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Highly Polarized Push-Pull Enediamines: Synthesis and characterization of novel α,α -diamino- β -cyano- β -arylaazoethylenes.

الأنيامينات عالية الاستقطاب: تحضير وخواص الفا الفا ثنائي أمينو بيتا بيتا أرويل أزو اثيلينز

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في هذا البحث تم تحضير بعض الأنيامينات من تفاعل بعض أصباغ الأزو الأروماتية للمالونونيتريل مع البيريدين والمورفولين وذلك بطريقة بسيطة بدلا من الطريقة المستخدمة سابقا في التحضير 6 خطوات . وتم دراسة تأثير الأحماض والهيدرازينات على المركبات الناتجة وقد تم اثبات المركبات الناتجة بواسطة التحليل الدقيق. الأشعة فوق الحمراء، الرنين النووي المغناطيسي للهيدروجين والكربون وكذلك تم اثبات تركيب المركب بواسطة أشعة أكس .

Abstract:

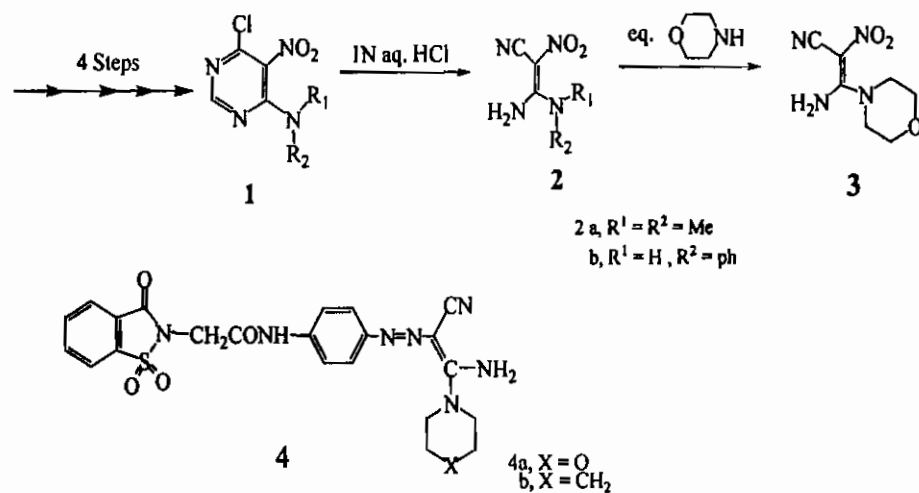
Enediamines was prepared by simple reaction of arylazomalononitriles with piperidine or morphilines in high yield. Reaction of the obtained enediamines with acid and hydrazines was studied. Structure of the novel enediamines was established by x-ray data as well as, spectroscopic and analytical data.

Introduction:

Recently the chemistry of push- pull enamines ^(1,2) is the subject of many reports owing to their successful utility as a starting materials for the synthesis of various substituted heterocycles. In spite of this

importance, very little attention was paid to the synthesis, rather than the utility of enediamines. The known method for enediamines of the type 3 was obtained³⁻⁶ by ring opening of 6- substituted amino-4-chloro-5-nitropyrimidines (1) under acid hydrolysis which was converted to the α,α -diamino- β -cyano- β -nitroethylenes (3) which mainly contaminated with by-products and obtained in poor yields after 6 successive steps (cf. Scheme 1). Also, only one known report ⁷ for the preparation of azaenediamines 4a,b described, for surprising, as colourless compounds.

Key Words: Arylazonitriles/ piperidine
/ morpholine/azaenediamines



Scheme 1

Results and Discussion:

In the present work, α,α -diamino- β -cyano- β -arylaazoethylene (6) was obtained in pure state and in high yields by heating the arylazomalononitriles 5 with piperidine or morphiline in a molar ratio (1:1.2) in ethanol for few minutes. Structure of the obtained

enediamines was established by elemental analysis, IR, ¹H-NMR, C¹³-NMR, and X-Ray analysis of 6c which confirm the E,E-configuration⁸ of the obtained enediamines (cf. experimental).

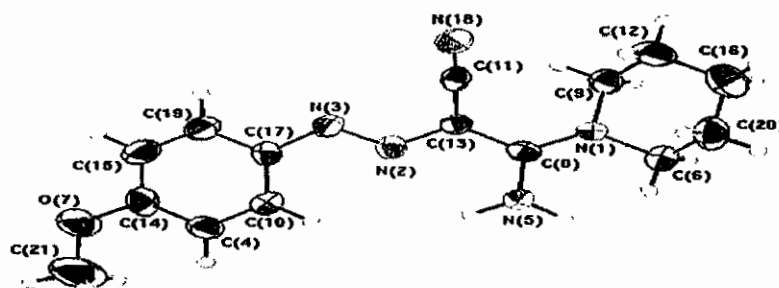


Figure 1: X-Ray crystal structure of 6c

Table 1: Selected Bond angles of 6c

INTRAMOLECULAR BOND ANGLES			
Bond length limits use covalent radii +0.20Å			
N(3)-N(2)-C(13)	118.7(3)	N(2)-N(3)-C(17)	111.0(3)
N(1)-C(8)-N(5)	119.2(4)	N(1)-C(8)-C(13)	123.1(4)
N(5)-C(8)-C(13)	117.7(4)	N(2)-C(13)-C(11)	122.2(4)
C(8)-C(13)-C(11)	121.3(4)		

Table 2: Selected Bond Lengths of 6c

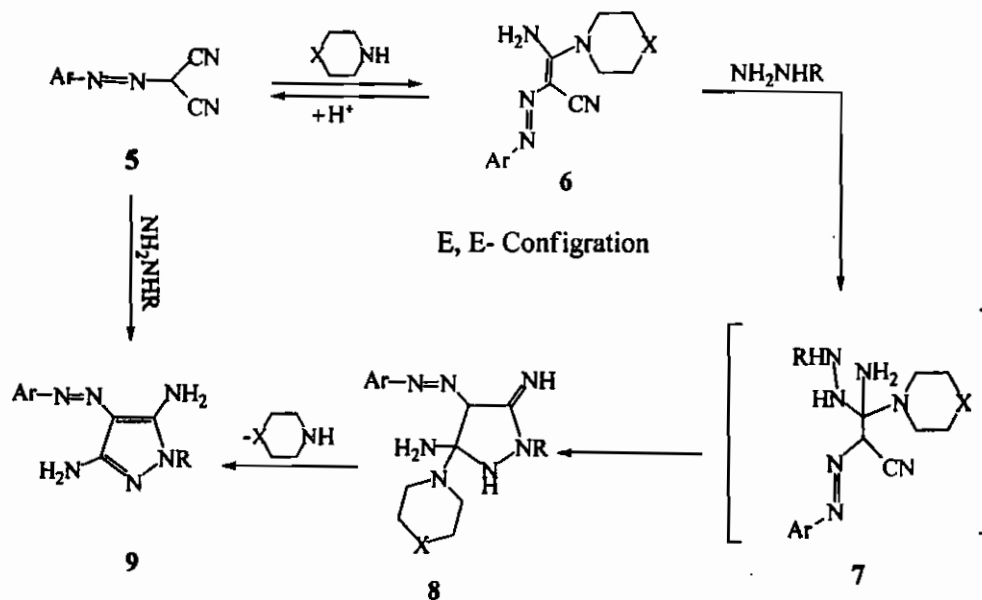
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In contrast to the reported formation of colourless arylazoenediamines derivatives⁷, deepening and lightening of colour was observed in conversion of 5 to 6. This is logic due to the presence of extra bathochromic group (NH₂ and tertiary amines) together with the increasing of conjugation pattern.

The obtained enediamines was converted to the starting arylazo analogues by the

action of acid (acetic acid glacial). Also, reaction of 6a-d with hydrazines gave easily the corresponding known 3,5-diaminopyrazoles^(9,10) 9a-d in high yields.

The most probable mechanism for formation of 9 may be summarized in Scheme 2. Compounds 9 was found identical with those obtained from reaction of 5 with hydrazines, via elimination of the more bulky substitute.



6	Ar	X
a	Ph	CH ₂
b	Ph	O
c	4-C ₆ H ₄ (COCH ₃)	CH ₂
d	4-C ₆ H ₄ (COCH ₃)	O

9	Ar	R
a	Ph	H
b	Ph	Ph
c	4-C ₆ H ₄ (OCH ₃)	H
d	4-C ₆ H ₄ (OCH ₃)	Ph

Scheme 2

Experimental:

Melting points were measured on Barnstead Electrochemical melting point apparatus and were not corrected. Elemental analysis for C, H and N were performed using a Thermo Finnigan Flash EA1112 instrument. -IR spectra were recorded (KBr) with Pye nicam SP-1100 spectrophotometer. - $^1\text{H-NMR}$ and C^{13} -NMR spectra were measured in DMSO on a Bruker 500 spectrophotometer and chemical shifts were expressed in ppm downfield from tetramethylsilane. Mass spectra were recorded on a Finnigan-MAT 8430 spectrometer at an ionization potential 70 ev.

Preparation of arylazoenediamines 6_{a-d} general Procedure- To a solution of **5** (0.01 mol) in absolute ethanol (30 ml) was added piperidine or morpholine (0.012 mol). The reaction mixture was refluxed for 2 hours. The precipitate formed on cooling was collected by filtration and crystallized from chloroform-ethanol mixture.

(EE)-3-amino-2-(phenyldiazinyl)-3-(piperidin-1-yl)acrylonitrile (6_a): Yield 93%, m.p. 168 °C dark orange crystals. -IR: $\nu = 3410-3272 \text{ cm}^{-1}(\text{NH}_2)$, 2183 (CN), - $^1\text{H-NMR}$: $\delta = 1.65(\text{m}, 6\text{H}, 3\text{CH}_2 \text{ piperidine})$, 3.29-3.55(m, 4H, 2CH₂ piperidine), 7.09-7.53 (m, 7H, ArH+NH₂).

(EE)-3-amino-2-(phenyldiazinyl)-3-(morpholin-1-yl)acrylonitrile (6_b): Yield 91%, m.p. 183 °C, bright brown crystals, -IR: $\nu 3440-3274 \text{ cm}^{-1}(\text{NH}_2)$, 2190 (CN). - $^1\text{H-NMR}$: $\delta = 3.59-3.69$, 3.71-3.72 (2t, 8H, $j = 4.73 \text{ Hz}$, CH₂ morph.), 7.1-7.6 (m, 7H, 5ArH+NH₂).

(EE)-3-amino-2-[(4-methoxyphenyl)diazinyl]-3-(piperidin-1-yl)acrylonitrile (6_c): Yield 84%, m.p. 158 °C, brown crystals. -IR: $\nu = 3390-3297 \text{ cm}^{-1}(\text{NH}_2)$, 2197 (CN), - $^1\text{H-NMR}$: $\delta = 1.61-1.64(\text{m}, 6\text{H}, 3\text{CH}_2 \text{ piperidine})$, 3.36-3.54 (m, 4H, 2CH₂ piperidine), 6.89-7.48, 3.76 (s, 3H, OCH₃), 6.89-7.48(m, 6H, ArH,+NH₂): $^{13}\text{C-NMR}$ - $\delta = 23.6$, 25.6(2C), 49.2(2C), 55.3, 91.8, 113.8, 117. -233 (2C), 121.3 (2C), 147.6, 152.4.

(EE)-3-amino-2-[(4-methoxyphenyl)diazinyl]-3-(morpholin-1-yl)acrylonitrile (6_d): Yield 89%, m.p. 193 °C, bright orange crystals. -IR: $\nu = 3440-3274 \text{ cm}^{-1}(\text{NH}_2)$, 2198 (CN), - $^1\text{H-NMR}$: $\delta = 3.32-3.50$, 3.69-3.71 (2t, 8H, $j = 4.59 \text{ Hz}$, CH₂ morph.), 3.71(s, 3H, OCH₃), 6.88-7.53(m, 6H, 4ArH+NH₂).

Preparation of 4-arylhydrazo-3,5-diaminopyrazole (9_{a-d})- general procedure- A mixture of each of **1_{a-d}** (2.0 g) and hydrazine hydrate or phenylhydrazine (2.5 ml) was heated on a boiling water bath for 30 minutes. The reaction mixture was triturated with ethanol and the resulting solid products **9_{a-d}** were crystallized from n-propanol.

3,5-Diamino-4-phenylazo-1H-pyrazole (9_a): Yield 85%, m.p. 263 °C (lit.⁹ m.p. 255 °C).

3,5-Diamino-4-phenylazo-1-phenylpyrazole (9_b): Yield 81%, m.p. 178 °C (lit.⁹ m.p. 174 °C).

3,5-Diamino-4-(4-methoxyphenylazo)-1H-pyrazole (9_c): Yield 78%, m.p. 261 °C, lit.¹⁰ m.p. 259 °C).

3,5-Diamino-4(4methoxyphenylazo)-1-phenylpyrazole (9_d): Yield 81%, m.p. 149 °C, lit.¹⁰ m.p. 157 °C).

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