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SPECIAL FEATURES OF THE STRUCTURE OF SOME SALTS OF TRIAZOLE BASES

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The structure of salts formed from nitroform and a number of 4-amino-1, 2, 4-triazole bases has been investigated. It was found that some of the salts contain two molecules of triazole base and one of nitroform. From IR spectra it is inferred that the salts contain the nitroform anion, and a proton bound to one of two triazole rings, the amino groups not participating in salt-formation. Formation of 2:1 salts of nitrogen bases is observed for the first time.

Recently the literature has recorded cases where salt formation has involved two molecules of base and one molecule of a monobasic acid. Thus a number of 2:1 salts between N-tert-butylacetamide and hydrohalogen acids have been prepared [1, 2]. There are antipyrine (2, 3-dimethyl-1-phenyl-5-pyrazolone) salts derived from $HAsF_6$ and $HSbF_6$ containing 2 molecules of base per molecule of acid [3]. N-oxides of pyridine, picoline, xylidine, quinoline, and acridine [4–7], also give 2:1 salts with $HSbF_6$, $HAsF_6$, and $HClO_4$.

From the IR spectra and X-ray analysis data, the authors of these papers [2–7] conclude that salt formation involves formation of short hydrogen bonds (~ 2.5 Å) with the oxygen of the base $(RO\ldots H\ldots OR)^+\ MeF_6^-$.

We have now investigated salts of nitroform with a number of 4-amino-1, 2, 4-triazoles, and found that some of the salts consist of two molecules of triazole base and one molecule of nitroform. This is the first case of formation of that kind of salt from nitrogen bases not containing oxygen.

As the free 4-amino-1, 2, 4-triazoles and their salts with nitroform were rather hygroscopic, steps were taken to protect them from the moisture of the air during preparation, and when measuring the spectra.

Information about the composition of the salts was obtained from elementary analysis data, gravimetric determination of nitroform with nitrone [8], and determination of the molecular weights of the salts using the UV spectra. The analytical results are given in Table 1.

UV spectra were determined in highly dilute aqueous solution. The 4-amino-1, 2, 4-triazoles themselves absorb very feebly (ε 10–1) and nonselectively in the 220–400 mμ region, while the nitroform anion gives an absorption band with λ_{max} 350 mμ, and molar extinction coefficient ε 14800, so that the molecular weight can be determined spectroscopically. The molecular weight was calculated from the formula $M=\frac{\varepsilon\cdot c\cdot l}{D}$, where D is the optical density of the salt under investigation, c is its concentration (g/l), and l the cell length (cm).

As can be seen from Table 1, the nitroform salts of 4-amino-1, 2, 4-triazole and its 3, 5-dimethyl and 3, 5-dihydroxmethyl derivatives comprise two molecules of triazole base and one of nitroform, while the nitroform salts of 3, 5-diethyl, 3, 5-di-n-propyl, 3, 5-α, α'-dihydroxyethyl, and 3, 5-β, β'-dihydroxyethyl-4-amino-1, 2, 4-triazoles are 1:1 compounds. Possibly the decrease in the molar base-acid ratio from 2:1 to 1:1 is connected with steric factors.

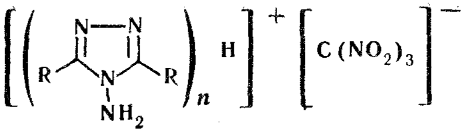
Study of IR spectra showed that the nitroform salts of 4-amino-1, 2, 4-triazoles have an ionic structure in the solid state. The nitroform is present as an anion. This structure is confirmed by the spectra of the salts exhibiting absorption bands characteristic of the trinitromethyl anion (cf. the potassium salt of nitroform which is known to have an ionic structure), and absence of absorption bands in regions characteristic of N—O valence vibrations in the unionized trinitromethyl group (~ 1600 and ~ 1300 cm^{-1}) (cf. nitroform, with a trinitromethyl group of covalent structure). Table 2 gives the experimental data.

Salt formation involving two molecules of 4-amino-1, 2, 4-triazole to one molecule of nitroform is rather unexpected and interesting. Up to the present, the reasons for this peculiar behavior of 4-amino-1, 2, 4-triazoles is unclear. This laboratory is now trying to clear up the fine structure of the salts by other independent physicochemical methods.

Otting [9] previously observed association of 1, 2, 4-triazoles unsubstituted at position 4. From the IR spectra he concluded that 1, 2, 4-triazoles not substituted at position 4 have a so-called ionogenic structure both in the solid state, and in non-polar solvents. This implies that the imino hydrogen of one molecule, in the form of a proton, links to the

Table 1

Nitroform Salts of 4-Amino-1, 2, 4-triazoles



R	n	Mp °C	Found						Calculated				
			C, %	H, %	N, %	Content of nitro-form, %	M	Empirical formula	C, %	H, %	N, %	Content of nitro-form, %	M
H	2	94.5— 95	19.02 18.90	3.10 3.08	48.55 48.43	47.24	330	$C_5H_9N_{11}O_6$	18.89	2.82	48.28	47.32	319
CH_3	2	136.5—137	28.64 28.69	4.79 4.76	41.72 41.73	41.05	388	$C_9H_{17}N_{11}O_6$	28.82	4.54	41.07	40.23	375
C_2H_5	1	72 — 73	29.14 29.35	4.57 4.58	33.63 33.68	52.20 51.53	303	$C_7H_{13}N_7O_6$	28.86	4.47	33.67	51.8	291
n-C_3H_7	1	—	—	—	—	47.10	—	$C_9H_{17}N_7O_6$	—	—	—	47.33	319
$HOCH_2$	2	99 —100	25.30 25.29	4.07 4.04	35.63 35.57	34.77	—	$C_9H_{17}N_{11}O_{10}$	24.60	3.87	35.08	34.39	439
$HOCH_2CH_2$	1	126 —127	26.60 26.51	4.33 4.39	30.60 30.41	46.62	—	$C_7H_{13}N_7O_8$	26.01	4.03	30.34	46.79	323
$CH_3CH(OH)$	1	129 —130	26.79 26.83	4.29 4.09	30.24 30.31	46.95	—	$C_7H_{13}N_7O_8$	26.01	4.03	30.34	46.79	323

Table 2

Absorption Bands of Nitroform Salts of 4-Amino-1, 2, 4-triazoles in Regions Characteristic of Nitroform and its Anion

Compound	Absorption bands $C(NO_2)_3$, cm^{-1}		Absorption bands of the anion $[C(NO_2)_3]^-$, cm^{-1}
	Antisymm ~ 1600	Symm ~ 1300	
Nitroform salt of 4-amino-1, 2, 4-triazole	None	None	1510s, 1290s, 1188 s } d 1170 s
Nitroform salt of 3, 5-dimethyl-4-amino-1, 2, 4-triazole	None	None	1495s, 1255s. w. 1165s } d 1152 s
Nitroform salt of 3, 5-diethyl-4-amino-1, 2, 4-triazole	None	None	1487s, 1290 vs.w. 1175s } d 1160s
K salt of nitroform	None	None	1520s, 1283s, 1182s
Nitroform	1605 s	1305 s	None None None

vs—very strong, s—strong, w—wide, d—doublet

Table 3

Some Absorption Bands in the IR Spectra of 4-Amino-1, 2, 4-triazoles and their Nitroform Salts (cm^{-1})

Compound	N—H valence vibrations		Absorption bands characteristic of ionogenic structures	
	Antisymm	Symm		
4-Amino-1, 2, 4-triazoles	3330m	3221 m } d 3280 m	None	None
Nitroform salt of 4-amino-1, 2, 4-triazole	3333 m	3265 m	2015 vs,w	2500 vs,w
3, 5-Dimethyl-4-amino-1, 2, 4-triazole	3250m	3154m	None	None
Nitroform salt of 3, 5-dimethyl-4-amino-1, 2, 4-triazole	3337m	3187m	1960 s, w	2400 vs,w
3, 5-Et_2-4-NH_2-1, 2, 4-triazole	3250m	3145m	None	None
Nitroform salt of 3, 5-Et_2-4-NH_2-1, 2, 4-triazole	3348m	3195 m, w	1944m	2552 m

vs—very strong, s—strong, m—medium, w—wide, d—doublet pyridine nitrogen of the other:

Formation of such a structure is accompanied by the appearance of two bands characteristic of the imino group $\gg\overset{+}{N}-H$: at about 1800 cm^{-1} with a wide band at 2500–2850 cm^{-1} [10].

The 4-amino-1,2,4-triazoles which we have investigated lack absorption bands in the solid state at 1800 cm^{-1} and 2500–2850 cm^{-1}. So, judging by their spectra, they do not have the ionogenic structure. Apparently, this is connected with the considerable decrease in mobility of the hydrogen atom in the amino group of 4-amino-1,2,4-triazoles, as compared with the hydrogen atom at position 4 in 1,2,4-triazole.

The picture changes sharply as we move to the nitroform salts of 4-amino-1,2,4-triazoles. Nitroform has a very mobile hydrogen, and the IR spectra of the salts show absorption bands in the same regions as with the ionogenic structures (see Table 3). This can be taken to indicate that in those salts the proton interacts with the triazole ring.

IR spectra data in the N–H valence vibrations region are evidence against protonization at the amino group. Table 3 shows that the N–H valence vibrations absorption bands in the salts are somewhat higher than in the free 4-amino-1,2,4-triazoles, whereas salt formation involving the amino group should lead to lowering of these frequencies, and further, the ammonium group generally does not absorb above 3250 cm^{-1} [11,12].

So it follows, from the evidence considered, that in solid salts the proton interacts with the thiazole ring. The amino group does not participate in salt formation.

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