# Theoretical Studies of Electronic Properties of Polyacene, Poly(1,4-dihydrobenzo-1,4-dihydrobenzene), Poly(*p*-phenylene), and Poly(*p*-1,4-dihydrobenzene) and Their Hetero (N, O, and S) Substituted Derivatives

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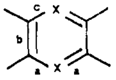
**Abstract:** A molecular-orbital-based molecular mechanics method (MOMM) has been employed to derive the structures of benzene, pyridine, pyrazine, 1,4-dihydrobenzene, 1,4-dihydropyrazine, 1,4-dioxin, and 1,4-dithiin. The oligomer structures of the above compounds have also been calculated by using the same method to derive the unit cells of polyacene, poly(pyridinopyridine), poly(pyrazinopyrazine), poly(1,4-dihydrobenzo-1,4-dihydrobenzene), poly(1,4-dihydropyrazino-1,4-dihydropyrazine), poly(1,4-dioxino-1,4-dioxin), *and* poly(1,4-dithiino-1,4-dithiin), poly(*p*-phenylene), poly(*p*-pyrazine), poly(*p*-1,4-dihydrobenzene), poly(*p*-1,4-dihydropyrazine), poly(*p*-dioxin), and poly(*p*-dithiin). The band structures, densities of states, ionization potentials, bandgaps, reduction potentials, and oxidation potentials of these polymers have then been calculated by using the Valence Effective Hamiltonian method (VEH). Poly(*p*-pyrazine) is predicted to have about the same conduction characteristics as poly(*p*-phenylene), the former being slightly less p-dopable by acceptors while being slightly more n-dopable by donors. In contrast to previously reported values and interpretation, our results are more in line with experimental data for poly(pyridinopyridine) and poly(pyrazinopyrazine). Pitfalls of the current VEH parametrization are discussed. Hetero atoms have been found to make considerable modifications for these polymers. Sulfur-substituted polymers are found to be particularly interesting in terms of conducting polymers. The structural effects on electronic properties are discussed.

Theoretical calculations have been widely applied to interpret and organize results and to resolve chemical mysteries. The most important role theoretical calculations may play for the future is probably to make correct predictions before any costly experimental work begins. Unfortunately, there is currently no single method that is adequate for all problems in terms of both the calculated accuracy and the required computer time. Thus, systematic studies should be encouraged. Such studies may be necessary for useful predictions because they increase the effectiveness of "cancellation of errors" and make systematic corrections possible.

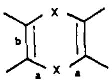
The general systematic approach we adopted in the previous work[1,2] is a multiple-stage approach, which makes use of the strength of each individual method. First, we select a set of model compounds for deriving a force field. Extensive ab initio calculations, using various basis sets, are then carried out for those model compounds whenever experimental data are not available or are questionable. Second, an appropriate force field to calculate accurate structures and energies is developed on the basis of Allinger's force field.[3] Calculations are then performed for large molecules. Finally, a special program such as the Valence Effective Hamiltonian (VEH) method[4] is employed to calculate ionization potentials, spectral properties, and electrochemical properties.

Conducting organic polymers represent one of the most challenging areas for theoretical scientists. In fact, they have recently been the focus of enormous interest.[5] It is due to the fact that certain organic polymers, upon doping with electron donors or acceptors, are transformed from insulators or semiconductors to "organic" metals. In addition, the reduced dimensionality of polymers leads to characteristic optical, magnetic, and transport properties that differ from those of traditional semiconductors.[5] Beyond the interest in conducting polymers, we view these polymers as key models for verifying or modifying theoretical tools for biopolymers and other macromolecules. Theoretical understanding of these polymers will certainly facilitate the design of new polymers. We view designing a macromolecule just like assembling a car. Thus, molecules studied in this work are equivalent to auto parts and they may become a portion of the polymer in mind.

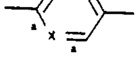
It is our intention in this paper to apply our systematic (multiple-stage) approach to study the electronic structures of polymers obtained from four similar classes of monomers. The unit cells of Classes I and III are conjugated six-membered rings (IA–ID, IIIA–IIIB) while those of Class II and IV compounds are homoconjugated six-membered rings (IIA–IID, IVA–IVD). Unit cells for each class are isoelectronic.



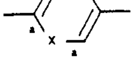
Class I
IA, X=CH
IB, X=N
IC, X=N or CH, C1 screw axis
ID, X=N or CH, C2 screw axis



Class II
IIA, X=CH2
IIB, X=NH
IIC, X=O
IID, X=S



Class III
IIIA, X=CH
IIIB, X=N



Class IV
IVA, X=CH2
IVB, X=NH
IVC, X=O
IVD, X=S

The VEH method has been chosen for this study since it yields ab initio (double-$\zeta$) quality results with negligible computer time.[4,6-8] The VEH method has been shown to give excellent

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(1) Kao, J.; Eyermann, C.; Southwick, E.; Leister, D. *J. Am. Chem. Soc.* **1985**, *107*, 5323. Kao, J.; Huang, T. *Ibid.* **1979**, *101*, 5546.

(2) Luke, L. A.; Kao, J.; Lilly, A. C. *J. Comp. Chem.*, in press.

(3) For example, see: Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(4) Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1979**, *70*, 2020; **1980**, *72*, 453.

(5) (a) Duke, C. B.; Ford, W. K. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1983**, *17*, 597. (b) Duke, C. B.; Ford, W. K. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 177. (c) Duke, C. B. In *Extended Linear Chain Compounds*; Miller, J. S.; Ed., Plenum: New York, 1982; pp 59–125.

(6) Bredas, J. L.; Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1982**, *76*, 3673.

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estimates of electronic properties such as ionization potentials (IP), band widths (BW), bandgaps ($E_g$), and electron affinities (EA).[4-8] $E_g$ values determine the conductivity properties of the undoped systems. IP and EA values of a polymer indicate how easily it can be ionized upon p-type and n-type doping, respectively. BW values of the highest occupied band (HOB) and the lowest unoccupied band (LUB) are a measure of electron delocalization of a polymer and can be roughly correlated with the mobilities of the charge carriers in these bands. It is hoped that systematic studies will give us a better understanding about the structural effects on electronic properties and, thus, provide us better skills in searching for a desirable compound.

VEH results for poly(*p*-phenylene), polyacene, poly(pyridinopyridine), and poly(pyrazinopyrazine) using assumed geometries have recently been reported.[6-8] However, some of these reported theoretical data are in contradiction to experimental results and various explanations have been proposed to account for these apparent differences. Reinvestigation of these polymers with use of better geometries is therefore called for.

## Computational Aspects

**MOMM Calculations.** The molecular structures are optimized with the Kao MOMM approach,[2,9,10] which was developed on the basis of the Allinger force field method.[11,12] The details and force field parameters of the Kao approach can be found in ref 2, 9, and 10. The force field or molecular mechanics (MM) method has been shown to be a very reliable, fast, and efficient way of determining molecular structures, energies, and other properties for a variety of compounds.[3]

In the MOMM approach, all-valence-electron or all-electron molecular orbital (MO) calculations are performed to derive or to modify MM parameters in cases where there are doubts about the capabilities of usual MM methods, while MM calculations are used in the structural optimizations. The CPU time required for MO calculations is then drastically reduced and this makes it feasible to calculate large molecules.

The basic assumptions used in MOMM for the linkage between MO and MM are very similar to those in MMPI and MMPI76.[11,12] Namely, the natural bond length ($l_0$) between atoms i and j, the stretching force constant ($k_s$) between atoms i and j, and the twofold torsional constant ($v_2$) across a double bond are simple functions of a descriptor (X) which can be derived from MO calculations, i.e.

$$l_0 = f(\mathrm{X}) \qquad (1)$$

$$k_s = g(\mathrm{X}) \qquad (2)$$

$$v_2 = h(\mathrm{X}) \qquad (3)$$

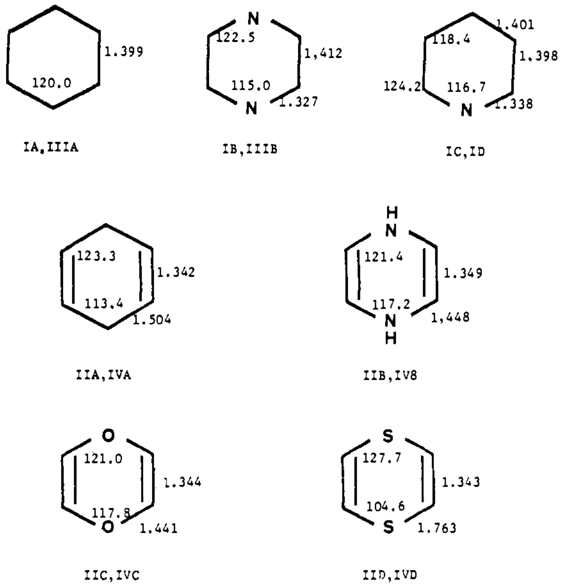
In the initial work,[9] the MNDO method[13] was arbitrarily chosen to test this methodology because of its popularity and X was taken to be the product of the MNDO bond order and core Hamiltonian between the atom pair i and j. However, it was found later that the bond index as defined by Armstrong et al.[14] is more appropriate for this type of approach and is used in the current version.[10] To further reduce CPU time and because of our increasing interest in organometallic compounds, the extended-Hückel method[15] is employed in our current MOMM version.[10]

Table I. Experimental and Theoretical Monomer Structures (Å or deg)

| monomer | structure[a] parameter | exptl[b] | calcd | difference (exptl − calcd) |
|---|---|---|---|---|
| benzene, IA | a | 1.399[c] | 1.399 | 0.000 |
| pyrazine, IB | a | 1.339[d] | 1.327 | 0.012 |
| | b | 1.403 | 1.412 | −0.009 |
| | aa′ | 115.6 | 115.0 | 0.6 |
| | ab | 122.2 | 122.5 | −0.3 |
| pyridine, IC | a | 1.340[e] | 1.338 | 0.002 |
| | b | 1.396 | 1.398 | −0.002 |
| | c | 1.394 | 1.401 | −0.007 |
| | aa′ | 117.0 | 116.7 | 0.3 |
| | ab | 123.8 | 124.2 | −0.4 |
| | bc | 118.5 | 118.4 | 0.1 |
| 1,4-dihydrobenzene, IIA | a | 1.496[f] | 1.504 | −0.008 |
| | b | 1.334 | 1.342 | −0.008 |
| | aa′ | 113.3 | 113.4 | −0.1 |
| | ab | 123.4 | 123.3 | 0.1 |
| 1,4-dioxin, IIC | a | 1.41 (3)[g] | 1.441 | −0.03 |
| | b | 1.35 (3) | 1.344 | 0.01 |
| | aa′ | 116 (4) | 117.8 | −2 |
| | ab | 122 (4) | 121.0 | 1 |
| 1,4-dithiin, IID | a | 1.78 (5)[h] | 1.762 | 0.02 |
| | b | 1.29 (5) | 1.336 | 0.04 |
| | aa′ | 100.2 (2.0) | 102.3 | −2.1 |
| | ab | 124.5 (2.0) | 126.3 | −1.8 |
| | $\varphi$ | 137.0 (2.0) | 150.0 | 13.0 |

[a] See Charts I and II for the parameter definitions. [b] The figures given in parentheses are reported standard deviations. [c] Reference 29a. [d] Reference 43. [e] Reference 44. [f] Reference 45. [g] Reference 46. [h] Reference 47.

Chart I. MOMM Planar Monomer Structures



All theoretical structures for monomers of Classes I–IV were first constructed and fully optimized with this method. Benzene, pyridine, and pyrazine are 6$\pi$-electron systems while the rest of the compounds can be considered to be 8$\pi$-electron systems. For cases where nonplanar (boat) forms are the most stable conformations, the planar forms were also calculated to derive conformational energies. Furthermore, due to our limited scope in the current study as well as our doubt on the accuracy of the current VEH parameters for nonplanar systems, we restrict ourselves to planar polymer systems. However, the recent VEH work[16] seems to indicate that nonplanarity of $\pi$ systems does not drastically change calculated results. Our calculated lowest energy structures are presented in Table I along with respective experimental data. The corresponding planar pentamers or hexamers for Classes I and II and trimers for Classes III and IV (with $C_{2h}$ symmetry if possible) were then constructed with use of planar monomer structures and were also optimized with the same method. The structure of a polymer was then derived by taking

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(7) Bredas, J. L.; Themans, B.; Andre, J. M. *J. Chem. Phys.* **1982**, *78*, 6137.

(8) Bredas, J. L.; Chance, R. R.; Silbey, R.; Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1982**, *77*, 371.

(9) Kao, J.; Leister, D.; Sito, M. *Tetrahedron Lett.* **1985**, *26*, 2403.

(10) Kao, J. *J. Am. Chem. Soc.*, in press.

(11) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893.

(12) Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975.

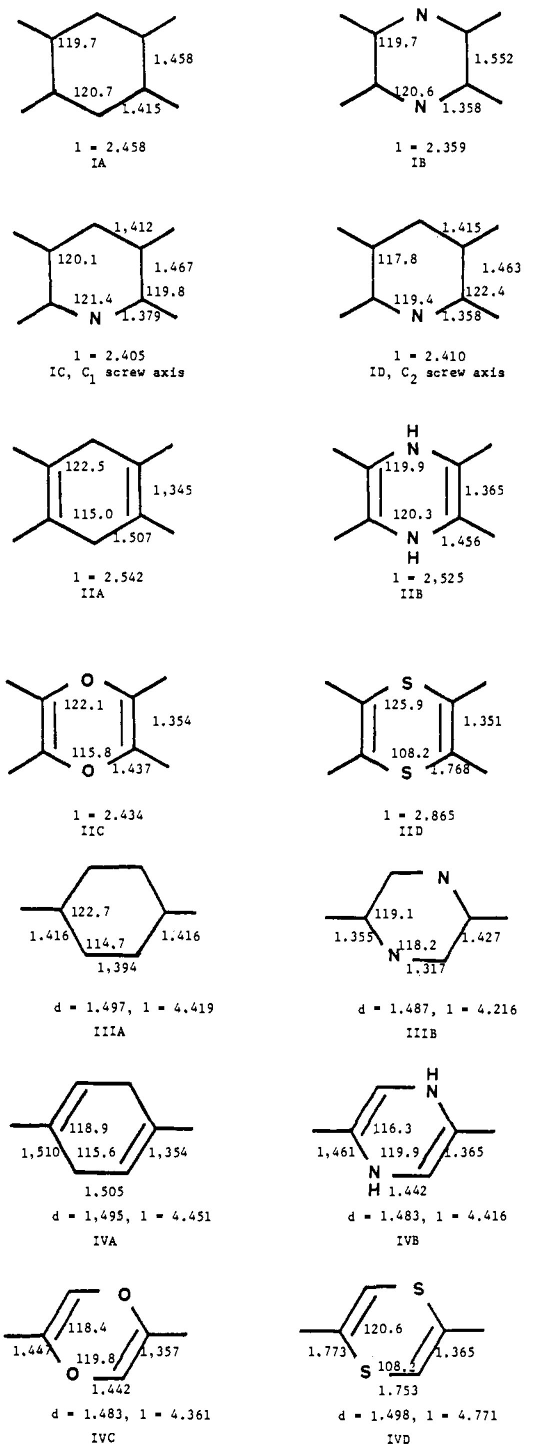
(13) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(14) Armstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc. Dalton Trans.* **1973**, 838.

(15) Hoffman, R. *J. Chem. Phys.* **1963**, *39*, 1937.

(16) Bredas, J. L.; Street, G. B; Themans, B.; Andre, J. M. *J. Chem. Phys.* **1985**, *83*, 1323.

**Chart II.** Unit Cell Structures Used in VEH Calculations



the middle ring structure of the oligomer for the unit cell. Structural parameters for monomers and polymers are presented in Charts I and II (where $l$ is unit cell length and $d$ is interring bond length). The existence of our MOLBUL (Molecular Builder)[17] program has made it a much easier job to construct structures and to derive unit cell lengths for calculations.

**VEH Calculations.** The theoretical method used in this study for calculating electronic properties is the VEH method of Durand and Nicolas[4] which has been adapted to the polymeric case by Andre et al.[18,19] This method has been applied by Bredas et al. to a large range of conducting polymers.[6-8,20-23] The VEH program of Bredas et al. was kindly provided to us and has been installed in our computer systems.

The details of the VEH method are given in ref 4, 18, and 19. In general, the model Hamiltonian consists of a kinetic operator and a sum of effective atomic potentials of the atoms within their specific chemical environment

$$f(\mathrm{i}) = -\frac{1}{2}\nabla_\mathrm{i}^2 + \sum_\mathrm{h}\sum_\mathrm{A} v_\mathrm{A}^\mathrm{h}(\mathrm{i}) \qquad (4)$$

The sums over h and A are for cells and atoms within cells, respectively. The effective potentials are sums of normalized Gaussian projectors, two of which $(t,u)$ are used for the 2s ($l$ = 0) and the 2p ($l$ = 1, $m$ = −1, 0, 1) functions on each atom A

$$V_\mathrm{A}^\mathrm{h}(\mathrm{i}) = \sum_l \sum_m \sum_{t,u} C^\mathrm{A}_{l,m,t,u} |{}^{\mathrm{Ah}}_{lmt}\rangle\langle{}^{\mathrm{Ah}}_{lmu}| \qquad (5)$$

The coefficients, $C^\mathrm{A}_{l,m,t,u}$, and exponents of the Gaussians are optimized in order to reproduce the Fock matrix of a pattern molecule. These parameters are then used in the polymer calculations. The parameters for the sulfur atom and the carbon atoms attached to the sulfur atom ($C_\alpha$) in IID and IVD were developed by Bredas et al.[8] as well as those for C and H atoms in hydrocarbons,[20] which were used for IA, IIA, IIIA, and IVA and for the H and non-$C_\alpha$ atoms in all remaining cases here. The parameters for the N atom and the $C_\alpha$ atoms attached to N were also developed by Bredas et al.[7] The parameters for the O-containing compounds were taken from our previous work.[2]

## Results and Discussion

**Structural Results.** From structural considerations, both boat (V) and planar conformations are possible for 1,4-dihydrobenzene (1,4-cyclohexadiene), 1,4-dihydropyridine, 1,4-dioxin, and 1,4-dithiin. Indeed, the preferred geomerties for these compounds and their derivatives have been the source of many investigations and the center of considerable controversy. While conflicting electron diffraction studies exist, the recent theoretical calculations and experimental studies (including vibrational spectroscopy and NMR) prefer the planar form for 1,4-dihydrobenzene.[24] Although planarity has been assessed both experimentally and theoretically for 1,4-dioxin,[25] the preferred conformation of its congener, 1,4-dithiin, is less certain.[1] Recently, it has been concluded that the conformational preference of 1,4-dithiin is different from that of 1,4-dioxin and the major factor to account for this is the very different natural bond angles for CSC and COC.[1] The small natural CSC bond angles of 1,4-dithiin cause the ring to flap in order to release unfavorable ring strains in the planar form.

V

Calculations here predict that the planar form is the most stable for 1,4-dihydrobenzene and all its hetero substitution derivatives with the exception of 1,4-dithiin. Theoretically, if the boat form is preferred (as the case in dithiin), the polymer can have two possible spatial arrangements (VI). However, even if the boat

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[17] Kao, J.; Day, V.; Watt, L. *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 129. Kao, J.; Eyermann, C.; Watt, L.; Maher, R.; Leister, D. *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 400.

[18] Andre, J. N.; Burke, L. A.; Delhalle, J.; Nicolas, G.; Durand, Ph. *Int. J. Quantum Chem.* **1979**, *S13*, 283.

[19] Nicolas, G.; Durand, Ph.; Burke, L. A. In *Lecture Notes in Physics*; Andre, J. M., et al., Eds.; Springer-Verlag: Berlin, 1980; No. 113, p 201.

[20] Bredas, J. L.; Chance, R. R.; Silbey, R.; Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1981**, *75*, 255.

[21] Bredas, J. L.; Elsenbaumer, R. L.; Chance, R. R.; Silbey, R. *J. Chem. Phys.* **1983**, *78*, 5656.

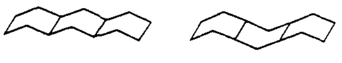
[22] Bredas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555.

[23] Andre, J. M.; Vercauteren, D. P.; Street, G. B.; Bredas, J. L. *J. Chem. Phys.* **1984**, *80*, 5643. Themans, B.; Andre, J. M.; Bredas, J. L. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 121.

[24] For example, see: Rabideau, P. W.; Lipkowitz, K. B.; Nachbar, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 3119.

[25] Gershbein, L. L. *Res. Commun. Chem. Pathol. Pharmacol.* **1975**, *11*, 445.

is preferred, the butterfly-flapping potential is *extremely* shallow and conformational equilibrium can easily be modified by solvent or other effects.[1] Thus, we shall limit our studies to *planar* systems.



VI

For Class III and IV compounds, the two X groups (X = $CH_2$, N, O, or S) attached to a bridge (interring) bond may be pointing in opposite (anti) or the same (syn) direction. We have attempted to explore this conformational preference by studying anti and syn conformations of their oligomers. In all cases, the most stable planar conformations are those with the two nearest X groups (i.e., one X from each ring) pointing in opposite directions. The conformational characteristics of these compounds can be understood by examining their dimers.

For an introduction, let us first look at the potential function of biphenyl. Steric crowding due to 1,6 (neighboring) H- - -H close contacts exists at the planar conformation. However, the conjugation energy is expected to favor the planar conformation and to disfavor the perpendicular form. A compromise of these two opposing forces is evident from experimental and theoretical data. The gas-phase value for the torsional angle about the central bond of biphenyl (**2**) is 42 + 5° experimentally,[26] and the MOMM value is 40°. Furthermore, previous various theoretical estimates[27] of the barrier heights for biphenyl are 1.2–4.8 kcal/mol at the planar form and 2.0–4.5 kcal/mol at the perpendicular form. MOMM predicted that the barrier heights are 1.8 and 1.5 kcal/mol respectively at the planar and perpendicular forms. Introducing N atoms into the phenyl rings at the 2 and 2′ positions will not only reduce interring van der Waals interactions but also favor the anti conformation due to dipolar interactions. Thus, the anti form of bipyrazyl is strongly favored over the syn conformation by ca. 6 kcal/mol.

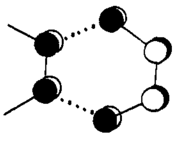
The preference of the anti conformation of IVA dimer over the syn form is calculated to be 3.2 kcal/mol, which is about the size of the syn–anti difference of 2,3-dimethylbutadiene. Thus, the conformational preference of the IVA dimer and 2,3-dimethylbutadiene may be rationalized in the same way.[10,28] The energy differences between syn and anti conformations are estimated to be 5, 5, and 4 kcal/mol respectively for IVB, IVC, and IVD dimers. Thus, a similar trend is observed for both Class III and IV compounds; heteroatom substitutions result in the increase of syn–anti energy difference.

Presented in Table I are calculated and experimental data for benzene, pyridine, pyrazine, 1,4-dihydrobenzene, 1,4-dihydropyrazine, 1,4-dioxin, and dithiin. As can be seen from Table I, the calculated structural parameters are all in good agreement with experimental values (mean deviation for bond length = 0.012 Å; mean deviation for bond angle = 0.8°). Theoretical monomer structures for planar conformations are also schematically presented in Chart I to facilitate our discussion.

In principle, we should calculate oligomers larger than pentamers or hexamers for Class I and II compounds and larger than trimers for Class III and IV compounds to derive corresponding polymer structures. However, because of the size of the compounds, we decided to limit ourselves to no more than 6 unit cells for this study. Moreover, the relatively small structural changes in going from a tetramer to a pentamer for Classes I and II as well as from a dimer to a trimer for Classes III and IV for several cases examined seem to justify the way we derive polymer structures for this study. The obtained unit cell structures are shown in Chart II.

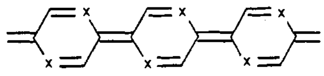
By comparing structures presented in Charts I and II, one observes several important and interesting structural changes in going from monomers to polymers (oligomers). There are substantial elongations of the central bonds for Class I compounds. While similar trends can also be recognized for Class II compounds, the changes are much smaller. These calculated bond elongations are consistent with experimental and theoretical data for benzene, naphthalene, anthracene, and tetracene. The experimental and theoretical (in parentheses) data for these central bonds are respectively 1.399 (1.399)[29a] Å for benzene, 1.422 (1.435)[29b] Å for naphthalene, 1.43 (1.447)[29c] Å for anthracene, as well as 1.420 (1.452) and 1.460 (1.455)[29d] Å for tetracene. One notes that changes in the experimental bond length in going from small to large molecules are well reproduced by the theory.

Theoretically, these bond elongations can be rationalized by considering oligomers as composed of two small parts. Class I compounds may be treated as an attachment of a 4$\pi$-electron system to a 2$\pi$-electron system (i.e., omitting the rest of the oligomer as a first approximation). The donor–acceptor interaction (VII) involves two electrons and will stabilize the system. The structural consequence due to interaction VII is a bond elongation of the donor bond. Donor–acceptor interactions may also be visualized for a 6$\pi$-electron system and a 2$\pi$-electron system to approximate Class II compounds. However, these interactions would be much smaller since the C–X single bond is longer and the overlap is therefore smaller.



VII

Bond elongations are observed for the C=C double bonds of Class III and IV polymers as compared with the corresponding monomers. They may be rationalized in terms of conjugation of double bonds across unit cells. Schematically, one may say that the resonance structure such as VIII is important for these compounds. Resonance structure VIII is expected to cause an increase in the C–X single bond, and this is indeed shown in the calculated results.



VIII

The ring structure of a trimer in Classes III and IV is similar to the corresponding monomer with the exception of the bond angles involving the interring atoms. The variation (<0.015 Å) of the interring bond distance, *d*, appears to be smaller than that of the bond angles involving interring atoms. This is as expected since it is easier to bend a bond angle than to stress a bond. In going from monomers to polymers, there is a consistent decrease of the CCX bond angle of a unit cell, which may be attributed to the steric repulsions between unit cells and/or to the rigidity of CCC in the polymer being higher than the counterpart, CCH, in a monomer. The calculated bridge bond lengths for III and IV range from 1,483 to 1.498 Å, which can be compared with the experimental value of 1.489 Å found in biphenyl.[30]

Variations in the calculated unit cell structures are large for all classes of polymers studied here. Thus, hetero substitutions have made significant structural modifications on these polymers, and their effects on electronic properties will be explored in the following.

**Electronic Properties.** The calculated band structures for the 14 polymers considered here are respectively given in Figure 1. They are computed by taking into account the screw axis symmetry of order two whenever it is present in the polymers. The potential quantities derived from band structure calculations which are useful in the prediction of conductivity are the theoretical

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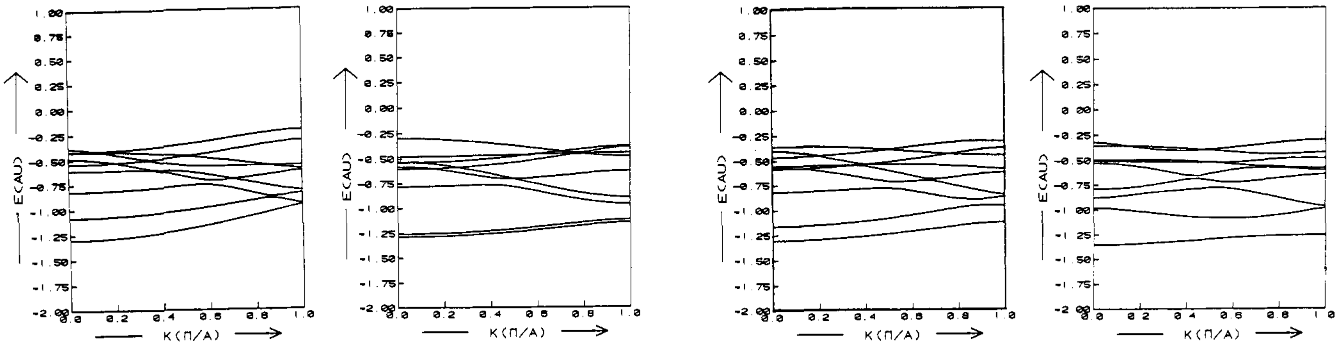
[26] Bastiansen, O.; Skancke, A. *Acta Chem. Scand.* **1967**, *21*, 587.

[27] Stolevik, R.; Thingstad, O. *Theochem.* **1984**, *106*, 333.

[28] Kavana-Saebo, K.; Saebo, S.; Boggs, J. E. *Theochem.* **1984**, *106*, 259.

[29] (a) Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243. (b) Bastiansen, O.; Skancke, P. N. *Adv. Chem. Phys.* **1961**, *3*, 323. (c) Mason, R. *Acta Crystallogr.* **1964**, *17*, 547. (d) Campbell, R. B.; Robertson, J. M.; Trotter, J. *Acta Crystallogr.* **1962**, *15*, 289.

[30] (a) Bastiansen, O.; Traetteberg, M. *Tetrahedron* **1962**, *17*, 147. (b) Almenningen, A.; Bastiansen, O. *Skr. K. Nor. Vidensk. Selsk* **1958**, *4*, 1.

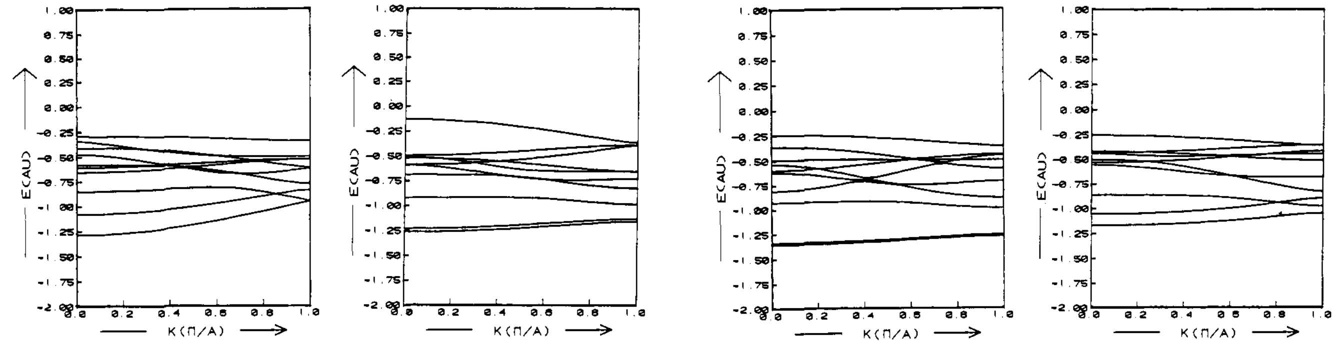


(1a) Polyacene

(1b) Polypyrazinpyrazine

(1c) Polypyridinopyridine ($C_1$ - screw axis)

(1d) Polypyridinopyridine ($C_2$ - screw axis)

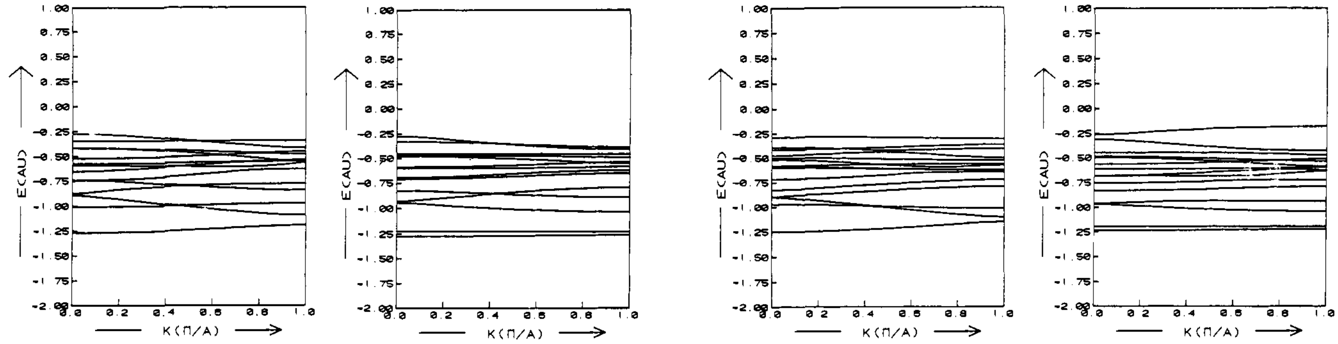


(1e) Poly(1,4-dihydrobenzo-1,4-dihydrobenzene)

(1f) Poly(1,4-dihydropyrazino-1,4-dihydropyrazine)

(1g) Poly(1,4-dioxino-1,4-dioxine)

(1h) Poly(1,4-dithiino-1,4-dithiin)

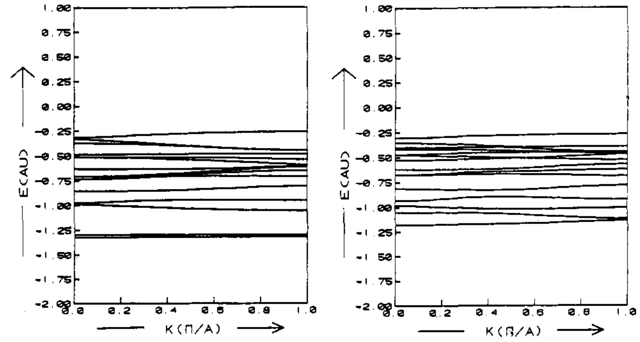


(1i) Poly(p-phenylene)

(1j) Poly(p-pyrazine)

(1k) Poly(p-1,4-dihydrobenzene)

(1l) Poly(p-1,4-dihydropyrazine)



(1m) Poly(p-1,4-dioxin)

(1n) Poly(p-1,4-dithiin)

**Figure 1.** Band structures.

ionization potential (IP), band width of the highest $\pi$ band (BW), and the bandgap ($E_g$). Electron affinity (EA) can be calculated in the usual way as IP - $E_g$. These results are presented in Table II. One notes that theoretical IP values shown in Table II have to be reduced by 1.9 eV in order to approximately account for the polarization energy of lattice.[6-8]

In order to compare these theoretical results to the experimental values in electrochemistry, oxidation ($E_O$) and reduction ($E_R$) potentials in volts vs. the saturated calomel electrode (SCE) have been calculated with relations 6 and 7. These calculated values are also listed in Table II. These empirical relationships between

$$E_O = \mathrm{IP} - 6.3 \tag{6}$$

$$E_R = \mathrm{EA} - 6.3 \tag{7}$$

theoretical quantities and experimental potentials have been found

**Table II.** Calculated Band Width (BW), Ionization Potential (IP), Bandgap ($E_g$), Electron Affinity (EA), Oxidation Potential ($E_O$), and Reduction Potential ($E_R$)[a]

| polymer | BW | IP | $E_g$ | EA | $E_O$ | $E_R$ | ref |
|---|---|---|---|---|---|---|---|
| IA | 5.3 | 6.0 | 0.2 | 5.8 | −0.3 | −0.3 | this work |
| | 5.9 | 5.8 | 0.0 | 5.8 | −0.5 | −0.3 | 7 |
| IB | 4.0[b] | 8.1[b] | 0.0 | 8.1 | 1.8 | 1.8 | this work |
| | 5.1[b] | 8.1[b] | 0.0 | 8.1 | 1.8 | 1.8 | 8 |
| | 4.3 | 10.4 | 2.2 | 8.2 | 4.1 | 1.9 | this work |
| IC | 3.9 | 8.7 | 2.9 | 5.7 | 2.4 | −0.6 | this work |
| | 4.3 | 8.7 | 3.0 | 5.7 | 2.4 | −0.6 | 8 |
| ID | 0.6 | 8.2 | 0.6 | 7.6 | 1.9 | 1.3 | this work |
| IIA | 1.5 | 8.1 | 6.1 | 2.0 | 1.8 | −4.3 | this work |
| IIB | 6.5 | 3.5 | 5.1 | −1.6 | −2.8 | −7.9 | this work |
| IIC | 3.2 | 6.6 | 8.6 | −2.0 | 0.3 | −8.3 | this work |
| IID | 2.6 | 6.8 | 2.7 | 4.1 | 0.5 | −2.2 | this work |
| IIIA | 3.8 | 7.3 | 2.9 | 4.4 | 1.0 | −1.9 | this work |
| | 3.5 | 7.5 | 3.5 | 4.0 | 1.2 | −2.3 | 8 |
| IIIB | 3.7 | 7.5 | 2.0 | 5.5 | 1.2 | −0.8 | this work |
| IVA | 0.7 | 7.6 | 4.2 | 3.4 | 1.3 | −2.9 | this work |
| IVB | 2.2 | 4.9 | 5.6 | −0.7 | −1.4 | −7.0 | this work |
| IVC | 1.7 | 7.0 | 6.2 | 0.8 | 0.7 | −5.5 | this work |
| IVD | 0.9 | 7.4 | 2.2 | 5.2 | 1.1 | −1.1 | this work |

[a] The values of $E_O$ and $E_R$ are with respect to the saturated calomel electrode (SCE). All units are in eV or volts. [b] Refer to the highest occupied $\sigma$ band, see text for discussion.

to hold for the IP and $E_g$ calculated by the VEH method for polyacetylene, poly(*p*-phenylene), polypyrrole, and polythiophene.[22] These relations are quite close to those found by taking experimental values of gas-phase IP and the first optical transition for molecules.[31]

Before we discuss VEH results, we shall discuss some potential VEH pitfalls which exist under the current parametrization. In our opinion, these pitfalls have to be carefully taken into consideration since they may greatly influence the interpretation of results for certain systems.

It has been mentioned in the early VEH publications[6,7] of Bredas et al. that excited $\sigma^*$ levels of propene and butadiene appear too close to the highest occupied $\pi$ levels and this fact may lead to the presence of spurious $\sigma^*$ bands unusually low in energy. However, by our experience, this VEH problem (presumably due to this version of parametrization) is probably more serious for certain cases than one would expect. In fact, we now tend to conclude that the current VEH universal parameters appear to have general problems with the relative stabilities of high-lying $\sigma$ and $\pi$ orbitals around the filled and unfilled boundary region. Thus, wrong ordering of orbitals may exist for certain compounds with conjugated $\pi$ systems. This is rather unfortunate since HOMO and LUMO (or HOB and LUB) are frontier orbitals and are of particular interest and importance to chemical processes. Nevertheless, one may overcome these shortcomings by systematic corrections. These findings are consistent with those stated in Bredas' papers. This will be illustrated by considering the following two examples.

Consider first the pyridine case. It has been shown experimentally[32] that $a_1$ and $a_2$ orbitals of pyridine have about the same energy (i.e., accidentally degenerate). However, according to Koopmans' theorem (KT)[33] and the VEH method, the $\pi$ orbital ($a_2$) is the HOMO for pyridine, being subtantially higher in energy than the $\sigma$ nonbonding ($a_1$) orbital by 1.2 eV. This problem is presumably due either to the fact that the current VEH pseudopotentials are derived from 4-31G energies and STO-3G MO coefficients or to the breakdown of KT, which is notable for the nitrogen-containing molecules.[32,34] However, the cause of inconsistency between theory and experiment is an unimportant issue here. What we need to know is that, as compared with experimental values, the IP value for the $\sigma$ lone pair orbital may be consistently and erroneously positioned with respect to $\pi$ orbitals for similar compounds by VEH calculations. In fact, by assuming that the VEH method systematically underestimates the stabilities of the highest occupied $\pi$ orbitals of the pyridyl ring, it was found that the corrected HOMO energies for a set of nicotine-related compounds are more in line with experimental IP values.[35] This provides us with confidence in our interpretation.

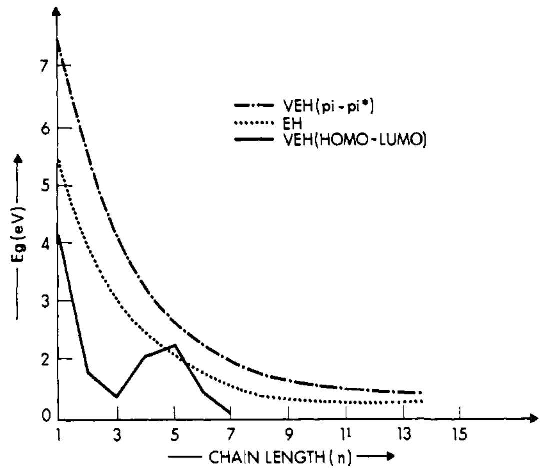


**Figure 2.** LUMO − HOMO (LUB − HOB) energy difference vs. chain length.

VEH calculations on the oligomers of IA provide another interesting example. It has been a general practice to predict polymer properties based on extrapolation from oligomer data. For instance, a smooth curve has been shown to exist between the (theoretical and experimental) bandgap (LUMO − HOMO) and chain length (or a reciprocal chain length) for a number of oligomers.[22,36] The VEH and extended-Hückel (EH) calculated results for oligomers of IA are presented in Table III. These theoretical data for the bandgap ($E_g$) vs. chain length ($n$, number of chain length) are plotted in Figure 2. As can be seen from Table III, EH correctly predicts the right orderings for HOMO and LUMO. On the other hand, $\pi$ orbitals have been erroneously displayed toward higher number of orderings by the VEH method. Indeed, a rather peculiar graph is obtained by plotting $E_g$ vs. $n$ for these VEH results without considering these wrong orderings. Fortunately, $\sigma$–$\pi$ separation can be applied to planar systems and one may thus omit these high-lying $\sigma$ orbitals without severe effects on results of interest to us. In fact, the bandgap corrected by eliminating spurious high-lying $\sigma$ orbitals is linearly correlated with the chain length.

In theory, no information pertaining to the excited states is included in deriving the universal atomic potentials of Bredas et al.[6-8] The results for unoccupied orbitals (including values derived from them) are thus expected to be inferior to those for occupied orbitals. This applies particularly to cases such as $\pi$–$\sigma^*$ and $\sigma$–$\pi^*$ transitions. For instance, without taking these shortcomings into consideration, one may erroneously predict metallic properties for compounds such as poly(*p*-phenylene) and poly(1,4-dihydrobenzo-1,4-dihydrobenzene). One must thus be careful in interpreting systems which are *aromatic*, *nonplanar*, and including *lone-pair* electrons. Because of these limitations, we will concentrate mainly on $\pi$–$\pi^*$ transitions of planar systems.

Consider in this case the excitation of only one electron, namely transitions normally associated with electronic absorption spectra. The usual SCF-LCAO-MO model is to approximate the excited state by a state resulting from the removal of an electron from an occupied MO to a virtual orbital. Thus, transitions calculated

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(31) Miller, L. L.; Norblum, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916. Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 5656. Loufty, R. O.; Still, I. W. J.; Thompson, M.; Leong, T. S. *Can. J. Chem.* **1979**, *57*, 638.

(32) Cederbaum, L. S.; Niessen, W. von *J. Chem. Phys.* **1975**, *62*, 3824.

(33) Koopmans, T. *Physica* **1933**, *1*, 104.

(34) Niessen, W. von; Diercksen, G. H. F.; Cederbaum, L. S. *Chem. Phys.* **1975**, *10*, 345.

(35) Kuhn, W.; Leister, D.; Kao, J.; Lilly, A. C. *Chem. Phys. Lett.*, in press.

(36) For example: Norinder, U.; Wennerstrom, O.; Wennerstrom, H. *Tetrahedron* **1985**, *41*, 713.

**Table III.** Orbital Types and Orderings and Energy Differences ($E_g$), in eV, between LUMO and HOMO of Linearly Fused Benzene Rings (IA)

| | | | | VEH | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| no. of unit cells | EH | | | uncorrected | | | corrected | | |
| | HOMO | LUMO | $E_g$ | HOMO | LUMO | $E_g$ | HOMO | LUMO | $E_g$ |
| 1 | $\pi(0)$ | $\pi(1)$ | 4.5 | $\pi(0)$ | $\sigma(1)$ | 3.1 | $\pi(0)$ | $\pi(2)$ | 6.8 |
| 2 | $\pi(0)$ | $\pi(1)$ | 2.9 | $\pi(0)$ | $\sigma(1)$ | 0.8 | $\pi(0)$ | $\pi(3)$ | 4.5 |
| 3 | $\pi(0)$ | $\pi(1)$ | 2.0 | $\sigma(0)$ | $\pi(1)$ | 0.4 | $\pi(1)$ | $\pi(3)$ | 3.2 |
| 4 | $\pi(0)$ | $\pi(1)$ | 1.5 | $\sigma(0)$ | $\pi(1)$ | 1.1 | $\pi(1)$ | $\pi(3)$ | 2.3 |
| 5 | $\pi(0)$ | $\pi(1)$ | 1.1 | $\pi(0)$ | $\sigma(1)$ | 1.3 | $\pi(2)$ | $\pi(4)$ | 1.7 |
| 6 | $\pi(0)$ | $\pi(1)$ | 0.8 | $\pi(0)$ | $\sigma(1)$ | 0.5 | $\pi(2)$ | $\pi(4)$ | 1.3 |
| 7 | $\pi(0)$ | $\pi(1)$ | 0.6 | $\sigma(0)$ | $\pi(1)$ | 0.1 | $\pi(2)$ | $\pi(4)$ | 1.0 |
| . | . | . | . | . | . | . | . | . | . |
| . | . | . | . | . | . | . | . | . | . |
| ∞ | | | 0.3[b] | | | | | | 0.5[b] |

[a] Numbers in parentheses correspond to the number of orderings above the highest occupied orbital. [b] Extrapolated value.

with the Hartree–Fock method are usually in poor agreement with experimental data since the differences in electronic correlation between the excited and ground states are not correctly accounted for. However, for some reasons, the $\pi$–$\pi^*$ bandgaps for several polymers are quite accurately reproduced by employing the VEH method.[6–8] This may be illustrated by considering the polyacene oligomers, where their IPs and $E_g$s are experimentally known.[37a] The experimental and VEH (in parentheses) IPs for benzene, naphthalene, anthracene, naphthacene, and pentacene (IA, number of unit cells = 1 ∼ 5) are respectively 9.24 (9.34), 8.15 (8.18), 7.40 (7.48), 7.01 (7.04), and 6.64 (6.74) eV. The agreement between experiment and theory is excellent. Similar good results were obtained from CNDO/S2 calculations,[37b] if a systematic correction of −0.8 eV is made from the negative of the HOMO eigenvalue. On the other hand, the $\pi$–$\pi^*$ transitions for these molecules appear to be less well reproduced by the VEH method. The experimental[37c] and VEH (in parentheses) values for $\pi$–$\pi^*$ transitions are 4.72 (6.79), 3.99 (4.54), 3,31 (3.18), 2.63 (2.32), and 2.12 (1.74) eV respectively for benzene, naphthalene, anthracene, naphthacene, and pentacene. One notes that although the agreement between experiment and theory is poor for small oligomers, the agreement becomes reasonable for medium-to-large oligomers. This observation is consistent with the good VEH results for polymers. However, the bandgaps obtained from the VEH method may have to be taken with reservation. The CNDO/S2 parametrization has been shown to accurately reproduce the first ($\pi$–$\pi^*$) singlet excitation energies for these compounds (4.75, 4.09, 3.36, 2.77, and 2.38 eV respectively for benzene, naphthalene, anthracene, naphthacene, and pentacene), presumably due the adequate inclusion of electronic correlation effects through configuration interactions.[37b]

As mentioned earlier, hetero substitutions have made significant structural modifications on these oligomers. Examination of calculated results reveals that the HOB contains contributions from all boundary atoms of a unit cell and heteroatoms. Thus, one expects large electronic consequences resulting from these modifications. This situation here is very different from the dibenzo case where the HOB contains no contributions from heteroatoms.[2] We shall discuss calculated electronic properties as a whole first and subsequently present them in terms of classes.

As can be seen in Figure 1, the HOBs of Classes II and IV do not interact with the rest of the bands. Due to fewer bridged atoms per unit cell, Class IV polymers appear to have weaker interactions among unit cells, which results in more flat $\pi$ HOBs. By examining calculated IP and BW values, one may conclude that, within each class, the –NH– functional group is the most effective in interacting with neighbors and the $-CH_2-$ the least effective.

IP values of monomers are 9.34, 9.55, 9.57, 8.77, 5.87, 7.98, and 7.77 eV respectively for benzene, pyridine, pyrazine, 1,4-dihydrobenzene, 1,4-dihydropyrazine, 1,4-dioxin, and 1,4-dithiin. The corresponding experimental IPs[38] are 9.24, 9.59, 9.62, 8.82, 8.13, and 8.15 eV respectively for benzene, pyridine, pyrazine, 1,4-dihydrobenzene, 1,4-dioxin, and 1,4-dithiin. The agreement between experimental and theoretical values is excellent. The 1,4-dihydropyrazine molecule appears to have the lowest IP value among all monomers studied here. Effects of the low IP value of 1,4-dihydropyrazine are manifested in polymers; both IIB and IVB have the lowest IP value within its class. Similarly, poly(*p*-aniline) has been calculated to have a lower IP value than both poly(*p*-phenylene sulfide) and poly(*p*-phenylene oxide).[23] Polymers with lower IP values can be p-doped with weaker acceptors. Thus, compounds with the –NH– unit should be more p-dopable than their $-CH_2-$, –O–, and –S– counterparts. This is an important concept in designing conducting polymers.

Changes in IP values from monomers to polymers reflect the extent of cell interactions in polymers. According to our calculations, only IA, IC, ID, IIIA, and IIIB show large changes (ca. 2 eV or larger) in IP values, this being consistent with the predicted low $E_g$ and moderate BW values for these polymers. Only sulfur-containing polymers among other polymers listed in Table II display low $E_g$ values. Since the IP and $E_g$ differences between monomers and polymers for IID and IVD are not much different from those for other Class II and IV compounds, the low $E_g$ value of sulfur-containing polymers is due to the low-lying nature of their LUBs. The LUB (LUMO) low-lying nature of these sulfur-containing compounds comes from the inherent nature of S atoms and their spatial requirements (see Chart I) in forcing close nonbonded C- - -C contacts. The lower $E_g$ of sulfur-containing polymers does not have much to do with $\pi$-electron delocalizations in the ground state.

It has been suggested that since polythiophene and polyacetylene can be n-doped by sodium naphthalide while polypyrrole cannot be, the $E_R$ of polypyrrole must be more negative than −2.9 V.[22] According to our calculations, IB, IC, ID, IID, IIIA, IIIB, and IVD should be n-dopable by sodium naphthalide.

**A. Class I Compounds.** Polyacene has been reported to exist as high molecular weight polymers.[39a] The VEH calculations on polyacene have been reported[6] previously, and they are also presented in Table II along with results obtained from this work. In both cases, similar (low IP and large BW) values are predicted. However, in contrast with previous results, we predict that the $E_g$ of polyacene is about 0.2 eV while it was shown to be zero for equal C=C bonds. The discrepancy comes from (a) the elimination of non $\pi$–$\pi^*$ transitions from consideration in this work and (b) the structures used in VEH calculations being different. MOMM optimized geometry is shown in Chart II, which is

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(37) (a) Clark, P. A.; Brogli, F.; Heilbronner, E. *Helv. Chim. Acta* **1972**, *55*, 1415. (b) Lipari, N. O.; Duke, C. B. *J. Chem. Phys.* **1975**, *63*, 1768. (c) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970; p 70.

(38) (a) Turner, D. W.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley-Interscience: London, 1970. (b) Gleiter, R.; Heilbronner, E.; Hornung, V. *Agnew. Chem., Int. Ed. Engl.* **1970**, *82*, 878. (c) Eland, J. H. D. *Int. J. Mass Spectrom. Ion Phys.* **1969**, *2*, 471. (d) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213. (e) Bloch, M.; Brogli, F.; Heilbronner, E.; Jones, T. B.; Prinzbach, H.; Schweikert, O. *Ibid.* **1978**, *61*, 1388. (f) Colonna, F.; Distefano, G. *J. Electron Spectrosc. Rel. Phenom.* **1980**, *18*, 75.

(39) (a) Kasatochkin, V. I.; Mel'nichenko, V. M.; Elizen, V. M. *Vis. Soed.* **1975**, *A17*, 1883. (b) Whangbo, M. H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London Ser.* **1979**, *A366*, 23.

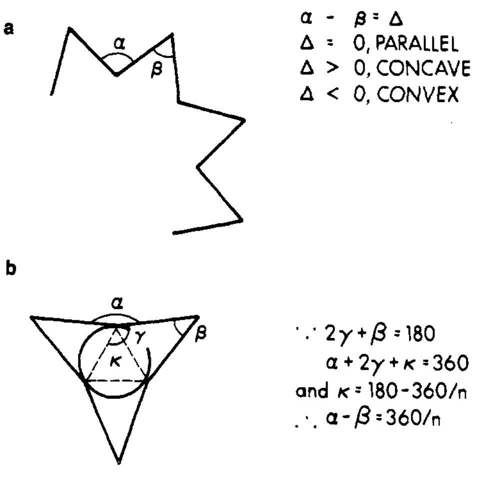
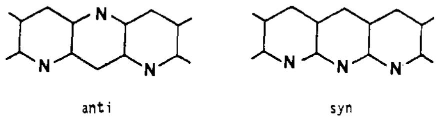


**Figure 3.** Distorsion of linear polymers.

somewhat different from the assumed geometry used in the previous work (1.40 Å for the two chains and 1.44 Å for the bonds connecting the two chains). Note that extrapolation from oligomers to polymers also appears to favor a small bandgap of ca. 0.5 eV for the VEH method. The EH bandgap extrapolated from oligomers is similar to this VEH value, which seems to contradict the well-known tendency that the EH method tends to predict small bandgaps.[7,39b]

Poly(pyrazinopyrazine) (paracyanogen) has been previously calculated with use of standard geometrical parameters and the VEH method.[7] It was predicted to be metallic, which is in disagreement with experimentally observed semiconducting behavior.[40] This discrepancy has been attributed to the low molecular weights of poly(pyrazinopyrazine) synthesized so far.[7] Although our calculated results using the MOMM optimized geometry are not much different from previous VEH results, we feel the VEH data can be interpreted in a different way by considering the $\pi$–$\pi^*$ transition. An $E_g$ value of 2.2 eV is obtained for the $\pi$–$\pi^*$ transition. Thus, poly(pyrazinopyrazine) should not have metallic properties.

Theoretically, poly(pyridinopyridine) can have two configurations, where heteroatoms may point in the same (syn) or opposite (anti) directions (IX). By symmetry, the anti form may have a twofold ($C_2$) screw axis. On the other hand, due to the inequivalence of bond angles CNC and NCN, the syn form is not a linear one-dimensional polymer and has no screw axis. Thus, without structural approximations (distortions) or program modification, the current VEH program may not be used to accurately calculate poly(pyridinopyridine). How accurate a calculation can be achieved by forcing a nonlinear polymer to become a linear one depends on the degree of distortion. The following analysis is performed in order to assess the degree of distortion and accuracy of calculations. Figure 3a schematically illustrates a possible structural distortion from linearity. The degree of distortion from linearity can be measured by calculating the difference in two bond angles, $\alpha$ and $\beta$. Another way to appreciate the curvature of a polymer is to calculate the number of unit cells ($n$) needed to make a complete circle. This is demonstrated in Figure 3b.



IX

MOMM calculations were carried out for the syn pentamer of IC by both full and partial optimizations. Partial optimization is obtained by restricting all heteroatoms on the same axis. Comparison of partially and fully optimized geometries shows that the distortions from linearity are very small. By considering the middle ring, the calculated parameters for the fully optimized pentamer are CNC = 121.4°, NCN = 119.6°, $\Delta \sim 2°$, $n \sim 180$. This indicates that the syn form of poly(pyridinopyridine) can be reasonably calculated by assuming a linear geometry. There is no surprise to find that our VEH results for the linear syn configuration are very similar to those reported earlier because the standard bond angles used in the previous work are good approximations for this case and the unit cell structures used in both calculations are similar. The predicted bandgap (3.0 eV) is large, which appears to be in contradiction to the experimentally observed high conductivity (5 S/cm) on pure poly(pyridinopyridine).[41]

VEH calculations for the anti form of poly(pyridinopyridine) (ID) are, on the other hand, straightforward since it is a linear polymer by symmetry. Calculated results for ID are somewhat different from those of IC. The IP, BW, and $E_g$ values of the former are respectively 0.5, 3.2, and 2.4 smaller than those of the latter. The small $E_g$ value of ID seems to imply that the experimentally observed conductivities for poly(pyridinopyridine) may correspond to a mixture of syn and anti forms. However, the discrepancy may also be attributed to the low molecular weights synthesized so far.[7]

**B. Class II Compounds.** Class II compounds have longer unit cell lengths than their Class I counterparts and $\pi$ delocalization is less effective in Class II than in Class I structures. As expected, calculated $E_g$ values for Class II compounds are substantially larger than the corresponding Class I compounds. Class II compounds are thus expected to have lower intrinsic conductivities as pure compounds than their Class I equivalents.

IID is of special interest since it is predicted to have a relatively small $E_g$ (2.7 eV) as well as moderate BW (2.6 eV) and IP (6.8 eV) values, which are all compatible with those of conjugated systems such as polypyrrole and polythiophene.[22] Similar observations have been found by Bredas et al. by comparing experimental and theoretical data of poly($p$-phenylene) and poly($p$-phenylene sulfide).[8] Thus, one may conclude that sulfur atoms play an effective role in connecting (either conjugated or nonconjugated) $\pi$ systems as far as conductivity is concerned. Sulfur atoms may thus be effectively used in improving the polymer conductivities by tinkering with its structure.

IIB is also theoretically interesting because of the calculated low IP and large BW values. Thus, IIB may be very unstable and can be easily p-doped by weak acceptors.

**C. Class III Compounds.** Our VEH results for poly($p$-phenylene) are similar to those reported previously,[8] and the corrected IP value (5.4 eV) is close to the 5.5 eV experimental estimate.[42a] There are small, yet significant differences and they can be ascribed to different geometries used in the calculations. As pointed out previously, the calculated wide bandgap explains the low intrinsic conductivity of IIIA, smaller than $10^{-15}$ S/cm at room temperature.[42b] The calculated $E_g$ value is 2.9 eV, which may be compared with the experimental estimate of 3.4 eV.[6] The large IP value is consistent with the fact that only strong acceptors, such as $AsF_5$, effectively dope IIIA.

Poly($p$-pyrazine) (IIIB) is of particular interest to us since it is calculated to have a bandgap which is about 0.9 eV smaller than

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(40) Paushkin, Y.; Vishnyakova, T. P.; Lunin, A. F.; Nizova, S. A. *Organic Polymer Semiconductor*; Wiley: New York, 1974.

(41) Teoh, H.; Metz, P. D.; Wilhelm, W. G. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 297.

(42) (a) Gelius, U. In *Electron Spectroscopy*; Shirley, D. A., Ed.; North-Holland: Amsterdam, 1972; p 311. (b) Ivory, D. M.; Miller, G. G.; Sowa, J. M.; Shacklette, L. W.; Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1979**, *71*, 1506.

(43) Bormans, B. J. M.; Dewith, G.; Mijbhoff, F. C. *J. Mol. Struct.* **1977**, *42*, 121.

(44) Mata, G.; Quintana, M. J.; Sorensen, G. O. *J. Mol. Struct.* **1977**, *42*, 1.

(45) Dallinga, G.; Toneman, L. H. *J. Mol. Struct.* **1967**, *1*, 117.

(46) Beach, J. Y. *J. Chem. Phys.* **1941**, *9*, 54. Lord, R. C.; Rounds, T. C. *J. Chem. Phys.* **1973**, *58*, 4344. Connett, J. E.; Creighton, J. A.; Green, J. H. S.; Kynaston, W. *Spectrochim. Acta* **1966**, *22*, 1859.

(47) Parham, W. E.; Wynberg, H.; Hasek, W. R.; Howell, P. A.; Curtis, R. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1954**, *76*, 4957. Howell, P. A.; Curtis, R. M.; Lipscomb, W. N. *Acta Crystallogr.* **1954**, *7*, 498.

that of IIIA. The IP and BW values of IIIB are compatible to those of IIIA. Thus, IIIB should have higher intrinsic conductivity than IIIA. Since only doped polyacetylene (ca. 1000 S/cm) provides higher conductivity than IIIA (ca. 500 S/cm),[42] IIIB would be of particular interest in the conducting polymers area.

Both the interring distance (*d*) and the unit cell length (*l*) are smaller in IIIB than in IIIA. This may account for the smaller $E_g$ value in the former, since smaller *d* and *l* values would increase the interaction between the basis functions on adjacent rings. Poly(*p*-pyridine) is another interesting polymer, but it is not calculated here due to its low symmetry. However, one may propose that poly(*p*-pyridine) should have electronic properties similar to poly(*p*-phenylene) and poly(*p*-pyrazine) on the basis of structural considerations.

**D. Class IV Compounds.** Class IV polymers have longer unit cell lengths than their Class III counterparts and $\pi$ delocalization is less effective in the latter than in the former. As expected, calculated $E_g$ values for Class IV are much larger than the corresponding Class III polymers. Class IV polymers are then predicted to have much less intrinsic conductivity than their Class III counterparts. Among all Class IV polymers, IVD appears to be of special interest. According to calculations, IVD should have higher intrinsic conductivity than IIIA since a lower $E_g$ value is obtained for the former (2.2 vs. 2.9 eV). However, the small BW value of IVD may limit its potential applications as a doped polymer. The lower $E_g$ of IVD clearly demonstrates the capability of S atoms in connecting two unsaturated units as far as conductivity is concerned. This type of capability is deemed to be very important in designing new conducting polymers.

## Conclusions

We have performed a systematic approach to study four classes (I–IV) of compounds using MOMM and VEH methods. The VEH method achieves its computation speed by evaluating only one-electron integrals and including no self-consistent-field iterative cycles. Hence, a theoretical or experimental structure is a prerequisite to carry out VEH calculations. Since the derivation of structures from the MOMM approach is much faster and is probably more accurate than other similar theoretical tools,[2,3,9,10] the potential benefits of a combination of MOMM and VEH are great. In our opinion, the combination of MOMM and VEH is a powerful tool for screening chemicals prior to their syntheses.

Pitfalls of the current VEH method have been presented and discussed. For certain cases, these pitfalls may lead to a very different interpretation of calculated results, such as polyacene and poly(pyrazinopyrazine). Whether these pitfalls can be avoided by reparametrization of atomic potentials needs to be further explored. The observed pitfalls presented here are in line with those reported in the previous papers by Bredas et al.

Poly(*p*-pyrazine) and poly(*p*-pyridine) are predicted to have similar intrinsic conductivities as poly(*p*-phenylene). As compared with poly(*p*-phenylene), poly(*p*-pyrazine) is calculated to be less p-dopable by acceptors while it is more no-dopable by donors. Poly(pyridinopyridine) can have two possible spatial arrangements, anti and syn. The anti configuration is calculated to have a lower bandgap than the syn form (0.6 vs. 2.9 eV). Thus, a mixture of syn and anti forms, instead of a pure syn configuration, may be needed to explain the experimentally observed high intrinsic conductivity of poly(pyridinopyridine).

Many interesting features have been revealed through systematic studies and structural analysis. This paper represents an interesting and important extension of previous activities in the influence of molecular architecture on the electronic properties of conducting polymers.[5-8] The –NH– functional group is found to be the most effective in lowering IP values for all cases studied here. This feature may be important in designing p-dopable polymers. The –S– unit is predicted to be the most effective in lowering the bandgap through decreasing the LUMO (or LUB) energy. Thus, the –S– functional group is a desirable element in designing intrinsic conducting polymers.

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**Registry No.** Benzene, 71-43-2; pyridine, 110-86-1; pyrazine, 290-37-9; 1,4-dihydrobenzene, 628-41-1; 1,4-dihydropyrazine, 3026-16-2; 1,4-dioxin, 290-67-5; 1,4-dithiin, 290-79-9; poly(pyridinopyridine), 108167-10-8; poly(pyrazinopyrazine), 95991-23-4; poly(1,4-dihydrobenzo-1,4-dihydrobenzene), 108232-80-0; poly(1,4-dihydropyrazino-1,4-dihydropyrazine), 108232-79-7; poly(1,4-dioxino-1,4-dioxin), 108150-06-7; poly(1,4-dithiino-1,4-dithiin), 108150-08-9; poly(*p*-phenylene), 25190-62-9; poly(*p*-pyrazine), 42319-72-2; poly(*p*-1,4-dihydrobenzene), 33040-25-4; poly(*p*-1,4-dihydropyrazine), 108150-02-3; poly(*p*-dioxin), 108150-03-4; poly(*p*-dithiin), 108150-04-5.

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# A Theoretical Study of Thermal Reactions of Bicyclo[2.1.0]pent-2-ene

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**Abstract:** Ab initio molecular orbital calculations, using 3-21G, 6-31G, and 6-31G* basis sets and including electron correlation through CASSCF and Møller–Plesset calculations up to fourth order, have been applied in a study of the thermal walk rearrangement in bicyclo[2.1.0]pent-2-ene (**1**). On the basis of our calculations and estimates, we conclude that this process occurs with inversion at the migrating center and that it probably is a two-step reaction. The activation energy for this symmetry-allowed walk rearrangement is found to be around 10 kcal/mol higher than that for the symmetry-forbidden disrotatory electrocyclic ring opening leading to cyclopentadiene. Estimates have been made of the influence that an electron-withdrawing substituent on the migrating carbon, the $-\mathrm{C}{\equiv}\mathrm{N}$ group, has on the activation energies. It is found that the substitution favors the walk reaction energetically relative to the ring opening, in accordance with experimental findings.

The walk rearrangement, defined as a reaction in which a divalent group such as –O–, –NR–, or $-\mathrm{CR_2}-$ moves along the surface of a conjugated cyclic $\pi$-electron system,[1] is of central importance in the discussion of the predictive power of the Woodward–Hoffmann symmetry rules.[2] If the rearrangement is a concerted reaction, it may be classified as a sigmatropic process in which orbital symmetry requirements lead to highly stereospecific reaction modes. These rules, applied to the circumam-

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(1) Klärner, F.-G. *Topics Stereochem.* **1984**, *15*, 1.

(2) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.