

ELECTRONIC SPECTRA OF SCHIFF'S BASES OF 3-(BENZYLIDENEAMINO)-4-HYDROXYTOLUENE AND N-(5-METHYLSALICYLIDENE)ANILINE TYPES

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Electronic spectra of twenty-one N-(5-methylsalicylidene)anilines and nineteen 3-(benzylideneamino)-4-hydroxytoluenes have been studied. The absorption bands have been ascribed to individual types of electronic transitions according to the influence of solvents and substituents and according to the previous works. Wave numbers of the main absorption bands of the second series of compounds correlate with the substituent constants σ resp. σ^- . The influence of solvents and hydrogen bonds has been characterized with the use of the experimental values of excitation energies of the corresponding hydroxy and O-methyl derivatives.

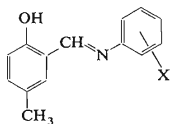
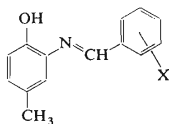
Electronic spectra of benzalanilines and salicylideneanilines are interesting from the point of view of inter- and intramolecular hydrogen bond formation as well as substituent influence. If, in the first approximation, only the structure of the compounds studied is taken into account, the benzalanilines should exhibit the same or, at least, similar transitions in spectra as azobenzene or stilbene eventually their conjugated acids. The spectra of benzalanilines do not, however, fit completely this analogy¹. The changed symmetry is the first reason of this. The *trans*-forms of azobenzene and stilbene belong to C_{2h} symmetry point group; the symmetry falls to C_{1v} group by substitution of one atom of the vinylene group. This causes such a lowering of the transition moment that, however $\pi \rightarrow \pi^*$ transition is encountered with benzalanilines at approximately the same wavelengths, its intensity is lower than that of the analogous transition in azobenzene or stilbene. At the same time the intensity of $\Phi_1 \rightarrow \pi_1^*$ transition is increased which becomes the main component of a complex band formed of $\pi_1 \rightarrow \pi_1^*$ and $\Phi \rightarrow \pi^*$ transitions. The complexity of these transitions and their superposition are the probable cause of the fact that the transition of the $\pi \rightarrow \pi^*$ type has not yet been found safely in the spectra of Schiff's bases. Jaffé's calculation¹ of the electron orbital energy levels shows that the energy of n -electrons of benzalanilines is approximately the same as the energy of those electrons in azobenzene. However, a substantially higher energy of the π_1^* level causes a hypsochromic shift of the $n \rightarrow \pi^*$ transition in benzalaniline, so that the corresponding band is covered by the neighbouring $\pi \rightarrow \pi^*$ transition. Ebara² and Brocklenhurst³ ascribe the difference between the spectrum of benzalaniline and those of structurally similar stilbenes and azobenzenes to a rotation of the aromatic nucleus bound to the nitrogen atom out of the plane of the molecule. Such deformation brings about a lowering

of π -electrons delocalization as compared to the planar molecule. However, a compensation can occur in the case of *o*-hydroxy analogs due to the intramolecular hydrogen bond; the free electron pair of *N*-salicylideneanilines will then be localized at the nitrogen atom to greater extent. The stabilization energy must be, therefore, smaller than in the case of benzalaniline.

In solid state the molecules can assume a planar configuration⁴ (5-chlorosalicylideneaniline) or a non-planar one⁵ (2-chloro-*N*-salicylideneaniline) or even various steric configurations in various polymorphous forms of a compound⁶ (4-chloro- and 4-bromoderivatives). Spectroscopic evidence, however, shows that isolated molecules in solutions are rather non-planar⁷. With respect to possible deviations from planar configuration, the molecules of benzalaniline can assume most different conformations in solutions. These can be influenced by a proton transfer (benzenoid — quinoid tautomerism) and geometrical isomerization at the double bond. *E.g.* such structural isomers of *N*-(2-hydroxy-1-naphthylidene)aniline⁸ and 2-phenylazo-1-naphthol⁹ were described by Lippert. A further complication is caused by a possibility of ionization and proton transfer from solvent system into the molecule. The only attempt of ascription of the absorption bands of benzalaniline on the basis of quantum calculations was carried out by Jaffé and coworkers¹. According to them the benzalaniline spectrum contains four main intensive absorption bands besides a weak badly developed $n \rightarrow \pi^*$ band.

The aim of the present work is a spectral study of the substituent influence on electronic transitions of *N*-(5-methylsalicylidene)anilines (*A*) (the compounds 1–21) and 3-(benzylideneamino)-4-hydroxytoluenes (*B*) (the compounds 22–40) and the solvent influence on spectral properties of the compounds studied. In computing the excitation energies we have also used the spectra of *N*-(3-methyl-6-methoxybenzylidene)aniline (41) and 3-(benzylideneamino)-4-methoxytoluene (42).

The formulae of the compounds of the type *A* and *B*.

*A**B*

| | | | |
|---------------------------|--|-------------------------------|--|
| 1, X = H | 12, X = 4-Cl | 22, X = H | 32, X = 4-CO ₂ H |
| 2, X = 2-OCH ₃ | 13, X = 4-NHCOCH ₃ | 23, X = 4-OH | 33, X = 4-CO ₂ CH ₃ |
| 3, X = 3-OCH ₃ | 14, X = 3-CO ₂ CH ₃ | 24, X = 2-OCH ₃ | 34, X = 3-CN |
| 4, X = 4-OCH ₃ | 15, X = 4-CO ₂ CH ₃ | 25, X = 3-OCH ₃ | 35, X = 4-CN |
| 5, X = 2-CH ₃ | 16, X = 3-COCH ₃ | 26, X = 4-OCH ₃ | 36, X = 2-NO ₂ |
| 6, X = 3-CH ₃ | 17, X = 4-COCH ₃ | 27, X = 2-Cl | 37, X = 3-NO ₂ |
| 7, X = 4-CH ₃ | 18, X = 4-CN | 28, X = 3-Cl | 38, X = 4-NO ₂ |
| 8, X = 3-F | 19, X = 3-NO ₂ | 29, X = 4-Cl | 39, X = 4-N(CH ₃) ₂ |
| 9, X = 4-F | 20, X = 4-NO ₂ | 30, X = 4-Br | 40, X = 3,4-CH ₂ O ₂ |
| 10, X = 2-Cl | 21, X = 4-N(CH ₃) ₂ | 31, X = 4-NHCOCH ₃ | |
| 11, X = 3-Cl | | | |

TABLE I
Anils Prepared

| Compound No | M.p. °C | Yield % Colour ^a | Formula (mol. wt.) | Calculated/Found | | |
|-------------|----------------|--------------------------------|--|------------------|--------------|----------------|
| | | | | % C | % H | % N |
| 8 | 79 | 48 y. | C ₁₄ H ₁₂ FNO (229·1) | 73·36 73·59 | 5·24 5·29 | 6·11 6·40 |
| 9 | 117 | 53 y. | C ₁₄ H ₁₂ FNO (229·1) | 73·36 73·04 | 5·24 5·00 | 6·11 6·30 |
| 13 | 215—217 | 61 y. | C ₁₆ H ₁₆ N ₂ O ₂ (268·3) | 71·62 71·35 | 6·01 6·30 | 10·44 10·45 |
| 14 | 91 | 74 o. | C ₁₆ H ₁₅ NO ₃ (269·3) | 71·36 71·11 | 5·61 5·49 | 5·20 5·11 |
| 15 | 171—172 | 74 y. | C ₁₆ H ₁₅ NO ₃ (269·3) | 71·36 71·49 | 5·61 5·95 | 5·20 5·00 |
| 16 | 96—97 | 69 y. | C ₁₆ H ₁₅ NO ₂ (253·3) | 75·87 75·44 | 5·97 5·61 | 5·53 5·29 |
| 17 | 140—141 | 78 y. | C ₁₆ H ₁₅ NO ₂ (253·3) | 75·87 75·99 | 5·97 6·11 | 5·53 5·75 |
| 18 | 148—149 | 70 o. | C ₁₅ H ₁₂ N ₂ O (236·3) | 76·25 76·44 | 5·12 5·35 | 11·86 11·45 |
| 23 | 220—223 | 52 p.y. | C ₁₄ H ₁₃ NO ₂ (227·3) | 73·99 74·09 | 5·77 5·62 | 6·16 6·16 |
| 30 | 83—84 | 57 y. | C ₁₄ H ₁₂ BrNO (290·2) | 57·95 58·15 | 4·17 4·40 | 4·83 5·09 |
| 32 | 310—314 | 71 y. | C ₁₅ H ₁₃ NO ₃ (255·3) | 70·58 70·25 | 5·13 5·39 | 5·49 5·69 |
| 33 | 137—139 | 61 y. | C ₁₆ H ₁₅ NO ₃ (269·3) | 71·36 71·23 | 5·61 5·85 | 5·20 5·38 |
| 34 | 146—148 | 62 y. | C ₁₅ H ₁₂ N ₂ O (236·3) | 76·25 76·26 | 5·12 5·38 | 11·86 11·62 |
| 35 | 155 | 66 y. | C ₁₅ H ₁₂ N ₂ O (236·3) | 76·25 75·97 | 5·12 5·37 | 11·86 11·62 |
| 40 | 129—130 | 51 y. | C ₁₅ H ₁₃ NO ₃ (255·3) | 70·58 70·74 | 5·13 5·34 | 5·49 5·41 |
| 42 | — ^b | 30 p.y. | C ₁₅ H ₁₅ NO (225·3) | 79·97 79·82 | 6·71 6·92 | 6·22 6·31 |

^a y. yellow, p.y. pale yellow, o. orange; ^b B.p. 53—55°C/0·1 Torr.

TABLE II
Electronic Spectra of Anils of the Type A

| Compound | Solvent ^a | Concentration · 10 ⁴ mol/l | λ_{\max} , nm (log ϵ) |
|----------|----------------------|--|--|
| 1 | A | 1.78 | 346 (4.01) + 319.5 s (4.01) + 304.5 s (4.03); 272 (4.11); 226.5 (4.29) + 206 s (4.25) |
| | B | 1.96 | 351 (4.01) + 320.5 s (3.96) + 304.5 s (3.99); 271 (4.12); 227.5 (4.31) + 207.5 s (4.22) |
| 2 | A | 1.66 | 351 (4.08); 271.5 (4.05); 232.5 (4.27) + 209 (4.32) |
| | B | 1.55 | 356 (4.07); 269.5 (4.08) |
| 3 | A | 1.87 | 347.5 (4.06); 270.5 (4.11); 211 (4.43) + 198.5 (4.45) |
| | B | 1.42 | 350.5 (4.04); 270 (4.11); 234 s (4.29) + 214 (4.37) + 202 s (4.32) |
| 4 | A | 1.31 | 352 (4.21) + 329 s (4.17) + 314—317 i (4.09); 272 (4.03) 229 (4.28) + 210 (4.26) |
| | B | 1.35 | 354 (4.17) + 329 (4.12) + 314—316 i (4.05); 271 (4.05) 222 (4.32) + 211.5 (4.24) |
| 5 | A | 2.16 | 347 (4.01) + 327 s (4.01) + 312—315 i (3.97); 270 (4.10); 233 (4.32) + 211 (4.25) |
| | B | 1.41 | 350 (4.01) + 329 s (3.96) + 313 s (3.92); 269 (4.11); 233 (4.31) + 209 (4.29) |
| 6 | A | 1.43 | 346 (4.04) + 321.5 (4.03) + 306 (4.04); 271.5 (4.10) 231 (4.31) + 209 (4.33) |
| | B | 1.63 | 350.5 (4.03) + 323 (3.98) + 306 (3.99) 270.5 (4.12); 233 (4.32) + 211 (4.30) |
| 7 | A | 1.37 | 347.5 (4.10) + 322.5 (4.10) + 308 (4.08) 271.5 (4.10); 231 (4.32) + 207 (4.27) |
| | B | 1.70 | 351 (4.18) + 323.5 (4.10) + 309 (4.13) 271 (4.21); 231 (4.42) + 209 (4.33) |
| 8 | A | 0.79 | 345 (4.03) + 317 s (4.03) + 298 s (4.09) 273 (4.17); 226 (4.32) + 207 (4.26) |
| | B | 0.77 | 351 (4.06) + 320 s (4.03) + 303 s (4.09) 271.5 (4.21); 226 (4.35) + 205.5 (4.30) |
| 9 | A | 0.76 | 345 (4.07) + 316 s (4.07) + 304 s (4.09) 272 (4.34) + 210 s (4.27) |
| | B | 0.75 | 352 (4.06) + 319 s (4.02) + 305.5 s (4.04) 270 (4.16); 221.5 (4.34) + 207 (4.27) |

TABLE II
 (Continued)

| Compound | Solvent ^a | Concentration · 10 ⁴ mol/l | λ_{\max} , nm (log ϵ) |
|----------|----------------------|--|--|
| 10 | A | 1·38 | 352 (4·00) + 327 s (4·01) + 305—310 i (4·02) 276 (4·14); 234 (4·30) + 211 (4·34) |
| | B | 1·37 | 357 (3·99) + 329 s (3·94) + 313 s (3·96) 272 (4·14); 234 (4·32) + 213 (4·31) + 200 (4·29) |
| 11 | A | 1·44 | 349 (4·00) + 322—326 i (3·99) + 298—303 i (4·05) 273·5 (4·15); 232 (4·31) + 212 (4·36) |
| | B | 1·44 | 355 (4·00) 323 s (3·95) + 303—305 i (4·00) 272·5 (4·16) |
| 12 | A | 0·45 | 349·5 (4·00) + 322 (4·01) + 309 (4·03) 273 (4·08); 232·5 (4·24) |
| | B | 0·46 | 354 (3·99) + 324 (3·35) + 310 (3·98) 272 (4·07); 234 (4·24) + 229·5 s (4·23) |
| 13 | A | 0·54 | 352 (4·28) + 331 s (4·26) 271·5 (4·19); 235 (4·33); 204·5 (4·34) |
| | B | 0·11 | 359 (4·20) + 332·5 (4·15) + 320 s (4·09) 272 (4·11); 238 (4·26) + 224 s (4·21) |
| 14 | A | 0·71 | 346 (3·98) 273 (4·15); 222 (4·12) |
| | B | 0·60 | 352 (4·13) 272 (4·28); 225 (4·54) |
| 15 | A | 0·63 | 356 (4·22) 277 (4·36); 243·5 (4·42); 198·5 (4·50) |
| | B | 0·43 | 349 (4·07) 282 (4·23); 242 (4·21); 205 (4·30) |
| 16 | A | 0·61 | 346 (4·06) 270·5 (4·23); 228·5 (4·46) + 206·5 s (4·22) |
| | B | 0·54 | 352 (4·07) 272·5 s (4·23) + 233·5 (4·46); 225 (4·46) + 204 s (4·25) |
| 17 | A | 0·63 | 352 (4·16) + 304 (4·30) 248·5 (4·11); 209 (4·35) |
| | B | 0·69 | 358 (4·14) + 302 s (4·22) + 280 (4·27) 247·5 (4·21); 204 (4·36) |
| 18 | A | 0·60 | 352 (4·09) + 284 (4·31) 240·5 (4·31); 207 (4·33) |
| | B | 0·65 | 359 (4·10) + 280 (4·27) 241 (3·47); 199 (4·36) |

TABLE II
(Continued)

| Compound | Solvent ^a | Concentration · 10 ⁴ mol/l | λ_{\max} , nm (log ϵ) |
|----------|----------------------|--|--|
| 19 | A | 1.32 | 350 (3.97) + 300 s (4.13) + 274 (4.32) 226 (4.33) |
| | B | 1.34 | 357 (3.97) + 300 s (4.09) + 272 (4.28) 229 (4.33) + 212 s (4.28) |
| 20 | A | 1.36 | 366 (4.19); 321.5 (4.23) 215.5 (4.34) + 203.5 (4.34) |
| | B | 1.15 | 368 (4.01); 311 (4.14) + 230—235 i (4.00); 202.5 s (4.21) |
| 21 | A | 1.82 | 384 (4.33) + 315—325 i (3.92) + 260—270 i (4.05) 244.5 (4.12) + 233—236 s (4.01) + 201.5 (4.36) |
| | B | 1.76 | 382 (4.37) + 315—325 i (3.93) + 265—270 i (4.54) 242 (4.31); 195 (4.51) |

^a A methanol, B n-heptane.

EXPERIMENTAL

The melting points were determined with the use of a Kofler apparatus. The samples for elemental analyses and spectral measurements were dried 24 hours over phosphorus pentoxide under reduced pressure (15 Torr).

Preparation of Schiff's Bases

All the anils were prepared by mixing equivalent amounts (0.01 mol) of methanolic solutions of the respective amines and aldehydes and isolated by the method given in our previous reports^{10,11}. The samples for analyses and spectral measurements were crystallized twice from methanol. The results are presented in Table I, the rest of anils *A* and *B* were described previously^{10,11}. The O-methyl derivative 42 (X = H) was prepared on a 0.1 mol scale; the syrupy product was obtained by distillation (53—55°C/0.1 Torr) after drying the etheric solution with sodium sulphate.

Measurements of Electronic Spectra

The spectra were measured with the use of a Unicam SP 800 B apparatus calibrated for the wavelengths of the absorption filters delivered with the apparatus and for extinctions by means of a solution of 120 mg potassium dichromate p.a. in 1000 ml 0.01 N-H₂SO₄. The accuracy of wavelength readings was ± 0.4 to ± 0.75 nm in the range of 190—450 nm. The error in the extinction readings did not exceed ± 0.03 units in the range of 0.1—1.2. The measurements were carried out in solutions of spectrally pure n-heptane and methanol at 25°C. The conditions and results of the measurements are presented in Tables II, III, and IV.

TABLE III
Electronic Spectra of Anils of the Type B

| Compound | Solvent ^a | Concentration · 10 ⁴ mol/l | λ_{\max} , nm (log ϵ) |
|----------|----------------------|--|--|
| 22 | A | 1.79 | 355 (3.66) 270—285 i (3.88); 244.5 (4.15); 208 (4.36) |
| | B | 1.94 | 369 (4.05) + 327—331 i (3.82) + 308—312 i (3.89) 272 (4.13); 241.5 s (3.96) + 227 s (4.12) + 205.5 (4.33) |
| 23 | A | 1.59 | 325.5 (3.61); 282 (3.90); 226.5 (3.73) |
| | B | 1.84 | 351 (3.52) 271 (3.84); 221.5 (3.73) |
| 24 | A | 1.21 | 356 (3.90); 325 (3.92); 257.5 (4.06) + 229—323 i (4.05); 208.5 (4.48) |
| | B | 1.52 | 365 (4.07); 323—328 i (3.92); 272.5 (4.04); 229 (4.07); 208 (4.39) |
| 25 | A | 1.25 | 355 (3.91) 260 (4.10); 208.5 (4.45) |
| | B | 1.73 | 368 (4.45) + 330—333 i (4.30) + 306—310 i (4.32); 273 (4.47) 213.5 (4.71); 205.5 (4.70) |
| 26 | A | 1.71 | 349.5 (3.92) 288 i (4.24) + 283 (4.26); 215—220 i (4.26) + + 207.5 (4.38) |
| | B | 1.61 | 359 (4.18) + 329—332 i (4.01) + 309—312 i (4.11) 291.5 (4.24); 206 (4.34) |
| 27 | A | 1.14 | 364 (3.78); 263.5 (3.99) + 248—251 i (3.94); 208.5 (4.36) |
| | B | 1.72 | 376 (4.02); 278 (4.07) + 248.5 s (3.98); 241 s (3.97) 208.5 (4.38) |
| 28 | A | 1.49 | 359 (3.99); 253 (4.09); 209.5 (4.50) |
| | B | 1.66 | 375 (4.04) + 330 s (3.81) + 314—316 i (3.89) 272.5 (4.09) + 248 s (4.00) + 239 s (4.02); 210.5 (4.48) |
| 29 | A | 1.52 | 358 (3.84); 261 (4.19); 210 (4.39) |
| | B | 1.55 | 373 (4.08) + 331 s (3.88) + 309—313 i (3.96) 278 (4.21) + 242.5 s (3.91); 204.5 (4.34) |
| 30 | A | 1.20 | 355 (3.91); 270.5 (4.19); 216.5 (4.09) |
| | B | 0.66 | 372 (4.09) + 315 i (—) 279.5 (4.22); 247.5 (3.86); 211.5 (4.22) |

TABLE III
(Continued)

| Compound | Solvent ^a | Concentration · 10 ⁴ mol/l | λ_{\max} , nm (log ϵ) |
|----------|----------------------|--|---|
| 31 | A | 0.71 | 349 (3.58); 292.5 (4.32); 223 (4.20) |
| | B | 0.24 | 366 (3.69) + 338 s (3.57) + 316 s (3.68) + 304 s (3.76) 295.5 (3.80); 292 i (3.79); 247 i (3.69) + 226 (3.65) |
| 32 | A | 1.39 | 359 (2.97); 285.5 (3.75); 248 (4.11); 215.5 (3.95) |
| | B | 0.09 | 286 (4.04) + 339 s (3.90) + 319 s (3.98) + 302 (4.07) 283 (4.12) + 235.5 (4.00); 220.5 (3.97) |
| 33 | A | 1.42 | 366 (3.89); 273 (4.14); 235.5 (4.01); 214.5 (4.02) |
| | B | 0.66 | 380 (4.07) + 309 (4.00) 280.5 (4.17) + 254 (3.94) + 233 (4.01); 211 (4.24) |
| 34 | A | 0.71 | 360 (3.68); 265 s (3.93) + 245 s (3.98) + 220 (4.31) |
| | B | 0.75 | 380 (3.49) + 316 s (3.81) 267.5 (4.08); 218.5 (4.37) |
| 35 | A | 0.74 | 368 (3.76) 270 (4.06) + 260 s (4.04); 232.5 (4.11); 212 (4.18) |
| | B | 0.73 | 390 (4.02); 338 (3.77) + 320 s (3.87) 279.5 (4.11) + 253 s (3.99); 238.5 (4.01) + 210.5 (4.21) |
| 36 | A | 1.15 | 360 (3.92); 271 (4.15) + 225—230 i (3.96); 205.5 (4.35) |
| | B | 1.13 | 374 (4.09) + 310—314 i (3.98) 278 (4.21) + 246.5 s (3.93); 227—230 i (4.03) + + 203 (4.40) |
| 37 | A | 1.73 | 363 (4.03) 258 (4.26); 223 (4.30) + 205.5 (4.35) |
| | B | 1.41 | 384 (3.92) 260 (4.13); 225 (4.29) + 201 (4.25) |
| 38 | A | 1.58 | 389 (3.92) 280 (4.18); 215—216 i (4.21) + 205.5 (4.29) |
| | B | 1.62 | 399 (4.13) + 374.5 s (3.89) + 329.5 s (3.97) + 311 s (4.03) 295—305 i (4.07) + 280 (4.16); 215—216 i (4.20) + + 206.5 (4.29) |

TABLE III
(Continued)

| Compound | Solvent ^a | Concentration · 10 ⁴ mol/l | λ_{\max} , nm (log ϵ) |
|----------|----------------------|--|--|
| 39 | A | 1.36 | 344.5 (4.31) + 300–310 i (4.04) 239.5 (4.05); 209 (4.40) |
| | B | 0.93 | 361 (4.26) + 325.5 s (4.07) 239.5 (3.93); 212–217 i (4.07) + 200 (4.22) |
| 40 | A | 1.37 | 349 (4.06) + 322 s (4.05) 280 (3.98); 231 (4.15) |
| | B | 0.71 | 361 (4.19) 280 (3.98); 231 (4.15) |

A methanol, B n-heptane.

TABLE IV
Electronic Spectra of O-Methyl Derivatives

| Anil | Solvent ^a | Anil concentration · 10 ⁴ mol/l | λ_{\max} , nm (log ϵ) |
|------|----------------------|---|---|
| 41 | A | 1.75 | 336 (3.19); 263.5 (4.07); 220.5 (4.28) + 210 s (4.23) |
| | B | 1.54 | 330 (4.03); 266.5 (4.11); 220.5 (4.33) + 203 s (4.30) |
| 42 | A | 1.47 | 335 (3.48); 287 s (3.67) + 250.5 (4.08); 216 (3.98) |
| | B | 1.23 | 334 (3.19); 394 (3.52); 241.5 (4.01); 212.5 (4.02) |

^a A methanol, B n-heptane.

RESULTS AND DISCUSSION

The vibration structure of the spectra of all the compounds studied in n-heptane is richer than that in methanol. Two main absorption regions can be clearly distinguished (Fig. 1 and 2). The one about 350 nm in the case of salicylideneanilines *A* and about 360–370 nm in spectra of the anils *B*. The other absorption region lies in the vicinity of 270 nm for all the compounds studied. The short-wave part

of the spectra cannot be distinguished so well. Anils *A* show a band at 220–230 nm and most of them also a band of a comparable intensity at 205–215 nm. In the series of anils *B*, only the shorter-wave of the both bands is distinguishable. The other one (the region of 230 nm) forms usually a part of a more complex system of inflex points and side maxima occurring in spectra of these compounds. Exceptions from the facts mentioned are encountered with the molecules carrying substituents with strong mesomeric influence. The respective absorption bands, except for the most short-wave ones, show considerable bathochromic shifts. The spectra are generally more simple, but, at the same time, they are influenced more strongly by the solvent character. Especially the first long-wave band is sensitive towards the influence of a hydroxylic solvent. The solvent change from *n*-heptane to methanol causes a shift of this band by 2–5 nm in average in the case of anils *A*, whereas in the case of anils *B* the respective shift is as much as three times as great. The instability of 4-nitro derivatives of the both types of compounds studied (the compounds 20 and 38) in alcohol is interesting. Their spectra change with time, and the changes found give evidence for a decomposition caused obviously by a protonation by solvent in accord to results of Cohen⁶.

The substituent influence can be judged from the 3- and 4-substituted derivatives. As it is seen from Tables II and III, the long-wave absorption maxima are sensitive to substitution. The both groups of Schiff's bases studied behave differently in this respect. Whereas in the case of anils *A* all the substituents cause bathochromic shifts

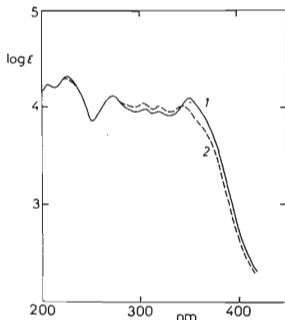


FIG. 1

Absorption Spectrum of *N*-(5-Methylsilylidene)aniline (*A*, *X* = H) in *n*-Heptane (Curve 1) and Methanol (Curve 2)

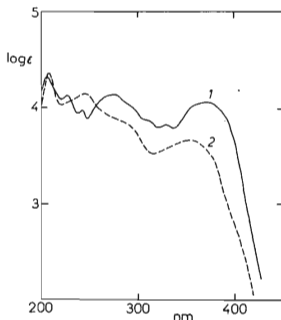


FIG. 2

Absorption Spectrum of 3-(Benzylideneamino)-4-hydroxytoluene (*B*, *X* = H) in *n*-Heptane (Curve 1) and Methanol (Curve 2)

only, in the case of anils *B* bathochromic and hypsochromic shifts occur by action of negative and positive substituents respectively. A correlation satisfying the modified form (1) of the Hammett equation can be found between substituent effects and the frequencies of the long-wave maxima for this group of compounds in *n*-heptane

$$\nu = \nu_0 + \rho\sigma, \quad (1)$$

solutions (see Fig. 3). Correlation analysis¹² for $n = 15$ gave $\nu_0 = 27412 \pm 461 \text{ cm}^{-1}$, $\rho = -1.899 \pm 0.081$, and $r = -0.989$. 4-Dimethylamino group represents an exception, neither normal nor any of dual substituent constants being satisfactory for it. The relation is fulfilled by using σ_p^- constants in the case of substituents of -M type. In the series of anils *A* the frequency shifts are roughly proportional to the absolute values of substituent constants, the significance of the correlation is, however, small.

The difference of the substituent influence between the both groups of compounds can have two basic causes. The first one is the arrangement of the atoms of vinylene group and the second one (which is directly connected to the first one) is the hydrogen bond between the hydroxyl group and the nitrogen atom of the linking chain. The problem of hydrogen bonds and their influence on the excitation energy of the molecules is illustrated by Figs 4 and 5. In the case of anils *A* in *n*-heptane solution the

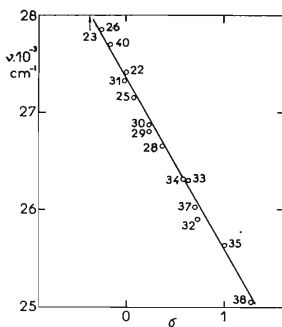


FIG. 3

Dependence of Wave Numbers of Long-Wave Absorption Maxima of 3-(Benzylideneamino)-4-hydroxytoluenes *B* on σ Constants

For numbers see the text. Values for the compound 23 (0.37; 28505)

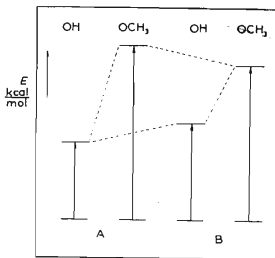


FIG. 4

Simplified Representation of Energies of $\pi \rightarrow \pi^*$ Transitions of Anil *A* ($X = H$) and its *O*-Methyl Derivative (41) with Respect to the Solvent Influence

displacement of the hydrogen bond (*i.e.* for compound 1 *vs.* 21) results in a change of the excitation energy from 81.48 to 86.46 kcal/mol, *i.e.* by 5.18 kcal/mol. The corresponding difference in methanol is 2.52 kcal/mol (85.12–82.60 kcal/mol). The intermolecular hydrogen bond formation thus competes with the six-membered hydrogen bond of the O—H—N type, the energy share due to solvation being 2.66 kcal/mol (5.18–2.52 kcal/mol) (see Fig. 4). $\pi \rightarrow \pi^*$ Transition of N-(3-methyl-6-methoxybenzylidene)aniline (compound 41) in *n*-heptane has practically the same energy (85.63 kcal/mol) as the corresponding transition of the parent anil of the type B (compound 22) (85.63 kcal/mol). The intramolecular hydrogen bond, however, changes the excitation energy far more fundamentally, *viz.* by 8.15 kcal/mol (85.63 to 77.48 kcal/mol). This phenomenon confirms the existence of a less firm five-membered chelate. The difference of the excitation energies in methanol is higher too, *viz.* 4.83 kcal/mol (85.37–80.54 kcal/mol). The effect of solvent is similar to that in the case of anil 1 *viz.* 3.32 kcal/mol (8.15–4.83 kcal/mol) (see Fig. 5).

With respect to the sensitivity of the long-wave transitions towards substituent influence and solvent system in the case of anils B, the transitions can be considered to be of $\pi \rightarrow \pi^*$ type with the B_u symmetry of the excited state and a polarization parallel with the approximately longitudinal axis of the molecule. The absorption band which lies near 270 nm for all the compounds is not practically influenced either by the substituent in the case of anils A or by solvent. If we use an analogy with the Jaffé ascription¹ and consider the transition to be of $\Phi \rightarrow \pi_1^*$ type with the polarization approximately perpendicular to the longitudinal axis of the molecule, it means that the solvation of salicylideneaniline occurs in such a way that the transverse polarity of the molecule is not influenced. From the analysis of the behaviour of the bands of $\pi \rightarrow \pi_1^*$ transitions we see that the solvent acts in the longitudinal axis of the molecule and hence the solvation obviously takes place at the hydroxyl group, an intermolecular O—H—O bond being formed.

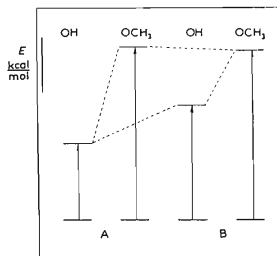


FIG. 5
Simplified Representation of Energies of $\pi \rightarrow \pi^*$
Transitions of Anil B(X = H) and its O-Methyl
Derivative (42)

This band which is, otherwise, well identifiable is strongly influenced by solvent in the case of anils of the type *B* (its positions in *n*-heptane and methanol differ by as much as 25 nm). This indicates obviously a solvation accompanied by a change of the transverse polarity of the molecule or by planarity lowering. The both bands described are accompanied by a number of side maxima and inflexes which are generally better distinguishable in *n*-heptane. The respective transitions are caused obviously by a symmetry perturbation of the parent molecule by the substituent. The last type of bands belongs quite surely to the $\Phi \rightarrow \Phi^*$ transition with the B_u symmetry of the excited state, and it is comparable to the benzalaniline band at 220 nm.

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