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Physics



Theoretical Study of Polymers Molecules Formed from A Series of P-Tert-Butyl Anisole Radical Cation

KEYWORDS	study habits, academic achievement, higher secondary school students				
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ABSTRACT In this wo stereosele	rk, we studied theoretically in the solvectivity of the reaction between the m	vent (acetonitrile) and without solvent, the possibility and the olecule p-tert-butyl anisole 1 and 2,2 '-dimethoxy -5,5 '-di-			

stereoselectivity of the reaction between the molecule p-tert-butyl anisole 1 and 2,2 '-dimethoxy -5,5 '-ditert-butylbiphenyl radical cation 2+. to form trimers molecules. Based on the different calculation methods such as ab-initio and DFT/B3LYP with the standard basis set 6-31G, we have given answers to scientists in experimental workshops concerning the possibility and the stereoselectivity of a new molecules such as tetramers and pentamers, respectively, obtained from the addition of four and five molecules of p-tert-butyl anisole radical cation 1+..

I/ Introduction

An experimental study was conducted on the electrochemical oxidation of p-tert-butylanisole <u>1</u> in acetonitrile [1, 2]. This study showed that a molecule is oxidized at the anode to form the radical cation <u>1</u>[±]. Thereafter the molecule <u>1</u> reacts with a p-tert-butylanisole radical cation <u>1</u>[±] to form the dimer <u>2</u> (Fig. 1). This dimer <u>2</u> oxidizes again at the anode to give the radical cation <u>2</u>[±]. Then, the authors showed that the formation of four different trimers structures <u>3</u>, <u>3b</u> and <u>3c</u>. The trimer <u>3a</u> was obtained either by addition of the monomer radical cation <u>1</u>[±] to the dimer radical cation <u>2</u>[±] or by the addition of a neutral monomer <u>1</u> to the dimer radical cation <u>2</u>[±]. Trimers <u>3b</u> and <u>3c</u> were obtained by addition of three molecules of monomer 1 (Fig. 2).





Fig 1



is only the trimer $\underline{3}$ is as crystal. Subsequently, the authors [2] show the existence of a tetramer $\underline{4a}$ obtained either by addition of the monomer radical cation $\underline{1^{\pm}}$ to the trimer radical cation $\underline{3^{\pm}}$ or by the addition of monomer <u>1</u> to the trimer radical cation $\underline{3^{\pm}}$ (Fig. 3). But the structure of a second tetramer $\underline{4a}$ was not proven experimentally until now. As S Hentati Besbes and al [2] were not sure tetramers while they proposed a single structure for the tetramer is the tetramer $\underline{4a}$ [2].

The study of the trimer structure by X-ray shows that there



We found interesting to make a theoretical study on these reactions and to give answers to scientists in experimental workshops. Based on the different calculation methods abinitio and DFT/B3LYP with the standard basis set 6-31G, we were able to propose a suitable structure of the tetramer. In order to give answers to the experienced before starting the experimental part, we optimized the geometry of trimer <u>3</u>. We then compared our theoretical results with experimental results for X Ray data [3,4]. In the second part of this work, we discussed the possibility of pentamers type <u>5a</u> and <u>5b</u> obtained from the addition of the monomer radical cation 1^{\pm} to the tetramer radical that we propose in our theoretical study. Using the more reliable calculation method for these molecules type in the first part of this study, we discussed from thermodynamic point of view the possibility and the

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stereoselectivity of these reactions (Fig. 5, Fig 6 and Fig 7).

II/ Calculation methods

This study was carried out using the Gaussian 03 program [5]. The calculations were performed at SCF/6-31G and DFT level with the standard basis set 6-31G. We used the B3LYP functional in which the exchange energy is calculated by Becke's three parameters method and the correlation method of Lee, Yang and Parr [6-8]. The choice of the last method is justified by its efficiency in the treatment of this systems type [9]. The geometry of various critical points on the potential energy surface was fully optimized with the gradient method available in GAUSSIAN 03. All structures are depicted with ORTEP program [10]. Calculations of harmonic vibrational frequencies were performed to determine the nature of each critical point.

III/ Results and discussion III.1/ Theoretical study of the trimer <u>3</u>

We determined by X Ray data, the structure of the trimer $\underline{3}$ (table 1). This structure allowed us to confirm the existence of the trimer $\underline{3}$. In order to determine the reliability of calculation methods, we optimized the geometry of compound $\underline{3}$ (Fig. 4) by the two methods SCF/6-31G and DFT/B3LYP with the standard basis set 6-31G. Putting in mind the stereochemistry of this molecule, we compared our theoretical results with experimental X ray data. Table 1 compiles some geometric parameters of the optimized molecule and the X Ray data. Fig 4 shows the stereochemistry of the molecule $\underline{3}$ optimized at the DFT level.



Fig 4: DFT/B3LYP optimized geometries of the trimer 3.

Table 1: Selected	optimized	geometrical	parameters	for
the trimer <u>3</u> .		-	•	

rameter	SCF/6-31G	B3LYP/6- 31G	X-ray data
O1C1	1.457	1.371	1.373
O1C19	1.562	1.407	1.401
O2C8	1.359	1.387	1.379
O2C20	1.429	1.399	1.408
O3C14	1.374	1.396	1.365
O3C21	1.42	1.431	1.418
C1C2	1.382	1.378	1.394
C1C6	1.392	1.392	1.38
C2C3	1.401	1.379	1.39
C2C7	1.552	1.51	1.508
C3C4	1.459	1.415	1.426
C3C13	1.49	1.564	1.506
C4C5	1.412	1.386	1.39
C4C22	1.574	1.531	1.526
C5C6	1.412	1.369	1.377
C7C8	1.454	1.391	1.384
C7C12	1.391	1.374	1.387

C8C9	1.394	1.361	1.359
C9C10	1.453	1.397	1.4
C10C11	1.352	1.367	1.378
C11C12	1 / 16	1 389	1 396
C11C26	1 576	1.507	1.576
C12C14	1.370	1.32	1.310
	1.431	1.39	1.371
C13C18	1.405	1.393	1.395
<u>C14C15</u>	1.477	1.389	1.387
C15C16	1.391	1.375	1.37
C16C17	1.434	1.391	1.394
C17C18	1.407	1.389	1.388
C17C30	1.537	1.511	1.507
C22C23	1 621	1 531	1 522
C22C2A	1.5/7	1.53/	1.522
C22C24	1 5547	1 5 2 7	1.550
624627	1.334	1.337	1.331
	1.497	1.4/5	1.400
C26C28	1.452	1.457	1.459
C26C29	1.439	1.491	1.485
C30C31	1.509	1.489	1.485
C30C32	1.497	1.439	1.44
C30C33	1.513	1.534	1.52
C101C19	116.8	117.5	117.7
C8O2C20	120.5	119.2	119.1
C14O3C21	119 5	118 5	118.6
010102	117.7	115 7	115 0
010102	124 /	124.4	124 5
	1120.0	124.4	124.5
	117.8	117./	117./
<u>C1C2C3</u>	127.6	120.3	120.4
C1C2C7	117.9	117.4	117.7
C3C2C7	124.6	120.8	121.9
C2C3C4	123.7	121.9	120.9
C2C3C13	116.3	118.3	116.1
C4C3C13	121.4	131.6	123
C3CAC5	1163	118.3	115 5
<u>C3C4C3</u>	127.9	120.0	126.7
	127.0	1120.0	120.7
	117.1	110.0	11/./
<u>C4C5C6</u>	129.2	119.3	124.1
C1C6C5	118.2	120.2	119.1
C2C7C8	131.7	121.7	122.6
C2C7C12	121.7	120.7	119.6
C8C7C12	119.6	119.7	117.8
O2C8C7	116.7	116.7	114.6
O2C8C9	127.7	126.3	124.8
C7C8C9	121.4	125.5	120.6
C8C9C10	120.3	120.2	120.2
C9C10C11	13/18	127.6	120.2
C10C11C12	114.0	115.0	115.0
C10C11C12	10.0	101.0	113.7
	123.7	121.0	122.0
<u>C12C11C26</u>	122.4	122.1	121.3
	121.6	121./	123./
<u>C3C13C14</u>	125.4	122.3	121.1
C3C13C18	122.1	121.1	120.2
C14C13C18	119.7	119.4	118.6
O3C14C13	116.1	118.1	117.4
O3C14C15	120.9	121.5	123.1
C13C14C15	117.3	119.3	119.4
C14C15C16	119.1	122.6	120.5
C15C16C17	121 2	121 1	122
	121.2	141.1	166
01010202	170 0	170 1	170
	1/0.2	1/0.1	1/7
	-2.5	-2./	-2./
01010605	1/6.4	169.2	1/8.1
02C8C7C2	-1.4	-1.9	-1.8
O2C8C7C12	177.4	191.3	175.5
O2C8C9C10	-172.3	-161.2	-175.3
C1C2C3C4	4.2	4.3	4.4
C1C2C3C13	-159.3	-181.2	-176.1
C1C2C7C8	113 5	102.5	104.6
C1C2C7C12	-71 5	-71 6	-72 7
C1C6C5C4	1.5	1 5	17
	1.0	1.0	1./
	107./	108.9	1/1.8
122010605	-3.2	-3.4	-3.3
C2C3C4C5	-5.5	-5.6	-5./
<u>C2C3C4C22</u>	171.6	162.7	173.8

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C2C3C13C18	-74.7	-76.8	-75.9
C2C7C8C9	177.1	172.3	178.2
C2C7C12C11	169.6	179.6	178.7
C3C2C1C6	0.2	0.3	0.3
C3C2C7C8	-73.1	-76.2	-77.3
C3C2C7C12	102.7	104.1	105.5
C3C4C5C6	2.8	2.7	2.7
C3C4C22C23	-149.7	-149.7	-156.8
C3C4C22C24	83.4	85.3	84.2
C3C4C22C25	-35.2	-37.3	-37.3
C3C13C14C15	-168.7	-168.7	-174.9
C3C13C18C17	168.4	169.5	176.4
C4C3C2C7	-169.7	-182.7	-173.8
C4C3C13C14	-81.5	-81.1	-80.6
C4C3C13C18	104.5	113.5	103.6
C5C4C3C13	173.4	185.7	174.8
C5C4C22C23	22.6	21 5	22.7
C5C4C22C24	-97.2	-92.3	-96.3
C5C4C22C25	141	143.1	142.2
C6C1O1C19	_9 1	_9 /	-9.5
C6C1C2C7	177 1	167.9	178 5
C6C5CAC22	-169 1	107.7	176.8
C7C2C3C13	5 /	5 5	5 7
C7C8O2C20	176 3	169 7	179.8
C7C8C9C10	170.5	107.7	177.0
C7C12C11C10	1.0	4.4	4.0
C7C12C11C10	1.7	177.2	177.2
$C^{2}C^{2}C^{1}C^{1}C^{1}C^{1}$	1 4	1 2	12
	1.0	1.5	1.5
	-1.3	-1.0	-1.0
C9C8C7C12	-0.2	-0.3	-0.5
	-4.0	-4.4	-4.4
	17/ 2	177 /	177 /
	140.1	177.4	122.4
	-140.1	-132.4	-132.4
	-8.8	-8.7	-8.9
	112.4	111.5	111.5
	44.3	46.4	40.4
	168.3	170.1	170.1
	-67.5	-69./	-69./
	-5.8	-5.6	-5.6
<u>C13C14O3C21</u>	1/9.3	179.1	179.1
<u>C13C14C15C16</u>	-1.5	-1.8	-1.8
<u>C13C18C1/C16</u>	-1.2	-1.1	-1.1
<u>C13C18C17C30</u>	-177.2	-178.6	-178.6
<u>C14C13C18C17</u>	0.4	0.5	0.5
C14C15C16C17	1.1	1.2	1.2
C15C14O3C21	-1.3	-1.4	-1.4
C15C14C13C18	1.1	1	1
C15C16C17C18	0.1	0.2	0.2
C15C16C17C30	179.1	177.8	177.8
C16C17C30C31	167.1	166.6	166.6
C16C17C30C32	-70.1	-71.6	-71.6
C16C17C30C33	49.3	48.5	48.5

Note: Distances are in angstroms (A °) and angles in degrees (°).

The calculation methods B3LYP/6-31G and SCF/6-31G give results which come close to experimental X-Ray of the trimer <u>3</u>. We notice that the DFT/B3LYP method gives results more efficient than those provided by the SCF/6-31G method. Therefore the B3LYP/6-31G calculation method is more reliable with these systems type of molecules [7].

As the calculation method DFT/B3LYP is the most reliable method for this system type, we finished the rest of our calculations with the DFT method using B3LYP functional and standard basis set 6-31G.

III.2/ Thermodynamic study

We conducted a thermodynamic study on the possibility and the stereoselectivity of these reactions (Fig. 5). Using the calculation method DFT/B3LYP with standard basis set 6-31G, we determined under standard conditions of temperature and pressure (298.15 K and 1atm = 100.325 kPa) the values of the different thermodynamic reaction state functions, such as energy $\Delta Er,$ free energy $\Delta Gr,$ enthalpy ΔHr and ZPE (Table 2).

As shown in Table 2, values of free reaction energy Δ Gr corresponding to reactions (II) (III) are positive. But values of free reaction energy Δ Gr corresponding to reaction (I) is negative. This allowed us to say that the formation of dimer <u>2</u> is theoretically possible and thermodynamically favored. But the formation of dimers <u>2a</u> and <u>2b</u> are not possible from the thermodynamic point of view. In the case of the formation trimers molecules, we found a positive value of free reaction energy Δ Gr corresponding to reactions (V), (VII) (VIII) and (IX). But, in the case of reactions (IV) and (VI), we found negative values of free reaction energy Δ Gr. This allowed us to say that the formation of the trimer <u>3</u> is possible and thermodynamic cally favoured. But the trimers <u>3'</u>, <u>3a</u> and <u>3b</u> are not possible from the thermodynamic point of view.

As the experimental study showed that the structure of trimer $\underline{3}$ was formed from the addition of tert-butyl anisole $\underline{1}$ to dimer radical cation $\underline{2^{\pm}}$ [2]. Therefore, our theoretical result confirms the result found experimentally.

We have subsequently discussed from thermodynamic point of view the possibility of the reaction between the tert-butylanisole radical cation 1[±] and trimer radical cation 3[±] to obtain tetramers molecules (Fig 5). As shown in Table 2, we noticed that the values of free reaction energy Δ Gr corresponding to reactions (XIII) (XIV) are positive. But values of free reaction energy Δ Gr corresponding to reactions (XII) and (XII) are negative. Therefore, the formation of tetramers 4a and 4b is possible and thermodynamically favored. But the formation of tetramers 4c and 4d is theoretically not possible. We also noted that the tetramer 4a is thermodynamically more stable than teramer 4b. For this reason the authors of tetramers 4a. But the tetramer 4b was not observed experimentally.

We have also studied from thermodynamic point of view these reactions (Fig. 5 and Fig 6) in the solvent (acetonitrile). As shown in Table 2, we found negative values of free energy reaction Δ Gr corresponding to reactions (I), (IV) (VI), (X) and (XI). This confirms again that the formation of trimer <u>3</u> is possible and thermodynamically favored. We can also confirm the existence of tetramers <u>4a</u> and <u>4b</u>. Moreover we can say that the tetramer <u>4a</u> is more stable thermodynamically than the tetramer <u>4b</u>. For this reason S.Hentati-Besbes et al [2] have determined the structure of tetramer <u>4b</u>.







Fig 6



Fig 7

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Table 2: Thermodynamic	results of	ΔEr,	∆Gr,	ΔHr	and	ZPE
for reactions (I - XIV).						

Reactions	Produits	∆Gr	ΔEr	∆Er + ZPE	ΔHr		
Without solvant (B3LYP/6-31G)							
Reaction I	2	-15,31	-17,59	-17,47	-21,27		
Reaction II	2a	11,86	12,19	12,18	7,35		
Reaction III	2b	12,39	12,83	12,73	7,44		
Reaction IV	3	-8,41	-9,35	-9,36	-13,79		
Reaction V	3'	14,71	8,37	8,47	5,68		
Reaction VI	3	-6,71	-8,26	-8,17	-12,37		
Reaction VII	3'	12,07	12,25	12,17	7,41		
Reaction VIII	3a	15,82	8,91	8,81	6,39		
Reaction IX	3b	16,34	9,65	9,64	7,27		
Reaction X	3c	16,48	15,51	15,62	11,01		
Reaction XI	4a	-14,92	-16,19	-16,18	-19,98		
Reaction XII	4b	-5,93	-7,34	-7,23	-11,74		
Reaction XIII	4c	15,98	9,12	9,11	6,83		
Reaction XIV	4d	12,44	12,97	12,87	7,52		
With solvant	(acetonitr	ile) (B3LY	P/6-31G)			
Reaction I	2	-14,55	-14,45	-18,29	-18,29		
Reaction II	2a	15,07	15,19	15,20	10,47		
Reaction III	2b	15,58	15,95	15,96	10,54		
Reaction IV	3	-5,21	-6,25	-6,26	-10,64		
Reaction V	3'	17,92	11,56	11,67	8,87		
Reaction VI	3	-3,50	-5,07	-5,17	-9,55		
Reaction VII	3'	15,28	15,46	15,37	10,62		
Reaction VIII	3a	19,01	12,12	12,22	9,58		
Reaction IX	3b	19,53	12,86	12,96	10,48		
Reaction X	3c	19,67	18,72	18,73	14,19		
Reaction XI	4a	-11,71	-12,97	-12,98	-16,79		
Reaction XII	4b	-2,74	-4,15	-4,25	-8,53		
Reaction XIII	4c	19,20	12,33	12,43	10,02		
Reaction XIV	4d	15.63	16,18	16.29	10.72		

In order to give answers to the scientists in experimental work shops before starting the experimental part, we studied from thermodynamic point of view the possibility and the stereoselctivity of pentamer molecules formed from the addition of five molecules of tert-butyl anisole radical cation $\underline{1^{\pm}}$ or formed from the addition of one molecule of tert-butyl-anisole radical cation $\underline{1^{\pm}}$ on the tetramer radical cation $\underline{4a^{\pm}}$ (Fig. 7).

As shown in Table 3, we found negative values of free energy reaction Δ Gr corresponding to reactions (XV) (XVI). This allowed us to say that the formation of pentamer type <u>5a</u> and <u>5b</u> is possible and thermodynamically favored. Furthermore, we noticed that the value of free energy reaction Δ Gr corresponding to reaction (XV) is higher in absolute value of free energy reaction which corresponds to the reaction (XVI). This shows that the pentamer <u>5a</u> is thermodynamically more stable than the pentamer <u>5b</u>.

According to the reaction that gives pentamers from the addition of five molecules of tert-butyl anisole radical cation $\underline{1}^{\pm}$. We found a negative value of free energy reaction Δ Gr which corresponds to reaction (XVII). But the free energy reaction Δ Gr which corresponds to reaction (XVIII) is positive. This allowed us to say that the formation of a pentamer type <u>5a</u> is theoretically possible and thermodynamically favored either from the addition of five molecules of tert-butyl anisole radical cation $\underline{1}^{\pm}$ or from the addition of tert-butyl anisole radical cation $\underline{1}^{\pm}$ to the tetramer radical cation $\underline{4a}^{\pm}$. We also determined in the solvent (acetonitrile), the values of free energy reaction Δ Gr for these reactions (XI), (XVI) (XVII) and (XVIII). We found negative values of free reaction energy corresponding to reactions (XV) and (XVIII). This allowed us to

say that the formation of pentamer $\underline{5a}$ is possible and thermodynamically favoured. But the formation of pentamer $\underline{5b}$ is not possible from thermodynamic point of view.

Our theoretical results are very important because they allowed us to give answers to the scientists in experimental workshops before starting the experimental section. Moreover, we can say that from experimental study we can easily obtain the pentamer $\underline{5a}$ by addition of tert-butyl-anisole radical cation $\underline{1^{\pm}}$ to tetramer radical cation $\underline{4a^{\pm}}$.



Fig 7

Table 3: Thermodynamic results of ΔEr , ΔGr , ΔHr and ZPE	
for reactions (XV - XVIII).	

Reactions	Produits	∆Gr	∆Er	∆Er + ZPE	ΔHr		
Without solvant (B3LYP/6-31G)							
Reaction XV	5a	-6,87	-8,32	-8,21	-12,58		
Reaction XVI	5b	-0,51	-2,99	-2,98	-7,23		
Reaction XVII	5a	-4,74	-6,75	-6,85	-10,78		
Reaction XVIII	5b	2,25	1,27	1,37	6,12		
with solvant (l'acétonitrile) (B3LYP/6-31G)							
Reaction XV	5a	-4,46	-5,91	-5,92	-10,16		
Reaction XVI	5b	1,91	-0,58	-0,68	-4,81		
Reaction XVII	5a	-1,62	-3,53	-3,52	-7,56		
Reaction XVIII	5b	5,47	1,95	1,96	8,9		

Conclusion:

In this work, we studied theoretically the possibility and the stereoselectivity of polymers reactions in a solvent (acetonitrile) and without a solvent. Our theoretical results show that the trimer 3 obtained by addition of tert-butyl-anisole radical cation 1^{\pm} to the dimer radical cation 2^{\pm} is thermodynamically favored. But the formation of trimers 3', 3a, 3b and 3c are not possible from thermodynamic point of view. These results also show that the formation of tetramers 4a and 4b is possible and thermodynamically favored. Furthermore, we showed that the tetramer <u>4a</u> is thermodynamically more stable than the tetramer <u>4b</u>. These theoretical results clearly confirm the experimental studies [1,2]. So, we were able to give answers to the scientists in experimental work shops before starting the experimental section, concerning the existence of a pentamer type 5a. Moreover, we can say that the formation of the pentamer 5a is easier by adding tert-butyl anisole radical cation 1^{\pm} to the tetramer radical cation $4a^{\pm}$.

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