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Comparative study of kinetics isomerization of substituted polyacetylene (Cl, F, Br and I): Semi empirical RM1 study



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Abstract The newly semi empirical RM1 was used to investigate the interconversions of substituted (F, Cl, Br and I) polyacetylene conformers in the vapor phase. The rates of this geometrical isomerization have been measured and the Arrhenius parameters evaluated. In the case of unsubstituted polyacetylene as the reference, the Arrhenius parameters obtained are $A_1 = 1.73 \cdot 10^{12} \text{ s}^{-1}$ and $E_a = 0.40 \text{ kcal mol}^{-1}$. The values of the equilibrium constant for the reaction have also been determined at various temperatures between 300 and 1000 K, and the value of the energy change calculated. The results also suggest that the straightforward kinetics characterizes the majority of substituted polyacetylene isomerizations above 300 K. The isomerization energies are positive, and the barrier heights $\Delta E_{\text{barrier}}$ are expected to be sensitive for the magnitude of halogen effects. According to geometry features the cis→trans isomerization in the gas phase is found to be influenced by the size and electronic character of substituted halogens.

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1. Introduction

Ground and excited-state properties of cis and trans-1,3,5-hexatriene have attracted considerable interest over the last years (Reid et al., 1993; Garavelli et al., 1997; Celani et al., 1994). In the beginning, this interest was stimulated by the fact that hexatriene (HT) and substituted hexatriene (SHT) play an

important role in visual pigments and in the energy-converting protein bacteriorhodopsin (Birge and Reu, 1981), it serves as a model for the biosynthesis of vitamin D (Jacobs and Havinga, 1979). Used as a fluorescent probe to investigate membrane molecular order it has also been proposed as a probe to analyze membrane heterogeneity (Aricha et al., 2004) and as an appropriate probe to investigate structural of specific membrane (Kuhry et al., 1985). In particular, fluorescent derivative diphenylhexatriene propionic acid (DPH-PA) was used for the evaluation of antioxidant activity, vitamin E and Trolox (Arora et al., 2000). These compounds form a promising class of organic materials with interesting characteristics for photonic applications (Nalwa, 2008). SHTs are interesting candidates, they have been widely studied due to their attractive structural characteristics on the molecular scale, extensive

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π -conjugation, good planarity, and strong electron donor and acceptor groups at opposite ends of the molecule and a non-centrosymmetric structure (Labidi and djebaili, 2010; Labidi et al., 2011). Substituents can have critical effects on the chemistry of polyenes. The interaction of electron donors and acceptors across double bonds may lead to lower π -bond orders permitting geometries significantly distorted from planarity to exist. The barriers to internal rotation around the carbon-carbon double bond can be substantially lowered by push-pull substituted polyene (Kalinowski and Kessler, 1973; Sandstroem, 1983). The rotational barriers of Z-1,3,5-hexatriene have also been reviewed. The mechanism for internal rotation around the carbon-carbon single bond of 1,3,5-hexatriene is normally discussed in terms of a dipolar transition. Intrinsic reaction coordinate (IRC) calculations lead to a detailed understanding of various conformer interconversion reactions and the calculated activation barriers are in good qualitative agreement with experimental values for the closely related molecules 1,3-butadiene and all-trans-octatetraene (Debora et al., 1999).

Theoretical calculations for the unsubstituted hexatriene have used the restricted Hartree Fock (RHF 6-31G*) calculation that predicts a lower barrier for s-cis-Z-s-trans (cZt) to s-trans-Z-s-trans (tZt)-hexatriene isomerization in hexatriene than for cis to trans isomerization in butadiene. The Becke (3) Lee-Yang-Parr parameter functional (B3LYP) density functional calculation predicts a higher barrier for the cis to trans isomerization for both butadiene and hexatriene (Henseler et al., 1999; Pullen et al., 1997; Fabiano and Della Sala, 2006). The parameters for the s-cis-Z-s-cis (cZc) to s-trans-Z-s-trans conformer (tZt) isomerization are less certain but may be estimated from quantum chemical calculations.

To our best knowledge no studies have been reported on the structures of substituted (F, Cl, Br and I) hexatriene treating the kinetic and thermodynamic parameters. The need to simulate large-sized molecules or to deal with large series of compounds is a challenging topic in computational chemistry. Bearing these factors in mind, we became intrigued by the ki-

netic and thermodynamic properties of these substituted compounds.

In this paper we address the kinetic and thermodynamic parameters of the cis to trans isomerization in the gas phase of substituted polyacetylene (F, Cl, Br and I) using accurate new semi empirical Recife Model 1 (RM1) (Rocha et al., 2006) method. We investigate also the geometries and conformations of the compounds, the interconversion rate constants k from reaction temperatures T and activation barriers $\Delta E_{\text{barrier}}$ provided by transition state theory (TST). Temperature effects on the rate constant of polyacetylene substituted (PAs) and substituents effects on the activation energy (E_a) are also discussed.

2. Methods

Kinetic and thermodynamic parameters for substituted PA were performed using the Hyperchem'08 software (HyperChem, 2009). The computational method used was the semi-empirical Recife Model 1 (RM1) method (Rocha et al., 2006). This semi-empirical method was an improvement over previous methods, such as semi-empirical (AM1) (Dewar et al., 1985), and was used for its ability to give fast and reasonable results (Anisimov and Cavasotto, 2011; Morse et al., 2011; Kumbhar and Sonawane, 2011; Fiedler et al., 2011; Chen et al., 2011; Lowicki et al., 2011; Marianovic et al., 2011). Ab initio molecular orbital calculations of the molecular structures are performed at the Hartree Fock (HF/6-31G), Becke (3) Lee-Yang-Parr parameter functional (B3LYP/6-31G) and Møller Plesant perturbation (MP2/6-31G) levels by using the GAUSSIAN 03 program (Frisch et al., 2003).

3. Results and discussion

3.1. Geometries and conformations

The molecular structures of unsubstituted trans- and cis-1,3,5-hexatriene calculated at the HF/6-31G, MP2/6-31G, and semi

Table 1 Calculated molecular structures of trans- and cis-1,3,5-hexatriene.

Parameters	Cis-1,3,5-hexatriene				Trans-1,3,5-hexatriene			
	HF	MP2	RM1	Exp ^a	HF	MP2	RM1	Exp ^b
C ₂ C ₃	1.462	1.471	1.441	1.462	1.460	1.468	1.443	1.457
C ₁ C ₂	1.329	1.360	1.323	1.336	1.329	1.360	1.324	1.337
C ₃ C ₄	1.337	1.369	1.331	1.362	1.334	1.366	1.332	1.367
C ₁ H ₇	1.073	1.089	1.077	1.090	1.072	1.089	1.077	1.103
C ₁ H ₈	1.075	1.092	1.076	1.090	1.075	1.091	1.076	1.103
C ₃ H ₁₀	1.076	1.095	1.089	1.090	1.077	1.097	1.089	1.103
C ₁ C ₂ C ₃	123.5	123.2	122.6	122.1	124.4	124.2	122.3	121.7
C ₃ C ₄ C ₅	127.1	126.7	123.9	125.9	124.2	124.0	122.4	124.4
C ₅ C ₆ H ₁₄	121.7	121.9	124.5	124.0	121.7	121.8	123.5	120.5
C ₃ C ₄ H ₁₁	117.7	117.8	119.6	124.0	119.4	119.0	121.1	120.5
C ₁ C ₂ H ₉	118.7	118.5	120.7	116.9	119.3	119.2	120.5	117.0
C ₄ C ₃ H ₁₀	117.7	117.8	119.6	118.0	119.4	119.0	121.1	115.0
C ₁ C ₂ C ₃ C ₄	180.0	180.0	180.0	–	180.0	180.0	180.0	–
C ₃ C ₄ C ₅ C ₆	180.0	180.0	180.0	–	180.0	180.0	180.0	–

In units of Å^o (bond lengths) and degrees (bond angles).

^a Turner et al. (1973).

^b Traetteberg (1968).

empirical RM1 levels are shown in Table 1. The numbering of atoms is given in Fig. 1. As expected, at the HF level, the value of the C=C bond length is clearly underestimated. The inclusion of electron correlation at different levels of calculation leads to values in closer agreement with the experiment. The value of the C-C bond length is less sensitive to the inclusion of electron correlation. As a consequence of this fact, the BLA is overestimated at the HF level. The inclusion of dynamical electron correlation through MP2 calculations corrects this error. A very similar result is obtained at the RM1 level of calculation. The value of the C-H bond lengths also changes with the inclusion of electron correlation, leading to a better agreement with experimental values. On the other hand, the value of the CCC and CCH bond angles is less sensitive to the level of calculation. These results show that the inclusion of electron correlation is necessary to obtain geometry parameters within the range of the experimental results. However, some of the geometry parameters are already well reproduced at lower levels of calculation.

The extent of differences in the bond lengths between the three theoretical levels is very similar for the trans and cis isomers. The angles $\theta(C_3C_4C_5)$, $\theta(C_3C_4H_{11})$ and $\theta(C_4C_3H_{10})$ of the cis isomer are calculated to be significantly different from those of the trans isomer at both theoretical levels, probably because of the steric effect in the former. It is important to note that a good agreement was found between experimental values bond lengths, bond angles and values calculated by the semi empirical RM1. The calculated ratio is considered to be ($R = \text{EXP}/\text{RM1}$). For the (C=C) double bond $R = 1.02$, and for (C-C) single bond the calculated ratio is $R = 1.01$.

However, for valence angles the ratio varies between $R = 0.97$ – 1.04 . RM1 method appeared to work well for our target systems.

For trans-cis-trans-hexatriene (Liu and Zhou, 1993) have found a planar (C_{2v}) structure at the Hartree Fock (HF) and Møller Plessant (MP2) levels of calculation, while the experimental data (Turner et al., 1973) suggest non planar structure with a dihedral angle of 10 degrees around the central C=C double bond. The calculated torsional potential curves around both central C=C double bond and the C-C single bond are very flat in the range between -10 and 10 degrees. This fact allows the effective relaxation of steric repulsion. The potential energy function corresponding to the rotation around the C-C single bond of butadiene has been studied by Guo and Karplus (1991). They showed that the form of the torsional potential in the region between $CCCC = 0$ – 120 degrees is not sensitive to the addition of polarization functions or inclusion of electron correlation.

In order to investigate the effects of substituents on polyacetylene geometry, we determined in Table 2 the bond length alternation factor BLA in the middle of molecule which represents the difference between the length of the simple and double bonds in the medium of the molecule ($BLA = R_{(C-C)} - R_{(C=C)}$) (Perpète and Champagne, 1999).

Table 2 shows the bond length alternation factor BLA for optimized cis and trans conformers (Fig. 1) using Recife Model 1 (RM1). According to the substituent effects great structural changes are produced. As expected, the central C=C bonds are longer in all substituted systems than that in the unsubstituted hexatriene. Furthermore, this bond is always shorter in

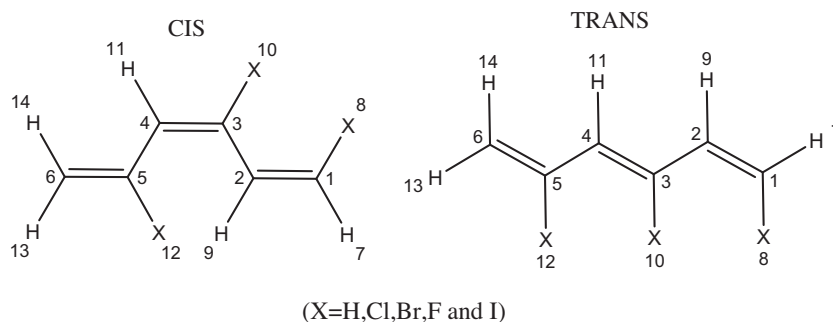


Figure 1 The numbering of atoms employed in Table 1 to describe optimized structure of (a) trans-1,3,5-hexatriene and (b) cis-1,3,5-hexatriene.

Table 2 Calculated bond length (Å), dipole moment (Debyes) and BLA (Å) for cis and trans-PAs-X₃ (X = Cl, F, Br and I) conformations using semi empirical RM1.

System	RM1							
	Cis			μ (D)	Trans			μ (D)
	C ₄ -C ₅	C ₃ =C ₄	BLA*		C ₄ -C ₅	C ₃ =C ₄	BLA*	
PA	1.4413	1.3320	0.1094	0.05	1.4427	1.3320	0.1107	0.00
PAs-F ₃	1.4445	1.3444	0.1001	1.39	1.4485	1.3433	0.1052	1.80
PAs-Cl ₃	1.4262	1.3279	0.0983	2.40	1.4280	1.3310	0.0970	4.36
PAs-I ₃	1.4284	1.3281	0.1002	2.58	1.4277	1.3286	0.0991	3.13
PAs-Br ₃	1.4267	1.3263	0.1003	2.45	1.4270	1.3282	0.0989	3.47
PAs-F ₆	1.4492	1.3568	0.0925	0.22	1.4518	1.3557	0.0961	0.00
PAs-I ₆	1.4080	1.3277	0.0803	0.18	1.3555	1.3186	0.0369	0.003

* ($BLA = R_{(C-C)} - R_{(C=C)}$).

the trans than in the cis isomer. The results first show that halogens acted to reduce the length of the double bond and to increase the length of the single bonds. As a result, the bond length alternation BLA in the middle is decreased by $\Delta l = 0.0055, 0.0116$ and $0.0118, 0.0137 \text{ \AA}$ for trans conformers (PAs-F₃, PAs-I₃, PAs-Br₃ and PAs-Cl₃, respectively). The same tendency was observed for the cis conformers where the BLA in the middle is decreased by $\Delta l = 0.0091, 0.0092, 0.0093, 0.0111 \text{ \AA}$ for PAs-Br₃, PAs-I₃, PAs-F₃ and PAs-Cl₃, respectively. In all cases, halogen substituents reduce the double bond character and consequently the BLA values, yielding dipolar species. As regards these substituted molecules, we are able to propose a decreasing classification, relatively to the BLA. The established order is as follows:

(i) Cis substituted conformation: $BLA(\text{PAs-Br}_3) > BLA(\text{PAs-I}_3) > BLA(\text{PAs-F}_3) > BLA(\text{PAs-Cl}_3)$. (ii) Trans substituted conformation: $BLA(\text{PAs-F}_3) > BLA(\text{PAs-I}_3) > BLA(\text{PAs-Br}_3) > BLA(\text{PAs-Cl}_3)$.

The decrease in bond alternancy, when halogen substitution is included can be explained in terms of molecular orbital energies at both highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals. The substitution of an atom of halogens (X = Cl, F or I) in the polyacetylene molecules increases molecular energy and decreases the energy gap between the two molecular orbitals HOMO–LUMO. For all these substituted polyacetylene, the HOMO and LUMO orbitals have opposite bonding properties for any two adjacent (C–X) atoms. An increase in the occupation of the LUMOs will therefore result in an elongation of the double bonds and shortening of the single bonds. The established order for trans substituted conformation is classified according to the size and thus according to the number of electrons of the halogen (Cl < Br < I). Except for fluorine atoms, the enhanced BLA value of the trans isomer can be explained by intramolecular hydrogen bonding contribution to band gap increasing.

For trans substituted PA, it can be seen that large substituent (I, Br and Cl) atoms, make greater structural changes as compared to cis structure, this can be explained in terms of the difference in unit cell for trans and cis conformation. The unit cell of trans PA consists only of one –CH=CH– segment, whereas a unit cell of cis PA consists of two –CH=CH– segments, as shown in Fig. 1. This makes the conjugation length of the trans polyene Π system longer than that of cis polyene. This demonstrates that the translational symmetry of trans PA is higher than that of cis PA. Clearly, the higher the translational symmetry the higher the delocalizability and the smaller the BLA. We can conclude that since BLA is one of the factors that increase band gaps, reduction of BLA could also contribute to the band-gap reductions observed for the substituted hexatriene.

The completely substituted molecule (PAs-F₆ and PAs-I₆) leads to the smallest value of BLA. Gould et al. (1999) synthesized PA by replacing all hydrogen atoms by fluorine and/or iodine atoms. Their experimental studies have shown that the incorporation of fluorine substituents into polymers leads to more stable structures with high thermal stability.

The comparison of alternation degree BLA presented in (Table 2) for cis and trans substituted PAs (X = Cl, Br, I and F), confirms that independently of the substituted halogens, the alternation degree of cis-conformations remains higher than that of trans ones:

$$BLA_{(\text{Cis})} > BLA_{(\text{Trans})}$$

The dipole moments for all neutral species are shown in Table 2. In substituted halogen systems, dipolar electronic structures are expected. Since the distance between the charges is larger in the trans forms than in the cis forms, the dipole moment of the trans forms is expected to be larger than that on the cis form for a given system. Indeed, the calculated dipole moments are greater for the trans form than for the cis form for all systems. The calculated dipole moments are also quite large for PAs-I₃ in this transition state (7.08 D). The large dipole moments suggest significant contribution from resonance form and are consistent significant donor effects.

3.2. Interconversion and barriers

According to Baker (1986) a suitable approximation of the favorable path of a chemical reaction is given by the eigenvector-following transition state search, which is defined as the maximum energy along a reaction coordinate on a potential energy surface. It locates the first-order saddle point; that is, the structure with only one imaginary frequency, having one negative eigenvalue. To find a first order saddle point (i.e., a transition structure), a maximum must be found in one (and only one) direction and minima in all other directions, with the Hessian (the matrix of second energy derivatives with respect to the geometrical parameters) being varied. So, a transition structure is characterized by the point where all the first derivatives of energy with respect to variation of geometrical parameters are zero (as for geometry optimization) and the second derivative matrix, the Hessian, has one and only one negative eigenvalue (Banerjee et al., 1985). Canonical transition-state theory CTST provides a simple tool for predicting interconversion rate constants k from reaction temperatures T and activation barriers ΔE :

$$k = A_h e^{\frac{-\Delta E_{ZP}}{RT}}$$

Table 3 RM1 calculated kinetic and thermodynamic parameters for substituted PA.

Reaction cis to trans	ln k				A_h (s ⁻¹)	E_a (kcal/mol)	$R = \frac{E_a(\text{PAs-X}_3)}{E_a(\text{PA})}$
	Temperature (K)						
	300	500	700	900			
PA	27.51	27.80	27.93	28.01	$1.725 \cdot 10^{12}$	0.40	1.0
PAs-F ₃	35.82	35.35	35.39	35.53	$6.328 \cdot 10^{14}$	-1.04	2.6
PAs-Cl ₃	38.91	37.43	37.04	36.95	$1.109 \cdot 10^{15}$	-2.54	6.4
PAs-I ₃	-81.22	-35.47	-15.65	-4.51	$1.625 \cdot 10^{14}$	67.93	169.8
PAs-Br ₃	46.38	43.86	43.14	42.93	$1.066 \cdot 10^{17}$	-4.28	10.7

k is the rate constant, R is the gas constant and T is the Kelvin temperature (K). The parameter A_h is called the Arrhenius prefactor (s^{-1}), and ΔE activation barriers (kcal/mol). Calculated vibrational frequencies for substituted, unsubstituted and transition state conformer using Recife Model 1 (RM1) may be used to estimate Arrhenius prefactor A_h in the limit of harmonic potentials.

The rate constants k predicted at different temperature values are shown in Table 3 and Fig. 2.

Fig. 2 shows RM1 Arrhenius plot of $\ln k$ versus $1/T$ for the cis-to-trans isomerization. The Arrhenius plot of $\ln k$ versus $1/T$ was found to be linear (Fig. 2) with a positive slope, with the exception for the substituted iodine hexatriene, the activation energy (E_a) was computed to be 0.40, -1.04 , -2.54 , 67.93

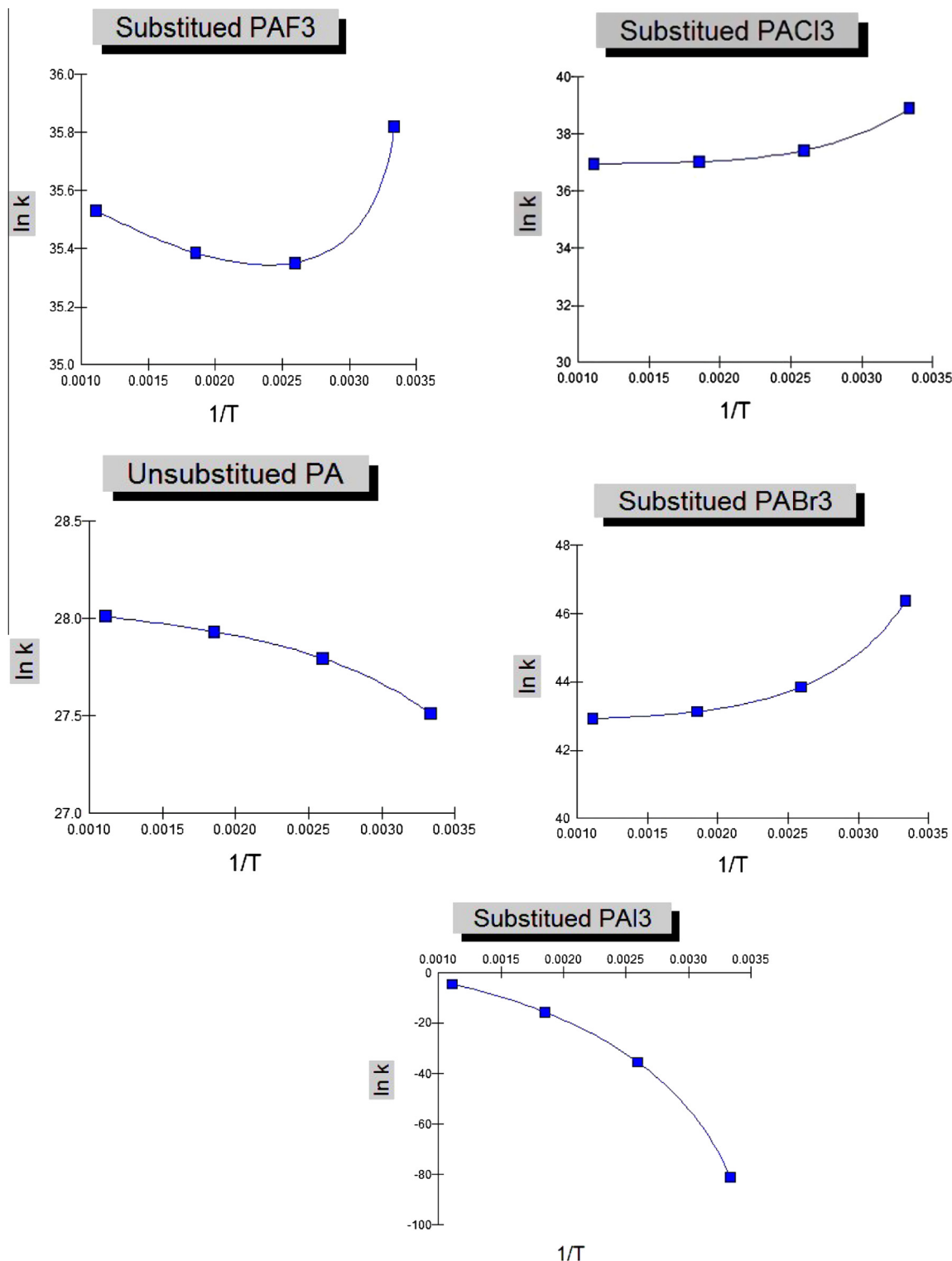


Figure 2 Arrhenius plot of $\ln k$ versus ($1/T$) for substituted polyacetylene (from hyperchem08).

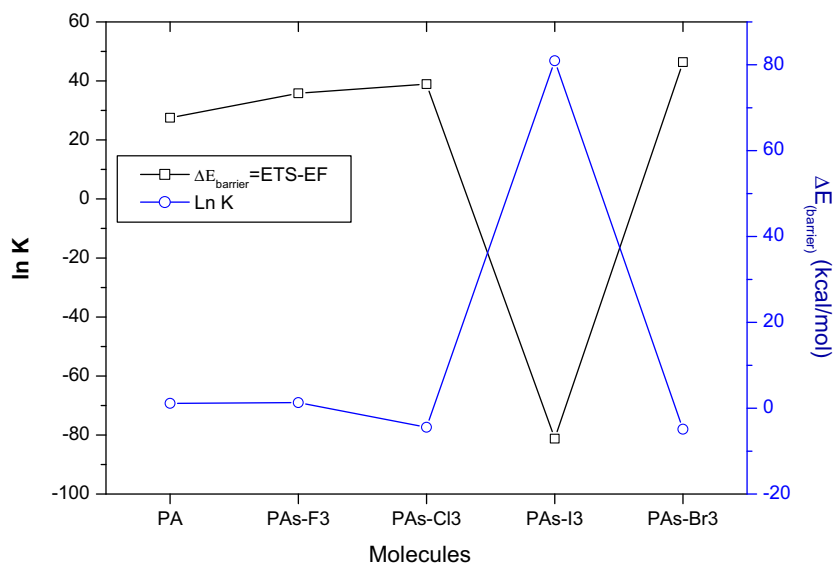


Figure 3 RM1 calculated variation rate constant $\ln k$ and $\Delta E_{\text{barrier}}$ for substituted PAs.

and -4.28 (kcal/mol) for PA, PAs-F₃, PAs-Cl₃, PAs-I₃ and PAs-Br₃, respectively.

Table 3 shows RM1 calculation yield values of Arrhenius prefactor $A_h = 1.73 \times 10^{12} \text{ s}^{-1}$ for unsubstituted conformer in the temperature range investigated here. This is slightly lower than the value of A_h calculated for the substituted conformer ($-F_3$, $-Cl_3$, $-I_3$ and $-Br_3$) ranging from $A_h = 1.6 \times 10^{14}$ to $1 \times 10^{17} \text{ s}^{-1}$. However the equilibrium Arrhenius prefactor (A_h) is an order of magnitude smaller for PAs-Br₃ ($1.06 \times 10^{17} \text{ s}^{-1}$) than the other substituted conformer ($-F_3$, $-Cl_3$ and $-I_3$) resulting in an absolute rate of decay that is faster for PAs-Br₃ than the other substituted conformer. The range of values for A_h estimated by transition state theory for cis to trans single bond isomerization is an order of magnitude lower than the value of $6 \times 10^{13} \text{ s}^{-1}$ determined from the data obtained in alkane solvents (Ahmasi Harris et al., 2006).

As Kauffmann et al. (1997) pointed out, the Arrhenius factor derived from a 10 ns time constant is by three orders of magnitude smaller than an experimental value obtained for all-trans-octatetraene. This is an indication that the time constant estimate of 10 ns is too large (Ackerman and Kohler, 1984). The observation made by Pullen et al. (1995) in their time resolved transient absorption studies that the spectrum at 100 ps differing very little from the equilibrium spectrum of 1,3,5-trans-hexatriene (tZt-HT) is in better agreement with the results found by Debora et al. (1999). For unsubstituted hexatriene at temperatures around 1000 K, the TS step is even faster than for the substituted hexatriene, due to the high preexponential factor for reaction which is decisive at this temperature. Even if the two preexponential factors were the same, for PAs-F₃ and PAs-I₃ the cis/trans transition state rate would only be 1.26 times as high as the rate for unsubstituted hexatriene. The experimentally determined ratio between the two rates could not be confirmed in this study. The RM1 calculated energy barrier ($\Delta E_{\text{barrier}} = E_{\text{TS}} - E_{\text{F}}$) for the cis to trans reaction is calculated to be 402 cm^{-1} (1.15 kcal/mol) which is in reasonable agreement with both calculated $350\text{--}400 \text{ cm}^{-1}$ (1.0–1.14 kcal/mol) (Henseler et al., 1999; Pullen et al., 1997).

Liu and Zhou (1993) have found a planar (C_{2v}) structure at the HF, MP2 and CASSCF levels of calculations with two possible cis/trans isomers with respect to the C=C bond. For each of them, the rotation around the C–C bonds can lead to s-trans and gauche conformations. The gauche-trans-trans, trans-cis-trans and gauche-cis-trans conformers have been found to be 3.0, 2.0 and 5.1 kcal/mol (Panchenko et al., 1992).

The semi empirical RM1 calculated barrier heights and rate constant for substituted polyacetylene are shown in Fig. 3.

Fig. 3 shows the variation of the rate constant $\ln k$ and barrier energy ($\Delta E_{\text{barrier}} = E_{\text{TS}} - E_{\text{F}}$) for substituted PAs and unsubstituted polyacetylene PA. The enhancement of rate constant $\ln k$ of these molecules is directly related to the barrier energy, an inverse relationship was found between $\Delta E_{\text{barrier}}$ and $\ln k$. Compounds with the large barrier energy value produce the larger rate constant K value. It could be interesting to synthesize compounds with F, Cl and Br substituent having the lowest barrier energy ($\Delta E_{\text{barrier}}$) values. It can be seen from Table 3 that, the substitution of iodine atoms, PAs-I₃, makes greater barrier energy changes due to the steric interaction as compared to the unsubstituted PA, the ratio $R = \Delta E_{\text{barrier}}(\text{PAs-I}_3)/\Delta E_{\text{barrier}}(\text{PA})$ is about 70 times larger. The barrier heights ($E_{\text{TS}} - E_{\text{trans}}$) are expected to be the sensitive probe for the magnitude of halogen effects. The isomerization energies are positive in all cases this means that the trans form is more stable than cis, except for PAs-Cl₃. This was attributed

Table 4 Linear regression coefficients (R^2) for substituted polyacetylene as function of temperature.

Linear regression ($Y = A + B.X$)	Correlation coefficient (R^2)
$\ln k = 34.73941 - 1.43451. \Delta E_{\text{barrier}}$	–0.994
$\ln k = 34.68845 - 0.87007. \Delta E_{\text{barrier}}$	–0.985
$\ln k = 34.88232 - 0.62836. \Delta E_{\text{barrier}}$	–0.970
$\ln k = 35.10251 - 0.49396. \Delta E_{\text{barrier}}$	–0.948

Table 5 Selected geometrical parameters for cis, trans and transition state (TS) for PAs-X₃ (X = Cl, F, Br and I), calculated at the semi empirical RM1 level.

PA				PAs-F ₃			
Parameters	Trans	Cis	TS	Parameters	Trans	Cis	TS
C ₂ C ₃	1.443	1.441	1.444	C ₂ C ₃	1.449	1.447	1.445
C ₁ C ₂	1.324	1.323	1.323	C ₁ C ₂	1.337	1.339	1.338
C ₃ C ₄	1.332	1.331	1.327	C ₃ C ₄	1.343	1.344	1.358
C ₁ H ₇	1.077	1.077	1.077	C ₁ H ₇	1.089	1.089	1.088
C ₁ H ₈	1.076	1.076	1.077	C ₁ F ₈	1.305	1.306	1.306
C ₃ H ₁₀	1.089	1.089	1.089	C ₃ F ₁₀	1.309	1.316	1.310
C ₅ H ₁₂	1.089	1.091	2.150	C ₅ F ₁₂	1.313	1.313	2.354
C ₁ C ₂ C ₃	122.3	122.6	122.5	C ₁ C ₂ C ₃	124.1	123.3	123.7
C ₃ C ₄ C ₅	122.4	123.9	122.0	C ₃ C ₄ C ₅	123.7	128.9	124.0
C ₅ C ₆ H ₁₄	123.5	124.5	123.6	C ₅ C ₆ H ₁₄	123.0	123.3	122.8
C ₃ C ₄ H ₁₁	121.1	119.6	116.7	C ₃ C ₄ H ₁₁	120.3	118.0	97.1
C ₁ C ₂ H ₉	120.5	120.7	120.6	C ₁ C ₂ H ₉	119.3	117.7	118.9
C ₄ C ₃ H ₁₀	121.1	119.6	120.7	C ₄ C ₃ F ₁₀	121.2	117.4	119.7
H ₇ C ₁ H ₈	112.1	112.1	112.1	H ₇ C ₁ F ₈	113.9	113.8	113.9
C ₁ C ₂ C ₃ C ₄	180.0	180.0	-177.5	C ₁ C ₂ C ₃ C ₄	180.0	180.0	-173.7
C ₃ C ₄ C ₅ C ₆	180.0	180.0	-93.9	C ₃ C ₄ C ₅ C ₆	180.0	180.0	173.3
μ (Debyes)	0.00	0.05	0.03	μ (Debyes)	1.80	1.39	1.29
PAs-Cl ₃				PAs-I ₃			
Parameters	Trans	Cis	TS	Parameters	Trans	Cis	TS
C ₂ C ₃	1.436	1.423	1.433	C ₂ C ₃	1.434	1.425	1.434
C ₁ C ₂	1.321	1.321	1.318	C ₁ C ₂	1.318	1.320	1.318
C ₃ C ₄	1.331	1.328	1.318	C ₃ C ₄	1.329	1.328	1.270
C ₁ H ₇	1.083	1.083	1.078	C ₁ H ₇	1.083	1.085	1.084
C ₁ Cl ₈	1.747	1.749	1.765	C ₁ I ₈	1.955	1.955	1.955
C ₃ Cl ₁₀	1.727	1.780	1.757	C ₃ I ₁₀	1.945	1.971	1.986
C ₅ Cl ₁₂	1.762	1.778	2.718	C ₅ I ₁₂	1.956	1.962	1.631
C ₁ C ₂ C ₃	129.1	129.2	122.5	C ₁ C ₂ C ₃	127.7	128.0	127.9
C ₃ C ₄ C ₅	129.0	131.0	128.4	C ₃ C ₄ C ₅	127.5	133.8	148.4
C ₅ C ₆ H ₁₄	123.9	123.6	124.5	C ₅ C ₆ H ₁₄	124.6	123.4	118.6
C ₃ C ₄ H ₁₁	118.0	116.6	101.7	C ₃ C ₄ H ₁₁	118.6	115.0	139.1
C ₁ C ₂ H ₉	116.2	115.6	121.5	C ₁ C ₂ H ₉	117.3	115.4	119.0
C ₄ C ₃ Cl ₁₀	121.9	112.5	119.0	C ₄ C ₃ I ₁₀	122.8	115.1	116.4
H ₇ C ₁ Cl ₈	111.0	110.7	113.0	H ₇ C ₁ I ₇	113.5	112.6	113.9
C ₁ C ₂ C ₃ C ₄	180.0	180.0	-81.7	C ₁ C ₂ C ₃ C ₄	180.0	180.0	-175.0
C ₃ C ₄ C ₅ C ₆	180.0	180.0	-162.0	C ₃ C ₄ C ₅ C ₆	180.0	180.0	-111.2
μ (Debyes)	4.36	2.40	1.24	μ (Debyes)	3.13	2.58	7.08

to better conjugation of the chlorine atoms lone pair with the π -system of C=C double bond in the cis form. The enhanced relative stability of the cis isomer of PAs-Cl₃ can be explained by intramolecular hydrogen bonding. A proton on the hexatriene chain and one substituted terminal halogens form a hydrogen-bond in the cis isomer. The Cl \cdots H distance is only 2.360 Å in cis-PAs-Cl₃ isomer. The F \cdots H distance is only 2.009 Å in cis-PAs-F₃, well within the range of the hydrogen bond. In the cis-PAs-I₃, the geometry is less favorable for hydrogen bonding. However, the I \cdots H distance is 2.757 Å. The isomerization energies are expected to be largely determined by steric interactions and they are relatively small in all cases.

Pullen et al. (1997) have reported for the cis to trans isomerization of hexatriene a barrier of 3.25 kcal/mol from a restricted Hartree Fock (RHF/6-31G) calculation. Panchenko and Bock (1992) have studied three high energy rotamers of octatetraene: g,T,t,T,t-, t,T,t,C,t- and g,t,t,c,t- where C and T refer to cis/trans isomerism around the C₁=C₂ and C₃=C₄ double bonds, while g and t refer to gauche and s-trans conformations around C₅-C₃, C₁-C₂ and C₄-C₆ single bonds. The

most stable structure is t,T,t,C,t-, which lies 1.9 kcal/mol above all trans conformer. The g,T,t,T,t- and g,T,t,C,t-conformations are 3.0 and 5.0 kcal/mol, respectively. Guo and Karplus (1991) have studied the potential energy corresponding to the rotation around the C-C (gauche conformation) bond of butadiene at the Møller Plesant (MP3/6-31G*) level, they found this conformation is 2.6 kcal/mol higher than the most stable s-trans conformation, in an excellent agreement with the experimental value of 2.7 kcal/mol (Durig et al., 1975). Several calculations have been reported comparing a variety of computational methods (Karpfen and Parasuk, 2004; Fabiano and Della Sala, 2006), calculated rotational barriers ranging from 2.5 to 4.0 kcal/mol with the most accurate calculations providing a reasonable estimate within (0.5 kcal/mol of the 3.10 kcal/mol experimental barriers).

The results in k and $\Delta E_{\text{barrier}}$ from Table 4 were subjected to a regression analysis and the output results of the regression analysis are summarized in Table 5. As noted in this table, the best correlation with $\ln k$ was for the temperature 300 K plotted in Fig. 4.

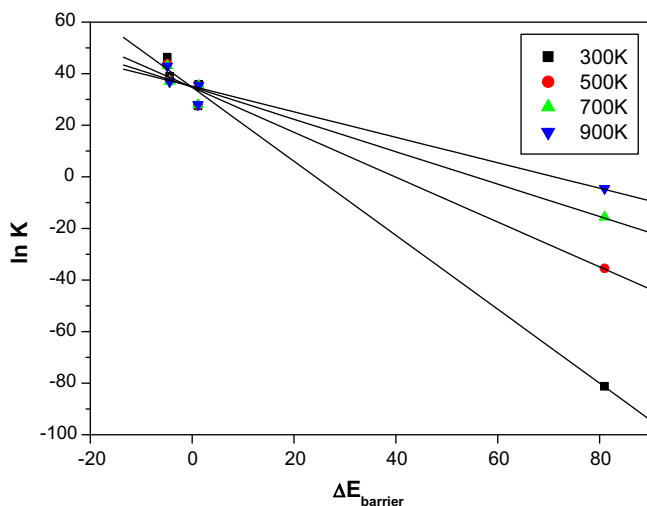


Figure 4 Fits of the rate constants obtained for the cis to trans isomerization as a function of temperature.

3.3. Temperature effects on the rate constant of PAs

As shown in Fig. 5, substitution of different halogens (F, Cl, Br and I) at different temperatures ranging from 300 to 1000 K leads essentially to very small variations of the rate constant, except for iodine atoms where the replacement changed considerably both $\ln k$ and the activation energy. For all-trans-octatetraene, the s-cis, s-trans isomerization of the terminal methylene group was studied in temperature dependent irradiation experiments with octatetraene in n-octane matrices (Fuss et al., 1996). The barrier in the s-cis to s-trans direction was determined to be 4.01 kcal/mol. For this reaction, the barrier is also expected to be slightly higher than for the second 1,3,5-cis-hexatriene (Z-HT) relaxation step as a result of the reduced sterical hindrance in E-substituted polyenes in comparison to 1,3,5-cis-hexatriene (Z-HT).

Debora et al. (1999) reported that after a few picoseconds concentrations of the conformers follow the development of the thermal equilibrium as determined by the solvent

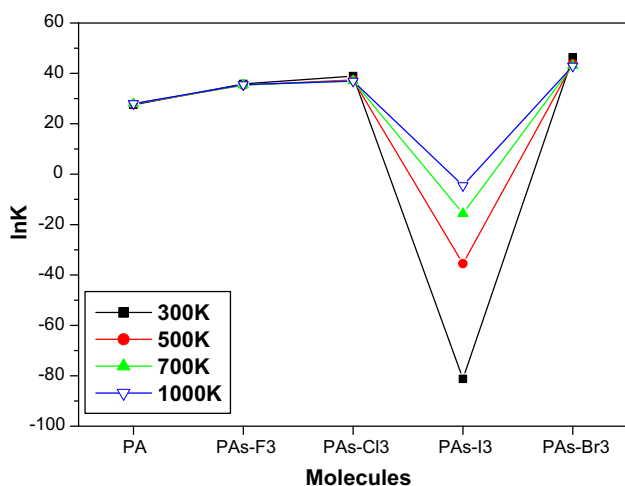


Figure 5 Temperature effects on the rate constant of substituted polyacetylene.

temperature. The fact that this substantial amount of trans-Z-trans-hexatriene (tZt) was not observed by Lawless et al. (1995), Reid et al. (1993) within 3 ns which again indicates some problems with the separation of conformational and thermal effects in the resonance Raman spectra. It is necessary to carry out further experimental as well as theoretical investigations on the kinetics of the relaxation step trans-Z-cis-hexatriene (tZc) in order to obtain a more detailed understanding of the ground-state dynamics of 1,3,5-cis-hexatriene (Z-HT).

4. Conclusion

The kinetics of the *cis*→*trans* isomerization of substituted polyacetylene in the vapor phase was studied by the new semi empirical RM1 as a function of temperature. The results suggest that the straightforward kinetics characterizing the majority of substituted polyacetylene isomerizations above 300 K also apply to unsubstituted polyacetylene as a reference. At these temperatures the isomerization proceeds with frequency factors of $1.725 \times 10^{12} \text{ s}^{-1}$ and $E_a = 0.40 \text{ kcal mol}^{-1}$. However, the value of the activation energy is very structure dependent, as shown by the excellent correlation between the activation energy and the rate constant of the substituted polyacetylene.

Theoretical calculation on target substrates in the gas was also performed based on RM1 method. Overall, the *cis*-to-*trans* isomerization energy barriers are found to be influenced by the size and electronic character of substituted halogens.

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