

Electronic structure of fully conjugated dendritic oligomers of β,β -dibromo-4-ethynyl styrene

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Abstract

Quantum-mechanical calculations of fully conjugated dendritic oligomers carried out at B3LYP/3-21G//HF/3-21G (d) and B3LYP/3-21G//PM3 levels of theory showed that loose dendritic architecture of β,β -dibromo-4-ethynyl styrene oligomers contributes little to the instability and conjugation disruption compared to 1 \rightarrow 2 branched polyacetylene, while Br terminal atoms in dendrimers strongly affect the electronic density distribution in studied molecules. On the one hand the bulky bromine atoms decrease the conjugation in Br-terminated dendrimers caused by steric hindrances, on the other hand, highly polarisable bromine atoms reduced significantly adiabatic ionisation potentials (IP_a) to be up to 1.5 eV lower than corresponding vertical potentials (IP_v). Another phenomenon contributing to the reducing of IP_a 's of all dendrimers is the flattening of molecular geometry accompanying the ionisation thus allowing better delocalisation of positive charge over the conjugated system while all aromatic ring except the very outer layer lost their aromaticity becoming essentially quinone by nature. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chemistry of dendritic molecules in general and of hyperbranched polymers particularly has experienced an explosive development since the late 1980s. Hyperbranched polymers combine high molecular weight with low solution viscosity, and high solubility with high concentration of terminal groups thus making them promising candidates for a number of applications [1]. Conjugated hyperbranched polymers represent an interesting class of dendritic molecules combining good solubility with high concentration of conjugated units unusual for linear conjugated polymers which is useful for potential applications. Moore et al. [2] synthesised a conjugated phenylacetylene

monodendron having a smooth gradient in electronic excitation energy from the periphery to the core. This molecule contains the essential features of an efficient exciton antenna. Miller and Neenan [3] published their efforts on all-hydrocarbon polyphenylene dendrimers. The present authors have recently reported the synthesis of fully conjugated hyperbranched polymers obtained by Pd-catalysed cross-coupling of β,β -dibromo-4-ethynyl styrene as well as step by step divergent synthesis of the respective well-defined oligomers [4,5]. The synthesised polymers and oligomers showed intense photo and electroluminescence.

A clear understanding of the structure–properties relationship is crucial for the directional design of hyperbranched conjugated polymers. As follows from the comparative theoretical analysis of linear

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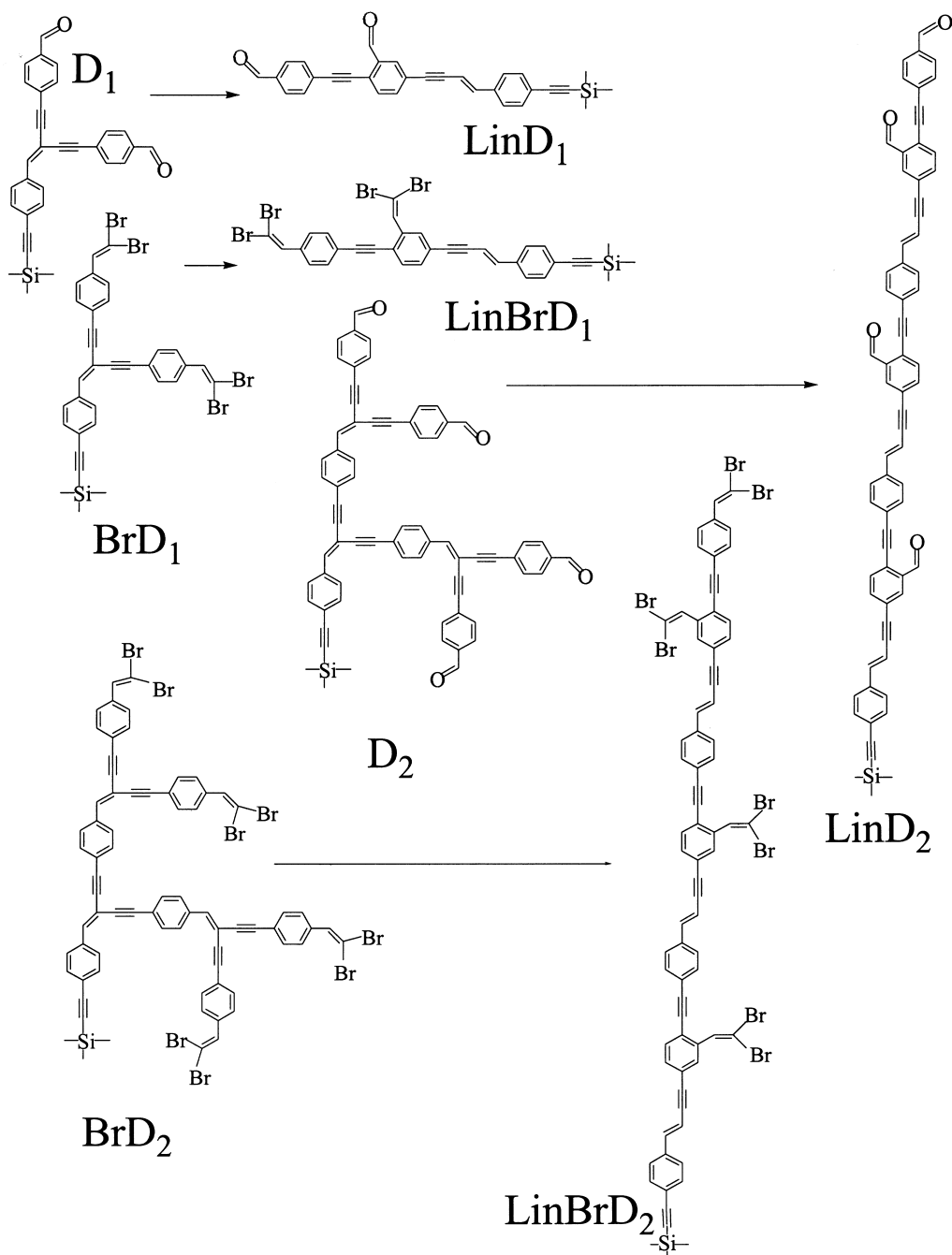


Fig. 1. Fully conjugated dendritic oligomers of β,β -dibromo-4-ethynyl styrene and corresponding linear model molecules.

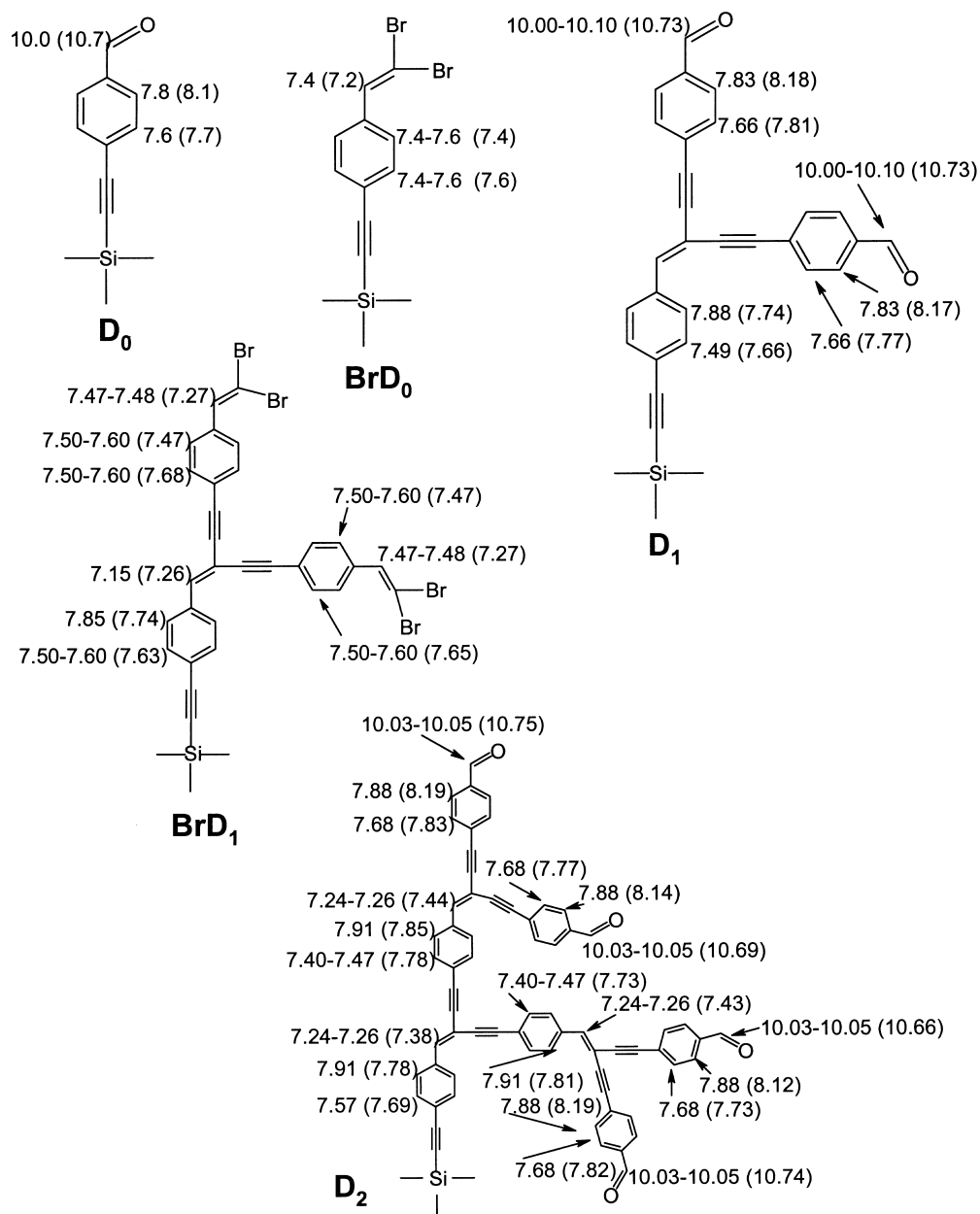


Fig. 2. Experimental and calculated (in brackets) ^1H NMR chemical shifts of dendritic molecules.

and hyperbranched polyacetylene [6] there is a significant difference in electronic structures between linear and hyperbranched structures arising from branched architecture and a great number of terminal groups in hyperbranched polymers. In spite of the importance of molecular modelling to gain better

understanding of the nature of conjugated dendritic molecules little is done in this area up to date. Bearing this in mind this article is devoted to the molecular modelling of well defined hyperbranched oligomers of β,β -dibromo-4-ethynyl styrene synthesised earlier [5] to refine the understanding

Table 1
Properties of dendritic molecules

Compound	IP _a ^a (eV)	IP _{v1} ^b (eV)	IP _{v2} ^c (eV)	IP _{v3} ^c (eV)	Eg ^d (eV)	Eg _{PM3} ^e (eV)	ΔE _{gHF} ^f (eV)	HOMO ^g (eV)	ΔE _{PM3} ^h (eV)	ΔE _{HF} ⁱ (kcal/mol)	ΔE _{PM3} ^j (kcal/mol)	ΔE _{HF} ^k (kcal/mol atom)
D0	8.13	8.38	8.40	4.20	4.72	4.72	4.72	8.99	—	—	—	—
BrD0	7.24	7.60	7.66	4.20	4.62	4.62	4.81	8.46	—	—	—	—
D1	6.71	7.07	7.12	3.29	3.33	3.22 ^l	3.49	3.36 ^m	2.10	2.87	0.036	0.049
BrD1	6.27	6.62	6.72	3.38	3.34	3.34 ^l	3.55	3.57 ^m	2.97	3.36	0.048	0.054
D2	6.02	6.53	6.57	3.11	2.91	2.87 ^l	3.09	3.07 ^m	6.50	8.96	0.055	0.076
BrD2	5.75	6.57	—	3.24	3.10	2.95 ^l	—	—	9.10	—	0.072	—

^a Adiabatic ionisation potential calculated as the difference of the total energies of the cation-radical and the neutral molecule at a B3LYP/3-21G//PM3 level of theory.

^b Vertical ionisation potential calculated as the difference of the total energies of the cation-radical and the neutral molecule at a B3LYP/3-21G//PM3 level of theory.

^c Vertical ionisation potential calculated as the difference of the total energies of the cation-radical and neutral molecule at aB3LYP/3-21G//HF/3-21G (d) level of theory.

^d Experimentally measured band gap (from absorption spectra).

^e A band gap calculated as the HOMO–LOMO energy differences at a B3LYP/3-21G//PM3 level of theory.

^f A band gap calculated as the HOMO–LOMO energy differences at a B3LYP/3-21G//HF/3-21G (d) level of theory.

^g Vertical ionisation potential taken as the negative HOMO energy at a HF/3-21G//HF/3-21G (d) level of theory.

^h Total energy difference between the dendritic and the respective linear molecules at a B3LYP/3-21G//PM3 level of theory.

ⁱ Total energy difference between the dendritic and the respective linear molecules at a B3LYP/3-21G//HF/3-21G (d) level of theory.

^j Total energy difference per atom between the dendritic and the respective linear molecules at a B3LYP/3-21G//PM3 level of theory.

^k Total energy difference per atom between the dendritic and the respective linear molecules at a B3LYP/3-21G//HF/3-21G (d) level of theory.

^l A band gap calculated as the HOMO–LOMO energy differences at a B3LYP/3-21G//PM3 level of theory for a hypothetical linear molecule.

^m A band gap calculated as the HOMO–LOMO energy differences at a B3LYP/3-21G//HF/3-21G (d) level of theory for hypothetical linear molecule.

of electronic structure of conjugated dendritic molecules.

2. Methods

All calculations were performed using GAUSSIAN-94 [7], Initial geometries were generated using CS Chem3D Pro Version 4.0 after preliminary optimisation with MM2 force field [8]. NMR spectra of dendrimers were simulated with the Gauge-Independent Atomic Orbital (GIAO) method [9] at 3-21G(d) level of theory using geometry optimised at the same level with 3-21G basis set used for Br atoms.

Including the electron correlation is very important for accurate modelling of conjugated molecules [10], therefore, the Becke three parameter hybrid (B3) exchange functional in combination with Lee–Yang–Parr (LYP) correlation functional (B3LYP) [11] with split valence basis set (3-21G) was used for *all* single point energy calculations at HF/3-21G(d) and PM3 optimised structures. As it was shown the B3LYP single point energy calculations run at PM3 or AM1 optimised geometry have better mean absolute deviation from experiment than the Hartree–Fock based methods [12]. The vertical ionisation potentials (IP_v) were calculated at both PM3 and HF/3-21G(d) optimised geometries while adiabatic ionisation potentials (IP_a) were computed at PM3 optimised structures with single point energy calculations at B3LYP/3-21G level of theory.

As it was recently discovered, B3LYP HOMO–LUMO energy differences gave excitation energies [energy gap (E_g)] in good agreement with experimental values as a result of partial cancellation of the particle-number discontinuities in the exchange–correlation functional associated with IP 's and electron affinities [13]. Therefore, B3LYP HOMO–LUMO energy differences were used to estimate E_g and to compare it with experimentally observed from absorption spectra [5].

3. Results and discussion

Fig.1 shows chemical structures of studied dendrimers. To estimate the stability of dendritic structure compared to linear one a scheme of homodesmotic reactions were used [14]. Using this approach the

contribution of dendritic architecture to the total energy of molecule could be estimated as the difference between total energies of the dendritic molecules and the hypothetical linear isomers shown in Fig.1. In order to evaluate the accuracy of HF/3-21G (d) and PM3 model chemistries in the geometry optimisation, NMR shielding tensors of dendritic molecules were computed at HF/3-21G (d)//HF/3-21G (d) level of theory and the simulated ^1H NMR spectra were compared with experimental data [5]. Computed NMR shielding tensors are known to be very sensitive to the molecular geometry [15]. The results of the calculations are presented in Fig. 2. As can be seen from the picture, the calculated proton chemical shifts agree reasonably well with experimentally observed values. For aldehyde protons only the difference is about 0.7 ppm, while for all other protons the deviations from experimental values do not exceed 0.35 ppm.

Taking this into account, the HF/3-21G (d) level of theory is reliable enough for an accurate geometry prediction of synthesised molecules. In contrast, when comparing HF/3-21G (d) and PM3 optimised structures the bond lengths and bond angles differed very little in the conjugated hydrocarbon part of molecules (0.01–0.02 Å and 1° – 2° respectively). However, C–Si and C–Br bond lengths in PM3 optimised structures differed by 0.04–0.09 Å and Br–C–Br angles even by 10° from these in HF/3-21G (d) optimised structures thus revealing certain deficiencies of the PM3 method in the accurate treatment of atoms heavier than second row elements. Fortunately, both HF/3-21G (d) and PM3 optimised geometry produced similar molecular properties when using B3LYP/3-21G single point energy calculations as seen from Table 1. Therefore, the most computationally demanding IP_a calculations were run at PM3-optimised geometries.

As previously found [6], 1 → 2 branched polyacetylenic dendrimers were less stable than isoelectronic linear *trans*-polyacetylenic oligomers due to steric hindrances, and the instability increased with molecular weight tending to a limit. The difference achieved 3 kcal/mol C atom (about 380 kcal/mol) for the fifth generation. This is also the case for the oligomers of β,β -dibromo-4-ethynyl styrene. As seen from the Table 1 at both B3LYP/3-21G//PM3 and B3LYP/3-21G//HF/3-21G (d) levels of theory the hypothetical

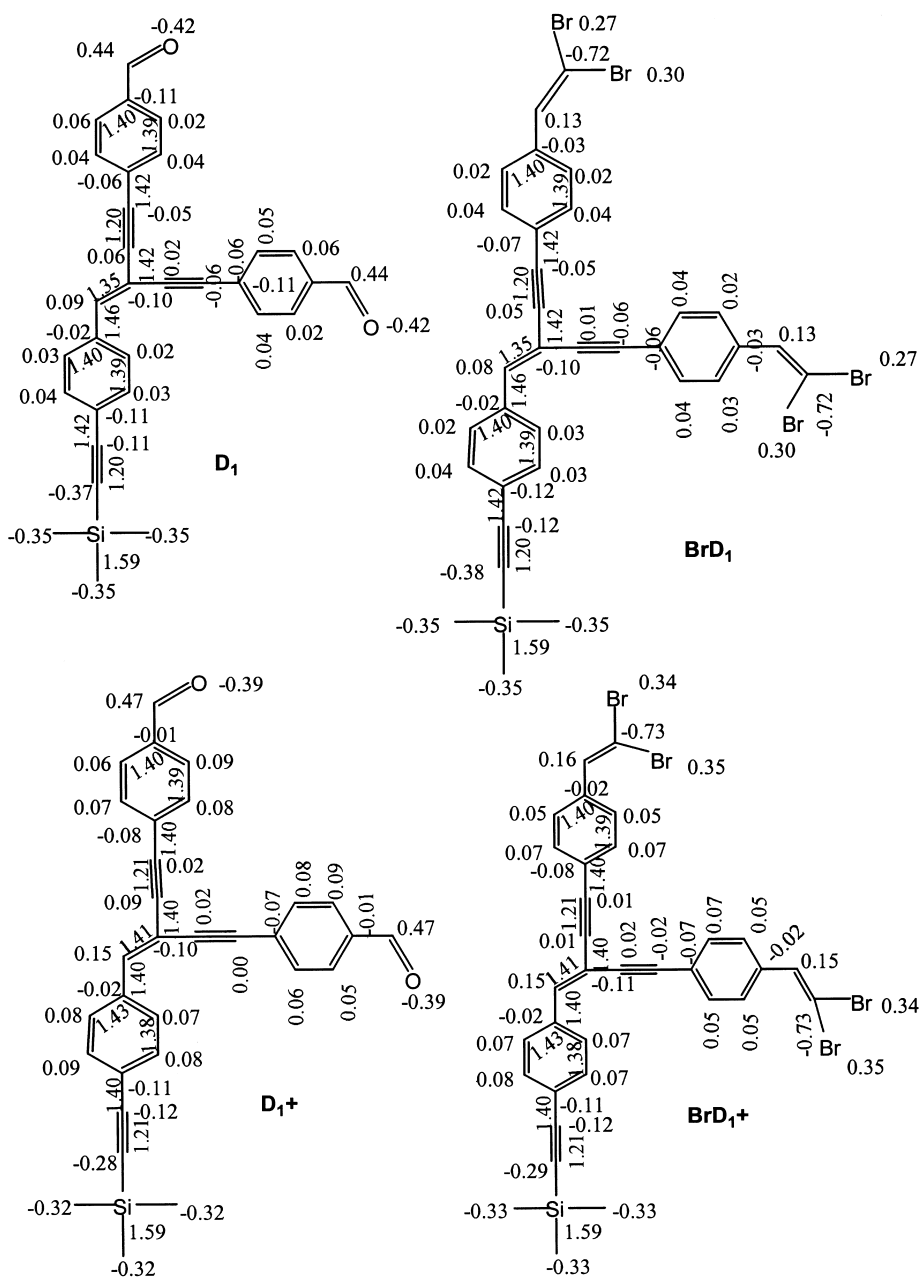


Fig. 3. Total atomic Mulliken charges with hydrogen atoms summed into heavy atoms and bond lengths for neutral and ionised D1 and BrD1 molecules, at a B3LYP/3-21G//PM3 level of theory.

linear molecules (Lin) are more stable than the respective dendrimers. The energy difference, however, is far less pronounced than in the case of branched polyacetylene owing to the loose structure of

β,β -dibromo-4-ethynyl styrene dendrimers. In a similar manner to hyperbranched polyacetylene, the instability increased as the generation number achieved 9.1 kcal/mol for the BrD2 molecule.

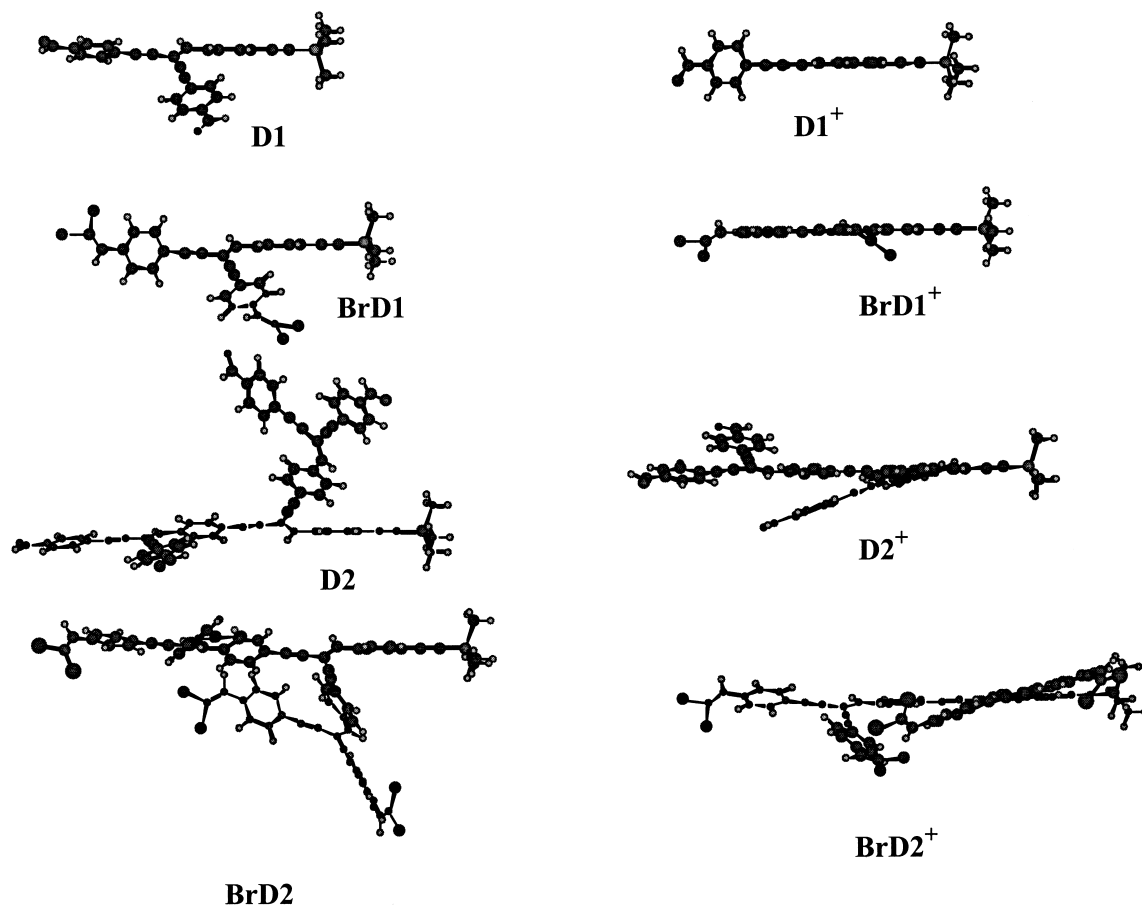


Fig. 4. PM3 optimised geometries of the dendrimers and the corresponding cation-radicals.

The calculated E_g of dendrimers and those of linear molecules are very similar (Table 1) revealing very little impact of dendritic architecture upon conjugation in this particular case because of the loose structure of dendritic molecules. It is noteworthy that there is a good agreement between calculated and measured E_g values, especially for large molecules in which the geometry optimisation method barely affected the calculated E_g . The loose structure of the dendrimers allows effective conjugation from both calculated and measured E_g values tending to decrease from D0 to D2 and from BrD0 to BrD2. However, Br-terminated dendrimers presented wider E_g compared with the respective formyl terminated molecules. This is because bulky bromine atoms impede the conjugation of terminal dibromovinyl groups with the rest of the

core as follows from optimised geometries of the dendrimers.

While Br-terminated dendrimers showed poorer conjugation than formyl-terminated ones their IPs are considerably lower than those of formyl-terminated molecules (Table 1). The difference is more pronounced for IP_a tending to decrease with the generation number. It seems that terminal bromine atoms are responsible for this behaviour. Fig. 3 presents total atomic Mulliken charges with hydrogen atoms summed into heavy atoms for neutral and ionised D1 and BrD1 molecules in, for example, the adiabatic ionisation process. As seen from the figure, in the case of D1+ the positive charge is distributed rather uniformly across the molecule, while in the case of the BrD1+ cation-radical, dibromovinyl

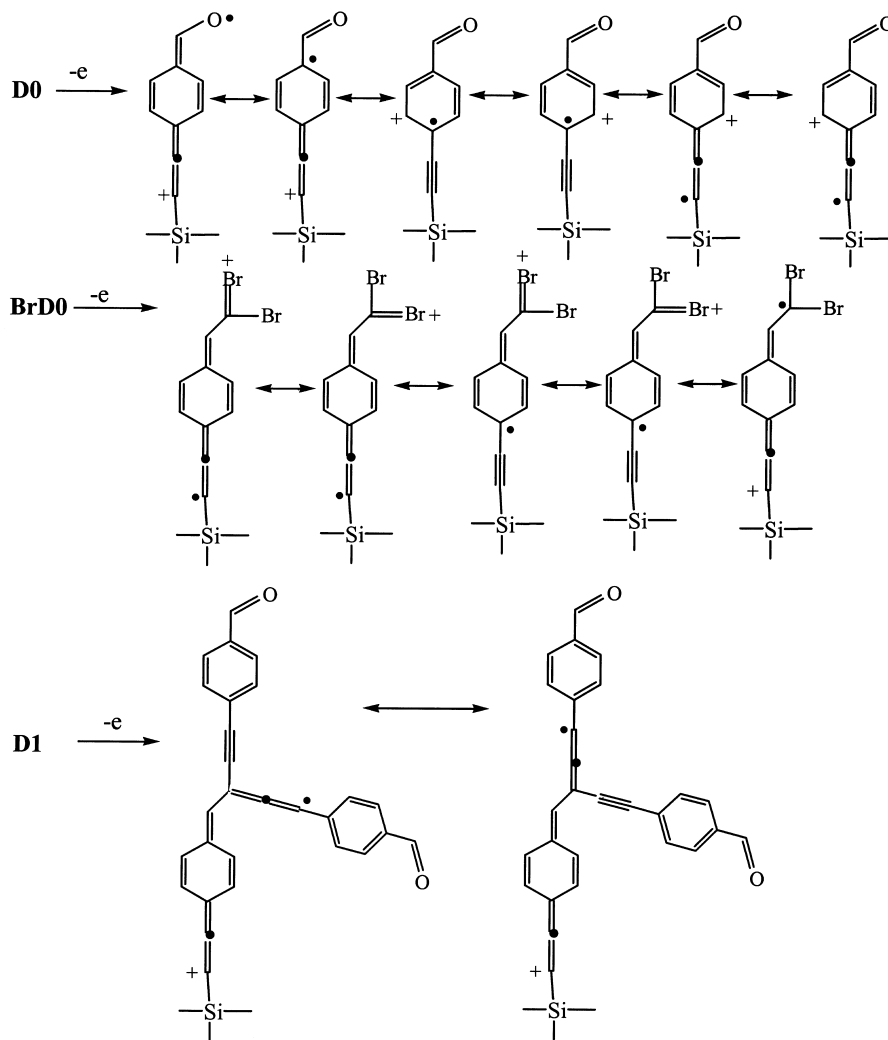


Fig. 5. Schematic representation of the charge and unpaired electron delocalisation in D0+, BrD0+ and D1+ molecules.

terminal groups accumulate about 25% of positive charge according to Mulliken's population analysis. This is the case for highly polarizable bromine atoms which contribute to the stabilisation of positive charge in cation-radicals and this holds for all other dendrimers. The contribution decreases from BrD0+ to BrD2+ (35% and 19% of positive charge, respectively), which agrees with the diminishing difference between the IPs for bromine- and formyl-terminated dendrimers.

As a rule IP_{aS} are lower than IP_{vS} , the energy difference accounts for the relaxation of molecular

geometry and electron density distribution following the ionisation process. This is also the case for the studied dendrimers, as seen from Table 1. The difference between IP_v and IP_a is greater for bromine terminated molecules, and tends to increase with the generation number. Fig. 4 shows the PM3 optimised molecular structures of the dendritic oligomers and the respective cation-radicals. As seen in the figure, there is a significant difference in shape between neutral molecules and cation-radicals. Ionisation causes flattening of the molecular geometry. This behaviour is similar to that observed for

hyperbranched polyacetylene cation-radicals [6], and the explanation is that flattening of the molecule allows better stabilisation of excessive positive charge by its delocalisation. The larger the conjugated system the better the stabilisation of excessive charge that can be achieved by the geometry adjustment, which agrees with the increase in the difference between IP_v and IP_a with generation number. It is noteworthy that while BrD1+ is almost completely planar in the D1+ molecule, one of the benzene rings is almost perpendicular (at 81°) to the rest of the molecule. From our point of view this difference in molecular geometry is caused by the influence of Br atoms. While in the planar BrD1+ molecule the energy gain as a result of charge delocalisation overcompensates the strain induced by the molecule flattening for polarisable bromine atoms participating in charge delocalisation, a completely flat conformation for D1+ is not so favourable, and the energy minimum is reached when one benzene ring is out of plane to decrease the steric hindrance in the rest of the completely flat molecule in order to achieve better delocalisation of excessive positive charge.

Taking into account the bond lengths in cation-radicals there is a significant contribution of quinone structures to these molecules (Fig. 3). As expected this phenomenon is most pronounced for D0+ and BrD0+ molecules. For the first and the second generation dendrimers the most affected is the focal point benzene ring, while the very outer layer of benzene fragments remains unchanged in cation-radicals. The difference between D1, BrD1 and the respective cation-radicals can be seen from Fig. 3. The results of geometry optimisation of D0+ at HF/3-21G (d) level of theory are similar to those obtained with the PM3 method predicting the essential contribution of the quinone structure to cation-radicals, therefore PM3 optimised structures of higher generation cation-radicals should be considered as rather reliable. It seems that a deficit (cation-radical) or an excess (anion-radical) of electrons in conjugated molecules destroys aromaticity of benzene rings involved in conjugation. This conclusion is confirmed by the fact that in all cases a significant change of bond lengths in benzene rings is observed only in the area of delocalisation of an unpaired electron. A similar observation was also made for anion-radicals of a phenylacetylene derivative [16].

Fig. 5 shows resonant structures that contribute most to D0+ BrD0+ and D1+ molecules according to the Mulliken charge, the spin density distribution and the bond lengths. As would be expected the positive charge in D0+ is mostly divided between three sites: the sp carbon connected to the trimethylsilyl group where the positive charge is stabilised by the strong electron-donating effect of this group; and two sp² carbons *meta* to carbonyl which are also capable of positive charge stabilisation. Resonant structures for BrD0+ clearly demonstrate the participation of a trimethylsilyl group and bromine atoms in stabilisation of positive charge and the essentially quinone nature of the cation-radical. The peculiarities of unpaired electron delocalisation in D1+ and higher generation dendritic cation-radicals (D2+, BrD1+ and BrD2+) affect the molecules in such a way that the outer benzene rings maintain their aromatic character, while inner and especially focal-point phenylenes show a great deal of contribution from quinone structures. A schematic representation of such a delocalisation for D1+ is shown in Fig. 5 as an example. In a similar way to the D0+ trimethylsilyl electron-donating group contributed to the stabilisation of positive charge, sp carbons attached to outer benzene rings accumulate about 25% of the total unpaired electron density.

4. Conclusions

The loose dendritic architecture of β,β -dibromo-4-ethynyl styrene oligomers contributes little to the instability and conjugation disruption compared with 1 → 2 branched polyacetylene. However, Br terminal atoms in BrD series of dendrimers strongly affect the electronic structure of studied dendrimers. On the one hand the bulky bromine atoms decrease the conjugation in bromine-terminated dendrimers caused by steric hindrance as follows from measured and calculated Eg. On the other hand, highly polarisable bromine atoms significantly reduced IP_a s to be 1.5 eV lower than corresponding IP_v s.

The ionisation of dendrimers is accompanied by flattening of the molecule thus allowing better delocalisation of positive charge over the conjugated system, while all aromatic rings except the very

outer layer lose their aromaticity becoming essentially quinone by nature.

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