

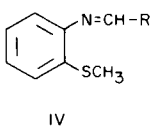
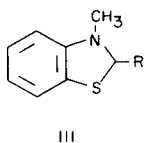
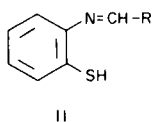
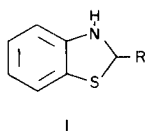
### Heterocyclic Tautomerisms. III. An Investigation of the 2-Arylbenzothiazoline-2-(Benzylideneamino)thiophenol Tautomerism. Part 3.

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The electronic spectra of various, substituted 2-arylbenzothiazoline (I)-2-(benzylideneamino)-thiophenol (II) tautomers were studied in order to determine what species were present in ethanol solution. In every case examined the absorption spectra closely resembled those of the correspondingly substituted 3-methyl-2-arylbenzothiazolines (III) and differed markedly from those of corresponding 2-(benzylideneamino)phenyl methyl sulfides (IV). These results indicate that, under the conditions examined, the 2-arylbenzothiazoline tautomer (I) predominates. Infrared spectra determined on solid samples of series I-II, III and IV were entirely in accord with structure I.

In preparation for a detailed study of 2-arylbenzothiazoline (I)-2-(benzylideneamino)thiophenol (II) equilibria, it was decided to examine the electronic (ethanol solution) and infrared (solid in fluorocarbon mull) absorption spectra of various potential 2-arylbenzothiazoline-2-(benzylideneamino)thiophenol tautomers (Table I) concurrently with appropriate model compounds.



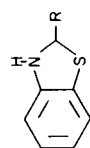
As models with electronic absorption properties characteristic of the 2-arylbenzothiazoline tautomers (I) their *N*-methylated analogs, the 3-methyl-2-arylbenzothiazolines (III), were prepared in high yield by the reaction of the appropriate aromatic aldehydes with *N*-methyl-2-mercaptoaniline (Table II). The electronic spectra of these compounds (Table III) rather closely resembled those of the potential 2-arylbenzothiazoline-(I)-2-benzylideneamino)-thiophenol (II) tautomers thus offering strong evidence

for the 2-arylbenzothiazoline structure for all compounds examined. In the infrared region these models, as would be expected, showed no absorption in the region characteristic of either N-H or S-H stretching frequencies and only feeble absorption in the region assignable to imine stretch near  $6.1 \mu$ .

As models with electronic absorption properties characteristic of the 2-(benzylideneamino)thiophenol tautomers (II) their *S*-methylated analogs, the 2-(benzylideneamino)phenyl methyl sulfides (IV), were prepared in high yield by the reaction of the appropriate aromatic aldehydes with 2-methylthioaniline (Table IV). The electronic spectra of these compounds (Table V) generally exhibited an absorption band much more bathochromic than the longest wavelength, near visible band of either the potential 2-arylbenzothiazoline-2-(benzylideneamino)thiophenol tautomers or the 3-methyl-2-arylbenzothiazoline models thus indicating the probable absence of appreciable quantities of the 2-(benzylideneamino)thiophenol tautomer under these conditions. In the infrared region these models showed strong absorption near  $6.1 \mu$ , characteristic of imine stretch (Table V), far stronger than any absorption in that region of compounds I-III or III.

It will now be feasible to examine spectra of 2-arylbenzothiazolines under various conditions with the possibility of simultaneously detecting both tautomers, I and II. Of course, it will be necessary in every solvent system and with every type of substitution to examine the spectra of all appropriate model compounds under analogous conditions in order to properly interpret the spectroscopic data.

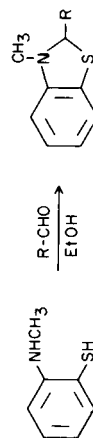
TABLE I



R in I or II	Infrared Spectra N-H Stretch Assignment		Ultraviolet Spectra (a)	
	$\lambda$ max in $\mu$	$\log \epsilon$	$\lambda$ max in $m\mu$	$\log \epsilon$
2-ethoxyphenyl	2.96	3.62	315.5	3.77
2-chlorophenyl	2.98	3.77	313.0	3.79
2,6-dichlorophenyl	2.95	3.73	315.0	3.79
2-hydroxyphenyl	3.06	3.79	312.5	3.79
2-hydroxy-5-chlorophenyl	3.06	3.79	315.0 (b)	3.71
2-hydroxy-5-bromophenyl	3.06	3.71	313.5 (b)	

(a) Only the most bathochromic, near visible maximum is given. (b) This absorption maximum occurred at a shoulder.

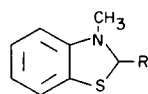
TABLE II



R	Melting Point $^{\circ}\text{C}$	Yield %	Formula	Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
phenyl	112-113 $^{\circ}$	(a)		—	—	—	—
2-methoxyphenyl	78-79 $^{\circ}$	67	$\text{C}_{15}\text{H}_{16}\text{NOS}$	70.04	70.18	5.84	5.73
2-chlorophenyl	88-89 $^{\circ}$	71	$\text{C}_{14}\text{H}_{12}\text{ClNS}$	64.24	64.22	4.59	4.69
2,6-dichlorophenyl	92-93 $^{\circ}$	85	$\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{NS}$	56.76	57.02	3.72	3.82
2-hydroxyphenyl	128-128 $^{\circ}$ (b)	82	$\text{C}_{14}\text{H}_{13}\text{NOS}$	69.14	69.25	5.35	5.44
2-hydroxy-5-chlorophenyl	152-153 $^{\circ}$ (b)	88	$\text{C}_{14}\text{H}_{12}\text{ClNOS}$	60.54	60.56	4.32	4.40

(a) Reported melting point: 112-113 $^{\circ}$ , ref. 1. (b) These compounds slowly discolor in air and become bright yellow on long standing. The nature of this oxidation has been determined and will be a topic of a future publication. These samples darkened during melting due to oxidation.

TABLE III



R	Ultraviolet Spectra (a)	
	$\lambda$ max in $m\mu$	log $\epsilon$
phenyl	314.0	3.63
2-methoxyphenyl	316.0	3.71
2-chlorophenyl	316.0	3.64
2,6-dichlorophenyl	320.0	3.76
2-hydroxyphenyl	315.0	3.72
2-hydroxy-5-chlorophenyl	315.5 (b)	3.77

(a) Only the most bathochromic, near visible maximum is given. (b) This absorption occurred at a shoulder.

EXPERIMENTAL

Preparation of 2-Arylbenzothiazolines.

2-Arylbenzothiazolines were prepared as described before (2). The 2-arylbenzothiazolines unreported elsewhere are listed in Table VI.

Preparation of 3-Methyl-2-arylbenzothiazolines (Table II).

An ethanol solution 1 molar each in aromatic aldehyde and *N*-methyl-2-mercapto aniline was refluxed under pure nitrogen for 15 minutes. The 3-methyl-2-arylbenzothiazoline was isolated by stepwise concentration and cooling. The analytical samples were recrystallized from absolute ethanol.

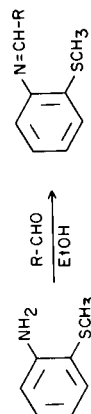
Preparation of Imines (Table IV).

The Imines, IV, were prepared and purified by the method applied to their para isomers (3).

Acknowledgment.

I would like to especially thank Prof. William J. Bailey for his constant help and encouragement. I would like to thank Prof. John T. Carruthers for his excellent work on the construction of the glass apparatus used in this work and Dr. Franz Kasler for performing the carbon-hydrogen analysis.

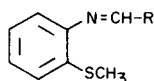
TABLE IV



IV

R	Melting Point $^{\circ}C$	Yield %	Formula	Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
phenyl	46-47	82	$C_{14}H_{13}NS$	74.00	73.73	5.73	5.79
2-methoxyphenyl	85-86	89	$C_{15}H_{16}NOS$	69.73	70.30	5.84	6.07
2-chlorophenyl	70-71	84	$C_{14}H_{12}ClNS$	64.24	63.98	4.59	4.07
2,6-dichlorophenyl	133-134	91	$C_{14}H_{11}Cl_2NS$	56.76	56.43	3.72	3.76
2-hydroxyphenyl	55-56	94	$C_{14}H_{13}NOS$	69.14	69.25	5.35	5.44
2-hydroxy-5-chlorophenyl	102-103	96	$C_{14}H_{12}ClNOS$	60.54	60.34	4.32	4.32
2-hydroxy-5-bromophenyl	107-108	99	$C_{14}H_{12}BrNOS$	52.17	51.87	4.04	3.77

TABLE V

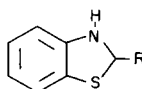


IV

R	Imine Stretch Assignment $\lambda$ max in $\mu$	Ultraviolet Spectra (a)	
		$\lambda$ max in $m\mu$	log $\epsilon$
phenyl	6.20	349.0	3.60
2-methoxyphenyl	6.20	319.0	3.95
2-chlorophenyl	6.18	367.0	3.55
2,6-dichlorophenyl	6.20	340.0 (b)	3.45
2-hydroxyphenyl	6.26	343.0	3.98
2-hydroxy-5-chlorophenyl	6.24	362.0	3.91
2-hydroxy-5-bromophenyl	6.24	363.5	3.99

(a) Only the most bathochromic, near visible maximum is given. (b) This absorption maximum was ill-defined.

TABLE VI



I

R	Melting Point $^{\circ}\text{C}$	Yield %	Formula	Carbon			
				Calcd.	Found	Calcd.	Found
2-ethoxyphenyl	75-76	52	$\text{C}_{14}\text{H}_{16}\text{NOS}$	70.04	70.14	5.84	6.03
2,6-dichlorophenyl	91-92	86	$\text{C}_{13}\text{H}_9\text{Cl}_2\text{NS}$	55.32	55.51	3.19	3.60
2-hydroxy-5-chlorophenyl	155-156	79	$\text{C}_{13}\text{H}_{10}\text{ClNOS}$	59.20	59.22	3.80	3.87
2-hydroxy-5-bromophenyl	148-149	83	$\text{C}_{13}\text{H}_{10}\text{BrNOS}$	50.65	50.38	3.25	3.50

## REFERENCES

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