Int. J. Chem. Sci.: 10(1), 2012, 63-79
ISSN 0972-768X
www.sadgurupublications.com

SIMULATION STUDY OF PHOTOCATALYTIC DECOLORIZATION OF BISMARCK BROWN –R USING DIFFERENT QUANTUM CALCULATION METHODS

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ABSTRACT

Simulation study of photocatalytic decolorization of bismarck brown- R, (4-[5-C 2, 4-diamino-5-methylphenyl) diazenyl-2-methylphenyl] diazenyl-6-methylbenzene-1, 3-diamine dihydrochloride has been carried out using quantum calculation methods (semiemprical and *Ab in tio*). Reactivity of bismarck brown-R molecule has been determined using potential energy stability compares between the mean bonds. Optimizing of probable structures of chemical species have been calculated using PM3 configuration interaction microstate (4 X 4). Thirty six transition states have been postulated and studied in order to estimate the real initiation step of photocatalytic decolorization reaction for different probable path ways.

Results show that hydroxyl radical can react with bismarck brown-R molecule through different active site (C7—N8, C12—N16, N16-N17 and N17—C18 bond) with lowest activation energy than other probable sites. The most probable transition states are investigated for all supposed pathways of photocatalytic decolorization Bismarck brown- R depending on energy barrier value of reaction, zero point energy and imaginary frequency for each one. The first initiation step mechanism of reaction is suggested for the path way at different conditions.

Key words: Simulation study, Quantum calculation methods, Photocatalytic decolorization, Bismarck brown-R.

INTRODUCTION

Azo compounds are common pollutants for the environment, which are coming out by different chemical and physical processes. These compounds cases damage for the live in earth due to the formation of harmful intermediates like potentially carcinogenic aromatic amines transferring into human and animal[1-3].

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The scientific investigation by UV-Vis spectroscopy gives key mechanistic features of the reactive chemistry for azo dyes due the high extinction coefficients that's stay unknown for long time ago. Their reaction products occur during oxidation complicate mechanism without clearless view about rate determining steps and intermediates[4]. A synthetic origin and complex aromatic molecular structures make azo dyes into more stable and more difficult to biodegrade. Azo dyes are classified for several classes and therefore, the reductive cleavage of azo linkages is responsible in formation of toxic amines in the effluent[5].

Decolorization and mineralization of bismarck brown-R (4-[5-C2, 4-diamino-5-methylphenyl) diazenyl-2-methylphenyl] diazenyl-6-methylbenzene-1, 3-diamine dihydro-chloride at various conditions have been studied extensively to estimate the efficiency of degradation reactions with respect to catalysts like ZnO and TiO_2[6,7].

The simulation study of chemical reactions depend on optimized geometries of chemical species and transition states. They are elementary keys to understand the chemical reactivity during the potential energy surface calculations. The first-order saddle point for minima transitions must be taken care to get on the most probable states than others[8,9]. Reaction mechanisms are started by first cleavage step, that's in usual lowest rate determining step than the faster latest steps[10].

In present work, we are interested in study of the mechanism of first cleavage step of bismarck brown-R in the photodecolorization reaction using different conditions and reactant species. Simulation study are taking pleased in several stage of calculations to estimate at last the suggested mechanism for the initiation step of decolorization reaction.

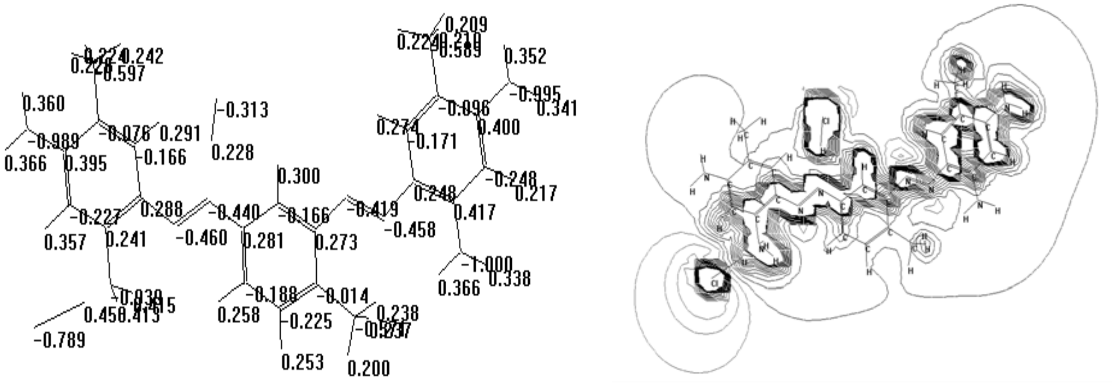
Computational details

Through this study, various theoretical methods according to molecular orbital theory have been used. The geometry structures of bismarck brown-R and their structures with another radical have been optimized at semiempirical configuration interaction (4 X 4) and *Ab in itio* (3-21G) level of theory[11,12]. Bond stability (length & torsion) for main bonds in bismarck brown-R molecule have been examined using PM3 method. The transition state for various reaction path techniques have been studied using quadratic synchronous transit method (**QST**) of HyperChem 7.52, which searches for a maximum along a parabola connecting reactants and products, and for a minimum in all directions perpendicular to the parabola. Vibrational frequencies of the proposed transition state structures have been calculated at UHF/RHF/3-21++G level of theory for characterization of the nature of stationary points and zero point energy (ZPE) calculations to compute the quantum energies of these reactions. All calculations have been carried out using HyperChem 7.52[13].

RESULTS AND DISCUSSION

Optimizing structure of bismarck brown-R

Optimizes real structure of bismarck brown-R are investigated through the results, since total energy equals to -565429.1 kJ.mol^{-1}. The heat of formation calculated by PM3 is equal to 317.599 kJ.mol^{-1}. Chemical properties of bismarck brown-R calculated at 3-21G level of theory is shown in Fig. 1. Estimation of the probable active site for the photoreaction achieved according to the orientation of atomic charge and electrostatic potential of bismarck brown-R molecule.



A- Charge of atoms B- - Electrostatic potential in 2D.

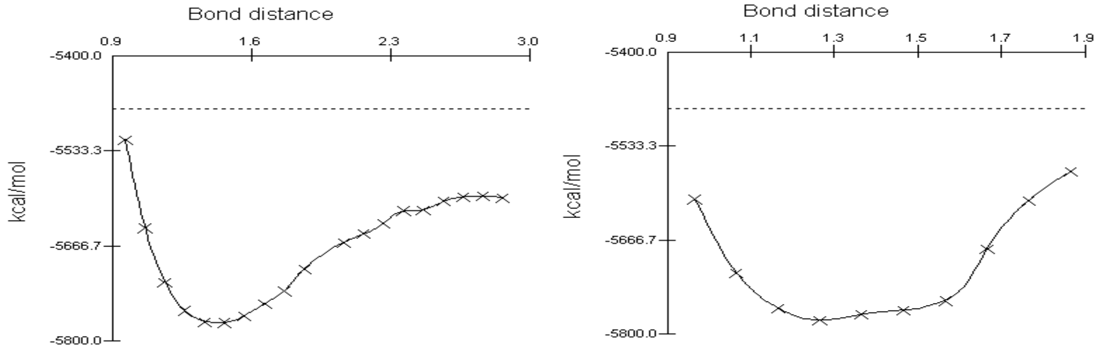
Fig. 1: Geometry optimization of bismarck brown-R calculated at 3-21G level of theory

Chemical reactivity of bismarck brown-R is achieved by comparing the bond stability of real molecular structure. Table 1 show the properties of main bond in bismarck brown-R. The N8—N9 and N16—N17 bonds are more stable than the other bonds, according to calculations of bond length and bond order. This means that low probability for participation in the photoreaction[14]. The bond angles of the N8—N9—C10 and N16—N17—C18 are equal to 114.048^o and 114.652^o, respectively. This bond angle is lower than the angle between the C7—N8—N9 and C12—N17—C18. That means the attack of the hydroxyl radical has lowest probability to the N8—N9—C10 and N16—N17—C18 than the other bonds.

Table 1: The properties of main bonds in bismarck brown-R calculated at 3-21G level of theory

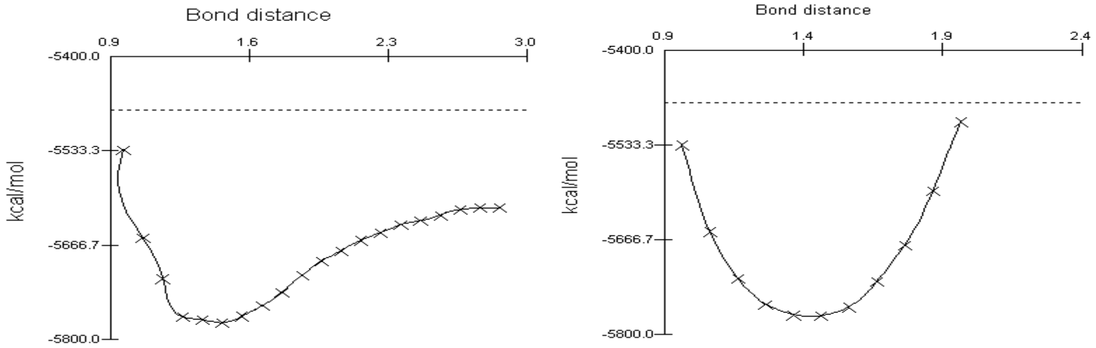
Bond	Bond order	Bond length Å	Bond	Bond angle (°)
C7—N8	1	1.364	C7—N8—N9	117.802
N8—N9	2	1.355	N8—N9—C10	114.048
N9—C10	1	1.381	C12—N16—N17	117.911
C12—N16	1	1.379	N16—N17—C18	114.652
N16—N17	2	1.342		
N17—C18	1	1.375		

This indicates that C7—N8, C12—N16 and N17—C18 bonds are broken at the lowest energy value than the other bond and therefore, these bonds are good sensitive active sites for photoreaction. Fig. 2 show potential energy surface calculations for the main bonds in bismarck brown-R.



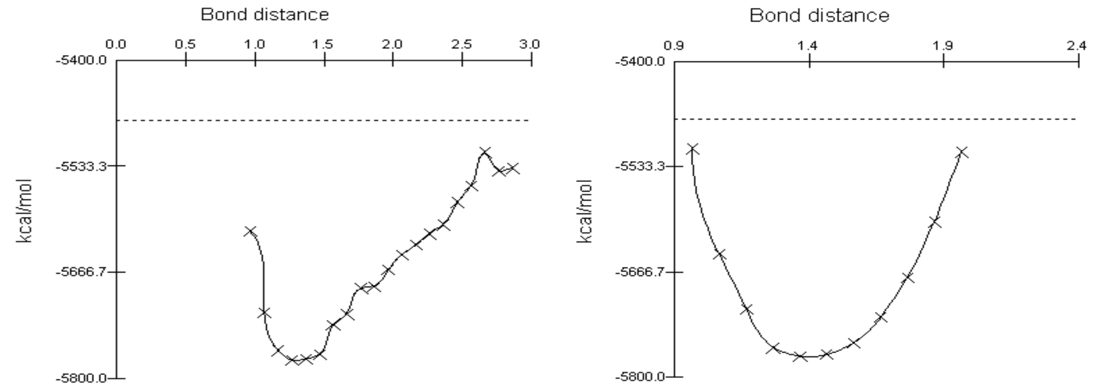
A- C7---N8 bond.

B- N8—N9 bond.

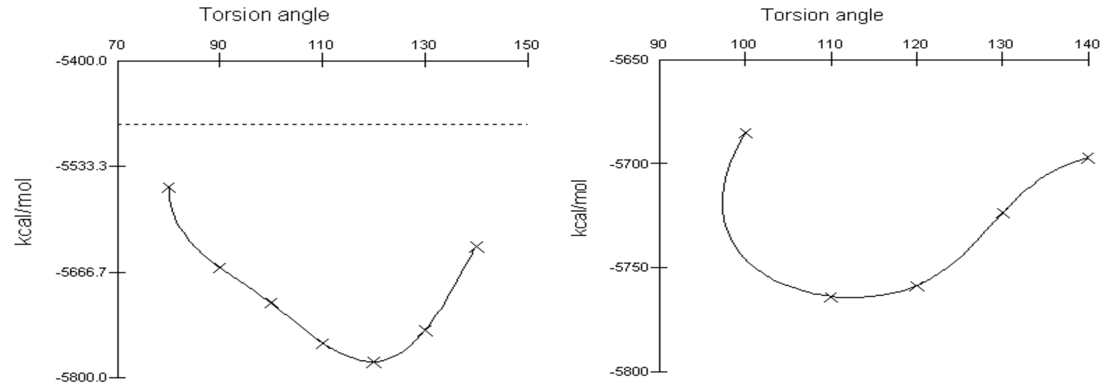


C- N9---C10 bond.

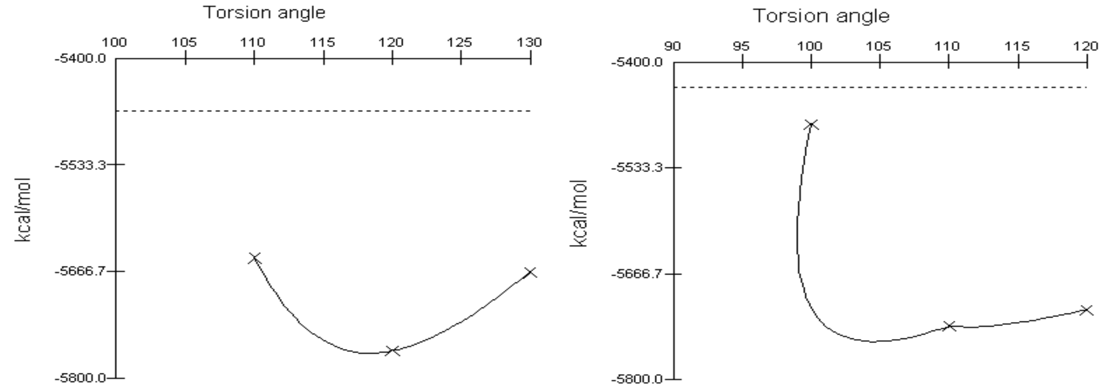
D- C12—C16 bond.



E- N16---N17 bond. F- N17---C18 bond.



I- C7—N8—N9 bond. J- N8—N 9—C10 bond.



H- C12—N16—N17 bond. K- N16—N17—C18 bond.

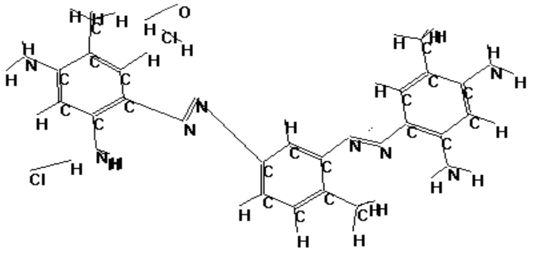
Fig. 2: The potential energy surface calculations of main bond in bismarck brown-R at PM3 CI (4 X 4)

Transition state

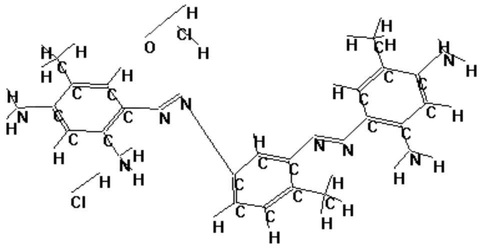
The simulation of photoreaction of bismarck brown-R can occur with several possibilities for transition state formation depending upon the effective side towards the attachment of chemical species and the path way of reaction[15]. Some atoms in bismarck brown-R have affinity to accept the negative charge, that is attacked by most chemical species like $^{\bullet}OH$ or $O_2^{-\bullet}$. The first step to cleavage depends on the transition state with high probability to give products with low energy barrier compared with other probable transition states.

Examination of transition state without catalyst

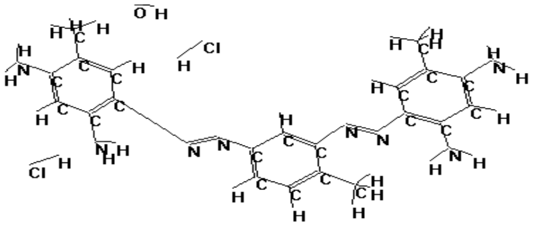
Probable confirmation Fig. 3 show stick view for fourteen transition states of bismarck brown-R. Hydroxyl radical is attached to the bismarck brown-R at active site with hydroxyl radical without catalyst. All the transition state structures have been studied through optimizing their geometry and calculating their vibration spectra. Tables 2 show that the activation energy for the forward reaction is less than the activation energy for the backward reaction. This means the reaction tends to the products for all transition states. The tenth transition state is the most probable state to give up the reaction products than other states due to lowest value of energy barrier of photoreaction (158319.576 kJ mol^{-1}), highest value of zero point energy (1213.653 kJ mol^{-1}) and lowest heat of formation (210.338 kJ mol^{-1})[16].



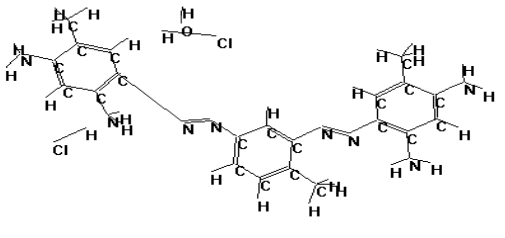
TS1



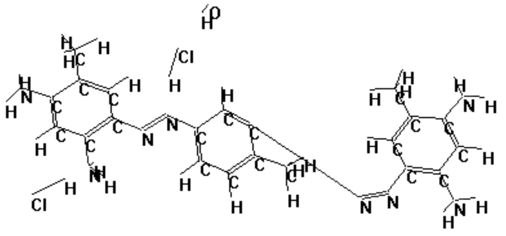
TS2



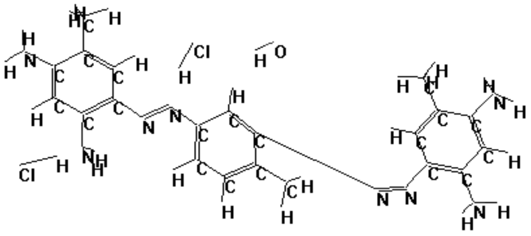
TS3



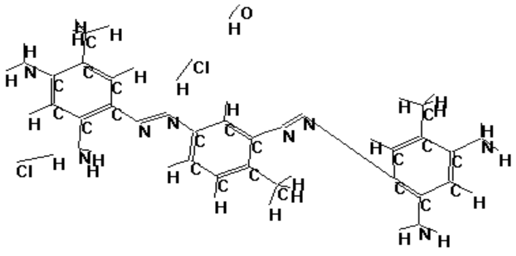
TS4



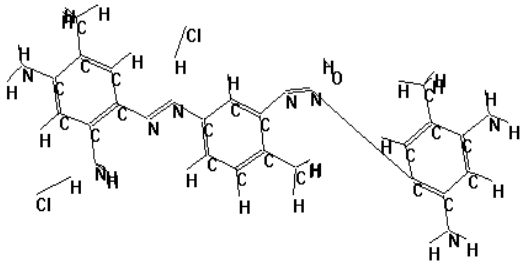
TS5



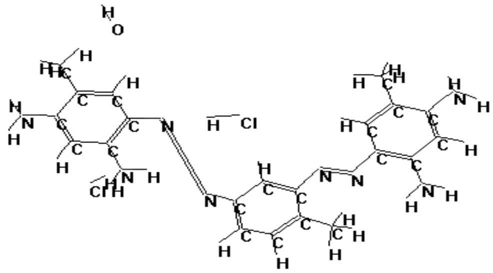
TS6



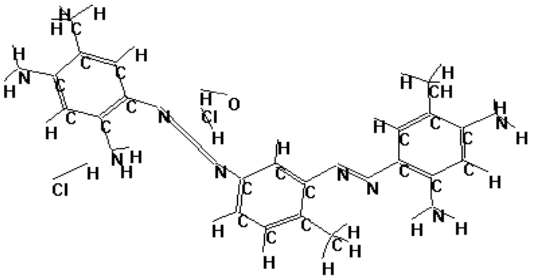
TS7



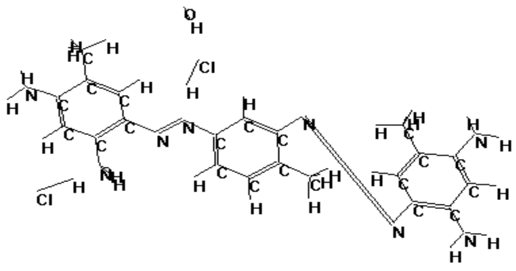
TS8



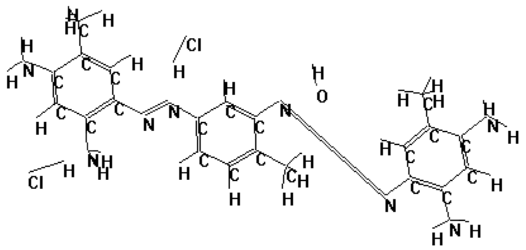
TS9



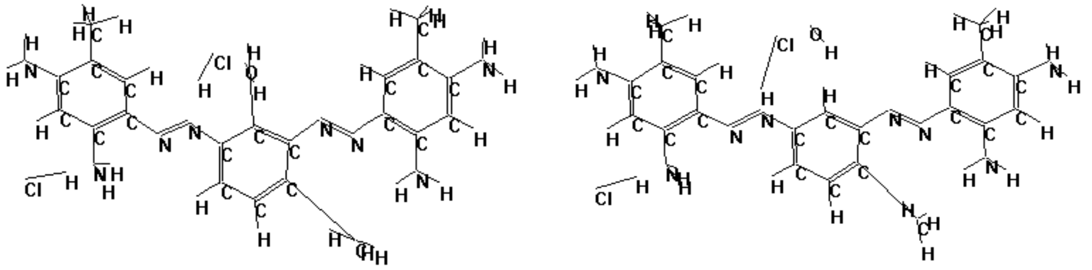
TS10



TS11



TS12



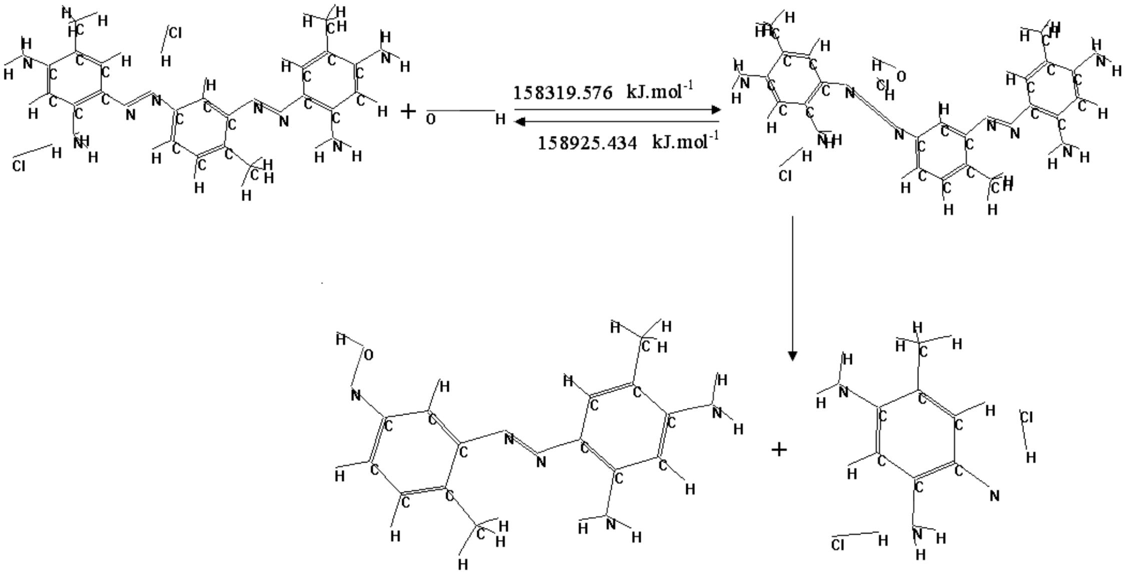
TS13 TSe14

Fig. 3: Stick view of transition states for the reaction of $^{\bullet}$OH with bismarck brown-R without catalyst calculated at PM3CI (4 X 4) in vacuum

Table 2: Energetic properties of probable transition states for bismarck brown-R without catalyst

TS	E_b of forward reaction (kJ.mol^{-1})	E_b of backward reaction (kJ.mol^{-1})	ZPE (kJ.mol^{-1})	Sing of first imaginary frequency	Heat of formation (kJ.mol^{-1})
1	158758.334	159051.178	1177.24	-	652.2061
2	158792.883	158072.342	1194.95	-	686.6153
3	158654.762	158651.453	1176.867	-	548.5893
4	158631.123	158684.334	1178.926	-	524.9414
5	158655.643	158904.343	1183.382	-	549.422
6	158662.915	158667.423	272.9432	-	556.7691
7	158671.586	158672.984	1176.445	-	565.3295
8	158564.378	158548.337	1209.184	-	458.1229
9	158754.897	158771.254	1132.621	-	647.8255
10	**158319.576**	**158925.434**	**1213.653**	**-**	**210.338**
11	158772.256	158742.323	10.67757	-	666.0468
12	158718.954	158555.664	1166.88	-	612.797
13	158782.456	158782.456	1172.474	-	675.8708
14	158712.523	158713.534	1190.047	-	606.3453

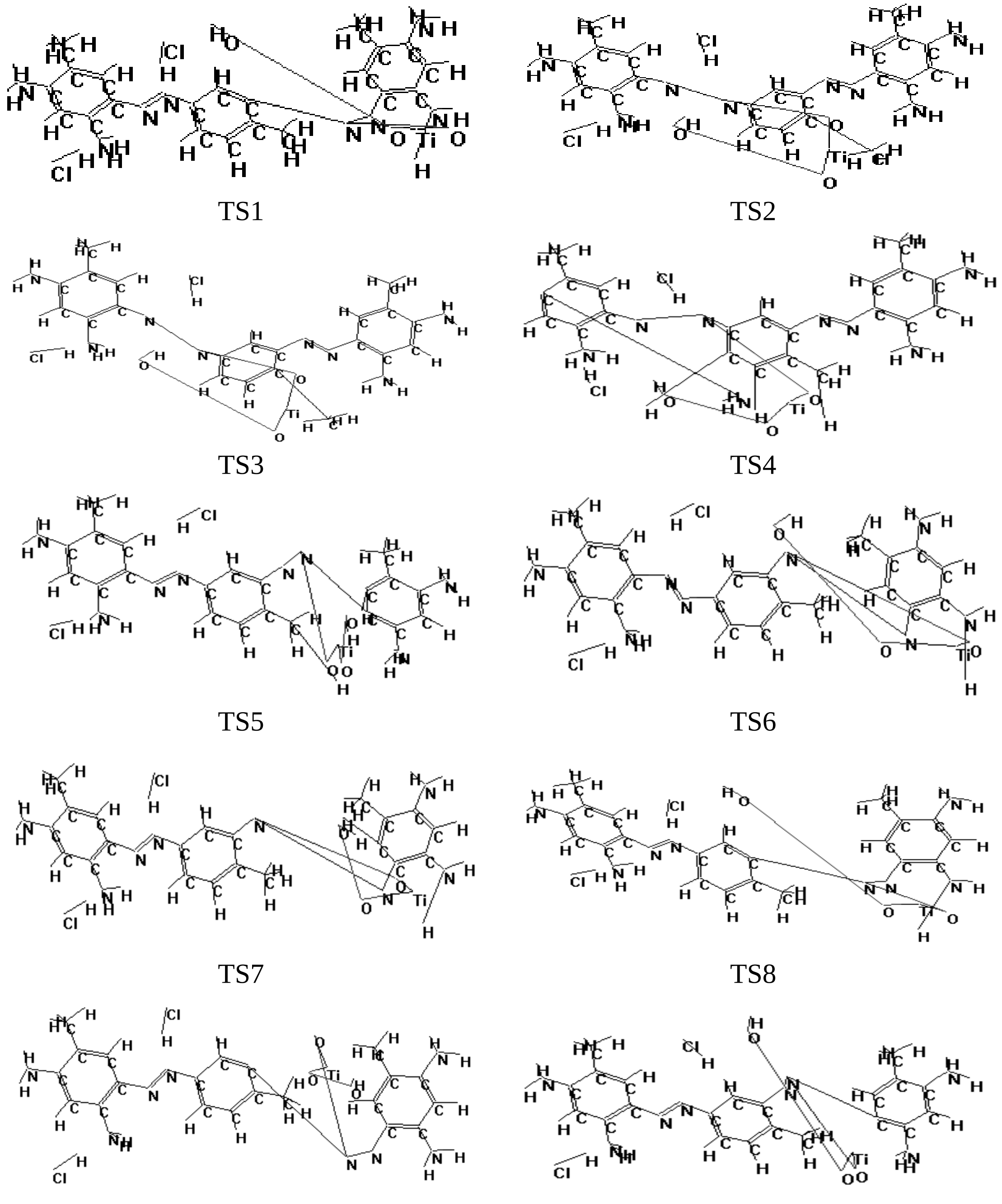
The initial step (lowest reaction step) of cleavage of the bismarck brown-R by the reaction with hydroxyl radical can be suggested through the tenth transition state for photodecolorization reaction to give up two new chemical moiety[17]. **Scheme 1** represents the suggested reaction mechanism of first initiation step of photodecolorization reaction.



Scheme 1: Suggested mechanism for first cleavage step of bismarck brown-R with $^{\bullet}$OH without catalyst in vacuum

Examination of transition state with catalyst and hydroxyl radical

Bismarck brown R can react with hydroxyl radical in the presence of TiO_2 catalyst in different suggested transition states. Fig. 4 show geometries of different possibilities for the reaction transition states. Tables 3 show that the energetic properties for suggested transition states with hydroxyl radical in presence of TiO_2. The activation energy for the forward reaction is less than the activation energy for backward reaction. This means the reaction tends to the products in all suggestions[18]. The transition state calculation shows that the TS5 and TS9 have the minimum activation energy equal to -0.79496 and -196.276 kJ.mol^{-1}, respectively. Zero point energy for the TS5 equal to 1220.326 kJ.mol^{-1}, which is higher than the other transition states. According to the results, the fifth transition state is the most probable state to give the first cleavage reaction step in this reaction map and the suggested mechanism can be proposed as in **Scheme 2**.



TS1 TS2

TS3 TS4

TS5 TS6

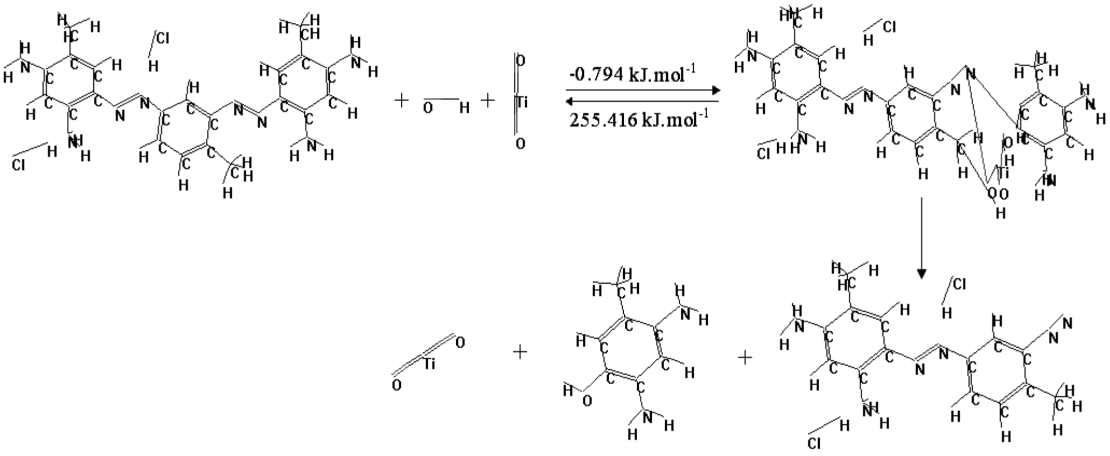
TS7 TS8

TS9 TS10

Fig. 4: Transition state of bismarck brown-R that is produced by hydroxyl radical and TiO_2 calculated at PM3 CI (4 x 4)

Table 3: Energetic properties for suggested transition state with hydroxyl radical in presence of TiO_2

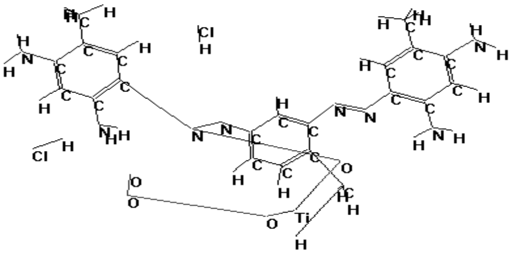
TS	E_b for forward reaction (kJ.mol^{-1})	E_b for backward reaction (kJ.mol^{-1})	ZPE (kJ.mol^{-1})	Imaginary frequency	Heat of formation H_f (kJ.mol^{-1})
1	179.025	646.695	981.876	-	238.4336
2	121.252	144.992	1037.113	-	191.941
3	528.079	633.993	1159.721	-	6.54796
4	612.725	1909.983	1173.721	-	91.19446
5	**-0.794**	**255.416**	**1220.326**	**-**	**-403.898**
6	151.1721	165.452	843.5028	-	-199.861
7	355.225	370.945	1181.352	-	-88.228
8	466.859	487.795	1190.829	-	-751.375
9	-196.276	375.836	1193.808	-	-444.596
10	342.803	414.349	1194.754	-	-788.174



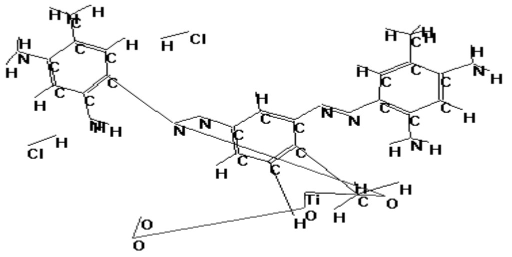
Scheme 2: Suggested mechanism of the first cleavage step of reaction bismarck brown-R with $^{\bullet}OH$ in presence of catalyst

Examination of transition state using super oxide anion and catalyst

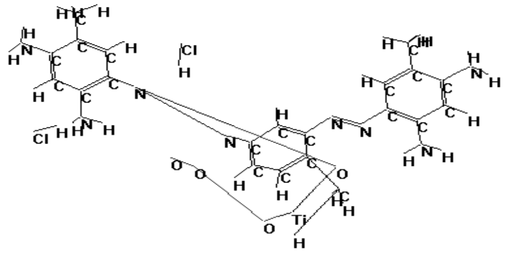
Fig. 5 show the stick view of the suggested transition state of bismarck brown-R with super oxide anion and TiO_2. All transition states structures have been studied through optimizing their geometry and calculating their frequencies. Table 4 show that the activation energy of forward reaction is less than the activation energy for backward reaction. Heat formation shows that the TS4, TS5, TS9 and TS10 have positive value, that means transition state absorbed energy of formation. The TS1, TS2, TS3, TS6, TS7, TS8, TS10 and TS12 have a negative value, since these transition states release the energy as heat to form the fundamental elements. According to transition state calculation, the sixth transition state has the lowest activation energy value of formation and the highest value of zero point energy to produce their products in a faster rate than the other probable transition state. Suggested mechanism of first initiation step for decolorization reaction of bismarck brown-R reaction with superoxide anion in the presence of the catalyst, that passes through the TS6 shown in **Scheme 3**.



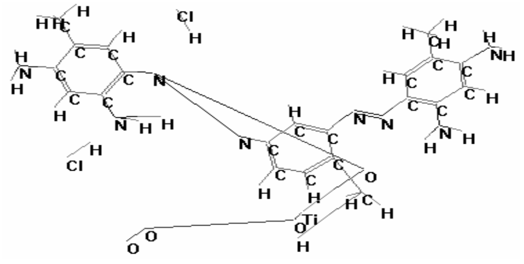
TS1



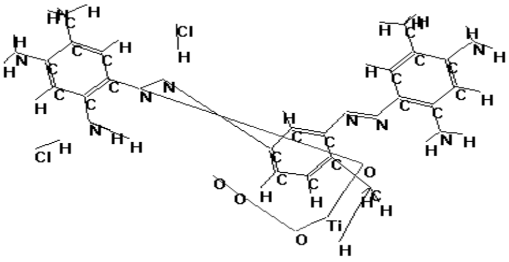
TS2



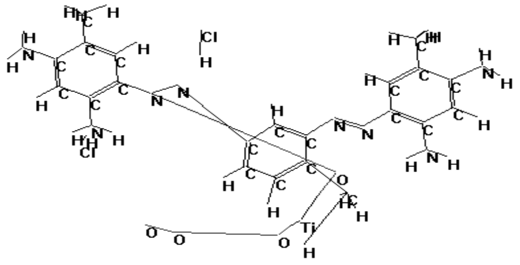
TS3



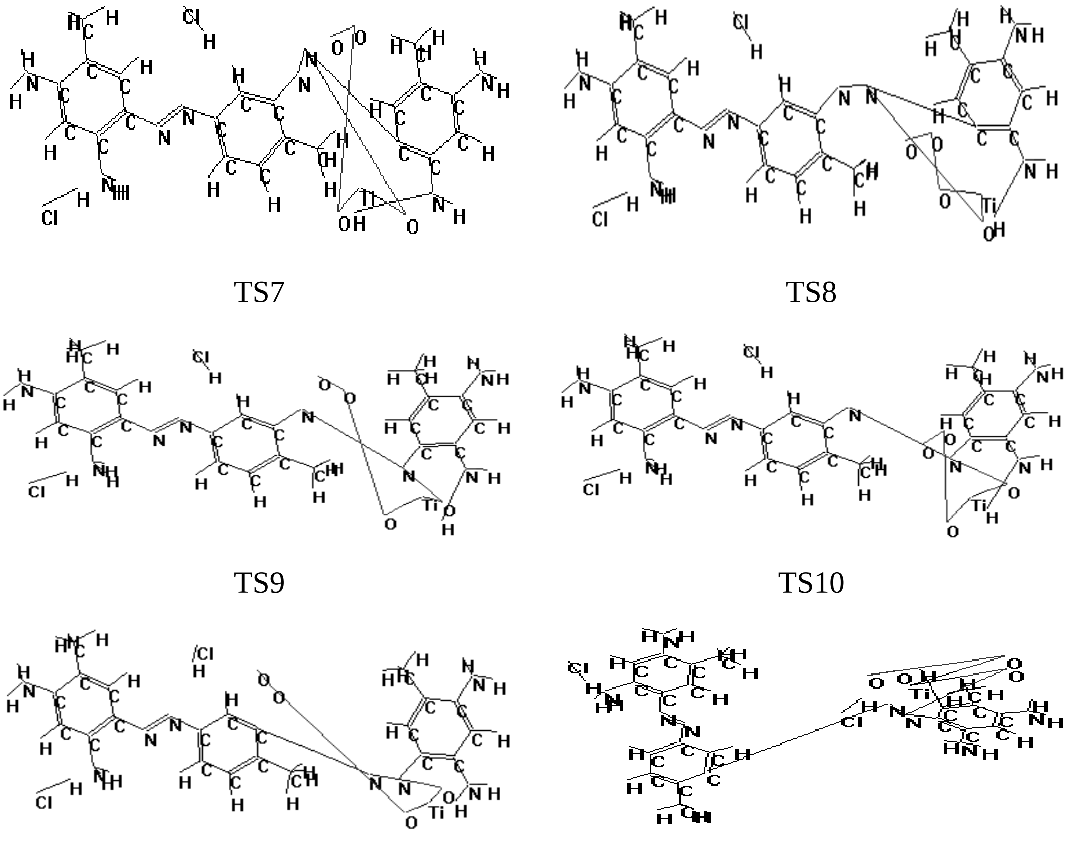
TS4



TS5



TS6



TS7 TS8

TS9 TS10

TS11 TS12

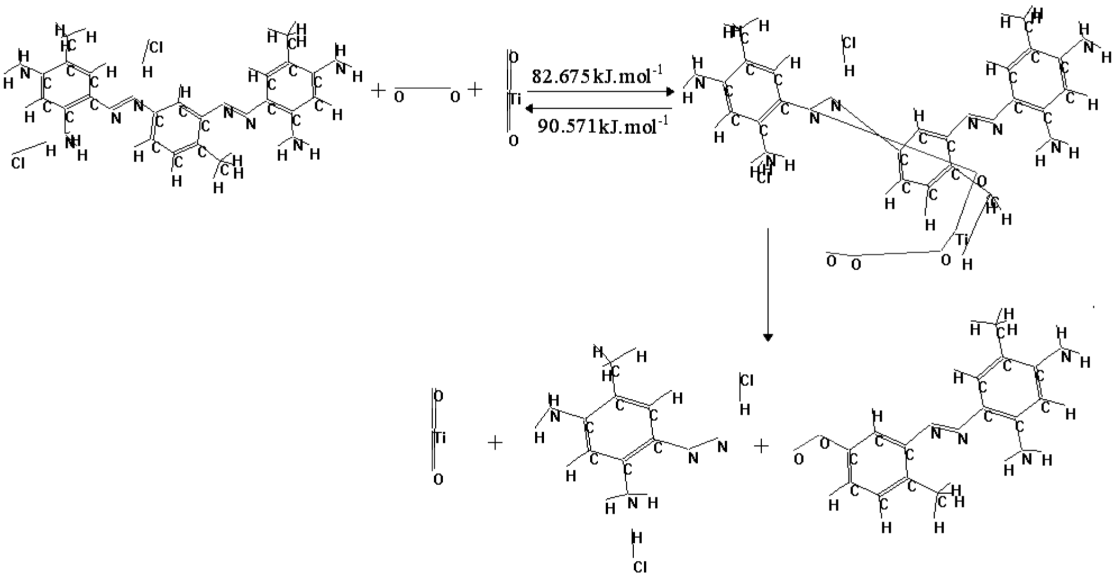
Fig. 5: Transition state of bismarck brown-R with superoxide anion in presence of TiO_2 calculated at PM3 method

Table 4: Energetic probabilities of transition state using super oxide anion in presence of TiO_2 calculated at PM3 method

TS	E_b for forward reaction ($kJ.mol^{-1}$)	E_b for backward reaction ($kJ.mol^{-1}$)	Zero point energy ($kJ.mol^{-1}$)	Imaginary frequency	Heat of formation ($kJ.mol^{-1}$)
1	154.515	309.544	1011.227	-	-167.557
2	183.426	194.639	711.7151	-	-138.633
3	274.641	278.123	970.3324	-	-47.4215

Cont…

TS	E_b for forward reaction (kJ.mol^{-1})	E_b for backward reaction (kJ.mol^{-1})	Zero point energy (kJ.mol^{-1})	Imaginary frequency	Heat of formation (kJ.mol^{-1})
4	428.713	436.663	1056.77	-	106.6543
5	441.755	445.018	704.3513	-	119.6708
6	**82.675**	**90.571**	**1026.967**	**-**	**-239.375**
7	136.063	141.260	1178.947	-	-514.615
8	591.182	610.332	1165.512	-	-59.5258
9	803.503	815.432	1140.349	-	152.8248
10	629.210	631.754	1172.599	-	-21.4848
11	510.393	517.447	989.0976	-	92.90572
12	828.574	833.047	1174.411	-	-264.63



Scheme 3: Suggested mechanism of the first cleavage step for reaction of the bismarck brown-R with super oxide anion in presence of catalyst

Investigating different reaction path ways for photoreaction of bismarck brown-R can be estimated through Fig. 6, 7 and 8 that show the reaction coordinate for different transition states with energy activation in different conditions.

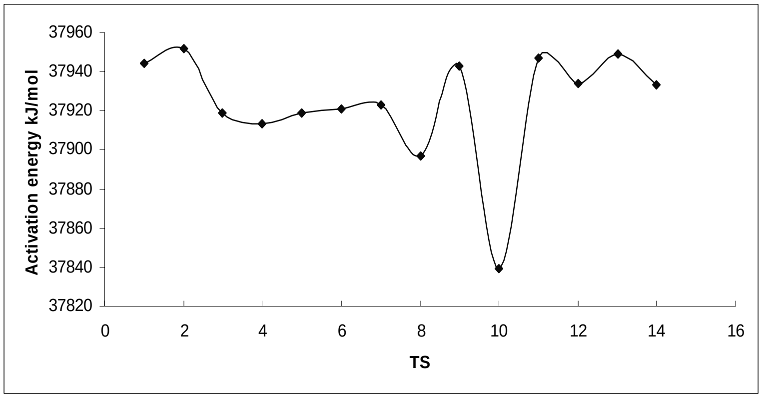


Fig. 6: Reaction coordinate of bismarck brown-R with hydroxyl radical

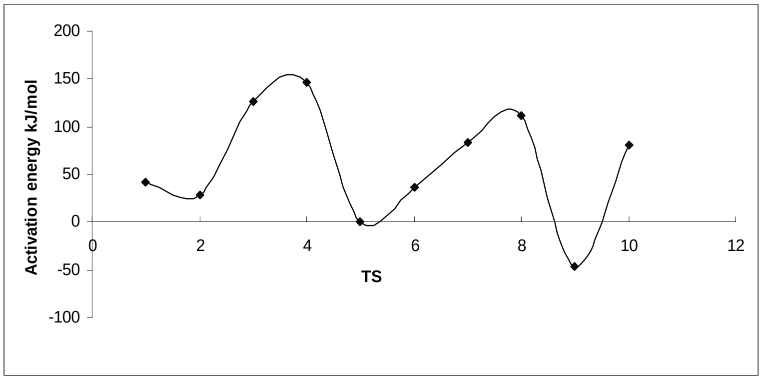


Fig. 7: Reaction coordinate of bismarck brown-R with hydroxyl radical in presence of catalyst

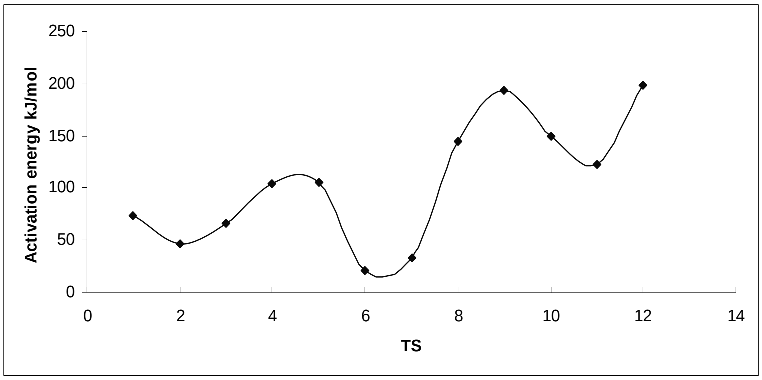


Fig. 8: Reaction coordinate of bismarck brown-R with super oxide anion in of presence catalyst

Tables 5 represents a comparison among the high probable transition states for reaction of bismarck brown-R for different paths. The results show that the fifth transition state represent the highest probable pathway to give up the first cleavage step through N16-N17 bond because the activation energy has the lowest value[19]. On the other hand, the highest value zero point energy and lowest enthalpy formation than the other states also favour it.

Table 5: Energetic values for transition states at different reaction path ways

Transition state	Activation energy ($kJ.mol^{-1}$)	Zero point energy ($kJ. mol^{-1}$)	Imaginary frequency	Heat of formation ($kJ. mol^{-1}$)
TS10	158319.518	1213.652	-	210.338
TS5	**-0.794**	**1220.326**	-	**-403.898**
TS6	82.675	1026.966	-	-239.375

CONCLUSION

Optimized structure of bismarck brown-R has been investigated using calculation methods to get the chemical reactivity towards different chemical species. There are three different transition states for three different reaction paths. The fifth state is most probable and reaction mechanism is the first cleavage step at N16-N17 bond due to lowest energy value using hydroxyl radical in the presence of TiO_2 catalyst.

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Revised : 25.09.2011 *Accepted : 28.09.2011*