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sym-TRIAZINE DERIVATIVES.

7.* STRUCTURE AND PROPERTIES OF TRIAZINYL DERIVATIVES OF CH ACIDS

K. F. Turchin, E. M. Peresleni,
Yu. N. Sheinker, G. A. Bogdanova,
I. V. Persianova, N. V. Alekseeva,
G. M. Vakhatova, V. V. Lapachev,
V. P. Mamaev,† and L. N. Yakhontov

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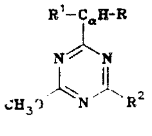
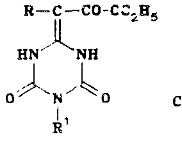
The structures, tautomerism, and acid-base properties of some sym-triazinyl-substituted CH acids were studied.

The tautomerism and acid-base properties of the previously obtained [2-4] sym-triazinyl derivatives of CH acids were studied. 2-(3',3'-Dimethyl-5'-oxo-6'-cyclohexen-1'-yloxy)-4,6-dimethoxy-sym-triazine (IIIb) was synthesized to accurately determine the structures of some of them.


I a-d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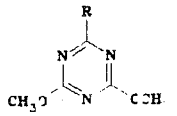
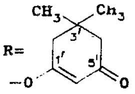
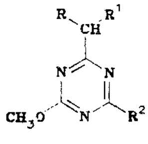

III a-c

Ia-c, IIa,c $R=COOC_2H_5$, Id, IIb,d $R=CN$; Ia,b $R^1=COOC_2H_5$, c,d $R^1=CN$, IIa,b $R^1=CH_3$, c,d $R^1=H$; Ia,c,d $R^2=OCH_3$, b $R^2=NH_2$; IIIa $R=H_3C_{(3')}-\underset{|}{\overset{}{C}}{}_{(2')}(O-)=HC_{(1')}-$ $-COOC_2H_5$; c $R=Cl$

IIIb R=


A single set of signals‡ in the ^1H spectra of 2-(dicarbethoxymethyl)-4,6-dimethoxy-sym-triazine (Ia) (Table 1) in both $CDCl_3$ and d_6-DMSO over the concentration range 10^{-1} to $3\cdot10^{-4}$ M; a singlet signal of the CH proton of a malonic residue is observed along with the signals of protons of OCH_3 and $COOC_2H_5$ groups. The presence of a CH group was confirmed by the ^{13}C NMR spectra (Table 2) (recorded without proton decoupling), in which the signal of the corresponding carbon atom is a doublet with spin-spin coupling constant $^1J_{CH}$ = 134 Hz. The virtual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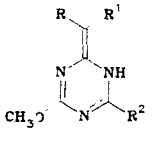
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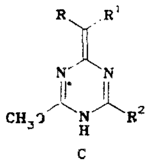
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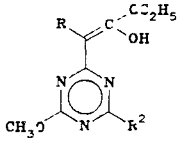
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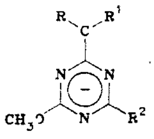
E

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*See [1] for Communication 6.

†Deceased.

‡The absence of an alternative set of signals can be ascertained with an accuracy of up to 10^{-4} M.

S. Ordzhonikidze All-Union Scientific-Research Institute, Moscow 119021. Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090.
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TABLE 1. Chemical Shifts of the Protons in Ia-d, IIa-d, and IIIa, b (δ, ppm)

Compound	Solvent	Protons of groups: CH*	NH	OCH_3, s	$CH_2(CH_2CH_3)$, q	$CH_3(CH_2CH_3)$, t	Other
Ia	$CDCl_3$	4,82 s	—	4,04	4,29	1,29	
Ia	d_6-DMSO	5,07 s	—	3,96	4,22	1,20	
IaA	d_6-DMSO /NaOH	5,07 s	—	3,96	4,22	1,20	
IaE		—	—	3,69	3,94		
IaA	d_6-DMSO /$(C_2H_5)_3N$	5,09 br.s	—	3,96 m.s	4,19 br.q	1,19	
IaE				3,72 m.s			
Ib	$CDCl_3$	4,70	—	3,94	4,27	1,29	5,48 br.s(NH_2)
IbA	d_6-DMSO	4,75	—	3,82	4,16	1,19	7,68 br.s(NH_2)
IbB		—	11,95 br.s	3,74	4,08	1,19	8,20, 8,25 br.s (NH_2)
IbA	d_6-DMSO /NaOH	4,71	—	3,82	4,16	1,20	7,65 br.s(NH_2)
IbE		—	—	3,65	3,92	1,12	6,45 br.s(NH_2)
IbA	d_6-DMSO /11N.HCl	4,75		3,81	4,12	1,16	7,76 br.s(NH_2)
Ib+	(10:1)						9,00 br.s(NH_2)
Ic	$CDCl_3$	—	12,80	4,11; 4,12	4,27	1,35	
Ic	d_6-DMSO		12,60	4,05; 3,98	4,19	1,24	
IcE	d_6-DMSO /$(C_2H_5)_3N$	—	—	3,77	3,93	1,14	
Id	d_6-DMSO (0,1 M)	—	—	3,95	—	—	—
Id	d_6-DMSO (0,01 M)	—	—	3,89	—	—	—
Id	d_6-DMSO (0,0003 M)	—	—	3,79	—	—	—
IdE	d_6-DMSO /NaOH	—	—	3,76	—	—	—
IIa	$CDCl_3$	—	12,35 br.s	—	4,26	1,38	3,31 s (N—CH_3)
IIa	d_6-DMSO	—	11,93 br.s	—	4,18	1,24 q	3,12 s (N—CH_3)
IIaE	d_6-DMSO /$(C_2H_5)_3N$	—	—	—	3,98	1,15	3,02 s (N—CH_3)
IIb	$CDCl_3$	—	11,68 br.s	—	4,30	1,35	3,34 s (N—CH_3)
IIb	d_6-DMSO	—	11,62 br.s	—	4,20	1,24	3,10 s (N—CH_3)
IIbE	d_6-DMSO /$(C_2H_5)_3N$	—	11,45 br.s	—	4,05	1,20	3,05 s (N—CH_3)
IIc	$CDCl_3$	—	12,36 br.s (2pu)	—	4,26	1,33	—
			8,68 br.s (2pu)		4,17	1,24	—
IId	d_6-DMSO	—	11,75 br.s 11,45 br.s	—	4,21	1,24	—
IIdE	d_6-DMSO /$(C_2H_5)_3N$	—	11,30 br.s 10,25 br.s	—	4,06	1,20	—
IIIa	$CDCl_3$	5,78 q	—	4,04	4,20	1,29	2,47 d (CH_3)
IIIb	$CDCl_3$	5,98 t	—	4,05	—	—	2,33, 2.55 s ($C_{(2')}$—CH_2, $C_{(4')}$—CH_2), 1,16 s ($C_{(3')}$—CH_3)

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*For IIIa, $^4J_{H,CH_3}$ = 1 Hz; for IIIb, $^4J_{H,CH_2}$ = 1.3 Hz.

coincidence of $^1J_{CH}$ in $CDCl_3$ and d_6-DMSO makes it possible to assert that the relative concentration of all the potentially tautomeric (IaB, IaC, IaD) or ionic (IaE) forms that could participate in rapid exchange with the CH form does not exceed 1%.

Evidence for the CH structure of Ia is also provided by its ^{14}N NMR spectrum, in which one observes a signal at −157 ppm, which corresponds to the nitrogen atoms of the aromatic triazine ring, which have close chemical shifts. This value is in good agreement with the chemical shift of the nitrogen atom in triazine (−100 ppm) and with the effect of two methoxy groups, which shift the signal 20-30 ppm to strong field [5].

The IR spectra of crystalline Ia [suspension in mineral oil: 1740 (CO), 1558 cm^{-1} (CN)] and of solutions of Ia (in $CHCl_3$: 1740, 1560 cm^{-1}; in DMSO; 1742, 1560 cm^{-1}) are also in agreement with the CH structure of Ia. Bands of OH or NH groups are absent in the high-frequency region of the spectrum. The UV spectra of Ia (Table 3) in nonpolar solvents are similar to the spectra of 2-chloro-4,6-dimethoxy-sym-triazine (IIIc); this is in agreement with the CH form of Ia. However, a band at 310-317 nm, the intensity of which depends markedly on the solvent and the concentration of the solution, appears in the spectra of Ia in polar solvents. This band is especially intense in the presence of strong bases; this makes it possible to assign it to the ionized form of Ia, i.e., to IaE.

TABLE 2. ^{13}C Chemical Shifts in Ia-d, IIb, c, and IIIa, b (δ, ppm)

Compound	Solvent	$C_{(6)}$	$C_{(4)}$	$C_{(2)}$	OCH_3	Protons of groups
Ia	$CDCl_3$	172,4	172,4	174,4	55,4	61,1 ($C_{(\alpha)}$); 165,1 (CO); 62,1 (CH_2); 14,0 (CH_3)
Ia	d_6-DMSO	171,8	171,8	174,1	55,3	60,3 ($C_{(\alpha)}$); 164,9 (CO); 61,6 (CH_2); 13,8 (CH_3)
IaE	d_6-DMSO /NaOH	169,8	169,8	171,3	53,1	87,2 ($C_{(\alpha)}$); 168,4 (CO); 57,6 (CH_2); 14,7 (CH_3)
IbA	d_6-DMSO	170,8	168,2	172,2	54,2	60,6 ($C_{(\alpha)}$); 165,7 (CO); 61,5 (CH_2); 13,9 (CH_3)
IbB		158,0	169,3	158,3	54,1	85,5 ($C_{(\alpha)}$); 167,4 (CO); 59,2 (CH_2); 14,3 (CH_3)
IbE	d_6-DMSO /NaOH	169,1	167,5	172,6	52,1	85,1 ($C_{(\alpha)}$); 169,0 (CO); 57,5 (CH_2); 14,8 (CH_3)
Ic	$CDCl_3$	168,7	161,7	163,5	56,5 56,6	68,3 ($C_{(\alpha)}$); 168,5 (CO); 61,1 (CH_2); 14,3 (CH_3); 115,9 (CN)
Ic	d_6-DMSO /HCl	169,0	162.0	164,1	56,9 56,2	65,9 ($C_{(\alpha)}$); 168,8 (CO); 60,6 (CH_2); 14,2 (CH_3); 116,6 (CN)
IcE	d_6-DMSO /$(C_2H_5)_3N$, 5:1	166,2	166,2	175,3	53,2	65,6 ($C_{(\alpha)}$); 170,5 (CO); 57,0 (CH_2); 14,9 (CH_3); 123,6 (CN)
Id	d_6-DMSO	162,3	162,3	172,4	55,9	49,8 ($C_{(\alpha)}$); 117,1 (CN)
IdE	d_6-DMSO /$(C_2H_5)_3N$, 5:1	171,8	171,8	178,5	55,4	49,4 ($C_{(\alpha)}$); 122,9 (CN)
IIb	d_6-DMSO	146,6	148,0	154,7		59,8 ($C_{(\alpha)}$); 167,4 (CO); 60,9 (CH_2); 14,0 (CH_3); 114, 3 (CN); 27,4 ($N_{(5)}$—CH_3)
IIc	$CDCl_3$	146,5	146,5	154,2		80,5 ($C_{(\alpha)}$); 168,4 (CO); 61,3 (CH_2); 14,0 (CH_3)
IIc	d_6-DMSO	147,2	147,2	154,5		78,5 ($C_{(\alpha)}$); 167,9 (CO); 60,6 (CH_2); 14,0 (CH_3)
IIcE	d_6-DMSO /NaOH	157,2 br	157,2 br	160,9		79 ($C_{(\alpha)}$); 168,7 (CO); 58,5 (CH_2); 14,5 (CH_3)
IIIa	$CDCl_3$	173,6	173,6	171,6	55,5	164,1 ($C_{(2')}$); 110,1 ($C_{(1')}$); 165,6 (CO); 60,2 (CH_2); 14,2 (CH_3); 17,9 ($C_{(3')}$)
IIIb	$CDCl_3$	173,6	173,6	171,2	55,6	168,6 ($C_{(1')}$); 116,3 ($C_{(6')}$); 198,7 ($C_{(5')}$); 41,8; 50,8 ($C_{(2')}$; $C_{(4')}$); 33,5 ($C_{(3')}$); 28,2 (CH_3)

TABLE 3. UV Spectra of Ia-d and IIIc

Compound	Solvent	λ_{max}, nm (lg ε)*
Ia	Dioxane	240 (3,52); 295—300 (2,7) sh
	DMF	[$1\cdot10^{-3}$] 317 (2,87); [$2\cdot10^{-4}$] 317 (3,12)
	DMSO	[$1,8\cdot10^{-3}$] 317 (3,37); [$1,8\cdot10^{-4}$] 317 (3,83)
	DMSO + $(C_2H_5)_3N$ †	317 (4,45)
	DMSO + 1N. KOH †	312 (4,54)
Ib	Dioxane	307 (2,65)
	$CHCl_3$	306 (2,72)
	C_2H_5OH	306 (3,38)
	DMSO	313 (3,92)
Ic	$CHCl_3$	305 (4,34)
	DMF	306 (4,59)
Id	C_2H_5OH	297 (4,57)
	DMSO	300 (4,54)
IIIc	Dioxane	237 (3,09); 295—300 (2,04)

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*The molar concentration of Ia in solution is indicated in brackets.

†In a ratio of 100:1 by volume.

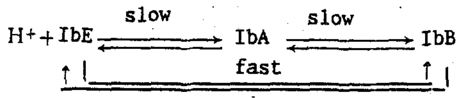
The acidic properties of Ia are also manifested in relatively fast deuterium exchange of the CH proton of the malonic residue in d_6-DMSO + CD_3OD (after <1 min) and in the exchange of this proton with the protons of the admixed H_2O in d_6-DMSO (1:500) at a rate of ~1 sec^{-1} (estimated by the method of saturation transfer [6]). The rate of proton exchange increases in the presence of triethylamine. A second set of signals, the intensity of which increases with an increase in the concentration of alkali, appears in the NMR spectra when NaOH is added to a solution of Ia in d_6-DMSO; the intensity of the signals of the CH form decreases in this case. A signal of the CH proton of the malonic residue is absent in the ^1H NMR spectra of such alkaline solutions for the second form, and in the ^{13}C NMR spectra recorded without proton decoupling the signal of the $C_{(\alpha)}$ carbon of the malonic residue of this form is a singlet that is shifted 27 ppm to weak field relative to the corresponding signal of the CH form of IaA. All of the signals in the ^{1}H and ^{13}C NMR spectra that correspond to the second form are identical to the signals of the spectrum of the sodium salt of Ia, which was previously isolated [2]. The data presented above make it possible to assign the second set of signals in the NMR spectra of alkaline solutions of Ia to ionized form IaE. Similar signals of the IaA and IaE forms – broad singlets of protons of the OCH_3 group – can be observed in the ^{1}H NMR spectrum of Ia in thoroughly dried d_6-DMSO in the presence of excess triethylamine.

Additional data on the acidity of Ia-d were obtained by comparison of the chemical shifts of the protons in the components of ternary mixtures – the sym-triazinyl derivative, a substituted phenol, and triethylamine. Thus the addition to a mixture of triethylamine with o-nitrophenol of an equimolar amount (with respect to o-nitrophenol) of Ia causes a 25% decrease in the degree of ionization of o-nitrophenol. Hence it may be concluded that Ia is an acid that is 0.5 of a pK_a unit weaker than o-nitrophenol, for which the pK_a in water is 7.2, as compared with 11 in DMSO [7, 8]. A pK_a value of 11 was obtained for Ia by potentiometric titration in DMSO. This indicates the validity of the assignment of the band at 310-317 nm in the UV spectra of Ia in polar solvents to ionized form IaE. An analysis of the concentration of the ionized form is high only in dilute solutions that are virtually inaccessible for study by means of NMR and IR spectra.

The properties of 2-(dicarbethoxymethyl)-4-amino-6-methoxy-sym-triazine (Ib) are similar in many respects to the properties of Ia. According to the data from the ^{1}H and ^{13}C NMR spectra, Ib exists in the CH form in $CDCl_3$. The same form is the preferred form, although not the only form, in d_6-DMSO. Two sets of signals with an intensity ratio of 7:1 are observed in the ^{1}H NMR spectrum of Ib in d_6-DMSO; a broad singlet at 11.95 ppm is present among the signals of the minor form. It was observed that δ values close to the indicated value are characteristic for NH protons that participate in an intramolecular hydrogen bond, in "enamine" forms of some sym-triazinyl ethers [10] and $N_{(5)}$-substituted IIa (see below). On the basis of this it can be concluded that in d_6-DMSO Ib exists in the form of an equilibrium mixture of tautomeric forms IbA $\rightleftarrows$ IbB in a ratio of 7:1; the NH proton of the IbB form participates in an intramolecular hydrogen bond. Data from the ^{13}C NMR spectra are in agreement with this conclusion; in these spectra the signals of two carbon atoms of minor form IbB are shifted by more than 10 ppm to strong field relative to the signals of CH form IbA; this constitutes evidence for disruption of the aromatic character of the sym-triazine ring. This sort of strong-field shift, which is evidently due to adjacency of the NH group, is absent in the ^{13}C NMR spectra of anion IbE (see below) and seems incompatible with structure IbD. The IR spectrum of Ib in CCl_4 [1735 (CO) and 3548, 3430 cm^{-1} (NH)] is in agreement with the conclusion that CH form IbA predominates in nonpolar solvents. At the same time, the presence of three bands at 1600-1800 cm^{-1} [a narrow band at 1748 cm^{-1} (CO) and broad bands at 1715 and 1669 cm^{-1} (CO)] is characteristic for the spectra in the crystalline state. The first of these bands coincides in frequency with the band for Ia and can be assigned to the CH form of Ib. The other two are evidently due to the presence of form IbB and may correspond to the CO band of ester groups attached to an unsaturated carbon atom; one of them (1669 cm^{-1}) participates in an intramolecular hydrogen bond, while the other (1715 cm^{-1}) does not [10]. (It might be assumed that the absorption band corresponding to NH_2 is located at 1660 cm^{-1} and that this is responsible for the greatest width of the band at 1669 cm^{-1}.)

The UV spectra of Ib depend on the polarity of the solvent. The intensity of the long-wave band is low in dioxane and chloroform, increases in ethanol, and is highest in DMSO. This is in agreement with the data presented above regarding the existence of only CH form IbA in nonpolar media and the presence of an appreciable amount of the NH form in the case of high polarity of the medium.

Like Ia, Ib displays acidic properties. As before, when NaOH is added to solutions of Ib in d_6-DMSO, in the ^{1}H and ^{13}C NMR spectra one observes two sets of signals, one of which contains the signal of a $C_{(\alpha)}H$ group, the other of which does not contain it. However, the ratio of the intensities of the signals of identical groups and the position of the signals in the set that does not contain the $C_{(\alpha)}H$ group are different than in neutral DMSO and depend on the ratio of the molar concentrations of Ib and NaOH. This is explained by the existence of an equilibrium between three forms, exchange between which proceeds at different rates:



In the NMR spectra one of the sets of signals corresponds to CH form IbA, while the other corresponds to the averaged signals of the rapidly interconverted anion IbE and NH form IbB. The addition of Ia to a solution containing anion IbE leads to ionization of Ia and conversion of an equimolar amount of anion Ib to the neutral form (the accuracy determined by the ^{1}H NMR method is no less than 3%). Consequently, derivative Ib is a weaker acid (by 1.5 or more pK_a units) than Ia. The ionization of Ib in neutral DMSO can therefore be appreciable (and be manifested in the UV spectra) only at concentrations that are substantially lower than in the case of Ia. In an acidic medium [DMSO + an 11 N solution of HCl in D_2O (10:1)] Ib is 30% protonated; this constitutes evidence for its relatively high basicity. The protonation of Ia under similar conditions could not be detected.

A single set of signals in each case is observed in the ^{1}H NMR and ^{13}C NMR spectra of 2-(carbethoxycyanomethylene)-4,6-dimethoxy-1,2-dihydro-sym-triazine (Ic) in both $CDCl_3$ and d_6-DMSO; a signal at 12.8 ($CDCl_3$) to 12.5 ppm (d_6-DMSO), which, on the basis of the information stated above, is related to the NH proton tied up in a hydrogen bond, is present in the ^{1}H NMR spectra. Thus, in contrast to derivatives Ia, b, Ic exists exclusively in the "enamine" NH form IcB.* A peculiarity of the NMR spectra of Ic is the nonequivalence of the signals of the carbon atoms in the 4 and 6 positions, as well as the carbon atoms and the protons of the methoxy groups in these positions; this is apparently due to the absence of free rotation relative to the $C_{(2)}=C_\alpha$ bond. Coalescence of the signals of the OCH_3 group occurs in the presence of triethylamine; this indicates facilitation of rotation relative to the $C_{(2)}=C_\alpha$ bond as a consequence of ionization. Compound Ic is a stronger acid than Ia, b. By means of the method examined above it was shown that Ic is a weaker acid by 0.5 of a pK_a unit than 2,4-dinitrophenol, the pK_a of which ≈4 (in H_2O) [11] and 5.2 (in DMSO) [8]. In the ^{14}N NMR spectrum of Ic one observes a broad signal at −260 ppm, i.e., at significantly stronger field than in the corresponding (NH—)-tautomeric form of the cyanoactic pyridine or pyrimidine derivative (∼−220 ppm) [12]. The broadening of the signal and its strong-field shift are evidently associated with the specific effects of the triazine ring. In particular, because of an increase in the acidity of the NH group and strengthening of the intramolecular hydrogen bond the polarization of the NH bond may be intensified (as compared with the pyrimidine derivatives) in the direction $\rangle N^- \ldots H^+$. It is known that an increase in the ionic character of the bond may lead to a strong-field shift of the signal [5].

Two bands at 1620 ($\nu_{C\equiv N}$) and 1655 cm^{-1} ($\nu_{C=O}$, having a hydrogen bond of the ester group attached to a double bond) are observed in the IR spectrum of Ic in $CHCl_3$ at 1600-1800 cm^{-1}. In the spectrum of this compound in the crystalline state these bands merge into a broad band with a maximum at 1623-1630 cm^{-1}.

A single absorption band, the intensity of which is minimal in $CHCl_3$ and maximal in DMF, is observed in the UV spectra of Ic in all solvents; this is explained by strong ionization of Ic in polar solvents (DMSO and DMF).

In the ^{1}H NMR spectrum of 2-(dicyanomethylene)-4,6-dimethoxy-1,4-dihydro-sym-triazine (Id) the signal of the proton of the malodinitrile residue is not observed separately from the signal of the admixed water in d_6-DMSO (the compound is insoluble in less polar aprotic solvents). According to the ^{13}C NMR spectra, in particular the significant strong-field shift of the signals of the $C_{(4)}$ and $C_{(6)}$ atoms [and, to a lesser extent, the $C_{(2)}$ atom], relative to the corresponding values for anion IdE, the triazine ring in Id is nonaromatic; the preferred tautomeric form is IdC. A marked dependence of the chemical shifts of the protons of the OCH_3 group on the concentration is observed for solutions of Id in d_6-DMSO over the concentration range 10^{-1} to $3 \cdot 10^{-4}$ M; this is evidently explained by the different degree of dissociation of this compound into ions. It was demonstrated by the method of ternary mixtures that, with respect to its acidity, Id occupies an intermediate position between 2,4-dinitrophenol (see above) and picric acid (pK_a 0.4 in H_2O [11] and 0.3 in DMSO [8]).

A single absorption band, which probably corresponds to ionized form IdE, is present in the UV spectra of Id above 215 nm.

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*We were unable to detect the presence of a CH form by NMR spectroscopy even in a solvent that was less polar than $CDCl_3$, viz., C_6D_{12} + $CDCl_3$ (10:1); however, see [13].

TABLE 4. pK_a Values of Some CH Acids and Their sym-Triazinyl Derivatives Obtained by ^1H NMR Spectroscopy Using the Acidities of Phenols in DMSO [8]

Compound	pK_a	Compound	pK_a	Compound	pK_a
$CH_2(COOC_2H_5)_2$*	13,3 [15]	$CH_2(CN)COOC_2H_5$*	9 [16]	$CH_2(CN)_2$*	11,2 [15]
Ia†	11,5	Ic†	5,5	Id†	3

*In H_2O.
†In DMSO. A pK_a value of 3.8 was obtained for Id by potentiometric titration in DMSO.

Several conclusions regarding the structures and properties of sym-triazinyl derivatives of CH acids can be drawn on the basis of the spectral data. From the closeness of the chemical shifts of the carbon atoms of the triazine ring in CH forms A and anions E of Ia, b one may conclude that there is relatively little perturbation of the electron structure of the triazine ring in the case of detachment of a proton from the residue of the CH acid on which the negative charge in the anion is evidently localized.* On the other hand, an appreciable difference, which is particularly great for the carbon atoms adjacent to the NH group, is observed between the chemical shifts of identical carbon atoms in the NH forms and anions of Ib-d. These changes on passing from the anion to the NH form are similar in sign and magnitude to the change in the chemical shift of the α-carbon atoms of the pyridine ring when it is protonated ($\Delta\delta = -7.8$ ppm) [14].

The differences between the chemical shifts of the carbon atoms of the residue of the CH acid [particularly $C_{(\alpha)}$] in the NH form and the anion are extremely slight. On the basis of this it may be concluded that the NH form is characterized by significant localization of the charges – the negative on the residue of the CH acid and the positive on the heteroring, i.e., with respect to electron structure it is similar to a dipolar ion. The sharp increase in the percentage of form IbB in the equilibrium IbA $\rightleftarrows$ IbB with an increase in the polarity of the solvent is in agreement with this conclusion.

In addition, the closeness of the λ_{max} and log ε values of the long-wave bands in the UV spectra of NH forms B and anions E indicates the relative similarity in the π-electron structures of these forms.†

An analysis of the data (Table 2) indicates the virtually complete independence of the chemical shifts of the carbon atoms in Ic on the solvent. This makes it possible to consider the possibility of a rapid equilibrium between the NH form and an appreciable amount of the enol form (type D) in DMSO to be unlikely. The conclusion drawn in [9] that an enol form (type D) is present was evidently based on an incorrect experimental procedure (deuterium exchange of a proton of the residue of the CH acid due to the admixed D_2O in the d_6-DMSO solvent is possible).

An increase in the basicity of the heteroring nitrogen atoms due to the introduction of an electron-donor substituent (Ia, b) shifts the tautomeric equilibrium of the sym-triazinyl derivative to favor the NH form.

Replacement of one of the methylene protons of the starting CH acid by a sym-triazinyl residue leads to substantially stronger acids as a consequence of the strong electron-acceptor effect of this substituent (Table 4).

We have previously studied some reactions of Ia and Ic [2, 4]; in particular, we isolated products of saponification of one of the methoxy groups. The compounds obtained were characterized as derivatives of 4-oxo-6-methoxy-1,2,3,4-tetrahydro-sym-triazine. However, a study of the structures of these products by means of their ^1H and ^{13}C NMR spectra showed that they are, respectively, 2-dicarbethoxymethylene (IIa) and 2-cyanocarbethoxymethylene (IIb) derivatives of 5-N-methyl-4,6-dioxohexahydro-sym-triazine. Evidence for this is pro-

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*The significant weak-field shift of the $C_{(\alpha)}$ atom relative to the CH form is due to a change in the hybridization of this atom.
†Disruption of the conjugation between the triazine ring and the residue of the CH acid in forms A leads to substantial differences in the UV spectra.

vided by the presence in their ^1H NMR spectra of a singlet of protons of the $>N-CH_3$ group at 3.3 ppm — at stronger field (by 0.6 ppm) than the signal of the protons of the methoxy groups in Ia-d. The signal at 27.4 ppm [at stronger field (by 25 ppm) than the signal of the carbon atom of the methoxy group in Ia-d] in the ^{13}C NMR spectrum corresponds to the carbon atom of the $N_{(5)}-CH_3$ group in IIb. The presence in the ^1H NMR spectrum of IIa of a lone signal at 12.35 ppm of NH groups with an intensity of 2 proton units (pu) constitutes evidence for symmetry of the molecule, i.e., the presence of a methyl group attached to the $N_{(5)}$ atom of the triazine ring. Compounds IIa, b are acids and undergo ionization in solutions that contain bases, as evidenced by the appreciable strong-field shift of the signals of the protons of the CH_2 and CH_3 groups in d_6-DMSO when $(C_2H_5)_3N$ is added. Similar changes in the chemical shifts are observed for IIc, d, which were described in [17, 18].

We have previously noted that the reaction of 2-chloro-4,6-dimethoxy-sym-triazine (IIId) with the sodium derivative of acetoacetic ester proceeds ambiguously [3]. The only product isolated was characterized as 2-carbethoxyacetylmethylene-4,6-dimethoxy-sym-triazine. A study of this compound by ^1H and ^{13}C NMR spectroscopy revealed a number of contradictions with the structure proposed for it. Thus the addition of $(C_2H_5)_3N$ and NaOH to solutions of it in d_6-DMSO had virtually no effect on the chemical shifts of the protons of the ethyl and methoxy groups, and the compound obtained consequently was not an acid; the CH proton of the ethyl acetoacetate residue did not undergo exchange with labile deuterons in either acidic or alkaline media; the signal of the corresponding carbon atom was observed at considerably weaker field (at 110.1 ppm) as compared with the expected value, while the signal of the carbon atom of the CO group of a ketone was completely absent. This indicated the incorrectness of the previously proposed structure and provided a basis for the conclusion that the product isolated was 2-(1'-carbethoxy-1'-propen-2'-yloxy)-4,6-dimethoxy-sym-triazine (IIIa). A similar derivative — 2-(3'-3'-dimethyl-5'-oxo-6'-cyclohexen-1'-yloxyl-4,6-dimethoxy-sym-triazine (IIIb) — was obtained by the reaction of dimedone with IIIc.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded with a Varian XL-200 (200 MHz) spectrometer at 200 MHz for the ^1H nuclei and at 50.3 MHz for the ^{13} nuclei; the solvents are indicated in the tables. The internal standard for solutions in $CDCl_3$ was tetramethylsilane (TMS) ($\delta_{1H} = \delta_{13C} = 0$); for solutions in d_6-DMSO as one of the components the internal standard for the ^{13}C NMR spectra was the signal of d_6-DMSO ($\delta_{13C} = 39.6$), while the internal standard for the ^1H NMR spectra was the signal of the admixed proton-containing DMSO [$CHD_2S(O)CD_3$] in the solvent ($\delta_{1H} = 2.50$). The ^{14}N NMR spectra were recorded with a Bruker CXP-3000 spectrometer (21.68 MHz) at 10-15% concentrations in $CHCl_3$ and 25°C. The chemical shifts are presented relative to CH_3NO_2 as the external standard. Negative signs correspond to a strong-field shift relative to the standard. The UV spectra were recorded with Hitache ESP-2 and Perkin—Elmer 575 spectrophotometers. The IR spectra were recorded with Perkin-Elmer 457 spectrometer. Solutions or mineral oil suspensions were used in IR spectroscopy.

2,(3'3'-Dimethyl-5'-oxo-6'-cyclohexene-1'-yloxy)-4,6-dimethoxy-sym-triazine (IIIb). A 3.5-g (25 mmole) sample of dimedone was added in a stream of argon to a suspension of 0.62 g (25 mmole) of sodium hydride in 30 ml of DMF. After hydrogen evolution was complete, the mixture was maintained at 20°C for 30 min. A 2.93-g (16.7 mmole) sample of 2-chloro-4,6-dimethoxy-sym-triazine (IIIc) was then added, and the course of the reaction was monitored by TLC on Silufol UV-254 [R_f 0.56; benzene—ethyl acetate (1:1)]. The reaction mass was maintained at room temperature for 24 h, after which the solvent was removed. The residue was triturated with ether (two 50-ml portions) and absolute ethanol (two 50-ml portions), and the ether and alcohol solutions were combined and evaporated. The residue was applied to a column packed with 250 g of Chemapol silica gel (40/160 μm). The reaction product was eluted with benzene—ethyl acetate (6:1). The yield was 2.62 g (56%). Mass spectrum, m/z: 279 (M^+), 264 ($M^+ - CH_3$), 251 ($M^+ - CO$), and 195 ($M^+ - CO-CH_2-C-CH_3-CH_3$). The colorless crystals, which were soluble in organic solvents, had mp 98-100°C (from heptane). Found: C 55.9; H 6.2; N 15.3%. $C_{13}H_{17}N_3O_4$. Calculated: C 55.9; H 6.1; N 15.4%.

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STABILIZATION OF POLYHETEROATOMIC AZA AND PHOSPHA ANALOGS OF CYCLOBUTADIENE AND BENZENE

M. N. Glukhovtsev, B. Ya. Simkin,
and V. I. Minkin

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A method is proposed for the stabilization of polyheteroatomic rings consisting only of nitrogen or phosphorus atoms by introduction of acceptors of the unshared electron pair of the heteroatom, particularly oxygen atoms, with the formation of oxide forms. The positions of introduction of the acceptor groups into four- and six-membered rings were determined. The conclusions drawn were confirmed by calculations by the MNDO method of tetrazete 1,3-dioxide and 1,3-ylid and hexaphosphorine 1,3,5-trioxide and 1,3,5-ylid.

An aromatic cyclic conjugated system in which the ring is formed by different heteroatoms may be stable. Borazine is a characteristic example [1, 2]. However, conjugated rings formed by heteroatoms of the same element are unstable [3, 4], and the possibility of their experimental detection frequently raises doubts.

The polyheteroatomic aza and phospha analogs of cyclobutadiene and benzene have π-electron systems that are similar to the π systems of cyclobutadiene $(CH)_4$ and benzene $(CH)_6$. Nevertheless, despite the closeness of the π-electron energies of the resonance of hexazine N_6 (I) and benzene $(CH)_6$ (II) [5], hexazine is exceptionally unstable, and doubts regarding its synthesis [6] were raised on the basis of the results of nonempirical calculations, which indicate the considerably higher (as compared with hexazine) stability of the acyclic N_6 structure [7, 8] (also see [5] and the literature cited therein). It is assumed that the experimental detection of tetrazete N_4 (III) [9] and the pentazole anion N_5^- (IV) [10, 11] is realizable only in the form of organometallic complexes. Nonempirical calculations [12], according to which the activation barrier of its cyclodecomposition to three P_2 molecules is 54 kJ/mole, provide evidence for the possibility of the experimental detection of hexaphosphorine P_6 (V) in an inert matrix at low temperatures.

Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rostov State University, Rostov-on-Don 344071. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 250-255, February, 1988. Original article submitted August 19, 1986.

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