



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 work, we studied theoretically in the solvent (acetonitrile) and without solvent, the possibility and the stereoselectivity of the reaction between the molecule *p*-tert-butyl anisole 1 and 2,2'-dimethoxy-5,5'-di-tert-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+.

1/ Introduction

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

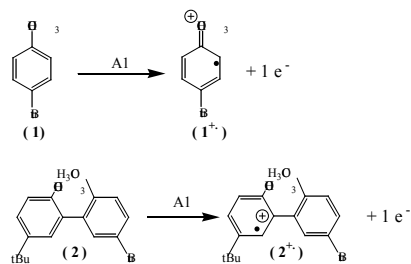


Fig 1

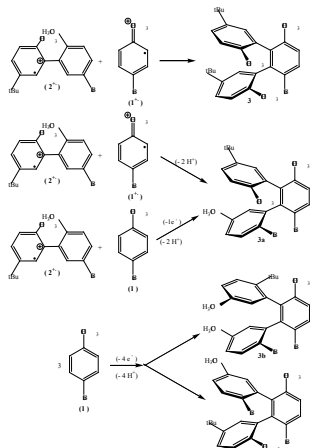


Fig 2

The study of the trimer structure by X-ray shows that there is only the trimer 3 is as crystal. Subsequently, the authors [2] show the existence of a tetramer 4a obtained either by addition of the monomer radical cation 1[±] to the trimer radical cation 3[±] or by the addition of monomer 1 to the trimer radical cation 3[±] (Fig. 3). But the structure of a second tetramer 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 4a [2].

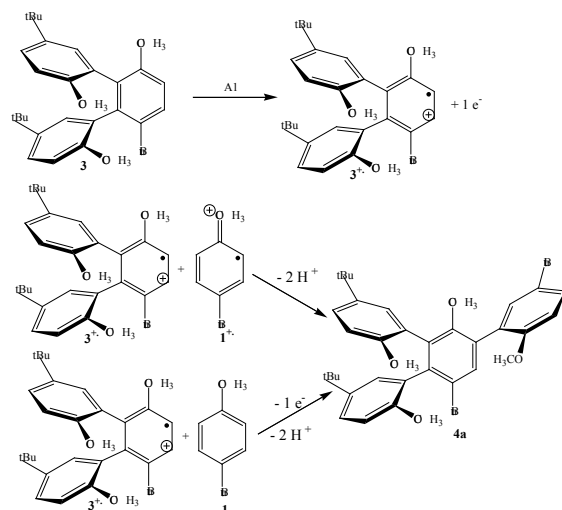


Fig 3

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 *ab-initio* 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 3. 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 5a and 5b obtained from the addition of the monomer radical cation 1[±] 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

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	-9.4	-9.5
C6C1C2C7	177.1	167.9	178.5
C6C5C4C22	-169.1	-176.1	-176.8
C7C2C3C13	5.4	5.5	5.7
C7C8O2C20	176.3	169.7	179.8
C7C8C9C10	4.5	4.4	4.6
C7C12C11C10	1.9	1.6	1.6
C7C12C11C26	-179.9	-177.3	-177.3
C8C7C12C11	1.6	1.3	1.3
C8C9C10C11	-1.3	-1.6	-1.6
C9C8O2C20	-0.2	-0.3	-0.3
C9C8C7C12	-4.8	-4.4	-4.4
C9C10C11C12	-1.5	-1.4	-1.4
C9C10C11C26	176.3	177.4	177.4
C10C11C26C27	-140.1	-132.4	-132.4
C10C11C26C28	-8.8	-8.9	-8.9
C10C11C26C29	112.4	111.5	111.5
C12C11C26C27	44.3	46.4	46.4
C12C11C26C28	168.3	170.1	170.1
C12C11C26C29	-67.5	-69.7	-69.7
C13C3C4C22	-5.8	-5.6	-5.6
C13C14O3C21	179.3	179.1	179.1
C13C14C15C16	-1.5	-1.8	-1.8
C13C18C17C16	-1.2	-1.1	-1.1
C13C18C17C30	-177.2	-178.6	-178.6
C14C13C18C17	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 (Å) 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 **3**. 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 ΔE_r , free energy ΔG_r , enthalpy ΔH_r and ZPE (Table 2).

As shown in Table 2, values of free reaction energy ΔG_r corresponding to reactions (II) (III) are positive. But values of free reaction energy ΔG_r corresponding to reaction (I) is negative. This allowed us to say that the formation of dimer **2** is theoretically possible and thermodynamically favored. But the formation of dimers **2a** and **2b** 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 ΔG_r 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 ΔG_r . This allowed us to say that the formation of the trimer **3** is possible and thermodynamically favoured. But the trimers **3'**, **3a** and **3b** are not possible from the thermodynamic point of view.

As the experimental study showed that the structure of trimer **3** was formed from the addition of tert-butyl anisole **1** to dimer radical cation **2[±]** [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 ΔG_r corresponding to reactions (XIII) (XIV) are positive. But values of free reaction energy ΔG_r corresponding to reactions (XI) 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 tetramer **4b**. For this reason the authors of the experimental study [2] have found only the structure of tetramer **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 ΔG_r corresponding to reactions (I), (IV) (VI), (X) and (XI). This confirms again that the formation of trimer **3** is possible and thermodynamically favored. We can also confirm the existence of tetramers **4a** and **4b**. Moreover we can say that the tetramer **4a** is more stable thermodynamically than the tetramer **4b**. For this reason S.Hentati-Besbes et al [2] have determined the structure of tetramer **4a** and they have not arrived to determine the structure of tetramer **4b**.

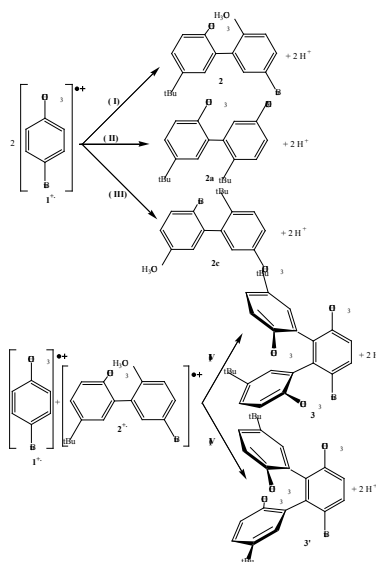
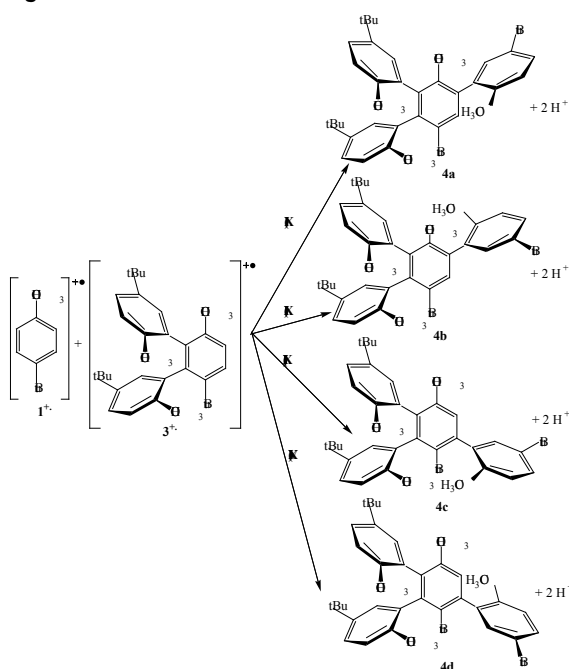


Fig 5

Table 2: Thermodynamic results of ΔE_r , ΔG_r , ΔH_r and ZPE for reactions (I - XIV).

Reactions	Products	ΔG_r	ΔE_r	$\Delta E_r + ZPE$	ΔH_r
Without solvent (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 solvent (acetonitrile) (B3LYP/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

Fig 6**Fig 7**

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 stereoselectivity of pentamer molecules formed from the addition of five molecules of tert-butyl anisole radical cation 1^\pm or formed from the addition of one molecule of tert-butyl-anisole radical cation 1^\pm on the tetramer radical cation $4a^{\pm}$ (Fig. 7).

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

According to the reaction that gives pentamers from the addition of five molecules of tert-butyl anisole radical cation 1^\pm . We found a negative value of free energy reaction ΔG_r which corresponds to reaction (XVII). But the free energy reaction ΔG_r which corresponds to reaction (XVIII) is positive. This allowed us to say that the formation of a pentamer type $5a$ is theoretically possible and thermodynamically favored either from the addition of five molecules of tert-butyl anisole radical cation 1^\pm or from the addition of tert-butyl anisole radical cation 1^\pm to the tetramer radical cation $4a^{\pm}$. We also determined in the solvent (acetonitrile), the values of free energy reaction ΔG_r 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 **5a** is possible and thermodynamically favoured. But the formation of pentamer **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 **5a** by addition of tert-butyl-anisole radical cation **1[±]** to tetramer radical cation **4a[±]**.

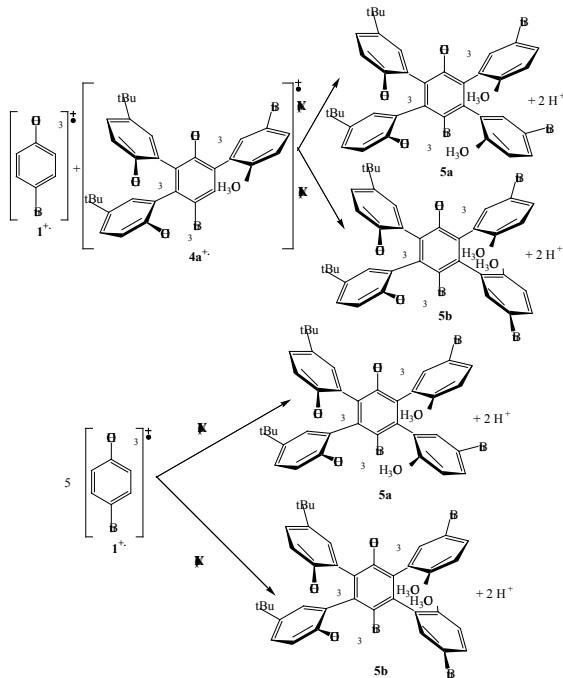


Fig 7

Table 3: Thermodynamic results of ΔE_r , ΔG_r , ΔH_r and ZPE for reactions (XV - XVIII).

Reactions	Products	ΔG_r	ΔE_r	$\Delta E_r + ZPE$	ΔH_r
Without solvent (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 solvent (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[±]** to the dimer radical cation **2[±]** 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 **4a** is thermodynamically more stable than the tetramer **4b**. These theoretical results clearly confirm the experimental studies [1,2]. So, we were able to give answers to the scientists in experimental workshops 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[±]** to the tetramer radical cation **4a[±]**.

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