



Effects of substituents on the electronic properties of polyacetylenes

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ABSTRACT

Hartree–Fock quantum mechanical calculations [at the RHF(ROHF)/6-31G(d) level] were performed to determine the electronic structure (ionization energies, electron affinities and singlet–triplet transition energies, $\Delta E(S_0 \rightarrow T_1)$) in a series of polyacetylenes with terminal substituents (neutral and charged), $=NH$ ($=NH_2^+$), $-NH_2$ ($-NH_3^+$), $-SH$ ($-S^-$), and $-SO_3H$ ($-SO_3^-$), for oligomers with between 2 and 30 conjugated double bonds. Neutral substituents had relatively modest effects on the electronic properties, primarily in systems with less than ~ 8 – 10 double bonds. The positively and negatively charged substituents were found to exert profound influences on these properties, which persisted in even the largest species studied. Negative terminal substituents lowered the ionization energies (relative to PA) by as much as 5 eV, even in systems with 30 double bonds, and the positive substituents decreased electron affinities by an equivalent amount. Both positive and negative substituents decreased values of the singlet–triplet transition energy by ~ 1 – 1.5 eV relative to the value in pristine PA. These effects were explained on the basis of a simple model of the effects of electron donors and acceptors on the frontier orbital (HOMO/LUMO) energies and charge distributions.

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1. Introduction

Because of their comparatively low manufacturing cost, ready processability, suitable band gaps (1.5–3.0 eV) and unique one-dimensional conductivity, polymers with conjugated π systems can potentially be utilized as the media for a less expensive, more versatile class of photovoltaic devices in the optical range of the spectrum than standard, silicon based semiconductors [1–5]. Unlike conventional semiconductors, in which the charge carriers are free to migrate independently, the photogenerated electrons and holes in conjugated polymers are bound together in “excitons” [6,7] and the additional energy required to separate the positive and negative charge carriers results in lowered energy conversion efficiencies. A number of methods have been proposed to alleviate this problem, including the use of block copolymers and appropriately placed substituents on the polymer backbone; however, results to date have not been entirely successful [1,4,5].

With a goal towards better understanding the effects of composition and substituents on electronic properties (e.g. ionization energy, electron affinity and optical transition energies) of conducting properties, we have completed investigations on block copolymers between polyacetylene and polymethineimine [$H-(CH=N-)_nH$] [8] and on 1-azapolyacetylenes [$H-(CH=CH)_{n-1}-CH=NH$] [9]. In both studies, it was observed that protonation of a nitrogen atom

had dramatic effects on the electronic properties, extending to oligomers with 20 or more double bonds.

Because of the marked impact of nitrogen protonation on the IEs, EAs and transition energies in 1-azapolyacetylenes, we have decided to further probe the effect of additional positively and negatively charged substituents on these properties in a series of substituted polyacetylenes. The computational methods and results are presented below.

2. Computational procedures

All calculations were performed using the Gaussian-98 [10] program suite on computers at the ASC/MSRC Supercomputer Center. The systems studied (with formula and acronym) were: (A) polyacetylene [$H-(CH=CH)_n$ PA], (B) 1-azapolyacetylene [$H-(CH=CH)_{n-1}-CH=NH$, APANH] and protonated form [$H-(CH=CH)_{n-1}-CH=NH_2^+$, APANH₂⁺] [11], (C) 1-aminopolyacetylene [$H-(CH=CH)_n-NH_2$, PANH₂] and protonated form [$H-(CH=CH)_n-NH_3^+$, PANH₃⁺], (D) 1-thiopolyacetylene [$H-(CH=CH)_n-SH$, PASH] and deprotonated form [$H-(CH=CH)_n-S^-$, PAS⁻], (E) 1-sulfonatopolyacetylene [$H-(CH=CH)_n-SO_3H$, PASO₃H] and deprotonated form [$H-(CH=CH)_n-SO_3^-$, PASO₃⁻]. Oligomers with even numbers of double bonds from 2 to 30 bonds were investigated. Ground state geometries of the oligomers in their all-trans conformations were optimized at the RHF/6-31G(d) level; all equilibrium structures represent energy minima.

Vertical ionization energies (IE) may be calculated as the energy difference of the radical cation [12] relative to the ground state,

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where cations represent species formed by removal of an electron from the π -system. Similarly electron affinities (EA) may be calculated from the radical anion (addition of an electron to a the π^* orbitals) energies via the relation, $EA = E(\text{Radical Anion}) - E(\text{Parent})$, and singlet–triplet excitation energies, $\Delta E(S_0 \rightarrow T_1)$, (representing the lowest $\pi \rightarrow \pi^*$ transition) from the energy of the lowest triplet.

It is expected that the quantitative values of these excited state properties may depend significantly upon both the size of the basis set as well as the inclusion of electron correlation. Therefore, we have computed values of $\Delta E(S_0 \rightarrow T_1)$, IE and EA using two basis sets, B1 = 6-31G(d) and B2 = 6-311+G(d) at the ROHF level for the two smallest oligomers [NDB = 2 double bonds and NDB = 6 double bonds], as well as at the ROMP2/6-311+G(d) level, to test the effect of electron correlation. The results for PA and all of the neutral species are contained in Table 1.

One observes from the table that for the smallest system (NDB = 2), values of $\Delta E(S_0 \rightarrow T_1)$ increase markedly from ROHF/B1 to ROHF/B2 results. However, for the slightly larger system (NDB = 6), the larger basis set has very little impact on the results. Although not shown, this was also found to be the case for larger oligomers. One finds further that values of IE are little affected by basis set size. There are significant differences between values of EA using the two bases, but it can be noted that the qualitative trends with increasing system size are similar using both basis sets. It may also be seen in Table 1 that the additional inclusion of electron correlation [ROMP2/B2] has relatively small effects on computed values of $\Delta E(S_0 \rightarrow T_1)$ and IE, but induces a drastic decrease in the electron affinity. However, again, qualitative trends in EA are preserved (decreasing EA with increasing oligomer size).

Ideally, one wants to utilize the highest basis set and include accurate correlation energies for all calculations. However, we found that the ROMP2/B2 calculations were not feasible for systems with more than 10–12 double bonds. Yet, some of the most interesting trends in the results are found in the larger systems, since the excited state properties often vary asymptotically towards a large molecule limit, and require calculations out to NDB = 20–30 (*vide infra*). Therefore, we adopted a compromise and calculated ionization energies and electron affinities at the ROHF/B2 level (i.e. with the triple zeta basis including a diffuse function). It was found that excitation energies (calculated at this level were very similar to ROHF/B1 results for small-medium oligo-

mer size, but would not converge to a stable solution in the larger systems. Therefore, unlike IE and EA results, values of $\Delta E(S_0 \rightarrow T_1)$ to be presented below are at the ROHF/B1 level.

We also note that in our recent study of 1-azapolyacetylenes [9], calculations were also carried out with larger basis sets, without yielding significant differences in IEs, EAs and transition energies. In addition, CASSCF calculations on the smaller oligomers of that series gave results for these parameters which were in good qualitative agreement with those from ROHF/6-31G(d) calculations. For a number of the systems investigated here, we also performed CIS/6-31G(d) calculations [13–15] to obtain the lowest singlet–triplet [$\Delta E(S_0 \rightarrow T_1)$] excitation energies. Although there were significant differences between quantitative values of the ROHF and CIS excitation energies, trends obtained using the two methods were very similar.

In our results and discussion below, it should be recognized that our goal is to interpret qualitative trends in the excited state properties as a function of oligomer size. Quantitative (and even semi-quantitative) values for these parameters would require even larger bases and higher levels of electron correlation (e.g. CCSD), and are not currently possible on the larger polyenes studied in this work.

It should be noted that all transition energies, ionization energies and electron affinities in this investigation were computed without zero-point vibrational energy corrections. This is expected to have only a small quantitative effect on numerical results and no impact on observed trends.

3. Results and discussion

3.1. Effects of electron acceptor/donor substituents on polyacetylene HOMOs and LUMOs

It is expected that if an electron acceptor, such as an amino group ($-\text{NH}_2$) or ammonium ion ($-\text{NH}_3^+$) is added to a polyacetylene chain, the mobile π electrons will be attracted to this substituent, leading to lowered energies of both the filled π orbitals (e.g. the “valence band” in semiconductor terminology) and virtual π^* orbitals (e.g. the “conduction band”). It is also expected that those orbitals with greater electron density in the vicinity of the acceptor will be lowered by a larger amount. Thus, one should find that orbitals located closer to the electron-accepting substituent will end up near the bottom of both the valence and conduction bands.

Table 1
Effect of basis set and correlation on electronic parameters^a

Molecule ^b	Method ^c	$\Delta E(S_0 \rightarrow T_1)$	$\Delta E(S_0 \rightarrow T_1)$	IE	IE	EA	EA
		NDB = 2	NDB = 6	NDB = 2	NDB = 6	NDB = 2	NDB = 6
PA	ROHF/B1	3.31	2.72	7.93	6.29	2.92	1.21
	ROHF/B2	6.04	2.72	8.07	6.47	2.16	0.87
	ROMP2/B2	6.46	2.55	8.91	7.04	1.46	−0.18
APANH	ROHF/B1	3.65	2.72	8.77	6.57	2.53	1.00
	ROHF/B2	6.49	2.75	8.91	6.75	1.73	0.66
	ROMP2/B2	7.51	2.58	10.17	7.36	1.52	−0.37
PANH ₂	ROHF/B1	3.30	2.71	6.81	5.94	3.53	1.40
	ROHF/B2	4.69	2.72	6.97	6.13	1.53	1.03
	ROMP2/B2	4.94	2.29	7.65	6.59	1.35	−0.02
PASH	ROHF/B1	3.22	2.71	7.45	6.23	2.61	1.12
	ROHF/B2	5.01	2.75	7.54	6.39	1.67	0.82
	ROMP2/B2	4.78	2.52	8.08	6.86	1.33	−0.21
PASO3H	ROHF/B1	3.28	2.67	8.91	6.76	1.31	0.44
	ROHF/B2	3.35	2.68	9.04	6.94	1.48	0.14
	ROMP2/B2	–	2.47	9.94	7.45	1.29	−0.81

^a Energies given in eV.

^b See text for molecule acronyms.

^c B1 = 6-31G(d); B2 = 6-311+G(d).

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