extract is dried over magnesium sulfate. The precipitate is filtered, and chloroform is distilled. Yield 77%, mp 79-80°C, IR spectrum: 1685 (C=O), 1620 cm^{-1} (C=N). PMR spectrum (CF_3COOH): 2.57 (3H, s, SCH_3); 3.57 ppm (3H, s, N_3CH_3).

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ELECTRONIC SPECTRA OF asym-TRIAZINYL GROUPS

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The induction, resonance, and Hammett constants of 3-, 5-, and 6-asym-triazinyl groups were calculated from the data of ^1H, ^{13}C, ^{19}F NMR spectra of isomeric aminophenyl-, hydroxyphenyl-, phenyl-, and fluorophenyl-asym-triazines.

Successive replacement of one, two, and more methine fragments in the benzene ring by a nitrogen atom leads to increase in the π-deficiency of the aromatic system in the series benzene, pyridine, diazines, triazines [1] and, as a result, to an increase in the electron-acceptor properties of the corresponding azinyl groups. The description of the electronic effects of different azinyl groups as substituents in the form of a given set of σ-constants may serve as a basis for establishing quantitative regularities with respect to the influence of aza-substitution on the induction and resonance characteristics of the above groups. In this regard it is of interest to examine the electronic effects of asym-triazinyl groups, in which three types of interactions of the heteroatoms in the six-membered ring are manifested simultaneously: 1, 2- as in pyridazine, 1,3- as in pyrimidine, and 1,4- as in pyrazine. However, no data are available in the literature, quantitatively characterizing the electronic effects of these groups.

The present work deals with the determination of σ-constants of 3-, 5-, and 6-asym-triazinyl groups (as-Tr) using the NMR method. For this purpose, we synthesized aryl-asym-triazines with phenyl- m-, and p-aminophenyl groups in the 3, 5, or 6-positions of the triazine ring, and also with m- and p-hydroxyphenyl and -fluorophenyl groups at the 3-position of the triazone ring (scheme), and recorded the ^1H, ^{13}C, ^{19}F NMR spectra in DMSO, selected as a standard solvent.

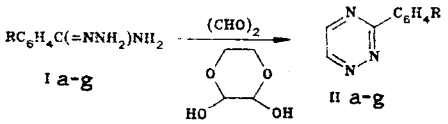

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TABLE 1. Characteristics of Aryl-asym-triazines

Compound	T_{mp}, deg C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
IIa	50—53 (52—55 [2])								
IIb	86—86,5	61,9	3,3	24,2	$C_9H_6FN_3$	61,7	3,4	24,0	10
IIc	106—107,5 (102—106 [2])								
IId	180—182	62,7	4,2	24,1	$C_9H_7N_3O$	62,4	4,1	24,3	27
IIe	236—238	62,7	4,0	24,3					66
IIf	106—107	53,3	2,9	27,8	$C_9H_6N_4O_2$	53,5	3,0	27,7	67
IIg*	176—178	53,2	3,1	27,6					70
IIh	131—133	62,9	4,9	32,3	$C_9H_8N_4$	62,8	4,7	32,5	38
IIi	198,5—199	62,7	4,7	32,3					62
IVa	100—102 (102 [3])								
IVf	142—144	53,3	3,1	27,8	$C_9H_6N_4O_2$	53,5	3,0	27,7	21
IVg	173—175	53,5	3,0	27,8					29
IVh	138—140	62,9	4,8	32,7	$C_9H_8N_4$	62,8	4,7	32,5	76
IVi	189—190	62,6	4,5	32,6					82
Va	83—85 (85 [3])								
Vf	135—137	53,4	3,1	27,6	$C_9H_6N_4O_2$	53,5	3,0	27,7	4
Vh	143—145	62,6	4,8	32,4	$C_9H_8N_4$	62,8	4,7	32,5	40
Vi	188—190	62,7	4,7	32,3					34

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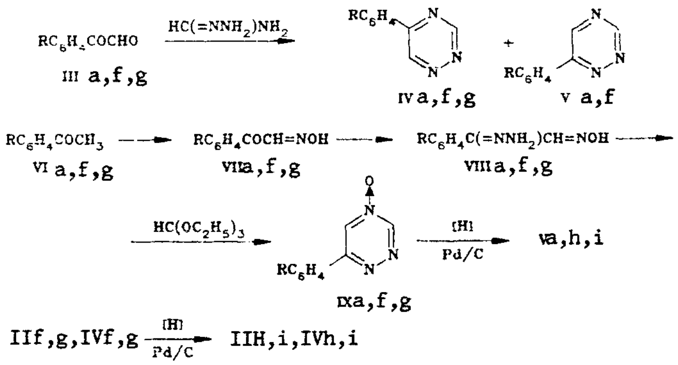
*In [4], compound IIg was used as the starting material, but its physical constants are not given.



I—IX ^{a} R=H, ^{b} R=m-F, c R=p-F, d R=m-OH, e R=p-OH, f R=m-NO_2, g R=p-NO_2, h R=m-NH_2, i R=p-NH_2

For the synthesis of 3-aryltriazines, the reaction of the corresponding substituted benzamidrazones with aqueous solution of glyoxal bisulfite derivative is usually used [2], but the yields of the products are not always reproducible. In this reaction, we obtained phenyl-, fluorophenyl-, and m-hydroxyphenyltriazines (IIa-d) in low yields, while p-hydroxyphenylhydrazine (IIe) and p-nitrophenylhydrazine (IIg) were isolated in trace amounts only. Using 2,3-dihydroxy-1,4-dioxane in an nonaqueous medium instead of glyoxal, we were able to obtain m-hydroxyphenyltriazine (IId) in satisfactory yield, and its p-isomer IIe and the two nitro derivatives IIf, g — in fair yields.

5-Nitrophenyltriazines (IVf, g) were synthesized from the corresponding arylglyoxals IIIf, g and formamidrazone under the conditions which were previously used [3] in the preparation of 5-phenyltriazine (IVa), and under which a small amount of 6-phenyltriazine (Va) is also formed. However, only in the case of m-nitrophenyl derivative were we able to isolate 6-(m-nitrophenyl)triazine (Vf) as a by-product together with the substituted derivative IVf.

For the preparative synthesis of 6-aryltriazines Va, h, i, we used the previously proposed [4] path consisting in successive introduction of an oximino group (isonitrosoketones VIIa, f, g) into the side chain of acetophenones VIa, f, g, leading to isonitrosoketone hydrazones (VIIIa, f, g) their reaction with orthoformic ester to form 6-aryltriazine N-oxides (IXa, f, g), and deoxygenation of the latter. In the case of nitrophenyl derivatives IXf, g, the deoxygenation under the catalytic hydrogenation conditions led directly to 6-aminophenyltriazines Vh, i. Under the same conditions, 3- and 5-nitrophenyl derivatives IIf, g and IVf, g

TABLE 2. Data of ^1H and ^{19}F NMR Spectra of Aryl-asym-triazines

Compound	Chemical shift, δ, ppm, multiplicity[1*]						Δδ[2*]	Δδ'[3*]	Δδ[4*]
	3-H	5-H	6-H,	Ar	NH_2 (OH)	F	NH_2 (OH)	NH_2 (OH)	F
IIa		8,92 d	9,40	7,44—7,70 m; 8,36—8,52 m					
IIb		8,98 d	9,46	7,66—8,43 m.		−50,51			−0,85
IIc		8,93 d	9,40	7,39 t; 8,49 dd		−53,76			−4,10
IId		8,89 d	9,36	6,90—7,53 m 7,81—8,00 m	(9,72)		(−0,49)	(−0,46)	
IIe		8,80 d	9,27	6,96 d; 8,32 d	(10,11)		(−0,88)	(−0,86)	
IIf		8,97 d	9,46	7,69—9,06 m					
IIg		9,01 d	9,47	8,40 d; 8,62 d					
IIh		8,89 d	9,37	6,72—9,06 m	5,33		−0,43	−0,40	
IIi		8,72 d	9,15	6,72 d; 8,19 d	5,84		−0,94	−0,92	
IVa	10,09d		9,77	7,47—7,76 m; 8,22—8,45 m					
IVf	10,26d		9,89	7,72—9,06 m					
IVg	10,20d		9,87	8,30—8,68 m					
IVh	9,96d		9,75	6,77—7,63 m	5,46		−0,56	−0,53	
IVi	9,81d		9,43	6,72 d; 8,07 d	6,10		−1,20	−1,18	
Va	9,80d	9,43		7,57—7,88 m; 8,14—8,40 m					
Vf	9,90	9,60		7,75—9,08 m					
Vh	9,74	9,28		6,71—7,57 m	5,38		−0,48	−0,45	
Vi	9,50	9,18		6,74 d; 7,93 d	5,84		−0,94	−0,92	

[1*] SSCC in triazine ring: $^5J_{36} = 2$, $^3J_{56} = 2.5$ Hz; in p-disubstituted benzene ring J = 8.5-9 Hz.

[2*] For compounds IId, e, relative to a signal of phenol in DMSO (9.23 ppm).

[3*] Taking into account an anisotropic correction for IIh, i, IVh, i, Vh, i, relative to a signal of aniline in DMSO (4.90 ppm).

[4*] Relative to a signal of fluorobenzene in DMSO (−49.66 ppm), the negative values correspond to a shift to weak field.

TABLE 3. Data of ^{13}C NMR Spectra of Phenyl-asym-triazines (in DMSO)

Compound	Chemical shift, δ, ppm							Δδ, ppm*		Δδ', ppm**	
	$C_{(3)}$	$C_{(5)}$	$C_{(6)}$	C_i	C_o	C_m	C_p	C_m	C_p	C_m	C_p
IIa	162,96	149,69	148,56	134,69	127,63	128,92	131,62	0,51	3,21	0,38	3,13
IVa	157,02	154,49	147,15	133,02	127,57	129,24	132,48	0,83	4,07	0,70	3,99
Va	156,05	147,42	161,34	133,07	126,87	129,14	130,86	0,73	2,45	0,60	2,37

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*Relative to a signal of benzene in DMSO (128.41 ppm).

**Taking into account the magnetic anisotropy of the triazine ring.

were reduced to aminophenyl derivatives IIh, i and IVh, i. The characteristics of the aryltriazines obtained are given in Tables 1-3.

The signals in the PMR spectra (Table 2) were assigned according to the data in [5] for an unsubstituted asym-triazine and its 5-phenyl-derivative in DMSO-D_6. The signals in the ^{13}C NMR spectra of phenyltriazines IIa, IVa, Va (Table 3) were assigned to the phenyl group and triazine ring carbon atoms based on spectral data for the same compounds in $CDCl_3$ [6].

The σ_I and σ_R^0 constants of the triazinyl groups were calculated according to correlational equations [7] based on chemical shifts (S) of m- and p-carbon atoms of phenyl groups in the ^{13}C NMR spectra of compounds IIa, IVa, Va. Into the experimental values of the CS, corrections were introduced for the magnetic anisotropy of the triazine ring: for C_m 0.13, for C_p 0.08 ppm. These corrections were calculated on the basis of the previously made evaluation of the effect of magnetic anisotropy of the aromatic ring of the phenyl group [8], taking into account the data in [9] on the anisotropy of the diamagnetic susceptibility of six-membered nitrogen heterocycles.

TABLE 4. σ-Constants of asym-Triazinyl Groups

Constant	Triazinyl group			Method of determination
	3-*as*-Tr	5-*as*-Tr	6-*as*-Tr	
σ_I	0,15	0,21	0,21	NMR ^1H $RC_6H_4NH_2$
	0,15			NMR ^1H RC_6H_4OH
	0,17	0,28	0,23	NMR ^{13}C RC_6H_5
	0,20			NMR ^{19}F RC_6H_4F
Mean	0,17±0,02	0,24±0,04	0,22±0,01	
$\sigma_R{}^0$	0,12	0,13	0,07	NMR ^{13}C RC_6H_5
	0,11			NMR ^{19}F RC_6H_4F
Mean	0,12±0,01			
σ_R	0,56	0,69	0,50	NMR ^1H $RC_6H_4NH_2$
	0,53			NMR ^1H RC_6H_4OH
Mean	0,55±0,02			
σ_m	0,35	0,48	0,39	
σ_p	0,72	0,94	0,72	

The resonance constants σ_R of the triazinyl groups were calculated together with the induction constants σ_I from the chemical shifts of the amino group protons [10] of the isomeric aminophenyltriazines IIh, i, IVh, i, Vh, i, taking into account the corrections for the magnetic anisotropy of the triazine ring (for m-NH_2 0.03, for p-NH_2, 0.02 ppm). The calculation of the same constants for the 3-triazinyl group using the data of ^{19}F NMR spectra [11] of the isomeric 3-fluorophenyltriazines IIb, c and the PMR spectra [10] of the isomeric 3-hydroxyphenyltriazines IId, e gave values which correlated well with one another (Table 4), despite the differences in the NMR methods and several assumptions and corrections thereby introduced.

From the values of induction and resonance constants found, we can evaluate the σ_m and σ_p-Hammett's constants of triazinyl groups, analogously to those calculated for other azinyl groups [10, 12]. In general, all three asym-triazinyl groups exhibit considerable electron-acceptor properties, comparable with those of the sym-triazinyl group (for comparison, for the sym-triazinyl group $\sigma_m = 0.39$, σ_p 0.88 [12]). However, the electron-deficient nature of the triazine ring affects the induction (3-as-Tr < 6-as-Tr ≈ 5-as-Tr) and resonance (6-as-Tr < 3-as-Tr < 5-asTr) constants of the triazinyl groups in different ways.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra of the solutions in dry DMSO under argon (in a concentration of 0.5 mole/liter) were recorded on a Varian A 56/60 A spectrometer at frequencies of 60 and 56.4 MHz, respectively; a ^{13}C- DMSO satellite and C_6F_6 were used as internal standards. The ^{13}C NMR spectra were recorded in a pulse regime on a Bruker HX-90 spectrometer at the frequency of 22.63 MHz, using TMS as internal standard. DMSO-D_6 (5%) was added to stabilize the resonance conditions. Pulse width 15 μsec, lag between pulses 10 sec, scanning width 5000 Hz, number of scannings 500-700.

The compounds wre isolated from the mixtures by chromatography on a column with silica gel, brand L 100/160; the eluent is given in description of the synthesis.

3-Phenyl-, 3-(m-fluorophenyl)- and 3-(p-fluorophenyl)-asym-triazines (IIa-c) are obtained according to [2], and 5-phenyl-asym-triazine (IVa) according to [3]. Compounds IIa and IIb are purified by crystallization from hexane, IIc from isopropanol, and IVa from petroleum ether with addition of $CHCl_3$.

3-(m-Hydroxyphenyl)asym-triazine (IId). A 1.8-g portion (17.5 mmoles) of triethylamine and 12.5 g (47 mmoles) of glyxal bisulfite derivative are added to a solution of 3.3 g (17.5 mmoles) of m-hydroxybenzamidrazone hydrochloride (Id) in 20 ml of water. The mixture is heated on a boiling water bath for 10 min, then cooled, filtered, made alkaline to pH 8, and extracted several times by ether. The extract is dried, evaporated to dryness, and the residue is dried in vacuo. Yield, 0.83 g (27%), mp 174-178°C. For the analysis, the material is chromatographed on silica gel (eluent—ethyl acetate), and then crystallized from isopropanol and sublimed in vacuo.

3-(p-Hydroxyphenyl)asym-triazine (IIe). A 0.84-g (4.5 mmole) of p-hydroxybenzamidrazone hydrochloride (Ie) is added with stirring to a solution of 0.60 g (5 mmoles) of 2,3-dihydroxy-1,4-diozane in 15 ml of absolute ethanol. Then, a solution of 0.45 g (4.5 mmoles) of triethylamine in 5 ml of absolute ethanol is added dropwise, and the solution is allowed to stand for 3 days. The precipitate is separated, washed with ethanol, the filtrate is evaporated in vacuc and the residue is chromatographed on silica gel. The material is eluted with ethyl acetate, the eluate is evaporated, and the residue is sublimed in vacuo. Yield, 0.49 g (66%). For the analysis, the compound is crytallized from butanol.

3-Nitrophenyl-asym-triazines (IIf, IIg). A 1.8-g portion (10 mmoles) of nitrobenzamidrazone (If, Ig) is added with stirring to a solution of 1.3 g (11 moles) of 2,3-dihydroxy-1,4-dioxane in 15 ml of absolute ethanol. The mixture is stirred at 20°C for 3 h, and after cooling, the precipitate is separated and dried in vacuo. For the analysis, compound IIf is crystallized from isopropanol, IIg from butanol, and both were then sublimed in vacuo.

5-Nitrophenyl-asym-triazines (Vf, IVg). A 2.69-g portion (84 mmoles) of anhydrous hydrazine in 40 ml of methanol is added with stirring to a solution of 8.74 g (84 mmoles) of formamidine acetate in 160 ml of methanol, and after 5 min this mixture is added dropwise to a solution of 15.15 g (84 mmoles) of nitrophenylglyoxal (IIIf, IIIg) in 160 ml of methanol. Then 8.48 g (84 mmoles) of triethylamine are added, and the mixture is allowed to stand overnight. The reaction mixture is evaporated, and the residue is chromatographed on a column with silica gel, using a mixture of petroleum ether—$CHCl_3$—ethyl acetate (1:1:1) as eluent. First the reaction by-products are eluted, and then the main fraction. The eluate is evaporated, and the residue is crystallized from isopropanol and sublimed in vacuo.

6-Phenyl-asym-triazine (Va) is obtained according to [3], starting from acetophenone, but the deoxygenation of 6-phenyl-asym-triazine 4-oxide (IXa) is carried out with hydrogen in the presence of palladium on carbon, as described below for the nitro derivatives IXf and IVg. THe deoxygenation product is chromatographed on silica gel (using diethyl ether as eluent), crystallized from petroleum ether, and sublimed in vacuo.

p-Nitro-ω-isonitrosoacetophenone (VIIg). Dry HCl is passed through a suspension of 17 g (103 mmoles) of p-nitroacetophenone (VIg) in 150 ml of ether, and, simultaneously, 13.7 g (117 mmoles) of isoamyl nitrite is added dropwise, with continuous boiling of the ether. After the addition of isoamyl nitrite, HCl is passed for another 30 min, and the mixture is left to stand overnight. It is then extracted by a 10% NaOH solution (5 × 75 ml), and the alkaline extract is slowly poured into a mixture of 40 ml of concentrated HCl and 100 g of ice. The precipitate is separated, washed with water, dried and crystallized from $CHCl_3$. Yield, 8 g (50%), mp 138-140°C. According to the data in [13], mp. 140°C.

m-Nitro-ω-isonitrosoacetophenone (VIIf) is obtained in a similar way as the p-isomer VIIg, in a 45% yield. mp 134-136°C. Found: C 49.7; H 3.11; N 14.2%. $C_8H_6N_2O_4$. Calculated: C 49.5; H 3.12; N 14.4%.

p-Nitro-ω-isonitrosoacetophenone hydrazone (VIIIg). A 3-g portion (60 mmoles) of hydrazine hydrate is added to a solution of 6 g (30 mmoles) of compound VIIg in 120 ml of ethanol, and the mixture is allowed to stand at 20°C for 24 h. The compound is separated, the filtrate is diluted with water and an additional amount of the reaction product is isolated. The product is crystallized from ethanol. Yield, 5.04 g (80%), mp 183-185°C. Found: C 46.2; H 3.89; N 26.4%. $C_8H_8N_4O_3$. Calculated: C 46.2; H 3.87; N 26.9%.

m-Nitro-ω-isonitrosoacetophenone hydrazone (VIIIf) is obtained in a similar way as the p-isomer VIIIg, in an 83% yield, mp 166-167°C. Found: C 45.8; H 3.98, N 27.1%. $C_8H_8N_4O_3$. Calculated: C 46.2; H 3.87; N 26.9%.

6-(p-Nitrophenyl)-asym-triazine 4-oxide (IXg). A mixture of 4.44 g (20 mmoles) of compound VIIIg, 15 ml of orthoformic ester, and 0.05 g of p-toluenesulfonic acid is boiled for 7 h, and the precipitate is separated, washed with ether, and crystallized from DMFA. Yield, 3.88 g (89%), mp 253-254°C. Found: C 49.3; H 2.81; N 25.4%. $C_9H_6H_4O_3$. Calculated: C 49.5; H 2.77; N 25.7%.

6-(m-Nitrophenyl-asym-triazine 4-oxide (IXf) is obtained in a similar way as the p-isomer IXg, in an 89% yield, mp 196-198°C. Found: C 49.6; H 2.65; N 25.6%. $C_9H_6N_4O_3$. Calculated: C 49.5; H 2.77; N 25.7%.

Aminophenyl-asym-triazines (IIh, i, IVh, i, Vh, i). A suspension of 5 moles of the nitrophenyl derivative IIf, g, IVf, g, IXf, g in 50 ml of absolute ethanol is hydrogenated in the presence of 0.15-0.20 g of 10% palladium on carbon. To complete the hydrogenation, the temperature of the reaction is raised to 40°C. The catalyst is filtered, washed with hot ethanol, and the filtrate is evaporated to dryness. The 3-aminophenyl derivatives IIh, i are purified by chromatography on silica gel (for IIh eluent $CHCl_3$, for IIi – ethyl acetate), and by sublimation in vacuo of 0.01 mm. 5-Aminophenylhydrazines IVh and IVi are purified by repeated sublimation in vacuo of 0.01 mm. 6-Aminophenyltriazines Vh and Vi are crystallized from acetonitrile and are sublimed in vacuo of 0.01 mm.

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