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An ab initio study of structural stability of poly(phenylacetylene) dimers and trimers

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Abstract

The energies of various stable isomers of poly(phenylacetylene) dimers and trimers were optimized by ab initio methods. The calculations were performed by using the 3-21G and 6-31G* basis sets. The stability of the dimers was predicted to increase in the order: dimer 2 > dimer 3 > dimer 1. From the calculated energies, dimer 2 (trans) is predicted to be about 2 kcal mol^{-1} lower in energy than dimer 3 (cis). The cis–trans (structures 1 and 3), and trans–trans (structures 5 and 6) trimers, were predicted to have the most stable isomers. Only trimer 3 can be formed from dimer 2. Thus, the polymer formation is most likely to occur based on this trimer with a tail–head–tail–head addition. © 1997 Elsevier Science B.V.

1. Introduction

The structure of conducting polymers has attracted considerable attention as a new emerging class of electronic materials [1,2]. The polymerization of acetylenic hydrocarbons, in particular, were of great interest to structural and synthetic chemists [3–8]. We were more interested in the mechanism and structural stability of poly(phenylacetylene), in which the stability of the oligomers formed at early stages of polymerization was not known.

In a very recent study the structural stability of different possible dimers and trimers of poly(1-propyne) as a model structure were investigated by employing the 3-21G basis set [8]. The ab initio method was thought to be a very reliable tool to study structural preference of polymers in the initial

polymerization. The predicted relative energies of poly(1-propyne) dimers and trimers suggested that the polymer formation is likely to be with the tail–head–tail–head addition [8].

As a continuation of this work, we are adopting the structure of poly(phenylacetylene) to investigate the reliability of the poly(1-propyne) model to predict the structural stability of the dimers and trimers of such important polymeric systems. The results of this study are presented herein.

1.1. Ab initio calculations

The GAUSSIAN 94 program was used to carry out the LCAO-MO-SCF restricted Hartree–Fock calculations [9]. The extended 3-21G and 6-31G* basis sets were employed in order to optimize the structures and predict the energies and dipole moments of both the dimers and trimers of poly(phenylacetylene). For

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poly(phenylacetylene) dimers, three geometrical isomers were determined (Fig. 1).

As for the trimers, the situation is more complex. There are four possible structural isomers, each of which can exist in at least two different geometrical forms (Fig. 2). In constructing the structure of the trimer, one must consider the orientation of both the vinyl groups and the phenyl rings with respect to the molecular plane. In comparison with 1,3-butadiene [10], the two vinyl moieties can be either trans (the CCCC dihedral angle is 180°) or gauche (the CCCC

Fig. 1. Molecular structure of stable isomers of poly(phenylacetylene) dimer.

dihedral angle is about 120°) to each other. The configuration of the phenyl rings depends on whether the molecular skeleton is planar (trans vinyl) or non-planar (gauche vinyl). In the case where the two vinyl moieties are trans to each other with a plane of symmetry, there are two orientations for the phenyl groups, one with the phenyl moieties in the same plane (torsional angle θ is $0°$), and the second in which the phenyl groups are perpendicular to the plane of the molecular chain (torsional angle θ is $90°$) according to symmetry restriction. When the two vinyl moieties are gauche to each other with no plane of symmetry, the torsion angles are between 0 and $90°$.

The isomers with high steric hindrance of the trimers were rolled out. This leads to a total of eighteen isomers, twelve planar ($C_3C_4C_5C_6$ is $180°$) and six non-planar ($C_3C_4C_5C_6$ is about $120°$). The structural parameters of the stable isomers of both the dimers and trimers of poly(phenylacetylene) were optimized by minimizing the energy with respect to most of the structural parameters. For a good approximation, only CCC and HCC bond angles of the phenyl groups were kept constant at $120°$.

The geometrical stability was determined by comparing the calculated energies of all the isomers. The relative energies were calculated with respect to the lowest energy isomer and summarized in Table 1 and Table 2. It was noticed that the torsion and CCCC angles remained unchanged at the end of the optimization of the planar trimers.

The calculated structural parameters of dimers 2 and 3 and trimers 3 are listed in Table 3 and Table 4 respectively. The C–H and C–C bond distances of the phenyl groups were optimized to be 1.071 and 1.075 and 1.386 and 1.088 Å at 3-21G and 6-31G* basis sets respectively.

2. Discussion

The polymerization of acetylenic hydrocarbons catalyzed by group VIIB and VIII transition metal complexes involve a coordinated metal acetylide [11–15]. The type of polymerization in such polymers can be determined from the examination of the dimeric and trimeric materials produced in the early stage of the polymerization process. For
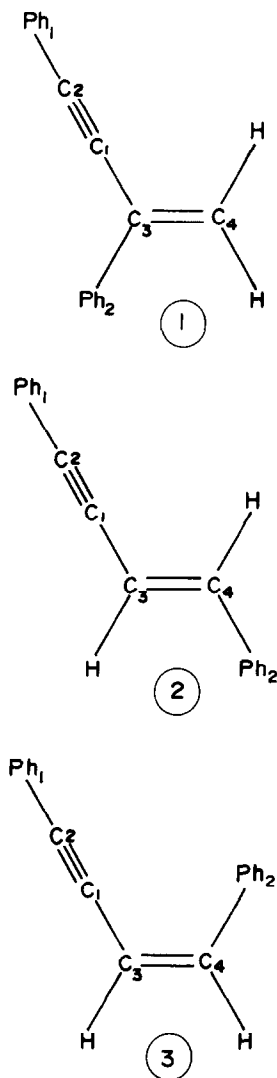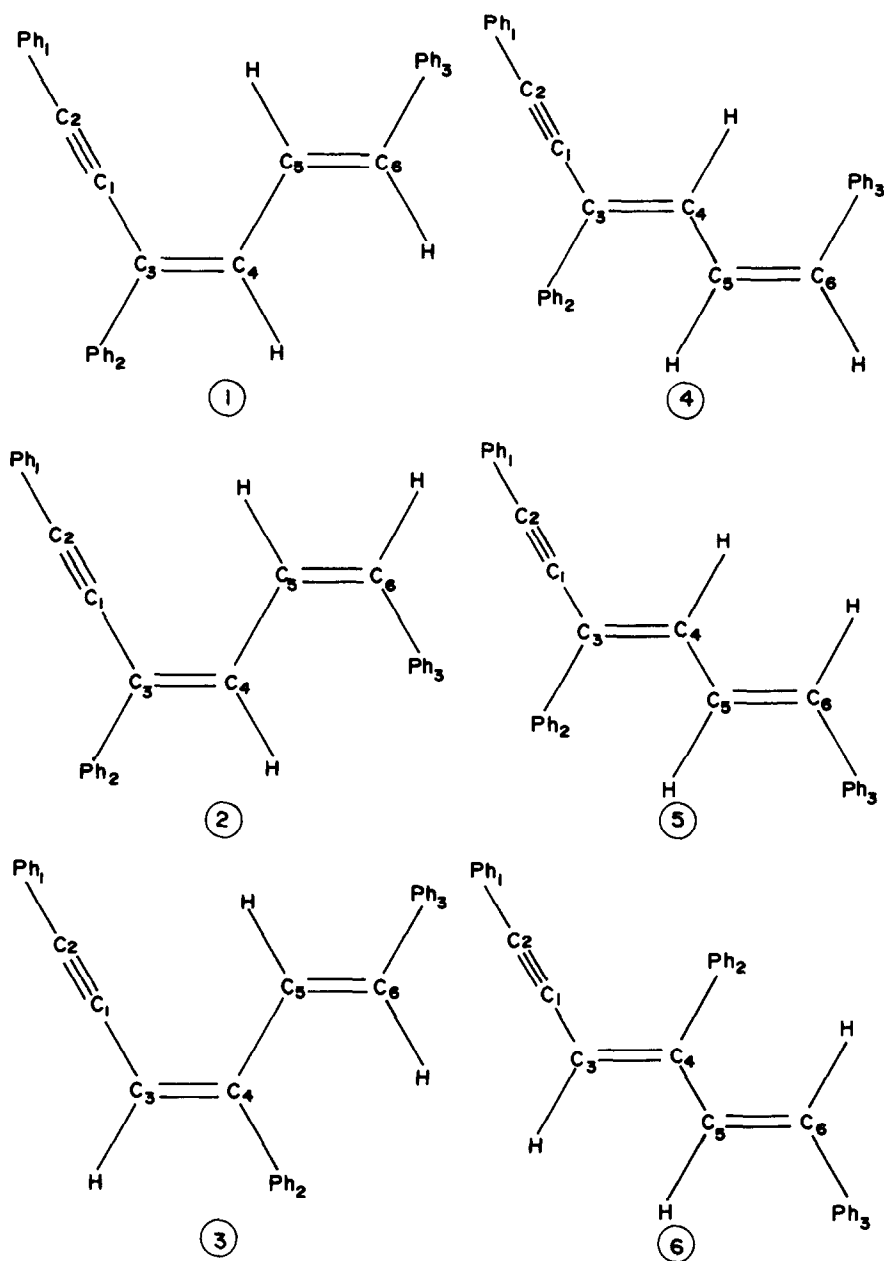
Fig. 2. Molecular structure of stable isomers of poly(phenylacetylene) trimer.

poly(phenylacetylene), the three dimers formed were identified as cis and trans $C_6H_5C \equiv C-CH=CHC_6C_5$ and $C_6H_5C \equiv C-C(C_6C_5H)=CH_2$. Four trimers have been separated, and all were found to be linear. No evidence of cyclic compounds was obtained. The metal acetylide is generated in solution by the reaction of the transition metal with the alkyne molecule. It then interacts with another alkyne molecule and through pi-bonding and ligand insertion reactions produce the poly(alkyne). The termination of the chain group may occur either by coupling of the metal–hydrogen and metal–alkenyl fragments (Scheme 1),

Table 1

Relative energies (kcal mol^{-1}) of the stable isomers of poly(phenylacetylene) dimers, calculated by 3-21G and 6-31G* basis sets

Geometrical isomers[a]	Geometry[a]	(θ_1, θ_2)[b]	Relative energy[c]		Polymerization
			HF/3-21G	HF/6-31G*	
2_1	trans	(0,0)	0.00	0.00	tail–head
2_2		(90,90)	2.37	3.30	
3_1	cis	(0,0)	2.01	2.13	tail–head
3_2		(90,90)	3.87	4.19	
1_1	—	(0,0)	3.92	3.81	head–tail
1_2		(90,90)	3.96	4.89	

[a] See Fig. 1. The trans and cis notation describe the geometry of the phenyl rings with respect to each other.

[b] θ_1 and θ_2 are the optimized dihedral angles of the two phenyl groups with respect to the plane of the molecule (θ is 0° for the planar form and 90° for the perpendicular form).

[c] Total energies of dimer 2_1 (trans) are − 609.40543 and − 612.82188 hartree, calculatd by 3-21G and 6-31G* basis sets respectively.

or by coupling of the alkynyl and acetylide ligands in the growing chain (Scheme 2).

According to Scheme 1, the hydrogen in the termination step would transfer from the metal hydride (M–H) to the growing polymer chain producing dimer 1. In Scheme 2, the interaction between the metal–acetylide catalyst and the metal would result in the formation of dimers 2 and 3. As shown in Table 1, the structural stability of the three dimers increases in the order: dimer 2 > dimer 3 > dimer 1. The relative thermodynamic stability of dimer 2 (trans) and dimer 3 (cis) is consistent with the metal–acetylide mechanism (Scheme 2) for the polymerization of poly(phenylacetylene). The calculated

Table 2

Relative energies (kcal mol^{-1}) of the stable isomers of poly(phenylacetylene) trimers, calculated by 3-21G and 6-31G* basis sets

Geometrical isomers[a]	Geometry[a]	Relative energy[c]				Polymerization[d]
		$(\phi, \theta_1, \theta_2, \theta_3)$[b]	3-21G	$(\phi, \theta_1, \theta_2, \theta_3)$[b]	6-31G*	
1_1	cis–trans	(180,0,0,0)	2.30		2.03	H–T–T–H
1_2		(180,90,90,90)	4.32		5.78	
1_3		(178, − 22, − 45, − 25)	0.0	(178, − 21, − 40, − 23)	0.00	
2_1	cis–cis	(180,0,0,90)	4.31		5.44	H–T–T–H
2_2		(180,90,90,90)	4.43		6.34	
2_3		(179,17,44, − 62)	2.40	(178,17,40, − 56)	3.18	
3_1	cis–trans	(180,0,90,0)	0.44		2.10	T–H–T–H
3_2		(180,90,90,90)	3.34		5.61	
3_3		(177, − 14, − 74, − 27)	0.14	(176, − 13, − 67, − 26)	1.60	
4_1	trans–cis	(180,0,90,90)	3.58		5.93	H–T–T–H
4_2		(180,90,90,90)	4.55		6.73	
4_3		(178, − 5, − 78, − 60)	3.21	(177, − 8, − 63, − 54)	4.90	
5_1	trans–trans	(180,0,90,0)	1.00		2.14	H–T–T–H
5_2		(180,90,90,90)	4.40		6.09	
5_3		(178, − 5, − 72, − 22)	0.84	(178, − 7, − 61, − 21)	1.90	
6_1	trans–trans	(180,0,90,0)	1.14		2.23	T–H–T–H
6_2		(180,90,90,90)	4.48		6.02	
6_3		(177, − 15, − 73, − 28)	0.77	(176, − 12, − 66, − 25)	1.80	

[a] See Fig. 1. The trans and cis notation describe the geometry of the phenyl rings with respect to each other.

[b] ϕ, θ_1, θ_2, and θ_3 are the optimized dihedral angles of the vinyl and the three phenyl groups with respect to the plane of the molecule respectively (θ is 0° for the planar form and 90° for the perpendicular form).

[c] Total energies of the non-planar trimer 3_3 are − 914.13297 and − 919.25761 hartree, calculated by 3-21G and 6-31G* basis sets respectively.

[d] Abbreviations used: H = head, and T = tail.

Table 3
Structural parameters and total dipole moment of poly(phenylacetylene) in the trans (structure 2) and cis (structure 3) dimers, calculated by 3-21G and 6-31G* basis sets

Parameter	Dimer 2				Dimer 3			
	HF/3-21G		HF/6-31G*		HF/3-21G		HF/6-31G*	
	(0,0)	(90,90)	(0,0)	(90,90)	(0,0)	(90,90)	(0,0)	(90,90)
Bond lengths (Å)								
$C_1 \equiv C_2$	1.193	1.192	1.192	1.191	1.194	1.192	1.193	1.191
C_1-C_3	1.426	1.432	1.433	1.439	1.424	1.431	1.433	1.439
$C_3=C_4$	1.328	1.322	1.330	1.324	1.331	1.322	1.333	1.325
C_5-C_2	1.433	1.436	1.442	1.444	1.434	1.436	1.442	1.444
C_6-C_4	1.479	1.493	1.479	1.494	1.477	1.491	1.479	1.493
C_3-H	1.073	1.075	1.075	1.077	1.075	1.075	1.076	1.077
C_4-H	1.075	1.075	1.077	1.078	1.076	1.075	1.078	1.078
Bond angles (deg)								
$C_1C_2C_5$	179.9	179.9	179.8	179.9	179.9	180.0	180.0	179.5
$C_3C_1C_2$	179.4	179.4	178.7	178.8	175.7	178.3	175.2	177.7
$C_4C_3C_1$	122.8	123.7	122.8	123.6	129.8	124.7	130.4	125.3
$C_6C_4C_3$	127.5	122.7	128.0	123.7	132.3	124.7	133.1	125.8
HC_3C_4	121.8	120.0	121.8	120.0	116.9	119.6	116.3	119.0
HC_4C_3	117.7	120.1	117.1	119.1	114.7	118.7	113.9	117.5
Dipole moment (D)	0.40	0.18	0.42	0.18	0.49	0.37	0.52	0.42

relative energies of the trimers by both basis sets, show that the cis–trans (structures 1 and 3) and trans–trans (structures 5 and 6) are thermodynamically the preferred geometrical isomers. The cis–trans (structure 3) trimer can only be formed from dimer 2 (trans), while the trans–trans (structure 6) trimer can be formed from dimer 3 (cis). The cis–trans (structure 1) and the trans–trans (structure 5) trimers can be formed from dimer 1. From the calculation, dimer 1 is predicted to have the lowest structural preference of the three dimers (Table 1). Accordingly, the mechanism with the termination step that involves a hydrogen transfer from M–H to the oligomeric growing chain is unlikely to take place. On the other hand, dimer 2 (trans) is predicted to be about 2 kcal mol^{-1} lower in energy than dimer 3 (cis). Therefore, the polymer formation of poly(phenylacetyle) can be assumed to occur mainly based on the cis–trans (structure 3) trimer with a tail–head–tail–head addition.

Furthermore, the cis–cis (structure 2), and trans–cis (structure 4) trimers, which cannot be formed from the trans and cis dimers were predicted to be thermodynamically less favorable than the cis–trans

(structure 3) trimer. This behavior again supports the proposed metal–acetylide mechanism.

For poly(phenylacetylene), both the conjugation and steric forces play an important role in controlling the strutural stability of the polymer. The conjugation forces tend to keep the phenyl groups in the same plane of the polymeric chain, while the steric torsional forces tend to keep the phenyl moieties out of the molecular frame. A comparison between the energies of the three dimers, particularly those calculated by 6-31G* basis set, shows that the planar isomers are relatively more favorable than the perpendicular ones. This indicates that the conjugation forces play a more important role than steric forces. This is not quite the case in the trimers, where the distances between the hydrogens of some of the phenyl and vinyl groups are calculated to be of about 0.4 Å. These close encounters highly destabilize the planar forms of the trimers as shown in Table 4.

As shown in Tables 3 and 4, the two forces affect several of the skeletal parameters. The C_5-C_2 and C_6-C_4 bond distances in the dimers and C_5-C_4, C_7-C_2 and C_8-C_4 bond distances in the trimers are calculated to be shorter in the planar than in the

Table 4
Structural parameters and total dipole moment (D) of poly(phenylacetylene) in trimer 3, calculated by 3-21G and 6-31G* basis set

Parameter	Trimer 3 (planar)				Trimer 3 (non-planar)	
	HF/3-21G		HF/6-31G*		HF/3-21G (−14,−74,−26)	HF/6-31G* (−13,−67,−26)
	(0,90,0)	(90,90,90)	(0,90,0)	(90,90,90)		
Bond lengths (A°)						
$C_1 \equiv C_2$	1.194	1.193	1.193	1.192	1.194	1.193
C_1-C_3	1.425	1.429	1.434	1.437	1.425	1.433
$C_3 \equiv C_4$	1.335	1.332	1.337	1.335	1.335	1.338
C_5-C_4	1.467	1.472	1.470	1.475	1.468	1.471
$C_5 \equiv C_6$	1.327	1.322	1.330	1.326	1.327	1.330
C_7-C_2	1.433	1.436	1.442	1.444	1.433	1.442
C_8-C_4	1.499	1.499	1.502	1.501	1.498	1.499
C_9-C_6	1.479	1.493	1.481	1.495	1.480	1.482
C_3-H	1.073	1.074	1.076	1.076	1.072	1.075
C_5-H	1.071	1.073	1.073	1.076	1.072	1.074
C_6-H	1.074	1.075	1.076	1.077	1.074	1.076
Bond angles (deg)						
$C_1C_2C_7$	179.5	179.8	179.7	180.0	178.7	177.8
$C_3C_1C_2$	178.4	178.6	177.7	178.0	179.8	180.0
$C_4C_3C_1$	125.2	125.0	125.8	125.6	125.0	125.8
$C_5C_4C_3$	122.7	122.8	122.0	122.0	122.4	121.5
$C_6C_5C_4$	123.9	124.5	124.6	125.2	124.6	125.6
$C_8C_4C_3$	118.6	118.9	118.6	118.9	118.7	118.5
$C_9C_6C_5$	127.4	122.6	127.8	123.5	125.5	125.5
HC_3C_4	119.1	119.2	118.9	118.9	119.1	118.9
HC_5C_4	114.7	115.7	114.6	115.6	115.0	115.0
HC_6C_5	118.1	120.6	117.9	120.0	119.1	119.1
$C_3C_4C_5C_6$	180.0	180.0	180.0	180.0	177.0	176.0
Dipole moment	0.59	0.39	0.57	0.37	0.56	0.52

perpendicular chains. This could be attributed to the stronger conjugation in the case of the planar forms. The calculation was performed at 6-31G* level to account for the effect of conjugation forces on structural parameters by including the polarization functions. As a result, better carbon–carbon bond distances were obtained by the 6-31G* basis set. Similarly, a slight improvement is noticed in calculated C–H bond lengths of the phenyl rings by the higher basis set.
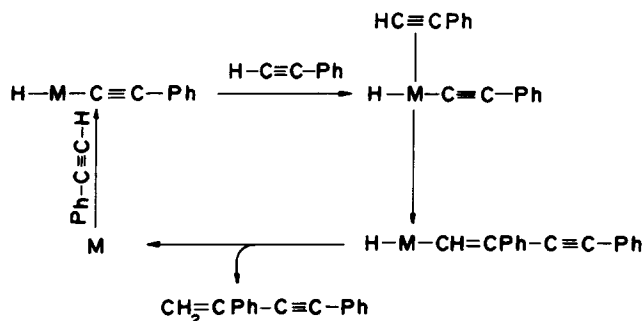
Scheme 1. The mechanism of the formation of dimer 1.
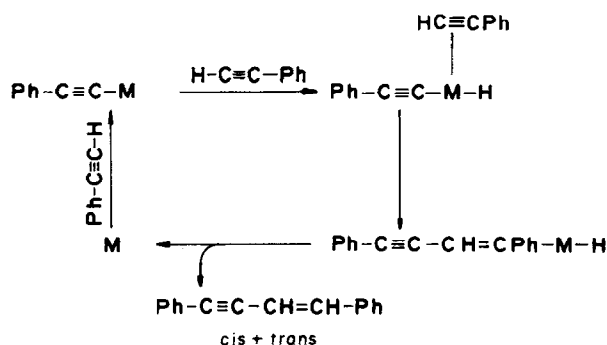
Scheme 2. The mechanism of the formation of dimers 2 (trans) and 3 (cis).

Several of the structural parameters seem to be influenced more by the steric forces. For example, a decrease of about 5° in the $C_6C_4C_3$ bond angle of the dimers was calculated as going from the planar to the perpendicular forms. A similar change was noticed in the $C_9C_6C_5$ bond angle in the planar trimers. This indicates that both forces have a competitive effect on the structural stability of the polymeric chain in poly(phenylacetylene).

From Tables 3 and 4, the dipole moments were calculated to be quite small. For a good approximation one can assume that the effect of solvent–solute interactions in the structural stability of the molecular system is negligibly small. However, the calculated energy differences between the most stable species in early polymerization of poly(phenylacetylene) were quite small. This would result in a complex polymerization at high temperatures.

Acknowledgements

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