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New C-arylation reaction found during a study on the interaction of aldohydrazones and arenediazonium chlorides

Natalia A. Frolova, Sergey Z. Vatsadze,* Natalia Yu. Vetokhina, Valery E. Zavodnik and Nikolay V. Zyk

Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation.
Fax: +7 495 932 8846; e-mail: szv@org.chem.msu.ru

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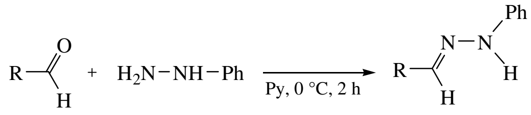
The interaction of 2-pyridinecarboxaldehyde phenylhydrazone 1a with aryldiazonium chlorides furnished in complex mixtures, from which (*E*)-phenylhydrazones of 2-pyridylarylketones 3a–c were isolated as the main products.

1,3,5-Triarylformazanes **2** are very useful substrates for the creation of heterocycles such as verdazyl radicals[1–5] and tetrazolium salts.[6–9] Owing to the presence of a chelating moiety in their structure, formazanes are also known to form metallochelates as a result of reactions with metal salts.[10–16] Attaching to the formazane metal complex molecules the donating units (*i.e.*, pyridines) could lead to a group of promising *exo*-polydentate metalloligands, which combine in their structure the intrinsic property of metal ion (redox, luminescent, catalytic, *etc.*) together with the ability of the whole molecule to act as a building block spanning two external metal centres. The necessary stage in the design of such metalloligands is the synthesis of respective hetaryl-substituted formazanes.

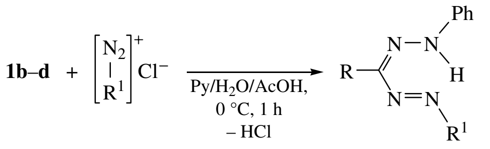


1a–d

a R = 2-Py **c** R = 4-Py
b R = 3-Py **d** R = 2-Thienyl

Scheme 1

Here, we describe a study on the interaction of phenylhydrazones **1a–d** with aryldiazonum salts. This reaction is a well known way to formation of hetarylformazanes. By using of a general synthetic scheme, formazanes **2a–k** were synthesised. Starting phenylhydrazones of 2-thienyl, 2-, 3- and 4-pyridine carboxaldehydes[†] **1a–d** were obtained by interaction of phenylhydrazone with suitable hetarylcarboxaldehydes in pyridine (Scheme 1, Table 1).



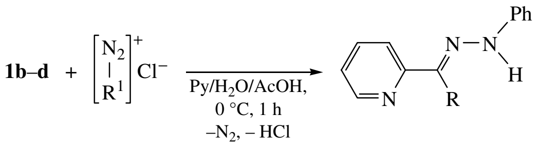
2a–k

2a R = 2-Thienyl, R^1 = Ph
2b R = R^1 = 3-Py
2c R = 3-Py, R^1 = 3-BrC$_6$H$_4$
2d R = 3-Py, R^1 = 3-MeC$_6$H$_4$
2e R = 3-Py, R^1 = 3,5-Me$_2$C$_6$H$_3$
2f R = 3-Py, R^1 = 4-NO$_2$C$_6$H$_4$
2g R = 4-Py, R^1 = 3-Py
2h R = 4-Py, R^1 = 3-BrC$_6$H$_4$
2i R = 4-Py, R^1 = 4-MeC$_6$H$_4$
2j R = 4-Py, R^1 = 3,5-Me$_2$C$_6$H$_3$
2k R = 4-Py, R^1 = 4-NO$_2$C$_6$H$_4$

Scheme 2

The reactions of hydrazones **1b–d** with aryldiazonium chlorides were performed under standard conditions. Formazanes **2a–k** were formed as single products (TLC monitoring) in good yields (Scheme 2, Table 1).[‡]

Contrary to the above data, the reactions of hydrazone **1a** with arenediazonium chlorides resulted in complex mixtures of several products (TLC monitoring). We successively found the procedure that allowed us to isolate major crystalline products from these reaction mixtures. Products **3a–c** were characterised by ^{1}H NMR[§] spectra (Scheme 3, Table 1) and, in the case of **3a**, additionally, by a single-crystal X-ray diffraction study (*vide infra*). A chromatographic study of the reaction mixtures[¶] showed the presence of target formazanes, starting hydrazone **1a**, and other unidentified products.



3a R = Ph
3b R = 4-MeC$_6$H$_4$
3c R = 3,5-Me$_2$C$_6$H$_3$

Scheme 3

Compound **3a** was obtained in two forms (**3a′** and **3a″**) as yellow and red crystals by crystallization from hexane–ethyl acetate (3:1). Although we were unable to separate these forms into individual components, we can state that the red form

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[†] ^{1}H NMR spectra (400 MHz) were recorded on a Bruker-Avance spectrometer in CDCl$_3$.

Phenylhydrazones **1a–c** were obtained previously.[17–19] **1d** was synthesised similarly to **1a–c**. ^{1}H NMR data for **1a** and **1d** are described for the first time in this paper.

1a: ^{1}H NMR, δ: 8.57 (ddd, 1H, α-H$_{\mathrm{Py}}$, J_1 5.0 Hz, J_2 1.8 Hz, J_3 1.1 Hz), 8.36 (s, 1H, NH), 8.03 (d, 1H, β′-H$_{\mathrm{Py}}$, *J* 8.0 Hz), 7.83 (s, 1H, CH=), 7.72 (dt, 1H, γ-H$_{\mathrm{Py}}$, J_1 7.5 Hz, J_2 1.2 Hz), 7.32 (t, 2H, *m*-H$_{\mathrm{Ph}}$, *J* 7.8 Hz), 7.23–7.15 (m, 3H, *o*-H$_{\mathrm{Ph}}$, β-H$_{\mathrm{Py}}$), 6.94 (t, 1H, *p*-H$_{\mathrm{Ph}}$).

1d: ^{1}H NMR, δ: 7.87 (s, 1H, CH=), 7.35–7.20 (m, 4H, *o*-H$_{\mathrm{Ph}}$, α-H$_{\mathrm{Thienyl}}$, NH), 7.12–7.06 (m, 3H, *m*-H$_{\mathrm{Ph}}$, β′-H$_{\mathrm{Thienyl}}$), 7.03 (dd, 1H, β-H$_{\mathrm{Thienyl}}$, J_1 4.9 Hz, J_2 3.5 Hz), 6.89 (t, 1H, *p*-H$_{\mathrm{Ph}}$, *J* 7.3 Hz).

[‡] Formazanes **2a–k** were obtained by a typical experimental procedure.[19]

1,5-Diphenyl-3-(2-thienyl)formazane **2a**: ^{1}H NMR, δ: 14.29 (s, 1H, NH), 7.74–7.64 (m, 5H, *o*-H$_{\mathrm{Ph}}$, α-H$_{\mathrm{Thienyl}}$), 7.48 (t, 4H, *m*-H$_{\mathrm{Ph}}$, *J* 7.8 Hz), 7.35–7.25 (m, 3H, *p*-H$_{\mathrm{Ph}}$, β′-H$_{\mathrm{Thienyl}}$), 6.89 (dd, 1H, β-H$_{\mathrm{Thienyl}}$, J_1 5.1 Hz, J_2 3.5 Hz).

3,5-Di(3-pyridyl)-1-phenylformazane **2b**: ^{1}H NMR, δ: 15.39 (s, 1H, NH), 9.37 (s, 1H, α′-H$_{\mathrm{Py(2)}}$), 8.84 (s, 1H, α′-H$_{\mathrm{Py(1)}}$), 8.62 (s, 1H, α-H$_{\mathrm{Py(2)}}$), 8.52 (d, 1H, α-H$_{\mathrm{Py(1)}}$, *J* 4.1 Hz), 8.36 (d, 1H, γ-H$_{\mathrm{Py(2)}}$, *J* 7.9 Hz), 8.05 (d, 1H, γ-H$_{\mathrm{Py(1)}}$, *J* 8.2 Hz), 7.76 (d, 2H, *o*-H$_{\mathrm{Ph}}$, *J* 7.3 Hz), 7.52 (t, 2H, *m*-H$_{\mathrm{Ph}}$, *J* 7.4 Hz), 7.39 (m, 3H, β-H$_{\mathrm{Py(2)}}$, β-H$_{\mathrm{Py(1)}}$, *p*-H$_{\mathrm{Ph}}$).

3-(3-Pyridyl)-1-phenyl-5-(3-bromophenyl)formazane **2c**: ^{1}H NMR, δ: 15.33 (s, 1H, NH), 9.36 (s, 1H, α′-H$_{\mathrm{Py}}$), 8.62 (d, 1H, α-H$_{\mathrm{Py}}$, *J* 3.8 Hz), 8.37 (d, 1H, γ-H$_{\mathrm{Py}}$, *J* 7.7 Hz), 7.83–7.74 (m, 3H, α′-H$_{\mathrm{Ph(2)}}$, *o*-H$_{\mathrm{Ph(1)}}$), 7.53 (m, 3H, α-H$_{\mathrm{Ph(2)}}$, *m*-H$_{\mathrm{Ph(1)}}$), 7.45–7.30 (m, 4H, β-H$_{\mathrm{Ph(2)}}$, γ-H$_{\mathrm{Ph(2)}}$, β-H$_{\mathrm{Py}}$, *p*-H$_{\mathrm{Ph(1)}}$).

3-(3-Pyridyl)-1-phenyl-5-(4-methylphenyl)formazane **2d**: ^{1}H NMR, δ: 15.50 (s, 1H, NH), 9.37 (s, 1H, α′-H$_{\mathrm{Py}}$); 8.58 (d, 1H, α-H$_{\mathrm{Py}}$, *J* 4.0 Hz), 8.39 (d, 1H, γ-H$_{\mathrm{Py}}$, *J* 8.3 Hz), 7.70 (d, 2H, *o*-H$_{\mathrm{Ph(2)}}$, *J* 8.6 Hz), 7.59 (d, 2H, *o*-H$_{\mathrm{Ph(1)}}$, *J* 8.3 Hz), 7.43 (t, 2H, *m*-H$_{\mathrm{Ph(1)}}$, *J* 7.5 Hz), 7.36 (td, 1H, β-H$_{\mathrm{Py}}$, J_1 7.2 Hz, J_2 4.6 Hz), 7.32 (t, 2H, *m*-H$_{\mathrm{Ph(2)}}$, *J* 8.1 Hz), 7.23 (t, 1H, *p*-H$_{\mathrm{Ph(1)}}$, *J* 7.0 Hz), 2.47 (s, 3H, Me).

3-(3-Pyridyl)-1-phenyl-5-(3,5-dimethylphenyl)formazane **2e**: ^{1}H NMR, δ: 15.50 (s, 1H, NH), 9.40 (s, 1H, α′-H$_{\mathrm{Py}}$), 8.60 (d, 1H, α-H$_{\mathrm{Py}}$, *J* 5.2 Hz), 8.41 (d, 1H, γ-H$_{\mathrm{Py}}$, *J* 8.1 Hz), 7.71 (d, 2H, *o*-H$_{\mathrm{Ph(1)}}$, *J* 8.1 Hz), 7.49 (t, 2H, *m*-H$_{\mathrm{Ph(1)}}$, *J* 7.6 Hz), 7.38 (dd, 1H, β-H$_{\mathrm{Py}}$, J_1 8.3 Hz, J_2 4.9 Hz), 7.35–7.30 (m, 3H, *o*-H$_{\mathrm{Ph(2)}}$, *p*-H$_{\mathrm{Ph(1)}}$), 6.99 (s, 1H, *p*-H$_{\mathrm{Ph(2)}}$), 2.44 (s, 6H, Me).

3-(3-Pyridyl)-1-phenyl-5-(4-nitrophenyl)formazane **2f**: ^{1}H NMR, δ: 14.79 (s, 1H, NH), 9.36 (s, 1H, α′-H$_{\mathrm{Py}}$), 8.67 (d, 1H, α-H$_{\mathrm{Py}}$, *J* 3.2 Hz), 8.37 (dt, 1H, γ-H$_{\mathrm{Py}}$, J_1 8.1 Hz, J_2 2.0 Hz), 8.30 (d, 2H, *o*-H$_{\mathrm{Ph(2)}}$, *J* 9.2 Hz), 7.96 (d, 2H, *o*-H$_{\mathrm{Ph(1)}}$, *J* 7.5 Hz), 7.64–7.56 (m, 3H, *m*-H$_{\mathrm{Ph(1)}}$, *p*-H$_{\mathrm{Ph(1)}}$), 7.51 (d, 2H, *m*-H$_{\mathrm{Ph(2)}}$, *J* 9.3 Hz), 7.41 (dd, 1H, β-H$_{\mathrm{Py}}$, J_1 7.5 Hz, J_2 4.7 Hz).

3-(4-Pyridyl)-5-(3-pyridyl)-1-phenylformazane **2g**: ^{1}H NMR, δ: 15.64 (s, 1H, NH), 8.86 (s, 1H, α′-H$_{\mathrm{Py(2)}}$), 8.71 (d, 2H, α-H$_{\mathrm{Py(1)}}$, *J* 6.0 Hz), 8.56 (s, 1H, α-H$_{\mathrm{Py(2)}}$), 8.06 (d, 1H, γ-H$_{\mathrm{Py(2)}}$, *J* 7.3 Hz), 8.00 (d, 2H, β-H$_{\mathrm{Py(1)}}$, *J* 6.0 Hz), 7.74 (d, 2H, *o*-H$_{\mathrm{Ph}}$, *J* 7.4 Hz), 7.52 (t, 2H, *m*-H$_{\mathrm{Ph}}$, *J* 7.6 Hz), 7.39 (m, 3H, β-H$_{\mathrm{Py(2)}}$, *p*-H$_{\mathrm{Ph}}$).

3-(4-Pyridyl)-1-phenyl-5-(3-bromophenyl)formazane **2h**: ^{1}H NMR, δ: 15.60 (s, 1H, NH), 8.69 (d, 2H, α-H$_{\mathrm{Py}}$, *J* 5.0 Hz), 8.13 (d, 2H, β-H$_{\mathrm{Py}}$, *J* 5.9 Hz), 7.83 (s, 1H, α′-H$_{\mathrm{Ph(2)}}$), 7.78 (d, 2H, *o*-H$_{\mathrm{Ph(1)}}$, *J* 8.1 Hz), 7.60–7.50 (m, 3H, α-H$_{\mathrm{Ph(2)}}$, *m*-H$_{\mathrm{Ph(1)}}$), 7.43 (m, 2H, β-H$_{\mathrm{Ph(2)}}$, γ-H$_{\mathrm{Ph(2)}}$), 7.36 (t, 1H, *p*-H$_{\mathrm{Ph(1)}}$, *J* 8.0 Hz).

3-(4-Pyridyl)-1-phenyl-5-(4-methylphenyl)formazane **2i**: ^{1}H NMR, δ: 15.75 (s, 1H, NH), 8.66 (d, 2H, α-H$_{\mathrm{Py}}$, *J* 5.4 Hz), 8.03 (d, 2H, β-H$_{\mathrm{Py}}$, *J* 6.1 Hz), 7.72 (d, 2H, *o*-H$_{\mathrm{Ph(2)}}$, *J* 8.5 Hz), 7.65 (d, 2H, *o*-H$_{\mathrm{Ph(1)}}$, *J* 7.6 Hz), 7.47 (t, 2H, *m*-H$_{\mathrm{Ph(1)}}$, *J* 7.4 Hz), 7.32 (d, 2H, *m*-H$_{\mathrm{Ph(2)}}$, *J* 8.0 Hz), 7.27 (t, 1H, *p*-H$_{\mathrm{Ph(1)}}$, *J* 7.0 Hz), 2.47 (s, 3H, Me).

3-(4-Pyridyl)-1-phenyl-5-(3,5-dimethylphenyl)formazane **2j**: ^{1}H NMR, δ: 15.73 (s, 1H, NH), 8.66 (d, 2H, α-H$_{\mathrm{Py}}$, *J* 4.9 Hz), 8.01 (d, 2H, β-H$_{\mathrm{Py}}$, *J* 4.6 Hz), 7.70 (d, 2H, *o*-H$_{\mathrm{Ph(1)}}$, *J* 7.3 Hz), 7.49 (t, 2H, *m*-H$_{\mathrm{Ph(1)}}$, *J* 7.5 Hz), 7.38–7.25 (m, 3H, *o*-H$_{\mathrm{Ph(2)}}$, *p*-H$_{\mathrm{Ph(1)}}$), 6.98 (s, 1H, *p*-H$_{\mathrm{Ph(2)}}$), 2.44 (s, 6H, Me).

3-(4-Pyridyl)-1-phenyl-5-(4-nitrophenyl)formazane **2k**: ^{1}H NMR, δ: 15.24 (s, 1H, NH), 8.66 (d, 2H, α-H$_{\mathrm{Py}}$, *J* 5.4 Hz), 8.03 (d, 2H, β-H$_{\mathrm{Py}}$, *J* 6.1 Hz), 8.30 (d, 2H, *o*-H$_{\mathrm{Ph(2)}}$, *J* 9.2 Hz), 7.95 (d, 2H, *o*-H$_{\mathrm{Ph(1)}}$, *J* 7.5 Hz), 7.63–7.53 (m, 3H, *m*-H$_{\mathrm{Ph(1)}}$, *p*-H$_{\mathrm{Ph(1)}}$), 7.50 (d, 2H, *m*-H$_{\mathrm{Ph(2)}}$, *J* 9.3 Hz).

[§] Hydrazones **3a–c** were obtained by an analogous experimental procedure as for **2**. Compounds **3a–c** were separeted for admixture by ablution of reaction mixture by diethyl ether.

*(*E*)-phenylhydrazone of 2-pyridyl phenyl ketone* **3a**: ^{1}H NMR, δ: 8.52 (d, 1H, α-H$_{\mathrm{Py}}$, *J* 4.9 Hz), 8.19 (d, 1H, β′-H$_{\mathrm{Py}}$, *J* 8.1 Hz), 7.80 (s, 1H, NH), 7.73 (td, 1H, γ-H$_{\mathrm{Py}}$, J_1 7.9 Hz, *J* 1.6 Hz), 7.61 (t, 2H, *m*-H$_{\mathrm{Ph(2)}}$, *J* 7.3 Hz), 7.53 (t, 1H, *p*-H$_{\mathrm{Ph(2)}}$, *J* 7.6 Hz), 7.39 (d, 2H, *o*-H$_{\mathrm{Ph(2)}}$, *J* 7.0 Hz), 7.29 (t, 2H, *m*-H$_{\mathrm{Ph(1)}}$, *J* 7.8 Hz), 7.17 (dd, 1H, β-H$_{\mathrm{Py}}$, J_1 7.2 Hz, J_2 6.3 Hz), 7.13 (d, 2H, *o*-H$_{\mathrm{Ph(1)}}$, *J* 7.7 Hz), 6.91 (t, 1H, *p*-H$_{\mathrm{Ph(1)}}$, *J* 7.3 Hz).

*(*E*)-phenylhydrazone of 2-pyridyl 4-methylphenyl ketone* **3b**: ^{1}H NMR, δ: 8.70 (s, 1H, NH), 8.37 (ddd, 1H, α-H$_{\mathrm{Py}}$, J_1 4.9 Hz, J_2 1.7 Hz, J_3 1.0 Hz), 8.25 (dt, 1H, β′-H$_{\mathrm{Py}}$, J_1 8.0 Hz, J_2 1.0 Hz), 7.81 (td, 1H, γ-H$_{\mathrm{Py}}$, J_1 8.3 Hz, J_1 1.8 Hz), 7.36 (d, 2H, *o*-H$_{\mathrm{Ph(2)}}$, *J* 7.1 Hz), 7.28–7.20 (m, 7H, *m*-H$_{\mathrm{Ph(2)}}$, *o*-H$_{\mathrm{Ph(1)}}$, *m*-H$_{\mathrm{Ph(1)}}$, β-H$_{\mathrm{Py}}$), 6.83 (tt, 1H, *p*-H$_{\mathrm{Ph(1)}}$, J_1 6.6 Hz, J_2 1.8 Hz), 2.43 (s, 3H, Me).

*(*E*)-phenylhydrazone of 2-pyridyl 3,5-dimethylphenyl ketone* **3c**: ^{1}H NMR, δ: 8.51 (d, 1H, α-H$_{\mathrm{Py}}$, *J* 3.0 Hz), 8.20 (d, 1H, β′-H$_{\mathrm{Py}}$, *J* 8.0 Hz), 7.78 (s, 1H, NH), 7.71 (td, 1H, γ-H$_{\mathrm{Py}}$, J_1 7.6 Hz, *J* 1.6 Hz), 7.61 (m, 2H, *m*-H$_{\mathrm{Ph(1)}}$, *J* 8.3 Hz), 7.19–7.09 (m, 4H, β-H$_{\mathrm{Py}}$, *p*-H$_{\mathrm{Ph(2)}}$, *o*-H$_{\mathrm{Ph(1)}}$), 6.97 (s, 2H, *o*-H$_{\mathrm{Ph(2)}}$), 6.88 (t, 1H, *p*-H$_{\mathrm{Ph(1)}}$, *J* 7.3 Hz), 2.44 (s, 6H, Me).

Table 1 Characterization of **1a**, **1d**, **2a**–**k**, **3a**–**c**.

Compound	Empirical formula	Elemental analysis (%), calculated (found)			Mp/°C	Yield (%)
		C	H	N		
1a	$C_{12}H_{11}N_3$	73.03 (73.46)	5.62 (5.32)	21.30 (21.62)	176 (EtOH)[a]	70
1d	$C_{11}H_{10}N_2S$	65.32 (65.12)	4.98 (5.00)	13.85 (13.78)	138–139 (EtOH)	77
2a	$C_{17}H_{14}N_4S$	66.64 (66.70)	4.61 (4.16)	18.29 (18.35)	138 (Et_2O)	70
2b	$C_{17}H_{14}N_6$	67.54 (67.50)	4.67 (4.56)	27.80 (27.55)	178–181 (Et_2O–$CHCl_3$, 3:1)	65
2c	$C_{18}H_{14}BrN_5$	56.86 (56.68)	3.71 (3.60)	18.42 (17.96)	128 (Et_2O)	40
2d	$C_{19}H_{17}N_5$	72.36 (72.09)	5.43 (5.57)	22.21 (22.38)	149 (Et_2O)	40
2e	$C_{20}H_{19}N_5$	72.93 (72.90)	5.81 (5.78)	21.26 (21.39)	148–149 (Et_2O)	32
2f	$C_{18}H_{14}N_6O_2$	62.42 (62.35)	4.07 (3.89)	24.26 (24.20)	205–208 (decomp.) (Et_2O)	63
2g	$C_{17}H_{14}N_6$	67.54 (67.50)	4.67 (4.72)	27.80 (27.62)	209 (EtOAc)	46
2h	$C_{18}H_{14}BrN_5$	56.86 (56.80)	3.71 (3.44)	18.42 (18.19)	159–160 (Et_2O)	23
2i	$C_{19}H_{17}N_5$	72.36 (72.45)	5.43 (5.30)	22.21 (22.34)	176–177 (Et_2O)	67
2j	$C_{20}H_{19}N_5$	72.93 (72.81)	5.81 (5.77)	21.26 (21.27)	181–182 (acetonitrile)	30
2k	$C_{18}H_{14}N_6O_2$	62.42 (62.03)	4.07 (4.15)	24.26 (24.50)	232–235 (decomp.) (Et_2O)	25
3a	$C_{18}H_{15}N_3$	79.10 (79.12)	5.53 (4.73)	15.37 (14.84)	148–150 (hexane–EtOAc, 3:1)	33
3b	$C_{19}H_{17}N_3$	79.41 (79.51)	5.96 (6.10)	14.62 (14.89)	168–169 (Et_2O)	45
3c	$C_{20}H_{19}N_3$	79.70 (79.59)	6.35 (6.58)	13.94 (13.89)	141–143 (Et_2O)	35

[a] Lit.,[17] mp 175 °C.

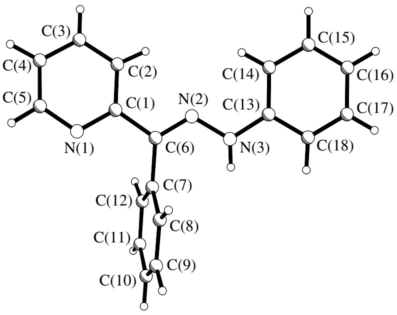

Figure 1 Molecular structure of **3a′**. Projection on the N(2)–N(3)–Ph [C(13) to C(18)] mean plane.

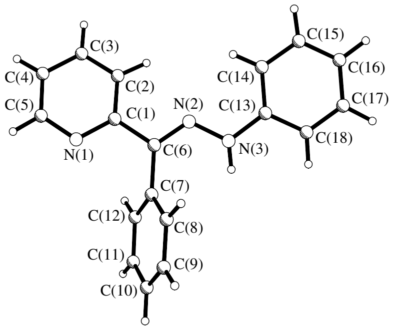

Figure 2 Molecular structure of **3a″**. Projection on the N(2)–N(3)–Ph [C(13) to C(18)] mean plane.

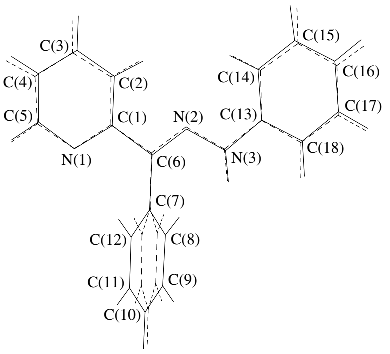

Figure 3 Difference in twisting of phenyl rings [C(7) to C(12)] in **3a′** and **3a″**.

dominates in the mixture. The single-crystal X-ray diffraction study[††] of these two forms showed that the isolated crystals are polymorph modifications of **3a**. The molecular structures of polymorphs are shown in Figures 1 and 2. Structures of molecules of **3a′**[‡‡] and **3a″** are very close to each other. Both contain an almost planar backbone, which includes a pyridine ring, a phenyl group [atoms C(13) to C(18)] and hydrazone C(7), N(2) and N(3) atoms. The structures differ in the degree of tilting of phenyl ring [containing atoms C(7) to C(12)] around the C(6)–C(7) single bond. The respective twisting angles are 73.8° for **3a′** and 44.0° for **3a″** (Figure 3).

According to the above data, products **3** do not possess azo fragments, which were expected for the products of aza-coupling reactions. Compounds **3** are the products of a new C-arylation reaction.

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¶ Column chromatography of **3a**–**c** was carried out on Silica gel (35/70) with a hexane–ethyl acetate (3:1) eluent.

[††] *Crystallographic data for* **3a′**: $C_{18}H_{15}N_3$, yellow prisms, $M = 273.34$, crystals are monoclinic, space group $P2_1/c$, $a = 10.796(2)$, $b = 9.326(2)$ and $c = 14.941(3)$ Å, $\beta = 106.25(3)°$, $V = 1444.2(5)$ Å^3, $Z = 4$, $d_{calc} = 1.257$ g cm^{-3}. Reflections were collected on an Enraf Nonius CAD4 diffractometer at 293 K [$\theta/2\theta$, λ(MoKα) = 0.71073 Å, β-filter]. The structure was solved by a direct method (SHELXS-97) and refined by the full-matrix least-square technique against F^2 for all non-hydrogen atoms (SHELXL-97), GOF = 0.976, $F(000) = 576$. Limiting indices $-12 \le h \le 12$, $0 \le k \le 11$, $0 \le l \le 17$. Reflections collected/unique, 2721/2611 ($R_{int} = 0.0179$), $R_1 = 0.0317$, $wR_2 = 0.0909$ [for 3283 reflections with $I > 2\sigma(I)$], $R_1 = 0.0841$, $wR_2 = 0.0953$ (for all data). Largest difference peak and hole, 0.132 and –0.129 eÅ^{-3}.

Crystallographic data for **3a″**: $C_{18}H_{15}N_3$, red prisms, $M = 273.34$, crystals are monoclinic, space group $P2_1/n$; $a = 12.204(2)$, $b = 8.149(2)$ and $c = 14.766(3)$ Å, $\beta = 99.84(3)°$, $V = 1446.9(5)$ Å^3, $Z = 4$, $d_{calc} = 1.255$ g cm^{-3}. Reflections were collected on an Enraf Nonius CAD4 diffractometer at 293 K [$\theta/2\theta$, λ(MoKα) = 0.71073 Å, β-filter]. The structure was solved by a direct method (SHELXS-97) and refined by the full-matrix least-square technique against F^2 for all non-hydrogen atoms (SHELXL-97), GOF = 1.007, $F(000) = 576$. Limiting indices $-0 \le h \le 14$, $0 \le k \le 9$, $-17 \le l \le 17$. Reflections collected/unique, 2818/2687 ($R_{int} = 0.0233$), $R_1 = 0.0293$, $wR_2 = 0.0882$ [for 3283 reflections with $I > 2\sigma(I)$], $R_1 = 0.0671$, $wR_2 = 0.0930$ (for all data). Largest difference peak and hole, 0.125 and –0.123 eÅ^{-3}.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 610460 and 610461 for **3a′** and **3a″**, respectively. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

[‡‡] **3a′** was obtained earlier[20] by a different method.

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