(21%) of VII with mp 176-177°C and R_f 0.67. Found: Cl 23.47; N 9.2%. $C_{15}H_{10}Cl_2N_2O$. Calculated: Cl 23.25; N 9.18%. IR spectrum: 1640 (C=N), 1690 (C=O), and 3100-3260 cm^{-1} (N–H). PMR spectrum: 5.98 (1H, s, 3-H) and 6.94-7.98 ppm (8H, m, aromatic protons).

B) A 0.7-g (2 mmole) sample of diazepinone V was chlorinated with 0.26 g (2 mmole) of NCS in 20 ml of carbon tetrachloride for 5 h. Workup gave 0.24 g (39%) of diazepinone VII with mp 176-177°C. No melting-point depression was observed for a mixture of this compound with the substance obtained in experiment A.

3,8-Dichloro-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (VIII). A solution of 0.67 g (5 mmole) of sulfuryl chloride in 5 ml of acetic acid was added dropwise to a mixture of 1.18 g (5 mmole) of diazepinone I and 0.51 g of aluminum chloride in 15 ml of acetic acid, and the mixture was stirred for 3 h. Workup gave 0.2 g (13%) of yellow chlorodiazepinone VII with mp 166-167°C and R_f 0.67. The filtrate was poured into ice water and worked up by chromatography with a column filled with silica gel to give 0.35 g (23%) of VIII with mp 190-191°C (from CCl_4) and R_f 0.72. Found: Cl 23.18; N 9.16%. $C_{15}H_{10}Cl_2N_2O$. Calculated: Cl 23.23; N 9.18%. IR spectrum: 1640 (C=N) and 3160-3280 cm^{-1} (N–H). PMR spectrum: 4.89 (1H, s, 3-H) and 6.89-7.95 ppm (7H, m, aromatic protons). Compound VIII was obtained by chlorination of 0.2 g (1.5 mmole) of 8-chloro-4-phenyl-2,3-dihydro-1,5-benzodiazepinone [5] with an equimolar amount of NCS in 15 ml of carbon tetrachloride by the method described above. Workup gave 0.15 g (33%) of diazepinone VII with mp 190°C and R_f 0.72.

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EFFECT OF SUBSTITUENTS ON THE CHEMICAL SHIFT OF THE RING PROTONS IN THE PMR SPECTRA OF MONOSUBSTITUTED sym-TRIAZINES

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UDC 543.422.25:547.87:541.67

A correlation equation that links the relative chemical shift of the protons of the triazine ring with the F and R constants of the substituents was obtained on the basis of data from the PMR spectra of solutions of sym-triazine and its monosubstituted derivatives [OCH_3, $N(CH_3)_2$, CH_3, C_6H_5, $COOC_2H_5$, and CN] in dimethyl sulfoxide (DMSO). The equation was analyzed by comparison with the corresponding equations for monosubstituted benzenes and pyrimidines.

Appreciable weakening of the inductive effect of substituents on the relative chemical shift of the ring protons adjacent to the nitrogen atom of the pyrimidine ring was previously noted [1, 2] during a study of the conductivity of electronic effects of substituents in the pyrimidine ring by PMR spectroscopy. To ascertain the common character of this effect we studied the dependence of the chemical shift of the protons of the sym-triazine ring on the electronic effects of the substituents in the PMR spectra of monosubstituted triazines in dimethyl sulfoxide (DMSO). We selected only monosubstituted derivatives as subjects of the investigation and

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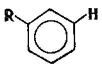
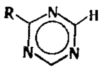
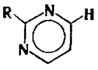
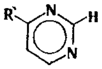
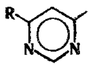
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 410-414, March, 1982. Original article submitted June 29, 1981.

0009-3122/82/1803-0310$07.50

TABLE 1. Chemical Shifts (Hz) of the Protons of the Triazine Ring in the PMR Spectra of Monosubstituted sym-Triazines at 60 MHz

Substituent	Solvent					
	CCl$_4$			DMSO		
	δ	Δδ	Δδ′	δ	Δδ	Δδ′
$N(CH_3)_2$	501	47	44	511	48	45
OCH_3	527,5	20,5	17,5	539,5	19,5	16,5
CH_3	537,5	10,5	7,5	550,5	8,5	5,5
C_6H_5	548	0	3	560	−1	2
H	548	0	0	559	0	0
$COOC_2H_5$	561	−13	−17	573,5	−14,5	−18,5
CN	561	−13	−19	576	−17	−23

TABLE 2. Conductivity of the Effects of Substituents in Six-Membered Aromatic Systems

Series	 1	 2	 3	 4	 5
γ_I	1,00	0,88	0,79	0,60	1,14
γ_R	1,00	3,18	2,00	2,98	2,92

excluded disubstituted triazines from consideration because of the fact that, according to the available data [3], the effect of substituents on the relative chemical shift of the protons of the triazine ring is not always additive, particularly when two electron-donor substituents such as diethylamino groups are present in the ring.

The series of monosubstituted sym-triazines described in the literature is limited and includes, as a rule, compounds with electron-donor substituents [$N(CH_3)_2$, OCH_3, and CH_3]. Our synthesis of previously unknown ethoxycarbonyl and cyano derivatives of triazine made it possible to not only substantially expand the scale of changes in the chemical shifts of the protons of the triazine ring (up to 1 ppm) but also to more adequately describe their dependence on the inductive and conjugation effects of the substituents.

To synthesize ethoxycarbonyl-sym-triazine we used the known method for the introduction of a substituent in the triazine ring by the reaction of triazine with the corresponding C-substituted formamidine. The disadvantage of this method, viz., the formation of side disubstitution products, did not introduce appreciable complications in the isolation of the monoethoxycarbonyl derivative, although it did lead to a decrease in the yield to 40%. By subsequent reaction with ammonia the product was converted to the carbamoyl derivative, which was subsequently converted to cyano-sym-triazine by the action of trifluoroacetic anhydride in the presence of pyridine. The cyanotriazine, which was isolated in only 17% yield, is unstable and darkens even when it is allowed to stand in an argon atmosphere in the dark. The structures of the synthesized triazine derivatives were confirmed by data from the vibrational spectra. The stretching vibrations of the $C\equiv N$ group, in particular, appear in the IR spectrum of the cyanotriazine in the form of a weak-intensity band at 2260 cm^{-1}, which was identified distinctly from the Raman spectrum.

To record the PMR spectra we used solutions of the compounds in DMSO and CCl_4 (Table 1). It is apparent from the data presented in Table 1 that for derivatives with electron-donor substituents the relative chemical shifts of the aromatic protons (Δδ) are virtually identical in both solvents and differ reliably only for the derivative with a strongly electron-acceptor group such as $C\equiv N$. The difference between triazine and aromatic systems of the carbocyclic series is displayed in the low sensitivity of the relative chemical shifts to the solvation effects of aprotic solvents (comparative data for substituted benzene rings are presented in [4]).

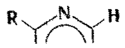
The specific features of azine systems in the conductivity of the electronic effects of substituents are displayed most distinctly when one compares the relative chemical shifts of the meta-aromatic protons found for the same derivatives of the benzene and triazine series in the same solvent (or in solvents with similar natures and solvation effects). Thus the relative shifts are very close for ethoxycarbonyltriazine and cyanotriazine in DMSO (Table 1) and for the same derivatives of the benzene series in dimethylacetamide (DMA) (12.4 and 17 Hz, respectively [5]). However, the relative shifts for methoxy derivatives of triazine (19.5 Hz) and benzene (4.3 Hz [5]) differ appreciably. This difference is even greater for dimethylamino derivatives of triazine

(48 Hz) and benzene (12.9 Hz [5]), which indicates significant intensification of the mesomorphic effect of the substituents in the triazine ring as compared with the benzene ring. Declerk and co-workers [3] have previously arrived at a similar conclusion in an examination of the PMR spectra of diethylamino- and methoxy-substituted triazines in CCl_4.

We made an analysis of the dependence of the measured (in DMSO) chemical shifts of the protons of the triazine ring on the electronic effects of substituents within the framework of the Swain–Lupton two-parameter correlation equation in the interpretation of Hansch and co-workers [6]. However, in the study of this dependence one must take into account the contribution of the purely electronic effect of the substituents on the local diamagnetic shielding of the resonating protons, excluding the effects of the magnetic anisotropy of the substituents, the effect of which on the shielding of the meta protons of the benzene ring is extremely substantial. The corrections that take into account the overall effect of the magnetic anisotropy of the substituent and the change in the magnetic anisotropy of the benzene ring when a given substituent is introduced into it on the shielding of the meta protons were estimated empirically [4] by comparison of their chemical shifts measured in solvents with markedly different polarities such as cyclohexane and DMA.

The legitimacy of the use of these corrections in series of triazine derivatives is based on the concept [7] of the small degree of perturbation of the aromatic system when methylidyne groups are replaced by nitrogen atoms and the data in [8] from a calculation of the induced "ring currents" in six-membered nitrogen heterocycles. In the case of phenyltriazine the anisotropic correction for the phenyl group was calculated by the method in [9] for the conformation in which the torsion angle is 27° [10] with allowance for the geometrical parameters of the triazine ring [11].

The chemical shifts of the protons of the triazine ring in the spectra of substituted triazines scaled relative to their shift in unsubstituted triazine and corrected with allowance for empirical corrections (see the $\Delta\delta'$ values in Table 1) were correlated with the inductive (F) and conjugation (R) constants of the substituents: $\Delta\delta' = -26.43F - 51.47R - 0.95$; r 0.998, s 1.7. Transmission factors γ_I and γ_R, which quantitatively characterize the change in conductivity of the inductive and conjugation effects of a substituent in the triazine ring (series 2) relative to the benzene ring (series 1), are presented in Table 2.

A comparison of the transmission factors for the triazine series (2) and for the analogous pyrimidine series (3-5) [2] indicates the higher transmitting capacity of the triazine ring with respect to the mesomeric effects of substituents. As regards the conductivity of the inductive effects (series 1-4), in the series of six-membered aromatic systems triazine occupies a position that is intermediate between benzene and pyrimidine. The transition from series 3 and 4 to series 2 (i.e., when the successive position of substituent R, the nitrogen atom, and the resonating proton in the  fragment is retained) leads to a small increase in γ_I; this may probably be due to shortening of the bonds in the indicated fragment for the triazine series (2) and consequently to an increase in the field component of the inductive effect of the substituent. An absolutely different situation arises when a nitrogen atom replaces the ring methylidyne group located between the carbon atoms that are directly bonded to the substituent and the resonating proton (the transition from series 5 to series 2), which leads to an appreciable decrease in γ_I from 1.14 to 0.88. The data obtained make it possible to assume that the effect of the free electron pair of the ring nitrogen atom on the shielding of the adjacent proton is also manifested in the triazine ring and to the same extent as in the pyrimidine ring [2].

EXPERIMENTAL

The IR spectra of samples of the compounds in KBr pellets were recorded with a UR-20 spectrometer. The Raman spectrum of a crystalline sample was recorded with a Coderg PH-1 apparatus equipped with a helium–neon laser. The PMR spectra of solutions (4%) of the compounds in CCl_4 and DMSO were recorded with a Varian A 56/60 A spectrometer with cyclohexane as the internal standard for solutions in CCl_4 [84.5 Hz from tetramethylsilane (TMS)] or the $^{13}C-H$ satellite of DMSO (221 Hz from TMS) as the internal standard for solutions in DMSO.

Known methods were used to obtain the following compounds: sym-triazine with mp 81-82°C (80-82.5°C [12]), 2-phenyl-sym-triazine with mp 66-67°C (64-65°C [13]), 2-methoxy-sym-triazine with bp 75-77°C (33 hPa) [71-73°C (28 hPa) [13]], and 2-dimethylamino-sym-triazine with mp 86-87°C (85-88°C [14]).

2-Methyl-sym-triazine. A 14.2-g (0.15 mole) sample of acetamidine hydrochloride was added with stirring to a solution of 3.2 g (0.14 mole) of sodium in 40 ml of methanol, the mixture was filtered, and the filtrate was added dropwise in the course of 40 min to a stirred solution of 8.1 g (0.1 mole) of sym-triazine in 5 ml of methanol. The reaction mixture was distilled with collection of the fraction (6 g) with bp 120-130°C [according to gas-liquid chromatography (GLC), the fraction contained 15% triazine, 20% dimethyltriazine, and traces of methanol as impurities]. The fraction was separated with a Prepakhrom No. 2 chromatograph [with a 15 mm by 5.6 m column filled with CKTH-1 (20%) on Chromosorb W-DMCS at 125°C] in a stream of nitrogen (3 ml/sec) to give 1.1 g (11%) of 2-methyl-sym-triazine containing 96% of the principal product. A reaction product with bp 123-124°C (124-124.3°C [15]) and mp 1-3°C (crystallization temperature 4°C [15]) was obtained by the freeze-out method.

2-Ethoxycarbonyl-sym-triazine. A mixture of 5.0 g (25.4 mmole) of 1-ethoxycarbonylformamidine hydrobromide [15], 2.06 g (25.4 mmole) of sym-triazine, and 20 ml of acetonitrile was refluxed with stirring for 1 h, after which it was cooled, the solution was decanted, and the acetonitrile was removed by vacuum distillation. The residue was treated with three 20-ml portions of boiling petroleum ether (bp 70-100°C), the extract was evaporated to one fourth of its original volume, and the concentrate was cooled. The resulting precipitate was separated and dried in vacuo to give 1.6 g (40%) of product. An analytical sample was obtained by crystallization from petroleum ether and subsequent sublimation in vacuo to give a product with mp 65.5-66°C. IR spectrum: 1740 (ester C = O) and 1190 cm^{-1} (ester C—O). PMR spectrum (in CCl_4): 9.31 (2H, s, triazine ring), 4.46 (2H, q, CH_2), and 1.44 ppm (3H, t, CH_3, J = 7.0 Hz). Found: C 47.3; H 4.59; N 27.5%. $C_6H_7N_3O_2$. Calculated: C 47.1; H 4.61; N 27.4%.

2-Carbamoyl-sym-triazine. A 2.4-g (19 mmole) sample of 2-ethoxycarbonyl-sym-triazine was added to a cooled solution of 2.7 g (160 mmole) of ammonia in 30 ml of ethanol, and the mixture was allowed to stand for 2 h. The precipitate was separated, washed with ethanol, and dried in vacuo to give 1.83 g (94%) of a product that did not melt when it was heated to 260°C but charred above 170°C. IR spectrum: 1640, 1700, 1720, 3170, 3330, and 3400 cm^{-1} ($CONH_2$). Found: C 39.0; H 3.45; N 44.9%. $C_4H_4N_4O$. Calculated: C 38.7; H 3.25; N 45.2%.

2-Cyano-sym-triazine. A 1.24-ml (8.9 mmole) sample of trifluoroacetic anhydride was added with stirring in the course of 1 h to an ice-cooled suspension of 1.0 g (8.1 mmole) of 2-carbamoyl-sym-triazine in 20 ml of anhydrous dioxane and 1.3 ml (16.2 mmole) of anhydrous pyridine, after which the mixture was stirred at 20°C for another 3 h. The precipitated pyridine trifluoroacetate was removed by filtration, and the filtrate was diluted with 20 ml of $CHCl_3$ and washed with two 5-ml portions of water and two 5-ml portions of a saturated solution of NaCl. It was then dried over $MgSO_4$ and evaporated in vacuo. The residue was extracted with three 5-ml portions of boiling hexane, and the extract was evaporated to a volume of 3 ml. The concentrate was cooled, and the precipitate was removed by filtration to give 0.15 g (17%) of product. An analytical sample was obtained by crystallization from hexane and vacuum sublimation to give a substance with mp 69-70°C. IR spectrum: 2260 cm^{-1} (C ≡ N). Raman spectrum: 2266 cm^{-1} (C ≡ N). Found: C 45.0; H 2.13; N 53.0%. $C_4H_2N_4$. Calculated: C 45.3; H 1.90; N 52.8%.

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