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Non-classical periodic boundary value problems with impulsive conditions

Sevda Nur Öztürk¹, Oktay Mukhtarov², Kadriye Aydemir³

Keywords

Non-classical periodic boundary value problems, Eigenvalues, Eigenfunctions, Impulsive conditions **Abstract** — This study investigates some spectral properties of a new type of periodic Sturm-Liouville problem. The problem under consideration differs from the classical ones in that the differential equation is given on two disjoint segments that have a common end, and two additional interaction conditions are imposed on this common end (such interaction conditions are called various names, including transmission conditions, jump conditions, interface conditions, impulsive conditions, etc.). At first, we proved that all eigenvalues are real and there is a corresponding real-valued eigenfunction for each eigenvalue. Then we showed that two eigenfunctions corresponding to different eigenvalues are orthogonal. We also defined some left and right-hand solutions, in terms of which we constructed a new transfer characteristic function. Finally, we have defined asymptotic formulas for the transfer characteristic functions and also for the eigenvalues. The results obtained are a generalization of similar results of the classical Sturm-Liouville theory.

Subject Classification (2020): 34B24, 34L10

1. Introduction

Since the middle of the 19th century, an extensive theory of Sturm-Liouville problems (SLP), as well as the spectral theory of linear differential operators in Hilbert spaces, has been developed in connection with applications in physics and engineering. Many mathematical physics problems, such as heat and mass transfer problems, the vibrations of a drum membrane or violin strings, and the motion of a particle in the matter, are modeled by SLPs [1]. For example, consider the wave equation

$$sw_{yy} = div\left(q\nabla w\right) - tw$$

with w = w(x, y) where x changes in the domain of interest belonging to the Euclidean space \mathbb{R}^2 or \mathbb{R}^3 , s(x) > 0, $q(x) \ge 0$, and $t(x) \ge 0$ are given functions of the spatial variables. Using the separation of independent variables method, we will look for a separate solution of the form $w = v(x)\theta(y)$. Such

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a separated solution satisfies the wave equation if and only if

$$\frac{\theta''}{\theta} = \frac{\operatorname{div}\left(q\nabla \upsilon\right) - t\upsilon}{(s-q)\upsilon}$$

holds for all (x, y). Both sides of this equality must be constant, here λ . Consequently, we have a simplest Sturm-Liouville equation

$$-\theta'' + \lambda\theta = 0$$

We know that, in typical real-world applications, the separation parameter λ is a negative number. So the separated solutions $w(x, y) = \theta(y)v(x)$ are periodic in time variable y. In particular, Sturm-Liouville equations with real periodic coefficients and/or with periodic boundary conditions have been paid much attention due to the need to solve many periodic phenomena that arise in natural sciences. A description of the most qualitative properties of periodic differential equations of second order, in part summarized, is given in books [1,2]. Further results relating to the spectral theory of differential equations are given in [3–5]. Various methods have also been developed to solve various types of Sturm-Liouville problems (see, for example, [2–8] and references cited therein)

Recently, there has been an increasing interest in Sturm-Liouville boundary value problems defined on two or more disjoint segments with common ends, the so-called many-interval SLPs (see, for example, [9–21] and references cited therein). To deal with such multi-interval boundary value problems, naturally, additional conditions (the so-called transmission conditions, jump conditions, interface conditions, and impulsive conditions) are imposed at these common endpoints.

In this study, we will consider the two-interval Sturm-Liouville equation

$$-u''(x) + (q(x) - \lambda) u(x) = 0, \ x \in [-1, 0] \cup (0, 1]$$
(1.1)

together with periodic boundary conditions, given by

$$u(-1) = u(1) \tag{1.2}$$

$$u'(-1) = u'(1) \tag{1.3}$$

and with additional conditions (the so-called transmission conditions or impulsive conditions) at the point of interaction x = 0, given by

$$u(0+) = u'(0-) \tag{1.4}$$

$$u'(0+) = \alpha u'(0-) - u(0-) \tag{1.5}$$

where α is a real number and q(x) is a real-valued function which is continuous on each of intervals [-1,0) and (0,1] and has a finite left and right-hand limit values $q(0\pm) = \lim_{x\to 0\pm} q(x)$.

2. Preliminaries

This section presents some of the basic notions employed in the following sections.

Theorem 2.1. If λ is an eigenvalue of the Sturm-Liouville boundary-value transmission problem (1.1)-(1.5), then it must be a real number.

Proof.

For brevity, we shall use the following notations

$$Lu := -u''(x) + q(x) u$$
$$P_1(u) := u(-1) - u(1), P_2(u) := u'(-1) - u'(1)$$

$$P_{3}(u) := u(0+) - u'(0-), P_{4}(u) := u'(0+) - \alpha u'(0-) + u(0-)$$

Let $u(x, \lambda)$ be an eigenfunction belonging to the eigenvalue λ , that is

$$Lu(.,\lambda) = \lambda \ u(.,\lambda) \tag{2.1}$$

$$P_i(u(.,\lambda)) = 0, \quad i = 1, 2, 3, 4$$
(2.2)

Then, by taking the complex-conjugates of the (2.1)-(2.2) and keeping in mind that the function q(x) is real valued and the coefficient α is a real number, we see that

$$L\overline{u(.,\lambda)} = \overline{\lambda} \ \overline{u(.,\lambda)}$$

$$P_i\left(\overline{u(.,\lambda)}\right) = 0, \quad i = 1, 2, 3, 4$$

$$(2.3)$$

It means that the function $\overline{u(x,\lambda)}$ is an eigenfunction belonging to the eigenvalue $\overline{\lambda}$. Using the above Equalities (2.1) and (2.3) we have

$$\overline{u(x,\lambda)}Lu(x,\lambda) - u(x,\lambda)L\overline{u(x,\lambda)} = \left(\lambda - \overline{\lambda}\right)u(x,\lambda)\overline{u(x,\lambda)}$$
(2.4)

Integrating (2.4) over [-1, 0) and (0, 1], we arrive at

$$\left(\lambda - \overline{\lambda}\right) \left(\int_{-1}^{0-} |u(x,\lambda)|^2 dx + \int_{0+}^{1} |u(x,\lambda)|^2 dx\right) = W\left(u(.,\lambda), \overline{u(.,\lambda)}; 1\right) - W\left(u(.,\lambda), \overline{u(.,\lambda)}; -1\right) \\ + W\left(u(.,\lambda), \overline{u(.,\lambda)}; 0-\right) \\ + W\left(u(.,\lambda), \overline{u(.,\lambda)}; 0+\right)$$

where $W\left(u\left(.,\lambda\right), \ \overline{u\left(.,\lambda\right)}; x\right)$ is the Wronskian of $u\left(x,\lambda\right)$ and $\overline{u\left(x,\lambda\right)}$, that is,

$$W\left(u\left(.,\lambda\right), \ \overline{u\left(.,\lambda\right)}; x\right) = u\left(x,\lambda\right) \ \overline{u'\left(x,\lambda\right)} - \overline{u\left(x,\lambda\right)}u'\left(x,\lambda\right)$$

Using boundary and transmission conditions, we get

$$W\left(u\left(.,\lambda\right), \ \overline{u\left(.,\lambda\right)}; 1\right) = W\left(u\left(.,\lambda\right), \ \overline{u\left(.,\lambda\right)}; -1\right)$$

$$(2.5)$$

and

$$W\left(u\left(.,\lambda\right), \ \overline{u\left(.,\lambda\right)}; 0+\right) = u\left(0+,\lambda\right), \ \overline{u'\left(0+,\lambda\right)} - \overline{u\left(0+,\lambda\right)}u'\left(0+,\lambda\right)$$
$$= u'\left(0-,\lambda\right)\left(\alpha \overline{u'\left(0-,\lambda\right)} - \overline{u\left(0-,\lambda\right)}\right) - \overline{u'\left(0-,\lambda\right)}(\alpha u'\left(0-,\lambda\right) - u\left(0-,\lambda\right))$$
$$= W\left(u\left(.,\lambda\right), \ \overline{u\left(.,\lambda\right)}; 0-\right)$$
(2.6)

respectively.

Equalities (2.5) and (2.6) permit us to restate Equality (2.5) as

$$\left(\lambda - \overline{\lambda}\right) \left(\int_{-1}^{0^{-}} |u(x,\lambda)|^2 dx + \int_{0^{+}}^{1} |u(x,\lambda)|^2 dx\right) = 0$$

$$(2.7)$$

Since the eigenfunction $u(x, \lambda)$ is a non-trivial solution of the problem (1.1)-(1.5), the last Equality (2.7) implies that $\lambda = \overline{\lambda}$. Thus the eigenvalue λ is real. \Box

Theorem 2.2. For every given eigenvalue λ , there is a real-valued eigenfunction corresponding to the given eigenvalue λ .

Proof.

Let $u(x,\lambda) = \eta(x,\lambda) + i\zeta(x,\lambda)$ be an eigenfunction corresponding to the eigenvalue λ , where η and ζ are real-valued functions. If we make the substitution $u = \eta + i\zeta$ in the problem (1.1)-(1.5) and separate real and imaginary parts, we have that both real-valued functions $\eta(x,\lambda)$ and $\zeta(x,\lambda)$ are

themselves eigenfunctions corresponding to the same eigenvalue λ . \Box

Definition 2.3. Let $L_2(-1,0) \oplus L_2(0,1)$ be the space consisting of all square-integrable functions on each of the intervals (-1,0) and (0,1). Then the number $\langle f,g \rangle$ defined by

$$\langle f,g\rangle := \int_{-1}^{0-} f(x)\overline{g(x)}dx + \int_{0+}^{1} f(x)\overline{g(x)}dx$$

is said to be the inner product of the functions f(x) and g(x).

Definition 2.4. Two eigenfunctions u(x) and v(x) are called orthogonal on the two-interval $[-1,0) \cup (0,1]$, if

$$\int_{-1}^{0-} u(x) \overline{v(x)} dx + \int_{0+}^{1} u(x) \overline{v(x)} dx = 0$$

Theorem 2.5. If λ_1 and λ_2 are distinct eigenvalues of the problem (1.1)–(1.5), then the corresponding eigenfunctions $u(x, \lambda_1)$ and $u(x, \lambda_2)$ are orthogonal.

Proof.

Multiplying the identities $Lu(x,\lambda_1) = \lambda_1 u(x,\lambda_1)$ and $L\overline{u(x,\lambda_2)} = \lambda_2 \overline{u(x,\lambda_2)}$ by $u(x,\lambda_2)$ and $u(x,\lambda_1)$, respectively, and then subtracting one from another, then using the well-known Lagrange identity [3], we have

$$W\left(u\left(.,\lambda_{1}\right),\overline{u\left(.,\lambda_{2}\right)};x\right) = \left(\lambda_{1} - \lambda_{2}\right)u\left(x,\lambda_{1}\right)u\left(x,\lambda_{2}\right)$$

Integrating this equality over the intervals $[-1,0) \cup (0,1]$, yields

$$(\lambda_1 - \lambda_2) \quad \left(\int_{-1}^{0-} u(x, \lambda_1) \,\overline{u(x, \lambda_2)} dx + \int_{0+}^{1} v(x, \lambda_1) \, v(\overline{x, \lambda_2}) dx \right) \\ = (Wu(., \lambda_1), u(., \lambda_2); x) \,|_{-1}^{1} + (Wu(., \lambda_1), u(., \lambda_2); x) \,|_{0-}^{0+}$$

As in the proof of the previous theorem, we can show that the right side of the last equality is equal to zero. Hence, the left side of this equality is also zero. Consequently, $\lambda_1 \neq \lambda_2$. \Box

Theorem 2.6. The periodic Sturm-Liouville boundary value transmission problem (1.1)-(1.5) is self-adjoint.

Proof.

Let ω and $\theta \in L^2[-1,0) \oplus L^2(0,1]$ that satisfies the given problem (1.1) - (1.5). Let it be

$$\Phi[\omega] := -\omega''(x) + q(x)\omega(x)$$

and

$$\Phi[\theta] := -\theta''(x) + q(x)\theta(x)$$

Multiplying the first by θ and the second by w and then subtracting yields,

$$\omega \Phi[\theta] - \theta \Phi[\omega] = \theta \omega'' - \omega \theta'' = \frac{d}{dx} \left(\theta \omega' - \omega \theta' \right)$$

By using, well known integral form of Lagrange's identity (see, for example, [3]), we obtain

$$\langle \omega, \Phi[\theta] \rangle - \langle \Phi[\omega], \theta \rangle = \left(\theta \frac{d\omega}{dx} - \omega \frac{d\theta}{dx} \right)_{-1}^{0-} + \left(\theta \frac{d\omega}{dx} \omega - \omega \frac{d\theta}{dx} \right)_{0+1}^{1-1}$$

That is,

$$\int_{-1}^{0-} \left(\omega\Phi[\theta] - \theta\Phi[\omega]\right) dx + \int_{0+}^{1} \left(\omega\Phi[\theta] - \theta\Phi[\omega]\right) dx = \left(\theta\frac{d\omega}{dx} - \omega\frac{d\theta}{dx}\right)_{-1}^{0-} + \left(\theta\frac{d\omega}{dx}\omega - \omega\frac{d\theta}{dx}\right)_{0+}^{1}$$
(2.8)

Since ω and θ satisfy the boundary transmission conditions (1.4) - (1.5), we have

$$\left(\theta \frac{d\omega}{dx} - \omega \frac{d\theta}{dx}\right)_{-1}^{0-} + \left(\theta \frac{d\omega}{dx} - \omega \frac{d\theta}{dx}\right)_{0+}^{1} = 0$$

Consequently, by Equality (2.8), we get

$$\langle \omega, \Phi[\theta] \rangle = \langle \Phi[\omega], \theta \rangle$$

3. Asymptotic Behaviours of the Left-Hand and Right-Hand Solutions

Let $v_1(x, \lambda)$ and $w_1(x, \lambda)$ be solutions of Equation (1.1) on the left interval [-1, 0) satisfying the initial conditions $v_1(-1, \lambda) = 1$, $v'_1(-1, \lambda) = 0$, and $w_1(-1, \lambda) = 0$, $w'_1(-1, \lambda) = 1$, respectively. Similarly, let $v_2(x, \lambda)$ and $w_2(x, \lambda)$ be solutions of Equation (1.1) on the right interval (0, 1], satisfying the initial conditions $v_2(1, \lambda) = 1$, $v'_2(1, \lambda) = 0$, and $w_2(1, \lambda) = 0$, $w'_2(1, \lambda) = 1$, respectively. We know that the functions $v_i(x, \lambda)$ and $w_i(x, \lambda)$ are entire functions of complex variable λ for each fixed x (see, [5]).

Theorem 3.1. Let $\lambda = z^2, z = t + is; t, s \in \mathbb{R}$. The following asymptotic formulas are valid as $|\lambda|$ tends to infinity.

$$v_1(x,\lambda) = \cos((1+x)z) + O\left(\frac{1}{|z|}\exp((1+x)|s|)\right)$$
(3.1)

$$v_1'(x,\lambda) = -z\sin((1+x)z) + O\left(\exp((1+x)|s|)\right)$$
(3.2)

$$w_1(x,\lambda) = \frac{1}{z}\sin((1+x)z) + O\left(\frac{1}{|z|^2}\exp((1+x)|s|)\right)$$
(3.3)

$$w_1'(x,\lambda) = \cos((1+x)z) + O\left(\frac{1}{|z|}\exp((1+x)|s|)\right)$$
(3.4)

$$v_2(x,\lambda) = \cos((1-x)z) + O\left(\frac{1}{|z|}\exp((1-x)|s|)\right)$$
 (3.5)

$$v_2'(x,\lambda) = z\sin((1-x)z) + O\left(\exp((1-x)|s|)\right)$$
(3.6)

$$w_2(x,\lambda) = -\frac{1}{z}\sin((1-x)z) + O\left(\frac{1}{|z|^2}\exp((1-x)|s|)\right)$$
(3.7)

$$w_2'(x,\lambda) = \cos((1-x)z) + O\left(\frac{1}{|z|}\exp((1-x)|s|)\right)$$
(3.8)

Proof.

The proof is similar to the Lemma 1.7. in [4]. \Box

4. The Transfer-Characteristic Function

This section defines a new concept for the problem (1.1)-(1.5), which we call the transfer-characteristic functions.

Definition 4.1. The determinant

$$A(\lambda) := \begin{vmatrix} v_1'(0,\lambda) - v_2(0,\lambda) & w_1'(0,\lambda) - w_2(0,\lambda) \\ \alpha v_1'(0,\lambda) - v_1(0,\lambda) - v_2'(0,\lambda) & \alpha w_1'(0,\lambda) - w_1(0,\lambda) - w_2'(0,\lambda) \end{vmatrix}$$

is called the transfer-characteristic function. Here v_1, v_2, w_1, w_2 are functions defined as in section 3.

Theorem 4.2. The number λ is an eigenvalue of the problem (1.1)-(1.5) if and only if $A(\lambda) = 0$.

Proof.

Since

$$W(v_1(.,\lambda), w_1(.,\lambda); -1) = W(v_2(.,\lambda), w_2(.,\lambda); 1) = 1$$
(4.1)

the left hand solutions v_1 and w_1 are linearly independent in the left interval [-1,0) and the right hand solutions v_2 and w_2 are linearly independent in the right interval (0,1]. Therefore, the general solution of the two-interval differential equation (1.1) can be represented in the form

$$u(x,\lambda) = \begin{cases} c_1 v_1(x,\lambda) + c_2 w_1(x,\lambda), x \in [-1,0) \\ c_3 v_2(x,\lambda) + c_4 w_2(x,\lambda), x \in (0,1] \end{cases}$$

If we try to satisfy the periodic boundary conditions (1.2)-(1.3), then we have $c_1 = c_3$ and $c_2 = c_4$. The requirement for validity of the transmission conditions (1.4)-(1.5) gives the following system of equations

$$\begin{cases} c_1 v_1'(0-,\lambda) - v_2(0+,\lambda) + c_2(w_1'(0-,\lambda) - w_2(0+,\lambda)) = 0\\ c_1 (\alpha v_1'(0-,\lambda) - v_1(0-,\lambda) - v_2'(0+,\lambda)) + c_2 (\alpha w_1'(0-,\lambda) - w_1(0-,\lambda) - w_2'(0+,\lambda)) = 0 \end{cases}$$

For this system of linear equations to have a non-trivial solution (with respect to the variables c_1, c_2). We would need the determinant of the coefficient matrix $A(\lambda)$ would need to be zero. \Box

Theorem 4.3. Let $\lambda = z^2, z = t + is : t, s \in \mathbb{R}$. Then, the transfer-characteristic function $A(\lambda)$ satisfies the asymptotic formula

$$A(\lambda) = z\sin(2z) + O\left(\exp|2s|\right), \text{ as } |\lambda| \to \infty$$
(4.2)

Proof.

By using asymptotic formulas (3.1)-(3.8) we can show that

$$\begin{aligned} v_1(0-,\lambda) &= \cos(z) + O\left(\frac{1}{|z|} \exp|s|\right) \\ v_1'(0-,\lambda) &= -z\sin(z) + O\left(\exp|s|\right) \\ w_1(0-,\lambda) &= \frac{1}{z}\sin(z) + O\left(\frac{1}{|z|^2} \exp|s|\right) \\ w_1'(0-,\lambda) &= \cos(z) + O\left(\frac{1}{|z|} \exp|s|\right) \\ v_2(0+,\lambda) &= \cos(z) + O\left(\frac{1}{|z|} \exp|s|\right) \\ v_2'(0+,\lambda) &= z\sin(z) + O\left(\exp|s|\right) \\ w_2(0+,\lambda) &= -\frac{1}{z}\sin(z) + O\left(\frac{1}{|z|^2} \exp|s|\right) \\ w_2'(0+,\lambda) &= -\cos(z) + \left(\frac{1}{|z|} \exp|s|\right) \end{aligned}$$

as $|\lambda| \to \infty$. Substituting these into $(A(\lambda) = 0)$ and simplifying, we arrive at the wanted formula (4.2). \Box

Theorem 4.4. The problem (1.1)-(1.5) has a countable number of eigenvalues $\lambda_1, \lambda_2, ...$ for which the

following asymptotic formula holds

$$z_n = \frac{n\pi}{2} + O\left(\frac{1}{n}\right) \cdot \lambda_n = z_n^2$$

Proof.

It is easy to see that the transfer-characteristic function $A(\lambda)$ is entire function and has countable many zeros. Take a circle S_n of the radius $r_n = \frac{n\pi}{2} + \frac{\pi}{4}$ in the z-plane, where n is a sufficiently large natural number. By using the well-known Rouche Theorem (see, for example, [3]), we can show that there are as many zeros of $A(\lambda)$ inside S_n as of the function $A_0(z^2) = z \sin(2z)$, i.e. 2n + 2. Consequently,

$$z_n = \frac{n\pi}{2} + a_n, \ n = 1, 2, \dots$$

where a_n is a bounded sequence and $|a_n| < \frac{\pi}{4}$ for each n. The equation $A(\lambda_n) = 0$ then takes the form

$$\left(\frac{n\pi}{2} + a_n\right)\sin\left(2\left(\frac{n\pi}{2} + a_n\right)\right) = 0$$

From this, it follows that $a_n = O(\frac{1}{n})$. Then, we have

$$z_n = \frac{n\pi}{2} + O\left(\frac{1}{n}\right)$$

5. Conclusion

In this paper, we study a new type of periodic boundary-value-transmission problem and generalize some results of classical Sturm-Lioville problems. This new approach may be further developed in the future by adding parameters to the boundary conditions of problems of the type described herein. Additionally, the properties of eigenvalues and eigenfunctions can be investigated for these problems that involve parameters in their boundary conditions.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

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A new host plant for Monochaetia monochaeta from Southern Anatolia

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Abstract — This study aims to report the endophytic fungal pathogen *Monochaetia monochaeta* (Desmazières) Allesch on *Quercus robur* Linnaeus (English oak) for the first time from Anatolia (Türkiye). The microscopic and macroscopic properties of the fungus, the symptoms it creates in the host plant, and the distribution of the disease in the world are explained. With the new host record revealed by this research, a contribution was made to the Turkish Mycoflora and the scientific world. Additionally, it has been emphasized that fungal diseases can cause serious yield loss and, therefore, significant economic losses in plants worldwide and that much more research should be done on these disease agents and host plants based on systematic and biological control studies.

Subject Classification (2020):

1. Introduction

Keywords:

New host,

Quercus robur,

Monochaetia

monochaeta,

English oak,

Türkiye

Endophytic fungi are commonly known as mycoparasitic fungi and occur in different parts of the world. They live in regions such as the Arctic and Antarctica and natural habitats in the oceans, rainforests, deserts, ferns, gymnosperms, and angiosperms [1]. Endophytic fungi live in the inner tissues of living plants, such as in leaves and root tissues, stems, flowers, fruits, and seeds [2]. These fungi cause severe damage to many plants living in their natural ecosystems. They can cause crop losses in wild fruit trees and shrubs [3]. The genus *Monochaetia* (Sacc.) Allesch. is characterized by brown median cells, a single cellular apical appendage, a single centric basal appendage (if present), and basal extension, morphologically acervular conidiomata, fusoid, and transverse septate conidia morphologically. *Monochaeta monochaeta* is reported to be common in host families such as *Fagaceae, Ericaceae*, *Aceraceae*, and *Myrtaceae*. *M. monochaeta* is a fungus that harms deciduous trees, especially *Quercus, Castanea, and Rhododendron* species, in their natural environment [1,4,5]. It is a pathogenic species that cause severe economic damage to *Castanea sativa* Mill. (Anatolian chestnut) [6]. In the long cultivation history of Quercus trees, fungal diseases have caused severe economic and ecological problems [7]. In this study, *Quercus robur*, infected by *Monochaetia monochaeta*, has been recorded as a new host plant in Türkiye.

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2. Materials and Methods

The material of this study consists of plant specimens infected by parasitic fungi collected in Manavgat (Antalya, Türkiye) between 2015–2017, especially in spring and autumn. During field studies, the sample species' necessary morphological and ecological properties were noted and photographed. The host samples were prepared according to established herbarium techniques. For the morphological examination of hosts and microfungi, a stereo microscope (SM) (Nikon C-Leds) and a light microscope (LM) (Nikon Eclipse E100) were used. Colonies and spores from the specimens were examined with a light microscope (Nikon Eclipse E100) and measured at least 15 times for each specimen (Figure 2). The host samples were identified using relevant literature [8,9]. In the identification of parasitic fungus, Dematiaceous Hyphomycetes [10], More Dematiaceous Hyphomycetes [11], Parasitische Pilze a Gefaesspflanzen in Europa [12], index fungorum website [13] and The Global Biodiversity Information Facility [14] have been used. The samples are preserved at the Laboratory of Manavgat Tourism Faculty, Akdeniz University (Türkiye). Figure 1 shows the *Q. robur* (English Oak) and *Fagaceae* localizations: Antalya, Manavgat, and Sorgun pine forests.



Figure 1. Satellite view of Manavgat city

3. Results and Discussion

Macro and microscopic features and the taxonomy of the fungus species are given below:

Taxonomy

Ascomycota

Sordariomycetes

Amphisphaeriales

Amphisphaeriaceae

Monochaetia (Sacc.) Allesch

Monochaetia monochaeta (Desm.) Allesch., Rabenh. Krypt.-Fl., Edn 2(Leipzig) 1(7): 667(1902)[1903]

Synonyms:

Hyaloceras monochaetum (Desm.) Died.

Hyaloceras monochaetum var. gallicola (Trotter) Died.

Monochaetia desmazieri Sacc. & D. Sacc.

Monochaetia desmazieri var. gallicola (Trotter) Sacc. & Traverso

Monochaetia monochaeta var. gallicola (Trotter) Allesch., Rabenh.

Pestalotia monochaeta Desm.

Pestalotia monochaeta var. gallicola Trotter

M. monochaeta forms black-bordered dark brown spots on both sides of the host leaf, $90-140\mu$ in size. Conidia, elliptical or narrow fusiform, broad spindle-shaped, light olive-colored, $13-21 \times 3-5\mu m$ in size, usually four cells, sometimes 5 or 3 apical cells thin-walled, naked, $3-12\mu m$ long simple appendage, middle cell barrel-shaped, basal cell truncated funnel-shaped simple appendage (Figure 2 a-d).

Specimen Examined – On *Q. robur* (English Oak) Fagaceae Türkiye: Antalya, Manavgat, Sorgun pine forest, at sea level, 12.10.2015, FA 3061 (Figure 1).



Figure 2. *M. monochaeta* on *Q. robur* a. Spots formed by fungus b. Stereo microscope images of spots

c. Conidiophores **d**. Conidia

The genus *Monochaetia* is reported on various hardwood hosts in many parts of the world. These fungi cause spots on tissues, leaves, and stems [15]. *M. taphrinicola* (Ellis & Everh.) Sacc. & D. Sacc. is reported on *Q. alba* L., *Q. nigra* L., and other *Quercus* species in the USA; *M. sinensis* N. I. de Silva, Phookamsak, Maharachch. & KD. Hyde is reported on dead leaves of *Quercus* sp. in China; *M. karstenii* (Sacc. & P. Syd.)

B. Sutton is reported on infected leaves of *Camellia japonica* L. in India [13], and *M. quercus* F. Liu, L. Cai & Crous has been recorded on *Q. eduardi* Trel. in Mexico [4]. Other records are as follows: *M. bicornis* (Durieu & Mont.) Sacc. & D. Sacc. has been recorded on *Q. coccifera* L. in Algeria and on *Q. nobilis* hort. ex K. Koch in Mexico; *M. hysteriiformis* (Berk. & M. A. Curtis) Guba has been recorded on *Q. nigra* L. in South Carolina and *Quercus* sp. in Georgia; *M. ilicina* (Sacc.) Nag Raj has been recorded on *Q. ilex* L. and *Q. pubescens* Willd. in Italy [3,4].

M. monochaeta is distributed in Asia, Europe, and North America and usually infects the host plant's living leaf tissues and stems [15]. It has been found originally on wilting and dry leaves of *Quercus ilex* L. in France, on dead areas on living leaves of *Rhododendron linearifolium* Siebold & Zucc. in Japan, on leaves of *R*. sp. in the USA and on *Castanea crenata* Siebold & Zucc. in Japan [4,15]. Besides, it is reported on *Q. robur* in the Netherlands; on *Q. pubescens* Willd. in Italy; on *Q. ilex* L. and on *Q. rubra* L. in France; on *Q. variabilis* Blume in China and Japan; on *Q. agrifolia* Née in California; on *Castanea crenata* Siebold & Zucc. in Japan; on *Acer rubrum* L. in North Carolina; on *Arbutus menziesii* Pursh. in Canada, on *R. macrosepalum* in Japan, and *Rhododendron* sp. in Washington [14,15].

In Türkiye, *M. monochaeta* has been recorded on *C. sativa* Mill. (Kastamonu) and *M. veneta* (Sacc.) Allesch. has been recorded on *Cornus mas* L. (Kastamonu) [6]. With this study, the endophytic fungal pathogen *M. monochaeta* is reported for the first time on *Q. robur* from Anatolia (Türkiye) [10-15].

4. Conclusion

Fungal diseases, which can be easily transmitted when they find suitable hosts, cause severe damage to both wild and cultivated plants worldwide. Diseases that occur in flowers, fruits, leaves, roots, or sometimes the whole plant cause significant yield losses and, thus, severe economic losses. Agricultural products, such as cereals, trees, and landscape plants, are the leading ones. Considering the ecological and economic importance of plant pathogenic fungi, it is observed that research studies in this field are pretty insufficient. Therefore, it is thought that studies in this field should be increased in our country and worldwide. Furthermore, studies that start with species identification based on morphological and molecular genetic methods should be continued with biological control studies, considering human and environmental health.

Author Contributions

All the authors equally contributed to this work. This paper is derived from the first author's master's thesis, supervised by the second author. They all read and approved the final version of the paper.

Conflict of Interest

All the authors declare no conflict of interest.

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Research Article





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Coating of AISI 1018 steel with the pack-boriding method

Ramazan Erarslan ¹ ^(D), Uğur Öztürk² ^(D), Fikret Yılmaz³ ^(D)

Keywords: AISI 1018 steel, Pack boriding, Wear properties, Hardness **Abstract** — In this study, AISI 1018 steel with low carbon content was coated with the packboriding method at 950 °C for 2h and 4h. A two-layer structure was observed in the 2h boronized material: the thin FeB phase and the more prominent Fe₂B phase. In addition to this two-phase structure, undesirable phases (SiC and Fe₃O₄) were detected in the material boronized for 4h. It was observed that the wear resistance and hardness of the boronized materials increased greatly, which is explained by the hard FeB and Fe₂B phases. In addition, as the heat treatment time increases, the thickness of the FeB phase increases while the thickness of the Fe₂B phase decreases.

Subject Classification (2020): 74A55, 76R50

1. Introduction

Boronizing enriches the material surface with boron atoms through thermochemical diffusion [1-4]. In this process, boron atoms diffuse into the metal matrix on the material surface using thermal energy, forming boride compounds with the atoms of the main material [5]. Compared to traditional surface coating methods, the most crucial advantage of this method is that the coated material shows very high wear and oxidation resistance [6, 7]. Boriding can be carried out in solid, liquid, or gaseous mediums. Pack boriding is the most commonly used boronizing method, which is easier and cheaper than the others [8]. The coated surface can be tetragonal Fe2B and/or orthorhombic FeB depending on the concentration of diffused boron atoms [9]. Although the FeB phase has a higher hardness value than Fe2B, it shows lower toughness [10]. In this respect, the FeB phase, which has a more brittle structure, is undesirable because the coating layer is easily broken when exposed to an external force.

Öztürk et al. [11] obtained a 150 μm Fe2B layer in thickness by coating the cylinder liner surface with the boronizing method. Another study found that very good thermal insulation is provided on boronized surfaces, thus improving performance parameters (thermal brake efficiency, brake-specific energy consumption, and fuel consumption) [12]. In addition, it has been observed that coated engines reduce harmful emission values. Türkmen et al. [13] coated SAE 1020 steel for 4, 8, and 12h for 850, 900, and 950 °C temperatures with the pack-boriding method. In that study, boric acid was used as a boron source. Homogeneous, mono-phase, and saw-tooth morphology Fe2B layers were observed in boronized materials. While the hardness value of the boronized layer was 1200-2000 HV0.1, the

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hardness value of the substrate was around 150 HV0.1. Motallebzadeh et al. [14] studied the hightemperature sliding wear characteristics of paste-borided 31CrMoV9 and X40CrMoV5-1 steels. A twolayer (FeB and Fe2B) structure was formed in both alloys. They found that the tribological properties at the test temperature of 500 °C were almost the same as at room temperature. In another study, AISI 316 L steel was coated with powder-pack boriding, and a two-layer (FeB-Fe2B) structure was detected on the surface [15]. These layers increased the tribocorrosion resistance of the steel by 1.5 times.

As can be seen from the studies, the properties, such as the structure, thickness, and hardness of the boron layers formed on the steel surface, are closely related to the process parameters and the steel composition. In addition, knowledge of materials' mechanical and tribological properties is crucial in determining their working conditions [16-18]. There are few studies on coating low-carbon steels by the boriding method in the literature. Among the low-carbon steels, AISI 1018 steel offers a good balance of toughness, strength, and ductility. However, they have low wear, corrosion resistance, and strength compared to high-carbon steels. In this respect, improving the surface properties of AISI 1018 steel is essential in increasing the cycle life.

In this study, low-carbon AISI steel was coated for different durations by the pack-boriding method. Boron compound layers formed on the surfaces were examined using scanning electron microscopy, xray diffraction method, hardness test, and wear test. The obtained results were evaluated in terms of the mechanical and tribological properties of the material.

2. Experimental

Commercial Ekabor-2 (Bortec) powder was used for coating AISI 1018 steel (Table 1). Firstly, the samples were cut with a diameter of 2 cm and a thickness of 3 mm and polished by metallographic methods up to 1 μ m. Then, the samples were buried in a 5x5x5 cm steel box filled with Ekabor-2 powder, and Ekrit (Bortec) powder was placed on it as a deoxidant. The samples were heat treated at 950 °C for 2 and 4h. The samples obtained are shown in Figure 1. The boronized products were molded with epoxy and polished by metallographic methods. It was then etched and prepared for Scanning Electron Microscopy (SEM) and hardness analysis. SEM (QUANTA 450 FEG) analyses were obtained in BSE (back scatter electron) mode. Hardness analyzes were performed with a Vickers hardness device (Highwood) under 200 gf force. Wear tests were performed with a pin on the disk set up for a total distance of 600 m at 150 rpm and 30 N loads. X-ray diffraction analysis (PANalytical Emperians) of the samples was performed under CuK α monochromatic beam in the range of 2 θ =10-90°.



Figure 1. Samples (a) Before boronizing and (b) After boronizing

Sample	C	Fe	Mn	P	S	BiC	SiC	KBF4
AISI 1018	0.14-0.20	98.81-99.26	0.60-0.90	< 0.040	< 0.050	-	-	-
Ekabor-2	-	-	-	-	-	5	90	5

Table 1. Chemical composition of AISI 1018 steel and Ekabor-2 powder (wt.%)

3. Results and Discussion

Figure 2 shows the XRD patterns of untreated and boronized steels. In untreated 1018 steel, all possible diffraction peaks of the Fe (ICSD: 98-018-0969) phase were detected. A two-layered structure was observed in the 2h boronized sample, the Fe₂B (ICSD: 98-060-3829) phase forming a large part of this structure. Apart from this, a small amount of FeB (ICSD: 98-042-5309), Fe₃B (ICSD: 98-061-3889), Fe₂Si (ICSD: 98-010-0094), and Fe₃O₄ (ICSD: 98-026-3009) phases were detected. A large amount of SiC (ICSD: 98-004-3291) and Fe₃C (ICSD: 98-001-6593) phases were observed in addition to a small amount of FeB phase in the 4h boronized sample. The XRD method can determine the material's crystal structure from the material surface. The penetration of X-rays on the surface is given by the formula [19],

$$I = I_0 e^{-\mu L}$$

where I_0 is the incident X-ray intensity, μ is the linear absorption coefficient, and L is the penetration distance. Since the X-ray intensity decreases exponentially, diffraction will not occur after a certain distance. In this respect, especially in the 4h boronized sample, the Fe₂B compound could not be detected by XRD because it did not form on the surface. The SiC phase is contained in Ekabor powder and diffused to the surface during heat treatment. SEM images were obtained to see the compounds formed on the surfaces in more detail.



Figure 2. XRD pattern of (a) 1018 steel, (b) 2h boronized, (c) 4h boronized steel

Figure 3 shows the SEM images obtained in BSE mode. A two-phase structure is seen in the material that has been heat treated for 2h (Figure 3b). A clear transition zone was not detected between the boron compound and the base material due to the low C content of the steel used in the study. The transition zone is formed by the repulsion of carbon atoms during the diffusion of boron atoms. A three-layer structure is seen in the material, subjected to 4h heat treatment. When the SEM images and XRD analyses are evaluated together, it is understood that the upper layer is 10µm thick SiC and Fe₃C. Since these phases are undesirable, they were removed by sanding before hardness and wear analysis. The middle layer is the FeB phase, and its thickness is around 20µm. The bottom layer is the Fe₂B phase and has a thickness of $75\mu m$. In addition, the saw-tooth structure of the Fe₂B phase in the 4h boronized material grew more unevenly compared to the 2h boronized material. As it can be understood from the SEM and XRD analyses, the increase in the heat treatment time caused the formation of undesired phases of the material and decreased the thickness of the Fe₂B phase. In general, the development of the boride layer increases with increasing time and/or temperature. Therefore, boron diffusion, which initially develops rapidly, slows down and finally stops with the decrease of boron in the powder media. In addition, the previously formed boride layer makes the diffusion of boron atoms difficult. In our case, the fact that the thickness of total boride layers (FeB and Fe_2B) are nearly the same in both samples indicated that the boron diffusion had taken place completely. On the other hand, the thickness of the FeB layer increases with increasing time while the thickness of Fe₂B decreases. This can be interpreted that increasing boronized time negatively affects the formation of the Fe₂B phase.



Figure 3 BSE images of boronized steel (a) 2h and (b) 4h

Figure 4 shows the mass loss plot of boronized samples and untreated steel for different distances. As seen in Figure 4, the mass loss of untreated steel increased up to about 0.16 grams for a sliding distance of 600 m. Mass loss in boronized samples is quite low, 0.002, and 0.004 g for 2h and 4h heat-treated samples, respectively. The results show that the wear resistance of the boronized samples is significantly increased. This can be explained by the hard boron compounds, FeB and Fe₂B, in agreement with the literature [20]. High wear resistance is attributed to the boride layer's saw-tooth and columnar morphology. This structure improves the bonding strength with a substrate. The higher mass loss of the 4h sample compared to the 2h sample can be explained by the more formation of brittle FeB phase formed on its surface. In addition, since the thermal expansion coefficient of FeB is higher than that of Fe₂B, cracks and fractures may occur easily under mechanical stress. Therefore, forming a single-phase Fe2B layer in boride coatings is desirable.



Figure 4. Mass losses of the samples for different sliding distances

Figure 5 shows the worn surface of the samples. Plastic deformation appears to predominate in untreated steel. The ductile nature of untreated steel can explain this. It is seen that grooves are dominant in the 2h boronized sample due to the hard and tough Fe_2B phase formed on the surface. On the other hand, in the 4h boronized sample, it is seen that microcracks are formed on the surface, as well as debris and oxides. This is due to the fact that the brittle FeB phase and an oxide layer formed on the surface were more dominant in the 4h boronized sample.



Figure 5. Worn surface of the samples (a) Untreated steel, (b) 2hboronized, (c) 4hboronized (100x and 5000x magnification)

Figure 6 shows the Vickers hardness values of the samples. It was determined that the hardness values of the boronized samples were approximately two times higher than those of the untreated steel, in agreement with the literature [21]. In addition, it was observed that the hardness of the 2h boronized sample was slightly higher than the 4h boronized sample. The results obtained can be explained by the fact that the Fe₂B phase is more dominant in the 2hboronized sample, in agreement with the wear tests and SEM images.



Figure 6. Vickers hardness of the samples. The inset picture shows the imprint image after indentation

4. Conclusions

In this study, AISI 1018 steel was coated with the pack boronization method for 2 and 4hours. The results obtained are summarized below:

- From the XRD analysis, a two-phase structure was formed in the 2hboronized material (FeB and Fe₂B), while undesirable phases were detected from the surface of the 4hboronized material (SiC and Fe₃O₄).
- Multilayer structures were observed in SEM analysis, consistent with XRD. In addition, it was observed that the thickness of the FeB layer increased while the thickness of the Fe₂B layer decreased in the 4h boronized material.
- From the wear tests, it was determined that the wear resistance of boronized materials was greatly increased. While the plastic deformation mechanism dominates untreated steel, grooves dominate in 2h boronized material. In the 4h boronized material, debris and microcracks are evident, which is explained by the more fragile FeB and oxide phases.
- The hardness values of the boronized samples are approximately 2 times that of the untreated sample due to the hard boron-iron compounds.
- > According to experimental studies, 2h boronized steel exhibited very promising results.

In this study, we obtained very promising results in the field of pack boriding. In future studies, we intend to investigate the effects of the mixture of Ekabor-2 and different powders, such as iron, cobalt, titanium, etc., on forming the boron layer.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

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Mersenne version of Brocard-Ramanujan equation

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Keywords Brocard-Ramanujan equation, Mersenne numbers, Diophantine equations Abstract — In this study, we deal with a special form of the Brocard-Ramanujan equation, which is one of the interesting and still open problems of Diophantine analysis. We search for the positive integer solutions of the Brocard-Ramanujan equation for the case where the right-hand side is Mersenne numbers. By using the definition of Mersenne numbers, appropriate inequalities for the parameters of the equation, and the prime factorization of n! we show that there is no positive integer solution to this equation. Thus, we obtain this interesting result demonstrating that the square of any Mersenne number can not be expressed as n! + 1.

Subject Classification (2020): 11D72, 11D61

1. Introduction

Diophantine equations are one of the important subjects of number theory. If there are two or more unknowns in an equation, this equation is called the Diophantine equation [1]. Usually, it is necessary to find all the integer solutions of these equations. However, there is no general method with finite numerical calculations for solving these equations in the set of integers. This theorem is the 10th problem among illustrious German mathematician Hilbert's 23 famous problems, which Matiyasevich proved in 1970. Matiyasevich demonstrated that there is no general method for showing whether an integer solution to an arbitrary Diophantine equation exists or not. Since there is no general method, for solving Diophantine equations, methods are being developed for solving a particular class of these equations. For instance, we can mention some of the existing methods by factoring method, parametric method, modular arithmetic method, solving Diophantine equations using inequalities, and other methods [2]. In this field, there are interesting works by prominent mathematicians, such as Fermat, Euler, Ramanujan, Puancare, and Erdös. One of the famous Diophantine equations is the Brocard-Ramanujan equation. This equation is still an open problem in number theory. The only known solutions to are $(n, m) \in \{(4, 5), (5, 11), (7, 71)\}$. This problem was formulated by Brocard and Ramanujan [3] in 1876 and 1911, respectively, as follows:

$$n! + 1 = m^2$$

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Although more than a century has passed, this problem has not been fully resolved. The solutions of this equation under some special conditions have been investigated by different mathematicians. Gerardin [4] put forward the idea that when m > 71, m must be a number with at least 20 digits. Lately, Berndt and Galway [5] proved that there are no other solutions up to $n = 10^9$. In addition, Marques [6] studied the form of the equation for Fibonacci numbers. Faco and Marques [7] studied the case where the right-hand side of the equation is Tribonacci numbers. Dabrowski and Ulas [8] investigated some varieties of the Brocard-Ramanujan equation. There are many studies [9–13] related to the famous number sequence and Diophantine equations in the literature.

2. Preliminaries

This section provides several basic notions to be needed for the following section.

Definition 2.1. Mersenne numbers are defined by $M_n = 2^n - 1, n \ge 1$.

Lemma 2.2. If $n \in N^*$, then

$$\frac{2}{n+1} \le (n!)^{\frac{-1}{n}} < \frac{e}{n+1} \tag{2.1}$$

holds.

Proof.

By arithmetic and geometric means inequality, we have

$$\frac{n+1}{2} \ge (n!)^{\frac{1}{n}}$$
$$\frac{2}{n+1} \le (n!)^{\frac{-1}{n}}$$

Then, we obtain

$$(n!)^{\frac{-1}{n}} < \frac{e}{n+1}$$

We use the induction method for this. If n = 1, then we get $1 < \frac{e}{2}$. Suppose that Inequality (2.1) is true for n = k and show that it holds for n = k + 1. We know that [14]

$$e^{\frac{1}{n+1}} \le 1 + \frac{1}{n} \le e^{\frac{1}{n}}, n \ge 1$$
 (2.2)

Thus, by assumption and Inequality (2.2), we obtain

$$\frac{1}{(k+1)!} < \left(\frac{e}{k+1}\right)^k \frac{1}{k+1} < \left(\frac{e}{k+2}\right)^{k+1}$$

Lemma 2.3. If $n \in N^*$, then

$$\frac{(n+1)^n}{3} > 2^{2n} - 2^{n+1} \tag{2.3}$$

holds for all $n \ge 11$.

Proof.

Suppose that n = 11. The

$$4^{11} > 2^{22} - 2^{12}$$

That is true. Besides, we assume that Inequality (2.3) is satisfied for n = k. Then, we must illustrate

for n = k + 1.

$$\left(\frac{k+2}{3}\right)^{k+1} > 2\left(\frac{k+1}{3}\right)^{k+1} = \frac{2(k+1)}{3}\left(\frac{k+1}{3}\right)^k > 2^{2k+3} - 2^{k+4} > 2^{2k+2} - 2^{k+2}$$

The prime factorization formula of n! provided in [15] can be summarized as follows: To acquire the prime factorization of n!, we must find, for each of these primes p, the exponent g_p of the greatest power of p that divides n!. The formula is connected to the relationship between n, p, and g_p . This formula belongs to the illustrious Legendre. In order to explain the formula, we first give the representation of the integer n according to the base p.

$$n = \sum_{i=0}^{k} r_i p^i$$

where $p^{k+1} > n, p^k \le n$ and $0 \le r_i \le p-1$, for all $i = 1, 2, \ldots, k$. Then, for $1 \le l \le k$,

$$\frac{n}{p^{l}} = \frac{\sum_{i=r}^{k} r_{i} p^{i}}{p^{l}} + \frac{\sum_{i=0}^{r-1} r_{i} p^{i}}{p^{l}}$$

thus

$$\sum_{i=0}^{r-1} r_i p^i \le (p-1) \sum_{i=0}^{r-1} p^i = p^r - 1 < p^r$$

we obtain that

$$\left[\frac{n}{p^{l}}\right] = \sum_{i=0}^{k-1} r_{k-i} p^{k-l-i}$$
(2.4)

for all $1 \leq l \leq k$, we know that, given for any prime $p \leq n$,

$$g_p = \sum_{i=1}^{k} \left[\frac{n}{p^k} \right] \tag{2.5}$$

where $p^{k+1} > n, p^k \le n$. For each $l(1 \le l \le k)$, we write Formula (2.4) and add side-by-side and using Formula (2.5), we get

$$g_p = \sum_{i=1}^k (r_i \sum_{j=1}^{i-1} p^{j-1}) = \frac{1}{p-1} \sum_{i=1}^k (r_i (p^i - 1)) = \frac{n - d_p}{p-1}$$
(2.6)

where $d_p = \sum_{i=0}^k r_i$.

3. Main Result

Theorem 3.1. In the following equation, there is no solution in N^*

$$n! + 1 = M_k^2 \tag{3.1}$$

Proof.

We investigate the following cases:

i. Suppose that n = k. Then, we must demonstrate there is no solution to the following equation:

$$n! = 2^{2n} - 2^{n+1}$$

Then, from Equation (3.1) and Inequality (2.1), we obtain

$$2^{2n} - 2^{n+1} = n! > \left(\frac{n+1}{3}\right)^n \tag{3.2}$$

However, according to Inequality (2.3) this is a contradiction for all $n \ge 11$. Moreover, we can demonstrate by simple numerical calculations that there is no solution for all $n \le 10$.

ii. Suppose that n > k. Then we have to prove there is no solution to the following equation:

$$n! = 2^{2k} - 2^{k+1} \tag{3.3}$$

By Lemma (2.3), we obtain

$$n! > 2^{2n} - 2^{n+1}$$

for all $n \ge 11$. In addition, we know n > k. Then, we get

$$n! > 2^{2n} - 2^{n+1} > 2^{2k} - 2^{k+1} \tag{3.4}$$

For all (k, n) pairs satisfying $11 \le k < n$ or $k < 11 \le n$. Then, by Inequality (3.4), we obtain that there is no solution of Equation (3.3) for these cases of n and k. Besides, for the remaining case k < n < 11, it can be shown by simple mathematical calculations that the equation there is no solution.

iii. Suppose that n < k. We see that the right-hand side of the equation is divided by 2^{k+1} , and from Formula (2.6), we obtain that the left-hand side is divided by 2^{n-d_2} . However, we see that $n - d_2 < n < k < k + 1$. This means that in this case, the equation there is no solution.

4. Conclusion

The Brocard-Ramanujan equation is one of the still open problems of Diophantine analysis. Although passed a hundred years, the authors solved only some special cases of this equation. In this article, we investigate the positive integer solutions of the Brocard-Ramanujan equation for the case where the right-hand side is Mersenne numbers. By using the definition of Mersenne numbers, appropriate inequalities for the parameters of the equation, and the prime factorization of n!, we proved that there is no positive integer solution to this equation. In addition, exciting results can be obtained in future studies by using the properties of number sequences and methods for solving Diophantine equations in the versions of this equation associated with k-Fibonacci, k-Lucas, Pell, Pell-Lucas, and Fermat numbers.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

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A comparative investigation for identification of N-(4-dimethylamino 3,5dinitrophenyl)maleimide

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Keywords:

N-(4-dimethylamino 3,5dinitrophenyl)maleimide, DFT-HF calculations, HOMO and LUMO, MEP, Molecular structure **Abstract** — This study has identified the characteristic behaviors of N-(4-dimethylamino 3,5dinitrophenyl)maleimide molecule using ab initio Hartree-Fock (HF) and density functional theory (DFT) based on Becke's three-parameter hybrid exchange functional combined with Lee-Yang-Parr non-local correlation function (HF/B3LYP and DFT/B3LYP) at 6-311G++(d,p) level of theory for the first time. On this basis, the optimized molecular structures, some thermodynamic features at 300 K, function groups of structures, charge distributions-dipole moments, molecular charge transfer regions, spectroscopic characteristic properties, vibrational frequencies, nuclear magnetic resonance chemical shifts of ¹³C-NMR and ¹H-NMR spectra, and corresponding vibrational assignments have been investigated in detail. Comparisons between some experimental findings and theoretical results are performed to test the reliability of the calculation method preferred in the study. The comparison results in high correlation parameters such as $R^2 = 0.976$ and $R^2 = 0.985$ for the molecular structures and vibrational frequencies in the DFT and HF calculation levels, respectively. Moreover, the obtained vibrational frequencies and calculated results are in good agreement with the experimental data. Additionally, the simulations of highest/lowest occupied/unoccupied molecular orbital (HOMO and LUMO), molecular electrostatic potential (MEP), and electrostatic potential (ESP) maps have shown that there appear strong non-uniform intramolecular charge distributions (ICT), electron engagements, lone pairs of electrons, π - π * conjugative effects based on the bond weakening, and intermolecular hydrogen bonding in the compound. Correspondingly, the molecule with the electrophilic reactive and nucleophilic regions has been noted to exhibit kinetical chemical stability. All the discussions have been confirmed by means of the findings of optimized molecular structures and vibrational frequencies belonging to the molecule.

Subject Classification (2020):

1. Introduction

Heterocyclic compounds have widely been utilized in the pharmaceutical industry due to their alluring properties, including the physicochemical, selective affinity towards biomolecules, and constructive as therapeutics agents. Maleimides are one of the most promising classes of heterocyclic compounds having the formula of H2C2(CO)2NH. The compound together with other organics have extensively been used in biological applications as anti-protozoal [1], anti-angiogenic [2], anti-bacterial [3], and anti-

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stress agents [4]. Especially, N-substituted ones are an essential part of electron acceptors that can form charge transfer complexes with several vinyl monomers [5,6].

In recent years, it has been reported that derivatives of maleimides could be used as selective inhibitors for monoglyceride lipase [7], Bfl-1 [8], and DNMT-1 protein [9]. Several researchers have investigated the biological activity of N-substituted derivatives of maleimides in the last ten years and obtained successful medical results on this issue. Zacchino and coworkers have reported that the N-substituted maleimides have shown anti-microbial activity against Candida spp [10]. They also observed that the maleimide framework had played a staminal role in the increase in the biological activity of these compounds. The structure-dependent antifungal activity of N-substituted maleimides was reported by Salewska et al. in 2012 [11]. Therefore, a great interest has begun in the synthesis of maleimides derivatives. In addition to the interest in the biological area, the N-substituted maleimides, with their excellent heat resistance, have also been used to prepare various polymers and copolymers. In other hands, the characteristic heat resistance property enables the N-substituted maleimides to be utilized in several areas, such as in rubber, plastics, and proteins [12,13]. Hence, the N-substituted maleimides are essential in organic chemistry, the polymer industry, and biological science.

Moreover, many studies on the N-substituted maleimides have been performed, and the scientific works have increased on the theoretical and experimental investigations of N-(4-dimethylamino 3,5-dinitrophenyl)maleimide, and its derivative organic compounds day by day. Reliable and effective results of theoretical investigations are much more important for the characteristic features of molecules as structural, thermodynamical, charge distributions-dipole moments, molecular charge transfer regions, and optical, spectroscopic, and electrochemical characteristic properties [14]. In other hands, a suitable quantum chemical method allows us to economically predict the compound characteristics and elucidate some experimental phenomena insightfully [15].

In the modern theoretical world, density functional theory (DFT) and ab initio Hartree Fock (HF) obtained considerable popularity as an effective general procedure to examine the physical, structural, thermodynamical, charge distributions dipole moments, molecular charge transfer regions, spectroscopic, and optical properties of the new synthesized molecules. In the current work, the molecular structures (optimized structures, bond lengths, bond angles, and bond dihedrals) and vibrational frequencies were calculated using ab initio Hartree-Fock (HF) and density functional theory (DFT) based on Becke's three-parameter hybrid exchange functional combined with Lee-Yang-Parr non-local correlation function (HF/B3LYP and DFT/B3LYP) at 6-311G++(d,p) level of theory. All the theoretical findings were compared to the experimental results obtained SDBS (13095) database [16]. It was found that the comparisons between experimental and theoretical findings have been noted to present a good correlation. This shows the reliability of the theoretical approach models used in the present three studies. Moreover, the vibrational frequencies, infrared intensities, and vibrational assignments were inspected.

Furthermore, the values of the energy band gap and transition states were examined concerning the frontier orbitals (the energy difference between HOMO and LUMO results). The maps relating to the molecular electrostatic potential (MEP), electrostatic potential (ESP), ¹³C, and ¹H chemical shifts of the compounds have been researched to find both the electrophilic/nucleophilic regions and the chemical stability (founded on the strong non-uniform intra-molecular charge distributions (ICT), electron engagements, lone pairs of electrons, π - π * conjugative effects, and intermolecular hydrogen bonding) of the compound studied. This study is interested in not only giving information about the identification of N-(4-dimethylamino 3,5-dinitrophenyl)maleimide and presenting in detail the vibrational modes but exhibit the way to future research, functionality in the medical areas (cytotoxic, anti-malarial, pharmacological activities), applications in biology and industry areas of this molecule.

2. Computational Details

The optimized molecular structures, thermodynamic features at 300 K, functional groups of structures, charge distributions-dipole moments, molecular charge transfers, spectroscopic properties, vibrational frequencies, corresponding vibrational assignments, and NMR chemical shifts of N-(4-dimethylamino 3,5-dinitrophenyl)maleimide molecule have been studied via Gaussian 09 package program [17,18] at HF and B3LYP/6-311++G(d,p) [19-22] level of theory for the first time. Besides, Electrochemical features such as highest/lowest occupied/unoccupied molecular orbitals (HOMOs and LUMOs), molecular electrostatic potential (MEP), and electrostatic potential (ESP) maps, energy band gap parameters, and transition states have been simulated.

3. Results and Discussion

According to Figure 1, the title compound possesses 32 atoms for a molecule and belongs to point group C1 including only the identity operation symmetry element; accordingly, all frequency modes (vibrations) are produced in only A species. As is well-known from the spectral analysis, the N atomic molecules provide 3N internal modes [23, 24] due to the existence of 3-dimensional space since every atom possesses 3 degrees of freedom. All the atoms are bonded and move translational, rotational, and vibrational. Thus, six modes (number of variables) appear for the translation and rotational modes for non-linear molecules. Three modes for the rotational movement stem from the rotations around three axes.



Figure 1. Optimized molecular structure of N-(4-dimethylamino 3,5-dinitrophenyl)maleimide

Correspondingly, 90 (3N–6) degrees of freedom constitute vibrational motion in the molecule. In this study, we have performed a frequency calculation analysis to obtain the spectroscopic signature of N-(4-dimethylamino 3,5-dinitrophenyl)maleimide. Vibrational frequencies have been calculated by using HF/6-311++G(d,p) and DFTB3LYP/6-311++G(d,p) methods. According to the literature, the vibrational frequencies are required to be scaled because they are mostly higher than the experimental ones. Hence, the vibrational frequencies computed at DFT-B3LYP/6-311++G(d,p) basis set were scaled by 0.958 for wavenumbers if the values are greater than 1700 cm⁻¹; otherwise, the scaling factor of 0.983 was used [25-28].

dinitrophenyl)maleimide molecule.

Moreover, the vibrational frequencies scaled by the factors of 0.9051 for HF/6-311++G(d,p) were given in Table 2. Thus, Tables 1 and 2 present the scaled vibrational frequencies compared with experimental values, Red. Masses, force Constant, IR intensities, Raman activity, Depolar(P) and Depolar(U) of the molecule, respectively. The correlation coefficient (R²) between the experimental and theoretical vibrational frequencies computed at DFT-B3LYP/6-311++G(d,p) basis set is found to be about 0.9996 (as provided in Figure 2), whereas the value of R² is observed to be about 0.9977 (see Figure3) for the HF/6-311++G(d,p) level of theory. It is found that the data obtained from the computational programs seem to be in good agreement with the experimental results. This shows that the theoretical method

As for the corresponding vibrational assignments of molecule studied, the existence of aromatic rings in a structure can easily be determined owing to the relation of C–H and C–C–C ring vibrations. As received, the multiplicity of C–H stretching bands seen between 3000 cm⁻¹ and 3150 cm⁻¹ are called the aliphatic C–H stretch [29]. For example, in a scientific study, the vibrations of C–H stretching bands have been observed in the 3120–3000 cm⁻¹ [30]. The vibrations related to the C–H stretching bands for the benzoxazole have been observed at 3085, 3074, 3065, and 3045cm⁻¹ band [31].

preferred is reliable for getting information about frequencies for the N-(4-dimethylamino 3,5-

In the present work, the vibrational values of aliphatic asymmetrical and symmetrical C–H stretching band for the molecule were calculated to be about 3114, 3096, 3095, and 3094 cm⁻¹ at B3LYP/6-311++G(d,p) level of calculation and 3086, 3070, and 3066 cm⁻¹ at HF/6-311++G(d,p) level of calculation, respectively. The bands have been experimentally observed in the range of 3082-3107 cm⁻¹. In the C–H stretching bands in the methyl groups, the vibration parameters were calculated to be about 2996, 2995, 2944, 2939, 2894, and 2887 cm⁻¹ at B3LYP/6-311++G(d,p) level of calculation and 2956, 2954 2916, 2914, 2868, and 2862 cm⁻¹ at HF/6-311++G(d,p) level of calculation, respectively. The C–H stretching bands in the methyl groups have experimentally been recorded as 2924 and 2964 cm⁻¹. Even is well known that the frequencies belonging to the methyl group have been noticed to appear at 2970–2950 or 2880–2860 cm⁻¹ [29]. All the calculations (especially performed by DFT method with superior correlations) have been observed to agree with the experimental measurement results.

Additionally, the maximum Raman activities have been calculated to be about 517.00 and 349.09 for the aromatic stretching usym(CH₃) vibrations by applying the B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) levels of theory, respectively. Moreover, we have calculated the stretching vibration bands (carbonyl group modes) between the carbon and oxygen atoms. On this basis, the aromatic v_{sym} (C=O2) modes have been observed to be approximately 1720 and 1706 cm⁻¹ in the experimental spectrum. The modes have been calculated to be about 1759 and 1706 cm⁻¹ at B3LYP/6-311++G(d,p) level of theory, while the bands have appeared at about 1862 and 1798 cm⁻¹ at HF/6-311++G(d,p) basis set. According to the comparisons, the DFT calculation level exhibits superior performance to the HF level of theory. Similar results have been seen in the literature [32].

Moreover, the differentiation in the stretching $v_{sym}(C=02)$ vibration bands has resulted from varied π - π^* conjugative effects and electron donating groups leading to the strong non-uniform intra-molecular charge distributions, actual position of the substituents, electron engagements, and lone pairs of electrons over the molecule. Among the IR intensities (in the unit of km/mol), the strongest IR bands have been noted to be about 626.4407 km/mol and 1003.786 km/mol for the stretching $v_{sym}(C=02)$ vibration bands at B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) levels of theory, respectively. As for the C–C stretching modes and C–C–C ring vibration bands in the benzene ring, in the literature, the inner modes have appeared at approximately 1315±65 and 1000cm⁻¹ bands, while the latter modes have been recorded at the bands of 1600, 1580, 1490 and 1440cm⁻¹ [30].

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In this study, the ring modes have been observed between 982 and 1593 cm⁻¹ bands at B3LYP/6-311++G(d,p) level of theory while the bands have appeared at intervals 1006-1666 cm⁻¹ at HF/6-311++G(d,p) basis set. The modes have experimentally been observed in the 1687-968 cm⁻¹. The main difference between the experimental findings and theoretical calculations stems from two main reasons: (I) the experimental results have been taken in the solid phase, and theoretical calculations have been performed in the gas phase. (II) in the theoretical calculations, the π - π * conjugative effects and electron donating groups leading to the strong non-uniform intra-molecular charge distributions, actual position of the substituents, electron engagements, and lone pairs of electrons over the molecule have been anticipated to be more homogenous than those in the experimental results [33]. In the literature, to illustrate the 3-(5-methyl thiazole-2-yl-diazenyl)-2-phenyl-1H-indole under C1 symmetry, the main C– C stretching bands have been calculated between 1071 and 1567cm⁻¹.

Besides, the C–C stretching modes and C–C–C ring vibration bands have been found in the ranges from 1600 cm⁻¹ to 1585 cm⁻¹ and 1500 cm⁻¹ to 1400 cm⁻¹ [34,35]. At the same time, the other aromatic stretching mode of C–N bands in the side chains always occurs with the other aromatic stretching bands and bending modes together. Thus, it is hard to separate the modes between them. The N–H stretching modes have been found at a high level. In the literature, the C–N stretching band has been observed at 1368 cm⁻¹ in benzamide [36].

Moreover, the stretching frequency mode for the C–N bands in the salicylic aldoxime has been recorded at 1617 cm⁻¹. Similarly, the frequency value of the N–H stretching modes has been observed at 3481 cm⁻¹ in the aniline [37]. In the present study, the C–N stretching vibration bands in the ring-b have appeared at 1759, 1593, 1322, 1308, 1262, 1217, 1186, 1143, and 895 cm⁻¹ at B3LYP/6–311++G(d,p) level of theory.

On the other hand, the related modes have been observed to be about 1862, 1666, 1415, 1368, 1255, 1226, 1195, 1168, and 947 cm⁻¹ at HF/6–311++G(d,p) basis set. The experimentally observed C–N stretching vibration bands have been found at 1720, 1687, 1630, 1249, 1236, 1186, and 1141 cm⁻¹. The C–N stretching vibration modes have been obtained at about 1086, 1076, 982, and 583 cm⁻¹ at B3LYP/6–311++G(d,p) calculation level while the modes have been observed to be in a range of 1116, 1107, 1006, and 606 cm⁻¹ at HF/6–311++G(d,p) basis set. The observed mode has been measured to be about 968 cm⁻¹ for the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide compound. At the same time, the other aromatic nitro compounds with asymmetric and symmetric stretching vibrational bands have been detected to be strong absorptions at 1485–1570 cm⁻¹ [38] and 1320–1370 cm⁻¹ [39], respectively. Likewise, the NO stretching vibrational modes are in a range of 1340–1450 cm⁻¹ [40]. In the current work, the NO stretching vibrational modes have been calculated to be in a range of 1524-762 cm⁻¹ at B3LYP/6–311++G(d,p) calculation level, while the modes have been observed to be in a range of 1625-821 cm⁻¹ at HF/6–311++G(d,p) basis set.

As for the appearance of bending modes in the compound, the C–H bending vibrational modes in the ring-a have been calculated between 1706-541 cm⁻¹ for the CCH bending vibrational modes at B3LYP/6–311++G(d,p) calculation level, whereas the modes have been determined to be in a range from 1798 cm⁻¹ to 556 cm⁻¹. In ring–b, the mode values intervals of 1524-392 cm⁻¹ and 1625-396 cm⁻¹ have been observed at B3LYP/6– 311++G(d,p) and HF/6–311++G(d,p) basis sets. The other bending modes (rocking, torsion, umbrella, breathing, wagging, scissoring, and twisting) have been provided in Tables 2 and 3.

	(cm ⁻¹) <i>DFT</i>							
Assignments	Scaled Freq.	Red. Masses	Frc Consts	IR Intent	Raman Actv	Depolar (P)	Depolar (U)	Exp. Freq.
$v_{sym}^{a}(CH)$	3114	1.1090	6.9036	0.26	247.14	0.1573	0.2719	3107
u _{asym} b(CH)	3096	1.0916	6.7205	14.14	24.69	0.7500	0.8571	
u _{sym} b(CH)	3095	1.0926	6.7244	0.075	46.97	0.0985	0.1793	3095
$v_{asym}^{a}(CH)$	3094	1.0894	6.6967	0.15	119.63	0.7500	0.8571	3082
v _{asym} (CH ₃)	2996	1.1005	6.3421	13.06	57.45	0.7137	0.8329	
v _{asym} (CH ₃)	2995	1.1003	6.3357	5.7304	9.89	0.7500	0.8571	
uasym(CH3)	2944	1.1053	6.1500	1.1152	43.06	0.6040	0.7531	2964
v _{asym} (CH ₃)	2939	1.1043	6.1255	35.4097	193.68	0.7500	0.8571	2924
Usym(CH3)	2894	1.0357	5.5697	80.6611	517.00	0.0681	0.1275	
Usym(CH3)	2887	1.0349	5.5422	31.2089	45.81	0.7500	0.8571	
$v_{sym}(C=O_2) + v^b(N-C)$	1759	12.4075	24.6547	0.5709	96.65	0.1764	0.2998	1720
$v_{sym}(C=O_2) + \gamma a(CCH)$	1706	12.4507	23.2754	626.4407	0.3024	0.7500	0.8571	1706
$v^{b}(C=C) + \gamma^{a}(CCH) + \gamma^{a}(CCH) + v^{b}(N-C)$	1593	7.1938	11.7271	107.8010	171.9320	0.5392	0.7006	1687-1630
$v^{a}(C=C) + \gamma^{a}(CCH) +$	1576	6.7274	10.7352	5.0778	42.4942	0.0442	0.0847	1543
$\upsilon(N=0)+\upsilon^a(C=C)+\Phi(CH_3)+\gamma^b(CCH)$	1524	12.0810	18.0348	290.6978	2.7197	0.7500	0.8571	1528
$v(N=0)+v^a(C=C)+\Phi^b(CCH)$	1522	8.8722	13.2033	383.6740	123.2386	0.4850	0.6532	
υ ^b (C=C)+ υ ^b (CCH)	1503	8.2232	11.9412	61.1878	7.6190	0.7500	0.8571	
υ(N=0)+3 ^b (CCH)	1494	2.2320	3.1986	153.7839	2.4706	0.7439	0.8532	
υ(N=0)+3 (CH ₃)	1444	1.2150	1.6276	3.3154	49.1572	0.4239	0.5954	1468
3 (CH ₃)	1439	1.0602	1.4102	25.9684	2.2021	0.7500	0.8571	1438
3 (CH ₃)	1434	1.0472	1.3832	26.1861	1.9936	0.7500	0.8571	
3 ^b (CCH)	1427	1.1043	1.4448	5.8453	12.9432	0.5427	0.7036	1422
υ(N=O)+ 3 (CH ₃)+ γ ^b (CCH)	1401	1.6170	2.0368	200.3489	29.4370	0.1697	0.2902	
$U b(CH_3) + v(N=0) + \gamma b(CCH)$	1390	1.1396	1.4148	0.2550	10.7982	0.7500	0.8571	
U (CH3)	1381	3.8179	4.6800	16.3654	2.8174	0.7500	0.8571	1377
$v^{b}(C=C)+\gamma^{b}(CCH)$	1370	4.5152	5.4442	70.2034	38.2015	0.4091	0.5807	1366
γ ^b (CCH)+ υ(N=O)+ 3 (CH ₃)+ υ ^b (N-C)	1322	3.7628	4.2226	281.3185	133.9973	0.2659	0.4200	
$v(N=0)+v^{b}(C=C)+\gamma^{b}(CCH)$	1313	11.0749	12.2675	344.0675	13.8591	0.7500	0.8571	
υ(N=O)+ υ ^b (N-C)+ γ ^b (CCH)	1308	9.2975	10.2110	42.9441	237.6281	0.1569	0.2712	
$\gamma^{b}(CCH) + v^{b}(C=C)$	1271	1.9399	2.0131	10.6930	11.9878	0.7500	0.8571	1284
$\gamma^{a}(CCH) + \upsilon^{b}(C=C) + \upsilon(CH_{3}) + \upsilon^{b}(N-C)$	1262	6.6373	6.7889	135.4079	17.9333	0.7500	0.8571	1249-1236
$\gamma^{b}(CCH) + \upsilon^{b}(N-C) + \upsilon(CH_{3})$	1217	2.2041	2.0975	77.9363	1.6895	0.7500	0.8571	
$B^{b} + {}^{\Phi}{}^{b}(CCH) + \upsilon^{b}(N-C) + \upsilon^{a}(C=C)$	1186	4.5375	4.1027	75.8744	49.1308	0.2579	0.4101	1186
v^{b} (C=C)+ v^{b} (CCH) + v (CH ₃)	1152	2.3175	1.9734	5.2908	0.2270	0.7500	0.8571	1177
υ(CH ₃)+ υ ^b (N-C)+3 ^b (CCH)	1143	1.7769	1.4902	31.5136	15.1952	0.2222	0.3637	1141
υ(CH ₃)+ γ ^b (CCH)	1103	1.4077	1.0998	5.5543	1.0360	0.7500	0.8571	1113
υ²(N-C)+ υ ^b (CCH)+ γ ^b (CCH)	1086	6.5545	4.9742	89.6597	11.8526	0.7500	0.8571	
$\upsilon(CH_3) + \gamma^b(CCC) + 3^b(CCH) + \upsilon^a(N-C) + 3^b(CCH)$	1078	2.1844	1.6303	42.6011	7.4200	0.6129	0.7600	1076
υ(CH ₃)+ γ ^b (CCH)	1071	1.2712	0.9375	2.0055	3.5920	0.6971	0.8215	
$3 \approx (CCH) + 3 \approx (CCH) + v \approx (C=C)$	1044	1.3026	0.9125	23.3185	25.6504	0.1849	0.3121	
υ(CH ₃)	1041	1.4899	1.0377	9.6567	0.5869	0.7500	0.8571	1036
$\gamma^{b}(CCH) + 3^{a}(CCH) + \gamma^{a}(CNC) + v^{a}(C=C)$	1002	3.8530	2.4870	8.4983	1.0230	0.7500	0.8571	
$B^{a} + v^{a}(N-C) + v^{b}(C=C) + 3^{a}(CCH)$	982	3.7321	2.3118	6.2692	4.6071	0.5477	0.7078	968
[♠] a(CCH)	936	1.2982	0.7310	0.0087	1.0154	0.5589	0.7171	
$B^{b} + v(CH_{3})$	931	3.3876	1.8884	36.3164	23.2198	0.3018	0.4637	926

 Table 1. Calculated DFT (cm⁻¹) frequencies and Experimental frequencies (cm⁻¹)

υ, stretching; ɣ, bending; υ, rocking; Ψ, torsion; U, umbrella; B, breathing; w, wagging; asy, asymmetric; sym, symmetric; 3, scissoring; ^Φ, twisting.

a – Ring1. b - Ring2

Table 1. Continued

	DFT							
	m ⁻¹)							
Assignments	д. (а	ş			>	\sim	\sim	
in the second seco	Frec	asse	ısts	t	Act	r (P	r (U	eq.
	lled	Ч. W	Cor	Intei	man	pola	pola	Ъ. Т
	Sca	Re	Frc	IR	Raı	Dej	Dej	ExJ
$\upsilon^{b}(N-C) + \upsilon(N=O) + \gamma^{a}(CCC) + \varphi^{b}(CCC)$	895	9.7180	5.0031	45.0523	0.8577	0.7500	0.8571	005
	895	1.4310	0.7355	0.1169	0.3266	0.7359	0.8479	895
3º(CCH)	8/4	1.6935	0.8302	20.3834	0.3072	0./500	0.85/1	020
	010	10.8181	4.8175	0.2108	1.1043	0.6400	0.7805	828
3°	762	2.1233	0.0937	12 2222	1.0700	0.7500	0.0571	777
$U(N=0)+3^{\circ}(CCH)+3^{\circ}(CNO)+$	762	7.7001 0.2E10	2.0745	13.2223	0.3570	0.7499	0.05/1	///
$\Phi_a \perp \pi (CNO) \perp \pi h(CCC) \perp$	720	0.2319 0.2319	2 2060	2 1 1.7 3 5 1	1 2701	0.0372	0.0717	
$v (ONO) \perp \phi_a \perp 3b(CCH) \perp$	736	8 5607	2.0009	1 0120	0 7039	0.7207	0.0451	
v(ONO) + vb(CCC) + vb(CCH) +	723	94167	3 1638	19 9119	0.7057	0.7500	0.8571	721-714
$v_{p}(CCC) + v_{p}(CCH)$	693	8.0478	2 4 8 2 7	16 8113	0.5729	0.7500	0.8571	696
$v_a(CCC) + v_a(CNC) +$	671	8.0038	2.1027	46 5940	2 2883	0.7500	0.8571	070
B molecule	660	6.0232	1.6857	0.3855	1.0092	0.5250	0.6886	
	627	4.8020	1.2108	0.7821	0.4819	0.7500	0.8571	
B molecule	602	10.0988	2.3482	20.9262	14.2229	0.0904	0.1657	
[•] molecule	601	2.4006	0.5576	4.3697	0.2282	0.7476	0.8556	
y ^b (CCH)+ 3 ^a (CCC)+ υ ^a (N-C)+ y ^a (NCO)+	583	3.8183	0.8356	12.6646	0.4722	0.7500	0.8571	
$v^{b}(CCH) + v^{a}(CCH) + v^{a}(NCO) +$	541	3.8823	0.7309	1.9633	0.6887	0.7500	0.8571	
$\Phi_b + \chi_b(NCO) + \chi(CNC) +$	521	5.7624	1.0072	5.9953	1.3013	0.2279	0.3712	
y (CNC) + y a(CCO) +	440	5.6444	0.7035	5.4487	2.2408	0.7200	0.8372	
$\chi^{a}(CCC) + \chi^{b}(CNC) +$	424	7.7694	0.8991	0.0907	0.9860	0.7500	0.8571	
w^{b} + χ^{a} (CNC)+ χ (CNO)+	401	8.4488	0.8742	0.6215	0.8359	0.7500	0.8571	
γ (CNC) + γ^{b} (CCH) + γ^{a} (NCO)	392	4.0042	0.3948	22.7896	1.4374	0.2831	0.4412	
γ(CNC)+ υ ^b	370	5.5737	0.4897	1.3311	0.4771	0.7500	0.8571	
γ (CNC) + Φ b + γ (CNO) +	357	4.9990	0.4115	0.0089	7.9951	0.3057	0.4683	
γ (CNC)+ γ^{a} (CNC)+	333	4.4450	0.3189	1.7528	0.8401	0.7500	0.8571	
B ^b +γ ^b (CNC)	290	8.7592	0.4765	1.0288	6.7781	0.3453	0.5134	
Фъ	277	4.1273	0.2041	0.0517	1.3244	0.6255	0.7696	
Ψ CH ₃ + γ ^b (CNC)	266	1.9291	0.0879	4.2420	0.2989	0.7500	0.8571	
Ψ CH ₃	247	1.0796	0.0424	0.0246	2.4677	0.6532	0.7902	
B ^b + Ψ CH ₃ + γ ^b (NCO)	238	5.4417	0.1976	6.9046	2.1431	0.1432	0.2506	
Ψ CH3+	238	3.0142	0.1095	0.0982	0.0925	0.7458	0.8544	
$\Psi CH_3 + \gamma^a (NCO)$	214	4.1046	0.1212	1.4124	1.6448	0.7500	0.8571	
Ψ CH ₃ + γ ^b (NCO)	193	3.3394	0.0803	4.8413	0.6067	0.7500	0.8571	
υ CH3+ γ ^b (NCO) +υ ^a	178	7.3127	0.1505	1.0282	3.6784	0.4127	0.5842	
^Φ ^b +υ CH ₃ +	165	5.7984	0.1016	2.0349	5.6968	0.6895	0.8162	
υ molecule	144	5.2548	0.0700	0.2366	1.7520	0.7500	0.8571	
υ molecule	121	9.9501	0.0945	9.1175	0.2971	0.7500	0.8571	
υ CH3+ λp (CCN)	106	4.2305	0.0311	10.1937	3.6734	0.5847	0.7380	
υ NO2+ Ψ CH3+ Ψ ^a	71	9.5781	0.0316	0.9047	2.4715	0.7500	0.8571	
w molecule	70	6.5069	0.0205	4.2314	0.5583	0.7500	0.8571	
υ NO ₂ + υ CH ₃	69	8.9288	0.0276	0.2660	3.4854	0.5551	0.7139	
^φ molecule	62	8.0780	0.0206	0.2173	0.6891	0.7500	0.8571	
w molecule	36	6.0630	0.0054	3.3309	1.2818	0.7500	0.8571	
w molecule	24	11.7827	0.0045	0.2885	4.1201	0.7242	0.8400	

υ, stretching; ɣ, bending; υ, rocking; Ψ, torsion; U, umbrella; B, breathing; w, wagging; asy, asymmetric; sym, symmetric; 3, scissoring; ^Φ, twisting.

a – Ring1. b - Ring2



Figure 2. Change of vibrational frequencies scaled by DFT-B3LYP/6-311++G(d,p) basis set versus experimental vibrational frequencies



Figure 3. Change of vibrational frequencies scaled by HF-B3LYP/6–311++G(d,p) basis set versus experimental vibrational frequencies

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Assignments	Scaled Freq. (cm ^{.1}) <i>HF</i>	Red. Masses	Frc Consts	IR Intent	Raman Actv	Depolar (P)	Depolar (U)	Exp. Freq.
υ _{sym} a(CH)	3086	1.11	7.62	0.48	173.47	0.1614	0.2779	3107
v _{asym} b(CH)	3070	1.09	7.42	9.26	26.20	0.7500	0.8571	
υ _{sym} b(CH)	3070	1.09	7.42	0.05	60.54	0.1128	0.2027	3095
v _{asym} a(CH)	3066	1.09	7.38	0.46	87.92	0.7500	0.8571	3082
v _{asym} (CH3)	2956	1.10	6.93	35.1349	42.38	0.7441	0.8533	
v _{asym} (CH3)	2954	1.10	6.9237	9.1717	16.94	0.7500	0.8571	
v _{asym} (CH3)	2916	1.1050	6.7596	0.3324	19.43	0.7475	0.8555	2964
v _{asym} (CH3)	2914	1.1043	6.7461	56.3837	148.90	0.7500	0.8571	2924
υ _{sym} (CH ₃)	2868	1.0363	6.1327	88.0587	349.09	0.0360	0.0695	

 Table 2. Calculated HF frequencies (cm⁻¹) and Experimental frequencies (cm⁻¹)

υ, stretching; ɣ, bending; υ, rocking; Ψ, torsion; U, umbrella; B, breathing; w, wagging; asy, asymmetric; sym, symmetric; 3, scissoring; ^Φ, twisting. a - Ring1. b - Ring2

Table 2. Continued Scaled Freq. (cm⁻¹) HF Masses Raman Actv **Depolar** (U) Assignments epolar (P) Consts . Freq. Intent Red.] ġ Frc К v_{sym}(CH₃) 2862 1.0352 6.1005 39.8838 23.9361 0.7500 0.8571 $v_{sym}(C=O_2) + v^b(N-C)$ 1862 12.2950 30.6740 6.6877 91.8958 0.2750 0.4314 1720 1798 12.4815 29.0102 1003.7862 1706 $v_{sym}(C=O_2) + \gamma a(CCH)$ 2.9709 0.7500 0.8571 $\upsilon^{b}(C=C) + \gamma^{a}(CCH) + \gamma^{a}(CCH) + \upsilon^{b}(N-C)$ 1666 9.2170 18.4192 372.0050 73.0194 0.5446 0.7052 1687-1630 $v^{a}(C=C) + \gamma^{a}(CCH) +$ 1632 13.7990 26.4563 747.5561 1.2899 0.7500 0.8571 1543 $\upsilon(N=0) + \upsilon^a (C=C) + {}^{\phi}(CH_3) + \gamma {}^{b}(CCH)$ 1625 6.6719 12.6709 1.1724 61.8098 0.0597 0.1127 1528 $v(N=0)+v^{a}(C=C)+\Phi^{b}(CCH)$ 1614 7.4546 13.9700 275.9697 105.3286 0.4830 0.6514 $v^{b}(C=C)+v^{b}(CCH)$ 1575 7.8892 14.0733 29.5236 3.1870 0.7500 0.8571 v(N=0)+3b(CCH)3.4516 307.5915 29.8872 0.3457 0.5138 1524 2.0656 42.8994 υ(N=0)+3(CH₃) 1487 10.0456 15.9799 55.0893 0.0481 0.0917 1468 372.9556 3 (CH₃) 1483 4.8848 7.7303 5.1759 0.7500 0.8571 1438 22.2763 3 (CH₃) 1479 1.3330 2.0975 10.6868 0.7494 0.8568 3 b(CCH) 1475 1.1940 1.8698 33.5022 1.1377 0.7500 0.8571 1422 $v(N=0)+3(CH_3)+\gamma^{b}(CCH)$ 15.7372 1464 1.0651 1.6419 2.0592 0.7500 0.8571 $U b(CH_3) + v(N=0) + \gamma b(CCH)$ 1455 1.0875 1.6582 9.0041 8.8913 0.7422 0.8520 U (CH₃) 1443 1.6317 2.4441 236.6356 2.5748 0.7313 0.8448 1377 1426 1.1492 1.6825 1.0932 4.1266 $v^{b}(C=C)+\gamma^{b}(CCH)$ 0.7500 0.8571 1366 $y^{b}(CCH) + v(N=0) + 3(CH_{3}) + v^{b}(N-C)$ 1415 4.6407 6.6877 130.3512 55.8562 0.1369 0.2408 1412 3.7955 $v(N=0)+v^{b}(C=C)+\gamma^{b}(CCH)$ 5.4482 17.6801 0.8523 0.7500 0.8571 1368 3.1122 $v(N=0)+v^{b}(N-C)+y^{b}(CCH)$ 4.1865 197.0477 2.7153 0.6981 0.8222 2.3328 6.6644 $\gamma^{b}(CCH) + \upsilon^{b}(C=C)$ 1312 1.8811 0.1565 0.7500 0.8571 1284 $\gamma^{a}(CCH) + \upsilon^{b}(C=C) + \upsilon(CH_{3}) + \upsilon^{b}(N-C)$ 1255 2.7401 3.1091 36.1686 0.3614 0.7500 0.8571 1249-1236 $\gamma^{b}(CCH) + \upsilon^{b}(N-C) + \upsilon(CH_{3})$ 1226 6.0448 6.5427 77.4441 25.0864 0.3527 0.5215 $B^{b} + \Phi^{b}(CCH) + \upsilon^{b}(N-C) + \upsilon^{a}(C=C)$ 1195 2.0472 2.1026 1.7835 0.6503 0.7500 0.8571 1186 $v^{b}(C=C)+v^{b}(CCH)+v(CH_{3})$ 1174 6.2008 6.1463 100.6400 5.1897 0.7500 0.8571 1177 $\upsilon(CH_3) + \upsilon^b(N-C) + 3^b(CCH)$ 1168 1.7032 1.6716 22.1894 8.0361 0.0529 0.1005 1141 $v(CH_3) + \gamma^{b}(CCH)$ 1139 1.4304 1.3352 17.4903 4.4130 0.7500 0.8571 1113 1116 2.4559 2.2002 51.3000 9.9660 0.3025 0.4645 $\upsilon^{a}(N-C) + \upsilon^{b}(CCH) + \gamma^{b}(CCH)$ **υ(CH₃)+ γ^b(CCC)+ 3^b(CCH)+ υ^a(N-C)+ 3^b(CCH)** 1107 6.2438 5.5078 56.3981 22.5867 0.7500 0.8571 1076 7.9686 0.2597 0.4123 $v(CH_3) + \gamma^{b}(CCH)$ 1102 1.2098 1.0564 21.6384 3a(CCH) + 3b(CCH) + vb(C=C)1070 1.4413 1.1867 12.1979 2.2950 0.7500 0.8571 1065 1.2918 1.0550 22.5989 22,9221 0.1146 0.2057 1036 v(CH₃) $\gamma^{b}(CCH) + 3^{a}(CCH) + \gamma^{a}(CNC) + \upsilon^{a}(C=C)$ 1034 3.6301 2.7922 7.2123 3.0356 0.7500 0.8571 $B^a + v^a(N-C) + v^b(C=C) + 3^a(CCH)$ 1006 3.3325 2.4265 1.5861 1.7559 0.7496 0.8569 968 [∲] a(CCH) 974 1.3039 0.8904 0.0102 3.4268 0.7275 0.8423 961 1.4420 0.9597 1.4030 0.1001 0.7370 0.8486 926 $B^{b} + v(CH_{3})$ $v^{b}(N-C) + v(N=0) + \gamma^{a}(CCC) +$ 947 10.8291 6.9852 33.9465 0.9672 0.7500 0.8571 ^ф ь(ССН) 47.3572 943 3.3106 2.1209 6.3296 0.3778 0.5484 895 3^b(CCH) 935 1.7125 1.0771 9.2910 0.0980 0.7500 0.8571 **B** molecule 871 11.8565 6.4734 0.4415 1.5150 0.1603 0.2762 828 92.9825 0.9381 0.7500 0.8571 3ª 853 2.1866 1.1442 v(N=0)+3b(CCH)+y(CNO)+7.1215 3.4588 8.4321 1.7575 0.7500 0.8571 777 821 799 8.9931 4.1322 0.7956 10.4168 0.2128 0.3510 **B** molecule $\Phi_a + \gamma$ (CNO) + γ_b (CCC) + 7.6097 3.3399 13.5348 13.0633 0.0105 0.0207 781 γ (ONO) + Φ_{a} + 3^b(CCH) + 768 7.9498 3.3809 2.4818 2.9888 0.7044 0.8266 γ (ONO)+ γ ^b(CCC)+ γ ^b(CCH)+ 0.7500 0.8571 758 8.8535 3.6709 26.3410 1.2116 721-714

u, stretching; ɣ, bending; u, rocking; Ψ, torsion; U, umbrella; B, breathing; w, wagging; asy, asymmetric; sym, symmetric; 3, scissoring; ^Φ, twisting.

a - Ring1. b - Ring2

Table 2. Continued

Assignments	Scaled Freq. (cm ⁻¹) <i>HF</i>	Red. Masses	Frc Consts	R Intent	Raman Actv	Depolar (P)	Depolar (U)	Exp. Freq.
$y^{b}(CCC) + y(ONO) + y^{b}(CCH)$	726	8.8684	3.3641	48.9181	0.5631	0.7500	0.8571	696
y ^a (CCC)+ y ^a (CNC)+	694	7.4396	2.5812	46.8675	0.6749	0.7500	0.8571	
B molecule	673	6.0625	1.9807	0.3736	0.5984	0.6251	0.7693	
^Φ molecule	650	4.0529	1.2328	0.6954	0.7164	0.7500	0.8571	
B molecule	627	2.5884	0.7333	0.7547	0.1638	0.7500	0.8571	
^Φ molecule	618	10.1004	2.7791	20.8632	11.2754	0.0621	0.1170	
ɣʰ(CCH)+ З¤(CCC)+ υ¤(N-C)+ ɣ¤(NCO)+	606	3.7415	0.9920	15.7006	0.4647	0.7500	0.8571	
ɣʰ(CCH)+ ɣª(CCH)+ ɣª(NCO)+	556	3.9346	0.8749	1.0464	0.2843	0.7500	0.8571	
$\Phi_{\rm b} + \gamma_{\rm b}(\rm NCO) + \gamma(\rm CNC) +$	541	5.8786	1.2406	4.8111	1.7530	0.1500	0.2609	
γ (CNC) + γ^{a} (CCO) +	449	6.7029	0.9735	19.2378	3.5610	0.5471	0.7073	
$\gamma^{a}(CCC) + \gamma^{b}(CNC) +$	432	7.8815	1.0600	5.9593	1.4424	0.7500	0.8571	
w ^b + y ^a (CNC)+ y (CNO)+	418	8.0107	1.0113	1.8791	0.7437	0.7500	0.8571	
γ (CNC) + γ^{b} (CCH) + γ^{a} (NCO)	396	4.1564	0.4698	23.8989	0.2866	0.4405	0.6116	
γ (CNC) + υ ^b	374	6.6844	0.6746	1.5637	0.4516	0.7500	0.8571	
γ (CNC)+ Φ b + γ (CNO)+	361	4.6053	0.4331	3.2154	5.5912	0.2183	0.3583	
γ (CNC)+ γ^{a} (CNC)+	333	4.7764	0.3812	0.3451	0.4837	0.7500	0.8571	
$B^{b}+\gamma^{b}(CNC)$	296	8.0882	0.5119	1.8302	3.5527	0.2192	0.3596	
Фъ	283	4.0688	0.2350	0.0000	1.5739	0.7389	0.8498	
Ψ CH ₃ + γ ^b (CNC)	255	3.3158	0.1555	3.4999	0.0304	0.7500	0.8571	
Ψ CH ₃	229	5.9895	0.2276	7.9920	3.0712	0.0914	0.1675	
B ^b + Ψ CH ₃ + γ ^b (NCO)	229	5.0768	0.1927	0.3671	0.3372	0.7500	0.8571	
Ψ CH3+	205	1.9021	0.0578	2.7224	0.3291	0.7500	0.8571	
$\Psi CH_3 + \gamma^a (NCO)$	204	1.0952	0.0329	0.0126	0.2490	0.7324	0.8455	
Ψ CH ₃ + γ ^b (NCO)	173	5.4882	0.1183	1.8249	4.1414	0.6985	0.8225	3107
υ CH3+ γ ^b (NCO) +υ ^a	166	7.1187	0.1420	0.7241	2.3864	0.5147	0.6796	
^Φ ^b +υ CH ₃ +	165	4.7326	0.0932	4.7627	1.6403	0.7500	0.8571	3095
u molecule	121	7.9518	0.0842	9.5198	0.2959	0.7500	0.8571	3082
u molecule	110	2.9202	0.0257	5.2397	0.5317	0.7500	0.8571	
υ CH3+ γ ^b (CCN)	86	4.0186	0.0215	10.3331	3.8506	0.5126	0.6777	
υ NO2+ Ψ CH3+ Ψ ^a	68	10.1695	0.0339	0.3789	1.3397	0.7500	0.8571	2964
w molecule	67	7.3680	0.0242	0.8278	1.7221	0.7340	0.8466	
υ NO2+ υ CH3	64	6.4184	0.0192	2.9143	0.4785	0.7500	0.8571	
[¢] molecule	61	7.1761	0.0192	0.5392	0.6427	0.7500	0.8571	
w molecule	42	5.7046	0.0071	2.7198	1.2168	0.7500	0.8571	
w molecule	20	11.8775	0.0035	0.2638	3.5809	0.7494	0.8568	

u, stretching; ɣ, bending; u, rocking; Ψ, torsion; U, umbrella; B, breathing; w, wagging; asy, asymmetric; sym, symmetric; 3, scissoring; ^Φ, twisting. a - Ring1. b - Ring2

The good agreement between the calculation levels of B3LYP/6-311++G(d,p) and HF/6-311++G(d,p)for the vibrational frequency bands has enabled us to determine the molecular geometric characteristics for the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide. In this respect, the selected molecular geometric features, including some selected bond lengths, bond angles, and dihedrals, have extensively been examined in detail by means of both the B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) levels of theories and determined the correlation between the calculation levels to identify the molecular geometric parameters. One can see the atomic numbered N-(4-dimethylamino 3,5dinitrophenyl)maleimide compound in Figure 1.

Besides, we have numerically depicted some selected molecular geometric features in Table 3. The bond lengths between the carbon atoms have been calculated to be about 1.39-1.50 Å and 1.38-1.50 Å at the B3LYP/6–311++G(d,p) and HF/6–311++G(d,p) levels of theories, respectively. The results obtained show that all the computations have been observed to agree with each other. As for the bond lengths between the nitrogenous and carbon atoms, the B3LYP/6–311++G(d,p) calculation level has displayed the lengths that have been gathered to be between about 1.37-1.49 Å. Similarly, we have computed the lengths between the nitrogenous and carbon atoms in the range of 1.37-1.49 Å at the HF/6–311++G(d,p) level of theory.

Moreover, the bond lengths between the carbon and hydrogen atoms have been calculated to vary from about 1.08 Å to 1.09 Å at the B3LYP/6-311++G(d,p) level of calculation whereas we have found between 1.07 Å and 1.08 Å for the bond distance values by using the HF/6-311++G(d,p) level of theory. The bond distance between the nitrogenous and oxygen has also been computed to be about 1.23 Å and 1.19 Å at the B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) basis sets, respectively. Moreover, the bond angles and bond dihedrals are in good agreement with each other (see Table 3). There seemed to be some differences in the calculations performed by the B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) levels of calculations due to the conjugation of π existing in both rings, different spatial electron (non-bonding lone pairs) distributions over the bonds in the molecule, and electron-withdrawing strength of high electronegative atoms. Besides, the electron density (electronegative, and electron-acceptor ability characteristics) delocalization, repulsive forces formation between positive or negative charged atoms, inhomogeneous charge distribution, and especially intra-molecular charge transfer (ICT) have led to vary the values of calculation models [41-46].

			U			1		
Bond Length(Å)	DFT	HF	Bond Angle(°)	DFT	HF	Bond Dihedrals(°)	DFT	HF
C1-C6	1.39	1.38	C1-C2-C3	120.02	119.82	C1-C2-H7-N18	0.75	0.42
C1-N18	1.42	1.42	C1-C2-H7	121.12	120.91	H7-C2-C3-N10	-7.52	-5.31
С6-Н8	1.08	1.07	C1-N18-C15	125.07	124.80	C3-C4-N9-O26	38.20	47.27
C3-N10	1.48	1.47	C1-N18-C12	125.07	124.80	C4-N9-C25-H32	13.93	
N10-024	1.23	1.19	C12-N18-C15	109.85	110.40	019-C12-N18-C15	179.86	179.50
C4-N9	1.37	1.37	C14-C15-O20	128.08	128.04	N18-C15-C14-H17	-179.88	-179.88
N9-C25	1.46	1.45	C13-C14-H17	129.48	121.60	C4-N9-C26-H28	-107.95	-113.20
C26-H28	1.09	1.08	C6-C5-N11	114.42	114.88	C4-N9-C25-H31	131.61	
C5-N11	1.49	1.47	C5-N11-O21	117.77	117.89	N9-C4-C3-N10	9.19	
C1-N18	1.42	1.42	C4-N9-C25	122.65	122.12	C3-C2-C1-N18	-177.33	-177.58
N18-C15	1.41	1.39	N9-C26-H28	112.05	111.71	C1-N18-C15-C14	-179.98	179.97
C15-O20	1.21	1.18				C1-C4-N9-C25	110.89	54.79
C12-C13	1.50	1.50				C1-C4-N9-C26	-69.12	-125.21

Table 3. Molecular geometric features of the compound

In the present work, the distribution of atomic charges for the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide have been calculated by the Mulliken method [47,48] at the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of calculation and all the computations for the atoms over the title molecule have been shown in Table 4. It has been observed that the magnitudes pertaining to the carbon atomic charges for the Mulliken calculation method are either positive or negative at the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) basis sets. These magnitudes have been noted to change between -1.25 and 0.26 for B3LYP/6-311++G(d,p) levels of calculation and between -0.57 and 0.22 for HF/6-311++G(d,p) levels of calculation. The magnitudes of charges calculated on N atoms excluding N28, decrease from HF to DFT calculation level. These values have been found to be 0.06 (N9), -0.39 (N10), -0.24 (N11), 0.44 (N18) at the B3LYP/6-311++G(d,p), and 0.29 (N9), -0.17 (N10), -0.17 (N11), 0.23 (N18) at the HF/6-31G(d,p) levels of calculations.

For O atoms, the magnitude of the charge is either positive or negative at the used basis sets. These magnitudes have been recorded to vary between -0.24 and 0.19 for the B3LYP/6-311++G(d,p) calculation and between -0.33 and 0.03 for the HF/6-311++G(d,p) level of theory. The magnitudes of charges calculated on O atoms have been detected to increase from the HF to DFT levels of calculations. In addition, the magnitudes of the hydrogen atomic charges have been observed to arrange from 0.12 to 0.30. The charge on H8 connected with C6 has been noticed to be the maximum magnitude (0.29 at the B3LYP/6-311++G(d,p) and 0.30 at the HF/6-311++G(d,p) levels of calculation). Although there seems to be a difference between the calculations performed by the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) basis set due to the presence of conjugation of π existing in both rings, non-bonding Ione pairs, inhomogeneous charge distributions, and especially intra-molecular charge transfer in the compound, it has been obvious that there has appeared a good agreement between the calculations.

The NMR examination is another identification study for organic compounds. There is a difference in the calculations performed by the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) calculation levels for the ¹³C-NMR and ¹H-NMR spectra because of the electron correlations. In more detail, no electron correlation effects have disappeared in the former method; however, in the latter calculation technique, the electronic energy has been treated as a function of the electron density of all electrons simultaneously, and thus the electron correlation effect has been taken in account for the calculations [49].

Label	DFT(B3LYP/6-311++(d,p))	HF (6-311++(d,p))
C1	-1.25	-0.57
C2	0.26	-0.28
C3	0.02	0.21
C4	0.09	-0.41
C5	0.13	0.21
C6	-0.18	-0.28
H7	0.26	0.30
H8	0.29	0.30
N9	0.06	0.29
N10	-0.39	-0.17
N11	-0.24	-0.17
C12	-0.30	0.11
C13	0.13	-0.09
C14	0.06	-0.09
C15	-0.03	0.11
H16	0.23	0.28
H17	0.24	0.28
N18	0.44	0.23
019	-0.20	-0.33
020	-0.24	-0.33
021	0.19	0.03
022	0.18	0.03
023	0.02	-0.01
024	0.11	-0.01
C25	-0.69	-0.36
C26	-0.27	0.22
H27	0.24	0.16
H28	0.12	0.16
H29	0.12	0.16
H30	0.23	0.22
H31	0.17	0.16
H32	0.17	0.16

Table 4: Atomic charges for optimized geometry of N-(4-dimethylamino 3,5-dinitrophenyl)maleimide

In this study, the GIAO ¹³C and ¹H NMR chemical shifts of N-(4-dimethylamino 3,5dinitrophenyl)maleimide have been calculated in the chloroform, and the obtained computations have numerically been depicted in Table 5. As for the comparison to the experimental results, the calculations performed at the B3LYP/6-311++G(d,p) calculation levels for the optimized geometry have been observed to be in good agreement with experimental results [16]. ¹H isotropic chemical shift values have been observed experimentally at 2.84–7.98 parts per million(ppm). On the other hand, the values have been calculated to be in the range of 0.41-7.41 ppm. At the same time, as seen in Table 5, all computations have been in good agreement with experimental data.

The CH proton (H8), observed to be about 7.98 ppm, is 7.13 ppm at the B3LYP/6-311++G(d,p)//HF/6-31G(d) calculation level and 7.41 ppm at B3LYP/6-311++G(d,p)//B3LYP/6-311+G(2d,p) level of theory. However, the chemical shift for the H13 atom has been obtained in good agreement with the experiment. In addition, ¹³C chemical shifts concerning TMS calculated at the same basis sets have been given in the same table. ¹³C chemical shift values were obtained at 51.2–165.0 ppm, whereas these values were experimentally observed at 42.3–168.2 ppm. The chemical shifts of C12 and C15 have been observed to be 168.2 ppm, whereas they have been noted to be at 155.8 ppm and 165.0 ppm at B3LYP/6-311++G(d,p)//HF/6-31G(d) and B3LYP/6-311++G(d,p)//B3LYP/6-311+G(2d,p) levels of theory, respectively. Nevertheless, the observed shift of C4 was noticed to be more different than the calculated ones because of the effect of chloroform solution on the compound.

		In CDCl ₃	In CDCl ₃	In CDCl ₃
Calculated	l Chemical Shift(ppm)	DFT-B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)	Experimental Value
	C12	165.0	155.8	168.2
	C15	163.0	155.8	168.2
	C4	159.0	134.6	138.6
	C13	149.7	124.7	134.6
ms	C14	148.9	124.7	134.6
Ato	C5	145.7	130.8	145.4
pon	C3	144.2	130.8	145.4
Car	C6	143.7	125.9	126.0
	C1	137.6	106.3	123.8
	C2	128.4	125.9	126.0
	C25	56.6	51.2	42.3
	C26	42.0	36.4	42.3
	H27	3.57	4.63	2.84
	Н8	7.41	7.13	7.98
	H16	7.01	5.95	6.92
smo	H17	6.85	5.95	6.92
n At	H7	6.07	7.13	7.98
086	H30	4.46	1.35	2.84
Hydr	H32	3.47	1.49	2.84
щ	H29	1.78	1.49	2.84
	H31	1.71	0.41	2.84
	H28	1.45	0.41	2.84

 Table 5. ¹³C and ¹H isotropic chemical shifts (concerning TMS, all values in ppm) for N-(4dimethylamino 3,5-dinitrophenyl)maleimide

 We have also determined some essential thermodynamics (including the total energy, zero-point energy, rotational constants, dipole moments, and the change in the total entropies such as rotational, vibrational, and translational) features with the aid of the B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) levels of calculations. One can see all the parameters computed in Table 6. Scale factors have been recommended [50] to predict the zero-point vibration energies accurately. Calculations of the HF/6-311++G(d,p) basis set for the energy parameters and rotational constants are the same as the B3LYP/6-311++G(d,p) level of theory. Moreover, HF data are generally smaller than DFT data for the entropy values.

Additionally, we have theoretically defined the frontier orbitals: the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which play a crucial role in quantum chemistry. The inner frontier orbitals (HOMO) are the outermost orbital containing electrons and tend to give the electrons such as an electron donor. On the other hand, the last frontier orbitals (LUMO) are the innermost orbital containing free places to accept electrons [51]. According to the molecular orbital theory, the interaction between HOMO and LUMO frontier orbitals for a structure is related to the transition state of π - π * type [52]. Therefore, the energy of the HOMO has directly been associated with the ionization potential, while the LUMO energy has been related to the electron affinity.

Besides, the energy difference between HOMO and LUMO orbital is called the band gap energy $|(\Delta E)|$, determining whether the structure is stable [53]. All the calculations about the frontier orbitals have numerically been depicted in Table 6. In addition, 3D plots of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) have been shown in Figure 4. According to the energy band gap (translation from HOMO to LUMO) deduced from the B3LYP/6–311++G(d,p) level of calculation, the value of $|(\Delta E)|$ has been calculated to be about 0.113 a.u. for the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide molecule while the band gap has been computed to be about 0.366 at the HF/6–311++G(d,p) level of calculation. The highest occupied molecular orbitals have been noted to localize on the title molecule but slightly on ring-1 mainly. On the other hand, the lowest unoccupied molecular orbitals have been determined to be about -0.128 and 0.025(a.u.) at B3LYP/6–311++G(d,p) and HF/6–311++G(d,p) basis sets, respectively. Conversely, the highest MO Eigenvalue has also been found to be -0.241 (a.u.) at B3LYP/6–311++G(d,p) and -0.341 (a.u.) at HF/6–311++G(d,p) calculation levels.



Figure 4. 3D plots of (left side) the HOMO and (right side) LUMO of the N-(4-dimethylamino 3,5dinitrophenyl)maleimide

In this part of the paper, we have focused wholly on the molecular electrostatic potential (MEP) behavior of the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide molecule. It is well known that at any

given point r(x, y, z) in the vicinity of a molecule, the molecular electrostatic potential V(r) is defined by the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r [54,55]. The molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions, as well as hydrogen-bonding interactions [56,57].

Table 6. Theoretically computed energies (a.u.), zero–point vibrational energies (kcal mol⁻¹), rotational constants (GHz) entropies (cal mol⁻¹ K⁻¹), dipole moment (Debye), and some of the calculated energy values as HOMO, LUMO and |(ΔE)| for N-(4-dimethylamino 3,5-dinitrophenyl)maleimide

	······································								
Compu	led Energies	DFT	HF						
	Total Energy	-1133.52	-1126.99						
ter	Zero-point Energy	141.40	152.71						
ame	Rotational Constant	0.43	0.45						
Par		0.21	0.21						
		0.16	0.16						
	Total	145.76	143.60						
v	Translational	43.05	43.05						
itroj	Rotational	34.38	34.33						
E	Vibrational	68.32	66.22						
	Dipole Moment	2.48	3.76						
ţ	НОМО	-0.241	-0.341						
anti	LUMO	-0.128	0.025						
Ŋu	ΔΕ	0.113	0.366						

In Figure 5, where negative (red) regions have presented the regions for the electrophilic attack, the regions for the nucleophilic reactivity wave have been displayed by MEP's positive (blue) regions. The figure shows that the red regions of the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide have been localized mainly on the oxygen and nitrogen atoms (especially N9, 021, and 022), whereas the regions of nucleophilic reactivity behavior have mainly been delocalized on the carboxylic protons. In this respect, the compound is useful to bond both metallically and interact intermolecularly.



Figure 5. 3D plots related to the map of molecular electrostatic potential obtained from DFT method of the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide (red color has displayed the negative regions while blue color has presented the positive regions of MEP). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article)

In this part, the electrostatic potential surface (ESP) has been mapped over the electron density that has shown the molecular size, shape, and charge distribution over the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide compound. Moreover, the ESP has enabled us to determine the molecular interaction with one another. We have extensively used the ESP maps to predict reactive behavior, inter and intra-molecular interaction of chemical systems, and hydrogen bonding [58]. On this basis, we have provided the ESP map belonging to the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide in Figure 6 to favor all the findings evaluated from the other parts of the paper. It is obvious from the figure that the most negative regions in the ESP map have been spread over the vicinity of oxygen atoms (electrophilic reactivity regions). Correspondingly, the π -electrons have been noted to delocalize fully over the oxygen atoms. On the other hand, the figure has guaranteed that the carboxyl groups have taken place in the nucleophilic reactivity regions.



Figure 6. 3D plot for an electrostatic potential map of the N-(4-dimethylamino 3,5dinitrophenyl)maleimide

4. Conclusion

In the current work, we have studied the full characterization of N-(4-dimethylamino 3,5-dinitrophenyl)maleimide molecule with the aid of quantum chemical calculation methods, including the HF/6-311++G(d,p) and DFT-B3LYP/6-311++G(d,p) methods. In this respect, we have determined the optimized molecular structures, vibrational frequencies, thermodynamic features, function groups of structures, nuclear magnetic resonance chemical shifts of C-NMR and H-NMR, charge distributions-dipole moments, molecular charge transfer regions, and spectroscopic characteristic properties for the first time.

Moreover, the observed vibrational frequencies have been compared to the calculated results, and it has been recorded that the experimental data are in good agreement with the computations. The correlation parameters are about R^2 =0.9996 and R^2 =0.9977 for the vibrational frequencies in the DFT and HF calculation levels, respectively. Thus, we have pointed out the reliability of calculation methods (especially for the DFT-B3LYP/6-311++G(d,p) method).

Besides, we have simulated the electrochemical properties, including the highest/lowest occupied/unoccupied molecular orbital, molecular electrostatic potential, and electrostatic potential maps for the N-(4-dimethylamino 3,5-dinitrophenyl)maleimide compound. The theoretical examinations have shown that the title molecule has exhibited strong non-uniform intra-molecular charge distributions and electron donating groups depending on the actual position of the substituents, electron engagements, lone pairs of electrons, π - π * conjugative effects, and intermolecular hydrogen bonding in the structure. Accordingly, the title compound, including the high electrophilic reactive and nucleophilic regions, can be selected to be a strong terminator for the antimicrobial, anticonvulsant, cytotoxic, antimalarial, and pharmacological microorganisms.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

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Determination of important biotechnical characteristics of some safflower (Carthamus tinctorius L.) cultivars

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Keywords:

Carthamus tinctorius, Sphericity, Coefficient of friction, a*, b* color characteristics **Abstract** — The study aimed to determine the biotechnical characteristics (physical properties, color characteristics, angle of repose, and coefficient of friction) of the seeds of safflower cultivars. Moisture contents of Asal, Balcı, and Dinçer cultivars were determined as 8.64%, 9.52%, and 8.57%, respectively. The width (4.04 mm) of the Dinçer cultivar gave higher values than other cultivars. Statistically significant (p < 0.01) differences were determined between the width values of safflower cultivars. There was no statistically significant difference in length, sphericity, surface area, and geometric mean diameter values between cultivars, but statistical differences at p < 0.05 level were determined between cultivars in thickness values. L^* brightness color value was higher (75.31) in Dinçer cultivar than in other cultivars. The rubber surface gave the highest values (0.360-0.384) in terms of coefficient of friction values. In the study, it is thought that the biotechnical characteristics (physical properties, color characteristics, coefficient of friction, and angle of repose values of the safflower seeds will contribute to obtaining important engineering data in the design of machinery, facilities, and systems to be used for sowing, harvesting and threshing mechanization and postharvest technologies.

Subject Classification (2020):

1. Introduction

In Türkiye, 1.5-1.7 million tons of edible oil is consumed annually. The amount obtained from different oil plants grown is approximately 600,000-700,000 tons. Accordingly, only about half of the consumed oil can be produced. The remaining oil needed (about 60% of the oil we consume) is imported in exchange for foreign currency (about 4.5 billion dollars). It can be said that one of the homelands of the safflower plant is Türkiye. It can be grown easily in every region, its root structure is deep and resistant to drought, and it is a plant that can contribute to the country's oil needs [1]. Safflower oil, which contains high oleic acid, seems promising as a diesel fuel that reduces air pollution by reducing CO2 emissions with the biofuel program since the 2000s [2,3].

Safflower (Carthamus tinctorius L.) is an oil plant that can be produced, especially in areas where other products with high economic gain cannot be cultivated. It is observed that safflower seeds can be easily processed in sunflower processing facilities. According to TUIK 2022 data [4], 30,000 tons of safflower were produced from 262,375 decares of land, and the yield was determined as 114 kg da-1. According to FAO 2020 data, 23,070 tons of production was cultivated from 32,612 ha in Africa, 7,074 kg ha-1, in

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Asia 353,221 tons from 473,677 ha, 7,457 kg ha-1, in Europe 17,518,296,739 tons of production was cultivated from the hectare area, and the yield was determined as 5,522 kg ha-1 [5].

In addition to pre-harvest factors, such as soil conditions, climate, and agricultural practices, harvesting methods and postharvest conditions, storage, and postharvest processes also significantly affect the product's quality. Agricultural products have irregular shapes and sizes. Geometric and gravimetric properties of agricultural products are essential biotechnical characteristics for sowing, harvesting, postharvest processing, storage, packaging, and quality control stages [6]. The design and development of special machinery and technology systems to obtain maximum product quality with minimum energy and labor consumption also make it necessary to know the biotechnical properties specific to the product [7]. The physical properties of seeds are a vast amount of data that can be useful in harvesting and storage or drying and other processes. This data is involved in designing machines for harvesting and in every part of the food processing chain. The main purpose of post-harvest biotechnical properties technology is to increase agricultural production through the dissemination of quality seeds of high-yielding varieties. This includes identifying varieties with high seed quality, thereby improving seedling and plant growth, and assessing seed quality using different methods [8].

It is seen that safflower seeds will be in a significant position in the coming years, both in terms of agricultural production, especially in terms of oil need, and as an alternative environmentally friendly biofuel, with the increasing importance of our country in recent years, being suitable for cultivation and developing the usage area. For this reason, it is seen that the comprehensive research of researchers in different fields related to the safflower plant will be important in directing the studies on a sectoral basis in terms of the production and postharvest technology of the safflower plant [9].

Some researchers on safflower have carried out certain studies: [10] seed and oil properties of the safflower plant, [11] physical and chemical properties of safflower genotypes, [12] some physical and mechanical properties of safflower seeds, [13] determined some physical properties of safflower seeds, [14] seed yield and yield components of some safflower cultivars, [15] moisture dependent physical and compression properties of safflower seed. This study aimed to determine critical biotechnical characteristics (physical properties, color characteristics, coefficient of friction, and angle of repose) of three important domestic safflower cultivars.

2. Materials and Methods

In this study, the safflower seeds for Asal, Balcı, and Dinçer cultivars were obtained from Tokat Gaziosmanpaşa University, Faculty of Agriculture, Department of Field Crops. To determine the geometric and volumetric properties of safflower seeds, a digital caliper with an accuracy of 0.01 mm in length (Ln), width (Wd), and thickness (Th) values were used for 100 samples. Samples for Asal, Balcı, and Dinçer cultivars were given Figure 1.



a) Asal



b) Balcı c) Dinçer Figure 1. Samples for Asal, Balcı, and Dinçer cultivars

The moisture content of safflower seeds was determined as dry bases (d.b%) as a result of drying the seed samples in a dry oven at $105\pm1^{\circ}$ C and 24 hours [16]. Moisture contents of Asal, Balcı, and Dinçer cultivars were determined as 8.64%, 9.52%, and 8.57% (d.b), respectively.

To determine the geometric and volumetric properties of safflower seeds, a digital caliper with an accuracy of 0.01 mm in length (L_n), width (W_d), and thickness (T_h) values were used for 100 samples. The sphericity (S_p), geometric mean diameter (G_{md}), and surface area (S_r) values of the seeds were calculated with the equations given below [17].

$$G_{md} = (L_n W_d T_h)^{1/3} (2.1)$$

$$S_p = \frac{(L_n W_d T_h)^{1/3}}{L_n} 100$$
(2.2)

$$S_r = \pi (G_{md})^2 \tag{2.3}$$

The masses (*M*) of the seeds were determined using an electronic digital balance with an accuracy of 0.001 g. To determine the thousand-grain weight (T_{sm}) of the seeds, the average weights of 100 seed samples with four replications were taken. The bulk density (B_d) of safflower seeds was determined using the hectoliter method. Seed volume (S_v) was calculated using the following equation. The liquid displacement method was used to determine the true density (T_d) values, and the porosity (P_r) was determined using the actual and bulk volume weight values [17].

$$T_y = \frac{\pi}{6L_n W_d T_h} \tag{2.4}$$

To determine the color characteristics of the seeds, L^* , a^* , and b^* color characteristics were determined with a Minolta brand CR-400 Model Tokyo-Japan colorimeter. In the determination of color characteristics, measurements were taken from a total of 15 samples for seeds. L^* , a^* , and b^* color characteristics, L^* indicates brightness, a^* scale indicates redness, and b^* scale indicates yellowness. Hue angle (a) and chroma (C) color characteristics were determined by the following equations [18]. Chroma indicates the vitality or pastel shade of the seeds. Vivid tones are close to 10, and pastel tones are close to 0 [19].

$$\alpha = \frac{1}{\tan \frac{b}{a}}$$
(2.5)

$$C = (a^2 + b^2)^{1/2}$$
(2.6)

PVC, laminate, rubber, and plywood surfaces were used to measure the friction coefficients of the seeds. In the measurement of the friction coefficient, the slope (inclination) angle read at the first moment when the seeds started to move in the experimental setup, which can be tilted via the screw arm, was taken as a basis [20] (Figure 2).

In determining the angle of repose, the inclination angle of the cone was taken into account by using a cylinder measuring 300×500 mm with an open top and bottom part and raising the seeds into the cylinder until a cone is formed on a flat surface [21](Figure 3). The relevant equation is as follows. The angle of repose is as follows:

$$As = \frac{1}{\tan\frac{H}{R}}$$
(2.7)

Here, As, H, and R denote Angle of repose (°), Height of the cone formed (cm), and Base radius of the cone formed (cm), respectively.



Figure 2. Measuring device for the coefficient of the friction



Figure 3. Measurement of the angle of repose

A normality test was performed before the analysis of variance to determine the suitability of the data in the study for statistical analysis. In the study, using a one-way analysis of variance, the effect of cultivars on biotechnical properties was determined by DUNCAN multiple comparison test.

3. Results and Discussions

3.1. Geometric Properties

The geometric properties and variance analysis results of safflower seeds are shown in Table 1. The width (4.04 mm) of the Dincer cultivar gave higher values than other cultivars. Statistically, differences were observed in the width values of safflower seeds in terms of cultivars (p < 0.01). There was no statistical difference between the cultivars in terms of length, sphericity, surface area, and geometric mean diameter (Table 1). The sphericity value varied between 61.52% and 63.38% in safflower cultivars.

	Table 1. Some geometrical properties of seeds of safflower cultivars								
Cultivars	Length (mm)	Width (mm)	Thickness (mm)	Geometric mean diameter (mm)	Surface area (mm²)	Sphericity (%)			
Asal	7.69 ± 0.24 ns	3.67±0.10b**	3.95±0.15a*	4.80±0.11 ns	72.60±3.40 ns	62.66±1.73 ns			
Balcı	7.85±0.20 ^{ns}	3.59±0.16b**	4.01±0.14a*	4.82 ± 0.14 ns	73.35±4.36 ^{ns}	61.52 ± 1.26 ns			
Dinçer	7.64 ± 0.23 ns	4.04±0.34a**	3.71±0.42b*	4.84±0.35 ^{ns}	74.23±10.83 ^{ns}	63.38±3.29 ns			
F value	2.46	11.81	3.72	0.09	0.13	1.72			
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*: p < 0,01, *: p < 0,05, π : non-significant. Differences between similar letters in the same columns are insignificant, \pm : standard deviation.

Ghareeb et al. [10] reported the geometric mean diameter values of safflower seeds as 4.98 mm and sphericity values as 65.20% in their study. Kobuk et al. [11] reported that the geometric mean diameter values are in the range of 4.58 - 5.08 mm, sphericity values are in the range of 56.93 - 65.90%, and

surface area values are in the range of 65.99 - 81.33 mm² for safflower seeds at the moisture content varied between 3.07% and 4.04%, respectively. Aktas et al. [12] reported that the length values varied from 7.27 to 7.81 mm, the width values changed from 3.50 to 3.79 mm, and the thickness varied from 2.80 mm to 3.50 mm; the geometric mean diameter was between 4.46 mm and 4.82 mm, and sphericity values changed from 47.14% to 48.83% at different moisture contents (7.4%, 8.1%, 8.7%, and 9.2%), respectively.

Çalışır et al. [13] reported that the length, width, thickness, and geometric mean diameter were 6.89 mm, 3.76 mm, 2.71 mm, and 4.13 mm at a moisture content of 5.61%, respectively. When the literature results are examined, it is seen that the geometric properties of safflower seeds show values close to the values found in this study.

3.2. Mass and Volumetric Properties

The values of seed mass and volumetric properties of safflower seeds are given in Table 2. The highest values for mass and bulk density were determined as 0.053 g and 557.76 kg m⁻³ in the Dincer cultivar. Statistically significant differences were determined in bulk density values of safflower cultivars (p < 0.01). No statistically significant difference between cultivars in porosity, true density and seed volume was observed.

	Table 2. Mass and volumente properties of secus of samower cultivars								
Cultivars	Mass (g)	Thousand seed mass (g)	Seed volume (mm³)	Bulk density (kg m ⁻³)	True density (kg m ⁻³)	Porosity (%)			
Asal	0.047±0.003b*	40.19±0.22b*	58.89±4.17 ns	468.71±18.27b**	1155.1±373.9 ^{ns}	54.21±18.14 ns			
Balcı	0.049±0.004b*	40.31±0.37b*	59.75 ± 5.36 ns	468.75±13.05b**	1182.3±285.3 ^{ns}	58.02 ± 10.71 ns			
Dinçer	0.053±0.005a*	50.02±0.11a*	61.31±13.51 ^{ns}	557.76±13.14a**	1102.3±271.2 ^{ns}	45.95±15.39 ns			
F value	5.32	9.16	0.20	175.69	0.25	2.52			

Table 2. Mass and volumetric properties of seeds of safflower cultivars

**: p < 0,01, *: p < 0,05, ns: non-significant. Differences between similar letters in the same columns are insignificant, \pm : standard deviation.

Ghareeb et al. [10] reported that the thousand seed mass of safflower seeds was 42.49 g, the seed volume was 0.048 ml, and the true density value was 103.97 g l^{-1} in their study. Kobuk et al. [11] reported that the bulk density values of safflower seeds were 537.07 g l^{-1} - 602.37 g l^{-1} , and the thousand-grain weight values were 31.15 g - 49.10 g.

Aktas et al. [12] determined the true density values of safflower seeds in the range of 0.78 g cm⁻³ - 0.73 g cm⁻³, and the porosity was 40.7% - 44.2%. Çalışır et al. [13], the seed mass and thousand seed mass values of safflower seeds were in the range of 0.035 g - 0.054 g and 36.1 g - 47.2 g, respectively. Moreover, the true density and porosity varied from 1096.7 to 1187.6 kg m⁻³, from 52.0 to 56.7%, at moisture contents ranging from 5.61% to 23.32%, respectively. The results of the study were observed to differ from the literature. This difference is thought to be due to the genetic differences between the safflower seeds used in the studies and the climate and growing conditions.

3.3. Color Characteristics

The results of the variance analysis of the color characteristics of safflower seeds are given in Table 3. The highest L^* value was 75.31 in the Dincer cultivar, and statistically, p < 0.01 level differences were observed between cultivars in terms of L^* value. The study determined that the difference between cultivars was statistically insignificant in terms of hue angle, chroma, a^* , and b^* color values.

Tuble 5. Goldi characteristics of seeds of samower califying										
Cultivars	L*	a*	b*	С	α(°)					
Asal	70.84±2.71b**	2.39±0.35 ns	11.67±1.27 ns	11.92±1.27 ns	78.36±1.75 ^{ns}					
Balcı	69.93±2.97b**	2.39±0.26 ns	12.67±1.45 ns	12.89±1.45 ns	79.22±1.33 ns					
Dinçer	75.31±2.31a**	2.65±0.43 ns	12.41±1.44 ns	12.69±1.46 ^{ns}	77.92±1.79 ^{ns}					
F value	17.37	2.52	2.06	2.05	2.46					

Table 3. Color characteristics of seeds of safflower cultivars

**: p < 0,01, *: p < 0,05, ns: non-significant. Differences between similar letters in the same columns are insignificant, \pm : standard deviation.

Kobuk et al. [11] reported that L^* and a^* color values of safflower seeds varied from 63.65 to 67.81 and from 3.41 to 3.97, respectively. Moreover, chroma and hue angle changed from 9.88 to 12.28, from 67.15 to 71.24°, respectively. Significant differences were observed in the results in terms of color characteristics. It is thought that this difference is due to the cultivar of safflower seeds used in the studies and the cultivation and climatic conditions.

3.4. The Angle of Repose and the Coefficient of Static Friction

The static coefficient of friction and angle of repose of safflower seeds were determined, and the results are given in Table 4. In terms of static friction coefficient values, statistically, p < 0.05 differences were observed between the cultivars on the rubber surface, while no statistically significant difference was observed between the cultivars on PVC and laminate surfaces. Statistically significant differences were determined in the natural aggregation angle values between safflower cultivars (p < 0.01).

Cultivora	Angle of				
Cultivals	Repose (°)	Plywood	Rubber	PVC	Laminate
Asal	8.65±1.09a**	0.368±0.016a**	0.384±0.025a*	0.302±0.022 ns	0.302±0.029 ns
Balcı	8.43±0.98a**	0.323±0.014b**	$0.360 \pm 0.016b^*$	0.306±0.027 ns	0.300±0.013 ns
Dinçer	7.27±0.77b**	0.327±0.019b**	0.374±0.010ab*	0.285±0.019 ns	0.289±0.014 ns
F value	9.03	22.67	4.44	2.41	1.28
**: <i>p</i> < 0,01, *: <i>p</i> <	< 0,05, ns: non-significant.	Differences between similar l	etters in the same columns are	e insignificant, ±: standard de	viation.

Table 4. Static coefficient of friction and angle of repose of seeds of safflower cultivars

Kobuk et al. [11] reported that the static coefficient of friction values ranged between 0.33 and 0.44, and the angle of repose values ranged from 23.17° - 26.23°. The angle of repose was found to be lower than in the literature. The difference is thought to be due to the difference in the ecological conditions and soil characteristics in which the seeds are grown, as well as the cultivar used.

4. Conclusion

In the study, width values were higher in the Dincer cultivar than in other cultivars. The highest value for mass and bulk density was determined in the Dincer cultivar. L* value was higher in the Dincer cultivar than in the other two cultivars. The highest static coefficient of friction value was found on the rubber surface. In agricultural applications, especially in sowing, harvesting, postharvest classification, storage, and transportation processes, important biotechnical properties of seeds should be considered.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

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Approximating of fixed points for Garsia-Falset generalized nonexpansive mappings

Seyit Temir¹, Oruç Zincir²

Keywords Generalized nonexpansive mapping, Fixed point, Uniformly-convex Banach spaces Abstract — This paper studies the convergence of fixed points for Garsia-Falset generalized nonexpansive mappings. First, it investigates weak and strong convergence results for Garsia-Falset generalized nonexpansive mappings using the Temir-Korkut iteration in uniformly convex Banach spaces. This paper then exemplifies Garsia-Falset generalized nonexpansive mappings, which exceed the class of Suzuki generalized nonexpansive mappings. Moreover, it numerically compares this iteration's convergence speed with the well-known Thakur iteration of approximating the fixed point of Garsia-Falset generalized nonexpansive mapping. The results show that the Temir-Korkut iteration converges faster than the Thakur iteration converges. Finally, this paper discusses the need for further research.

Subject Classification (2020): 47H09, 47H10

1. Introduction

In mathematics and many disciplines, the concept of a fixed point is crucial. The conditions under which maps have solutions are provided by fixed point results. In particular, fixed-point approaches have been used in various disciplines, including biology, chemistry, economics, engineering, and informatics. Even if establishing the existence of a fixed point is an essential first step, the major and probably last stage in finding a solution is to find the exact value of the intended fixed point. An iterative procedure is one of the common ways to obtain the intended fixed point. In the last 65 years, many authors have been interested in these areas and established many iterative processes to approximate fixed points for nonexpansive mappings and a broader class of nonexpansive mappings.

Especially, some generalizations of nonexpansive mappings and the study of related fixed point theorems have been intensively carried out over the past decades [1–9]. A class of generalized nonexpansive mappings (GNMs) on a nonempty subset K of a Banach space X has been defined by Suzuki [5]. Such mappings were referred to as belonging to the class of mappings satisfying condition (C) (also referred as Suzuki GNM), which properly includes the class of nonexpansive mappings. Recently, fixed point theorems for Suzuki generalized nonexpansive mappings have been studied by a number of authors [10–14]. Every self-mapping Ψ on K providing condition (C) has an almost fixed point sequence for a nonempty bounded and convex subset K. Two new classes of GNMs that are wider

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than those providing the condition (C) were presented in 2011 by Garsia-Falset et al. [2], while retaining their fixed point properties. They investigated Garsia-Falset GNMs, named as condition (E). Later in 2019, for a general class of nonexpansive mappings that are not necessarily continuous on their domains, Pandey et al. [3] presented fixed point results and showed how several other classes of nonexpansive type mappings are appropriately included inside this class. Recently, Usurelu et al. [7] investigated the visualization of convergence behaviors of various iterative processes and some fixed point outcomes for this class of mappings.

Some related properties to the aforesaid topics are as follows: Let K be a nonempty subset of a Banach space X. A mapping $\Psi : K \to K$ is said to be nonexpansive if $||\Psi u - \Psi v|| \leq ||u - v||$, for all $u, v \in K$. A mapping $\Psi : K \to K$ is called quasi-nonexpansive if $||\Psi u - p|| \leq ||u - p||$, for all $u \in K$ and $p \in F(\Psi)$ (where $F(\Psi)$ denotes the set of all fixed points of Ψ). Therefore, the class of quasi-nonexpansive mappings is weaker than the class of nonexpansive mappings. Suzuki [5] presented the concept of GNMs, known as condition (C), in 2008. Let K be a nonempty convex subset of a Banach space X, a mapping $\Psi : K \to K$ satisfies condition (C) on K if, for all $u, v \in K$, $\frac{1}{2}||u - \Psi u|| \leq ||u - v|| \Rightarrow ||\Psi u - \Psi v|| \leq ||u - v||$. Suzuki [5] showed that the mapping satisfying condition (C) is weaker than nonexpansiveness and stronger than quasi-nonexpansiveness.

Recently, Garsia-Falset et al. [2] studied GNMs satisfying condition (E) that have a weaker property than Suzuki GNMs. Let K be a nonempty subset of a Banach space X. A mapping $\Psi : K \to X$ satisfies condition (E_{μ}) on K, if there exists $\mu \geq 1$ such that

$$||u - \Psi v|| \le \mu ||u - \Psi u|| + ||u - v||$$

for all $u, v \in K$. Moreover, it is said that Ψ satisfies condition (E) on K, whenever Ψ satisfies condition (E_{μ}) , for some $\mu \geq 1$. It is clearly seen that if $\Psi : K \to X$ is nonexpansive, then it satisfies condition (E_1) and from Lemma 7 in [5], we know that if $\Psi : K \to K$ satisfies condition (C) on K, then Ψ satisfies condition (E_3) (see [2]). Proposition 1 in [2], we know also that if $\Psi : K \to X$ a mapping which satisfies condition (E) on K has some fixed point, then Ψ is quasi-nonexpansive. Example 2 that is in [2] shows the converse is not true. Hence, the class of Garcia-Falset GNMs exceeds the class of Suzuki GNMs (also the class of nonexpansive mappings), however, it still remains stronger than quasi-nonexpansiveness.

The generalized α -nonexpansive mappings (which includes α - nonexpansive mappings [1]) of nonexpansive type mappings are introduced by Pant and Shukla [4] in 2017. They have attained some fixed point results for this class of mappings. A mapping $\Psi : K \to K$ is called a generalized α -nonexpansive mapping if, for each $u, v \in K$, there exists an $\alpha \in [0, 1)$ such that

$$\frac{1}{2}\|u - \Psi u\| \le \|u - v\| \Rightarrow \|\Psi u - \Psi v\| \le \alpha \|\Psi u - v\| + \alpha \|\Psi v - u\| + (1 - 2\alpha)\|u - v\|$$

In recent years, many iterations have been used to approximate fixed points of GNMs. In particular, with iteration development, a faster approach to the fixed point has gained importance. Iterations, such as the Thakur iteration [11] and the Temir-Korkut iteration [15], have recently been introduced and used to approximate the fixed points of GNMs. Usurelu et al. [7] studied the Thakur iteration in the new context of GNMs enriched with condition (*E*). The underlying setting of their method is a uniformly convex Banach space (UCBS). Thakur iteration: For $\{\zeta_n\}, \{\varsigma_n\}, \{\tau_n\} \in (0, 1)$ and arbitrary $u_1 \in K$ construct a sequence $\{u_n\}$ defined by

$$z_n = (1 - \tau_n)u_n + \tau_n \Psi u_n$$

$$y_n = (1 - \varsigma_n)z_n + \varsigma_n \Psi z_n$$

$$u_{n+1} = (1 - \zeta_n)\Psi z_n + \zeta_n \Psi y_n$$
(1.1)

For generalized α -nonexpansive mappings in UCBS, Temir and Korkut [15] recently presented an iteration (named the Temir-Korkut iteration) and proved some convergence results using this iteration. Temir-Korkut iteration: For $\{\zeta_n\}, \{\varsigma_n\}, \{\tau_n\} \in (0, 1)$ and arbitrary $u_1 \in K$ construct a sequence $\{u_n\}$ defined by

$$z_{n} = \Psi((1 - \tau_{n})u_{n} + \tau_{n}\Psi u_{n})$$

$$y_{n} = \Psi((1 - \varsigma_{n})\Psi u_{n} + \varsigma_{n}\Psi z_{n})$$

$$w_{n} = \Psi((1 - \zeta_{n})y_{n} + \zeta_{n}\Psi y_{n})$$

$$u_{n+1} = \Psi w_{n}$$
(1.2)

In this study, we use the Temir-Korkut iteration motivated by the above to prove weak and strong convergence results for Garsia-Falset GNMs, which is the generalization of Suzuki GNMs in the setting of UCBS. Moreover, we provide an example of Garsia-Falset GNM, which is not Suzuki GNM. In addition, we numerically show that the Temir-Korkut iteration converges to a fixed point of Garsia-Falset GNM faster than the Thakur iteration.

2. Preliminaries

This section recalls some basic notations to be used in main results.

Definition 2.1. [16] A Banach space X will be said to be uniformly convex if for each $\varepsilon \in (0, 2]$, there corresponds a $\delta(\varepsilon) > 0$ such that the conditions ||u|| = ||v|| = 1, $||u - v|| \ge \varepsilon$ imply $\frac{||u+v||}{2} \le 1 - \delta(\varepsilon)$.

Definition 2.2. [17] A Banach space X is said to satisfy *Opial's condition* if, for each sequence $\{u_n\}$ in X, the condition $u_n \to u$ (weakly) as $n \to \infty$ and for all $v \in X$ with $v \neq u$ imply that

$$\liminf_{n \to \infty} \|u_n - u\| < \liminf_{n \to \infty} \|u_n - v\|$$

Definition 2.3. [18] Let $\{u_n\}$ be a bounded sequence in a Banach space X and $u \in X$. Then,

i. the asymptotic radius of $\{u_n\}$ at u is the number $r(u, \{u_n\}) = \limsup ||u_n - u||$.

ii. the asymptotic radius of $\{u_n\}$ relative to K is defined by $r(K, \{u_n\}) = \inf\{r(u, \{u_n\}) : u \in K\}$.

iii. the asymptotic center of $\{u_n\}$ relative to K is the set $A(K, \{u_n\}) = \{u \in K : r(u, \{u_n\}) = r(K, \{u_n\})\}$.

It is known that $A(K, \{u_n\})$ consists of exactly one-pointin UCBS.

Lemma 2.4. [19] Suppose that X is a UCBS and $0 < k \le t_n \le m < 1$ for all $n \in \mathbb{N}$. Let $\{u_n\}$ and $\{v_n\}$ be two sequences of X such that $\limsup_{n \to \infty} ||u_n|| \le \kappa$, $\limsup_{n \to \infty} ||v_n|| \le \kappa$ and $\limsup_{n \to \infty} ||t_n u_n + (1 - t_n)v_n|| = \kappa$ hold for $\kappa \ge 0$. Then, $\lim_{n \to \infty} ||u_n - v_n|| = 0$.

Definition 2.5. [20] Let $\{u_n\}$ in K be a given sequence. $\Psi : K \to X$ with the nonempty fixed point set $F(\Psi)$ in K is said to satisfy condition (I) with respect to the $\{u_n\}$ if there is a nondecreasing function $\varphi : [0, \infty) \to [0, \infty)$ with $\varphi(0) = 0$ and $\varphi(\kappa) > 0$ for all $\kappa \in (0, \infty)$ such that for all $n \in \mathbb{N}$, $\|u_n - \Psi u_n\| \ge \varphi(d(u_n, F(\Psi)).$

Theorem 2.6. [2] Let K be nonempty subset of a Banach space X. Let $\Psi : K \to X$ be a mapping. Then, $u = \Psi u$, if

i. there exists $\{u_n\}$ for Ψ in K such that $\lim_{n\to\infty} ||u_n - \Psi u_n|| = 0$ and $u_n \to u \in K$ (weakly).

- *ii.* Ψ satisfies condition (*E*) on *K*,
- *iii.* $(X, \|.\|)$ satisfies the Opial's condition.

3. Convergence of Garsia-Falset GNMs

This section proves weak and strong convergence theorems for (1.2) of Garsia-Falset GNMs in UCBS.

Lemma 3.1. Let K be a nonempty closed convex subset of a uniformly convex Banach space X, $\Psi: K \to K$ be a Garsia-Falset GNM with $F(\Psi) \neq \emptyset$. For arbitrary chosen $u_1 \in K$, let $\{u_n\}$ be a sequence generated by (1.2), then $\lim_{n\to\infty} ||u_n - p||$ exists for any $p \in F(\Psi)$.

Proof.

Assume that $F(\Psi) \neq \emptyset$. Ψ is a quasi-nonexpansive because $\Psi : K \to K$ is a Garsia-Falset GNM. In order to prove, we follow Lemma 3.1 in [15]. By (1.2) and for any $p \in F(\Psi)$, because of Ψ quasi-nonexpansive mapping, then we have

$$\begin{aligned} \|z_n - p\| &= \|\Psi((1 - \tau_n)u_n + \tau_n \Psi u_n) - p\| \\ &\leq \|(1 - \tau_n)(u_n - p) + \tau_n(\Psi u_n - p)\| \\ &\leq (1 - \tau_n)\|u_n - p\| + \tau_n\|u_n - p\| \\ &= \|u_n - p\| \end{aligned}$$
(3.1)

From (1.2) and (3.1), we have

$$||y_{n} - p|| = ||\Psi((1 - \varsigma_{n})\Psi u_{n} + \varsigma_{n}\Psi z_{n}) - p||$$

$$\leq ||(1 - \varsigma_{n})(\Psi u_{n} - p) + \varsigma_{n}(\Psi z_{n} - p)||$$

$$\leq (1 - \varsigma_{n})||u_{n} - p|| + \varsigma_{n}||u_{n} - p||$$

$$= ||u_{n} - p||$$
(3.2)

From (1.2) and (3.2), we get

$$\|w_{n} - p\| = \|\Psi((1 - \zeta_{n})y_{n} + \zeta_{n}\Psi y_{n}) - p\|$$

$$\leq \|(1 - \zeta_{n})(y_{n} - p) + \zeta_{n}(\Psi y_{n} - p)\|$$

$$\leq (1 - \zeta_{n})\|u_{n} - p\| + \zeta_{n}\|u_{n} - p\|$$

$$= \|u_{n} - p\|$$
(3.3)

Moreover, from (1.2) and (3.3), we have

$$||u_{n+1} - p|| = ||\Psi w_n - p|| \le ||w_n - p|| \le ||u_n - p||$$

This implies that $\{||u_n - p||\}$ is bounded and non-increasing for all $p \in F(\Psi)$. Hence, $\lim_{n \to \infty} ||u_n - p||$ exists.

Theorem 3.2. Let K be a nonempty closed convex subset of a UCBS X. For $\mu \ge 1$, let $\Psi : K \to K$ be a Garsia-Falset GNM. For arbitrarily chosen $u_1 \in K$, let $\{u_n\}$ be a sequence in K defined by (1.2) with $\{\zeta_n\}$, $\{\varsigma_n\}$ and $\{\tau_n\}$ real sequences in (0, 1), then $F(\Psi) \neq \emptyset$ if and only if $\{u_n\}$ is bounded and $\lim_{n\to\infty} ||u_n - \Psi u_n|| = 0$.

Proof.

Suppose $F(\Psi) \neq \emptyset$ and let $p \in F(\Psi)$. Then, from Lemma 3.1, $\lim_{n \to \infty} ||u_n - p||$ exits and $\{u_n\}$ is bounded. In this part of the proof, we follow Theorem 3.1 in [15]. Put $\lim_{n \to \infty} ||u_n - p|| = \kappa$. Since a GNM satisfying the condition (E) is quasi-nonexpansive mapping and from (1.2), we have

$$\limsup_{n \to \infty} \|z_n - p\| \le \limsup_{n \to \infty} \|u_n - p\| = \kappa$$
$$\limsup_{n \to \infty} \|w_n - p\| \le \limsup_{n \to \infty} \|y_n - p\| \le \limsup_{n \to \infty} \|u_n - p\| = \kappa$$

and

$$\limsup_{n \to \infty} \|\Psi u_n - p\| \le \limsup_{n \to \infty} \|u_n - p\| = \kappa$$

Besides, $||u_{n+1} - p|| \le ||w_n - p||$. Therefore, $\kappa \le \liminf_{n \to \infty} ||w_n - p||$. Thus, we have $\kappa = \lim_{n \to \infty} ||w_n - p||$. Using here, we can get $\kappa = \liminf_{n \to \infty} ||w_n - p|| \le \liminf_{n \to \infty} ||y_n - p||$. Thus, we have $\kappa = \lim_{n \to \infty} ||y_n - p||$. Moreover,

$$\begin{aligned} \|y_n - p\| &= \|\Psi((1 - \varsigma_n)\Psi u_n + \varsigma_n\Psi z_n) - p\| \\ &\leq \|(1 - \varsigma_n)(\Psi u_n - p) + \varsigma_n(\Psi z_n - p)\| \\ &\leq (1 - \varsigma_n)\|\Psi u_n - p\| + \varsigma_n\|\Psi z_n - p\| \\ &\leq (1 - \varsigma_n)\|u_n - p\| + \varsigma_n\|z_n - p\| \end{aligned}$$

Hence,

$$||y_n - p|| - ||u_n - p|| \le \frac{||y_n - p|| - ||u_n - p||}{\varsigma_n} \le ||z_n - p|| - ||u_n - p||$$

implies that $||y_n - p|| \le ||z_n - p||$. Thus, we have $\kappa = \lim_{n \to \infty} ||z_n - p||$. Again from (1.2), we have

$$\lim_{n \to \infty} \|(1 - \tau_n)(u_n - p) + \tau_n(\Psi u_n - p)\| = \kappa$$

Thus, by Lemma 2.4, we have

$$\lim_{n \to \infty} \|u_n - \Psi u_n\| = 0$$

Conversely, suppose that $\{u_n\}$ is bounded $\lim_{n\to\infty} ||u_n - \Psi u_n|| = 0$. Let $p \in A(K, \{u_n\})$. Since Ψ satisfies condition (E) with $\mu \ge 1$, one has

$$r(\Psi p, \{u_n\}) = \limsup_{n \to \infty} \|u_n - \Psi p\| \leq \limsup_{n \to \infty} (\mu \|\Psi u_n - u_n\| + \|u_n - p\|)$$
$$\leq \limsup_{n \to \infty} \|u_n - p\| = r(p, \{u_n\})$$

This implies that for $\Psi p \in A(K, \{u_n\})$. For closed-bounded convex subsets of UCBSs, the asymptotic center consists of exactly one point. Therefore, $\Psi p = p$, i.e $F(\Psi) \neq \emptyset$, and the proof is complete.

Next, we prove the following strong convergence theorems of Garsia-Falset GNMs.

Theorem 3.3. Let X be a real UCBS and K a nonempty compact convex subset of X and $\Psi : K \to K$ be a Garsia-Falset GNM for $\mu \geq 1$. Let Ψ and $\{u_n\}$ be as in Theorem 3.2. If $F(\Psi) \neq \emptyset$, then $\{u_n\}$ defined by (1.2) converges strongly to a fixed point of Ψ .

Proof.

Suppose $F(\Psi) \neq \emptyset$. Thus by Theorem 3.2, we have $\lim_{n \to \infty} ||\Psi u_n - u_n|| = 0$. Since K is compact, there exists a subsequence $\{u_{n_k}\}$ of $\{u_n\}$ such that $u_{n_k} \to p$ as $k \to \infty$ for some $p \in K$. Since Ψ satisfies condition (E) with $\mu \geq 1$, then we have, for all $k \in \mathbb{N}$,

$$||u_{n_k} - \Psi p|| \le \mu ||\Psi u_{n_k} - u_{n_k}|| + ||u_{n_k} - p||$$

Letting $k \to \infty$, we get $u_{n_k} \longrightarrow \Psi p$. Thus $\Psi p = p$, i.e. $p \in F(\Psi)$. Furthermore, $\lim_{n \to \infty} ||u_n - p||$ exists for every $p \in F(\Psi)$, thus $\{u_n\}$ converges strongly to a fixed point of Ψ .

Moreover, we give below our second strong convergence theorem of Garsia-Falset GNMs satisfying condition (I).

Theorem 3.4. Let K be a nonempty closed convex subset of a UCBS X and $\Psi : K \to K$ be a Garsia-Falset GNM for $\mu \geq 1$. Let Ψ and $\{u_n\}$ be as in Theorem 3.2 and $F(\Psi) \neq \emptyset$. If Ψ satisfies condition (I), then $\{u_n\}$ defined by (1.2) converges strongly to a fixed point of Ψ .

Proof.

Using the same argument as in Theorem 3.5 in [7], we obtain the strong convergence theorem of Garsia-Falset GNMs satisfying condition (I).

Finally, we give the following weak convergence theorem of Garsia-Falset GNMs in a UCBS satisfying Opial's condition.

Theorem 3.5. Let K be a nonempty closed convex subset of a UCBS X endowed with Opial's condition and $\Psi: K \to K$ be a Garsia-Falset GNM for $\mu \geq 1$. Let Ψ and $\{u_n\}$ be as in Theorem 3.2 and $F(\Psi) \neq \emptyset$. Then, $\{u_n\}$ converges weakly to a fixed point of Ψ .

Proof.

Since $F(\Psi) \neq \emptyset$, let p be a fixed point of Ψ . By Theorem 3.2, the sequence $\{u_n\}$ is bounded and $\lim_{n\to\infty} \|\Psi u_n - u_n\| = 0$ and by Lemma 3.1, $\lim_{n\to\infty} \|u_n - p\|$ exists. Because X is uniformly convex, Xis reflexive. Due to the reflexiveness of X, there exists a subsequence $\{u_{n_j}\}$ of $\{u_n\}$ such that $\{u_{n_j}\}$ converges weakly to some $\nu_1 \in X$. Since K is closed and convex subset of X, according to Mazur's Theorem, $\nu_1 \in K$. Hence, by Theorem 2.6, we obtain $\Psi \nu_1 = \nu_1$, consequently $\nu_1 \in F(\Psi)$. Arguing by contradiction, suppose that $\{u_n\}$ has two sub-sequences $\{u_{n_j}\}$ and $\{u_{n_k}\}$ converging weakly to ν_1 and ν_2 , respectively. $\Psi \nu_2 = \nu_2$ is obtained in the same way which is used $\Psi \nu_1 = \nu_1$. After that, the uniqueness will be proved. By Lemma 3.1, $\lim_{n\to\infty} \|u_n - \nu_1\|$ and $\lim_{n\to\infty} \|u_n - \nu_2\|$ exist. Suppose that $\nu_1 \neq \nu_2$, afterward by the Opial's condition, we obtain

$$\lim_{n \to \infty} \|u_n - \nu_1\| = \lim_{j \to \infty} \|u_{n_j} - \nu_1\| < \lim_{j \to \infty} \|u_{n_j} - \nu_2\| = \lim_{n \to \infty} \|u_n - \nu_2\|$$
$$= \lim_{k \to \infty} \|u_{n_k} - \nu_2\| < \lim_{k \to \infty} \|u_{n_k} - \nu_1\| = \lim_{n \to \infty} \|u_n - \nu_1\|$$

which is a contradiction. Hence, $\nu_1 = \nu_2$. Therefore, $\{u_n\}$ converges weakly to a fixed point of Ψ . This completes the proof.

4. Illustrative Example

This section exemplifies Garsia-Falset generalized nonexpansive mappings, which exceed the class of Suzuki generalized nonexpansive mappings.

Example 4.1. Let $K = [0,1] \subset \mathbb{R}$ endowed with usual norm in \mathbb{R} and $\Psi : [0,1] \to [0,1]$ be a mapping defined by

$$\Psi u = \begin{cases} \frac{\arctan u}{2}, & u \neq 1\\ \frac{5}{7}, & u = 1 \end{cases}$$

Here, Ψ is a Garsia-Falset GNM. We prove next that Ψ satisfies condition $(E_{\frac{7}{2}})$. For Ψ , satisfying condition $(E_{\frac{7}{2}})$ explicitly means to check if the following inequality holds:

$$||u - \Psi v|| \le \frac{7}{2} ||u - \Psi u|| + ||u - v||, \text{ for all } u, v \in [0, 1]$$

$$(4.1)$$

To verify that Ψ satisfies the condition $(E_{\frac{7}{2}})$, we consider the following cases.

Case I: Let u = 1 and $v \in [0, 1)$. Then, (4.1) is written as follows for this particular case

$$\left| \begin{aligned} 1 - \frac{\arctan v}{2} \right| &\leq \frac{7}{2} \left| 1 - \frac{5}{7} \right| + \left| 1 - v \right| \\ 1 - \frac{\arctan v}{2} &\leq 1 + 1 - v \end{aligned}$$

Then, we have

$$v - rac{\arctan v}{2} \leq 1$$

which is ultimately equivalent to condition $f(v) = v - \frac{\arctan v}{2} \leq 1$. Since $f(v) = v - \frac{\arctan v}{2}$ is nondecreasing over the interval [0, 1), then $Im(f) = [f(0), f(1)) = [f(0), 1 - \frac{\pi}{8})$; therefore, this inequality is satisfied.

Case II: Let $u \in [0, 1)$ and v = 1. Then, (4.1) is written as follows for these particular assignments

$$\begin{aligned} u - \frac{5}{7} \middle| &\leq \frac{7}{2} \left| u - \frac{\arctan u}{2} \right| + |u - 1| \\ &\leq \frac{7u}{2} - \frac{7\arctan u}{4} + 1 - u \\ &\leq \frac{5u}{2} - \frac{7\arctan u}{4} + 1 \end{aligned}$$

Taking this time the function $g(u) = \frac{5u}{2} - \frac{7arctanu}{4} + 1$. Since the function $g(u) = \frac{5u}{2} - \frac{7arctanu}{4} + 1$ also is nondecreasing over the interval [0,1), then $Im(g) = [g(0),g(1)) = \left[1,\frac{7}{2} - \frac{7\pi}{16}\right]$. Hence, $g(u) \ge 1 > \left|u - \frac{5}{7}\right|$, for all $u \in [0,1)$. Therefore, this inequality is satisfied.

Case III: Let $u, v \in [0, 1)$. One has

$$||u - \Psi v|| \le ||u - \Psi u|| + ||\Psi u - \Psi v|$$

Substituting, we attain

$$\left|u - \frac{\arctan v}{2}\right| \le \frac{7}{2} \left|u - \frac{\arctan u}{2}\right| + \frac{1}{2} \left|\arctan u - \arctan v\right|$$

From the mean value theorem, we have

$$\begin{vmatrix} u - \frac{\arctan v}{2} \end{vmatrix} \leq \frac{7}{2} \begin{vmatrix} u - \frac{\arctan u}{2} \end{vmatrix} + \frac{1}{2} |u - v| \\ \leq \frac{7}{2} \left| u - \frac{\arctan u}{2} \right| + |u - v| \end{vmatrix}$$

which is precisely (4.1), for $u, v \in [0, 1)$. Thus, this inequality is satisfied.

Case IV: Let u = 1, v = 1. Then, (4.1) which needs to be fulfilled is

$$\begin{vmatrix} 1 - \frac{5}{7} \\ \frac{2}{7} &\leq \frac{7}{2} \begin{vmatrix} 1 - \frac{5}{7} \\ 1 - 1 \end{vmatrix}$$

$$\frac{2}{7} &\leq 1$$

and it is obviously satisfied.

Finally, if u = 1, v = 0.8 is taken, then

$$\frac{1}{2}\|u - \Psi u\| = \frac{1}{2}\left|1 - \frac{5}{7}\right| = \frac{1}{7} = 0.1428 < 0.2 = \|u - v\|$$

and

$$\|\Psi u - \Psi v\| = \left|\frac{5}{7} - \frac{\arctan(0.8)}{2}\right| = 0.37693 > 0.2 = \|u - v\|$$

Hence, Ψ does not satisfy condition (C).

Next, since an example of the Garsia-Falset GNM is provided, we will give it to a numerical reckoning for the iteration stated in the introduction. The observations are given in Table 1 and Figure 1.
4.1. Numerical Results

The convergence behaviors of (1.2) and (1.1) implementing Example 4.1 is compared. Let $\{\zeta_n\} = \{\varsigma_n\} = \{\tau_n\} = 0.75$, for all $n \ge 1$. 0 is the fixed point of the mapping defined in Example 4.1.

	Temir-Korkut iteration	Thakur iteration
u_1	0.80000000	0.80000000
u_2	0.01258820	0.15303068
u_3	0.00023817	0.03411124
u_4	0.00000451	0.00765877
u_5	0.00000009	0.00172020
u_6	0	0.00038637
u_7	0	0.00008678
u_8	0	0.00001949
u_9	0	0.00000438
u_{10}	0	0.00000098
u_{11}	0	0.00000022
u_{12}	0	0.00000005
u_{13}	0	0.00000001
u_{14}	0	0

Table 1. Sequences generated by (1.2) and (1.1) for mapping Ψ of Example 4.1.



Figure 1. Convergences of the Temir-Korkut iteration and the Thakur iteration to the fixed point 0 of the mapping defined in Example 4.1.

5. Conclusion

This paper has studied the convergence of (1.2) to fixed points for the Garsia-Falset GNMs in UCBS. An illustrative numerical example has been presented, one of the crucial of this paper. Example 4.1 satisfies condition (E). However, this example does not satisfy condition (C). This is intended to show numerically that the Garcia-Falset GNMs class is actually wider than the Suzuki GNMs class. Moreover, Table 1 and Figure 1, obtained from Example 4.1, can be observed that the Temir-Korkut iteration converges faster than the Thakur iteration. New iterations that converge faster than those presented herein can be developed in future studies. Additionally, more complex examples can be studied to compare the results obtained in this paper.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

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Crabronidae (Insecta: Hymenoptera) fauna of Kelkit Valley, Türkiye part I: subfamilies Astatinae and Dinetinae

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Dinetinae,				
Kelkit Valley				

Abstract — This study is the first part of the faunistic, and systematic research conducted in 2013-2018 to determine the Crabronidae species in Kelkit Valley, and the subfamilies Astatinae and Dinaetinae were evaluated in this part. In this study, 10 species and one subspecies of *Astata* and two species and one subspecies of *Dryudella* belong to the subfamily Astatinae and one species of *Dinetus* belongs to the subfamily Dinetinae have been recorded. Most of the identified species were recorded for the first time from Kelkit Valley. In addition, data on the seasonal and vertical distributions of the identified species are also presented. Distribution of species in the research area, Türkiye, and the world is included.

Subject Classification (2020):

1. Introduction

Astatinae and Dinetinae are two subfamilies of the solitary wasp family Crabronidae. Members of the subfamily Astatinae are relatively large wasps measuring 4 to 16 mm in size and are special predators of the order Hemiptera [1]. Astatinae contains 161 species in four genera worldwide. Most of the species are included in the two well-known genera, Astata and Dryudella, with 82 and 58 species, respectively [2]. Thus far, 16 taxa belonging to the genus Astata and seven taxa belonging to the genus Dryudella have been reported from Türkiye [3]. Dinetinae is the smallest subfamily of the Crabronidae family, with a single genus, Dinetus, containing only 14 species in the world [1]. These brightly colored small wasps usually have a black-yellow body pattern. Members of this group make their nests on the sand dunes and prey on hemipteran insects like the subfamily Astatinae [4]. *Dinetus pictus* is the only species representing this subfamily in Türkiye [3].

Kelkit Valley is the longest valley of the Yeşilırmak Basin, located in the inner parts of the Central Black Sea region in the east-west direction from Gümüşhane to Amasya. The valley, whose altitude decreases from 1500 m to 230 m from Kelkit to Taşova, is surrounded by Yeşilırmak and Canik mountains with an average height of 1400 - 1500 m. It is found in a transition zone between the humid Black Sea climate and the arid Central Anatolian climate. In addition, the Mediterranean climate and vegetation locally found in the Valley contribute to the diversity of habitats throughout the region [5]. The geographic location and habitat diversity of the valley has made it one of the richest faunal areas in Türkiye, and therefore the determination of insect diversity will provide important data. Although various insect

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species have been identified in the region to date [6-17], studies on the subfamilies Astatinae and Dinetinae are very limited [18-24]. Only four species are known from Kelkit Valley belonging to these two subfamilies, i.e., *Astata boops, A. kashmirensis, A. miegi scapularis and A. minor.*

The family Crabronidae was investigated comprehensively by field expeditions in the Kelkit Valley between 2013 and 2018. In this first part of the study, faunistic data concerning the subfamilies Astatinae and Dinetinae were included, together with some ecological observations about the species.

2. Material and Methods

In this study, adult insect specimens belonging to the Astatinae and Dinetinae subfamilies (Insecta: Hymenoptera) of the Kelkit Valley were collected. Totally, 230 specimens belonging to Astatinae and 16 specimens belonging to Dinetinae were collected from 34 localities between 2013 and 2018. Table 1 presents information about the collecting localities and habitat types of five provinces in the valley. All the specimens collected were prepared as standard museum materials and deposited in the Entomology Research Laboratory of the Biology Department in Tokat Gaziosmanpaşa University. The identification of the samples was made according to Bitsch et al. [25]. Identified taxa and collection localities of the specimens are given in alphabetical order in the following list.

Locality	Localities	Latitude/Longitu	Altitude (m)	Habitat	Collectors
1	Amasya, Central district, Ziyaret	40.696 / 35.853	435	Steppe	F. T. Çubuk
2	Amasya, Central district, Sarılar	40.677 / 35.893	1120	Steppe	F. T. Çubuk
3	Erzincan, Refahiye, Sakaltutan	39.870 / 39.092	1970	Steppe	İ. Can
4	Erzincan, Refahiye, Sağlık	39.920 / 38.777	1670	Farmland, Steppe	İ. Can
5	Erzincan, Refahiye, Akçiğdem	39.926 / 38.813	1720	Farmland, Steppe	İ. Can
6	Erzincan, Refahiye, Çat	40.021 / 38.774	1250	Steppe	İ. Can
7	Giresun, Alucra, Gürbulak	40.290 / 38.805	1560	Shrubs, Steppe	İ. Can
8	Giresun, Çamoluk, Hacıören	40.183 / 38.821	1410	Steppe	İ. Can
9	Giresun, Şebinkarahisar, Central	40.320 / 38.435	1200	Shrubs, Steppe	İ. Can
10	Gümüşhane, Kelkit, Ağıl	39.976 / 39.474	1660	Forest	İ. Can
11	Gümüşhane, Kelkit, Çilhoroz	40.159 / 39.290	1550	Oak Forest	İ. Can
12	Gümüşhane, Şiran, Güreşköy	40.112 / 38.950	1190	Steppe	İ. Can
13	Gümüşhane, Şiran Fındıkbeli	40.266 / 38.946	1675	Steppe	İ. Can
14	Gümüşhane, Şiran, Seydibaba	40.096 / 39.055	1450	Gallery Forest	İ. Can
15	Sivas, Akıncılar, Şenbağlar	40.060 / 38.396	1140	Shrubs, Steppe	İ. Can
16	Sivas, Gölova, Arslanca	40.068 / 38.771	1180	Shrubs	İ. Can
17	Sivas, Gölova, Çobanlı	40.015 / 38.585	1290	Shrubs	İ. Can
18	Sivas, İmranlı, Aşağıçulha	39.905 / 38.130	1830	Steppe	İ. Can
19	Sivas, Koyulhisar, İskenderşeyh	40.259 / 37.839	750	Steppe	F. T. Çubuk
20	Sivas, Koyulhisar, Kılıçpınarı	40.247 / 38.005	1200	Steppe	F. T. Çubuk
21	Sivas, Suşehri, Aşağısarıca	40.155 / 38.147	930	Steppe	İ. Can
22	Sivas, Suşehri, Boyalıca	40.150 / 38.126	975	Steppe	F. T. Çubuk
23	Sivas, Suşehri, Çokrak	40.133 / 38.093	1040	Steppe	İ. Can
24	Sivas, Suşehri, Akşar	40.050 / 38.184	1110	Steppe	İ. Can
25	Sivas, Suşehri, Geminbeli	39.990 / 37.986	2010	Galary forest	İ. Can
26	Sivas, Zara, Kumoğlu	39.955 / 37.925	1660	Steppe	İ. Can
27	Tokat, Erbaa, Karayaka	40.750 / 36.571	360	Shrubs, Steppe	F. T. Çubuk
28	Tokat, Erbaa, Tepekışla	40.680 / 36.670	230	Steppe, Shrubs	F. T. Çubuk
29	Tokat, Erbaa, Eryaba	40.707 / 36.713	900	Forest, Shrubs	F. T. Çubuk
30	Tokat, Niksar, Akıncı	40.424 / 37.083	600	Forest, Shrubs	F. T. Çubuk
31	Tokat, Niksar, Dönekse	40.522 / 36.907	320	Steppe	F. T. Çubuk
32	Tokat, Reşadiye, Zinav	40.450 / 37.277	970	Forest, Shrubs	F. T. Çubuk
33	Tokat, Reşadiye, Soğukpınar	40.360 / 37.301	780	Forest, Shrubs	F. T. Çubuk
34	Tokat, Reşadiye, Karlıyayla	40.395 / 37.512	1320	Forest, Steppe	F. T. Çubuk

Table	1	Collecting	localities	in	Kelkit	Vallev
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3. Results

Famliy Crabronidae Latreille, 1802

Subfamily Astatinae Lepeletier de Saint Fargeau 1845

Genus Astata Latreille, 1796

Astata affinis radoszkowskii Pulawski, 1957 (Figure 1a)

Material examined: Erzincan: Refahiye, Çat, 1250 m, 01.VIII.2017, 2 99; Sivas: Akıncılar, Şenbağlar, 1140 m, 18.VIII.2015, 9.

Distribution in the world: Algeria, Germany, Greece, Iran, Italy, Morocco, Spain, Türkiye, Ukraine [2].

Distribution in the Türkiye: Bilecik, Erzurum, Hatay, Kars, Konya, Tokat, Tunceli [3].

Remarks: New record for Erzincan and Sivas provinces

Astata boops (Schrank, 1781) (Figure 1b, c)

Material examined: Erzincan: Refahiye, Çat, 1250 m, 11.VIII.2016, 2 ♀♀; 01.VIII.2017, ♀; 12.VII.2018, 3 ♀♀; 27.VII.2018, ♀, ♂; Refahiye, Sağlık, 1660 m, 29.VI.2017, ♀; Refahiye, Sakaltutan, 1970 m 12.VII.2018, 2 ♂♂; Giresun: Çamoluk, Hacıören, 1410 m, 20.VII.2017, ♀; Gümüşhane: Kelkit, Ağıl, 1700 m, 13.VII.2016, ♀; Şiran, Güreşköy, 1190 m, 03.VII.2018, ♀; Şiran, Fındıkbeli, 1700 m, 13.VII.2016, 2 ♂♂; 24.VII.2016, ♂; Sivas: Akıncılar, Şenbağlar, 1140 m, 18.VII.2016, ♀; 03.VIII.2016, 4 ♀♀; 01.VIII.2017, ♀; 12.VIII.2017, ♀; 11.VII.2018, ♂; Gölova, Çobanlı, 1290 m, 13.VII.2017, 2 ♂♂; 23.VI.2017, ♂; Koyulhisar, İskenderşeyh, 750 m, 03.VIII.2016, ♂; Suşehri, Aşağısarıca, 930 m, 02.VI.2018, ♀; Suşehri, Çokrak , 1040 m, 05.VII.2018, ♀; Suşehri, Geminbeli, 2010 m, 12.VIII.2017, ♀; Zara, Kumoğlu, 1660 m, 09.VIII.2016, ♂; Tokat: Erbaa, Eryaba, 900 m, 21.III.2015, ♀.

Distribution in the world: Albania, Algeria, Austria, Azerbaijan, Belarus, Belgium, Bulgaria, China, Croatia, Cyprus, Czechia, Denmark, Egypt, England, Estonia, Finland, France, Germany, Greece, Hungary, India, Iran, Ireland, Israel, Italy, Kazakhstan, Korea, Kuwait, Latvia, Libya, Lithuania, Luxembourg, Malta, Morocco, Netherlands, Norway, Oman, Poland, Portugal, Romania, Russia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Tajikistan, Tunisia, Türkiye, Turkmenistan, Ukraine, Uzbekistan [2].

Distribution in the Türkiye: Adana, Afyonkarahisar, Ankara, Artvin, Aydın, Bayburt, Bilecik, Bingöl, Burdur, Bursa, Çanakkale, Erzurum, Eskişehir, Hatay, Isparta, İzmir, Kahramanmaraş, Kars, Kayseri, Kocaeli, Konya, Mersin, Niğde, Rize, Tokat, Trabzon, Tunceli [3].

Remarks: New record for Erzincan, Giresun, Gümüşhane, and Sivas provinces.

Astata costae A. Costa, 1867 (Figure 1d, e)

Material examined: Amasya: Central district, Ziyaret, 435 m, 07.VII.2013, σ; Erzincan: Refahiye, Akçiğdem , 1700 m, 13.VII.2017, σ; Refahiye, Çat , 1250 m, 11.VIII.2016, ♀; Refahiye, Sakaltutan , 1970 m, 11.VII.2018, ♀, σ; 27.VII.2018, σ; Giresun: Alucra, Gürbulak , 1600 m, 13.VII.2016, ♀, 3 σσ; 24.VII.2016, σ; 11.VII.2017, 2 σσ; Çamoluk, Haciören , 1410 m, 20.VII.2017, ♀; Gümüşhane: Kelkit, Ağıl , 1560 m, 13.VII.2016, ♀; Şiran, Fındıkbeli , 1700 m, 13.VII.2016, 2 σσ; Sivas: Zara, Kumoğlu, 1660 m, 22.VII.2015, 4 σσ; 09.VIII.2016, σ; Tokat: Erbaa, Tepekışla, 230 m, 03.VI.2017, σ; Reşadiye, Soğukpınar, 780 m, 18.X.2014, σ.

Distribution in the world: Algeria, Azerbaijan, Bulgaria, Croatia, Cyprus, Czechia, France, Greece, Hungary, Iran, Italy, Kazakhstan, Malta, Morocco, Portugal, Russia, Slovakia, Spain, Switzerland, Tajikistan, Tunisia, Türkiye, Turkmenistan, Ukraine [2].

Distribution in the Türkiye: Ağrı, Antalya, Artvin, Bingöl, Diyarbakır, Edirne, Erzurum, Hatay, Iğdır, Kars, Konya, Kütahya, Samsun, Tunceli [3].

Remarks: New record for Amasya, Erzincan, Giresun, Gümüşhane, Sivas and Tokat provinces.

Astata diversipes Pulawski, 1955 (Figure 1f)

Material examined: Sivas: Zara, Kumoğlu, 1660 m, 22.VII.2016, 2 ♂♂; Tokat: Niksar, Akıncı, 600 m, 13.V.2014, 9.

Distribution in the world: Syria, Türkiye [2].

Distribution in the Türkiye: Erzincan, Hatay, Sivas [3].

Remarks: New record for Tokat province.

Astata gallica de Beaumont, 1942

Material examined: Tokat: Niksar, Dönekse, 320 m, 28.V.2015, *s*; Reşadiye, Sarıyayla, 1250 m, 15.VIII.2015, *s*; Sivas: Koyulhisar, Kılıçpınarı, 1200 m, 22.VI.2016, *s*.

Distribution in the world: Czechia, France, Italy, Morocco, Poland, Portugal, Slovakia, Spain, Türkiye [2].

Distribution in the Türkiye: Erzurum, Kars, Samsun [3, 26].

Remarks: New record for Sivas and Tokat provinces.

Astata graeca de Beaumont, 1965 (Figure 1g, h)

Material examined: Erzincan: Refahiye, Çat , 1250 m, 12.VII.2018, ♀, ♂; 27.VII.2018, ♀; Refahiye, Sağlık , 1660 m, 13.VII.2017, ♂; Refahiye, Sakaltutan , 1970 m, 12.VII.2018, 3 ♂♂; Giresun: Alucra, Gürbulak , 1560 m, 24.VII.2016, ♂; Şebinkarahisar, Central district, 1200 m, 02.VII.2018, ♀; Sivas: Koyulhisar: Kılıçpınarı, 1200 m, 03.VIII.2016, ♀; Suşehri, Geminbeli, 2010 m, 12.VIII.2017, ♂; Zara, Kumoğlu, 1660 m, 18.VII.2017, ♂.

Distribution in the world: Azerbaijan, Cyprus, France, Greece, Iran, Israel, Italy, Türkiye, United Arab Emirates [2].

Distribution in the Türkiye: Ankara, Artvin, Kars, Tokat [3, 27].

Remarks: New record for Erzincan, Giresun, and Sivas provinces.

Astata kashmirensis Nurse, 1909 (Figure 1i, j)

Material examined: Erzincan: Refahiye, Sakaltutan, 1970 m, 12.VII.2018, *d*; 27.VII.2018, *d*; Giresun: Alucra, Gürbulak, 1560 m, 28.VI.2017, *d*; Çamoluk, Hacıören, 1410 m, 11.VIII.2016, *d*; 28.VI.2017, 6 *dd*; 11.VII.2017, *d*; 20.VII.2017, *d*; Şebinkarahisar, Central district, 1250 m, 02.VII.2018, *d*; Gümüşhane: Kelkit, Çilhoroz, 1550 m, 26.VII.2017, *d*; 02.VII.2018, *d*; Şiran, Güreşköy, 1190 m, 03.VII.2018, *d*; Sivas: Akıncılar, Şenbağlar, 1140 m, 23.VI.2017, *d*; 02.VI.2018, *d*; Suşehri, Çokrak, 1040 m, 17.VII.2018, *d*; Suşehri, Geminbeli, 2010 m, 22.VII.2015, *d*; 01.VIII.2017, *d*; 12.VIII.2017, 2 *dd*; Zara, Kumoğlu, 1660 m, 22.VII.2015, *d*; 18.VII.2016, *Q*; 09.VIII.2016, 2 *dd*; Tokat: Erbaa, Tepekışla, 230 m, 03.VI.2017, *d*.

Plants collected on: Euphorbia virgata

Distribution in the world: Austria, Azerbaijan, Bulgaria, China, Cyprus, Czechia, France, Germany, Greece, Hungary, India, Iran, Italy, Kazakhstan, Poland, Portugal, Russia, Slovakia, Slovenia, Spain, Switzerland, Türkiye, Turkmenistan, Ukraine, Uzbekistan [2].

Distribution in the Türkiye: Amasya, Ankara, Bilecik, Bingöl, Denizli, Diyarbakır, Erzincan, Erzurum, Hatay, Iğdır, Isparta, Kars, Konya, Mersin, Şanlıurfa, Tokat, Tunceli [3].

Remarks: New record for Giresun, Gümüşhane and Sivas provinces.

Astata miegii scapularis (Kohl, 1889) (Figure 1k, l)

Material examined: Amasya: Central district, Sarılar, 1120 m, 01.VII.2013, σ'; Erzincan: Refahiye, Çat, 1250 m, 11.VIII.2016, 4 σ'σ'; 26.VII.2017, σ'; 12.VII.2018, 2 ♀♀; Giresun: Çamoluk, Hacıören, 1410 m, 24.VII.2016, ♀, 2 σ'σ'; 11.VII.2017, σ'; 20.VII.2017, ♀, σ'; 07.VIII.2017, ♀; Şebinkarahisar, Central district, 1260 m, 02.VII.2018, 2 σ'σ'; 24.VII.2018, σ'; Gümüşhane: Kelkit, Çilhoroz, 1550 m, 02.VII.2018, 2 σ'σ'; Sivas: Akıncılar, Şenbağlar, 1140 m, 11.VII.2018, σ'; Suşehri, Akşar, 1110 m, 18.VII.2017, ♀; 29.VIII.2018, 4 σ'σ'; Suşehri, Boyalıca, 975 m, 03.VIII.2016, σ'; 18.VII.2017, 5 σ'σ'; Suşehri, Çokrak, 1040 m, 05.VII.2018, σ'; 17.VII.2018, ♀; Tokat: Reşadiye, Soğukpınar, 780 m, 18.X.2014, σ'; Reşadiye, Zinav, 970 m, 17.VIII.2014, σ'.

Distribution in the world: Armenia, Bulgaria, Greece, Türkiye, Ukraine [2].

Distribution in the Türkiye: Aksaray, Amasya, Ankara, Antalya, Bilecik, Bingöl, Çankırı, Erzincan, Erzurum, Gümüşhane, Isparta, İzmir, Kars, Kırıkkale, Kütahya, Manisa, Nevşehir, Tokat, Tunceli [3, 27].

Remarks: New record for Giresun and Sivas provinces.

Astata minor Kohl, 1885 (Figure 1m, n)

Material examined: Erzincan: Refahiye, Çat, 1250 m, 12.VII.2018, 2 99; 27.VII.2018, 9; Refahiye, Sakaltutan, 1970 m, 11.VII.2018, 9 99, 2 & d; 27.VII.2018, 2 99, d; Giresun: Alucra, Gürbulak, 1560 m, 11.VII.2017, d; Çamoluk, Hacıören, 1460 m, 18.VI.2017, d; 28.VI.2017, 2 dd; 02.VII.2017, d; 24.VII.2018, 4 99, d; Şebinkarahisar, Central district, 1200 m, 02.VII.2018, 9; Sivas: Akıncılar, Şenbağlar, 1140 m, 18.VIII.2015, 9; 23.VI.2017, d; 02.VII.2017, d; 01.VIII.2017, 2 99; 05.VII.2018, 2 99; 11.VII.2018, 3 99; Gölova, Çobanlı, 1290 m, 23.VI.2017, 9; İmranlı, Aşağıçulha, 1830 m, 24.VII.2017, d; Koyulhisar, İskenderşeyh, 750 m, 03.VIII.2016, d; 1150 m, 13.VII.2017, d; Suşehri, Geminbeli, 2010 m, 24.VII.2017, 9; 01.VIII.2017, 2 99; 12.VIII.2017, 9; Zara, Kumoğlu, 1660 m, 22.VII.2015, 2 dd; 17.VII.2018, 9; Tokat: Erbaa, Karayaka, 360 m, 09.V.2015, 2 dd; Erbaa, Tepekışla, 230 m, 16.V.2015, 9; Niksar, Çamiçi, 900 m, 21.VI.2013, d; Reşadiye, Karlıyayla, 1320 m, 20.VI.2015, d.

Plants collected on: Euphorbia virgata

Distribution in the world: Algeria, Austria, Azerbaijan, Belarus, Belgium, Bulgaria, Croatia, Cyprus, Czechia, Denmark, Finland, France, Germany, Greece, Hungary, Iran, Israel, Italy, Kazakhstan, Lithuania, Luxembourg, Morocco, Netherlands, Poland, Portugal, Romania, Russia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Tunisia, Türkiye, Turkmenistan, Ukraine, Uzbekistan [2].

Distribution in the Türkiye: Ağrı, Ankara, Artvin, Bilecik, Bingöl, Diyarbakır, Erzincan, Erzurum, Gümüşhane, Hatay, Iğdır, Isparta, Kars, Tokat, Tunceli [3, 27].

Remarks: New record for Giresun and Sivas provinces.

Astata pontica Pulawski, 1958

Material examined: Sivas: Koyulhisar, Suşehri road 20. km, 700 m, 27.VII.2014, ♂; Tokat: Erbaa, Tepekışla, 230 m, 02.VII.2014, ♂.

Distribution in the world: Bulgaria, Czechia, Greece, Russia, Türkiye [2].

Distribution in the Türkiye: Isparta, Niğde [3].

Remarks: New record for Sivas and Tokat provinces.

Astata rufipes Mocsáry, 1883 (Figure 1o, p)

Material examined: Erzincan: Refahiye, Sakaltutan, 1900 m, 29.VI.2017, σ'; 11.VII.2018, 2 σσ'; Giresun: Çamoluk, Hacıören, 1410 m, 28.VI.2017, 3 σσ'; 20.VII.2017, σ'; Şebinkarahisar, Central district, 1250 m, 06.VIII.2015, ♀; Gümüşhane: Kelkit, Çilhoroz, 1550 m, 02.VII.2018, σ'; Şiran, Seydibaba, 1450 m, 26.VII.2017, σ'; Sivas: Akıncılar, Şenbağlar, 1140 m, 23.VI.2017, 2 σσ'; 01.VIII.2017, 2 σσ'; Zara, Kumoğlu, 1660 m, 01.VII.2016, 4 σσ.

Plants collected on: Euphorbia virgata

Distribution in the world: Austria, Bulgaria, Czechia, France, Greece, Hungary, Italy, Kazakhstan, Libya, Poland, Russia, Slovakia, Spain, Switzerland, Tajikistan, Türkiye, Turkmenistan, Ukraine [2].

Distribution in the Türkiye: Bitlis, Kars, Tokat, Tunceli [3].

Remarks: New record for Erzincan, Giresun, Gümüşhane and Sivas provinces.

Genus *Dryudella* Spinola, 1843

Dryudella freygessneri (Carl, 1913) (Figure 1q, r)

Material examined: Erzincan: Refahiye, Sakaltutan, 2010 m, 27.VII.2018, σ; Sivas: Zara, Kumoğlu, 1660 m, 18.VII.2016, ♀, σ; İmranlı, Aşağıçulha, 1830 m, 18.VII.2017, σ.

Distribution in the world: France, Italy, Switzerland, Türkiye [2].

Distribution in the Türkiye: Erzincan, Erzurum, Kütahya [3].

Remarks: New record for Sivas province.

Dryudella tricolor (Vander Linden, 1829) (Figure 1s)

Material examined: Erzincan: Refahiye, Sakaltutan, 1970 m, 11.VII.2018, 9; 27.VII.2018, 9; Tokat: Erbaa, Tepekışla, 230 m, 02.VII.2014, 9; Reşadiye, Zinav, 970 m, 12.X.2014, 9.

Distribution in the world: Austria, Belarus, Bulgaria, Czechia, France, Greece, Hungary, Iran, Italy, Kazakhstan, Kuwait, Libya, Morocco, Portugal, Romania, Russia, Slovakia, Spain, Switzerland, Tajikistan, Türkiye, Ukraine [2].

Distribution in the Türkiye: Erzincan, Kars, Kayseri [3].

Remarks: New record for Tokat province.

Dryudella tricolor eurygnatha (Pulawski, 1967) (Figure 1t)

Material examined: Erzincan: Refahiye, Çat, 1250 m, 12.VII.2018, σ'; Sivas: Gölova, Arslanca, 1180 m, 24.VII.2016, σ'; Suşehri, Akşar, 1110 m, 09.VIII.2016, σ' Zara, Kumoğlu, 1660 m, 22.VII.2016, 2 σσ.

Distribution in the world: Azerbaijan, Bulgaria, Greece, Iran, Kazakhstan, Romania, Russia, Türkiye [2].

Distribution in the Türkiye: Amasya, Aydın, Balıkesir, Bingöl, Diyarbakır, Erzincan, Erzurum, Hatay, Konya, Mersin, Nevşehir, Sinop, Tunceli [3].

Remarks: New record for Sivas provinces.



Figure 1. Some identified species belonging to subfamily Astatinae: a) *Astata affinis* (\$); b) *Astata boops* (\$); c) *Astata boops* (\$); d) *Astata costae* (\$); e) *Astata costae* (\$); f) *Astata diversipes* (\$); g) *Astata graeca* (\$); h) *Astata graeca* (\$); i) *Astata kashmirensis* (\$); j) *Astata kashmirensis* (\$); k) *Astata miegi scapularis* (\$); l) *Astata miegi scapularis* (\$); m) *Astata minor* (\$); n) *Astata minor* (\$);
o) *Astata rufipes* (\$); p) *Astata rufipes* (\$); q) *Dryudella freygessneri* (\$); r) *Dryudella freygessneri* (\$); s) *Dryudella tricolor* (\$); t) *Dryudella tricolor eurygnatha* (\$)

Subfamily Dinetinae W. Fox, 1895

Genus Dinetus Panzer, 1806

Dinetus pictus (Fabricius, 1793) (Figure 2a, b)

Material examined: Giresun: Alucra, Gürbulak, 1560 m, 11.VII.2017, 3 ♂♂; 20.VII.2017, 1 ♂; Sivas: Zara, Kumoğlu, 1660 m, 22.VII.2015, 2 ♀♀, 1 ♂; 06.VIII.2015, 3 ♀♀, 1 ♂; 18.VII.2016, 3 ♀♀; Tokat: Erbaa, Tepekışla, 230 m, 03.VI.2017,1 ♀; 03.VII.2017,1 ♀.

Distribution in the world: Albania, Algeria, Austria, Belarus, Belgium, Bulgaria, Croatia, Czechia, Denmark, Estonia, Finland, France, Germany, Great Britain, Greece, Hungary, Italy, Kazakhstan, Latvia, Netherlands, Poland, Portugal, Romania, Russia, Slovakia, Slovenia, Spain, Switzerland, Syria, Türkiye, Ukraine [2].

Distribution in Türkiye: Bayburt, Bingöl, Bursa, Erzincan, Erzurum, Isparta, İstanbul, Kayseri, Konya, Niğde, Sinop, Tokat [3, 27].

Remarks: New record for Giresun and Sivas provinces.





4. Conclusion

In this study, samples were caught with collection nets from the field and plant species on which samples were collected were determined as much as possible. During field studies, most of the specimens were caught in sandy or stony areas with sparse vegetation. Therefore, plant records for most specimens could not be given, probably because they were not active at the time of collection, or they were caught in the air during flight. *Euphorbia virgata* was the only plant species on which specimens belonging to three species, *Astata kashmirensis, A. minor* and *A. rufipes*, could be collected.

As listed above, 14 taxa from Astatinae and one species from Dinetinae were identified, among which the most common ones were *Astata boops, A. costae, A. kashmirensis* and *A. miegii scapularis*. Except for *Astata boops, A. kashmirensis, A. miegi scapularis* and *A. minor*, all identified taxa were recorded for the first time from Kelkit Valley. Moreover, detecting *Astata diversipes, A. pontica, A. rufipes, Dryudella freygessneri* and *D. tricolor* is an important faunistic record, since these species are rare and distributed in a narrow area in Türkiye.

The species, *Astata jucunda*, which was previously recorded from Erzincan by Yıldırım and Ljubomirov [21], could not be determined in this study. This is probably because the specific locality of the species has not been clearly defined or it has been overlooked during our field studies.

According to our results, species belonging to subfamilies Astatinae and Dinetinae are actively flying from March to October, mostly in July and August. *Astata boops* has the longest flight period among others. It is known that this species, which repeats at least three generations in a year, is seen from June to September [28]. This species was found to be active from late March to mid-August in the study area.

Although collections were made between March and October in the region, no samples were found in April and September (Figure 3). There may be different reasons for the unavailability of samples during these months. For example, climatic conditions, vegetation characteristics, the low prey population of these predatory insects or the inactivity of insects during visits.



Figure 3. Seasonal distribution of Astatinae and Dinetinae species in Kelkit Valley

The vertical distribution of the species according to the samples caught in the research area ranged from 200 to 2100 m. The highest number of species is detected between 1500-2000 m (Figure 3). It can be concluded that this altitude range has suitable ecological conditions for the identified species. *Astata costae, A. kashmirensis,* and *A. minor* have the widest vertical distribution range as they are found at almost all elevations.



Figure 4. Vertical distribution of Astatinae and Dinetinae species

A total of 24 taxa are known in Türkiye belonging to Astatinae and Dinetinae subfamilies. The detection of 15 taxa belonging to these subfamilies in Kelkit Valley is an indication of the rich fauna. Additionally, some of these taxa are new records for the Crabronidae fauna of the provinces in the region (Table 2).

Province	Number of taxa			
riovilice	Literature	New records	Current	
Amasya	96	1	97	
Erzincan	107	5	112	
Giresun	22	8	30	
Gümüşhane	25	4	29	
Sivas	61	13	74	
Tokat	151	5	156	

Table 2. Number of taxa belonging to Crabronidae in Kelkit Valley

It is very valuable to document the distribution of insect species, which constantly changes with the effect of global warming, destruction of habitats, decrease in food sources, or other environmental factors, with new data. This study provided essential data for future studies, including new species records from the research area and some ecological data of the identified species.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper. This paper is derived from the first and the second authors' doctoral dissertations supervised by the third author.

Conflicts of Interest

All the authors declare no conflict of interest.

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