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Pyrolysis of 4-aryl-5-amino-v-triazolines affords, generally, amidines and/or benzanilides. Pyrolysis of 4-aryl-5-morpholino-v-triazolines **6**, together with the expected amidines **7** and/or aryanilides **8**, produced the morpholinopyrroles **9**. The reaction mechanism of this unusual transformation is discussed. Influence of solvent dipole moment in pyrrole formation is suggested. Pyrrole **9a** [*i.e.* 2-(3-morpholin-4-yl-2,4-pyrrol-1-yl)-benzotrile] has been fully characterized and its molecular structure has been determined by X-ray diffraction analysis.

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Many studies, mainly from our research group, have been carried out on the thermal behaviour of 5-amino-1-aryl-4,5-dihydro-1,2,3-triazoles [2]. All transformation patterns involve ring cleavage and nitrogen elimination

except for the deamination to aromatic 1,2,3-triazoles. Recently we have investigated the behaviour of 5-amino-4-aryl-4,5-dihydro-1,2,3-triazoles bearing on N-1 a substituted phenyl group. A typical outcome of the thermal reaction of the above compounds is their transformation into a mixture of amidines and aryanilides (Scheme 1).

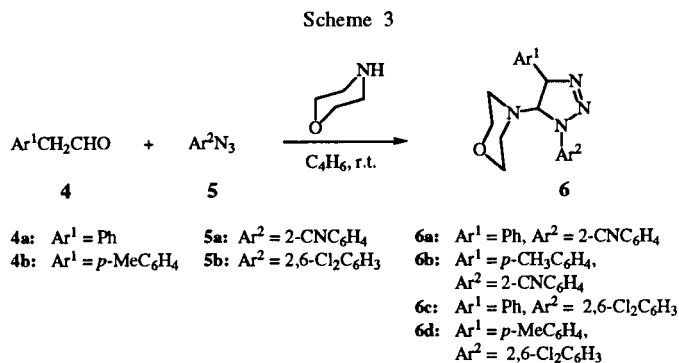
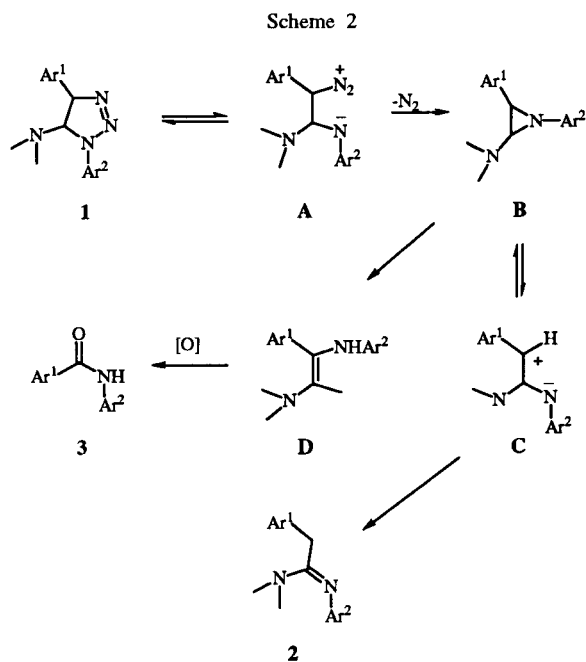
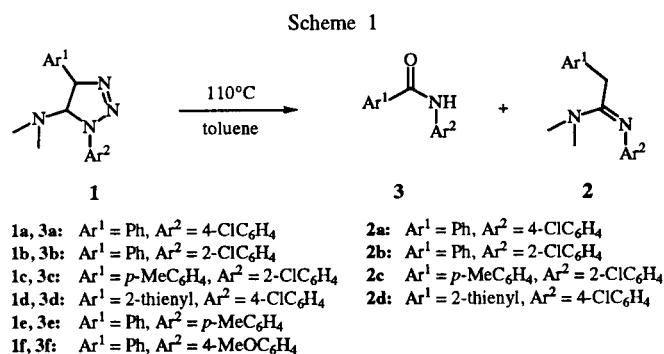
These results have been explained by mechanisms suggested to account for both products [3] and depicted, in simplified form, in Scheme 2.

Scheme 2 comprises highly reactive intermediates, and new mechanistic pathways are dependent upon the presence of an aryl group at both C-4 and N-1.

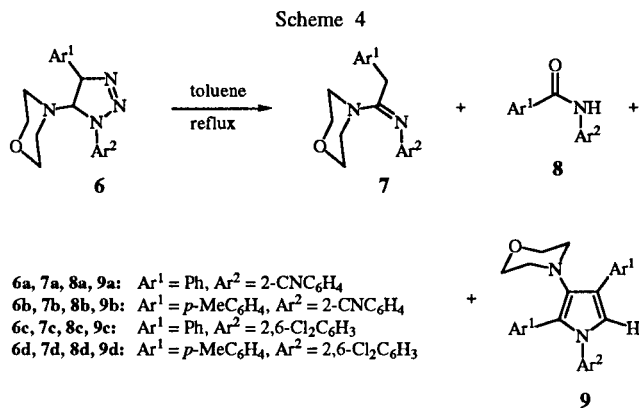
We have studied triazolines where the N-1 aryl group is 2-cyanophenyl or 2,6-dichlorophenyl, to evaluate, in intermediate **C**, the effect of Ar<sup>2</sup> on inducing other transformation modes.

## Results and Discussion.

The reaction of equimolar amounts of phenylacetaldehyde **4a** or 4-methylphenylacetaldehyde **4b** with morpholine and 2-cyanophenylazide **5a** or 2,6-dichlorophenylazide **5b** in benzene at room temperature resulted in direct formation of v-triazolines **6a-d** [4] through 1,3-dipolar cycloaddition of azide to an enaminic intermediate (Scheme 3).



The structure of products **6** was confirmed by analytical and spectroscopic data, mainly  $^1\text{H}$ -nmr spectra showing the typical A-B system associated with H-4 and H-5 (*trans*-configuration) (see Experimental). Compounds **6a-d** when heated in boiling toluene afforded, in short reaction times (70-90 minutes), mixture of transformation products (Scheme 4). Starting from **6a,b** a mixture of compounds was obtained. Expected products were amidines **7a,b** along



with a minor amount of the corresponding benzanilides **8a,b**. However careful analysis and work-up of the reaction mixture allowed detection and isolation of small amounts (about 2%) of a third group of compounds, *i.e.* pyrroles **9a,b**. Different results were obtained starting from 2,6-dichlorophenyl-substituted triazolines **6c,d**: only amidines **7c,d**, with a small amount of pyrroles **9c,d** were obtained [6]. Pyrroles **9a-d**, though obtained in low yield, represent nevertheless interesting results, because their formation can further clarify and complete the pattern of triazolone transformations. Moreover 2,2,4-triaryl-3-tertiaryaminopyrroles are unknown in the literature to our knowledge. Their substitution pattern was inferred from nmr data. Few aminopyrroles are known in the literature and the structure assignment to compounds **9** was made on the basis of  $^1\text{H}$ -nmr and  $^{13}\text{C}$ -nmr by comparison with available data. The  $^1\text{H}$ -nmr of compound **9a** possesses two multiplets at 2.8 and 3.6  $\delta$ , typical for protons of the morpholino group linked with an aromatic structure, and a singlet at 6.96  $\delta$ . The latter is a typical signal of H- $\alpha$  in a pyrrole ring with nitrogen bearing a phenyl group [8a-c]; accordingly it was associated with H-5. The  $^{13}\text{C}$ -nmr of pyrrole **9a** exhibits a signal at 120.54 ppm, related to C-5. This value, too, is in agreement with CH in the  $\alpha$ -carbon of *N*-arylpyrrole [9a,b]. Comparison with available data indicates that the signal at 132.6 ppm should be associated with a  $\beta$ -carbon bearing a morpholino substituent. To this substituent was assigned position 3 because for a structure bearing the morpholino group and the hydrogen substituent on the same side of the ring a higher shift for the CH hydrogen had to be expected [10].

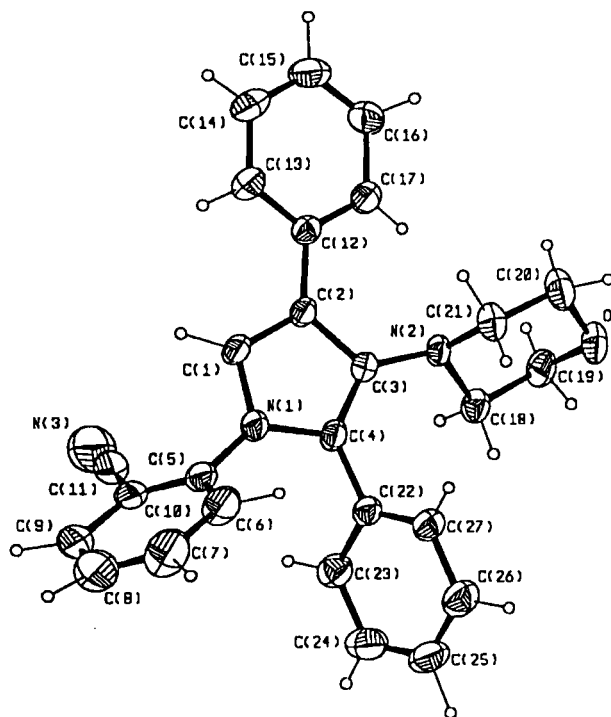


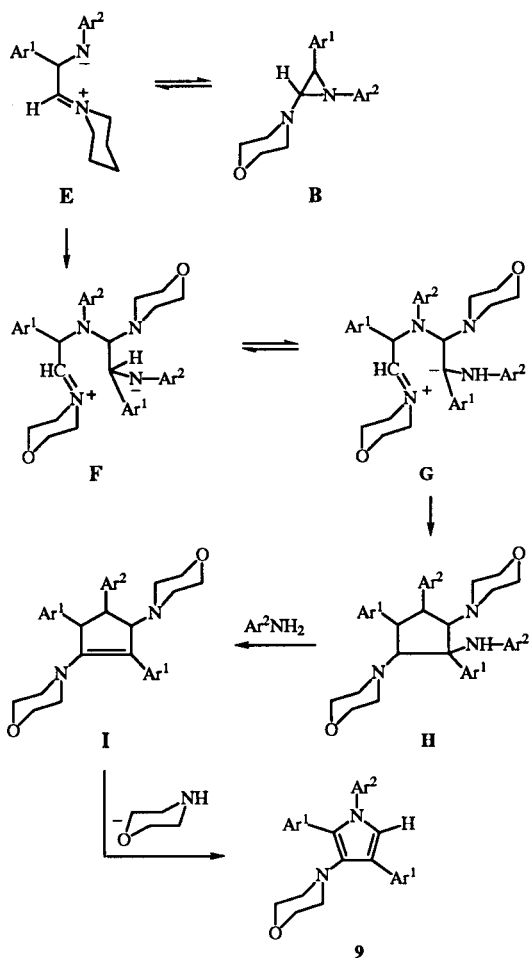
Figure 1. Perspective view of 2-(3-morpholin-4-yl-2,4-diphenylpyrrol-1-yl)benzonitrile (**9a**). Elipsoids are at 40% of probability [18].

The molecular structure of compounds **9** was obtained by X-ray diffraction analysis of pyrrole **9a**.

A perspective ORTEP view of the molecule is shown in Figure 1 together with the atom numbering scheme. In the morpholine ring the torsion angles are in the range  $54.5(4) \rightarrow (61.0(3))^\circ$  averaging  $58.0^\circ$  (referred to absolute values) which is higher than the ideal value of  $54.7^\circ$  for a pure chair conformation. The bonds to the nitrogen atom N(2), having the substituent in an equatorial position, show the expected pyramidal conformation with two about equal N(sp<sup>3</sup>)-C(sp<sup>3</sup>) (1.456 av.Å) lengths, somewhat larger than the third N(2)-C(3) of 1.417(3) Å where some electron delocalization from the pyrrole moiety could be present. This is suggested also by the lengthening of the C(3)-C(4) bond of 1.376(4) Å with respect to the C(1)-C(2) bond of 1.351(4)Å in the pyrrole moiety. The orientation of the aromatic substituents with respect to the pyrrole plane is characterized by the dihedral angles of  $158.1(1)^\circ$  and  $54.1(1)^\circ$  for the two unsubstituted C(12) phenyl and C(22) phenyl, while the substituted C(5) phenyl is rotated of  $61.3(1)^\circ$  with the cyano moiety in the less hindered position towards the unsubstituted C(1) carbon. The shortest intermolecular contact present in the crystal cell is H(1)---O' 2.32(2) Å where H(1) is linked to C(1) of the pyrrole moiety [C(1)-H(1)---O angle is  $163^\circ$ ] ('at x-0.5, 0.5-y, z-0.5).

An examination of the structure of pyrrole **9** [11] provides evidence that it is derived from a reaction of two fragments coming from the starting triazoline after  $N_2$ -elimination. Species **B** or its dipolar form **C** and/or **D** in Scheme 2 can be considered as precursors. Under these conditions the

Scheme 5



consumption of intermediate **D** was excluded owing to oxidation. Indeed, it was previously demonstrated that intermediate **D** is stable until contact with  $O_2$  [3]. However, also under these conditions the yield of compound **9** was not increased, as had to be expected owing to the longer life of intermediate **D**. This result rules out both the origin of pyrrole from an autocondensation reaction of **D** and from the reaction of **D** with **B** and/or **C**. The pyrrole must derive from **B** or from a zwitterionic form different from **C**, through a condensation reaction. In Scheme 5 is depicted a reasonable mechanistic pathway to explain pyrrole formation.

One might consider that the cleavage of the aziridine bond between the N-atom and the C-atom bearing the morpholine residue affords both the diaminoethylene intermediate **D**, mentioned above, and a new zwitterionic intermediate **E**. This latter reacts with **B**, *via* nucleophilic addition, linking the C atom bearing the morpholino residue to give a second dipole **F** in equilibrium with **G**. This tautomer affords the five-ring **H** from which the final aromatic product **9** derives through elimination of substituted aniline and a secondary amine. Expectedly, this reaction mechanism should be favoured by factors enhancing the stability of intermediate **E**. Owing to its zwitterionic character, **E** should be more stable in highly polar solvents. A series of experiments has been performed reacting triazoline **6c** in different solvents. The absolute yield of pyrrole **9c** and the ratio of **9c** to amidine **7c** was measured by hplc analysis. Table 1 lists the experimental results together with the dipole moments [12a,b] of the reaction solvent.

Though a synthetically useful yield of the pyrrole derivative could not be obtained, a clear enhancement of its yield was nevertheless observed with increasing the dipole moment of the reaction solvent. The above view on the origin of the pyrrole by-product was then confirmed by the demonstration that, an increase in  $\mu$ , shifts the reaction path of intermediate **E** towards the formation of pyrrole derivatives, even to the detriment of formation of the 'normal' product, *i.e.* the amidine.

Table 1  
Experimental Conditions to Obtain Pyrrole **9c**

Solvent	$\mu$ (debyes)	T°C time	Heating pyrrole <b>9c</b>	Yield % amidine <b>7c</b>	Yield % % ratio	Pyrrole/amidaine
benzene	0.00	80	12 hours	2.4	87	2.8
toluene	0.36	110	70 minutes	2.2	77	2.9
1-propanol	1.68	97	2.5 hours	2.5	74	3.4
nitromethane	3.46	101	1.5 hours	4.7	63	7.4
dimethylformamide	3.82	154	45 minutes	5.5	84	6.5
acetonitrile	3.92	82	14 hours	4.9	72	6.7
benzonitrile	4.08	190	1 hour	6.0	84	7.2
phthalonitrile [a]	6.19	150	70 minutes	9.9	69	14.4
phthalonitrile: benzonitrile (5:1) [b]	-	110	2 hours	13	70	18.8

[a] Phthalonitrile (mp 139-140°C) was melted, triazoline **6c** was added and the mixture heated for the above indicated time. [b] Phthalonitrile and benzonitrile were mixed in the indicated ratio and fused at 110°C. Triazoline **6c** was added and heated.

Table 2  
Analytical and Spectral Data of Compounds **6c,d** and **7c,d**

Compound No.	Yield (%)	Mp (°C)	<sup>1</sup> H-NMR (δ ppm)	Molecular Formula	Analysis (%)		
					Calcd./Found C	H	N
<b>6c</b>	85	137	2.42-2.86 (m, 4H, CH <sub>2</sub> NCH <sub>2</sub> ), 3.52-3.68 (m, 4H, CH <sub>2</sub> OCH <sub>2</sub> ), 5.27 (d, 1H, J = 5.1Hz, 5-H), 5.47 (d, 1H, J = 5.1Hz, 4-H), 7.17-7.43 (m, 8H, Ar-H)	C <sub>18</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>4</sub> O	57.30	4.80	14.85
					57.22	4.88	14.74
<b>6d</b>	96	140	2.36 (s, 3H, CH <sub>3</sub> ), 2.4-2.85 (m, 4H, CH <sub>2</sub> NCH <sub>2</sub> ), 3.5-3.7 (m, 4H, CH <sub>2</sub> OCH <sub>2</sub> ), 5.26 (d, 1H, J = 5Hz, 5-H), 5.47 (d, 1H, J = 5Hz, 4-H), 7.11-7.49 (m, 7H, Ar-H)	C <sub>19</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>4</sub> O	58.31	5.15	14.31
					58.64	5.21	14.0
<b>7c</b>	75	104	3.52-3.62 (m, 10H, morpholine and CH <sub>2</sub> ), 6.8-7.35 (m, 8H, Ar-H)	C <sub>18</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>2</sub> O	61.91	5.19	8.02
<b>7d</b>	53	103	2.30 (s, 3H, CH <sub>3</sub> ), 3.53 (s, 2H, CH <sub>2</sub> ), 3.55 (s, 8H, morpholine), 6.8-7.25 (m, 7H, Ar-H)	C <sub>19</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>2</sub> O	61.54	5.38	7.99
					62.81	5.55	7.76
					62.53	5.23	7.45

Table 3  
Analytical and Spectral Data of Pyrroles **9a-d**

Compound No.	Yield [a] (%)	Mp (°C)	<sup>1</sup> H-NMR (δ ppm)	MS m/z (% Relative Intensity)	Molecular Formula	Analysis (%)		
						Calcd./Found C	H	N
<b>9a [b]</b>	0.23	207	2.78-2.88 (m, 4H, CH <sub>2</sub> NCH <sub>2</sub> ), 3.58-3.66 (m, 4H, CH <sub>2</sub> OCH <sub>2</sub> ), 6.96 (s, 1H, H-5), 7.12-7.85 (m, 14H, Ar-H)	406 (M <sup>+</sup> +1, 30), 405 (M <sup>+</sup> , 95), 347 (40), 346 (95), 243 (15), 217 (24), 189 (20), 105 (75)	C <sub>27</sub> H <sub>23</sub> N <sub>3</sub> O	79.97	5.71	10.36
						79.81	5.83	10.09
<b>9b [c]</b>	0.26	208	2.30 (s, 3H, CH <sub>3</sub> ), 2.38 (s, 3H, CH <sub>3</sub> ), 2.78-2.92 (m, 4H, CH <sub>2</sub> NCH <sub>2</sub> ), 3.56-3.6 (m, 4H, CH <sub>2</sub> OCH <sub>2</sub> ), 6.92 (s, 1H, H-5), 6.95-7.72 (m, 12H, Ar-H)	434 (M <sup>+</sup> +1, 35), 433 (M <sup>+</sup> , 97), 376 (32), 374 (58), 360 (28), 230 (15), 179 (15), 102 (65)	C <sub>29</sub> H <sub>27</sub> N <sub>3</sub> O	80.34	6.28	9.69
						80.21	6.33	9.44
<b>9c [d]</b>	0.5	225	2.82-2.87 (m, 4H, CH <sub>2</sub> NCH <sub>2</sub> ), 3.61-3.67 (m, 4H, CH <sub>2</sub> OCH <sub>2</sub> ), 6.72 (s, 1H, H-5), 7.1-7.91 (m, 13H, Ar-H)	452 (17), 451(31), 450 (71), 449 (M <sup>+</sup> , 52), 448 (98), 447 (15), 390 (11), 389 (12), 273 (119), 134 (13)	C <sub>26</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>2</sub> O	69.49	4.93	6.23
						69.29	5.09	6.62
<b>9d [e]</b>	0.67	oil	2.28 (s, 3H, CH <sub>3</sub> , <b>9d</b> ), 2.34 (s, 3H, CH <sub>3</sub> , <b>furan</b> ), 2.38 (s, 3H, CH <sub>3</sub> , <b>9d</b> ), 2.41 (s, 3H, CH <sub>3</sub> , <b>furan</b> ), 2.82-2.9 (m, 4H, CH <sub>2</sub> NCH <sub>2</sub> , <b>9d</b> ), 3.18-3.25 (m, 4H, CH <sub>2</sub> NCH <sub>2</sub> , <b>furan</b> ), 3.6-3.7 (m, 4H, CH <sub>2</sub> OCH <sub>2</sub> , <b>9d</b> ), 3.82-3.9 (m, 4H, CH <sub>2</sub> OCH <sub>2</sub> , <b>furan</b> ), 6.68 (s, 1H, H-5, <b>9d</b> ), 6.78 (s, 1H, H-4, <b>furan</b> ), 6.98-7.85 (m, 11H, Ar-H, <b>9d</b> , and m, 8H, Ar-H, <b>furan</b> )		C <sub>28</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>2</sub> O			

[a] For **9a**, **9b**, **9c**, the yields refer to compounds recrystallized from isopropyl ether. [b] Spectra ir (Nujol):  $\nu = \text{cm}^{-1}$ : 2222 (CN) and <sup>13</sup>C-nmr (deuteriochloroform): 53.2 (CH<sub>2</sub>NCH<sub>2</sub>), 68.1 (CH<sub>2</sub>OCH<sub>2</sub>), 111.9 (C-CN), 116.8 (CN), 120.5 (CH-5), 122.5 (C-4), 127.8 (C-2), 126.6, 127.9, 128.0, 128.1, 128.4, 128.6, 129.7, 132.3, 133.4 (14 ArCH), 132.6 (C-3), 135.3 and 135.6 (2Cq-C-1"-phenyl), 143.3 (C-1'-cyanophenyl). [c] Spectra ir (Nujol):  $\nu = \text{cm}^{-1}$ : 2222 (CN). [d] <sup>13</sup>C-nmr (deuteriochloroform): 53.4 (CH<sub>2</sub>NCH<sub>2</sub>), 68.2 (CH<sub>2</sub>OCH<sub>2</sub>), 118.9 (CH-5), 121.5 (C-4), 126.2, 127.8, 128.2, 128.6, 130.1, 131.6 (13 ArCH), 127.4 (C-2), 133.0 (C-3), 134.0 (2C, C-Cl), 136.1 and 136.2 (2Cq, C-1"-phenyl), 136.7 (C-1'-dichlorophenyl). [e] Compound **9d** is mixed with furan (80:20) as determined by <sup>1</sup>H-nmr. The signals of both compounds are indicated above.

## EXPERIMENTAL

Melting points were determined using a Buchi 510 (capillary) and Electrothermal 9100 apparatuses. The ir spectra were measured using a JASCO IR Report 100 instrument. The <sup>1</sup>H and <sup>13</sup>C-nmr spectra with tetramethylsilane as the internal standard were recorded with an EM Varian at 200 MHz and a Bruker AC 200

Spectrometer (<sup>1</sup>H 200.13 MHz, <sup>13</sup>C 50.32 MHz) equipped with an ASPECT 3000 data system; multiplicities were determined with APT pulse sequence. J values are given in Hz for solutions in deuteriochloroform. The apparatus for hplc was Perkin-Elmer 1020 LC. Mass spectra data were obtained on a Varian MAT 1H COS 50 instrument using electron-impact ionization techniques. Column chromatography was performed on Kieselgel 60

Table 4

Selected Bond Lengths (Å) and Angles (°) for C<sub>27</sub>H<sub>23</sub>N<sub>3</sub>O, **9a**

O-C(19)	1.427(4)	O-C(20)	1.427(4)
N(1)-C(1)	1.381(4)	N(1)-C(4)	1.389(3)
N(1)-C(5)	1.417(4)	N(2)-C(3)	1.417(3)
N(2)-C(18)	1.451(4)	N(2)-C(21)	1.461(4)
N(3)-C(11)	1.154(6)	C(1)-C(2)	1.351(4)
C(2)-C(3)	1.434(3)	C(2)-C(12)	1.477(4)
C(3)-C(4)	1.376(4)	C(4)-C(22)	1.475(4)
C(5)-C(6)	1.386(6)	C(5)-C(10)	1.383(5)
C(6)-C(7)	1.375(7)	C(7)-C(8)	1.374(8)
C(8)-C(9)	1.372(9)	C(9)-C(10)	1.395(5)
C(10)-C(11)	1.431(6)	C(16)-C(17)	1.389(6)
C(18)-C(19)	1.500(4)	C(20)-C(21)	1.505(4)
C(26)-C(27)	1.394(5)		
C(19)-O-C(20)	110.2(3)	C(4)-N(1)-C(5)	126.4(2)
C(1)-N(1)-C(5)	122.9(2)	C(1)-N(1)-C(4)	108.8(2)
C(18)-N(2)-C(21)	111.2(2)	C(3)-N(2)-C(21)	115.9(2)
C(3)-N(2)-C(18)	118.1(2)	N(1)-C(1)-C(2)	109.4(2)
C(1)-C(2)-C(12)	124.3(2)	C(1)-C(2)-C(3)	106.6(2)
C(3)-C(2)-C(12)	129.1(2)	N(2)-C(3)-C(2)	123.8(2)
C(2)-C(3)-C(4)	108.3(2)	N(2)-C(3)-C(4)	127.7(2)
N(1)-C(4)-C(3)	106.9(2)	C(3)-C(4)-C(22)	133.2(2)
N(1)-C(4)-C(2)	119.8(2)	N(1)-C(5)-C(10)	120.3(3)
N(1)-C(5)-C(6)	119.7(3)	C(6)-C(5)-C(10)	120.0(3)
C(5)-C(6)-C(7)	119.7(4)	C(6)-C(7)-C(8)	119.9(4)
C(7)-C(8)-C(9)	121.6(6)	C(8)-C(9)-C(10)	118.6(4)
C(5)-C(10)-C(9)	120.1(3)	C(9)-C(10)-C(11)	118.6(3)
C(5)-C(10)-C(11)	121.3(3)	N(3)-C(11)-C(10)	175.4(5)
N(2)-C(18)-C(19)	108.3(2)	O-C(19)-C(18)	110.2(2)
O-C(20)-C(21)	112.0(3)	N(2)-C(21)-C(20)	109.4(2)
C(4)-C(22)-C(27)	120.9(3)	C(4)-C(22)-C(23)	120.2(3)
C(23)-C(22)-C(27)	118.9(3)	C(22)-C(23)-C(24)	120.4(3)
C(23)-C(24)-C(25)	120.4(4)	C(24)-C(25)-C(26)	119.9(4)
C(25)-C(26)-C(27)	120.4(3)	C(22)-C(27)-C(26)	119.8(3)

Table 5

Atomic Coordinates (x 10<sup>4</sup>) for C<sub>27</sub>H<sub>23</sub>N<sub>3</sub>O and Equivalent Isotropic Displacement Coefficients (U) (Å<sup>2</sup>x10<sup>3</sup>)

Atom	x	y	z	Ueq
O	7380 (2)	2065 (3)	6835 (1)	65 (8)
N(1)	4961 (2)	2544 (3)	3128 (1)	48 (8)
N(2)	6026 (1)	2450 (3)	5312 (1)	425 (7)
N(3)	4225 (3)	5984 (5)	2043 (2)	104 (2)
C(1)	4188 (2)	2801 (3)	3421 (2)	46 (1)
C(2)	4460 (2)	2751 (3)	4249 (2)	41 (9)
C(3)	5456 (2)	2440 (3)	4488 (2)	39 (8)
C(4)	5746 (2)	2279 (3)	3788 (2)	43 (9)
C(5)	4879 (2)	2226 (4)	2292 (2)	54 (1)
C(6)	5104 (3)	828 (5)	2072 (2)	78 (2)
C(7)	4978 (3)	496 (7)	1257 (3)	113 (2)
C(8)	4655 (3)	1562 (8)	669 (3)	118 (3)
C(9)	4436 (3)	2958 (6)	872 (2)	87 (2)
C(10)	4562 (2)	3296 (4)	1698 (2)	62 (1)
C(11)	4359 (2)	4765 (5)	1910 (2)	69 (1)
C(12)	3813 (2)	2948 (3)	4771 (2)	45 (9)
C(13)	2845 (2)	2733 (3)	4439 (2)	54 (1)
C(14)	2225 (2)	2936 (4)	4913 (2)	68 (1)
C(15)	2555 (3)	3337 (4)	5727 (2)	74 (1)
C(16)	3503 (3)	3537 (4)	6061 (2)	71 (1)
C(17)	4133 (2)	3358 (4)	5591 (2)	55 (1)
C(18)	6949 (2)	3148 (4)	5490 (2)	49 (1)
C(19)	7291 (2)	3426 (4)	6397 (2)	57 (1)

Table 5 (continued)

Atom	x	y	z	Ueq
C(20)	6484 (3)	1340 (5)	6664 (2)	67 (1)
C(21)	6071 (3)	1061 (4)	5761 (2)	56 (1)
C(22)	6674 (2)	1985 (3)	3644 (2)	47 (1)
C(23)	7036 (2)	2950 (4)	3170 (2)	58 (1)
C(24)	7904 (3)	2679 (5)	3031 (2)	77 (1)
C(25)	8425 (2)	1474 (5)	3372 (2)	78 (2)
C(26)	8074 (2)	501 (5)	3834 (2)	71 (1)
C(27)	7195 (2)	747 (4)	3972 (2)	57 (1)

(Merck) 0.063-0.200 mm with ethyl acetate/cyclohexane (ratios indicated in Experimental). Arylacetaldehyde **4a** is a commercial product, **4b** [13] has already been described. Arylazides **5a** [14] and **5b** [15] were prepared as described in the literature.

General Procedure for the Preparation of 4,5-Dihydro-5-morpholino-1-aryl-1,2,3- triazoles **6a-d**.

A stirred solution of the aryl azide **5** (50 mmoles) in benzene (70 ml) was mixed with an equimolar amount of the suitable aldehyde (50 mmoles). A benzene solution of morpholine (4.4 ml, 50 mmoles) was added dropwise to the previously prepared mixture, which was then stirred at room temperature until the starting aldehyde had disappeared (tlc). The solution was dried with sodium sulfate and the benzene was evaporated under reduced pressure. The crude products were crystallized from diisopropyl ether to afford pure compounds **6a-d**. Compounds **6a,b** are known [5]. Yield, physical and analytical data of **6c,d** are collected in Table 2.

General Procedure for Thermolysis of Triazoline **6a-d**.

The triazolines **6** (4 mmoles) dissolved in toluene (30 ml) were heated under reflux for 70-90 minutes, progress of the reaction being followed by tlc. After disappearance of the starting material solvent was removed *in vacuo* and the viscous oil worked up in three different ways, as described below:

a) The crude mixture, from **6a** and **6b**, was chromatographed on a silica gel column eluted with ethyl acetate/cyclohexane (4:6). From first fraction, pyrrole **9a** or **9b** was isolated (data collected in Table 3); the second fraction contained the known benzanilides **8a** [16] or **8b** [17]; the third fraction was amidine **7a** [5] or **7b** [5].

b) The crude residue from **6c** was chromatographed on a silica gel column and eluted with ethyl acetate/cyclohexane (2:8). The first fraction yielded pyrrole **9c** (data in Table 3), the second fraction was identified as amidine **7c** (data in Table 2).

c) The reaction mixture from **6d** was chromatographed on a silica gel column and eluted with ethyl acetate/cyclohexane (5:95). The first fraction was identified as a mixture of pyrrole **9d** and 3,5-diaryl-2-morpholinofuran (see Results and Discussion: Note [6]) (data in Table 3); the second fraction was amidine **7d** (for data see Table 2). In all cases amidines **7a-d** and pyrroles **9a-c** were crystallized from diisopropyl ether.

Checking the Effect of Solvent Dipole Moment with Respect to Pyrolysis of Triazoline **6c**: Increase of Pyrrole **9c**. HPLC Analysis.

Triazoline **1c** (1.13 g, 3 mmoles) was dissolved or suspended in 10 ml of solvent and heated as shown in Table 1. The decomposition times were related to the solvent boiling points. The reaction

progress was monitored by tlc (eluent: ethyl acetate/cyclohexane 2:8). The solvent was usually removed at reduced pressure. Phthalonitrile, or a mixture of phthalonitrile/benzonitrile, was previously separated from the crude reaction by silica gel column chromatography (eluent ethyl acetate/cyclohexane 3:7) before the hplc analysis. The crude oily residue was then qualitatively and quantitatively analyzed by hplc. A solution of the crude residue (6 mg) in 20 ml of ethyl acetate/*n*-hexane (15:85) was injected (column: Hypersil 5  $\mu$ , 250 x 4.6, uv detector: 254 nm; ethyl acetate/*n*-hexane (15:85); 1 ml/minute).

The chromatogram showed two principal peaks: first peak, smaller in area, was identified as pyrrole **9c** and the second peak, wider in area, was amidine **7c**, respectively by comparison with authentic samples, previously obtained.

#### X-Ray Crystallography of Pyrrole **9a**.

Crystal data  $C_{27}H_{23}N_3O$ , (**9a**)  $M = 405.50$ , monoclinic, space group  $P2_1/n$ ,  $a = 14.702(3)$ ,  $b = 9.057(3)$ ,  $c = 16.957(4)$  Å,  $\beta = 106.09(3)^\circ$ ;  $V = 2169(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.24$  Mg m<sup>-3</sup>,  $\lambda = (\text{MoK}\alpha) = 0.71069$  Å,  $\mu(\text{MoK}\alpha) = 0.80$  cm<sup>-1</sup>,  $F(000) = 856$ ,  $T = 294$  K.

A prismatic yellow crystal of dimensions 0.44 x 0.20 x 0.52 mm was centered on a four-circle Philips PW1100 diffractometer with graphite-monochromated  $\lambda(\text{MoK}\alpha)$  radiation. The orientation matrix and preliminary unit-cell dimensions were determined from 30 reflections found by mounting the crystal at random, varying the orientation angles  $\chi$  and  $\Phi$  over a range of  $120^\circ$ , with  $7 \leq \theta \leq 9^\circ$ . For the determination of precise lattice parameters, 30 strong reflections with  $10 \leq \theta \leq 12^\circ$  were considered. Integrated intensities for  $hkl$  reflections ( $h = \pm 19$ ;  $k = 0/11$ ,  $l = 0 \rightarrow 22$ ) were measured in the interval  $\theta = 3\text{--}28^\circ$ , using  $\theta/2\theta$  scans. Two standard reflections, 4,1,0 and -4,1,1, were collected every 200 reflections. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-Polarization effects but not for absorption.

#### Structure Solution and Refinement.

The structure was solved by direct methods (SIR 92) [18] and refined by full-matrix least-squares on  $F^2$  (SHELXL 93) [19] with anisotropic thermal parameters for all non-H atoms and isotropic for hydrogen atoms whose positions were detected from difference Fourier maps. The function minimized was  $\Sigma w(F_o^2 - F_c^2)^2$  and  $w^{-1} = \sigma^2(F_o)^2 + (aP) + bP$ , where  $3P = (2F_c^2 + F_o^2)$  and  $a$  and  $b$  are constants adjusted by the program. The final  $wR(F)^2$  was 0.11 with conventional  $R(F)$  0.045 ( $R$  factors defined in ref. 19) for 372 parameters and 2144 reflections having  $(F_o)^2 \geq (3\sigma(F_o)^2)$ , g.o.f. = 0.97, maximum  $\Delta/\rho$  0.3 eÅ<sup>-3</sup>. Final geometrical calculations were carried out with PARST [20], drawing with ORTEP II [21] programs. Selected bond lengths and angles are given in Table 4 and atomic coordinates in Table 5. Thermal parameters and full list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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