

Molecular modelling of hyperbranched polyacetylene

Serguei Fomine*, Lioudmila Fomina, Patricia Guadarrama

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacán, México DF 04510, México

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SUMMARY: *Ab initio* and density functional theory calculations carried out on linear and dendritic polyacetylenic (PA) oligomers of different size showed that acetylenic dendrimers are less stable than *trans*-PA oligomers and that the instability increases with molecular weight reflecting the strain in crowded hyperbranched structures. However, the energy difference between linear and dendritic structure is rather small and tends to a limit with molecular weight. Twisting of the double bonds decreases the conjugation in hyperbranched PA compared to linear *trans*-PA. However, the conjugation though less effective than in *trans*-PA is extended up to the 4th or 5th generation of dendrimers. It was shown that bromine end groups strongly affect the electronic properties of acetylenic dendrimers decreasing even more the conjugation due to the sterical hindrances, however, highly polarizable bromine atoms reduced significantly the adiabatic potentials of ionization to be very close to that for *trans*-PA oligomers.

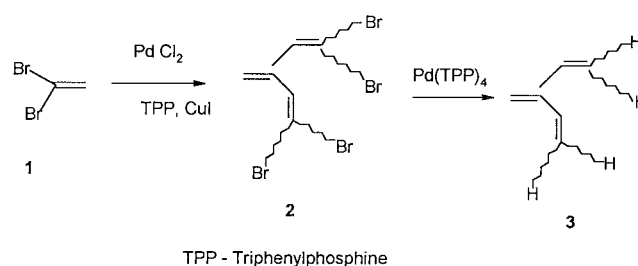
Introduction

Hyperbranched polymers obtained from AB₂ type monomers are attracting increasing interest. Some advantages of hyperbranched polymers are the high solubility compared with their linear analogues and the high concentration of end groups even for high-molecular-weight polymers. It is also known that the polyconjugated polymers which show conductivity and non-linear optical properties are mostly insoluble unless they contain long aliphatic spacers. These spacers deteriorate the polymer properties related with the conjugation and interchain interactions such as conductivity, non-linear optical properties *etc.* Fully conjugated hyperbranched polymers are an alternative to conjugated polymers with long aliphatic spacers. They should combine solubility with high concentration of conjugated units. The present authors have recently reported the synthesis and molecular modelling of fully conjugated hyperbranched polymers obtained by Pd-catalyzed cross-coupling of β,β -dibromo-4-ethynylstyrene. The polymer was soluble in hot chlorinated aromatic hydrocarbons, showed \bar{M}_w of 70000 and exhibited strong photoluminescence¹⁾. Molecular modelling of poly(β,β -dibromo-4-ethynylstyrene) at AM1 level of theory showed that conjugation in the polymer is partially disrupted by twisting of the benzene rings.

Hyperbranched PA can be generated by the Heck reaction according to the Scheme 1 starting from 1,1-dibromoethylene (1). The resulting hyperbranched PA will contain bromine end-groups (2). The bromine end groups can be replaced with hydrogen by the treatment of Br-terminated hyperbranched PA with Pd(TPP)₄ to produce hyperbranched PA with hydrogen end group (3).

Although a few theoretical studies of dendritic molecules have now appeared²⁻⁵⁾ little is known about the elec-

Scheme 1: A route to hyperbranched polyacetylene



tronic structure of conjugated hyperbranched polymers and their importance for application properties as their potentials of ionization (IP) and energy gaps (E_g), how those values depend on molecular weight and the nature of end groups, and how they are related with those properties of linear analogues. This paper is devoted to a comparative theoretical study of hyperbranched and linear *trans*-polyacetylene (PA) as simplest representative of conjugated hyperbranched polymers using semiempirical, *ab initio* and density functional (DFT) methods.

Five generations of acetylenic dendrimers shown in Fig. 1 were studied as idealized models of hyperbranched PA molecules at the different stages of growth. The respective bromine-terminated acetylenic dendrimers up to the 4th generation were also examined to clarify the effect of bulky and polarizable bromine terminal groups on geometry and electronic properties of hyperbranched PA. In order to compare the electronic structure of hyperbranched PA with that of the linear analogue, the geometry optimization and single point energy calculation were carried out also for *trans*-PA oligomers corresponding to the respective dendrimer generation (**Lin1–Lin5**).

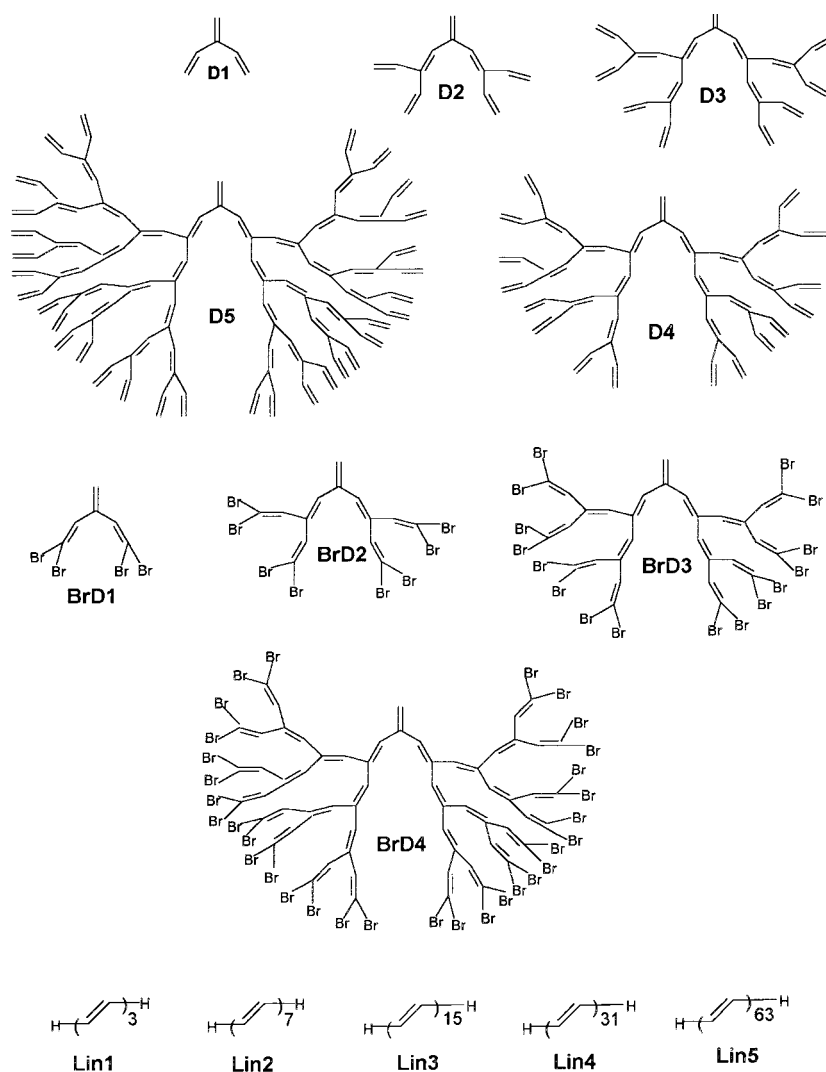


Fig. 1. Studied dendritic and linear acetylenic oligomers

Methods

All calculations were performed using Gaussian-94⁶; initial geometries were generated using CS Chem3D Pro Version 4.0 after preliminary optimization with MM2 force field⁷. First, the geometries of **Lin1**, **D1** and **D2** molecules were fully optimised at PM3⁸, RHF/3-21G and B3LYP/3-21G⁹ levels of theory and the results were compared with one another and with experimental data available for **Lin1**¹⁰. All methods reproduced bond lengths and angles for **Lin1** within 0.01–0.02 Å and 1°–2°, respectively, giving very similar results for the rest of molecules tested. The PM3 model Hamiltonian was chosen for the geometry optimization as the computationally less demanding alternative.

Including electron correlation is very important for accurate modelling of polyenes¹¹, therefore, the Becke three parameter hybrid (B3) exchange functional in combination with the Lee-Yang-Parr (LYP) correlation func-

tional (B3LYP)⁹ with split valence basis set (3-21G) was used for single point energy calculations. It has been shown that the B3LYP single point energy calculations run at PM3 or AM1 optimized geometry have better mean absolute deviation from experiment than the Hartree-Fock based methods¹². The vertical ionization potentials (IP) were calculated as the negative HOMO energies taken from RHF/3-21G single point energy calculation according to Koopman's theorem¹³ since all DFT methods give negative HOMO energies too low compared to experimental IPs¹⁴. However, B3LYP HOMO-LUMO energy differences gave excitation energies (energy gap (E_g)) in good agreement with experimental values due to partial cancellation of the particle-number discontinuities in the exchange-correlation functional associated with IPs and electron affinities¹⁴. Adiabatic IPs were obtained as B3LYP energy difference between cation-radical and neutral molecule calculated at PM3 optimized geometries.

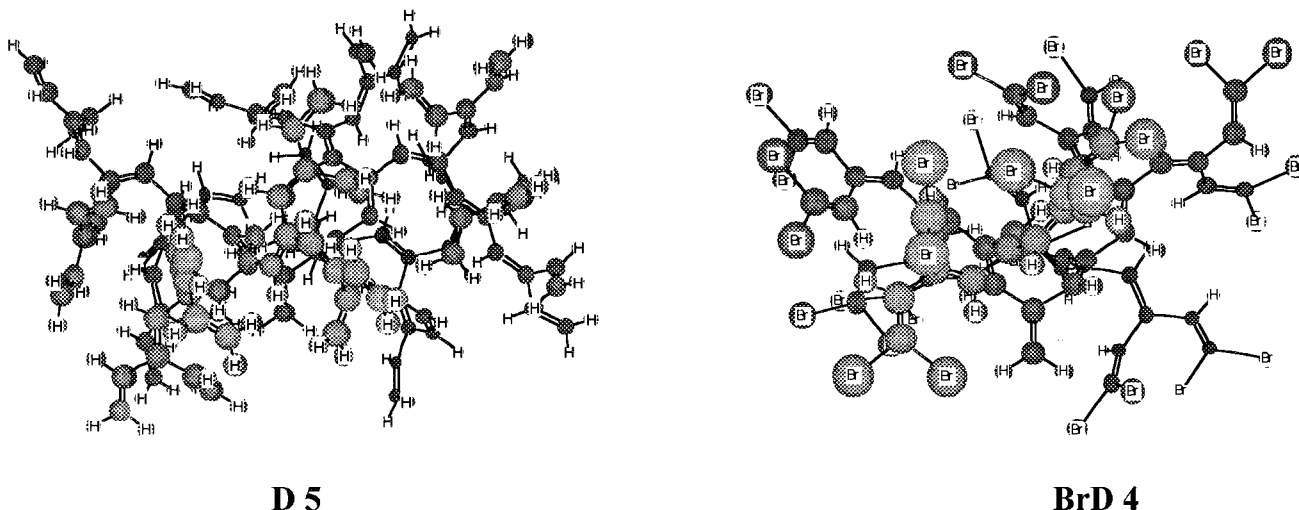


Fig. 2. PM3 optimized geometries of **D5** and **BrD4** dendritic molecules

While the ground state geometry of linear *trans*-PA, the planar zig-zag centrosymmetric chain¹⁵, is well established, this is not the case for hyperbranched PA. When the geometry of large acetylenic dendrimers is optimized starting from arbitrarily chosen structures, it is very possible that different local minima will be located which may hamper the comparison between different dendrimer generations. To minimize this problem the optimized geometry of the dendrimer of n generation was obtained by the replacing terminal hydrogen atoms in the optimized structure of dendrimer of $n-1$ generation with vinyl groups followed by full minimization of the obtained structure first by MM2 and then by the PM3 method. A similar procedure was applied to bromine terminated oligomers **BrD1–BrD4**. In addition, to estimate the effect of conformation on the electronic structure of dendrimers, several molecular dynamic cycles followed by geometry optimization with the PM3 method and a single point energy calculation at B3LYP/3-21G and RHF/3-21G levels of theory were run for **D2** and **D3** molecules. A new implementation of Norman L. Allinger's MM2 force field based in large measure on work done by Jay W. Ponder of Washington University, incorporated in the Chem 3D Pro 4.0 program, was used in molecular dynamic calculations⁷.

Results and discussion

Fig. 2 shows optimized structures of **D5** and **BrD4** molecules as the largest ones in this study. In all cases there was no clear evidence of bond lengths' change with the dendrimer generation number. The lengths of the formal double bonds were between 1.33 Å for the outer and 1.35 Å for inner layers of the dendrimer while the lengths of

the formal single bonds were between 1.46 and 1.47 Å for **D1–D5** molecules. This was very close to those of linear acetylenic oligomers (terminal C=C 1.33 Å, inner C=C 1.34 Å and C–C 1.45 Å). In a similar manner in all bromine-terminated dendritic molecules the lengths of outer and inner double bonds were 1.32 and 1.35 Å, respectively, while the lengths of the formal single C–C and C–Br bonds were in the range of 1.46–1.47 and 1.86–1.87 Å, respectively. In addition, the bond angles in the dendrimers did not show any tendency to change with the generation number. Bearing this in mind it follows that in spite of the crowded architecture of the dendrimers, especially those with bromine terminal groups, the molecules were essentially not strained. The effect of molecular weight of **D1–D5** dendrimers on their relative stability can be estimated from the difference between total energies of a dendrimer and the respective linear oligomer. Fig. 3 shows $\Delta E = (E_d - E_l)/N$ values plotted against N , where E_d is the total RHF or B3LYP energy of **D1–D5**, E_l is the respective total energy of linear oligomer of the same formula and N is the number of carbon atoms in the molecule. As could be expected the linear *trans*-PA chain is more stable than branched structures and ΔE increases with the molecular weight. The difference in stability is, however, rather small. Both RHF and B3LYP methods gave the energy difference between linear and dendritic structure not to exceed 3.5 kcal/mol C atoms. Moreover, as seen from the Fig. 3, ΔE tends to a limit with molecular weight, being almost the same for **D3**, **D4** and **D5**. These results suggest that high molecular weight hyperbranched polyacetylene should be rather stable and not excessively strained.

Tab. 1 shows calculated IPs and E_g 's for all molecules shown in Fig 1. A good agreement observed between calculated and experimentally determined vertical IP and E_g

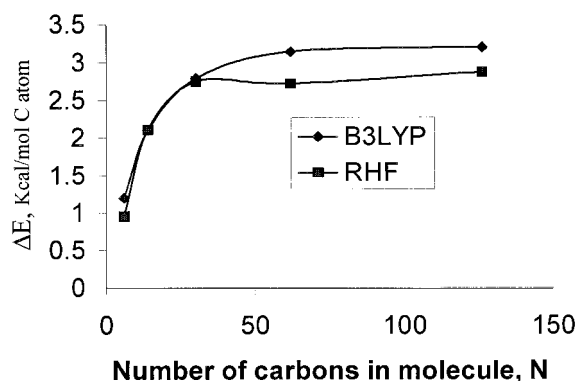


Fig. 3. $\Delta E = (E_d - E_l)/N$ plotted against N , where E_d is the total RHF or B3LYP energy of **D1–D5**, E_l is the respective total energy of linear oligomer of the same formula and N is the number of carbon atoms in the molecule

available for **Lin1** and E_g 's for **Lin2** and **Lin5** molecules, respectively, shows that the level of theory chosen for modelling is adequate. Both oligomer series, **D1–D5** and **BrD1–BrD4**, follow the same trend as linear *trans*-PA oligomers (**Lin1–Lin5**). Both E_g 's and IPs decrease with molecular weight due to the expanding of the conjugated system tending to a limit for high-molecular-weight dendrimers. Experimentally found E_g for *trans*-PA (1.9 eV) agrees well with that calculated for **Lin5** ($C_{126}H_{128}$) (1.94 eV) allowing us to extrapolate E_g 's for the dendrimers of the **D** and **BrD** series with infinite molecular weight to 3.30–3.25 and 3.55–3.50 eV, respectively. As seen from the Tab. 1, E_g 's and vertical PIs of **D** and especially **BrD** series dendrimers are constantly higher than those of *trans*-PA oligomers. This reflects the twisting of conjugated double bonds in the dendrimers, which is especially notable for dendrimers of the **BrD** series due to large bromine terminal groups.

While in linear polymers the number of terminal groups per repeat unit tends to zero with molecular weight not affecting properties of high-molecular-weight polymers, the situation is completely different for hyperbranched polymers. The polymerization of AB_2 type monomer leads to a hyperbranched polymer similar to dendrimers of the **BrD** series, where the number of terminal groups per repeat unit approaches 1 not 0 with molecular weight thus affecting the properties of the hyperbranched polymer. The effect of terminal bromine groups on the electronic properties of hyperbranched PA can be clearly seen from Tab. 1. While the vertical IPs of **BrD** dendrimers are constantly higher than those of **D** dendrimers due to steric hindrances for conjugation caused by the bromine atoms, the adiabatic IP's are significantly lower for bromine containing dendrimers and very close to those of linear *trans*-PA oligomers. All other things being equal, the vertical IP reflects the conjugation in the neutral molecule while the adiabatic IP also accounts for

Tab. 1. Calculated energy gaps (E_g), vertical (IP_v) and adiabatic (IP_a) ionization potentials (in eV) of linear and dendritic acetylenic oligomers

Compound	Formula	E_g ^{a)}	IP_v ^{b)}	IP_a ^{c)}	IP_v^{exp}	E_g^{exp}
Lin1	C_6H_8	4.71	7.91	7.66	8.29 ^{d)}	4.95 ^{e)}
D1	C_6H_8	5.26	8.43	8.13	–	–
BrD1	$C_6H_4Br_4$	5.02	8.84	7.59	–	–
Lin2	$C_{14}H_{16}$	3.06	6.69	6.06	–	3.18 ^{f)}
D2	$C_{14}H_{16}$	3.97	7.55	7.09	–	–
BrD2	$C_{14}H_8Br_8$	4.25	8.51	6.89	–	–
Lin3	$C_{30}H_{32}$	2.32	6.20	5.07	–	–
D3	$C_{30}H_{32}$	3.76	7.41	6.89	–	–
BrD3	$C_{30}H_{16}Br_{16}$	3.72	8.29	4.55	–	–
Lin4	$C_{62}H_{64}$	2.03	6.02	–	–	–
D4	$C_{62}H_{64}$	3.32	7.03	5.55	–	–
BrD4	$C_{62}H_{32}Br_{32}$	3.60	8.24	–	–	–
Lin5	$C_{126}H_{128}$	1.94	5.96	–	–	1.7–1.9 ^{g)}
D5	$C_{126}H_{128}$	3.30	6.87	–	–	–

a) Band gap calculated as HOMO-LUMO energy difference at B3LYP/3-21G//PM3 level of theory.

b) Vertical ionization potential calculated as negative HOMO energy at HF/3-21G//PM3 level of theory.

c) Adiabatic ionization potential calculated as difference of total energies of cation-radical and neutral molecule at B3LYP/3-21G//PM3 level of theory.

d) Cf. ref.¹⁶⁾

e) Cf. ref.¹⁷⁾

f) Cf. ref.¹⁸⁾

g) Cf. ref.¹⁹⁾

the relaxation of molecular geometry and electron density distribution following the ionization process. Fast ionization produced by a photon impact when nucleus and electrons have no time to relax follows the vertical mechanism, whereas the ionization related with slow electron transfer (chemical oxidation) is an adiabatic process. Fig. 4 shows total atomic Mulliken charges with hydrogens summed into heavy atoms for neutral and ionized **D1**, **BrD1**, **D2** and **BrD2** molecules, respectively, calculated at B3LYP/3-21G level of theory after full geometry optimization with the PM3 method. In the case of **BrD1** and **BrD2** cation-radicals, 72% and 74% of positive charge, respectively, is stabilized at the expense of highly polarizable bromine terminal groups thus explaining the reduction of adiabatic IP for **BrD1** compared with **D1**. This also holds for other dendrimer generations. It is known that doping of conjugated polymers with oxidizing agents, leading to a drastic increase in conductivity, consists in electron transfer from a polymer to an oxidant. *trans*-PA shows the highest conductivity in the doped state among all conjugated polymers¹⁴⁾. Bearing in mind the low adiabatic IP's found for Br-terminated hyperbranched polyacetylenic oligomers, hyperbranched PA 2 with terminal Br-groups may combine solubility with high conductivity in the doped state. It is noteworthy that

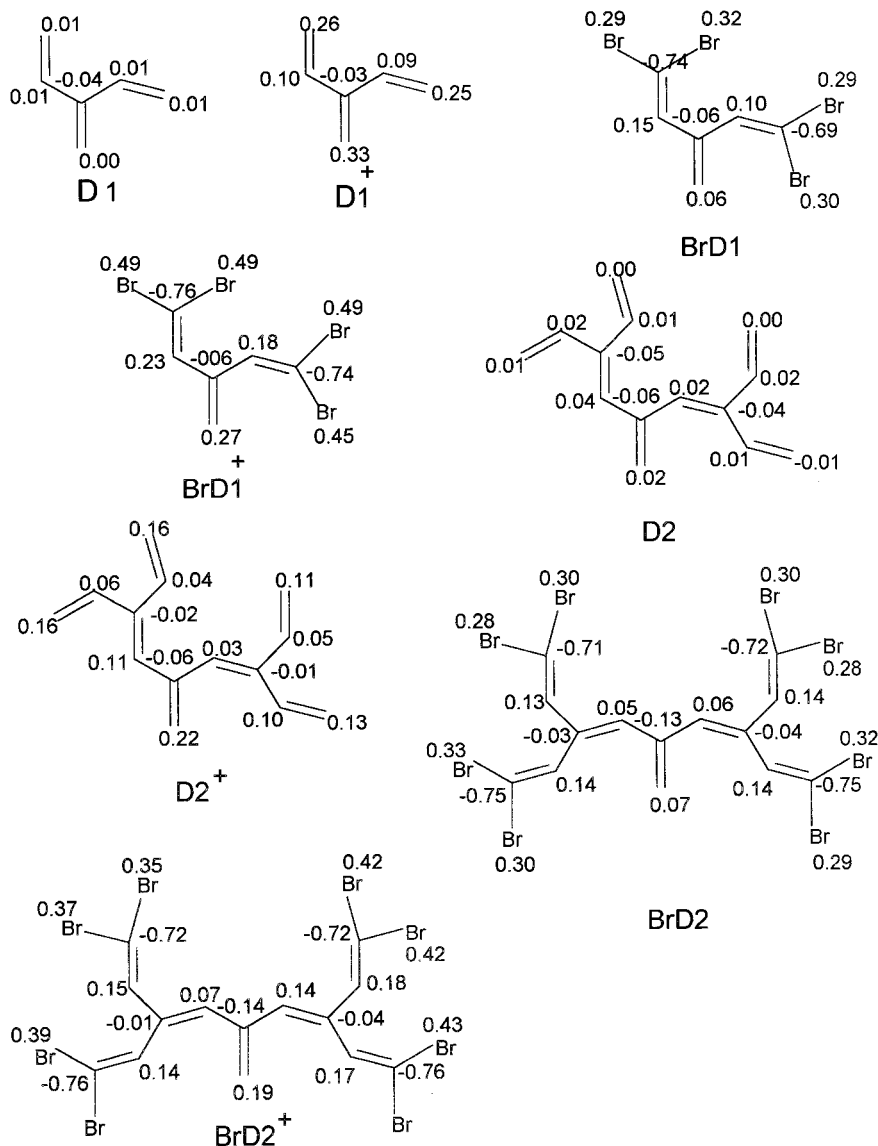


Fig. 4. Total atomic Mulliken charges with hydrogens summed into heavy atoms for neutral and ionized **D1**, **BrD1**, **D2** and **BrD2** molecules, at B3LYP/3-21G level of theory after full geometry optimization with the PM3 method

the ionization of the dendrimer leads to some flattening of the molecule. This is especially pronounced for the **D1** molecule which becomes completely flat on the ionization. The flattening of the molecule in the cation-radical form allows better stabilization of the excessive positive charge. As a result of a decrease in number of bonding π -electrons in cation-radicals the formal double bonds become longer by some 0.05–0.06 Å while the formal single bonds shorten from 1.47–1.46 to 1.42–1.43 Å. The observed decrease in the bond length alternation in cation-radicals could be attributed to the more efficient conjugation favoured by the geometry changes induced by the ionization.

As already noted, when a large molecule is optimized various local minima are located depending on the initial

geometry. In the optimization of large dendritic molecules this is just the case. To examine how calculated E_g 's and IPs depend on the conformation, molecular dynamics calculations were run for **D2** and **D3** molecules and the results are listed in Tab. 2. After each 100 ps run the geometry was optimized first by MM2 and then by the PM3 method followed by RHF/3-21G and B3LYP/3-21G single point energy calculations to estimate the total energy, E_g and vertical PI of the conformer. As seen from Tab. 2 the initially located conformers of **D2** and **D3** are local not global minima in the conformational space according to both RHF and B3LYP calculations. However, while for **D3** 3 out of 8 located conformers were more stable than the initially found one (using B3LYP results as more reliable) in the case of **D2** dendrimer only 1 out of 8 was

Tab. 2. Molecular dynamics simulation results for **D2** and **D3** molecules. (The simulations were carried out at 273 K, a heating rate, from 0 to 273 K, of 1 kcal/(fs · mol of atoms), and a time step of 2 fs)

Run	Time in ps	D3				D2			
		IP _v ^{a)}	E _g ^{b)}	ΔE _{RHF} ^{c)}	ΔE _{B3LYP} ^{d)}	IP _v ^{a)}	E _g ^{b)}	ΔE _{RHF} ^{c)}	ΔE _{B3LYP} ^{d)}
		eV		kcal/mol		eV		kcal/mol	
0	0	7.41	3.76	0	0	7.55	3.97	0	0
1	100	7.65	4.15	2.17	2.56	7.87	4.58	-5.08	-0.97
2	200	7.65	4.12	-9.23	-7.27	7.91	4.43	-1.01	4.81
3	300	7.55	3.99	2.52	0.89	7.56	4.52	-4.99	1.09
4	400	7.61	4.22	0.07	0.12	7.94	4.38	-1.62	2.28
5	500	7.70	4.10	-10.13	-7.53	7.91	4.55	-5.69	1.45
6	600	7.40	3.98	-4.43	-5.23	7.83	4.25	8.10	11.90
7	700	7.21	3.75	3.55	0.87	7.42	3.77	4.09	2.78
ΔE _{max} ^{e)}		0.49	0.47	-	-	0.52	0.81	-	-
Mean		7.52	4.00	-	-	7.75	4.31	-	-

^{a)} Calculated as HOMO energy at RHF/3-21G//PM3 level of theory.

^{b)} Calculated as LUMO-HOMO energy difference at B3LYP/3-21G//PM3 level of theory.

^{c)} Total energy difference calculated at RHF/3-21G//PM3 level of theory between starting conformer and that of the corresponding run.

^{d)} Total energy difference calculated at B3LYP/3-21G//PM3 level of theory between starting conformer and that of the corresponding run.

^{e)} Dispersion of PI and E_g.

0.97 kcal/mol more stable than initially located. It is due to the adopted building concept that for low-molecular-weight dendrimers the minima closer to the global minimum were located. As can be seen, the dispersions in E_g' and IP decrease significantly from **D2** to **D3**. This is due to the fact that in high-molecular-weight dendrimers the majority of available conformations show about the same conjugation owing to the averaging effect of the great number of atoms resulting in similar IP's and E_g's. Moreover, there is a good correlation between mean IPs and E_g's shown in Tab. 2 and those calculated initially. On this basis the data of Tab. 1 obtained for higher generations of dendrimers should be considered as reliable.

Conclusions

Total energies of the **D** series of acetylenic dendrimers calculated at both RHF/3-21G and B3LYP/3-21G levels of theory are higher than those of linear *trans*-PA oligomers and increase with molecular weight reflecting strain in the crowded hyperbranched structure. However, the energy differences between linear and dendritic structures are rather small and do not exceed 3.5 kcal/mol C atom. Moreover, the difference tends to a limit with molecular weight, being almost the same for **D3**, **D4** and **D5**. This suggests that high-molecular-weight hyperbranched polyacetylene should be rather stable and not excessively strained.

Twisting of the double bonds decreases the conjugation in hyperbranched PA compared to linear *trans*-PA as fol-

lowed from calculated E_g's and vertical PIs constantly higher for hyperbranched PA oligomers than those for *trans*-PA ones. However, the conjugation though less effective than in *trans*-PA is extended up to the 4th or 5th generation in dendrimers.

Bromine terminal groups affect strongly the electronic structure of hyperbranched PA. On the one hand the bulky bromine atoms decrease even more the conjugation in bromine-terminated acetylenic dendrimers due to sterical hindrances as followed from calculated E_g's and vertical PI's constantly higher for **BrD** series dendrimers than those for the **D** series. On the other hand highly polarizable bromine atoms reduced significantly the adiabatic IP's to be very close to that for *trans*-PA oligomers.

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