Anilide XIX was similarly obtained in 95% yield from XVIII.

α-(1-Imidazolyl)ethyl Furan-2-carboxylate (XX). A) A 13.8-g (0.1 mole) sample of I was added dropwise at 20-30° to a mixture of 6.8 g (0.1 mole) of IX and 0.83 g of pulverized potassium hydroxide in 50 ml of acetone, after which the mixture was stirred for 1 h and worked up to give 13.8 g (85.2%) of XX with mp 80-81° (heptane).

B) A mixture of 6.8 g (0.1 mole) of IX and 13.8 g (0.1 mole) of I was stirred at 20° for 3 h, after which it was allowed to stand overnight. Workup gave 11.1 g (53.3%) of XX with mp 80-81°. Esters XXI-XXIV were similarly obtained (see Table 1).

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RING – CHAIN TRANSFORMATIONS WITH PARTICIPATION OF THE C = N GROUP

IV.* QUANTITATIVE STUDY OF THE TAUTOMERISM OF 3-(m- or p-X-ARYLAMINO)-3-PHENYLPHTHALIDES

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UDC 547.588.21:543.422.6

The ring–chain tautomeric equilibrium constants (K) of aryl-ring-substituted 3-arylamino-3-phenylphthalides in dioxane were measured by UV spectroscopy. A satisfactory linear correlation between log K/K_0 and the σ^+ constants of the substituents in the aryl ring was found.

It has been shown [2] that the tautomeric equilibrium I$\rightleftharpoons$II is observed in solutions of 3-arylamino-3-phenylphthalides (II).

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*See [1] for communication III.

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TABLE 1. Ring-Chain Tautomeric Equilibrium Constants (K = [II]/[I]) in Dioxane Solutions of 3-Arylamino-3-phenylphthalides

Compound	X	I⇄II		III		K	lg K/K_0	σ [3]	σ⁺ [4]
		λ, nm	ε	λ, nm	ε				
a	4-OCH_3	348	1119	348	4122	2,69±0,20	−0,250	−0,268	−0,778
b	4-CH_3	334	615	328	2974	3,83±0,27	−0,096	−0,170	−0,311
c	3-CH_3	326	389	325	2417	5,21±0,37	−0,037	−0,069	−0,066
d	H	324	405	322	2345	4,78±0,34	0	0	0
e	4-I	332	667	334	3787	4,67±0,36	−0,010	0,18	0,135
f	4-$COOC_2H_5$	332	445	324	3959	7,94±0,49	0,220	0.45	0,482
g	4-$COCH_3$	330	446	328	4750	9,61±0,63	0,303	0,502	—

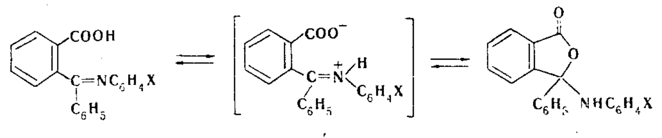
TABLE 2. 3-Arylamino-3-phenylphthalides (IIc, f, g) and Substituted o-Carbomethoxybenzophenone Anils (IIIa-c, e-g)

Compound	X	mp, °C*	Empirical formula	Found, %			Calc., %			IR spectra of dioxane solutions, ν, cm⁻¹			
										C=O		C=N	
				C	H	N	C	H	N	ν	ε	ν	ε
IIc	3-CH_3	201—202	$C_{21}H_{17}NO_2$	80,0	5,3	4,4	80,0	5,4	4,4	1772 1727	690 130		
IIf	4-$COOC_2H_5$	182—183	$C_{23}H_{19}NO_4$	74,7	5,1	3,8	74,0	5,1	3,8	1779 1718	660 585		
IIg	4-$COCH_3$	201—202	$C_{22}H_{17}NO_3$	76,8	4,9	4,0	77,0	5,0	4,1	1778 1729 1684	710 80 470		
IIIa	4-OCH_3	133—134	$C_{22}H_{19}NO_3$	76,4	5,7	4,3	76,5	5,6	4,1	1730	545	1620	170
IIIb	4-CH_3	106—107	$C_{22}H_{19}NO_2$	80,3	5,7	4,3	80,2	5,8	4,3	1729	525	1625	165
IIIc	3-CH_3	91—93	$C_{22}H_{19}NO_2$	80,5	5,8	4,6	80,2	5,8	4,3	1732	540	1626	185
IIIe	4-I	112—113	$C_{21}H_{16}INO_2$	I —29,0		3,2	I —28,8		3,2	1727	550	1626	195
IIIf	4-$COOC_2H_5$	106—108	$C_{24}H_{21}NO_4$	74,9	5,6	3,6	74,4	5,5	3,6	1728	735	1630	160
IIIg	4-$COCH_3$	167—168	$C_{23}H_{19}NO_3$	78,4	5,3	3,9	77,3	5,4	3,9	1734 1687	560 475	1632	165

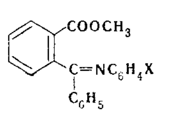
*The following crystallization solvents were used: acetic acid for IIb, 50% ethanol for IIf, ethanol for IIg, and cyclohexane for IIIa-c, e-g.

In the present research we set out to give a quantitative evaluation of the effect of substituents in the aryl ring on the state of this equilibrium.

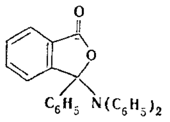
We used UV spectroscopy for the quantitative measurement of the equilibrium constants (K = [II]/[I]). A long-wave absorption band in the UV spectra of model compounds with fixed open structures – o-carbomethoxy-benzophenone anils (IIIa-g) – is observed at 322-348 nm. A model compound with a fixed chain structure – 3-(N,N-diphenylamino)-3-phenylphthalide (IV) – does not absorb at ~320 nm. Having assumed that the intensities of the long-wave band in the spectra of tautomeric form I and the corresponding model compound III, in which the hydrogen of the carboxyl group is replaced by a methyl group, are equal, we calculated the equilibrium constants from the molar extinction coefficients (Table 1).



I I′ II



III



IV

I, II, III a X=OCH_3; b X=4-CH_3; c X=3-CH_3; d X=H; e X=4-I; f X=4-$COOC_2H_5$; g X=4-$COCH_3$

It was established that the intensity of the long-wave band in the spectra of solutions II and III in dioxane does not change when the solutions are allowed to stand at room temperature for 3 days. Ethanol proved to be unsuitable as a solvent for these measurements, inasmuch as slow solvolysis is realized when solutions of 3-arylamino-3-phenylphthalides in ethanol are allowed to stand at room temperature for 24 h, and the intensity of the long-wave band decreases gradually in 24 h.

The measured tautomeric equilibrium constants correlate approximately with the σ constants of substituents X ($\log K/K_0 = 0.58\sigma$; r = 0.94, and s = 0.20. A better correlation is observed with the electrophilic substituent constants [4] ($\log K/K_0 = 0.35\sigma^+$; r = 0.97, and s = 0.07). A similar phenomenon was observed [5] in the correlation of the constants of the ring–chain tautomeric equilibrium 2-aryl-4,4-dimethyloxazolidines $\rightleftharpoons$ Schiff basis with the σ and σ^+ constants of the substituents in the aryl ring.

This is evidently explained by the fact that the equilibrium I $\rightleftharpoons$ II is realized through ionic structure I', in which the electron-donor substituents are in direct polar conjugation with the nitrogen atom bearing an integral positive charge.

The ring–chain tautomeric equilibrium constants are two orders of magnitude higher for 2-benzoylbenzoic acid anils than for 2-benzoylbenzoic acid itself (K = 0.033 [6] and K = 0.07 [7], determined by IR spectroscopy of dioxane solutions). This is due to the fact that, despite the lower reactivity of the C =NAr group as compared with the keto group, the high basicity of the nitrogen atom makes it possible to easily form a $C=\overset{+}{N}HAr$ group, the carbon atom of which has greater electrophilicity [8].

EXPERIMENTAL

The UV spectra of solutions of the compounds (10^{-4} M) were recorded with a Specord UV-Vis spectrophotometer. Prior to recording of the spectra, the solutions were maintained at 20° in a thermostat for 3 h. The IR spectra of dioxane solutions of the compounds ($5 \cdot 10^{-2}$ M, l = 0.011 cm) were recorded with an IKS-14A spectrometer. The errors in the equilibrium constants were calculated with allowance for the systematic errors in the measurement of the optical densities and the preparation of solutions of given concentrations.

Compounds IIa, b, d, e, IId, and IV were characterized in [2]; the remaining compounds (IIc, f, g, and IIIa-c, e-g) were obtained for the first time via previously described methods [2], and their characteristics are presented in Table 2.

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