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Mendeleev Commun., 2020, **30**, 490–493

Mendeleev Communications

Perchlorylamino furazans and their salts: new high-energy-density materials with high sensitivity

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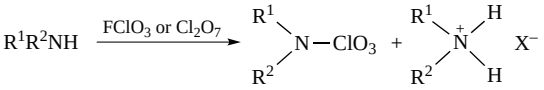
DOI: 10.1016/j.mencom.2020.07.028

The first perchlorylamino heterocycles, perchlorylamino-furazans, were obtained by the reaction of N-lithiated and N-silylated aminofurazans with $FClO_3$ or Cl_2O_7. Energetic salts comprising nitrogen-rich 1,2,4-triazol-based cations and 3-nitro-4-(perchlorylamino)furazan anion whose predicted explosive performance was close or superior to that of HMX were synthesized and characterized. Although the explosive output of perchlorylaminofurazan salts is better compared to relative nitraminofurazan ones, they would more readily degrade (explode!) upon impact, friction or heating.

Keywords: perchlorylamines, furazans, perchloryl fluoride, dichlorine heptoxide, explosives.

Nitric acid amide, nitramide (H_2NNO_2),[1] and its organic derivatives[2] have a rich history in the chemistry of energetic compounds, and their positive enthalpy of formation, high density, attractive oxygen contents, and stability make the nitramino group a prized key structural motif in the design of explosives and propellants ingredients.[3] In contrast, almost nothing is known on their analogues bearing N–ClO_3 moiety instead of N–NO_2 one. In 1956, Engelbrecht and Atzwanger synthesized the first known perchloric acid amide derivatives, ammonium, silver and barium salts.[4] Since then, only a few other similar salts have been obtained and studied.[5] The first example of organic perchloric acid amide, *N*-perchlorylpiperidine was described by Gardner in 1964.[6] Later, several *N*-perchloryl-alkylamines were synthesized by treating primary and secondary alkylamines with perchloryl fluoride ($FClO_3$)[7] and dichlorine heptoxide (Cl_2O_7)[8] (Scheme 1), although in some cases amines reacted in other ways.[9] Although the first perchlorylamines were documented more than half a century ago, less than 20 representatives of this type are known so far.



R^1, R^2 = H, Alk; X = F, ClO_4

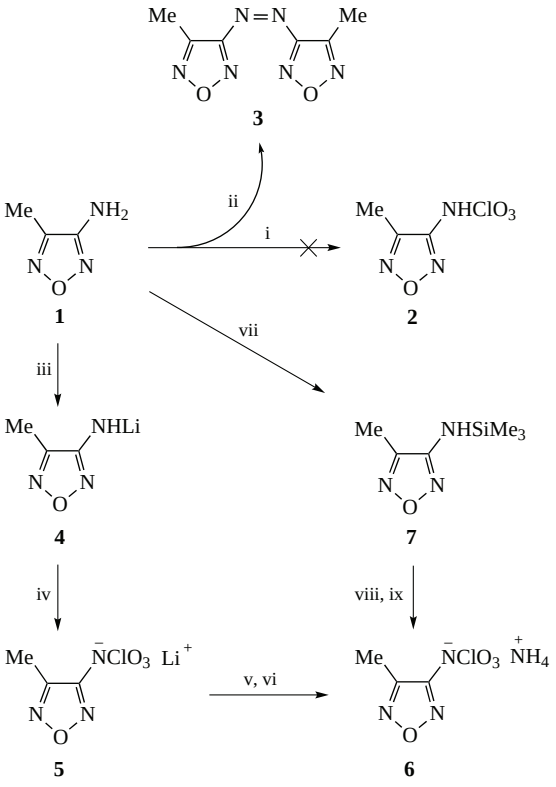
Scheme 1

The presence of N–ClO_3 moiety obviously increases the enthalpy of formation compared with similar nitramines, probably due to the relative weakness of the N–Cl and Cl–O bonds compared to the N–N and N–O one in N–NO_2. The same factors cause a decrease in the thermodynamic stability of perchlorylamines. Indeed, all *N*-perchlorylalkylamines described are highly explosive, shock and friction-sensitive compounds and should be handled with extreme care.[6,8(*a*),(*b*)] Inorganic perchlorylamide salts are sensitive to pulsed laser initiation, and their initiation threshold is lower than that of pressed $Pb(N_3)_2$ charges.[10]

The five-membered heterocyclic motif is in the top amongst modern energetic compounds.[11] Earlier, we synthesized energetic compounds incorporating both furazan ring and oxygen-rich nitramine group.[12] To the best of our knowledge, there are no reports describing the preparation of azoles bearing perchlorylamino group as an explosophore.

Herein, the first examples for the preparation of perchloryl-amino-substituted furazans are reported. In the beginning, we attempted direct N-perchlorination of 3-amino-4-methylfurazan **1** as a model precursor (Scheme 2) under typical for alkylamines conditions using $FClO_3$ (excess of $FClO_3$, H_2O or EtOH or Et_2O, 20 °C). However, under conditions tested only the starting material was recovered. Reactions of compound **1** with Cl_2O_7 (CCl_4, 0 °C) also failed to give the desired 3-(perchlorylamino)furazan **2** yielding 4,4′-dimethyl-azofurazan **3** instead as the major product (see Scheme 1). Evidently, this resulted from low nucleophilicity of the amino group attached to furazan ring.

To overcome these problems, we turned attention to our previous work on N-lithiation of aminofurazans by their deprotonation.[13] For this purpose, compound **1** was lithiated to **4** with BuLi in THF at –30 °C for 1 h (Scheme 2, optimized conditions). Next, the solution of N-Li intermediate **4** was treated with $FClO_3$ in CH_2Cl_2 at –30 °C to give the desired 3-(perchloryl-amino)furazan **2** that due to the high acidity of its NH proton would form Li salt **5** which precipitated along with the accompanying inorganic salts. This extremely dangerous compound **5** was isolated in 12% yield by crystallization. Notably, replacing $FClO_3$ with 0.2 N solution of Cl_2O_7[14] in CCl_4 provided somewhat higher yield of 27%, however, this reagent can be applied only at –80 °C inasmuch as addition of the Cl_2O_7 solution at a slightly higher temperature led to an instantaneous



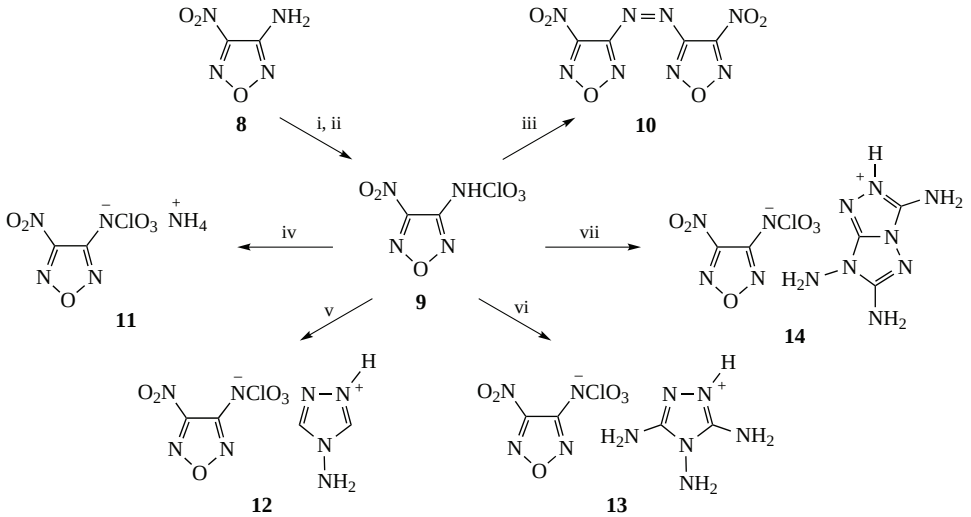
Scheme 2 *Reagents and conditions*: i, $FClO_3$, H_2O, 20 °C; ii, Cl_2O_7, CCl_4, 0 °C; iii, BuLi (1.1 equiv.), THF, –30 °C, 1 h; iv, $FClO_3$ (1.5 equiv.), CH_2Cl_2, –30 °C; v, H_2O, 2 N H_2SO_4, 0 °C, Et_2O; vi, NH_3, Et_2O, –15 °C; vii, $HN(SiMe_3)_2$, PhMe, reflux; viii, $FClO_3$, 1,2-dichloroethane, 0 °C, 24 h; ix, NH_3, $CHCl_3$, 0 °C.

fire. The colourless solid **5** left in light would spontaneously detonate without additional stimuli, and it almost always exploded on contact with a Teflon spatula, at attempts to dissolve it in DMSO, or when treated with any acid. However, after acidification of ~5% aqueous solution of salt **5** with 2 N H_2SO_4 at 0 °C, free perchlorylamine **2** could be extracted into diethyl ether to afford an unstable solution. Attempts to concentrate this ethereal solution caused explosions. The treatment of ethereal solution of perchlorylamine **2** at *ca*. –15 °C with an excess of gaseous ammonia led to precipitation of colourless ammonium salt **6** (see Scheme 2). Only decomposition was observed in attempted syntheses of hydrazine or hydroxylamine salts of compound **2**; these reactions were exothermic and some colourless gas was released.

The IR spectra of salts **5** and **6** contained the characteristic absorption bands for the perchlorylamino group[15] in the 1050–1110, 950–990 and 620–640 cm^{-1} regions, while the sharp double absorption bands at *ca*. 3450 and 3350 cm^{-1} typical of NH_2 group at the furazan ring were absent. In the ^{13}C NMR spectra of both salts, three signals in the expected range for the methylfurazan framework carbon atoms[16] were present similar to those of (nitramino)furazan derivatives.[12(*a*),17]

The above method of producing (perchlorylamino)furazans turned to be extremely dangerous and difficult to reproduce. In view of the well-established propensity of aminofurazans to form *N*-trimethylsilyl derivatives,[13,18] we were pleased to find that the use of *N*-silyl derivative **7** instead of lithium one **5** (see Scheme 2) in the reaction with $FClO_3$ can provide a more convenient synthesis of the desired perchlorylamines. In fact, the reaction of amine **1** with hexamethyldisilazane in toluene afforded silylated compound **7**. After removing the solvent, compound **7** could be used without further purification. Its solution in 1,2-dichloroethane was reacted with an excess of $FClO_3$ at 0 °C for 24 h under dry conditions and, after removing residual $FClO_3$ and volatile Me_3SiF under reduced pressure, was quenched at 0 °C with a solution of NH_3 in $CHCl_3$ to give a precipitate of the colorless ammonium salt **6**. Using this simpler and more reliable protocol, salt **6** was obtained in an overall yield of 31%. Light friction, shock, heating or shining bright light caused the detonation of compound **6**. When stored in the dark, compound **6** may explode spontaneously.

Following the same protocol, 3-amino-4-nitrofurazan **8** was converted into relative perchlorylamine **9** (Scheme 3). Compound **9** was found to be somewhat stable within 2 h in a 1,2-dichloroethane solution at 0 °C, however on longer storage it underwent self-condensation into 4,4′-dinitroazofurazan **10**. The direct treatment of the solution of perchlorylamine **9** with ammonia in $CHCl_3$ gave salt **11**. Acidification of the aqueous solution of salt **11** resulted in recovering of compound **9** which, when treated with an NH_3 solution, was re-converted into the same salt **11** with no changes in the NMR and IR spectra. When ammonia was replaced by some nitrogen-rich bases, ionic compounds **12**–**14** were obtained (see Scheme 3). However, our attempts to prepare analogous hydroxylammonium, guanidinium, aminoguanidinium, diaminoguanidinium and triaminoguanidinium salts failed, and



Scheme 3 *Reagents and conditions*: i, $HN(SiMe_3)_2$, PhMe, reflux; ii, $FClO_3$, 1,2-dichloroethane, 0 °C; iii, 1,2-dichloroethane, 20 °C, 24 h; iv, NH_3, $CHCl_3$, 0 °C; v, 4*H*-1,2,4-triazol-4-amine, MeOH, 20 °C; vi, 4*H*-1,2,4-triazole-3,4,5-triamine, MeOH, 20 °C; vii, 7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole-3,6,7-triamine, MeOH, 20 °C.

Table 1 Physical and calculated energetic properties of perchlorylamines salts compared with those of 3-nitramino-4-nitrofurazan ammonium salt **15**.

Compound	M_W	α^a	ρ^b/g cm^{-3}	Δ_fH^0 (*s*)^c/kJ mol^{-1} (kJ g^{-1})	D^d/m s^{-1}	$P_{C-J}{}^e$/GPa
$C_2H_4ClN_5O_6$ **11**	229.53	1.08	1.88	388 (1.69)	9180	39.40
$C_4H_5ClN_8O_6$ **12**	296.58	0.62	1.87	712 (2.40)	9125	39.31
$C_4H_7ClN_{10}O_6$ **13**	326.61	0.56	1.84	678 (2.08)	9027	37.81
$C_5H_7ClN_{12}O_6$ **14**	366.64	0.48	1.79	904 (2.47)	8763	34.54
$C_2H_4N_6O_5$ **15**[17]	192.09	0.83	1.81	200 (1.04)	9011	34.90

[a] Oxygen coefficient. For a compound with the molecular formula of $C_xH_yCl_vN_wO_z$, $\alpha = (z + v/2)/(2x + y/2)$; when $\alpha > 1$, compound is an oxidizer. [b] Pycnometric density. [c] The enthalpy of formation for the solid state calculated by the additive method.[20] [d] Detonation velocity at maximal density (at *ca*. 25 °C). [e] Detonation pressure.

full decomposition occurred (in some cases, mixing the reagents led to a violent reaction with ignition followed by an explosion).

Wherein salts **11**–**14** can be stored at ambient temperature in the dark for a long time, they are more sensitive to any provocation (heat, shock and friction) and treacherous than salts **5** and **6**.† For example, these salts often exploded during the preparation of samples for recording spectra. Nevertheless, we managed to fully characterize them by IR and NMR spectroscopy and elemental analyses.‡ Similarly to salts **5** and **6**, the three characteristic infrared absorption bands at *ca*. 1100, 960 and 630 cm^{-1} confirm the presence of *N*-perchloryl group. In the ^{13}C NMR spectra, salts **11**–**14** show two expected signals around 151 ppm for carbon atoms of the nitrofurazan unit,[19] which are very similar to those of nitro(nitramino)furazan derivatives.[17] The X-ray quality crystals of the ammonium salt **11** were grown from the slow evaporation of methanol solutions. However, after transferring the single crystal to goniometer hold and switching on X-ray beam, explosion occurred. For safety reasons, other efforts were not pursued. The density of all compounds was determined by the pycnometric method (Table 1).

The high positive enthalpies of formation for all perchlorylamines of this study arise from high nitrogen content and the presence of weak N–Cl and Cl–O bonds. Based on the enthalpies of formation and densities, the explosive performance was predicted using the method developed by Smirnov *et al*.,[21] and the data are provided in Table 1. The detonation velocities (*D*) of these salts range from 8763 to 8180 ms^{-1}, and detonation pressures (*P*) from 34.5 to 39.4 GPa. Ammonium salt **11** displays the highest detonation values in this series, exhibits a better detonation performance than related ammonium salt **15**,[17] and its energetic performance is superior to those of high explosive benchmark octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (*D*: 9059 ms^{-1}; *P*: 39.2 GPa).

In conclusion, the N-lithiation or N-trimethylsilylation of aminofurazans followed by reaction with $FClO_3$ or Cl_2O_7 opens up first routes to perchlorylamino heterocycles. It has been demonstrated that the explosive performance of the (perchloryl-amino)furazans are superior to that of similar (nitramino)-furazans. However, all (perchlorylamino)furazan derivatives are thermally not stable enough and extremely sensitive (explode upon heating or weak mechanical shock) for practical applications. Obviously, to develop the energetic materials chemistry, it is important to understand at least the gross factors that determine the balance between high performance, acceptable stability and molecular structure. This vital development is impossible without revealing new structure–property relationships.

† Attempts to use machines for testing primary explosives have been unsuccessful. The sensitivity of our perchlorylamine salts is beyond their measurement capabilities. Minimum loads during shock and friction tests led to explosions.

‡ For spectral characteristics and elemental analyses of compounds **6**, **11**–**14**, see Online Supplementary Materials.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.07.028.

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Received: 26th February 2020; Com. 20/6144