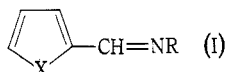


THE ELECTRONIC AND INFRARED SPECTRA OF *N*-ARYL FURFURYLIDENE- AND THENYLLIDENE-IMINES*

By R. J. HEAD† and R. ALAN JONES‡

In the course of our investigations¹ of the structure of 2-pyrrolylmethylene-imines (I; X = NH, NCH₃) we also prepared the corresponding furan and thiophen compounds (I; X = O and S). We now record the electronic and infrared spectra of these compounds (Table 1).



All of the compounds with the aryl ring directly attached to the imine nitrogen atom have two high intensity absorption bands above 270 mμ, but the lower intensity band usually observed in the 220–230 mμ region for 2-substituted furans and

TABLE 1
ELECTRONIC ABSORPTION MAXIMA (IN ETHANOL) AND C=N STRETCHING FREQUENCIES
(IN CHLOROFORM)

R	λ (mμ)	10 ⁻³ ε	λ (mμ)	10 ⁻³ ε	λ (mμ)	10 ⁻³ ε	ν(C=N) (cm ⁻¹)	ε
Furans (I; X = O)								
C ₆ H ₄ N(CH ₃) ₂ - <i>p</i>	284	10.8			388	15.4	1626	350
C ₆ H ₄ OCH ₃ - <i>p</i>	288	13.4			340	17.1	1629	330
C ₆ H ₄ CH ₃ - <i>p</i>	289	13.3			328	14.4	1632	220
C ₆ H ₅	290	11.0			319.5	10.6	1632	240
C ₆ H ₄ F- <i>p</i>	290	14.5			322	14.9	1633	300
C ₆ H ₄ Cl- <i>p</i>	293	15.4			325	16.9	1631	280
C ₆ H ₄ Br- <i>p</i>	294	14.5			327	15.8	1630	260
C ₆ H ₄ NO ₂ - <i>p</i>	(—)				344	21.5	1632	300
C ₆ H ₅ CH ₂	273	18.8					1645	240
Thiophenes (I; X = S)								
C ₆ H ₄ N(CH ₃) ₂ - <i>p</i>	263	12.3	288 ^a	8.9	390	15.1	1615	600
C ₆ H ₄ OCH ₃ - <i>p</i>	272	9.7	296	10.3	345	15.0	1618	350
C ₆ H ₄ CH ₃ - <i>p</i>	271	10.2	306 ^a	11.4	333	13.7	1620	280
C ₆ H ₄ CH ₃ - <i>m</i>	270	13.1	307 ^a	15.0	328	15.7	1617	350
C ₆ H ₅	270	9.8			324	12.1	1618	310
C ₆ H ₄ Cl- <i>p</i>	272	10.7			330	14.5	1614	400
C ₆ H ₄ Br- <i>p</i>	272.5	11.2			331	16.0	1614	370
C ₆ H ₄ Cl- <i>m</i>	272	10.9			323	14.1	1613	180
C ₆ H ₄ CO ₂ C ₂ H ₅ - <i>p</i>	273	16.6			332	18.5	1622	230
C ₆ H ₅ CH ₂	255	11.4	283	8.9			1632	260

^a Inflexion.

* Manuscript received March 28, 1966.

† School of Chemical Sciences, University of East Anglia, Norwich, England.

‡ Department of Organic Chemistry, University of Adelaide; present address: School of Chemical Sciences, University of East Anglia.

¹ Jones, R. A., *Aust. J. Chem.*, 1964, **17**, 894.

thiophens² was obscured by a higher intensity end absorption. Comparison with the spectra of the *N*-benzylimines shows that the long-wavelength absorption band of the *N*-arylimines results from conjugation of the heterocyclic ring with the aryl ring. As was found for the pyrrole compounds, this band is shifted bathochromically by both electron-donating and electron-withdrawing substituents on the aryl ring.

TABLE 2
COMPOUNDS INVESTIGATED

R	B.P. or M.P.		Ref.	N Analysis (%)	
	Observed	Lit.		Found	Calc.
Furans (I; X = O)					
C ₆ H ₄ N(CH ₃) ₂ - <i>p</i>	100–101°	100–101°	a		
C ₆ H ₄ OCH ₃ - <i>p</i>	66–66.5	—		7.0	7.0
C ₆ H ₄ CH ₃ - <i>p</i>	41–42	43–44	b		
C ₆ H ₅	54–56	58	b		
C ₆ H ₄ F- <i>p</i>	126/5 mm	—		7.5	7.4
C ₆ H ₄ Cl- <i>p</i>	50	48–50	a		
C ₆ H ₄ Br- <i>p</i>	58–58.5	—		5.1	5.6
C ₆ H ₄ NO ₂ - <i>p</i>	140	139–140	a		
C ₆ H ₅ CH ₂	137/5 mm	155/11 mm	b		
Thiophens (I; X = S)					
C ₆ H ₄ N(CH ₃) ₂ - <i>p</i>	134–135	—		11.9	12.2
C ₆ H ₄ OCH ₃ - <i>p</i>	45	45–46	c		
C ₆ H ₄ CH ₃ - <i>p</i>	61–62	62	d		
C ₆ H ₄ CH ₃ - <i>m</i>	130–132/0.5 mm	—		7.0	7.0
C ₆ H ₅	120–122/2 mm	122–125/2 mm	e		
C ₆ H ₄ Cl- <i>p</i>	69–70	69–69.5	c		
C ₆ H ₄ Br- <i>p</i>	88–89	90	d		
C ₆ H ₄ Cl- <i>m</i>	49–50	—		6.6	6.3
C ₆ H ₄ CO ₂ C ₂ H ₅ - <i>p</i>	86–87	—		5.3	5.4
C ₆ H ₅ CH ₂	118–120/2 mm	—		7.0	7.3

^a Fischer, E., *J. prakt. Chem.*, 1920, **100**, 109.

^b De Chalmot, G., *Liebigs Ann.*, 1892, **271**, 11.

^c Angert, L. G., Goldfarb, Y. L., Gorushkina, G. I., Zenchenko, A. I., Kuzminskii, A. S., and Federov, B. P., *Zh. priklad. Khim.*, 1959, **32**, 408 (*Chem. Abstr.* 1959, **53**, 13132f).

^d Hantzsch, A., and Witz, R., *Ber. dt. chem. Ges.*, 1901, **34**, 841.

^e Drisko, R. W., and McKennis, H., *J. Am. chem. Soc.*, 1952, **74**, 2626.

These results are readily explained in terms of the relative stabilization or destabilization of the ground and excited states of the molecule by the electron-donating and electron-withdrawing substituents, and by the fact that, as a result of the electron-donating effect of the heterocyclic rings, the excited state of the molecule is not identical for the two types of substituent.¹

The C=N stretching frequency was observed at 1622–1613 cm⁻¹ and 1632–1629 cm⁻¹ for the *N*-aryl thiophen and furan compounds respectively, compared

² Jaffe, H. H., and Orchin, M., "Theory and Applications of Ultraviolet Spectroscopy." (John Wiley: New York 1962.)

with 1627–1618 cm^{-1} for the corresponding pyrroles. All compounds showed infrared absorption bands characteristic of the substituted benzene rings^{3–5} and of the 2-monosubstituted furan⁶ or thiophen⁷ ring. The majority of the remaining bands with $\epsilon \geq 15$ could be assigned to the substituent on the aryl ring. The spectra will be submitted for publication with the Documentation of Molecular Spectroscopy.

Experimental

Spectra

The electronic spectra of all the compounds were measured for $c. 10^{-5}\text{M}$ solutions in ethanol in 10-mm cells using a Unicam SP700 spectrometer.

The infrared spectra in the region 2000–800 cm^{-1} were measured for 0.202M solutions in chloroform in 0.099-mm compensated cells on a Perkin–Elmer 125 spectrometer.

Compounds

The thenylideneimines were prepared by refluxing stoichiometric amounts of 2-formyl-thiophen and the aromatic amine in benzene for 1 hr. The benzene solution was dried over magnesium sulphate and evaporated to give the imines which were purified by distillation or recrystallizations.

The furfurylideneimines were prepared by mixing stoichiometric amounts of furfural and the aromatic amine in benzene. The temperature of the mixture was kept near 5° for 1 hr by ice cooling and the mixture then worked up as described for the thiophens.

Properties and analytical data are given in Table 2. Analyses were carried out in the School of Chemical Sciences, University of East Anglia, and by the Australian Microanalytical Service, Melbourne.

Acknowledgment

We acknowledge the award of a Science Research Council Grant (R.J.H.).

³ Katritzky, A. R., and Lagowski, J. M., *J. chem. Soc.*, 1958, 4155.

⁴ Katritzky, A. R., and Simmons, P., *J. chem. Soc.*, 1959, 2051.

⁵ Katritzky, A. R., and Simmons, P., *J. chem. Soc.*, 1959, 2058.

⁶ Katritzky, A. R., and Lagowski, J. M., *J. chem. Soc.*, 1959, 657.

⁷ Katritzky, A. R., and Boulton, A. J., *J. chem. Soc.*, 1959, 3500.