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Synthesis and Characterization of Benzylidene Derivatives of Benzothiazole

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Abstract: ***A series of some novel benzothiazole derivatives were synthesized from the 2-(4-aminophenyl) benzothiazol-5-ol, which was synthesized by the Jacobson method using Lawesson's reagent. Benzylidene derivatives (P201-P205) were synthesized by catalyzed condensation and acylation method,named as 2-(4-((4 hydroxybenzylidene)amino) phenyl) benzothiazole-5-ol (P201), 2-(4-((4- methoxybenzylidene) amino)phenyl)benzothiazole-5ol(P202),2-(4-((4-chlorobenzylidene) amino)phenyl)benzothiazole-5-ol(P203), (4-((furan-2-ylmethylene) amino)phenyl)benzothiazole-5-ol(P204), Dimethyl(4(5hydroxy benzothiazol2yl)phenyl)carbonimidodithioate(P205)The structures of the compounds were confirmed by NMR and IR spectral data.***

Keywords: Benzothiazole, Synthesized, Benzylidene,Lawesson's reagent.

I. INTRODUCTION

The best of biologically active agrochemicals and pharmaceuticals used in industrial application extending from cosmectics, data storage, reprography and plastics are heterocyclic in nature. Heterocycles make an enormously significant class of compounds. In the study of organic chemistry heterocycles have occupied a major and magnificent research area.[1-3]

Heterocycles are also useful compounds for their synthetic value as synthetic intermediate, protecting group, chiral auxillaries, organic reagents in organic synthesis.[4-6] Therfore, new methods developed to synthesized heterocycles have been paid too much attention. The alkaloids have a main cluster of naturally occurring heterocyclic compounds. Alkaloids such as Ergotamine: indole based and Cinchonine : quinolone based exhibited antimigraine and antimalarial activities respectively, they contain basic N-atoms. A triazole based alkaloid: Posaconazole has also been used as antifungal drug.[7-10]

Heterocyclic compounds can be segregated into heteroaromatic and hetero alicyclic types. In general, the chemistry of hetero alicyclic compounds is identical to that of their aliphatic parallel such as ether, amide, amines, thioether etc. Their properties are especially impacted by the occurrence of ring strain.[11-13]

The compounds enclosing benzothiazole fraction are of excessive attention and have been broadly used in pharmaceutical chemistry and agricultural division. In calculation, benzothiazole forms an imperative pharmacophore in herbicidal, fungicidal and insecticidal agents.[14,15]

Benzylidene derivatives have the property of 'Schiff base'due to the azomethine group (-HC=N-). They are obtained by condensation of ketones (or) aldehydes under acids or base catalysis or with heat.They were first described by HugoSchiff in 1864.[16-18]

The mesomorphic behaviour of benzylidene derivatives of benzothiazole is due to its molecular structure including linking, terminal and core groups.[19-21]

The benzylidene benzothiazole exhibit nematic phase in the form of droplet texture under polarizing microscope and on cooling, fan shaped texture was observed.[22]

The Aim of the present study is to synthesize bezylidene derivatives of benzothiazole from 2-(4-aminophenyl)benzothiazol-5-ol as starting compound in which NH_2 and endocylic N functions are suitably situated to enable reaction with common electrophillic agents to form a variety of fused heterocyclic derivatives.

II. EXPERIMENTAL

A. Synthesis of 2-(4-aminophenyl)benzothiazol-5-ol (1) [23]

It was synthesized in four steps as follows:

1) *Step I:* Preparation of [(4-hydroxyphenyl)-4-azaneyl) (4-nitrophen)] methanone (a) To a solution of p-amino phenol and p-nitrobenzoylchloride,pyridine (40 ml) was added followed by the addition of toluene (30 ml) and the mixture was refluxed for 5hrsThe product obtained was recrystallized from alcohol. Yield: 60%, m.p- 150^{0}C

2) *Step II:* Preparation of N-(4-hydroxyphenyl)-4nitrobenzo thioamide (b) To an ethanolic solution of compound a, Lawesson's reagent [2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide] (0.6 molar eq) was added. The mixture was heated for 2hrs after which it was dried and recrystallised from alcohol. Yield: 65%, m.p :160^{0}C
3) *Step III:* Preparation of 2-(4-nitrophenyl)benzothiazol-6-ol (c) To a benzene solution of compound b,0.5 ml ethanol and 1ml NaOH was added. The freshly prepared aqueous potassium ferricynide(2-3 molar equivalent) was added to a cooled solution in an ice bath and stirred at room temperature. Then the mixture was neutralized with 1M HCl. The organic layer was removed and residue was washed with water and recrystallised from alcohol. Yield: 50 % ,m.p-120^{0}C
4) *Step IV:* Preparation of 2-(4-aminophenyl)benzothiazol-5-ol (1) To an ethanolic solution of compound c, 10 ml water,4 g iron powder and 7g ammonium chloride was added. The mixture was stirred at 850C for one hr. cooled at room temp. then filtered and washed with water and recrystallised from alcohol. Yield: 65%,m.p-148^{0}C.

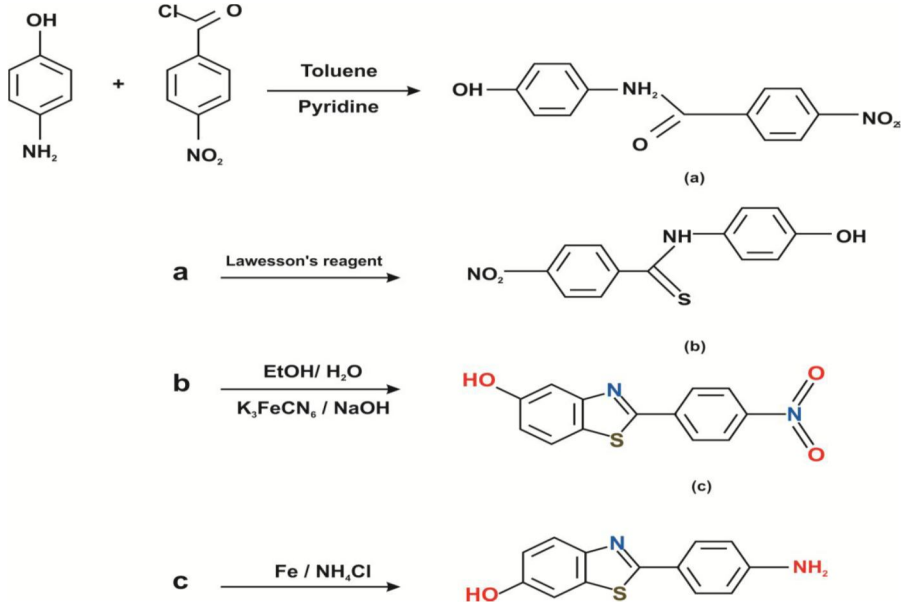

Fig 1 - Synthesis of 2-(4-aminophenyl)benzothiazol-5-ol (1)

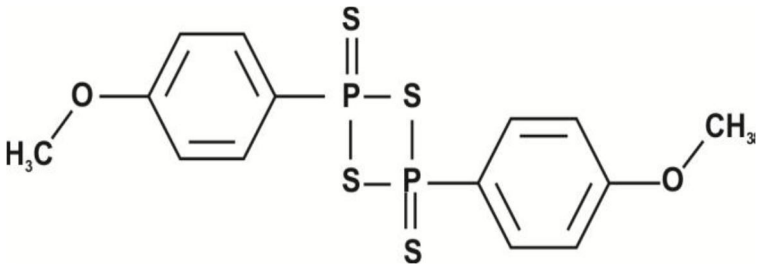

Fig 2 - Lawesson's Reagent

B. Synthesis of Benzothiazole derivatives (P201-P204)[24]

A solution of 2-(4-aminophenyl) benzothiazol-5-ol(1) (0.0055 mole) and 4-hydroxy, 4-methoxy, 4-chloro benzaldehyde and furfuraldehyde (20mol) was prepared in absolute ethanol (100ml) and refluxed for 3hrs in the presence of acetic acid.The product obtained,was washed with water, dried and recrystallized from alcohol.

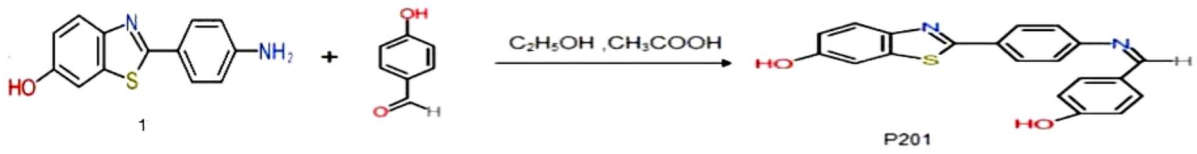

Fig 3- synthesis of 2-(4-[(4-hydroxybenzylidene)amino]phenyl)benzothiazole-5-ol (P201)

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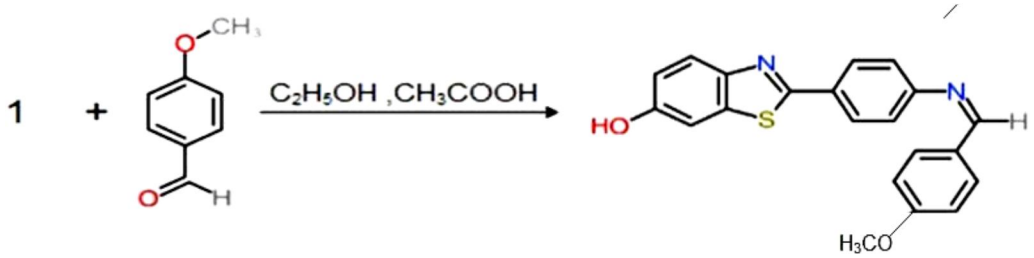
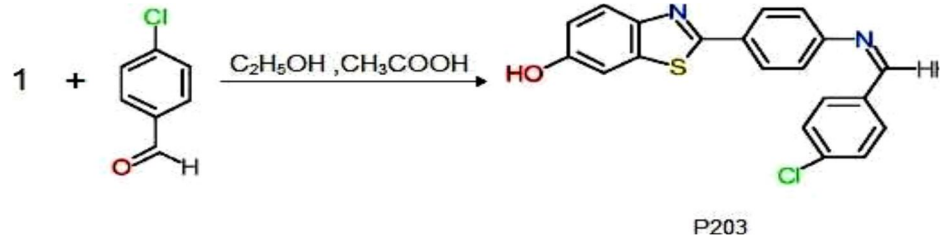
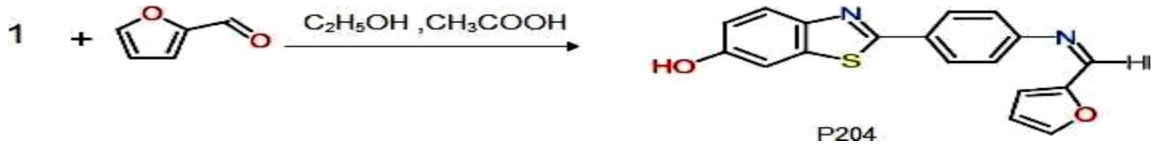


Fig 4- synthesis of 2-(4-[(4-methoxybenzylidene) amino]phenyl) benzothiazole-5ol (P202)



P203

Fig 5-synthesis of 2-(4-[(4-chlorobenzylidene)amino]phenyl)benzothiazole-5-ol(P203)



P204

Fig 6- synthesis of 2-(4-[(furan-2-ylmethylene)amino]phenyl)benzothiazole-5-ol(P204)

C. Synthesis of dimethyl[4-(5-hydroxybenzothiazol-2- yl)phenyl]carbonimidodithioate (P205) [25]

To a well stirred ice cold solution of 1 (0.05 mole) in DMF (20 ml) , an aqueous solution of 10 M NaOH (5ml),carbondisulphide (0.10 mole) and methyl iodide (0.05 mole) was added in sequence at an interval of 30 min. with continous stirring for 3hrs. Then mixture was poured into ice cold water. The product P205 was obtained ,washed with water and recrysatallised from alcohol.

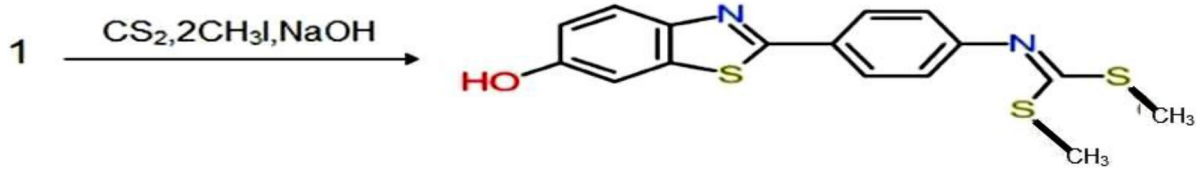


Fig 7- synthesis of Dimethyl(4-(5-hydroxybenzothiazol-2 yl) phenyl) carbonimidodithioate (P205)

III. RESULTS AND DISCUSSIONS

A. Proposed mechanism for the synthesis of (P201-P204)

This is acid catalysed condensation between 1 and 2 giving P201-P204

B. Proposed mechanism for the synthesis of P205

The mechanism involves the base catalyzed reaction of CS_2 with amine group of 1 forming a diamine (i) which then undergoes S-alkylation with CH_3I forming dimethyl (4-(5-hydroxybenzothiazol -2-yl)phenyl) carbonimidodithioate (P205)

C. The Spectral data of the synthesized compounds are as followes-

Spectral data of 2-(4-[(4-hydroxy benzylidene)amino]phenyl) benzothiazol-5ol(P201)

IR(KBr)Cm^{-1}	3427.52(Ar-OH)etc.
^{1}HNMR(400MHzDMSO)ppm	8.32 & 8.14(Ar-OH),6.06-7.71(Ar-H),5.90(=CH)
^{13}CNMR(400MHzDMSO)ppm	167.57,165.91,163.02,159.76,154.12,152.48,151.56,148.87,140.78,136.90,130.52,128.10,122.31,119.43,115.67,114 .74,112.59,112.54

Spectral data of 2- (4[(4methoxybenzylidene)amino]phenyl)benzothiazole -5ol(P202)

IR(KBr)Cm^{-1}	3291.9(O-H) 1108.4(O-CH_3)etc.
^{1}HNMR(400MHzDMSO)ppm	10.30(Ar-OH),6.5-8.32(Ar-H)3.75(OCH_3)
^{13}CNMR(400MHzDMSO)ppm	162.92,134.05,148.63,128.97,114.85,79.12,40.11,39.70,39.07,38.86

Spectral data of 2-(4-[(4-chloro benzylidene)amino]phenyl) benzothiazol-5-ol(P203)

IR(KBr)Cm^{-1}	3371(O-H),803.76(C-Cl)etc.
^{1}HNMR(400MHz DMSO)ppm	8.19(O-H),6.05-7.34(Ar-H),4.32(=CH)
^{13}CNMR(400MHzDMSO)ppm	167.57,163.02,159.76,151.56,136.90,132.01,130.52,128.91,123.33,122.05, 119.43,115.67,113.14,112.54

Spectral data of 2-(4-[(furan-2-ylmethylene)amino]phenyl) benzothiol- 5 -ol(P204)

IR(KBr)Cm^{-1}	3377(O-H) etc.
^{1}HNMR(400MHzDMSO) ppm	8.1(Ar-OH),6.0-7.34(Ar-H),4.32(=CH)
^{13}CNMR(400MHzDMSO)ppm	155.44,134.61,127.65,125.91,122.41,118.66,108.65,79.25,78.92 ,78.60,40.1139.27,39.00,38.85

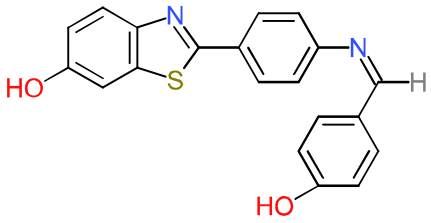
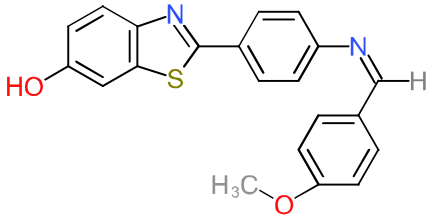
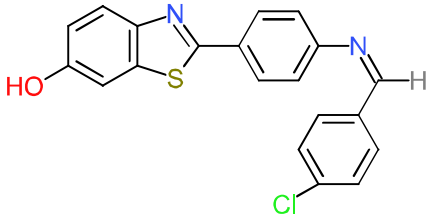
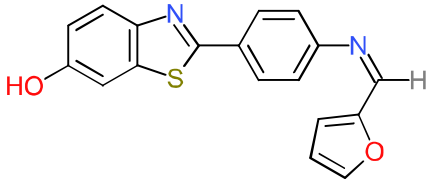
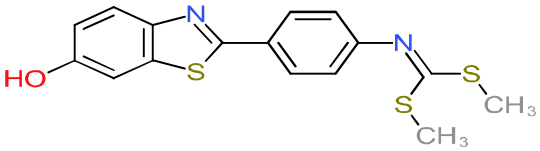
Spectral data of Dimethyl [4-(5-hydroxy benzothiazole-2-yl)phenyl] carbonimid odithioate (P205)

IR(KBr)Cm^{-1}	3258.28(O-H) ,1658.45(C=N) etc.
^{1}HNMR(400MHzDMSO) ppm	9.3035(O-H),6.51-8.32(Ar-H) ,2.51(CH_3)
^{13}CNMR(400MHzDMSO) ppm	162.92,154.05,148.78,140.63,130.02,122.24,114.85

IV. CONCLUSSION

The present work describes convenient methods for the synthesis of Benzothiazole derivatives. Benzothiazole derivatives were synthesized from the 2-(4-aminophenyl) benzothiazol-5-ol, which was synthesized by the Jacobson method using Lawesson's reagent.Five benzylidene derivatives (P201-P205) were synthesized by catalyzed condensation and acylation method,named as 2-(4-((4 hydroxybenzylidene)amino) phenyl) benzothiazole-5-ol **(P201)**, 2-(4-((4- methoxybenzylidene) amino)phenyl)benzothiazole-5ol **(P202)**, 2-(4-((4-chlorobenzylidene) amino)phenyl)benzothiazole-5-ol **(P203)**, (4-((furan-2-ylmethylene) amino)phenyl)benzothiazole-5-ol **(P204),** Dimethyl(4(5hydroxy benzothiazol2yl)phenyl)carbonimidodithioate**(P205)**

Table : Summary of the synthesized compounds.

Product code	Structure
P201	
P202	
P203	
P204	
P205	

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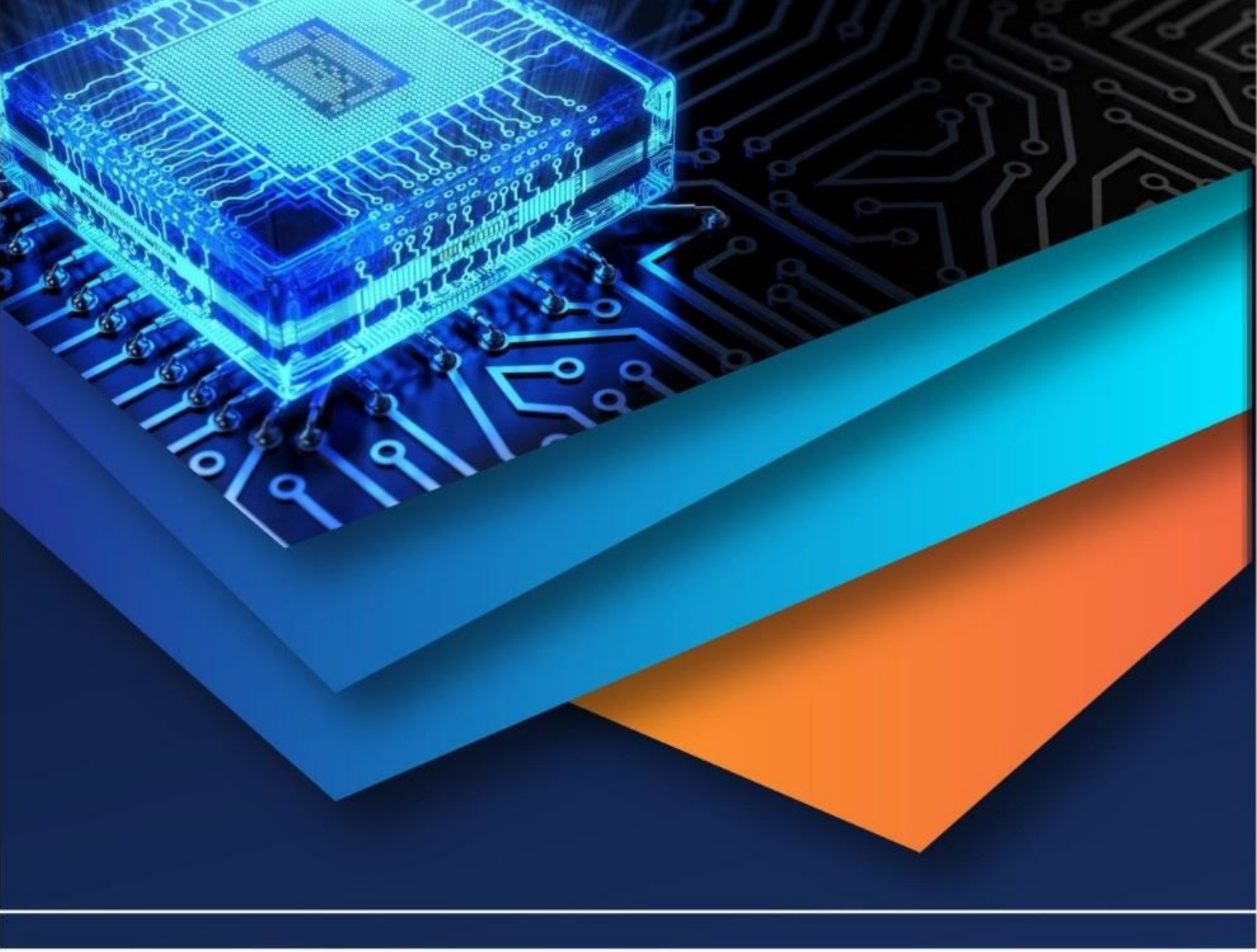

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