

MOLECULAR AND ELECTRONIC STRUCTURE OF SUBSTITUTED BITHIOPHENES

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Several substituted bithiophenes were prepared and their electronic structure studied by photoelectron spectroscopy and semi-empirical MO calculations. Comparison of the spectra of related molecules and analysis of calculated molecular geometries gave an indication of molecular conformations in the gas phase.

INTRODUCTION

Much interest has been generated recently in studies of electrically conducting polymers, especially polyheterocycles such as polythiophene. Our knowledge of their properties and factors which influence them is still incomplete, however. The study of model molecules ('building blocks') for these polymers is thus a natural step in an attempt to rationalize their design for technological purposes. The simplest model molecules are various isomeric bithiophenes. Whereas most reported work involved unsubstituted 2,2'-bithiophene, it is interesting to gain an insight into the possible influence of substituents on the conducting polymer.

In this paper we describe the synthesis and electronic and molecular structures of substituted bithiophenes on the basis of photoelectron spectra (PES) and semi-empirical AM1 MO calculations. The results by Nagashima *et al.*¹ have shown that semi-empirical methods when applied within Koopmans' approximation provide a good description of photoelectron spectra and molecular structures.

SYNTHESES OF BITHIOPHENE DERIVATIVES

The synthetic scheme for the bithiophene derivatives is depicted in Figure 1. The syntheses of 2,3'- (**1**) and 2,2'-bithiophene (**1a**) were performed using established

literature procedures² involving Grignard coupling of 2-thienylmagnesium bromide with 3-bromothiophene and 2-bromothiophene, respectively, in the presence of a catalyst [NiCl₂(dppp)] [dppp = Ph₂P(CH₂)₃PPh₂]. Nitration of (**1a**) was performed using acetic acid-concentrated nitric acid mixtures in tetrahydrofuran to afford 5-nitro-2,2'-bithiophene (**2**) in 69% yield, an improvement over the use of acetic anhydride-nitric acid mixtures.³ Chlorination of (**1a**) with *N*-chlorosuccinimide afforded 5,5'-dichloro-2,2'-bithiophene (**3**), whereas iodination with iodine monochloride afforded 5,5'-dijodo-2,2'-bithiophene (**4**). The latter represents a novel synthetic approach to **4**. 5,5'-Dibromo- (**5a**) and 3,3',5,5'-tetrabromo-2,2'-bithiophene (**6**) were synthesized by direct bromination.⁵ In this reaction, 3,5,5'-tribromo-2,2'-bithiophene (**5**) was established as an intermediate since it may be derived from the dibromo compound (**5a**) with 1 mol equiv. of bromine, whereas addition of 2 mol equiv. of bromine afforded the tetrabromo compound (**6**). Previously, (**5**) has been synthesized with copper (II) bromide as the brominating agent.⁶

In the above syntheses, selective reaction at the 5,5'-positions occurs unless more than 2 mol equiv. of electrophilic reagents are present, whence reaction would occur at the 3,3'-positions. This result is to be expected since molecular orbital calculation on bithiophenes⁷ has indicated that the 5-position is the most reactive to electrophiles and the next most reactive site is the 3-position.

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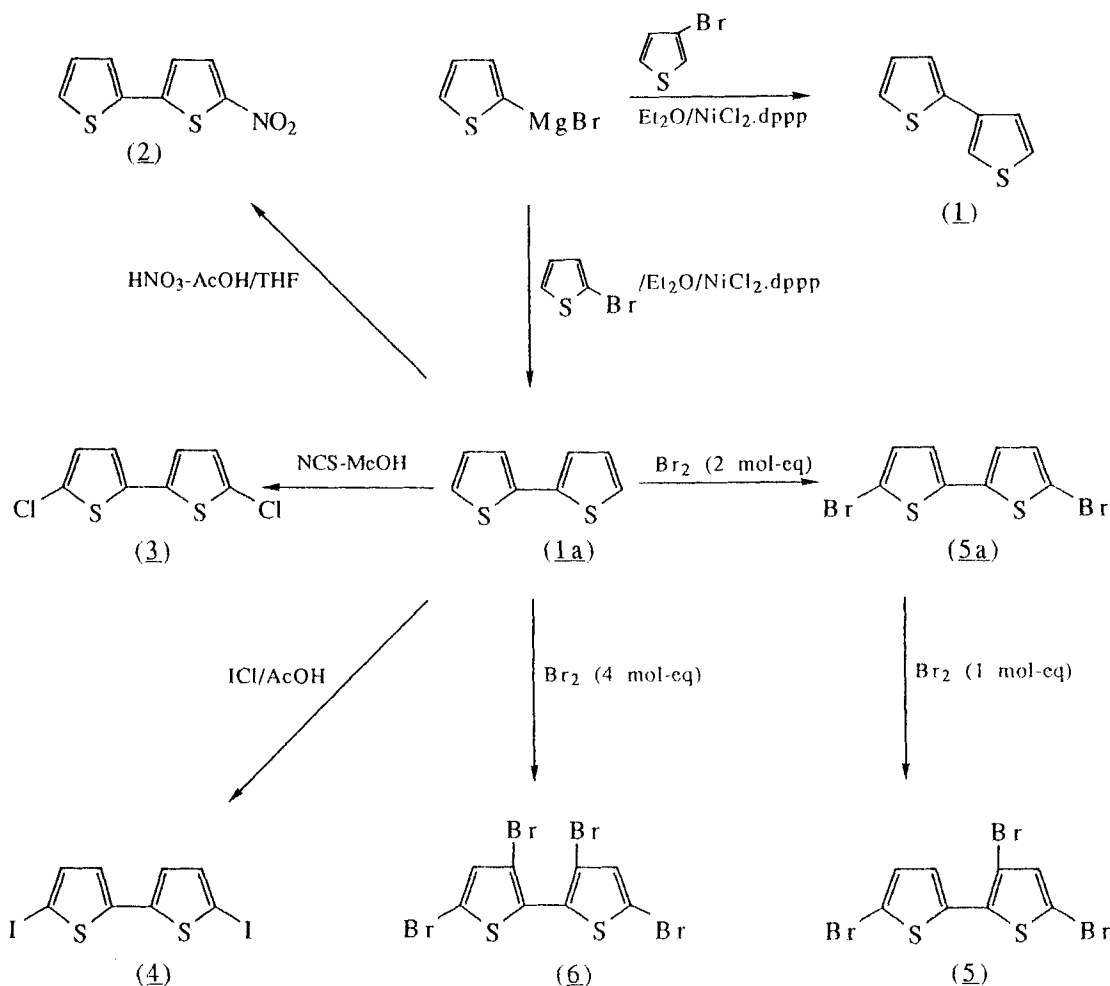


Figure 1. Synthetic scheme for bithiophene derivatives

RESULTS AND DISCUSSION

He I photoelectron spectra of the molecules studied are shown in Figures 3 and 4. They were recorded on Vacuum Generators UV-G3 and Leybold-Heraeus UPG-200 spectrometers with a spectral resolution (measured at the $\text{Ar}^+ \text{}^2\text{P}_{3/2}$ and $\text{}^2\text{P}_{1/2}$ lines) of ca 25 meV. The Ar lines were also used for calibration. The temperatures of the sample inlet probe during spectral measurements were 363–423 K.

The AM1 SCF MO program obtained from QCPE was used in the calculations. All the molecular geometries were fully optimized during the calculation. The initial geometric parameters were obtained from an electron diffraction study of 2,2'-bithiophene⁸ and microwave spectra of halothiophenes.⁹ The results obtained reveal two important pieces of information

about the molecules: their electronic structure and their gas-phase molecular conformation.

In order to facilitate discussion of the electronic structure, a qualitative MO diagram is shown in Figure 2. The diagram explains possible inter-ring conjugation and the relationship of thiophene and 2,2'-bithiophene π -orbitals. From it one deduces that π_3 orbitals of thiophene give rise to π_3 (bonding combination) and π_6 (antibonding combination) orbitals in the bithiophene molecule. The $\pi_6 - \pi_3$ energy gap can thus be considered a useful indicator of the extent of inter-ring conjugation. The π_2 orbital of thiophene, on the other hand, has a low electron density in the α -position and the π_5 and π_4 orbitals of 2,2'-bithiophene which correlate with it are virtually degenerate and insensitive to conformational (inter-ring conjugation) changes.

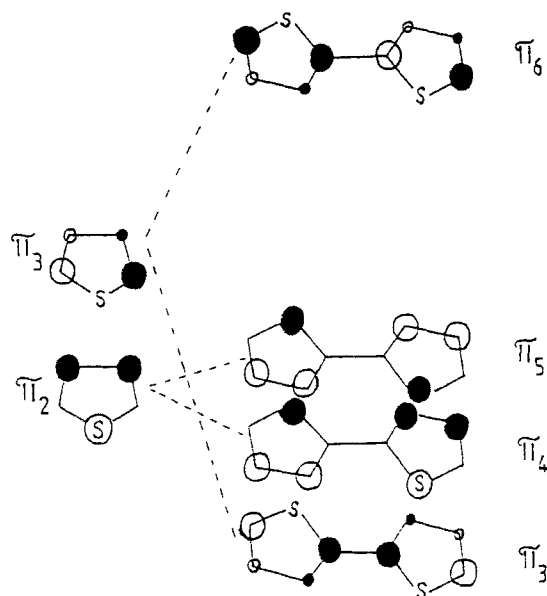


Figure 2. Schematic diagram of π -orbitals in thiophene and 2,2'-bithiophene

Assignment of the photoelectron spectra can be readily achieved through comparison with previously reported data on substituted thiophenes¹⁰⁻¹² and

bithiophenes¹³ and is confirmed by AM1 calculations. The first four bands correspond to π orbital ionizations whereas the sharp resolved bands at higher ionization energies can be attributed to halogen lone pairs. The assignment of the sulphur lone pair (σ -symmetry) remains ambiguous owing to the multitude of bands observed at higher ionization energies. The assignment of the nitro derivative can be deduced on the basis of comparison with PES of 2-nitrothiophene.¹⁴

Figures 5 and 6 reveal that the π orbital ionization energies are insensitive to halogen substitution but are strongly shifted to higher values for the nitro derivative (electron-withdrawing substituent). AM1 results show that the $\pi_6 - \pi_3$ orbitals are not delocalized into the NO_2 moiety, suggesting a predominantly inductive effect of the nitro group. It is important to add that the band at 10.95 eV observed in the PES of nitro-bithiophene possibly contains up to two ionizations from predominantly NO_2 group localized orbitals. This conclusion can be reached on the basis of the band intensity and in view of the fact that NO_2 group ionizations in 2-nitrothiophene were observed in the range 10.8–11.4 eV.¹⁴ The reason for the insensitivity of π orbitals to halogen substitution can be explained in terms of the energy difference between halogen p and bithiophene π orbitals. Figure 5 indicates that such an argument is plausible because the least sensitive (π_6) orbital also has the largest energy separation from the

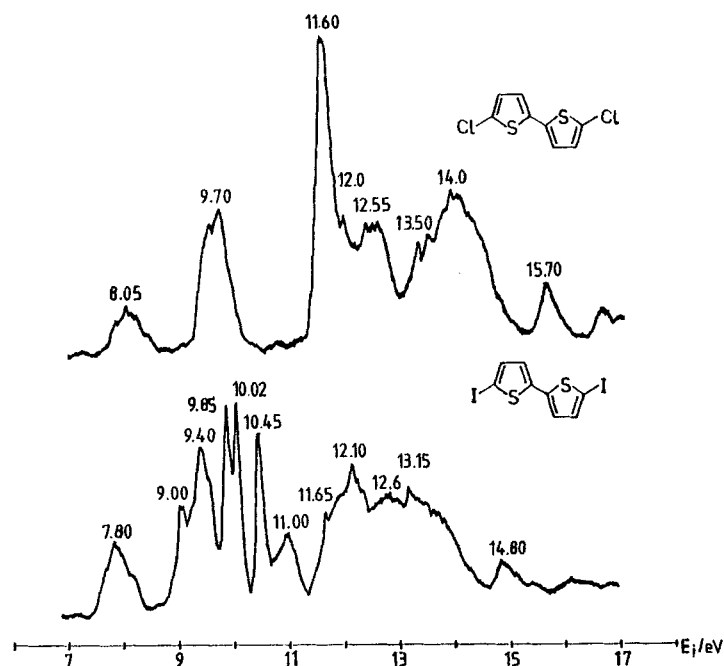


Figure 3. He I photoelectron spectra of 5,5'-dichloro- and 5,5'-diiodo-2,2'-bithiophene

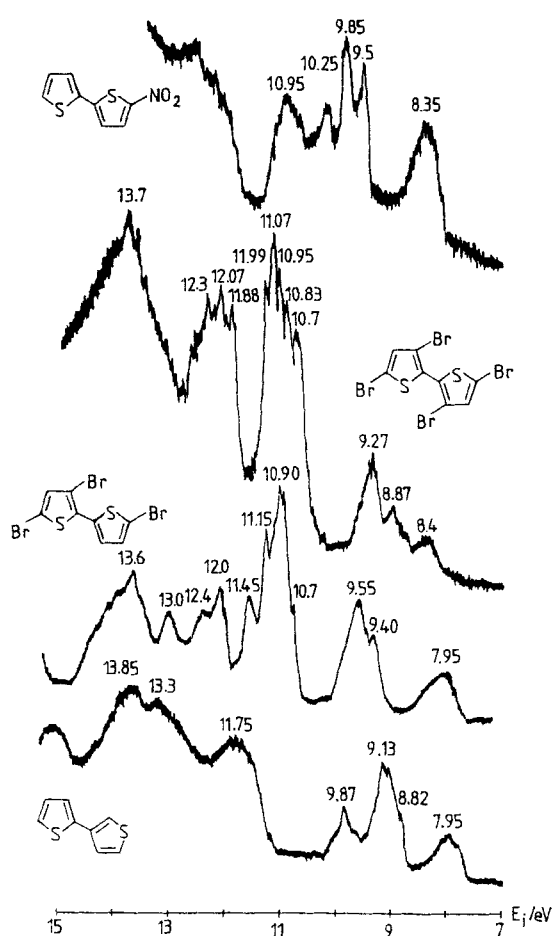


Figure 4. He I photoelectron spectra of 2,3'-bithiophene, 3,5,5'-tribromo-2,2'-bithiophene, 3,5,3',5'-tetrabromo-2,2'-bithiophene and 5-nitro-2,2'-bithiophene

halogen p orbital. The halogen p orbitals form out-of-phase combinations with π_6 and π_3 orbitals.

Photoelectron spectroscopy is not well suited for conformational analysis except in favourable cases. Nonetheless, the present spectra in combination with AM1 calculations provide some information about gas-phase conformations (Table 1). Almennigen *et al.*⁸ demonstrated using gas-phase electron diffraction that 2,2'-bithiophene is non-planar with an angle of twist of 34° . The angle was not obtained very accurately, however, and authors suggested⁸ the possibility of a virtually free ring rotation within 0 – 84° . This result agrees with our AM1 calculations, which predict a slightly non-planar conformation (Table 1).

Comparison of the $\pi_6 - \pi_3$ energy gap in 2,2'-bithiophene with those in 2,3'-bithiophene and 5-nitro-2,2'-bithiophene (Figure 6) suggests that similar

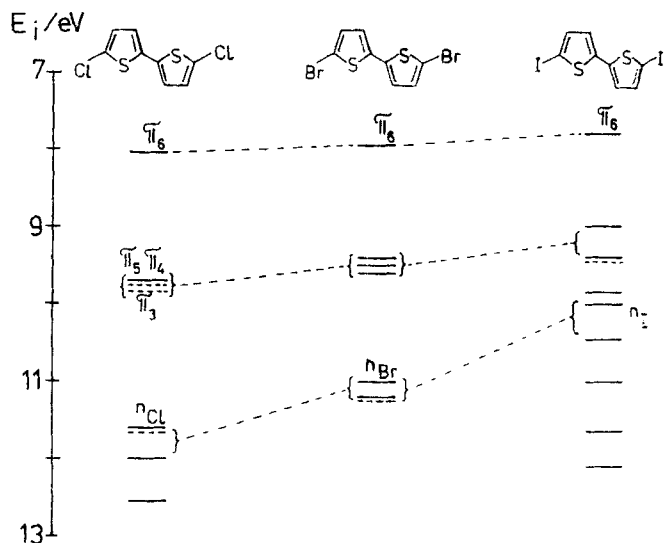


Figure 5. Energy level diagram (deduced from PES) for thiophenes and bithiophenes

non-planar *anti* conformations apply to the latter two molecules also. 5,5'-Dibromo-2,2'-bithiophene has been shown to exist in a non-planar conformation in the gas phase on the basis of the photoelectron spectrum¹³ with no definite angle of twist reported. Our AM1 results support this conclusion.

The size of the $\pi_6 - \pi_3$ energy gap in the tribromo derivative again indicates that it probably exists in a similar non-planar gas-phase conformation. The substituent effect of additional bromine does not affect the π ionization pattern (Figure 6). The tetrabromo derivative, on the other hand, reveals a different pattern of π ionizations with a significantly reduced $\pi_6 - \pi_3$ separation, which is indicative of a conformation different from those of the dibromo and tribromo derivatives. It is possibly due to a large angle of twist which results in

Table 1. AM1 conformations and dipole moments of bithiophenes^a

Molecule	θ ($^\circ$)	μ (10^{-30} cm)
2,2'-Bithiophene	2.0	0.05
2,3'-Bithiophene	1.5	1.17
3,3'-Bithiophene	9.3	0.14
5-Nitro-2,2'-bithiophene	1.0	20.35
5,5'-Dichloro-2,2'-bithiophene	7.0	0.33
5,5'-Dibromo-2,2'-bithiophene	10.3	0.54
5,5'-Diiodo-2,2'-bithiophene	7.0	0.33
3,5,5'-Tribromo-2,2'-bithiophene	17.5	2.80
3,5,3',5'-Tetrabromo-2,2'-bithiophene	44.2	0.73

^aTwist angles refer to planar *anti* conformation.

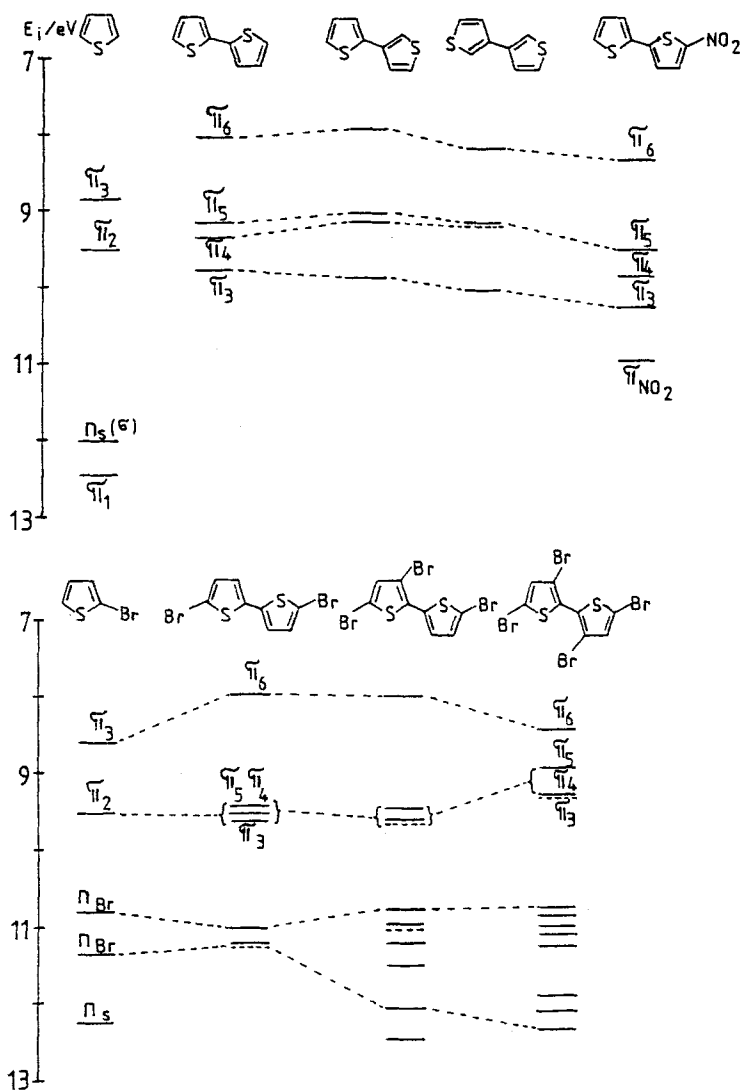


Figure 6. Energy level diagram (deduced from PES) for substituted bithiophenes

a loss of inter-ring π conjugation and reduced $\pi_6 - \pi_3$ separation (Figure 2). The AM1 results (Table 1) indicated a much larger angle of twist for the tetrabromo than for any other derivative. Such pronounced non-planarity can be rationalized in terms of electron density and internuclear repulsion between S and Br atoms situated in the neighbouring rings. If one accepts a 35° angle of twist in 2,2'-bithiophene and its derivatives as a good estimate, then the angle in tetrabromo derivative must definitely be much larger.

The magnitude of such repulsive interactions is nonetheless probably small. Comparison of π ionizations in the 5,5'-dibromo derivative (where there is no such

interaction) and the 3,5,5'-tribromo derivative (with one S-Br interaction) shows similar molecular conformations, which supports the original conclusion. On the other hand, two repulsive interactions together with a small inter-ring rotation barrier lead to significant distortion from coplanarity in the tetrabromo compound. Hydrogen bonding is likely to be insignificant, as shown by the non-planarity of the parent 2,2'-bithiophene molecule.

In conclusion, the electronic structures of substituted bithiophenes are similar and only moderately influenced by substituents. The gas-phase conformations of the molecules studied are non-planar with an especially

large angle of twist in the tetrabromo derivative. These conformations are therefore very different from the nearly planar conformations observed in the solid state.⁶

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