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T. E. Ezell
University of Arkansas at Little Rock

Jerry A. Darsey
University of Arkansas at Little Rock

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SCF-MO Conformational Analysis of Polycroconaine

T.E. Ezell and J.A. Darsey
Department of Chemistry
University of Arkansas at Little Rock
Little Rock, Arkansas 72204

Abstract

Ab initio calculations at the STO-3G basis set level using GAUSSIAN 92 were conducted on the monomer unit of polycroconaine, a conducting polymer with conductive properties similar to several metals, in order to determine the most probable conformation of the monomer. We also compared the energy difference between the highest occupied and lowest unoccupied molecular orbitals. Successive calculations were performed at dihedral angle intervals of 30° around the central bond of the monomer. Minimum energy was observed at 0° bond rotation, consistent with a theory that the polymer owes many of its conductive properties to a planar configuration in combination with extensive conjugation of the C-C double bonds in the structure.

Introduction

Polycroconaine is one of a series of recently prepared organic polymers that are more like metals in their intrinsic electrical properties than any previously known polymers. The polycroconaines and related polysquaraines are more metal-like because they have some of the smallest band gaps ever observed in organic polymers. The band gap of a metal is the amount of energy needed to promote an electron from the highest occupied energy level (the valence band) to the empty band immediately above it (the conductance band). This gap determines the intrinsic electronic and optical properties of a material since a smaller band gap corresponds to an increase in the material's electrical conductivity. Metals, which have zero band gap, are excellent electrical conductors because their electrons can readily be promoted to the conductance band. Insulators, on the other hand, have a very large band gap which greatly restricts the flow of electrons.

Conjugated organic polymers have currently found great interest with respect to their potential conductive properties. Several polymers have been prepared which conduct electricity when doped with an oxidizing or a reducing agent. The band gap in most of these doped polymers, which are semiconductors, generally ranges from 1.5 to 4 eV. In recent years research has been focused in preparing polymers with increasingly smaller energy gaps, so as to make an organic material with a band gap as close to zero as possible. These polymers would not need doping in order to conduct in a similar manner to metals.

A group of polymers whose band gap is as small as 0.5 eV has recently been synthesized (Havinga et al., 1992). These polymers, polycroconaine and polysquaraine, contain strong electron-donating and electron-

accepting moieties in a regular alternating pattern. It is believed this close alternation causes a broadening of the energy bands which, in turn, leads to a smaller band gap. The electron donor in polycroconaine is a conjugated heterocyclic ring system containing nitrogen and sulfur atoms. The acceptor is croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione) in the case of polycroconaine, or squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) for polysquaraine. These polymers are stable in air at room temperature and can be heated to 300°C in air without degradation. The smallest band gap exists for polycroconaine, measured at 0.5 eV (Havinga et al., 1993). Samples with this band gap were found to be up to seven times more conductive (10^{-5} Siemens/cm) than other undoped organic polymers, which are generally insulators. While this is still far less conductive than a metal such as copper (conductivity 10^6 Siemens/cm), samples of polycroconaine which have been heavily doped with iodine show conductivities between 10^{-3} and 1 Siemens/cm, similar to that of undoped amorphous silicon (Havinga et al., 1993).

Materials and Methods

Because of the unique, semi-metallic electrical conductivity of polycroconaine, it would be useful to know if the polymer's properties are related to the extended conjugation offered by a planar structure for the monomer and possibly for extended sections of the polymer chain. Additionally, it would be useful to determine the energy differential between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and compare this value to the reported band gap for the polymer. In order to obtain these energy val-

ues, *ab initio* self-consistent field molecular orbital calculations were performed on the monomer or repeating unit of the polymer.

The segment of polycroconaine used for this research is the repeating unit shown in Fig. 1. Each end of the repeating unit was capped with a hydrogen atom in lieu of a representation of the remainder of the polymer chain. It was necessary to restrict this study to the single monomer unit because of the molecular size restrictions imposed by th *ab initio* program used. The procedure used was to optimize the geometry of the monomer unit using the GAUSSIAN 92 (Frisch et al., 1992) *ab initio* program, determine the potential energy function for rotation around the central bond of the monomer, and to determine the energy differential between the HOMO and the LUMO. These calculations were carried out on an IBM 3090 at the Cornell National Supercomputer Facility, a VAX 7000, and a 386DX/40 Microcomputer.
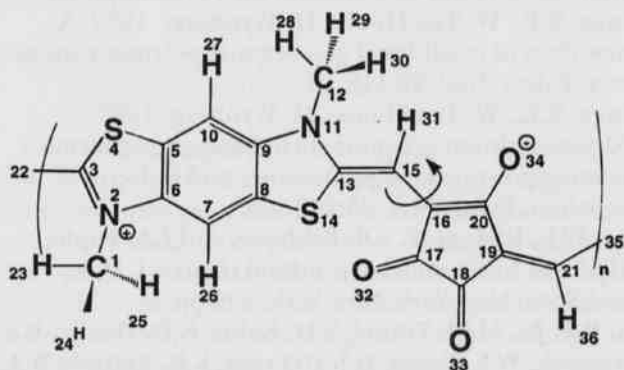

Fig. 1. Structure of polycroconaine with atomic labels used in calculations.

The geometry of the polycroconaine monomer had to be optimized before other calculations could be performed. An internal coordinate data set was created in the Z-matrix format which included the three-dimensional orientation of the atoms, as well as bond lengths, bond angles, and dihedral angles with respect to the appropriate reference atoms (Hehre et al., 1986). The atomic labels, initial geometric parameters and structure are shown at Fig. 1. To insure the Z-matrix geometry was correct, the atomic coordinates derived from the matrix were used to plot the atoms in three dimensions and visually check the geometry. To optimize the initial geometry, GAUSSIAN 92 was used to optimize first all bond lengths, then all bond angles using the STO-3G basis set. Once optimization was completed, the geometry was again visually checked to insure the optimized parameters appeared reasonable.

The rotational potential energy function was created by rotating the croconic acid moiety around the central

backbone of the monomer in 30° increments until the dihedral angle had been rotated through 360°. Again, each Z-matrix geometry was plotted and visually checked to insure a reasonable structure. These rotations were represented by a series of twelve rotation data sets used in the specific calculations. A point calculation (holding all parameters constant) was performed using GAUSSIAN 92 for each rotational increment. These calculations produced a set of 12 rotations with their corresponding energies listed in hartrees, or atomic units. These energies were converted to kilocalories per mole and plotted against the corresponding dihedral angle to generate the potential energy function.

A second point calculation was performed using GAUSSIAN 86 (Hout et al., 1986) to obtain a molecular orbital population analysis for the optimized molecule at the geometry with the lowest potential energy.

Results and Discussion

The results for the optimized geometry of the polycroconaine monomer are given in Table 1. All bond lengths are listed in Ångstroms; all bond angles are listed in degrees. It is interesting to note that these results predict that the two ring structures lie in the same plane, allowing maximum through-conjugation for the aromatic rings, the conjugated double bonds, and the nonbonding electron pairs from the hetero atoms in the structure.

Once the optimized geometry was determined, total energies were calculated at rotational intervals of 30° around the bond linking the heterocyclic ring to the croconic acid ring. The potential energy function created by this rotation is shown at Fig. 2. Energy minima are seen at 0° rotation with lesser local minima between 240° to 300°. Energy maxima occur between 30° to 90° rotation and again near 120° to 210°. Minimum energy is observed at 0° dihedral, where both rings lie in the same plane and the negatively-charged oxygen of the croconic acid ring is on the opposite side of the structure from the neighboring sulfur atom and its two nonbonding electron pairs. High rotational energies are observed between 30° and 90° and near 330°, likely because of repulsion between the electron pairs of the sulfur (S14) and the two neighboring oxygens on croconic acid. The bond length for the charged oxygen atom (C20-O34) is approximately 10% longer (1.360 Å) than the carbon-oxygen bond lengths for the carbonyl groups (C17-O32 and C18-O33; 1.215 Å), increasing the interaction between O34 and the sulfur electron pairs at these angles of rotation. Local minima are observed at 240° and 300° as the electron pairs on the oxygen rotate out of plane and away from the sulfur; however, some stability may also be lost due to loss of conjugation as the pi orbitals of the conjugated

double bonds move out of same plane. This is evidenced by the high energy observed at 270° where the croconic acid ring is at right angles to the heterocyclic ring. Finally, we calculated the energy differential between the HOMO and LUMO for the monomer unit to be 0.17896 hartrees, or atomic units. This is equivalent to 112.65 kcal/mol, or 4.869 eV.

Table 1. Optimized geometry of polycroconaine.

Bond Lengths: (Angstroms)

N2-C1 = 1.49	S14-C13 = 1.74	H26-C7 = 1.08
C3-N2 = 1.34	C15-C13 = 1.32	H27-C10 = 1.08
S4-C3 = 1.61	C16-C15 = 1.48	H28-C12 = 1.09
C5-S4 = 1.61	C17-C16 = 1.49	H29-C12 = 1.09
C6-N2 = 1.56	C18-C17 = 1.49	H30-C12 = 1.09
C7-C6 = 1.38	C19-C18 = 1.49	H31-C15 = 1.09
C8-C7 = 1.38	C20-C19 = 1.53	O32-C17 = 1.22
C9-C8 = 1.38	C21-C19 = 1.32	O33-C18 = 1.22
C10-C5 = 1.38	H22-C3 = 1.08	O34-C20 = 1.36
N11-C9 = 1.52	H23-C1 = 1.09	H35-C21 = 1.08
C12-N11 = 1.49	H24-C1 = 1.09	H36-C21 = 1.08
C13-N11 = 1.52	H25-C1 = 1.09	

Interatomic Angles: (degrees)

C1-N2-C3 = 109.0	N2-C3-S4 = 109.0	C3-S4C5 =109.0
C1-N2C6 = 141.0	C3-N2-C2 = 110.0	N2-C6-C7 = 126.9
C6-C7-C8 = 120.0	C7-C8-C9 = 120.0	S4-C5-C10 = 141.0
C8-C9-N11 = 108.0	C9-N11-C12 = 109.0	C9-N11-C13 = 109.0
C12-N11-C13 = 142.0	N11-C13-S14 = 109.0	N11-C13-C15 = 125.0
S14-C13-C15 = 126.0	C13-C15-C16 = 123.5	C15-C16-C17 = 110.0
C16-C17-C18 = 105.0	C17-C18-C19 = 110.0	C18-C19-C20 = 105.0
C18-C19-C21 = 123.5	C20-C19-C21 = 131.5	N2-C3-H22 = 131.5
S4-C3-H22 = 119.5	N2-C1-H23 = 109.5	N2-C1-H24 = 109.5
H23-C1-H24 = 109.4	N2-C1-H25 = 109.5	H23-C1-H25 = 109.4
H24-C1-H25 = 109.4	C6-C7-H26 = 116.0	C8-C7-H26 = 124.0
C5-C10-H27 = 116.0	N11-C12-H28 = 109.5	N11-C12-H29 = 109.5
H28-C12-H29 = 109.4	N11-C12-H30 = 109.5	H28-C12-H30 = 109.4
H29-C12-H30 = 109.4	C13-C15-H31 = 119.5	C16-C15-H31 = 117.0
C16-C17-O32 = 121.0	C18-C17-O32 = 82.3	C17-C18-O33 = 121.0
C19-C18-O33 = 79.8	C19-C20-O34 = 128.6	C19-C21-H35 = 119.0
C19-C21-H36 = 119.0	H35-C21-H36 = 122.0	

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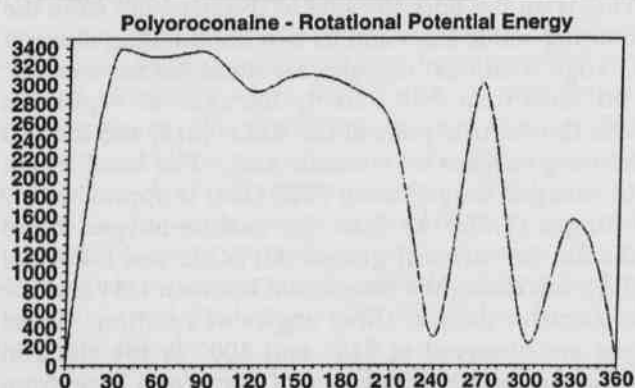

Fig. 2. Two dimensional rotational potential energy function, rotational angle vs. total energy in kcal/mol.