

Theoretical analysis of model compounds of substituted poly(acetylenes): conformation versus electronic properties

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ABSTRACT

The influence of the conformation of conjugated molecules on their electronic properties has been investigated using the extended Hückel theory. Dimers of acetylene and methylacetylene have been taken as model compounds of poly(acetylene) and poly(methylacetylene). Upon increasing the torsional angle between the two repeat units, both the band gap and the ionization potential increase, but the change is more pronounced with the former variable. This increase is not regular and becomes more important at angles larger than 30°. Non-planar conformations are then expected with poly(methylacetylene) and other n-alkyl monosubstituted poly(acetylenes) and explain their large band gap (i.e. blue shifting) in comparison with that of poly(acetylene). In addition, similar ionization potentials are expected for n-alkyl substituted poly(acetylenes) and, therefore, their different reactivity in presence of oxidizing agents has to be explained by the size of their substituents.

INTRODUCTION

The influence of the conformation of conjugated polymers on their optical and electronic properties has been widely studied in recent years (1-11). For example, Brédas et al. (7) and Orchard and Tripathy (10) have investigated the variation of band gap and ionization potential of aromatic polymers and poly(diacetylenes), respectively, upon conformation. These calculations have shown a strong influence of conformation on these two parameters for angles larger than 40°.

Furthermore, UV-visible spectroscopy experiments on poly(diacetylenes) (1-3) and poly(silanes) (4) have shown a major modification of the polymer electronic structure with conformation. Similarly, a correlation between conformation and UV absorption spectra has been demonstrated with poly(acetylene) derivatives (8). This relation reveals a significant blue shift of the optical absorption spectra with the loss of backbone planarity and, therefore, conjugation.

In order to confirm the relation between conformation and electronic properties of poly(acetylene) derivatives, band gap and ionization potentials were calculated in this article as a function of the torsional angle between repeat units. Dimers of acetylene and methylacetylene have been taken as model compounds of poly(acetylene) and poly(methylacetylene). The electronic properties of these models were calculated as a function of the conformation using the extended Hückel theory (EHT) (12, 13).

METHODOLOGY

At variance with the standard Hückel theory, the extended Hückel method takes into account all the valence electrons of the molecule under investigation and, therefore, can be used to study non-planar molecules. However, it neglects two-electron repulsion terms which limits its application to non-polar molecules (14).

With this theory, the molecular orbitals are approximated as linear combinations of the valence atomic orbitals of the atoms:

$$\psi_j = \sum_k c_{jk} \phi_k \quad (1)$$

where ψ_j are molecular orbitals, ϕ_k atomic orbitals and c_{jk} the coefficients of the atomic orbitals. Each molecular orbital contains contributions from four atomic orbitals on each carbon atom (one 2s and three 2p) and from one 1s atomic orbital atom on each hydrogen atom. The atomic orbitals used in this work are Slater-type orbitals and the required Slater coefficients are reported in Table I.

The secular equation, Eq. (2), and the equation for the molecular coefficients, Eq. (3), were solved using Roothan's method (15):

$$\det(H_{jk} - e_i S_{jk}) = 0 \quad (2)$$

$$\sum_k (H_{jk} - e_i S_{jk}) c_{jk} = 0 \quad (3)$$

where S_{jk} are overlap integrals, H_{jk} resonance integrals, H_{jj} Coulomb integrals and e_i energies of the molecular orbitals. All overlap integrals are considered and they are evaluated using Mulliken equations (16), H_{jk} being calculated from:

$$H_{jk} = 0.5K (H_{jj} + H_{kk}) S_{jk} \quad (4)$$

where $K = 1.75$ and H_{jj} are taken from atomic ionization potentials (Table I). Using the Hamiltonian and overlap matrices, Equation (2) is solved with two matrix diagonalizations (13). The total energy is evaluated from:

$$E_{tot} = 2 \sum e_i \quad (5)$$

TABLE I: Atomic Parameters for the Extended Hückel Calculations

Atom	Orbital	Slater exponent	Valence-state ionization potential (eV)
H	1s	1.30	-13.6
C	2s	1.625	-21.4
C	2p	1.625	-11.4

Bond angles and bond lengths of the models used were identical to those used by Hoffmann (13) and the calculations were optimized for side-group rotations. The method employed in this study cannot calculate the electronic band structure of the molecule but, for comparison purposes, band gaps were defined as the difference in energy between the Lowest Unoccupied Molecular Orbital (LUMO) and the Highest Occupied Molecular Orbital (HOMO). Following Koopman's theorem, the ionization potentials were taken as the inverse of the energy of HOMO (15). The energy values thus calculated are different from those of the corresponding polymers; however, the conformational and structural dependences of these models are expected to follow the same trends in both series.

RESULTS

Figure 1 shows the dependence of band gap and ionization potential of dimers of acetylene and methylacetylene upon conformation. These two parameters increase with the torsional angle, but the variation is not linear; it becomes significant for angles larger than 30°. It can also be observed that ionization potentials are less dependent upon conformation than band gaps. From 0 to 90°, band gaps increase by more than 1.3 eV, while ionization potentials increase by only 0.3 eV.

The presence of a methyl substituent on methylacetylene decreases slightly the ionization potentials and the band gaps calculated as compared to those of acetylene, but no difference is observed in their conformational dependence. From these results, substituted poly(acetylenes) are expected to have similar or even better electrical properties as compared to unsubstituted poly(acetylene), assuming similar conformations. However, the substitution on poly(acetylene) causes a deviation to planarity (5, 8) which leads to the sort of increase of the band gap and ionization potential shown in Fig. 1.

Using the extended Hückel method, the preferred conformation of methylacetylene dimers was calculated as shown in Figure 2. The more stable conformation has a torsional angle of 100°, in agreement with the value found in a CNDO conformational analysis of poly(hexafluorobut-2-yne) (17). In an earlier publication (8), a minimum energy angle of 130° was calculated using molecular mechanics, as compared to 90° in Ref. 5. This last value does not appear to be realistic: such an obtuse angle between repeat units would lead to a breakage of conjugation and this polymer would not be orange. It then appears that poly(methylacetylene) has a non-planar conformation with a torsional angle in the 100-130° range; it is difficult to tell at this point which value is the best one, each method of calculation being subjected to a certain number of systematic errors which are difficult to assess.

DISCUSSION

As shown above, a small red shift in UV absorption is predicted with the methyl substitution of butadiene (and presumably poly(acetylene)) but, on the other hand, a blue shift is calculated when the torsional angle between repeat units increases. The influence of a non-planar conformation is more important than that of the alkyl substitution, especially for angles larger than 30°, and this factor can explain the shift at short wavelengths of the absorption limit of substituted poly(acetylenes) on increasing the size of their substituent (8) or, in other words, on increasing their deviation to planarity. In a previous study (8), a correlation has been found between torsional angle and

Figure 1: Evolution of band gap and ionization potential of acetylene and methylacetylene dimers with conformation.

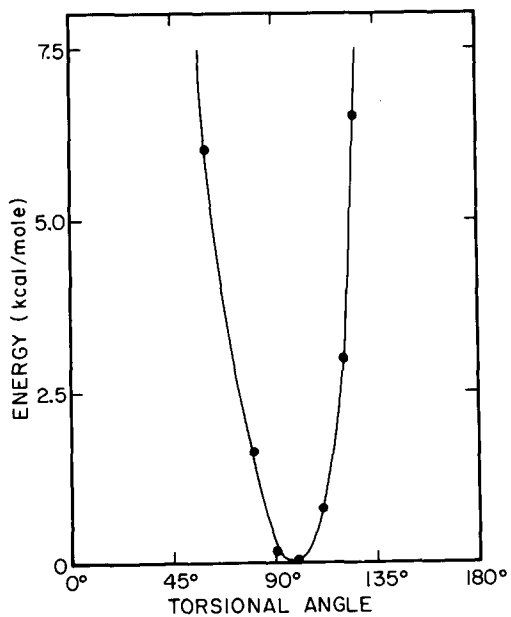
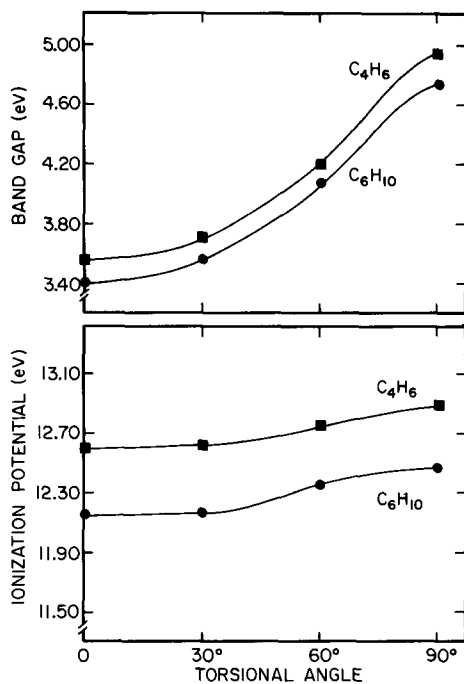


Figure 2: Conformational dependence of the potential energy function of methylacetylene dimer.

absorption in the UV spectra of substituted poly(acetylenes); this empirical relation is reported in Figure 3. The calculated band gaps of the methylacetylene dimer are also plotted in this figure as a function of torsional angle. The two curves have the same shape and this similarity confirms that the band gaps calculated from UV absorption values are directly related to the conformation of the molecule.

In this study, a continuous deformation along the main polymer chain is assumed and the blue shift of the band gap is attributed to the loss of conjugation related to this deformation. This model is equivalent to the wormlike (Porod-Kratky) chain model (18, 19) used by Wenz et al. (3) to explain the yellow phase of some poly(diacetylenes). Another approach of this problem would consist to introduce into the chain an uncorrelated strong disorder (90° twist) to break up the conjugation and to create sub-molecules with different conjugation lengths. With this latter model, calculations have shown a blue shift of the band gap which can be useful to explain the color transitions of poly(diacetylenes) (11, 20). However, even if some local disorder can be introduced into substituted poly(acetylenes), thus creating sub-molecules in the polymer, these sub-units cannot be planar and the influence of torsional angle upon the conjugation must be again analyzed. The model used in this study then appears to be more adequate.

Another important parameter to investigate is the ionization potential of the molecules which indicates the capability of a p-type dopant to ionize them. As shown in Figure 1, ionization potentials of model compounds depend weakly upon their substituent and conformation. This weak dependence of ionization potentials upon torsional angle was also reported by Tripathy et al. (5) for poly(methylacetylene) and poly(acetylene-co-methylacetylene). Therefore, it is suggested that poly(methylacetylene), poly(ethylacetylene), poly(propylacetylene) and poly(pentylacetylene) have about the same ionization potentials since they have similar conformations (8). The same assumption was used by Brédas et al. (7) for substituted poly(pyrroles): from the ionization potentials of these polymers, they have derived torsional angles which are in good agreement with theoretical calculations.

In an earlier work (21), substituted poly(acetylenes) were doped with iodine and it was found that the maximum dopant concentration varies with the size of the substituent. For example, poly(methylacetylene) can be doped up to 4.0 mole % while poly(pentylacetylene) shows a maximum doping concentration of 1.2%. Taking into account the weak variation of ionization potential with conformation and the similar conformations of these polymers, these different doping levels cannot be explained by different ionization potentials. The only other parameter which can influence the doping level is the bulkiness of the substituents. In Figure 4, the difference in doping levels is related to Hancock's steric coefficient (E_s^c) (22) of each polymer, confirming this hypothesis.

CONCLUSIONS

There is a close relationship between conformation and band gap in conjugated polymers. A planar conformation yields a relatively small band gap while any deviation to planarity gives an increase of the band gap value. A simultaneous consequence of a non-planar conformation is the blue shifting of the UV absorption spectrum from which the band gap value is measured. This relationship is such that not only the UV spectrum can be calculated from the knowledge of the polyene most stable

Figure 3: Conformational dependence of the band gap for methyl-acetylene dimer (theoretical curve) and for several substituted poly(acetylenes) (experimental curve).

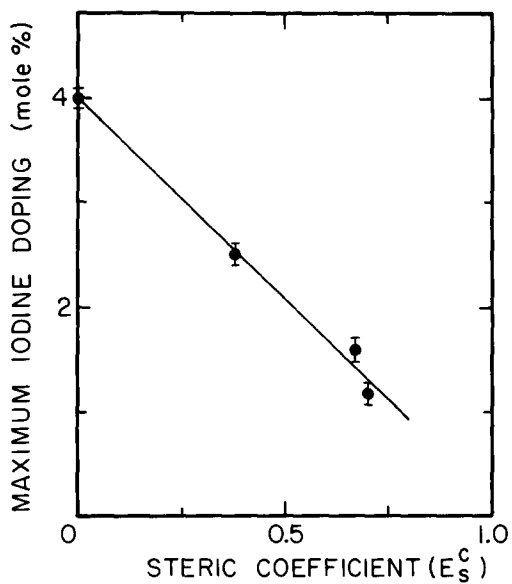
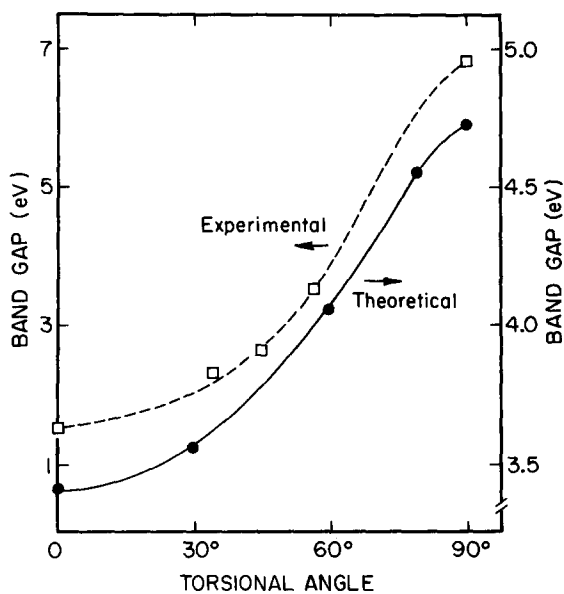


Figure 4: Correlation between the maximum iodine doping level and the steric coefficient of several substituted poly(acetylenes).

conformation but also the conformation of substituted poly(acetylenes) can be determined from their UV absorption spectra.

The calculations carried out in this article indicate clearly that the presence of a substituent on the acetylene dimer (and poly(acetylene)) does not modify significantly the band gap value, for similar conformations. In other words, similar band gaps are calculated with acetylene and methylacetylene (and, therefore, with poly(acetylene) and poly(methylacetylene)), in agreement with recent calculations of Brédas et al. (23). However, substituted poly(acetylenes) cannot have a planar conformation and this is the basic reason for their different band gaps.

The strong influence of conformation on electrical properties can also be invoked to explain the low conductivity of non-planar N-substituted poly(pyrroles) (24) as compared to un-substituted poly(pyrroles). In fact, only planar polymers exhibit good conductivity levels. For example, poly(1,6-heptadiyne) which is planar due to its bridge structure shows the best conductivity observed for a poly(acetylene) derivative (25). Some non-planar polymers, like poly(β,β' -dimethylpyrrole), can reach a high conducting level but theoretical calculations (7) have shown the possibility for these polymers to adopt a planar structure in the doped state.

The relationship between conformation and electronic properties seems to be quite general. It is applicable not only to the substituted poly(acetylenes) studied in this article, and to poly(pyrroles), but it can be used in the interpretation of the spectroscopic changes observed with poly(diacetylenes) and poly(silanes). The thermochromic transitions observed with the latter polymers can be explained by a transition from a planar to a non-planar conformation (2, 26). This conformational transition perturbs the conjugation along the polymer chain leading to a shift in the UV absorption.

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