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A Theoretical Investigation of the Electronic Properties and Structure of Some Model Poly(diacetylenes)

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ABSTRACT: The electronic properties of some model poly(diacetylenes) were investigated by using AM1 and, to a limited extent, MNDO and PM3 semiempirical SCF–MO methods. The capped-bond option allowed for simulation of polymer structures but the option has limitations when computing electronic properties of conjugated polymers. With optimized geometries, AM1-computed structures for poly(diacetylene) models favor the enyne structure. The chemical and electronic effects of substituents on the structure of the polymer backbone were investigated, and the Koopman ionization potential and bandgap were computed and discussed. The changes in HOMO and LUMO energies as a function of nonplanarity along the backbone were also calculated. The bandgaps of some diacetylene monomers and several oligomers were computed for comparison with experimental values of diacetylene monomers and polymers. Finally, some AM1 calculations are included showing variations in geometry, atomic charge, and bandgap with chain length in a series of oligomeric diacetylenes.

Poly(diacetylenes) are organic polymers with fully conjugated carbon backbones. Polymers with delocalized π-electron systems can have large nonlinear polarizabilities; therefore, physical and chemical properties of poly(diacetylenes) as soluble species, thin films, and very thin crystals have attracted considerable interest in nonlinear optics studies.[1]

Diacetylene polymers have the unique feature that allows the synthesis of many of them in single-crystal form by irradiation of crystals of the monomer.[2] If all diacetylene monomers crystallized in a polymerizable arrangement, polymer chemists could readily optimize the nonlinear optical properties of poly(diacetylenes) by synthesizing the monomers that would lead to the desirable polymers. Unfortunately, not all crystalline diacetylene monomers polymerize.[1]

Many of the experimental studies of poly(diacetylenes) have included structural data obtained from X-ray crystallographic investigations, making it easy to compare theoretical and experimental data on geometries. This along with the general interest of theoreticians in conjugated systems has prompted a number of theoretical papers devoted to a deeper understanding of the electronic, structural, and spectroscopic properties of these systems.[3-5]

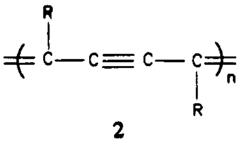
There are two reasons why we have chosen to evaluate poly(diacetylenes) using theoretical methods. First, we would like to find a reliable method useful in predicting which diacetylene monomers will be polymerizable in their crystalline form. If such a method were available, a considerable amount of unnecessary trial and error monomer synthesis could be avoided. Future papers will address our approaches to this problem. Second, theoretical methods can assist in monomer design if the method can predict how various functional groups affect monomer and polymer properties. In the present study we are evaluating one very popular theoretical method to see if it warrants further use in the two areas mentioned above.

There are a number of theoretical methods that we could evaluate for our application. With monomeric and polymeric diacetylenes, the structural types are wide-ranging and, in many cases, quite large. For practical reasons ab initio calculations were not evaluated because they are limited to small systems, while various semiempirical methods can be used to compute structures and properties of larger systems. For computation of structures and properties of polymeric systems, even the semiempirical methods are limited; hence one must wisely choose the method that is best suited to the problem of interest. The semiempirical methods developed by Dewar, e.g., MNDO[6] and AM1,[7] are the most generally acceptable for reproduction of a wide variety of properties of molecules. Karpfen[4] and Orchard and Tripathy[5] have reported some calculations of poly(diacetylenes) using the MNDO method. Our chief objective here is to evaluate the suitability of the more recently developed AM1 method for the prediction of structures and some properties of monomeric and oligomeric diacetylenes. As we began this study, a new "NDO"-type method called PM3[8] was introduced. PM3 is a semiempirical SCF–MO method that is similar to AM1 in that it has spherical Gaussian core–core repulsion functions. We have therefore included some calculations where MNDO, AM1, and PM3 may be compared. However, only AM1 calculations were carried out for the diacetylene oligomers.

Polymerization of a poly(diacetylene), e.g., **1** → **2**, gives a repeat unit consisting of four carbon atoms in the

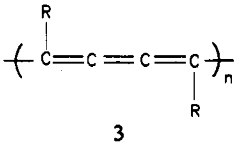
$R—C\equiv C—C\equiv C—R \longrightarrow$

1



$\left[=\overset{R}{C}-C\equiv C-\underset{R}{C}=\right]_n$

2



$\left[\overset{R}{C}=C=C=\underset{R}{C}\right]_n$

3

backbone and two bulky pendant groups. In some ab initio calculations[4] these pendant groups are replaced by hydrogen atoms due to the limitation of computers. It has been shown, however, that, for some type polymers, pendant groups may have a significant influence on the electronic properties of the backbone.[9] Theoretical verification of this has been described.[5] It is not necessary

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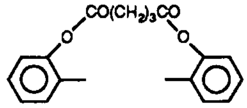
Table I
X-ray Diffraction Data for Some Poly(diacetylenes)[a,b]

II, R = R′	abbrev	r_1	r_2	r_3	α	β	ref
CH_2OSO_2-*p*-$C_6H_4CH_3$	PTS	1.191	1.428	1.356	115.8	121.9	*c*
CH_2OSO_2-*p*-$C_5H_4OCH_3$	MBS	1.195	1.424	1.364	115.1		*d*
$CH_2OCONHC_6H_5$	HDU-1	1.21	1.42	1.36			*e*
$CH_2N(Ph)_2$	THD	1.205	1.426	1.359	117.1	119.1	*f*
			1.427	1.360	119.9	120.1	
	BPG	1.29	1.38	1.42	116.0	119.2	*g*

[a] Bond lengths are in angstroms and bond angles are in degrees. [b] r_1, r_2, r_3, α, and β are shown in system II. [c] Kobelt, D.; Paulus, E. F. *Acta Crystallogr., B* **1974**, *30*, 232. [d] Williams, R. L.; Ando, D. J.; Bloor, D.; Hursthouse, M. B. *Polymer* **1980**, *21*, 1269. [e] Hadicke, E.; Mez, E. C.; Krauch, C. H.; Wegner, G.; Kaiser, J. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 266. [f] Enkelmann, V.; Schleier, G. *Acta Crystallogr., B* **1980**, *36*, 1954. [g] Reference 13 and Lando, J. D.; Day, D.; Enkelmann, V. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 73.

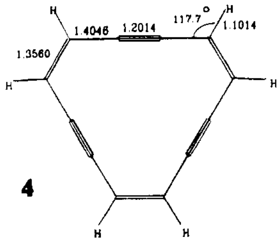
to severely restrict the size of pendant groups when using semiempirical methods.

Intuitively we believe that electron-donating and electron-withdrawing groups have opposite effects on some properties but not on others. In understanding a semiempirical theoretical method, it is important that we evaluate whether or not the expected effect is observed. Therefore, to investigate the influence of pendant groups having different electronic properties, we have chosen chlorine as an electron-withdrawing substituent and a methyl group to model an electron-donating group. In this paper, we report detailed investigations concerning the influence of these groups on the molecular geometry and electronic properties of the backbone. It should be emphasized at this point that various conformations of some bulky pendant groups may lead to steric strain on the backbone; the groups used here lack sufficient bulk to show this sort of influence in poly(diacetylenes). With one diacetylene system we look at how the AM1 method predicts the structure and properties change as the molecular chain length is increased.

Many poly(diacetylenes) show drastic color changes in the solid state or in solution when the temperature or solvent is changed.[10,11] These changes have been interpreted in terms of different resonance contributions or changes of planarity. However, despite the great effort devoted to the elucidation of this effect, to date there is no experiment that unambiguously explains the nature of the color changes. Since these changes can be related to molecular orbital energies, we have calculated the changes in the energies of the HOMO and LUMO and considered the bandgap variations as a function of the degree of nonplanarity.

Results and Discussion

Model for Calculations. Poly(diacetylenes) may exist in two forms, i.e., structures 2 and 3. The structure for most of the poly(diacetylenes) investigated by X-ray diffraction can be best represented by the enyne structure; e.g., structure 2 (see Table I). However, there are a few examples that exhibit characteristics of the butatrienic backbone, e.g., 3. It is difficult to computationally model structures 2 and 3 because the two forms are not isomeric. Karpfen[4] and Orchard and Tripathy[5] approached the solution in different ways and obtained similar results. Both ab initio at the STO-3G level and MNDO favored the enyne form, structure 2. Karpfen estimated the favored form using cyclic trimers 4 and 5, which *are* isomers. Since this model facilitates a computational solution without introducing serious concerns,[5] we have used the cyclic trimers in order to compare the AM1 method with those previously used. Our results show that the enyne structure, isomer 4, is more stable by 12.1 kcal/mol per repeat unit. This is essentially the same result obtained by the other theoretical methods.[4,5] Therefore, in this work we have use models, i.e., structures I and II, that allow features of the more stable enyne form to be computed.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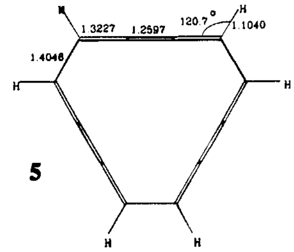
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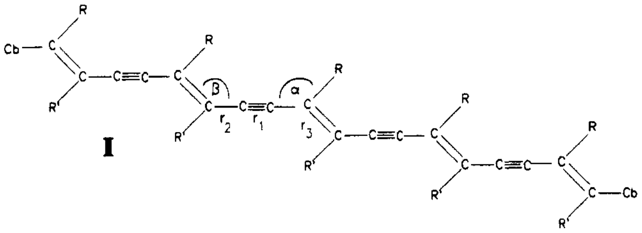
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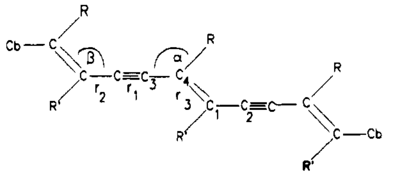

II

For computing electronic properties, conjugated systems are normally modeled as possessing an extended planar trans structure with hydrogen atoms serving as substituents to satisfy the backbone valence geometry. In this work the "capped-bond" (Cb)[12] atom is chosen in order to satisfy the backbone valence structure. The Cb atom is a designated end group that is used to satisfy valency requirements of atoms for which some bonds are not completed. Alternatively, using hydrogen atoms to complete the normal valency in polymers has the defect that the electronegativity of a hydrogen atom is different from that of carbon. The Cb atom behaves like a monovalent atom, with the exception that it can alter its electronegativity to achieve an exactly zero charge in whatever environment it finds itself.

In order to check the influence of an extension of the lattice on the equilibrium geometry and to investigate the effect of the Cb atom on the molecular structure of the backbone, some calculations have been carried out on

Table II
AM1 Calculations of Bond Angles and Lengths in Systems I and II[a]

	r_1	r_2	r_3	α	β
system I	1.2022	1.4038	1.3414	113.9	122.3
system II	1.2005	1.4029	1.3405	114.3	122.4
Δ	−0.0017	−0.0009	−0.0009	0.4	0.1
% Δ	−0.14	−0.06	−0.07	0.35	0.08

[a] Geometries are optimized using the AM1 Hamiltonian; bond lengths are in angstroms and angles are in degrees; changes are from system I to II.

systems I and II, using the AM1 method. The optimized molecular geometries are summarized in Table II. It is clear from Table II that optimized bond lengths and bond angles are similar for the two systems, and no significant changes in the equilibrium structure can be observed. This is what one may expect from the diacetylenes, because the elementary cell chain is comparatively large.

In order to compare the Cb atom with hydrogen in completion of the normal valency in polymer backbones, we have performed some similar calculatkons on systems I and II, replacing the Cb atom with hydrogens. With hydrogen end groups, the angle β changes by 1°, indicating less similarity between systems I and II. Because of the similarity of I and II, we have chosen system II as a model for calculation of electronic properties and molecular structure of some mono- and disubstituted poly(diacetylenes).

Equilibrium Geometry of the Poly(diacetylene) Backbone. By varying the large organic substituents R and R′ of structure II more than 200 different materials have been synthesized and reported in the literature. The experimental data for molecular geometries of several poly(diacetylenes) are available from X-ray crystallographic investigations; some of these are compiled in Table I. It can be seen from this table that, except for BPG, the equilibrium geometry of the backbone chains can be best represented by the enyne structure. BPG is prepared from a monomer that represents a case of limited reactivity; its crystal structure analysis was carried out with a crystal containing only 35% polymer.[13]

The molecular geometries for some methyl- or chloro-substituted poly(diacetylenes) are calculated by using MNDO,[6] AM1,[7] and PM3[8] semiempirical SCF-MO methods and are included in Table III. All calculations were carried out on a CRAY X-MP/24 computer using version 5.04 of the MOPAC package.[12] It is clear that angle α is affected by varying substituents more than the other parameters of r_1, r_2, r_3, and β. Therefore, one may not be able to compare this angle with the observed data in Table I, but bond lengths are in good agreement with the experimental data. When the substituents are varied from hydrogen to methyl, MNDO calculations show a 1.7° change in angle α. Thus holding angle α to fixed values, as was the case in the study by Karpfen[4] of poly(diacetylenes), is not reasonable. Changes in angle β by variation of substituents are assumed to be less in comparison to the large changes of angle α. This assumption is refined by our calculations. For unsubstituted poly(diacetylene), ab initio calculations using the STO-3G basis set[4] give values of 115.3° and 123.9° for angles α and β, respectively. These values are in good agreement with those obtained by the AM1 and MNDO methods in this work. The PM3 method, however, slightly overestimates angle α.

By comparing the results obtained from different semiempirical methods, one may draw a general conclusion that all three methods are reliable in reproducing the molecular geometry of poly(diacetylenes), especially those that are calculated in this work. Choosing the best method for optimization of the molecular geometry of methyl- or chloro-substituted poly(diacetylenes) demands experimental data that are not available.

Effect of the Chemical and Electronic Nature of the Substituents on the Electronic Properties of the Polymer Backbone. In order to study the effect of substituents on the electronic properties of the backbone, we have chosen a methyl group as an electron-donating substituent and a chlorine atom as an electron-withdrawing substituent. The MNDO[6] and AM1-calculated[7] charge densities for some chloro- and methyl-substituted poly(diacetylenes) are included in Table IV. The MNDO[6] atomic point charges on atoms 1 and 2 of unsubstituted poly(diacetylene) are in reasonable agreement with those of previous calculations[5] on the same system. We suspect that the slight differences reflect the fact that angles α and β are optimized in this work, while they were held fixed in the previous calculations.[5] Although the trend of atomic charge densities of atoms 1, 2, and 4 obtained by using the MNDO method in this work is in agreement with the previously calculated[5] results, the differences in absolute values are large. This can be attributed to the considerable changes in the angles α and β of a single methyl-substituted poly(diacetylene) with respect to the unsubstituted polymer (see Table III).

It can be seen from Table IV that the electron-withdrawing property of a chloro group and the electron-donating property of a methyl group are satisfactorily reproduced by the MNDO method. In the case of the monochloro-substituted poly(diacetylene), the carbon atom C_4 bearing the chlorine atom has 178% more positive charge than that carbon atom bearing a hydrogen (in the unsubstituted polymer). These changes are smaller for atoms 1 and 2, which are farther away from the chlorine atom. This is in agreement with the fact that the effect of a substituent rapidly diminishes as the distance from the site of substitution increases. As indicated in Table IV, the MNDO-calculated charge concentration about the connecting backbone atom C_1 in the case of the dichloro-substituted poly(diacetylene) decreases by 219%, while the dimethyl-substituted polymer shows a 47% increase when comparing each polymer to the unsubstituted analogue. This means that the inductive effect of a chlorine atom is much stronger than the methyl group for short-range interactions. One disturbing point from Table IV relates to the ability of the AM1 method to reproduce the electron-withdrawing properties of chlorine but not the electron-donating characteristics of the methyl group; the methyl group is surprisingly predicted to be an electron-withdrawing group. However, the methyl group's electron-donating properties are seen in the AM1 orbitals shifts.

In order to investigate the effect of substituents on the macroscopic electronic properties of poly(diacetylene) chains, the Koopman ionization potential, and the bandgap of chloro- and methyl-substituted poly(diacetylenes), calculations performed with the MNDO and AM1 methods are compared with those of unsubstituted species (Table IV). It can be seen that the ionization potential increases upon substitution of the electron-withdrawing group (chlorine) and decreases upon substitution of the electron-donating methyl group. This confirms our intuitive belief that the chloro and methyl groups have opposite effects on the stabilities of the polymers' highest occupied molecular orbital (HOMO). It is clear from Table V that the chloro group has a more pronounced effect in comparison to the methyl group. This is in agreement with the conclusion drawn from evaluation of the atomic point

Table III
Calculated Geometries for Derivatives of Structure II

II							
R	R′	method	r_1	r_2	r_3	α	β
H	H	MNDO	1.2026	1.4166	1.3436	114.6	122.8
		AM1	1.2005	1.4029	1.3405	114.3	122.4
		PM3	1.1964	1.4095	1.3370	117.7	123.0
Cl	H	MNDO	1.2033	1.4136	1.3466	113.7	124.2
		AM1	1.2018	1.3994	1.3422	117.3	123.3
		PM3	1.1962	1.4068	1.3433	117.9	122.5
Cl	Cl	MNDO	1.2020	1.4157	1.3436	111.6	124.9
		AM1	1.1994	1.4051	1.3489	114.7	120.6
		PM3	1.1962	1.4078	1.3488	116.7	122.5
CH_3	H	MNDO	1.2027	1.4147	1.3546	117.8	126.9
		AM1	1.2012	1.4021	1.3430	117.0	122.5
		PM3	1.1968	1.4072	1.3448	118.1	123.5
CH_3	CH_3	MNDO	1.2041	1.4271	1.3606	112.9	119.2
		AM1	1.2029	1.4103	1.3480	112.5	119.4
		PM3	1.1962	1.4157	1.3516	117.0	118.7

Table IV
MNDO- and AM1-Calculated Charge Densities[a] for Derivatives of Structure II

II			MNDO			AM1		
R	R′	atom	q_i	Δ	% Δ	q_i	Δ	% Δ
H	H	1	0.0370	0.0000	0.00	-0.0299	0.0000	0.00
		2	-0.1156	0.0000	0.00	-0.1324	0.0000	0.00
		4	0.0370	0.0000	0.00	-0.0299	0.0000	0.00
Cl	H	1	0.0557	0.0187	50.54	-0.0387	-0.0088	-29.43
		2	-0.0790	0.0366	31.66	-0.0902	0.0422	31.87
		4	0.1029	0.0659	178.11	0.0396	0.0695	232.44
Cl	Cl	1	0.1183	0.0813	219.73	0.0312	0.0611	204.35
		2	-0.0683	0.0473	40.92	-0.0937	0.0387	29.33
		4	0.1183	0.0813	219.73	0.0312	0.0611	204.35
CH_3	H	1	0.0588	0.0218	58.92	-0.0455	-0.0156	-52.17
		2	-0.1189	-0.0033	-2.85	-0.1238	0.0086	6.50
		4	-0.0053	-0.0423	-114.32	0.0348	0.0647	216.39
CH_3	CH_3	1	0.0194	-0.0176	-47.57	0.0233	0.0532	177.93
		2	-0.1119	0.0037	3.20	-0.1266	0.0058	4.38
		4	0.0194	-0.0176	-47.57	0.0233	0.0532	177.92

[a] The changes in atomic point charges, q_i, are with respect to the unsubstituted case.

Table V
MNDO- and AM1-Calculated Ionization Potential and Bandgap for Derivatives of Structure II[a]

II				
R	R′	method	IP, eV	bandgap, eV
H	H	MNDO	8.65	8.22
		AM1	8.79	8.14
Cl	Cl	MNDO	9.57	7.93
		AM1	9.13	7.68
CH_3	CH_3	MNDO	8.56	8.00
		AM1	8.39	7.89
$\Delta(Cl)_2$		MNDO	0.92	-0.29
		AM1	0.34	-0.47
$\Delta(CH_3)_2$		MNDO	-0.10	-0.22
		AM1	-0.39	-0.26

[a] The changes in the electronic properties are with respect to the unsubstituted polymer.

charges included in Table IV, indicating that the methyl group is not as good an electron donor as the chlorine is an electron withdrawer.

The effect of substituents on the bandgap is different. Specificially, the bandgap for both dichloro- and dimethyl-substituted poly(diacetylenes) is lower than that of the unsubstituted polymer. This shift in the bandgap implies that the absorption edge will be significantly red shifted. The decrease in the bandgap of the dichloro-substituted species indicates that a chloro group has considerable effect on the lowest unoccupied molecular orbital (LUMO) and will stabilize this orbital. The observed effects are in agreement with qualitative MO theory.

Conformations of the Poly(diacetylene) Chain. Many poly(diacetylenes) show "red-to-blue" shifts in the solid state or in solution when the temperature or the solvent is changed.[10,11] Berlinsky et al.[18] have proposed a theory for the rod-to-coil transition in the poly(diacetylene) 4BCMU and related polymers. That theory is based on the hypothesis that the yellow phase consists predominantly of the cis structure, while the red phase is trans. Patel et al.[19] identified the red phase as a planar conformation, because the red color is associated with the small transition energy expected for long conjugation length, while the yellow is characteristic of conjugation length of only a few monomer units. It is also proposed by Baughman and Chance[20] that conjugation in the yellow phase is interrupted by "orbital spin flips" about the single bonds. More recently, Schweizer[21] has developed a statistical mechanical theory that leads him to suggest that the coupled conformational–electronic transitions in poly(diacetylenes) both in liquid solution and in solid films are driven by configuration-dependent polymer–solvent interactions that arise from electron delocalization along the polymer backbone. We sought to apply the AM1 semiempirical method to this problem to see if this would provide insight into this phenomenon.

To investigate the relation between electronic transitions and nonplanarity of the poly(diacetylene) chains, we examined the dichloro- and dimethyl-substituted polymers as models. The nonplanar backbones were generated by introducing alternating rotations of $\pm\phi°$ about the single bond formed between carbon atoms 3 and 4. After each

Table VI
AM1-Calculated Ionization Potential, Total Energy, and Optimized Molecular Geometry for Dimethyl-Substituted Structure II as a Function of the Backbone Dihedral Angle[a-c]

	0°	5°	10°	20°	30°	60°	90°
IP, eV	8.39	8.39	8.42	8.44	8.49	8.69	8.85
tot energy, eV	−2302.3	−2302.3	−2302.3	−2302.3	−2302.3	−2302.3	−2302.3
ΔE_{tot}, kJ/mol	0.00	3.47	−0.19	−1.45	0.00	5.60	4.15
r_1	1.2029	1.2014	1.2006	1.1989	1.1977	1.2004	1.1994
r_2	1.4103	1.4140	1.4147	1.4118	1.4123	1.4148	1.4112
r_3	1.3480	1.3501	1.3484	1.3477	1.3461	1.3449	1.3486
α	112.50	113.3	112.0	112.9	112.3	113.7	115.7
β	119.4	118.6	118.7	119.6	118.7	118.0	118.2

[a] Total energy changes, ΔE_{tot}, are with respect to the planar structure. [b] Molecular geometries are shown for system II. [c] Bond lengths in angstroms; bond angles in degrees.

Table VII
AM1-Calculated Ionization Potential, Total Energy, and Optimized Molecular Geometry for Dichloro-Substituted Structure II as a Function of the Backbone Dihedral Angle[a-c]

	0°	5°	10°	20°	30°	60°	90°
IP, eV	9.13	9.14	9.13	9.15	9.20	9.26	9.34
tot energy, eV	−3527.1	−3527.1	−3527.1	−3527.2	−3527.2	−3527.1	−3527.2
ΔE_{tot}, kJ/mol	0.000	0.10	1.26	−0.77	−1.35	0.00	−1.06
r_1	1.1994	1.1996	1.1995	1.1998	1.1997	1.1985	1.1992
r_2	1.4051	1.4047	1.4035	1.4055	1.4056	1.4080	1.4071
r_3	1.3489	1.3485	1.3500	1.3481	1.3456	1.3475	1.3443
α	114.7	114.6	114.7	114.7	114.9	114.6	113.6
β	120.6	120.9	120.7	120.4	122.1	120.7	121.4

[a] Total energy changes, ΔE_{tot}, are with respect to the planar structure. [b] Molecular geometries are shown in system II. [c] Bond lengths in angstroms; bond angles in degrees.

Table VIII
AM1-Calculated Energies of the HOMO, LUMO, and Bandgap for Dichloro-Substituted Structure II as a Function of the Backbone Dihedral Angle[a]

	0°	5°	10°	20°	30°	60°	90°
E_{HOMO}	−9.1295	−9.1345	−9.1259	−9.1500	−9.1973	−9.2601	−9.3419
E_{LUMO}	−1.4531	−1.4577	−1.4626	−1.4362	−1.4281	−1.3360	−1.3094
bandgap, eV	7.68	7.68	7.66	7.71	7.77	7.92	8.03
Δ_{HOMO}	0.0000	−0.0050	0.0036	−0.0205	−0.0678	−0.1306	−0.2124
% Δ_{HOMO}	0.00	−0.05	0.04	−0.22	−0.74	−1.43	−2.33
Δ_{LUMO}	0.0000	−0.0046	−0.0095	0.0169	0.0250	0.1171	0.1437
% Δ_{LUMO}	0.00	−0.32	−0.65	1.16	1.72	8.06	9.89
Δ_{BG}, eV	0.00	0.00	−0.01	0.03	0.09	0.24	0.35
% Δ_{BG}	0.00	0.01	−0.17	0.49	1.21	3.23	4.64

[a] The changes in energies and bandgaps are with respect to the planar polymer.

rotation all bond lengths and bond angles were fully optimized by using the AM1 semiempirical MO method. The calculated Koopman ionization potentials, changes in total energies, and optimized molecular geometries of the dimethyl and dichloro polymers as a function of the degree of nonplanarity along the backbone are summarized in Tables VI and VII, respectively. For both the methyl- and chloro-substituted species, the ionization potential increases as the degree of nonplanarity increases. This increment is, however, more pronounced for the methyl-substituted species as compared to the chloro-substituted polymer. It can be seen from Tables VI and VII that changes in bond lengths are very small but not negligible. The internal barriers to rotation about the C_3–C_4 bond are 7.1 and 2.5 kJ/mol for the dimethyl- and dichloro-substituted poly(diacetylene), respectively. These small barriers suggest that, within the solid state, rotation about the single bonds may be possible for these polymers.

AM1-calculated energies of the HOMO, LUMO, and bandgaps for the dichloro-substituted poly(diacetylene) as a function of rotation angle ϕ are included in Table VIII, and variation in the bandgap is shown (dashed line) in Figure 1. The bandgap shows a small increase at 5° and a decrease at 10° and then starts to increase with increasing rotation angle ϕ. A decrease in the bandgap at 10° can be mainly attributed to the stabilization of the LUMO. In this respect we note that caution must be applied to interpretation of results based on the computed energies of unoccupied molecular orbitals since these orbitals have little physical significance within the framework of the Hartree–Fock approximation.

Table IX and Figure 1 (solid line) indicate that variation of the bandgap as a function of nonplanarity for the dimethyl-substituted poly(diacetylene) has a different appearance. In this case the bandgap increases continuously as the rotation angle increases. This behavior is consistent with the fact that, by losing order, the bandgap will increase as a result of the loss of delocalization. Table IX shows that as the degree of nonplanarity increases, the HOMO is more stabilized and the LUMO is more destabilized, resulting in a blue shift in the bandgap. It is clear from data included in Tables VIII and IX that the overall trend of variation of the bandgap as a function of increase in the degree of nonplanarity is a red-to-blue transition. Therefore, our calculations suggest that by changing the temperature, the conformation of poly(diacetylene) chains with a small barrier to rotation will deviate from planarity. This deviation, in turn, has an effect on the energies of the molecular orbitals and, therefore, influences the spectroscopic properties or the polymers. These results seem to be consistent with Schweizer's conclusions.[21] Clearly though, one can expect solvent changes to drastically

Table IX
AM1-Calculated Energies of the HOMO, LUMO, and Bandgap for Dimethyl-Substituted Structure II as a Function of the Backbone Dihedral Angle[a]

	0°	5°	10°	20°	30°	60°	90°
E_{HOMO}	-8.3947	-8.3940	-8.4154	-8.4403	-8.4898	-8.6907	-8.8472
E_{LUMO}	-0.5068	-0.4779	-0.4649	-0.4540	-0.4027	-0.2108	-0.0796
bandgap, eV	7.89	7.92	7.95	7.99	8.09	8.48	8.77
Δ_{HOMO}	0.0000	0.0007	-0.0207	-0.0456	-0.0951	-0.2960	-0.4525
% Δ_{HOMO}	0.00	0.01	-0.25	-0.54	-1.13	-3.53	-5.39
Δ_{LUMO}	0.0000	0.0289	0.0419	0.0528	0.1041	0.2960	0.4272
% Δ_{LUMO}	0.00	5.70	8.27	10.42	20.54	58.40	84.29
Δ_{BG}, eV	0.00	0.03	0.06	0.10	0.20	0.59	0.88
% Δ_{BG}	0.00	0.36	0.79	1.25	2.53	7.50	11.15

[a] The changes in energies and bandgaps are with respect to the planar polymer.

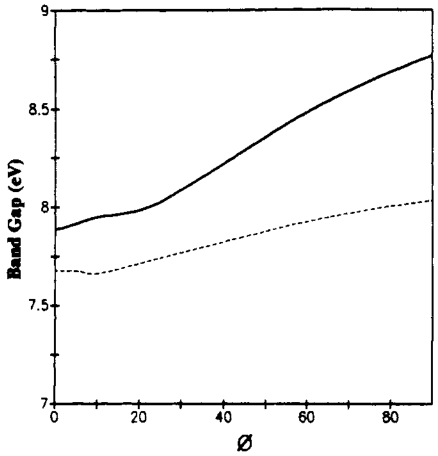


Figure 1. AM1-computed bandgap as a function of dihedral angle of the methyl- (—) and chloro-disubstituted (- - -) poly(diacetylene) models.

Table X
Comparison of Bandgaps of Some Diacetylene Monomers with Those of Structure II

II		monomer		structure II		
R	R′	bandgap	Δ	bandgap	Δ	ΔΔ
H	H	11.1	0.0	8.1	0.0	3.0
Cl	H	10.5	-0.6	7.9	-0.2	2.6
Cl	Cl	10.0	-1.0	7.7	-0.4	2.3
CH_3	H	10.6	-0.4	8.0	-0.1	2.6
CH_3	CH_3	10.3	-0.8	7.9	-0.2	2.4

[a] The changes in bandgaps are with respect to the unsubstituted species (Δ) and from monomer to polymer (ΔΔ). Both have units of eV.

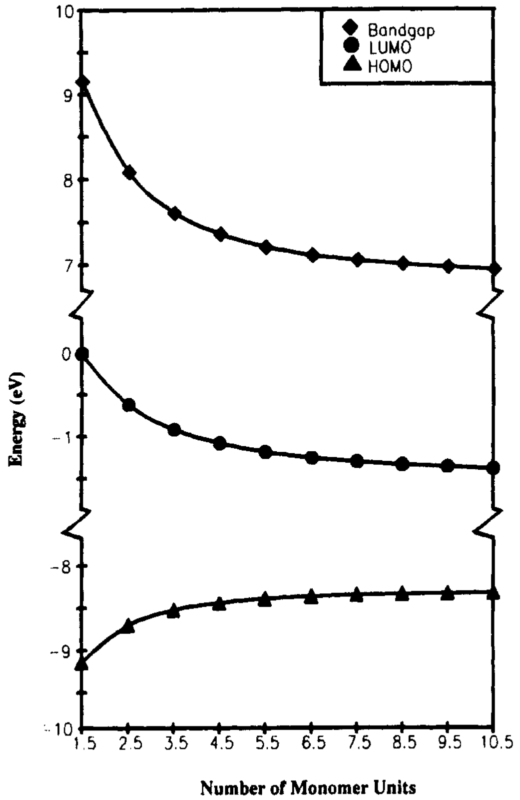


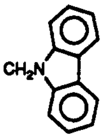
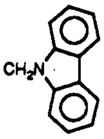
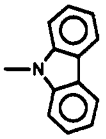
Figure 2. AM1-computed HOMO and LUMO energies and the bandgap as a function of chain length.

affect solvation of polymers and result in much larger relative conformational energies; the present AM1 calculations are not suitable for modeling solvent effects.

Comparison of Electronic Properties of Some Diacetylene Monomers with Corresponding Polymers. Most of the diacetylene monomer crystals are transparent if pure, i.e., free of residual polymer, and their optical properties will change upon polymerization. It is known that increasing the conjugation length of a molecule lowers the energy of elementary excitations of a conjugated chain.[22,23] To elucidate this concept, the AM1-calculated bandgaps of some diacetylene monomers are compared with those of their analogous polymers in Table X. Predictably, all poly(diacetylenes) computed (Table X) have smaller bandgaps than their analogous monomers. Our calculation shows that the HOMO experiences an upward and the LUMO a downward shift in energy, and the bandgap decreases upon the extension of length of the polymer chain (Figure 2). This is consistent with what one may expect from fully conjugated systems. In the case of the unsubstituted polymer, the bandgap is enormously reduced (by 2.9 eV) going from monomer to the polymer of structure II, while differences between the bandgaps of structures I and II are still significant (0.68 eV) but much smaller. The smaller value between I and II is obviously due to the fact that the elementary cell chain of these polymer models is comparatively large. The bandgap between structure I and its higher ($n + 1$) analogue is even less (0.21 eV) and establishes a trend to smaller and smaller bandgaps for conjugated high polymers with similar molecular weights.

It is clear from Table X that substitution has a small effect on the optical transition of monomers, and the effect is even smaller for the corresponding polymers. Substitution of one chlorine reduces the bandgap of the monomers and its analogous poly(diacetylenes) by 5.33% and 3.24%, respectively. In the case of the dichloro species the bandgap increases 9.42% and 5.75% for the monomer and its analogous polymer, respectively. For the monomer and polymer of the methyl-substituted diacetylene the changes in the bandgap are smaller. Therefore, one may conclude that it is the electronic structure of the backbone rather than that of the substituents that provides the major influence of the electronic properties of poly(diacety-

Table XI
Experimental Bandgaps for Diacetylene Monomers (1) and Polymers (2)

R	R′	abbrev	bandgap, eV			ref
			monomer	polymer	$\Delta\Delta$[a]	
CH_2OSO_2-*p*-$C_6H_4CH_3$	CH_2OSO_2-*p*-$C_6H_4CH_3$	PTS	7.1	2.0	5.1	*b*
$(CH_2)_4OCONHC_6H_5$	$-(CH_2)_4-OCONHC_6H_5$	TCDU		2.33		*c*
		DCHD		1.9		*d*
	CH_2OH	CPDO		1.6		*e*

[a] Change from monomer to polymer. [b] Tokura, Y.; Mitani, T.; Koda, T. *Chem. Phys. Lett.* **1980**, *75*, 324. [c] Muller, H.; Eckhardt, C. J.; Chance, R. R.; Baughman, R. H. *Chem. Phys. Lett.* **1977**, *50*, 22. [d] Hood, R. J.; Müller, H.; Eckhardt, C. J.; Chance, R. R.; Yee, K. C. *Chem. Phys. Lett.* **1977**, *54*, 295. [e] Matsuda, H.; Nakanishi, H.; Minami, N.; Kato, M. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 241.

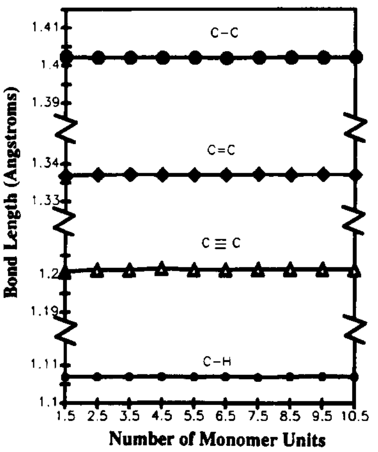


Figure 3. AM1-computed bond lengths in the terminal monomer unit for a series of oligomeric diacetylenes.

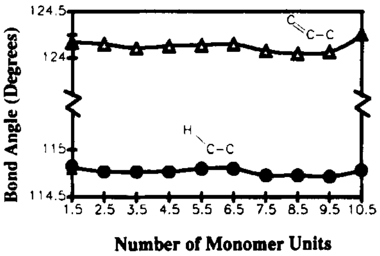


Figure 4. AM1-computed bond angles in the terminal monomer unit for a series of oligomeric diacetylenes.

lenes). This is in contrast to the situation encountered with conventional polymers having σ-bonded backbones where the substituents play the dominant role.

Comparison of calculated and experimental bandgap values for diacetylene monomers and polymers requires some guesswork since the actual molecules we have calculated have not been studied experimentally. Also, experimental measurements of first ionization potentials for poly(diacetylenes) are rare. However, first IPs for the polymers like CPDO (Table XI) are ca. 7 ± 1 eV, while for the simpler polymers we calculate values ca. 1.4–2.6 eV higher. The bandgaps calculated for our simple models are also higher than measured values of known derivatives that are more complex molecules (see Table XI). This failure to mimic experiment may be due to three factors that we can identify. First, since these methods do not include electron correlation, the computed HOMO energies are probably too negative. Second, our calculation assumes that the polymer is perfectly modeled by the enyne structure (2); in fact, there is speculation[1] that some of the polymer's observed electronic properties are the result of the presence of bond rotation that may produce 12–15 monomer units that might have carbene, radical, or cationic sites. In this connection, the recent work of Tanaka et al.[3] is especially pertinent. They computed poly(diacetylene) bandgaps of 9.36 eV, which dropped to 1.59 eV when a cation concentration of 25 mol % was assumed. Finally, as we noted above, there is a large change in the computed bandgap on going from monomer to structure I, the polymer model. We suspect that our polymer model is insufficient, and we treat that possibility below.

Since we noted that the difference in the computed bandgap on going from the simplest polymer model (i.e., structure II) to the higher homologue (i.e., structure I) is substantial, we began to suspect that the capped bond does not properly account for conjugation effects of the extended chain. To verify this we calculated bandgaps for several chain-extended models that represent oligomeric diacetylenes having hydrogen end groups. The results of these calculations are shown in Figure 2. The trends for the HOMO, LUMO, and bandgap energies discussed above are shown to continue by these extended calculations. The graphs also show that the capped-bond option does lead to erroneous predictions for electronic properties if small models are used. With the extended models, we can now extrapolate a lower limit for the bandgap of ca. 6 eV for a poly(diacetylene) having 30–40 monomer units. This computed bandgap is still some 4 eV higher than the bandgaps measured experimentally (e.g., Table XI).

Orchard and Tripathy[5] calculated the electronic band structure of diacetylene polymers using the valence effective Hamiltonian method and obtained bandgaps that are more accurate than the ones calculated here by the AM1 method. However, for the prediction of trends, we only need *relative* energies, which we believe the AM1 can reliably produce. Also, we believe that AM1 (and PM3) offers speed and flexibility not available in other methods that have been applied to complex diacetylene polymers.

AM1 Calculations of Oligomeric Diacetylenes. The above calculations and bandgaps for oligomeric diacetylenes (compare Table V and Figure 2) show that the capped-bond option is insufficient in modeling certain features of polymers, especially conjugated polymers. Therefore, we decided to look at some other features of

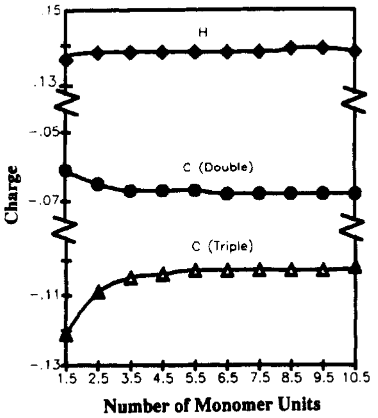


Figure 5. AM1-computed charge in the terminal monomer unit for a series of oligomeric diacetylenes.

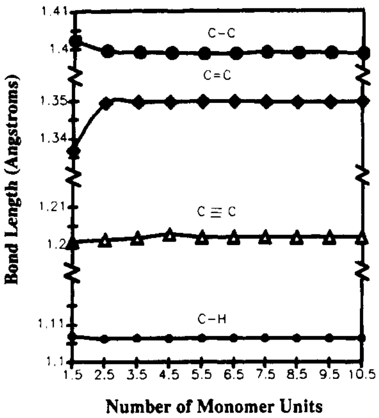


Figure 6. AM1-computed bond lengths in the central monomer unit for a series of oligomeric diacetylenes.

the calculations of oligomers to see how the properties of the chain-extended models vary. In Figures 3–5 we show the trends for bond lengths, bond angles, and charge, respectively, for the atoms or groups closest to the end group (hydrogen) in each structure. The data shown in Figures 6–8 are for bond lengths, bond angles, and charge, respectively, in the same set of structures, but using data from the central most atom or unit. Note that the geometries settle down quite rapidly but the atomic charges on carbon are still variable at fairly long chain lengths. We think these data suggest that AM1 calculations of oligomers and conjugated polymers using less than about four monomer units for diacetylenes (and probably eight or more for polyacetylenes) are not representative of the conjugated system.

Conclusion and Summary

Poly(diacetylenes) with fully conjugated backbones are suitable models for theoretical investigation of the electronic properties of conjugated polymers. Theoretical elucidation of poly(diacetylenes) in this paper accompanies three goals as follows:

(1) Since ab initio calculations are not feasible for optimizing molecular geometries of substituted poly(diacetylenes), the reliability of some semempirical SCF–MO methods in reproducing the molecular geometries and electronic properties were investigated. The MNDO-, AM1-, and PM3-calculated bond lengths of chloro- and methyl-substituted poly(diacetylene) backbones are in good agreement with the experimental data. The calculated angles α and β of poly(diacetylene) obtained by using the MNDO and AM1 methods are in reasonable agreement with ab initio[4] results, but the angle α is slightly overestimated by the PM3 method.

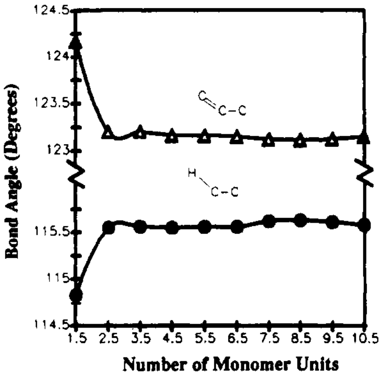


Figure 7. AM1-computed bond angles in the central monomer unit for a series of oligomeric diacetylenes.

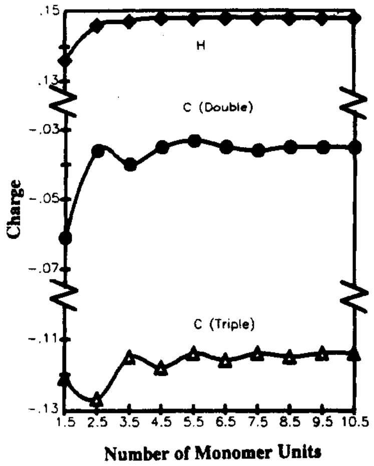


Figure 8. AM1-computed charge in the central monomer unit for a series of oligomeric diacetylenes.

(2) The methyl group as an electron-donating substituent and a chlorine atom as an electron-withdrawing substituent are chosen to elucidate the substitution effect on the molecular geometry and electronic properties of poly(diacetylene) backbones. Changing the substituents has a small effect on the bond lengths of the polymer backbone and insignificant effect on the angle α.

The charge concentration about the carbon atom (C_4) of the backbone connecting the substituents decreases in the case of chlorine and increases by a smaller amount when a methyl group is the substituent. These changes are smaller for C_1 and C_2, which are more distant from the substituents. These results confirm that the effect of substituents rapidly diminishes as the distance from the site of substitution increases. Also the inductive effect of a chloro group is indicated to be much stronger than that of a methyl group for short-range interactions.

(3) The Koopman ionization potential, the energies of the HOMO and LUMO, and the variation of the bandgap as a function of the degree of nonplanarity were investigated in this work. For both chloro- and methyl-substituted species, the ionization potential increases as the degree of nonplanarity increases. This increment is more pronounced for the methyl-substituted polymer as compared to the chloro-substituted polymer. As the degree of nonplanarity increases, the HOMO is more stabilized and the LUMO is more destabilized, resulting in a blue shift in the bandgap. The overall variation of the bandgap as a function of an increase in nonplanarity is a red-to-blue shift. Therefore, one may conclude that the conformation of poly(diacetylene) backbones, with a small barrier to rotation, changes by variation of temperature. This deviation from nonplanarity will change the energies

of the HOMO and LUMO, and therefore the optical properties of the polymers will change.

The bandgaps of chloro- and methyl-substituted poly(diacetylene) monomers are compared with those of the corresponding polymers. All poly(diacetylenes) of interest in this work have smaller bandgaps than the analogous monomers. Substitution for hydrogen by a chlorine atom or a methyl group changes the bandgap by at most 10%, while this parameter changes considerably upon polymerization. This indicates that it is the electronic structure of the backbone rather than that of the substituents that controls the electronic properties of the poly(diacetylenes). The effect on properties of conjugating groups were not considered in this article but will be reported when work currently underway is complete.

The capped bond does not allow calculation of some properties of long-chain conjugated polymers. In particular, we found that the calculations of bandgaps and charges were especially affected by chain length; therefore, calculations of oligomers rather than short-chain models were required to obtain good AM1 calculations of the polymers.

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Registry No. 1 (R,R = H), 460-12-8; 1 (R = Cl, R = H), 6089-44-7; 1 (R,R = Cl), 51104-87-1; 1 (R = CH_3, R = H), 4911-55-1; 1 (R,R = CH_3), 2809-69-0; II (R,R′ = H), 131105-49-2; II (R,R′ = H) (SRU),61565-16-0; II (R = Cl, R′ = H), 131105-50-5; II (R,R′ = Cl), 131105-51-6; II (R,R′ = Cl) (SRU), 131130-25-1; II (R = CH_3, R′ = H), 131105-52-7; II (R,R′ = CH_3), 131105-53-8; II (R,R′ = CH_3) (SRU), 131105-58-3; II (R = Cl, R′ = H) (SRU), 131378-80-8; II (R = CH_3, R′ = H) (SRU), 131378-81-9.