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Electronic Structure and Conformation of Polymers from Cluster Molecular Orbital and Molecular Mechanics Calculations: Polyimide

Sherif A. Kafafi,[*,†] John P. LaFemina,[*,⊥] and Jeffrey L. Nauss[§]

Contribution from the Division of Environmental Chemistry, The Johns Hopkins University, 615 North Wolfe Street, Baltimore, Maryland 21205, Battelle Pacific Northwest Laboratory,[‡] Molecular Science Research Center, P.O. Box 999, Richland, Washington 99352, and the Department of Gastroenterology, The Walter Reed Army Institute of Research, Washington, D.C. 20307. *Received April 30, 1990*

Abstract: Full geometry optimizations using molecular mechanics and the quantum chemical AM1 method have been carried out to determine the minimum energy conformation of pyromellitic dianhydride–oxydianiline polyimide (PMDA–ODA PI). The phenyl–imide twist angle for this compound was determined to be $\sim$30°. These computations also provided a quantitative determination of the energy gap (7 eV), electron affinity (–2 eV), and ionization potential (8.97 eV). Computations on the PMDA–ODA PI radical anion provided an estimate of the "hopping" barrier for an electron to hop from one chain to another (3.2 eV), the mechanism believed responsible for photoconduction. Moreover, the use of qualitative molecular orbital theory (QMOT) arguments provided an interpretation of these results in a simple molecular orbital framework.

I. Introduction

The electronic structure of organic polymers is an area of research that has attracted a great deal of interest over the past decade due to the promise these materials hold as chemically tunable electronic systems.[1] The class of materials known as polyimide (PI) has found wide application in the electronics and space industries because of their superior thermal and mechanical properties and low dielectric constant.[2] In addition, PIs can be etched with well-defined features by using UV radiation,[3] thus making it a potentially important material in microelectronics and electronic packing technologies.[4] Because of the potential industrial applications, much of the work on PIs to date has focused on the characterization of the laser ablation process and the elucidation of the ablation mechanism.[5]

There have been some theoretical studies that have sought to understand the photophysical properties of pyromellitic dianhydride–oxydianiline (PMDA–ODA) PI (Figure 1) on a molecular level.[6-8] These studies revealed that the electronic processes in PMDA–ODA PI are highly localized,[6,7] thus enabling the polymer to be successfully modeled via a macromolecular representation, and provided quantitative understanding of the optical absorption data and emission mechanism of PI.[7,8]

A periodic band structure calculation on PMDA–ODA PI, reported by Bredas and Clarke (BC) using the valence effective hamiltonian (VEH) method,[6b] was the first to recognize the localization of the electronic processes in this system, though it had several deficiencies. First was the assumption that the phenyl–imide twist angle was 0°. X-ray diffraction data on related compounds indicated that the phenyl rings were twisted by $\sim$60°.[9] Subsequent CNDO/S3 computations that examined the dependence of the optical absorptions on the phenyl–imide twist angle suggested that a value of $\sim$30° was more appropriate[7]—a result consistent with the results of a study of core-level shifts for PMDA–ODA PI by Silverman et al.[10] which concluded that the torsional angle was greater than 0° but less than 60°. The second drawback, common to all reported computations on this material, is the lack of any geometry optimization.

Finally, none of the previously reported computations are expected to provide a reasonable estimate for the lowest unoccupied orbital. Accordingly, the calculated energy gap (E_g), ionization potential (IP), and electron affinity (EA) of PMDA–ODA PI are expected to be unreliable. These quantities are crucial for understanding the electron-transfer capabilities of the polymer.[8,11] The IP indicates whether a given acceptor (p-type dopant) is capable of ionizing the polymer chains. E_g determines the electrical properties of the substance. The latter, when subtracted from the IP, yields the EA, the quantity important in n-type doping processes.

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[*] The author to whom correspondence should be addressed.

[†] The Johns Hopkins University.

[⊥] Battelle Pacific Northwest Laboratory.

[§] The Walter Reed Army Institute of Research.

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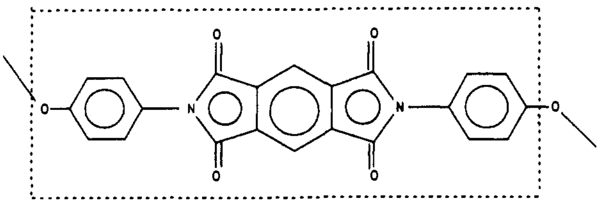


Figure 1. Polyimide unit cell.

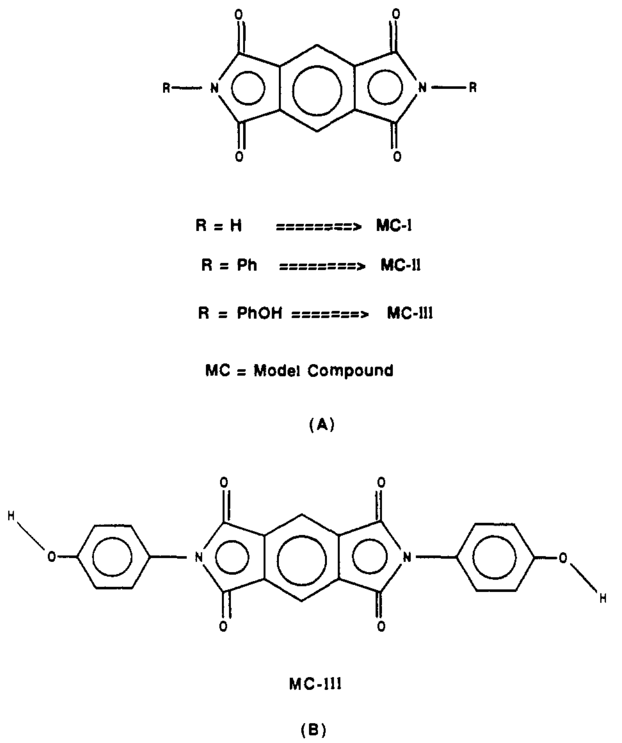


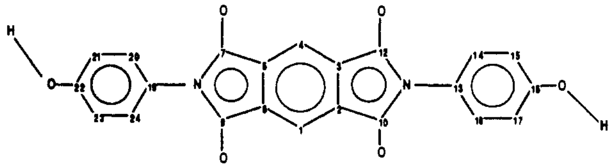
Figure 2. The model compounds studied in this work.

In this work, we use molecular mechanics, MM2,[12] the quantum chemical AM1 method,[13] and qualitative molecular orbital theory (QMOT)[1,14] to address the question of the minimum energy conformation of PMDA-ODA PI in order to determine its molecular orbital (MO) characteristics and associated electronic properties (E_g, IP, and EA).

All of the computations reported in this work are cluster calculations. The model compounds chosen for this study are shown in Figure 2. The computations were performed on both the neutrals and anion radical species of these model compounds. The calculations on the corresponding singly charged anion radicals are important in understanding the nature of electron transport in PI.

The paper is organized as follows. Section II is a brief description of the computational methods. The results of the computations are presented in section III. Section IV contains a discussion of the results in the context of QMOT along with a qualitative discussion of the photoconduction process in PMDA-ODA PI. In section V we present AM1 and MM2 computations on an expanded unit cell of PI to test the convergence of the electronic properties computed from the model compounds. We conclude with a synopsis.

Table I. The Minimum Energy Geometric Parameters for the Neutral and the Radical Anion of MC-III Obtained from the AM1 Method[a]



parameter	MC-III neutral	MC-III anion
R(C1–C2)	1.3908	1.3863
R(C2–C3)	1.4162	1.4476
R(C3–C4)	1.3908	1.3874
R(C3–C12)	1.5026	1.4715
R(C12=O)	1.2306	1.2411
R(C12–N)	1.4274	1.4400
R(N–C13)	1.4144	1.4029
R(C13–C14)	1.4109	1.4155
R(C14–C15)	1.3902	1.3891
R(C15–C16)	1.4004	1.3990
R(C16–O)	1.3753	1.3826
R(O–H)	0.9684	0.9672
R(C1–H)	1.1013	1.0993
R(C18–H)	1.1028	1.1037
R(C17–H)	1.0996	1.0990
∠(C1–C2–C3)	122.2	121.6
∠(C2–C3–C4)	122.3	122.0
∠(C3–C4–C5)	115.4	116.0
∠(O–C12–C3)	127.1	129.0
∠(C2–C3–C12)	108.1	108.0
∠(C3–C12–N)	106.6	107.0
∠(C14–C13–N)	120.5	121.1
∠(C15–C14–C13)	120.3	121.0
∠(C16–C15–C14)	119.9	120.1
∠(H–O–C16)	108.0	107.4
(phenyl–imide) dihedral angle	30.4	26.2

[a] The bond lengths and angles are given in angstroms and degrees, respectively.

II. Computational Methods

All of the calculations reported in this work were done with MM2[12] and Dewar et al.[13,15a] AM1 methods. For each of the computations, the geometry was fully optimized. No symmetry constraints were imposed in any optimization. Therefore, in MM2 the equilibrium configuration of the species of interest corresponds to a minimum in the molecular potential energy function. This function takes into account the interactions between all possible atomic pairs in the molecule. In AM1, on the other hand, the restricted Hartree–Fock (RHF) method, using minimal basis sets consisting of Slater type orbitals (STO), was employed and the minimum energy geometries were located with use of analytical gradients. The half-electron option implemented in the AM1 method was used for all radical anions.

In this work, the MM2 computations were carried out on all the neutral species of interest. The AM1 method was used to predict the molecular conformation of the PI fundamental unit cell and its corresponding anion radical. The electronic properties of these species will then be derived from the AM1 cluster calculations on the model compounds shown in Figure 2.

III. Results

While computations were performed for all of the compounds shown in Figure 2, the results are sufficiently similar so that the discussion will focus on those for MC-III.

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(i) **Equilibrium Geometries.** Table I lists the minimum energy geometric parameters calculated from AM1 for the neutral and radical anion of MC-III. As shown in Table I, the phenyl–imide twist angles for these species are 30° and 26°, respectively, in agreement with earlier CNDO/S3 computations.[7] This small difference in the torsional angles for the neutral and charged MC-III, along with the observation that they have similar minimum energy geometric parameters, implies that the addition of an electron is a relatively small perturbation to the nuclear frame. The corresponding equilibrium geometries obtained from MM2 are similar to those calculated from AM1.

(ii) **The Relative Energy between Planar and Nonplanar Conformations of PI.** The relative energy between the planar and nonplanar conformations of MC-III was calculated to be 2.2 kcal/mol for the neutral species and 1.6 kcal/mol for the charged species. These values were obtained from the difference in heats of formations of the nonplanar and planar conformers. MM2 computations on the planar and nonplanar neutral MC-III yielded a value of 3 kcal/mol. In view of the reliability of AM1 and MM2 in estimating relative energies between conformers,[12,13,15] these values should be considered as an upper limit for this energy difference.

(iii) **The Electronic Properties of PMDA–ODA PI.** The IP, EA, and E_g[16] of PMDA–ODA PI can be derived from the electronic properties of MC-III. The IP can be estimated by using Koopmans theorem,[17] which relates the IP to the energy of the highest occupied MO (HOMO). The EA can be obtained from the difference between the heats of formation of the neutral species and its corresponding radical anion.[18] Finally, the E_g can be estimated as the HOMO–LUMO energy difference. By using these approximations, the IP is computed to be 8.97 eV, as obtained from AM1. This value is in good agreement with the corresponding experimental value of 9.1 eV reported by Kowalczyk et al.[6a] The corresponding IP calculated by BC[6b] using the VEH method is 8.0 eV. The EA computed from AM1 is −2.9 eV. However, since AM1 tends to overestimate the stability of anions by 10–20 kcal/mol,[13,15,18] our estimate of the EA of PMDA–ODA PI is ca. −2 eV. Accordingly, we estimate the E_g of PI to be $\sim$7 eV.

The EA of PI has not been determined experimentally. However, our estimated value, −2 eV, falls in the range of EAs embraced by the maleimide derivatives that are substitutionally related to PI.[18]

(iv) **Photoconduction in PMDA–ODA PI.** Photoconduction in PI is believed to proceed via a two-step mechanism. First, an electron is transferred to the pyromellitimide moiety, either from a dopant in donor-loaded films (intermolecular charge transfer) or from the diphenyl ether moiety in the virgin polymer (intramolecular charge transfer).[8,11] Once the radical anion is formed, step two involves photoconduction via field-assisted hopping between adjacent pyromellitimide units. The energy barrier to this hopping process can be equated to the IP of the radical anion. The hopping barrier in PMDA–ODA PI is computed to be 3.2 eV, as obtained from the AM1 method. This value of the IP of the radical anion could be overestimated by 0.5 eV.[13]

Studies on the effects of interchain interactions on the conformation and electronic properties of polyimide are currently underway.

IV. The QMOT Description of PI

Over the years, QMOT arguments have been found to be useful in predicting the broad outlines of MO computations.[1,14,19] They allow one to understand the computational results by providing significant insights into molecular structure, conformation, and chemical reactivity via the identification of the controlling orbital interactions in the system. In this section we apply QMOT to the model compound MC-III (Figure 2) to aid in the understanding of the electronic and molecular structure of PMDA–ODA PI.

(i) **The QMOT Description of Neutral PMDA–ODA PI.** Figure 3 illustrates the occupied sixteen π-MOs (1–7, 10, 11, 16, 17, and 20–24), the highest filled eight σ-MOs (8, 9, 12–15, 18, and 19), and the lowest unoccupied π-MO (25) of MC-III. These orbitals are constructed from the results of AM1/STO full geometry optimization on the neutral, uncharged, MC-III constrained to planar geometry. The AM1 orbital energies are also given in Figure 3. For clarity purposes, the following should be noted: (1) The p_z AOs whose coefficients are less than 0.02 in all π-MOs are assigned a node. These AOs are not expected to have any significant effect on the geometrical preference of the system. (2) Only the AOs that are expected to affect the overall conformation of MC-III are shown in the σ-MOs. (3) The MOs displayed in Figure 3 correspond to half of MC-III. The AO phases of the other half could be predicted by using symmetry arguments. (4) The shape of the p_z AOs as drawn in the π-MOs (1–7, 10, 11, 16, 17 and 20–24) should not be confused with the hydrogen s AOs of the σ-orbitals (8, 9, 12–15, 18, and 19).

As discussed in section III, the energy minimum of MC-III is nonplanar. This preference for the nonplanar structure could be understood by examining the first-order energy change of each occupied MO in Figure 3 as the phenyl ring is slightly twisted around the C–N bond.

First, let us examine how the π-MOs sketched in Figure 3 will respond to this perturbation. The torsional perturbation will slightly destabilize MOs 1, 2, and 7 due to the loss of through-space bonding interactions between the p_z AOs located on the carbon atoms of the phenyl ring and the corresponding p_z AOs on the phthalimide part of the molecule. The energies of MOs 3, 6, and 20–22 are not expected to change to first order. This is due to the presence of nodes on the carbon atoms of the phenyl and/or five-membered ring(s) as shown in Figure 3. Also, the energies of MOs 4, 16, and 17 should not be affected because as the molecule becomes nonplanar, the energy lowering due to the decrease in through-space out-of-phase interactions is nearly balanced by the energy rise resulting from the loss of through-space bonding ones, as shown by the arrows drawn in these MOs. Using similar arguments, we can show that MOs 5, 10, 11, 23, and 24 will be stabilized by the torsional perturbation. Therefore, out of the sixteen occupied π-MOs, three are expected to be destabilized, eight will not be affected, and five will stabilize due to the torsional perturbation. The net effect on the total energy of MC-III is thus stabilizing, in agreement with the computational results obtained from the AM1 method.

With use of similar arguments as those described above for the σ-orbitals shown in Figure 3, the torsional perturbation will stabilize MOs 14, 15, 18, and 19, destabilize 9, 12, and 13, and not affect MO 8 to first order. Again, the nonplanar conformation of MC-III is also preferred by the σ-framework. Therefore, the σ- and π-MOs cooperatively contribute to the nonplanarity of MC-III.

By examining the σ-orbitals sketched in Figure 3, we can understand why hydrogen bonding did not occur between the phthalimide–oxygen atoms and the hydrogen atoms, nearest to the oxygens, of the phenyl ring in MC-III. MOs 14, 15, 18, and 19 show out-of-phase through-space interactions between the AOs located on these atoms. MOs 9, 12, and 13 show in-phase

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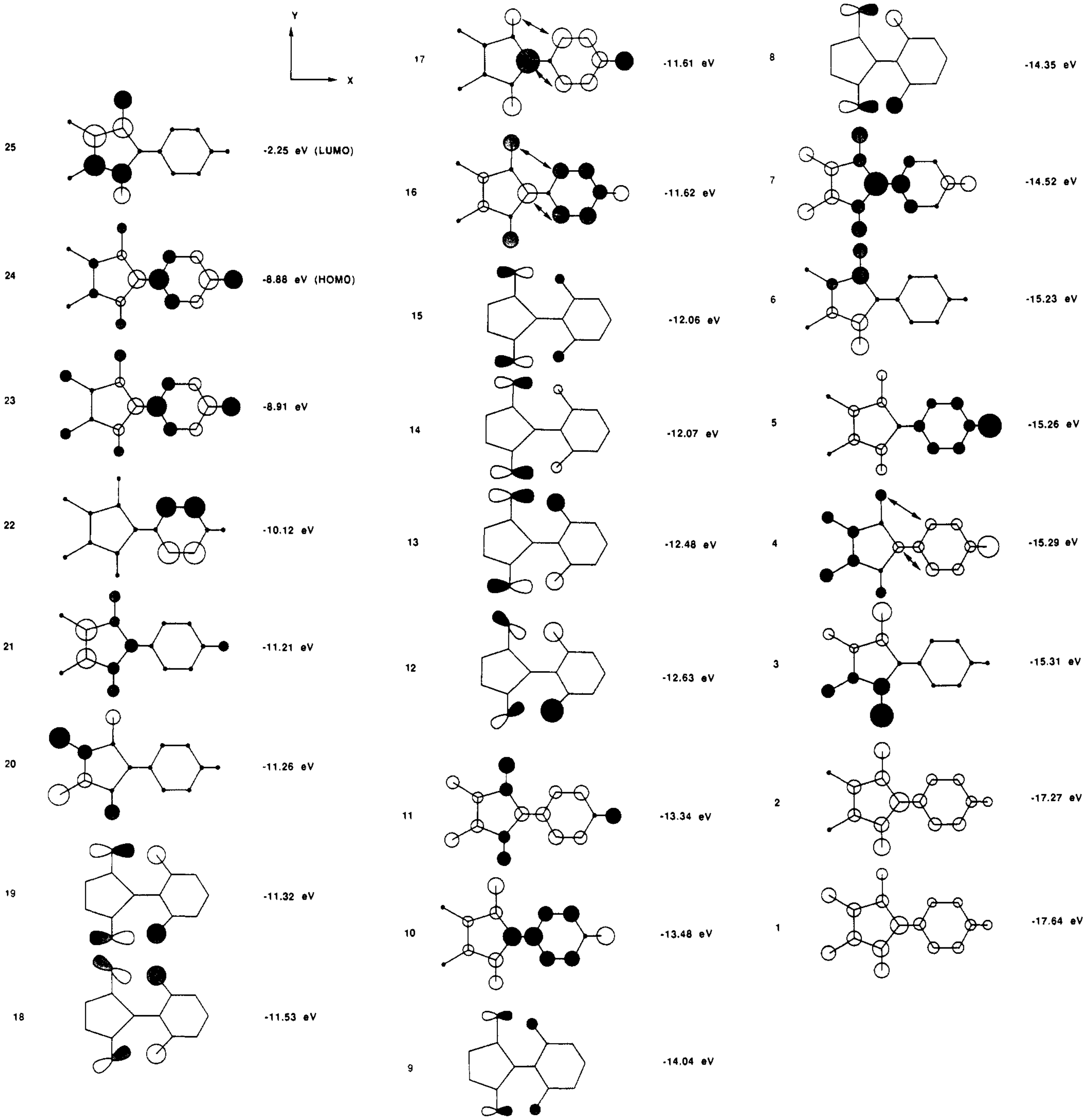

Figure 3. The highest occupied sixteen π-MOs and eight σ-MOs and the lowest unoccupied π-MO of MC-III. The orbital energies are given in eV.

through-space overlap. Therefore, we have a net repulsive interaction between the O$\cdots$H atom pairs. Accordingly, intramolecular hydrogen bonding did not occur in MC-III.

As a consequence of the nonplanarity of MC-III, the σ- and π-MOs are no longer orthogonal and all the energy levels will consist of a mixture of both. The degree of σ–π mixing depends on the energy separation between the levels and the phthalimide–phenyl torsional angle. Since the σ-orbitals generally occur at lower energies than the π-levels, the low-lying filled π-MOs in MC-III will mix with the σ-orbitals more than the higher filled ones, as is actually observed in the results of the AM1 computations on MC-III. This and the fact that the computed phenyl–imide twist angle is not so large, 30°, explain why the HOMO and LUMO are dominated by the p_z AOs, $\sim$95%.

(ii) **The QMOT Description of Radical Anion PMDA–ODA PI.** Adding an electron to MC-III produces its corresponding radical anion. If planar, this electron will occupy the nonbonding π-MO 25 (LUMO) shown in Figure 3.

As explained in the previous section, the total energy of the fully occupied MO's 1–24 favors a nonplanar structure. The singly occupied π-MO of MC-III is nonbonding. To first order, the torsional perturbation described above will not affect the energy of this orbital. Therefore, similar to the neutral compound, the radical anion of MC-III favors a nonplanar conformation over its planar one. This explains why the minimum energy geometrical parameters of the anion of MC-III are similar to the corresponding ones in the neutral species as shown to be in the case in Table I. Accordingly, the relative energy between the planar and nonplanar forms in neutral, 2.2 kcal/mol, and radical anion, 1.6 kcal/mol, MC-III species was found to be comparable.

The geometric parameters that did change could have been qualitatively predicted from the shape of the LUMO. For example, the carbonyl C=O interaction is antibonding, hence the bond length should increase. Examination of Table I will reveal that the carbonyl C=O bond length increased from 1.2306 Å in the neutral to 1.2411 Å in the radical anion.

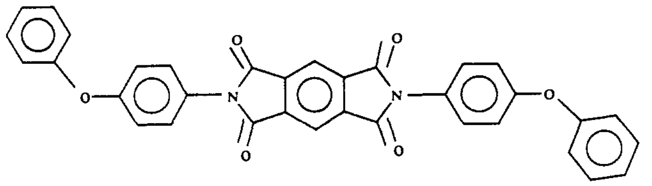

Figure 4. The model compound, MC-IV, investigated to test the convergence of the electronic properties of MC-III.

The nodal plane in the LUMO running along the chain axis and through the imide–phenyl linkage site indicates that the nature of the LUMO in the radical anion will be independent of the nature of the substituent attached to the imide nitrogen.

V. The Converged Electronic Properties of PMDA–ODA PI

An important question that needs to be answered when cluster calculations are performed to estimate the electronic properties of polymers is the following: Did the electronic properties calculated for the polymer of interest from cluster calculations converge?

To answer this question, a full geometry optimization was performed with use of the AM1 and MM2 methods on the neutral form of the model compound MC-IV shown in Figure 4 and AM1 optimizations on the corresponding radical anion. The results of the AM1 computations on the neutral species showed that its IP is 8.91 eV, that is, almost equal to the corresponding one of MC-III, 8.97 eV. In addition, the phenyl–imide torsional angle in the neutral form of MC-IV is 30°, and its remaining minimum energy geometric parameters are almost identical with the corresponding ones in neutral MC-III. The torsional angle between the planes containing the benzene rings in the diphenyl ether moiety is 40°, in good agreement with the X-ray crystal results for substitutionally related compounds that give a value of 45°.[9] The MM2 results were similar to those obtained from AM1. The LUMO energy of MC-IV is −2.25 eV, that is, identical with the corresponding one in MC-III. Furthermore, its EA was found to be equal to that of MC-III, −2.9 eV. As mentioned above, AM1 tends to overestimate the stability of anions by 10–20 kcal/mol. Therefore, the EA of MC-IV is thus ca. −2 eV. Accordingly, the E_g is also similar to that of MC-III, $\sim$7 eV.

In summary, increasing the size of the model compound did not have any significant effect on the magnitudes of the electronic properties computed for MC-III. This is an indication that the latter properties have converged. Accordingly, the computed electronic properties of MC-III provide reliable estimates of the corresponding ones in PI.

VI. Synopsis

The minimum energy conformation for several PMDA–ODA PI model compounds has been determined via molecular mechanics (MM2) and quantum chemical AM1 computations. The phenyl–imide torsional angle was found to be 30°. Computations on both the neutral and radical anion model compounds provided quantitative determination of the energy gap (7 eV), electron affinity (−2 eV), and ionization potential (8.97 eV). In addition, the barrier to intrachain electron hopping was estimated at 3.2 eV. Finally, qualitative molecular orbital theory was used to aid in the understanding of the electronic and molecular structure of this polymer in a simple orbital interaction context.

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Registry No. (PMDA)(ODA)PI (copolymer), 25038-81-7; MC-III, 14027-98-6; MC-III$^-$, 129731-77-7; MC-IV, 51601-64-0; MC-III (SRU), 25036-53-7.

Methane Formation during Ethylene Decomposition on (1×1)Pt(110)

E. Yagasaki and R. I. Masel*

Contribution from the School of Chemical Sciences, University of Illinois, 1209 West California Street, Urbana, Illinois 61801.
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Abstract: Previous work on the decomposition of ethylene on a variety of single-crystal surfaces and inorganic clusters indicates that the carbon–carbon bond usually stays intact until after the ethylene is largely dehydrogenated. However, in this paper we find that when ethylene adsorbs on (1×1)Pt(110), the carbon–carbon bond breaks near room temperature yielding methane. The methane desorbs in two peaks centered at 250 and 320 K. There also is evidence for production of a species containing CH_3 groups between 220 and 250 K. By comparison no significant production of methane has been observed during ethylene decomposition on any face of any transition metal studied previously. No methane formation is observed during ethylene decomposition on (2×1)Pt(110) even though all of the sites present on (1×1)Pt(110) are also present on (2×1)Pt(110). This kind of remarkable structure sensitivity has not been observed previously. We propose a speculative mechanism to explain these results involving some special steric hindrances on the (2×1)Pt(110) surface.

Introduction

Over the last 15 years, there have been over a hundred papers which examined ethylene adsorption on various transition-metal surfaces and cluster compounds.[1,2] Generally, the ethylene adsorbs molecularly and then dehydrogenates. There are a few examples where the carbon–carbon bond scission occurs at moderate temperatures.[3-5] There also has been one example where a tiny

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