at 170-180°C for 1 h. The reaction mixtures were then dissolved in benzene, and the solutions were washed successively with 10% alkali solution and water and dried over calcium chloride. The benzene solution was passed through a column filled with 90 g of Al_2O_3 (elution with benzene), the benzene was removed from the eluate by distillation, and the residue was recrystallized. The yields of the ketones are presented in Table 1. The reaction of 3-benzoyldibenzothiophene [3.6 g (0.0125 mole)] with benzoyl chloride [1.75 g (0.0125 mole)] was carried out similarly in the presence of 0.02 g of $FeCl_3$ or $ZnCl_2$, and the diketone was purified as described above.

3-Benzoyldibenzothiophene. This compound was purified by successive recrystallization from benzene—alcohol and glacial acetic acid and had mp 149°C, M^+ 288 (by mass spectrometry), and R_f 0.87. Found, %: C 78.9; H 4.2; S 11.0. $C_{19}H_{12}OS$. Calculated, %: C 79.1; H 4.2; S 11.1. IR spectrum: 1655 (C=O), 700-800 (C-S bonds), 957 (C=C bonds in a heterocyclic compound), and 829 cm^{-1} (1,2- and 1,2,4-substituted aromatic compounds).

3-(p-Chlorobenzoyl)dibenzothiophene. This compound was recrystallized from glacial acetic acid and had mp 118°C, M^+ 322 (by mass spectrometry), and R_f 0.51. IR spectrum: 1665 (C=O), 700-800 (C-S bonds), 950 (C=C bonds in a heterocyclic compound), and 822 cm^{-1} (1,2- and 1,2,4-substituted aromatic compounds). According to the data in [3], this compound has mp 114-116°C.

3,6-Dibenzoyldibenzothiophene. This compound was purified by successive recrystallization from benzene—alcohol and glacial acetic acid and had mp 172°C, M^+ 392 (by mass spectrometry), and R_f 0.13. Found, %: C 79.2; H 3.6; S 8.2. $C_{26}H_{16}O_2S$. Calculated, %: C 79.5; H 4.1; S 8.2. IR spectrum: 1657 (C=O), 700-800 (C-S bonds), 960 (C=C bonds in a heterocyclic compound), and 829 cm^{-1} (1,2- and 1,2,4-substituted aromatic compounds).

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CONVERSION OF 2-ACETAMIDO-1-THIOCHROMONE TO THE CORRESPONDING 4-CHLORO AND 4-AMINO DERIVATIVES

O. M. Glozman, L. A. Zhmurenko, and V. A. Zagorevskii

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2-Acetimido-4-chloro-2H-1-thiochromene, in which the chlorine atom is exchanged by hydroxy and amino groups, was synthesized by the action of phosphorus oxychloride on 2-acetamido-1-thiochromone. It was established on the basis of the IR, UV, PMR, and mass spectra that the product of the reaction of this compound with aniline has the 2-acetamido-1-thiochromene structure.

It has been previously established that 2-aminochromones [1], 2-aminothiochromones [2], and their N-acyl derivatives [2, 3] exist in the aminochromone tautomeric form and that the introduction of the strong electron-acceptor trichloroacetylene does not shift the equilibrium to favor the 4-hydroxycoumarin form, in contrast to some other systems with a smaller difference in the energies of the two tautomeric forms (for example, see [4]). In conformity with the general position regarding the dependence of tautomeric equilibria on the acidities of the tautomeric forms [5] it might have been expected that replacement of the oxygen atom of the pyrone carbonyl group by the more basic imino group would promote a shift of the equilibrium to favor the formation of the 2-imino-4-amino form.

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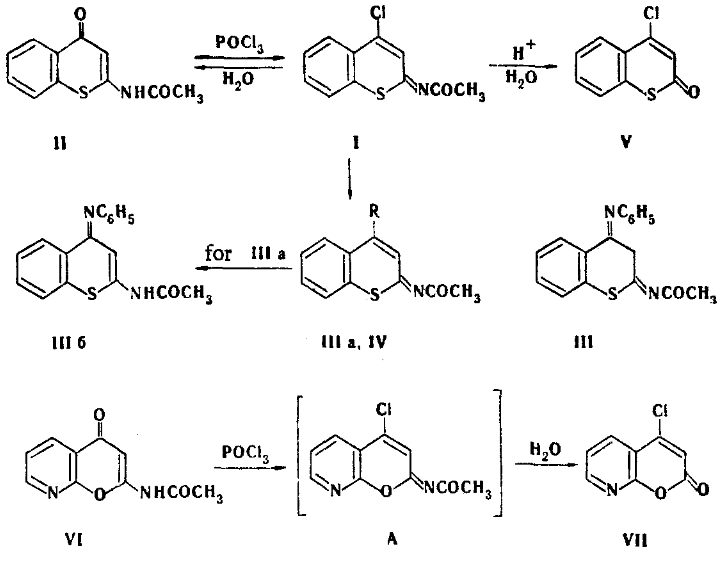

III a R=NHC$_6$H$_5$; IV R=NC$_5$H$_{10}$

To synthesize compounds with this structure we first obtained 2-acetimido-4-chloro-2H-1-thiochromene (I) by the action of phosphorus oxychloride on the known 2-acetamido-1-thiochromone (II) [2]. The chlorine atom in I, which is the cyclic vinylog of an imino acid chloride, is quite easily exchanged by a hydroxyl or amino group. In the first case starting II is formed, whereas in the second case 4-amino derivatives (III and IV) are formed. If hydrolysis is carried out by the addition of acid (protonation of the imine nitrogen atom), the reaction proceeds in a different direction with splitting out of an acetimido group to give the known 4-chloro-1-thiocoumarin (V) [6]. Consequently, I is appreciably more resistant to hydrolysis than the oxygen analogs (the products of hydrolysis of the latter cannot be isolated [7]) because of the more pronounced electrophilic effect of the sulfur atom directly bonded to the electrophilic center.

An attempt to obtain compound A (an analog of chloride I) by the action of phosphorus oxychloride on acetamido-4-oxo-4H-chromeno[2,3-b]pyridine (VI) was unsuccessful, since compound A was hydrolyzed to 2-oxo-4-chloro-2H-pyrano[2,3-b]pyridine (VII) upon subsequent treatment with water, regardless of the pH of the medium.

The structures of I and VII were confirmed by the PMR and mass-spectral data (see the experimental section). The fragmentation of VII, which is the aza analog of 4-chlorocoumarin [8], is identical to the fragmentation of the latter. The molecular ions of VII undergo fragmentation via two pathways: 1) successive elimination of two CO molecules and a Cl atom, and 2) vice versa, successive ejection of a Cl atom and two CO molecules. The fragmentation of I also proceeds via two pathways: 1) successive splitting out by the molecular ions of $CH_3^{\bullet}$, CO, $CN^{\bullet}$, and $Cl^{\bullet}$ particles and, 2) successive ejection of $Cl^{\bullet}$, $CH_3CO^{\bullet}$, and $CN^{\bullet}$ particles. Both paths lead to the same ion with m/e 133,* the subsequent fragmentation of which involves splitting out of a CS molecule. It is interesting to note the chloride V, in contrast to 4-chlorocoumarin, its aza analog VII, and I undergo fragmentation via the same pathway: successive ejection of CO, $Cl^{\bullet}$, and CS particles by the molecular ions.

Compound III in the condensed state and in solutions (in chloroform, DMSO, and alcohol) has primarily the IIIb form. The IR spectrum of tautomer IIIb in chloroform is characterized by NH stretching vibrations (3410-3440 cm^{-1}) and an increased frequency of the vibration (as in the case of II [2]) of the amide carbonyl group (1695-1705 cm^{-1}). The band at 1515 cm^{-1} (amide II), the intensity of which is comparable to the intensity of the carbonyl absorption, vanishes in the case of deuteration. The highest frequency in the IR spectrum of IV, which can be regarded as a model compound with respect to form IIIa, in the region of the vibrations of the double bonds is observed at 1618 cm^{-1}. The PMR spectrum (in d$_6$-DMSO) of IIIb contains a singlet of the 3-H proton with an intensity of one proton unit at 6.5 ppm; this excludes form IIIc (and constitutes evidence for homogeneity of the structure). It should be noted that splitting of the ν_{NH} band with the appearance of bands with different intensi-

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*Here and subsequently, the numbers that characterize the ion are the ratios of the mass to the charge.

ties at 3440 and 3410 cm^{-1} is observed in the IR spectrum of IIIb (in chloroform); this can be explained by the presence of nonequivalent conformations of the $NHCOCH_3$ grouping. The alternative explanation that the second band in the ν_{NH} region is the first overtone of the carbonyl absorption band [9] is unacceptable in this case, since both indicated bands vanish in the case of deuteration of IIIb.

The mass spectrometric study of the latter may provide additional information regarding the tautomeric structure of III. One's attention is drawn to the fact that the mass spectrum of III contains an ion at 279 corresponding to detachment of 15 amu (a CH_3 group)* from the molecular ion, as well as an ion with 251 corresponding to ejection of an acetyl group from the molecular ion; the ratios of the intensities of the ions $I_{[M-CH_3]^+}/I_{M^+}$ and $I_{[M-COCH_3]^+}/I_{M^+}$ are, respectively, 0.17 and 1.67. Under electron impact III simultaneously undergoes the fragmentation characteristic for acetamido derivatives II and VI (as in the case of 2-acylaminochromones): splitting out of an acetyl group is accompanied by migration of a hydrogen atom of the acetyl group to the NH group (the ratio of the intensities of the ion peaks $I_{[M-COCH_2]^+}/I_{M^+}$ is 0.63). One should next take into account the fact that the mass spectrum of I with a fixed acetamido grouping in the 2 position contains peaks of $M - CH_3^+$ (222) and $M - COCH_3^+$ (194) ions (the ratios of the intensities of the ion peaks $I_{[M-CH_3]^+}/I_{M^+}$ and $I_{[M-COCH_3]^+}/I_{M^+}$ are, respectively, 2.0 and 0.14) but does not contain the peak of an ion corresponding to splitting out of an acetyl group from M^+ with migration of a hydrogen atom. The detachment of methyl and acetyl groups in the fragmentation of III, which is not, by the way, observed in the mass spectra of II, VI, and 2-acetamidochromone [2, 10], can be explained by the existence of a certain amount of form IIIa (in addition to the IIIb form) in the gaseous state. A shift of the tautomeric equilibrium to favor the formation of the IIIa form probably occurs during vaporization of the compound into the ion source.

In conclusion, it must be stated that whereas 4-hydroxycoumarin and 4-hydroxythiocoumarin are energetically considerably more favorable than the 4H-chromene system, 2-aminochromone, 2-acylaminochromone, and their 1-thio analogs, and even 2-acylamino-4-phenylimino-1-thiochromene, are clearly more stable than the corresponding tautomeric forms with a 2H-chromene system.

EXPERIMENTAL

The UV spectra of alcohol solutions of the compounds were recorded with a Perkin–Elmer 402 spectrophotometer. The IR spectra of mineral oil suspensions, KBr pellets, and solutions of the compounds in DMSO, $CHCl_3$, or absolute alcohol were obtained with a Perkin–Elmer 457 spectrometer. The PMR spectra were recorded with a Varian T-60 spectrometer with HMDS as the standard (internal for solutions in $CHCl_3$, $CDCl_3$, and CF_3COOH and external for solutions in d_6-DMSO). The mass spectra were obtained with a Varian MAT-112 chromatographic mass spectrometer with a system for direct introduction of the samples into the ion source at 150°C, an ionizing voltage of 80 V, and an ionization-chamber temperature of 200°C. Aluminum oxide (alkaline form, activity II) was used for thin-layer chromatography (TLC) with benzene as the solvent.

2-Acetimido-4-chloro-2H-1-thiochromene (I). A mixture of 0.5 g (23 mmole) of II [2] in 20 ml of phosphorus oxychloride was heated to the boiling point and allowed to stand for 16 h, after which the small amount of precipitate was removed by filtration, and the filtrate was poured into a mixture of 70 g of sodium carbonate, 200 ml of water, and 100 g of ice. The mixture was neutralized to pH 7, and the resulting precipitate was removed by filtration and washed with water to give 0.4 g (74%) of I with mp 111-112°C (from heptane) and R_f 0.75. IR spectrum (in CCl_4): 1652 ($\nu_{C=O}$; 1642 in oil), 1593, and 1485 cm^{-1}. PMR spectrum (in CCl_4): 2.27 (s, CH_3), 7.16 (s, 3-H), and 7.30-8.33 ppm (C_6H_4). Mass spectrum, m/e (relative intensity in percent): 239 (19), 238 (7), 237 (51), 224 (39), 223 (14), 222 (100), 202 (7), 196 (3), 194 (6), 170 (28), 169 (9), 168 (70), 159 (52), 133 (12), 132 (9), 115 (9), 114 (14), 89 (19), 69 (33). Found, %: Cl 15.2; N 5.8; S 13.4. $C_{11}H_8ClNOS$. Calculated, %: Cl 14.9; N 5.9; S 13.4.

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*The assignment of the indicated fragment precisely to CH_3 in the fragmentation of III and I was proved by high-resolution mass spectroscopy. We sincerely thank A. B. Belikov for obtaining these data.

2-Oxo-4-chloro-2H-pyrano[2,3-b]pyridine (VII). This compound was obtained under similar conditions from 2.04 g (10 mmole) of VI [10]. The yield of product with mp 148-149°C (from benzene) and R_f 0.6 was 1.2 g (66%). IR spectrum (in $CHCl_3$): 1730 (C=O) and 1605 cm^{-1} (C=C). UV spectrum, λ_{max} (log ε): 262 (3.74), 272 (3.72), and 308 nm (4.03). PMR spectrum (in $CDCl_3$): 6.66 (s, 3-H), 7.47 (two d, J_1 = 10 Hz, J_2 = 6 Hz, 6-H), 8.34 (two d, J_1 = 8 Hz, J_2 = 2 Hz, 5-H), and 8.67 ppm (two d, J_1 = 7 Hz, J_2 = 2 Hz, 7-H). Mass spectrum, m/e (relative intensity in percent): 183 (35), 182 (13), 181 (100), 155 (21), 154 (8), 153 (65), 152 (7), 146 (16), 127 (7), 126 (6), 125 (25), 118 (87), 90 (35), 63 (57). Found, %: C 52.8; H 2.3; Cl 19.5; N 8.2. $C_8H_4ClNO_2$. Calculated, %: C 52.9; H 2.2; Cl 19.5; N 7.7.

Hydrolysis of 2-Acetimido-4-chloro-2H-1-thiochromene (I). A) An 0.3-g (1.3 mmole) sample of I was refluxed in 20 ml of 10% hydrochloric acid for 5 h, after which the precipitate was removed by filtration to give 0.2 g (81%) of chloride V with mp 98-99°C (from heptane) and R_f 0.65 (mp 92°C [6]). IR spectrum (in oil): 1635 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 264 (3.62), 294 (3.64), and 303 nm (3.63). Mass spectrum, m/e (relative intensity in percent): 198 (13), 197 (4), 196 (32), 170 (40), 169 (10), 168 (100), 133 (23), 132 (9), 106 (6), 93 (9), 89 (40).

B) Water (0.05 ml) was added to a solution of 0.1 g (0.42 mmole) of IV in 4 ml of DMSO, and the mixture was allowed to stand overnight. Water (2 ml) was added, and the precipitate was removed by filtration to give 0.07 g (76%) of II, which decomposed above 320°C (from alcohol) and had R_f 0.52. The properties of II were identical to those of a genuine sample [2] (with respect to the R_f values and the ability to dissolve in NaOH).

2-Acetamido-4-phenylimino-1-thiochromene (IIIb). An 0.49-g (5 mmole) sample of anhydrous aniline was added to a solution of 0.6 g (2.5 mmole) of I in 20 ml of absolute benzene, and the mixture was stirred for 2 h. The resulting precipitate was removed by filtration and washed with water to give 0.5 g (60%) of the hydrochloride of IIIb with mp 279-280°C (dec., from alcohol). IR spectrum (in oil): 1710 (C=O) and 1600 cm^{-1}. PMR spectrum (in CF_3COOH): 1.97 (s, CH_3), 6.72 (s, 3-H), 7.0-7.33 (C_6H_5), and 7.40-8.33 ppm (C_6H_4). Found, %: Cl 10.8; S 9.8. $C_{17}H_{15}ClN_2OS$. Calculated, %: Cl 10.7; S 9.7. The hydrochloride of IIIb was treated with aqueous sodium carbonate solution for a few hours, and the resulting precipitate was removed by filtration and washed with water to give base IIIb with mp 221-222°C (dec., from benzene) and R_f 0.41. IR spectrum (in KBr): 3203 (ν_{NH}), 1695 (amide I), 1612 and 1515 cm^{-1} (very intense band; probably amide II). IR spectrum (in $CHCl_3$): 3440 and 3410 (ν_{NH}), 1705 (amide I), 1603, 1585, 1551, and 1520 cm^{-1} (amide II). IR spectrum (in $CHCl_3 + D_2O$): 2540, 1692, 1608, 1590, 1551, 1496, and 1483 cm^{-1}. IR spectrum (in DMSO): 1695 (amide I), 1598, 1581, 1548, and 1515 cm^{-1}. IR spectrum (in absolute alcohol): 1685, 1575, and 1547 cm^{-1}. UV spectrum, λ_{max} (log ε): 275 (inflection, 4.27), 349 (4.20), and 364 nm (shoulder, 4.18). PMR spectrum (in d_6-DMSO): 2.0 (s, CH_3), 6.5 (s, 3-H), and 6.66-7.66 ppm (10H, NH and benzene ring protons). Mass spectrum, m/e (relative intensity in percent): 294 (60), 279 (10), 253 (12), 252 (38), 251 (100), 236 (8), 226 (6), 225 (24), 224 (23), 223 (44), 222 (15), 219 (9), 218 (10), 212 (6), 211 (6), 210 (15), 197 (8). Found, %: N 9.4; S 11.1. $C_{17}H_{14}N_2OS$. Calculated, %: N 9.5; S 10.9.

2-Acetimido-4-piperidino-2H-1-thiochromene (IV). A mixture of 0.60 g (2.5 mmole) of I, 0.42 g (5 mmole) of piperidine, and 20 ml of absolute benzene was refluxed for 4 h, after which it was cooled and filtered. The filtrate was evaporated, and the residue was treated with a mixture of petroleum ether and ether. Workup gave 0.60 g (83%) of IV with mp 130-131°C (from heptane) and R_f 0.72 (activity IV Al_2O_3, elution with chloroform). IR spectrum (in KBr): 1618, 1577, 1531, and 1465 cm^{-1}. UV spectrum, λ_{max} (log ε): 251 (4.13), 282 (4.82), and 387 nm (4.37). PMR spectrum (in $CDCl_3$): 1.70 (6H) and 3.12 (4H) (CH_2 groups of the piperidine ring), 2.33 (s, CH_3), 6.66 (s, 3-H), and 7.16-8.0 ppm (C_6H_4). Found, % : N 9.8; S 11.1. $C_{16}H_{18}N_2OS$. Calculated, %: N 9.8; S 11.2.

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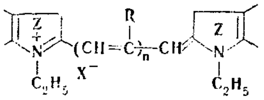
QUANTUM-CHEMICAL CALCULATIONS OF THE ELECTRONIC STRUCTURES OF POLYMETHYLIDYNE DYES

P. I. Abramenko and V. A. Kosobutskii UDC 547.749'829:541.67:668.819.45

The energies of the transitions of unsubstituted and substituted thia-, thiazolo-, and thienothiazolocarbocyanines, as well as quinocyanines and carbocyanines with a condensed thiophene, furan, selenophene, or pyridine ring, to the excited singlet states and their electronic structures were calculated by the MO LCAO method within the Pariser—Parr—Pople approximation. The nature of the long-wave and short-wave absorption bands in the spectra of these dyes and the peculiarities of the color of thieno-, furo-, and selenophenothiazolo- and -pyridocyanines, as well as the effect of substituents on their electronic characteristics as a function of the position in the heteroresidues and the nature of the latter, are discussed.

Polymethylidyne dyes are of interest as spectral sensitizers of motion picture photographic materials. Information regarding their electronic structures is extremely valuable for the interpretation and prediction of their various properties.



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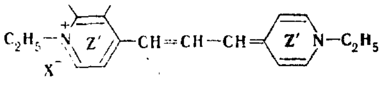

II

In the present research we investigated the electronic structures and colors of a number of cyanine dyes with structures I and II, in which Z is unsubstituted or substituted thiazolyl, benzothiazolyl, furo- and thieno[3,2-d]thiazolyl, benzoxazolyl, 3,3-dimethylindoleninyl, 1-ethylbenzimidazolyl, 2-pyridyl, 2-quinolyl, thieno-, selenopheno-, or furo-[2,3-b]-6-pyridyl, Z' is 4-pyridyl, 4-quinolyl, 5-vinyl-4-pyridyl, thieno-, furo-, or selenopheno[2,3-b]-4-pyridyl, n = 0–3, R = H, CN, or $N(C_2H_5)_2$, and X^- is an acid residue.

The calculations were made by the Pariser—Parr—Pople method with the program described in [1]. The $\gamma_{\mu\nu}$ integrals were calculated from the Mataga—Nishimoto formula [2]. The $\beta_{\mu\nu}$ resonance integrals were calculated with the "variable β" approximation [3, 4]. The principal parameters and the details of the calculation were presented in [5]. The parameters for nitrogen in the heteroresidues were determined from the tables of Hinze and Jaffe [6] by the Pariser—Parr procedure [7]. The constants for variation of $\beta_{\mu\nu}$ for the C-S bond and the W_μ and $\gamma_{\mu\mu}$ values for the sulfur atom were borrowed from [8]. At the beginning of the calculation, all of the rings were considered to be regular polygons with bond lengths of 1.40 Å. The C-C and C=C bond lengths were assumed to be 1.48 and 1.36 Å, respectively, and the valence angles were assumed to be 120°. However, during the calculation the geometrical characteristics were recalculated in conformity with the procedure proposed in [9]. The parameters for the N and O atoms in the NO_2 and OCH_3 groups, the C and N atoms in the CN

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