

2-ARYL DERIVATIVES OF CONDENSED FIVE-MEMBERED
N-HETEROCYCLIC COMPOUNDS. II.*ULTRAVIOLET ABSORPTION SPECTRA OF 2- AND 4-SUBSTITUTED
PHENOLS AND NAPHTHOLSJ. DURMIS^a, M. KARVAŠ^a and Z. MAŇÁSEK^b^a *Research Laboratory, Dimitrov Chemical Works, and*^b *Institute of Polymers, Slovak Academy of Sciences, Bratislava*

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The absorption spectra, in the near ultraviolet region, were measured of 23 phenols, 7 anisoles substituted in position 2 with 2-(4,5)-areneazolyl and 2-indolyl groups and 8 2-phenyl (4,5)-areneazole and indole derivatives in solvents of varying polarity and in acidic and alkaline media. The effect of the structure of the heterocyclic skeleton on the absorption bands is discussed. The effects of the intermolecular hydrogen bond on the UV spectra of 3-substituted phenols and of the intramolecular hydrogen bond on the UV spectra of 2-substituted phenols were studied. The transition energy corresponding to the longest wavelength band of 2-substituted phenols was correlated with *Z*-value. It was found that with increasing polarity of the solvent the intramolecular hydrogen bond in 2-substituted phenols is cleaved in dependence on the character of the proton-accepting substituent and on steric arrangement and conjugation conditions in the molecules of the studied compounds. In an acidic and an alkaline medium $\Delta\bar{\nu}$ of the longest wavelength bands correlate well with Hammett σ_p constants.

The ultraviolet absorption spectra of 2-phenyl derivatives of [4,5]areneazoles were studied by several authors¹⁻⁶. Substituent effects on the 2-phenyl group have not yet been studied only with indole derivatives. Little attention has been paid also to indazole derivatives⁷. The effect of hydrogen bonding on the UV absorption spectra of phenols has been studied at length⁸⁻¹³. The effect on intramolecular hydrogen bonding on UV absorption spectra is as a rule more complicated and is usually interpreted in different terms by different authors. Lutsjikij¹⁴ and Sawicki¹⁵ had assumed that a strong intramolecular hydrogen bond may result in the formation of a new absorption band. This view was however questioned¹⁰. Yarborough and coworkers¹⁶ concluded that absorption characteristics of the compounds with strong intramolecular hydrogen bond are mostly independent of the concentration of the compound, solvent and temperature. A comparatively greatest attention to this problem was paid by Dearden and Forbes^{10,17,18} who demonstrated that intramolecular hydrogen bond in 2-substituted phenols can be studied by electronic spectroscopy with the use of three different approaches: 1) comparison of the spectra of 2- and 3-substituted phenols similar in structure, 2) comparison of the spectra of 2-substituted phenols and 2-substituted anisoles, and 3) study of solvent effects in an inert or a polar solvent.

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In the present work we deal with the effect of the structure on the individual absorption bands of the compounds of types A–E, as well as with the effect of intramolecular hydrogen bonding on the electronic spectra of 2-substituted phenols with 2-[4,5]areneazolyl substituent. The spectra of 2-substituted phenols are compared with the spectra of corresponding 3- and 4-substituted phenols and 2-substituted anisoles. The effect of solvent polarity on the electronic spectra of the studied compounds and on the relative strength of their intramolecular hydrogen bond is also discussed.

EXPERIMENTAL

Melting points, measured with "Boetius" apparatus, are uncorrected. Prepared compounds were dried over P_2O_5 at 100°C under the pressure of 1 Torr. Compounds I, III, VI, VIII, XI, XIII, XVI, XVIII, XXI, XXII, XXIV, XXIX, XXXI, XXXIV, XXXVI, XXXIX and XL were obtained by the already reported methods¹⁹. Compounds II, IV, VII, IX, X, XX and XXXVII were prepared according to known procedures, compound XIV was synthesized by a modified procedure⁵, and compounds XIX, XXIII, XXVII and XXXII were obtained in the usual way²⁰. Their melting points agreed well with literature data.

3-(2-Naphtho[1,2-d]triazolyl)phenol (XII) was obtained⁵ in 26% yield. The crude product was purified by crystallization from ethanol, sublimation at 190°C/1 Torr, followed by twofold crystallization from 60% ethanol, m.p. 207–208°C. For $C_{16}H_{11}N_3O$ (211.2) calculated: 73.54% C, 4.24% H, 16.09% N; found: 73.51% C, 4.40% H, 16.25% N.

3-(2-Benzimidazolyl)phenol (XVII) was prepared by the reported procedure²⁰. The reaction mixture was boiled with ammonia and then filtered, affording the crude product in 51.4% yield. Its recrystallization from ethanol, followed by sublimation at 260°C/1 Torr and repeated crystallization yielded the product melting 282–284°C. For $C_{13}H_{10}N_2O$ (210.3) calculated: 74.30% C, 4.78% H, 13.32% N; found: 74.14% C, 4.87% H, 13.27% N.

3-(2-Benzoxazolyl)phenol (XXV). The procedure²⁰ and the work-up of the reaction mixture described in the preceding paragraph afforded the crude product in 66.4% yield. This was recrystallized from ethanol and chloroform, yielding white needles melting 243–244°C (lit.^{21,22} gives m.p. 237°C). For $C_{13}H_9NO_2$ (211.2) calculated: 74.07% C, 4.30% H, 6.63% N; found: 73.96% C, 4.20% H, 6.62% N.

3-(2-Benzothiazolyl)phenol (XXX). The crude product, obtained by the procedure²⁰, was purified by crystallization from 60% ethanol. M.p. 173–174°C. For $C_{13}H_9NSO$ (227.3) calculated: 68.90% C, 4.00% H, 6.06% N, 14.12% S; found: 68.84% C, 3.92% H, 6.16% N, 14.14% S.

3-(2-Indolyl)phenol (XXXV). The crude product, obtained by the procedure²³, was recrystallized from ethanol and a benzene–cyclohexane mixture. M.p. 175–176°C. For $C_{14}H_{11}NO$ (209.2) calculated: 80.40% C, 5.30% H, 6.69% N; found: 80.49% C, 5.22% H, 6.72% N.

2-(2-Benzotriazolyl)anisole (V). A mixture of 5.2 g (0.034 mol) 1-nitro-2-nitrosobenzene and 4.16 g (0.034 mol) 2-methoxyaniline was dissolved in 44 ml glacial acetic acid and 25 ml ethanol. The reaction mixture was stirred at room temperature for 8 h. 2-Nitro-2'-methoxyazobenzene was precipitated by diluting the reaction mixture with water. The crude product (70%) was dried and reduced²⁴. The product was isolated by extraction with benzene and distillation *in vacuo* as yellowish, viscous liquid boiling 128°C/0.9 Torr. For $C_{13}H_{11}N_3O$ (225.2) calculated: 68.93% C, 4.90% H, 18.79% N; found: 69.12% C, 4.92% H, 18.66% N.

2-(2-Naphtho[1,2-d]triazolyl)anisole (XV). The intermediate product, 2-amino-2-methoxy-1-naphthylazobenzene, was prepared by the procedure analogous to that described in ref.²⁴. Its

oxidation²⁴ yielded the crude product (25%) which was recrystallized from ethanol-benzene. M.p. 116.5–118°C. For $C_{13}H_{13}N_3O$ (275.3) calculated: 74.35% C, 4.77% H, 15.27% N; found: 74.19% C, 4.57% H, 15.24% N.

2-(2-Benzoxazolyl)anisole (XXVIII). The crude product, obtained by the procedure²⁰ (yield 8%), was isolated by neutralization of the reaction mixture with NaOH solution, followed by vacuum evaporation of water and extraction of dry residue with ethanol. After recrystallization and sublimation at 100°C/1 Torr, the compound had m.p. 120–122°C. For $C_{14}H_{11}NO_2$ (225.2) calculated: 74.80% C, 4.92% H, 6.21% N; found: 74.69% C, 4.97% H, 6.28% N.

2-(2-Benzothiazolyl)anisole (XXXIII), prepared according to lit.²⁰ (21%), was sublimed at 110°C/1 Torr and crystallized from ethanol. M.p. 132–134°C (lit.²⁵ records m.p. 92°C). For $C_{14}H_{11}NOS$ (241.3) calculated: 69.77% C, 4.60% H, 5.81% N, 13.30% S; found: 69.51% C, 4.43% H, 5.75% N, 13.47% S.

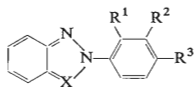
2-(2-Indolyl)anisole (XXXVIII) obtained according to the procedure²³ (25.9%) was chromatographed, using the Al_2O_3 column and benzene as the eluent. M.p. 84–85°C (ethanol). For $C_{15}H_{13}NO$ (223.3) calculated: 80.67% C, 5.60% H, 6.62% N; found: 80.90% C, 5.80% H, 6.30% N. UV absorption spectra were recorded with Model ORD/UV-5 (Japan Spectroscopic Co., Tokyo) and Unicam SP-700 (Unicam, England) instruments and measured with Zeiss VSU-1 spectrophotometer (Jena, GDR). Spectrograde solvents were commercial products and were used without further purification. HCl and NaOH were of analytical purity grade. The $2 \cdot 10^{-5} M$ solutions of the compounds were measured in 1 cm thick cell at $25 \pm 0.5^\circ C$.

RESULTS AND DISCUSSION

The interpretation of the UV spectra of unsubstituted five-membered N-heterocyclic compounds meets with difficulties not only in correlating the spectra with other physico-chemical properties, but also in assigning individual electron transitions²⁶. The introduction of 2-phenyl group complicates even more the situation. Our observations support the conclusion of Passerini¹, reached in the study of benzoxazoles, that the benzene and not the heterocyclic nucleus should be regarded as basic chromophor. The UV spectra of [4,5]areneazoles and indole are very similar to the spectrum of the parent hydrocarbon, indene. This is by no way exception, because also the spectra of other heterocyclic compounds are usually comparable with those of parent hydrocarbons. The spectra of 2-phenyl substituted derivatives exhibit both the primary and the secondary benzene band (the classification taken from ref.²⁷). These bands are to be found also in the spectra of unsubstituted derivatives and are modified by conjugation of the heterocycle with the phenyl group. In addition, a new intense band appears at wavelengths nearer to the visible region. The new chromophor, originated from the conjugation of the 2-phenyl group with the heterocycle, is probably the main reason of the electron transition which results in the formation of the above mentioned band (further referred to as C-band). The secondary benzene band either coincides with the new bathochromically shifted band or appears as a shoulder on the short-wavelength side of this band. This is illustrated for the compounds of type A in Fig. 1 and for the compounds of type C in Fig. 2. Similar situation arises also with derivatives of types B and E, containing naphthalene ring, except that here the naphthalene ring should be considered as basic chromophor. As Table I shows, the spectrum of compound XIV, besides primary bands, exhibits also the intense C-band at longer wavelengths.

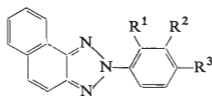
The UV spectra of all the 2-phenyl derivatives show in the near UV region two bands, the first primary benzene band and the C-band. The spectra of derivatives XIV and XXXIII show also second primary bands (Table II). The fact that with derivative XIV this band is apparent contrarily to naphthalene (Table I) and that with benzothiazole XXXII the bathochromic shift

of the band is greatest of all the 2-phenyl-[4,5]benzenazoles studied can be explained by an increased conjugation of the benzene ring with the heterocycle, since sulphur atom readily yields the electron pair needed for sufficient conjugation in the heterocyclic ring. A similar situation arises also with the first primary band (Table III). On going to 2-substituted phenols, the second primary band undergoes bathochromic shift (Table II). Further shift of the band towards visible region occurs in 3-substituted phenols, while with 4-substituted derivatives hypsochromic shift, relative to the 3- and 2-substituted derivatives, is observed, with the exception of compound *XIII*. The second primary bands of derivatives *III*, *VIII*, *XXII*, and *XXXVI* occur therefore in the far UV region. In the case of 2-substituted anisoles a hypsochromic shift of this band with respect



A

- I*, X = N; R¹ = OH; R², R³ = H
II, X = N; R¹, R³ = H; R² = OH
III, X = N; R¹, R² = H; R³ = OH
IV, X = N; R¹, R², R³ = H
V, X = N; R¹ = OCH₃; R², R³ = H
VI, X = CH; R¹ = OH; R², R³ = H
VII, X = CH; R¹, R³ = H; R² = OH
VIII, X = CH; R¹, R² = H; R³ = OH
IX, X = CH; R¹, R², R³ = H
X, X = CH; R¹ = OCH₃; R², R³ = H



B

- XI*, R¹ = OH; R², R³ = H
XII, R¹, R³ = H; R² = OH
XIII, R¹, R² = H; R³ = OH
XIV, R¹, R², R³ = H
XV, R¹ = OCH₃; R², R³ = H

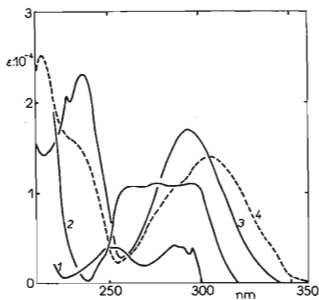


FIG. 1

UV Absorption Spectra of 1 Indazole (in Ethanol⁴³), 2 2-Methylindazole, 3 2-Phenylindazole and 4 2-(2-Indazolyl)phenol in Methanol

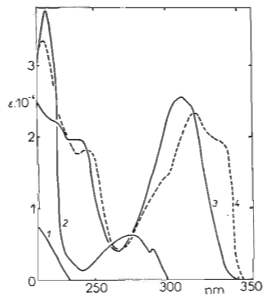


FIG. 2

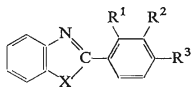
UV Spectra of 1 Pyrrole and 2 Indole in Ethanol⁴² and of 3 2-Phenylindole and 4 2-(2-Indolyl)phenol in Methanol

TABLE I

Absorption Characteristics of Naphthalene, 1,2,3-Triazole and Its Derivatives Containing Naphthalene Ring

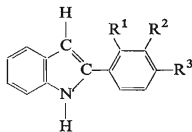
 λ is given in nm, ϵ in $l \text{ mol}^{-1} \text{ cm}^{-1}$.

Compound		2-nd Primary band	1-st Primary band	Secondary band	C-band
Naphthalene ^a	λ	221	286	312	—
	ϵ	133 000	9 300	289	—
XIV	λ	225	278	—	334
	ϵ	72 800	32 000	—	21 720
XXXIV	λ	224	276	284	331
	ϵ	72 500	14 920	14 520	6 000
1,2,3-Triazole ^b	λ	—	285	—	—
	ϵ	—	4 500	—	—

^a Lit.²⁷. ^b Lit.⁴.

C

XVI, X = NH;	$R^1 = \text{OH}; R^2, R^3 = \text{H}$
XVII, X = NH;	$R^1, R^3 = \text{H}; R^2 = \text{OH}$
XVIII, X = NH;	$R^1, R^2 = \text{H}; R^3 = \text{OH}$
XIX, X = NH;	$R^1, R^2, R^3 = \text{H}$
XX, X = NH;	$R^1 = \text{OCH}_3; R^2, R^3 = \text{H}$
XXI, X = N—CH ₃ ;	$R^1 = \text{OH}; R^2, R^3 = \text{H}$
XXII, X = N—CH ₃ ;	$R^1, R^2 = \text{H}; R^3 = \text{OH}$
XXIII, X = N—CH ₃ ;	$R^1, R^2, R^3 = \text{H}$
XXIV, X = O;	$R^1 = \text{OH}; R^2, R^3 = \text{H}$
XXV, X = O;	$R^1, R^3 = \text{H}; R^2 = \text{OH}$
XXVI, X = O;	$R^1, R^2 = \text{H}; R^3 = \text{OH}$
XXVII, X = O;	$R^1, R^2, R^3 = \text{H}$
XXVIII, X = O;	$R^1 = \text{OCH}_3; R^2, R^3 = \text{H}$
XXIX, X = S;	$R^1 = \text{OH}; R^2, R^3 = \text{H}$
XXX, X = S;	$R^1, R^3 = \text{H}; R^2 = \text{OH}$
XXXI, X = S;	$R^1, R^2 = \text{H}; R^3 = \text{OH}$
XXXII, X = S;	$R^1, R^2, R^3 = \text{H}$
XXXIII, X = S;	$R^1 = \text{OCH}_3; R^2, R^3 = \text{H}$



D

XXXIV, $R^1 = \text{OH}; R^2, R^3 = \text{H}$
XXXV, $R^1, R^3 = \text{H}; R^2 = \text{OH}$
XXXVI, $R^1, R^2 = \text{H}; R^3 = \text{OH}$
XXXVII, $R^1, R^2, R^3 = \text{H}$
XXXVIII, $R^1 = \text{OCH}_3; R^2, R^3 = \text{H}$

to the bands of the 2-phenyl derivatives, is observed with compounds *XV* and *XXXIII*, whereas the bands of the other derivatives show bathochromic shift.

The first primary bands of all the studied compounds are presented in Table III. From the table it is evident that the bathochromic shift of these bands is greatest with the 4-substituted phenols while with the 3-substituted phenols the bands appear only as shoulders on the long-wavelength side of the primary band. The shift of this band in the visible region decreases in the order 4-OH > 2-OH > 3-OH. In the case of the 2-substituted anisoles the first primary band occurs in the region near to the 2-phenyl derivatives or to the 2-substituted phenols. The exceptions are derivatives *V* and *XV* in which, because of steric hindrance which deviates the molecule from co-planarity, the conjugation is decreased^{4,6}, this resulting in the great hypso- and hypochromic shift. These bands of the studied compounds may be compared with the bands of disubstituted benzene derivatives containing one electron-donating and

TABLE II

Second Primary Bands of Derivatives of 2-Aryl-Substituted [4,5]Areneazoles and of Indole in Methanol

λ in nm, ϵ in $1 \text{ mol}^{-1} \text{ cm}^{-1}$.

Compound	λ ϵ	Compound	λ ϵ	Compound	λ ϵ	Compound	λ ϵ	Compound	λ ϵ
<i>IV</i>	<210 —	<i>I</i>	212 21 200	<i>II</i>	217 16 400	<i>III</i>	<210 —	<i>V</i>	212 20 400
<i>XIV</i>	225 72 800	<i>XI</i>	226 38 500	<i>XII</i>	224 38 700	<i>XIII</i>	228 33 900	<i>XV</i>	217 40 200
<i>IX</i>	<210 —	<i>VI</i>	214 25 200	<i>VII</i>	216 28 800	<i>VIII</i>	<210 —	<i>X</i>	216 21 300
<i>XIX</i>	<210 —	<i>XVI</i>	211 36 200	<i>XVII</i>	216 22 800	<i>XVIII</i>	<210 —	<i>XX</i>	212 17 900
<i>XXIII</i>	<210 —	<i>XXI</i>	215 38 500	—	—	<i>XXII</i>	<210 —	—	—
<i>XXVII</i>	<210 —	<i>XXIV</i>	<210 —	<i>XXV</i>	<210 —	<i>XXVI</i>	<210 —	<i>XXVIII</i>	215 16 200
<i>XXXII</i>	224 16 200	<i>XXIX</i>	215 28 800	<i>XXX</i>	221 25 500	<i>XXXI</i>	213 21 850	<i>XXXIII</i>	214 25 000
<i>XXXVII</i>	<210 —	<i>XXXIV</i>	214 33 450	<i>XXXV</i>	222 21 000	<i>XXXVI</i>	<210 —	<i>XXXVIII</i>	214 32 400
—	— —	<i>XXXIX</i>	224 72 500	—	—	<i>XL</i>	<210 —	—	—

one electron-accepting substituent. The great bathochromic shift observed with the 4-substituted phenols can be ascribed to facile electron transfer in this system²⁸.

The C-band changes in dependence on the structure of the arene-like heterocycle. The influence of the heterocyclic portion as a substituent on the position of this band is complex. It can be roughly said that the intensity of the band increases with its increasing bathochromic shift (Table IV). In the case of monosubstituted benzene derivatives, this band is nearest to the visible region in the derivative *IX* and is obviously influenced by the presence of the naphthalene ring in the molecule. The nearest to the far UV region is the band of the derivative *XXIII*, whose hypsochromic shift, relative to compound *XIX*, is understandable when interaction on the N—CH₃ hydrogens with the hydrogen in position 2 of the phenyl group, which results in deviation from the co-planarity of the molecule, is taken into account.

TABLE III

First Primary Bands of Derivatives of 2-Aryl-Substituted [4,5]Areneazoles and of Indole in Methanol

λ in nm, ϵ in $l \text{ mol}^{-1} \text{ cm}^{-1}$.

Compound	λ ϵ	Compound	λ ϵ	Compound	λ ϵ	Compound	λ ϵ	Compound	λ ϵ
<i>IV</i>	217 15 800	<i>I</i>	236 10 300	<i>II</i>	230 ^a 14 500	<i>III</i>	251 5 580	<i>V</i>	— ^c
<i>XIV</i>	278 32 000	<i>XI</i>	276 22 800	<i>XII</i>	276 27 500	<i>XIII</i>	284 22 800	<i>XV</i>	240 12 600
<i>IX</i>	235 23 000	<i>VI</i>	231 ^a 15 600	<i>VII</i>	230 ^a 26 000	<i>VIII</i>	245 9 500	<i>X</i>	236 ^a 12 300
<i>XIX</i>	240 12 900	<i>XVI</i>	234 ^b 12 300	<i>XVII</i>	236 ^a 11 500	<i>XVIII</i>	249.5 15 400	<i>XX</i>	241 11 160
<i>XXIII</i>	233 14 600	<i>XXI</i>	234 7 000	—	—	<i>XXII</i>	247 12 200	—	—
<i>XXVII</i>	234 7 850	<i>XXIV</i>	— ^c	<i>XXV</i>	— ^c	<i>XXVI</i>	— ^c	<i>XXVIII</i>	215 16 000
<i>XXXII</i>	248 ^d 6 740	<i>XXIX</i>	248 ^e 7 000	<i>XXX</i>	248 ^{a,f} 7 580	<i>XXXI</i>	250 ^g 5 160	<i>XXXIII</i>	248 ^h 7 780
<i>XXXVII</i>	237 18 600	<i>XXXIV</i>	244 18 300	<i>XXXV</i>	245 14 600	<i>XXXVI</i>	246 18 300	<i>XXXVIII</i>	244 16 950
—	—	<i>XXXIX</i>	276 14 920	—	—	<i>XL</i>	233 31 850	—	—

^a Shoulder. ^b Also shoulder at 239 nm (12 000). ^c Bands cannot be identified. ^d Also band at 255 nm (6 790). ^e Also band at 256 nm (7 400). ^f Shoulder at 258 nm (6 640). ^g Shoulder at 257 nm (4 900). ^h Also band at 258 nm (7 810).

The hyper- and bathochromic shift of the C-band observed, as expected, with the 4-substituted phenols is in accordance with similar phenomenon established with other phenols. The greatest shift in the spectrum of derivative XXXI is not surprising, since also the other bands already discussed are shifted similarly. A comparatively great shift of the band of benzotriazole derivative III is unexpected in view of a relatively weak mesomeric effect occurring in the derivatives of 2-phenylbenzotriazole²⁹. The band of indolyl derivative XXXVI is surprisingly shifted only little, relative to the band of 2-phenyl derivative XXVII. The intensities and maxima of the absorption bands of 3-substituted phenols differ only slightly from those of 2-phenyl derivatives. This finding only further supports the conclusions made for benzotriazolylphenols²⁴ and for [1,2-*d*]triazolylphenols⁶. Dearden³⁰ assumes the formation of "hybrid spectra" with analogous 3-substituted benzene derivatives, similarly as with 2-substituted derivatives. As the result, another absorption band should appear in the spectrum, which originates from the electron transition due predom-

TABLE IV

C-Bands of Derivatives of 2-Aryl-Substituted [4,5]Areneazoles and of Indole in Methanol
 λ in nm, ϵ in $l\ mol^{-1}\ cm^{-1}$.

Compound	λ ϵ	Compound	λ ϵ	Compound	λ ϵ	Compound	λ ϵ	Compound	λ ϵ
IV	306 25 200	I	327 17 400	II	308 20 850	III	319 26 600	V	287 14 900
XIV	334 21 720	XI	347 19 900	XII	336 20 630	XIII	342 24 300	XV	329 10 900
IX	294 17 500	VI	306 14 000	VII	298 17 800	VIII	299 13 900	X	296 14 300
XIX	302 24 200	XVI	315 23 500	XVII	301 21 600	XVIII	304 36 800	XX	312 22 800
XXIII	287 16 300	XXI	319 ^a 3 300	—	—	XXII	292 21 100	—	—
XXVII	298 23 800	XXIV	318 16 600	XXV	298 18 100	XXVI	305 29 000	XXVIII	318 16 700
XXXII	296 19 500	XXIX	331.5 18 400	XXX	299 17 500	XXXI	316 31 500	XXXIII	331 17 300
XXXVII	308 26 000	XXXIV	319 23 300	XXXV	317 22 800	XXXVI	309 28 250	XXXVIII	318 23 300
—	—	XXXIX	331 6 000	—	—	XL	332 14 800	—	—

^a Shoulder.

antly to the action of phenolic portion of the molecule. In the case of 3-substituted phenols with non-heterocyclic substituents this band is characterized as secondary phenolic band. With 4-substituted phenols, due to a strong conjugation of the electron-attracting substituent in position 4 with the basic chromophor, the molecule shows only one absorption band corresponding to the respective electron transition. Although suitable conditions for strong conjugation should have been formed with 2-substituted derivatives, this in fact is not the case, since steric effects play important role and unfavourably affect the extent of the conjugation. As the result, the spectra of these derivatives have also hybrid character, both portions of the disubstituted benzene reflecting in corresponding electron transitions. The 2-substituted phenols with heterocyclic substituent do show two absorption regions (Table IV), contrarily to 4- and 3-substituted derivatives, the exceptions being indolyl derivative *XXXIV* and naphthotriazolyl derivative *XI*. Especially the absence of the second band in the spectrum of the naphthotriazolyl derivative is surprising, as this band appears in both benzotriazolyl derivatives *I* and *XXXIX*. This can only be accounted for by the confluence of this band with a comparatively intense first primary band. In the spectrum of the indolyl derivative the above band appears only as a shoulder on the short-wavelength side of the C-band.

The spectra of anisole derivatives *XX*, *XXVIII* and *XXXIII* closely resemble those of 2-substituted phenols *XVI*, *XXIV* and *XXIX* (Fig. 3). As they are also 2-substituted derivatives, both substituents in the benzene ring manifest themselves in electron transitions and the spectra are therefore hybrid, too. This fact excludes the possibility

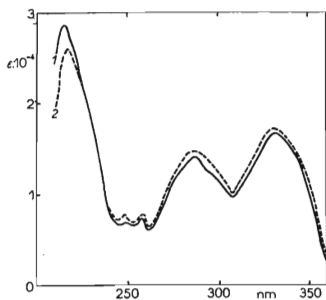


FIG. 3

UV Spectra of 1 2-(2-Benzothiazolyl)phenol and 2 2-(2-Benzothiazolyl)anisole in Methanol

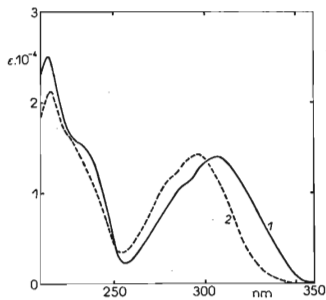
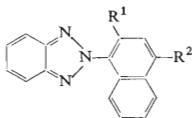


FIG. 4

UV Spectra of 1 2-(2-Indazolyl)phenol and 2 2-(2-Indazolyl)anisole in Methanol

that the splitting of the C-band of 2-substituted phenols is due to intramolecular hydrogen bonding in these compounds. While in anisoles *XX*, *XXVIII* and *XXXIII* the intramolecular bond is absent, their C-bands still show splitting. In this case the intramolecular hydrogen bonds influence the patterns of the spectra only little. Different situation arises with compounds *V*, *X* and *XV*. Both substituents attached to the benzene ring should sterically interact with one another, similarly as in 2-(2-methylphenyl)benzotriazole⁴, which results in angular displacement of the phenyl group around the N—C bond, reduced extent of conjugation and hypsochromic shift of the C-bands, relative to the respective 2-substituted phenols (Fig. 4). It can be assumed that in the case of the 2-substituted phenols the steric effect of the hydroxyl group is smaller and also that the intramolecular hydrogen bond aids in keeping the molecules of compounds *I*, *VI* and *IX* planar. This creates more favourable conditions for conjugation, which results in bathochromic shift of the C-bands. The naphthol *XXXIX* has obviously similar properties, since it has the same structure of the heterocyclic substituent as derivatives *I*, *VI* and *XI*. Compound *XXI* behaves analogously to substance *XVI*, except that the steric effect of the N—CH₃ group is by far greater in the former than in the latter derivative. Consequently, the anisole derivative, with the great steric effect³, is not co-planar and its C-band shows a hypsochromic shift. The intramolecular hydrogen bond effect in derivative *XXI* prevails over the steric effect only in aprotic solvents. In such a case the molecule of the compound is co-planar and its spectrum resembles the spectrum of substance *XVI*. The intramolecular hydrogen bond in derivative *XXI* strongly influences the ultraviolet spectrum of this compound, and in this sense this derivative behaves similarly as derivatives *I*, *VI*, *XI* and *XXXIX*. Indoles *XXXIV* and *XXXVIII*, which are similar in structure to benzothiazolyl, benzimidazolyl and benzoxazolyl derivatives, are co-planar, due to the resonance effect. Compound *XXXIV* does not form intramolecular hydrogen bond and can thus be employed in comparing with other derivatives of 2-substituted phenols possessing this bond.

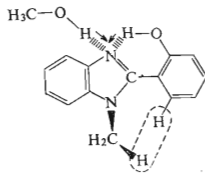
When studying the effect of solvents on the C-bands and secondary phenolic band of 2-substituted phenols, we have found that while the latter are influenced



E

XXXIX, R¹ = OH; R² = H

XL, R¹ = H; R² = OH



F

by solvent polarity only little (Table V), the former are very sensitive to the polarity of solvents (Table VI). This may be connected with the fact that C-bands are strongly influenced by intramolecular hydrogen bonding, as already stated. With 4-substituted phenols, due to the formation of intermolecular hydrogen bond in dioxane, which is the main factor influencing shifts of absorption band on changing the solvent, the C-bands show hyperchromic shift, with respect to the chloroform solution (Table VII). Furthermore, derivatives *III*, *XIII*, *XXII* and *XXXI* exhibit the expected bathochromic effect, which has already been observed³¹ with 4-substituted phenols with non-heterocyclic substituent. The hypsochromic shift in the case of compounds *XVIII* and *XXXVI* is influenced above all by the possibility of the formation of another type of the intermolecular hydrogen bond N—H...O. Hypsochromic shifts in the spectra of compounds *VIII* and *XXVI* are less expected. The observed changes in C-bands on going from chloroform to dioxane indicate that the effect of solvent on these bands is quite complex, which can be related to the structure of the hetero-

TABLE V

Solvent Effects on Secondary Phenolic Bands of 2-Substituted 2-[4,5]-Areneazoly- and (2-Indolyl)phenols and of 1-(2-Benzotriazolyl)-2-naphthol
 λ in nm, ϵ in $l \text{ mol}^{-1} \text{ cm}^{-1}$.

Compound	n-Heptane	Chloroform	Dioxane	96% Ethanol	Methanol	50% Dioxane
<i>I</i>	295 14 400	299 ^a 10 400	298 16 500	296 12 620	296 20 000	296 16 500
<i>VI</i>	288.5 11 500	290 10 050	287.5 14 500	287.5 ^a 13 000	288 ^a 13 120	287 ^a 15 000
<i>XVI</i>	293 ^b 10 000	294 14 400	292 15 000	290 13 050	291 16 250	291.5 18 500
<i>XXI</i>	291 14 150	293 15 050	292 14 600	— —	288 12 600	292 8 100
<i>XXIV</i>	292 25 800	294 20 150	293 22 500	292 17 310	292 22 500	292.5 22 540
<i>XXIX</i>	288 16 100	290 15 050	288 17 700	287 13 780	287 15 300	287 17 300
<i>XXXIV</i>	301 ^a 14 700	302 ^a 13 000	300 ^a 14 500	298 ^a 13 180	297 ^a 15 250	297.5 ^a 16 000
<i>XXXIX</i>	319 13 000	320 14 200	317 7 400	318 ^a 5 500	318 ^a 5 500	319 ^a 5 300

^a Shoulder. ^b Measured saturated solutions (low solubility).

cyclic substituent, which, along with the phenolic group, can also be considered as a functional group.

Contrarily to the 4-substituted phenols the C-bands of the 2-substituted derivatives (excepting derivative *XXXIV* which does not form intramolecular hydrogen bond) show either hypsochromic shift on going from chloroform to dioxane, or they do not change (derivative *XXI*). This indicates that dioxane, due to its proton-acceptor properties, cleaves the intramolecular hydrogen bond. The bathochromic shift observed with derivative *XXXIV* has been expected and can be explained similarly as in the case 4-substituted phenols, by the formation of the intermolecular hydrogen bond O—H...O. In dioxane medium, the intramolecular hydrogen bond is undoubtedly completely cleaved in compound *XXXIX* (Fig. 5), which fact is connected with steric hindrance in the molecule, since derivative *XXXIX* can be regarded as 2',6'-disubstituted 2-phenylbenzotriazole. Such derivatives were found to be non-coplanar^{6,32}. The compound *XXXIX* in *n*-heptane solution is co-planar, due to the intramolecular hydrogen bond, and its UV spectra are similar to the spectra of other 2-substituted phenols studied. However, already such a strong proton-acceptor solvent as dioxane is able to cleave the intramolecular hydrogen bond, which is due to steric effects. This results in angular displacement of the naphthyl around the

TABLE VI

Z-Values (in Parentheses) and Energies (*E*, kcal/mol) Corresponding to Electron Transitions of C-Bands of 2-Substituted 2-[4,5]Areneazolyl- and 2-Indolylphenols and of 1-(2-Benzotriazolyl)-2-naphthol in Solvents of Varying Polarity

Compound	<i>E</i> , in							
	benzene	<i>n</i> -heptane	chloroform	pyridine	dioxane	96% ethanol	methanol	50% dioxane
	(54.0) ^a	(60.1) ^b	(63.2) ^a	(64.0) ^a	(75.5) ^c	(80.8) ^a	(83.6) ^a	(87.5) ^a
<i>I</i>	85.2	85.4	85.7	—	86.4	86.7	87.4	88.3
<i>VI</i>	89.4	89.9	89.9	—	91.4	92.6	93.5	94.4
<i>XI</i>	—	82.0	81.8	—	82.0	82.2	82.3	81.8
<i>XVI</i>	89.1	89.4	89.4	89.4	90.1	90.6	90.9	91.2
<i>XXI</i>	89.1	89.1	89.4	89.4	89.4	89.6	89.6	89.9
<i>XXIV</i>	88.9	89.1	89.4	88.9	89.6	89.9	89.9	90.3
<i>XIX</i>	85.1	85.2	85.6	—	85.8	85.9	86.3	86.9
<i>XXXIV</i>	90.3	89.9	89.1	87.4	88.3	89.4	89.6	89.4
<i>XXXIX</i>	79.9	80.4	80.4	—	86.7	—	86.4	86.4

^a Taken from lit.³⁷. ^b Value for iso-octane. ^c Calculated by extrapolating the values recorded in ref.⁴¹.

N—C bond and, as a consequence, in a strong hypso- and hypochromic shift of the longest wavelength band. With the 2-substituted phenols forming strong intramolecular hydrogen bond in the nonpolar solvent, this bond is not completely cleaved in dioxane, a comparatively most extensive cleavage occurring obviously with derivative VI.

Upon substitution of dioxane for methanol the situation becomes still more complicated (Tables III and VII), since methanol is the solvent with both electron-acceptor and electron-donor properties. As follows from the results given in Tables III and VII, those 2-phenyl derivatives which can form only intermolecular hydrogen bond of the type $N\cdots H-O$ (except for 2-phenylindole and 2-phenylbenzimidazole) exhibit hypsochromic shift, similarly as anilines³³, which fact is obviously due to the reduced electron density on the functional group during excitation³⁴. With 2-phenylindole and 2-phenylbenzimidazole the bond of type $N-H\cdots O$, if formed, should be by far weaker than the bond of type $N\cdots H-O$ ³¹. The introduction of hydroxyl group to the 2-position of the phenyl ring complicates again the situation. From the hypsochromic shift of all the 2- and 4-substituted hydroxy derivatives (except derivative XXXI) it can be deduced (Tables III and VII) that either the strongest bond is the hydrogen bond of type $N\cdots H-O$ or that the solvent methanol exerts greater effect on the heterocyclic substituent than on the phenolic part of the molecule. This is in harmony with the observation of Chandra and Basu³⁵ and of Baba³⁶, who found that the $N\cdots H-O$ bond is stronger than $O\cdots H-O$ bond, and it agrees well also with our earlier results¹⁹.

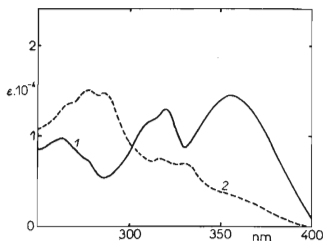


FIG. 5

UV Spectrum of 1-(2-Benzotriazolyl)-2-Naphthol in n-Heptane 1 and Dioxane 2

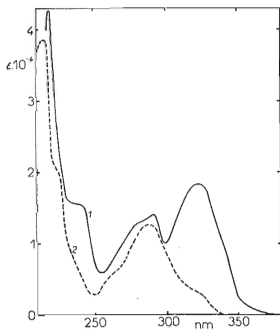


FIG. 6

UV Spectrum of 2-(N-Methyl-2-benzimidazolyl)phenol in n-Heptane 1 and Methanol 2

In the case of the 2-substituted phenols the $N\cdots H-O$ bond decreases the electron density on the nitrogen and by this effect the present intramolecular hydrogen bond is weakened. The hypsochromic shift is therefore greater with the derivatives in which the hydrogen bond strongly affects the UV spectrum (compounds *I*, *VI*, *XXXIX*). Compound *XI* exhibits a small solvent effect, which can be due to the lesser steric accessibility toward solvent of the nitrogen engaged in the intramolecular hydrogen bond. Derivative *XXI*, with significant steric effects in the molecule, behaves similarly as derivative *XXXIV* in dioxane (Fig. 6). As in the molecule of compound *XXI* along with steric effects, which tend to decrease co-planarity of the molecule, there is also intramolecular hydrogen bond which is oppositely operating, the decisive factor becomes the magnitude of these effects. In aprotic solvents (Table VII) the strength of the intramolecular hydrogen bond is great enough to overcome steric effects and the molecule is co-planar. In methanol or other protic solvents the proton donor weakens or cleaves the intramolecular hydrogen bond to such an extent that the

TABLE VII

C-Bands of Derivatives of 2-Aryl-Substituted [4,5]Areneazoles and of Indole in Chloroform (C) and in Dioxane (D)

Compound	C	D	$\Delta\lambda^a$	Compound	C	D	$\Delta\lambda^a$	Compound	C
<i>I</i>	334 17 850	331 22 750	- 3	<i>III</i>	320 23 900	325 25 800	+ 5	<i>IV</i>	308 24 800
<i>VI</i>	318 19 900	313 22 000	- 5	<i>VIII</i>	307 20 750	303 24 300	- 4	<i>IX</i>	298 15 310
<i>XI</i>	350 24 050	349 22 750	- 1	<i>XIII</i>	344 21 300	346 24 050	+ 2	<i>XIV</i>	336 18 700
<i>XVI</i>	320 21 100	317.5 24 750	- 2.5	<i>XVIII</i>	309 22 800	306 41 300	- 3	<i>XIX</i>	303 28 200
<i>XXI</i>	320 20 900	320 17 800	0	<i>XXII</i>	295 18 400	297 23 900	+ 2	<i>XXIII</i>	290.5 16 800
<i>XXIV</i>	320 18 590	319 19 500	- 1	<i>XXVI</i>	307 28 650	305.5 36 750	- 1.5	<i>XXVII</i>	300 23 700
<i>XXIX</i>	334 16 850	333.5 20 300	- 0.5	<i>XXXI</i>	315 25 400	317.5 31 000	+ 2.5	<i>XXXI</i>	298 18 800
<i>XXXIV</i>	321 18 850	324 23 400	+ 3	<i>XXXVI</i>	312 28 850	308 34 600	- 4	<i>XXXVI</i>	309 24 800
<i>XXXIX</i>	356 12 750	330 7 000	- 26	<i>XL</i>	323 15 100	323 18 000	0	—	—

^a $\Delta\lambda = \lambda_{\max}(\text{dioxane}) - \lambda_{\max}(\text{chloroform})$.

effect of steric factors is prevailing, which results finally in the extinction of the hydrogen bond (F). This manifests itself by a strong decrease in the intensity of C-band, or by the fact that this band appears only as a shoulder on the long-wavelength side of the secondary phenolic band.

The effect of various solvents on the position of the C-band is summarized in Table VI. The Z -values³⁷ were taken as the measure of solvent polarity. In a study of the dependence of $\pi - \pi^*$ and $n - \pi^*$ transitions of benzophenone derivatives on Z -value, Dilling³⁸ has reported that protic solvents behave differently from aprotic ones. Typical dependence of C-band energy on Z -values for 2-(2-indazolyl)phenol and 2-(2-benzotriazolyl)phenol is shown in Fig. 7a. This dependence is linear in both types of the solvents. The break on the curve occurs, however, on going from aprotic to protic solvents. This indicates that the intermolecular hydrogen bond $N \cdots H - O$, which forms in protic solvents, is the strongest of all the types of intermolecular hydrogen bonds which could have occurred in the studied compounds. The position of the C-band of the derivatives with extensive conjugation is much less influenced by the polarity of solvents (Fig. 7b) than of the derivatives of type A (Fig. 7a). In the case of 2-(2-benzoxazolyl)phenol the break on the curve does not occur even on going to

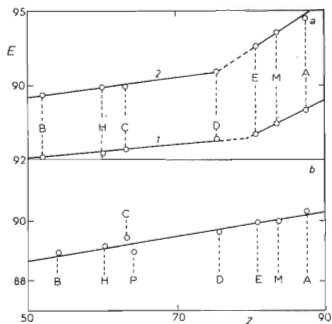


FIG. 7

Dependence, on Z -Values, of Energies (E , kcal/mol) Corresponding to Electron Transitions of C-Bands of *a* 2-(2-Benzotriazolyl)phenol 1, 2-(2-Indazolyl)phenol 2 and *b* 2-(2-Benzoxazolyl)phenol

B Benzene, H *n*-heptane, C chloroform, P pyridine, D dioxane, E 96% ethanol, M methanol, A 50% aqueous dioxane.

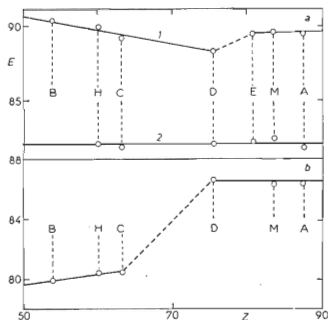


FIG. 8

Dependence, on Z -Values, of Energies (E , kcal/mol) Corresponding to Electron Transitions of C-Band of *a* 2-(2-Indolyl)phenol 1, 2-(2-Naphthol [1,2-*d*]triazolyl)phenol 2 and *b* 1-(2-Benzotriazolyl)-2-Naphthol

Solvents see Fig. 7.

protic solvents (Fig. 7*b*). This speaks for a comparatively strong intramolecular hydrogen bond in this derivative in protic solvents, which has already been established in a study of dissociation constants¹⁹. Derivatives *XI*, *XXI* and *XXXIX* are exceptions to the rules established with other derivatives, undoubtedly due to the already mentioned steric reasons. The exceptional behaviour of derivative *XXIV* is obviously due to the absence of intramolecular hydrogen bond (Fig. 8).

The ultraviolet spectra of 2- and 4-substituted phenols in 0.05M-HCl and in 0.05M-NaOH are reported in Table VIII. In the case of 4-substituted phenols the expected batho- and hyperchromic shift of the C-band corresponding to the phenolate anion occurs on going from acidic to alkaline medium. We have found that $\Delta\bar{\nu}$ of 4-substituted phenols with heterocyclic substituents can be linearly correlated with σ_p^- constants, similarly as Simpson and coworkers³⁹ found with 4-substituted 2-chlorophenols and Rapport and coworkers⁴⁰ with 4-substituted 2-nitrophenols. The values of $\Delta\bar{\nu} = \bar{\nu}_A - \bar{\nu}_{HA}$, where $\bar{\nu}_{HA}$ is the wavenumber of the C-band in the acidic medium and $\bar{\nu}_A$ is the wavenumber in the alkaline medium are presented in Table VIII. The correlation has the form

$$\Delta\bar{\nu} = -4.176 + 4173\sigma_p^- ; s = 142 ; r = 0.988 ; n = 8 ;$$

(*s* is the standard deviation, *r* the correlation coefficient and *n* the number of members of the series). While secondary phenolic bands are rather insensitive to the change in pH, the C-bands, similarly as in the case of 4-substituted phenols with non-heterocyclic substituent, are strongly influenced by the medium. With 2-substituted phenols containing heterocyclic substituent the bathochromic effect is observed, as expected, but hyperchromic shift of C-bands on going to ionised forms does not occur. Instead, the shift is rather hypochromic. Distinct hypochromic shift occurs with all the 2-substituted phenols the intramolecular hydrogen bond of which aids the co-planarity of the molecule (compounds *I*, *VI* and *XI*). Deviations from co-planarity are indicated by a marked decrease in absorbancy, since the formed phenolate anion, which is responsible for a bathochromic shift of the spectrum, is no more in effective conjugation with the N-heterocyclic ring. In the above mentioned compounds there are two factors which compete with one another and reflect in the spectra. In derivatives *XXI* and *XXXIX*, with deviations from co-planarity already in the non-ionised form, only phenolic portion of the molecule exerts effect and the spectrum shows batho- and hyperchromic effect, similarly as phenols without *ortho*-effect. Also comparison of ionised and non-ionised forms of 2- and 4-substituted phenols is of interest. 2-Substituted phenols, when compared with 4-substituted ones, have C-bands shifted bathochromically in non-ionised forms of all the studied compounds. The C-bands of ionised forms of 2-substituted phenols are shifted relative to the bands of 4-substituted derivatives only in those compounds the intramolecular hydrogen bond of which does not influence significantly the ultraviolet spectrum. Contrarily, reverse effect

TABLE VIII
Secondary Phenolic Bands of 2-Substituted and C-Bands of 2- and 4-Substituted [4,5]Arenazoaryl- and Indolylphenols and 2-Benzotriazolyl-naphthols in 0.05M-HCl and in 0.05M-NaOH

Compound	λ_1^a	λ_2^b	λ_3^c	λ_4^d	Compound	λ_5^a	λ_6^c	$\Delta\lambda_1^e$	$\Delta\lambda_2^f$	$\Delta\lambda_3^g$	$\Delta\bar{\nu}^h$	σ_p^{-i}
I	325	296	344	277	III	312.5	360	19	-12.5	+16	4 220	1.020
	19 000	18 000	6 000	15 500		29 200	22 500					
VI	309.5	287 ^o	324	287.5	VIII	305	324.5	14.5	-4.5	+0.5	1 970	0.487
	14 000	3 000	10 750	9 750		18 500	21 200					
XI	350	277	350	-j	XIII	346	372	0	-4	+22	2 120	0.487
	16 450	19 900	7 400			21 000	24 700					
XVI	325 ^k	297	353	296	XVIII	305 ^l	323	39	-9	-30	1 830	0.480
	21 500	13 500	20 750	24 700		41 000	46 100					
XXI	304 ^m	283	320	286	XXII	295 ⁿ	316	2	-23	-4	2 250	0.578
	8 700	11 500	8 700	5 950		16 400	27 600					
XXIV	318	292.5	361	286	XXVI	306	336	43	-12	-25	2 920	0.684
	20 250	15 500	15 750	16 000		28 800	45 200					
XXIX	329	291 ^o	380	292.5	XXXI	320	353	51	-9	-27	2 920	0.652
	19 400	6 700	21 300	15 500		27 800	43 300					
XXXIV	320	297 ^o	351	295	XXXVI	309	326	31	-11	-25	1 690	0.389
	22 750	8 500	24 250	11 500		26 000	39 800					
XXXIX	331	287	355	278	XL	323	374	24	-8	+19	4 220	-
	6 400	8 100	17 800	27 800		15 400	14 150					

^a C-band in 0.05M-HCl. ^b Secondary phenolic band in 0.05M-HCl. ^c C-band in 0.05M-NaOH. ^d Secondary phenolic band in 0.05M-NaOH. ^e $\lambda_3 - \lambda_1$. ^f $\lambda_5 - \lambda_1$. ^g $\lambda_6 - \lambda_3$. ^h $\bar{\nu}_5 - \bar{\nu}_6$. ⁱ Taken from ref. 19. ^j Coincides with the primary band. ^k At pH 7 for undissociated form: λ 314 nm and ϵ 27 500. ^l Determined at pH 7; in 0.05M-HCl λ 312 nm and ϵ 25 000. ^m At pH 7 λ 318 nm and ϵ 3 800. ⁿ Determined at pH 7; in 0.05M-HCl λ 302 nm and ϵ 23 400. ^o Shoulder.

is observed with compounds *I*, *VI*, *XI* and *XXXIV* and it can be attributed to the already discussed non-coplanarity of the ionised forms, in which the intramolecular hydrogen bond cannot be formed and the spectra of which are therefore influenced mainly by steric effects.

CONCLUSION

All the studied derivatives have similar electronic spectra which exhibit besides the bands of the basic benzene chromophor, also the band which can be ascribed to the electron transition arising in the main from a chromophor formed by 2-aryl substituent of N-heterocyclic nucleus grouping. When using electronic spectra, the intramolecular hydrogen bond in the phenols substituted in position 2 by N-heterocyclic group can be best studied by comparing phenols with respective 2-substituted anisoles or by examining solvent effect. On the other hand, 3-substituted phenols are not suitable for examination of the intramolecular hydrogen bond in the series of studied compounds, since their spectra differ from the spectra of 2-substituted derivatives. When compared with 3-substituted phenols, 4-substituted derivatives are more suitable for the study of intramolecular hydrogen bond in the studied compounds, owing to similarity of the electronic effects of substituents in positions 2 and 4 of the benzene ring. The intramolecular hydrogen bond influences the electronic spectra mainly in that it aids the coplanarity of molecules, which is especially important in the cases where mesomeric effects cannot compete with steric effects tending, by contrast, to deviate the molecule from coplanarity. Owing to the increased stabilisation of coplanarity, which results in more efficient conjugation, the spectrum shows a bathochromic shift. In compounds with extensive conjugation and small or no steric effect, the intramolecular hydrogen bond exerts only small effect on the near ultraviolet spectrum. The strength of the intramolecular hydrogen bond or its resistance to the cleavage by proton donors is greater in those derivatives the UV spectra of which are less influenced by this bond.

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