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Conformations and Electronic Structures of Poly(ketene) and Related Conjugated Polymers: Reduction of the n–π^* Band Gap

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Abstract: In an effort to design polymers with smaller band gaps, the conformations and electronic structures of poly(ketene) (PKT) and related polymers have been studied by semiempirical and ab initio quantum chemical methods. The band structure of PKT indicates that the oxygen lone pair bands are very close to the Fermi level independent of the conformation of the polymer. Two related hypothetical polymers, $[(COCHCOH)(CH)_2]_x$ and $[CHCOCHCHCOCH]_x$, have small band gap values (calculated to be around 1 eV). The small band gaps for these polymers can be attributed to a delocalized oxygen lone pair band lying between the occupied π and empty π^* bands, which creates the lone pair (n)–π^* band gaps. The band width of this lone pair band is large enough (1.5 eV) to allow electrical conduction in this unusual lone pair band upon doping.

I. Introduction

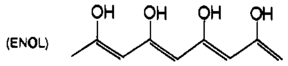
Since the discovery of a large increase in conductivity of polyacetylene, polythiophene, and polypyrrole upon doping,[1] the effect of substitution and ring fusion on their electronic properties has been extensively studied both theoretically and experimentally.[2] The studies show that the substitutions and ring fusions on the backbones of these conjugated polymers will substantially influence their band gaps.[1,2]

Recently two research groups have claimed the synthesis of an unusual conjugated backbone polymer, poly(ketene) (PKT **1**), with very high molecular weight, having the backbone of polyacetylene.[3] The onset of absorption at about 2.0 eV in the UV–vis linear absorption spectra (at both room and liquid nitrogen temperatures) indicates a conjugated π-system in accordance with the IR and NMR data. The very broad onset of the absorption gives evidence that delocalized π-segments are separated by nonconjugated groups. The polymer is an insulator with very low electrical conductivity ($\sigma < 10^{-8}$ S cm^{-1}).[3] Exposure of the powder to iodine vapor increases the conductivity by only 4 orders of magnitude ($\sigma = 10^{-4}$ S cm^{-1}).[3] The pure polymer has essentially no unpaired spins.[3] The elemental and spectral analyses indicate the following possible structure suggested by Olah et al.[3a] and Khemani and Wudl.[3b]

$$[(COCH_2)_m(COHCH)_n]_x$$

Khemani and Wudl give $m = 0.63$ and $n = 0.37$.[3b]

As far as the conformation is concerned, PKT has remarkable flexibility as compared with other polymers, which often have two competing forms, such as a quinoid one and an aromatic one.[3] In contrast, poly(ketene) can be in three different forms: the enol, keto and enol–keto forms as shown in **1a**, **1b**, and **1c**, respectively. The IR spectrum shows great similarity between PKT and 2,4,6-heptanetrione in terms of local structures, indicating that major contributions to the structure might be the enol–keto (**1c**) and keto forms (**1b**).[3] Because all of the above three conformations are possible, the study of the energetics of these conformations is an essential step in understanding the electronic and physical properties of PKT and furthermore designing polymers with smaller band gaps.



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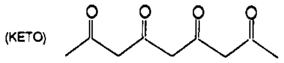

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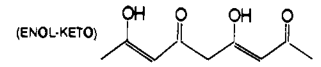

1c

In this work the conformational properties of PKT will be investigated by calculations of the torsional potential curves for the three different forms of PKT. Their relative stabilities and electronic structures will be calculated. Two related hypothetical polymers, $[(COCHCOH)(CH)_2]_x$ and $[CHCOCHCHCOCH]_x$, with full conjugation also will be included due to the fact that they have oxygen lone pair levels close to the Fermi level like PKT, which can lead to small band gaps and might form a new type of conducting polymer.

II. Methods

The semiempirical MNDO-AM1[4a] (Modified Neglect of Diatomic Overlap–Austin Model 1) crystal orbital approach,[4b,5] where a screw axis of symmetry has been taken into account,[6] will be used for the calculations of the geometrical structures of the systems under study. In this approach the polymer is assumed to be in a perfectly regular, i.e. translationally symmetrical or helical, conformation. As compared with the MNDO method, the MNDO-AM1 technique overcomes some of the weaknesses of the MNDO method, in particular the failure to reproduce hydrogen bonding.[4] Due to the fact that torsional barriers around single bonds and conjugation energies are usually underestimated by the MNDO-AM1 approach, the torsional potentials will be calculated by the extended Hückel theory (EHT)[7] on the basis of the MNDO-AM1 optimized structures. It has been shown that this combination of the MNDO and EHT methods can produce much more reasonable rotational barriers, especially for conjugated systems.[2e] Comparisons with the oligomer calculation results of the ab initio approach[8] will be made in order

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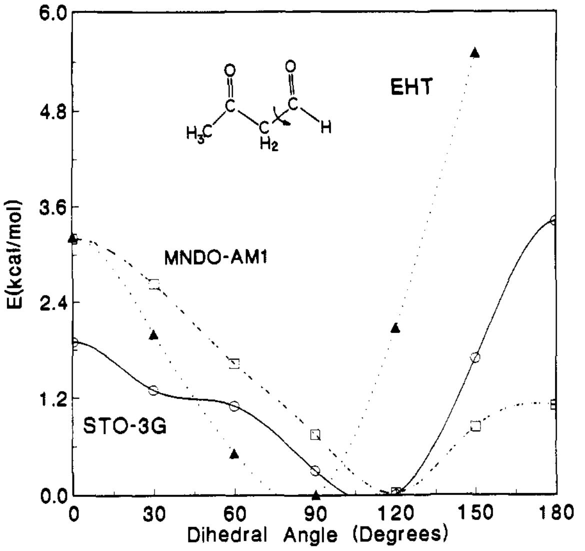


Figure 1. Torsional potential curves of the keto form of diketene with three different methods as a function of the dihedral angle around the middle C–C bond of the molecule.

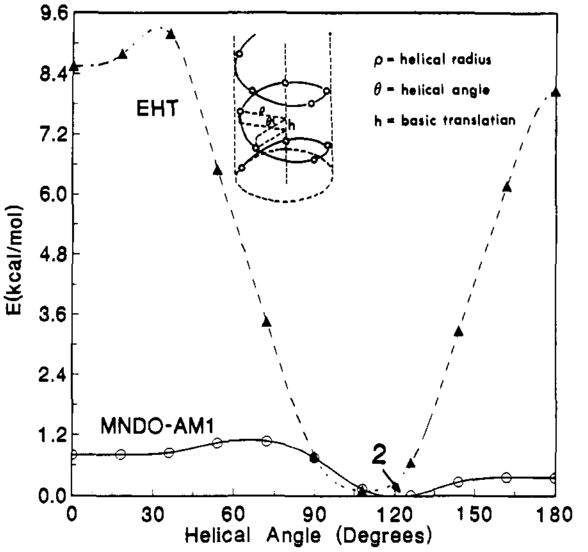


Figure 2. Torsional potential curves of the keto form of poly(ketene). The insert shows the helical angle, θ, and helical radius, ρ.

to check the overall quality of the semiempirical calculations. The band structures have been calculated by the extended Hückel approach,[7b] which is known to produce reasonable band gap values for semiconductors while all Hartree–Fock type methods, such as the MNDO approach, are known to overestimate band gaps.[5]

III. Torsional Potential Curves of PKT

A. Keto Form of PKT. To compare the different methods used in this work, the torsional potentials of diketene, the total energies as a function of the dihedral angle around the middle C–C bond at the ab initio, MNDO, and EHT levels, are presented in Figure 1. Often ab initio calculations at the modest STO-3G level can predict reasonable torsional barriers.[2e,8a] The results of the three methods, ab initio, MNDO, and EHT, indicate that diketene has a nonplanar structure with a CCCC dihedral angle of about 120° by the ab initio and MNDO-AM1 approaches and 88° by the EHT method, respectively. As far as the planar conformation is concerned, the MNDO-AM1 calculations estimate that all-trans planar diketone is more stable than the planar cis conformation, in contrast to both ab initio and EHT calculations. To further check the methods we have looked at the more refined ab initio 6-31G CCCC dihedral angle (118°) for diketene, which is close to the STO-3G value. Thus, the keto form of PKT is expected to be nonplanar on the basis of the dimer calculations.

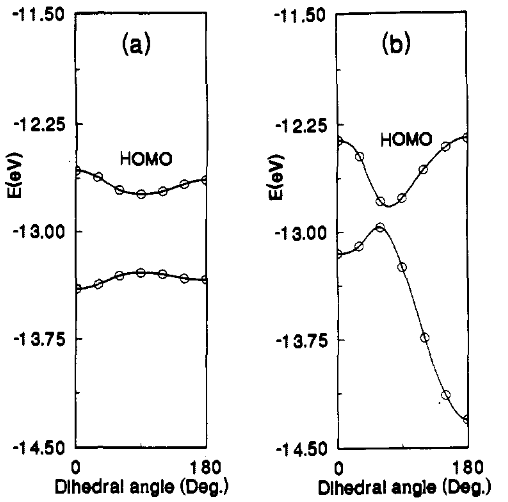
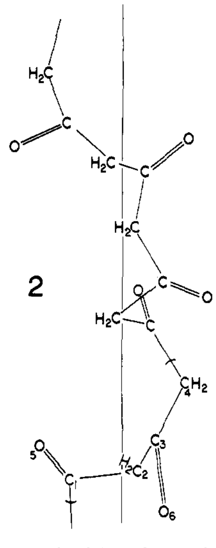


Figure 3. (a) Walsh diagram for **4**. (b) Walsh diagram for HOOH as calculated in the present work.

The torsional potential curves of the keto form of PKT, i.e., the total energies per $C_4O_2H_4$ unit as a function of the helical angle by the EHT and MNDO-AM1 methods, are shown in Figure 2. The helical angle is defined as the rotation angle for a screw operation, $S(\theta)$, which describes a rotation through an angle of θ around the screw axis followed by a translation. Further details about using helical symmetry in quantum chemistry can be found elsewhere.[6] Similar to the dimer calculations, a nonplanar gauche structure is estimated to be most stable. The optimized structure of the keto form of PKT is presented in **2**.



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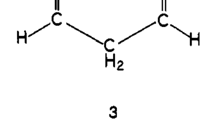
An analysis of the chemical bonding of the dimer can be the starting point toward understanding why the keto form of PKT is nonplanar. We use malondialdehyde (**3**) as a model system, which can be derived from diketene by replacing the CH_3 group



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on diketene with a hydrogen atom. Therefore, the stable conformation of malondialdehyde is not expected to be significantly

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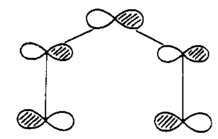
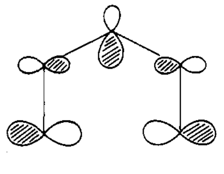
different from that of diketene. Indeed, malondialdehyde is calculated to have a nonplanar structure with a CCCO dihedral angle of about 90° by the EHT method, which is close to the value of 88° for diketene at the same level calculation. The Walsh diagram[9] for this system is shown in Figure 3a. One can clearly see that as the CCCO dihedral angle decreases from 180° the energy of the HOMO goes down and that of the second HOMO goes up. At the dihedral angle of about 90° the HOMO reaches the minimum and the second HOMO the maximum while the total energy reaches the minimum. Continuing to increase the dihedral angle from 90° the orbital energies run in the opposite direction and the total energy goes up. The frontier molecular orbitals of the planar malondialdehyde (**3**) are shown in **4**, which can be used to understand the way the orbital energy changes with the dihedral angle in Figure 3a. This is similar to the orbital energy changes of the HOMO and the second HOMO in the Walsh diagrams of HOOH and HSSH. They have a dihedral angle of about 90° as shown in Figure 3b for hydrogen peroxide.[9c] In the case of HOOH and HSSH π lone pair repulsions are responsible for their nonplanar structures.[9] For malondialdehyde (**3**) the HOMO and the second HOMO are σ-type orbitals. As a result, the σ electron repulsions should be responsible for the nonplanar structures of malondialdehyde and the keto form of PKT (**2**). Specifically, the repulsions between $C{=}O$ and the next C—C bonds as well as the repulsions between oxygen atoms are responsible for the nonplanar structure of this polymer. Before discussing the band structures of the various forms of PKT, let us turn to the enol form.

HOMO (2)



HOMO (1)



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B. Enol Form of PKT. The enol form of PKT (**1a**) may be characterized by the existence of intrapolymer hydrogen bonding. The hydrogen atom of each hydroxyl group (O–H) forms a hydrogen bond with the oxygen atom of the next hydroxyl group (O–H). At the same time the polymer can be a fully conjugated chain. Both of the above effects make a planar structure more favorable. The torsional potential curve of the enol form of diketene at the STO-3G level supports the above arguments, as shown in Figure 4. The large distortion from the planar structure will lead to a significant increase in energy due to the loss of conjugation energy and the breaking of hydrogen bonds. As a result, the most stable form of the polymer is expected to be in the conformation in which all hydroxyl groups are on the same side and the polymer is as close to planarity as possible. However, the two nearest CCC bond angles are inequivalent. The structure of a polymer, which is closest to such a nearly planar chain, has to be a helix with a large helical radius. The helical radius is estimated to be 143 Å from the two different CCC bond angles (124° and 125° at the STO-3G level, repsectively) and the optimized C–C bond lengths on the basis of the diketene calculations.

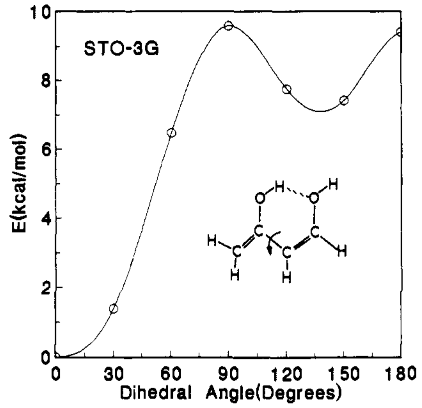
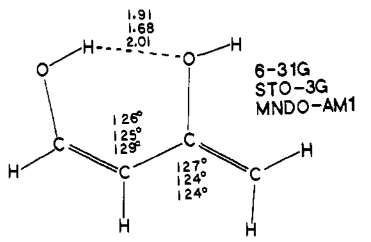


Figure 4. Ab initio torsional potential curves of the enol form of diketene.

To check if we can use the MNDO-AM1 method to calculate the torsional potential curve of the enol form of PKT, comparative calculations have been performed on the enol form of diketene at the MNDO-AM1, STO-3G,and 6-31G levels. The optimized CCC bond angles and hydrogen bond distances are presented in **5**. At the MNDO-AM1 level the difference between the two different CCC bond angles is 5° while at the ab initio STO-3G and 6-31G levels the above difference is only about 1°. The hydrogen bond distance of 2.01 Å obtained by the MNDO-AM1 approach is larger than those (1.68 and 1.91 Å at the STO-3G and 6-31G levels, respectively) by the ab initio calculations. The estimated helical radius of the infinite polymer from the diketene calculations at the ab initio STO-3G and 6-31G levels is about 143 Å while this value at the MNDO-AM1 level is 28 Å. If the polymer is linear and planar, all of the CCC bond angles must be the same. When the polymer is forced to be linear and planar, the structural constrains introduced at the MNDO-AM1 level are much larger than those at the ab initio level. Therefore, the MNDO-AM1 method is not appropriate for studying the enol form of PKT.



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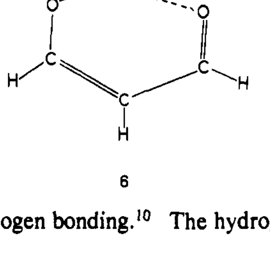
It is expected that if the ab initio crystal orbital approach would be used for the calculation of the torsional potential curve of the enol form of PKT, the torsional potential curve would be similar to that in Figure 4. The optimized structure for the linear enol form of PKT is expected to be a nearly planar structure with a large helical radius.

C. Enol–Keto Form of PKT. Before starting to discuss the conformation of the enol–keto form of PKT let us discuss the bonding in the closely related molecule malonaldehyde (**6**). Malonaldehyde has attracted a great deal of attention due to its intramolecular hydrogen bonding.[10] The hydrogen bond between



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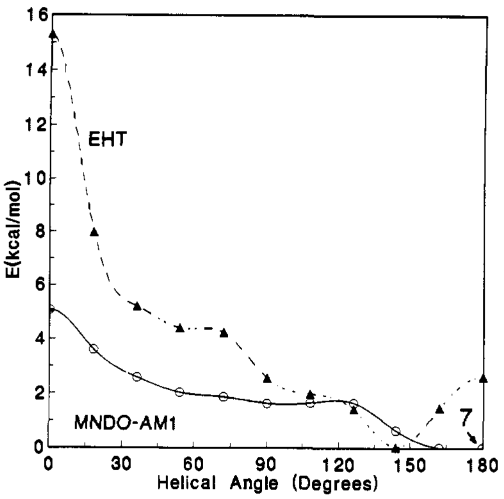
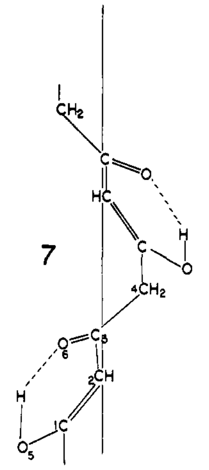


Figure 5. Torsional potential curves of the enol–keto form of poly(ketene).

the hydrogen atom of the hydroxyl group and the oxygen atom of the carbonyl group gives malonaldehyde extra stability. In the enol–keto form of PKT (**1c**) the hydrogen bonding will stabilize the enol segments of the polymer, and therefore the enol–keto form of PKT should be built up from malonaldehyde-like rings.

The torsional potential curves of the keto–enol form of PKT at the MNDO-AM1 and EHT levels are shown in Figure 5. Both MNDO-AM1 and EHT calculations give one minimum, and both potential surfaces are very flat around the minimum. The MNDO-AM1 optimized structure is given in **7**, indicating that the malonaldehyde rings exist in the polymer. This minimum is more stable than the structurally crowded linear planar PKT (**1c**), where all carbonyl and hydroxyl groups are on the same side of the polymer. (Actually **1c** as shown would be a slightly nonplanar helix with a large helical radius.)



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The geometrical parameters optimized by the MNDO-AM1 approach for the three different forms of PKT are summarized in Table I.

IV. Relative Stabilities and Transformations of the Different Forms of PKT

The calculated relative energies of the three different forms of PKT are listed in Table II, by the EHT and MNDO-AM1 crystal orbital approaches for the polymer and by the ab initio technique at the 6-31G level for the three different forms of diketene.

All calculations indicate that the enol form of PKT is the least stable, in agreement with the generally known experimental results on molecules with enol groups.[11] It is well-known that an enol group is thermodynamically unstable and will undergo ketonization, but often has a long half-life. A typical example is vinyl alcohol which has a half-life of about 30 min.[11] The ketonization can be catalyzed by bases, acids, and water. Under catalyzed condition no enol group can be detected.[11]

Table I. Optimized Geometrical Parameters of PKT

parameters	enol (**1a**)[a]	keto (**2**)	enol–keto (**7**)
	Bond Lengths (Å)		
C1–C2	1.455	1.508	1.356
C2–C3	1.358	1.506	1.451
C3–C4	1.455	1.505	1.511
C4–C1′	1.357	1.504	1.476
C1–O5	1.377	1.233	1.361
C3–O6	1.376	1.233	1.243
	Bond Angles (deg)		
C1C2C3	124.4	111.2	125.3
C2C3C4	123.9	116.7	116.2
C3C4C1′	124.4	112.4	113.8
C4C1′C2′	124.2	116.7	122.5
O5C1C2	111.4	120.9	126.0
O6C3C2	124.5	121.4	123.8
	Dihedral Angles (deg)		
C1C2C3C4	178.4	121.1	127.7
C2C3C4C1′	149.4	89.8	51.3
C3C4C1′C2′	178.3	78.4	116.4
C4C1′C2′C3′	149.3	86.6	177.2
O5C1C2C3	32.3	92.8	0.1
O6C3C4C1′	3.6	92.6	131.1
	Helical Angles (deg)[b]		
	0.0	120.1	180.0

[a] Atom numbering is the same as in **2**. **1a** is the least stable form. [b] Dependent variable.

Table II. Comparison of Relative Stability of Different Forms of PKT

method	keto (**2**)	enol–keto (**7**)	enol (**1a**)[a]
MNDO-AM1[b]	−70.8	−70.8	−63.9
EHT[c]	0.0	13.1	33.9
ab initio (6-31G)[c] (diketene)	4.6	0.0	13.8

[a] **1a** is the least stable form. [b] Heat of formation per $C_4O_2H_4$ unit in kcal/mol. [c] Relative to the most stable conformation in kcal/mol.

The ab initio calculations on diketene at the 6-31G level indicate that the enol–keto form is even more stable than the keto form by 4.8 kcal/mol. This can be simply attributed to the formation of an intramolecular hydrogen bond which can stabilize the enol segment, as we pointed out for malonaldehyde, and the compromise between the loss of hydrogen bonding and the formation of keto groups which gains energy. The present calculations do not clearly distinguish between the stabilities of the keto and enol–keto forms. Depending on the conditions, such as the presence of water or bases or acids, the ratio of the enol and keto segments might vary. This conclusion is in concordance with the structural assignment of PKT by Khemani and Wudl.[3b]

V. Electronic Structure of PKT

The band structures of the three different forms of PKT calculated by the EHT approach are shown in Figure 6, in which VB indicates the highest occupied valence band and CB the lowest empty conduction band. For the keto and enol–keto forms the MNDO-AM1 optimized geometries are used. For the enol form the geometry is derived from the ab initio calculations on the enol form of diketene at the 6-31G level and is assumed to be a planar linear structure. The band structures are represented in the pseudo-Brillouin zone which corresponds to the smallest repeat

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(10) (a) Frisch, M. J.; Scheiner, A. C.; Schaefer, H. F., III *J. Chem. Phys.* **1985**, *82*, 4194. (b) Seliskar, C. J.; Hoffmann, R. E. *J. Mol. Spectrosc.* **1982**, *96*, 146. (c) Fluder, E. M.; de la Vega, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 5265.

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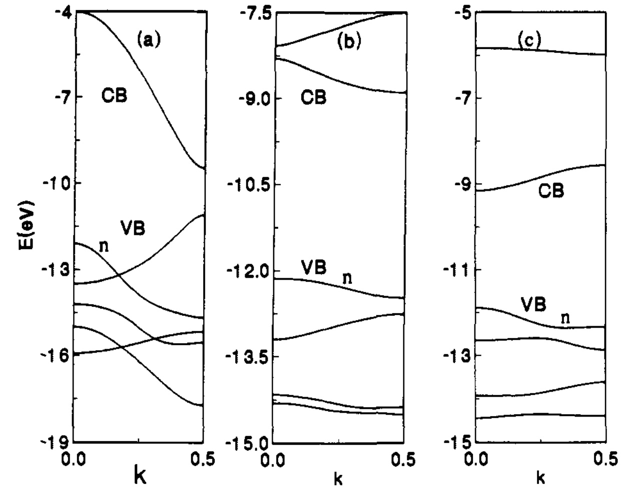


Figure 6. EHT band structures of keto (a), enol (b), and enol-keto (c) forms of poly(ketene) based on the MNDO-AM1 optimized geometries. For the enol form only the band structure at the planar geometry (**1a**) is given. **n** indicates the oxygen lone pair band.

unit and is described elsewhere.[6]

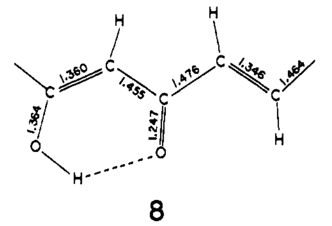
The enol form has a band gap of 1.8 eV due to the conjugation along the polymer backbone while both enol-keto and keto forms have a much larger band gap of about 3.0 eV because the CH_2 groups interrupt the conjugation. As discussed above, the pure enol form of PKT is unstable, and there is an equilibrium among the keto, enol, and keto-enol forms of PKT. Therefore, the above band structures might not be a good description for the real electronic structure of PKT in the condensed phase. A complete description of the electronic structure of PKT should correspond to a random mixture of all different conformations and distributions of the keto and enol segments. This can be done by the use of a combination of molecular dynamics and quantum chemical calculations[12] and is beyond the scope of the present work. However, the combination of the band structures in Figure 6 and the energetics in Table II still can offer us a qualitative picture of the electronic structure of PKT. It is reasonable to conclude that PKT cannot be a fully conjugated chain and there exist various lengths of the keto and enol segments. Therefore, PKT is not a good candidate for an electronically conducting polymer.

Checking the band structures of the three different forms of PKT, it is noteworthy that the oxygen lone pair band is very close to the Fermi level for the enol form of PKT while it is the valence band for the keto and enol-keto forms. Is there any possibility of making a polymer with an oxygen lone pair band lying between π and π^* bands? This question will be considered in the next section.

VI. Optimized Geometries and Band Structures of Two Hypothetical Polymers

Let us introduce a model polymer which is a copolymer, $[(COCOHCH)(CH)_2]_x$, of poly(ketene) (keto-enol form **1c**) and polyacetylene. This polymer is less crowded than PKT. Therefore, it is expected to be planar.

The geometry of the model polymer optimized by the MNDO-AM1 approach is shown in **8**. The existence of the malonaldehyde rings is an important structural feature of the polymer. It is very particular to this structure that the bond alternation is interrupted in such a way that every double bond is followed by two single bonds.



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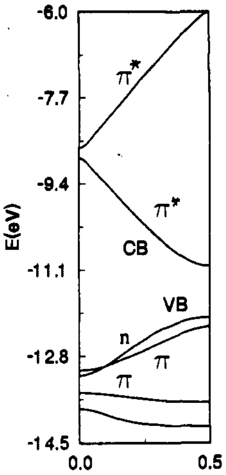
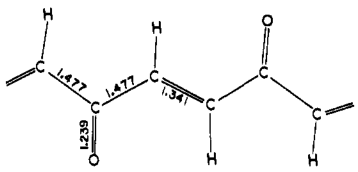


Figure 7. EHT band structure of **8** based on the MNDO-AM1 optimized geometry. **n** indicates the oxygen lone pair band.

The present suggestion is different from that due to Jenekhe,[13] who proposed that with the insertion of =CR— units in polythiophene one might end up with small band gap polymers. The theoretical calculations indicated that these odd π-electron systems might have somewhat reduced band gaps relative to polyacetylene.[14] A similar case has been found for certain polypyrrole analogues.[15] The presently discussed systems have an even number of π electrons per chemical repeat unit although the oxygen π lone pairs are in an "exo-position", i.e. in a location outside of the main chain.

The band structure of polymer **8** is shown in Figure 7, indicating a relatively moderate band gap of 1.2 eV. Obviously this polymer might become a conducting polymer. Note that the oxygen lone pair band is between the π and π^* bands.

The other hypothetical polymer, $[CHCOCHCHCOCH]_x$, as shown in **9**, is designed on the basis of the electronic structure of benzoquinone (**10**). The perfluoro effect in the photoelectron spectroscopy of benzoquinone shows that the two oxygen lone pair orbitals (n_g and n_u) are between the π and π^* orbitals.[16] The n_g and n_u levels are separated by 1.4 eV due to the through-bond interaction of the lone pairs.[17] This has been further confirmed by the ab initio calculations at the configuration interaction level.[18]



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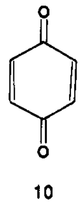

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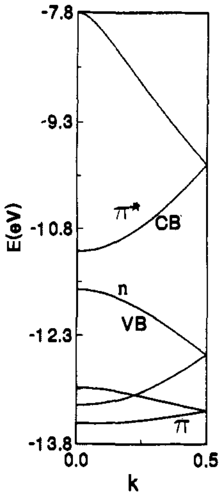

Figure 8. EHT band structure of **9** based on the MNDO-AM1 optimized geometry. **n** indicates the oxygen lone pair band.

Therefore, one can expect that the band width of the lone pair band corresponding to n_g and n_u is on the order of 1.4 eV.[19] The band gap of polyacetylene between the π and π^* bands is ca. 1.5 eV.[1] If the lone pair band falls in the middle of the π and π^* bands, the band gap may be reduced substantially.

The MNDO-AM1 optimized geometrical parameters for this system are shown in **9**. The hypothetical polymer (**9**) is expected to have the oxygen lone pair band lying between the occupied and unoccupied π bands. That may lead to a reduced band gap. Indeed, the band structure obtained by the EHT method on the basis of the MNDO-AM1 optimized geometry confirms this expectation. The calculated band gap is only 0.8 eV as shown in Figure 8. This value is comparable to the calculated band gap of polyacetylene at this level of theory. The 1.5 eV band width of the lone pair band can be traced back to the through-bond interactions[17] and is sufficiently broad to allow electrical conduction and high mobility of the electron in the band upon doping.

VII. Conclusions

The conformation and electronic structure of poly(ketene) have been studied by semiempirical and ab initio quantum chemical methods. Ab initio oligomer calculations can provide very useful information concerning the reliability of semiempirical calculations. The ground states of the keto and enol–keto forms of PKT are calculated to be helical structures with helical angles of around 120° and 180°, respectively, while the enol form is nearly planar. The reason for the formation of a helix of the keto form of PKT is electronic, which has been attributed to bonding electron pair repulsions. The enol form is not stable as compared with the keto and enol–keto forms while the stability of the enol–keto form is comparable to that of the keto form. The stabilization of the enol–keto form of PKT comes from the formation of intramolecular hydrogen bonds. Mixing of the enol and keto segments of PKT and transformation between the keto and enol groups are expected from known experimental data of small molecules. This is in concordance with the present calculations. Band structure calculations indicate that the keto and the enol–keto forms of PKT have a large band gap of about 3.0 eV while the unstable enol form has a smaller band gap of 1.8 eV. This can explain why the conductivity of PKT is increased by only 4 orders of magnitude upon doping.

The geometric and electronic structures of two hypothetical polymers, $[(COCHCOH)(CH)_2]_x$ and $[CHCOCHCHCOCH]_x$, have been calculated in an effort to design polymers with small band gaps. Band gaps of 1.2 and 0.8 eV have been obtained by the EHT method for the above two hypothetical polymers, respectively. The small band gap of the latter polymer can be attributed to the quite delocalized nature of the oxygen lone pair band lying between the π (occupied) and π^* (empty) bands creating a lone pair (n)–π^* band gap. This is completely different from traditional conducting polymers with π–π^* band gaps. The band width of 1.5 eV for the lone pair band comes from through-bond interactions of the oxygen lone pairs[18] and should allow high electrical conduction of these materials upon doping.

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Registry No. 1, 31455-32-0; **8**, 133551-04-9; **9**, 133551-02-7.

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