

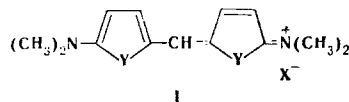
MONO- AND DIMETHINE DYES FROM 2-DIMETHYLAMINO-5-FORMYLFURANS,
-THIOPHENES, AND -SELENOPHENES

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The chromaticity of diverse mono- and dimethine dyes obtained from 2-dimethylamino-5-formylfurans, -thiophenes, and -selenophenes was examined by means of the Kiprianov-Brooker deviation method. It is shown that the heterocyclic rings have considerably higher basicity than the 4-dimethylaniline ring, that the 2-dimethylamino-5-furan ring is the most basic ring, and that the 2-dimethylamino-5-thiophene ring is the least basic ring, whereas the analogous ring of the selenophene occupies an intermediate position that is closer to the thiophene ring.

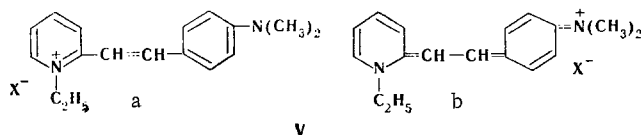
Our development [1] of a method for the preparation of heteroanalogs I, with furan, thiophene, and selenophene rings ($Y = O, S, Se$), of the diphenylmethane dye Michler's blue hydrol (I, $Y = CH=CH$) enables us to use the Kiprianov-Brooker "deviation" method [2, 3] to estimate the electronic symmetry of polymethine dyes containing such rings and, in addition, to find the position of the latter in the order of "basicities" of rings that form polymethine dyes [4].



$Y = O, S, Se, CH=CH$

For this purpose, we obtained unsymmetrical mono- and dimethine dyes V-XII by condensation of 2-dimethylamino-5-formylfuran (II), -thiophene (III), and -selenophen (IV) with various heterocycles with an active methyl or methylene group and also with dimethylaniline. The absorption maxima, the molar extinctions, and the deviations of these dyes, i.e., the hypsochromic shift of the absorption maxima of the unsymmetrical dye from the arithmetical mean of the maxima of the corresponding symmetrical dyes with absorption maxima and deviations of the analogous dyes with benzene rings, are compared in Table 1. The strongly basic 2-pyridine ring, the 2-quinoline and indolenine rings of medium basicity, and the least basic 4-dimethylaniline ring [4] were selected as rings R from the order of basicities. In the case of intraionoid dyes IX-XII rings R were selected in such a way that they differed markedly with respect to their "acidities" [5].

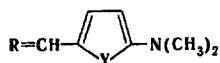
The structure of dye V ($Y = CH=CH$) is determined by the energies of boundary structures a and b, but structure a is predominant, inasmuch as the aromatic character of the pyridine and benzene rings is disrupted in structure b.



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TABLE 1. Spectral Characteristics of Dyes of the General Formula



| Dye | R | λ_{max} , nm ($\epsilon \cdot 10^{-4}$), deviation, nm | | | |
|------|---|---|--------------------|--------------------|--------------------------|
| | | Y=O | Y=S | Y=Se | Y=CH=CH |
| V | | 536 (5,3) 36,5 | 524 (5,4) 50,5 | 536 (5,6) 45 | 461 ⁴ 123 |
| VI | | 587 (11,0) 6,5 | 582 (9,5) 13,5 | 590 (10,7) 11,5 | 525 ⁴ 80 |
| VII | | 555 (13,1) 9 | 560 (14,8) 6 | 565 (15,2) 7,5 | 546 ⁴ 30 |
| VIII | | 530 (4,5) 65 | 558 (6,3) 39 | 558 (6,7) 45,5 | — |
| IX | | 529 (4,1) 28,5 | 520 (5,6) 39,5 | 531 (5,6) 35 | 466 ⁵ 103 |
| X | | 503 (5,0) 7 | 495 (4,9) 17 | | 467 ⁵ 54,5 |
| XI | | 520 (10,5) 1,5 | 511 (10,1) 12,5 | | 481 ⁵ 52 |
| XII | | 506 (11,0) 15 | 506 (12,5) 17 | | 490 ⁵ 42,5 |

The high electronic asymmetry of this dye is attested to by its large deviation. The replacement of the benzene ring in dye V by a thiophene ring, which has a lower resonance energy [6], leads to a drawing together of the weights of the boundary structures, i.e., to equalization of the electron density and to a decrease in the deviation. The furan ring, which has even lower resonance energy than the thiophene ring [6], causes a further decrease in the deviation. On the other hand, in combination with the least basic 4-dimethylaniline ring (dye VIII) the cation charge is located to a greater extent on the heterocyclic ring and is more symmetrical (less deviation) for the dye with the more aromatic (as compared with the furan ring) thiophene ring. Data on the resonance energy of the selenophene ring are unavailable, but, according to the assumptions in [7, 8], it should be close to the

TABLE 2. Absorption Maxima of Dyes IX and XII in Various Solvents

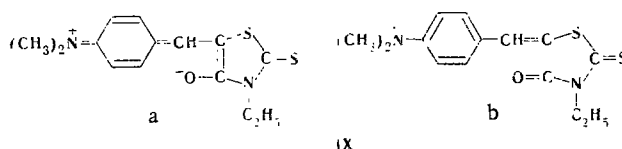
| Dye | λ_{max} , nm | | |
|---------------|----------------------|---------|---------|
| | methanol | acetone | benzene |
| IX (Y=O) | 528 | 521 | 513 |
| XII (Y=CH=CH) | 494 | 490 | 485 |
| XII (Y=O) | 501 | 503 | 508 |

resonance energy of thiophene, although, it seems to us, somewhat lower because of the decrease in the conjugation over the longer C-Se bonds as compared with C-S bonds. The deviations of dyes V and VIII with a selenophene ring confirm this - they lie between the deviations of dyes with furan and thiophene rings but closer to the latter.

The 2-dimethylamino-5-furan, -thiophene, and -selenophene rings can be arranged in the order of "basicities" of the rings that form the polymethine dyes with respect to the deviations of dyes VIII [4].

Whereas the deviations are large and differ from one another in dyes VI and VII (Y = CH=CH), dyes VI and VII (Y = O, S, Se) have deviations that are small and comparable with one another. In this case, in accordance with the "sensitivity rule" [3], the deviations do not change appreciably as the basicity of the rings changes in the case of high symmetry of the electron density distribution.

Nonpolar structure b predominates in intraionoid dye IX (Y = CH=CH) because of the disadvantageousness in structure a of the quinone ring and the charge separation; this is apparent from its large deviation.



The thiophene ring in dye IX (Y = S) draws the energies of structures a and b together and reduces the deviation, whereas the furan ring causes a further decrease in the deviation similar to what is observed for dyes V. As in the case of dyes V and VIII, the deviation of dye IX, which has a selenophene ring, is closer to the values of its thiophene analog.

Although transition to more "acidic" pyrazolone, indanedione, and thiobarbituric acid rings in dyes containing a benzene ring increases the symmetry of the electron density of the chromophore (and therefore reduces the deviation), the structure of dye XII (Y = CH=CH) is nevertheless closer to a nonpolar structure; this is evident from its positive solvatochromism [9] (Table 2). Replacement of the benzene ring by a furan ring brings about a situation in which the electron density is symmetrical in dye XI (Y = O), in which the deviation is insignificant, whereas in dye XII (Y = O), which has a greater deviation, a dipolar structure predominates (which is confirmed by its negative solvatochromism [9]), in contrast to dyes IX (Y = O) and XII (Y = CH=CH).

It should be noted that all of the dyes having furan, thiophene, and selenophene rings are more deeply colored than their benzene analogs, although symmetrical dyes I (Y = O, S, Se) are more highly colored [1] than dye I (Y = CH=CH) [4].

EXPERIMENTAL

Dyes V-VII and IX-XII. These dyes were obtained by heating α -picoline (dye V) and quinaldine (VI) ethiodides, 2,3,3-trimethylindolenine methylperchlorate (VII), N-ethylrhodanine (IX), 1-phenyl-3-methyl-5-pyrazolone (X), 1,3-indanedione (XI), and 1,3-diethyl-2-thiobarbituric acid (XII) with a three-fold excess of aldehydes II-IV at 120° for 30 min in the case of dyes VI, VII, and IX-XII and at 140° for 4 h in the case of V with the addition of a few drops of pyridine in order to reduce sublimation of the aldehydes. Dyes VI, VII, and IX-XII can be obtained in good yields by refluxing the components in acetic anhydride for 3 min.

TABLE 3. Analytical Characteristics of the Dyes Obtained

| Dye | Name | mp, °C | Empirical formula | Found, % | Calc., % | Yield, % |
|------------|---|--------|--|----------|----------|----------|
| V O | 2-[1-(5-Dimethylamino-2-furyl)-2-vinyl]-1-ethylpyridinium iodide | 233 a | C ₁₅ H ₁₉ IN ₂ O | I 34,3 | I 34,3 | 63 |
| V S | 2-[1-(5-Dimethylamino-2-thienyl)-2-vinyl]-1-ethylpyridinium iodide | 272 a | C ₁₅ H ₁₉ IN ₂ S | I 32,7 | I 32,8 | 41 |
| V Se | 2-[1-(5-Dimethylamino-2-selenienyl)-2-vinyl]-1-ethylpyridinium iodide | 269 a | C ₁₅ H ₁₉ IN ₂ Se | N 6,5 | N 6,5 | 49 |
| VI O | 2-[1-(5-Dimethylamino-2-furyl)-2-vinyl]-1-ethylquinolinium iodide | 221 a | C ₁₉ H ₂₁ IN ₂ O | I 30,1 | I 39,2 | 49 |
| VI S | 2-[1-(5-Dimethylamino-2-thienyl)-2-vinyl]-1-ethylquinolinium iodide | 249 a | C ₁₉ H ₂₁ IN ₂ S | I 29,1 | I 29,2 | 46 |
| VI Se | 2-[1-(5-Dimethylamino-2-selenienyl)-2-vinyl]-1-ethylquinolinium iodide | 250 a | C ₁₉ H ₂₁ IN ₂ Se | N 5,8 | N 5,8 | 33 |
| VII O | 2-[1-(5-Dimethylamino-2-furyl)-2-vinyl]-1,3,3-trimethyl-(3H)indolinium perchlorate | 244 b | C ₁₉ H ₂₃ ClN ₃ O ₅ | Cl 9,1 | Cl 9,0 | 61 |
| VII S | 2-[1-(5-Dimethylamino-2-thienyl)-2-vinyl]-1,3,3-trimethyl-(3H)indolinium perchlorate | 239 a | C ₁₉ H ₂₃ ClN ₃ O ₄ S | S 8,1 | S 7,8 | 78 |
| VII Se | 2-[1-(5-Dimethylamino-2-selenienyl)-2-vinyl]-1,3,3-trimethyl-(3H)indolinium perchlorate | 225 a | C ₁₉ H ₂₃ ClN ₃ O ₄ Se | Cl 7,8 | Cl 7,7 | 50 |
| VIII O | 4-(5-Dimethylamino-2-furfurylidenyl)-2,5-cyclohexadienyliden-1-yldimethylammonium iodide | 248 a | C ₁₅ H ₁₉ IN ₂ O | I 34,5 | I 34,3 | 30 |
| VIII S | 4-(5-Dimethylaminothienylyliden-2-yl)-2,5-cyclohexadienyliden-1-yldimethylammonium perchlorate | 224 a | C ₁₅ H ₁₉ ClN ₂ O ₄ S | S 9,1 | S 9,0 | 53 |
| VIII Se | 4-(5-Dimethylamino-2-selenienylmethyl)-2,5-cyclohexadienyliden-1-yldimethylammonium perchlorate | 226 a | C ₁₅ H ₁₉ ClN ₂ O ₄ Se | Cl 8,7 | Cl 8,7 | 46 |
| IX O | 5-(5-Dimethylaminofurfuryliden-2-yl)-3ethylrhodanine | 239 c | C ₁₂ H ₁₄ N ₂ O ₂ S ₂ | S 22,7 | S 22,7 | 92 |
| IX S | 5-(5-Dimethylaminothienylyliden-2-yl)-3-ethylrhodanine | 129 d | C ₁₂ H ₁₄ N ₂ OS ₃ | S 32,3 | S 32,2 | 65 |
| IX Se | 5-(5-Dimethylamino-2-selenienylmethyl)-3-ethylrhodanine | 123 e | C ₁₂ H ₁₄ N ₂ OS ₂ Se | N 7,8 | N 8,1 | 70 |
| X O | 4-(5-Dimethylaminofurfuryliden-2-yl)-3-methyl-1-phenyl-5-pyrazolone | 200 c | C ₁₇ H ₁₇ N ₃ O ₂ | N 14,3 | N 14,2 | 35 |
| X S | 4-(5-Dimethylaminothienylyliden-2-yl)-3-methyl-1-phenyl-5-pyrazolone | 119 f | C ₁₇ H ₁₇ N ₃ OS | S 10,4 | S 10,3 | 42 |
| XI O | 2-(5-Dimethylaminofurfuryliden-2-yl)-1,3-indanedione | 226 c | C ₁₆ H ₁₃ NO ₃ | N 5,3 | N 5,2 | 55 |
| XI S | 2-(5-Dimethylaminothienylyliden-2-yl)-1,3-indanedione | 229 e | C ₁₆ H ₁₃ NO ₂ S | S 11,3 | S 11,3 | 70 |
| XII O | 5-(5-Dimethylaminofurfuryliden-2-yl)-1,3-diethyl-2-thiobarbituric acid | 216 e | C ₁₅ H ₁₉ N ₃ O ₃ S | N 13,2 | N 13,1 | 48 |
| XII S | 5-(5-Dimethylaminothienylyliden-2-yl)-1,3-diethyl-2-thiobarbituric acid | 269 e | C ₁₅ H ₁₉ N ₃ O ₂ S ₂ | S 19,2 | S 19,0 | 90 |

a) From ethanol; b) from methanol; c) from benzene; d) from carbon tetrachloride-heptane (1:2); e) from xylene; f) from carbon tetrachloride.

Dyes VIII. A 1-mmole sample of phosphorus oxychloride was added dropwise at 20° to a solution of 1 mmole of aldehyde III or IV and 3 mmole of dimethylaniline in 1 ml of hydrogen chloride-free dry chloroform at 20° [in the case of dye VIII (Y = O), 1 mmole of aldehyde II, 10 mmole of dimethylaniline, 2 mmole of phosphorus oxychloride, and 1 ml of chloroform were subjected to reaction at 0°]. The resulting dyes were washed with ether and precipitated from ethanol solution by the addition of sodium iodide (Y = O) or sodium perchlorate (Y = S, Se). According to its absorption spectra in nitromethane and methylene chloride, dye VIII (Y = S) proved to be identical to the dye of the same structure obtained by the method in [10].

The names, melting points, analytical characteristics, and yields of the dyes are presented in Table 3.

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