THEORY AND PRACTICE OF ENERGETIC MATERIALS

(VOL. IX)

Edited by

LI Shengcai
NIU Peihuan

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Proceedings of the 2011 International Autumn Seminar on

Propellants, Explosives and Pyrotechnics

Nanjing, Jiangsu, China, September 20–23, 2011

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State Key Laboratory of Explosion Science and Technology
Beijing Institute of Technology
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Introduction of Content

This monograph is the Proceedings of the 2011 International Autumn Seminar on Propellants, Explosives and Pyrotechnics (2011 IASPEP). Collected in this volume are 194 papers from 14 countries. These papers cover the following aspects: Synthesis and Manufacture, Characterization and Analysis, Combustion and Detonation, Modeling and Calculation, and Miscellaneous. Many novel research results on propellants, explosives and pyrotechnics achieved during the last few years are mentioned in the proceedings.

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PREFACE

Following the success of the eight previous International Autumn Seminars on Propellants, Explosives and Pyrotechnics which were held in China's Beijing(1996), Shenzhen(1997), Chengdu(1999), Shaoxing(2001), Guilin(2003), Beijing(2005), Xi'an(2007), Kunming(2009), the ninth seminar with the same theme is to be held in Nanjing, Jiangsu Province, China, on September 20–23, 2011. The purpose of this seminar is to foster the exchange of ideas, evaluate new methods and new lines of investigation, and bring together scientists from all over the world, working in universities and research institutions.

Collected in the proceedings are 194 papers accepted for presentation at the Seminar. These papers are contributed by 581 authors and co-authors from 14 countries which are: Australia, Belgium, Canada, China, Czech Republic, Egypt, India, Iran, Japan, Korea, Pakistan, Russia, Switzerland and USA. The contents of the proceedings have also been recorded in electronic form and provided on CDROM in color. I believe that the proceedings will benefit not only the participants of the meeting but also all of colleagues engaging in the research and development of propellants, explosives and pyrotechnics.

I wish to thank Academician ZHU Jianshi, Mr. Rutger WEBB and Prof. Karl RINK for their outstanding and dedicated contributions as the seminar co-chairmen. Thanks are also given to the members of International Advisory Committee of the Symposium for their tremendous contributions, and to all the authors for their valuable papers. And I also would like to express my sincere thanks to the National Natural Science Foundation of China for supporting this seminar.

In addition, I would like to express my sincere thanks to the staffs of the Editorial Department of *Journal of Safety and Environment* for their tireless efforts and outstanding services in the administration and preparation of the manuscript of the proceedings, to the staffs of Science Press for their diligence in publishing the proceedings.

Finally, I wish all participants a most enjoyable and informative experience.

Dr. FENG Changggen

冯长根

Vice-President of the China Association for Science and Technology
Professor of the Beijing Institute of Technology
Secretary General of 2011 International Autumn Seminar on Propellants, Explosives and Pyrotechnics
Beijing, China, July 2011

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SYNTHESIS AND MANUFACTURE

Synthesis and Characterization of 3,6-di(nitramino)-1,2,4,5-tetrazines

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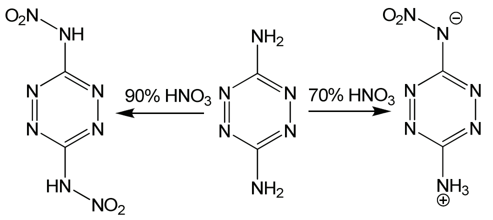
Abstract: The synthesis of 3(6)-nitramino-1,2,4,5-tetrazines via nitration of 3,6-disubstituted s-tetrazines with nitric acid is reported. The effect of 3(6)-amino-1,2,4,5-tetrazine structure and nitric acid concentration on the direction of the nitration reaction is shown. The synthesized products have been characterized by IR, UV, NMR spectroscopy, and DSC analysis.

Keywords: 3,6-disubstituted 1,2,4,5-tetrazines; nitration; nitramines; thermal stability

1 Introduction

The 3,6-substituted 1,2,4,5-tetrazines have attracted much attention in the field of energetic compounds chemistry. These high-nitrogen substances have good density and high positive heat of formation. In view of high energy content, high density, and good thermal stability many of these substances have been proposed as ingredients in some energetic compositions[1-16]. By now a whole number of symmetrical and unsymmetrical derivatives of 1,2,4,5-tetrazines have been explored, among them energetic ones, which contain substituents in the 3- and 6-positions. However, little information is available in literature on the synthesis of nitramino-1,2,4,5-tetrazines[4,15,16]. Only a few examples of these functionalized tetrazines have been reported that makes it difficult to evaluate properties of such materials (Scheme 1).

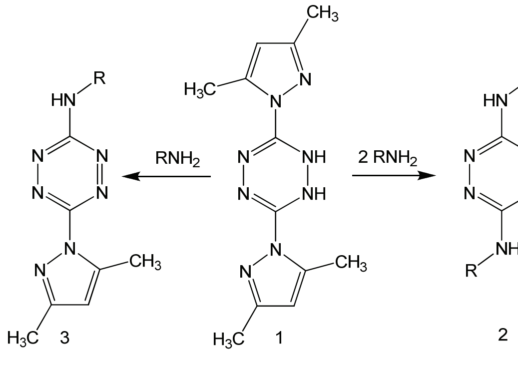


Scheme 1 Nitration of 3,6-diamino-1,2,4,5-tetrazine

To elucidate the relationship between the chemical structure of nitramino substituent and thermal stability of substituted tetrazines, a series of symmetrical 3,6-di(nitramino)-1,2,4,5-tetrazines have been synthesized and characterized in the present work.

2 Results and Discussion

The synthesis of 3(6)-nitramino-1,2,4,5-tetrazines was realized in two steps starting from readily available 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (1)[17].



R = H(a), CH_3(b), C_2H_5(c), i-Pr(d), t-Bu(e), $HOCH_2CH_2$(f), $CH_3CH(OH)CH_2$(g)

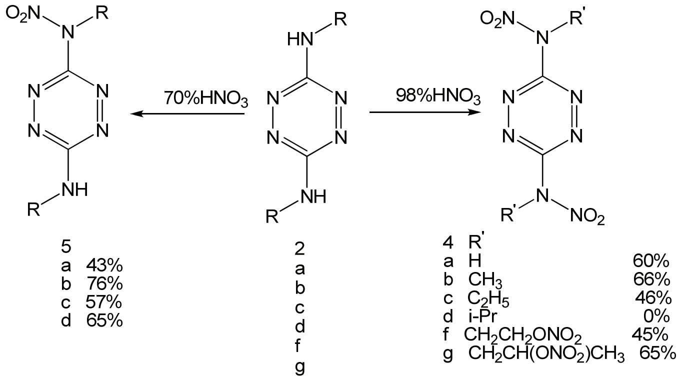
Scheme 2 Synthesis 3(6)-alkylamino substituted 1,2,4,5-tetrazines (2, 3)

The nucleophilic substitution of the dimethylpyrazol moiety with different alkylamines[18], aminoalkohols, and ammonia was carried out in acetonitrile, ethanol, and NMP in the presence of water or without it. We have found that the nucleophilic substitution occurs in two steps with spontaneous oxidation of the heterocycle (Scheme 2). The reaction of substitution proceeds selectively, and the yield of 3,6-bis(alkylamino)-1,2,4,5-tetrazines (2a-d,f,g) (30-76%) depends on the final product isolation and purification methods.

Investigation of the nitration reaction was performed in 70%, 98% nitric acid and mixtures of sulfuric and nitric acids. The course of the reaction was monitored by TLC. The structure of obtained products was confirmed by IR, UV, and NMR spectroscopy.

It was found that nitration in concentrated nitric acid leads to formation of bis(alkylnitramino)-1,2,4,5-tetrazines (4a-g), except for N,N'-diisopropyl-1,2,4,5-tetrazine-3,6-diamine (2d) (Scheme 3). The rate of nitration reaction is slightly dependent on the nature of the substituent (reaction time is 1-2 hours) and the yield of nitration products is 45-66%. In the case of amino alcohol derivatives (2f,g) the N-nitration occurs together with the O-nitration (4f,g).

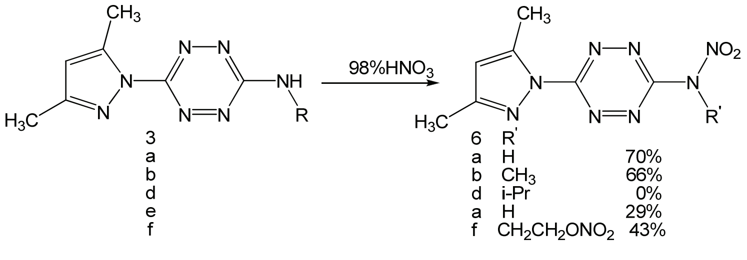
Reaction in dilute nitric acid (56-70%) leads to the selective formation of mono nitration products (5a-d). Increasing the temperature and reaction time did not give positive results.



Scheme 3 Nitration of 3,6-bis(alkylamino)-1,2,4,5-tetrazines (2)

The nature of the substituent at the amine nitrogen atom plays a significant role in the nitration of 3,6-bis(alkylamino)- and mono(alkylamino)-1,2,4,5-tetrazines. Nitration of 6-(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine-3-amine (3a) and 6-(3,5-dimethyl-1H-pyrazol-1-yl)-N-methyl-1,2,4,5-tetrazine-3-amine (3b) with concentrated nitric acid form nitramines in good yields. 6-(3,5-Dimethyl-1H-pyrazol-1-yl)-N-isopropyl-1,2,4,5-tetrazine-3-amine (3d) does not form nitration products even when heated in the presence of ammonium chloride or in reaction with sulfuric-nitric acid mixture (Scheme 4). The behavior of 3e in concentrated nitric acid is different from the nitration of 2-(t-butylamino)-4,6-bis(trinitromethyl)-1,3,5-triazine[19]. The reaction is accompanied by gas evolution at room temperature and leads to formation of 6-(3,5-dimethyl-1H-pyrazol-1-yl)-N-nitro-1,2,4,5-tetrazine-3-amine (6a).

Intermediate N-(t-butyl)-6-(3,5-dimethyl-1H-pyrazol-1-yl)-N-nitro-1,2,4,5-tetrazine-3-amine (6e) was not recorded, therefore the mechanism of nitration is not clear and requires further study. The reaction can proceed both on the mechanism of substituted nitration, and with prior removal of t-butyl group under acidic conditions.



Scheme 4 Nitration of 3-alkylamino-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazines (3)

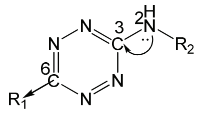
In contrast to bis(alkylamino)-1,2,4,5-tetrazines, mono(alkylamino)-1,2,4,5-tetrazines (3) do not form nitramines in the reaction with 70% nitric acid. This fact can be explained by strong deactivating effect of the dimethylpyrazol moiety, similar to nitramine group. Quantum chemical calculations performed on the basis of 3-21G, show that the presence of these substituents at position 6 decreases the bond length between the nitrogen atom in position 3 and the heterocycle (d/C_3N_2/, Table 1). The results show that there is a shift of electron density from the amino group to the s-tetrazine ring. This effect may explain the negative results of nitration of monoalkylamino-1,2,4,5-tetrazine in 70% nitric acid.

Influence of NNO_2 and DMP substituents on the electronic system of tetrazines can be explained on the basis of analysis of UV spectra. Using ethylamino-1,2,4,5-tetrazine derivatives as an example, it has been shown that the transition from 2c to 3c and 5c is accompanied by a strong hypsochromic shift of the visible spectrum, corresponding to n-π* transition (60 and 80 nm, respectively, in methanol). This indicates to a substantial delocalization of the heterocycle electronic system and, as a consequence, the conjugation of electrons of the substituent in position 3 with the tetrazine cycle.

All the synthesized nitro derivatives of 3(6)-alkylamino-1,2,4,5-tetrazine are colored crystalline substances with melting points from 70 to 150°C. Product 4g was isolated as a viscous oil and, as it follows from the results of NMR spectroscopy, was a racemic mixture.

The thermal behavior of new tetrazines has been studied by means of DSC analysis. Exothermic decomposition of all samples is observed at 100-195℃ (Table 2). As could be expected, mononitro-1,2,4,5-tetrazine derivatives exhibit higher stability compared with 3,6-bis(nitramino)-1,2,4,5-tetrazines. The decomposition of 4b,f,g and 5b reveals two distinct exotherms.

Table 1 Calculated charge (q) and bond length (d) of 6-substituted 3-amino-1,2,4,5-tetrazines at the B3LYP/3-21G level



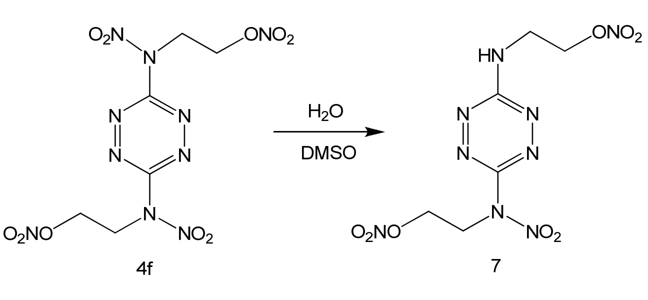
R_1	R_2	q (C_3)	q (N_2)	d /C_3N_2/,Å	Bond Order
NH_2	H	0,968	-0,944	1,352	0.998
$NHNO_2$	H	1,019	-0,938	1,330	1.108
DMP*	H	1,006	-0,941	1,336	1.052
CH_3NH	CH_3	1,003	-0,928	1,350	1.075
CH_3NNO_2	CH_3	1,030	-0,927	1,337	1.137
DMP	CH_3	1,037	-0,928	1,336	1.070
C_2H_5NH	C_2H_5	1.005	-0.922	1.352	1.069
$C_2H_5NNO_2$	C_2H_5	1.053	-0.923	1.330	1.175
DMP	C_2H_5	1.042	-0.928	1.339	1.060

*DMP – 3,5-dimethylpyrazol-1-yl

Table 2 DSC data

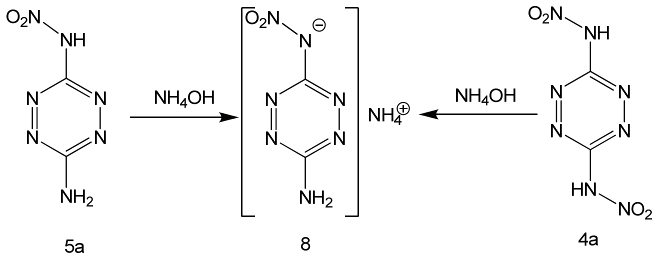
Compound	T_{onset}/℃	$T_{max}{}^1$/℃	$T_{max}{}^2$/℃	Q_{dec}/(kJ·kg^{-1})	Q_{dec}/(kJ·kg^{-1})
5a	163	177	-	1041	164
4a	103	130	-	2357	476
5b	122	148	195	807	149
4b	137	163	171-	1738	400
5c	113	148	-	707	151
4c	130	155	-	1459	376
4f	119	148	154	1750	665
4g	96	123	152	1394	569

3,6-Bis(nitramino)-1,2,4,5-tetrazines are chemically stable in the dry state, but their solutions in the presence of moisture undergo denitration reaction at different rates. Investigation of this process by NMR spectroscopy, carried out by the example of polyfunctional nitro compound 4f, has showed that hydrolysis occurs by one nitrogen atom to form stable compound 7 (Scheme 5).



Scheme 5 Denitration of 4f

In contrast to the 1,3,5-triazine[19,20], alkaline hydrolysis of 4 leads to formation of mono(nitramino)-1,2,4,5-tetrazines. In this way 4a reacts with aqueous ammonia to form ammonium salt of N-nitro-1,2,4,5-tetrazine-3,6-diamine (8), previously synthesized from 5a[10] (Scheme 6).



Scheme 6

The structures of compounds 4a–e were confirmed by ^1H NMR and IR spectroscopy. In the IR spectra, an absorption maximum is observed at 1548-1583 см$^{-1}$ and 1257-1283 см$^{-1}$, which is typical of NO_2 group. Compounds 5a-d give strong stretching absorption bands at 3250-3370 см$^{-1}$ in IR spectra and resonance signals of the NH proton in the range 6.03-6.09 ppm as singlet in ^1H NMR spectra.

The analysis of the IR spectra suggests the presence of strong interaction between the functional group in the *para*-position and the nitroamine fragment. The replacement of alkyl by hydrogen results in the appreciable shift in antisymmetrical vibration band of NO_2 to the high-frequency region. In the IR spectra of 4-6a, the symmetrical vibrations of the nitro group are recorded in the ordinary region (1274, 1294, 1278 см$^{-1}$), and the field of the antisymmetrical vibrations depends on the properties of substituent in the *para*-position of heterocycle (1629, 1616, 1604 см$^{-1}$). Replacing of the amino group by dimethylpyrazole or nitramine fragments leads to higher rigidity of NO_2 group because of increasing conjugation of NNO_2 with the electronic system of 1,2,4,5-tetrazine.

3 Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Mercuryplus instrument (400,46 MHz for ^1H and 100,70 for ^{13}C) in DMSO-d6 or $CDCl_3$ solution. Chemical shifts are reported in ppm relative to TMS as an internal reference. The IR spectra of new compounds were measured on a Termo Nicolet 360 FTIR spectrometer in range 400-4000 cm^{-1} in KBr pellets. UV spectra were recorded on a Specord M-40 spectrometer. LC-MS analyses were conducted on a Thermo Finnigan mass spectrometer, using APCI interface in the negative- and positive-ion modes.

The melting points were measured on Boetius heating table at the heating rate 4°C min^{-1}. DSC studies of the thermal stability were performed on a DSC-600 instrument. The Heating rate was 8°C min^{-1} in the temperature range 20-350°C. The course of the reaction was monitored by TLC using Sorbfil PTLC-AF-A-UV plates.

Compound 1 was synthesized using a published procedure[21]. Characteristics of 2a-f, 3a-f, 4a, 5a, 8 are in accordance with previously published data[10,16,18,22,23]. Compounds 2g and 3g were synthesized for the first time using analogous procedure.

***N,N'*-di(2-hydroxypropyl-1)-1,2,4,5-tetrazine-3,6-diamine (2g)**: yield 30%, crimson crystals, mp 102-105°C, R_f=0.33 (EtOAc); UV (MeOH), λ_{max} (lgε): 255 (4.84), 469 (3.23), 502 (3.16); IR (KBr), ν (cm^{-1}): 3473, 3348, 3250, 3107, 2969, 2932, 2900, 1544, 1426, 1371, 1098, 1049, 932, 837; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 5.53 (br.s, 1H, NH), 4.05-4.12 (m, 1H, CH), 3.62-3.68 (m, 1H, CH_2), 3.31-3.38 (m, 1H, CH_2), 4.87 (br.s, 1H, OH), 1.27 (d, 3H, CH_3, J=6.4); ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 160.68, 64.80, 48.36, 21.21.

6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-*N*-(2-hydroxypropyl-1)-1,2,4,5-tetrazin-3-amine (3g): yield 65%; orange crystals, mp 117-120°C, R_f=0,33 (EtOAc); UV (MeOH), λ_{max} (lgε): 273 (4.47), 469 (3.19), 502 (2.73); IR (KBr), ν (cm^{-1}): 3455, 3259, 3141, 3070, 2965, 2928, 1593, 1569, 1482, 1416, 1280, 1098, 1043, 974, 794, 553; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.76 (br.s, 1H, NH), 6.16 (br.s, 1H, CH), 4.83 (br.s, 1H, OH), 3.89 (br.s, 1H, CH), 3.36-3.40 (m, 2H, CH_2), 2.36 (br.s, 3H, CH_3), 2.20 (br.s, 3H, CH_3), 1.11 (d, 3H, CH_3, J=5.0 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 161.20, 156.41, 149.66, 140.98, 108.08, 64.03, 48.06, 20.85, 13.06, 11.90.

***N,N'*-dimethyl-*N,N'*-dinitro-1,2,4,5-tetrazine-3,6-diamine (4b):** yield 66%, pink crystals, mp 140-144°C, R_f=0.78 (ЭA:heptane/3:1); IR (KBr), ν (cm^{-1}): 3048, 3023, 2835, 1566, 1437, 1395, 1275, 1183, 1134, 967, 931, 749, 528; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 4.04 (s, 3H, CH_3).

***N,N'*-diethyl-*N,N'*-dinitro-1,2,4,5-tetrazine-3,6-diamine (4c):** yield 46%, pink crystals, mp 68-69°C, R_f=0.76 (EtOAc:heptane/3:1); IR (KBr), ν (cm^{-1}): 2985, 2938, 2876, 1573, 1549, 1421, 1257, 1165, 1186, 985, 823, 748, 550; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 4.51-4.56 (m, 2H, CH_2), 1.50 (d, 3H, CH_3, J=7.1 Hz).

***N,N'*-di(2-nitroxyethyl-1)-*N,N'*-dinitro-1,2,4,5-tetrazine-3,6-diamine (4f):** yield 45%, pink crystals, mp 82-84°C, R_f=0.82 (EtOAc:heptane/3:1); IR (KBr), ν (cm^{-1}): 3044, 2962, 2917, 2889, 2844, 1640, 1583, 1413, 1277, 1148, 973, 892, 849, 746, 706, 530; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 4.87 (t, 2H, CH_2O, J=4.6 Hz), 4.93 (t, 2H, CH_2N, J=4.6 Hz).

***N,N'*-di(2-nitroxypropyl-1)-*N,N'*-dinitro-1,2,4,5-tetrazine-3,6-diamine (4g):** yield 65%, red oil, R_f=0.87 (EtOAc:heptane/3:1); IR (KBr), ν (cm^{-1}): 3388, 3146, 2992, 2933, 2852, 1635, 1569, 1277, 1056, 882, 852, 755, 571; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 4.05-4.11 (m, 2H, CH_2), 3.77-3.84 (m, 2H, CH_2), 1.42 (d, 3H, CH_3), 5.54-5.63 (m, 1H, CH).

***N,N'*-dimethyl-*N*-nitro-1,2,4,5-tetrazine-3,6-diamine (5b):** yield 76%; orange crystals, mp 90-91°C, R_f=0.71 (EtOAc:heptane/3:1); IR (KBr), ν (cm^{-1}): 3370, 3060, 2950, 2876, 1609, 1547, 1483, 1446, 1414, 1380, 1285, 1151, 1052, 979, 951, 837, 788, 754, 630, 556; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 6.03 (br.s, 1H, NH), 3.84 (s, 3H, CH_3NNO_2), 3.27 (d, 3H, CH_3NH, J=5.5 Hz).

***N,N'*-diethyl-*N*-nitro-1,2,4,5-tetrazine-3,6-diamine (5c):** yield 57%; orange crystals, mp 97-100°C, R_f=0.38 (CH_2Cl_2); IR (KBr), *ν* (cm^{-1}): 3255, 3147, 3071, 2986, 2940, 2892, 1593, 1554, 1474, 1345, 1305, 1269, 1127, 1085, 1055, 976, 931, 826, 806, 685, 569; ^{1}H NMR ($CDCl_3$, 400 MHz), *δ* (ppm): 6.09 (br.s, 1H, NH), 4.29 (d, 2H, CH_2NNO_2, *J*=6.8 Hz), 1.70 (t, 2H, CH_2NH), 1.38 (d, 6H, CH_3, *J*=5,03 Hz).

***N,N'*-diisopropyl-*N*-nitro-1,2,4,5-tetrazine-3,6-diamine (5d):** yield 65%; orange crystals, mp 96-97°C, R_f=0.44 (CH_2Cl_2); IR (KBr), *ν* (cm^{-1}): 3251, 3147, 3071, 2975, 1599, 1548, 1493, 1282, 1124, 1055, 985, 819, 758, 709, 553; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 5.91 (br.s, 1H, NH), 5.07-5.14 (m, 1H, $CHNNO_2$), 4.33-4.42 (m, 1H, CHNH), 1.36-1.40 (m, 12H, CH_3).

6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-*N*-nitro-1,2,4,5-tetrazin-3-amine (6a): yield 70%, pink crystals, mp 137-140°C, R_f=0.56 (EtOAc:MeOH/5:1); IR (KBr), *ν* (cm^{-1}): 3430, 2967, 2932, 2659, 1615, 1583, 1498, 1461, 1294, 1265, 1089, 1007, 944, 815, 746, 553; ^{1}H NMR (DMSO-d6, 400 MHz), *δ* (ppm): 6.23 (s, 1H, =CH), 2.73 (s, 3H, CH_3), 2.48 (br.s, 1H, NH), 2.43 (br.s, 3H, CH_3).

6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-*N*-methyl-*N*-nitro-1,2,4,5-tetrazin-3-amine (6b): yield 66%, pink crystals, mp 85-88°C, R_f=0.62 (EtOAc:heptane/2:1); IR (KBr), *ν* (cm^{-1}): 3003, 2931, 2854, 1583, 1499, 1453, 1281, 1174, 1109, 1064, 964, 823, 769, 634, 540; ^{1}H NMR ($CDCl_3$, 400 MHz), *δ* (ppm): 6.21 (s, 1H, =CH), 3.98 (s, 3H, CH_3NNO_2), 2.74 (s, 3H, CH_3), 2.39 (s, 3H, CH_3).

6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-*N*-(2-nitroxyethyl-1)-*N*-nitro-1,2,4,5-tetrazin-3-amine (6f): yield 43%, pink crystals, mp 114-116°C, R_f=0.80 (EtOAc); IR (KBr), *ν* (cm^{-1}): 3005, 2957, 2906, 1637, 1589, 1571, 1504, 1460, 1432, 1418, 1328, 1288, 1274, 1250, 1138, 1127, 1108, 957, 932, 885, 855, 818, 768, 758, 675, 563; ^{1}H NMR ($CDCl_3$, 400 MHz), *δ* (ppm): 6.22 (br.s, 1H, =CH), 4.93 (t, 2H, CH_2O, *J*=5.0 Hz), 4.79 (t, 2H, CH_2N, *J*=5.0 Hz), 2.74 (s, 3H, CH_3), 2.39 (s, 3H, CH_3).

4 Conclusions

The synthesis and characterization of 3(6)-nitramino-s-tetrazines have been conducted in this study. Nitration of 3(6)-amino derivatives of s-tetrazine with nitric acid of different concentrations has been studied. The depth of nitration of 3,6-bis (alkylamino)-1,2,4,5-tetrazines has been shown to depend on both concentration of nitric acid and nature of alkyl substituent at the exocyclic nitrogen. The synthesized 3(6)-nitramino-s-tetrazines have been investigated in order to find relationships between the structure and thermal stability.

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Nitration of Derivatives of 2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane

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Abstract: An HPLC and HPLC-MS study of the product composition and rate of nitration 2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (TAIW), 2,4,6,8,12-pentaaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (PAIW), 2,4,6,8,10,12-hexaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (GAIW) and 2,6,8,12-tetraacetyl-4,10-diformyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADFIW) in sulfuric-nitric acid mixtures. It is shown that rate of nitration TAIW and GAIW are similar, rate of nitration PAIW several times more slowly.

Keywords: 2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane; 2,4,6,8,12-pentaaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane; 2,4,6,8,10,12-hexaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane; 2,6,8,12-tetraacetyl-4,10-diformyl-2,4,6,8,10,12-hexaazaisowurtzitane, nitration

1 Introduction

In recent decades, has been synthesized a number of promising compounds, which include hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20)[1]. Scheme of its synthesis involves three main stages: building isowurtzitane cage, reductive debenzylation, nitration.

HNIW can be obtained from a number of starting compounds: 2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (TAIW), its mono- and di- formate salts, 2,6,8,12-tetraacetyl-4,10-diformyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADFIW), 2,6,8,10,12-hexaacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADBIW), dinitro- and dinitroso derivatives, 2,4,6,8,12-pentaaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane(PAIW), 2,6,8,10,12-hexaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (GAIW) and other derivatives[2,3]. Industrial application has nitration using TAIW and TADFIW. On nitration GAIW reported in[4], data on the rate of nitration PAIW in the literature not available. Nitration of isowurtzitane derivatives a multistep process, as a result which is formed series of nitro compounds, their composition by influences to quality of the GNIW.

The literature shows methods of nitration of hexaazaisowurtzitane derivatives using as a are different nitrating systems: nitric acid, solution of ammonium nitrate in concentrated nitric acid, sulfur-nitric acid mixtures[2]. In this study, we used sulfuric-nitric acid mixture, providing a higher rate compared with nitric acid and ammonium nitrate solution in it.

2 Experiment

We have studied of the composition intermediates products from the nitration TAIW, PAIW, GAIW and TADFIW. TAIW was obtained by the standard scheme two stepwise debenzylation of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane, its purification was carried out by recrystallization from aqueous dimethylformamide. PAIW and GAIW synthesized from it by acylation a mixture of acetic acid and acetic anhydride[3] , TADFIW obtained by formylation TAIW formic acid. The identity and purity of obtained compounds was confirmed by IR and NMR spectroscopy, gas and liquid chromatography-spectroscopy. In the table 1 shows the retention times and a relative contents of substances formed by nitration of derivatives hexaazaisowurtzitane.

Table 1 Retention times and a relative contents of substances formed by nitration of derivatives hexaazaisowurtzitane

Number of NO_2 groups	Name of compounds	RT/min	Initial compound		
			TAIW	PAIW	GAIW
1	PANIW	0.56	100	100	100*
2	2,6,8,12-TA-4,10-DNIW	0.89	50	60	4
	unidentified TADNIW	0.99	-	-	traces
	2,6,10,12-TA-4,8-DNIW	1.03	-	40	10
	unidentified TADNIW	1.21	-	-	9
3	6,8,12-TA-2,4,10-TNIW	1.75	50	45	traces
	4,10,12-TA-2,6,8-TNIW	2.11	-	5	10
	6,10,12-TA-2,4,8-TNIW	2.56	-	50	90
4	8,12-DA-2,4,6,10-TNIW	2.79	20	-	*
	unidentified DATNIW	3.14	-	-	
	6,12-DA-2,4,8,10-TNIW	3.34	80	40	
	unidentified DATNIW	3.76	-	60	
5	2-APNIW	4.32	100	85	65
	4-APNIW	4.57	-	15	45
6	HNIW	5.44	100	100	100

* - mixture of isomers

Hypersil-ODS 100*5 mm, CH_3CN-H_2O from 20/80 to 80/20 in 10 minutes.

To isolate the products of nitration sample was diluted with water and neutralized by sodium bicarbonate, extraction with ethyl acetate. Analysis of nitro compounds was carried out by liquid chromatography (LC) and liquid chromatography-mass spectrometry (LC-MS) with chemical ionization at atmospheric pressure and the registration of negative ions. It should be noted that the molecular ions of all compounds except the HNIW fixed in the form adducts with formate ion ($[M+45]^-$). Some of the intermediate products were isolated by using preparative thin layer chromatography and characterizations by IR and NMR spectroscopy. Spectral data are presented in tables 2 and 3.

The nitration of TAIW, PAIW, GAIW and TADFIW was carried out in systems containing 78% HNO_3, 21% H_2SO_4,1% H_2O and 89% HNO_3, 10,5% H_2SO_4, 0,5% H_2O at temperatures 30°C, 40°C, 60°C and 75 °C and reaction time from 30 min to 240 min.

Table 2 NMR spectra of derivatives isowurtzitane

Substance	Chemical shift, ppm				
Solvent	-$COCH_3$	-CHO	-NH	C-H, position3, 5, 9, 11	C-H,position 1, 7
TAIW DMSO d6	2.00 (s, 12 H)		4.2 (br. s 1H)	5.33 (s, 4 H)	6.13-6.3 (br. m, 2 H)
TAIW D_2O	2.01 (s, 12 H)	-	-	5.54-5.45 (m, 4 H)	6.16- 6.57 (m, 2 H)
PAIW DMSO d6	2.03 (s, 12H) 2.30 (s, 3H)	-	4.53-4.76 (m, 1H)	5.56 (s, 4 H)	6.22-6.73 (m, 2H)
PAIW DMSO d6	2.06 (s, 12 H) 2.28 (s, 3H)	-	-	6.45-6.66 (m, 4H)	6.93 (s, 2H)
TADFIW DMSO d6	2.07-1.98 (m,12H)	8.26 (s, 2H)	-	6.71-6.75 (m, 4H)	6.19- 6.60 (m, 2H)
2,6,8,12-TA-4,10-DNIW, DMSO d6	2.10 (s, 12H)	-	-	7.37 (s, 4 H)	6.67 (br. s, 1 H) 6.84 (br. s, 1 H)
6,8,12-TA-2,4,10-TNIW, DMSO d6	2.09 (s, 3H) 2.12 (s, 6H)	-	-	7.29 (br. s, 1H) 6.53-7.38 (m, 3H)	6.85 (br. s, 1H) 7,77 (d, J=7.8, 1H)
6,12-DA-2,4,8,10-TNIW, DMSO d6	2.07 (s, 3H) 2.14 (s, 3H)	-	-	-	7,59 (dd, J=8.15, 2.85, 1H) 7,79 (dd, J=8.15, 2.85, 1H)
6,12-DA-2,4,8,10-TNIW, DMSO d6	2.11 (s, 6H)	-	-	7.52 (m, J=7.74, 2H) 7.84, (m J=7.74, 2H)	7.38(s, 2 H)
2-APNIW, DMSO d6	2.13 (s, 3H)	-	-	7.85-7.95 (m, 4H)	7.51 (d, J=5.6, 1H) 7.61 (dd, J=8.23, 2.74, 1H)
HNIW DMSO d6	-	-	-	7.99 (s, 4H)	8.06 (s, 2H)

Table 3 IR spectra of derivatives isowurtzitane in KBr

Substance (initial compound)	-C=O/cm^{-1}	-C-N-/cm^{-1}	-NO_2/cm^{-1}	-NO_2/ cm^{-1}
TAIW	1658	1399	-	-
PAIW	1672	1404	-	-
GAIW	1669	1412	-	-
TADFIW	1669	1415	-	-
2,6,8,12-TA-4,10-DNIW (from the TAIW)	1674	1404	1566	1284, 1301
6,8,12-TA-2,4,10-TNIW (from the TAIW)	1687	1389	1577	1310, 1264
6,12-DA-2,4,8,10-TNIW (from the TAIW)	1695	1403	1590	1320, 1266
2-APNIW (from the TAIW)	1702	1388	1594	1316, 1266
DADFDNIW (from the TADFIW)	1697	1410	1557, 1580	1310
ADFTNIW (from the TADFIW)	1703	1409	1587, 1561	1304
4-FPNIW (from the TADFIW)	1723	1429	1590, 1557	1276, 1326
2,6,8,10,12-PA-4-NIW (from the GAIW)	1674	1393	1559	1303
TADNIW (from the GAIW)	1678	1402	1577, 1534	1311
TATNIW (from the GAIW)	1688, 1680	1397	1586	1323
DATNIW (from the GAIW)	1693	1382	1592	1322, 1284

3 Results and Discussion

For comparison the reactivity of the derivatives of hexaazaisowurtzitane we studied the nitration TAIW, PAIW, GAIW and TADFIW in sulfuric - nitric acid mixtures containing 23.3 and 34.3% wt. sulfuric acid [5]. Some results are shown in Fig. 1, the lowest rate of nitration demonstrated TADFIW is consistent with the published data[2]. The highest rate of nitration showed is TAIW, the formation of HNIW of GAIW is 2-2,5 times slower. Unexpectedly PAIW demonstrated low nitration reaction rate, in nitrating mixture containing 23.3% sulfuric acid rate of formation HNIW similar to that observed for TADFIW, if they contain sulfuric acid of 34,3% is 1,5-2 times higher.

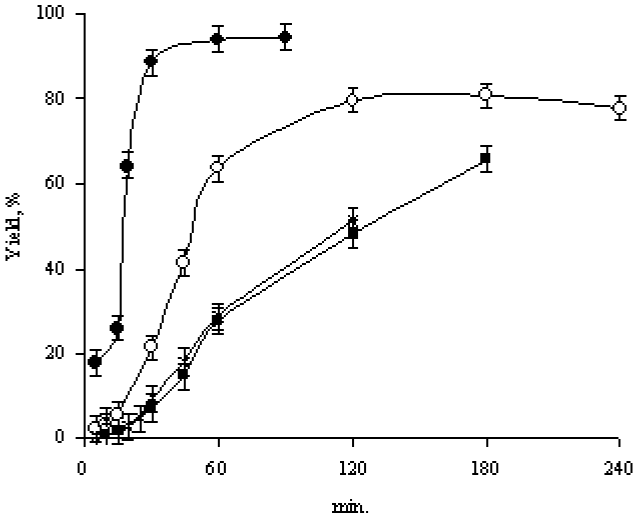

Fig.1 Dependence of the yield GNIW of time for nitration TAIW (●), PAIW (*),GAIW (○) and TADFIW (■) in the acid mixture containing 23.3% wt. H_2SO_4, 75 ° C

The analysis of the mixtures and purified compounds by HPLC, LC-MS and NMR spectroscopy showed by the presence of the single dinitro compound ($[M+CHO_2]^-=471$) was identified as 2,6,8,12-tetraacetyl-4,10-dinitro-2 ,4,6,8,10,12-hexaazaisowurtzitane (2,6,8,12-TA-4,10-DNIW). In addition to his mix contains a single isomer trinitro compound ($[M+CHO_2]^-=474$) - identified as 2,6,8-triacetyl-4,10,12-trinitro-2,4,6,8,10,12-hexaazaisowurtzitane (6,8,12-TA-2,4,10-TNIW), two isomers tetranitro compounds ($[M+CHO_2]^-=477$) - identified as the 2,10-diacetyl-4,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (90 %, 6,12-DA-2,4,8,10-TNIW) and 2,8-diacetyl-4,6,10,12- tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (10%, 8,12-DA-2,4,6,10-TNIW) and pentanitro compound ($[M+CHO_2]^-=480$) - 2-acetyl-4,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane (2-APNIW). These results are consistent with data published in the paper[5]. In such a way the process of nitration TAIW can be presented by the following scheme (Fig.2):

In contrast of TAIW at the first stage of the nitration PAIW is observed the formation of 2,6,8,10,12-pentaacetyl-4-nitro-2,4,6,8,10,12-hexaazaisowurtzitane which can be isolated from the reaction mixture. When the reaction time 60 min at 30 ° C it is the main product Next, the formation of two isomers TADNIV in the ratio the near to 2:1, the first of these corresponds to 2,6,8,12-tetraacetyl-4,10-dinitro-2,4,6,8,10,12-hexaazaisowurtzitane, second compound probably contains the nitro group in positions 2 and 8. Introduction of a third nitro group (60 min at 40° C) followed by the formation of three isomers in a ratio of 9:1:11. The first of these corresponds to 2,6,8-tracetyl-4,10,12-trinitro-2,4,6,8,10,12-hexaazaisowurtzitane. Continued of the nitration resulted to a mixture of two tetranitro compounds a ratio of 2 to 3, the first of which are corresponds to 2.10-diacetyl-4,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane. The second one probably corresponds of 10.12-diacetyl-2,4,6,8-tetranitro-2,4,6,8,10,12- hexaazaisowurtzitane Next stages the formation of two pentanitro compounds containing acetyl group at 2 and 4 positions. In such a way the process of nitration TAIW can be presented by the following scheme (Fig.3):

The nitration of GAIW is more complicated, in this case, is observed all the four possible isomers dinitro compounds, three major trinitro compounds, the two main isomers tetranitro compounds and two pentanitro compounds. The proposed scheme of nitration GTIV shown in the fig.4. Thus, nitrolysis of acyl groups located at 4 and 10 positions cage is slower than the 2, 6, 10 and 12.

Under nitration TADFIW is possible as a substitute for the acyl and formyl groups. It is known that the latter subjected nitrolysis much slower and the main impurities in GNIV obtained in this way is 2,6,8,10,12-pentanitro-4-formyl-2,4,6,8,10,12-hexaazaisowurtzitane [2]. We carried out a study of the composition of intermediate products of nitration TADFIW in the systems containing 67,5% HNO_3, 31% H_2SO_4, 1,5% H_2O and 0,3% NO_2 at 75° C and reaction time of 20 and 45 minutes. The resulting mixture analyzed by HPLC and LC-MS. It was shown that at the stage formation of mono and dinitro derivatives occurs substitution of acyl groups to the formation 6,8,12-triacetyl-4,10-diformyl-2-nitro-2,4,6,8,10,12-hexaazaisowurtzitane (TADFNIW,

$[M+CHO_2]^-$=440) and diacetyldiformyldinitrohexaazaisowurtzitane (DADFDNIW, $[M+CHO_2]^-$= 443). The introduction of the third nitro group gives a mixture of acetyldiformyltrinitrohexaazaisowurtzitane (ADFTNIW, $[M+CHO_2]^-$=446) and diacetylformyltrinitrohexaazaisowurtzitane (DAFTNIW, $[M+CHO_2]^-$=460), contents of the last at 6-8 times less. Next the same process of substitution of an acyl or formyl groups and formed diformyltetranitrohexaazaisowurtzitane (DFTNIW, $[M+CHO_2]^-$=449) and acetylformyltetraanitrohexaazaisowurtzitane (AFTNIW, $[M+CHO_2]^-$=463) in a ratio of 2 to 1. Next they turn into formyltpentanitrohexaazaisowurtzitane (4-FPNIW, $[M+CHO_2]^-$=466), acetyltpentanitrohexaazaisowurtzitane ($[M+CHO_2]^-$=480) is observed only in trace amounts.

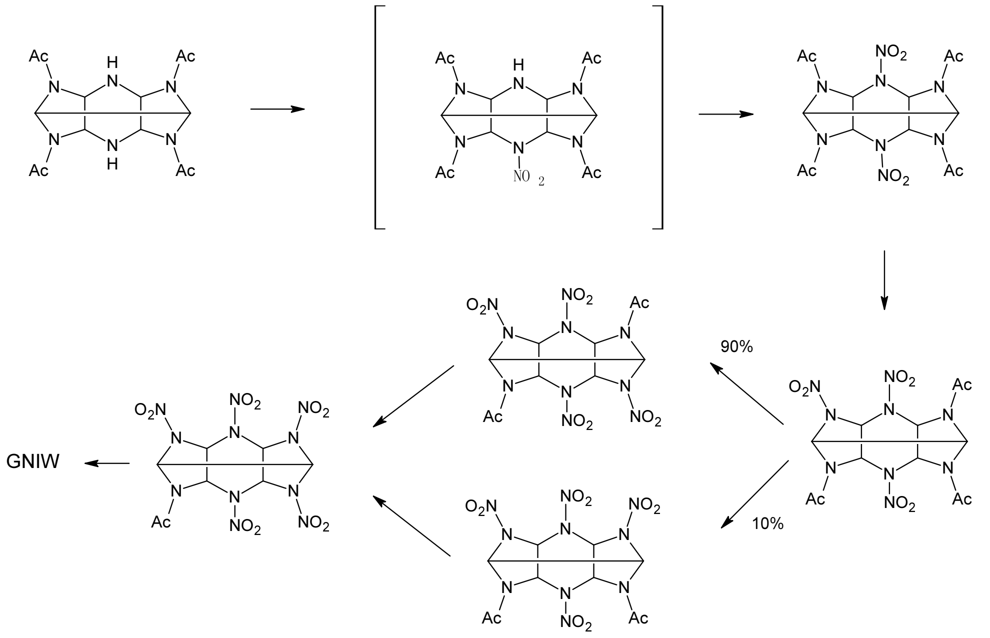

Fig.2 Scheme of nitration TAIW

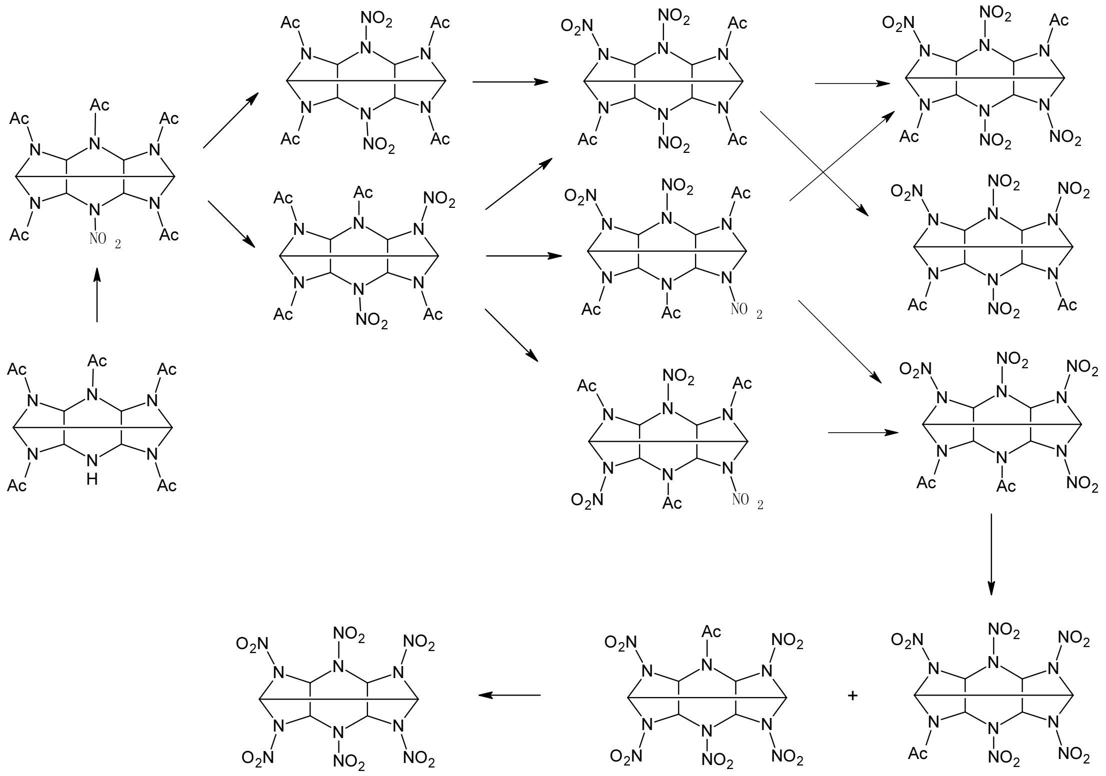

Fig.3 Scheme of nitration PAIW

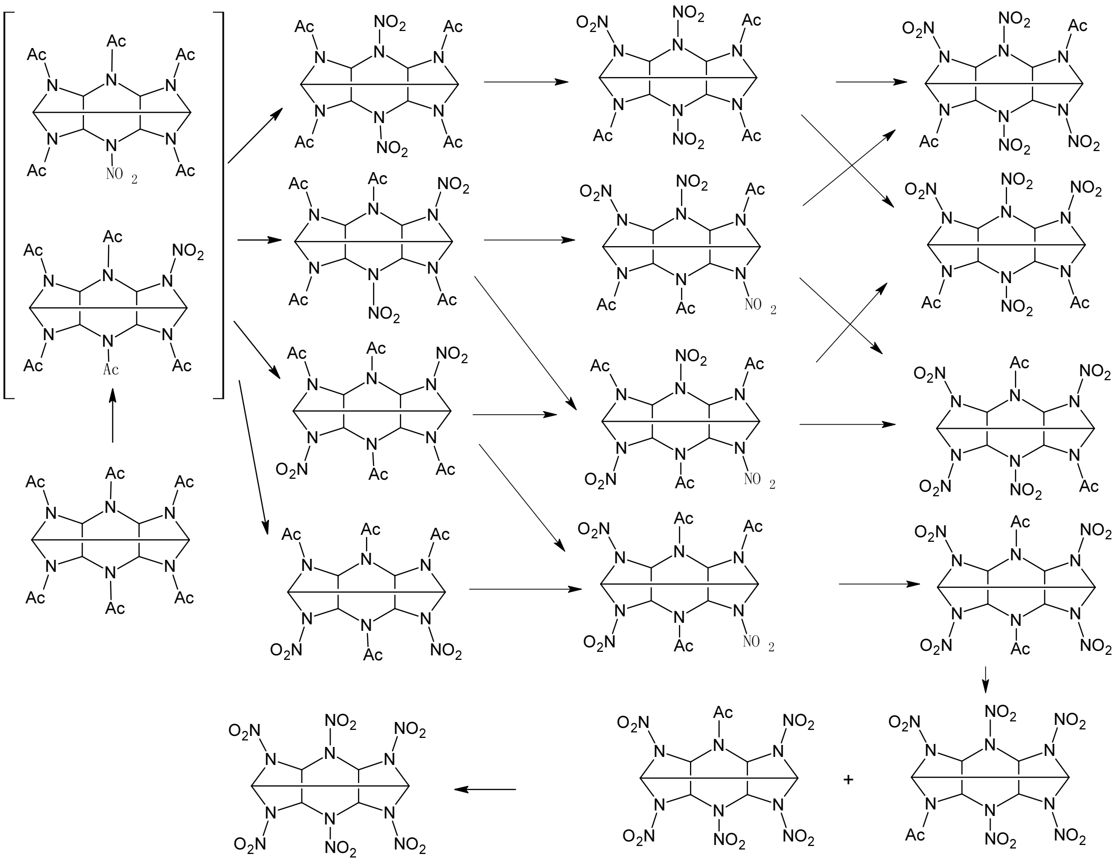

Fig.4 Scheme of nitration GAIW

4 Conclusion

The two free secondary amines of TAIW are nitrated firstly and then the four acetyl groups of TAIW are nitrolyzed one after. Under nitration GAIW and PAIW substitution of acyl groups located at 4 and 10 positions of the cage is slower than the 2, 6, 10 and 12. By nitration TADFIW the reaction path involves concurrent substitution formyl and acyl groups, formyl group replaced more slowly.

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Preparation Nano Sized HMX by Using Ultrasonic Waves

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Abstract: The researches done on particle size of explosive materials show that with reducing of particle size of explosive materials, reduced impact, friction and shock waves sensitivity, also by using of ultrafine explosive materials in propellant in comparison to larger particle size improved density, stability, calory and mechanical properties. Meanwhile the reduction of particle size of explosive materials influence on combustion mechanism of propellant and reduced burning rate and exponent pressure of different methods used for reduction of particle size, for example, milling, crystallization and etc. In this article for preparation of ultrafine HMX the method of solvent-anti solvent has been used by assistance of ultrasonic device. In optimum state the average size of particle is 106 nm and size distribution is narrow.

Keywords: sedimentary crystallization; ultrasonic; reduce particle size; HMX

1 Introduction

By the development of explosive materials with improvement performance and the reduction of sensitivity to mechanical stimuli such as impact and friction is one of the important researches goals in energetic fields. With reducing particle size of explosive materials decrease crystal defects and inclusion. This will reduce the sensitivity of explosive materials. Therefore safety of materials increases during handelling, processing, warehousing, and transportation. There searches done on the role of superfine particles of explosive materials in propellant show that with reducing of particles size increase density, calory, stability, and mechanical properties. Also one of the most important affecting issues on burning rate of propellant is the particles size of explosive materials. By using these ultrafine explosive materials in the propellant, the burning rate and exponent pressure decrease [1]. Various methods used for the reduction of the particles size of materials that the selection methods depend materials and expected properties such as the particles size distribution. Two general methods used for the reduction of the particles size up to down method including mechanical methods (grinding) and down to up method, including crystallization method (sediment crystallization fusion, supercritical fluid, and etc) . In the reduction of particles size in mechanical technique reduction of particles size in mechanical technique, solids construction elements have been broken by mechanical forces and increasing the mass distribution happens. To reduce the particles size with mechanical method used various equipment such as pinned disk mill, jet mill, colloid mill, ball mill, etc. Mentioned methods have disadvantages such as static, electricity, pressure, and trituration that with considering the disadvantages, these methods are powerless and insecure to produce these ultrafine explosive materials [2-6]. Crystallization is the conversion of one or more material from liquid or gas state to crystalline state. This method used for modifying the physical properties of substance. In addition, the crystallization is a process for thickening pure material from solution, melt or gas phase‹ one of the suitable methods for producing these ultrafine crystal of explosive materials is sedimentary crystallization method (solvent-anti solvent). Because in method nucleation is high and high degree of saturation is seen. Although crystallization methods for preparing explosive materials have significant and advantages and crystals can grow slowly away from stress and obtain an ideal crystal. These methods have disadvantages such as [6-9]:

A: Sample should be soluble in one or more solvent solution and precipitate with reduction of temperature or increasing of anti-solvent.

B: Contaminate crystals to solvent and other solvate.

C: They spend too much energy.

D: Having lower yield (Because occurs in several stages)

A new method to produce ultrafine explosive is the kinetic spray crystallization that submicron size HMX and RDX are prepared with this method. The obtained particles size distribution with this method is very narrow. This schematic has been shown in Fig.1 [10] Solvent/anti-solvent for spray solution by air into anti-solvent is used to produce ultrafine HMX The average of the obtained particles size with this method is 245 nm [1]. Also Mr. Lee and et al. by using sedimentary crystallization method have achieved HMX with an average particle size of 300 nm [11].

In this research solvent/anti-solvent method has been used for producing ultrafine HMX by the assistance of ultrasonic device. In this method for controlling the crystallization process, the ultrasonic energy is used. To create ultrasonic waves, piezoelectric converters are used. These converters converted electrical energy into mechanical vibration with the same frequency. Mechanism to reduce the particles size of solid and emulsions by ultrasonic waves is cavitation. Cavitation is used as the center of nucleation of new crystals and growing. Also producing bubbles and bursting them caused trituration and grinding of solid particles [12].

2 Safety

Generally by development of nanotechnology and producing nano particles in different scientific fields duet to the specific nature of nano particles produced and creating risk for human health, Considering the work, safety during producing, transportation, warehousing, and applying of nano particles should be considered. Therefore at the same time by growing the technology in producing nano particles, safety problems and diseases have been considered. In Considering the risks of toxicity of nano material in three contact areas in human body with the environment can be mentioned: skin, respiratory system, lungs, digestive system (mouthesophagus).These three elements are the enteries for the nano particles in human body and from the way it can be entered in blood stream and internal systems and nervous. Of course it should be mentioned that the safety hints for producing nano explosive materials are not available. There fore, the respiratory mask, gloves, and suitable ventilation system can be away to control damages[13].

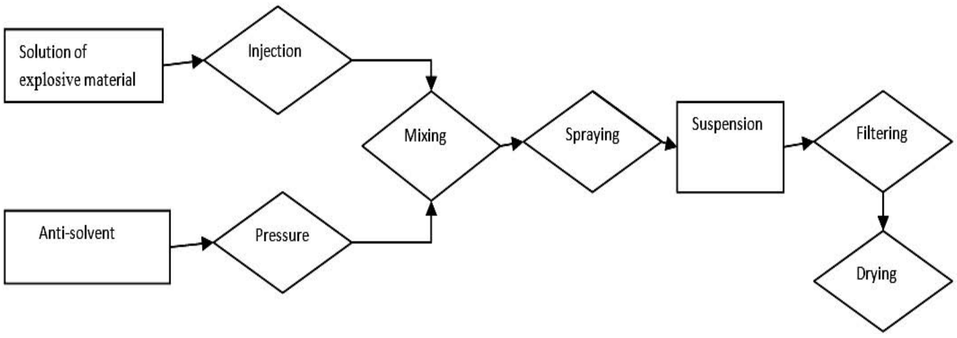

Fig.1 Principle of kinetic spray crystallizing method [10]

3 Experiment

3.1 Equipment

Ultrasonic device used H80 model is made in Elma Company of Germany. To determine the morphology and particle size of electronic Microscope XL30 manufactured in Philips Company of Dutch has been used. Installed equipment for doing the experiment is shown in Fig.2.

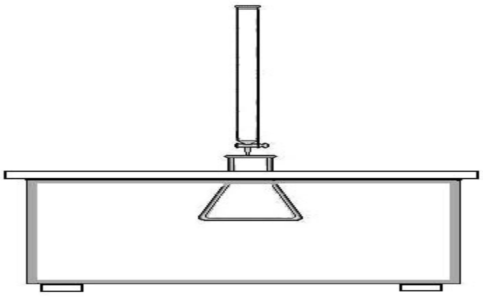

Fig.2 Installed Equipment

3.2 Procedure

In this method certain concentrations of HMX in acetone solvent prepared at room temperature (table1) and then by using of a burette of 0.5 cc are injected into an erlenmeyer flask containing anti–solvent (water) that its temperature is zero degrees Celsius. Solvent injection rate is about 0.7 ml per minute. Ultrasonic frequency is 80 Hz and its power is 750 Watt.

Table 1 Characteristic of produced samples

Sample name	Amount of HMX/gr.	Solvent (acetone)/ml	Anti-solvent(water)/ml	Anti-solvent Temperature (centigrade degree)
Sample-1	0.1	5	80	0
Sample-2	0.1	10	80	0
Sample-3	0.1	20	80	0

4 Results and Discussion

SEM image and the particles size distribution graph of sample respectively have been shown in Fig 3 and 4. Also SEM image and the particles size distribution graph of sample-2 in Fig 5, 6 and sample-3 in Fig 7, 8 have been shown respectively.

According to the images and the particles size distribution graph, it is observed with reduction of concentration samples can be achieved to smaller particle size. The best particle size is related to sample -3 that have the lowest concentration among the prepared solutions. The obtained average particles size is 106 nm. The reason for the reduction of the particles size with reduction of concentration is expressed with the degree of relative supersaturated theories. In other words, with reduction of samples