

FULL PAPER

Alternating Planarity/Nonplanarity in n-Doped Odd-Membered, All-Trans Polyenes: Molecular Structures of $\text{NaC}_n\text{H}_{n+2}$ ($n = 3, 5, 7,$ and 9)

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Abstract The electronic structures of small, odd-membered, all-*trans* polyenes doped with one Na atom at various positions have been investigated using Hartree-Fock and density functional (B3LYP) theory with a 6-31G(d) basis set. Two distinctly different structural motifs have been identified. In one motif, the dopant atom interacts with an allylic polyene unit in a 4π -electron interaction that results in a planar polyene backbone. The other motif has the dopant atom interacting with a pentadienyl polyene unit in a 6π -electron interaction, which produces a significantly warped polyene backbone. Independent of structural motif at the doping site, the portion of the polyene structure outside the interaction region remains largely undisturbed in terms of planarity and bond length alternation. For a particular formula unit and potential energy surface, the stationary points corresponding to minima and transition states are remarkably close in energy despite the pronounced changes that occur in the dihedral angles of the polyene backbone at the dopant sites. Whereas internal and external instabilities are found in the Hartree-Fock wavefunctions for NaC_7H_9 and $\text{NaC}_9\text{H}_{11}$ structures, the restricted B3LYP wavefunctions are stable for all structures investigated.

Keywords Polyenes, n-doped, B3LYP, Na

Introduction

Although polyacetylene is classified as a poor semiconductor ($\kappa \sim 10^{-10} \text{ S cm}^{-1}$), n- or p-doped polyacetylenes are semiconductors and heavily doped polyacetylenes display metallic conductivity. The nature of the conductivity and the

mechanisms responsible for these physical changes are not well understood [1]. Extended models have been produced for band structure calculations, but molecular models are much less well defined for conductivity based on dynamical changes involving dopants. Molecular species systematically formed by appropriately chosen small polyenes (C_nH_{n+2}) plus dopant atoms or groups may serve as model systems for the long chain, doped polyacetylenes and may be amenable to high level computational studies using first principles electronic structure methods. In previous work [2], we investigated the structural and vibrational aspects of

Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

selected allyl ($n = 3$) and pentadienyl ($n = 5$) lithium and sodium species at the RHF/3-21G level of theory. We studied structures in which the metal atom was positioned above the central carbon atom (molecular C_s symmetry) and discovered a pronounced flexing of the pentadienyl chain near the dopant site. Calculations were also carried out for octatetraenyl disodium and a similar distortion of the polyene chain was observed. The bridged allyl Li, allyl Na, and pentadienyl Na structures were all calculated to be minima. Normal mode analysis showed that a stationary point, which appeared to represent a pentadienyl Li structure, was in fact only a transition state for the transfer of the Li atom between the ends of the carbon chain. Our work demonstrating the distortion of polyene backbones induced by Li or Na dopant atoms suggests the involvement of one or more dynamical processes in the conductivity of such species.

Model units examined by others include even-numbered polyene chains with and without defects or dopants, and odd-membered neutral and charged polyene radicals. In particular, Dupuis et al. [3-5] have studied the effect of electron correlation through comparison of RHF/UHF methods with MCSCF methods. Geometry optimization with methods that include electron correlation diminishes the double bond/single bond alternancy in neutral, singly, and doubly ionized C_nH_{n+2} ($n = 4, 6, 8,$ and 10) species; correlation effects also attenuate the charge density waves in the cations and the alternancy of bond orders for radicals with $n = 5, 7, 9,$ and 11 . Tanaka et al. [6-8] have calculated electronic structures for a number of polyene-dopant complexes, including some that we also present in this account, at the HF/3-21G level,

but they did not test the nature of the stationary points and performed only partial geometry optimization in certain cases [6]. The *allyl + metal* group forms the integral carrier unit in doped polyacetylene according to these authors. The allyl sodium complex had been of interest to several groups previously [2,9,10], and it was Schleyer et al. [10] who first described the bonding in this and related species on the basis of *ab initio* electronic structure calculations.

The considerable carbon chain deformation that we observed in pentadienyl Li and Na [2] (ca. 40° dihedral angle changes) has led us to explore larger chains for the presence of this motif. Here, we present structural and energetic results for some small odd-membered, all-*trans* polyenes doped with a single Na atom, NaC_nH_{n+2} ($n = 3, 5, 7,$ and 9), obtained from first principles electronic structure calculations which employ polarized basis sets and both Hartree-Fock and density functional levels of theory. A discussion of computational results on analogous Li or K doped polyenes will be presented elsewhere.

Computational details

A number of computational methods incorporated into the Gaussian 98 suite of electronic structure programs were used in this investigation [11]. Geometry optimizations were carried out at the restricted Hartree-Fock (RHF) [12] and B3LYP (RB3LYP) [13] levels of theory with the standard split valence plus polarization 6-31G(d) basis set [14]. Normal mode

Figure 1 End-, top-, and side-views of RB3LYP/6-31G(d) optimized structures of NaC_5H_7 isomers: **3** (left column) and **2** (right column). Selected dihedral angles are given

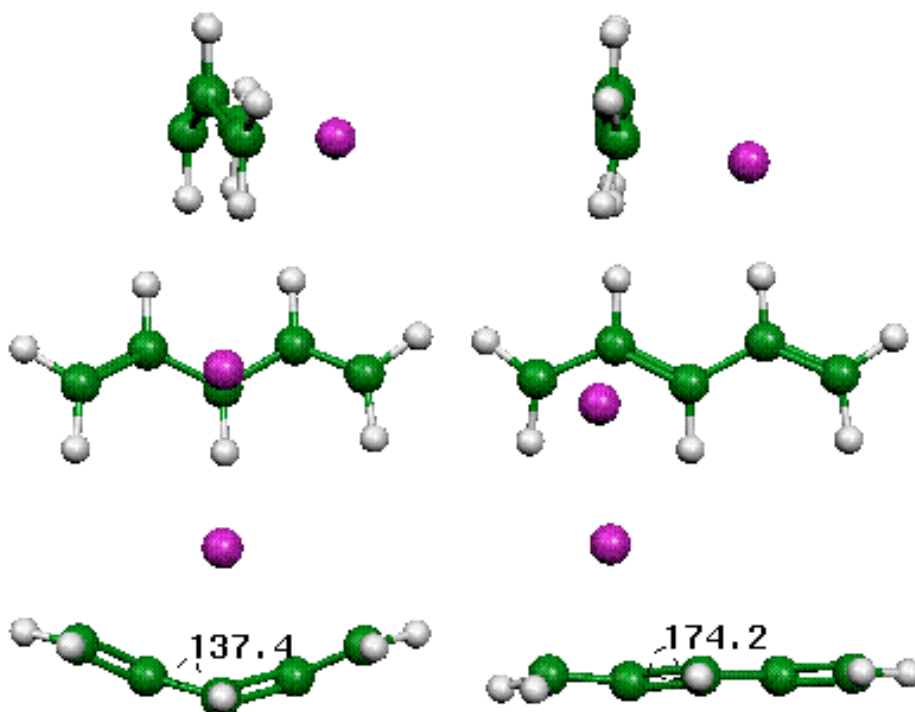
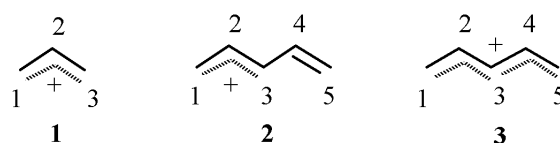


Table 1 Selected structural parameters for the optimized structures of $\text{Na}[2]\text{C}_3\text{H}_5$, $\text{Na}[2]\text{C}_5\text{H}_7$, and $\text{Na}[3]\text{C}_5\text{H}_7$. All calculations employed the 6-31G(d) basis set

Molecule Parameter	$\text{Na}[2]\text{C}_3\text{H}_5$		$\text{Na}[2]\text{C}_5\text{H}_7$		$\text{Na}[3]\text{C}_5\text{H}_7$	
	RHF	RB3LYP	RHF	RB3LYP	RHF	RB3LYP
NaC_{i-1}	2.504	2.468	2.472	2.412	2.582	2.548
NaC_i	2.444	2.397	2.460	2.429	2.448	2.457
NaC_{i+1}			2.585	2.626		
NaC_{i+2}			3.628	3.615	2.899	2.841
C_1C_2	1.393	1.405	1.397	1.415	1.363	1.381
C_2C_3			1.389	1.395	1.417	1.418
C_3C_4			1.452	1.442		
C_4C_5			1.332	1.352		
$\text{NaC}_i\text{-H}(\text{C}_i)$	115.6	115.3	115.2	113.5	86.8	87.5
$\text{H}(\text{C}_1)\text{C}_1\text{C}_2\text{Na}$	-82.7	-82.9	-85.4	-88.9		
$\text{H}'(\text{C}_1)\text{C}_1\text{C}_2\text{Na}$	126.6	126.4	126.0	123.9		
$\text{C}_1\text{C}_2\text{C}_3\text{Na}$					70.7	70.5
$\text{C}_1\text{C}_2\text{C}_3\text{C}_4$			-178.5	-174.2	141.3	137.4
$\text{C}_2\text{C}_3\text{C}_4\text{C}_5$			-172.1	-177.6		

analysis was performed to ascertain the nature of all structures identified as stationary points on the potential energy surfaces. Tests were conducted for internal and external stability of the (spin- and space-) restricted wavefunctions obtained at the optimized geometries [15]. The electronic structure of selected isomers were also computed using unrestricted methods (UHF, UB3LYP) [16]. Molecular wavefunctions were analyzed using the traditional Mulliken population procedure [17]. Figures were generated with the Molekel program [18].

Results

Since our principal interest lies in modeling metal doped polyenes, we will be concerned only with structural isomers in which the dopant atom (Na) interacts with the polyenic π -system in a charge-transfer, ion-pair type manner (viz., Na^+ -polyene $^-$). We find two distinct types of Na-polyene interaction pockets in our model systems. In each pocket type, the Na atom occupies a position close to the central carbon atom (C_i) of a chain containing either three ($\text{C}_{i-1}\text{C}_i\text{C}_{i+1}$) or five ($\text{C}_{i-2}\text{C}_{i-1}\text{C}_i\text{C}_{i+1}\text{C}_{i+2}$) sequential carbon atoms. A structural isomer in which Na is positioned in close proximity to carbon atom C_i in a polyene of composition C_nH_{n+2} will be denoted $\text{Na}[i]\text{C}_n\text{H}_{n+2}$. Data (geometrical parameters, relative energies,

and partial atomic charges) mentioned in the text refer to the RB3LYP/6-31G(d) level of theory, unless stated otherwise.

NaC_3H_5

The electronic structure of allylsodium, $\text{Na}[2]\text{C}_3\text{H}_5$ (**1**, C_s symmetry), has been discussed in detail elsewhere [2,6,9,10], and we present in Table 1 the salient structural parameters solely for reference purposes. $\text{Na}[2]\text{C}_3\text{H}_5$ is the prototypical species presenting the first of the basic structural motifs: the dopant Na atom is located "inside" an allylic pocket defined by a triad of carbon atoms, formally engaged in a 4π -electron interaction. The Na atom is situated 2.40 Å from C_2 and 2.47 Å from C_1 and C_3 ; the computed $\text{C}_1\text{-C}_2$ bond length is 1.40 Å [19]. As discovered by Schleyer et al. [9], the $p(\pi)$ -orbitals on the terminal carbon atoms reorient toward the bridging metal atom to increase electrostatic interactions and the interacting allyl fragment is no longer completely planar. Both RHF and RB3LYP wavefunctions for **1** satisfied all stability tests.

NaC_5H_7

There are two possible bridging positions in the pentadienyl isomers, $\text{Na}[2]\text{C}_5\text{H}_7$ (**2**) and $\text{Na}[3]\text{C}_5\text{H}_7$ (**3**). Es-

Table 2 Isomer energies (au), relative energies (kcal mol⁻¹), parenthesis after the total energy (0 = minimum; 1 = transition state) and the result of wavefunction stability tests. The number of imaginary frequencies for a particular isomer is shown in

Isomer	RHF	E(rel)	Stable	RB3LYP	E(rel)	Stable
Na[2]C ₃ H ₅	-278.29493 (0)		yes	-279.57534(0)		yes
Na[2]C ₅ H ₇	-355.18508 (0)	0.00	yes	-356.98401(0)	0.00	yes
Na[3]C ₅ H ₇	-355.18055 (0)	2.84	yes	-356.98298(0)	0.65	yes
Na[2]C ₇ H ₉	-432.07571 (0)	0.00	no[a]	-434.39363(0)	0.00	yes
Na[3]C ₇ H ₉	-432.07015 (1)	3.49	no[b]	-434.38970(1)	2.47	yes
Na[4]C ₇ H ₉	-432.07459 (0)	0.70	no[c]	-434.39119(0)	1.53	yes
Na[2]C ₉ H ₁₁	-508.96549 (0)	0.00	no[d]	-511.80260(0)	0.00	yes
Na[3]C ₉ H ₁₁	-508.96032 (1)	3.24	no[e]	-511.79903(1)	2.24	yes
Na[4]C ₉ H ₁₁	-508.96497 (0)	0.33	no[f]	-511.80076(0)	1.15	yes
Na[5]C ₉ H ₁₁	-508.96049 (0)	3.14	no[g]	-511.79955(0)	1.92	yes
Na[4']C ₉ H ₁₁	-508.96047 (1)	3.15	no[h]	-511.79942(1)	2.00	yes

[a] UHF/6-31G(d) = -432.07809 (1.49 kcal mol⁻¹ below RHF)

[b] UHF/6-31G(d) = -432.07075 (0.38 kcal mol⁻¹ below RHF)

[c] UHF/6-31G(d) = -432.07511 (0.33 kcal mol⁻¹ below RHF)

[d] UHF/6-31G(d) = -508.97219 (4.20 kcal mol⁻¹ below RHF)

[e] UHF/6-31G(d) = -508.96514 (3.02 kcal mol⁻¹ below RHF)

[f] UHF/6-31G(d) = -508.96915 (2.62 kcal mol⁻¹ below RHF)

[g] UHF/6-31G(d) = -508.96410 (2.27 kcal mol⁻¹ below RHF)

[h] UHF/6-31G(d) = -508.96416 (2.32 kcal mol⁻¹ below RHF)

sequential structural parameters are presented in Table 1 and Figure 1 shows views of the two NaC₅H₇ isomers. **2** structurally resembles **1** in the dopant pocket, but asymmetry has been induced since the Na atom in **2** is shifted over toward the C₁C₂ bond (NaC₁ = 2.41 Å, NaC₂ = 2.43 Å, NaC₃ = 2.63 Å). The polyene backbone remains essentially planar in **2**. The C-C distances inside the dopant pocket are in the 1.40-1.42 Å range and those outside the pocket are closely similar to those of a regular conjugated polyene with alternating single (~ 1.44 Å) and double (~ 1.35 Å) bonds. The RB3LYP structure presents a more delocalized (less alternating) backbone than does the RHF structure, in accord with the findings of Villar and Dupuis [3,4].

The central Na binding site is symmetrical (C_s symmetry) but produces a strongly warped (<C₁C₂C₃C₄ = 137.4°) polyene backbone (Figure 1, left). The Na atom is located essentially vertically above the C₃ atom (<H(C₃)C₃Na ~ 90°; <C₁C₃C₅Na ~ 10°). The immediate Na-C interaction distances (NaC₃ = 2.46 Å, NaC₂ = 2.55 Å) are only slightly longer in **3** than in **2**, and even the distance to the terminal carbon atom is relatively short (NaC₁ = 2.84 Å). The C₁C₂ bond length is 1.38 Å and the C₂C₃ bond length is 1.42 Å. The magnitudes of these NaC and CC distances show that the entire polyene π-system in **3** interacts with the Na atom. **3** is thus the prototypical example of the second structural motif we encounter: a Na atom and a full pentadienyl unit formally engaged in a 6π-electron interaction extending over a nonplanar backbone. We mention in passing that **3** remains significantly warped at the explicitly electron-correlated MP2/6-31G(d), CISD/6-31G(d), and CASSCF(4,4)/6-31G(d) levels (<C₁C₂C₃C₄ = 137.0°, 139.0°, and 145.5°, respectively).

We find that **2** is more stable than **3** by 2.8 kcal mol⁻¹ at the RHF level but only by 0.6 kcal mol⁻¹ at the RB3LYP level

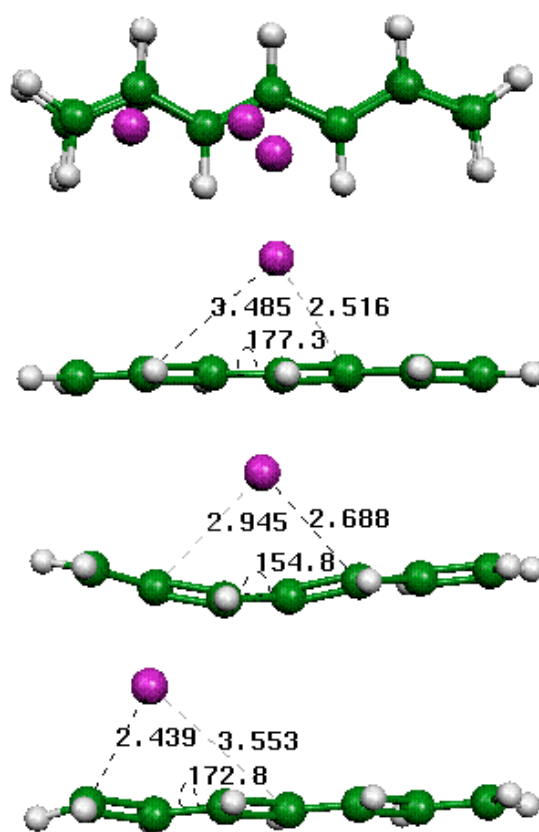
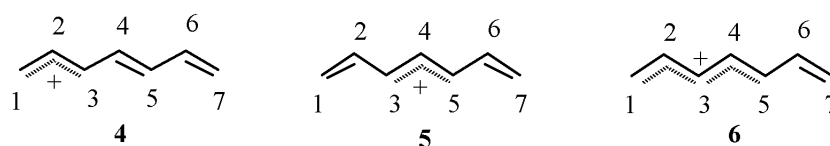


Figure 2 Views of RB3LYP/6-31G(d) optimized structures of NaC₇H₉ isomers. From bottom to top: **4**, **6** (a transition state, see text), **5**, and a composite top-view with the three structures superimposed. Selected bond lengths and dihedral angles are given

Table 3 Selected structural parameters for the optimized structures of $\text{Na}[2]\text{C}_7\text{H}_9$, $\text{Na}[3]\text{C}_7\text{H}_9$, and $\text{Na}[4]\text{C}_7\text{H}_9$. All calculations employed the 6-31G(d) basis set

Molecule Parameter	$\text{Na}[2]\text{C}_7\text{H}_9$		$\text{Na}[3]\text{C}_7\text{H}_9$		$\text{Na}[4]\text{C}_7\text{H}_9$	
	RHF	RB3LYP	RHF	RB3LYP	RHF	RB3LYP
NaC_{i-1}	2.500	2.437	2.815	2.945	2.543	2.516
NaC_i	2.462	2.428	2.435	2.442	2.464	2.406
NaC_{i+1}	2.568	2.610	2.508	2.426		
NaC_{i+2}			2.814	2.688		
C_1C_2	1.388	1.408	1.348	1.364	1.332	1.352
C_2C_3	1.397	1.401	1.433	1.433	1.452	1.443
C_3C_4	1.442	1.430	1.399	1.403	1.392	1.405
C_4C_5	1.341	1.366	1.380	1.403		
C_5C_6	1.457	1.442	1.453	1.443		
C_6C_7	1.328	1.349	1.331	1.351		
$\text{NaC}_i\text{H}(\text{C}_i)$	115.2	113.0	89.6	90.3	115.1	113.4
$\text{H}(\text{C}_1)\text{C}_1\text{C}_2\text{Na}$	-82.9	-87.1				
$\text{H}'(\text{C}_1)\text{C}_1\text{C}_2\text{Na}$	124.6	122.7				
$\text{C}_{i-1}\text{C}_i\text{C}_{i+1}\text{Na}$			79.3	87.1	119.1	114.0
$\text{C}_1\text{C}_2\text{C}_3\text{C}_4$	-178.8	-172.9	153.0	159.8	171.0	174.4
$\text{C}_2\text{C}_3\text{C}_4\text{C}_5$	-172.3	-178.7	-151.6	-154.8	-179.6	177.3
$\text{C}_3\text{C}_4\text{C}_5\text{C}_6$	-179.1	-179.2	-179.0	179.2		
$\text{C}_4\text{C}_5\text{C}_6\text{C}_7$	179.5	179.9	173.1	173.4		

(Table 2). The transition state for interconversion of the two isomers is just $0.7 \text{ kcal mol}^{-1}$ (RB3LYP) above **3** [20]. The RHF and RB3LYP wavefunctions are stable for both isomers.

NaC_7H_9

The optimized geometry representing $\text{Na}[2]\text{C}_7\text{H}_9$ (**4**, Table 3) shows a virtually planar backbone, the conventional model for a doped polyene. The structural parameters pertaining to the dopant pocket are very similar to those in **2**, including the asymmetric location of the Na atom favoring the C_1C_2 bond region and the remainder of the structure rapidly reverting structurally to a regular polyene (Figure 2).

The $\text{Na}[4]\text{C}_7\text{H}_9$ structure (**5**, C_s symmetry) represents a second minimum with a virtually planar polyene backbone (Figure 2) and a Na atom positioned symmetrically well into the $\text{C}_3\text{C}_4\text{C}_5$ pocket, which is slightly more compact than the one computed for **3** (Table 3). The C-C bond lengths in the pocket are near 1.40 \AA , whereas the C-C bond lengths outside the pocket vary as expected for a conjugated polyene.

We have not been able to locate a $\text{Na}[3]\text{C}_7\text{H}_9$ structure as a minimum, despite numerous attempts. It is possible to locate a stationary point on the potential energy surface which

has the Na atom in the vicinity of C_3 (**6**), but this structure is only a transition state for Na migration between the minima represented by **4** and **5**. Transition state **6** does share several structural features with the minimum structure **3**, including the distinct nonplanarity exhibited by the polyene backbone (Figure 2) [21].

Isomer **4** is computed to be more stable than **5** by $1.5 \text{ kcal mol}^{-1}$ at the RB3LYP level ($0.70 \text{ kcal mol}^{-1}$ /RHF, Table 2). The transition state **6** lies $2.5 \text{ kcal mol}^{-1}$ above **4**, i.e., only $0.9 \text{ kcal mol}^{-1}$ above **5** (RB3LYP). Although only the delocalized 4π -electron allylic interactions, flanked by essentially localized polyene fragments, produce minima for NaC_7H_9 (**4**, **5**), the 6π -electron delocalized interaction extending over a nonplanar backbone (**6**), assisted by a localized 2π -electron interaction, is nevertheless remarkably stabilizing. The RB3LYP wavefunctions are stable for all three structures investigated, whereas the RHF wavefunctions are all triplet unstable and spatially unrestricted wavefunctions of lower energy exist (Table 2). Geometry optimization of **5** at the unrestricted Hartree-Fock level (UHF/6-31G(d), singlet) preserves the planarity of the backbone, lengthens the C-C bond lengths by $\sim 0.01 \text{ \AA}$ or less, and lowers the energy by only 0.0004 au relative to the UHF energy obtained at the RHF geometry.

$\text{NaC}_9\text{H}_{11}$

The two structural motifs established above by the dopant sites in the C_3 , C_5 , and C_7 polyenes are clearly illustrated in the $\text{NaC}_9\text{H}_{11}$ series of isomers (**7-10**, Table 4, Figure 3). In both the $\text{Na}[2]\text{C}_9\text{H}_{11}$ (**7**) and $\text{Na}[4]\text{C}_9\text{H}_{11}$ (**9**) isomers, we observe virtually planar backbones in which the structural parameters of the allyl-type Na-pockets are similar to those calculated for the pockets in **2** and **4**, and the remainder of each structure is polyene-like, a hexatriene in the case of **7** and an ethylene plus a butadiene in the case of **9**.

The optimized structures for $\text{Na}[3]\text{C}_9\text{H}_{11}$ (**8**) and $\text{Na}[5]\text{C}_9\text{H}_{11}$ (**10**) show significantly warped backbones at the dopant site. Structure **8** is only a transition state for interconversion of **7** and **9**, whereas **10** is a genuine, but shall-

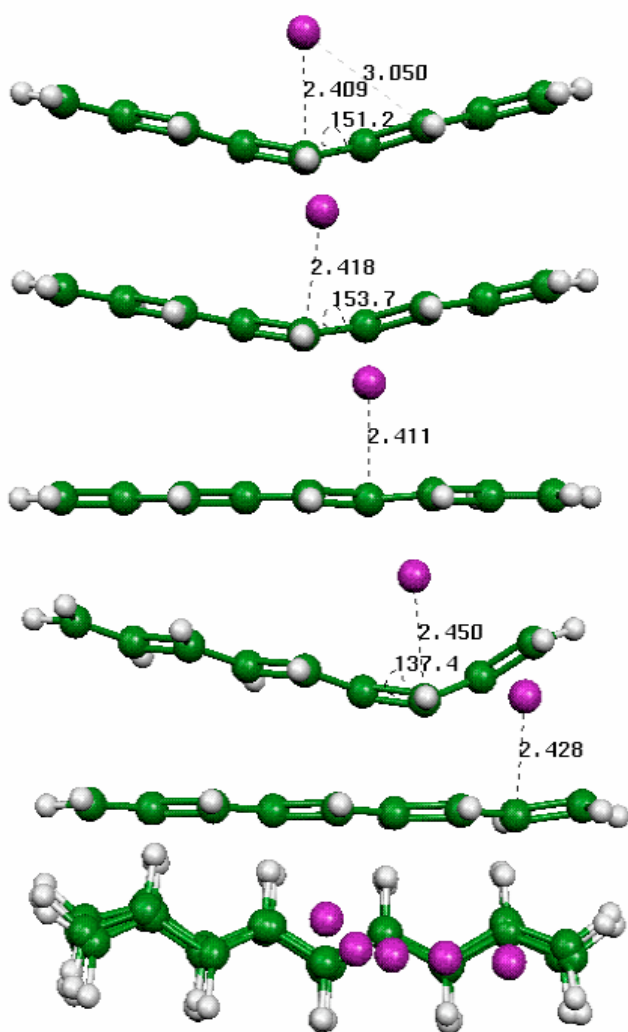


Figure 3 Views of RB3LYP/6-31G(d) optimized structures of $\text{NaC}_9\text{H}_{11}$ isomers. From top to bottom: **10**, $\text{Na}[4']\text{C}_9\text{H}_{11}$ (a transition state, see text), **9,8** (a transition state, see text), **7**, and a composite with the five structures superimposed. Selected bond lengths and dihedral angles are given

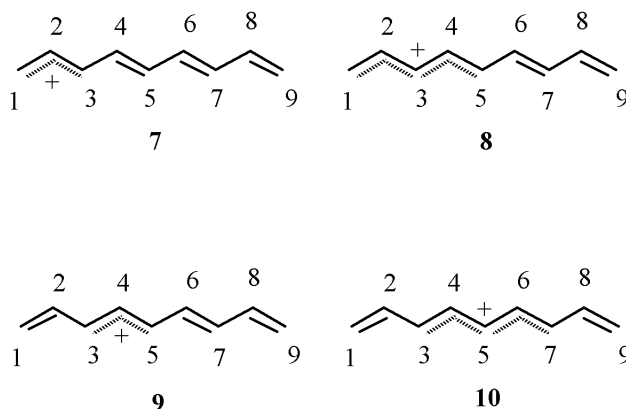
low, minimum; **10** is, however, highest in energy of the three $\text{NaC}_9\text{H}_{11}$ minima: 1.9 kcal mol⁻¹ above the most stable isomer **7** and 0.8 kcal mol⁻¹ above **9**. Transition state **8** is 2.2 kcal mol⁻¹ above the minimum **7** and hence 1.1 kcal mol⁻¹ above **9**. We have also located the transition state between **9** and **10** (labeled $\text{Na}[4']\text{C}_9\text{H}_{11}$ in Tables 2 and 4), a structure which has the Na atom positioned above the C_4C_5 bond (Figure 3). The activation energy barrier relative to **10** is particularly low (0.08 kcal mol⁻¹) and, in accord with the Hammond Principle [22], the transition state structure is much more similar to that of **10**, which is the reactant closer in energy content. For example, the dihedral angle in the chain varies from only 151.2° in **10** to 153.7° in $\text{Na}[4']\text{C}_9\text{H}_{11}$, whereas this angle is nearly 180° in **9**. The range of relative energies (0-2 kcal mol⁻¹) presented by these $\text{NaC}_9\text{H}_{11}$ structures provide some indication of the flatness of the potential energy surface with respect to Na migration above the polyene π -system.

The RHF solutions for all the $\text{NaC}_9\text{H}_{11}$ isomers are triplet unstable, whereas all the RB3LYP solutions are stable (Table 2). Upon reoptimization as a singlet using UHF/6-31G(d) theory and a spatially asymmetric wavefunction, **9** does maintain its warped character although the puckering decreases slightly.

Planarity/nonplanarity of isomers

A simple argument based on partial atomic charges may be presented to rationalize the presence of the two interaction motifs described above. In the extreme of charge transfer, we may consider the alkali-doped polyene as a Na^+ ion interacting with a polyene anion. The net atomic charges of the carbon atoms in the polyene anion follow a pattern in which the odd numbered centers are the primary carriers of the negative charge with the two terminal carbon atoms carrying the most charge, whereas the even numbered carbon atoms are essentially charge neutral. For example, the net atomic charges for $\text{C}_9\text{H}_{11}^-$ (Mulliken charges with H-atom contributions summed in) are $\text{C}_1 = -0.28(3)$, $\text{C}_2 = 0.02(0)$, $\text{C}_3 = -0.12(4)$, $\text{C}_4 = -0.05(0)$, and $\text{C}_5 = -0.12(7)$. Thus, when the Na^+ ion is doped into the [2] pocket (defined by the atoms $\text{C}_1\text{C}_2\text{C}_3$) or into the [4] pocket (defined by $\text{C}_3\text{C}_4\text{C}_5$), it is stabilized by Coulombic interaction with the odd-membered carbon atoms located on its immediate "sides" at the termini of the pocket. The Na^+ ion will be symmetrically positioned in the [4] pocket, but pulled toward the distinctly larger charge density on C_1 when inside the [2] pocket. The interaction unit involves three carbon atoms in an allylic array and the Na atom, a total of four π -electrons and the polyene backbone remains planar. In a [3]- or [5]-interaction site, the Na^+ ion experiences strong attraction to the central atom defining the pocket (C_3 or C_5). To gain additional Coulombic stabilization it is, however, necessary to bypass the neighboring, even-numbered, essentially neutral carbon atoms and instead involve the next set of odd-membered carbon atoms, which do carry negative charge. We thus achieve a warped interaction site consisting of a non-planar pentadienyl unit and the Na atom containing

Table 4 Selected structural parameters for the optimized structures of $\text{Na}[2]\text{C}_9\text{H}_{11}$, $\text{Na}[3]\text{C}_9\text{H}_{11}$, $\text{Na}[4]\text{C}_9\text{H}_{11}$, and $\text{Na}[5]\text{C}_9\text{H}_{11}$. All calculations employed the 6-31G(d) basis set

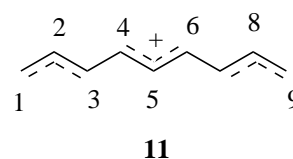


Molecule Parameter	$\text{Na}[2]\text{C}_9\text{H}_{11}$		$\text{Na}[3]\text{C}_9\text{H}_{11}$		$\text{Na}[4]\text{C}_9\text{H}_{11}$		$\text{Na}[5]\text{C}_9\text{H}_{11}$	
	RHF	RB3LYP	RHF	RB3LYP	RHF	RB3LYP	RHF	RB3LYP
NaC_{i-1}	2.516	2.456	2.786	2.913	2.567	2.543	2.626	2.568
NaC_i	2.464	2.428	2.435	2.440	2.467	2.411	2.423	2.409
NaC_{i+1}	2.559	2.599	2.526	2.438	2.535	2.515		
NaC_{i+2}			2.861	2.736			3.060	3.050
C_1C_2	1.384	1.403	1.348	1.363	1.331	1.352	1.329	1.350
C_2C_3	1.401	1.404	1.434	1.433	1.454	1.443	1.455	1.442
C_3C_4	1.438	1.425	1.396	1.401	1.386	1.402	1.366	1.387
C_4C_5	1.345	1.372	1.382	1.405	1.399	1.410	1.415	1.417
C_5C_6	1.449	1.430	1.445	1.431	1.444	1.432		
C_6C_7	1.3336	1.363	1.339	1.365	1.341	1.366		
C_7C_8	1.460	1.443	1.458	1.442	1.457	1.442		
C_8C_9	1.326	1.347	1.327	1.348	1.327	1.349		
$\text{NaC}_i\text{H}(\text{C}_i)$	115.1	112.7	89.9	90.3	114.7	112.4	91.1	93.6
$\text{H}(\text{C}_i)\text{C}_1\text{C}_2\text{Na}$	-81.6	-85.8						
$\text{H}'(\text{C}_i)\text{C}_1\text{C}_2\text{Na}$	123.9	121.7						
$\text{C}_{i-1}\text{C}_i\text{C}_{i+1}\text{Na}$			-78.2	-86.5	-118.3	-113.2	76.6	80.2
$\text{C}_1\text{C}_2\text{C}_3\text{C}_4$	-179.0	-172.0	-153.0	-159.0	-172.1	-175.2	-176.1	-177.0
$\text{C}_2\text{C}_3\text{C}_4\text{C}_5$	-172.2	-179.3	152.0	-155.4	-179.9	-177.4	-179.9	-178.3
$\text{C}_3\text{C}_4\text{C}_5\text{C}_6$	-179.0	-178.8	179.4	-177.9	-179.6	175.4	151.8	151.2
$\text{C}_4\text{C}_5\text{C}_6\text{C}_7$	179.5	179.5	-174.2	-175.5		171.2	176.4	
$\text{C}_5\text{C}_6\text{C}_7\text{C}_8$	180.0	-179.8	-179.1	-179.1		179.2	179.2	
$\text{C}_6\text{C}_7\text{C}_8\text{C}_9$	179.8	179.8	179.8	179.8	-179.7	-179.7		

a total of six π -electrons. In these structures, the Na atom is positioned almost straight above the central carbon atom (C_i), equidistant from and interacting with both C_{i+2} and C_{i-2} .

Overall, the isomers containing three carbon, 4π -electron interaction sites appear favored relative to the isomers containing the five carbon, 6π -electron sites. Either interaction site provides the opportunity for the remainder of the molecule to form regular, conjugated polyene fragments. If we attempt to force a three carbon, 4π -electron interaction site

from a five carbon, 6π -electron dopant site, we create open-shell radical polyene fragments on either side of the dopant site (viz. **11**).



Spin coupling of the two radicals to a singlet leads back to the five carbon, 6π -electron model, and spin coupling to a (π, π^*) -type triplet state is apparently not very favorable. The lower lying triplet states in the Na-doped polyenes with [2]- or [4]-type allylic dopant pockets place one electron in a polyene π -orbital and one electron in a Na orbital (not in a π^* -type orbital); the triplet state of lowest energy has an electron in a Na $3s$, $3p_z$ -type hybrid orbital, Figure 4 (z is defining the direction of the polyene π -type AO's). This orbital occupancy in effect transfers charge back to the Na^+ ion, and the triplet state dissociates upon geometry optimization to form a neutral Na atom and a polyene radical. The primary interacting orbital on the Na atom in all the doped polyene structures (planar or nonplanar) is always a $3s$ orbital, which has mixed some $3p_z$ directionality into it. We see no interactions involving the $3p_{x,y}$ orbitals on Na in any of the species studied here [6].

The observation that the lowest triplet state in all the metal-doped polyenes involves one electron in a Na sp_z -type hybrid orbital may provide a second rationalization for the alternating planarity/nonplanarity of the polyene backbone based on

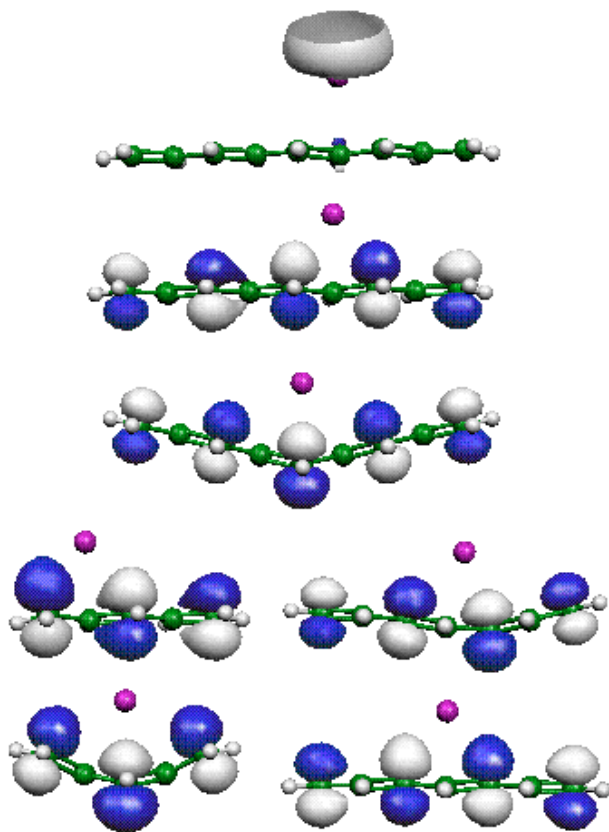


Figure 4 Contour plots of RB3LYP/6-31G(d) frontier molecular orbitals. From top to bottom: LUMO of **9**; HOMO of **9**; HOMO of **10**; HOMO's of **2** (left) and **5** (right); and HOMO's of **3** (bottom left) and **6** (bottom right)

a frontier orbital interaction picture. As examples, let us consider the structures of NaC_5H_7 through $\text{NaC}_9\text{H}_{11}$ in which the dopant atom is located at the central carbon atom (**3**, **6**, and **10**) or immediately next to the central atom (**2**, **5**, and **9**). The HOMO of an odd-membered polyene has a nonzero coefficient on odd numbered atoms and coefficients of zero on even numbered atoms (Figure 4). The center atom for $n = 3, 7, 11$, etc. is even numbered and thus its coefficient in the HOMO is zero, while the center atom for $n = 5, 9, 13$, etc. is odd numbered. However, it is a particular property of the HOMO for all odd-membered polyenes that the coefficients on the next nearest neighbors of any one carbon up and down the chain (i.e. atoms C_{i+2} and C_{i-2}) are in phase with each other. Thus, when the Na atom is above an atom with a nonzero coefficient, the orbital contributions to the HOMO from the two next nearest carbon $2p_z$ AOs are in phase and can interact favorably with the Na $3sp_z$ orbital. This leads to a warped backbone (Figure 4). When the Na atom is above an even numbered carbon atom, then the AO coefficient on any next nearest neighbor is also zero, leading to interaction with only the nearest neighbors and no warping of the backbone. If we let m denote the total number of π -electrons (one from each carbon atom of the polyene plus one from the Na atom), then the systems considered here (odd-membered polyenes plus one Na atom) give rise to $(4n)$ or $(4n+2)$ π -electron systems ($n = 1, 2, 3, \dots$). When $m = (4n+2)$, the central carbon atom is odd numbered and a warped backbone will result, when the Na atom is above the center. The opposite holds true for $m = 4n$ systems.

Summary and conclusions

Two types of structural pockets and interaction motifs have been clearly identified in these singly alkali metal doped polyenes: the previously documented *allyl* + *metal* coordination site which involves four π -electrons and leads to an overall planar backbone, and a *pentadienyl* + *metal* coordination site which involves six π -electrons and results in significantly warped structures. In these small polyenes, the three carbon interaction sites result in more stable isomers than the five carbon interaction sites; furthermore, for a given composition, the [2] isomer (terminal pocket interaction) is always the most stable. Remarkably small energy differences are obtained among structural isomers and transition states, a particularly striking result when we consider the substantial structural differences and distortions that are involved.

Finally, RB3LYP wavefunctions were always internally and externally stable and have been found to be so up to at least the $\text{NaC}_{25}\text{H}_{52}$ isomers [23], in contrast to RHF wavefunctions which became unstable starting with the NaC_7H_9 isomers. This aspect of instability would complicate any calculations on these species which include electron correlation on the basis of RHF solutions (e.g. MP2), and properly developed density functional theory models, such as B3LYP, do thus appear to be highly promising computational vehicles for studies of doped polyenes.

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Supplementary material available Optimized RB3LYP/6-31G(d) geometries of structures **1-10** (XYZ-format).

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