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# CRYSTAL STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF 4-AZIDO-2-(4-METHOXYPHENYL)-5-(2-NITROPHENYL)-2H-1,2,3-TRIAZOLE SYNTHESIZED ON THE BASIS OF DIBROMODIAZADIENE

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**Abstract.** The newly synthesized title compound was subjected to characterization *via* NMR and single crystal X-ray diffraction techniques. A Hirshfeld surface analysis was performed to analyze intermolecular interactions. Stabilization of molecular packing is achieved by a strong C---H…O hydrogen bond, C---H…π and π-π interactions.

***Keywords:*** *Triazole, hirsfield surface analyse, noncovalent interactions.*

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## 1. Introduction

Our research team develops effective synthesis of new type of 1,2-diaza-1,3-diene derivatives with two chloride atoms in the heminal position of the C=C double bond (Nenajdenko *et al*., 2017; 2023; Shikhaliyev *et al*., 2018, 2019, 2021; Maharramov *et al*., 2018; Askerova *et al*., 2024). Due to the electron accepting aza-group, these azadienes have demonstrated to be highly reactive electrophiles. It is from this point of view that dichlorodiazadienes with their unique structures have found wide application in the synthesis of several important compounds in the recent years (Muzalevskiy *et al*., 2023; Tsyrenova *et al*., 2020a, 2021, 2020b; Shastin *et al*., 2018). Their use as heterodienes in some reactions is especially noteworthy. The synthesis of various nitrogen heterocycles on the basis of dichlorodiazadienes especially bears mentioning (Sergeev *et al*., 2020). Synthesis of 6-aminopiridazine derivatives via the reaction of dichlorodiazadienes with malonitrile by Nenajdenko and his colleagues can be pointed out (Sergeev *et al*., 2020). Authors used various 1,2-diaza-1,3-dienes, different from the electronic and steric point of view. As a result of this research, the impact of the nature

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of the functional groups of the dichlorodiazadienes on the course of the reaction has been determined. At the same time it is important to note the synthesis of α-keto ester arylhydrazones via the solvolysis of dihalogendiazadienes and synthesis of azide triazoles via the reaction of dihalogendiazadienes with $NaN_3$. The present article is devoted to the synthesis of biologically active azide triazole via the reaction of dibromodiazadienes with $NaN_3$ and study of its structural characteristics.

## 2. Materials and Methods

The syntheses of compounds were carried out at the Organic Chemistry Department of Baku State University (Baku, Azerbaijan). Unless stated otherwise, all the reagents used in this study were obtained from the commercial sources (Aldrich, TCI-Europe, Strem, ABCR). NMR spectra were recorded on a Bruker Avance 300 (1H: 300 MHz, Karlsruhe, Germany); chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references ($CDCl_3$ δH = 7.26 ppm, δC = 77.16pp). The X-ray analyses of compound was carried out using the Bruker APEX II CCD (T 296 K, λMoK α - radiation, graphite monochromator, φ - and ω - scan) diffractometer.

### *2.1. Synthesis of 4-azido-2-(4-methoxyphenyl)-5-(2-nitrophenyl)-2H-1,2,3-triazole*

Dye was synthesized according to a literature protocol (Maharramov *et al*., 2018). A 20 ml screw-neck vial was charged with DMSO (20 ml), (E)-1-(2,2-dibromo-1-(2-nitrophenyl)vinyl)-2-(4-methoxyphenyl)diazene (440 mg, 1 mmol) and sodium azide ($NaN_3$; 390 mq; 3 mmol). After 1–3 h (until TLC analysis showed complete consumption of the corresponding triazole), the reaction mixture was poured into a 0.01 M solution of HCl (100 ml, pH = 2–3) and extracted with dichloromethane (3 * 20 ml). The combined organic phase was washed with water (3 * 50 ml), brine (30 ml), dried over anhydrous $Na_2SO_4$ and concentrated in vacuo using a rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (v/v: 3/1–1/1). Yield 65%, yellow, $T_{melt=}$ 75, $^1$H NMR (300 MHz, Chloroform-d) δ 7.92 (t, *J* = 7.3 Hz, 3H), 7.75 – 7.62 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 159.1, 148.4, 143.6, 132.9, 132.6, 131.6, 129.7, 124.8, 124.5, 119.7, 115.0, 114.3, 55.5. Compound was dissolved in dichloromethane and then left at room temperature for slow evaporation; red crystal of compound suitable for X-rays started to form after ca 2 d.

### *2.1.Single crystal X-ray diffraction*

X-ray diffraction data were collected at 100 K for the title compound on a Rigaku XtaLAB Synergy-S, HyPix-6000HE area-detector diffractometer using a single wavelength X-ray source ($CuK_\alpha$ radiation: λ = 1.54184 Å) from a micro-focus sealed X-ray tube and an Oxford liquid-nitrogen Cryostream cooler. The selected suitable single crystal was mounted on a goniometer head. Pre-experiment, data collection, data reduction and analytical absorption correction were performed with the program suite CrysAlisPro 1.171.43.92a (Rigaku, 2023; Table 1). Using WinGX (Farrugia, 2012), the structures were solved with the SHELXT small molecule structure solution program (Sheldrick, 2015a) and refined with the SHELXL 2018/3 package (Sheldrick, 2015b) by

full-matrix least-squares minimization on $F^2$. All H atoms were placed in calculated positions (C–H = 0.95 and 0.98 Å) and were constrained to ride on their parent atoms, with $U_{iso}$(H) = 1.2 or 1.5$U_{eq}$(C). The PLATON program was used to check the results of the X-ray analysis, crystal packing and molecular drawings molecular drawings (Spek, 2020). The three nitrogen atoms of the azido group attached to the 1,2,3-triazole ring of the title molecule are disordered at two positions with a ratio of 0.859(5):0.141(5). Constraints were made for atoms in the disordered part of the molecule using the SADI, DFIX and EADP commands.

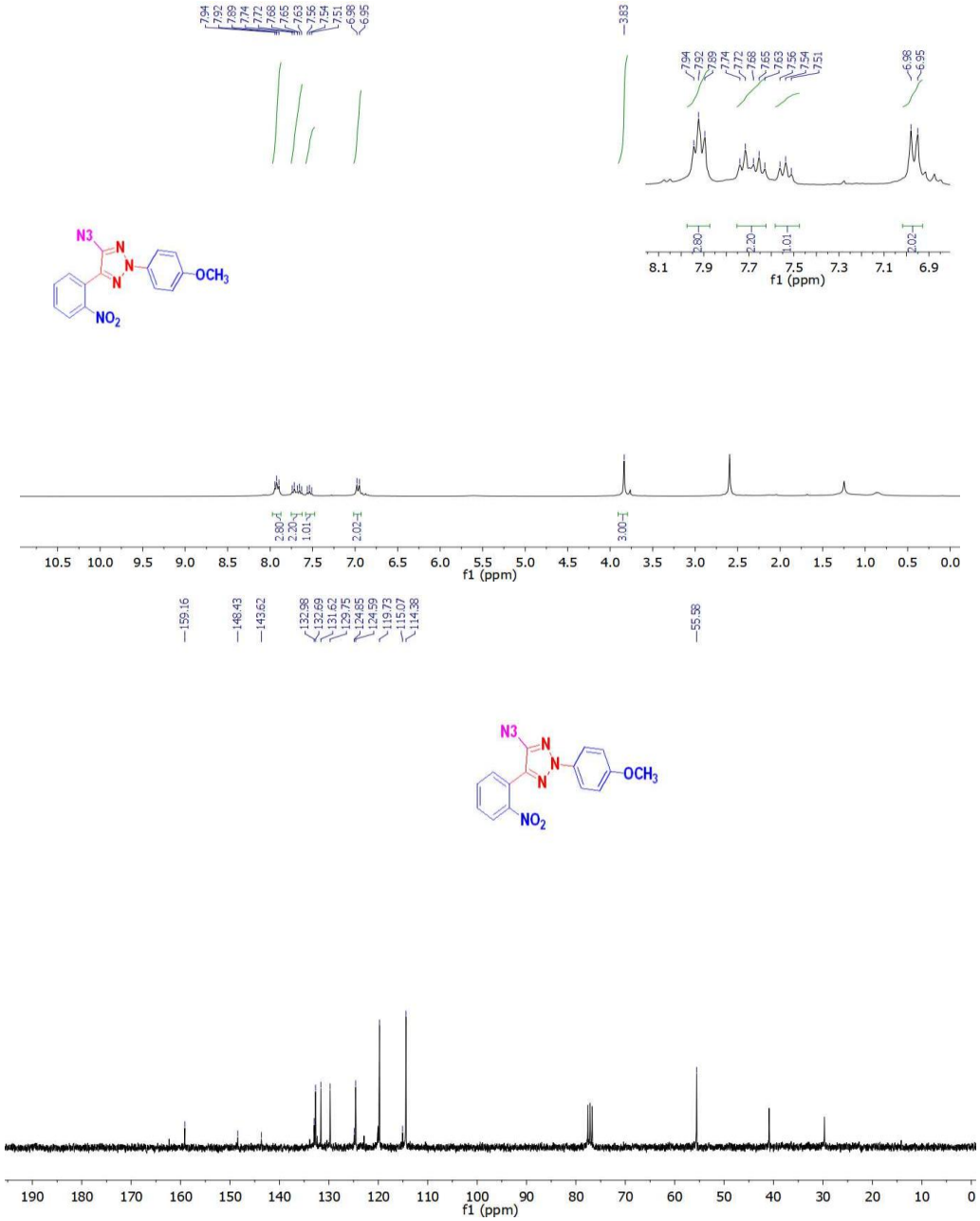


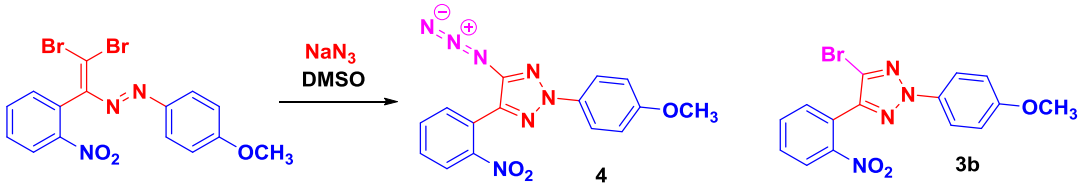

**Figure 1.** 1H and 13C spectra for (E)-1-(2,2-dibromo-1-(2-nitrophenyl)vinyl)-2-(4-methoxyphenyl)diazene

**Table 1.** Experimental details

| | |
|---|---|
| CCDC number | 2351101 |
| Chemical formula | $C_{15}H_{11}N_7O_3$ |
| $M_r$ | 337.31 |
| Crystal system, space group | Triclinic, *P*-1 |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 7.5592 (1), 10.2870 (2), 10.5481 (2) |
| α, β, γ (°) | 74.088 (2), 74.385 (2), 75.403 (2) |
| *V* (Å$^3$) | 745.50 (3) |
| *Z* | 2 |
| Radiation type | Cu *K*α |
| μ (mm$^{-1}$) | 0.93 |
| Crystal size (mm) | 0.25 × 0.21 × 0.15 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 16382, 3219, 3133 |
| $R_{int}$ | 0.027 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.638 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.040, 0.104, 1.06 |
| No. of reflections | 3219 |
| No. of parameters | 237 |
| No. of restraints | 4 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.23, −0.32 |

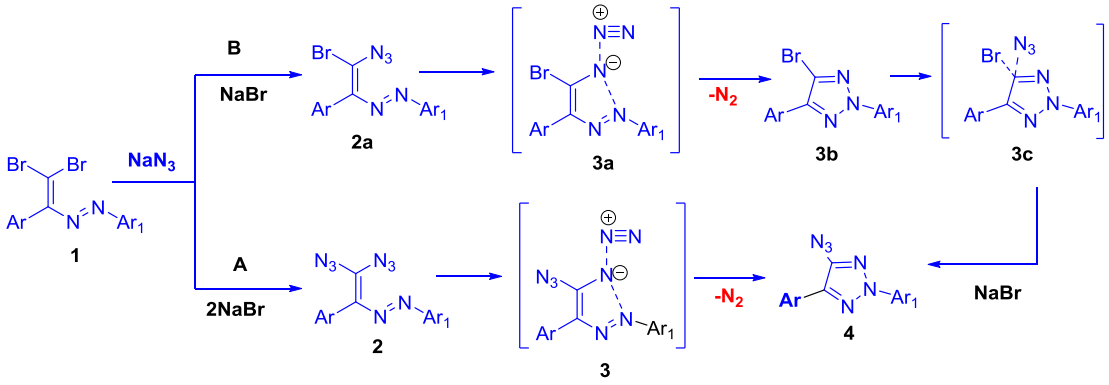
## 3. Results and Discussion

Generally speaking, dichlorodiazadienes are rich in synthetic possibilities and provide opportunity to obtain various nitrogen-containing heterocycles. Thus, the present article is devoted to a topic that is currently very important – the synthesis of biologically active azide triazoles via the reaction of dichlorodiazadienes with $NaN_3$. To justify the presented mechanism, the research with dibromodiazadienes have been continued. In order to do this, the reaction of dibromdiazadienes (synthesized on the basis of o-nitrobenzoyl aldehyde) with $NaN_3$ has been thoroughly studied and the obtaining of two products has been determined using X-ray method of structural analysis. Thus, it has been proven that htere are both molecules in the obtained monocrystal.




**Scheme 1.** General scheme for the preparation of (E)-1-(2,2-dibromo-1-(2-nitrophenyl)vinyl)-2-(4-methoxyphenyl)diazene

In the course of studying the mechanism of the reaction, it has been suggested that the reaction proceeds in two directions. In the **A** direction, both bromide atoms are substituted simultaneously via the nucleophilic attack of azide anion, obtaining bis azide **2**, then as a result of its intramolecular cyclization **3** the transformation into azide triazole **4** occurs. It has been suggested that in the **B** direction, the bromide atoms are substituted sequentially. Thus, thin-layer chromatography study of reaction mixture has showed that two products are obtained and the products have been removed from the reaction mixture via column chromatography, their structures were confirmed via NMR and X-ray methods. Due to the obtaining of 4-bromtriazole **3b**, it can be said that the reaction does also proceed in the **B** direction, but the small reaction yield gives reason to claim that the reaction mainly proceeds in the **A** direction.




**Scheme 2.** Probable mechanism of preparation of (E)-1-(2,2-dibromo-1-(2-nitrophenyl)vinyl)-2-(4-methoxyphenyl)diazene

Thus, in the course of X-ray study of the compound obtained from reaction mixture, it has been found that 3b and 4 compounds crystallize together (in other words, both molecules are present in the crystal) (Figure 2). It should be noted that **3b** comprises **3%**, while **4** comprises **97%** of the crystal. Therefore, the obtaining of 4-bromtriazole **3b** proves that the reaction does proceed in the **B** direction. But here, just as in the case of the reaction with dichlorodiazadiene, the small yield of 4-bromtriazole gives a substantial reason to claim that the reaction mainly proceeds in the **A** direction (in the **A** direction, both chloride atoms are simultaneously substituted via the nucleophilic attack of azide anion, obtaining bis azide **2**, then its intramolecular cyclization **3** occurs and as a result it transforms into azide triazole **4**). Thus, we have unequivocally proven that the synthesis of triazole via the reaction of dihalogendiazadienes with $NaN_3$ proceeds according to the mechanism presented above.

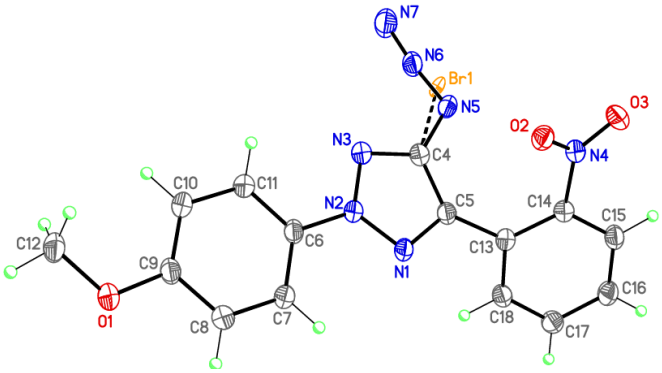



**Figure 2.** Molecular structure of (E)-1-(2,2-dibromo-1-(2-nitrophenyl)vinyl)-2-(4-methoxyphenyl)diazene

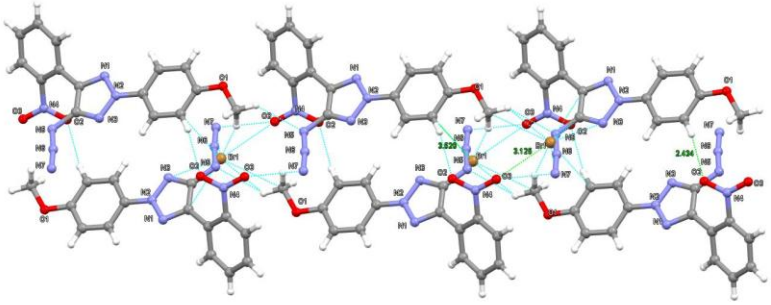


**Figure 3.** Intermolecular relationships in the structure of (E)-1-(2,2-dibromo-1-(2-nitrophenyl)vinyl)-2-(4-methoxyphenyl)diazene (Br···O [3.125Å], O···N [3.007Å])

### *3.1. Description of molecular and crystal structure*

The three nitrogen atoms of the azido group attached to the 1,2,3-triazole ring of the title molecule are disordered at two positions with a ratio of 0.859(5) : 0.141(5). As seen in Figure 4, the 4-methoxyphenyl and 2-nitrophenyl rings make angles of 4.50 (7) and 44.56 (7)°, respectively, with the 1,2,3-triazole ring.

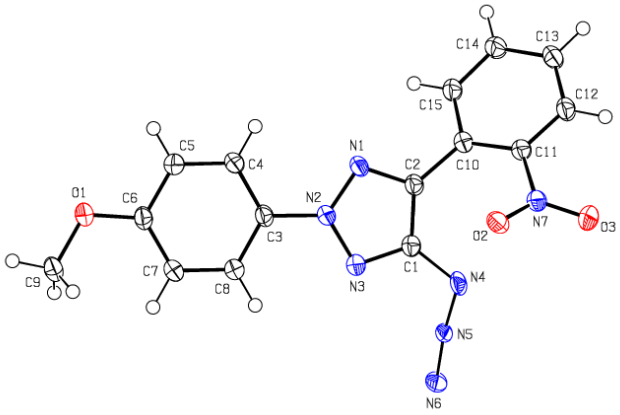



**Figure 4.** The molecular structure of the title compound, with atom labelling. The displacement ellipsoids are drawn at the 50% probability level. Only the major component of the disorder part is shown

The angle between the 4-methoxyphenyl and 2-nitrophenyl rings is 41.55 (6)°. The bond length and angle values in Table 2 of the title molecule are at normal values and can be compared with those of the similar structures which are *4-azido-2-(3,5-dimethylphenyl)-5-(4-nitrophenyl)-2H-1,2,3-triazole* (Maharamov *et al*., 2023) and *1-[4-chloro-3-(trifluoro-methyl)phenyl]-4-phenyl-1H-1,2,3-triazole* (Altimari *et al*., 2012).

In the *crystal*, *pairs* of *C---H…O hydrogen bonds* link the *molecules* into inversion dimers with R $R^2_2(22)$ ring motifs (Bernstein *et al*., 1995; Table 3; Figures 5, 6 and 7).

**Table 2.** Bond Distances (A), bond angles (°) and torsion angles (°)

| | | | |
|---|---|---|---|
| O1---C6 | 1.3618(17) | O1---C9 | 1.4331(18) |
| O2---N7 | 1.2266(15) | O3---N7 | 1.2313(16) |
| N1---N2 | 1.3344(15) | N1---C2 | 1.3405(16) |
| N2---N3 | 1.3410(16) | N2---C3 | 1.4239(17) |
| N3---C1 | 1.3271(17) | N4---N5 | 1.198(3) |
| N4---C1 | 1.422(2) | N5---N6 | 1.166(3) |
| N7---C11 | 1.4708(18) | | |
| C6--O1--C9 | 116.97(11) | N1--N2--N3 | 115.33(10) |
| N1--N2--C3 | 123.02(11) | N3--N2--C3 | 121.65(10) |
| N2--N3--C1 | 102.83(10) | N5--N4--C1 | 114.71(17) |
| N4--N5--N6 | 172.6(2) | O3--N7--C11 | 117.84(11) |
| O2--N7--C11 | 118.19(11) | O2--N7--O3 | 123.93(12) |
| N2--N1--C2--C1 | 0.55(14) | C2--N1--N2--N3 | -0.38(15) |
| N5--N4--C1--C2 | -172.66(17) | O2--N7--C11--C10 | -27.88(17) |
| C9--O1--C6--C7 | 9.4(2) | | |

**Table 3.** Hydrogen-bond geometry (Å, º)

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C7—H7···O2$^{i}$ | 0.95 | 2.43 | 3.3494 (17) | 162 |

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

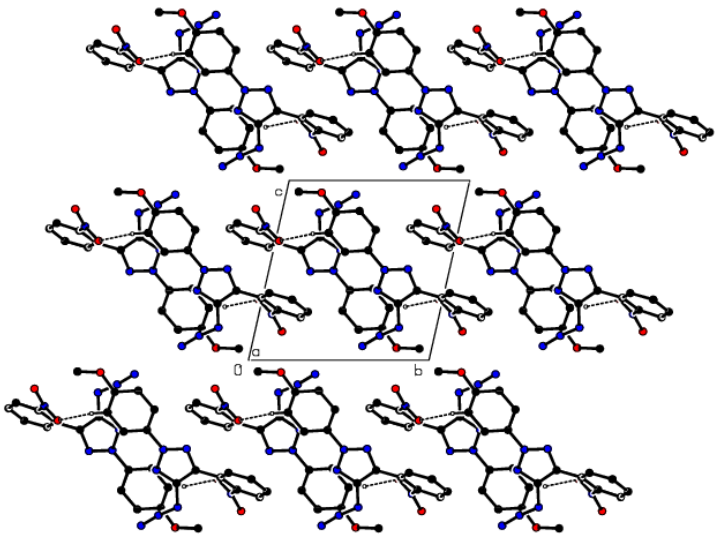



**Figure 5.** C---H...O hydrogen bonds along the a-axis

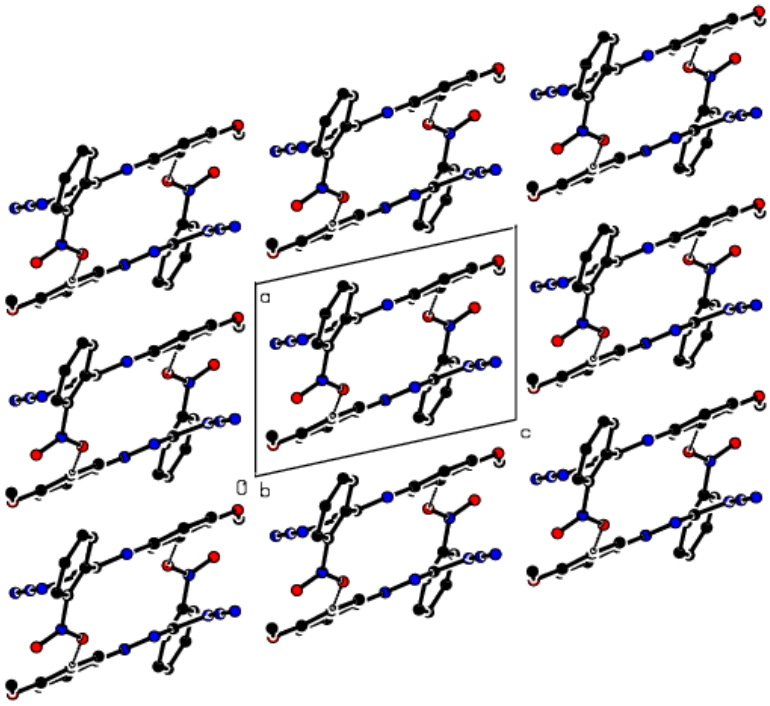



**Figure 6.** C---H...O hydrogen bonds along the b-axis

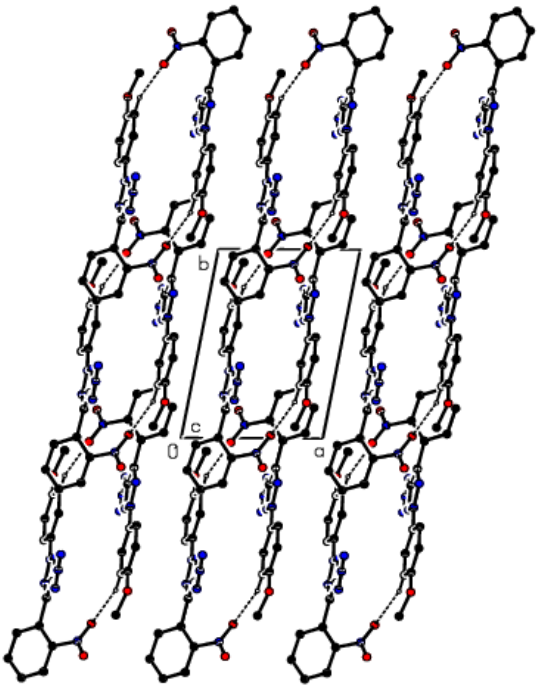



**Figure 7.** C---H...O hydrogen bonds along the c-axis

Additionally, molecules are linked by N---N…π and π-π interactions, forming layers parallel to the (0 0 1) plane (Figures 8, 9 and 10). Crystal structure stability is achieved by van der Waals interactions between these layers.

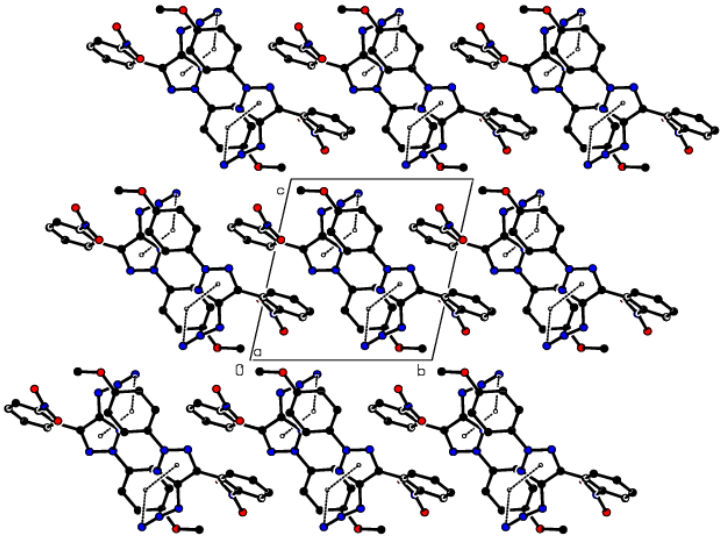



**Figure 8.** N---N...π and π--π interactions along the a-axis

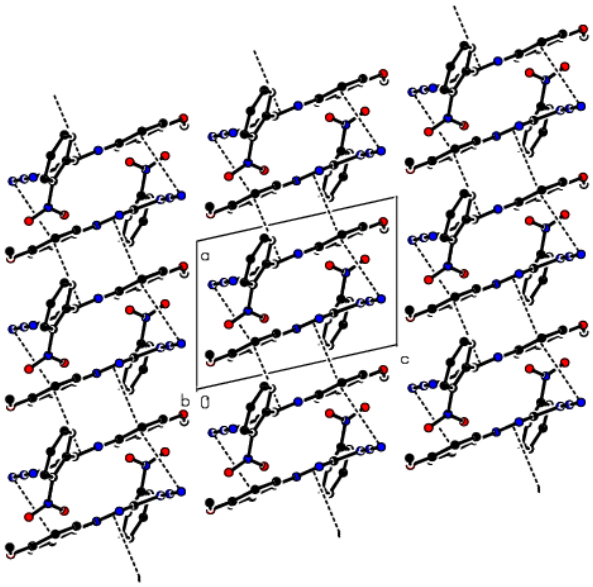



**Figure 9.** N---N...π and π--π interactions along the b-axis

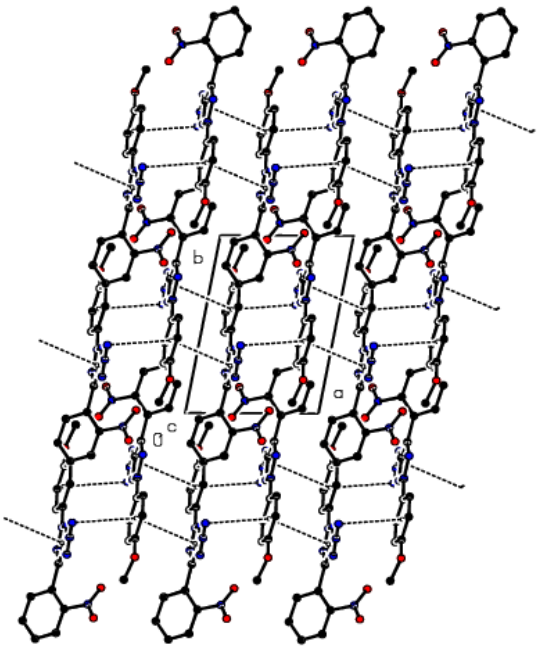



**Figure 10.** N---N...π and π--π interactions along the c-axis

### *3.2. Hirshfeld surface analysis*

A Hirshfeld surface analysis was carried out using *CrystalExplorer 17.5* (Spackman *et al*., 2021) to analyse the intermolecular interactions. The three-dimensional Hirshfeld surface mapped over the normalized contact distance ($d_{\mathrm{norm}}$) is shown in Figure 11. The bright-red spots indicate shortened contacts and correspond to the C—H···O intermolecular hydrogen bonds.

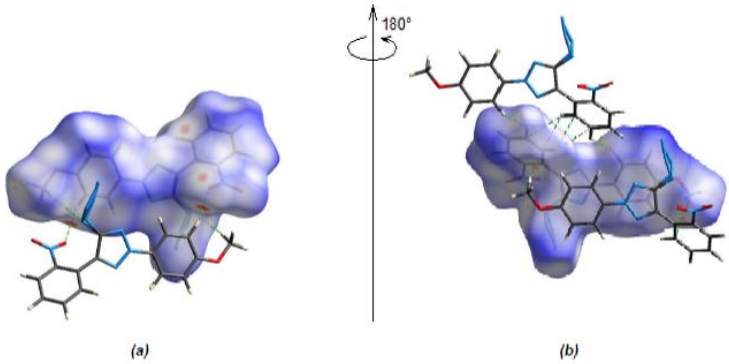



**Figure 11.** (*a*) Front and (*b*) back sides of the three-dimensional Hirshfeld surface of the title compound mapped over $d_{norm}$

The two-dimensional fingerprint plots show the N…H/H…N (Figure 12*b*; 25.9%) contacts to be the most common, followed by H…H (Figure 12*c*; 23.1%), O…H/H…O (Figure 12*d*; 16.7%) and C…H/H…C (Figure 12*e*; 10.7%) and N…C/C…N (Figure 12*f*; 10.7%) contacts. The O…N/N…O (4.9%), O…C/C…O (4.5%), C…C (2.7%) and N...N (0.7%) contacts have little directional influence on the molecular packing.

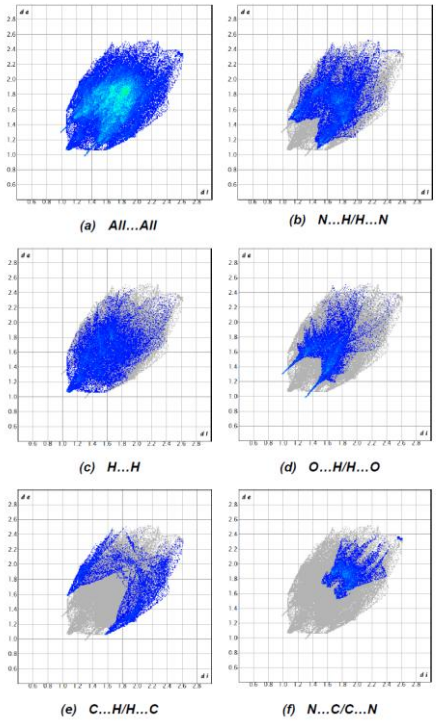



**Figure 12.** The two-dimensional fingerprint plots, showing (*a*) all interactions and delineated into (*b*) N···H/H···N, (*c*) H···H, (*d*) O···H/H···O, (*e*) C···H/H···C and (*f*) N···C/C···N interactions. $d_e$ and $d_i$ represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively

## 4. Conclusion

In this study, we synthesized the title compound and reported its crystal structure. The solid-state structure of the title compound is stabilized by C---H…O, C---H…π and π-π interactions. Hirshfeld surface highlights key short contacts crucial for stabilizing the crystal structure. Other interactions also significantly contribute to the stabilization of the respective molecular dimers of the title compound.

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