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Towards to the trans-bromination of 2-styrylpyridine with a palladacycle intermediary and structure analysis for trans-1,2-dibromo-2-styrylpyridine

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ABSTRACT

The simple halogenation of alkynes in conventional organic reactions gives a blend of cis and trans isomers. It is proposed then, a synthesis of stereospecific halogenation of alkynes in trans position, using palladacycle as intermediaries. The recrystallization of the compound obtained by bromination of 2-Styrylpyridine, with cyclepalladium intermediary results in a single crystal, which is subjected to X-ray diffraction.

The crystal packing is established through weak interactions of three types. The first one is of the type π × π interactions, from symmetry operation, between the centroids. The second one is of the type C—X···π interactions. And the last type is an anomalous intermolecular interaction between halogens, C—X···X—C, with bond distances smaller than the sum of the van der Waals radii. The conformation on the C=C bond is trans and the dihedral angle between the aromatic rings is (with esd approximate) 18.1(3)°.

1. Introduction

Textbook mechanism of the trans-bromination of alkynes via a more or less symmetrically bridged bromonium ion does not always apply [1].

Therefore, studies for new routes of bromination have continued to attract the interest of researchers due to the difficulty of controlling the product stereoselectivities [2–4]. The bromination of alkynes through cyclepalladated includes the coordination of the heteroatom to palladium followed by an interaction of the triple bond with the metal center [5]. The intermolecular nucleophilic attack of bromide ion binding to CtripleC coordinated to atom of palladium results in a palladacycle thermodynamically stable [6]. As a consequence of interactions palladium-alkyne, the formation of a wide range of cyclopalladated derivatives of amines and thioethers propargylic differently functionalized occurs [7]. The palladacycles have been receiving closer attention lately because of the possibility of its application in several areas [8]. As examples, it can be cited: organic synthesis [9,10]. Development of new materials to obtain liquid crystals [11]. Bio-organometallic chemistry and antitumor chemotherapeutic agent [12]. Photochemical reactions of electron transfer [13]. In catalysis as catalyst precursors in a wide range of reactions such as hydrogenation [14,15].

This work have proposed a new stereospecific synthesis, as a reaction intermediate cyclepalladated. A departure complex cyclepalladated was obtained and characterized as previously described in [16,17] by changing the reaction's temperature to 0 °C which increases the yield of the reaction. The product characterization was done by analyzing one single crystal of it through the X-ray diffraction.

2. Methods

2.1. Synthesis of pyridinyl-phenyl-ethyne

The functionalized alkyne pyridinyl-phenyl-ethyne was obtained by stoichiometric reaction between 2-bromo-pyridine and phenylacetylene, using diethylamine as a solvent and 0.1 t% Pd Cl_2 $(PPh_3)_2$/CuI in equal proportions as a catalyst. The reaction was performed during 3 h on constant agitation in argon atmosphere and at a temperature of 0 °C, using an ice bath. The diethylamine was then removed by distillation at reduced pressure. The catalyst was removed by filtration on Celite (L = 3.0 cm, Ø = 3.0 cm) and the product was purified by extraction with hexane followed by micro distillation at reduced pressure (te = 74 °C, $P = 10^{-1}$ mm Hg) after hexane evaporation. The product, a brown liquid with high boiling point, was isolated with 80% of yield. The NMR spectra of ^1H {^{13}C} and ^{13}C{^1H} were performed on a Brucker AC-200 spectrometer. ^1H NMR (δppm, DCCl3): 8.60–8.56 (m, 2H, Py), 7.67–7.53 (m, 7H, Ar) 13C (1H) NMR (δppm, DCCl3): 90.0 (s, py—*C≡C—), 90.6 (s,—C≡C *—Ø), 123.0(—*C(phe)—C≡). The IR spectrum was measured on a spectrometer Perkin–Elmer, mod. Spectrum-100 spectrophotometer, in the region 4000–400 cm^{-1}, using a resolution of 2 cm^{-1}, using Nujol emulsion

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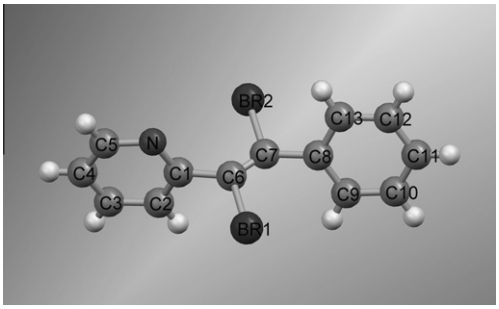

Fig. 1. The perspective view [22] of the trans-1,2-dibromo-2-styrylpyridine.

Table 1
Bond lengths (Å) and angles (°), with esd approximate.

Br1—C6	1.965(1)	C2—C1—C6	119.3(7)
Br2—C7	2.025(1)	C1—C2—C3	117.5(8)
N—C1	1.346(1)	C4—C3—C2	119.9(7)
N—C5	1.348(9)	C3—C4—C5	119.6(8)
C1—C2	1.366(1)	N—C5—C4	122.8(8)
C1—C6	1.499(1)	C7—C6—C1	132.6(1)
C2—C3	1.391(1)	C7—C6—Br1	114.3(9)
C3—C4	1.340(1)	C1—C6—Br1	113.1(7)
C4—C5	1.361(1)	C6—C7—C8	135.5(1)
C6—C7	1.167(1)	C6—C7—Br2	113.6(9)
C7—C8	1.503(1)	C8—C7—Br2	110.9(6)
C8—C9	1.379(1)	C9—C8—C13	119.1(7)
C8—C13	1.381(9)	C9—C8—C7	121.5(7)
C9–10	1.365(1)	C13—C8—C7	119.4(7)
C10—C11	1.347(1)	C10—C9—C8	119.4(7)
C11—C12	1.344(1)	C11—C10—C9	122.1(8)
C12—C13	1.369(1)	C12—C11—C10	118.0(8)
C1—N—C5	116.6(7)	C12—C12—C13	122.9(8)
N—C1—C2	123.5(7)	C12—C13—C8	118.5(8)
N—C1—C6	116.8(7)		

technique, where we observe the vibrational normal mode of the stretching —C≡C— at 2219 cm^{-1}.

2.2. Palladacycle synthesis

A Li_2PdCl_4 solution was prepared by dissolution of $PdCl_2$ and LiCl, using a molar ratio of 1:2, respectively in heated methanol. At the end of reaction, a reddish-brown solution was formed, which was filtered to remove solid residues. After cooling the reactional mixture to room temperature, the previously synthezised pyridinyl-phenyl-ethyne, which had been previously dissolved in methanol in a 1:1 stoichiometric ratio in relation to the Li_2PdCl_4, as slowly added by using an addition funnel during 24 h on constant stirring at room temperature and inert atmosphere. At the end of the reaction, a yellow precipitate was isolated by filtration, and washed with ethanol and acetone and dried under vacuum.

Table 2
Crystal data and structure refinaments for trans-1,2-dibromo-2-styril-pyridine.

Empirical formula	$C_{13}H_9Br_2N$
Formula weight	339.03
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
a	8.8465(9) Å
b	10.496(2) Å
c	13.309(2) Å
β	97.11(1)°
Volume	1226.2(3) A^3
Z	4
Calculated density	1.836 Mg/m^{-3}
Absorption coefficient	6.581 mm^{-1}
F(0 0 0)	656
Crystal size	0.5 × 0.4 × 0.4 mm
θ	2.32–28.04°
Limiting indices	$-11 < h < 11$ $-13 < k < 0$ $0 < l < 17$
Reflections collected/unique	3100/2973
R (int)	0.0303
Absorption correction	Psi-scan
Max. and min. transmission	0.3522 and 0.3028
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2973/0/145
Goodness-of-fit on F^2	1.030
R_1, wR_2 [$I > 2\sigma(I)$]	0.0558, 0.1380
R_1, wR_2 (all data)	0.1700, 0.1709
Largest diff. peak and hole	1.142 and −0.676 e $Å^{-3}$

The complex {Pd*[(Ph)—*C═C(Cl))—(Py—*N)]} (μ-Cl)}$_2$ was then recrystallized in toluene with 65% of yield. The symbol (*) indicates pallacycle ring bonds. (C, H, N, % calc; % Enc) C (43.8, 43.7), H (2.5, 2.6), N (3.9, 4.0).

2.3. Bromination of the palladacycle complex synthesis

The reaction of palladacycle complex {Pd*[(Ph)—*C═C(Cl))—(Py—*N)]} (μ-Cl)}$_2$ and bromine was performed in a 1:2 stoichiometric amounts respectively in chloroform at room temperature on constant stirring during 1 h. After the reaction, the solution obtained was filtered on Celite to remove the metallic palladium formed and the solvent slowly evaporate at room temperature. The large, white, needle-shaped crystals obtained were then analyzed by X-ray diffraction and identified as a **trans[Py—C(Br)═C(Br)—Ø]**.

3. Results

A single crystal was sealed in a thin-walled glass capillary with approximate dimensions of 0.5 mm along [1 0 0], 0.4 mm along

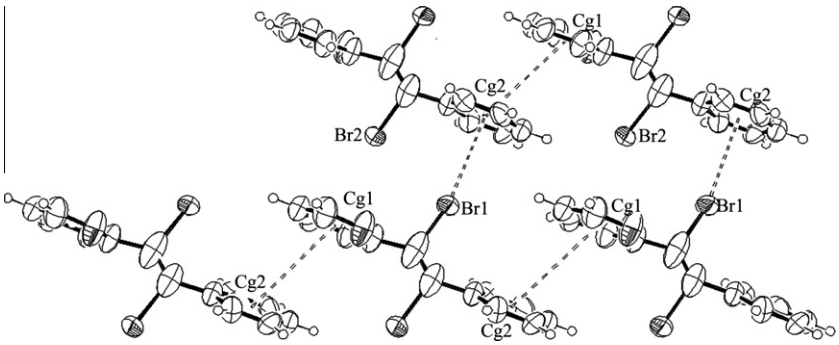

Fig. 2. Intermolecular interactions [23] of the types: π × π interactions, from symmetry operation [x, ½ − y, −½ + z], and C—X···π interactions, from [−1 + x, y, z].

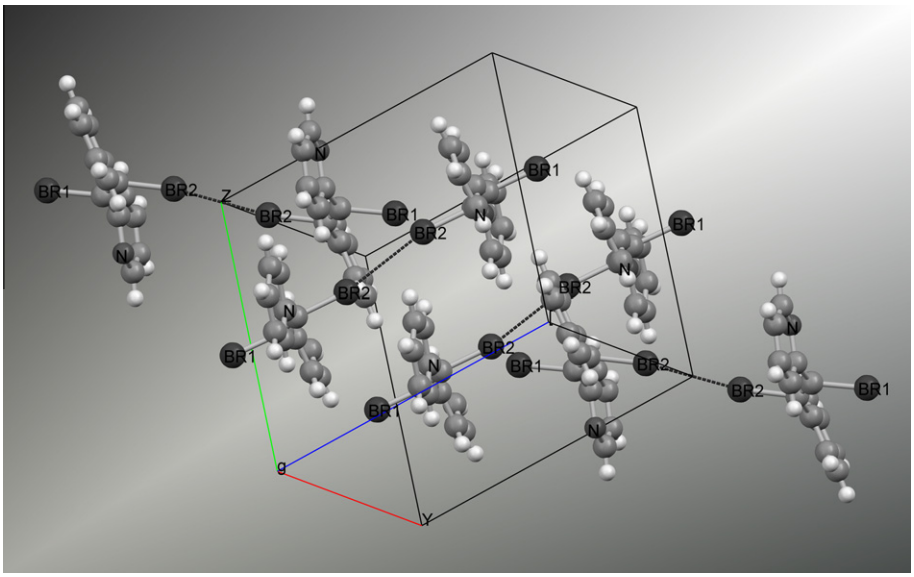

Fig. 3. Intermolecular interactions of the type C—X···X—C [22].

[0 1 0] and 0.4 mm along [0 0 1]. The reflexions in one quadrant for reciprocal space were measured, by using graphite-monochromated [μ (MoKα) = 0.71073] radiation with ω-2θ scan technique at room temperature. Intensities were corrected for Lorentz and polarization effects and semi-empirical absorption, and the data reduction was carried out using PSI-SCAN [18], with Fourier smoothing equal to 7.

The structure was solved by direct methods using WINGX system [19]. All the non-hydrogen atoms were refined by SHELXL97 program [20] on F^2 anisotropically by full-matrix least-squares method. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The structural analysis was performed by the PLATON system [21].

4. Discussion

The measuring has been made in a diffractometer CAD-4, the radiation was MoKα 0.71073 Å at 293 K. Crystallographic data: *a* 8.847(1) Å, *b* 10.496(2) Å, *c* 13.309(2) Å, β 97.11(1)°, *V*

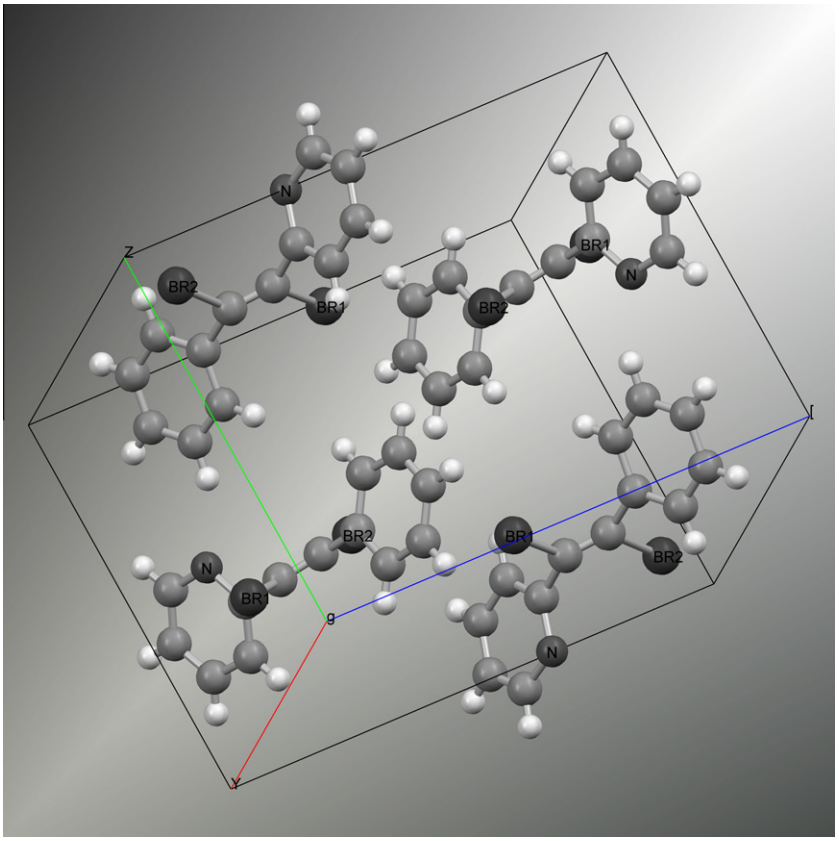

Fig. 4. Crystalline packing [22].

1226.2(2) Å^3, D 1.84 Mg m^{-3}, Z = 4, non-centrosymmetric. The systematic absences analysis indicated the presence of a rotation axis, order 2, and a glide in direction, with a primitive cell: space group P21/c. The perspective view [22] of the **Trans-1,2-dibromo-2-styril-pyridine** is shown in Fig. 1.

The 2973 reflections were held and the agreement between the real and the obtained model was evaluated by the disagreement factors $R(F)$ and $Rw(F^2)$, which were 5.6% and 17.1% respectively, and S 1.030. Selected bond distances and angles are given in Tables 1. Crystal data and structure refinaments are shown in Table 2.

The crystalline packing presents two types of intermolecular interactions is shown in Fig. 2. The first one is $\pi \times \pi$ interactions, from symmetry operation $[x, ½ - y, -½ + z]$, between the centroids, Cg1···Cg2 (4.2362 Å) [where Cg1 is the centroid of the ring {N1, C1, C2, C3, C4, C5} and Cg2 {C8, C9, C10, C11, C12, C13}]. The second one is C—X···π interactions, from $[-1 + x, y, z]$, C6—Br1···Cg2 (3.5999 Å).

The delocalization of π electrons of the double bond can be seen upon the C6, therefore, the bond distances and angles between the halogen and carbon are not equal (Table 1). This occurrence also implies in short contacts between halogens, in crystal packing.

In the present case, the short anomalous intermolecular interaction is smaller than the sum of the van der Waals radii, {Br2···Br2—C7 equal 3.502 Å < 3.70 Å}, and they are coming an stereospecific interaction between these atoms. Van der Waals radii to Br is 1.86 Å [24]. This interaction is shown in Fig. 3, symmetry operation $[2 - x, 1 - y, -z]$.

The merger of all these contacts gives rise to supramolecular assembly, with parallel layers along the crystal lattice (Fig. 4). The pyridine ring and the phenyl ring are all planar. The angle between the minimum square planes through the phenyl and the pyridinyl is 18.1(3)°.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-798560. Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-(0)1223-762910 or via www.ccdc.cam.ac.uk/data-request/cif.

5. Conclusions

The **trans-1,2-dibromo-2-styrylpyridine** molecular structure shows the phenyl and the pyridinyl rings attached to the double bond and located *trans* to the pyridine ring. The bromines present in the molecule are in trans position, the torsion angle Br1—C6═C7—Br2 is 178.8(4)° and the distances of halogens in relation to the best minimum square plane through the molecule is 2.05(1) and 1.82(1) Å to Br1 and Br2, respectively.

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