Open Access **Baghdad Science Journal** **P-ISSN: 2078-8665**
Published Online First: January, 2023 **2023, 20(4): 1352-1358** **E-ISSN: 2411-7986**

DOI: https://dx.doi.org/10.21123/bsj.2023.7380

Degradation of Indigo Dye Using Quantum Mechanical Calculations

Halla T. Mohammed [1] ***Ahmed M. Kamil*** [2] ***Hayder M. Abduljalil*** [3]
Abbas A-Ali Drea [4] ***Mohammed A. Al-Seady*** [5,6*]

[1] Anesthesia Techniques Department, Al-Mustaqbal University College, Iraq.
[2] Ministry of Education, Babylon Education Directorate, Iraq.
[3] Physics Department, College of Science, University of Babylon, Babylon, Iraq.
[4] Chemistry Department College of Science, University of Babylon, Babylon, Iraq.
[5] Environmental Research and Studies Centre, University of Babylon, Babylon, Iraq.
[6]Department of Theoretical Physics, University of Debrecen, H-4010 Debrecen, Bem ter 18/B, Hungary
*Corresponding author: muhammad.alsaadi@uobabylon.edu.iq
E-mail addresses: halah.thamer@mustaqbal-college.edu.iq, ahmedmuslimkamil@yahoo.com, hyder.abduljalil1@gmail.com, abbasdrea@gmail.com.

Received 4/5/2022, Revised 2/8/2022, Accepted 4/8/2022, Published Online First 20/1/2023, Published 1/8/2023

This work is licensed under a Creative Commons Attribution 4.0 International License.

Abstract:

The semiempirical (PM3) and DFT quantum mechanical methods were used to investigate the theoretical degradation of Indigo dye. The chemical reactivity of the Indigo dye was evaluated by comparing the potential energy stability of the mean bonds. Seven transition states were suggested and studied to estimate the actually starting step of the degradation reaction. The bond length and bond angle calculations indicate that the best active site in the Indigo dye molecule is at C10=C11. The most possible transition states are examined for all suggested paths of Indigo dye degradation predicated on zero-point energy and imaginary frequency. The first starting step of the reaction mechanism is proposed. The change in enthalpy, Gibbs free energy and change in entropy of the overall reaction are equal to -548268.223 kcal/mol, 30831.951 kcal/mol and 48.552 cal/mol.deg, respectively. The activation energy is 46176.405 kcal/mol. The reaction rate is equal to $22.867 \times 10^{11}\ s^{-1}$.

Keywords: Degradation, DFT, Indigo dye, PM3, superoxide free radical.

Introduction:

One of the main environmental problems in the world is wastewater. The contamination of water sources such as rivers and lakes occurs when untreated wastewater is released into these sources. Plants and species living in or around the aquatic system can be harmed by polluted water. It can also cause harm to those who consume it, including humans, plants, and animals [1]. Pathogens, inorganic substances, organic material, and macroscopic pollutants are the four basic types of water pollution. Dye is one of the most significant of these pollutants, and it is becoming a major environmental and public health hazard. Dyes in water cause issues for instance lowering the levels of oxygen in the water, interfering with sunlight diffusion through waters, slowing photosynthesis as well as interfering with the solubility of gases in water bodies [2].

Indigo is a natural dye prepared from Indigofera tinctoria and Isatis tintoria plants. Due to a scarcity of natural blue dyes, indigo has played a key part in the economics of many countries since its inception, mostly for textile dyeing and printing, and it is still utilized in the fabric business today [3].

Chemical oxidation[4], adsorption[5], biodegradation [6], and photolysis [7] are some of the current technologies utilized to treat wastewater. Chemical oxidation technology employs a sequence of oxidants and catalysts to remove organic molecules from wastewater. Oxidants are used in chemical oxidation processes to destroy contaminants and transform them into less hazardous by-products or end products (e.g., carbon dioxide, water). Ozone, oxygen, peroxide, permanganate, and other oxidants are widely applied [8].

Baghdad Science Journal
2023, 20(4): 1352-1358
P-ISSN: 2078-8665
E-ISSN: 2411-7986

Researchers have been applying computation methods to descript the molecular structure and reactivity of compounds in recent years. Chemical reaction simulations require optimal geometry of chemical compounds and transition states. When computing the potential energy surface, they are found the key to chemical reactivity [9]. For minimum transitions, the first-order saddle point must be carefully considered to order to land on the most possible states. The reaction mechanisms begin with the first cleavage step, which is usually the slowest deciding step compared to the faster later steps [10, 11].

In this paper, the mechanisms of the first cleavage step for the degradation of indigo dye with superoxide anion radical have been studied using quantum chemical calculations**.**

Material and methods:

In this article, depending on molecular orbital theory different theoretical calculations were performed using the semiemperial PM3 method in the Hyperchem package 8.02 [12]. All reactants, suggested transition states and products have been optimized by DFT, 6-31G / B3LYP by Gaussian 09 program. The bond stability of main bonds in indigo dye molecule was studied using the PM3 method. Vibrational frequencies of suggested transition state structures were calculated. The parameters of thermodynamics (ΔG, ΔH and ΔS) have been estimated at DFT, 6-31G / B3LYP by Gaussian 09 program [13].

Results and Discussion:

Optimizing the structure of Indigo dye

Electronic properties of Indigo dye were studied at the PM3 level shown in Fig. 1. The atomic charge orientation and electrostatic potential of the Indigo dye molecule were used to estimate the possible active site that reacts toward O_2^- radicals [14].

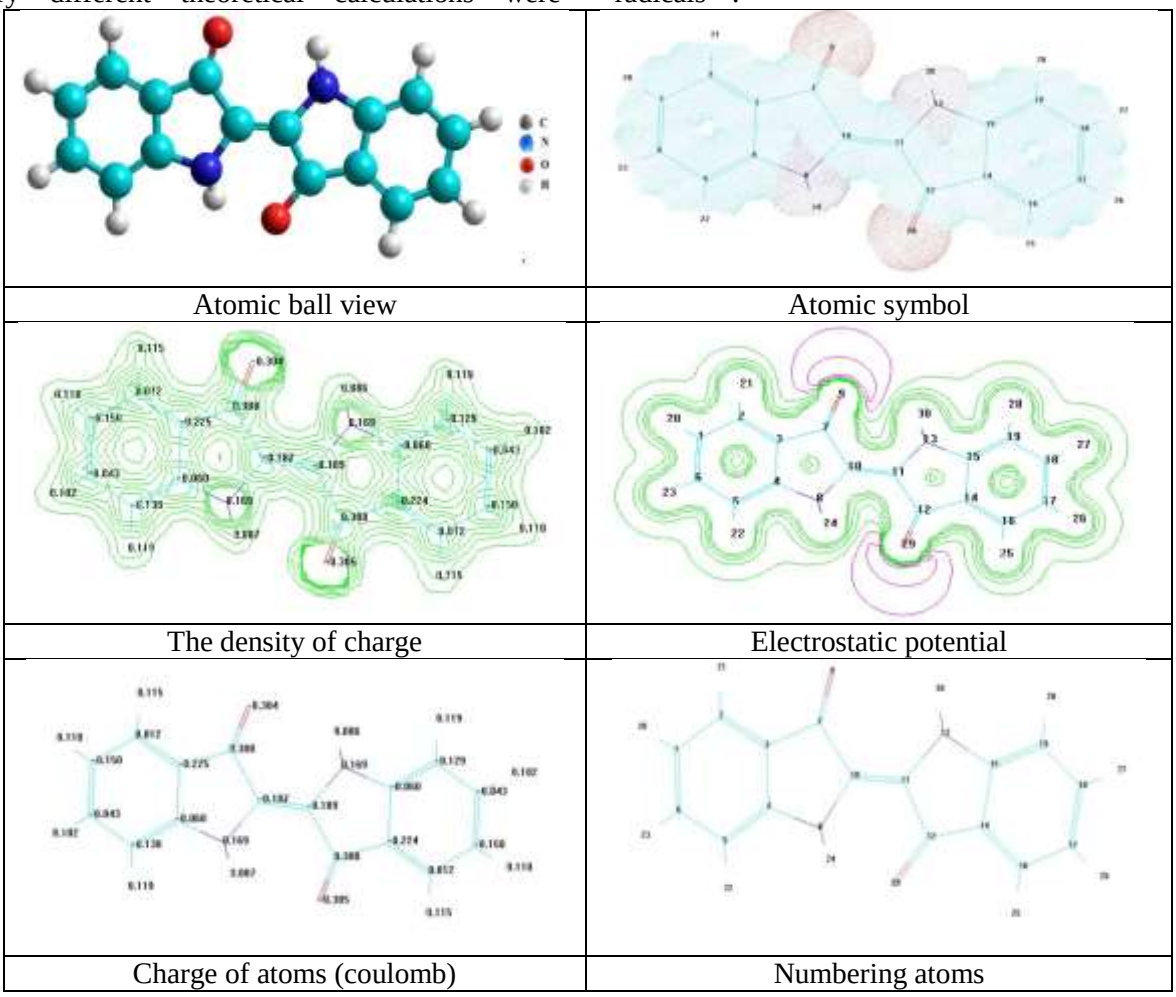

Figure 1. The optimizing properties of indigo dye calculated in 2 D.

Because of the high value of electronegativity, the negative charge densities are highlighted by the red color and dispersed on the oxygen and nitrogen atoms. The green color represents positive charge concentrations, which are dispersed across the carbon atoms. The total potential energy surface of free Indigo dye is -875.225 kcal /mol.

The bond length of indigo dye bonds C10=C11, C7=O9 and N8—H24 are 1.351, 1.212

Baghdad Science Journal
2023, 20(4): 1352-1358
P-ISSN: 2078-8665
E-ISSN: 2411-7986

and 0.992 Aº respectively. Due to these results, the C10=C11 bond is more active to react [15].

Bond strength was measured for the main important bonds as shown in Table 1. Fig. 2 illustrates the stability of bonds C10=C11, C7— O9 and N8—H24 calculated by the PM3 method. The results indicate that the C10=C11 is the best active site due to the lowest bond dissociation energy [16].

Table 1. Potential energy stability and dissociation of main bonds in indigo compound calculate at semiempirical PM3 method.

bond	bond order	bond length Å	Potential energy stability (kcal/mol)	Potential energy stability (kcal/mol)	Bond dissociation energy (kcal/mol)
C10=C 11	2	1.351	-3583.077	-3484.009	99.068
C7=O 9	2	1.212	-3591.152	-3364.9836	226.168
N8—H24	1	0.992	-3591.976	-3458.704	133.271

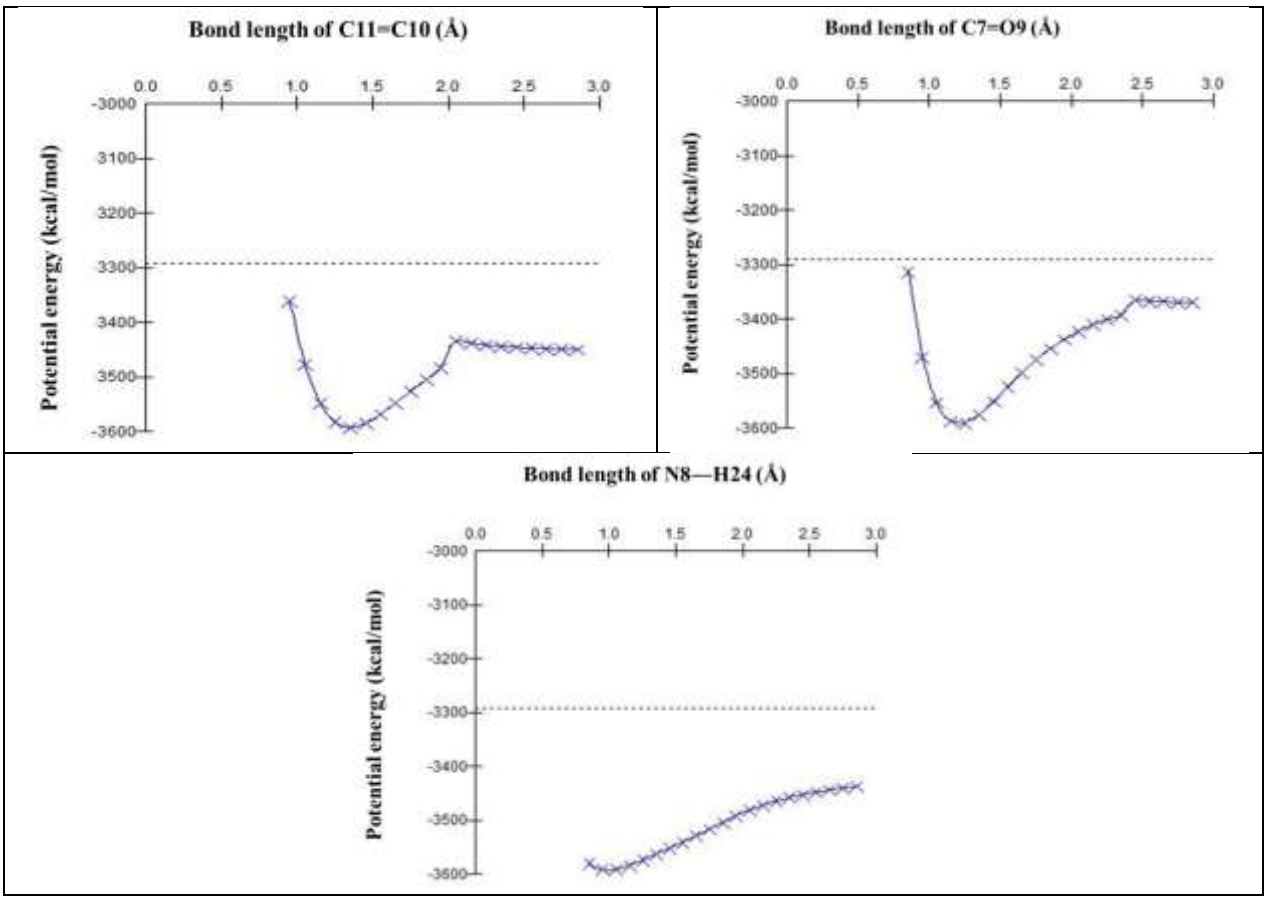

Figure 2. Potential energy stability of bonds in indigo molecule calculated at semiempirical PM3.

The bond angles of the O9=C7—C10, C7—C10=C11, N8—C10=C11 and C10—N8—H24 are equal to 127.142°, 128.06°, 124.062° and 117.886°, respectively. These bond angles are higher than the other angles. That is, the O9=C7—C10 and C7—C10=C11 bonds are more likely to be attacked by the superoxide anion radical than the other bonds [17]. Fig. 3 shows the potential energy stability of bonds in indigo.

Baghdad Science Journal
2023, 20(4): 1352-1358
P-ISSN: 2078-8665
E-ISSN: 2411-7986

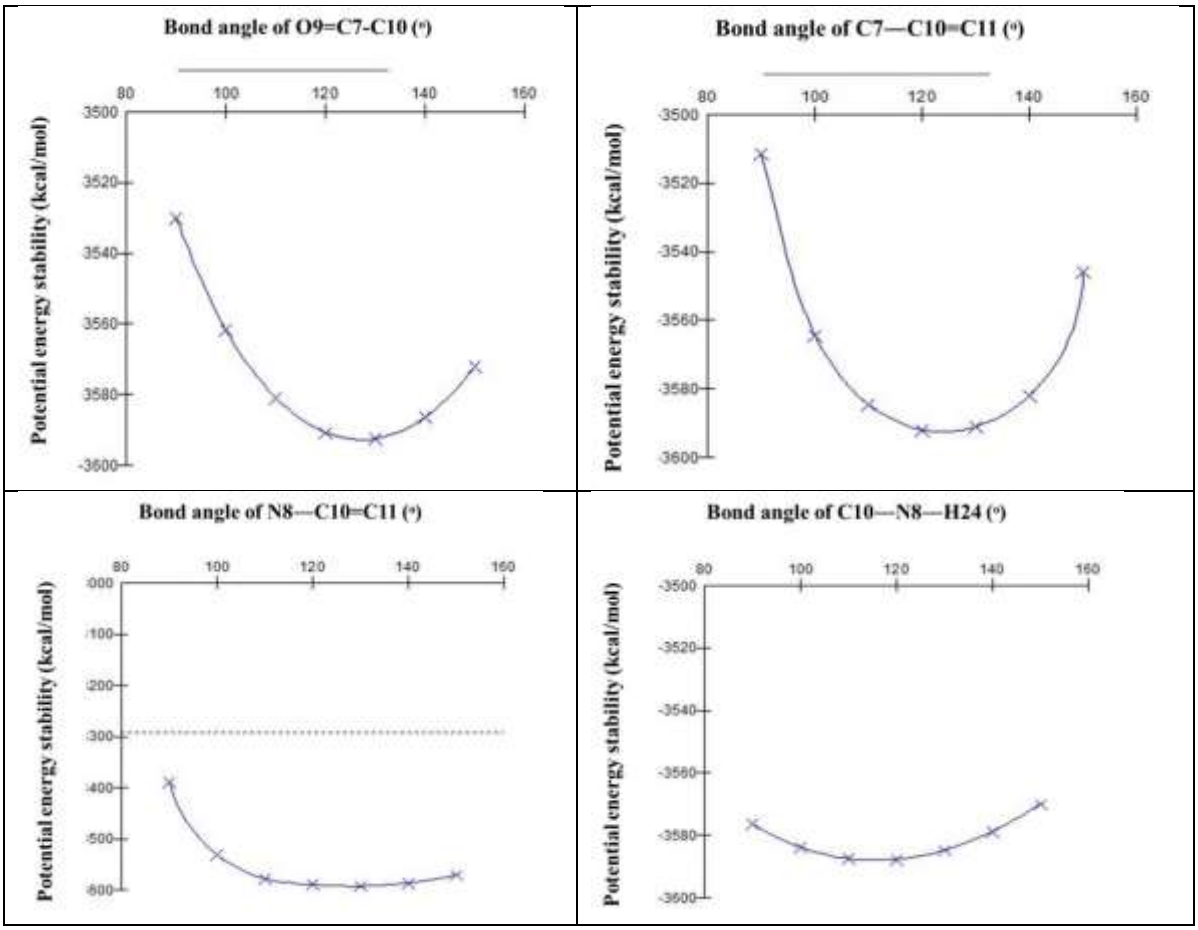

Figure 3. Potential energy stability of bonds angle in indigo molecule calculated at semiempirical PM3.

Different seven transition states have been suggested for indigo dye degradation. As indicated in Fig. 4, all transition states were investigated to determine the most likely transition state to give the product. Table 2 shows the Energetic values for suggested transition states. The first transition state is the most likely to give up reaction products than other states since it has the highest value of zero-point energy and the lowest heat of formation [18].

Table 2. Energetic values of suggested transition states for indigo degradation by superoxide anion free radical using semiempirical PM3.

TS	Total energy (kcal/mol)	Heat of formation (kcal/mol)	ZPE (kcal/mol)	Imaginary frequency
TS1	-81771.082	-44.044	147.061	-
TS2	-81779.010	-36.084	146.744	+
TS3	-81778.983	-43.986	146.815	+
TS4	-81766.256	-31.259	145.393	+
TS5	-81700.412	34.584	144.804	-
TS6	-81724.547	10.450	143.774	-
TS7	-81666.798	68.199	143.399	-

Baghdad Science Journal
2023, 20(4): 1352-1358
P-ISSN: 2078-8665
E-ISSN: 2411-7986

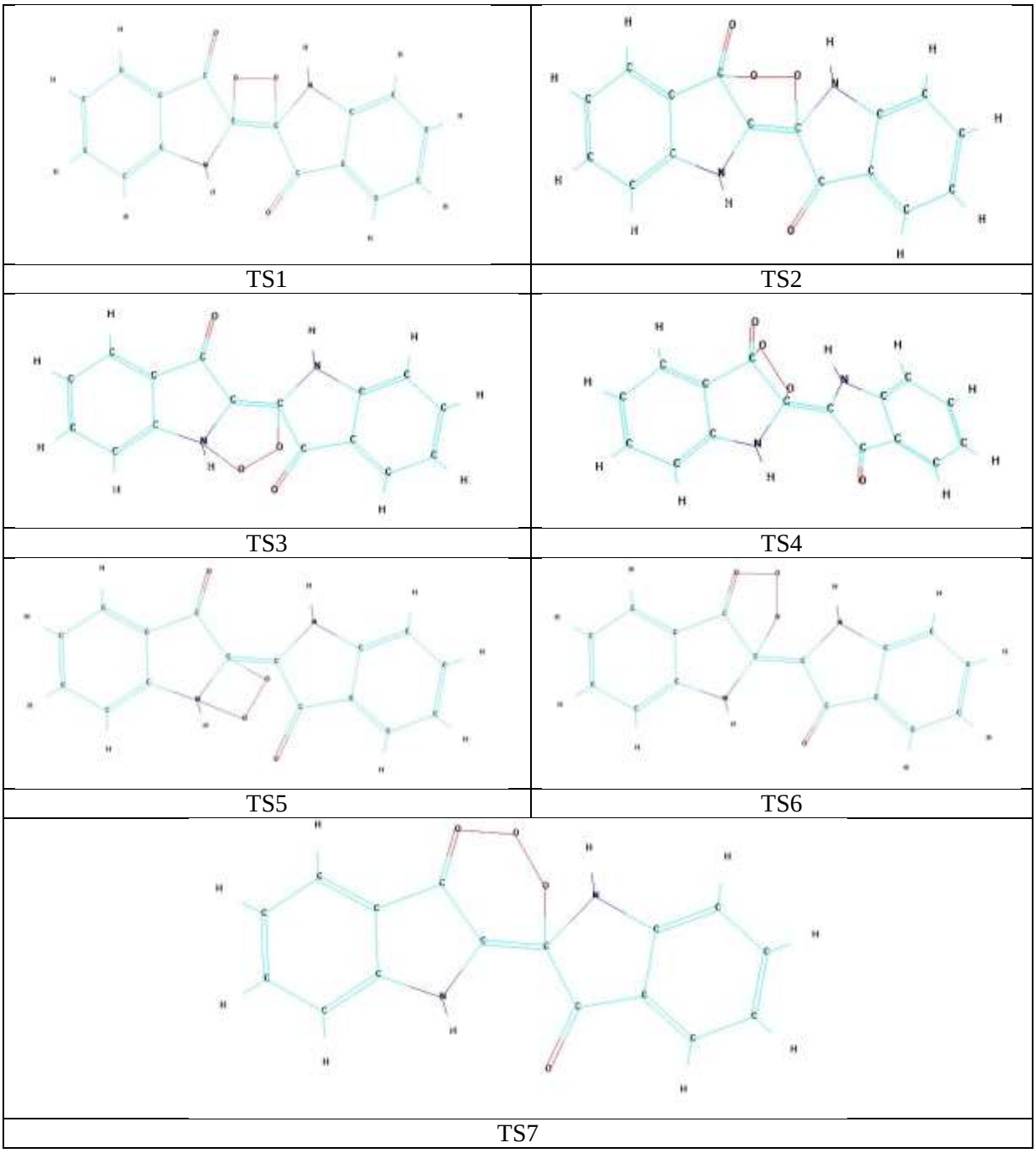

Figure 4. Proposed transition states for indigo degradation by superoxide anion free radical using semiempirical PM3.

The initial broken step of the Indigo dye by the reaction with superoxide anion radical was proposed from the first transition state to produce Isatin. The proposed reaction mechanism for the initiating step of the reaction is shown in Scheme 1. The energy barrier value of the forwarding reaction is -548436.731 kcal mol^{-1}, while the backward reaction is -89.039 kcal mol^{-1}. These results indicate the reaction goes to the product Isatin [19]. The energetic properties of reactant and transition state and product are listed in table 3.

Schem1. The suggested mechanism for the first broken step of indigo dye with $O_2^{\cdot-}$.

Table 3. Energetic properties for indigo, superoxide anion free radical, TS1, and Isatin using B3LYP/6-31G.

	Indigo	superoxide anion free radical	TS1	Isatin
Total energy (kcal/mol)	-875.225	-94294.523	-643526.479	-321719.281
Heat of formation (kcal/mol)	-875.224	-94293.931	-643156.698	-321718.689
ΔS° (cal/mol.deg)	118.753	48.867	129.991	108.086
ΔG° (kcal/mol)	-875.280	-94308.501	-643564.643	-321750.915
Zero-point energy (kcal/mol)	-875.239	-94296.23	-643536.741	-321541.628

The change in enthalpy, Gibbs free energy and change in entropy of the overall reaction are equal to -548268.223 kcal/mol, 30831.951 kcal/mol and 48.552 cal/mol.deg, respectively. These results indicate that the reaction is exothermic[20] and nonspontaneous[21] at 298.15 K. The activation energy is 46176.405 kcal/mol. The reaction rate is equal to $22.867 \times 10^{11}\ s^{-1}$.

Conclusion:

The chemical reactivity of indigo dye optimized structure has been examined utilizing computational methods towards superoxide anion radical. The active site in the dye molecule was determined using the bond strength and bond angles calculations. The first transition state is the most probable and the reaction mechanism is the first cleavage step at the C10—C11 bond due to the lowest energy value.

Acknowledgments:

The authors thank Al-Mustaqbal University College for its support of this research.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Babylon.

Authors' contributions statement:

H. T. M. wrote a part of the manuscript and ran a section of the work on her computer. A. M. K. wrote another part of manuscript. H. M. A. worked on performing a section of the calculations on his computer. A. A-A. D. worked to explain some of the results. M. A. A. worked on interpreting some of the results and publishing the research.

References:

1. Kamil A, Abdalrazak F, Halbus A, Hussein F. Adsorption of bismarck brown R dye onto multiwall carbon nanotubes. J Environ Anal Chem. 2014; 1(104): 2.
2. Salahuddin N, Abdelwahab MA, Akelah A, Elnagar M. Adsorption of Congo red and crystal violet dyes onto cellulose extracted from Egyptian water hyacinth. Nat. Hazards. 2021; 105(2): 1375-94. DOI: 10.1007/s11069-020-04358-1
3. Franchi D, Calamante M, Coppola C, Mordini A, Reginato G, Sinicropi A, et al. Synthesis and characterization of new organic dyes containing the indigo core. Molecules. 2020; 25(15): 3377.
4. Kamil AM, Mohammed HT, Balakit AA, Hussein FH, Bahnemann DW, El-Hiti GA. Synthesis, characterization and photocatalytic activity of carbon nanotube/titanium dioxide nanocomposites. Arab J Sci Eng. 2018; 43(1): 199-210, DOI: 10.1007/s13369-017-2861-z
5. Cheng Z, Tan ALK, Tao Y, Shan D, Ting KE, Yin XJ. Synthesis and characterization of iron oxide nanoparticles and applications in the removal of heavy metals from industrial wastewater, Int. J Photoenergy. 2012; 2012: 1-5 , DOI: 10.1155/2012/608298
6. Chen X, Yang Y, Ke Y, Chen C, Xie S. A comprehensive review on biodegradation of tetracyclines: Current research progress and prospect. Sci Total Environ. 2022: 814: 1-13 . DOI: 10.1016/j.scitotenv.2021.152852
7. Shi X, Chen Z, Liu X, Wei W, Ni B-J. The photochemical behaviors of microplastics through the lens of reactive oxygen species: Photolysis mechanisms and enhancing photo-transformation of pollutants. Sci Total Environ. 2022: 846: 157498. DOI: 10.1016/j.scitotenv.2022.157498
8. Deng Y, Zhao R. Advanced oxidation processes (AOPs) in wastewater treatment. Curr Pollut Rep. 2015; 1(3): 167-76.
9. Kubba RM, Mohammed MA, Ahamed LS. DFT Calculations and Experimental Study to Inhibit Carbon Steel Corrosion in Saline Solution by Quinoline-2-One Derivative. Baghdad Sci J. 2021; 18: 113-123 .
10. Mohammed HT, Abbas A, Drea A. Simulation Study of Adrenaline Synthesis from Phenylalanine. J Adv Chem. 2017; 12: 3888-3901.

11. Drea A, Naman S, Jaffer B. Theoretical degradation study of methomyl. J Appl Chem. 2012; 1: 126-137 .
12. TM H. HyperChem TM for windows molecular modeling system. 8.0.9 ed: Hypercupe, Inc. 2011.
13. Parks C, Alborzi E, Akram M, Pourkashanian M. DFT Studies on Thermal and Oxidative Degradation of Monoethanolamine. Ind Eng Chem Res. 2020; 59(34): 15214-15225.
14. Kubba RM, Mohammed MA. Theoretical and Experimental Study of Corrosion Behavior of Carbon Steel Surface in 3.5 NaCl and 0.5 M HCl with Different Concentrations of Quinolin-2-One Derivative. Baghdad Sci J. 2022;19: 105-120 .
15. Noureddine O, Issaoui N, Al-Dossary O. DFT and molecular docking study of chloroquine derivatives as antiviral to coronavirus COVID-19. J King Saud Univ Sci. 2021; 33(1): 101248.
16. Wen M, Blau SM, Spotte-Smith EWC, Dwaraknath S, Persson KA. BonDNet: a graph neural network for the prediction of bond dissociation energies for charged molecules. Chem Sci J. 2021; 12(5): 1858-68.
17. Guthardt R, Bruhn C, Färber C, Siemeling U. Effect of the Lead (II) Bond Angle on the Reactivity of Diaminoplumbylenes toward Ammonia: From Inertness to Immediate Ammonolysis. Organometallics. 2020; 39(23): 4174-7.
18. Birkholz AB, Schlegel HB. Using bonding to guide transition state optimization. J Comput Chem. 2015; 36(15): 1157-66.
19. Chen B, Tian F, Wang M, Peng C. Electron transfer and energy barrier co-modulation: unravelling the role of sequential fluorination in high-rate CO2 photoreduction on conjugated organic polymers. Appl Catal A: Gen. 2022: 638: 118618.
20. Chen L, Qi X, Tang J, Xin H, Liang Z. Reaction pathways and cyclic chain model of free radicals during coal spontaneous combustion. Fuel. 2021; 293: 120436.
21. Guo J, Xie T, Yang S, Xie Q, Liu Q, Qin J. Free-Radical and Non-Free-Radical Based Reaction Pathways of Iodide Oxidation by Hydrogen Peroxide in Acid Solution–Ab Initio Calculations. Russ J Phys Chem A. 2021; 95(1): S15-S22.

تكسير صبغة الانديجو باستخدام حسابات ميكانيك الكم

هالة ثامر محمد[1] **احمد م. كامل[2]** **حيدر محمد عبد الجليل[3]** **عباس عبدعلي دريع[4]**
محمد اياد السعدي[6,5]

[1]قسم تقنيات التخدير، كلية المستقبل الجامعة، بابل، العراق
[2] وزارة التربية، مديرية تربية بابل، بابل، العراق
[3] قسم الفيزياء، كلية العلوم، جامعة بابل، بابل، العراق
[4]قسم الكيمياء، كلية العلوم، جامعة بابل، بابل، العراق
[5] جلمعة بابل، مركز البحوث والدراسات البيئية، بابل، العراق
[6] قسم الفيزياء النظرية, جامعة دبرسين, H-4010 مقاطعه بم تير B/18, المجر

الخلاصة:

استخدمت طرق ميكانيك الكم النظرية الكثافة الوظيفية والشبه التجريبية لدراسة التكسير الحراري النظري لصبغة الانديجو. قيمت الفعالية الكيميائية لصبغة الانديجو عن طريق مقارنة استقرارية طاقة الجهد للاواصر الرئيسية في المركب. اقترحت سبع حالات وسطية لتحديد الخطوة الابتدائية الفعلية لتفاعل التكسير. حددت المواقع الفعالة والملائمة لبداية التكسير في صبغة الانديجو باستخدام حسابات اطوال وزوايا الاواصر ووجد بان اصرة C10=C11 هي افضل موقع فعال. اختيرت افضل حالة وسطية لتكسير صبغة الانديجو بالاعتماد على طاقة نقطة الصفر والتردد الخيالي. افترضت ميكانيكية الخطوة الاولى لتفاعل التكسير وتم قياس التغير في الانثالبي وطاقة كبس الحرة والتغير في الانتروبي لهذا التفاعل وكانت تساوي -548268.223 kcal/mol و 30831.951 kcal/mol و 48.552 cal/mol.deg على التوالي48.552 cal/mol على التوالي. وجد بان طاقة التنشيط وثابت سرعة التفاعل لهذا التفاعل تساوي 46176.405 kcal/mol و $22.867 \times 10^{11}\ s^{-1}$.

الكلمات المفتاحية: التكسير، نظرية الكثافة الوظيفية، صبغة الانديجو، الشبه التجريبية، جذر فوق الاوكسيد الحر.