

Article

Positional Methyl Effects in Benzo[*e*][1,2,4]triazines—Synthesis and Crystal Structure Analysis of 5-Methyl-3-phenylbenzo[*e*][1,2,4]triazine and Its Precursor, *N'*-(3-Methyl-2-nitrophenyl)benzohydrazide

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Abstract

We report the synthesis, spectroscopic characterization, and single-crystal X-ray structures of 5-methyl-3-phenylbenzo[*e*][1,2,4]triazine (**I**) and its precursor *N'*-(3-methyl-2-nitrophenyl)benzohydrazide (**IV**). Compound **IV** was obtained by nucleophilic aromatic substitution of 1-fluoro-3-methyl-2-nitrobenzene with benzohydrazide and was converted to **I** through a reductive cyclodehydration/oxidative aromatization sequence. The present study provides a concise route to the 5-methyl regioisomer together with full structural characterization and examines how methyl substitution at the 5-position influences molecular geometry and crystal packing relative to the previously reported 6- and 8-methyl analogs. X-ray analysis shows that **IV** adopts a conjugated hydrazide framework with a twisted N–N linkage and an out-of-plane nitro group. In the crystal, it forms one-dimensional N–H···O hydrogen-bonded chains further assembled by weaker intermolecular contacts. By contrast, **I** displays an essentially planar benzo[*e*][1,2,4]triazine core with an almost coplanar phenyl substituent and packs into slipped π -stacked columns reinforced by secondary C–H···N contacts. Comparison with the previously reported methyl regioisomers shows that relocation of the methyl group to the 5-position has little effect on the intrinsic molecular geometry of the benzo[*e*][1,2,4]triazine scaffold, while subtly modulating the stacking arrangement and secondary packing interactions in the solid state. These results further define the role of methyl-substituent position in shaping the supramolecular organization of 3-phenylbenzo[*e*][1,2,4]triazines.

Keywords: benzohydrazides; benzo[*e*][1,2,4]triazines; Blatter radicals; π – π stacking



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1. Introduction

Benzo[*e*][1,2,4]triazines (**Btz**, Figure 1) are a distinct subclass of 1,2,4-triazines [1–3] that have attracted increasing attention in recent decades due to their biological, electronic, photonic, and energetic properties, leading to applications in pharmacology and materials science [4–8]. Substitution at the C3 position has a pronounced effect on biological activity. For example, 3-amino derivatives have been reported to exhibit antimalarial [9] and anti-tumor activity [10,11], whereas 3-phenyl substitution has been associated with antiviral activity [12].

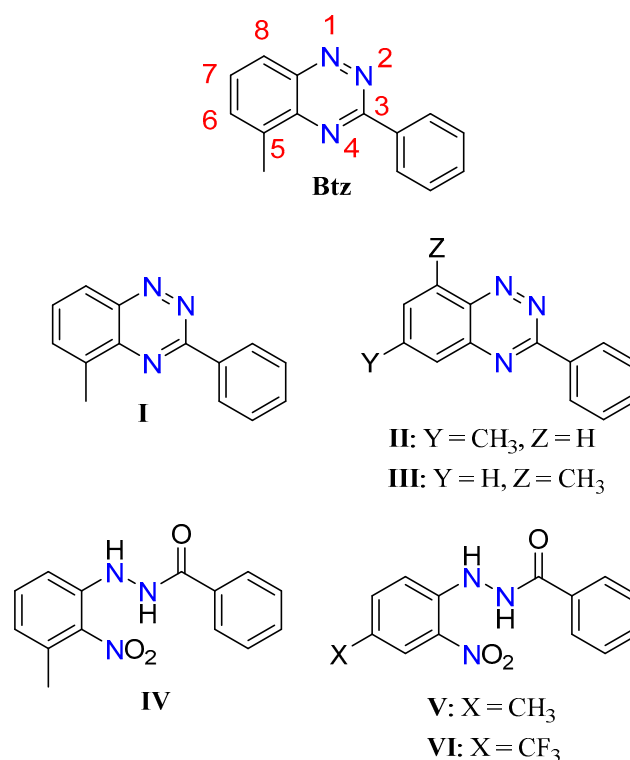


Figure 1. Molecular structures of (i) the parent benzo[*e*][1,2,4]triazine (**Btz**), with nomenclature ring-atom numbering in red; (ii) methyl-substituted benzo[*e*][1,2,4]triazines **I–III**; and (iii) methyl- and trifluoromethyl-substituted *N'*-phenylbenzohydrazides **IV–VI**.

Benzo[*e*][1,2,4]triazines bearing aromatic heterocyclic substituents at C6 have been reported as PAD enzyme inhibitors [13], while C6-methyl derivatives have shown promise for the treatment or amelioration of cancer [14]. In parallel, benzo[*e*][1,2,4]triazines have been used as key components in light-emitting materials [15,16] and as precursors to Blatter radicals [17], which are of interest for applications in molecular magnetism and spintronics [17–25]. Recent reviews have summarized the synthesis, reactivity, medicinal relevance, and broader chemistry of 1,2,4-triazines and benzotriazines, including benzo[*e*][1,2,4]triazine derivatives and their benzo-fused analogs [26–28].

The main compound examined in this study, 5-methyl-3-phenylbenzo[*e*][1,2,4]triazine (**I**, Figure 1), has shown promise for enhancing the performance of electroluminescent devices [29]. More broadly, benzo[*e*][1,2,4]triazines fused with heteroaromatic moieties have been reported as electron-acceptor units for n-type semiconductors [30,31]. Despite this wide range of applications, there are comparatively few systematic studies that correlate substituent effects with their electronic structure, molecular geometry, and solid-state organization [32–38]. In nitrogen-rich heteroaromatic systems, electronic communication between the aromatic framework and the ring nitrogens can strongly influence π -delocalization and, in radical derivatives, spin delocalization. In the solid state, these compounds commonly adopt supramolecular arrangements dominated by π – π stacking between heteroaromatic cores, underscoring the importance of packing on their functional properties. Accordingly, the benzo[*e*][1,2,4]triazine scaffold provides a useful platform for probing structure–property relationships through systematic functionalization of the aromatic rings.

Reported crystal structures of 6-methyl- and 8-methyl-3-phenylbenzo[*e*][1,2,4]triazines (**II–III**, Figure 1) show similar one-dimensional π -stacked columns, with parallel π – π interactions that are offset both longitudinally and laterally [37,38]. Additional short contacts, including weak hydrogen-bond-type interactions, further rigidify the solid-state

assemblies. Because relocating the methyl substituent from C6 to C8 has little effect on the overall supramolecular arrangement, we sought to examine the related 5-methyl derivative, in which the substituent lies in closer proximity to the π surfaces involved in stacking and could therefore exert a stronger influence on packing.

Herein, we report the synthesis and single-crystal X-ray structures of 5-methyl-3-phenylbenzo[*e*][1,2,4]triazine (**I**) and its precursor *N'*-(3-methyl-2-nitrophenyl)benzohydrazide (**IV**). Although 5-methyl-3-phenylbenzo[*e*][1,2,4]triazine (**I**) has been previously reported [29], the purpose of the present work is to establish a concise preparative route to this regioisomer, provide full spectroscopic and crystallographic characterization, and evaluate how methyl substitution at the 5-position influences molecular geometry and solid-state organization relative to the previously characterized 6- and 8-methyl analogs [38]. For clarity, two numbering schemes are used in this work. IUPAC ring-atom numbering (Figure 1) is used to denote substituent positions in the benzo[*e*][1,2,4]triazine framework, whereas crystallographic atom numbering is used in the discussion of molecular geometry, crystal packing, and intermolecular interactions.

2. Materials and Methods

All reagents, chemicals, and solvents were sourced from Sigma-Aldrich (St. Louis, MO, USA) and used directly without any further purification. NMR spectra for both ^1H and ^{13}C were recorded on a Bruker Avance 400 MHz spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany). Residual solvent signals were used as internal references, and all chemical shifts are expressed in parts per million (ppm). High-resolution mass spectrometry (HRMS) and associated fragmentation data were collected using a Waters Xevo G2-XS QToF mass spectrometer (Waters Corporation, Wilmslow, Cheshire, United Kingdom) operating in positive electrospray ionization (ESI^+) mode. The measurements were performed by direct flow injection at a flow rate of 0.2 mL/min, using a 95:5 (*v/v*) methanol–water solvent system as the mobile phase. Single-crystal X-ray diffraction data were obtained using a Rigaku MicroMax-007HF diffractometer (Rigaku Corporation, Tokyo, Japan). Melting points were determined with a Mel-Temp (Stanford Research Systems (SRS), Sunnyvale, CA, USA) melting point apparatus.

2.1. Synthesis of *N'*-(3-Methyl-2-nitrophenyl)benzhydrazide (**IV**)

A solution of 1-fluoro-3-methyl-2-nitrobenzene (2.33 g, 15.0 mmol) and benzohydrazide (2.11 g, 15.5 mmol) in dry DMSO (3 mL) was stirred at 80 °C for 2 days under anhydrous conditions. After cooling, ethyl acetate (100 mL) followed by H_2O (150 mL) were added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted twice with small portions of ethyl acetate. The combined organic layers were dried (Mg_2SO_4), the solvent was evaporated, and the solid residue was crystallized (DCM/Cyclohexane), giving 1.08 g (26% yield) of the hydrazide as yellow crystals: mp = 144.9–147.8 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 9.03 (1H, s), 8.06 (1H, s), 8.01 (1H, s), 7.89 (2H, d, J = 7.4 Hz), 7.61 (1H, m), 7.52 (2H, m), 7.32 (1H, d, J = 6.9 Hz), 7.10 (1H, d, J = 8.6 Hz), 2.33 (3H, s); ^{13}C NMR (CDCl_3 , 400 MHz) δ 167, 143, 137, 133, 132, 129, 127, 126, 115, 114, 20; HRMS (ES^+) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_3$: 272.1035, found 272.1039; EI-MS (70eV): m/z = 105, 77 (100%).

2.2. Synthesis of 5-Methyl-3-phenylbenzo[*e*][1,2,4]triazine (**I**)

N'-(3-methyl-2-nitrophenyl)benzhydrazide (1.08 g, 4.0 mmol) was dissolved in glacial acetic acid (42 mL), Sn powder (2.0 g, 16.9 mmol) was added, and the solution was stirred vigorously at room temperature for 1 hr. The reaction was then heated at 120 °C for 20 min. Upon cooling, methylene chloride (150 mL) followed by H_2O (200 mL) were added,

and the resulting biphasic mixture was passed through a layer of Celite. The organic layer was separated and the aqueous layer was extracted with methylene chloride. The combined organic extracts were washed with sat. NaHCO_3 and dried (MgSO_4). The solvent was removed, the solid residue was dissolved in a $\text{MeOH}/\text{CH}_2\text{Cl}_2$ mixture (1:1, 84 mL), and solid NaIO_4 (1.28 g, 6.0 mmol) was added. The mixture was stirred until the initial dihydro derivative was no longer observed by TLC (30 min). Inorganic salts were filtered, solvents were evaporated, and the resulting yellow solid residue was passed through a short SiO_2 column ($\text{AcOEt}/\text{hexane}$, 1:5) giving 0.13 g (14.8% yield) of 5-methyl-3-phenylbenzo[*e*][1,2,4]triazine as a yellow solid. Subsequent sublimation (120 °C) gave 14.1 mg (1.6% yield) of pure product: mp: 139.2–141.3 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.77 (dd, 2H, $J = 7.6, 2.2$ Hz), 8.43 (d, 1H, $J = 8.6$ Hz), 7.88 (1H, s), 7.69–7.67 (m, 1H), 7.64–7.59 (m, 3H), 2.68 (s, 3H); ^{13}C NMR (CDCl_3 , 400 MHz) δ 160, 147, 145, 141, 136, 133, 131, 130, 129, 128, 127, 22; HRMS (ES+) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{N}_3$: 222.1031, found 222.1023; EI-MS (70 eV): $m/z = 222, 192, 179, 165$ (100%), 152, 104, 89, 77.

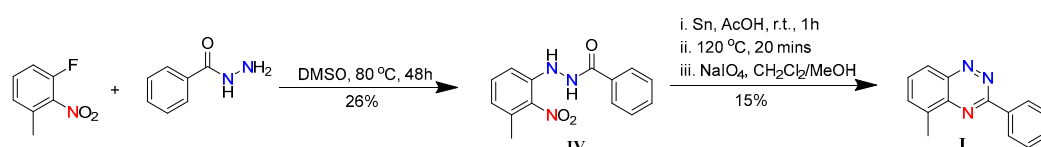
2.3. Crystal Structure Determination

Unit cell parameters were refined using *CrysAlis PRO* version 1.171.43.130a [39]. Indexing and image collection were performed based on strategy calculations from *DTREK 9.9.9.4 W9RSSI* [40]. Absorption correction was carried out using spherical harmonics via the *SCALE3 ABSPACK* algorithm from *CrysAlis PRO*. The structure was solved with the *ShelXT 2018/2* [41] solution program using dual methods and *Olex2 1.5-alpha* [42] as the graphical interface. Final structure refinement was achieved using full matrix least-squares minimization within *SHELXL 2019/3* [43]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were positioned geometrically and refined under the riding model.

CCDC 2533925 and 2533926 contain the Supplementary Crystallographic Data for *N'*-(3-methyl-2-nitrophenyl)benzohydrazide (**IV**) and 5-methyl-3-phenylbenzo[*e*][1,2,4]triazine (**I**), respectively. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/structures> (accessed on 1 March 2026) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

The synthesis of 5-methyl-3-phenylbenzo[*e*][1,2,4]triazine (**I**) was accomplished in two steps from commercially available 1-fluoro-3-methyl-2-nitrobenzene (Scheme 1). In the first step, the corresponding *N'*-(3-methyl-2-nitrophenyl)benzohydrazide (**IV**) was obtained via a nucleophilic aromatic substitution of the activated aryl fluoride by benzohydrazide in dry DMSO under anhydrous conditions at 80 °C (2 days), followed by standard aqueous workup and recrystallization to afford **IV** as yellow crystals. This hydrazide formation is consistent with our prior protocols for preparing *N'*-(2-nitrophenyl)benzohydrazides from fluoro-nitroarenes and benzohydrazide under similar conditions [34].



Scheme 1. Synthesis of 5-methyl-3-phenylbenzo[*e*][1,2,4]triazine (**I**) via hydrazide formation, reductive cyclodehydration, and oxidative aromatization.

In the second step, hydrazide **IV** was converted to benzotriazine **I** using a one-pot reductive cyclodehydration/oxidative aromatization sequence that parallels our reported route to the 6- and 8-methyl-3-phenylbenzo[*e*][1,2,4]triazines [35]. Treatment of **IV** with tin

in glacial acetic acid at room temperature followed by brief heating promotes reduction in the nitro group and intramolecular ring closure to a dihydrobenzotriazine intermediate, which was observed by TLC. Subsequent oxidation with NaIO₄ in a MeOH/CH₂Cl₂ mixture afforded the fully aromatized benzo[e][1,2,4]triazine **I**. The overall synthetic route provides direct access to **I** from readily available starting materials and matches the general strategy previously used for closely related methyl regioisomers in this series [35].

Crystal Data for C₁₄H₁₃N₃O₃ (CCDC 2533925): $M_r = 271.27$, monoclinic, $P2_1/c$ (No. 14), $a = 17.1527(4)$ Å, $b = 4.96670(10)$ Å, $c = 16.4805(4)$ Å, $\beta = 116.330(3)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 1258.35(6)$ Å³, $T = 100.00(10)$ K, $Z = 4$, $Z' = 1$, $\mu(\text{Cu K}\alpha) = 0.858$, 10,970 reflections measured, 2559 unique ($R_{\text{int}} = 0.0155$) which were used in all calculations. The final wR_2 was 0.0849 (all data) and R_1 was 0.0311 ($I \geq 2\sigma(I)$).

Crystal Data for C₁₄H₁₁N₃ (CCDC 2533926): $M_r = 221.26$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 4.6031(2)$ Å, $b = 14.1189(7)$ Å, $c = 16.8936(7)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 1097.93(9)$ Å³, $T = 100.01(10)$ K, $Z = 4$, $Z' = 1$, $\mu(\text{Cu K}\alpha) = 0.650$, 8338 reflections measured, 2195 unique ($R_{\text{int}} = 0.0505$) which were used in all calculations. The final wR_2 was 0.1758 (all data) and R_1 was 0.0647 ($I \geq 2\sigma(I)$).

3.1. Geometry Characteristics of the Molecular Structure

Compound **IV** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 2). The hydrazide fragment adopts the expected amide-like geometry, with a short carbonyl distance ($d(\text{O1}-\text{C7}) = 1.2315(13)$ Å) and a shortened C(O)-N bond ($d(\text{C7}-\text{N1}) = 1.3561(14)$ Å), consistent with significant conjugation across the O=C-N linkage. This is closely aligned with our previously reported *N'*-(2-nitrophenyl)benzohydrazides, where planarity at the acyl nitrogen was taken as evidence of N-C(O) delocalization [37]. The local geometry around N1 in **IV** indicates a near-trigonal arrangement evident by the angles at N1 ($116(1)^\circ$, $122(1)^\circ$, $118.03(9)^\circ$; $\Sigma \text{angles} \approx 356.03^\circ$) and a small out-of-plane displacement of 0.147 Å from the N2-C7-H1 plane.

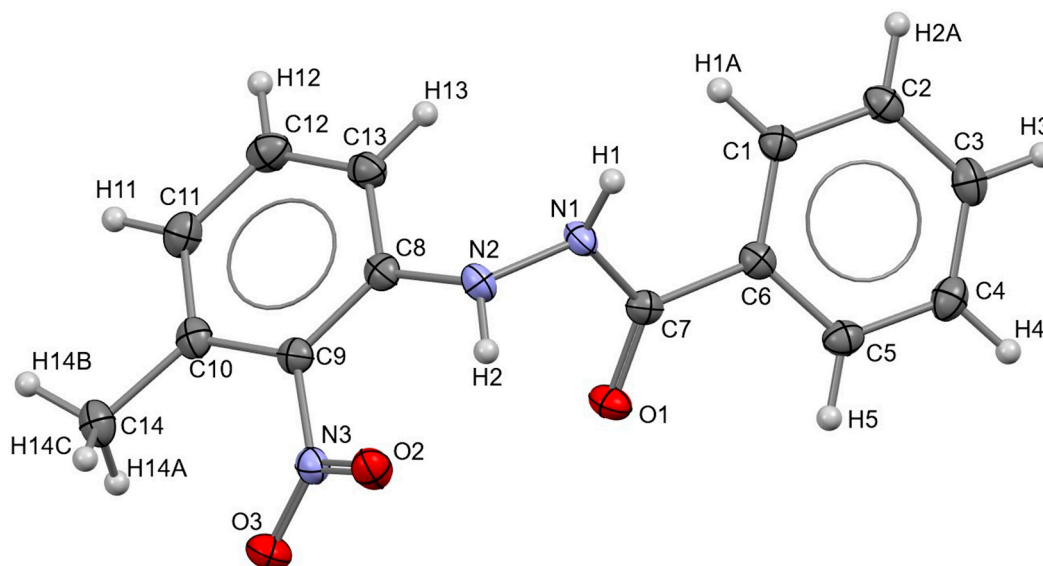


Figure 2. Molecular structure of *N'*-(3-methyl-2-nitrophenyl)benzhydrazide (**IV**) (ORTEP, 50% probability ellipsoids) with atom labeling.

In contrast, the terminal nitrogen N2 is noticeably pyramidalized (0.276 Å from the C8-H2-N1 plane), and the hydrazide bond is strongly twisted ($\angle(\text{C7}-\text{N1}-\text{N2}-\text{C8}) = -86.74(12)^\circ$). Together with the relatively long N2-C8 bond ($1.3910(14)$ Å), these features indicate that conjugation is localized primarily on the amide side (O=C-N1) rather than

extended through N2 into the nitroaryl ring. This structural feature is qualitatively closer to that observed for *N'*-(4-methyl-2-nitrophenyl)benzohydrazide (**V**) [37], and contrasts with *N'*-(2-nitro-(4-trifluoromethyl)phenyl)benzohydrazide (**VI**) [37], in which planarization at *N'* and an unusually short C8–N2 distance are consistent with greater π -delocalization along the *N'*-aryl bond into the nitro-substituted ring, leading to an almost parallel arrangement of the two aromatic rings [44–57]. Notably, the pyramidalization at N2 in **IV** (0.276 Å) is smaller than in the methyl analog **V** (0.326 Å), indicating a modest increase in delocalization while still well short of full planarity.

Two additional intramolecular distortions are evident and consistent with the steric congestion created by adjacent methyl and nitro substituents on the same aromatic ring. First, the nitro group is rotated out of the aromatic plane ($\angle(\text{O2–N3–C9–C8}) = 29.80(14)^\circ$), most plausibly due to steric congestion with the adjacent methyl substituent, which offsets the electronic tendency toward coplanarity and π -conjugation. Second, the amide carbonyl is also twisted relative to the benzoyl ring ($\angle(\text{C5–C6–C7–O1}) = -25.69(15)^\circ$), indicating that conjugation on the benzoyl side is likewise moderated by torsional distortion arising from steric and/or packing effects.

Compound **I** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit (Figure 3). Although **I** is an achiral molecule, crystallization in the Sohncke space group $P2_12_12_1$ is not unusual. In this case, the refined Flack parameter should be interpreted with caution because the structure contains only weak anomalous scatterers and the benzo[*e*][1,2,4]triazine framework is essentially planar. The angle between the benzo-fused ring plane (C2–C7) and the amidrazonyl moiety (N1–N2–C8–N3) is only 1.74° . Bond lengths and angles within the N-rich core are consistent with aromatic delocalization, with $d(\text{N1–N2}) = 1.312(4)$ Å, $d(\text{N3–C8}) = 1.311(4)$ Å, and C–N distances clustered around 1.36 Å ($d(\text{N1–C6}) = 1.363(4)$ Å; $d(\text{N3–C7}) = 1.364(4)$ Å). These values are consistent with those reported for the 6-methyl and 8-methyl-benzo[*e*][1,2,4]triazines (**II** and **III**) analogs [38], where triazine-ring distances (1.311–1.374 Å) were interpreted as intermediate between single and double bonds owing to π -conjugation.

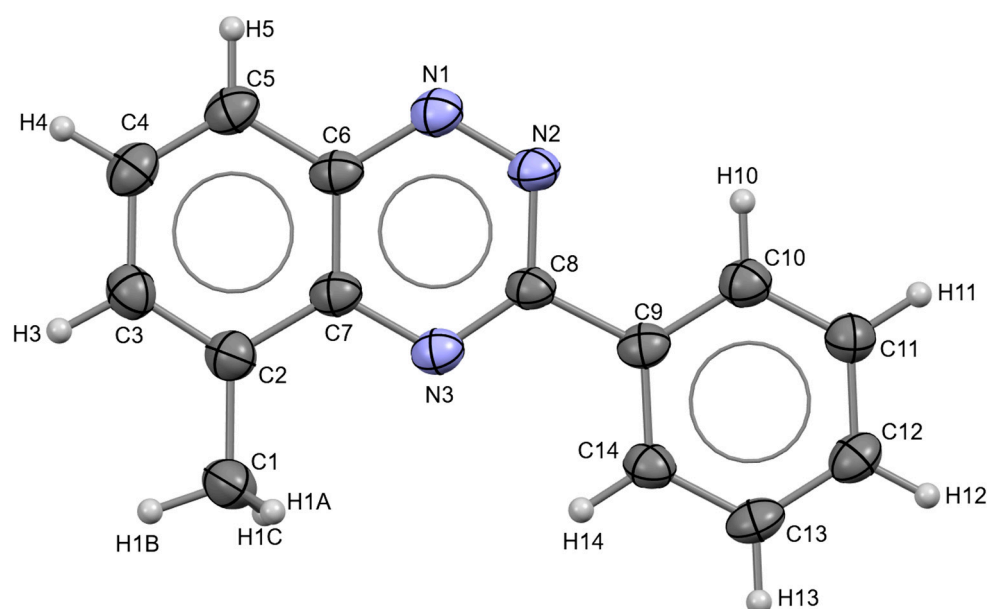


Figure 3. Molecular structure of 5-methyl-3-phenylbenzo[*e*][1,2,4]triazine (**I**) (ORTEP, 50% probability ellipsoids) with atom labeling.

A noticeable conformational feature in benzotriazine **I** is the orientation of the pendant 3-phenyl ring. In **I**, the phenyl ring is essentially coplanar with the benzotriazine π -

surface ($\angle(\text{N3-C8-C9-C14}) = -2.5(5)^\circ$), indicating an extended conjugated system across the C8–C9 bond. This degree of coplanarity is comparable to, and in fact greater than, that reported for the 6- and 8-methyl regioisomers (**II** and **III**), where the dihedral angle between the benzotriazine core and the pendant phenyl ring is $9.68(4)^\circ$ for the 6-methyl-benzo[*e*][1,2,4]triazine (**II**) and $4.37(5)^\circ$ for the 8-methyl-benzo[*e*][1,2,4]triazine (**III**) [38]. Thus, in the 5-methyl regioisomer **I**, the methyl substituent does not induce steric twisting of the aryl substituent. Rather, the molecular conformation is governed primarily by the inherent planarity and π -delocalization of the benzo[*e*][1,2,4]triazine framework.

3.2. Supramolecular Arrangement

Crystal packing in **IV** is compact, with intermolecular contacts extending in all three crystallographic directions. Because hydrogen atoms were treated using a conventional IAM/riding model, X–H distances and H-involving short contacts should be regarded as standard crystallographic descriptors and interpreted with appropriate caution. The most prominent directional interaction occurs along the *b* axis (Figure 4), where neighboring molecules are linked into a one-dimensional chain (1D) through an N1–H1 $\cdots$ O1 hydrogen bond ($d(\text{H1} \cdots \text{O1}) = 1.97(1) \text{ \AA}$, $\angle(\text{N-H} \cdots \text{O}) = 165(1)^\circ$, $d(\text{N1} \cdots \text{O1}) = 2.843(1) \text{ \AA}$), as shown in Figure 4. Within the same chain, close aromatic contacts are also present ($d(\text{C2} \cdots \text{C5}) = 3.387(2) \text{ \AA}$), consistent with efficient packing of the phenyl fragments.

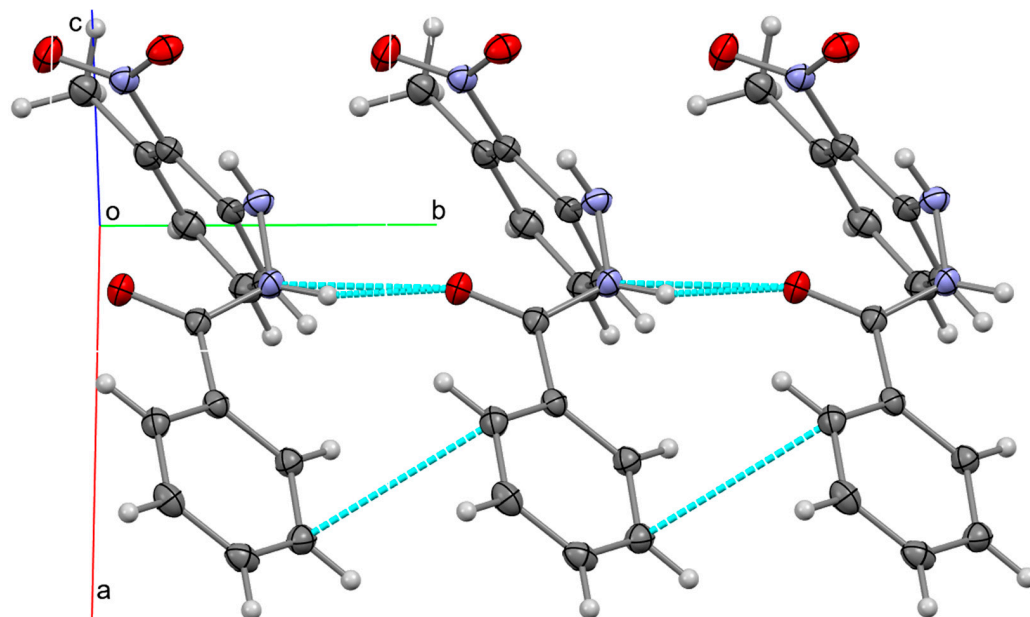


Figure 4. Packing along the *b* axis showing the N1–H1 $\cdots$ O1 hydrogen-bonded chain and the closest aromatic contacts.

Additional organization is evident along the *c* axis, where molecules adopt an antiparallel arrangement to form a ribbon motif (Figure 5). The ribbon is supported primarily by short contacts that are best described as proximity interactions between aromatic fragments (for example, $d(\text{H13} \cdots \text{C3}) = 2.821 \text{ \AA}$ and $d(\text{H2A} \cdots \text{C7}) = 2.855 \text{ \AA}$), together with an $\text{O3} \cdots \text{C3}$ contact of $3.154(1) \text{ \AA}$. A weak hydrogen-bond-like contact involving the terminal hydrazide N–H is also present ($\text{N2-H2} \cdots \text{C4}$, $d(\text{H2} \cdots \text{C4}) = 2.72(2) \text{ \AA}$, $\angle(\text{N2-H2} \cdots \text{C4}) = 119(1)^\circ$, $d(\text{N2} \cdots \text{C4}) = 3.232(1) \text{ \AA}$). Along the *a* axis, the structure again adopts an antiparallel ribbon arrangement (Figure 6), which includes a weak C–H $\cdots$ O contact ($d(\text{H14C} \cdots \text{O3}) = 2.6477 \text{ \AA}$, $\angle(\text{C14C-H14C} \cdots \text{O3}) = 114.18^\circ$, $d(\text{C14C} \cdots \text{O3}) = 3.178(2) \text{ \AA}$).

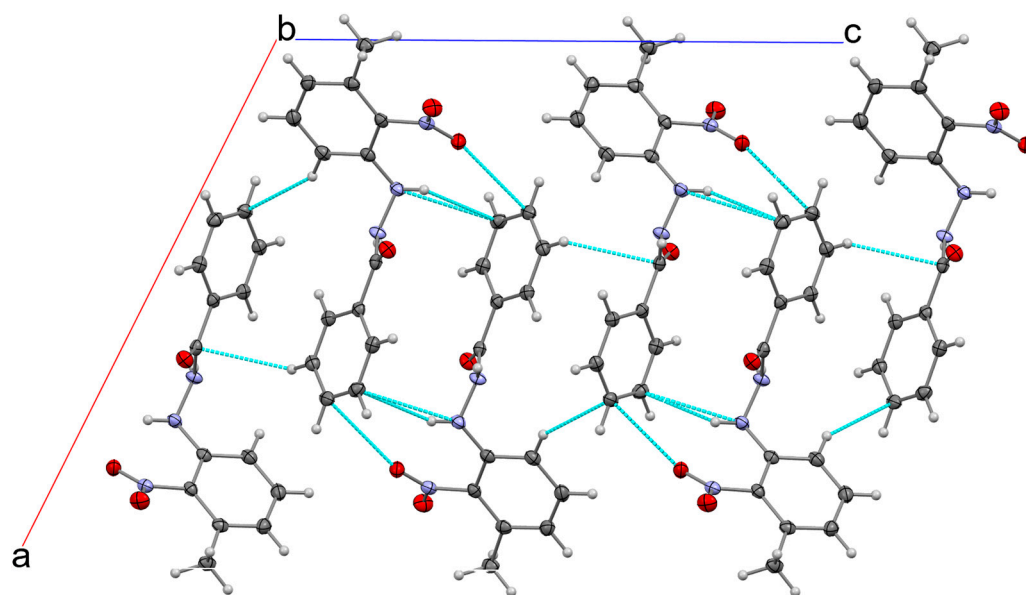


Figure 5. Packing along the *c* axis showing the antiparallel ribbon arrangement and the key short contacts.

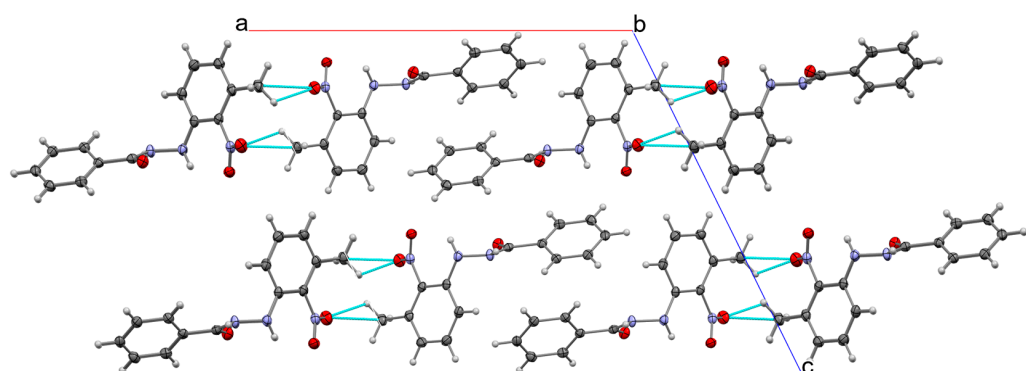


Figure 6. Packing along the *a* axis highlighting the weak C–H $\cdots$ O contact.

Overall, the packing motif of **IV** differs from that reported for *N'*-(4-methyl-2-nitrophenyl)benzohydrazide (**V**) and *N'*-(2-nitro-(4-trifluoromethyl)phenyl)benzohydrazide (**VI**) [37], where π – π stacking between aromatic rings drives the formation of centrosymmetric one-dimensional columns of dimers, reinforced by symmetric N–H $\cdots$ O hydrogen bonds. In benzohydrazide **IV**, the dominant motif is instead a hydrogen-bonded chain along *b* with additional ribbon-like antiparallel organization along *a* and *c*, stabilized by a network of weaker proximity contacts. The distinct packing motif observed for **IV** is consistent with the more torsionally flexible hydrazide geometry observed for **IV**, including a twisted nitro group and non-coplanarity of the carbonyl with the benzoyl ring, which can disfavor the highly regular π -stacked dimer columns seen in the previously reported benzohydrazides [34].

Crystal packing in **I** is likewise dense, with extensive intermolecular contacts across all axes. The dominant supramolecular feature is a one-dimensional (1D) column of slipped π -stacked benzotriazines running along the *a* axis (Figure 7). The interplanar spacing between benzotriazine cores is regular at 3.299 Å (defined using the ten atoms of the benzotriazine core), with longitudinal and latitudinal slippage angles of 41.98° and 20.36°, respectively. Within this stack, short intrachain C $\cdots$ C contacts are consistent with significant aromatic overlap ($d(\text{C6} \cdots \text{C8}) = 3.394(5)$ Å and $d(\text{C4} \cdots \text{C7}) = 3.339(5)$ Å).

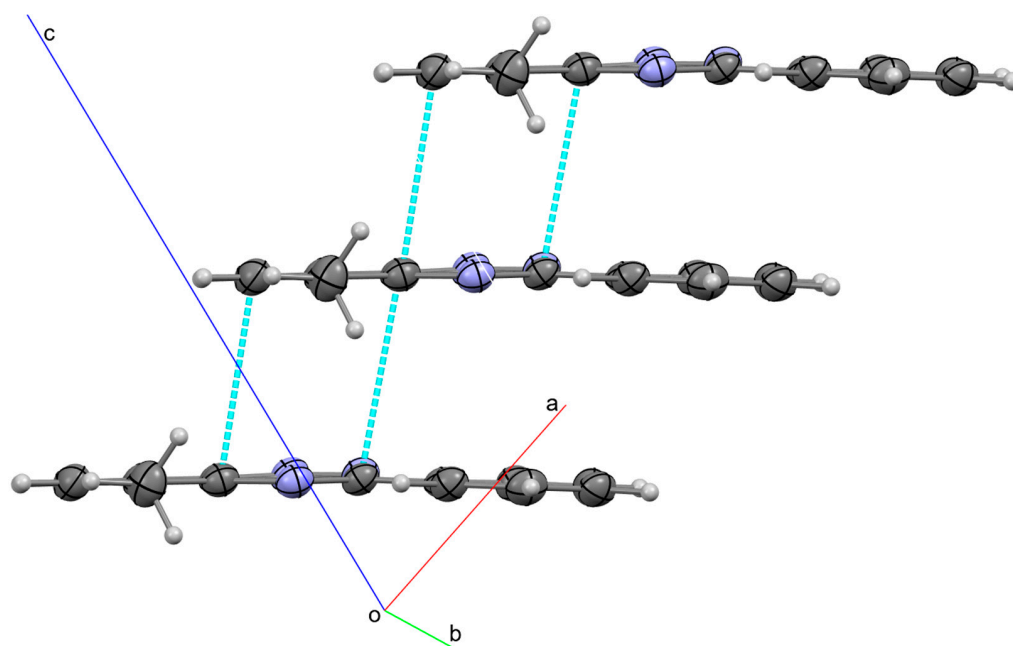


Figure 7. Packing along the *a* axis showing the slipped π -stacked column and the closest intrastack contacts.

Packing connectivity beyond the *a* axis column is evident in the *bc* plane (Figure 8). The structure can be viewed as chains running along *b*, with adjacent chains arranged antiparallel along *c* to maintain a tight packing and to position methyl groups in regions that reduce steric congestion between neighboring benzotriazines. Interchain association is supported by weak C–H $\cdots$ N contacts, including a bifurcated interaction from C3–H3 to N1 and N2 ($d(\text{H3} \cdots \text{N1}) = 2.504 \text{ \AA}$, $\angle(\text{C13}–\text{H3} \cdots \text{N1}) = 157.9^\circ$, $d(\text{C3} \cdots \text{N1}) = 3.402(4) \text{ \AA}$; $d(\text{H3} \cdots \text{N2}) = 2.622 \text{ \AA}$, $\angle(\text{C3}–\text{H3} \cdots \text{N2}) = 150.6^\circ$, $d(\text{C3} \cdots \text{N2}) = 3.480(4) \text{ \AA}$). Additional short contacts such as $d(\text{C13} \cdots \text{H5}) = 2.803 \text{ \AA}$ also contribute to close packing between neighboring fused aromatic fragments.

To place **I** in the broader structural context of 3-phenylbenzo[*e*][1,2,4]triazines, it is useful to compare it with the previously reported 6-methyl and 8-methyl regioisomers **II** and **III** [38] as well as the parent [34] and dimethyl-substituted analogs [58]. Across this family, the benzo[*e*][1,2,4]triazine core remains essentially planar and the key N–N and C–N bond distances remain within the narrow range expected for a delocalized heteroaromatic system. Likewise, the 3-phenyl substituent remains only slightly twisted from the fused azaaromatic core. In the 6-methyl **II** and 8-methyl isomers **III**, the corresponding dihedral angles are $9.68(4)$ and $4.37(5)^\circ$, respectively, while in **I** the phenyl ring is nearly coplanar with the benzo[*e*][1,2,4]triazine π -surface. The dominant supramolecular motif across the series is π – π stacking, although the detailed stacking registry differs. The 6-methyl isomer **II** forms alternating dimers with interplanar separations of 3.257 and $3.304 \text{ \AA}$, the 8-methyl isomer **III** forms regular translational stacks with a $3.366 \text{ \AA}$ spacing, and the parent 3-phenylbenzo[*e*][1,2,4]triazine [34] also adopts π -stacked columns, whereas the 5,7-dimethyl derivative shows a more dimeric stacking mode [58]. Taken together, these comparisons indicate that methyl substitution has only a minor effect on the intrinsic molecular geometry of the benzo[*e*][1,2,4]triazine core, but measurably influences the stacking registry and secondary intermolecular contacts in the crystal.

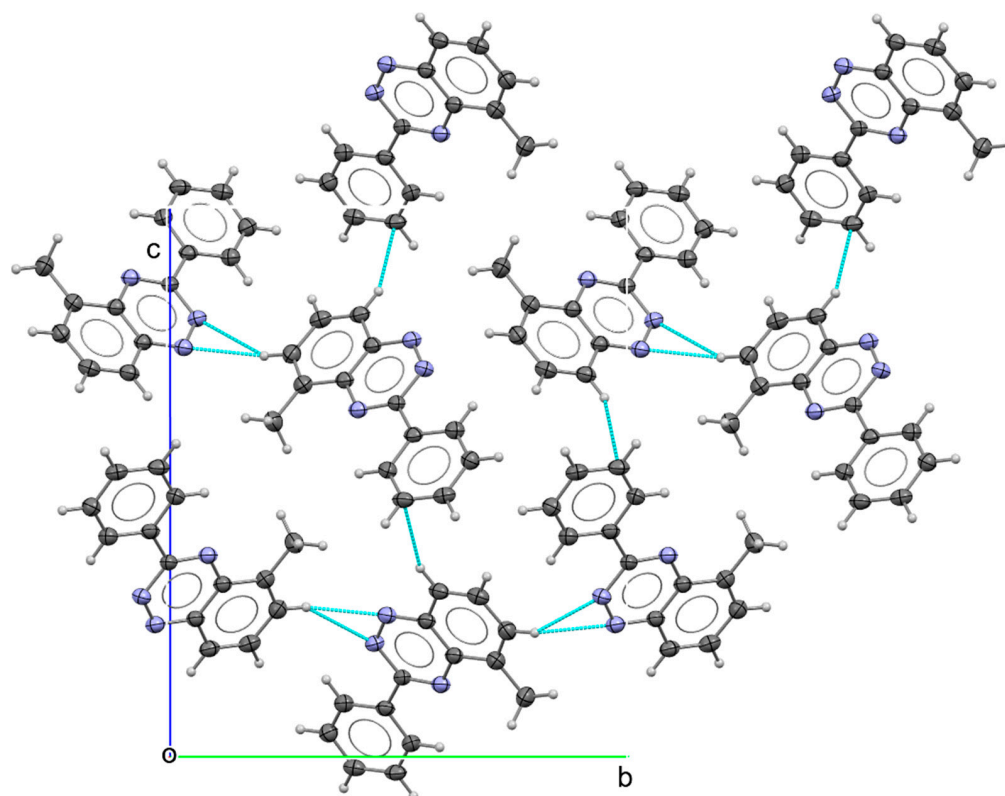


Figure 8. Packing in the *bc* plane showing interchain contacts, including the bifurcated C–H···N interactions.

4. Conclusions

In summary, compound **IV** forms a robust one-dimensional hydrogen-bonded chain through N1–H1···O1 interactions, with the three-dimensional packing further stabilized by ribbon-like motifs supported by weaker C–H···O and C–H···C contacts. In contrast to the previously reported benzohydrazides, **IV** does not assemble into highly regular π -stacked dimer columns, a difference that is consistent with its more torsionally flexible hydrazide conformation, including nitro-group twisting and non-coplanarity of the carbonyl group with the benzoyl ring. Compound **I** displays an essentially planar benzo[*e*][1,2,4]triazine framework with an almost coplanar pendant phenyl ring, maintaining an extended conjugated system comparable to the 6- and 8-methyl analogs. Its supramolecular organization is dominated by slipped π -stacked columns of benzotriazines, reinforced by secondary C–H···N contacts, and the interplanar separation within the stack is slightly shorter than that reported for the corresponding methyl regioisomers, indicating efficient aromatic overlap in the solid state.

Within our broader effort to examine how methyl-substituent position affects the molecular and supramolecular behavior of benzo[*e*][1,2,4]triazines, the present study demonstrates that relocation of the methyl group to the 5-position in regioisomer **I** preserves the essential planarity of the benzo[*e*][1,2,4]triazine framework while subtly influencing the crystal packing arrangement. Comparison with the previously reported 6-methyl and 8-methyl regioisomers (**II** and **III**) shows that the overall preference for π – π -stacked columnar organization is maintained across the series, whereas the detailed intermolecular contacts, molecular offsets, and steric accommodation within the lattice vary with substituent position. Collectively, these findings reinforce the importance of methyl-group migration as a means of modulating supramolecular architecture in substituted benzo[*e*][1,2,4]triazines.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/cryst16030206/s1>. Figure S1. ^1H NMR spectrum of N' -(3-methyl-2-nitrophenyl)benzhydrazide (IV); Figure S2. ^{13}C NMR spectrum of N' -(3-methyl-2-nitrophenyl)benzhydrazide (IV); Figure S3. ^1H NMR spectrum of 5-methyl-3-phenylbenzo[e][1,2,4]triazine (I); Figure S4. ^{13}C NMR spectrum of 5-methyl-3-phenylbenzo[e][1,2,4]triazine (I); Figure S5. HRMS and pattern fragmentation of N' -(3-methyl-2-nitrophenyl)benzhydrazide (IV); Figure S6. HRMS and pattern fragmentation of 5-methyl-3-phenylbenzo[e][1,2,4]triazine (I); Crystal Data of N' -(3-methyl-2-nitrophenyl)benzhydrazide (IV); Crystal Data of 5-methyl-3-phenylbenzo[e][1,2,4]triazine (I).

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