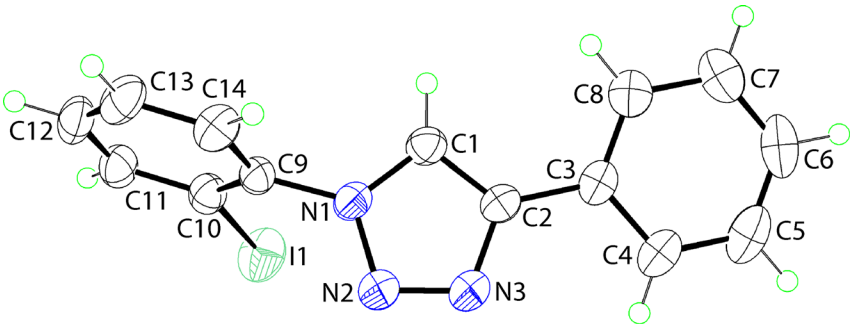
Ignez Caracelli*, Wystan K. O. Teixeira, Danilo Yano de Albuquerque, Ricardo S. Schwab and Edward R. T. Tiekink

The crystal structure of 1-(2-iodophenyl)-4-phenyl-1*H*-1,2,3-triazole, $C_{14}H_{10}IN_3$



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Abstract

$C_{14}H_{10}IN_3$, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.0778(6) Å, b = 11.1909(10) Å, c = 14.3114(12) Å, V = 1293.72(19) Å^3, Z = 4, $R_{gt}(F)$ = 0.0312, $wR_{ref}(F^2)$ = 0.0790, T = 290 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless irregular
Size:	0.36 × 0.22 × 0.08 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.46 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9322, 2639, 0.056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2397
$N(param)_{refined}$:	163
Programs:	SADABS [1], Bruker [2], SIR2014 [3], SHELX [4], WinGX/ORTEP [5]

Source of material

To a solution of 1-azido-2-iodobenzene (0.15 mmol, 1.0 equiv.) and phenylacetylene (0.15 mmol, 1.0 equiv.) in methanol (3 mL) was added CuF_2 (60.6 mg, 0.3 mmol, 2.0 equiv.). The reaction was placed in a microwave reactor and the temperature was kept at 378 K for 30 min. The solvent was removed under vacuum and the crude product was purified by flash chromatography using silica gel (*n*-hexane-EtOAc, 8:2) affording the 1-(2-iodophenyl)-4-phenyl-1*H*-1,2,3-triazole (I). Crystals were obtained by slow evaporation from a dichloromethane solution of (I) and characterised by X-ray crystallography.

Experimental details

The carbon-bound H-atoms were placed in calculated positions (C–H = 0.93 Å) and were included in the refinement using the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq} of the parent (C). The absolute structure was established by refinement of the Flack parameter: 0.01(2) from 933 quotients using the Parsons' method [6].

***Corresponding author: Ignez Caracelli,** Departmento de Física, BioMat, Universidade Federal de São Carlos, C. P. 676 13565-905 São Carlos SP, Brazil, E-mail: ignez@df.ufscar.br
Wystan K. O. Teixeira, Danilo Yano de Albuquerque and Ricardo S. Schwab, Departamento de Química, Laboratório de Síntese, Catálise e Modelagem Molecular (SintCatMol), CERSusChem, Universidade Federal de São Carlos, C. P. 676, 13565-905 São Carlos, SP, Brazil, E-mail: wystan852@gmail.com (W.K.O. Teixeira), danilo_ya@hotmail.com (D.Y. de Albuquerque), rschwab@ufscar.br (R.S. Schwab)
Edward R. T. Tiekink, Research Centre for Crystalline Materials, School of Medical and Life Sciences, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, E-mail: edwardt@sunway.edu.my. https://orcid.org/0000-0003-1401-1520

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4836 (6)	0.6265 (4)	0.5549 (4)	0.0355 (11)
H1	0.407661	0.683651	0.574636	0.043*
C2	0.5744 (6)	0.6270 (4)	0.4743 (3)	0.0323 (11)
C3	0.5759 (6)	0.7139 (5)	0.3971 (3)	0.0339 (11)
C4	0.6514 (7)	0.6845 (5)	0.3119 (4)	0.0461 (13)
H4	0.703740	0.610976	0.305167	0.055*
C5	0.6486 (9)	0.7631 (7)	0.2386 (4)	0.0603 (18)
H5	0.698820	0.742408	0.182370	0.072*
C6	0.5721 (9)	0.8728 (6)	0.2473 (5)	0.0604 (18)
H6	0.569121	0.925264	0.196884	0.072*
C7	0.5001 (8)	0.9041 (6)	0.3311 (4)	0.0532 (16)
H7	0.450221	0.978492	0.337640	0.064*
C8	0.5018 (7)	0.8247 (5)	0.4060 (4)	0.0425 (13)
H8	0.452923	0.846364	0.462359	0.051*
C9	0.4663 (6)	0.4805 (4)	0.6869 (3)	0.0324 (11)
C10	0.3563 (7)	0.3857 (5)	0.6890 (3)	0.0365 (11)
C11	0.2959 (7)	0.3471 (5)	0.7747 (4)	0.0404 (12)
H11	0.221803	0.283554	0.777409	0.049*
C12	0.3459 (7)	0.4032 (5)	0.8560 (4)	0.0452 (13)
H12	0.304888	0.376979	0.913166	0.054*
C13	0.4548 (7)	0.4967 (6)	0.8535 (4)	0.0468 (14)
H13	0.487990	0.533606	0.908679	0.056*
C14	0.5150 (7)	0.5360 (5)	0.7687 (4)	0.0423 (13)
H14	0.588430	0.599949	0.766623	0.051*
N1	0.5279 (6)	0.5256 (4)	0.5996 (3)	0.0354 (10)
N2	0.6421 (6)	0.4650 (4)	0.5499 (3)	0.0512 (13)
N3	0.6709 (6)	0.5276 (4)	0.4741 (3)	0.0482 (12)
I1	0.27255 (6)	0.30037 (4)	0.56765 (3)	0.05942 (17)

Comment

1,2,3-Triazoles are a privileged class of heterocyclic compounds as they find applications in several major technological areas, especially in drug discovery [7]. In recent years, several synthetic strategies have been reported for the synthesis of compounds containing fused triazoles [8]. In particular, 2-iodo-phenyl-1,2,3-triazole (I) has been used as an important building block for the construction of polycyclic fused triazole heterocycles. A particularly interesting approach for the synthesis of the polycyclic triazolic core construction was reported by Kumar and co-workers [9]. In this work, the homo-condensation of two molecules of (I), via a palladium catalyzed domino coupling reaction, furnished triazolo[1,5-*f*] phenanthridines. Later, the same group developed a new copper-mediated, one-pot tandem synthesis of 1,2,3-triazolo-cinnolinone from (I) and terminal alkynes [10]. It was in the context of such considerations that the title compound, (I), previously reported [11], was investigated crystallographically.

The molecular structure of (I) is shown in the figure (50% displacement ellipsoids) and comprises a central triazole ring flanked by a N2-bound 2-iodo-phenyl ring and a C2-bound phenyl ring. The five-membered ring is strictly planar with maximum deviations of ±0.005(5) Å for the N3 and C2 atoms. The 2-iodo-phenyl ring forms a dihedral angle of 74.1(3)° with the triazole ring, a conformation which minimises the repulsion between the iodine atom with the central ring. The triazole ring forms a dihedral angle of 13.4(3)° with the C2-appended phenyl ring, consistent with a small twist. The dihedral angle between the phenyl rings is 64.3(3)° indicating a conrotatory relationship between the outer rings. Within the five-membered ring, there is a clear indication of considerable delocalisation of π-electron density, in particular in the shortening of the N1–N2 [1.348(6) Å], C1–N1 [1.347(7) Å] and C2–N3 [1.357(6) Å] bond lengths and the lengthening of the N2–N3 [1.313(6) Å] and C1–C2 [1.367(7) Å] bonds.

A search of the crystallographic literature for related structures did not reveal many analogues despite the preponderance of the triazole scaffold. For example, there were no direct analogues of the triazole-N2-bound 2-iodo-phenyl residue. However, when the substitution pattern of the central ring in (I) was held constant, and the C-bound group was constrained to be a phenyl ring, seven direct analogues were found where the iodine atom in the 2-position was substituted by another residue, hereafter designated as Y. Three examples of relatively simple substituents were apparent, i.e. Y = NO_2 [12], C(=O)OH [13] and Ph [14] which exhibited triazole/2-YC_6H_4 dihedral angles of 56.06(9), 78.18(6) and 57.27(7)°, respectively. Two organoselenium examples are known, namely Y = SeC_6H_4OMe-2 [15] and $SeC_6H_2Me_3$-2,4,6 [16], which had similar dihedral angles of 42.40(7)° and 47.57(6)°, respectively. The remaining two structures are phosphane derivatives. In the first of these, Y = PPh_2 with the two molecules comprising the asymmetric-unit having triazole/2-YC_6H_4 dihedral angles of 44.44(6) and 52.70(6)° [17]. A more complicated molecule is found in the last example whereby two N-bound phenyl rings are bridged in the 2-position of each by a single PPh residue [18]. The two independent dihedral angles span a large range, i.e. 47.39(6) –85.20(6)°. This last consideration suggests other factors come into play, over and above steric congestion, to dictate the magnitude of the triazole/2-YC_6H_4 dihedral angle in these species.

The most prominent directional interaction in the crystal of (I) is a (2-iodo-phenyl)-C–H$\cdots\pi$(phenyl) contact [C11–H11$\cdots$Cg(C3–C8)^i: H11$\cdots$Cg(C3–C8)^i = 2.63 Å with angle at H11 = 148° for symmetry operation (i): 1/2 – *x*, 1 – *y*, 1/2 + *z*] which gives rise to a supramolecular layer in the

ab-plane. The connections between layers are type II I1···N2 halogen bonding contacts [C10–I1···N2^{ii} = 3.572(5) Å with angle at I1 = 149.88(15)° for (ii): $-1/2 + x$, $1/2 - y$, $1 - z$]. This separation is longer than the nominal van der Waals radii of 3.53 Å [19].

Further insight into the molecular packing was achieved by calculating the contributions to the Hirshfeld surface following established methods [20] and CrystalExplorer17 [21]. This analysis revealed that 92.6% of all contacts involve H atoms. However, the major contribution to the surface contacts were of the type C···H/H···C [34.2%] followed by H···H [28.1%], I···H/H···I [16.2%] and N···H/H···N [14.1%] contacts.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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