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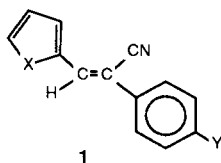
The ¹H-nmr data of some (Z)-α-(p-substituted-phenyl)-β-(2-furyl), -β-(2-pyrrolyl), and -(N-methyl-2-pyrrolyl)-acrylonitriles have been investigated to indicate the preferred conformation and to establish the conformational preferences of the β-heterocyclic ring. The ultraviolet spectra have been discussed in order to obtain information about the chromophores responsible for the absorption. The infrared spectra have been analyzed for the identification of the main absorption frequencies of cyano and ethylenic groups and to assign the characteristic absorption bands to specific normal vibrations of the heteroaromatic nuclei.

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Our previous studies were related to the spectroscopic properties of some thienyl and furyl compounds [1,2]. Recently we reported a conformational study of (E)-α,β-diarylethylenes containing a -COOH or a -NO₂ group in α-position and a five-membered heterocyclic nucleus in β-position [3,4], and a ¹H-nmr approach to the conformations of some α,β-diarylacrylonitriles [5].

Following this research work we report here ¹H-nmr, ultraviolet and infrared spectra of some (Z)-α-(p-substituted-phenyl)-β-(2-furyl), -β-(2-pyrrolyl) and -(N-methyl-2-pyrrolyl) acrylonitriles I with the aim to establish the conformational preferences of the β-heterocyclic ring, to elucidate the

signment. As previously found on (E)- and (Z)-α,β-diarylacrylonitriles, ¹H-nmr data exhibited a singlet in the (E) structure that changed into a complex pattern in the (Z) isomer [5]. Because of poor solubility at low temperature we could not have low temperature ¹H-nmr spectra to provide insight on the population of S-trans and S-cis rotamers of the acrylonitriles containing a β-heterocyclic nucleus. However it is possible to establish the preferred conformations from ¹H-nmr data at room temperature (Scheme 1). The signal of H-5 in the (E)- and (Z)-α,β-diarylacrylonitriles exhibited a noticeable stereospecific long-range spin-spin coupling (0.7 Hz) with the ethylene proton



X = O (1a), NH (1b), NCH₃ (1c)

Y = H, CH₃, CH₃O, Cl, NO₂

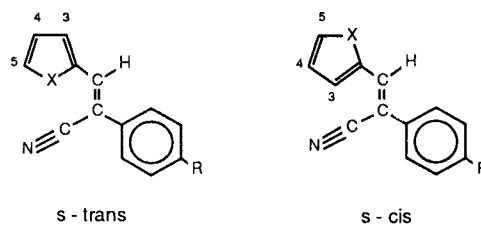
chromophores responsible for the absorption, to identify the main absorption frequencies of cyano and ethylenic groups, and to assign the characteristic absorption bands to specific normal vibrations of the heteroaromatic nuclei.

Results and Discussion.

Although it is known that the base catalyzed reaction of aldehydes with acetonitriles forms α-β-diarylacrylonitriles only of Z configuration [1,6-12], we used the ¹H-nmr spectral data to confirm the preferred Z configurations of α-phenyl-β-heteroarylacrylonitriles I and to establish the conformational preferences of the β-heterocyclic rings.

For α-phenyl-β-heteroarylacrylonitriles I the shape of the phenyl signal can be used for the configurational as-

Scheme 1



[5]. A multiplicity of eight lines (first-order) appeared because of the couplings with H₃, H₄ and ethylene proton. As known, a trans coplanar disposition (dihedral angle 0°) is necessary for the ⁵J_{H,H} (W-plan) couplings [3,12-16] (Scheme 2). No coupling was observed between H-4 and the

Scheme 2

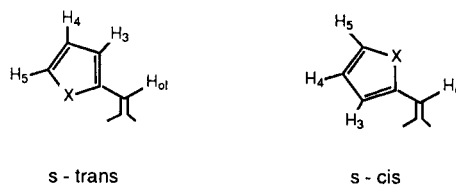
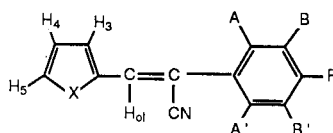


Table 1
Chemical Shifts (δ , ppm) of the Protons of Compounds I in Deuteriochloroform



No.		H _{ol}	H ₃	H ₄	H ₅	H _{AA'}	H _{BB'}	J _{H_{ol}-H₄} (Hz)	N-H
1	Ia, X = O, Y = H	(7.36-7.62)		6.35	7.20	(7.36-7.62)		0.5	
2		CH ₃	7.30	7.59	6.57	7.20	7.55	7.19	
3		CH ₃ O	7.26	7.57	6.55	7.15	7.57	6.93	0.5
4		Cl	7.54	7.63	6.69	7.23	7.48	7.31	0.55
5		NO ₂	7.53	7.76	6.65	7.34	7.82	8.31	
1	Ib, Y = NH, Y = H		7.36	6.66	6.33	7.05	(7.20-7.47)		N-H
2		CH ₃	7.26	6.68	6.33	7.05	7.31	7.46	9.93
3		CH ₃ O	7.28	6.63	6.31	7.03	6.95	7.50	9.76
4		Cl	(7.37-7.58)	6.70	6.37	7.08	(7.37-7.58)		9.72
5		NO ₂	7.81	7.09	6.41	7.16	8.26	7.75	9.82
1	Ic, X = NCH ₃ , Y = H	(7.30-7.55)	7.61	6.26	6.76	(7.30-7.55)			10.75
2		CH ₃	7.28	7.46	6.25	6.75	7.18	7.47	0.75
3		CH ₃ O	7.23	7.40	6.28	6.80	6.93	7.53	0.57
4		Cl	(7.26-7.60)	7.51	6.31	6.83	(7.26-7.60)		
5		NO ₂	7.51	7.64	6.36	6.92	8.28	7.75	

olefinic proton. The H-4 signal appearing as a clear first-order quartet (doublet of doublets) because of the spin-spin couplings with H-3 and H-5. The *s-trans* conformation so seems to be preferred by those (*E*)- and (*Z*)- α - β -diarylacrylonitriles [5]. In the compounds where the *S-cis* conformation was preferred the signal of H-4 exhibited a stereospecific long-range spin-spin coupling with the ethylene proton. No coupling was observed between H-5 and the olefinic protons [5]. As previously found the shape of the phenyl signal in the α -phenyl- β -heteroaryl acrylonitriles I here studied show a complex pattern, indicating the (*Z*) conformation of these compounds (Table 1).

In the case of the (*Z*)- α -phenyl- β -(2-furyl)acrylonitriles (Ia) a 5J_w of about 0.5 Hz between H₄ and H_{ol} is observed, whereas no coupling occurs H₅-H_{ol}. Moreover a marked deshielding is noticed on H₃ because of the magnetic anisotropy of cyano group. So it is evident that the *S-cis* conformation is preferred by (*Z*)- α -phenyl- β -(2-furyl)acrylonitriles (Ia). This can be ascribed to the destabilization of the thermodynamically favoured *S-trans* conformation [17,18] owing to electrostatic interaction between the negative charged oxygen and the cloud of the cyano group. This interaction appears to be similar to that previously observed for some (*E*)- α , β -diarylethylenes containing a -COOH or a NO₂ group in α position and a furyl ring in β position [3,8,12].

The nmr spectra of (*Z*)- α -phenyl- β -(2-pyrrolyl)acrylonitriles (Ib) reveal that the N-H proton is strongly deshielded

and the H₃ proton resonates between H₄ and H₅ at the usual fields. To detect the stereospecific couplings we reduced the multiplicity of the heterocyclic protons by N-H deuteration. The spectra of the deuterated compounds exhibit $^5J_{H_{ol}-H_4} = 0.0$. This behaviour indicates that the *S-trans* conformation is preferred by the 2-pyrrolyl compounds (Ib).

The (*Z*)- α -phenyl- β -(*N*-methyl-2-pyrrolyl)acrylonitriles (Ic) assume the *S-cis* conformation because of steric hindrance between the bulky N-CH₃ and cyano group. The spectra of *N*-methyl-2-pyrrolyl derivatives in fact show the deshielding effect on H₃, owing to the magnetic anisotropy of the cyano group and the stereospecific coupling H_{ol}-H₄ due to their *trans* disposition ($^5J_{H_{ol}-H_4} \sim 0.75$). As expected nmr spectral data of (*Z*)- α -phenyl- β -(*N*-methyl-2-pyrrolyl)acrylonitriles show that H₃ resonates at the lowest fields among the heterocyclic protons and a marked deshielding was displayed by H₃ (about 1 ppm). Thus, differently from the 2-pyrrolyl derivatives, the *S-cis* conformation is preferred by the *N*-methyl-2-pyrrolyl compounds.

Ultraviolet Spectra.

The ultraviolet spectral data of the compounds are listed in Table 2.

The spectrum of *trans*-stilbene shows an intense band at 295 nm. This band was considered a conjugation band and the assignment was in agreement with the results of PPP calculations and INDO |S-CI calculations [19]. By the introduction of the α -cyano group in the stilbene framework

Table 2

Ultraviolet Spectral Data of Compounds I				
No.		λ max		$\log \epsilon$
1	Ia, X = O, Y = H	236		3.70
		342		4.46
2	Y = CH ₃	239		4.02
		344		4.46
3	Y = CH ₃ O	240		3.99
		353		4.46
4	Y = Cl	239		4.05
		346		4.49
5	Y = NO ₂	235		3.95
		271		3.76
6	Ib, X = NH, Y = H	242		4.01
		367		4.48
7	Y = CH ₃	245		4.13
		278 [a]		3.64
8	Y = CH ₃ O	369		4.54
		242		4.03
9	Y = Cl	307 [a]		3.66
		369		4.48
10	Y = NO ₂	249		4.04
		373		4.54
11	Ic, X = NCH ₃ , Y = H	250 [a]		3.78
		414		4.49
12	Y = CH ₃	243		4.02
		280 [a]		3.49
13	Y = CH ₃ O	373		4.47
		245		4.04
14	Y = Cl	281		3.37
		375		4.48
15	Y = NO ₂	245		4.05
		290		3.60
16	Y = Cl	378		4.47
		244		4.08
17	Y = NO ₂	280 [a]		3.45
		375		4.55
18	Y = NO ₂	253		3.75
		325		3.59
19	Y = NO ₂	416		4.34

[a] Inflection.

the conjugation band is shifted bathochromically by about 20 nm. The intensity of the conjugation band in the *trans*-stilbene is reduced in its cyano derivative by steric inhibition of resonance and the angle of twist of the phenyl was calculated to be 26° [19]. The substitution of a 2-furan, 2-pyrrole or *N*-methyl-2-pyrrole for a benzene ring produces a bathochromic shift in the conjugation band.

Trans-2-styrylfuran is characterized by an inflection at 234 nm ($\log \epsilon = 3.95$), and absorption bands at 240 nm ($\log \epsilon = 3.91$), 305 nm ($\log \epsilon = 4.40$), 316 nm ($\log \epsilon = 4.42$), and 330 nm ($\log \epsilon = 4.36$) [20]. *Trans*-2-styrylpyrrole shows absorptions at 236 nm ($\log \epsilon = 3.92$), 242 nm ($\log \epsilon = 3.90$) and 330 nm ($\log \epsilon = 4.44$) [21] *N*-methylation of *trans*-2-styrylpyrrole produces a slight bathochromic shift and a considerable hypochromic shift of the conjugation. The absorption bands are at 239 nm ($\log \epsilon = 4.02$), 244 nm (\log

Table 3

Frequency of the Longest Wavelength Band (cm ⁻¹) of Compounds I					
No.	X =	-CH=CH- [a]	O	NH	NCH ₃
1	Y = H	32260	29240	27250	26810
2	CH ₃	31445	29070	27100	26670
3	CH ₃ O	30210	28330	27100	26455
4	Cl	31445	28900	26810	26670
5	NO ₂	29940	27030	24155	24040

[a] (Y = substituent, λ max nm 95% ethanol, ref synthesis); H, ref [26]; CH₃, 230, 4.16; 318, 4.39; J. Serges and A. Bruylants, *Helv. Chim. Acta.*, **40**, 561 (1957); CH₃O, 233, 4.08; 331, 4.36; S. S. Kulp and C. B. Caldwell, *J. Org. Chem.*, **45**, 171 (1980); Cl, 229, 4.12; 319, 4.42; S. S. Kulp and C. B. Caldwell, *J. Org. Chem.*, **45**, 171 (1980); NO₂, 222, 4.07; 334, 4.43; A. Schonne, E. Braye and A. Bruylants, *Bull. Soc. Chim. Belg.*, **62**, 155 (1953).

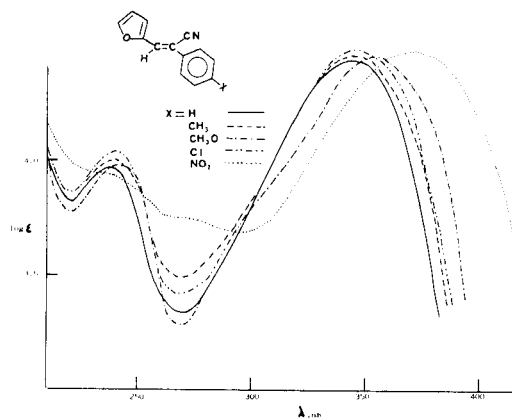


Figure 1. Ultraviolet spectra of (*Z*)- α -(*p*-substituted-phenyl)- β -(2-furyl)acrylonitriles.

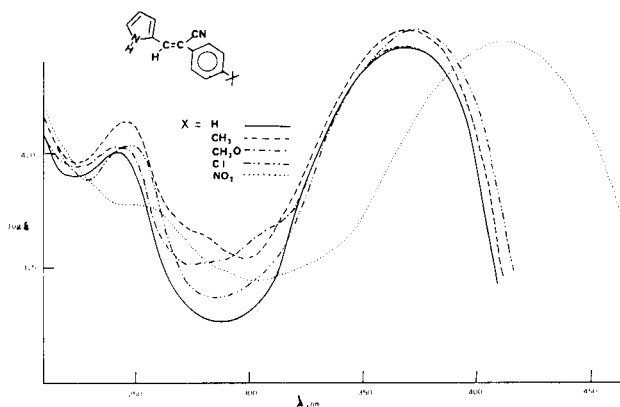


Figure 2. Ultraviolet spectra of (*Z*)- α -(*p*-substituted-phenyl)- β -(2-pyrrolyl)acrylonitriles.

$\epsilon = 3.98$), and 339.5 nm ($\log \epsilon = 4.35$) [22]. The effects of the α -cyano substitution on the spectral characteristics of (*Z*)- α -(phenyl)- β -(2-furyl), -(2-pyrrolyl) or -(*N*-methyl-2-pyrrolyl)acrylonitriles I are analogous to those induced in the stilbene spectrum shifting the conjugation bands bathochromically by about 20 nm (Figures 1-3).

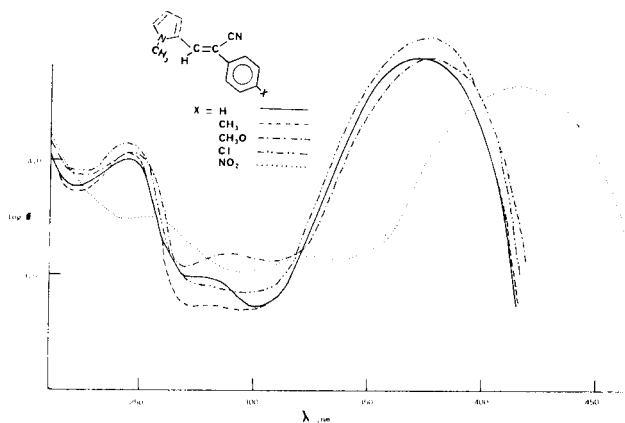


Figure 3. Ultraviolet spectra of $(Z)\text{-}\alpha\text{-}(p\text{-substituted-phenyl})\text{-}\beta\text{-}(N\text{-methyl-2-pyrrolyl})\text{acrylonitriles}$.

The uv spectra are useful to assign the geometry of the compounds here reported. A linear relationship is obtained plotting λ max of p -substituted *trans*-stilbenes [22,23] where Y is constant but X varies in I against the λ max of the corresponding α,β -diarylacrylonitriles, indicating that the compounds here reported are in the *Z* configuration. Figure 4 shows as an example the plot of λ max of p -substituted-*trans*-2-styrylpyrroles [22] and the λ max of the corresponding $\alpha\text{-}(p\text{-substituted-phenyl})\text{-}\beta\text{-}(2\text{-pyrrolyl})\text{acrylonitriles}$.

We can compare the energies of the electronic transition from the ground to the first excited state in compounds I. This is proportional to the frequency of the longest wavelength band (Table 3).

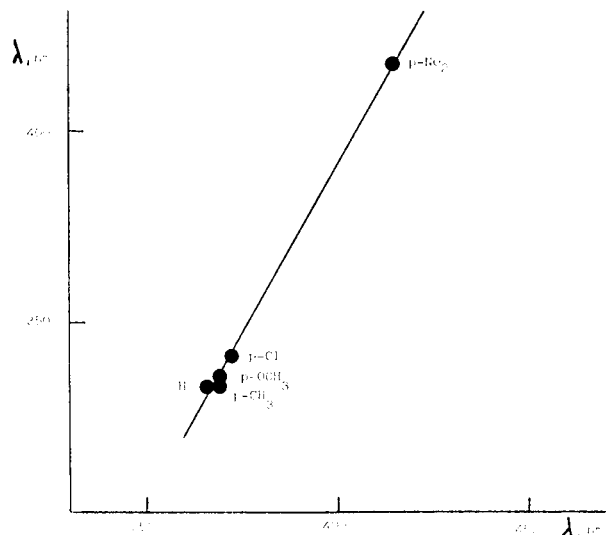


Figure 4. Plot of λ max of p -substituted-*trans*-2-styrylpyrroles against λ max of the corresponding $\alpha\text{-}(p\text{-substituted-phenyl})\text{-}\beta\text{-}(2\text{-pyrrolyl})\text{acrylonitriles}$ (Ib).

The effect of the substituents in the benzenoid compounds is measured by the differences between the values for the substituted compounds and that for the unsubstituted derivative. These differences are all negative ($X = \text{H}$, $Y = \text{CH}_3$, -815 ; $Y = \text{CH}_3\text{O}$, -2050 ; $Y = \text{Cl}$, -815 ; $Y = \text{NO}_2$, -2320) showing that the introduction lowers the energy of transition to the excited state. The size of the effect varies with the substituent being $\text{NO}_2 > \text{OCH}_3 > \text{Cl} = \text{CH}_3$, as found in *trans*-styryl compounds [24]. The effect depends on the conjugation power of the substituent

Table 4

Infrared Spectral Data of $(Z)\text{-}\alpha\text{-}(p\text{-Y-Phenyl})\text{-}\beta\text{-}(2\text{-furyl})\text{acrylonitriles}$ (Ia)

No.		ν CN	ν C=C	I	II	III	V	VI	VII	VIII	IX	X
1	Y = H	2207 s	1593 s	1573 m	1494 m	1392 m	1248 m	1140 m	1085 s	1025 s	932 s	885 s
2	CH ₃	2206 s	1614 s	1590 m	1509 s	1389 m	1249 m	1141 m	1086 s	1022 s	930 s	883 s
3	CH ₃ O	2210 s	1603 s	1573 m	1510 s	1384 m	1254 s	1138 m	1084 s	1023 s	930 s	884 s
4	Cl	2210 s	1596 s	1570 m	1491 s	1408 m	1249 m	1143 m	1093 s	1027 s	932 s	886 s
5	NO ₂	2209 s	1597 s	1582 s	1510 s	1381 m	1254 m	1147 m	1090 s	1024 s	934 s	884 s

s = strong, m = medium.

Table 5

Infrared Spectral Data of $(Z)\text{-}\alpha\text{-}(p\text{-Y-Phenyl})\text{-}\beta\text{-}(2\text{-pyrrolyl})\text{acrylonitriles}$ (Ib)

No.		ν NH	ν CN	ν C=C	I	II	III	ν NH [a]	VI	VII	VIII	IX
1	Y = H	3390 s	2204 s	1597 s	1549 m	1452 m	1424 m	1128 s	1095 m	1000 m	903 m	879 m
2	CH ₃	3386 s	2200 s	1603 s	1555 m	1446 m	1414 s	1127 s	1096 s	997 m	897 m	878 m
3	CH ₃ O	3330 s	2202 s	1602 s	1569 m	1451 m	1430 s	1137 s	1102 s	1014 m	896 m	880 m
4	Cl	3398 s	2199 s	1598 s	1561 m	1458 m	1412 s	1129 s	1093 s	1001 m	907 m	878 m
5	NO ₂	3362 s	2207 s	1600 s	1562 m	1458 m	1428 s	1124 s	1094 s	1002 m	914 m	876 m

[a] NH in-plane deformation, s = strong, m = medium.

Table 6

Infrared Spectral Data of (*Z*)- α -(*p*-Y-Phenyl)- β -(*N*-methyl-2-pyrrolyl)acrylonitriles (Ic)

No.		ν CN	ν C=C	I	II	IV	VI	VII	VIII
1	Y = H	2207 s	1586 s	1529 m	1482 s	1378 m	1099 m	1005 m	900 s
2	CH ₃	2198 s	1588 s	1530 m	1482 s	1382 m	1093 m	1007 m	887 m
3	CH ₃ O	2203 s	1606 s	1523 m	1484 s	1381 m	1091 m	1012 m	890 s
4	Cl	2198 s	1596 s	1534 m	1479 s	1382 m	1094 m	1004 m	891 m
5	NO ₂	2197 s	1578 s	1532 m	1485 s	1382 m	1095 m	1009 m	901 m

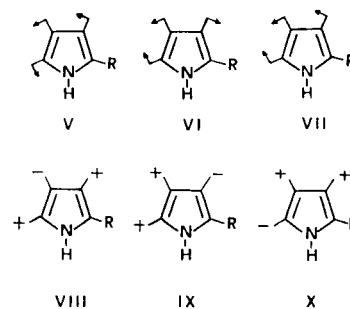
s = strong, m = medium.

but not on whether it is an electron-acceptor or -donor. The effect on the heterogroup in the unsubstituted heterocyclic compounds is indicated by the differences between their frequencies and that of (*Z*)- α , β -diphenylacrylonitrile. These differences (X = O, Y = H, -3020; X = NH, -5010; X = NCH₃, -5450) are in the same order as the electron-donating properties of the heterocyclic rings [22].

Infrared Spectra.

The infrared data of the compounds I for cyano, ethylenic and heteroaromatic nuclei are listed in Tables 4-6. The position of the CN absorption band is insensitive to structural changes and it is located in the 2197-2210 cm⁻¹ region [1,25]. The ethylenic absorption band for (*Z*)- α -(*p*-substituted-phenyl)- β -(2-furyl)acrylonitriles (Ia) is in the range 1593-1614 cm⁻¹ (Table 4). The normal vibrations of the furan can be divided into: (a) ring stretching modes; (b) CH-in-plane deformation modes; (c) ring breathing mode; (d) CH-out-of-plane deformation modes. Furan shows bands at 1590, 1487 and 1381 cm⁻¹ [26], and they were assigned to the normal stretching modes I-III [27]. The ring stretching mode IV was not found in this region [1]. The absorption bands shown by 2-substituted furan derivatives (Ia) at 1570-1590, 1491-1510, 1381-1408 cm⁻¹ are assigned to the ring stretching modes I-III respectively, according to the Katritzky numbering convention [25]. The CH-in-plane deformations are at 1248-1254 (V), 1138-1147 (VI), and 1084-1093 cm⁻¹ (VII). The band at 990 cm⁻¹ for furan has been assigned to the ring breathing mode VIII. 2-Substituted furan derivatives show a corresponding band at 1002-1032 cm⁻¹ [1,25]. Compounds Ia show this band at 1011-1027 cm⁻¹. The CH-out-of-plane deformation are at 930-934 (IX) and 884-886 cm⁻¹ (X). Many investigations have been made on the infrared spectra of pyrrole and 24 normal vibrational modes have been assigned to observed absorption bands [28]. The normal vibrations of the pyrrole nucleus can be divided into: (a) N-H stretching mode near 3400 cm⁻¹; (b) CH stretching modes near 3100 cm⁻¹; (c) C-C and C-N stretching vibrations in the region 1600-1350 cm⁻¹; (d) CH-in-plane deformations near 1250-100 cm⁻¹; (e) CH-out-of-plane deformations near 1000-700 cm⁻¹; (f) NH-in and -out-of-plane deformations; (g) a ring breathing mode [28,29]. The NH-out-of-plane deformation causes absorption in the region of 500 cm⁻¹ and then it will

not be treated. In Table 5 are listed the main absorption bands for (*Z*)- α -(*p*-substituted-phenyl)- β -(2-pyrrolyl)acrylonitriles (Ib). The NH stretching vibration of compounds Ib is located at 3300-3398 cm⁻¹ [28,30]. Absorption due to the ring stretching modes (I-IV) for 2-substituted pyrroles should be similar to those found for pyrrole. Lord and Miller [31] reported bands at 1531, 1466, 1418 and 1384 cm⁻¹, corresponding to those modes for pyrrole. In the spectra of 2-substituted pyrroles only three bands were observed which probably correspond to the vibration modes I-III [29]. In the spectra of (*Z*)- α -(*p*-substituted-phenyl)- β -(2-pyrrolyl)acrylonitriles (Ib) only three bands are observed at 1549-1569 (I), 1446-1458 (II) and 1412-1430 cm⁻¹ (III). The ethylenic absorption band for *trans*-2-styrylpyrroles is in the range 1633-1637 cm⁻¹ [22]. Conjugation with the cyano group displaces the ν C=C by 20-40 cm⁻¹ below its normal position [32]. Compounds Ib and Ic show the ν C=C absorption at 1578-1606 cm⁻¹. The band at 1124-1137 cm⁻¹ has been assigned to the NH-in-plane deformation mode. For pyrrole this mode was found at 1138 cm⁻¹ and for other 2-substituted pyrroles at 1110-1122 cm⁻¹ [29]. Five membered rings with three adjacent hydrogen atoms will have three-in-plane (V-VII) and three out-of-plane deformation modes (VIII-X) [29]. The bands at 1093-1102



cm⁻¹ and at 1038-1048 cm⁻¹ are assigned to modes VI and VII respectively. The mode corresponding to V was not found [29]. The bands at 896-914 and 876-880 cm⁻¹ probably correspond to modes VIII and IX. The strongly Raman band of pyrrole at 1144 cm⁻¹ has been assigned to the ring breathing frequency of pyrrole. However, its complete absence from the Raman and infrared spectrum of pyrrole-N-d places some doubt on this assignment [29]. An absorption band near 870-990 cm⁻¹ has been assigned to

the ring breathing mode of polysubstituted pyrroles by analogy with the spectra of other aromatic systems [33]. Several discrepancies are in the assignments for the ring breathing mode [29] and therefore we have not assigned this mode. Table 6 lists the main absorption bands of (*Z*)- α -(*p*-substituted-phenyl)- β -(*N*-methyl-2-pyrrolyl)acrylonitriles (Ic). Three bands at 1523-1534, 1479-1485, and 1378-1382 cm^{-1} are assigned to the modes I, II, and IV respectively. These positions correspond closely to those of absorption bands of other 1- and 2-substituted pyrroles as found by Jones [34].

Absorption bands at 1091-1099, 997-1014 cm^{-1} are assigned to the modes VI and VII. The band at 887-901 cm^{-1} is due the CH-out-of-plane deformation (VIII). No absorption band could be assigned with any certainty to the ring breathing vibration.

EXPERIMENTAL

Acrylonitriles I were prepared by condensation of heterocyclic aldehydes with the appropriate arylacetonitrile in the presence of base [1]: a solution of the aldehyde (0.02 mole) and arylacetonitrile (0.02 mole) were shaken in warm ethanol with a few drops of 30% aqueous potassium hydroxide. The substance precipitated was washed with water, and recrystallized from ethanol.

(*Z*)- α -(Phenyl)- β -(2-furyl)acrylonitrile had mp 43-44° [35]; (*Z*)- α -(*p*-methyl-phenyl)- β -(2-furyl)acrylonitrile had mp 79-80° [5]; (*Z*)- α -(*p*-methoxyphenyl)- β -(2-furyl)acrylonitrile had mp 61-62° [35]; (*Z*)- α -(*p*-chlorophenyl)- β -(2-furyl)acrylonitrile had mp 80-81° [35]; (*Z*)- α -(*p*-nitrophenyl)- β -(2-furyl)acrylonitrile had mp 73-74° [36].

(*Z*)- α -(Phenyl)- β -(2-pyrrolyl)acrylonitrile had 98-99° [5]; (*Z*)- α -(*p*-methylphenyl)- β -(2-pyrrolyl)acrylonitrile had mp 104-105° [5]; (*Z*)- α -(*p*-methoxyphenyl)- β -(2-pyrrolyl)acrylonitrile had mp 118-119°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$: C, 74.98; H, 5.39; N, 12.49. Found: C, 75.11; H, 5.31; N, 12.57.

(*Z*)- α -(*p*-Chlorophenyl)- β -(2-pyrrolyl)acrylonitrile had mp 122-123°.

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{ClN}_2$: C, 72.73; H, 4.22; N, 6.52. Found: C, 72.85; H, 4.30; N, 6.61.

(*Z*)- α -(*p*-Nitrophenyl)- β -(2-pyrrolyl)acrylonitrile had mp 206-207°.

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_2$: C, 65.27; H, 3.79; N, 17.56. Found: C, 65.35; H, 3.68; N, 17.63.

(*Z*)- α -(Phenyl)- β -(*N*-methyl-2-pyrrolyl)acrylonitrile had mp 99-100° [5]; (*Z*)- α -(*p*-methylphenyl)- β -(*N*-methyl-2-pyrrolyl)acrylonitrile had mp 100-101° [5]; (*Z*)- α -(*p*-methoxyphenyl)- β -(*N*-methyl-2-pyrrolyl)acrylonitrile had mp 110-111°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$: C, 75.60; H, 5.92; N, 11.75. Found: C, 75.71; H, 5.99; N, 11.84.

(*Z*)- α -(*p*-Chlorophenyl)- β -(*N*-methyl-2-pyrrolyl)acrylonitrile had mp 184-185°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{ClN}_2$: C, 69.28; H, 4.57; N, 11.54. Found: C, 69.12; H, 4.63; N, 11.67.

(*Z*)- α -(*p*-Nitrophenyl)- β -(*N*-methyl-2-pyrrolyl)acrylonitrile had mp 290-291°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2$: C, 66.39; H, 4.38; N, 16.59. Found: C, 66.51; N, 4.47; N, 16.68.

The ^1H -nmr spectra were performed on 5% solutions with ca. 1% TMS as the internal standard. A Bruker WP 80 spectrometer was used. Deuteriochloroform of commercial quality was employed as solvent. The J values were measured directly from the spectra run at maximum scale width. The uv spectra were obtained with a Hitachi Perkin-Elmer EPS-3T spectrometer, using 5×10^{-5} M solutions in 95% ethanol. The ir spectra were obtained using a Perkin-Elmer 237 spectrometer. All compounds investigated were compressed into potassium bromide pellets. Wave

number were accurate to $\pm 1 \text{ cm}^{-1}$.

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