REACTIONS OF AZINIUM CATIONS.

8.* ELECTRON STRUCTURES OF 3-SUBSTITUTED 1,2,4-TRIAZINES AND PROTONATION, QUATERNIZATION, AND REACTIONS WITH NUCLEOPHILES

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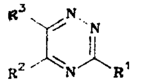
The electron structures of 3-substituted 1,2,4-triazines and isomeric N-methyltriazinium salts were calculated by the CNDO/2 method. The results of the calculations were compared with the parameters of the ^{13}C, ^{15}N, and ^{14}N NMR spectra, as well as with experimental data on the protonation, N-alkylation, and reactions of 1,2,4-triazines with simple nucleophiles. The protonation centers of 1,2,4-triazines were determined by means of ^{1}H, ^{13}C, and ^{14}N NMR spectroscopy. The covalent adducts formed by the proton salts of 3-methoxy-, 3-methylthio-, 3-morpholino-, and 3-pyrrolidino-1,2,4-triazine with water and methanol were recorded by ^{1}H NMR spectroscopy.

Although extremely limited, the literature data on the structures of N-protonated and N-alkylated 1,2,4-triazinium cations provide evidence that the protonation and quaternization of 1,2,4-triazines can, in principle, take place at any of the ring nitrogen atoms; the direction of the reaction is determined by both electronic and steric factors [1-6].

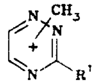
It was previously established by ^{1}H and ^{13}C NMR spectroscopy that the quaternization of 3-cycloalkylamino-substituted 1,2,4-triazines by alkylating agents takes place only at the $N_{(1)}$ atom [1].

In the present communication we present computational indexes for the molecules of a number of 3-substituted triazines and 1,2,4-triazinium cations, which, in conjunction with experimental data on protonation and quaternization, as well as with the characteristics of the ^{1}H, ^{13}C, ^{15}N, and ^{14}N NMR spectra, give an idea of the electron density distribution in triazines and triazinium salts and make it possible to evaluate the relative stabilities of isomeric triazinium cations and ascertain the most probable centers of protonation, quaternization, and nucleophilic addition.

The quantum-chemical calculations of triazines Ia-e and N-methyltriazinium cations IIa, c-e with a methyl group attached to the $N_{(1)}$, $N_{(2)}$, and $N_{(4)}$ atoms were made by the CNDO/2 method with "averaged" geometries of the molecules [7]. The geometry of the triazine ring for all of the compounds was assumed to be invariable with the following bond lengths: C—C 13.83, C—N 13.51, N—N 13.26, and C—H 10.80 nm. As a result of the quantum-chemical study we obtained the distributions of the charges in Ia-e and IIa, c-e and calculated the resonance energies of the bonds (Tables 1 and 2).



I a-j



II a-g

I a—g $R^3=R^2=H$; I h, j $R^3=H$, $R^2=CH_3$; I i $R^3=CH_3$, $R^2=H$; I, II a $R^1=H$, b $R^1=NH_2$, c $R^1=N(CH_3)_2$, d $R^1=OCH_3$, e $R^1=SCH_3$, f $R^1=$morpholine, g $R^1=$ pyrrolidine; I h, i $R^1=SCH_3$; I j $R^1=OCD_3$

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TABLE 1. Electron Structures of 1,2,4-Triazines Ia-e

Compound	Charges on the atoms, units of electron charge						
	$N_{(1)}$	$N_{(2)}$	$C_{(3)}$	$N_{(4)}$	$C_{(5)}$	$C_{(6)}$	R^3
Ia	−0,043	−0,101	0,155	−0,134	0,099	0,040	−0,007 (H)
			0,150[a]		0,093[a]	0,017[a]	
			0,135b		0,091b	0,035b	
Ib	−0,029	−0,147	0,264	−0,181	0,112	0,015	−0,211 (N)
Ic	−0,018	−0,167	0,287	−0,207	0,118	0,004	−0,149 (N)
Id	−0,024	−0,140	0,309	−0,184	0,114	0,017	−0,215 (O)
Ie	−0,034	−0,119	0,201	−0,159	0,105	0,026	−0,064 (S)

[a],[b]Literature data: [a][1], [b][9].

TABLE 2. Electron Structures of N-Methyl-1,2,4-triazinium Cations IIa, c-d

Compound	Nitrogen atom	Charges on the atoms, units of electron charge						E_b^R, au
		$N_{(1)}$	$N_{(2)}$	$C_{(3)}$	$N_{(4)}$	$C_{(5)}$	$C_{(6)}$	
IIa	$N_{(1)}$[a]	0,164	−0,029	0,182	−0,018	0,118	0,090	−14,251
	$N_{(2)}$	0,026	0,119	0,204	−0,063	0,164	0,068	−14,245
	$N_{(4)}$	0,089	−0,013	0,185	0,065	0,130	0,057	−14,219
IIc	$N_{(1)}$	0,179	−0,127	0,327	−0,094	0,135	0,045	−21,303
	$N_{(2)}$	0,036	0,029	0,338	−0,139	0,180	0,031	−21,261
	$N_{(4)}$	0,057	−0,136	0,343	0,070	0,169	−0,001	−21,263
IId	$N_{(1)}$	0,174	−0,080	0,342	−0,071	0,131	0,062	−17,787
	$N_{(2)}$	0,040	0,067	0,358	−0,121	0,175	0,043	−17,772
	$N_{(4)}$	0,106	−0,081	0,347	0,008	0,141	0,033	−17,748
IIe	$N_{(1)}$	0,157	−0,064	0,200	−0,044	0,121	0,068	−16,980
	$N_{(2)}$	0,043	0,122	0,214	−0,124	0,154	0,042	−16,983
	$N_{(4)}$	0,100	−0,055	0,190	0,015	0,129	0,042	−16,947

[a]Quaternized atom.

The results of calculations of the electron structures of 1,2,4-triazines Ia-e presented in Table 1 are in good agreement with the literature data obtained by the same method for unsubstituted triazine Ia [8, 9] (Table 1). In particular, the calculated dipole moment of Ia μ = 2.36 D is close to the value μ = 2.16 D presented in [10]. It is apparent from the data in Table 1 that for all 1,2,4-triazines Ia-e the positive charge on the carbon atoms decreases in the order $C_{(3)} > C_{(5)} > C_{(6)}$.

The relative positioning of the ^{13}C NMR signals of triazines Ia-f (Table 3) shows that the $C_{(3)}$ atom has the greatest electron-density deficit; the chemical shifts (CS) of the carbon atoms in Ib-f* change in the same order as the charges on atoms: $\delta C_{(3)} > \delta C_{(5)} > \delta C_{(6)}$. In the case of unsubstituted triazine Ia the weakest-field signal is also the signal of the $C_{(3)}$ atom, and the ^{13}C CS of the $C_{(5)}$ and $C_{(6)}$ atoms have close values.

The change in the basicity of the nitrogen atoms in triazines Ia-g can be judged from the localization of the negative charge, which, according to the calculated data, decreases in the order $N_{(4)} > N_{(2)} > N_{(1)}$ (Table 1). This order is in good agreement with the CS of the nitrogen atoms in the ^{15}N and ^{14}N NMR spectra of triazines Ia, b, d-f (Table 4).

Thus, in the absence of steric effects and under the condition that the reaction is controlled by the charge, as a result of protonation and N-alkylation of unsubstituted triazine Ia, one should expect the formation of primarily $N_{(4)}$-protonated or $N_{(4)}$-alkylated cation. The presence of substituents in the 3 position should hinder N-alkylation of the $N_{(3)}$ and $N_{(4)}$ atoms and increase the yield of $N_{(1)}$-alkyl salts.

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*Quantum-chemical calculations of triazines If, g were not made, since it is evident that their electron structures differ little from the electron structure of 3-dimethylamino-substituted 1,2,4-triazine Ic.

TABLE 3. ^{13}C Chemical Shifts of Triazines Ia-f in $CDCl_3$

Compound	^{13}C CS, δ, ppm				Literature
	$C_{(3)}$	$C_{(5)}$	$C_{(6)}$	R^1	
Ia	158,3	149,2	150,7	—	[11]
	158,1	149,6	150,8		[8, 12]
	157,89[a]	149,98[a]	151,10[a]		[13]
Ib	161[a]	148[a]	139[a]	—	[14]
Ic	160	148	138	36 ($N(CH_3)_2$)	[14]
Id	166,1	151,6	145,5		[11]
	164	150	143	54 (OCH_3)	[14]
	165,6[a]	152,0[a]	145,6[a]		[15]
Ie	174,33	148,01	145,19	13,57 (SCH_3)	—
	174,7	148,5	145,6		[11]
If	161,11	148,55	140,13	43,65 (NCH_2) 66,40 (OCH_2)	[1]

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[a] In d_6-DMSO.

TABLE 4. Characteristics of the ^{14}N and ^{15}N NMR Spectra of the 1,2,4-Triazines

Compound	Nitrogen atom	^{14}N NMR data			^{15}N CS,[a] ppm (in DMSO [16]
		solvent	^{14}N[a] CS, ppm	$\nu_{1/2}$,[b] Hz	
Ia[c]	$N_{(1)}$	$(C_2H_5)_2O$	422	286	420,0
	$\check{N}_{(2)}$		378	276	382,0
	$N_{(4)}$		299	217	318,0
Ib	$N_{(1)}$		—	—	415,7
	$\check{N}_{(2)}$				369,0
	$N_{(4)}$				250,0
Id	$N_{(1)}$	$CHCl_3$	435	1000	416,0
	$\check{N}_{(2)}$		335	700	322,0
	$N_{(4)}$		261	750	253,6
	$N_{(1)}$	$CHCl_3 + CF_3COOH$	421	1350	—
	$\check{N}_{(2)}$		326	1250	
	$N_{(4)}$		266	1300	
Ie	$N_{(1)}$	$CHCl_3$	430	1300	412,0
	$\check{N}_{(2)}$		366	1000	351,0
	$N_{(4)}$		288	950	282,0
	$N_{(1)}$	$CHCl_3 + CF_3COOH$	416	4700	—
	$\check{N}_{(2)}$		362	3500	
	$N_{(4)}$		290	3500	
If	$N_{(1)}$	$CHCl_3$	432	1200	—
	$\check{N}_{(2)}$		338	850	
	$N_{(4)}$		265	1200	
	N (morph)		90	1100	
	$N_{(1)}$	$CHCl_3 + CF_3COOH$	406	1750	—
	$\check{N}_{(2)}$		326	1800	
	$N_{(4)}$		264	1500	
	N (morph)		91	1150	

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[a] Relative to liquid ammonia, δ = 0.0 ppm. [b] Width of the ^{14}N signal at half the height; the quadrupole broadening of the lines and chemical exchange processes lead to broadening of the ^{14}N signals. [c] Literature data [17, 18].

Quantum-chemical calculations of the isomeric salts show that $N_{(1)}$- and $N_{(2)}$-alkyltriazinium salts IIa, c-e have the minimal resonance energies of the valence-bonded atoms E_b^R (Table 2), i.e., they are the most stable. This is explained by the fact that in 1,2,4-triazines, just as in pyridazine [19], interaction of the unshared electron pairs leads to deviation of the p orbitals of the nitrogen atoms from the plane perpendicular to the skeleton of the molecule, thereby decreasing the effectiveness of cyclic conjugation of the π electrons. The formation of triazinium $N_{(1)}$- and $N_{(2)}$-cations is more favorable than the formation of $N_{(4)}$-cations, since in this case interaction of the n orbitals of the $N_{(1)}$ and $N_{(2)}$ atoms due to the formation of an N—R bond (where R = H or Alk) is eliminated. Thus the

TABLE 5. Data from the ^{1}H NMR Spectra of 1,2,4-Triazines Id-i

Compound	Chemical shifts of the protons, δ, ppm			$^3J_{5,6}$, Hz	Solvent	$\Delta\delta_{H_i}$^{a}, ppm			$\Delta\,^3J_{5,6}$^{a}, Hz
	6-H	5-H	R^1			6-H	5-H	R	
Id	9,01	9,30	4,50 (OCH_3)	2,0	CF_3COOH	0,05	0,77	0,26	−0,2
	9,06	8,53	4,24 (OCH_3)	2,2	$CDCl_3$	—	—	—	—
	9,00^b	8,56	—	—	$CDCl_3$	—	—	—	—
	9,16^c	8,56	5,15 (OCH_3)	2,3	$CDCl_3$	—	—	—	—
Ie	9,08	9,25	2,98 (SCH_3)	2,0	CF_3COOH	0,12	0,84	0,31	−0,3
	8,96	8,41	2,67 (SCH_3)	2,3	$CDCl_3$	—	—	—	—
	8,85^b	8,30	—	—	$CDCl_3$	—	—	—	—
	9,00^c	8,46	2,64 (SCH_3)	2,3	$CDCl_3$	—	—	—	—
If	8,91	8,45	4,16 (morph)	1,8	CF_3COOH	0,37	0,31	0,31	−0,3
	8,54^d	8,14	3,85 (morph)	2,1	$CDCl_3$	—	—	—	—
Ig	8,91	8,45	3,6—4,1 and 2,0—2,5 (pyrr)	1,8	CF_3COOH	0,39	0,31	0,2—0,3	−0,3
	8,52^d	8,14	3,4—3.8 and 1,8—2,2 (pyrr)	2,2	$CDCl_3$	—	—	—	—
Ih	8,87	—	2,92 (SCH_3)	—	CF_3COOH	0,10	—	0,28	—
	8,77	—	2,64 (SCH_3)	—	$CDCl_3$	—	—	—	—
	8,82^c		2,66 (SCH_3)	—	$CDCl_3$	—	—	—	—
Ii	—	9,17	2,95 (SCH_3)	—	CF_3COOH	—	0,95	0,49	—
	—	8,22	2,46 (SCH_3)	—	$CDCl_3$	—	—	—	—

^{a}Effect of protonation: $\delta_{H_i\,CF_3COOH} - \delta_{H_i\,CDCl_3}$; $^3J_{5,6}$ (CF_3COOH) − $^3J_{5,6}$ ($CDCl_3$). $^{b-d}$Literature data. ^{b}[11], ^{b}[12], ^{d}[1].

high stabilities of the $N_{(1)}$- and $N_{(2)}$-cations may be one of the factors that determine the direction of quaternization of triazines. The results of the calculations (Table 1) show that the nitrogen atom of the exocyclic amino group may also be a quaternization center in aminotriazines Ib, c, f, g.

In the ^{1}H NMR spectra of 3-methoxy- and 3-methylthiotriazine Id, e (Table 5) the 5-H signals (0.77 and 0.84 ppm) undergo the greatest shifts to weak field on passing from $CDCl_3$ to CF_3COOH, and the signals of the 6-H proton and substituent R^1 experience smaller shifts. The assignment of the 5-H and 6-H signals was made by means of experiments involving recording of the ^{13}C NMR spectra of Ie under conditions of selective decoupling of the coupling of the protons with the ^{13}C atoms and is in good agreement with the literature data (Table 5 [11]). The signal of the $C_{(2)}$ atom in the ^{13}C NMR spectrum of triazine Ie was identified from the absence of a direct constant of spin-spin coupling through one bond ^{1}H(CH), and the signals of the $C_{(5)}$ and $C_{(6)}$ atoms were assigned on the basis of literature data (Table 3 [11]).

It is known that the signal of the proton in the β position relative to the protonated nitrogen atom experiences a large shift to weak field when azines are protonated [20]. Applying this principle to the dependence of the chemical shifts of the 5-H and 6-H protons in the ^{1}H NMR spectra of triazine Ie on the acidity of the medium one may conclude that the $N_{(1)}$-protonated form makes a significant contribution to the spectrum (Fig. 1).

Cycloalkylamino-substituted triazines If, g have an additional protonation center — the nitrogen atom of the exocyclic amino group. This is apparent both from calculation of their structural analog Ic (Table 1) and from the Δδ values obtained from the ^{1}H NMR spectra of triazines If, g (Table 5). In the latter commensurable changes in the CS of the 5-H and 6-H protons and the protons of substituent R^1 are observed on passing from $CDCl_3$ to CF_3COOH; this may indicate the contribution of not only $N_{(1)}$-, $N_{(2)}$- and $N_{(4)}$-protonated forms but also protonation of the exocyclic nitrogen atom.

The dependence of the parameters of the ^{13}C NMR spectra of triazine Ie on the acidity of the medium (Fig. 2) also has complex character. As CF_3COOD is added to a solution of triazine Ie in $CDCl_3$ up to a concentration of 39% (by volume), the signal of the $C_{(6)}$ atom is shifted to strong field, reaching at this point δ = 141.83 ppm ($\Delta\delta$ = −3.36 ppm), while the $C_{(3)}$ and $C_{(5)}$ signals are shifted to weak field by 2.00 and 8.82 ppm (Fig. 2). The shift of the signal of the α-carbon atom to strong field is one of the diagnostic signs in establishing the protonation and quaternization centers [20]. Proceeding from this, it might be concluded that protonation takes place primarily at the $N_{(1)}$ atom. The changes in the CS of the

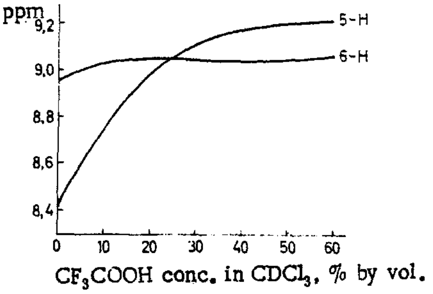

Fig. 1

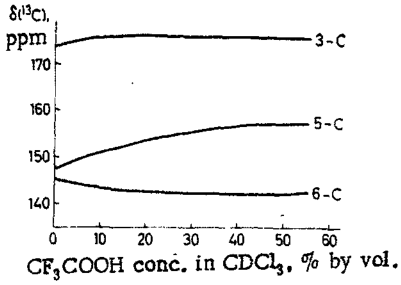

Fig. 2

Fig. 1. Change in the chemical shifts of the 5-H and 6-H protons of triazine Ie as a function of the acidity of the medium.

Fig. 2. Dependence of the ^{13}C chemical shifts for triazine Ie on the concentration of CF_3COOH in $CDCl_3$.

^{13}C atom of triazine Ie at this point are completely comparable to the effects of quaternization of 3-morpholino-1,2,4-triazine (If) with methyl iodide at the $N_{(1)}$ atom [1]. The following facts also constitute evidence for protonation at the $N_{(1)}$ atom: a) the increase in the direct SSCC through one bond $^1J(C_{(5)}, H_{(5)})$ from 187.2 to 194.6 Hz and $^1H(C_{(6)}, H_{(6)})$ from 188.9 to 195.8 Hz, b) the decrease in the $^2J(C_{(5)}, H_{(6)})$ value from 9.6 to 8.8 Hz and the increase in $^2J(C_{(6)}, H_{(5)})$ from 9.6 to 10.5 Hz.*

The character of the dependence changes with a further increase in the CF_3COOD concentration from 39% to 55%. The signal of the $C_{(6)}$ atom is shifted to the weak-field region, the signal of the $C_{(5)}$ atom in the ^{13}C NMR spectra with complete decoupling of the protons becomes appreciably broadened, and in addition to broadening, the intensity of the $C_{(5)}$ signal decreases. These effects evidently can be explained by the existence of spin-spin coupling (SSC) between the α-^{13}C atoms and the $^{14}N^+$ nuclei ($I = 1$) of the azine system [20-22]. This character of the changes in the spectra may indicate protonation of triazine Ie at the $N_{(2)}$ atom or at the $N_{(4)}$ atom. It is difficult to say which of the protonated forms — $N_{(2)}$ or $N_{(1)}$ — makes the greater contribution to the averaged spectrum on the basis of the data presented above.

We found that ^{14}N NMR spectroscopy is more informative for determining the protonation centers of 3-substituted triazines Id-f. The assignment of the signals in the ^{14}N NMR spectra of triazines Id-f and their protonated forms (Table 4) was made taking into account the literature ^{15}N NMR data on Ia, b, d, e (Table 4 [16]) and the ^{14}N NMR data on unsubstituted triazine Ia (Table 4 [17, 18]). Since the use of an external standard in ^{14}N NMR spectroscopy creates definite difficulties in the accurate determination of the ^{14}N CS values, the narrow signal of dissolved molecular nitrogen at 315.3 ppm (relative to liquid ammonia) was used as a stable internal standard. The sensitivity of the device under the conditions used to record the ^{14}N NMR spectra (see the experimental section) makes it possible to record this signal.

It is apparent from Table 4 that the addition of CF_3COOH to solutions of triazines Id-f in $CDCl_3$ leads to broadening of the ^{14}N NMR signals; this indicates protonation of all three ring nitrogen atoms of the triazine system. The greatest shift of the signal of the $N_{(1)}$ atom of triazines Id-f by 14-26 ppm to strong field (Table 4) indicates preponderance of the $N_{(1)}$-protonated form in solution. The contribution of the $N_{(2)}$-protonated forms of triazines Id-f is also significant, as is apparent from the changes in the ^{14}N CS of the $N_{(2)}$ atoms, although it is smaller than the contribution of $N_{(1)}$-triazinium salts. Since the signal of the $N_{(4)}$ atom of Id, e experiences shifts of 5 and 2 ppm to the weak-field region, it may be concluded that the protonation of this center in triazines Id, e is insignificant. However, in the case of 3-morpholinotriazine If the signal of the $N_{(4)}$ atom has a tendency to undergo a shift to strong field; this may indicate a higher percentage of the $N_{(4)}$-protonated form than in the case of Id, e (Table 4). This explains the difference between the data from the

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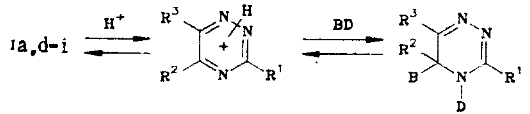
*The SSCC of triazine Ie were measured at 0% and 20% concentrations of CF_3COOD in $CDCl_3$.

^{1}H NMR spectra of the proton salts of triazines If, g and the spectral characteristics of the salts of triazines Id, e (Table 5). The small broadening (50 Hz) and the insignificant shift of the signal of the exocyclic nitrogen atom of the proton salt of If to weak field by 1 ppm indicate that the protonation of triazine If virtually does not involve this atom.

It is known [23, 24] that the reactivities of azines and their chemical transformations in reactions with nucleophiles depend in many respects on the structure and lability of the covalently bonded intermediates.

It has been previously shown that the protonated salts of unsubstituted 1,2,4-triazine (Ia) and 6-substituted 3-amino-1,2,4-triazines add simple nucleophiles to the $C_{(5)}-N_{(4)}$ bond [2, 26-29]. In the present research we established that the proton salts of 3-methoxy- and 3-methylthio-1,2,4-triazine (Id, e) in trifluoroacetic acid also give products IIIe, j of the covalent addition of water (Table 6). Methoxy adducts IIIf, k with a similar structure were detected in the ^{1}H NMR spectra of triazines Id, e in d_4-methanol in the presence of CF_3COOH, but the degree of conversion of salts of 3-substituted triazines Id, e to adducts IIIe, f, j, k is only 20-40%. Since the spectral characteristics of adducts IIIe, f, j, k differ from the literature data on the products of covalent addition of O-, N-, and C-nucleophiles IIIa-d, g-i (Table 6), to prove their structures we carried out experiments with model 5-methyl- and 6-methyl-3-methylthio-1,2,4-triazine (Ih, i).



IIIa,e,f,j-p

III^a $R^1=H$; III^{e,f} $R^1=OCH_3$; III $^{g-m}$ $R^1=SCH_3$; III o $R^1=$ morpholino III p $R^1=$ =pyrrolidino ; III a,e,j,m B=DO; III f,k,*l*,o-p B=D_3CO; III a,e,f,j,k,o,p $R^2=R^3=H$; III *l* ,m $R^2=H$, $R^3=CH_3$; III n $R^2=CH_3$, $R^3=H$

It was established that the presence of a methyl group in the 5 position of triazine Ih completely blocks the formation of products of addition of O-nucleophiles in $CF_3COOH-D_2O$ and $CF_3COOH-CD_3OD$, whereas a very small amount* of methoxy adduct IIIn, which was recordable from the signlet 6-H signal at 7.34 ppm, is formed in d_4-methanol in the presence of CF_3COOH. In d_4-methanol 6-methyl derivative Ii is converted completely to the product of covalent addition of methanol III*l*, which was detectable from the 5-H singlet at 5.30 ppm, when CF_3COOH was added. The formation of adduct III*l* is also observed when a solution of triazine Ii in CF_3COOH is treated with d_4-methanol (Table 6). A comparison of the spectral characteristics of adducts III*l*, m, n and IIIe, f, j, k shows that the addition of methanol and water to 3-methoxy- and 3-methylthiotriazine Id, e also takes place at the $C_{(5)}$ atom. The formation of methoxy adducts IIIf, k, which with time (Table 6) are converted to products of covalent addition of water† IIIe, j, is initially observed when d_4-methanol is added to solutions of triazines Id, e in trifluoroacetic acid. The formation of adducts IIIe, j was confirmed by experiments with heavy water. A similar phenomenon is also observed in the case of the 6-methyl derivative.

The proton salts of triazines If, g are less active in reactions with nucleophiles — they do not form covalent adducts with water but, like the salts of triazines Id, e, give $C_{(5)}$-adducts IIIo, p with methanol.

These are the peculiarities of the protonation of 1,2,4-triazines and the formation of covalent adducts from them. Despite the existence of a mixture of $N_{(1)}$-, $N_{(2)}$-, and $N_{(4)}$-protonated forms in solutions, only the thermodynamically stable $C_{(5)}$-triazines with nucleophiles.

The steric factor has a determining effect in the alkylation of 1,2,4-triazines [1, 5], and $N_{(1)}$-alkyltriazinium salts, which are distinguished by the smallest E_D^R values (Table 2) as compared with the other isomeric salts, are therefore formed in the quaternization of 3-substituted triazines Id-f [1, 3]. The distribution of the charges on the carbon atoms in

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*The formation of methoxy d: -derivative Ij (6-H singlet at 8.97 ppm) is also recorded in the reaction mixture. Signal ratio IIIn:Ij:Ih = 1:2:19.

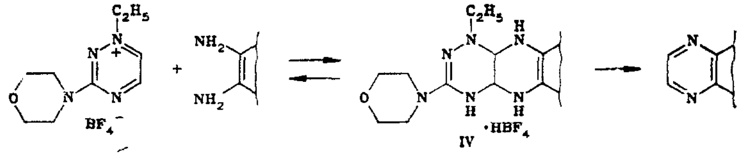
†The water is formed as a result of the side reaction $CF_3COOH + CH_3OH \rightleftarrows H_2O + CF_3COOCH_3$.

TABLE 6. ^{1}H NMR Spectra of Adducts IIIa-p

pound	Adduct		Chemical shift, δ, ppm			$^3J_{5,6}$[a], Hz	Solvent	Note
	R¹	B	6-H	5-H	R¹			
IIIa	H	DO	8,55	6,60	7,60	—	CF_3COOH	[2]
IIIb	H	NH_2	6,65	4,15	7,40	—	NH_3(l)	[11]
IIIc	OCH_3	NH_2	6,73	4,56	—	—	NH_3(l)	[11]
IIId	OCH_3	CH_3	6,62	3,48	3,72	2,0	$CDCl_3$	[25]
IIIe	OCH_3	DO	7,46	5,81	4,28	3,0	CF_3COOH	+118 μl D_2O
IIIf	OCH_3	CD_3O	7,49	5,49	4,33	2,9	CF_3COOH	+60 μl CD_3OD
IIIe	OCH_3	DO	7,51	5,87	4,35	3,0	CF_3COOH	+60 μl CD_3OD after 1 h
IIIf	OCH_3	CD_3O	7,40	5,40	4,17	—	CD_3OD	+72 μl CF_3COOH
IIIg	SCH_3	NH_2	6,52	4,10	—	—	NH_3(l)	[11]
IIIh	SCH_3	CH_3	6,57	3,48	2,39	2,0	$CDCl_3$	[25]
IIIi	SCH_3	C_6H_5	6,64	4,56	2,38	2,0	$CDCl_3$	[25]
IIIj	SCH_3	DO	7,56	5,65	2,76	3,0	CF_3COOH	+90 μl D_2O
IIIf	SCH_3	CD_3O	7,56	5,36	2,79	3,0	CF_3COOH	+60 μl CD_3OD
IIIl	SCH_3	DO	7,59	5,73	2,81	2,9	CF_3COOH	+60 μl CD_3OD after 1 day
IIIk	SCH_3	CD_3O	7,49	5,24	2,75	3,1	CD_3OD	+86 μl CF_3COOH
IIIl	SCH_3	CD_3O	—	5,38	2,84	—	CF_3COOD	+36 μl CD_3OD
IIIm	SCH_3	DO	—	5,74	2,90	—	CF_3COOD	+36 μl CD_3OD after 1 day
IIIn	SCH_3	CD_3O	7,34		2,62	—	CD_3OD	+48 μl CF_3COOH
IIIl	SCH_3	CD_3O	—	5,30	2,76	—	CD_3OD	+48 μl CF_3COOH
IIIo	Morpholino	CD_3O	7,41	5,11	3,4—3,9	3,0	CD_3OD	+48 μl CF_3COOH
IIIp	Pyrrolidino	CD_3O	7,29	5,10	1,9—2,3 and 3,4—3,7	3,0	CD_3OD	+48 μl CF_3COOH

[a] Accuracy in the determination of the SSCC was ±0.2 Hz.

isomeric triazinium cations IIa, c-e retains the same order as in the basis, regardless of the position of the N-methyl group. $C_{(3)} > C_{(5)} > C_{(6)}$. The effect of quaternization is manifested in the fact that the differences in the deficit of positive charge on the unsubstituted $C_{(5)}$ and $C_{(6)}$ atoms become not so pronounced as in the case of the bases; this is particularly clear in the case of the $N_{(1)}$-methyl cations (Tables 1 and 2). Proceeding from this, one should expect that in the reactions of 1,2,4-triazinium cations nucleophilic attack may be directly at both the $C_{(5)}$ and $C_{(6)}$ atoms. With respect to their chemical properties N-alkyl-1,2,4-triazinium salts actually differ from their proton analogs. As demonstrated in [1, 30], they add two molecules of indole at the $C_{(5)}$ and $C_{(6)}$ atoms. The ability of $N_{(1)}$-alkyl salts to undergo diaddition is also displayed in their reactions with o-diamines, which lead to the formation of condensed pyrazines through cyclic adducts IV [31].



EXPERIMENTAL

The quantum-chemical calculations were made within the CNDO/2 approximation with an EC-1022 computer by means of the modified program in [32] that makes it possible to accomplish energy separation in accordance with Fisher and Kollmar [33] and to calculate the "forces on the atoms" via the Pulay scheme [34]. The resonance energy of the valence-bonded atoms E_b^R was calculated by summation of all of the two-center resonance energies E_{A-B}^R for the A and B atoms, between which there is a chemical bond: $E_b^R = \sum\limits_A^A \sum\limits_B^B E_{AB}^R$.

The ^{1}H NMR spectra of solutions of the investigated substances in $CDCl_3$, CD_3COD, CF_3COOH, and CF_3COOD were measured with Perkin-Elmer R-12-B (60 MHz) and Bruker WH-90 (90 MHz) spectrometers with respect to tetramethylsilane (δ = 0.00 ppm) as the internal standard. The ^{13}C NMR spectra of solutions of triazine Ie in $CDCl_3$ and $CDCl_3$ in the presence of CF_3COOD were recorded with a Bruker WH-90 (22.62 MHz) spectrometer with respect to the signal of the solvent (δ = 77.0 ppm). The ^{14}N NMR spectra of triazones Id-f and their protonated forms were recorded with a Bruker CXP-300 spectrometer at 21.68 MHz. The CS values of the ^{14}N atoms were measured relative to the signal of molecular nitrogen (δ_{N_2} = 315.3 ppm), which was used as the internal standard, and were converted to the δ scale relative to liquid ammonia. The error in their measurement $\delta \approx \pm\nu_{1/2}/300$ ppm. We used 0.5 M solutions of Id-f in $CDCl_3$ for recording of the ^{14}N NMR spectra. In the study of the protonation of triazines Id-f CF_3COOH (30 µl) was added to their solutions.

Triazines Id-i were obtained by known methods [1, 2, 25].

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