A computational study of the reactivity of diethenylnaphthalenes towards anionic polymerization

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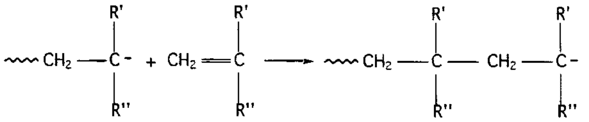
Diethenyl, di(1-methylethenyl), and di(1-phenylethenyl) naphthalenes are known to be difunctional initiators used in the synthesis of thermoplastic elastomers. Semiempirical (AM1, PM3) and *ab initio* calculations (HF/6-31G, HF/6-31G*) have been carried out to determine the reactivity of these compounds towards anionic polymerization. For this purpose, geometrical parameters, electrostatic potentials, and frontier orbitals have been analyzed. Reaction paths starting from the diethenylnaphthalenes and reaching the proposed products have been studied, and transition structures along the paths have been located. The minimum energy conformers were determined through a conformational search around single bonds for a series of diethenylnaphthalenes. We have attempted to predict how the location of the vinyl groups affects the reactivity of diethenylnaphthalenes. Our results have revealed that the most suitable difunctional initiators for anionic polymerization are the compounds where the substituents lie away from the naphthalene bridge. We have also found that in some cases the substituents are conjugated with each other and di(1-phenylethenyl)naphthalenes are more reactive than diethenylnaphthalenes which in turn are more reactive than di(1-methylethenyl)naphthalenes towards anionic polymerization.

Introduction

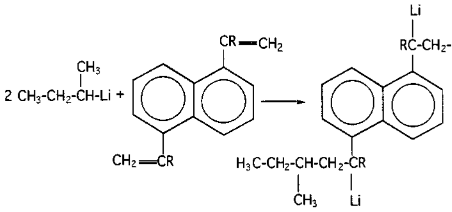
Vinyl-diene triblock copolymers are among the most extensively investigated thermoplastic elastomers because they were the earliest to be produced and commercialized. Thermoplastic elastomers are block copolymers that exhibit rubberlike elasticity[1] without requiring chemical crosslinking. The term "rubberlike elasticity" implies that a material can be extended to several times its original length, yet return rapidly to nearly its initial dimensions upon removal of the deforming force. Block copolymers that behave as thermoplastic elastomers are described as either ABA or $(AB)_n$ polymers, according to the number and type of repeating units per macromolecule.

Homogeneous anionic polymerization methods[2–4] provide close control of the molecular weight, molecular weight distribution and composition of each block in the ABA copolymers. Certain vinyl, diene and cyclic monomers can be polymerized by an anionic mechanism with no termination step.[3,4] Since the growing chain remains active in such "living polymers", different monomers may be added stepwise to build each block in sequence. Anionic polymerization proceeds by the addition of monomers to active centers bearing a whole or a partial negative charge. The active center is regenerated in each step. The chain propagation is illustrated in eqn. (1).



$$\sim\mathrm{CH_2}-\overset{R'}{\underset{R''}{\mathrm{C}^-}} + \mathrm{CH_2}{=}\overset{R'}{\underset{R''}{\mathrm{C}}} \longrightarrow \sim\mathrm{CH_2}-\overset{R'}{\underset{R''}{\mathrm{C}}}-\mathrm{CH_2}-\overset{R'}{\underset{R''}{\mathrm{C}^-}} \quad (1)$$

Difunctional anionic initiators are used because triblock copolymers can be synthesized in only two or one monomer addition steps.[5] Difunctional initiators are also important when the second monomer is incapable of reinitiating the polymerization of the first monomer.[6] The synthesis of the difunctional anionic initiators has generally followed two methods: (i) the generation of ion–radical species which couple to yield the dicarbanionic initiator,[7,8] (ii) the reaction of butyllithium with a diethenyl compound.[9] For vinyl and diene monomers alkyl lithiums are particularly favored initiators. The reaction between 1,5-diethenylnaphthalene and *sec*-butyllithium has produced a new difunctional organolithium initiator [eqn. (2)]



(2)

which is soluble in non-polar solvents and effective in the synthesis of the styrene–isoprene–styrene triblock copolymer.[10]

The purpose of this research is to assist experimentalists by giving a means of predicting reactivity trends of diethenylnaphthalenes towards *sec*-butyllithium. We have attempted to understand how the location of the vinyl groups and the nature of the substituent on the vinyl groups will affect the reactivity of the diethenylnaphthalenes towards anionic polymerization. To this end, we have modeled several diethenylnaphthalenes, di(1-methylethenyl)naphthalenes and di(1-phenylethenyl)naphthalenes. Our approach was to determine the most stable conformer of each species and to analyze its properties of interest such as the transition structures for the addition of *sec*-butyllithium, the frontier orbitals and the electrostatic potentials. The nomenclature used in the discussion is shown in Fig. 1, the terms e*xy*, m*xy*, p*xy* have been used to denote diethenylnaphthalenes, di(1-methylethenyl)naphthalenes and di(1-phenylethenyl)naphthalenes respectively where *x* and *y* show the position of the substituent on the naphthalene ring. The numbering system used throughout this article is shown in Fig. 2.

Methodology

All possible conformers for diethenylnaphthalenes, di(1-methylethenyl)naphthalenes and di(1-phenylethenyl)naphthalenes have been investigated using the MM2 force field provided with-

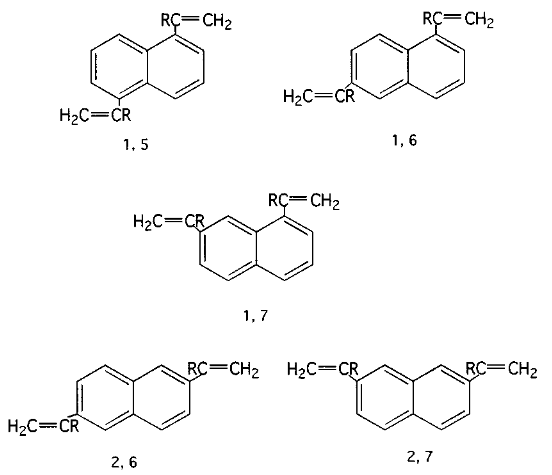


Fig. 1 Nomenclature for diethenylnaphthalenes. R = H, diethenylnaphthalenes: e15, e16, e17, e26, e27; R = CH_3, di(1-methylethenyl)-naphthalenes: m15, m16, m17, m26, m27; R = Ph, di(1-phenylethenyl)-naphthalenes: p15, p16, p17, p26, p27.

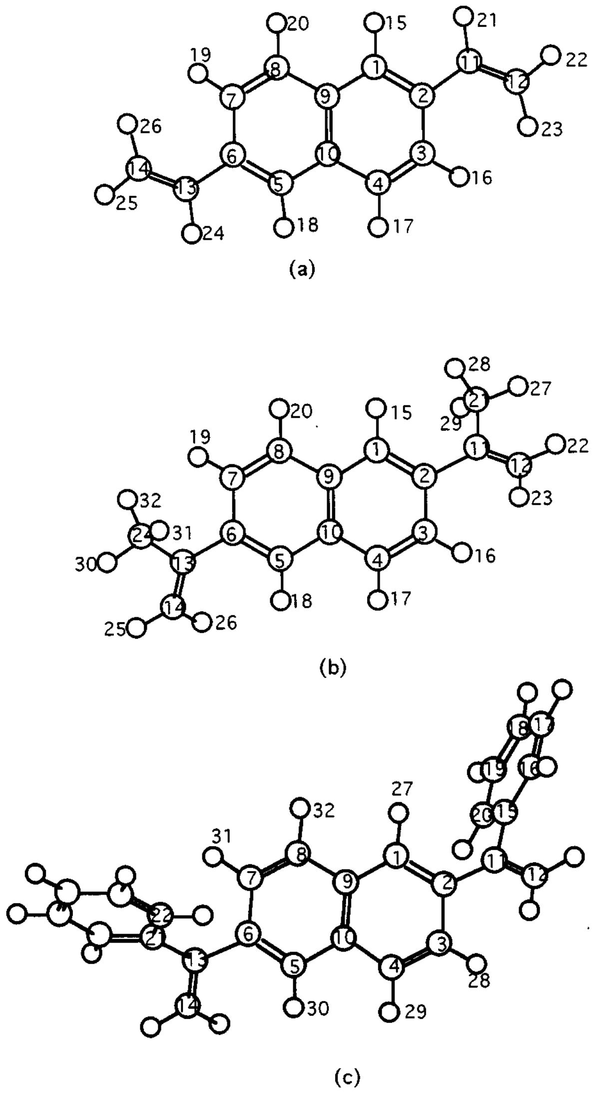


Fig. 2 Numbering system used for diethenylnaphthalenes.

Table 1 Relative energies (kcal mol^{-1}) with respect to the most stable compounds[a]

Compound	ΔH_f(rel) AM1	E_r(rel) HF/6-31G	E_t(rel) HF/6-31G*//HF/6-31G
e15	3.35	5.54	11.72
e16	1.59	2.62	2.59
e17	1.65	2.64	2.62
e26[b]	0.00	0.00	0.00
e27	0.02	0.64	7.06
m15	3.72	4.86	4.47
m16	1.80	2.26	2.07
m17	1.77	2.39	2.20
m26[c]	0.00	0.00	0.00
m27	0.02	0.02	0.04
p15	3.86		
p16	1.92		
p17	2.06		
p26[d]	0.00		
p27	0.13		

[a] Energies are given for the most stable conformer of each compound. [b] $\Delta H_f = 73.74$ kcal mol^{-1}. E_t (HF/6-31G = −536.933525 H, HF/6-31G* = −537.121.332 H). [c] $\Delta H_f = 61.47$ kcal mol^{-1}. E_t (HF/6-31G = −614.97209 H, HF/6-31G* = −615.19194 H). [d] $\Delta H_f = 129.37$ kcal mol^{-1}.

in the Spartan package.[11] The following parameters have been investigated: for diethenylnaphthalenes, free rotation around the naphthalene–vinyl bond; for di(1-methylethenyl)naphthalenes free rotation around the naphthalene–vinyl and the vinyl–methyl bonds, for di(1-phenylethenyl)naphthalenes free rotation around the naphthalene–vinyl and the phenyl–vinyl bonds. The stationary points having the minimum energy with the MM2 force field—three for each molecule—have been chosen as potential candidates for further study employing semiempirical methods. The choice of the semiempirical method to be used is based upon a comparison between the experimental and calculated values for the torsion angle between the vinyl group and naphthalene in 1-vinylnaphthalene. The high resolution NMR spectra of 1-vinylnaphthalene have been used to deduce a value of 36.7–45.9° for the angle between the vinyl group and the ring planes.[12] The value calculated by AM1 is 40.1° whereas PM3 has set this value to 0°. Based on these findings, AM1 has been chosen for further investigations. For each compound, the conformers located as minima on the potential energy surface have been further optimized with HF/6-31G using the GAUSSIAN94 program.[13] The energetics have also been reported with single point HF/6-31G* (HF/6-31G*//HF/6-31G) calculations (Table 1). Selected dihedral angles are gathered in Table 2, bond lengths are given in Table 3.

The activation barriers for the addition of *sec*-butyllithium to diethenylnaphthalenes have been evaluated by considering a stepwise addition of the lithium salt (Figs. 3 and 4). The transition structures are four centered: the C=C bond and the Li–C bonds break, whereas new C–Li and C–C bonds form (Fig. 5). Due to the size of the compounds, this reaction path has been modeled for 2,6-diethenylnaphthalenes only. The parameters for Li are available in PM3 (tm) but not in AM1, thus the PM3 method has been used to evaluate the relative energies for the addition reaction.

Many different reactivity measures have been introduced to quantify the chemical activity of various groups or sites of molecules.[14,15] To name a few, free valencies, frontier orbitals and the molecular electrostatic potentials can be used as the indicators of molecular reactivity. The magnitude of the coefficients of the lowest unoccupied molecular orbitals (LUMO's) is an indication of the sites which are more susceptible to attack by a nucleophile. Any electric charge distribution creates an electrostatic potential. For example, the nucleus and the electrons of the atoms give rise to a potential field around the receptor molecule. The sign of the potential *V*(r) in any particular region depends on whether the potential of the nuclei or of the electrons is the dominating factor. The molecular electrostatic potential of the receptor creates favorable binding

Table 2 Selected dihedral angles (°) for diethenylnaphthalenes, di(1-methylethenyl)naphthalenes (HF/6-31G) and di(1-phenylethenyl)naphthalenes (AM1)

Dihedral angle	e15	e16	e17	e26	e27
C12–C11–C1–C2	45.0	43.6	44.1	—	—
C12–C11–C2–C3	—	—	—	0.72	0.5
C14–C13–C5–C6	−45.0	—	—	—	—
C14–C13–C6–C5	—	−177.6	—	−179.3	—
C14–C13–C7–C6	—	—	2.4	—	−153.5
	m15	m16	m17	m26	m27
C12–C11–C1–C2	78.4	78.5	−79.0	—	—
C12–C11–C2–C3	—	—	—	−32.0	−32.4
C14–C13–C5–C6	78.4	—	—	—	—
C14–C13–C6–C5	—	148.8	—	−45.5	—
C14–C13–C7–C6	—	—	134.7	—	−32.5
H27–C21–C11–C12	4.5	4.4	−4.4	7.8	7.2
H30–C24–C13–C14	4.6	7.8	4.4	4.2	7.8
	p15	p16	p17	p26	p27
C12–C11–C1–C2	112.9	−71.1	114.0	—	—
C12–C11–C2–C3	—	—	—	−40.1	40.2
C14–C13–C5–C6	−112.6	—	—	—	—
C14–C13–C6–C5	—	39.4	—	−39.6	—
C14–C13–C7–C6	—	—	42.9	—	40.1
C20–C15–C11–C1	−38.9	−38.6	−39.4	—	—
C20–C15–C11–C2	—	—	—	−40.9	40.6
C22–C21–C13–C5	38.9	—	—	—	—
C22–C21–C13–C6	—	39.8	—	−40.3	—
C22–C21–C13–C7	—	—	−138.8	—	40.7

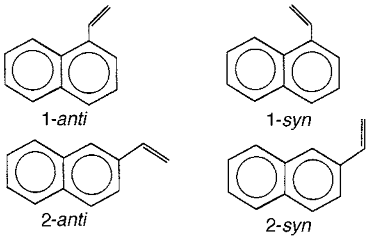
sites for the ligands or restricts the approach of the ligands to certain regions of the molecule. An approaching nucleophile would move favorably towards regions of positive V(r). To investigate the reactivity of the studied diethenylnaphthalenes, we analyzed the frontier orbitals resulting from AM1 optimization. We have also created the electrostatic potential at the molecular surfaces. To create the electrostatic potentials, first Mulliken charges for the optimized geometries were determined. Then, using Mulliken charges, the electrostatic potential was determined at the molecular surfaces using the Grasp program.[16] Since the nucleophilic attachment site for the *sec*-butyl anion is the end vinylic carbon, only the surface points which are within 2.5 Å from the end vinylic carbon with a potential larger than 20 kT (about 0.5 eV at room temperature) were assumed to form the reactive region. Changing the radius and the threshold potential did not affect the relative trend of the reactivity of the compounds.

Results and discussion

A. Energetics and geometries of diethenylnaphthalenes

The energetics of the compounds considered are seen to depend upon the position of the substituents on the rings. The relative energies (Table 1) show that substitutions at 2,6- or 2,7-positions give rise to the more stable compounds while substitutions at 1,5-positions near the bridge produce isomers which are less stable. As expected 1,6- and 1,7-substituted naphthalenes lie in between and are almost isoenergetic. We have also optimized 1,8-substituted naphthalenes which turned out to be highly energetic in comparison to the rest of the compounds. Obviously, steric hindrance is the major factor affecting the relative stability of these compounds. When positions away from the bridgehead are occupied the compound is more stable. It is interesting to notice that the ranking of the compounds is not sensitive to the method used, both AM1 and HF/6-31G produce the same trend regarding their stabilities. For all the compounds studied, 2,6-substituted isomers are found to be more stable than the others whereas 1,5-substituted isomers are found to be less stable than the others.

The internal rotation in styrene and substituted styrenes has been investigated by a large variety of techniques including microwave,[17a] infrared,[17b] Raman,[17c] ultraviolet,[17d] fluorescence,[17e] photoelectron[17f] and NMR spectroscopy,[17g] molecular rotatory polarization,[17h] calorimetric,[17i] molecular mechanics calculations,[17j] semiempirical[17k] and *ab initio* molecular orbital calculations.[17l] The consensus from these investigations is that the internal rotation in styrene is governed largely by a two-fold barrier with the planar form being the most stable. For styrene, the magnitude of the observed quadrupolar splittings with high resolution deuterium NMR spectra were used to calculate the average value of the dihedral angle between the vinyl and ring planes as 16.5°.[18] Klemm *et al.* concluded on the basis of ultraviolet spectroscopy that 1-vinylnaphthalene exists in a non-planar *anti* conformation, 1-*anti* whereas 2-vinylnaphthalene exists in a coplanar conformation 2-*syn*.[12] Similar conclusions were reached on the basis of ^{1}H NMR chemical shifts.[19]



On the basis of proton–proton nuclear Overhauser effects, it was concluded that the minimum energy conformation for 1-vinylnaphthalene was 1-*anti* with the deviation of the torsion angle a from planarity being equal to 38°. The same torsional angle a determined by high-field NMR spectroscopy was shown to be 41.8 ± 4.1° for 1-vinylnaphthalene and as 18.3 ± 3.1° for 2-vinylnaphthalene.[18]

In our calculations, analyses of the dihedral angles between the vinyl group and the naphthalene ring planes have demonstrated that the substituents orient themselves in such a way as to minimize their interaction with the ring and with each other (Table 2). We have compared the optimum geometries

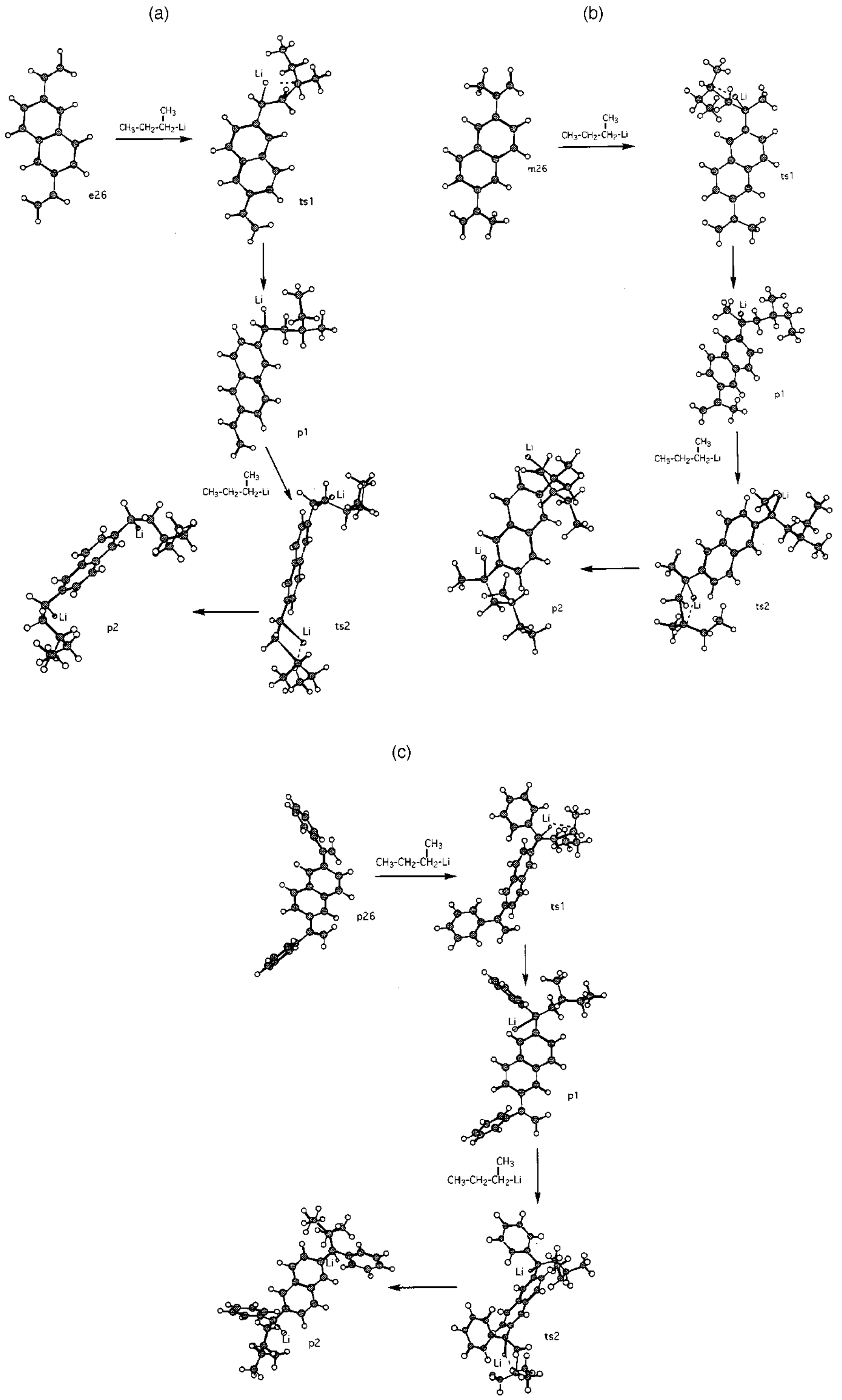


Fig. 3 Reaction path for the addition of *sec*-butyllithium to a, 2,6-diethenylnaphthalene, b, 2,6-di(1-methylethenyl)naphthalene, c, 2,6-di(1-phenylethenyl)naphthalene.

with HF/6-31G for diethenylnaphthalenes with the findings in the literature for ethenylnaphthalenes. The vinyl group at position 1 for compounds e15, e16 and e17 is *anti* to the bridge and tilted by approximately 45° from planarity in agreement with the experimental findings for 1-vinylnaphthalene.[18] The compounds with vinyl substituents at positions 2, 6 and 7 can be compared to 2-vinylnaphthalene. Similar to experimental results for 2-vinylnaphthalene, HF/6-31G calculations also give rise to coplanar vinyl groups with the naphthalene ring in e16, e17, e26 and e27. However, the vinyl group adopts an *anti* orientation with respect to the bridge in these compounds except for position 7 in e27. We have found out that the energies of different conformers for a given diethenylnaphthalene compound are within 2 kcal mol^{-1} of each other. The substituents might affect each other's orientation with respect to the naphthalene ring. The value of the dihedral angle between the vinyl group and the naphthalene ring increases by substituting methyl and phenyl groups on the vinyl group in compounds m15, m16, m17, p15, p16 and p17. For compounds m26, m27, p26 and p27 the dihedral angle C12–C11–C2–C3 is greater than zero, the coplanar situation of the vinyl group with respect to naphthalene is destroyed, due to the presence of bulky substituents. For di(1-methylethenyl)naphthalenes one of the H's of the methyl group is eclipsed with the vinylic double bond, this may be due to long range stabilizing interactions between the π electrons and the hydrogen.

Table 3 Bond lengths (Å) of diethenylnaphthalenes, di(1-methylethenyl)naphthalenes (HF/6-31G) and di(1-phenylethenyl)naphthalenes (AM1)

Bond length	e15	e16	e17	e26	e27
C1–C2	1.369	1.369	1.369	1.370	1.369
C3–C2	1.410	1.413	1.412	1.424	1.423
C4–C3	1.361	1.360	1.360	1.360	1.360
C10–C4	1.421	1.420	1.418	1.421	1.418
C10–C5	1.434	1.417	1.418	1.418	1.418
C6–C5	1.369	1.368	1.360	1.370	1.360
C7–C6	1.410	1.422	1.420	1.424	1.423
C8–C7	1.361	1.361	1.370	1.358	1.369
C8–C9	1.421	1.423	1.420	1.421	1.417
C9–C1	1.434	1.432	1.434	1.416	1.419
C10–C9	1.417	1.414	1.414	1.409	1.411
C11[a]	1.482	1.482	1.482	1.477	1.478
C12–C11	1.326	1.326	1.326	1.327	1.327
C13[b]	1.482	1.477	1.478	1.474	1.478
C14–C13	1.326	1.327	1.327	1.327	1.327
	m15	m16	m17	m26	m27
C1–C2	1.366	1.368	1.367	1.369	1.369
C3–C2	1.412	1.414	1.414	1.425	1.425
C4–C3	1.360	1.360	1.360	1.360	1.360
C10–C4	1.422	1.420	1.418	1.420	1.418
C10–C5	1.433	1.419	1.419	1.417	1.418
C6–C5	1.366	1.368	1.360	1.369	1.360
C7–C6	1.412	1.423	1.422	1.424	1.425
C8–C7	1.360	1.360	1.369	1.361	1.369
C8–C9	1.421	1.421	1.421	1.419	1.419
C9–C1	1.433	1.431	1.433	1.418	1.419
C10–C9	1.417	1.412	1.413	1.409	1.408
C11[a]	1.500	1.499	1.500	1.491	1.492
C12–C11	1.326	1.326	1.326	1.330	1.330
C13[b]	1.500	1.491	1.492	1.492	1.492
C14–C13	1.326	1.330	1.329	1.329	1.330
C21–C11	1.512	1.512	1.512	1.512	1.512
C24–C13	1.512	1.512	1.512	1.512	1.512
	p15	p16	p17	p26	p27
C1–C2	1.380	1.380	1.381	1.381	1.380
C3–C2	1.413	1.414	1.413	1.424	1.424
C4–C3	1.372	1.372	1.372	1.371	1.372
C10–C4	1.422	1.422	1.421	1.422	1.421
C10–C5	1.430	1.421	1.422	1.419	1.421
C6–C5	1.380	1.380	1.371	1.380	1.372
C7–C6	1.413	1.423	1.423	1.423	1.424
C8–C7	1.372	1.371	1.380	1.372	1.380
C8–C9	1.422	1.423	1.421	1.422	1.421
C9–C1	1.430	1.429	1.430	1.420	1.421
C10–C9	1.421	1.419	1.419	1.418	1.418
C11[a]	1.472	1.472	1.472	1.467	1.467
C12–C11	1.341	1.341	1.341	1.343	1.343
C13[b]	1.472	1.467	1.467	1.467	1.467
C14–C13	1.341	1.343	1.342	1.343	1.343
C15–C11	1.466	1.466	1.466	1.466	1.467
C21–C13	1.466	1.466	1.466	1.467	1.467

[a] C1 in 1,5-, 1,6- and 1,7-diethenylnaphthalenes; C2 in 2,6- and 2,7-diethenylnaphthalenes. [b] C5 in 1,5-; C6 in 1,6- and 2,6-; C7 in 1,7- and 2,7-diethenylnaphthalenes.

It is expected that variations in bond distances will provide evidence for the conjugation effect (Table 3). The bond lengths in the naphthalene ring adjacent to the substituents are longer than their homologues: for example in e15 the C1–C2, C1–C9, C5–C6, C5–C10, C9–C10 bonds are longer by 0.01–0.02 Å than C3–C4, C2–C3. The same is true for all the compounds. This elongation of the bonds vicinal to the substituents may be interpreted as a reflection of the electron withdrawing character of the vinyl groups. On the other hand, the C=C bond in the vinyl group is shorter by about 0.03 Å than the double bonds in naphthalene, indicating that delocalization of π-electrons over the naphthalene ring does not extend to the external vinylic fragment with the same efficiency. The C–C bond between the

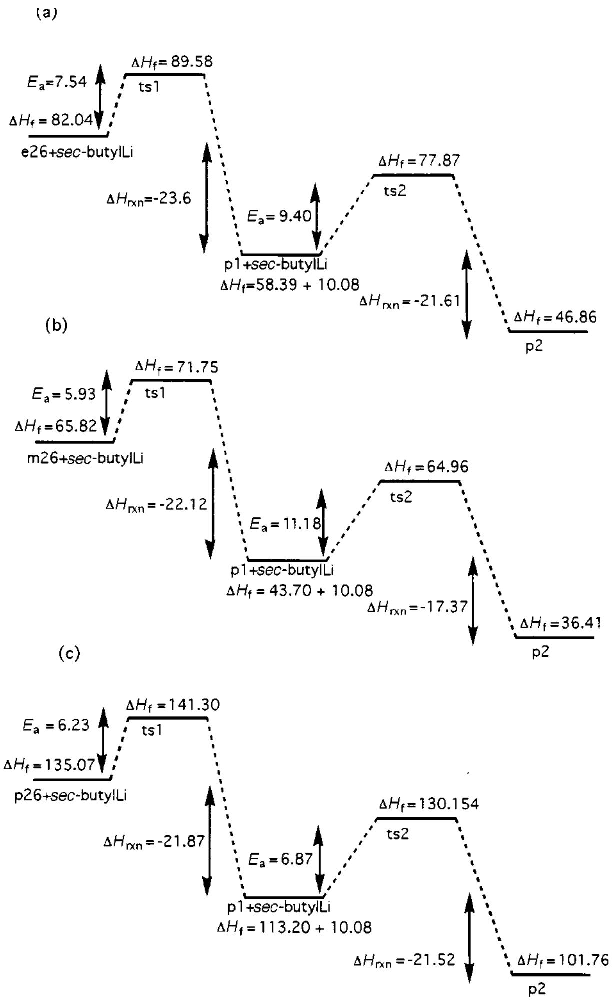
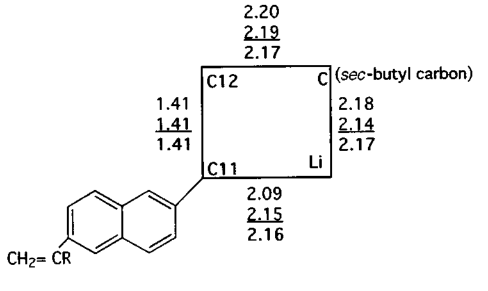


Fig. 4 Energetics for the addition reaction of *sec*-butyllithium to a, 2,6-diethenylnaphthalene, b, 2,6-di(1-methylethenyl)naphthalene, c, 2,6-di(1-phenylethenyl)naphthalene.



a) First transition state

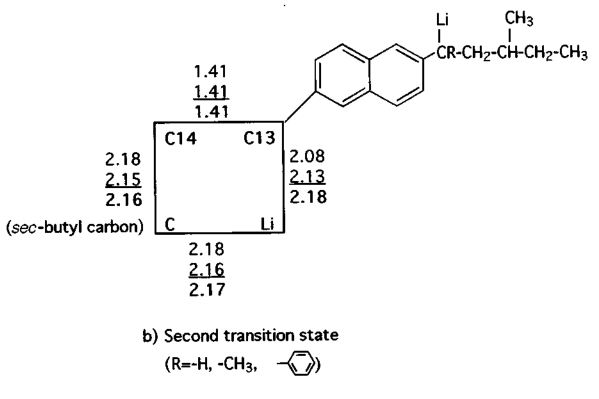


Fig. 5 Geometry for the transition states for the addition of *sec*-butyllithium to disubstituted naphthalenes. Distances are given in plain for R = H, in underlined for R = CH_3 and in bold for R = Ph.

Table 4 The coefficients for the LUMO in diethenylnaphthalenes

	C11	C12	C13	C14
e15				
s	0.00051	−0.01915	0.00053	−0.01923
p_x	0.09952	0.20076	−0.09929	0.20025
p_y	0.01370	0.00739	−0.01342	−0.00803
p_z	0.05323	−0.08027	−0.05282	0.07943
e16				
s	0.01440	−0.00692	0.00064	−0.01779
p_x	0.10579	−0.19086	0.09410	−0.16029
p_y	−0.05147	0.11083	−0.05121	0.09337
p_z	0.01493	−0.03366	−0.04489	0.12049
e17				
s	−0.00049	−0.01908	−0.00161	0.00811
p_x	0.03841	−0.03633	0.10425	−0.20693
p_y	−0.11072	0.22102	−0.03943	0.07014
p_z	0.03180	−0.04400	0.05742	−0.09191
e26				
s	0.00128	−0.00847	−0.00128	0.00847
p_x	−0.04280	0.09848	−0.04280	0.09848
p_y	0.00320	0.00044	0.00320	0.00044
p_z	0.13550	−0.24946	−0.13550	0.24946
e27				
s	0.00164	−0.00607	0.00164	−0.00607
p_x	−0.02047	0.03917	0.02047	−0.03917
p_y	−0.10399	0.18730	0.10399	−0.18730
p_z	−0.03123	0.07325	−0.03123	0.07325

vinyl group and the ring is longer for methyl and phenyl substituted compounds. This result can be justified by noting that methyl or phenyl substitution increases the steric interactions of the substituent with the naphthalene ring and the vinyl group tends to be away from the ring. However, comparison of positions 1 and 2 in terms of the bond length between the vinyl group and the ring indicates that this bond is shorter in position 2 because at this position, the substituent suffers less from steric repulsions. Also, due to the quasi planarity of these compounds migration of electrons towards the vinyl group can cause shortening of the bond. For substituents at positions 2, 6 and 7, differences in the length between double and single bonds diminish in comparison to positions 1 and 5. π electrons are more delocalized in compounds which are 2,6,7-substituted rather than 1 and 5 substituted ones, confirming the extra stability of the former compounds over the others. The trends observed for the bond lengths in the ring with HF/6-31G for diethenylnaphthalenes and di(1-methylethenyl)naphthalenes is also observed with di(1-phenylethenyl)naphthalenes. For di(1-phenylethenyl)naphthalenes, the C–C bond distance between the substituent and the ring is only 0.05 Å longer than the single bond in the ring, the same value is 0.06 Å for the ethenyl substituents and 0.08 Å for the methylethenyl substituents. These findings are due to the electron withdrawing character of the phenyl group which pulls the electrons from the naphthalene ring more than hydrogen and methyl species.

B. Modeling the addition of *sec*-butyllithium to diethenylnaphthalenes

We have considered the addition reaction of *sec*-butyllithium to the most stable 2,6-diethenylnaphthalenes in Fig. 3 where ts1 and ts2 represent the first and second transition states, p1 and p2 stand for the first and second products after the addition of one and two moles of *sec*-butyllithium respectively. The addition of *sec*-butyllithium to the first vinylic double bonds is an exothermic reaction. For all the substituents, the first step is more exothermic than the second one. The first activation barrier is considered as the rate determining step since the second barrier can be overcome by the energy given off during the first step. The energetics displayed in Fig. 4 suggest that the substituents lower the activation barrier. The methyl group with its electron donor ability and the phenyl group with its electron withdrawing character polarize the double bond towards the addition reaction. The geometry of the transition states is such that the double bond character of the vinylic double bond (1.33 Å) has disappeared (1.41 Å). The C–Li bond elongates from 2.01 Å in *sec*-butyllithium to 2.18 Å. The other sides of the quadrilateral are of 2.20 Å and 2.09 Å respectively. As seen from Fig. 5 the nature of the substituent does not affect the geometrical parameters of the transition structures.

C. Frontier orbitals

The LUMO's of the disubstituted naphthalenes have been considered since the attacking anion will be accommodated in the atomic orbitals with higher coefficients. Consideration of Tables 4–6 shows that coefficients for C12 and C14 are larger than the ones for C11 and C13. As expected the anion will attack the end carbons (C12 and C14) rather than the central vinylic carbons (C11 and C13).

Comparison of the coefficients at different positions indicates that the LUMO's have larger coefficients at positions 2, 6 and 7 which are away from the bridgehead. Thus, naphthalenes with substituents at positions 2, 6 and 7 are preferentially attacked by the alkyl anion. For the symmetrical 2,6- and 2,7-diethenylnaphthalenes, both positions, 2 and 6 or 2 and 7 are equally susceptible towards the nucleophilic attack.

The ratio of the coefficients has been considered for the comparison of the three substituents (R = H, CH_3, Ph): when the vinyl groups are away from the bridgehead positions, the phenyl group favors the attack of the anion somewhat more than methyl and hydrogen. On the other hand when the vinyl groups are close to the bridgehead the substitution effect is not observed.

D. Electrostatic potential

The reactivity of molecules can be calculated from the electrostatic potential $V(\mathrm{r})$ in several ways. The molecular surface potentials of the studied naphthalenes are reported in Figs. 6 and 7. The electrostatic potential energy of an anion with a charge $q = -1$ would be $U(\mathrm{r}) = qV(\mathrm{r}) = -V(\mathrm{r})$. The most straightforward analysis would be to calculate the patch area on the surface defining the reaction region. If one assumes random collisions between the reacting molecules, the reaction rate would simply be proportional to the reaction patch area. In this, it is implicitly assumed that the contribution to the reactivity is the same in each part of the reaction patch regardless of the value of the electrostatic potential. Results of this type of analysis are reported in Table 7 under PA, the patch area. As described in the Methodology section, the reaction region was defined as the surface points which have an energy lower than 20 kT and are within a distance of 2.5 Å from the vinylic end carbon atoms. A slightly more complicated analysis would weight the contributions of different regions of the reaction zone with an appropriate Boltzmann factor

$$NK_{\mathrm{a}} = A\int_{\mathrm{S}} \mathrm{e}^{-\beta u} da \qquad (3)$$

where A is a proportionality constant and da is the infinitesimal area element of the integrated surface. This type of analysis has been used before in determining the association constant of reactions. Because of the exponential dependence, points with large potentials would dominate the integral NK_{a}. Therefore, the observed trend in the maximum value of the electrostatic potential $V(\mathrm{r})$ and in the weighted sum of the above integral are the same. It should however be kept in mind that the electrostatic potentials were generated when the anionic ligand was not in the vicinity. Therefore, since they will

Table 5 The coefficients for the LUMO in di(1-methylethenyl)-naphthalenes

	C11	C12	C13	C14
m15				
s	−0.00009	0.02737	0.00009	−0.02739
p_x	0.01027	−0.02139	0.02547	−0.02139
p_y	0.06443	−0.10891	0.01680	−0.10891
p_z	0.00486	−0.06474	0.05774	−0.06474
m16				
s	0.00059	0.02649	0.00076	0.01719
p_x	0.04344	−0.04400	0.10622	−0.17718
p_y	0.02100	−0.07586	0.04370	−0.10024
p_z	0.04370	−0.09252	−0.00217	−0.00395
m17				
s	0.00031	0.02698	−0.00006	0.01266
p_x	−0.02516	0.01398	0.01316	−0.05787
p_y	0.03027	−0.10130	−0.06724	0.12188
p_z	−0.05110	0.07899	−0.08255	0.14856
m26				
s	0.00104	0.01829	−0.00104	−0.01829
p_x	0.06801	−0.14488	0.06801	−0.14488
p_y	0.01208	−0.03473	0.01208	−0.03473
p_z	−0.10235	0.16726	0.10235	−0.16726
m27				
s	0.00122	0.01540	0.00122	0.01540
p_x	−0.08224	0.13280	0.08220	−0.13274
p_y	0.02851	−0.06501	−0.02851	0.06501
p_z	−0.04854	0.09583	−0.04853	0.09580

Table 6 The coefficients for the LUMO in di(1-phenylethenyl)-naphthalenes

	C11	C12	C13	C14
p15				
s	−0.00423	−0.02602	−0.00425	−0.02609
p_x	0.00158	−0.06261	−0.00164	0.06269
p_y	−0.04225	−0.08230	0.04176	−0.08151
p_z	−0.06510	0.10078	0.06447	−0.09940
p16				
s	0.00358	0.02732	0.00110	0.01134
p_x	−0.01967	0.08319	0.04134	−0.04445
p_y	0.02887	−0.04404	−0.01141	0.04473
p_z	0.04681	−0.04939	0.12956	−0.23738
p17				
s	0.00330	0.02564	−0.00213	−0.01744
p_x	0.04221	−0.12196	−0.03361	0.05203
p_y	−0.03419	0.05837	0.05680	−0.12566
p_z	−0.04986	0.04857	−0.11125	0.17901
p26				
s	0.00136	0.01371	0.00212	0.01745
p_x	0.08671	−0.18943	0.07733	−0.16484
p_y	−0.10385	0.16327	0.11346	−0.18176
p_z	−0.03163	0.04909	0.02990	−0.04626
p27				
s	0.00198	0.01422	0.00198	0.01421
p_x	0.03644	−0.04197	−0.08357	0.13634
p_y	−0.10905	0.19349	0.03740	−0.04999
p_z	0.00407	−0.01260	0.06989	−0.13554

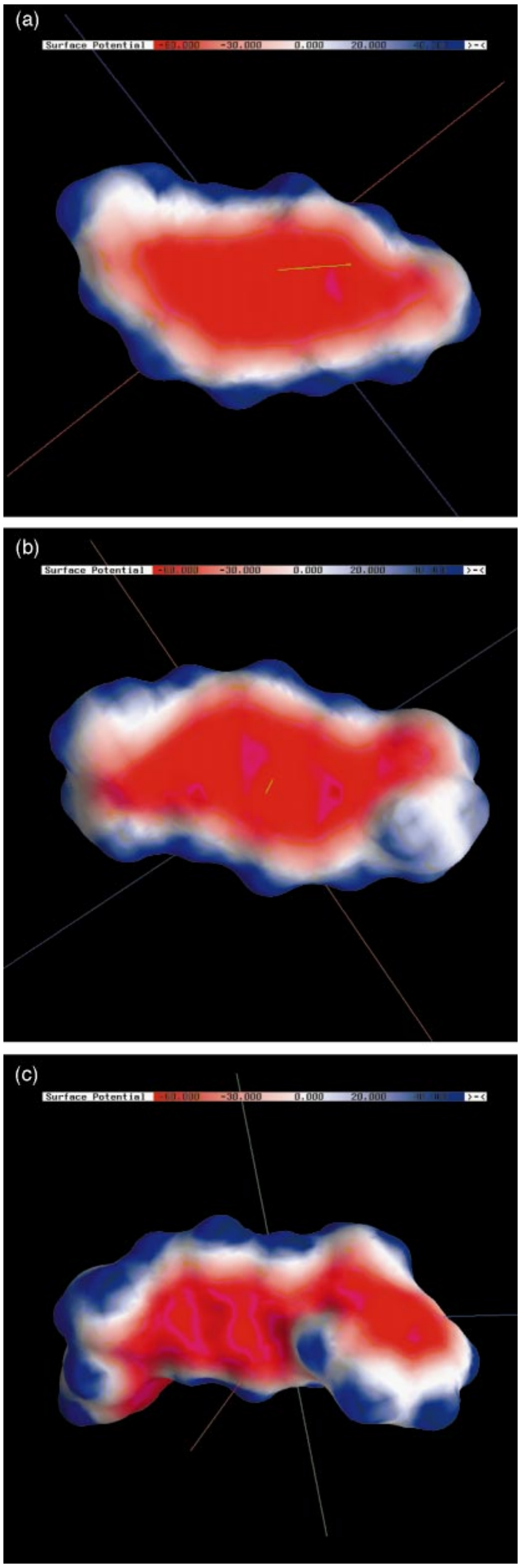


Fig. 6 Electrostatic potential at the molecular surfaces of 2,6-substituted diethenylnaphthalenes. The orientation of the molecule is such that one of the vinyl groups is facing the reader on the left upper corner, and the other is looking into the page on the right. a, e26, b, m26, and c, p26.

be affected less, the reaction patch area sizes might be a better indicator of the polymer's stability. Results reported in Table 7 show that positions away from the bridgehead are more susceptible to being attacked by the anion and the 1,5-substituted compounds are the least reactive ones toward the anionic polymerization. This can be justified by steric restrictions around the bridgehead limiting the access to the binding site. Among other substitutions, 1,7-substitution is not favored either, which might be due to the fact that in this configuration the substitutions are placed very close to each other. Compounds with the 1,6-, 2,6- and 2,7-substitutions are more

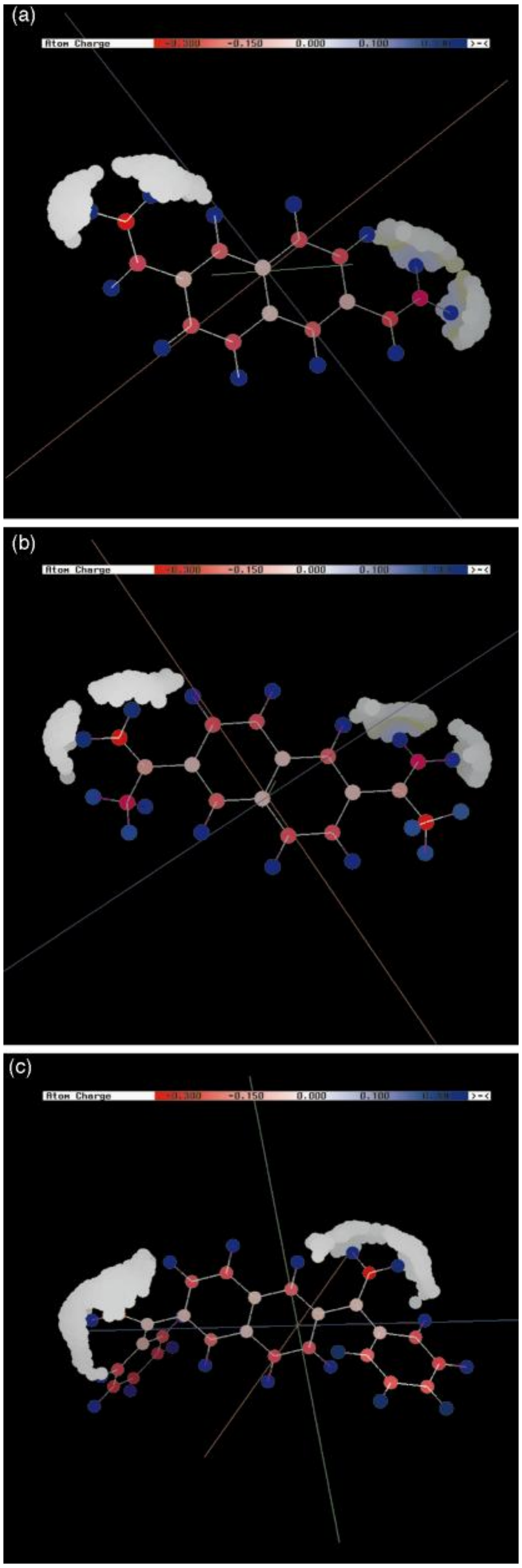


Fig. 7 Reactive patch areas reported in Table 7 for the 2,6-substituted diethenylnaphthalenes. Small white spheres around the vinyl groups show the defined reactive molecular surface regions. a, e26, b, m26, and c, p26.

Table 7 Electrostatic potentials in the reaction region[a]

Compound	e15	e16	e17	e26	e27
PA	1.13	1.33	1.25	1.34	1.34
log10 (NK_a)	−3.26	−2.11	−2.39	1.16	2.82
V_{max}(r)	44.9	48.7	48.1	56.4	60.2
Compound	**m15**	**m16**	**m17**	**m26**	**m27**
PA	0.68	0.89	0.81	1.00	1.07
log10 (NK_a)	−4.54	1.92	−3.43	0.00	1.25
V_{max}(r)	41.7	58.2	45.6	53.2	56.1
Compound	**p15**	**p16**	**p17**	**p26**	**p27**
PA	0.91	1.23	1.02	1.23	1.59
log10 (NK_a)	−1.43	1.56	−0.65	3.62	−0.05
V_{max}(r)	49.5	57.3	52.2	62.1	53.0

[a] The reaction region is described in the text. PA is the reaction patch area, log10 (NK_a) is the base 10 logarithm of the association constant calculated using eqn. (3). Both the PA and NK_a are normalized with their respective values for the m26 compound. V_{max}(r) is the largest V(r) among the surface points of the reaction region in the units of k_BT where k_B is the Boltzmann's constant and T is the temperature.

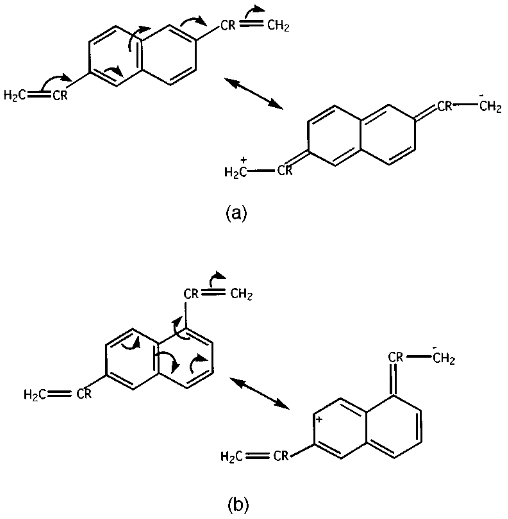


Fig. 8 Delocalization in diethenylnaphthalenes. a, 2,6-diethenylnaphthalenes, b, 1,6-diethenylnaphthalenes.

susceptible to a nucleophilic attack. Judging from the patch areas the 2,7-substituted compounds would polymerize slightly better than the equivalent 1,6- and 2,6-substituted ones.

The observed trend in the maximum value of the electrostatic potential V(r) reflects the effect of the substituents on the reactivity of the compounds of interest. The values for V(r) in the reaction region for 1,5-, 1,7- and 2,6-substituted compounds are seen to mimic the electron withdrawing abilities of the substituents, phenyl substituted compounds have the greatest V(r) while methyl substituted compounds have the lowest V(r). This trend is not observed for 1,6- and 2,7-substituted compounds. We have explained this difference in behavior between these two classes of compounds by drawing resonance structures for representatives of each class. Fig. 8 shows that for 1,5-, 1,7- and 2,6-substituted compounds the two substituents are in resonance with each other through a continuous delocalization path. This will enhance the electron withdrawing abilities of the substituents. On the other hand, it is difficult to predict a trend for compounds with 1,6- and 2,7-substituents where the two substituents are not conjugated due to a discontinuous delocalization path.

Conclusions

The following conclusions can be drawn from the results presented.

1. Both AM1 and HF/6-31G can be used to sufficiently discuss the geometries and energies of the compounds of interest.

2. Substitution away from the bridgehead of naphthalene has generated stable compounds due to the delocalization which

was possible because of the quasi planarity of these compounds.

3. Frontier orbitals and electrostatic potentials have shown that positions 2, 6 and 7 are more reactive than the other positions.

4. Methyl and phenyl substituted vinyl compounds have been shown to decrease the activation barriers in comparison to the non-substituted vinyl groups. These findings are confirmed by the presence of coefficients for end carbons in the LUMO's.

5. Electrostatic potential analysis results further support the conclusion that the 1,6-, 2,6- and 2,7-substituted compounds are more susceptible to a nucleophilic attack, and therefore, should have better polymerization characteristics.

6. In some cases—1,5-, 1,7- and 2,6-substituted compounds—the substituents are in conjugation with each other. It is then possible to state that the phenyl group with its electron withdrawing character enhances polymerization more than hydrogen and methyl groups.

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