



# Syntheses, spectroscopy, and crystal structures of 3-(4-bromophenyl)-1,5-diphenylformazan and the 3-(4-bromophenyl)-1,5-diphenylverdazyl radical and the crystal structure of the by-product 5-anilino-3-(4-bromophenyl)-1-phenyl-1H-1,2,4-triazole

Received 18 January 2018

Accepted 1 February 2018

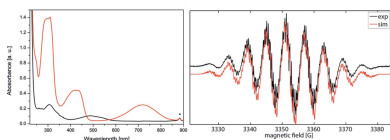
Edited by A. J. Lough, University of Toronto, Canada

**Keywords:** crystal structure; H-atom transfer; tautomerism; hydrogen bonding; radical; dye; heterocycle.**CCDC references:** 1821241; 1821240; 1821239**Supporting information:** this article has supporting information at journals.iucr.org/eGregor Schnakenburg<sup>a</sup> and Andreas Meyer<sup>b\*</sup><sup>a</sup>University of Bonn, Institute of Inorganic Chemistry, Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany, and <sup>b</sup>University of Bonn, Institute of Physical and Theoretical Chemistry, Wegelerstrasse 12, 53115 Bonn, Germany. \*Correspondence e-mail: meyer@pc.uni-bonn.de

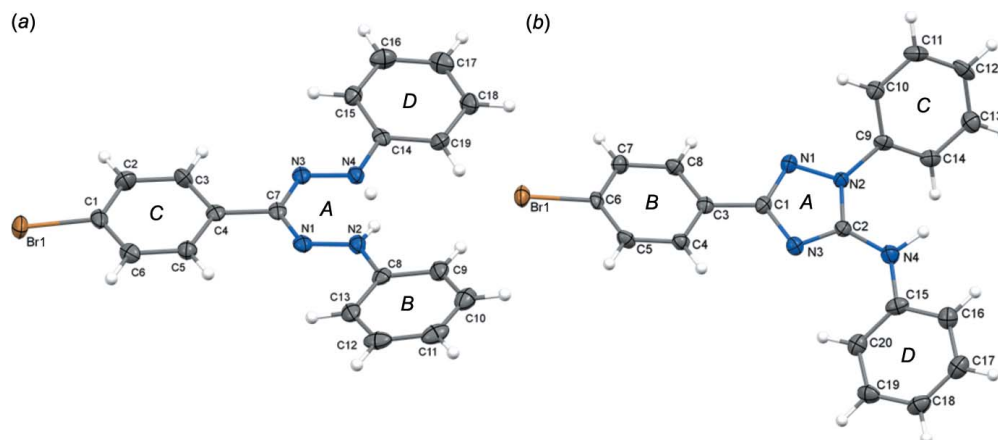
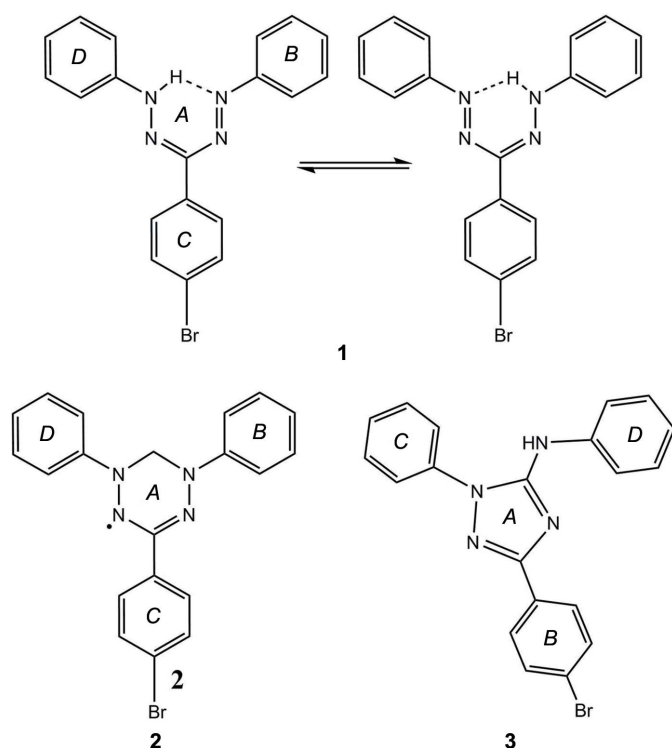
The title compounds, C<sub>19</sub>H<sub>15</sub>BrN<sub>4</sub>, C<sub>20</sub>H<sub>16</sub>BrN<sub>4</sub> and C<sub>20</sub>H<sub>15</sub>BrN<sub>4</sub>, are nitrogen-rich organic compounds that are related by their synthesis. The verdazyl radical, in which stacking leads to antiferromagnetic interactions, was reported previously [Iwase *et al.* (2013). *Phys. Rev. B*, **88**, 184431]. For this compound, improved structural data and spectroscopic data are presented. The other two compounds have been crystallized for the first time and form stacks of dimers, roughly along the *a*-axis direction of the crystal. The formazan molecule shows signs of rapid intramolecular H-atom exchange typical for this class of compounds and spectroscopic data are provided in addition to the crystal structure. The triazole compound appears to be a side-product of the verdazyl synthesis.

## 1. Chemical context

Verdazyl radicals are a family of organic radicals first reported by Kuhn & Trischmann (1963) who emphasized their intense green color and their stability. These Kuhn-verdazyls require formazan precursors, which are intensely red in color and interesting in their own respect (Nineham, 1955; Scudiero *et al.* 1988). A few years after Kuhn's discovery, syntheses leading to the orange 6-oxo- and 6-thioxoverdazyls were developed (Neugebauer & Fischer, 1980; Neugebauer *et al.*, 1988). As of late, verdazyls experience renewed interest, partially as a result of the improvements concerning their syntheses, enabling the introduction of a large variety of substitution patterns (Paré *et al.*, 2005; Bancarz *et al.*, 2012; Matuschek *et al.*, 2015; Le *et al.*, 2017). Such tailor-made radicals have possible applications as fundamental building blocks in molecular magnets or in spintronic materials (Koivisto & Hicks, 2005; Train *et al.*, 2009; Ratera & Veciana, 2012). Verdazyls often avoid stacking, preventing the occurrence of strong magnetic interactions. However, some exceptions to this rule have been reported, where strong antiferromagnetic coupling occurs as a consequence (Koivisto *et al.*, 2006; Eusterwiemann *et al.*, 2017). With respect to applications in spintronics, tetrathiafulvalene-substituted verdazyl compounds represent interesting examples (Chahma *et al.*, 2006; Venneri *et al.*, 2015). Herein, the preparation and crystal structures of three molecules involved in verdazyl synthesis are reported.



3-(4-Bromophenyl)-1,5-diphenylformazan,  $C_{19}H_{15}N_4Br$  (**1**), was used as the educt to obtain the 3-(4-bromophenyl)-1,5-diphenylverdazyl radical  $C_{20}H_{16}N_4Br$  (**2**). Additionally, 5-anilino-3-(4-bromophenyl)-1-phenyl-1*H*-1,2,4-triazole,  $C_{20}H_{15}N_4Br$  (**3**), could be crystallized, representing a possible side-product in verdazyl synthesis. The identification of such by-products might aid future efforts to further elucidate the so-far poorly understood mechanism of verdazyl formation. The crystal structures of all three molecules could be obtained and are discussed in detail for **1** and **3**. The structure of **2** has already been discussed by Iwase *et al.* (2013) and a dataset with improved residuals is provided herein. In addition to the crystal structures, spectroscopic data for **1** and **2** are presented.



**Figure 1**  
The molecular structures of (a) **1** and (b) **3** with displacement ellipsoids drawn at the 50% probability level.

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for **1**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2\cdots N4$	0.80 (10)	1.93 (10)	2.566 (5)	137 (9)
$N4-H4\cdots N1$	0.81 (12)	2.40 (11)	2.803 (5)	112 (9)
$N4-H4\cdots N2$	0.81 (12)	1.86 (12)	2.566 (5)	145 (10)
$C19-H19\cdots Br1^i$	0.95	3.05	3.921 (4)	153
$C9-H9\cdots Br1^i$	0.95	3.14	4.014 (5)	153

Symmetry code: (i)  $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$ .

## 2. Structural commentary

The molecular structures of **1** and **3** are shown in Fig. 1*a* and *b*, respectively. Compound **2** has a structure typical for verdazyls, for details see Iwase *et al.* (2013). For **1**, interesting structural features are the bond lengths in the central NNCNN atomic chain. Taking into account the  $3\sigma$  criterion, the bond lengths  $N1-N2$  and  $N3-N4$  are identical [1.309 (5) and 1.300 (5)  $\text{\AA}$ , respectively] and the same is true for  $N1-C7$  and  $N3-C7$  [1.350 (5) and 1.364 (5)  $\text{\AA}$ , respectively]. These bond lengths lie between values typical for single and double bonds. The pairwise identical bond lengths are in agreement with rapid intramolecular H-atom exchange (Nineham, 1955; Otting & Neugebauer, 1969; Buemi *et al.*, 1998). Correspondingly, the H atom was considered to be split between the two possible positions at N2 and N4. In both positions, an intramolecular hydrogen bond is formed with  $H\cdots A$  distances amounting to 1.93 (10)  $\text{\AA}$  for  $N2-H2\cdots N4$  and 1.86 (12)  $\text{\AA}$  for  $N4-H4\cdots N2$  (Table 1). Finally, it is noted that the molecule is essentially planar with angles between the normal vectors of the NNCNN mean plane A and the three rings B, C, and D amounting to 9.71 (16) ( $A/B$ ), 5.28 (3) ( $A/C$ ), and 12.18 (13) $^\circ$  ( $A/D$ ).

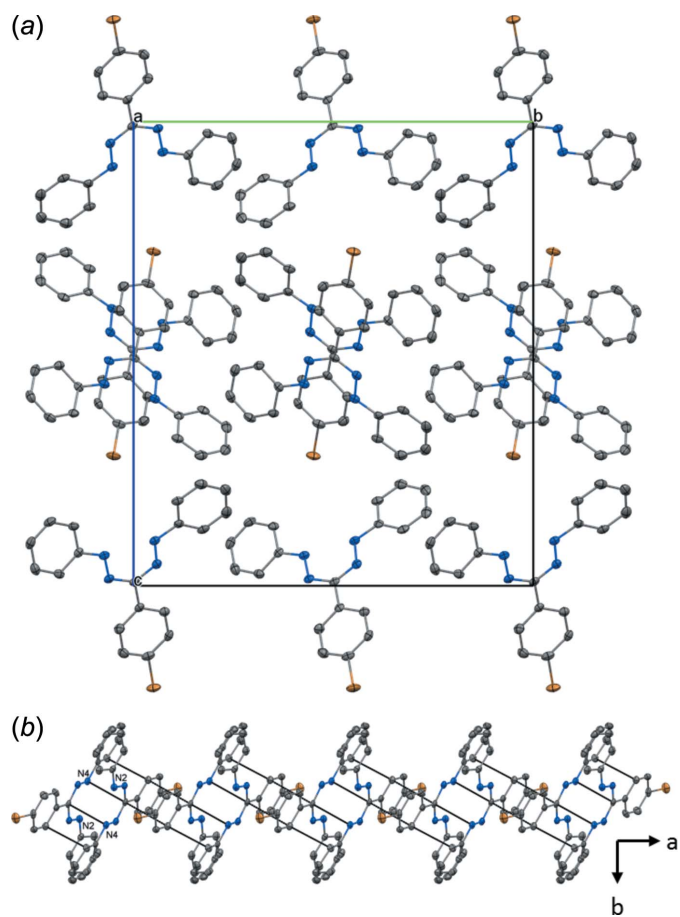
Compound **3** was isolated in later fractions of the column that was used to purify **2**. Such triazole compounds have been identified as products of thermal verdazyl decomposition at 473 K or after four days of refluxing at 353 K in benzene (Neugebauer *et al.*, 1972). Here, the formation of **3** was observed under much less harsh conditions. The bond lengths within ring A suggest bond orders between single and double bonds, in accordance with the aromatic character of 1,2,4-

**Table 2**  
Hydrogen-bond geometry (Å, °) for **3**.

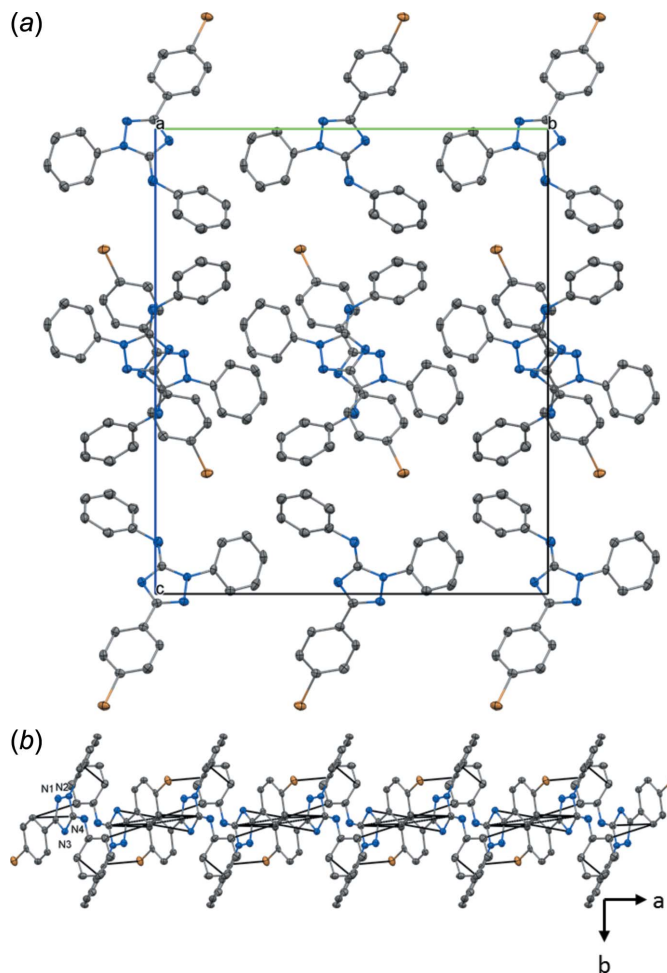
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C14-H14\cdots Br1^i$	0.95	2.99	3.814 (4)	146 (1)
$C10-H10\cdots C20^{ii}$	0.95	2.75	3.575 (5)	146 (1)
$C17-H17\cdots C19^{iii}$	0.95	2.84	3.694 (6)	150 (1)

Symmetry codes: (i)  $-x+2, -y+1, -z+1$ ; (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $x-\frac{1}{2}, y, -z+\frac{3}{2}$ .

triazoles. Closer inspection reveals that three of the five bonds are considerably longer than the other two [ $N1-N2 = 1.375$  (4),  $N2-C2 = 1.358$  (5), and  $N3-C1: 1.370$  (5) Å compared to  $N1-C1 = 1.321$  (5) and  $N3-C2 = 1.326$  (5) Å], indicating that the resonance structure given in Fig. 5 is the most important one. The amino-nitrogen  $N4$  is connected to ring *A* by a bond of similar character to the bonds within the ring [ $N4-C2 = 1.371$  (5) Å] whereas its bond to phenyl ring *D* has essentially single-bond character [ $N4-C15 = 1.426$  (6) Å]. The bonds connecting ring *A* with rings *B* and *C* also have mostly single-bond character [ $C1-C3 = 1.479$  (5) and  $N2-C9 = 1.441$  (5) Å]. The mean planes of rings *B*, *C*, and *D* are tilted with respect to the mean plane of *A* and are arranged in a



**Figure 2**  
(a) Unit cell of **1** viewed parallel to the (100) plane. (b) Stacks of dimers formed along the *a*-axis direction. Two nitrogen atoms of two molecules are labelled.



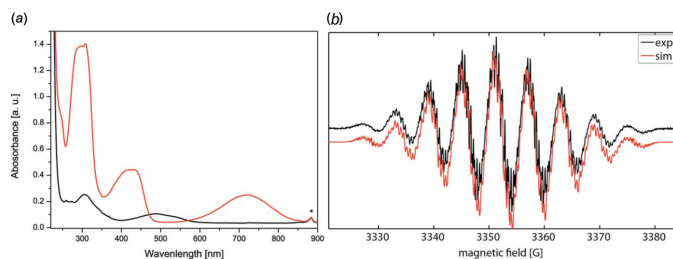
**Figure 3**  
(a) Unit cell of **3** viewed parallel to the (100) plane. (b) Stacks of dimers formed along the *a*-axis direction. The nitrogen atoms of one molecule are labelled.

propeller-like manner [angles between normal vectors:  $A/B = 14.47$  (14),  $A/C = 40.42$  (14), and  $A/D = 20.67$  (16)°].

### 3. Supramolecular features

Compound **1** crystallizes with orthorhombic symmetry in space group *Pbca*, in which head-to-tail dimers between two molecules are stacked along the *a*-axis direction (Fig. 2). Within a dimer, the shortest contacts are 3.213 (5) and 3.372 (6) Å for  $N4\cdots C7$  and  $C19\cdots C5$ , respectively. The short  $C5\cdots C7$  contact [3.277 (6) Å] connects pairs of dimers. The Br atom is not involved in halogen bonding, which is a structural motive attracting increasing attention (Metrangolo *et al.*, 2008; Gilday *et al.*, 2015). Relatively short contacts between H19 as well as H9 and the Br1 atom of another molecule connect different stacks (Table 1). However, the observed distances of 3.05 Å ( $C19-H19\cdots Br1$ ) and 3.14 Å ( $C9-H9\cdots Br1$ ) are still longer than the sum of the van der Waals radii of H and Br, meaning that these are at best very weak hydrogen bonds.

The packing of **2** leading to antiferromagnetic coupling has already been described (Iwase *et al.*, 2013).



**Figure 4**  
 (a) UV-Vis spectra of **1** (black line, 2.3  $\mu\text{M}$ , DCM) and **2** (red line, 11  $\mu\text{M}$ , DCM). (b) EPR spectrum of **2** in degassed deuterated DCM (black line) along with its simulation (red line) obtained using the program *EasySpin* (Stoll & Schweiger, 2006).

Compound **3** has a similar structure to **1** in space group *Pbca* and with pairs of molecules stacked along the *a*-axis direction (Fig. 3). Here, the centroid-to-centroid distances of the *A* rings are 3.564 (3) and 4.661 (3) Å within and between the dimers, respectively. However, the shortest intra-dimer contact is a C—H $\cdots\pi$  interaction (Table 2) between rings *C* and *D* (C10—H10 $\cdots$ C20, 2.75 Å). A similar contact is found between H17 and C19 (C17—H17 $\cdots$ C19, 2.84 Å), forming a contact between different stacks.  $\pi$ -Stacking is observed between rings *A* and *B*, connecting pairs of dimers, with the shortest contacts being 3.229 (6) (C8 $\cdots$ N3), 3.318 (6) (C8 $\cdots$ C2), and 3.378 (6) Å (C7 $\cdots$ C2). As with **1** and **2**, no halogen bonding is observed, but the Br atom is involved in a very weak hydrogen bond (C14—H14 $\cdots$ Br1, 2.99 Å; Table 2).

#### 4. Spectroscopy

Fig. 4*a* shows the UV-Vis spectra of **1** and **2**, while Fig. 4*b* represents the EPR spectrum of **2** and its simulation (black and red lines, respectively). The UV-Vis spectra of **1** and **2** are typical for formazans and verdazyls, respectively, with the peaks in the visible range at 490 nm (**1**) as well as at 425 and 720 nm (**2**) being responsible for their intense red (**1**) or green colors (**2**). The EPR spectrum of **2** was simulated by assuming a *g* value of 2.00354 and hyperfine coupling constants (HFCC) of 16.77 and 16.48 MHz for the two pairs of nitrogen nuclei. In addition, the approximate values for the HFCC of the phenyl ring protons could be obtained, amounting to 0.01 (CH<sub>2</sub>), 3.04 (H, rings *B* and *D*, *ortho*), 1.14 (H, rings *B* and *D*, *meta*), 3.34

(H, rings *B* and *D*, *para*), 1.14, (H, ring *C*, *ortho*), and 0.52 MHz (H, ring *C*, *meta*). The assignment of the protons is in accordance with that of Kopf *et al.* (1971).

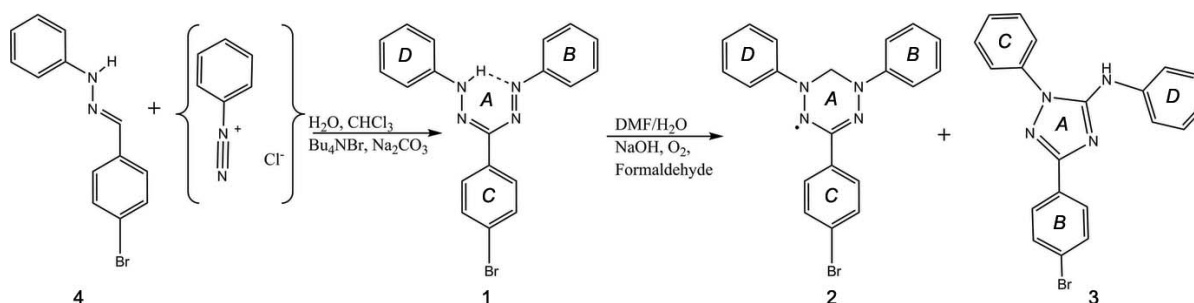
#### 5. Database survey

The Cambridge Structural Database (CSD, Version 5.36; Groom *et al.*, 2016) was queried for other formazans, verdazyls, and 1,2,4-triazoles. The search revealed 21 examples of formazans if the only restriction was to have carbon substituents in the 1,3,5-positions. This number reduced to nine if all of these substituents were required to be phenyl-based, one of these nine examples being a metal complex of a formazan. The remaining eight structures include examples in which the bond lengths in the NNCNN unit alternate, as well as examples in which they are pairwise equal in a similar manner to that described herein. Interestingly, 3,5-diphenyl-1-(4-bromophenyl)formazan (regioisomer of **1**, CCDC code EMEVUO; Tunç & Yıldırım, 2010) shows alternating bond lengths, which reflects the fact that the two nitrogen atoms are chemically inequivalent in this molecule. An example with split hydrogen positions is 1,5-diphenyl-3-(*p*-nitrophenyl)formazan (GUHCIW; Iqbal *et al.*, 2009), which shows a similar stacking to that observed in **1** and can be formally derived from **1** by replacing the bromine with a nitro group. 33 examples for 1,3,5-aryl-substituted verdazyls were found in the CSD, only 14 of them Kuhn-verdazyls. The largest hitlist was obtained for 1,3,5-substituted 1,2,4-triazoles (1001 entries). This number reduced drastically if purely organic compounds were considered exclusively (42 hits) and even further if the substituent at C5 was required to be a nitrogen atom (four hits, no further restriction).

#### 6. Synthesis and crystallization

The syntheses were performed following Berry *et al.*, 2009 (Fig. 5). The hydrazone **4** required for the synthesis of **1** was synthesized by refluxing a solution of *p*-bromobenzaldehyde with phenylhydrazine in ethanol and collecting the slightly yellow precipitate that formed after cooling the solution down to room temperature (rt).

To synthesize **1**, 450 mg (1.72 mmol) of **4** and 80 mg (0.25 mmol) of tetrabutylammonium bromide were dissolved in 11 mL of dichloromethane (DCM) and combined with 1.4 g



**Figure 5**  
 Synthesis of **1**, **2**, and **3**.



**Table 3**  
Experimental details.

	<b>1</b>	<b>2</b>	<b>3</b>
<b>Crystal data</b>			
Chemical formula	C <sub>19</sub> H <sub>15</sub> BrN <sub>4</sub>	C <sub>20</sub> H <sub>16</sub> BrN <sub>4</sub>	C <sub>20</sub> H <sub>15</sub> BrN <sub>4</sub>
<i>M<sub>r</sub></i>	379.26	392.28	391.27
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Orthorhombic, <i>Pbca</i>	Orthorhombic, <i>Pbca</i>
Temperature (K)	100	123	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.7930 (5), 19.0947 (16), 22.1843 (17)	7.0881 (3), 21.2183 (11), 22.2028 (9)	7.7989 (9), 18.971 (3), 22.455 (4)
<i>V</i> (Å <sup>3</sup> )	3301.1 (4)	3339.2 (3)	3322.4 (8)
<i>Z</i>	8	8	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	2.50	2.47	2.48
Crystal size (mm)	0.33 × 0.06 × 0.04	0.15 × 0.12 × 0.06	0.32 × 0.16 × 0.1
<b>Data collection</b>			
Diffractometer	Bruker D8 Venture	Stoe IPDS 2T	Bruker X8 Kappa APEXII
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2015)	Integration ( <i>X-RED32</i> ; Stoe & Cie, 2009)	Multi-scan ( <i>SADABS</i> ; Bruker, 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.550, 0.746	0.254, 0.620	0.583, 0.746
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	60778, 3975, 2652	70879, 3640, 3397	19450, 3999, 2708
<i>R<sub>int</sub></i>	0.147	0.128	0.098
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.661	0.639	0.660
<b>Refinement</b>			
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.057, 0.153, 1.03	0.029, 0.076, 1.10	0.056, 0.126, 1.05
No. of reflections	3975	3640	3999
No. of parameters	224	226	229
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	1.76, -1.08	0.72, -0.65	1.46, -0.84

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *X-AREA* (Stoe & Cie, 2009), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

of sodium carbonate in 11 mL of water to form a biphasic system, which was stirred at 273 K for 30 min. During this time, 1.8 mL (186 mg, 2 mmol) of aniline were dissolved in 4.5 mL of dilute hydrochloric acid (*ca* 12%) and stirred at 273 K. To this solution, 55 mg (3.3 mmol) of sodium nitrite in 3 mL of water were added dropwise over the course of ten minutes, leading to the occurrence of a slight yellow color. This yellow solution was added carefully to the biphasic solution of **4** and an intense red color evolved within minutes. After one h, 20 mL of water were added and the temperature was allowed to increase to rt. After stirring for another 30 minutes at rt, the phases were separated. The organic phase was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub> before removing the solvent under reduced pressure. The raw product was subjected to column chromatography using aluminum oxide (AlOx, water content 5%) as stationary phase and DCM/cyclohexane (1:4). The red fractions were collected, yielding **1** as red solid in 66% yield (307 mg). Crystals of **1** were obtained by dissolving the solid in a mixture of DCM and hexane which was left to evaporate.

To obtain **2**, 119 mg (0.31 mmol) of **1** were dissolved in 10 mL of dimethylformamide and mixed with 0.7 mL 2 *M* aqueous sodium hydroxide solution and 0.65 mL of 37% formaldehyde solution. The mixture was stirred at rt in an open vessel with contact to air, leading to a change of color from red to green over the course of an hour. 20 mL of water and diethyl ether were then added to the solution and the

phases were separated from each other. After drying the organic phase over Na<sub>2</sub>SO<sub>4</sub>, the raw product was subjected to column chromatography using AlOx (water content 5%) and diethylether/cyclohexane (1:5) as eluent. The green fractions were collected and the solvent was removed under reduced pressure (yield: 37 mg, 30%). Crystals of **2** were obtained by dissolving the product in a mixture of DCM and hexane and leaving the green solution to evaporate.

Compound **3** was obtained by collecting the slightly yellow fractions that eluted from the column after **2** and removing the solvent. Dissolving the resulting brownish solid in a mixture of DCM and hexane and leaving the solution to evaporate afforded crystals suitable for X-ray crystallography.

**Additional analytical data for 1 and 2.** **1:** <sup>1</sup>H NMR (400 MHz, DCM-*d*<sub>2</sub>): δ 15.45 (*s*, 1H); 8.08 (*dt*, *J* = 8.8 MHz, 2.2 MHz, 2H); 7.75 (*dm*, *J* = 8.4 MHz, 4H); 7.61 (*dt*, *J* = 8.8 MHz, 2.2 MHz, 2H); 7.52 (*ddt*, *J* = 8.4 MHz, 7.2 MHz, 1.6 MHz, 4H); 7.36 (*tt*, *J* = 7.2 MHz, 1.2 MHz, 2H). ESI-MS (positive, *m/z*): calculated 377.04 ([*M* - H]<sup>+</sup>), found 377.04. UV-Vis: see above.

**2:** ESI-MS (positive, *m/z*): calculated 391.06 ([*M*]<sup>+</sup>), found 391.06. UV-Vis and EPR: see above.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were refined

using a riding model with  $C-H = 0.95-0.99 \text{ \AA}$  and  $U_{iso}(H) = 1.2U_{eq}(C)$ . N-bound H atoms were located in a difference-Fourier map and refined with  $U_{iso}(H) = 1.2U_{eq}(N)$ .

## Acknowledgements

Professor Dr O. Schiemann and Professor Dr. A. C. Filippou are gratefully acknowledged for providing access to the laboratory and spectrometers and for financial support (AM) as well as access to the X-ray diffractometers (GS).

## Funding information

Funding for this research was provided by: Rheinische Friedrich-Wilhelms-Universität Bonn (contract to Gregor Schnakenburg; scholarship to Andreas Meyer).

## References

- Bancerz, M., Youn, B., DaCosta, M. V. & Georges, M. K. (2012). *J. Org. Chem.* **77**, 2415–2421.
- Berry, D. E., Hicks, R. G. & Gilroy, J. B. (2009). *J. Chem. Educ.* **86**, 76–79.
- Bruker (2015). *APEX2, SADABS and SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Buemi, G., Zuccarello, F., Venuvanalingam, P., Ramalingam, M. & Ammal, S. S. C. (1998). *Faraday Trans.* **94**, 3313–3319.
- Chahma, M., Wang, X. S., Est, A. van der & Pilkington, M. (2006). *J. Org. Chem.* **71**, 2750–2755.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Eusterwiemann, S., Dresselhaus, T., Doerenkamp, C., Janka, O., Niehaus, O., Massolle, A., Daniliuc, C. G., Eckert, H., Pöttgen, R., Neugebauer, J. & Studer, A. (2017). *Chem. Eur. J.* **23**, 6069–6082.
- Gilday, L., Robinson, S. W., Barendt, T. A., Langton, M. J., Mullaney, B. R. & Beer, P. D. (2015). *Chem. Rev.* **115**, 7118–7195.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Iqbal, A., Moloney, M. G., Siddiqui, H. L. & Thompson, A. L. (2009). *Tetrahedron Lett.* **50**, 4523–4525.
- Iwase, K., Yamaguchi, H., Ono, T., Hosokoshi, Y., Shimokawa, T., Kono, Y., Kittaka, S., Sakakibara, T., Matsuo, A. & Kindo, K. (2013). *Phys. Rev. B*, **88**, 184431.
- Koivisto, B. D. & Hicks, R. G. (2005). *Coord. Chem. Rev.* **249**, 2612–2630.
- Koivisto, B. D., Ichimura, A. S., McDonald, R., Lemaire, M. T., Thompson, L. K. & Hicks, R. G. (2006). *J. Am. Chem. Soc.* **128**, 690–691.
- Kopf, P., Morokuma, K. & Kreilick, R. (1971). *J. Chem. Phys.* **54**, 105–110.
- Kuhn, R. & Trischmann, H. (1963). *Angew. Chem. Int. Ed. Engl.* **2**, 155.
- Le, T.-N., Trevisan, T., Lieu, E. & Brook, D. J. R. (2017). *Eur. J. Org. Chem.* **2017**, 1125–1131.
- Matuschek, D., Eusterwiemann, S., Stegemann, L., Doerenkamp, C., Wibbeling, B., Daniliuc, C. G., Doltsinis, N. L., Strassert, C. A., Eckert, H. & Studer, A. (2015). *Chem. Sci.* **6**, 4712–4716.
- Metrangolo, P., Meyer, F., Pilati, T., Resnati, G. & Terraneo, G. (2008). *Angew. Chem. Int. Ed.* **47**, 6114–6127.
- Neugebauer, F. A. & Fischer, H. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 724–725.
- Neugebauer, F. A., Fischer, H. & Siegel, R. (1988). *Eur. J. Inorg. Chem.* **121**, 815–822.
- Neugebauer, F. A., Otting, W., Smith, H. O. & Trischmann, H. (1972). *Eur. J. Inorg. Chem.* **105**, 549–553.
- Nineham, A. W. (1955). *Chem. Rev.* **55**, 355–483.
- Otting, W. & Neugebauer, F. A. (1969). *Eur. J. Inorg. Chem.* **102**, 2520–2529.
- Paré, E. C., Brook, D. J. R., Brieger, A., Badik, M. & Schinke, M. (2005). *Org. Biomol. Chem.* **3**, 4258–4261.
- Ratera, I. & Veciana, J. (2012). *Chem. Soc. Rev.* **41**, 303–349.
- Scudiero, D. A., Shoemaker, R. H., Paull, K. D., Monks, A., Tierney, S., Nofziger, T. H., Currens, M. J., Seniff, D. & Boyd, M. R. (1988). *Cancer Res.* **48**, 4827–4833.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Stoe & Cie (2009). *X-AREA and X-RED32*. Stoe & Cie, Darmstadt, Germany.
- Stoll, S. & Schweiger, A. (2006). *J. Magn. Reson.* **178**, 42–55.
- Train, C., Norel, L. & Baumgarten, M. (2009). *Coord. Chem. Rev.* **253**, 2342–2351.
- Tunç, T. & Yildirim, L. T. (2010). *The Open Crystallogr. J.* **3**, 54–58.
- Venneri, S., Wilson, J., Rawson, J. M. & Pilkington, M. (2015). *ChemPlusChem* **80**, 1624–1633.

## supporting information

*Acta Cryst.* (2018). E74, 292-297 [https://doi.org/10.1107/S2056989018001913]

## Syntheses, spectroscopy, and crystal structures of 3-(4-bromophenyl)-1,5-diphenylformazan and the 3-(4-bromophenyl)-1,5-diphenylverdazyl radical and the crystal structure of the by-product 5-anilino-3-(4-bromophenyl)-1-phenyl-1*H*-1,2,4-triazole

Gregor Schnakenburg and Andreas Meyer

### Computing details

Data collection: *APEX2* (Bruker, 2015) for (1), (3); *X-AREA* (Stoe & Cie, 2009) for (2). Cell refinement: *SAINT* (Bruker, 2015) for (1), (3); *X-AREA* (Stoe & Cie, 2009) for (2). Data reduction: *SAINT* (Bruker, 2015) for (1), (3); *X-AREA* (Stoe & Cie, 2009) for (2). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for (2), (3). For all structures, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### *N'*-Anilino-4-bromo-*N*-(phenylimino)benzene-1-carboximidamide (1)

#### Crystal data

$C_{19}H_{15}BrN_4$	$D_x = 1.526 \text{ Mg m}^{-3}$
$M_r = 379.26$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, <i>Pbca</i>	Cell parameters from 9908 reflections
$a = 7.7930 (5) \text{ \AA}$	$\theta = 3.0\text{--}27.7^\circ$
$b = 19.0947 (16) \text{ \AA}$	$\mu = 2.50 \text{ mm}^{-1}$
$c = 22.1843 (17) \text{ \AA}$	$T = 100 \text{ K}$
$V = 3301.1 (4) \text{ \AA}^3$	Needle, clear red
$Z = 8$	$0.33 \times 0.06 \times 0.04 \text{ mm}$
$F(000) = 1536$	

#### Data collection

Bruker D8 Venture diffractometer	$T_{\min} = 0.550$ , $T_{\max} = 0.746$
Radiation source: microfocus sealed X-ray tube, Incoatec $I\mu\text{s}$	60778 measured reflections
Mirror optics monochromator	3975 independent reflections
Detector resolution: $7.9 \text{ pixels mm}^{-1}$	2652 reflections with $I > 2\sigma(I)$
$\omega$ and $\varphi$ scans	$R_{\text{int}} = 0.147$
Absorption correction: multi-scan (SADABS; Bruker, 2015)	$\theta_{\max} = 28.0^\circ$ , $\theta_{\min} = 2.3^\circ$
	$h = -10 \rightarrow 10$
	$k = -25 \rightarrow 25$
	$l = -28 \rightarrow 29$

#### Refinement

Refinement on $F^2$	$S = 1.03$
Least-squares matrix: full	3975 reflections
$R[F^2 > 2\sigma(F^2)] = 0.057$	224 parameters
$wR(F^2) = 0.153$	0 restraints

Hydrogen site location: mixed  
H atoms treated by a mixture of independent  
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 12.5159P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.76 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.08 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	-0.16420 (6)	0.55022 (3)	0.27999 (2)	0.03107 (17)	
N1	0.2728 (4)	0.55820 (18)	0.54659 (16)	0.0192 (7)	
N2	0.3581 (4)	0.5531 (2)	0.59722 (16)	0.0203 (8)	
H2	0.400 (12)	0.516 (6)	0.605 (4)	0.024*	0.54 (7)
N3	0.3438 (4)	0.43883 (18)	0.51495 (15)	0.0192 (7)	
N4	0.4238 (4)	0.4268 (2)	0.56531 (16)	0.0193 (8)	
H4	0.431 (14)	0.461 (6)	0.587 (5)	0.023*	0.46 (7)
C1	-0.0210 (5)	0.5366 (2)	0.34853 (19)	0.0240 (10)	
C2	0.0685 (6)	0.4745 (3)	0.3551 (2)	0.0278 (10)	
H2A	0.0650	0.4396	0.3247	0.033*	
C3	0.1633 (5)	0.4645 (2)	0.4072 (2)	0.0246 (9)	
H3	0.2257	0.4221	0.4120	0.029*	
C4	0.1701 (5)	0.5148 (2)	0.45276 (18)	0.0186 (8)	
C5	0.0796 (5)	0.5773 (2)	0.44382 (19)	0.0223 (9)	
H5	0.0836	0.6127	0.4738	0.027*	
C6	-0.0146 (5)	0.5881 (2)	0.39252 (19)	0.0228 (9)	
H6	-0.0753	0.6308	0.3871	0.027*	
C7	0.2672 (5)	0.5027 (2)	0.50893 (18)	0.0183 (8)	
C8	0.3693 (5)	0.6134 (2)	0.63337 (18)	0.0191 (9)	
C9	0.4789 (5)	0.6102 (2)	0.68286 (19)	0.0247 (9)	
H9	0.5375	0.5679	0.6920	0.030*	
C10	0.5026 (6)	0.6688 (3)	0.7187 (2)	0.0294 (10)	
H10	0.5793	0.6668	0.7520	0.035*	
C11	0.4152 (6)	0.7304 (3)	0.7065 (2)	0.0304 (11)	
H11	0.4326	0.7706	0.7308	0.036*	
C12	0.3018 (6)	0.7325 (2)	0.6580 (2)	0.0298 (11)	
H12	0.2400	0.7744	0.6499	0.036*	
C13	0.2776 (5)	0.6748 (2)	0.62164 (19)	0.0250 (10)	
H13	0.1993	0.6768	0.5889	0.030*	
C14	0.5102 (5)	0.3628 (2)	0.57135 (18)	0.0182 (8)	
C15	0.5307 (5)	0.3138 (2)	0.52541 (19)	0.0221 (9)	
H15	0.4798	0.3215	0.4871	0.027*	
C16	0.6253 (6)	0.2540 (2)	0.5358 (2)	0.0298 (10)	
H16	0.6399	0.2205	0.5045	0.036*	



C17	0.6999 (6)	0.2424 (2)	0.5923 (2)	0.0293 (10)
H17	0.7645	0.2011	0.5993	0.035*
C18	0.6798 (6)	0.2907 (2)	0.6376 (2)	0.0280 (10)
H18	0.7328	0.2832	0.6756	0.034*
C19	0.5834 (5)	0.3500 (2)	0.62810 (19)	0.0219 (9)
H19	0.5663	0.3824	0.6600	0.026*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0285 (2)	0.0471 (3)	0.0176 (2)	0.0039 (2)	-0.00492 (18)	0.0059 (2)
N1	0.0146 (15)	0.0221 (19)	0.0208 (18)	-0.0026 (14)	0.0021 (14)	0.0024 (15)
N2	0.0178 (17)	0.025 (2)	0.0176 (18)	-0.0008 (15)	-0.0007 (13)	0.0045 (16)
N3	0.0152 (16)	0.0239 (19)	0.0184 (17)	-0.0030 (14)	0.0024 (13)	0.0039 (14)
N4	0.0148 (16)	0.025 (2)	0.0175 (18)	-0.0009 (14)	-0.0008 (14)	0.0029 (15)
C1	0.0139 (19)	0.039 (3)	0.019 (2)	-0.0017 (18)	0.0004 (16)	0.0078 (19)
C2	0.030 (2)	0.029 (2)	0.025 (2)	0.004 (2)	0.0002 (18)	-0.006 (2)
C3	0.022 (2)	0.026 (2)	0.025 (2)	0.0079 (19)	-0.0024 (18)	0.0022 (18)
C4	0.0147 (17)	0.022 (2)	0.019 (2)	-0.0035 (17)	0.0046 (16)	0.0046 (17)
C5	0.020 (2)	0.025 (2)	0.021 (2)	-0.0013 (17)	0.0008 (17)	0.0008 (18)
C6	0.021 (2)	0.020 (2)	0.027 (2)	0.0000 (17)	0.0031 (18)	0.0077 (18)
C7	0.0126 (17)	0.024 (2)	0.018 (2)	-0.0054 (16)	0.0023 (15)	0.0052 (17)
C8	0.0183 (19)	0.023 (2)	0.016 (2)	-0.0047 (16)	0.0054 (15)	0.0018 (17)
C9	0.022 (2)	0.033 (3)	0.019 (2)	-0.0018 (19)	0.0015 (17)	0.0047 (18)
C10	0.026 (2)	0.039 (3)	0.023 (2)	-0.010 (2)	0.0032 (19)	-0.001 (2)
C11	0.034 (2)	0.028 (3)	0.030 (3)	-0.011 (2)	0.014 (2)	-0.004 (2)
C12	0.031 (2)	0.025 (2)	0.034 (3)	0.0007 (19)	0.017 (2)	0.004 (2)
C13	0.021 (2)	0.035 (3)	0.019 (2)	-0.0011 (19)	0.0046 (17)	0.0080 (19)
C14	0.0113 (17)	0.021 (2)	0.022 (2)	-0.0040 (16)	0.0011 (16)	0.0049 (17)
C15	0.020 (2)	0.027 (2)	0.019 (2)	-0.0057 (17)	0.0001 (17)	-0.0017 (18)
C16	0.031 (2)	0.022 (2)	0.036 (3)	-0.0025 (19)	0.006 (2)	-0.007 (2)
C17	0.029 (2)	0.022 (2)	0.037 (3)	0.0026 (19)	0.006 (2)	0.010 (2)
C18	0.027 (2)	0.034 (3)	0.023 (2)	0.006 (2)	0.0010 (19)	0.011 (2)
C19	0.022 (2)	0.027 (2)	0.017 (2)	0.0022 (18)	0.0035 (16)	-0.0002 (18)

*Geometric parameters (Å, °)*

Br1—C1	1.904 (4)	C8—C13	1.398 (6)
N1—N2	1.309 (5)	C9—H9	0.9500
N1—C7	1.350 (5)	C9—C10	1.385 (7)
N2—H2	0.80 (10)	C10—H10	0.9500
N2—C8	1.405 (6)	C10—C11	1.385 (7)
N3—N4	1.300 (5)	C11—H11	0.9500
N3—C7	1.364 (5)	C11—C12	1.392 (7)
N4—H4	0.81 (12)	C12—H12	0.9500
N4—C14	1.401 (5)	C12—C13	1.379 (7)
C1—C2	1.384 (6)	C13—H13	0.9500
C1—C6	1.386 (6)	C14—C15	1.393 (6)

C2—H2A	0.9500	C14—C19	1.404 (6)
C2—C3	1.384 (6)	C15—H15	0.9500
C3—H3	0.9500	C15—C16	1.379 (6)
C3—C4	1.395 (6)	C16—H16	0.9500
C4—C5	1.400 (6)	C16—C17	1.398 (7)
C4—C7	1.476 (6)	C17—H17	0.9500
C5—H5	0.9500	C17—C18	1.373 (7)
C5—C6	1.370 (6)	C18—H18	0.9500
C6—H6	0.9500	C18—C19	1.375 (6)
C8—C9	1.392 (6)	C19—H19	0.9500
N2—N1—C7	119.3 (4)	C10—C9—C8	120.0 (4)
N1—N2—H2	117 (7)	C10—C9—H9	120.0
N1—N2—C8	117.5 (4)	C9—C10—H10	119.8
C8—N2—H2	126 (7)	C11—C10—C9	120.5 (4)
N4—N3—C7	116.9 (4)	C11—C10—H10	119.8
N3—N4—H4	113 (8)	C10—C11—H11	120.4
N3—N4—C14	117.8 (4)	C10—C11—C12	119.3 (4)
C14—N4—H4	128 (8)	C12—C11—H11	120.4
C2—C1—Br1	119.8 (3)	C11—C12—H12	119.5
C2—C1—C6	121.0 (4)	C13—C12—C11	121.0 (4)
C6—C1—Br1	119.1 (3)	C13—C12—H12	119.5
C1—C2—H2A	120.8	C8—C13—H13	120.3
C1—C2—C3	118.4 (4)	C12—C13—C8	119.5 (4)
C3—C2—H2A	120.8	C12—C13—H13	120.3
C2—C3—H3	119.0	N4—C14—C19	115.6 (4)
C2—C3—C4	122.0 (4)	C15—C14—N4	124.8 (4)
C4—C3—H3	119.0	C15—C14—C19	119.6 (4)
C3—C4—C5	117.7 (4)	C14—C15—H15	120.2
C3—C4—C7	121.6 (4)	C16—C15—C14	119.7 (4)
C5—C4—C7	120.7 (4)	C16—C15—H15	120.2
C4—C5—H5	119.5	C15—C16—H16	119.9
C6—C5—C4	121.1 (4)	C15—C16—C17	120.2 (4)
C6—C5—H5	119.5	C17—C16—H16	119.9
C1—C6—H6	120.1	C16—C17—H17	119.9
C5—C6—C1	119.8 (4)	C18—C17—C16	120.2 (4)
C5—C6—H6	120.1	C18—C17—H17	119.9
N1—C7—N3	128.8 (4)	C17—C18—H18	119.9
N1—C7—C4	114.6 (4)	C17—C18—C19	120.2 (4)
N3—C7—C4	116.5 (4)	C19—C18—H18	119.9
C9—C8—N2	116.9 (4)	C14—C19—H19	119.9
C9—C8—C13	119.7 (4)	C18—C19—C14	120.1 (4)
C13—C8—N2	123.3 (4)	C18—C19—H19	119.9
C8—C9—H9	120.0		
Br1—C1—C2—C3	-176.2 (3)	C3—C4—C7—N3	-2.6 (6)
Br1—C1—C6—C5	176.0 (3)	C4—C5—C6—C1	0.0 (6)
N1—N2—C8—C9	-171.6 (3)	C5—C4—C7—N1	-5.7 (5)

N1—N2—C8—C13	8.0 (6)	C5—C4—C7—N3	176.7 (3)
N2—N1—C7—N3	-1.7 (6)	C6—C1—C2—C3	0.8 (6)
N2—N1—C7—C4	-179.0 (3)	C7—N1—N2—C8	176.3 (3)
N2—C8—C9—C10	176.9 (4)	C7—N3—N4—C14	-177.1 (3)
N2—C8—C13—C12	-177.3 (4)	C7—C4—C5—C6	-178.2 (4)
N3—N4—C14—C15	6.4 (6)	C8—C9—C10—C11	1.3 (6)
N3—N4—C14—C19	-175.3 (3)	C9—C8—C13—C12	2.4 (6)
N4—N3—C7—N1	5.4 (6)	C9—C10—C11—C12	0.7 (6)
N4—N3—C7—C4	-177.3 (3)	C10—C11—C12—C13	-1.1 (6)
N4—C14—C15—C16	176.9 (4)	C11—C12—C13—C8	-0.4 (6)
N4—C14—C19—C18	-176.0 (4)	C13—C8—C9—C10	-2.8 (6)
C1—C2—C3—C4	0.3 (7)	C14—C15—C16—C17	0.2 (6)
C2—C1—C6—C5	-1.0 (6)	C15—C14—C19—C18	2.3 (6)
C2—C3—C4—C5	-1.2 (6)	C15—C16—C17—C18	-0.3 (7)
C2—C3—C4—C7	178.1 (4)	C16—C17—C18—C19	1.4 (7)
C3—C4—C5—C6	1.1 (6)	C17—C18—C19—C14	-2.4 (7)
C3—C4—C7—N1	175.0 (4)	C19—C14—C15—C16	-1.2 (6)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 $\cdots$ N4	0.80 (10)	1.93 (10)	2.566 (5)	137 (9)
N4—H4 $\cdots$ N1	0.81 (12)	2.40 (11)	2.803 (5)	112 (9)
N4—H4 $\cdots$ N2	0.81 (12)	1.86 (12)	2.566 (5)	145 (10)
C19—H19 $\cdots$ Br1 <sup>i</sup>	0.95	3.05	3.921 (4)	153
C9—H9 $\cdots$ Br1 <sup>i</sup>	0.95	3.14	4.014 (5)	153

Symmetry code: (i)  $-x+1/2, -y+1, z+1/2$ .

## 6-(4-Bromophenyl)-2,4-diphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazin-1-yl (2)

## Crystal data

$C_{20}H_{16}BrN_4$   
 $M_r = 392.28$   
 Orthorhombic,  $Pbca$   
 $a = 7.0881$  (3)  $\text{\AA}$   
 $b = 21.2183$  (11)  $\text{\AA}$   
 $c = 22.2028$  (9)  $\text{\AA}$   
 $V = 3339.2$  (3)  $\text{\AA}^3$   
 $Z = 8$   
 $F(000) = 1592$

$D_x = 1.561$   $\text{Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$   
 Cell parameters from 8857 reflections  
 $\theta = 2.7\text{--}29.5^\circ$   
 $\mu = 2.47$   $\text{mm}^{-1}$   
 $T = 123$  K  
 Plate, clear green  
 $0.15 \times 0.12 \times 0.06$  mm

## Data collection

STOE IPDS 2T  
 diffractometer  
 Radiation source: sealed X-ray tube, 12 x 0.4  
 mm long-fine focus  
 Plane graphite monochromator  
 Detector resolution: 6.67 pixels  $\text{mm}^{-1}$   
 rotation method scans  
 Absorption correction: integration  
 (X-RED32; Stoe & Cie, 2009)

$T_{\min} = 0.254$ ,  $T_{\max} = 0.620$   
 70879 measured reflections  
 3640 independent reflections  
 3397 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.128$   
 $\theta_{\max} = 27.0^\circ$ ,  $\theta_{\min} = 2.7^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -26 \rightarrow 26$   
 $l = -28 \rightarrow 28$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.076$   
 $S = 1.10$   
 3640 reflections  
 226 parameters  
 0 restraints

Primary atom site location: structure-invariant  
 direct methods  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 1.3621P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.72 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.65 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.68387 (3)	0.06162 (2)	0.45203 (2)	0.02595 (8)
N1	0.66003 (19)	0.27769 (7)	0.22407 (6)	0.0176 (3)
N2	0.63370 (19)	0.31170 (6)	0.17288 (6)	0.0177 (3)
N3	0.5658 (2)	0.22196 (6)	0.11776 (6)	0.0184 (3)
N4	0.59259 (19)	0.18478 (6)	0.16660 (6)	0.0177 (3)
C1	0.6208 (2)	0.21623 (7)	0.21812 (7)	0.0168 (3)
C2	0.5041 (2)	0.28635 (7)	0.12838 (8)	0.0196 (3)
H2A	0.5096	0.3112	0.0907	0.024*
H2B	0.3731	0.2870	0.1438	0.024*
C3	0.6287 (2)	0.17818 (7)	0.27390 (7)	0.0169 (3)
C4	0.6697 (2)	0.11391 (8)	0.27170 (8)	0.0203 (3)
H4	0.6898	0.0942	0.2338	0.024*
C5	0.6815 (2)	0.07845 (8)	0.32404 (8)	0.0219 (3)
H5	0.7076	0.0346	0.3221	0.026*
C6	0.6550 (2)	0.10777 (8)	0.37910 (7)	0.0188 (3)
C7	0.6106 (2)	0.17127 (8)	0.38283 (8)	0.0201 (3)
H7	0.5912	0.1908	0.4208	0.024*
C8	0.5950 (2)	0.20578 (7)	0.32989 (7)	0.0182 (3)
H8	0.5606	0.2490	0.3319	0.022*
C9	0.7103 (2)	0.37250 (7)	0.16939 (7)	0.0169 (3)
C10	0.8613 (2)	0.38881 (8)	0.20700 (8)	0.0203 (3)
H10	0.9078	0.3594	0.2356	0.024*
C11	0.9424 (3)	0.44801 (8)	0.20224 (8)	0.0230 (4)
H11	1.0434	0.4593	0.2282	0.028*
C12	0.8777 (3)	0.49117 (8)	0.15982 (8)	0.0230 (3)
H12	0.9363	0.5312	0.1560	0.028*
C13	0.7268 (3)	0.47506 (8)	0.12329 (8)	0.0236 (3)
H13	0.6818	0.5044	0.0944	0.028*
C14	0.6404 (2)	0.41659 (8)	0.12830 (8)	0.0204 (3)

H14	0.5344	0.4066	0.1039	0.024*
C15	0.5678 (2)	0.19397 (7)	0.06049 (7)	0.0173 (3)
C16	0.4641 (2)	0.21964 (8)	0.01255 (7)	0.0195 (3)
H16	0.3903	0.2565	0.0185	0.023*
C17	0.4698 (2)	0.19094 (8)	-0.04350 (7)	0.0218 (3)
H17	0.3998	0.2085	-0.0759	0.026*
C18	0.5761 (3)	0.13688 (8)	-0.05301 (8)	0.0236 (4)
H18	0.5797	0.1176	-0.0916	0.028*
C19	0.6775 (2)	0.11138 (8)	-0.00510 (8)	0.0238 (4)
H19	0.7506	0.0744	-0.0112	0.029*
C20	0.6733 (2)	0.13926 (8)	0.05142 (8)	0.0202 (3)
H20	0.7420	0.1212	0.0838	0.024*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.02689 (12)	0.02657 (12)	0.02438 (12)	-0.00268 (6)	-0.00495 (6)	0.00843 (6)
N1	0.0164 (6)	0.0181 (6)	0.0184 (7)	0.0001 (5)	0.0007 (5)	0.0015 (5)
N2	0.0176 (6)	0.0169 (6)	0.0186 (6)	-0.0016 (5)	-0.0021 (5)	0.0006 (5)
N3	0.0206 (7)	0.0166 (6)	0.0180 (6)	0.0007 (5)	-0.0028 (5)	-0.0001 (5)
N4	0.0166 (6)	0.0183 (6)	0.0181 (6)	0.0002 (5)	-0.0011 (5)	0.0017 (5)
C1	0.0105 (7)	0.0190 (7)	0.0207 (8)	0.0002 (6)	0.0004 (6)	-0.0008 (6)
C2	0.0171 (7)	0.0178 (7)	0.0238 (8)	0.0009 (6)	-0.0038 (6)	-0.0009 (6)
C3	0.0106 (7)	0.0190 (7)	0.0211 (8)	-0.0020 (6)	-0.0005 (6)	0.0008 (6)
C4	0.0201 (8)	0.0200 (8)	0.0209 (8)	-0.0002 (6)	-0.0003 (6)	-0.0028 (6)
C5	0.0198 (8)	0.0176 (7)	0.0282 (9)	0.0005 (6)	-0.0013 (6)	0.0011 (7)
C6	0.0148 (7)	0.0219 (8)	0.0197 (8)	-0.0033 (6)	-0.0021 (6)	0.0053 (6)
C7	0.0180 (8)	0.0215 (8)	0.0209 (8)	-0.0017 (6)	0.0008 (6)	-0.0009 (6)
C8	0.0156 (7)	0.0176 (7)	0.0213 (8)	-0.0010 (6)	0.0008 (6)	-0.0002 (6)
C9	0.0156 (7)	0.0150 (7)	0.0202 (8)	0.0003 (5)	0.0031 (6)	-0.0009 (6)
C10	0.0200 (8)	0.0199 (8)	0.0210 (8)	-0.0003 (6)	-0.0020 (6)	0.0014 (6)
C11	0.0211 (8)	0.0223 (8)	0.0256 (9)	-0.0024 (6)	-0.0032 (7)	-0.0015 (6)
C12	0.0240 (8)	0.0166 (7)	0.0284 (9)	-0.0026 (6)	0.0022 (7)	-0.0005 (6)
C13	0.0246 (8)	0.0193 (8)	0.0268 (9)	0.0030 (7)	-0.0019 (7)	0.0019 (7)
C14	0.0189 (8)	0.0191 (8)	0.0231 (8)	0.0002 (6)	-0.0033 (6)	-0.0005 (6)
C15	0.0153 (7)	0.0186 (7)	0.0180 (7)	-0.0044 (6)	-0.0001 (6)	0.0004 (6)
C16	0.0169 (7)	0.0190 (7)	0.0227 (8)	-0.0025 (6)	-0.0022 (6)	0.0011 (6)
C17	0.0197 (8)	0.0255 (8)	0.0203 (8)	-0.0049 (7)	-0.0043 (6)	0.0031 (6)
C18	0.0249 (9)	0.0266 (9)	0.0193 (8)	-0.0057 (7)	0.0017 (6)	-0.0052 (6)
C19	0.0234 (9)	0.0214 (8)	0.0266 (9)	-0.0015 (6)	0.0018 (7)	-0.0035 (7)
C20	0.0185 (8)	0.0195 (8)	0.0227 (8)	-0.0014 (6)	-0.0027 (6)	0.0008 (6)

*Geometric parameters (Å, °)*

Br1—C6	1.9034 (16)	C9—C10	1.401 (2)
N1—N2	1.3592 (19)	C9—C14	1.398 (2)
N1—C1	1.340 (2)	C10—H10	0.9500
N2—C2	1.452 (2)	C10—C11	1.385 (2)



N2—C9	1.402 (2)	C11—H11	0.9500
N3—N4	1.3544 (18)	C11—C12	1.392 (2)
N3—C2	1.454 (2)	C12—H12	0.9500
N3—C15	1.404 (2)	C12—C13	1.385 (3)
N4—C1	1.339 (2)	C13—H13	0.9500
C1—C3	1.479 (2)	C13—C14	1.388 (2)
C2—H2A	0.9900	C14—H14	0.9500
C2—H2B	0.9900	C15—C16	1.404 (2)
C3—C4	1.395 (2)	C15—C20	1.395 (2)
C3—C8	1.395 (2)	C16—H16	0.9500
C4—H4	0.9500	C16—C17	1.386 (2)
C4—C5	1.387 (2)	C17—H17	0.9500
C5—H5	0.9500	C17—C18	1.389 (3)
C5—C6	1.385 (2)	C18—H18	0.9500
C6—C7	1.386 (2)	C18—C19	1.393 (3)
C7—H7	0.9500	C19—H19	0.9500
C7—C8	1.389 (2)	C19—C20	1.388 (2)
C8—H8	0.9500	C20—H20	0.9500
C1—N1—N2	113.94 (13)	C14—C9—N2	120.97 (15)
N1—N2—C2	117.33 (13)	C14—C9—C10	119.65 (15)
N1—N2—C9	118.79 (13)	C9—C10—H10	120.1
C9—N2—C2	123.25 (13)	C11—C10—C9	119.71 (15)
N4—N3—C2	117.38 (13)	C11—C10—H10	120.1
N4—N3—C15	118.51 (13)	C10—C11—H11	119.6
C15—N3—C2	123.22 (13)	C10—C11—C12	120.76 (16)
C1—N4—N3	114.49 (13)	C12—C11—H11	119.6
N1—C1—C3	116.15 (14)	C11—C12—H12	120.4
N4—C1—N1	126.88 (15)	C13—C12—C11	119.24 (16)
N4—C1—C3	116.66 (14)	C13—C12—H12	120.4
N2—C2—N3	105.55 (12)	C12—C13—H13	119.5
N2—C2—H2A	110.6	C12—C13—C14	120.96 (16)
N2—C2—H2B	110.6	C14—C13—H13	119.5
N3—C2—H2A	110.6	C9—C14—H14	120.2
N3—C2—H2B	110.6	C13—C14—C9	119.61 (15)
H2A—C2—H2B	108.8	C13—C14—H14	120.2
C4—C3—C1	120.79 (15)	N3—C15—C16	121.15 (14)
C8—C3—C1	120.70 (14)	C20—C15—N3	119.24 (14)
C8—C3—C4	118.51 (15)	C20—C15—C16	119.60 (15)
C3—C4—H4	119.6	C15—C16—H16	120.2
C5—C4—C3	120.90 (16)	C17—C16—C15	119.68 (15)
C5—C4—H4	119.6	C17—C16—H16	120.2
C4—C5—H5	120.4	C16—C17—H17	119.5
C6—C5—C4	119.19 (15)	C16—C17—C18	121.01 (15)
C6—C5—H5	120.4	C18—C17—H17	119.5
C5—C6—Br1	120.35 (13)	C17—C18—H18	120.5
C5—C6—C7	121.36 (15)	C17—C18—C19	119.00 (15)
C7—C6—Br1	118.28 (13)	C19—C18—H18	120.5

C6—C7—H7	120.7	C18—C19—H19	119.5
C6—C7—C8	118.69 (15)	C20—C19—C18	120.90 (16)
C8—C7—H7	120.7	C20—C19—H19	119.5
C3—C8—H8	119.4	C15—C20—H20	120.1
C7—C8—C3	121.26 (14)	C19—C20—C15	119.79 (16)
C7—C8—H8	119.4	C19—C20—H20	120.1
C10—C9—N2	119.37 (14)		

*Hydrogen-bond geometry* (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C10—H10 $\cdots$ N1 <sup>i</sup>	0.95	2.65	3.519 (2)	153

Symmetry code: (i)  $x+1/2, y, -z+1/2$ .**5-Anilino-3-(4-bromophenyl)-1-phenyl-1*H*-1,2,4-triazole (3)***Crystal data*C<sub>20</sub>H<sub>15</sub>BrN<sub>4</sub> $M_r = 391.27$ Orthorhombic, *Pbca* $a = 7.7989$  (9) Å $b = 18.971$  (3) Å $c = 22.455$  (4) Å $V = 3322.4$  (8) Å<sup>3</sup> $Z = 8$  $F(000) = 1584$  $D_x = 1.564$  Mg m<sup>-3</sup>Mo *K*α radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1652 reflections

 $\theta = 2.8$ – $23.1^\circ$  $\mu = 2.48$  mm<sup>-1</sup> $T = 100$  K

Plank, clear light yellow

0.32 × 0.16 × 0.1 mm

*Data collection*Bruker X8 Kappa APEXII  
diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 8 pixels mm<sup>-1</sup>fine slicing  $\omega$  and  $\varphi$  scansAbsorption correction: multi-scan  
(SADABS; Bruker, 2015) $T_{\min} = 0.583$ ,  $T_{\max} = 0.746$ 

19450 measured reflections

3999 independent reflections

2708 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.098$  $\theta_{\max} = 28.0^\circ$ ,  $\theta_{\min} = 3.0^\circ$  $h = -6 \rightarrow 10$  $k = -24 \rightarrow 25$  $l = -29 \rightarrow 29$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.056$  $wR(F^2) = 0.126$  $S = 1.05$ 

3999 reflections

229 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 6.8615P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 1.46$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.84$  e Å<sup>-3</sup>*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	1.11136 (5)	0.36858 (2)	0.25928 (2)	0.02548 (14)
N1	0.7607 (4)	0.57251 (19)	0.48352 (14)	0.0201 (7)
N2	0.6739 (4)	0.58069 (18)	0.53638 (14)	0.0179 (7)
N3	0.7073 (4)	0.46533 (19)	0.52531 (15)	0.0193 (7)
N4	0.5536 (4)	0.5068 (2)	0.61156 (16)	0.0249 (8)
H4	0.487 (6)	0.549 (3)	0.626 (2)	0.030*
C1	0.7806 (5)	0.5035 (2)	0.48020 (17)	0.0178 (8)
C2	0.6420 (5)	0.5157 (2)	0.55932 (17)	0.0191 (9)
C3	0.8667 (4)	0.4696 (2)	0.42895 (17)	0.0183 (8)
C4	0.8470 (5)	0.3977 (2)	0.41832 (18)	0.0195 (9)
H4A	0.7837	0.3694	0.4454	0.023*
C5	0.9206 (5)	0.3673 (2)	0.36779 (18)	0.0216 (8)
H5	0.9072	0.3184	0.3601	0.026*
C6	1.0134 (4)	0.4094 (2)	0.32914 (17)	0.0174 (8)
C7	1.0376 (5)	0.4806 (2)	0.33950 (18)	0.0220 (9)
H7	1.1034	0.5085	0.3128	0.026*
C8	0.9637 (5)	0.5105 (2)	0.38984 (18)	0.0203 (9)
H8	0.9795	0.5593	0.3977	0.024*
C9	0.6007 (5)	0.6479 (2)	0.55219 (17)	0.0176 (8)
C10	0.5417 (5)	0.6904 (2)	0.50640 (18)	0.0216 (9)
H10	0.5527	0.6759	0.4661	0.026*
C11	0.4660 (5)	0.7548 (2)	0.5203 (2)	0.0266 (10)
H11	0.4264	0.7849	0.4893	0.032*
C12	0.4485 (5)	0.7750 (2)	0.5792 (2)	0.0274 (10)
H12	0.3939	0.8184	0.5886	0.033*
C13	0.5099 (5)	0.7328 (2)	0.6240 (2)	0.0269 (10)
H13	0.4985	0.7471	0.6643	0.032*
C14	0.5883 (5)	0.6694 (2)	0.61057 (18)	0.0219 (9)
H14	0.6334	0.6407	0.6415	0.026*
C15	0.5186 (5)	0.4420 (2)	0.64132 (19)	0.0237 (9)
C16	0.3863 (5)	0.4433 (3)	0.68331 (19)	0.0276 (10)
H16	0.3253	0.4858	0.6904	0.033*
C17	0.3441 (6)	0.3832 (3)	0.7144 (2)	0.0313 (11)
H17	0.2541	0.3846	0.7429	0.038*
C18	0.4312 (6)	0.3214 (3)	0.7045 (2)	0.0302 (11)
H18	0.3998	0.2798	0.7253	0.036*
C19	0.5661 (6)	0.3199 (2)	0.66360 (19)	0.0268 (10)
H19	0.6285	0.2775	0.6576	0.032*
C20	0.6096 (5)	0.3798 (2)	0.63171 (18)	0.0249 (9)
H20	0.7006	0.3785	0.6036	0.030*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0214 (2)	0.0350 (3)	0.0200 (2)	0.00676 (19)	0.00321 (17)	-0.00357 (19)

N1	0.0195 (16)	0.023 (2)	0.0179 (17)	0.0000 (14)	0.0018 (14)	-0.0011 (14)
N2	0.0199 (16)	0.0151 (19)	0.0186 (17)	0.0001 (13)	0.0037 (13)	-0.0002 (14)
N3	0.0164 (16)	0.019 (2)	0.0223 (18)	-0.0010 (14)	0.0001 (13)	-0.0017 (15)
N4	0.0240 (18)	0.023 (2)	0.0283 (19)	0.0022 (15)	0.0046 (15)	0.0009 (16)
C1	0.0120 (18)	0.024 (2)	0.0180 (19)	-0.0008 (16)	-0.0004 (15)	0.0017 (17)
C2	0.0179 (19)	0.020 (2)	0.019 (2)	0.0022 (16)	-0.0001 (15)	0.0007 (16)
C3	0.0143 (18)	0.022 (2)	0.0182 (19)	0.0018 (16)	-0.0024 (15)	-0.0003 (16)
C4	0.0168 (18)	0.018 (2)	0.023 (2)	0.0009 (16)	0.0009 (15)	0.0015 (17)
C5	0.0208 (19)	0.015 (2)	0.029 (2)	-0.0001 (17)	0.0007 (16)	-0.0008 (18)
C6	0.0104 (17)	0.024 (2)	0.0179 (19)	0.0058 (16)	0.0000 (15)	-0.0016 (16)
C7	0.0167 (18)	0.025 (3)	0.025 (2)	0.0012 (17)	0.0040 (16)	0.0028 (18)
C8	0.0205 (19)	0.015 (2)	0.025 (2)	-0.0013 (17)	-0.0007 (17)	-0.0007 (17)
C9	0.0143 (17)	0.013 (2)	0.026 (2)	-0.0047 (15)	-0.0005 (16)	0.0029 (15)
C10	0.0191 (19)	0.025 (3)	0.021 (2)	-0.0003 (17)	-0.0007 (16)	-0.0001 (17)
C11	0.022 (2)	0.023 (3)	0.035 (3)	-0.0014 (18)	-0.0046 (18)	0.012 (2)
C12	0.024 (2)	0.013 (2)	0.046 (3)	0.0018 (17)	0.0001 (19)	-0.002 (2)
C13	0.027 (2)	0.026 (3)	0.027 (2)	-0.0007 (19)	-0.0026 (18)	-0.0048 (19)
C14	0.021 (2)	0.021 (2)	0.024 (2)	-0.0017 (17)	-0.0023 (17)	0.0037 (17)
C15	0.025 (2)	0.023 (3)	0.023 (2)	-0.0075 (18)	-0.0061 (18)	0.0047 (18)
C16	0.027 (2)	0.029 (3)	0.027 (2)	0.000 (2)	0.0024 (19)	-0.0022 (19)
C17	0.032 (2)	0.037 (3)	0.025 (2)	-0.005 (2)	0.0035 (19)	0.001 (2)
C18	0.038 (3)	0.026 (3)	0.026 (2)	-0.009 (2)	-0.0014 (19)	0.0046 (19)
C19	0.033 (2)	0.017 (2)	0.030 (2)	-0.0013 (18)	-0.0049 (18)	-0.0012 (18)
C20	0.023 (2)	0.029 (3)	0.022 (2)	-0.0040 (19)	-0.0010 (17)	-0.0018 (17)

*Geometric parameters (Å, °)*

Br1—C6	1.909 (4)	C9—C14	1.376 (6)
N1—N2	1.375 (4)	C10—H10	0.9500
N1—C1	1.321 (5)	C10—C11	1.392 (6)
N2—C2	1.358 (5)	C11—H11	0.9500
N2—C9	1.441 (5)	C11—C12	1.384 (6)
N3—C1	1.370 (5)	C12—H12	0.9500
N3—C2	1.326 (5)	C12—C13	1.373 (6)
N4—H4	1.00 (5)	C13—H13	0.9500
N4—C2	1.371 (5)	C13—C14	1.382 (6)
N4—C15	1.426 (6)	C14—H14	0.9500
C1—C3	1.479 (5)	C15—C16	1.398 (6)
C3—C4	1.393 (6)	C15—C20	1.394 (6)
C3—C8	1.395 (6)	C16—H16	0.9500
C4—H4A	0.9500	C16—C17	1.376 (6)
C4—C5	1.397 (6)	C17—H17	0.9500
C5—H5	0.9500	C17—C18	1.374 (7)
C5—C6	1.384 (6)	C18—H18	0.9500
C6—C7	1.384 (6)	C18—C19	1.396 (6)
C7—H7	0.9500	C19—H19	0.9500
C7—C8	1.390 (6)	C19—C20	1.385 (6)
C8—H8	0.9500	C20—H20	0.9500

C9—C10	1.386 (5)		
C1—N1—N2	102.6 (3)	C14—C9—C10	120.7 (4)
N1—N2—C9	120.5 (3)	C9—C10—H10	120.5
C2—N2—N1	108.4 (3)	C9—C10—C11	119.1 (4)
C2—N2—C9	129.5 (3)	C11—C10—H10	120.5
C2—N3—C1	101.8 (3)	C10—C11—H11	120.0
C2—N4—H4	116 (3)	C12—C11—C10	119.9 (4)
C2—N4—C15	127.1 (4)	C12—C11—H11	120.0
C15—N4—H4	116 (3)	C11—C12—H12	119.9
N1—C1—N3	115.7 (4)	C13—C12—C11	120.3 (4)
N1—C1—C3	121.9 (4)	C13—C12—H12	119.9
N3—C1—C3	122.3 (4)	C12—C13—H13	119.9
N2—C2—N4	121.9 (4)	C12—C13—C14	120.2 (4)
N3—C2—N2	111.4 (3)	C14—C13—H13	119.9
N3—C2—N4	126.7 (4)	C9—C14—C13	119.8 (4)
C4—C3—C1	120.6 (4)	C9—C14—H14	120.1
C4—C3—C8	119.7 (4)	C13—C14—H14	120.1
C8—C3—C1	119.6 (4)	C16—C15—N4	116.2 (4)
C3—C4—H4A	120.0	C20—C15—N4	124.1 (4)
C3—C4—C5	119.9 (4)	C20—C15—C16	119.7 (4)
C5—C4—H4A	120.0	C15—C16—H16	119.9
C4—C5—H5	120.5	C17—C16—C15	120.3 (4)
C6—C5—C4	119.0 (4)	C17—C16—H16	119.9
C6—C5—H5	120.5	C16—C17—H17	119.8
C5—C6—Br1	119.4 (3)	C18—C17—C16	120.4 (4)
C5—C6—C7	122.0 (4)	C18—C17—H17	119.8
C7—C6—Br1	118.7 (3)	C17—C18—H18	120.1
C6—C7—H7	120.7	C17—C18—C19	119.7 (4)
C6—C7—C8	118.6 (4)	C19—C18—H18	120.1
C8—C7—H7	120.7	C18—C19—H19	119.7
C3—C8—H8	119.7	C20—C19—C18	120.5 (4)
C7—C8—C3	120.7 (4)	C20—C19—H19	119.7
C7—C8—H8	119.7	C15—C20—H20	120.4
C10—C9—N2	117.7 (4)	C19—C20—C15	119.3 (4)
C14—C9—N2	121.7 (4)	C19—C20—H20	120.4

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C14—H14 $\cdots$ Br1 <sup>i</sup>	0.95	2.99	3.814 (4)	146 (1)
C10—H10 $\cdots$ C20 <sup>ii</sup>	0.95	2.75	3.575 (5)	146 (1)
C17—H17 $\cdots$ C19 <sup>iii</sup>	0.95	2.84	3.694 (6)	150 (1)

Symmetry codes: (i)  $-x+2, -y+1, -z+1$ ; (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $x-1/2, y, -z+3/2$ .