

## Synthesis of CL-20 by clean nitrating agent dinitrogen pentoxide

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**Abstract :** CL-20 is a high energy material. It is usually prepared via nitration with concentrated nitric and sulfuric acid, but this technique pollutes the environment. In this article, CL-20 was synthesized with 2,6,8,12-tetraacetylhexaazatetracyclo[5,5,0,0<sup>3,11</sup>,0<sup>5,9</sup>]dodecane (TAIW) and clean nitrating agent dinitrogen pentoxide. By the use of new nitrating agent, the reaction eliminated the use of concentrated sulfuric acid and was environmental friendly with high atom economy. The structure of the compound was characterized by elemental analysis, IR, <sup>1</sup>H NMR and MS. Meanwhile, the effects of reaction temperature, time and other factors on yield were analyzed. Through the separation of intermediate, the nitration course and mechanism were also discussed.

**Keywords :** CL-20, dinitrogen pentoxide, synthesis, explosive.

### Introduction

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5,5,0,0<sup>3,11</sup>,0<sup>5,9</sup>]dodecane or hexanitrohexaazaisowurtzitane (HNIW) is a high-energy material with a cage structure; today it is considered as the most powerful explosive. In view of its superior performance, HNIW, popularly known as CL-20, can be regarded as a high-energy material of the next generation. Its attributes of great interest are high density ( $\rho > 2 \text{ g cm}^{-3}$ ) and heat of formation ( $\Delta H_f = 100 \text{ kcal mol}^{-1}$ ), which exceed the same parameters of cyclotetramethylenetetranitramine or HMX ( $\rho = 1.91 \text{ g cm}^{-3}$  and  $\Delta H_f = 17 \text{ kcal mol}^{-1}$ , respectively). The high performance of CL-20 is due to a strained cage structure carrying 6NO<sub>2</sub> substituents. The production technology is studying all over the world.

Now, the synthesis of CL-20 is the nitration of its precursors by mixture of concentrated nitric and sulfuric acid. The disadvantages of the process are giving off NO<sub>2</sub>; hard disposal of spent acid; polluting environment; very low yields, which lead to the production in small batches. Our team succeeded in preparing CL-20 using N<sub>2</sub>O<sub>5</sub> as nitrating agent. The techniques not only enhances the yield, but also avoids the use of mixture of concentrated nitric and sulfuric acid, which accords with the demand of environmental protection.

Dinitrogen pentoxide is a new clean nitrating agent. Advantages of using N<sub>2</sub>O<sub>5</sub> in comparison to conventional

nitrating agents are : (a) ease of temperature control, the reaction give off less heat; (b) absence of spent acid for disposal; (c) simple isolation of the product; (d) high selectivity in position of attack with poly functional substrates; (e) no oxidation occurs; (f) feasibility towards the reaction in acidic medium to offer strong nitrating system; (g) very high yields.

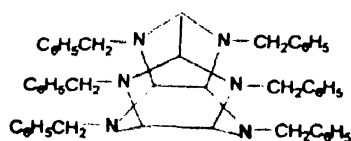
Meanwhile, the nitration by N<sub>2</sub>O<sub>5</sub> in acidic medium is non-selective, it can be exploited to nitrate deactivated precursors<sup>1-3</sup> while nitration by N<sub>2</sub>O<sub>5</sub> dissolved in an organic solvent (especially chlorinated hydrocarbons) is an effective means for selective nitration of substrates where there is more than one possible nitration site in the molecule. This unique dichotomy of dinitrogen pentoxide chemistry may lead to a wide variety of products of interest to energetic materials community.

### Synthesis :

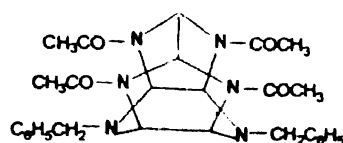
#### Dinitrogen pentoxide :

Dinitrogen pentoxide can be generated using different approaches. Solid N<sub>2</sub>O<sub>5</sub> can be prepared on a laboratory scale by the reaction of chlorine with solid silver nitrate as well as during the reaction of nitryl chloride/fluoride with metal nitrate and by the dehydration of nitric acid by P<sub>2</sub>O<sub>5</sub><sup>4</sup>. However, these methods produce low yields of poor quality product contaminated with small quantities of HNO<sub>3</sub>. Electrochemical synthesis of dinitrogen pentoxide by controlled potential oxidation of N<sub>2</sub>O<sub>4</sub> in

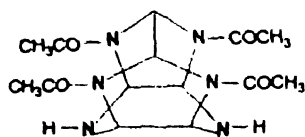
anhydrous nitric acid at platinum or titanium supported iron oxide anodes is established by several researchers<sup>5</sup>. Preparation of  $N_2O_5$  by reacting  $N_2O_4$  with ozone is considered one of the most versatile methods to obtain high purity  $N_2O_5$ <sup>6</sup>. The reaction is as follows:  $N_2O_4 (l) + O_3 (g) = N_2O_5 (s) + O_2 (g)$ .  $N_2O_4$  was poured in a round bottom flask cooled down to  $-20\text{ }^\circ\text{C}$ , and then oxygen containing 6% ~ 7% ozone was introduced. The reaction was finished instantaneously, which can be judged by the color of reaction mixture.  $N_2O_5$  is a white crystal, which was kept under  $-20\text{ }^\circ\text{C}$ .



(HBIW)



(TADBIW)



(TAIW)

Scheme 1. Precursors of CL-20.

There are many precursors of CL-20, such as hexabenzylisowurtzitane (HBIW), 4,10-dibenzyl-2,6,8,12-tetraacetylhexaazatetracyclo[5,5,0,0<sup>3,11</sup>,0<sup>5,9</sup>]dodecane (TADBIW) and 2,6,8,12-tetraacetylhexaazatetracyclo[5,5,0,0<sup>3,11</sup>,0<sup>5,9</sup>]dodecane (TAIW). They are all synthesized as follows<sup>7-10</sup>.

The first step in CL-20 synthesis involves creation of basic cage structure, the caged polyazapolycyclic intermediate HBIW is prepared by condensation of stoichiometric quantities of benzylamine and glyoxal in aqueous acetonitrile solvent at  $25\text{ }^\circ\text{C}$  in the presence of formic acid catalyst.

The second isolated intermediate TADBIW is prepared in 75% yield by reductive acetylation of HBIW in acetic

anhydride, DMF solvent with HBr as catalyst ( $H_2$ ,  $Pd(OH)_2$ ,  $45\text{ }^\circ\text{C}$ , 8 h). After washing by acetone, the isolated TADBIW is quite pure and may be employed for the next step without further purification.

TAIW can be prepared by adding TADBIW into the mixture of methanol and acetic acid with  $Pd/C$  (containing 5%  $Pd$ ) as catalyst ( $40\text{ }^\circ\text{C}$ , 18 h). The product is extracted by DMSO, and the yield can reach 78%.

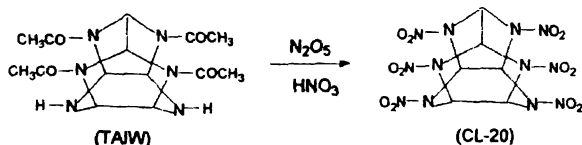
Table 1. Characterization data of HBIW, TADBIW and TAIW

HBIW	M.p. ( $^\circ\text{C}$ ) : 152-154 Elemental analysis ( $C_{48}H_{48}N_6$ , %) : C, 81.32; H, 6.84; N, 11.84 IR ( $\text{cm}^{-1}$ ) : 3388, 3024, 2832, 1598, 1490, 1450, 1340, 1170, 1064, 984, 832 $^1\text{H}$ NMR ( $\delta$ ) : 7.20-7.24 (20H, m, Ph), 4.16-4.09 (12H, s, $\text{CH}_2$ ), 4.03-3.57 (6H, s, CH) Mass ( $m/z$ ) : 709 ( $M + H$ ) <sup>+</sup> , 708 ( $M$ ) <sup>+</sup>
TADBIW	M.p. ( $^\circ\text{C}$ ) : 321-325 Elemental analysis ( $C_{28}H_{32}N_6O_4$ , %) : C, 65.09; H, 6.24; N, 16.27 IR ( $\text{cm}^{-1}$ ) : 2926, 2866, 1690, 1654, 1408, 1358, 1306, 1128, 1078, 990, 776 $^1\text{H}$ NMR ( $\delta$ ) : 7.25-7.60 (10H, m, Ph), 5.65-5.10 (4H, b, CH), 4.20-3.85 (4H, d, $\text{CH}_2$ ), 2.20-1.65 (12H, m, $\text{CH}_3$ ) Mass ( $m/z$ ) : 517 ( $M + H$ ) <sup>+</sup> , 516 ( $M$ ) <sup>+</sup>
TAIW	M.p. ( $^\circ\text{C}$ ) : 321 Elemental analysis ( $C_{14}H_{20}N_6O_4$ , %) : C, 49.99; H, 5.99; N, 24.99 IR ( $\text{cm}^{-1}$ ) : 3368, 3046, 1660, 1400, 1296, 1254, 1160, 1108, 1018, 974, 908, 800, 710 $^1\text{H}$ NMR ( $\delta$ ) : 6.4 (2H, m, CH), 5.50-5.29 (4H, m, CH), 2.0-1.9 (12H, m, $\text{COCH}_3$ ) Mass ( $m/z$ ) : 337 ( $M + H$ ) <sup>+</sup> , 336 ( $M$ ) <sup>+</sup>

### CL-20 :

HBIW/TADBIW/TAIW (7 g/5 g/3 g, 0.01 mol) was placed in a three-neck 250 ml flask, stirred and kept at certain temperature. 9 g  $N_2O_5$  dissolved in 100% nitric acid ( $30\text{ cm}^3$ ) was cooled to  $-10\text{ }^\circ\text{C}$  and then decanted into an addition funnel and added to the flask dropwise over a 10 min period. The mixture was stirred for several hours and the temperature was kept the same. After reaction, the mixture was poured on the crushed ice. The solid precipitate was filtrated and then dissolved in ethyl acetate and neutralized with sodium bicarbonate solution. The organic layer was separated and concentrated. The concentrated liquid obtained was chromatographed through

silica gel column using mixture of ethyl acetate and hexane as eluent. The fractions were concentrated under vacuum.

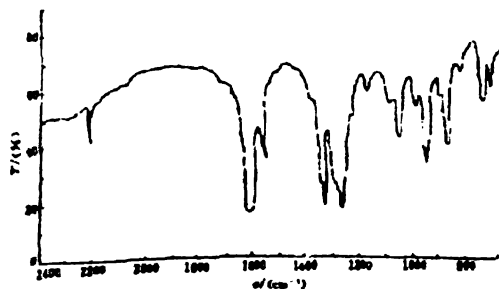


## Results and discussion

The use of dinitrogen pentoxide in nitration is one of the major challenges faced by the high-energy materials (HEMs) community. In this study, the nitration by dinitrogen pentoxide enriched nitric acid was attempted. Reaction of HBIW with  $\text{N}_2\text{O}_5$  enriched  $\text{HNO}_3$  led to the formation of low melting compound. The IR spectrum of the product indicated the cleavage of the cage structure for the competing nitration of phenyl rings<sup>11</sup>. Subsequently, well-reported precursor TADBIW obtained by reductive debenzoylation of HBIW was subjected to nitration by dinitrogen pentoxide. Nitration of TADBIW in  $\text{N}_2\text{O}_5$  enriched  $\text{HNO}_3$  yielded a product. IR revealed the presence of both C- $\text{NO}_2$  and N- $\text{NO}_2$  suggesting that nitration of both isowurzitane nitrogen as well as phenyl ring<sup>11</sup>. Consequently, completely debenzylated precursor TAIW may be the best choice for  $\text{N}_2\text{O}_5$  nitration. The nitration in  $\text{N}_2\text{O}_5$  enriched nitric acid led to the formation of white amorphous material, which was resolved by column chromatography and dried at 60 °C under vacuum. After re-crystallization, the  $\epsilon$ -CL-20 was prepared. Its formation was confirmed by elemental analysis, IR, as well as  $^1\text{H}$  NMR and MS.

M.p. (°C) : 228–236 (decompose); elemental analysis (%), measured (calcd.  $\text{C}_6\text{H}_6\text{N}_{12}\text{O}_{12}$ ) : C, 16.45 (16.44); H, 1.38 (1.38); N, 38.36 (38.38); O, 55.19 (55.20); C, H, N and O contents obtained by elemental analysis were close to theoretical values.

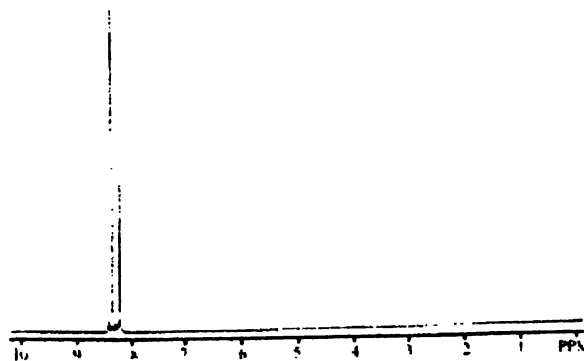
*Spectrums of CL-20 are as follows :*



**Fig. 1. IR of CL-20.**

**IR (KBr),  $\gamma$  (cm<sup>-1</sup>) : 2190, 1600, 1566, 1269, 1328, 1094**

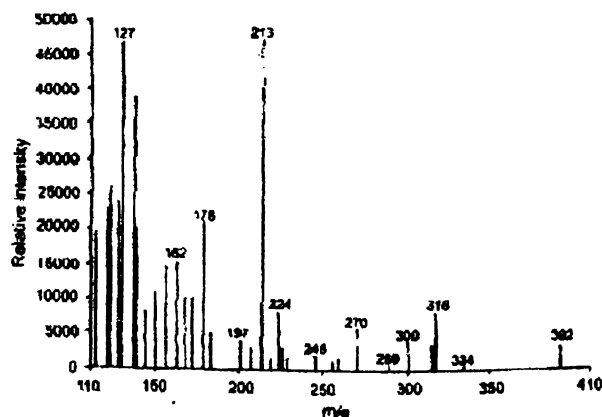
1600 and 1328  $\text{cm}^{-1}$  is the vibrating absorption of N- $\text{NO}_2$ , which means - $\text{NO}_2$  has been successfully connected to heterocyclic N.



**Fig. 2.**  $^1\text{H}$  MNR of CL-20.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ (ppm) : 8.21 (2H, s, CH), 8.34 (4H, s, CH).

There is no other characteristic peaks of H, which means the nitration reacted completely.



**Fig. 3. MS of CL-20.**

**Mass (%) : 392, 316, 300, 213, 127**

392 is formed by  $[M + H]^+$  losing one nitril; 300 is formed by  $[M + H]^+$  losing three nitril; 316, 213 and 127 is formed by recombination of fragments.

*Effect of reaction temperature on yield :*

When  $\text{N}_2\text{O}_5/\text{HNO}_3$  was dripped, the yield of CL-20 was various by different reaction temperature, the relation between yield and temperature was shown in Table 2.

**Table 2.** Effect of reaction temperature on yield<sup>a</sup>

Sl. no.	Temp. (°C)	Reaction degree <sup>b</sup>	Yield <sup>c</sup> (%)
1.	-40	Incomplete	26
2.	-20	Incomplete	32
3.	0	Complete	62
4.	20	Complete	45
5.	40	Complete	32

<sup>a</sup>The reaction time was 1 h.<sup>b</sup>Reaction degree was tested by TLC. It is completed when only one spot on the thin layer, and purity > 95% (HPLC normalization); if it is incomplete, two or more spots accrued, they are MAPN and DATN separately.<sup>c</sup>Yield was calculated by TAIW.

There is a significant effect of reaction temperature on the yield. The positive effect of elevated temperature would probably be due to the enhanced nitration of nitrogen, but more N<sub>2</sub>O<sub>5</sub> decomposed and the outgrowth increased too, so the temperature can't be too high. If the reaction temperature is very low, the reaction rate is so slow as to the overstock of N<sub>2</sub>O<sub>5</sub>/HNO<sub>3</sub>, which may lead to the prompt temperature-raise and materials' dash-out. As a result, the reaction temperature and dripping rate of N<sub>2</sub>O<sub>5</sub>/HNO<sub>3</sub> are both essential. The best yield is 62% when the reaction temperature is controlled around 0 °C.

*Effect of reaction time on yield :*

Reaction time is another effect on the yield of CL-20. Several hours later after the dripping of N<sub>2</sub>O<sub>5</sub>/HNO<sub>3</sub>, the difference was slight as to the yield, which is shown in Table 3.

**Table 3.** Effect of reaction time on yield<sup>a</sup>

Sl. no.	Time (h)	Reaction degree	Yield (%)
1.	0.5	Incomplete	49
2.	1	Complete	62
3.	2	Complete	64
4.	4	Complete	68
5.	8	Complete	66

<sup>a</sup>The reaction temperature is 0 °C.

It is clear from Table 3 that the reaction went on very fast and almost completed in 1 h. When the time was less than 1 h, the nitration hasn't reacted completely, so the

yield was low. Increasing the reaction time led to higher yield, but after reacting 1 h, the yield increased little as the time passed, and the purity quotient became worse. So, one hour is the best reaction time for this nitration.

*Effect of N<sub>2</sub>O<sub>5</sub>/HNO<sub>3</sub> ratio and amount on yield :*

Thus, all experiments had utilized a large excess of N<sub>2</sub>O<sub>5</sub>/HNO<sub>3</sub>, which had fulfilled the role of solvent as well as reagent. It was of interest to know if such large excess were actually necessary. A series of reactions was therefore conducted in which the ratio of the N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> and the N<sub>2</sub>O<sub>5</sub>/HNO<sub>3</sub> to TAIW were varied.

**Table 4.** Effect of reagent ratio on yield<sup>a</sup>

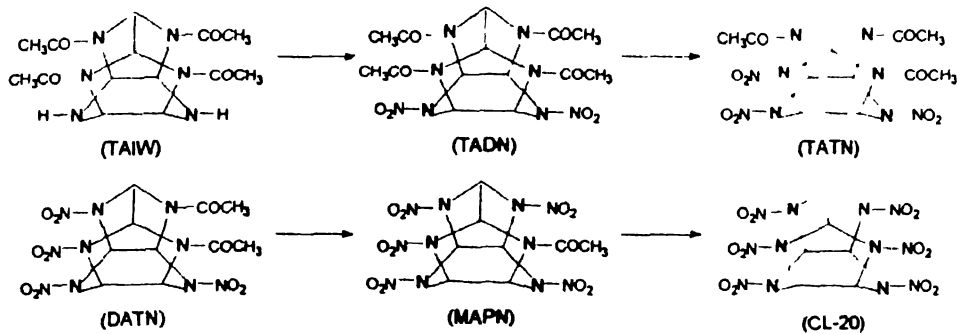
Sl. no.	TAIW (mol)	N <sub>2</sub> O <sub>5</sub> (mol)	HNO <sub>3</sub> (ml)	Yield (%)
1.	0.01	0.01	30	14
2.	0.01	0.05	30	39
3.	0.01	0.08	30	62
4.	0.01	0.10	30	64
5.	0.01	0.20	30	71
6.	0.01	0.08	15	28
7.	0.01	0.08	20	44
8.	0.01	0.08	60	67

<sup>a</sup>The reaction was proceeded in 1 h at 0 °C.

The purpose of alerting the ratio and amount of nitrating agent is to find the best synthesizing way. In testing, we fixed the moles of TAIW, changed the amount of N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> to find the relationship among them. As the results shown in Table 4, there is a significant effect on the yield when alerting N<sub>2</sub>O<sub>5</sub>. At a little higher N<sub>2</sub>O<sub>5</sub> concentrations with respect to TAIW (< 8 : 1), the yield increases rapidly as the amount of N<sub>2</sub>O<sub>5</sub> grows. When the amount of N<sub>2</sub>O<sub>5</sub> is seven times more than TAIW, the more N<sub>2</sub>O<sub>5</sub> doesn't lead to much higher yield. Comparing N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub> is less important to yield much more HNO<sub>3</sub> only induce a littler higher yield. Of course, HNO<sub>3</sub> is not only a nitrating agent, but also solvent, the reacting system cannot contact fully with too little HNO<sub>3</sub>.

*The nitration course :*

Through the separation and token of intermediates, the two dissociated amidocyanogen and four acetyl are nitrated separately. So, the reaction course is brought forward :

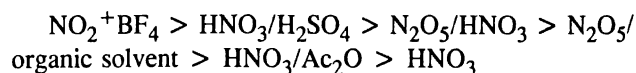


It is known to us all that the yield of nitrating secondary amine with strong basicity is very low. As far as TAIW with special construction is concerned, the electron-withdrawing inductive effect of four acetyl highly weaken the basicity of the two secondary amine in the cage, which makes the two dissociated amidocyanogen easy to be nitrated, the dinitroamine intermediate TADN is gained with good yield. There are two ways for other four acetyl to be nitrated to nitroamine : one is nitril substituting acetyl directly; another is N-acetyl hydrolyzing to become dissociated amidocyanogen, and then be nitrated. After forming trinitro-intermediate TATN, three isomers may be existed when importing the forth nitril :

than nitril, so the fourth nitril is imported to the same heptatomic ring as the third one, rather than another heptatomic ring containing two acetyl (cisoid conformation). It is clear that the import of the forth nitril is a highly tridimensional selective reaction, which is totally proved by the crystal structural identification of  $3^{12}$ .

*Discuss on the nitration mechanism :*

The nitration agent is one kind that can import nitril to organic molecule, its general expression is  $X-NO_2$ , and it can produce  $NO_2^+$ , which is an effective nitrating attacking agent. In terms of three effective concentration, the nitrating capability is arranged as follows<sup>13</sup> :

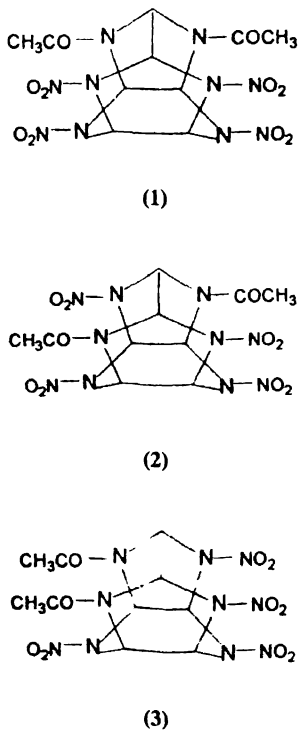


It can be seen that  $\text{N}_2\text{O}_5/\text{HNO}_3$  is an efficient nitrating agent, which is only a little inferior to  $\text{HNO}_3/\text{H}_2\text{SO}_4$ . So, it can create much  $\text{NO}_2^+$ . As an acid amide compound with double N-substituent,  $\text{NO}_2^+$  attack the N in the HAIW molecular and form  $\text{N}^+$ , then acetyl with positive charge is divorced from amidocyanogen N under the nucleophile, N- $\text{NO}_2$  is formed through this process. This mechanism is the same as the nitrosification mechanism of tertiary amine in nitrous acid or hydrolyzation mechanism of acid amide in nitrous acid. As the result, the mechanism of HAIW nitration in  $\text{N}_2\text{O}_5/\text{HNO}_3$  is described as follows :

There is no water in the system, which is the guarantee of enough  $\text{NO}_2^+$  in the system. Furthermore, the amount of relatively cheap nitrating agent is more than TAIW, the reaction can be finished under lower temperature with higher yield and purity.

**Conclusion :**

This paper brings out the potential of  $\text{N}_2\text{O}_5$  as versatile nitrating agent for the synthesis of CL-20. It discusses the method used for synthesis of high purity  $\text{N}_2\text{O}_5$  by interacting  $\text{N}_2\text{O}_4$  with  $\text{O}_3$ . Despite various routes available for CL-20 synthesis and production, the current cost



Result shows the product is isomer 3. It may be that the acetyl rotated quickly to form more steric inhibition

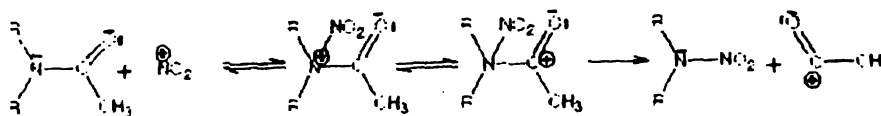


Fig. 4. Sketch map of nitrating mechanism.

of the material is high and the mixed acid is harmful to the environment. The experiments on  $\text{N}_2\text{O}_5$  aided nitration of CL-20 precursors brought out that TAIW is a material of choice for the synthesis of CL-20. By the use of new nitrating agent, the reaction eliminated the use of concentrated sulfuric acid and was environmental friendly. Furthermore, through the separation and token of intermediates, the separated nitration mechanism is brought forward.

#### Acknowledgement

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