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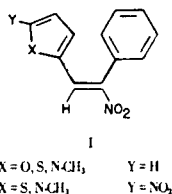
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The 60 MHz room temperature pmr data of some  $\alpha$ -nitro- $\beta$ -arylstyrenes are used to assign the stereochemical configuration. The variable temperature pmr spectra exclude the presence of a rotational isomerism. The preferred conformation are then established by analysis of the chemical shifts of the heterocyclic protons.

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In previously reported conformational analyses on (*E*)-1,2-diaryl substituted ethylene systems (3,4) containing a heterocyclic ring we observed that the interaction between the heteroatom and the  $\pi$ -cloud of the adjacent phenyl ring represents a relevant contribution to the determination of the conformational preferences.

We now wish to report further results about some (*E*)- $\alpha$ -nitro- $\beta$ -arylstyrenes I which are structurally similar to the systems before investigated (3-6).



The  $\alpha$ -nitrostyrenes derivatives I were synthesized by Knoevenagel reaction starting from the suitable heterocyclic Schiff's base and phenylnitromethane (see Experimental).

Only the compounds I (X = O, S; Y = H) were described in the literature (7), but no configuration assignment was reported.

#### Results and Discussion.

The assignments of the configuration of the styrene derivatives I were deduced by analysis of their room temperature pmr spectra (Table I). The resonance lines of olefinic proton in all these compounds show a strong deshielding effect which cannot be interpreted with a (*Z*)-structure where the interaction between the phenyl

ring and the olefinic proton should be the same of structurally similar molecules, *i.e.* the (*Z*)- $\alpha$ -phenyl- $\beta$ -arylacrylic acids (4-6) and the (*Z*)- $\alpha$ -phenylcinnamic acids (8). Consequently, not too downfield chemical shift values for the ethylene proton should be observed. It seems, therefore, that the (*E*)-configuration can be inferred to the molecules I, in which a marked anisotropic deshielding occurs on the ethylene proton owing to the adjacent nitro group; the same effect is caused by the carboxyl in the (*E*)- $\alpha$ -phenyl- $\beta$ -arylacrylic acids (4-6).

The differences between the olefinic proton chemical shift values of the molecules I can be ascribed to a different inductive and anisotropic effect of the various heterocyclic rings and to a contribution caused by their different conformational behaviour (9).

Electronic spectral data (Table II) seem to be in agreement with the hypothesis of the (*E*)-configuration. As previously observed for molecules containing a *trans*- $\beta$ -nitrostyrene structure 1a (10-12), which is strictly similar

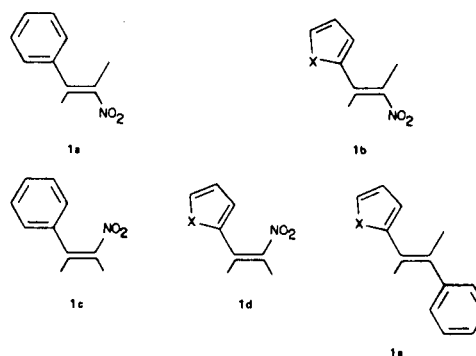
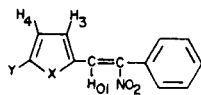


Table I

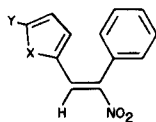
Chemical Shifts ( $\delta$  ppm) and Stereospecific Coupling Constants (Hz) of the Protons of some (*E*)- $\alpha$ -Nitro- $\beta$ -arylstyrenes



		H <sub>01</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	J <sub>H<sub>01</sub>-H<sub>5</sub></sub>	J <sub>H<sub>01</sub>-H<sub>4</sub></sub>
X = S	Y = H	8.45	7.25-7.62	7.00	7.25-7.62	0.6	0.0
X = S	Y = NO <sub>2</sub>	8.30	7.62	7.77	---	---	0.0
X = O	Y = H	8.15	6.13	6.38	7.22-7.55	0.0	0.5
X = N-CH <sub>3</sub>	Y = H	8.32	5.53	5.98	6.83	0.0	0.6
X = N-CH <sub>3</sub>	Y = NO <sub>2</sub>	8.28	5.42	7.08	---	---	0.6

to the main chromophore **1b** of the compounds I, the electronic spectra exhibit a strong absorption beyond 300 nm.

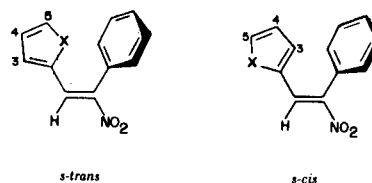
Table II

Electronic Spectral Data of the (*E*)- $\alpha$ -Nitro- $\beta$ -arylstyrenes

		$\lambda$ max, nm	(log $\epsilon$ )
X = S	Y = H	294 (i)	(4.13)
		315	(4.18)
		360 (i)	(3.77)
X = S	Y = NO <sub>2</sub>	282	(3.70)
		369	(4.24)
X = O	Y = H	314	(3.96)
		362 (i)	(3.59)
X = N-CH <sub>3</sub>	Y = H	234	(4.02)
		409	(4.25)
X = N-CH <sub>3</sub>	Y = NO <sub>2</sub>	275	(4.02)
		379	(4.26)

No absorption at the high wavelengths showed by the compounds I should be caused by the presence of a *cis*- $\beta$ -nitrostyrene chromophore **1c** (10-12) or, analogously, by a strictly similar structure **1d**, neither by a *trans*- $\beta$ -arylstyrene chromophore **1e** (13,14).

The (*E*)-styrenes I can assume both *s-trans* and *s-cis* conformations.

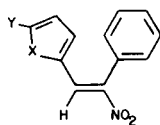


In order to determine the relative populations of the two rotamers we have undertaken a low temperature pmr study. Pmr spectra of the (*E*)- $\alpha$ -nitro- $\beta$ -(2-thienyl) and  $\beta$ -[2-(5-nitro)thienyl]styrene I (X = S; Y = H, NO<sub>2</sub>) are unchanged down to -90°.

Because of the strong conjugation between the heterocyclic ring and the nitro group (see electronic spectral data, Table II), the barrier to the rotation may reasonably be considered higher than the one observed for the 2-formyl derivatives of furan, pyrrole and thiophene (about 10 Kcal/mole) (15-17) and similar to the barrier in the parent (*E*)- $\alpha$ -phenyl- $\beta$ -arylacrylic acids. Therefore, no free rotation averaging the two rotamers' signals can be thought at lowest temperatures.

Sufficient differences between the two rotamers' spectral features are expected depending on the different chemical environment of the 3-heterocyclic proton in the *s-cis* or in the *s-trans* isomer. Hence, the presence of a rotational isomerism would have been detected. We may therefore suggest that the compounds I (X = S; Y = H, NO<sub>2</sub>) exist in only one conformation. The room temperature chemical shift values of the 3-heterocyclic proton can be used to decide which is the actual conformation. The inspection of Table I reveals no shielding effect on the 3-heterocyclic proton, which should be present in the

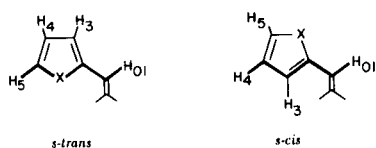
Table III

Melting Points and Analytical Data of the (*E*)- $\alpha$ -Nitro- $\beta$ -arylstyrenes

		M.p. (°C)	Formula	Analyses		Found
				C%	H%	Calcd.
						N%
X = S	Y = H	126-127 (a)				
X = S	Y = NO <sub>2</sub>	184-185	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> S	52.07	2.80	10.10
				52.17	2.92	10.14
X = O	Y = H	88-89 (a)				
X = N-CH <sub>3</sub>	Y = H	136-137	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	67.80	5.25	12.01
				68.41	5.30	12.27
X = N-CH <sub>3</sub>	Y = NO <sub>2</sub>	163-164	C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub>	56.92	4.04	15.27
				57.14	4.06	15.38

(a) Reference 7.

*s-cis* preferred conformation (3,4) owing to the diamagnetic anisotropic effect of the phenyl ring current. The 3-proton values are in fact substantially similar to those of the (*E*)- $\alpha$ -phenyl- $\beta$ -(2-thienyl)acrylic acids, where no diamagnetic effect was evidenced by comparison with the corresponding (*Z*)-isomers (3). In addition in the compound I ( $X = S$ ;  $Y = H$ ) the resonance lines of the 5-heterocyclic proton show a characteristic stereospecific  $W_5$  plan coupling (0.6 Hz) (4, 18-20) with the olefinic proton according to the *trans*-coplanar disposition of the two protons in the *s-trans* conformation, whereas no coupling is observed between the  $H_{O1}$  and the 4-heterocyclic proton.



Therefore we can conclude that the molecules I ( $X = S$ ;  $Y = H$ ,  $NO_2$ ) occur only in the *s-trans* conformation.

As can be evidenced by the inspection of the molecular model, the compounds I ( $X = N-CH_3$ ;  $Y = H$ ,  $NO_2$ ) are biased in the *s-cis* conformation because of the steric interaction between the  $N-CH_3$  and the adjacent phenyl ring in the *s-trans* rotamer. Consequently, the 3-heterocyclic proton should be strongly shielded (Table I) by the electronic current (3-4) of the  $\pi$ -cloud of the perpendicular (21) benzene nucleus. This is experimentally observed (Table I) and further evidenced by comparison of  $H_3$  chemical shift values with those of  $H_4$  and  $H_5$ . In fact in the compound I ( $X = N-CH_3$ ;  $Y = H$ ), among the three heterocyclic protons, the 3-proton absorbs at highest field values, whereas, generally, in substituted pyrroles containing in the 2-position a withdrawing substituent the 4-proton gives the resonance at highest field (22).

According to the *trans*-coplanar disposition of the  $H_{O1}$  and  $H_4$  in the *s-cis* rotamer, a stereospecific coupling ( $J_{H_{O1}, H_4}^S = 0.6$  Hz) is observed. No coupling is noticed between  $H_{O1}$  and  $H_5$ .

No broadening of the heterocyclic proton lines is observed in the pmr low temperature spectrum of the (*E*)- $\alpha$ -nitro- $\beta$ -(2-furyl)styrene I ( $X = O$ ;  $Y = H$ ) down to  $-80^\circ$ , this indicating the presence of only one rotational isomer. The splitting of the 4-heterocyclic proton is very significant to decide which rotamer is present. In fact we observe eight lines (ddd) because of the further presence of the stereospecific  $W_5$  plan coupling with the olefinic proton ( $J_{H_{O1}, H_4} = 0.5$  Hz). No coupling with the olefinic proton is observed on the  $H_5$  signal. In addition,  $H_3$  (Table I) shows its resonance at higher field than  $H_4$  and  $H_5$ , differently from what generally observed for furan derivatives containing a withdrawing substituent in the 2-position (22). A shielding effect is then evidenced, as observed for the (*N*-methyl)pyrrolylstyrene derivatives I.

It can be concluded that also the molecule I ( $X = O$ ,  $Y = H$ ) populates only the *s-cis* conformation.

The different conformational behaviour of the 2-thienyl and 2-furylstyrene derivatives I can be ascribed to the different interaction between the negatively charged heterocyclic oxygen and the  $\pi$ -electrons of the phenyl ring (3).

To observe the possible transition to the other conformation, we performed high temperature pmr measurements of the compounds I ( $X = S$ ,  $O$ ;  $Y = H$ ) in the range from  $+40^\circ$  to  $+135^\circ$ . No change of the spectral features is observed in both compounds, such as chemical shift values, spin-spin coupling constants and line widths of the heterocyclic protons. The population of the alternative conformation, *i.e.* the *s-cis* in the 2-thienyl and the *s-trans* in the 2-furyl derivative, seems to be hindered, at least until to  $+135^\circ$ , by its sufficiently higher energy with respect to the existing rotamer. The presence of only one conformation is then proved conclusively.

## EXPERIMENTAL

The samples of the (*E*)- $\alpha$ -nitro- $\beta$ -arylstyrenes were synthesized adding to a solution (about 4 *M*) of phenylnitromethane in glacial acetic acid, equal molar amounts of the appropriate Schiff's base (23) of the heterocyclic aldehyde with *n*-butylamine. The precipitation of the reaction product begins within 1 hour. To complete the crystallization the mixture is allowed to stand overnight at room temperature, then the solid is filtered, washed with water and crystallized in all cases from absolute ethanol.

Melting points and analytical data are summarized in Table III.

Room temperature 60 MHz pmr spectra were recorded in 5% solutions with *ca.* 1% of TMS as internal standard. In all cases deuteriochloroform of commercial quality was used, except for I ( $X = N-CH_3$ ;  $Y = NO_2$ ) where  $DMSO-d_6$  was employed.

Low temperature pmr spectra were performed in a mixture of acetone- $d_6$ :dichloromethane- $d_2$  (2:1). High temperature pmr spectra were obtained in 5% dimethylformamide solutions. A Varian A-60D spectrometer with variable-temperature accessories was used.

Electronic spectra were recorded in 95% ethanol (Hitachi-Perkin Elmer EPS-3T spectrometer).

Acknowledgments.

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