $V_{\text{in vacuo}}$ the small potential barrier of which is flattened by the application of an intermolecular potential $V_{\text{lattice}}$. If this is the case the dynamics of the system [26] will show some peculiarities:

(i) The vibrational quantum levels for the torsional motion about $\theta$ are very close and the 0–1 quantum transition must occur at very low frequencies in the far infrared (for biphenyl see ref. 27).

(ii) At room temperature many quantum levels due to the torsional motion are appreciably populated and the mean vibrational amplitudes are very large. Such chain molecules in the solid state will thus show a large thermally activated conformational flexibility about the C—C bonds. The large Debye–Waller factor in scattering experiments on solids should then be measured. Intramolecular energy transfer due to anharmonic terms in the vibrational potential can also easily occur between higher energy transitions and the manifold of torsional levels coupled with low energy lattice modes resulting in an appreciable temperature-dependent broadening of the infrared and/or Raman lines (for the known case of biphenyl see ref. 28). New experiments are needed which may provide information on the shape of the potential near $\theta=0^\circ$.

(iii) Upon lowering the temperature the contribution by $V_{\text{lattice}}$ increases and also its symmetry may change, the shape of $V_{\text{total}}$ changes with the consequent changes in the minimum energy structure, flexibility, etc. In general several crystalline phases and molecular conformations have been observed in such systems (e.g. paraterphenyl and paraquaterphenyl from the data of Raman spectroscopy [28] and X-ray diffraction [29]).

The structural situation encountered when bithiophene is embedded in a liquid crystal [19] requires some comment. Since it is known experimentally that in the gas phase ($V_{\text{in vacuo}}$) the most stable structure has $\theta=34^\circ$ the existence of both anti and syn isomers observed by NMR in the nematic liquid crystal phase proves that interactions take place between the molecule and its environment as if the contribution by $V_{\text{lattice}}$ starts being turned on. As discussed earlier in this paper, so far no quantum chemical calculations have accounted for this kind of intermolecular contribution; thus the comparison of NMR data with quantum chemical calculations is not rigorous.

4. Early results from quantum chemical calculations

Following the concepts discussed in Section 3 use of the results from any kind of quantum chemical calculations on the kind of polyaromatic molecules studied in this work must be made with great caution since they all refer to a system 'in vacuo'.

A classification of the calculations can be proposed as follows:
(i) The results from calculations which include the torsional angle $\theta$ as one of the variables to be minimized can be compared freely with the experimental data of the molecules in the gas or solution state. For polyaromatics dissolved in a ‘good solvent’ to a first approximation we can consider $V_{\text{lattice}} = 0$ in eqn. (2) only if intermolecular interactions which cause molecules to aggregate in solution are shown not to take place. In this class we consider the calculations by Orti et al. [30, 31] who first obtained $\theta = 0^\circ$ for Py2 by INDO methods allowing a limited freedom in the energy minimization. These authors have extended their work to Py2 with 'ab initio' calculations using both STO-3G and 4-31G basis sets which gave $\theta = 0^\circ$ and $\theta = 32.4^\circ$ respectively. STO-3G calculations by Brédas et al. on Py2 and Th2 yielded $\theta = 0^\circ$ [32].

(ii) If in the calculations energy minimization is carried out with the constraint that $\theta = 0^\circ$ the geometry obtained may be closer to the relaxed geometry taken up by the molecule in the crystal (i.e. in the minimum of $V_{\text{total}}$). However, the actual shape of $V_{\text{total}}$ for any value of $\theta$ will never be available unless $V_{\text{lattice}}$ is somehow taken into account in the calculation. Calculations on Th2 by Brédas et al. [32, 33] and more recently by Nagashima et al. [6] are examples for this case.

5. New MNDO calculations

We have carried out MNDO calculations [34] on Th2, Th3, Py2 and Py3 as systems 'in vacuo' with a full geometry optimization including the inter-ring torsional angle $\theta$ in Th2 and Py2 and angles $\theta$ and $\theta'$ in Th3 and Py3. The calculations reported here were carried out with MOPAC 2.0. More recently new versions of this program became available (MOPAC 4.0) with new parametrization of the S atom [35]. We have recalculated the data for Th2 and Th3 with MOPAC 4.0 and have found no substantial differences. In order to obtain the full potential function $V_{\text{in vacuo}}(\theta)$ calculations were made in steps of $\theta = 0^\circ$ (anti), $10^\circ$, $20^\circ$, $35^\circ$, $60^\circ$, $90^\circ$ (perpendicular structure), $120^\circ$, $150^\circ$ and $180^\circ$ (syn). For every step of $\theta$ calculations were made by relaxing all other geometrical parameters. At each step we calculated minimum energy geometry, heat of formation, ionization potential $I_p$ and bond orders. Similar calculations for Th2 have been presented by Barone et al. [36].

For Py3 and Th3 there are two $\theta$ angles which are independent variables. Our calculations were restricted to the case in which the two external rings were rotated, one in the anticlockwise direction and the other in the clockwise direction of the same angle $\theta$. Only for Py2 and Th2 at $\theta = 0^\circ$ and $\theta = 60^\circ$ have we calculated the harmonic force field, the vibrational frequencies and infrared intensities.

The sets of harmonic force constants $F_x$ are obtained from the standard MNDO programs in terms of the $3N$ cartesian coordinates ($N=$ number of atoms in the molecule). We then transformed them into a complete set of force constants $F_S$ in terms of non-redundant internal coordinates $S$ (46 for
Py2 and 42 for Th2) following the method of Pulay et al. [37]. The internal coordinate associated with the torsion about the inter-ring C–C bond is defined as the sum of all possible dihedral angles. The transformation from $F_x$ to $F_S$ is obtained from the relation

$$F_S = \mathbf{B}^{-1} F_x \mathbf{B}^{-1}$$

where the matrix $\mathbf{B}$ is suitably constructed with the standard Wilson GF method [38, 39].

6. Results and discussion

6.1. $V_{in\ vacuo}(\theta)$: conformational flexibility

The heats of formation as a function of $\theta$ for the four molecules studied are plotted in Fig. 2. For all the molecules the minimum is found for $\theta \approx 60^\circ$. The calculated value of $\theta$ is larger than the only one measured experimentally for Th2 in the gas phase ($\theta \approx 34^\circ$). The calculated barriers to rotation for all the four molecules are smaller than those obtained from 'ab initio' methods as reported in Table 1.

As already discussed by Dewar et al. [40] it is known that the aromatic character is overestimated by MNDO calculations and other semiempirical methods giving more weight to the non-bonded interactions; conversely it is underestimated at the HF/STO-3G level especially in the rigid rotor

![Fig. 2. MNDO calculated electronic energies as a function of the inter-ring torsional angle for a few oligomers of thiophene and pyrrole.](image)
TABLE 1
Calculated barriers to rotation in 2,2'-bithiophene and 2,2'-bipyrrrole

<table>
<thead>
<tr>
<th>2,2'-Bipyrrrole</th>
<th>2,2'-Bithiophene</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0 (ref. 32, STO-3G)</td>
<td>4.2 (ref. 32, STO-3G)</td>
</tr>
<tr>
<td>4.6 (ref. 31, STO-3G)</td>
<td></td>
</tr>
<tr>
<td>4.4 (ref. 31, STO-3G)</td>
<td></td>
</tr>
<tr>
<td>1.8 (ref. 31, 4-31G/STO-3G)</td>
<td>1.8 (ref. 31, 4-31G)</td>
</tr>
<tr>
<td>1.1 (this work, MNDO)</td>
<td>0.77 (this work, MNDO)</td>
</tr>
</tbody>
</table>

approximation [41, 42] (see also ref. 6). While Orti et al. point out that full minimization may change the potential barrier [30], Brédas shows that this is not the case at the STO-3G level, the correction being very small [5].

We are not particularly interested in the actual value of the potential barrier but in the general shape of \( V_{\text{in vacuo}}(\theta) \). Independent from any accurate determination, we observe qualitatively that the whole potential function is broad and fairly flat about the minimum structure. As in the case of the solid phase this indicates that such polyheteroaromatic chains have a very large conformational flexibility with reasonably low potential barriers. It follows that in solution (see Section 4 (i)) these chains can be quite flexible and the angle \( \theta \) can vary in a very broad range, thus allowing a temperature-dependent broad distribution of \( \theta \) values. Moreover, in going to the crystalline state relatively weak lattice forces can easily constrain the molecule to become coplanar (\( \theta = 0 \)) (see Section 4 (ii)).

We also notice that for both classes of molecule studied the \( V_{\text{in vacuo}}(\theta) \) functions of Fig. 2 are asymmetrical showing a slight preference of the system to twist with \( \theta \approx 120^\circ \). This state is, however, a metastable plateau. More extended 'ab initio' calculations with full minimization are needed for exploring whether this metastable plateau evolves into a second energy minimum.

6.2. \( I_p(\theta) \)

The ionization potential of the four molecules as a function of \( \theta \) are given in Fig. 3. The largest values of \( I_p \) are found at \( \theta = 90^\circ \) where no \( p_z \) overlap takes place since the rings are orthogonal and \( I_p \) is that of the monomer. For all the four molecules studied \( I_p \) is obviously the lowest at \( \theta = 0^\circ \) (maximum delocalization) and changes very little in the range of \( \theta \) from 0° to \( \approx 30^\circ \) and then increases slowly with increasing \( \theta \). The calculated values should be scaled for a comparison with the experiments; we discuss here only the trend in the values.

This information is relevant to the understanding of the doping process of these systems in solution. Theory suggests that the work done to extract an electron from a distorted Th2 molecule (small values of \( I_p \)) is practically
the same as that for the coplanar molecule. This means that (i) since oligomers of Th (and perhaps Py) are soluble in organic solvent they are conformationally distorted in the so-called \( \Sigma_0 \) structures (see ref. 17), but they could still be doped in solution almost as well as in the solid, and (ii) if substitution in \( \beta \) or \( \beta' \) positions forces the polythiophene molecule to be conformationally distorted because of steric hindrance the material can still as easily be doped in solution [13].

6.3. Geometry versus \( \theta \)

As expected (and as pointed out by many authors) the inter-ring C–C bond length increases with increasing \( \theta \) since at \( \theta = 0 \) the delocalization of \( p_z \) electrons is maximum and goes to zero at \( \theta = 90^\circ \). The bond order decreases with increasing \( \theta \) because the contribution by the higher energy quinoid configuration decreases.

The calculated values of bond length and bond order for the inter-ring C–C show that the contribution by the quinoid structure is small even at \( \theta = 0 \). This is consistent with the calculated low energy barriers.

7. Vibrational properties and molecular dynamics

While the problem of detailed interpretation of the vibrational infrared and Raman spectra of Th, Th2, Th3, PTh and polyalkylthiophenes are discussed
elsewhere [17, 43–45] we limit ourselves here to the collection of theoretical and experimental data which may give further support that the bithiophene molecule is not coplanar in the solution state (i.e. $V_{in\ vacuo}$) as we predict in this work on the basis of MNDO calculations.

We recorded the vibrational spectra of Th2 in the solid and solution phases. Our main aim, at this stage, was to carry out a vibrational assignment in order to identify bands which may be used as probes for conformational distortion. The combination of vibrational assignment and group theory provides a way to obtain structural information.

We calculated the MNDO force field, normal vibrations and dipole transitions (intensities) and compared them with the experimental data.

7.1. Molecular force fields

We limited our calculations to Th2 at $\theta=0^\circ$ and $\theta=60^\circ$ and have obtained force constants, frequencies and infrared intensities for the dipole allowed fundamental transitions for both models. While calculations at $\theta=60^\circ$ present no problems, for the case of $\theta=0^\circ$ we had to accept some compromises. At $\theta=0^\circ$ we calculated the second derivatives of the potential energy at the top of a small potential barrier, i.e. in a non-equilibrium geometry, i.e. at a point of instability of the system. We consider the calculations still possible and meaningful since the barriers to rotation are very small compared with the heat of formation and the changes in geometry with $\theta$ are extremely small about $\theta=0^\circ$. For the above reasons we neglected the numbers obtained for the force constants and frequencies related to the inter-ring torsional coordinate. Both numbers turn out to be extremely small and negative and the corresponding normal modes are fully decoupled from the other intramolecular modes.

For the comparison between calculated and experimental frequencies the calculated force constants have been scaled, as is customary in quantum chemical calculations, by scaling factors suitably calculated by the method of Pulay et al. [37].

7.2. Vibrational spectrum of Th2

Since the molecule in the solid state is transplanar it belongs to the symmetry point group $C_{2h}$ and its 42 normal modes are distributed in the four irreducible representations as indicated in Table 2. We neglected space group selection rules in this work. If the molecule in solution is twisted its symmetry is reduced to the point group $C_2$ with only two species. The correlation between selection rules for $C_{2h}$ and $C_2$ point groups are included in Table 2.

First the IR and Raman spectra of solid Th2 are assigned on the basis of the results of MNDO calculations with $\theta=0^\circ$. In general for the Raman spectrum a few of the totally symmetric $A_g$ normal modes are strong in the Raman while all the others (including the $B_g$ modes) have vanishing intensity. The vibrational assignment for Th2 in the solid coplanar case is reported
TABLE 2
Irreducible representation, distribution of normal modes and symmetry correlations between C_{2a} and C_{2} point groups for the bithiophene molecule

<table>
<thead>
<tr>
<th>C_{2a}</th>
<th>C_{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>15A_g</td>
<td>22A</td>
</tr>
<tr>
<td>14B_u</td>
<td>20B</td>
</tr>
</tbody>
</table>

TABLE 3
Vibrational frequencies (cm^{-1}) for normal modes of 2,2'-bithiophene calculated from scaled MNDO force constants compared with the experimental data

<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
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<tr>
<td>A_g</td>
<td></td>
<td></td>
<td>B_g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C-H) str.</td>
<td>3107</td>
<td>3095</td>
<td>(C-H) def.</td>
<td></td>
<td>880</td>
</tr>
<tr>
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<td>3078</td>
<td>(C-H) def.</td>
<td></td>
<td>804</td>
</tr>
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<td>620</td>
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<tr>
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<td>1467</td>
<td>ring tors.</td>
<td></td>
<td>534</td>
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<tr>
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<td>1355</td>
<td>ring tors.</td>
<td></td>
<td>251</td>
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<tr>
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<td>C-H def.</td>
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<td>288</td>
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<td></td>
</tr>
<tr>
<td>B_u</td>
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<td></td>
<td>A_u</td>
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<td>1108</td>
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<td>1073</td>
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<td></td>
<td></td>
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<tr>
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<td>894</td>
<td>910</td>
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<td>857</td>
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<tr>
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<tr>
<td>ring def.</td>
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in Table 3. The fitting between the calculated and experimental spectra [17] is quite satisfactory.

In going to the twisted C_{2} structure the theoretical information we feel relevant is that the out-of-plane deformation mode calculated for \(\theta=0^\circ\) at
716 cm\(^{-1}\) (exp. 703 cm\(^{-1}\) in the solid) shifts downward to 710 cm\(^{-1}\) calculated for \(\theta=60^\circ\) (exp. 690 cm\(^{-1}\) in solution). Such evidence of conformational twist for the Th2 solution adds to the others previously mentioned.

We can also add that, because of symmetry, in principle we expected to find in the IR (Raman) originally Raman (IR) active transitions. Because of the above reasons the Raman spectrum is not useful in this case. We then looked at the IR spectrum and, with the help of MNDO calculations on the two Th2 models, we tried to locate bands which originate from the vibrational transitions originally silent in the centrosymmetric coplanar structure. No unquestionably new bands were found, thus indicating that the molecule cannot be in a \(\Sigma_\theta\) structure with large values of \(\theta\).

8. Conclusions

A discussion has been presented on the various contributions to the torsional potential for flexible aromatic oligomers and polymers by intramolecular and intermolecular phenomena. The resulting shapes of the potential functions have been qualitatively described and the consequences in the vibrational dynamics and spectra have been outlined. Many of these straightforward predictions still need experimental verification. The usefulness and limitations of the data from quantum mechanical calculations on these systems have been presented in the light of their comparison with the few experimental data available.

The MNDO calculations carried out in this work on Th2, Th3, Py2 and Py3 with full minimization and including the inter-ring torsional angle \(\theta\) provide information which, according to the criteria presented at the beginning of this paper, can only be compared with the molecules in the gas or solution state. Only geometrical parameters for the system with the constraint \(\theta=0\) can be compared with those of the molecule in the crystal.

In solution molecules are twisted with an angle \(\theta\) which is predicted from calculation to be \(\theta=60^\circ\), too large if compared with the only experimental datum available for gaseous Th2 (\(\theta=34^\circ\)). On the other hand, the fact that the molecule becomes distorted in solution is also clearly indicated by the change of the HOMO–LUMO transition in the electronic spectrum.

The shape of the calculated potential \(V_{in\,vacuo}(\theta)\) about the equilibrium indicates that these kinds of systems in solution may possess a large conformational flexibility. A broad and temperature-dependent distribution of twisted geometries is then likely to occur for these systems in solution. The conformational flexibility should give rise to the broadening of a few infrared or Raman lines.

But even if distorted the effective delocalization of \(p_z\) electrons is large enough to keep the ionization potential almost as low as for the coplanar case. This accounts for the fact that these systems can or could also be doped in solution, as recently shown for polyalkythiophenes. Lastly, in spite of the fact that MNDO calculations overestimate \(p_z\) conjugation, the contri-
bution by the 'quinoid' configuration to the ground state wavefunction turns out to be small.

The MNDO scaled force field has allowed us to carry out a detailed vibrational assignment of the spectrum of Th2 in the solid state (i.e. in the \( \Sigma^* \) structure). From the analysis of the vibrational infrared spectrum further clear evidence is found that the Th2 molecule is twisted in solution.

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Appendix

As pointed out by the referee, after submitting this paper, a work by J. L. Brédas and A. J. Heeger has been published (Macromolecules, 23 (1990) 1150). These authors report on calculations with the 3-21G basis set for bithiophene. From these calculations the molecule turns out to be anti coplanar with a barrier height of 2.6 kcal/mol. Certainly the calculations by these authors are more powerful since they use an ‘ab initio’ method with a large basis set. In the light of what is discussed in this paper we are faced with the challenging fact that for the molecule ‘in vacuo’ MNDO calculations are in better agreement with the experimental data (electron diffraction in the gas phase, changes of electronic and vibrational spectra from solid to solution).