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Synthesis and Theoretical Calculations of 2-(*p*-Tolyl)-2,3-Dihydro-1*H*-Perimidine using Density Functional Theory

VISHNU A. ADOLE[1]* and GANESH B. YELMAME[2]

[1]Department of Chemistry, Mahatma Gandhi Vidyamandir's Arts, Science and Commerce College, Manmad, Nashik-423 104, India. (Affiliated to SP Pune University, Pune).
[2]Department of Chemistry, Mahatma Gandhi Vidyamandir's SPH Arts, Science and Commerce College, Nampur, Nashik- 423204, India. (Affiliated to Savitribai Phule Pune University, Pune).

Abstract

In the present study, 2-(*p*-tolyl)-2,3-dihydro-1*H*-perimidine (**TDHP**) is synthesized from 1,8-naphthalenediamine and 4-methylbenzaldehyde by embedding a one-carbon unit between the nitrogen followed by ring closure using green chemistry approach. ^{1}H NMR and ^{13}C NMR spectral techniques were used to validate the structure of the **TDHP**. The synthesized perimidine **TDHP** is studied using density functional theory (DFT) to provide valuable insights into structural, chemical, and thermochemical study.The structural and chemical properties of **TDHP** were computed using the DFT method on the B3LYP/6-311G(d,p) basis package. Bond lengths were predicted from the optimized molecular structure, and the physical and chemical properties of the molecules were inferred as a consequence. The HOMO and LUMO are computed, and quantum chemical parameters are determined using electronic energies. The calculated HOMO-LUMO energy gap is 4.25 eV indicating charge transfer phenomenon within the molecule. The electron density and chemical behaviour of the **TDHP** was predicted using Mulliken atomic charges and the molecular electrostatic surface potential plot. Amongst all carbon atoms, the C8 carbon as more positive and C27 as more negative carbon atoms. The high global electrophilicity index suggests electrophilic character of the **TDHP**. The harmonic vibrational frequencies were used to measure total energy, total molar entropy, and molar heat capacity.

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CONTACT Vishnu A. Adole ✉ vishnuadole86@gmail.com Department of Chemistry, Mahatma Gandhi Vidyamandir's Arts, Science and Commerce College, Manmad, Nashik-423 104, India. (Affiliated to SP Pune University, Pune).

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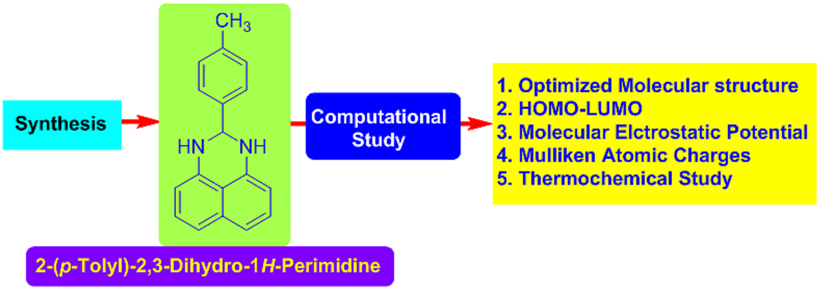


Graphical abstract

Introduction

Perimidine is a tri-cyclic heterocycle comprising two nitrogen atoms at the first and third positions, which enhances pi-electrons' delocalization to the naphthalene ring from the fused heterocyclic ring. Perimidines' biological behaviour has been the topic of numerous journal entries in recent years. Perimidines are robust motifs and an interesting family of N-heterocycles that have advanced significantly in recent years as a result of their wide range of uses in life sciences, medicine, and industrial research. Their way to interact molecularly with protein molecules, form complexes with metal, and behave differently in different light wavelengths renders themselves increasingly enticing for potential use.Perimidines are of great interest to researchers because of their broad variety of biological activities.[1,2] The biological profile of several perimidine hybrids is found to be explored in numerous applications such as Pd(II) complexes derived from perimidine ligand for *in-vitro* antimicrobial applications,[3] antioxidant properties of transition metal complexes of perimidine ligand,[4] anti-inflammatory studies of transition metal complexes of 1*H*-perimidine derivatives,[5] 2-phenylazonaphtho[1,8-*ef*][1,4] diazepines and 9-(3-arylhydrazono) pyrrolo [1,2-*a*] perimidines as antitumor agents,[6] oxo-7*H*-benzo [*e*] perimidine-4-carboxylic acid derivatives as potent, nonpeptidecorticotropin releasing factor (CRF) receptor antagonists,[7] and 3-Chloro-1-(4-perimidine methylcarbonylamino)-4-phenyl-azetidin-2-one for antibacterial and antifungal activities.[8] Besides, 1-alkylperimidineruthenium (II) complexes were used for catalytic applications,[9] N-xylyl-N′-methylperimidinecarbene iridium complexes as catalysts for C–H activation and dehydrogenativesilylation,[10] perimidin-2-ylidene rhodium(I) complexes for transfer hydrogenation reaction,[11] Perimidine based synthetic receptors for identification of cupric ionin water solution,[12] 2,3-dihydroperimidine derivatives for lubricants,[13] etc.

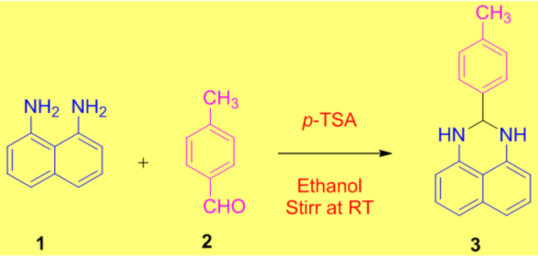
Theoretical calculations such as DFT has been used to identify various structural, molecular and spectral properties(*E*)-7-(arylidene)-indanones,[14] 2-(3-bromophenyl)-4-(4-bromophenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine,[15] 2-(2-hydrazineyl) thiazole derivatives,[16] (3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-1-yl)(phenyl) methanone,[17] 2-(5-methyl-1-benzofuran-3-yl) acetic acid,[18] 2,4-dibromoaniline,[19] 5-Methoxy-1*H*-benzo[*d*]imidazole-2(3*H*)-thione,[20] etc. Besides, DFT methodology has been efficiently used for studying electronic and structural properties of graphyne oxide for CO, CO_2 and NH_3 adsorption phenomena,[21] exploration of structural and mechanical properties of pristine and adsorbed puckered arsenene nanostructures ,[22] investigation of kinetics and mechanism of oxidation of bromothymol blue,[23] etc.The DFT method with appropriate basis set is found to envisage spectroscopic properties like UV-Visiblein terephthalic acid,[24] 7-hydroxy-3(4-methoxyphenyl)chromone,[25] bis(thiourea)nickel chloride,[26] NMR study inN,N′-bis(salicylidene)-1,2-phenylenediamine,[27] 3-fluorophenylboronic acid,[28] 5-bromo-2-ethoxyphenylboronic acid (monomer and dimer structures),[29] 5-(3-pyridyl)-4*H*-1,2,4-triazole-3-thiol,[30] veratrole,[31] Raman investigation[32-35] and IRassignments' study in5-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole,[36] (*E*)-1-(2,3-dihydrobenzo [*b*][1,4] dioxin-6-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one,[37] dihydropyrimidinones,[38] (2*E*)-3-(2,6-dichlorophenyl)-1-(4-fluoro)-prop-2-en-1-one,[39] ethyl-4-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate,[40] indole-3-carboxylic acid.[41]

The DFT approach with the B3LYP functional has been shown to predict theoretical properties that are in good agreement with experimental spectroscopic results.[42-45] Using the B3LYP functional with a 6-311G(d,p) basis set, the assignment of absorption bands and, as a result, the prediction of electronic and chemical properties of molecules is found to be accurate. [46, 47] Energized by all above mentioned aspects, in the present study, we have synthesized, characterized and studied 2-(*p*-tolyl)-2,3-dihydro-1*H*-perimidine using DFT method with B3LYP/6-311G(d,p) basis set.This is first report on DFT study of the **TDHP**compound. For the **TDHP** molecule, no work on DFT analysis for the exploration of structural, electronic, and chemical parameters has been done to date.Structural parameters using optimized molecular structure have been obtained. The optimized structure provides the information of geometrical parameters, stability of the molecule and also polarity. With the help of geometry optimization, HOMO-LUMO energies are computed and these are further used for the determination of electronic and global reactivity parameters. I have predicted the electronic properties such asionization potential energy (I)electron affinity (A) and global reactivity attributes such as hardness (η), softness (S), electronegativity (χ), chemical potential (μ) and electrophilic index (ω) with the help of HOMO-LUMO energies.The band gap energy and frontier molecular orbitals (FMOs) are established and examined. The molecular electrostatic surface potential is established by using optimized structure and being used to locate sites for electrophilic and nucleophilic attacks.

Materials and Methods

General Remarks

The 1,8-diamino naphthalene (Purity: 99%, Make: sigma Aldrich) and *p*-Tolualdehyde (Purity: 98%, Make: Alfa aesar) chemicals were purchased from Virion Enterprises, Mumbai. The chemicals were used exactly as they were obtained, with no further purification needed.Melting point was determined in open capillary and uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker using DMSO-*d*6 solvent on 400 MHz NMR Spectrometer. Thin-layer chromatography using aluminium sheets with silica gel 60 F254 (Merck) was used to track the completion of the reaction.



Scheme 1 Synthesis of title compound

Table 1: Physicochemical and spectral data of title compound

Systematic Name of the Product	2-(*p*-tolyl)-2,3-dihydro-1*H*-perimidine
Abbreviation used	**TDHP**
Physicochemical data	Yield: 85 %, M.P: 147^{0}C, Colour: Faint brown
^{1}H NMR (400 MHz, DMSO)δ	9.98 (s, 1H), 8.34 – 8.22 (m, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.35 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.99 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.71 (t, *J* = 18.7 Hz, 1H), 6.64 (s, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 6.51 (d, *J*= 8.1 Hz, 1H), 4.61 (s, 1H), 2.44 (s, 3H)
^{13}C NMR (400 MHz, DMSO) δ	143.59, 139.31, 138.18, 134.83, 129.15, 128.25, 127.28, 115.62, 112.92, 104.72, 66.62, 21.27

Synthesis of TDHP

In the past, the *p*-TSA was employed for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one derivatives.[48] Based on this we tried the synthesis of **TDHP** using *p*-TSA using 2 mol% catalyst dose and to our credit, we got good results in terms of synthetic efficiency. We did not switch our attention for optimizing the reaction conditions as our main goal of the present research is study of structural, electronic and chemical nature of the **TDHP** molecule.In a standard reaction procedure, a mixture containing naphthalene-1,8-diamine (**1**, 0.01mol), *p*-toluene benzaldehyde (**2**, 0.01 mol) and p-TSA (2 mol%) in ethanol (5 mL) were taken in a conical flask and stirred at room temperature for 30 minute on magnetic stirrer. After completion of the reaction (monitored by TLC), the crude product was obtained simply filtration and the it was purified by recrystallization to provide the perimidine derivative (**3**): 2-(*p*-tolyl)-2,3-dihydro-1*H*-perimidine **(Scheme 1**). The physicochemical and spectral data of title compound is given in **Table 1.**

Table 1: Optimized geometrical parameters of TDHP by DFT/ B3LYP with 6-311G (d,p) basis set

Bond lengths (Å)			
C1-C2	1.3788	C11-H27	1.103
C1-C6	1.4111	C11-N33	1.4712
C1-H13	1.0864	C11-N35	1.4571
C2-C3	1.4198	C17-C18	1.3991
C2-H14	1.0863	C17-C19	1.399
C3-C4	1.4298	C18-C20	1.3926
C3-C7	1.4211	C18-H21	1.0869
C4-C5	1.4253	C19-C22	1.3953
C4-C8	1.431	C19-H23	1.0858
C5-C6	1.3839	C20-C24	1.4022
C5-N35	1.4157	C20-H25	1.0872
C6-H15	1.0858	C22-C24	1.3999
C7-C10	1.3776	C22-H26	1.0872
C7-H12	1.086	C24-C29	1.5103
C8-C9	1.3853	C29-H30	1.0971
C8-N33	1.3979	C29-H31	1.0946
C9-C10	1.4118	C29-H32	1.0936
C9-H28	1.087	N33-H34	1.0139
C10-H16	1.0865	N35-H36	1.0142
C11-C17	1.5149	-	-

Computational Details

DFT measurements of a **TDHP** molecule were conducted using the Gaussian 03 software package.[49] The molecular structure of the **TDHP**molecule in the ground state was optimized using the density functional theory (DFT/B3LYP)[50, 51] with the 6-311G(d,p) basis set.[52, 53] All the quantum chemical calculations for the **TDHP** compound were performed at B3LYP/6-311G(d,p) level and corresponding molecular drawing was done with the aid of the Gauss View 4.1.2 visualization programme.[54] Thermochemical data were obtained using harmonic vibrational frequencies.

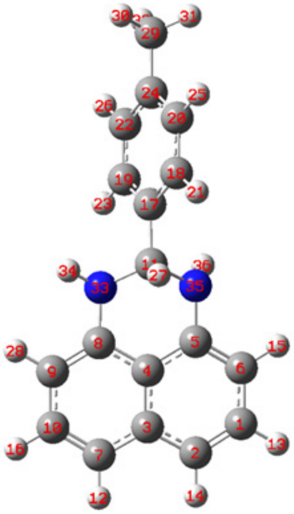


Fig.1:Optimized molecular structure TDHP by DFT/ B3LYP with 6-311G(d,p) basis set

Results and Discussion

Geometrical Parameters

The optimized molecular structure of the title molecule is given in **Figure 1. Table 1** shows the optimized geometric parameter bond lengths by B3LYP with the 6-311G(d,p) basis set. The B3LYP method is well known for predicting geometrical parameters that are closer to experimental results, as discussed in the literature.[55] B3LYP/6-311G(d,p) is taken into consideration for these purposesin the present discussion.The information about bond lengths is very crucial to get insights into inter and intra molecular interactions, hydrogen bonding effects and also chemical reactivity patterns.[56-58] For the title compound, the bonds C5-N35 and C8-N33 are having 1.4157 Å and 1.3979 Å respectively. This will makenitrogen atom of C5-N35 bond better nucleophile since the bonding electrons are more polarized due to longer bond length.When acidic nature of H34 and H36 is compared, it is observed that H36possessmore acidic strength which is supported by their bond lengths and Mulliken atomic charge values. The bond length values of N33-H34 and N35-H36 bonds are 1.0139 Å and 1.0142 Å respectively. In the naphthalene ring of the **TDHP** compound, C1-C2 andC7-C10 bonds possess nearly same bond lengths and importantly these two bonds are found to contain maximum double bond character and thereby render electrophilic aromatic substitution reactions more probable at these bonds. The C2 and C9 positions are more prone towards electrophilic attack. In this way the knowledge about bond length values provides valuable insights into physical and chemical properties of the **TDHP** compound.

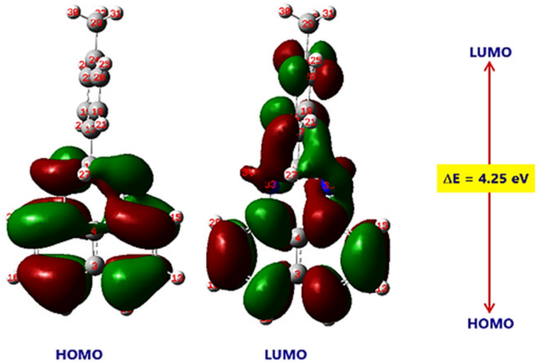


Fig. 2: Frontier molecular orbitals and HOMO-LUMO energy gap

Table2: The HOMO–LUMO energy and reactivity descriptor values of the TDHP Molecule calculated in the gas phase

Molecular properties	Calculated values
E_{HOMO} energy	-4.85 eV
E_{LUMO} energy	-0.60 eV
$E_{LUMO} – E_{HOMO}$ energy gap (ΔE)	4.25 eV
Electron affinity (A)	0.60 eV
Ionization energy (I)	4.85 eV
Chemical hardness (η)	2.12 eV
Chemical softness (S)	0.47eV-1
Chemical potential (μ)	-2.72 eV
Electrophilicity index (ω)	1.75 eV

Frontier Molecular Orbital Analysis

HOMO and LUMO are called as frontier molecular orbitals (FMOs) and very crucial for assessing a molecule's reactivity and stability. HOMO and LUMO are linked with electron-donating and electron-accepting capabilities respectively. The narrower the energy difference between HOMO and LUMO, the more stable a molecule becomes. A decrease in stability, polarizability, and electron transport in a molecule occurs as the HOMO-LUMO energy gap is increased. Since they relate to ionization potential energy and electron affinity, respectively, the HOMO and LUMO energy values are very important to understand the electronic nature of the molecules. The HOMO-LUMO pictures are given in Figures 2. The HOMO–LUMO energy and reactivity descriptor values of the **TDHP** Molecule are calculated in the gas phase and presented in **Table 2.** The HOMO is observed to be principally on naphthalene ring. The HOMO energy in the title molecule is -4.85 eV and LUMO energy is -0.60 eV. When predicting the reactivity pattern between the **TDHP** compound and other molecules, the HOMO-LUMO values of the **TDHP** compound could be compared to the HOMO-LUMO values of the other molecules. The estimated band gap value is 4.25 eV. The electron affinity and ionization potential values are 0.60 and 4.85 eV. The global reactivity parameter values are calculated using Koopman's theorem.[59]The global reactivity parameters like chemical hardness (η), chemical softness (S), chemical potential (μ) and electrophilicity index (ω) are calculated using HOMO-LUMO energies. The calculated chemical hardness and chemical softness values are 2.12 eV and $0.47eV^{-1}$ respectively.These two values are critical in determining the polarizability of the **TDHP** compound. The existence of intermolecular interactions and chemical reactivity may be predicted by comparison with other molecules. The electrophilicity index value in the title molecule is 1.75 eV.The electrophilicity index is greater than 1.5 eV that indicates the **TDHP**compound could accept the electrons.[58] The chemical potential value is 2.72 eV.

Mulliken Atomic Charges

Mulliken charges for the **TDHP** molecule are determined using the B3LYP/6-311G(d,p) method and are described in **Figure 3** and **Table 3** to estimate the net atomic populations in the **TDHP** molecule. Mulliken atomic charges calculation remains essential in the implementation of quantum chemical calculations to molecules because atomic charges impact several attributes of molecules. The two nitrogen atoms of the title molecule are found to be most negative in terms of Mulliken atomic charge with -0.610591 and -0.596207Mulliken atomic charge values for N33 and N35 atoms. The C8 atom is the most positive atom with Mulliken atomic charge value of 0.289643. All hydrogen atoms in the title molecule are positive in terms of Mulliken atom charge.

Table 3: Mulliken atomic charges computed at B3LYP/6-311G (d,p) method

Atom	Mulliken atomic charge
1 C	-0.093114
2 C	-0.140902
3 C	0.091281
4 C	0.051997
5 C	0.248417
6 C	-0.123987
7 C	-0.144325
8 C	0.289643
9 C	-0.145986
10 C	-0.090983
11 C	0.169852
12 H	0.074204
13 H	0.080591
14 H	0.076251
15 H	0.078505
16 H	0.079317
17 C	0.037742
18 C	-0.104867
19 C	-0.113417
20 C	-0.123714
21 H	0.090465
22 C	-0.125990
23 H	0.103043
24 C	0.128424
25 H	0.081299
26 H	0.081192
27 H	0.100655
28 H	0.067192
29 C	-0.381613
30 H	0.128129
31 H	0.118828
32 H	0.113955
33 N	-0.610591
34 H	0.246391
35 N	-0.596207
36 H	0.258324

Molecular Electrostatic Surface Potential and Thermochemistry Analysis

The molecular electrostatic surface potential (MESP) plotof the **TDHP** molecule given in **Figure4** is used to investigate the chemical reactivity of the title molecule, and it is plotted over the optimized electronic structure of the title compound using density functional B3LYP level with 6-311G(d,p) basis collection. Since it was established in space around a molecule by the charge distribution, the MESP plot is quite valuable in studying the reactive sites for nucleophilic and electrophilic attacks, hydrogen bonding interactions and also in the biorecognition processes. Different colours represent different electrostatic potential values: red symbolizes negative electrostatic potential, blue denotes positive electrostatic potential, and green depicts less positive electrostatic potential. In the title molecule the negative potential is around nitrogen atom and also around naphthalene ring system indicating high electron density which indicatesits reactivity as nucleophile. The highest positive potential is found around hydrogen atoms attached to the nitrogen atoms. The hydrogen atoms are expected to react with bases to form anions. The *p*-tolyl ring system possesses less positive electrostatic potential values.

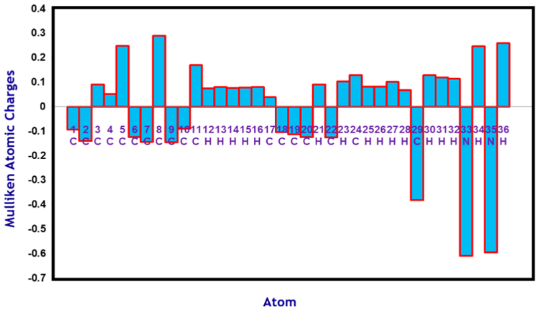


Fig. 3: graphical presentations of Mulliken atomic charges

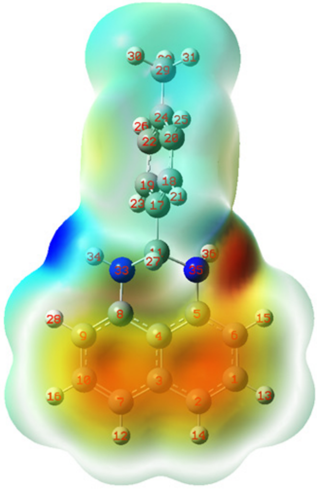


Fig. 4: MESP plot of title compound

The statistical analysis thermodynamic functions: total thermal energy, heat capacity, and entropy for the **TDHP** compound were obtained from the theoretical harmonic frequencies and described in Table 4 based on vibrational analysis at the B3LYP/6-311G(d,p) stage.

Table 4: Thermodynamic functions of title compound calculated in the gas phase

Entry	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Electronic	196.199	64.274	128.241
Translational	0.000	0.000	0.000
Rotational	0.889	2.981	42.568
Vibrational	0.889	2.981	33.847
Total	194.422	58.312	33.847

Conclusion

The **TDHP** compound was synthesized using green chemistry approach and ^{1}H and ^{13}C NMR spectroscopy was used to affirm the molecular structure of the synthesised compound **TDHP**. DFT calculations were used to determine the molecular structural parameters, HOMO–LUMO analysis, MESP plot, Mulliken atomic charges, and thermodynamic properties of the title compound for optimized geometry. The geometry was optimised using the DFT/B3LYP/ method with the 6-311G(d,p) basis set without any symmetry constraints. According to the optimized molecular structure and bond length details, C1-C2 and C7-C10 bonds are more vulnerable to electrophilic attack. N35 was revealed to be more reactive to acidic reagent. The two nitrogen atoms in the title molecule are the most negative and on the other hand hydrogen atoms in the title molecule are positivein terms of Mulliken atomic charge. According to MESP, negative potential around the nitrogen atom and even around the naphthalene ring structure in the title molecule shows a high electron density, suggesting its reactivity as a nucleophile. Besides, some thermochemical insights are provided. We conclude that the results of this analysis will allow for further research into the physical and chemical properties of the **TDHP** and related perimidine derivatives.

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Conflict of Interest

Authors declared that they do not have any conflict of interest regarding this research article.

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