Abstract: The compound \(N-(5-(4-chlorobenzyl)-1,3,5-triazinan-2-ylidene)nitramide\) (C\(_{10}H_{12}ClN_5O_2\), \(M = 269.70\)) was synthesized and structurally confirmed by \(^1\)H NMR, \(^{13}\)C NMR, HRMS and single-crystal x-ray diffraction. The crystal belongs to the monoclinic system with space group \(P2_1/c\). The title compound consisted of a benzene ring and a 1,3,5-triazine ring. All carbon atoms in the benzene ring were nearly coplanar with a dihedral (C6–C5–C10 and C7–C8–C9) angle of 1.71° and all non-hydrogen atoms of the 1,3,5-triazine ring were not planar, but exhibited a half-chair conformation. The crystal structure was stabilized by a strong intramolecular hydrogen bonding interaction N(3)–H(3)···O(2) and three intermolecular hydrogen bonding interactions, N(2)–H(2)···O(1), N(2)–H(2)···N(4) and N(3)–H(3)···Cl(1). The preliminary bioassay showed that the title compound showed not only aphicidal activity against \(Sitobion miscanthi\) (inhibition rate: 74.1%) and \(Schizaphis graminum\) (77.5%), but also antifungal activities against \(Pythium aphanidermatum\) (62.0%). These results provide valuable guidelines for the design and synthesis of novel aphid control agents and fungicides.

Keywords: synthesis; crystal structure; nitramide; aphicidal activity; antifungal activity

1. Introduction

Substituted triazine compounds have attracted more and more attention in recent years for their use as medicines [1–3] and agrochemicals [4–6], such as adenosine A antagonists, anticonvulsants, antimicrobials, antioxidant agents, bactericides, herbicides and insecticides. Among these triazines, hexahydro-1,3,5-triazine, is endowed with simple structure and very important pharmaceutical activities, such as insecticidal [7], antifungal [8], herbicidal [9] and antiviral [10] activities. In addition, the electron-withdrawing group of NO\(_2\) plays a crucial role in providing insecticidal properties [11], such as those against \(Myzus persicae\) [12], \(Aphis gossypii\) [13], \(Aphis medicaginis\) [14], \(Nilaparvata lugens\) [15] and \(Spodoptera littoralis\) [16]. Besides, benzyl groups exhibited outstanding activities, such as in insecticidal activity of Pyridaben and fungicidal activity of Cyflufenamid. However, during the past decade, resistance and cross-resistance have increased in a range of species due to their frequent applications in field [17–20].

As part of our ongoing work in exploring triazine active chemical structures, we noticed that a type of 2-nitroimino-hexahydro-1,3,5-triazine (NHT) derivatives displayed biological activity against the apterous adult aphids of \(M. persicae\) [21,22] and \(Acyrthosiphon pisum\) [23]. In the view of these facts and in order to further search for NHT derivatives with high bioactivity and broad-spectrum, the titled compound \(N-(5-(4-chlorobenzyl)-1,3,5-triazinan-2-ylidene)nitramide\) (1), was designed by introducing benzyl group active substructure into NHT scaffold. The Compound 1 was synthesized.
through combining nitro guanidine, formaldehyde and 4-chlorobenzylamine via the Mannich reaction using the one-pot method in protic solvent (Scheme 1). The structure of the corresponding compound was characterized by \(^1\)H NMR, \(^{13}\)C NMR, HRMS and single-crystal x-ray diffraction. Furthermore, the insecticidal activity against different aphid species was evaluated. Moreover, compounds containing NHT group have been discovered to showed antifungal activity [24–26]. Herein, we have also estimated the antifungal activity of Compound 1.

![Scheme 1. Synthetic approach of the title Compound 1.](image)

**2. Materials and Methods**

**2.1. General Techniques**

Melting point of the Compound 1 was determined on an X-5 binocular (Fukai Instrument Co., Beijing, China) with an uncorrected thermometer. \(^1\)H NMR spectra were measured on a Bruker DPX300 spectrometer (Bruker, Bremen, Germany). Chemical shifts were reported in \(\delta\) (ppm) with TMS as the internal standard and DMSO-d6 as the solvent. \(^{13}\)C-NMR spectra were obtained by using a Bruker DPX300 spectrometer (75 MHz) with DMSO-d6 as a solvent. The chemical shifts (\(\delta\)) were reported in parts per million using the solvent peak. High-resolution mass spectral data were acquired by a FTICR-MS Varian 7.0 T FTICR-MS instrument (Varian, Palo Alto, CA). A single-crystal x-ray structure was recorded on a Gemini E x-ray single crystal diffractometer (Rigaku, Tokyo, Japan). Nitro guanidine, formaldehyde and 4-chlorobenzylamine were purchased from Beijing Ouhe Technology Co., Ltd. (Beijing, China). All the other reagents were acquired from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China) and used without further purification.

**2.2. Synthesis of N-(5-(4-Chlorobenzyl)-1,3,5-Triazinan-2-Ylidene)Nitramide**

The target Compound 1 was prepared according to a modified procedure based on the published methods [27]. The synthetic approach of Compound 1 is shown in Scheme 1. To a solution of 4-chlorobenzylamine (58 mmol) and nitro guanidine (48 mmol) in ethanol (20 mL), 37% formaldehyde (120 mmol) was added dropwise. The reaction mixture was stirred at 60 °C for 6 h. After it was cooled to room temperature, the mixture was filtered and the filtrate was washed with cold ethanol and acetone, respectively, then dried under infrared lamp to obtain the white solid Compound 1 with a yield of 65.3%. m.p.: 201–203 °C. \(^1\)H NMR (DMSO-d6, 300 MHz), \(\delta\) (ppm): 8.79 (brs, 2H, NH), 7.34–7.40 (m, 4H, ArH), 4.24 (s, 4H, CH\(_2\)), 3.78 (s, 2H, Ar-CH\(_2\)). \(^{13}\)C NMR (DMSO-d6, 75 MHz), \(\delta\) (ppm): 155.80, 136.70, 132.15, 130.69, 128.44, 59.58, 53.25. HRMS calculated for C\(_{10}\)H\(_{12}\)ClN\(_5\)O\(_2\) (M+H\(^+\)): 270.0752, found 270.0747.

**2.3. Structure Determination**

Single crystals suitable for x-ray diffraction were obtained from slow evaporation of a solution of the title compound 1 in dichloromethane/petroleum ester (v/v = 3/1) at temperature of 4 °C. Compound 1 exists in the form of colorless crystals. A crystal of Compound 1 (0.36 mm × 0.20 mm × 0.14 mm) was selected for data collection and mounted in inert oil, which was transferred to the cold gas stream of the Gemini E x-ray single crystal diffractometer (Rigaku, Tokyo, Japan) equipped with a graphite-monochromatic \(\mu\)MoK\(\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)) at temperature 109(10) K. In a range of
6.59 < 2θ < 58.972°, a total of 9949 reflections were collected by using an ω scan mode, of which 3246 were unique with Rint = 0.0332 and 2794 were observed with I > 2σ(I). The structure of Compound 1 was solved via Direct Methods and the solutions were refined by full-matrix least squares techniques on F2 by SHELXL-2014 program [28]. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located theoretically. The final R = 0.0468, wR = 0.0864 (w = 1/[σ2(Fo)2 + (0.0311P)2]), where P = (Fo2 + 2Fc2)/3, S = 1.066, (Δσ)max = 0.859, (Δσ)max = 0.291 and (Δσ)min = −0.288 eÅ−3 included 169 parameters. Crystal data and structure refinement data of Compound 1 are shown in Table 1.

| Compound | 1 |
|----------|---|
| CCDC No. | 1973548 |
| Empirical formula | C10H12ClN5O2 |
| Formula weight | 269.70 |
| Temperature/K | 109.35 |
| Crystal system | monoclinic |
| Space group | P21/c |
| a/Å | 5.46593(17) |
| b/Å | 24.7334(6) |
| c/Å | 8.6800(3) |
| α/° | 90.00 |
| β/° | 95.218(3) |
| γ/° | 90.00 |
| Volume/Å³ | 1168.59(6) |
| Z | 4 |
| ρcalc mg/mm³ | 1.533 |
| μ/mm⁻¹ | 0.330 |
| F(000) | 560 |
| Crystal size/mm³ | 0.36 × 0.20 × 0.14 |
| 2Θ range for data collection | 6.59 to 58.972° |
| Index ranges | −7 ≤ h ≤ 7, −33 ≤ k ≤ 34, −7 ≤ l ≤ 11 |
| Reflections collected | 9949 |
| Independent reflections | 2794[R(int) = 0.0332, Rsigma = 0.0355] |
| Data/restraints/parameters | 2794/0/169 |
| Goodness-of-fit on F² | 1.066 |
| Final R indexes [I > 2σ (I)] | R₁ = 0.0383, wR₂ = 0.0814 |
| Final R indexes [all data] | R₁ = 0.0468, wR₂ = 0.0864 |
| Largest diff. peak/hole / e Å⁻³ | 0.29/−0.29 |

2.4. Aphidical Activity

The in vivo aphidical activities of Compound 1 against *Myzus persicae*, *Sitobion miscanthi*, *Rhopalosiphum padi*, *Schizaphis graminum* and *Metopolophium dirhodum* were measured using the reported method [29,30]. Compound 1 was dissolved in DMSO to a concentration of 2000 mg/L and then diluted to 200 mg/L with 0.05% Triton X-20. Wheat seedlings (for wheat aphids) or cabbage leaf discs (for *M. persicae*) were dipped into the test solution for 15 s. And then, the seedlings or discs were infested with 20 ± 3 apterous adult aphids and incubated under constant temperature (25 ± 1 °C) and light period (light : dark = 8:16) for 48 h. The number of dead aphids was then recorded, and the inhibition rates were corrected using Abbott’s formula [31]. Each experiment was conducted in triplicates. The LC₅₀ values were also determined based on the preliminary aphid mortality rates. The commercial insecticide Pymetrozine was used as a positive control while the solvent was set as a negative control.
2.5. Antifungal Activity

The in vitro antifungal activities of the Compound 1 were evaluated against six plant fungal pathogens (*Rhizoctonia solani*, *Pythium aphanidermatum*, *Valsa mali*, *Botrytis cinerea*, *Fusarium moniliforme*, *Alternaria solani*). The mycelium growth rate method was used according to references [32,33]. Compound 1 was dissolved in DMSO to prepare the 10 mg/mL stock solution, then mixed with PDA (Potato Dextrose Agar) medium to a concentration of 50 mg/L and was poured into sterilized Petri dishes. After the dishes were cooled, the mycelia disks were inoculated in the center of the Petri dishes and incubated at 25 °C. Each experiment was repeated three times. After 2–3 d of culturing, the colony diameter of each strain was measured. The commercial fungicide, Difenoconazole, with broad spectrum against fungus was used as the positive controls.

3. Results and Discussion

3.1. Crystal Structure

The title Compound 1 crystallized in the monoclinic system. The molecular structure of the Compound 1 is depicted in Figure 1. Selected molecular structure parameters, including bond lengths, bond angles and torsion angles of Compound 1 are summarized in Table 2 and Supplementary Materials Table S1, S2 and S3. Other parameters of fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3), hydrogen atom coordinates (Å × 10^4) and isotropic displacement parameters (Å^2 × 10^3) are listed in Supplementary Materials Table S4, S5 and S6. The Hydrogen bonds and crystal packing of Compound 1 are displayed in Figure 2. The molecule crystal structure of Compound 1 had been deposited in the Cambridge Crystallographic Data Centre; the recorded CCDC number was 1,973,548. Crystallographic data for Compound 1 can be obtained free of charge at the following website: http://www.ccdc.cam.ac.uk/data_request/cif.

![Figure 1. Crystal Structure of Compound 1.](image1)

![Figure 2. Hydrogen bonds (dashed lines) and crystal packing in Compound 1.](image2)
Table 2. Selected molecular structure parameters.

| Bond                | Distance (Å) | Bond                | Distance (Å) |
|---------------------|--------------|---------------------|--------------|
| Cl(1)–C(8)          | 1.7538(15)   | N(3)–C(3)           | 1.472(2)     |
| O(1)–N(5)           | 1.2459(17)   | N(4)–N(5)           | 1.3405(17)   |
| O(2)–N(5)           | 1.2500(16)   | N(4)–C(1)           | 1.3707(19)   |
| N(1)–C(2)           | 1.4476(18)   | C(4)–C(5)           | 1.506(2)     |
| N(1)–C(3)           | 1.4453(19)   | C(5)–C(6)           | 1.390(2)     |
| N(2)–C(1)           | 1.3310(19)   | C(5)–C(10)          | 1.396(2)     |
| N(2)–C(2)           | 1.4743(19)   | C(7)–C(8)           | 1.380(2)     |
| N(3)–C(1)           | 1.3277(19)   | C(8)–C(9)           | 1.387(2)     |

| Angle (°)           | Angle (°)   |
|---------------------|-------------|
| C(2)–N(1)–C(4)      | 112.61(11)  | N(1)–C(2)–N(2)      | 111.42(12)   |
| C(3)–N(1)–C(2)      | 108.67(12)  | N(1)–C(3)–N(3)      | 111.35(12)   |
| C(1)–N(2)–C(2)      | 123.18(13)  | N(1)–C(4)–C(5)      | 111.81(12)   |
| C(1)–N(3)–C(3)      | 119.53(13)  | C(6)–C(5)–C(10)     | 118.68(14)   |
| N(5)–N(4)–C(1)      | 119.53(12)  | C(7)–C(6)–C(5)      | 121.47(15)   |
| O(1)–N(5)–O(2)      | 121.48(12)  | C(8)–C(7)–C(6)      | 118.35(14)   |
| O(1)–N(5)–N(4)      | 114.46(12)  | C(7)–C(8)–C(9)      | 122.04(14)   |
| N(3)–C(1)–N(2)      | 119.06(14)  | C(8)–C(9)–C(10)     | 118.62(15)   |
| N(3)–C(1)–N(4)      | 128.22(14)  | C(9)–C(10)–C(5)     | 120.81(14)   |

As shown in Table 2, all bond lengths and angles are generally within normal ranges and in a good agreement with those reported previously [34–40]. The C–C bond lengths of benzene ranged from 1.380(2) to 1.396(2) Å, which were extremely close to C–C bond lengths (1.373(3) to 1.393(2) Å) of benzene in compound (E)-5-benzyl-1-methyl-N-nitro-1,3,5-triazinan-2-imine [34]. In the 1,3,5-triazine ring (C1/C2/C3/N3/N2–N1), four of the six amino C–N bonds were shortened equivalent C–N single bond (1.49 Å) [41]. The bond lengths of N(2)–C(2), N(3)–C(3), N(1)–C(2) and N(1)–C(3) were 1.4743(19) Å, 1.472(2) Å, 1.4476(18) Å and 1.4453(19) Å, respectively. The remaining two amino bonds N(2)–C(1) [1.3310(19) Å] and N(3)–C(1) [1.3277(19) Å] were equivalent partial double bonds [37], shorter than that of N(2)–C(2), N(3)–C(3), N(1)–C(2) and N(1)–C(3), which suggested that the electron density of the imino C(1)–N(4) bond p-electrons was delocalized among N(2)–C(1)–N(4) and N(3). This phenomenon also existed in other crystal structures bearing NHT ring, such as (E)-5-benzyl-1-methyl-N-nitro-1,3,5-triazinan-2-imine [34], 1,5-dimethyl-2-nitroimino-1,3,5-triazinan [35], 1-(2-chloro-1,3-thiazol-5-ylmethyl)-3,5-dimethyl-2-nitrimino-1,2,3,4,5,6-hexahydro-1,3,5-triazine [36] and 2-nitrimino-5-nitro-hexahydro-1,3,5-triazine [37]. The length of the imino bond C(1)=N(4) was 1.3707(19) Å, which was significantly longer than above two amino bonds N(2)–C(1) and N(3)–C(1) in the 1,3,5-triazine ring. The distances of resemble guanidine structures with nitro group were found in literatures with similar values from 1.342 to 1.389 Å [34–37,41,42]. However, these distance values were longer than those of reported C=N bonds with nitro group with values between 1.267 and 1.275 Å [43–47]. Bracutti commented molecular interaction and intermolecular H-bonds in crystal structure had responsibilities for this elongation of hydrazine C=N bond [37]. Meanwhile, the length of nitrimino bond N(4)–N(5) (1.3405(17) Å), a partial double bond, was similar with reported nitrimino bond distance (1.322–1.362 Å) [34,35,37,41]. In particular, it was similar with the distance of nitrimino bond in 1,5-dimethyl-2-nitroimino-1,3,5-triazinan, regardless of trans and cis configuration [35]. But it was longer than the length of nitrimino bond (1.294 Å) in...
1-(2-chloro-1,3-thiazol-5-ylmethyl)-3,5-dimethyl-2-nitrimino-1,2,3,4,5,6-hexahydro-1,3,5-triazine [36].

The Cl(1)–C(8) bond length was 1.7538(15) Å, which corresponds to typical values for the C(sp2)–Cl bond length.

The title compound consisted of a benzene ring and a 1,3,5-triazine ring. All carbon atoms in the benzene ring were nearly coplanar with a dihedral (C6–C5–C10 and C7–C8–C9) angle of 1.71° and all non-hydrogen atoms of the 1,3,5-triazine ring were not planar, but exhibited a half-chair conformation. This half-chair conformation could be also found in some crystal structures with 1,3,5-triazine ring, such as in structures of CCDC codes 859,274 [48], 840,152 [42], 774,302 [34], 700,528 [35], 674,453 [36] and 224906 [37]. On the other side, the conformation of 1,3,5-triazine ring in other compounds presented different. For instance, those conformations from structures of CCDC codes 842,778 [49], 957,651 [50] were not half-chair, but planar. The 1,3,5-triazine ring in Compound 1 displayed a large distortion due to the nature of its non-conjugated system. For example, the torsion angels of C(2)–N(2)–C(1)–N(3), C(2)–N(1)–C(3)–N(3) and C(1)–N(3)–C(3)–N(1) were 6.7(2)°, 58.45(15)° and –35.90(18)°, respectively. The 1,3,5-triazine ring formed two planes C3/C2/N2/C1/N3 and N1/C3/C2, respectively, with a dihedral angle of 49.08° between them. The atoms N(2)–C(1)–N(4) and N(3) were nearly planar. The bond angles of N(1)–C(4)–C(5), C(3)–N(1)–C(2) and N(3)–C(1)–N(2) were 111.81(12)°, 108.67(12)° and 119.06(14)°, respectively. The N atom in the nitro group and C atom in the Schiff base were nearly coplanar, with a torsion of –3.4(2)° for C(1)–N(4)–N(5)–O(2).

The hydrogen bonds and crystal packing characteristics of Compound 1 in the unit cell are described in Figure 2. Analysis of the crystal packing indicates that molecules were linked by the intermolecular and intramolecular interactions. An intramolecular N–H···O hydrogen bonding interaction occurred, resulting in the formation of a six-membered nearly planar ring (N(3)/H(3)/O(2)/N(5)/N(4)/C(1)). In the crystal structure, molecules were stabilized by intermolecular N–H···N, N–H···O and N–H···Cl hydrogen bonding interactions, forming a S-shaped chain along the c axis. The distances between donor (D) and acceptor (A) were 2.957 Å for N(2)–H(2)···O(1)#1, 3.170 Å for N(2)–H(2)···O(1) and 2.613 Å for N(3)–H(3)···O(2), respectively. The N–Cl distances between donor (D) and acceptor (A) were 3.528 (6) Å for N(2)–H(2)···Cl(1), a weak hydrogen bond. Details of the hydrogen bonding in this crystal structure are listed in Table 3.

### Table 3. Hydrogen bonding interactions of Compound 1.

| D–H···A  | d(D–H)/Å | d(H···A)/Å | d(D···A)/Å | <(DHA)/Å |
|---------|----------|-----------|-----------|----------|
| N(2)–H(2)···O(1)#1 | 0.824 | 2.570 | 3.170 | 130.84 |
| N(2)–H(2)···N(4)#2 | 0.824 | 2.136 | 2.957 | 174.88 |
| N(3)–H(3)···O(2) | 0.808 | 2.015 | 2.613 | 130.42 |
| N(3)–H(3)···Cl(1)#3 | 0.808 | 2.950 | 3.528 | 130.42 |

Symmetry transformations used to generate equivalent atoms: #1: -x + 2, -y, -z + 2; #2: -x + 2, -y, -z + 2; #3: x, -y + 1/2, z + 1/2.

3.2. Spectroscopic Properties

The structure of Compound 1 was confirmed by 1H NMR, 13C NMR and HRMS analysis. In the 1H-NMR spectrum, one wide single peak with chemical shifts of δ 8.79 ppm exhibited the presence of N–H proton. The signals of the proton in the benzene ring were clearly discovered at δ 7.34–7.40 ppm. The protons of two methylene in the NHT ring and one methylene connected to the benzene ring were observed at 4.24 ppm and 3.78 ppm, respectively. The four methylene protons in 1,3,5-triazine ring had the same chemical shift. In the 13C NMR spectrum, the carbons of C2/C3 in NHT ring, C6/C10 and C7/C9 in benzene ring appeared as doublets at 59.58 ppm, 130.69 ppm and 128.44 ppm, respectively. The CH2 carbon C4 and the imino carbon C1 located the highest (53.25 ppm) and the lowest (155.80 ppm) field strength, respectively. The recorded HRMS spectral data of Compound 1 were in good accordance with the theoretical value.

| D–H···A  | d(D–H)/Å | d(H···A)/Å | d(D···A)/Å | <(DHA)/Å |
|---------|----------|-----------|-----------|----------|
| N(2)–H(2)···O(1)#1 | 0.824 | 2.570 | 3.170 | 130.84 |
| N(2)–H(2)···N(4)#2 | 0.824 | 2.136 | 2.957 | 174.88 |
| N(3)–H(3)···O(2) | 0.808 | 2.015 | 2.613 | 130.42 |
| N(3)–H(3)···Cl(1)#3 | 0.808 | 2.950 | 3.528 | 130.42 |

Symmetry transformations used to generate equivalent atoms: #1: -x + 2, -y, -z + 2; #2: -x + 2, -y, -z + 2; #3: x, -y + 1/2, z + 1/2.
3.3. Biological Activity

3.3.1. Aphicidal Activity

The aphicidal activity of Compound 1 and the positive control Pymetrozine against *M. persicae*, *S. mischanthi*, *R. padi*, *S. graminum* and *M. dirhodum* are shown in Table 4. The preliminary bioassay results (at a concentration of 200 mg/L, for 48 h) indicated that Compound 1 exhibited insecticidal activity against all of the tested aphid species. The aphicidal activities against *M. persicae*, *R. padi* and *M. dirhodum* were moderate, with inhibition rates of 58.5%, 63.5% and 51.0%, respectively. Its inhibition rates of *S. mischanthi* and *S. graminum* reached 74.1% and 77.5%. However, the aphicidal activities of Compound 1 were lower than that of commercial Pymetrozine. The structure of Compound 1 showed a partially similar features to neonicotinoids (Figure 3: 1, 2, 3 and 4 represent aromatic heterocycle, flexible linkage, electron-withdrawing group and hydro-heterocycles or guanidine/amidine, respectively). It contained parts 3 and 4, but did not contain parts 1 and 2. However, the structure of control Pymetrozine was screened from many compounds. It is highly effective against aphids via blockage of stylet resulting in irreversible stop of feed [51]. The structure property of Compound 1 might lead to lower aphicidal activity than commercial Pymetrozine. In the future, introduction of aromatic heterocycle on part 1 and flexible linkage on part 2 to the scaffold structure of Compound 1 are recommended. On the basis of the primary experimental results, aphid species exhibiting a mortality rate higher than 70% were chosen to determine the LC\textsubscript{50} values. As shown in Table 5, Compound 1 exhibited a high aphicidal activity against *S. miscanthi* and *S. graminum*, with LC\textsubscript{50} values of 47.8 mg/L and 33.6 mg/L, respectively. However, the aphicidal activities of Compound 1 were lower than Pymetrozine with LC\textsubscript{50} values of 13.8 mg/L and 8.1 mg/L, respectively.

**Table 4.** The in vivo aphicidal activity of Compound 1.

| Compound | Inhibition Rates of Compounds at Concentration 200 mg/L (%)** |
|----------|---------------------------------------------------------------|
|          | *M. Persicae*       | *S. Mischanthi*     | *R. Padi*       | *S. Graminum*     | *M. Dirhodum*     |
| 1        | 58.5 ± 2.8          | 74.1 ± 2.2          | 63.5 ± 2.9      | 77.5 ± 1.8        | 51.0 ± 2.2        |
| Pymetrozine* | 84.0 ± 3.6             | 92.3 ± 3.7          | 87.1 ± 3.5      | 89.5 ± 4.2        | 74.5 ± 4.0        |

* Pymetrozine was used as a positive control; ** Average of three replicates, mean ± sd.

**Figure 3.** Structure features of neonicotinoids.

**Table 5.** The LC\textsubscript{50} of Compound 1.

| Compound | *S. Miscanthi* | *S. Graminum* |
|----------|---------------|---------------|
|          | LC\textsubscript{50} (95% FL), mg/L | Toxic Regression Equation | R | LC\textsubscript{50} (95% FL), mg/L | Toxic Regression Equation | R |
| 1        | 47.8 (37.2–61.0) | y = 1.312x−2.268 | 0.969 | 33.6 (23.7–44.7) | y = 0.924x−1.411 | 0.903 |
| Pymetrozine* | 13.8 (8.3–19.2) | y = 1.083x−1.235 | 0.952 | 8.1 (2.5–14.3) | y = 0.738x−0.671 | 0.939 |

3.3.2. Antifungal Activity

The in vitro antifungal activity of Compound 1 against six plant fungal pathogens, *R. solani*, *P. aphanidermatum*, *V. mali*, *B. cirerea*, *F. moniliforme* and *A. solani* was estimated. The results are shown
in Table 6. The data suggested that all compounds had weak to moderate antifungal activity. The preliminary bioassay indicated that Compound 1 exhibits weak inhibition activity towards R. solani, V. mali and F. moniliforme. Its inhibition rates of P. aphanidermatum, B. circerea and A. solani reached 62.0%, 56.4% and 56.1% at 50 mg/L, respectively. Unfortunately, Compound 1 showed activities sometime comparable but usually lower activities for these plant fungal pathogens compared with the Difenoconazole control. However, these results indicated that Compound 1 could be further used as a lead compound to develop novel fungicides, particularly against P. aphanidermatum. Thus starting from lead Compound 1, further studies could be envisaged and searched by intermediate derivatization approach, an effective method for the discovery of new biologically active molecules [52], by introduction of active substructure or by synthesis of new analogues and reporting the structure activity relationships.

Table 6. The in vitro antifungal activity of Compound 1.

| Compound         | R. Solani (%) | P. Aphanidermatum (%) | V. Mali (%) | B. Circerea (%) | F. Moniliforme (%) | A. Solani (%) |
|------------------|---------------|-----------------------|------------|----------------|-------------------|--------------|
| 1                | 30.3 ± 0.8    | 62.0 ± 2.4            | 27.1 ± 2.1 | 56.4 ± 2.7     | 23.0 ± 1.2        | 56.1 ± 1.5   |
| Difenoconazole   | 80.2 ± 2.0    | 65.4 ± 0.9            | 100.0 ± 0.0| 83.8 ± 1.1     | 92.2 ± 1.7        | 83.1 ± 2.0   |

4. Conclusions

In summary, the compound, N-(5-(4-chlorobenzyl)-1,3,5-triazinan-2-ylidene)nitramide, has been prepared by Mannich reaction and characterized by $^1$H NMR, $^{13}$C NMR, HRMS and single-crystal x-ray structural determination. The biological activity results showed that the title compound, Compound 1, had favorable insecticidal activity against the aphids of S. miscanthi and S. graminum and exhibited moderate antifungal activities. The bioassay results demonstrate that this compound has a wide range of biological activities. This study offered valuable clues and will lay the foundation towards the design and synthesis of novel aphid control agents and fungicides.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/4/245/s1, Table S1: Bond Lengths for Compound 1, Table S2: Bond angles for Compound 1, Table S3: Torsion angles for Compound 1, Table S4: Fractional atomic coordinates (Å$\times$10$^4$) and equivalent isotropic displacement parameters (Å$^2$×10$^3$) for Compound 1, Table S5: Anisotropic displacement parameters (Å$^2$×10$^3$) for Compound 1, Table S6: Hydrogen atom coordinates (Å$\times$10$^4$) and isotropic displacement parameters (Å$^2$×10$^3$) for Compound 1.

Author Contributions: Y.-G.Q. synthesized the crystalline material, carried out experimental work, analyzed the crystal data, conducted bioassays and wrote the manuscript; Z.-K.Y. helped in the NMR spectra analysis and the bioassay experiments; J.F. and X.J. helped in the bioassay experiments; J.-L.C., J.F., and X.-L.Y. supervised the entire study and revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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