

Synthesis of bis(benzotriazol-1-yl)methane derivatives by cobalt-catalyzed formation of C-C bonds

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Abstract: The compounds bis(benzotriazol-1-yl)phenylmethane and bis(benzotriazol-1-yl)pyridin-2-ylmethane were prepared by reacting (benzotriazol-1-yl)methanone and benzaldehyde or pyridine-2-carboxaldehyde using CoCl₂ as catalyst under neat conditions. The products were characterized spectroscopically and the solid-state structures were ascertained by single-crystal X-ray diffraction.

Keywords: 1H-benzotriazole, (benzotriazol-1-yl)methanone, cobalt catalysis, C-C bond formation.

1. Introduction

The first example of CoCl₂-catalyzed reaction between 1,1'-carbonyldiazoles and carbonyl compounds was reported by Thé and Peterson in 1973, obtaining 2,2-bis(pirazol-1-yl)propane from bis(pyrazol-1-yl)methanone and acetone [1]. The study was extended to several other ketones and aldehydes and to methyl-substituted bis(pyrazol-1-yl)methanone derivatives, with the isolation of the corresponding bis(pirazol-1-yl)alkanes by elimination of CO₂. A reaction mechanism was subsequently proposed [2], indicating the crucial role of the coordination of the metal centre to the free nitrogen atoms for the activation of the N-C(O) bonds in the bis(pyrazol-1-yl)methanone skeleton. The synthetic approach was then extended by other research groups to functionalized aldehydes [3], with the aim of preparing pyrazole-based ligands to be applied in coordination [4], bioinorganic [5], organometallic chemistry and homogeneous catalysis [6].

To the best of our knowledge, the cobalt-catalyzed reaction was never applied for the synthesis of bis(benzotriazol-1-yl)methane derivatives, and species such as bis(benzotriazol-1-yl)phenylmethane are actually obtained following different synthetic approaches with variable selectivity [7]. Benzotriazole is considered an ideal synthetic auxiliary in organic chemistry [8] and it is present as donor moiety in heteroscorpionate ligands [9]. These outcomes prompted us to start an investigation on the possible use of bis(benzotriazol-1-yl)methanone as reactant, and in this communication we report the straightforward preparation of bis(benzotriazol-1-yl)phenylmethane and bis(benzotriazol-1-yl)pyridin-2-ylmethane from bis(benzotriazol-1-yl)methanone and the proper aldehyde, using CoCl₂ as catalyst under neat conditions. The products were characterized spectroscopically and their solid structures were ascertained by single-crystal X-ray diffraction.

2. Methods

Commercial solvents (Aldrich) were purified following literature methods [10]. 1H-benzotriazole, triphosgene, triethylamine, benzaldehyde and pyridine-2-carboxaldehyde were Aldrich products, used as received. Anhydrous CoCl₂ was obtained from the corresponding hexahydrated salt (Alfa Aesar) using an Abderhalden's drying pistol heated with refluxing toluene

and in the presence of P_4O_{10} . Reactions involving triphosgene were carried out in a glove-box (MBraun Labstar, N_2 atmosphere) for safety reasons.

The compound bis(benzotriazol-1-yl)methanone was synthesized by modifying a reported procedure and avoiding the use of phosgene [11]. In a jacketed reactor cooled down with cold nitrogen gas 1.246 g of triphosgene (4.2 mmol) were placed and dissolved in 50 mL of dry diethyl ether. Triethylamine (3.5 mL, 25.2 mmol) was added, then 3.002 g (25.2 mmol) of 1H-benzotriazole were slowly introduced into the reactor when the temperature had reached $-70\text{ }^\circ\text{C}$. The solution was left under stirring and allowed to slowly reach room temperature. The following work-up was conducted outside the glove box. The white precipitate, mostly composed by the product and tetraethylammonium chloride, was filtered and dried in vacuo. The solid was then dissolved in dichloromethane (40 mL) and washed with distilled water ($2 \times 20\text{ mL}$). The aqueous phase was washed three times with 15 mL of dichloromethane and the organic fractions were collected together and dried with Na_2SO_4 . The solution was filtered, the solvent was concentrated in vacuo and diethylether (10 mL) was added. The white solid thus obtained was filtered, washed with diethylether and dried under vacuum. Yield: 85%. Characterization data agree with those reported in the literature [11].

Synthesis of bis(benzotriazol-1-yl)phenylmethane. In a Schlenk apparatus 0.528 g (2.0 mmol) of bis(benzotriazol-1-yl)methanone, 0.20 mL (2.0 mmol) of benzaldehyde and a catalytic amount (ca. 0.004 g) of $CoCl_2$ were added. The solids were heated to $150\text{ }^\circ\text{C}$ until they melted, and the formation of CO_2 was observed. The reaction mixture was stirred at this temperature for 2 hours, and then it was allowed to cool to room temperature. The solids were dissolved in dichloromethane (20 mL) and the solution was washed with distilled water (20 mL). In order to increase the yield, the aqueous phase was subsequently extracted with 15 mL of dichloromethane three times and all the organic fractions were collected and dried with Na_2SO_4 . The organic phase was filtered, the solvent was concentrated in vacuo and diethylether (10 mL) was added. The white solid that separated was collected by filtration, washed with diethylether and dried under vacuum. Crystals suitable for X-ray diffraction were obtained from slow evaporation of dichloromethane solutions.

Synthesis of bis(benzotriazol-1-yl)pyridin-2-ylmethane. The compound was obtained on the basis of the method previously described for bis(benzotriazol-1-yl)phenylmethane, using pyridine-2-carboxyaldehyde (0.19 mL, 2.0 mmol) as reactant. The temperature was kept at $85\text{ }^\circ\text{C}$ to avoid decomposition. When the evolution of CO_2 terminated the reaction mixture was allowed to cool at room temperature. The product was dissolved with hot cyclohexane (75 mL) and the yellow solution was concentrated by rotary evaporation. The product was isolated as light orange solid by addition of diethylether (10 mL), filtered and dried under vacuum. Crystals suitable for X-ray diffraction were obtained by slowly cooling hot cyclohexane solutions.

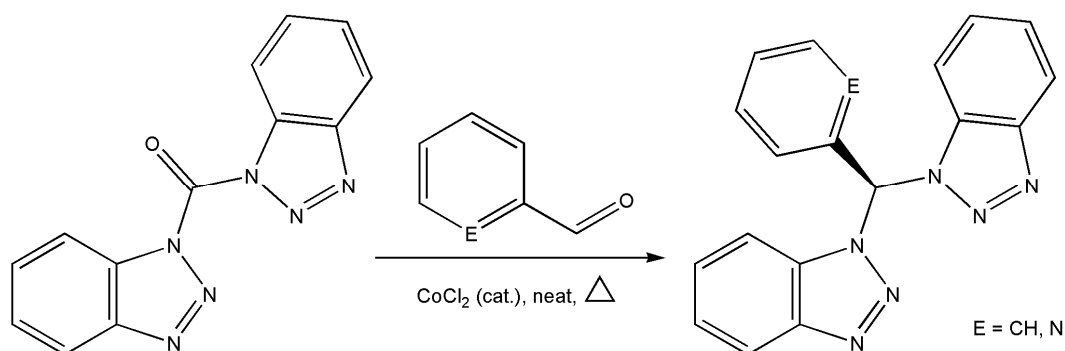
Elemental analyses (C, H, N) were carried out at the University of Padua using a Fison EA1108 microanalyzer. Melting point measurements were performed with a modified Falc 360 D apparatus equipped with a video recording device. IR spectra were collected in the range $4000 - 400\text{ cm}^{-1}$ using a Perkin-Elmer Spectrum One spectrophotometer. The mono- and bidimensional nuclear magnetic resonance (NMR) spectra were collected for $CDCl_3$ solutions employing Bruker Avance 300 and Avance 400 instruments operating respectively at 300.13 MHz and 400.13 MHz of 1H resonance. 1H and ^{13}C NMR spectra are referred to the partially deuterated fraction of the solvent, itself referred to tetramethylsilane.

Crystallographic data were collected at CACTI (Univ. of Vigo) at 100 K (CryoStream 800) using a Bruker D8 Venture Photon 100 CMOS detector and Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) generated by a Incoatec high brilliance $I\mu S$ microsource. The software APEX3 [12] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [12] for integration of intensity of reflections, and SADABS [12] for scaling and empirical absorption correction. The

crystallographic treatment was performed with the Oscale program [13], solved using the SHELXT program [14]. The structure was subsequently refined by a full-matrix least-squares based on F^2 using the SHELXL program [15]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters.

3. Results and Discussion

The CoCl_2 -catalyzed reaction between bis(benzotriazol-1-yl)methanone and benzaldehyde or pyridine-2-carboxaldehyde is depicted in Scheme 1. Characterization data of the products bis(benzotriazol-1-yl)phenylmethane and bis(benzotriazol-1-yl)pyridin-2-ylmethane are collected in Tables 1 and 2. Elemental analyses are in agreement with the proposed formulations. The IR spectra show the complete disappearance of the carbonyl moiety of the reactant. The ^1H NMR spectra show a singlet in the high-frequency region around 9.0 ppm attributable to the methyne fragment, corresponding to a ^{13}C resonance in the range 72 – 74 ppm. In the aromatic region the resonances of the benzotriazolyl and phenyl or pyridinyl moieties are observable, and in the case of bis(benzotriazol-1-yl)pyridin-2-ylmethane the different heterocycles are easily distinguishable in the ^1H NMR spectrum, as observable in Figure 1.



Scheme 1. Synthesis of bis(benzotriazol-1-yl)phenylmethane and bis(benzotriazol-1-yl)pyridin-2-ylmethane.

Table 1. Analytical data of the compounds.

Compound	Formula	Mr	$\omega_i(\text{calc.}), \%$			M.p. ($^{\circ}\text{C}$)	Yield, %
			$\omega_i(\text{found}), \%$				
			C	H	N		
bis(benzotriazol-1-yl)phenyl methane	$\text{C}_{19}\text{H}_{14}\text{N}_6$	326.35	69.92 69.64	4.32 4.34	25.75 25.65	144	70
bis(benzotriazol-1-yl)pyridin-2-yl methane	$\text{C}_{18}\text{H}_{13}\text{N}_7$	327.34	66.04 65.78	4.00 4.02	29.95 29.83	105	55

Table 2. IR and NMR data of the compounds.

Compound	Spectral data
bis(benzotriazol-1-yl)phenylmethane	<p>IR, $\tilde{\nu}$ /cm⁻¹: 3100-2950 (C-H), 1610-1450 (C=C, C=N).</p> <p>¹H NMR (CDCl₃, 25 °C) δ: 9.05 (s, 1H, CH), 8.10 (dt, 2H, $J_{\text{HH}} = 8.2$ Hz, $J_{\text{HH}} = 0.9$ Hz, benzotriazole), 7.66 (dt, 2H, $J_{\text{HH}} = 8.4$ Hz, $J_{\text{HH}} = 1.0$ Hz, benzotriazole), 7.53-7.39 (m, 7H, benzotriazole and phenyl), 7.15 (d, 2H, $J_{\text{HH}} = 7.9$ Hz, phenyl).</p> <p>¹³C {¹H} NMR (CDCl₃, 25 °C) δ: 142.29 (ipso), 132.44 (ipso), 132.34 (ipso), 129.92 (phenyl), 129.17 (phenyl), 128.58 (benzotriazole), 127.11 (phenyl), 124.81 (benzotriazole), 120.31 (benzotriazole), 110.80 (benzotriazole), 72.48 (CH).</p>
bis(benzotriazol-1-yl)pyridin-2-ylmethane	<p>IR, $\tilde{\nu}$ /cm⁻¹: 3060-2950 (C-H), 1610-1430 (C=C, C=N).</p> <p>¹H NMR (CDCl₃, 25 °C) δ: 9.00 (s, 1H, CH), 8.66 (ddd, 1H, $J_{\text{HH}} = 4.8$ Hz, $J_{\text{HH}} = 1.7$ Hz, $J_{\text{HH}} = 0.9$ Hz, pyridine-H₆), 8.10 (dt, 2H, $J_{\text{HH}} = 8.3$ Hz, $J_{\text{HH}} = 0.9$ Hz, benzotriazole), 7.82 (td, 1H, $J_{\text{HH}} = 7.8$ Hz, $J_{\text{HH}} = 1.7$ Hz, pyridine-H₄), 7.67 (dt, 2H, $J_{\text{HH}} = 8.4$ Hz, $J_{\text{HH}} = 1.0$ Hz, benzotriazole), 7.49 (ddd, 2H, $J_{\text{HH}} = 8.1$ Hz, $J_{\text{HH}} = 7.0$ Hz, $J_{\text{HH}} = 1.1$ Hz, benzotriazole), 7.42 (dd, 1H, $J_{\text{HH}} = 7.8$ Hz, $J_{\text{HH}} = 4.8$ Hz, pyridine-H₅), 7.41 (dt, 2H, $J_{\text{HH}} = 8.2$ Hz, $J_{\text{HH}} = 7.0$ Hz, $J_{\text{HH}} = 1.0$ Hz, benzotriazole), 7.32 (ddd, 1H, $J_{\text{HH}} = 7.8$ Hz, $J_{\text{HH}} = 1.7$ Hz, $J_{\text{HH}} = 0.9$ Hz, pyridine-H₃).</p> <p>¹³C {¹H} NMR (CDCl₃, 25 °C) δ: 151.56 (ipso), 150.11 (pyridine-C₆), 146.28 (ipso), 137.35 (pyridine-C₄), 132.64 (ipso), 128.59 (benzotriazole), 124.78 (benzotriazole), 124.54 (pyridine-C₅), 122.48 (pyridine-C₃), 120.33 (benzotriazole), 110.68 (benzotriazole), 73.43 (CH).</p>

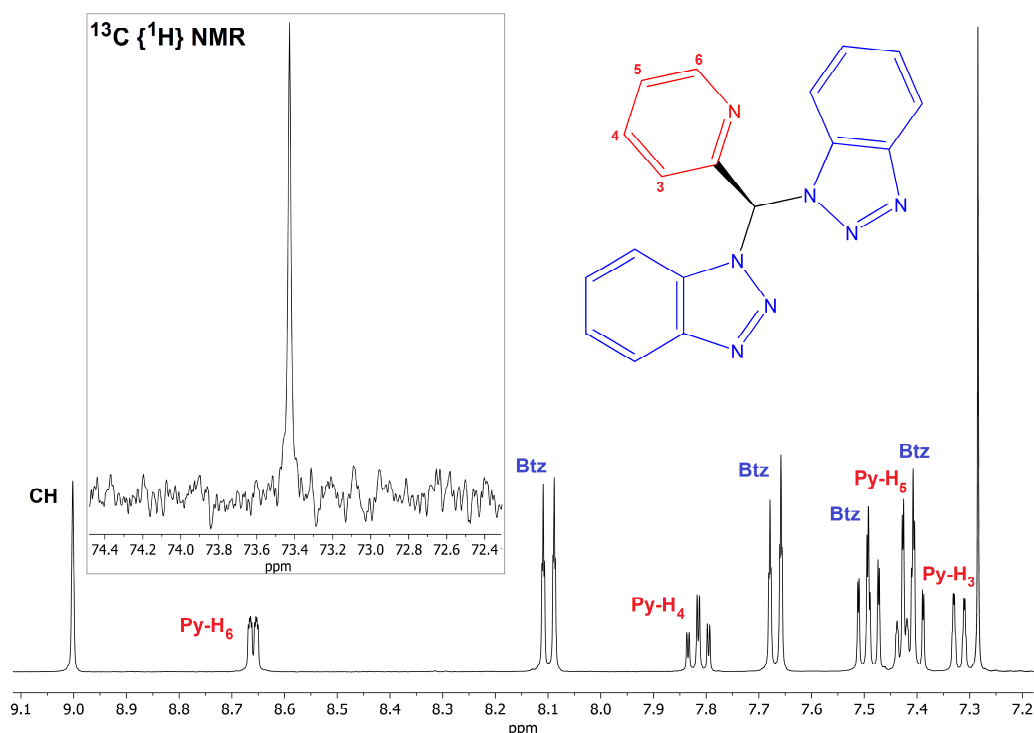


Figure 1. ^1H NMR spectrum of bis(benzotriazol-1-yl)pyridin-2-ylmethane in CDCl_3 at 25°C . Inset: ^{13}C NMR methyne resonance.

To the best of our knowledge, the product bis(benzotriazol-1-yl)pyridin-2-ylmethane was never reported. The structures of both compounds were unambiguously established for the first time by single-crystal X-ray diffraction techniques. Figures 2 and 3 contain ORTEP plots of both compounds [16]. They consist of an helicate built around a tertiary carbon atom with formula $\text{CHR}_2\text{R}'$, where R is a N(1)-benzotriazol-1-yl and R' is a six-membered phenyl or 2-pyridyl ring. Although the structures resemble heteroscorpionate ligands such as classical tris(azolyl)borates [17], they are more related with known tris(azolyl)methane derivatives as tris(pyrazolyl)methane [18] or tris(3,4,5-trimethylpyrazolyl)methane [19]. In the compounds described in this paper one of the azolyl ring was changed by a six-membered ring, and this situation was already found in the closely related bis(benzoindazol-1-yl)pyridin-2-ylmethane, described early [20]. It is worth noting that compounds based on comparable bis(pyrazol-1-yl)pyridin-2-ylmethane skeleton were recently used for the preparation of coordination compounds acting as catalysts towards ethylene oligomerization and polymerization [21]. The three cycles adopt a helical conformation (see a superimposition of both molecules drawn along the H(1)-C(1) vector in Scheme 2; torsion angles are collected in Table 3). Distances and angles in the compounds are in the expected range and do not deserve many comments. Bond parameters around C(1) are set out in Table 4 and show distances around 1.45 \AA for the C-N bonds and 1.52 \AA for the C-C bonds; the angles are between 110 and 115° (extreme values for the pyridyl derivative), all of them characteristics of a sp^3 carbon atom. The disposition of the three rings is in such a way that the nitrogen atoms (if present) are as far as they can, in an anti- or pseudo trans conformation. A similar way occurs in bis(benzotriazol-1-yl)methane [22] and also in some pyrazolyl compounds such as bis(pyrazolyl)bipyridinylmethane [23], but quite different disposition was found in 2-[bis(3,5-diphenyl-1H-pyrazol-1-yl)methyl]pyridine [24] or in bis(benzotriazol-1-yl)methanethione [25], where the two nitrogen atoms in 2-position in both rings are pointing to each other. Figure 4 shows as both benzotriazolyl rings are in opposite direction, one of them with the benzene ring to the right and the other to the left. Sterical requirements for the benzene moieties rather than electronic features could be the reason for this conformation.

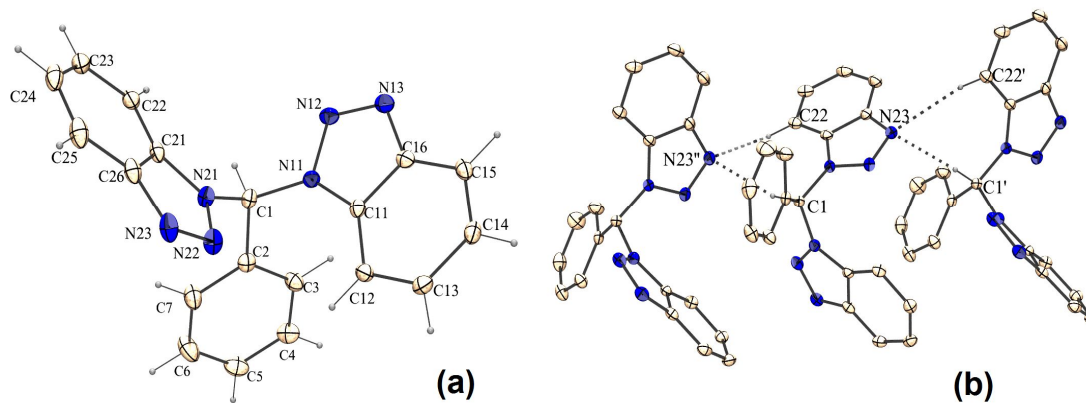


Figure 2. (a) X-ray structure of bis(benzotriazol-1-yl)phenylmethane. (b) Intermolecular interactions.

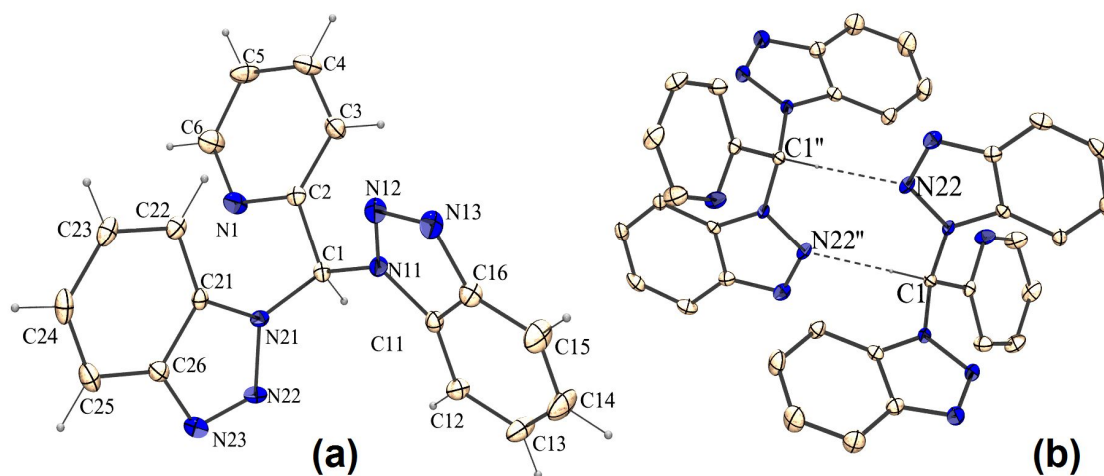
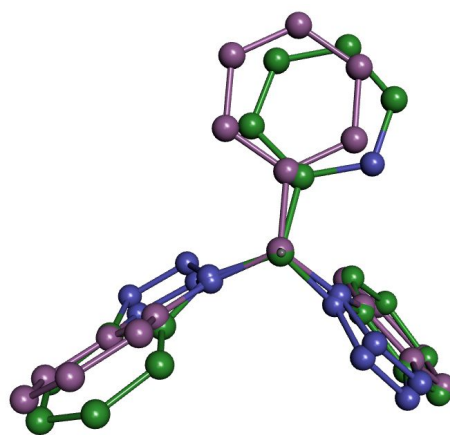


Figure 3. (a) X-ray structure of bis(benzotriazol-1-yl)pyridin-2-ylmethane. (b) Intermolecular interactions.



Scheme 2. Superimposition of both molecules drawn along the H(1)-C(1) vector. Violet carbons: bis(benzotriazol-1-yl)phenylmethane. Green carbons: bis(benzotriazol-1-yl)pyridin-2-ylmethane.

Table 3. Selected torsion angles with H(1)-C(1) bond.

Bis(benzotriazol-1-yl)pyridin-2-ylmethane		Bis(benzotriazol-1-yl)phenylmethane	
H(1)-C(1)-N(11)-N(12)	161.34	H(1)-C(1)-N(11)-N(12)	13.26
H(1)-C(1)-N(11)-C(11)	31.40	H(1)-C(1)-N(11)-C(11)	-175.55

H(1)-C(1)-N(21)-N(22)	16.51	H(1)-C(1)-N(21)-C(21)	-7.32
H(1)-C(1)-N(21)-C(21)	165.86	H(1)-C(1)-N(21)-N(22)	177.74
H(1)-C(1)-C(2)-N(1)	78.87	H(1)-C(1)-C(2)-C(3)	86.94
H(1)-C(1)-C(2)-C(3)	97.81	H(1)-C(1)-C(2)-C(7)	-85.02

Table 4. Bond lengths [Å] and angles [°] around central C(1).

Bis(benzotriazol-1-yl)phenylmethane		Bis(benzotriazol-1-yl)pyridin-2-ylmethane	
C(1)-N(11)	1.4511(16)	C(1)-N(11)	1.4548(14)
C(1)-N(21)	1.4595(16)	C(1)-N(21)	1.4542(14)
C(1)-C(2)	1.5199(17)	C(1)-C(2)	1.5285(16)
N(11)-C(1)-N(21)	110.45(10)	N(11)-C(1)-N(21)	109.86(9)
N(11)-C(1)-C(2)	114.23(10)	N(11)-C(1)-C(2)	115.05(9)
N(21)-C(1)-C(2)	112.20(10)	N(21)-C(1)-C(2)	110.72(9)

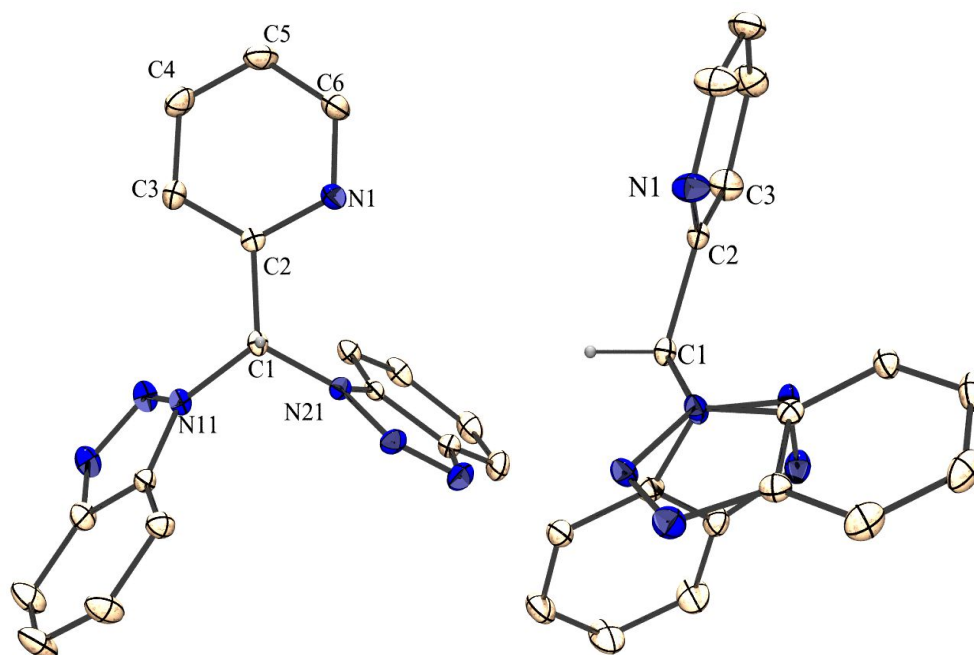


Figure 4. Two views of bis(benzotriazol-1-yl)pyridin-2-ylmethane, left along the C(1)-H(1) bond, and right, 90° y-rotated.

The benzotriazole rings are more or less planar, the root mean square deviation from the planarity for the 8 atoms implicated are between 0.0134 and 0.0196 Å. Dihedral angles between them are 76.49(3)° for the phenyl derivative and 78.80(3)° for the pyridyl one. However, some differences are found in the dispositions of the third ring (py or Ph ring), since the dihedral angle between the benzotriazole rings and the pyridine are 51.08(4) and 70.75(4)°, while between the benzotriazole rings and the phenyl ring for the other compound are 74.89(3) and 79.98(4)°.

The supramolecular structure does not contain the classical π,π -stacking between the rings in the molecule [22], probably because the above mentioned helical disposition around the central C(1)

atom of the scorpionate molecule prevents such interactions. Instead, non-classical C-H...N hydrogen bond are found (parameters in Table 5). These interactions are quite different between these molecules. Figure 2 shows these interaction for bis(benzotriazol-1-yl)phenylmethane, and they continue growing in the *b*-direction. However for bis(benzotriazol-1-yl)pyridin-2-ylmethane these interaction generates only dimers as shows Figure 3, in a similar way that related pyrazolyl compounds [26].

Table 5. Hydrogen bonds for bis(benzotriazol-1-yl)phenylmethane and bis(benzotriazol-1-yl)pyridin-2-ylmethane [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
bis(benzotriazol-1-yl)phenylmethane				
C(1)-H(1)...N(23 ⁱ)	1.00	2.27	3.1285(17)	143.6
C(22)-H(22)...N(23 ⁱ)	0.95	2.61	3.3776(17)	138.1
bis(benzotriazol-1-yl)pyridin-2-ylmethane				
C(1)-H(1)...N(22 ⁱⁱ)	1.00	2.36	3.3625(15)	175.6

Symmetry transformations used to generate equivalent atoms: i: $x, 1.5-y, z-0.5$; ii: $1-x, 1-y, -z$.

4. Conclusions

In this paper it was shown that the CoCl_2 -catalyzed approach for the formation of C-C bonds, applied in the past to bis(pyrazol-1-yl)methanone and related species, can be successfully extended to bis(benzotriazol-1-yl)methanone. The new product bis(benzotriazol-1-yl)pyridin-2-ylmethane represents an example of neutral homoscorpionate ligand, and studies concerning its coordination chemistry are actually in progress.

Acknowledgments

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