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# New 1H-1-alkyl-6-methyl-3-phenyl-7-phenylazo-pyrazolo[5,1-c][1,2,4]triazoles through regioselective alkylation of 1H-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazoles

**Research Article**

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**Abstract:** 1*H*-1-Alkyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazoles (**2aa-ad**) were obtained by regioselective alkylation of 1H-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazoles (**2a**). 1*H*-1-Alkyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazoles **2aa** and **2ab** were also prepared by coupling phenyldiazonium chloride with 1*H*-1-alkyl-6-methyl-3-phenyl-pyrazolo[5,1-c][1,2,4]triazoles **1aa** and **1ab**. The new compounds were characterized by IR, UV-VIS, $^{1}$H-NMR, $^{13}$C-NMR, and $^{15}$N-NMR spectroscopy and their structures and actual tautomeric forms were established unequivocally.

**Keywords:** *Pyrazolo[5,1-c][1,2,4]triazole • Regioselective N-alkylation • Azo compound • Tautomerism*



## 1. Introduction

Azomethinic and azo dyes derived from pyrazolo[5,1-*c*][1,2,4]triazoles are key intermediates in the preparation of photosensitive color materials, inks and toners [1-4], and in other areas of interest [5-8]. The literature on the subject of synthesis and properties of these compounds, except the patent literature, is, to our knowledge, rather scarce.

There have been studies, described in the literature, on the annular tautomerism of pyrazoles [9-13] and aza-3a-pentalene systems containing 10 π electrons, which include the pyrazolo[5,1-*c*][1,2,4]triazole system [14,15], where it has been reported that one of the tautomeric forms predominates, but to our knowledge there has been no research done on the nature of the compounds formed in the functionalization reactions of these tautomers.

It was shown in our previous studies that the coupling reaction of phenyldiazonium chloride with 1*H*-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (1a) leads to the azo dye 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2a) [16], while the alkylation of 1*H*-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]- triazole (1a) and 1*H*-7-ethoxycarbonyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (3a) occurs regioselectively, with the formation of 1*H*-1-alkyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazoles (1aa-ab) and 1*H*-1-alkyl-7-ethoxycarbonyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazoles (3aa-ad), respectively, as proven by $^{1}$H-NMR and $^{13}$C-NMR [17] spectroscopy (Scheme 1).

In this work we extended the study of the alkylation reaction to 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2a), employing $^{1}$H-NMR, $^{13}$C-NMR and $^{15}$N-NMR spectroscopy for the structure determination of the compounds formed

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using two alternative syntheses. Thus, in this study the structure of the alkylation products and the actual tautomeric forms in which they exist were established unequivocally by 2D-NMR.

## 2. Experimental procedure

The chemical reagents were purchased from commercial sources (Merck, Fluka) and used in syntheses with no further purification. 1*H*-6-Methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2a) [16], 1*H*-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (1a) [1], 1*H*-6-alkyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazoles (1aa-ab) [1] and 1*H*-7-ethoxycarbonyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (3a) [1] were prepared by methods described in literature. The methods used for *N*-alkylation of pyrazolo[5,1-c][1,2,4] triazoles are modifications of these used in *N*-alkylation of 1,2,4-triazole [18].

The melting points were determined on a Böetius PHMK apparatus (Veb Analytik Dresden). TLC was performed on 60 $F_{254}$ Merck silica gel plates using benzene-ethyl acetate 1:1 (v/v) as eluent. The IR spectra were recorded in KBr pellets, using a Jasco FT/IR-410 spectrometer. The $^{1}H$, $^{13}C$ and $^{15}N$-NMR spectra were recorded on a Bruker Avance DRX 400 (400 MHz for $^{1}H$, 100 MHz for $^{13}C$ and 40 MHz for $^{15}N$) spectrometer, using TMS as internal reference.

### 2.1. Procedure for the preparation of 1H-1-alkyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazoles (2aa-ab) through azo coupling

The solution of diazonium salt prepared from aniline (1 mmole) is added at 0-5°C to a solution of 1*H*-1-alkyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (1aa, 1ab) (1 mmole) in ethyl alcohol (5 mL) and $CH_3COONa$ (4 mmoles) in water (0.5 mL). The azo dye formed is extracted with ethyl acetate (25 mL) and the organic layer is washed successively with NaOH 2.5% (2×5 mL) and water (5 mL). After drying on anhydrous $Na_2SO_4$, decantation and removal of the solvent to dryness, the chromatographically pure azo dyes are obtained.

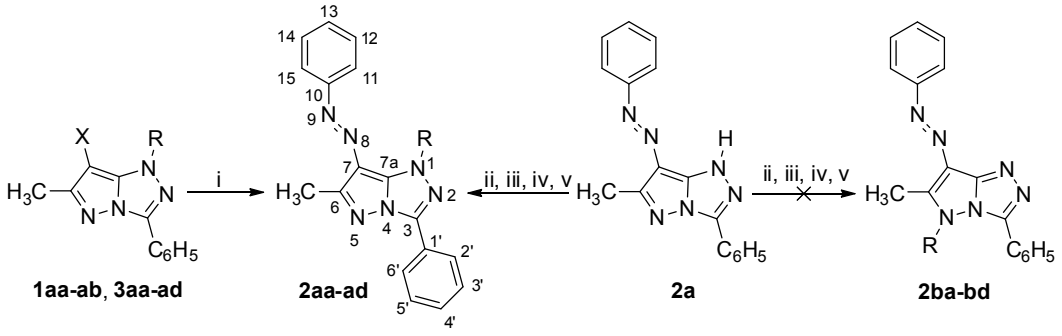
1,6-Dimethyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2aa). Dark yellow powder. Yield 55%; m.p. 196-198°C. IR (KBr) $\nu_{max}$: 3462, 3060, 3029, 2931, 2872, 2823, 1572, 1491, 1452, 1415, 1378, 1242, 1182, 1073, 976, 764, 689 $cm^{-1}$. UV-VIS: $\lambda_{max}$ ($\varepsilon_{max}$ x $10^4$) = 379.6 nm (2.845). $\delta_H$ ($CDCl_3$, 400 MHz): 8.39 (dt, 2H, $J_{2'\text{-H, }3'\text{-H}}$ = 7.2 Hz, $J_{2'\text{-H, }4'\text{-H}}$ = 1.2 Hz, 2′-H, 6′-H), 7.75 (dd, 2H, $J_{11\text{-H, }12\text{-H}}$ = 7.2 Hz, $J_{11\text{-H, }13\text{-H}}$ = 1.2 Hz, 11-H, 15-H), 7.55-7.43 (m, 5H, 3′-H, 4′-H, 5′-H, 12-H, 14-H), 7.32 (tt, 1H, $J_{13\text{-H, }14\text{-H}}$ = 7.2 Hz, $J_{13\text{-H, }15\text{-H}}$ = 1.2 Hz, 13-H), 4.41 (s, 3H, 1-N-C$\underline{H}_3$), 2.74 (s, 3H, 6-C-C$\underline{H}_3$); $\delta_C$ ($CDCl_3$, 100 MHz): 159.9 (6-C), 153.4 (10-C), 139.3 (3-C), 139.2 (7a-C), 130.4 (4′-C), 128.9 (12-C, 14-C), 128.8 (3′-C, 4′-C), 128.4 (13-C), 126.6 (2′-C, 6′-C), 125.1 (1′-C), 121.2 (11-C, 15-C), 118.2 (7-C), 39.8 (1-N-$CH_3$), 13.1 (6-C-$\underline{C}H_3$); $\delta_N$ ($CDCl_3$, 40 MHz): 286.2 (2-N), 254.2 (5-N), 158.6 (1-N). Calcd. (%) for $C_{18}H_{16}N_6$: C 68.34; H 5.10; N 26.56. Found (%): C 68.07; H 4.97; N 26.18.

1-Ethyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2ab). Yellow powder. Yield 29%; m.p. 191-193°C. IR (KBr): 3450, 3059, 3023, 2975, 2935, 1567, 1489, 1295, 1197, 1147, 1072, 962, 763, 688 $cm^{-1}$. UV-VIS: $\lambda_{max}$ ($\varepsilon_{max}$ x $10^4$) = 380.0 nm (2.942). $\delta_H$ ($CDCl_3$, 400 MHz): 8.38 (dt, 2H, $J_{2'\text{-H, }3'\text{-H}}$ = 8.2 Hz, $J_{2'\text{-H, }4'\text{-H}}$ = 1.4 Hz, 2′-H, 6′-H), 7.72 (d, 2H, $J$ = 7.6 Hz, 11-H, 15-H), 7.51-7.40 (m, 5H, 3′-H, 4′-H, 5'-H, 12-H, 14-H), 7.33-7.26 (m, 1H, 13-H), 4.81 (q, 2H, $J$ = 7.0 Hz, -C$\underline{H}_2$CH$_3$), 2.74 (s, 3H, 6-C-C$\underline{H}_3$), 1.51 (t, 3H, $J$ = 7.0 Hz, -CH$_2$C$\underline{H}_3$); $\delta_C$ ($CDCl_3$, 100 MHz): 160.0 (6-C), 153.5 (10-C), 139.2 (3-C), 138.9 (7a-C), 130.4 (4′-C), 128.9 (12-C, 14-C), 128.8 (3′-C, 5′-C), 128.4 (13-C), 126.6 (2′-C, 6′-C), 125.2 (1′-C), 121.2 (11-C, 15-C), 118.5 (7-C), 47.9 (-$\underline{C}H_2CH_3$), 16.3 (-$CH_2\underline{C}H_3$), 13.1 (6-C-$\underline{C}H_3$); $\delta_N$ ($CDCl_3$, 40 MHz): 284.1 (2-N), 254.3 (5-N), 173.7 (1-N). Calcd. (%) for $C_{19}H_{18}N_6$: C 69.07; H 5.49; N 25.44. Found (%): C 68.90; H 5.22; N 25.25.

### 2.2. Preparation of 1H-1-alkyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazoles (2aa-ad) through regioselective alkylation of 1H-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazole (2a)

General procedure for the preparation of 1,6-dimethyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2aa) and 1-ethyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2ab) through alkylation of 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2a) with dimethyl sulfate and diethyl sulfate, respectively.

$Me_2SO_4$ and $Et_2SO_4$ (1.2 mL) were added at room temperature to a solution of 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2a) (0.6 and 0.33 mmoles, respectively) in NaOH 5% (3.0 and 1.5 mL, respectively) and ethanol (10 and 5 mL, respectively), and the mixture is stirred for 30 minutes. The reaction mass is filtered, the precipitate is washed with water, dried and recrystallized from ethanol.




X=H; R=-$CH_3$ (**1aa**), -$C_2H_5$ (**1ab**)

X=-N=N-$C_6H_5$; R=-$CH_3$ (**2aa**), -$C_2H_5$ (**2ab**), -$CH_2$-$CH$=$CH_2$ (**2ac**), -$CH_2$-$C_6H_5$ (**2ad**)

X=-$COOC_2H_5$; R=-$CH_3$ (**3aa**), -$C_2H_5$ (**3ab**), -$CH_2$-$CH$=$CH_2$ (**3ac**), -$CH_2$-$C_6H_5$ (**3ad**)

i= $C_6H_5N_2]^+Cl^-$ / $C_2H_5OH$-$H_2O$ / NaOH

ii= $(CH_3)_2SO_4$ / DMF / NaOH; iii= $(C_2H_5)_2SO_4$ / DMF / NaOH

iv= $CH_2$=CH-$CH_2Br$ / MEK / $K_2CO_3$; v= $C_6H_5CH_2Br$ / MEK / $K_2CO_3$

**Scheme 1.** The reaction conditions and the products obtained.

## 2.3. Preparation of the azo dye 1-allyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazole (2ac) through alkylation of 1H-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazole (2a) with allyl bromide

To a suspension of 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2a) (0.33 mmoles) and allyl bromide (0.07 mL) in ethanol (5 mL), a NaOH 5% solution (0.8 mL) is added at room temperature, and the orange solution formed is kept 10 minutes at room temperature. The yellow suspension formed is poured into water (25 mL) and then filtered. The compound obtained is chromatographically pure.

## 2.4. Preparation of the azo dye 1-benzyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazole (2ad) through alkylation of 1H-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4]triazole (2a) with benzyl chloride

To a solution of benzyl chloride (0.091 mL) and KI (0.06 g) in acetone (15 mL), finely powdered $K_2CO_3$ (0.109 g) and 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2a) (0.33 mmoles) are added at 50°C. After refluxing for 2 hours, the yellow-reddish suspension formed is cooled, filtered and the precipitate is washed with acetone. After removing the solvent under low pressure, compound 2ad is obtained chromatographically pure.

1,6-Dimethyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2aa). Yellow powder. Yield 56%; m.p. 196-198°C. The spectroscopic data are identical with those of the same compound obtained previously through azo coupling. Calcd. (%) for $C_{18}H_{16}N_6$: C 68.34; H 5.10; N 26.56. Found (%): C 68.07; H 4.98; N 26.23.

1-Ethyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2ab). Yellow powder. Yield 55%; m.p. 191-193°C. The spectroscopic data are identical with those of the same compound obtained previously through azo coupling. Calcd. (%) for $C_{19}H_{18}N_6$: C 69.07; H 5.49; N 25.44. Found (%): C 68.94; H 5.36; N 25.22.

1-Allyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2ac). Yellow powder. Yield 98%; m.p. 89-92°C. IR (KBr): 3065, 3029, 2964, 2935, 2916, 2835, 1643, 1564, 1489, 1449, 1285, 1195, 1151, 765, 713, 689, 674 $cm^{-1}$. UV-VIS $\lambda_{max}$ ($\varepsilon_{max}$ x $10^4$) = 379.2 (2.740). $\delta_H$ ($CDCl_3$, 400 MHz): 8.41 (dt, 2H, $J_{2'\text{-H, }3'\text{-H}}$ = 6.8 Hz, $J_{2'\text{-H, }4'\text{-H}}$ = 1.6 Hz, 2′-H, 6′-H), 7.76 (dd, 2H, $J_{11\text{-H, }12\text{-H}}$ = 8.4 Hz, $J_{11\text{-H, }13\text{-H}}$ = 1.2 Hz, 11-H, 15-H), 7.56-7.44 (m, 5H, 3′-H, 4′-H, 5′-H, 12-H, 14-H), 7.33 (tt, 1H, $J_{13\text{-H, }14\text{-H}}$ = 7.2, $J_{13\text{-H, }15\text{-H}}$ = 1.2 Hz, 13-H), 6.90 (qt, 1H, $J_{2''\text{-H, }3''\text{-Hb}}$ = 17.2 Hz, $J_{2''\text{-H, }3''\text{-Ha}}$ = 10.4 Hz, $J_{2''\text{-H, }1''\text{-H}}$ = 5.6 Hz, 2”-H), 5.45 (dt, 2H, $J_{1''\text{-H, }2''\text{-H}}$ = 5.6 Hz, $J_{1''\text{-H, }3''\text{-H}}$ = 1.2 Hz, 2x1”-H), 5.28 (dd, 1H, $J_{3''\text{-Hb, }2''\text{-H}}$ = 17.2 Hz, $J_{3''\text{-Hb, }3''\text{-Ha}}$ = 1.2 Hz, 3”-$H_b$), 5.23 (dd, 1H, $J_{3''\text{-Ha, }2''\text{-H}}$ = 10.4 Hz, $J_{3''\text{-Ha, }3''\text{-Hb}}$ = 1.2 Hz, 3”-$H_a$), 2.76 (s, 3H, 6-C-C$\underline{H}_3$); $\delta_C$ ($CDCl_3$, 100 MHz): 160.0 (6-C), 153.5 (10-C), 139.8 (3-C), 139.0 (7a-C), 133.1 (2”-C), 130.5 (4′-C), 129.0 (12-C, 14-C); 128.8 (3′-C, 5′-C), 128.5 (13-C), 126.8 (2′-C, 6′-C), 125.1 (1′-C), 121.2 (11-C, 15-C), 118.5 (3”-C), 118.3 (7-C),

54.6 (1"-C), 13.1 (6-C-$\underline{C}H_3$); $\delta_N$ ($CDCl_3$, 40 MHz): 284.6 (2-N), 255.2 (5-N), 169.6 (1-N). Calcd. (%) for $C_{20}H_{18}N_6$: C 70.16; H 5.30; N 24.54. Found (%): C 70.15; H 5.10; N 24.29.

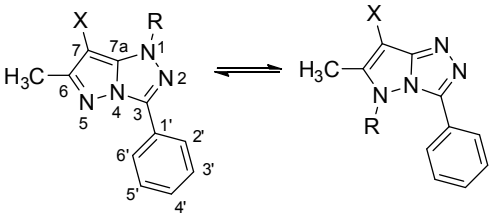
1-Benzyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2ad). Light yellow powder. Yield 77%; m.p. 146-149°C. IR (KBr): 3153, 3054, 3029, 2979, 2937, 2898, 2878, 1563, 1488, 1451, 1263, 1192, 1153, 978, 770, 689 $cm^{-1}$. UV-VIS $\lambda_{max}$ ($\varepsilon_{max}$ x $10^4$) = 380 (3.053). $\delta_H$ ($CDCl_3$, 400 MHz): 8.44 (d, 2H, $J_{2'\text{-H, }3'\text{-H}}$ = 6.8 Hz, 2′-H, 6′-H), 7.81 (d, 2H, $J_{11\text{-H, }12\text{-H}}$ = 7.6 Hz, 11-H, 15-H), 7.58-7.46 (m, 7H, 3′-H, 4′-H, 5′-H, 2"-H, 6"-H 12-H, 14-H), 7.40-7.30 (m, 4H, 13-H, 3"-H, 4"-H, 5"-H), 6.08 (s, 2H, -$\underline{C}H_2$-Ph), 2.82 (s, 3H, 6-C-$\underline{C}H_3$); $\delta_C$ ($CDCl_3$, 100 MHz): 150.2 (6-C), 153.4 (10-C), 139.9 (3-C), 138.7 (7a-C), 136.5 (1"-C), 130.5 (4′-C), 129.0 (12-C, 14-C), 128.8 (3′-C, 5′-C), 128.7 (3"-C, 5"-C), 128.5 (13-C), 128.2 (2"-C, 6"-C), 128.0 (4"-C), 126.8 (2′-C, 6′-C), 125.2 (1′-C), 121.2 (11-C, 15-C), 118.2 (7-C), 55.5 (-$\underline{C}H_2$-Ph), 13.1 (6-C-$\underline{C}H_3$); $\delta_N$ ($CDCl_3$, 40 MHz): 284.8 (2-N), 255.6 (5-N), 172.1 (1-N). Calcd. (%) for $C_{24}H_{20}N_6$: C 73.45; H 5.14; N 21.41. Found (%): C 73.21; H 5.04; N 21.14.

## 3. Results and discussion

Theoretically, 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (1), 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2) and 1*H*-7-ethoxycarbonyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (3) can exist as two tautomeric forms a and b (Fig. 1): a 1*H*-tautomeric form (a), in which the hydrogen is bonded to the nitrogen in position 1 (1-N), and a 5*H*-tautomeric form (b), in which the hydrogen is bonded to the nitrogen in position 5 (5-N).

Based on the analysis of the 2D $^1$H-$^{15}$N NMR spectra recorded, we can affirm that 6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (1), 6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2) and 7-ethoxycarbonyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (3) exist only as 1*H*-tautomeric forms (a), a fact that explains their regioselective alkylation occurring exclusively at the 1-N nitrogen.

Thus, in the 2D HMBC $^1$H-$^{15}$N spectrum of 6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (1) the long-range couplings between the four nitrogen atoms of the pyrazolo-triazole system and three different protons is observed: one at 12.94 ppm (N-$\underline{H}$), one at 5.69 ppm (7-C-$\underline{H}$) and one at 2.34 ppm (6-C-C$\underline{H}_3$). The signals of the four nitrogen atoms in this heterocyclic system appear at 153.7, 225.9, 252.3 and 276.3 ppm, respectively. In the 2D HMQC $^1$H-$^{15}$N spectrum of 1*H*-




**1a, 2a, 3a** **1b, 2b, 3b**

X= H, R= H (**1a**, **1b**)
X= N=N-$C_6H_5$, R= H (**2a**, **2b**)
X= $COOC_2H_5$, R= H (**3a**, **3b**)

**Figure 1.** Tautomeric forms in the 3,6-di- and 3,6,7-trisubstituted pyrazolo[5,1-c][1,2,4]triazole system.

6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (1) the direct coupling $^1J$ between the nitrogen atom at 153.7 ppm and the proton at 12.94 ppm can be observed, which indicates that the proton at 12.94 ppm is either 1-N-$\underline{H}$ (1a) or 5-N-$\underline{H}$ (1b). The nitrogen atom at 252.3 ppm long-range couples with the protons at 2.34 ppm (6-C-C$\underline{H}_3$). The only nitrogen atom that is able to long-range couple ($^3J$) with the 6-C-C$\underline{H}_3$ protons is the 5-N atom, because all the other nitrogen atoms are located at distances longer than three bonds. Therefore the nitrogen atom at 252.3 ppm is the 5-N atom. Since no direct coupling between the 5-N atom and any proton is observed, the only direct coupling being between the nitrogen at 153.7 ppm and the proton at 12.94 ppm, and since the nitrogen at 153.7 ppm does not couple with the 6-C-C$\underline{H}_3$ protons, we can conclude that the nitrogen at 153.7 ppm is 1-N. From the above spectroscopic observations one can draw a conclusion that the tautomeric form in which compound 1 exists is 1a, not 1b.

In the 2D HMBC $^1$H-$^{15}$N spectrum of compound 1a, the long-range couplings between the nitrogen atom at 225.9 ppm and the protons 1-N-$\underline{H}$ at 12.94 ppm and 7-C-$\underline{H}$ at 5.69 ppm, respectively, are observed. The only nitrogen atom that can simultaneously long-range couple ($^3J$) with these protons is the 4-N nitrogen. Also, the vicinal coupling between the nitrogen at 276.3 ppm and the 1-N-$\underline{H}$ proton at 12.94 ppm is observed, a coupling ($^2J$) possible only for the 2-N nitrogen.

In the 2D HMBC $^1$H-$^{13}$C spectrum of compound 1a the $^2J_{7a\text{-}\underline{C},\ 1\text{-N-}\underline{H}}$, $^2J_{7a\text{-}\underline{C},\ 7\text{-C-}\underline{H}}$, $^2J_{6\text{-}\underline{C},\ 6\text{-C-C}\underline{H}3}$, $^3J_{7\text{-}\underline{C},\ 6\text{-C-C}\underline{H}3}$ and $^3J_{3\text{-}\underline{C},\ 1\text{-N-}\underline{H}}$ long-range couplings are also observed. In conclusion, in conformity with the above-presented spectroscopic data, we can state with certainty that 1*H*-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole 1 exist as the tautomeric form 1a, and the four nitrogen atoms in the heterocycle appear at the following values: 1-N at 153.7 ppm, 2-N at 276.3 ppm, 4-N at 225.9 ppm and 5-N at 276.3 ppm.

The elucidation of the structure of compound 1a was necessary, because in the case of compound 2a no signal for the 1-N-H proton appears in the $^{1}$H-NMR spectrum, even though various solvents were employed (DMSO-$d_6$, $CDCl_3$, $C_6D_6$ and $CD_3CN$) and the studies were conducted at low temperature (-30°C in $CDCl_3$ and $CD_3CN$). Due to the absence of the signal for the 1-N-H proton, there are no signals for the 1-N, 2-N and 4-N nitrogen atoms in the 2D HMBC $^{1}$H-$^{15}$N-NMR spectrum, because of the lack of the $^{1}J_{1\text{-}N,\ 1\text{-}N\text{-}H}$ direct coupling and the $^{2}J_{2\text{-}N,\ 1\text{-}N\text{-}H}$ and $^{3}J_{4\text{-}N,\ 1\text{-}N\text{-}H}$ long-range couplings. Only the signal for the 5-N nitrogen atom appears at 256.9 ppm, due to the long-range coupling with the 6-C-C$H_3$ protons ($^{3}J_{5\text{-}N,\ 6\text{-}C\text{-}CH3}$). The absence of the signal for the 1-N-H proton was also observed for other previously synthesized 1*H*-7-arylazo-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole derivatives variously substituted on the aryl ring [16]. It is interesting that, in the case of 1*H*-7-ethoxycarbonyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4] triazole (3a), the signal for the 1-N-H proton exists and appears in the $^{1}$H-NMR spectrum at 13.95 ppm in DMSO-$d_6$, and therefore the four nitrogen atoms could be identified based on their direct and long-range couplings at 163.6 ppm (1-N), 222.8 ppm (4-N), 257.7 ppm (5-N) and 278.3 ppm (2-N). A possible explanation for the absence of the signal of the 1-N-H proton in the case of 1*H*-7-arylazo-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4] triazole compounds could be the formation of intermolecular hydrogen bonds in a six-atom ring between the 1-N-H proton and the azo nitrogen atom attached to the aryl ring, as shown in Fig. 2. The intermolecular hydrogen bond formed can lead to a rapid proton exchange between the two nitrogen atoms (the heterocyclic and the azo), which causes the proton's decoupling from the 1-N nitrogen atom and renders its coupling with this atom unobservable.

For the two analyzed compounds 1a and 3a it can be observed in the 2D-HMBC $^{1}$H-$^{15}$N spectra that the shielding of nitrogen atoms in the pyrazolo-triazole system decreases in the order 1-N > 4-N > 5-N > 2-N; thus the most shielded nitrogen atom is 1-N, while the least shielded is 2-N.

In the 2D-HMBC $^{1}$H-$^{15}$N spectrum of 1,6-dimethyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2aa), there are long-range couplings observed between the three nitrogen atoms at 158.6 ppm, 254.2 ppm and 286.2 ppm, and two types of protons, the ones at 4.41 ppm assigned to the 1-N-C$H_3$ methyl group and those at 2.74 ppm assigned to the 6-C-C$H_3$ methyl group. The nitrogen atoms at 158.6 ppm and 286.2 ppm couple with the methyl protons at 4.41 ppm (1-N-C$H_3$), while the nitrogen atom at 254.2 ppm couples with the methyl protons at 2.74 ppm (6-C-C$H_3$). Taking into account the

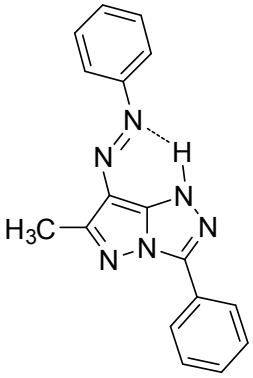



**Figure 2.** Formation of an intermolecular hydrogen bond in 1H-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-c][1,2,4] triazole compounds.

previous assignments of the signals corresponding to the nitrogen atoms in compounds 1a and 3a, and the fact that the only nitrogen atom in compound 2aa able to long-range couple ($^{3}J$) with the 6-C-C$H_3$ protons is the 5-N nitrogen atom, we can safely assign the signal at 254.2 ppm to this atom. Similarly, in agreement with the attributions previously made for compounds 1a and 3a, the other two nitrogen atoms that can long-range couple ($^{2}J$ and $^{3}J$) with the protons of the N-C$H_3$ group are the 1-N atom at 158.6 ppm and the 2-N atom at 286.2 ppm, respectively.

Based on the absence of the coupling ($^{2}J$) between the 5-N nitrogen atom and the methyl group, introduced through alkylation, at 4.41 ppm (N-$CH_3$), we can conclude that the alkylation of 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (1) occurs regioselectively, exclusively at the 1-N nitrogen atom, and the alkylated compound obtained exists only as the 1*H*-1-methyl isomer (2aa).

Another argument in favor of the 1*H*-1-methyl isomer (2aa) is the existence in the 2D-HMBC $^{1}$H-$^{13}$C spectrum of the long-range coupling ($^{3}J$) between the 7a-C carbon atom and the methyl protons at 4.41 ppm, a coupling which wouldn't be possible if the alkylation occurred at the 5-N nitrogen atom, since it would be a four-bond coupling ($^{4}J$).

Also, in the case that the alkylation had occurred on the tautomeric form 2b, at the 5-N nitrogen atom, maximum two long-range couplings between the nitrogen atoms and protons would have been observed in the 2D-HMBC $^{1}$H-$^{15}$N spectrum of the alkylated compound, that is for the 5-N and 4-N nitrogen atoms, because the couplings for the 2-N and 1-N atoms, respectively, are impossible to observe, as they are over distances longer than three bonds.

Similarly to the 2D-HMBC $^{1}$H-$^{15}$N spectrum of the *N*-methylated compound 2aa, in the spectra of *N*-ethylated 2ab, *N*-allylated 2ac and *N*-benzylated 2ad

compounds long-range couplings are observed between three nitrogen atoms and the following protons: that of the 1-N and 2-N atoms with the 1-N-C$\underline{H}_2$- methylene protons and that of the 5-N atom with the 6-C-C$\underline{H}_3$ methyl protons.

In the 2D-HMBC $^{1}$H-$^{13}$C spectra of the three above-mentioned compounds (2ab, 2ac and 2ad), the long-range couplings between the 7a-C carbon and the 1-N-C$\underline{H}_2$- methylene groups are also observed.

Interpretation of the NMR spectroscopic data for the *N*-ethyl (2ab), N-allyl (2ac) and *N*-benzyl (2ad) compounds, respectively, using the same reasoning as for the *N*-methyl compound (2aa), certifies that in these cases the alkylation also occurred regioselectively and exclusively at the 1-N nitrogen atom, in agreement with the tautomeric form 2a.

Two of these 1*H*-1-alkyl-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole dyes, 2aa and 2ab, were also prepared by coupling phenyldiazonium chloride with 1*H*-1-alkyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazoles 1aa and 1ab, respectively, using the method described in literature [9]. Their identity with the compounds 2aa and 2ab obtained through the alkylation of 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2a) was established by comparing their physical characteristics and using IR, UV-VIS, $^{1}$H-NMR, $^{13}$C-NMR and $^{15}$N-NMR spectroscopy.

## 4. Conclusions

Although 1*H*-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (1a) and 1*H*-7-ethoxycarbonyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazole (3a) have been well-known in the literature for a long time, each time they are presented exclusively as the tautomeric form 1a, without providing any scientific reason for this. In this study we elucidated the structure of these compounds using 2D $^{1}$H-$^{15}$N-NMR and $^{1}$H-$^{13}$C-NMR spectroscopy, clearly showing that they exist solely as the tautomeric form 1a and 3a, respectively. Also, for the first time, the corresponding chemical shifts were assigned to the four heterocyclic nitrogen atoms in these two compounds, based on the 2D $^{1}$H-$^{15}$N-NMR spectra.

It was demonstrated that the monoalkylation of 1*H*-6-methyl-3-phenyl-7-phenylazopyrazolo[5,1-*c*][1,2,4]triazole (2a) with various alkylating agents occurs regioselectively, yielding 1-*N*-alkylated compounds 2aa-ad, as proved through 2D HMBC $^{1}$H-$^{15}$N-NMR and $^{1}$H-$^{13}$C-NMR spectroscopy and through comparison of their identity with compounds 2aa and 2ab obtained alternatively by the coupling of phenyldiazonium chloride with 1*H*-1-alkyl-6-methyl-3-phenylpyrazolo[5,1-*c*][1,2,4]triazoles 1aa and 1ab. Also, the chemical shifts corresponding to the heterocyclic nitrogen atoms in the alkylated compounds were attributed, based on the long-range couplings with protons observed in the 2D $^{1}$H-$^{15}$N-NMR spectra.

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