

## State-of-the-art Advances in the Ignition Selay Reduction of N,N-dimethylethanamine

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Propellant is a core fuel in defense and aerospace applications. However, conventional hydrazine fuel is highly volatile, toxic, and carcinogenic, resulting in huge threats to the human body and environment. N,N-dimethylethanamine (DMAZ) is a green, high-energy fuel with a low freezing point, high density, high specific impulse, and high combustion rate, and it is a promising substitute of conventional hydrazine fuel. Nevertheless, the industrial application of DMAZ is limited by long ignition delay. In this study, the mechanism of ignition of DMAZ was explored by summarizing current methods to reduce the ignition delay of DMAZ, including the addition of catalyst, fuel formulation, and tuning molecular structure. This study provides references for applications of amine azide.

**Keywords:** N,N-dimethylethanamine, green propellant, high-energy fuel, reduction of ignition delay.

### 1. INTRODUCTION

In defense and aerospace applications, hydrazine has been widely used as the fuel of pyrophoric liquid propellant. However, hydrazine is highly volatile, toxic, and carcinogenic, resulting in huge threats to the human body and environment [1]. Hence, developing green fuel is an urgent challenge for the liquid propellant industry. Liquid azide fuel is a kind of organic compound with azide-containing groups and low molecular weight, including azides, azido esters, azide low molecular polyether, and amine azides. Among them, amine azide fuel is denoted as high specific impulse, non-carcinogenic pyrophoric fuel (CINCH) because of its high density, no toxicity, clean combustion products, high specific impulse, and high combustion rate [2, 3]. A typical example of amine azide fuel is N,N-dimethylethanamine (DMAZ). It has been demonstrated that DMAZ has a high enthalpy of formation, high boiling point, high density, and low freezing point, and it is almost non-toxic and non-carcinogenic. The introduction of azide groups increases the nitrogen content of the system and reduces the hydrocarbon content, which can effectively reduce the flame temperature and temperature signal of fuel. Therefore, it is considered a new type of liquid fuel that can be used as a single-component [4], dual-component [5], gel [6], and functional liquid propellant. Although DMAZ has good overall performance, ignition is the primary problem that needs to be solved when replacing hydrazine fuel. Unsymmetrical dimethylhydrazine ignites immediately upon contact with strong oxidants (e.g., red-fuming nitric acid,  $N_2O_4$ , and  $H_2O_2$ ), and the ignition delay is less than 10 ms. In contrast, the current DMAZ ignition delay of tens of milliseconds [7, 8], which will seriously affect the application of DMAZ. As a potential green and high-energy energy source, if it can break through the limitation of ignition delay time, whether as a single component fuel, two-component fuel, or additive,

it can provide great help for the development of aerospace and military. It can effectively replace current hydrazine fuels as core fuels and solve the hazards of hydrazine toxicity and cancer treatment. The ignition delay, i.e., the time elapsed from the moment when the ignition propellant components come into contact with each other to the time when they ignite, has an important impact on the engine performance and fuel economy. When the ignition delay is long (generally more than 25 ms), the unburned propellant and incomplete combustion products will accumulate in the combustion chamber, resulting in a steep increase in the pressure of the combustion chamber after ignition occurs, damaging the engine [9]. Therefore, to avoid pressurization and to guarantee the combustion effect, it is necessary to shorten the ignition delay or to design a larger combustion chamber, which is the key problem to be solved when replacing hydrazine with DMAZ.

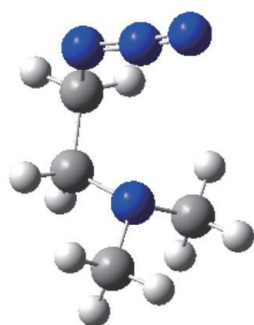
### 2. ADVANCES IN THE MECHANISM OF IGNITION OF DMAZ

In recent years, using theoretical computational simulations to study chemical reaction processes has been a very effective method to investigate mechanisms. Density functional theory is a quantum mechanical method for studying the electronic structure of multi-electron systems, which can be used to describe and determine the properties of the system [10]. As structure determines nature, DMAZ has multiple conformations. McQuaid et al. [11] determined the geometric parameters of 12 equilibrium conformations of DMAZ based on DFT and analyzed the mid-infrared absorption spectra of DMAZ fuel vapors based on the calculation results. As indicated, the most stable conformation is that the central N atoms of azide groups are aligned on amine lone pair electrons, as shown in Fig. 1.

Since this structure may inhibit proton transfer to the amine site, it can protect the electrons from the attack of

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nitric acid protons, which may be a key step to limit the ignition of DMAZ and NA(Nitric Acid).



**Fig. 1.** The most stable structure of DMAZ

After obtaining a stable conformation of DMAZ, Zhang et al. [12] studied the reaction of DMAZ with pure NA based on DFT and identified two important low-temperature reaction pathways. (1) proton transfer reaction between DMAZ and the nitrogen atom of NA amine in the NA liquid phase; (2) hydrogen extraction between DMAZ and  $\text{NO}_2$  in the gas phase.

Zhao et al. [13] calculated the barrier, reaction rate constant, and reaction activation energy of DMAZ stable conformation and  $\text{NO}_2$  hydrogen extraction based on DFT. As indicated, DMAZ first undergoes a decomposition reaction to generate  $\text{N}_2$ ; after the decomposition of NTO(3-nitro-1,2,4-triazole-5-one),  $\text{NO}_2$  is generated, and  $\text{NO}_2$  is hydrogen extracted in the subsequent process to generate  $\text{HNO}_2$ . Subsequently, the  $\text{N}_2$ -removed DMAZ undergoes C-C cleavage to form  $\text{C}_3\text{H}_8\text{N}$  and  $\text{CH}_2\text{N}$ . Based on the test results that the ignition delay of DMAZ is shorter than that of TMEDA (Tetramethylethylenediamine) and NTO, the rate at which the potential energy of the system increases to its maximum value and the generation rate of  $\text{HNO}_2$  is used as the basis for calculating and analyzing the ignition delay of the compound fuel and NTO. It has been demonstrated that after adding 5 wt.% pyrrole to DMAZ, the time required for the system to reach the maximum energy is greatly shortened, and the generation rate of  $\text{HNO}_2$  is greatly increased. This is because the pyrolysis of the pyrrole ring configuration can easily form small molecule radicals, such as H radicals and HCN radicals, thus accelerating the reaction between DMAZ and  $\text{NO}_2$  radicals and increasing the generation rate of  $\text{HNO}_2$ . Therefore, the addition of pyrrole can effectively shorten the ignition delay.

Zhao et al. [13] combined theoretical calculations with experimental verification, not only analyzed the process and mechanism of molecular bond breaking from a microscopic point of view but also verified the mechanism with experiments and proposed a hydrogen extraction mechanism during the ignition reaction between amine azide and NTO. At the same time, based on the hydrogen extraction mechanism, the experiment of adding pyrrole was designed to accelerate the rate of hydrogen extraction further and verify the hydrogen extraction mechanism. This method provides a better idea and method to shorten the ignition delay of amine azide.

### 3. METHODS TO REDUCE IGNITION DELAY OF DMAZ

Based on the above studies on the mechanism of amine azide's ignition delay, researchers have adopted methods of adding catalysts, compounding, and changing the molecular structure to accelerate the reaction process and shorten the ignition delay.

Catalysts can effectively improve the ignition performance of DMAZ. Catalytic ignition is a catalytic decomposition reaction that aims to decompose to generate heat and release gases rapidly. Hence, researchers have tried various catalysts to improve the ignition performance of DMAZ.

The decomposition of DMAZ begins with the adsorption of DMAZ molecules on the acidic active centers on the catalyst surface, and the azide groups are extremely unstable under the condition of Lewis acid catalysis, which can decompose rapidly and release nitrogen. The unstable intermediate state continues to release nitrogen under the action of catalyst active centers. It gives rise to ethane and ethylene, rapidly desorbed on the catalyst surface, where further decomposition of the intermediate states may be the rate-determining step [14]. Based on the above decomposition process studies, catalysts for the ignition of DMAZ, such as Ir-based, Fe-based, and composite catalysts, have been investigated.

Darren et al. [15] utilized an Ir catalyst. When the catalyst bed was heated to above  $177\text{ }^\circ\text{C}$ , the fuel contact catalyst bed would decompose rapidly, producing a large amount of gas and releasing a large amount of heat, which could maintain the continuous reaction. When DMAZ entered the reactor at  $204\text{ }^\circ\text{C}$ , it could decompose rapidly, and the pressure increased rapidly, but the delay time of this process was only 2 ms.

Pakdehi et al. [16] found that the DMAZ conversion of  $\gamma\text{-Al}_2\text{O}_3$  loaded with Ir at  $190\text{ }^\circ\text{C}$  under Ar flow was higher, but the catalyst's mechanical strength decreased when the loading exceeded a certain value. The catalyst had the best effect on DMAZ when the Ir mass fraction was 34 %.

Ultramet company (USA) invented a kind of  $\text{FeCl}_3$  and  $\text{FeCl}_2$  catalyst, which could rapidly catalyze the decomposition of DMAZ at low temperatures. Among them,  $\text{FeCl}_3$  had a better effect, and these two catalysts were more suitable for catalyzing fuel to ignite at low temperatures. At  $30\text{ }^\circ\text{C}$ , the granular anhydrous  $\text{FeCl}_3$  with a surface area of only  $0.29\text{ m}^2/\text{g}$  could catalyze the decomposition of DMAZ. The disadvantages of  $\text{FeCl}_3$  are low melting point ( $306\text{ }^\circ\text{C}$ ) and low decomposition temperature ( $315\text{ }^\circ\text{C}$ ). It is generally required that the melting point and decomposition temperature of the catalyst should exceed the flame temperature ( $\sim 900\text{ }^\circ\text{C}$ ) of DMAZ decomposition. However, the high melting and boiling points of solid  $\text{FeCl}_2$  produced by  $\text{FeCl}_3$  decomposition also has high catalytic activity, which can catalyze the decomposition of DMAZ above  $80\text{ }^\circ\text{C}$ , thus compensating the above disadvantages of  $\text{FeCl}_3$ . It was also found that at room temperature,  $\text{FeCl}_3$  without carriers could heat DMAZ from  $-30\text{ }^\circ\text{C}$  to  $376\text{ }^\circ\text{C}$  in only 0.037 s, while the small  $\text{Al}_2\text{O}_3$  particles formed by anhydrous  $\text{FeCl}_3$  carriers were found to be suitable for propellant ignition.

Alternatively, Mach I, Inc. (USA) [17] developed an iron phosphotungstate-based catalyst with higher activity, more stable performance, and lower cost, which could catalyze DMAZ and be used as a single-component propellant, making regenerating easier.

Fortini et al. [18] synthesized platinum-non-platinum self-adjusting catalysts for the decomposition of azide-based fuels. The platinum metals are mainly iridium, ruthenium, or iridium ruthenium alloys; the non-platinum metal compounds are mainly cerium oxide mixed with barium hafnate, barium zirconate, yttrium chromate or lanthanide chromates (e.g., lanthanum chromate, ytterbium chromate, erbium chromate, neodymium chromate, and their mixtures), etc., and non-platinum not only serves as a catalyst carrier but also a catalyst for propellant decomposition, during the catalytic process. If a platinum metal is eroded by high temperature or washed off by chemical substances in the catalytic process, causing local defects in the catalytic bed, the non-platinum metal as carriers can make up for this deficiency and continue to promote the decomposition of DMAZ.

Hallit et al. [19] investigated a self-ignition catalyst (HF-57J) for rocket-grade  $H_2O_2$  and DMAZ. They combined DMAZ with 8 wt.% anhydrous cobalt butyrate as a catalyst and 96 ~ 98 wt.%  $H_2O_2$  as oxidant, achieving the ignition delay of this dual-component propellant of only 1 ~ 2 ms. The performance of this dual-component system was very stable, but the ignition delay increased when the mass fraction of cobalt butyrate was reduced to 5 % ~ 6 %. Additionally, manganese butyrate and cobalt caprylate were found to catalyze self-ignition, but had such shortcomings as longer ignition delay and poorer fuel storage stability.

Hallit et al. [20] reported that for a mixture of DMAZ and cobalt isooctanoate solvent oil containing 12 % cobalt ethylhexanoate in the ratio of 85:15 by volume, the ignition delay was less than 16 ms when the mass fractions of Co and  $H_2O_2$  were 1.2 % and 90 %, respectively. If the volume ratio of DMAZ to cobalt (II) isooctanoate solvent oil was 50:50, and the mass fraction of  $H_2O_2$  was 98 %, the ignition delay was less than 16 ms.

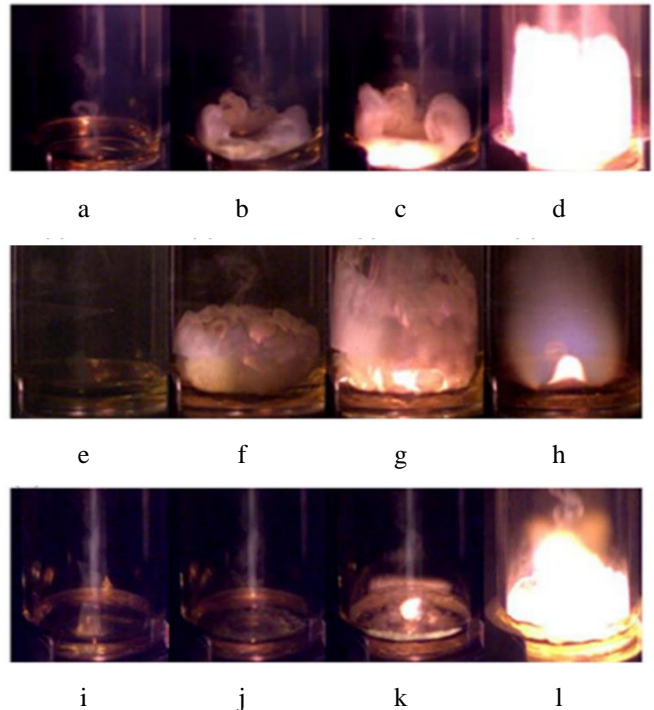
The ignition reaction of amines with nitric acid is the interaction of the N atoms of the amine group with the protons in the nitric acid. The transfer of protons from the NA to the amine N atoms in the fuel may be a key step in controlling the reaction. Using formulation, fuel mixing can produce a synergistic effect to accelerate the fuel ignition, thus shortening the fuel's ignition delay.

Generally, the ignition delay of tertiary amine fuel is 20–30 ms, while that of hydrazine fuel is 3–10 ms. Adding azides to tertiary amine fuel improves its density and energy, and the presence of azides reduces the ignition delay of tertiary amine fuel to the level of hydrazine fuel [21].

William et al. investigated the system with red-fuming nitric acid as the oxidant. They determined that the ignition delay of monomethylhydrazine was about 3–15 ms, that of N,N,N'-tetramethylethylenediamine was about 14 ms, and that of DMAZ was about 26 ms, all measured at 30 °C. The ignition delay of 33.3 % DMAZ compounded with 66.7 % N,N,N',N'-tetramethylethylenediamine to form a mixed fuel can be shortened to 9 ms [22]. The ignition delay of triazidoethylamine and red-fuming nitric acid was about

43 ms. The ignition delay could be reduced to 8 ms after N, N, N', N'-tetramethylethylenediamine compounded with triazidoethylamine in different proportions.

Wang et al. [23] explored the ignition delay of white fuming nitric acid with N, N, N', N'-tetramethylethylenediamine (DMAZ) and the mixture of 66.7 % N, N, N', N'-tetramethylethylenediamine and 33.3 % DMAZ under different pressures. Fig. 2 shows drop experiments of DMAZ, N, N, N', N'-tetramethylethylenediamine and their mixture with white-fuming nitric acid under 500 kPa pressure.

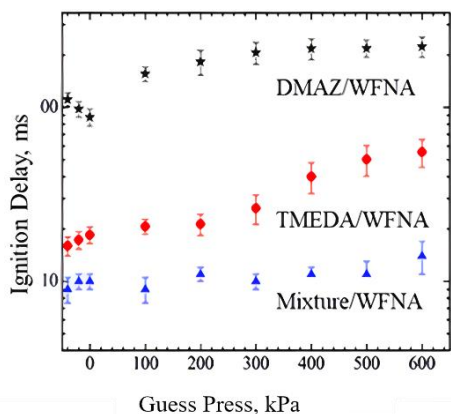


**Fig. 2.** Drop experiments of DMAZ, N, N, N', N'-tetramethylethylenediamine and their mixture with white fuming nitric acid under 500 kPa: a–t = 0 ms; b–t = 100 ms; c–t = 218 ms; d–t = 230 ms; e–t = 0 ms; f–t = 33 ms; g–t = 50 ms; h–t = 100 ms; i–t = 0 ms; j–t = 5 ms; k–t = 11 ms; l–t = 20 ms

Ignition delays of DMAZ, N, N, N', N'-tetramethylethylenediamine and their mixture with white-fuming nitric acid under different pressures were investigated. As shown in Fig. 3, the ignition delay of the mixture of N, N, N', N'-tetramethylethylenediamine and DMAZ was shorter than that of N, N, N', N'-tetramethylethylenediamine or DMAZ.

Compared with pure DMAZ, the addition of N, N, N', N'-tetramethylethylenediamine increases the heat release of the DMAZ salt formation reaction, thereby shortening the ignition delay period. Compared with pure N, N, N', N'-tetramethylethylenediamine, the addition of DMAZ brings azide groups, and its reaction temperature may be lower than the temperature required for decomposing N, N, N', N'-tetramethylethylenediamine salts or other secondary reactions. The combination of these two factors results in a shorter ignition delay period for the mixture. Based on the stable conformations of DMAZ obtained by DFT, the central N atoms of azide groups are aligned on the lone pair electrons of amine group N. This structure inhibits the

transfer of protons to the amine group and thus protects the electrons from the attack of nitrate protons.

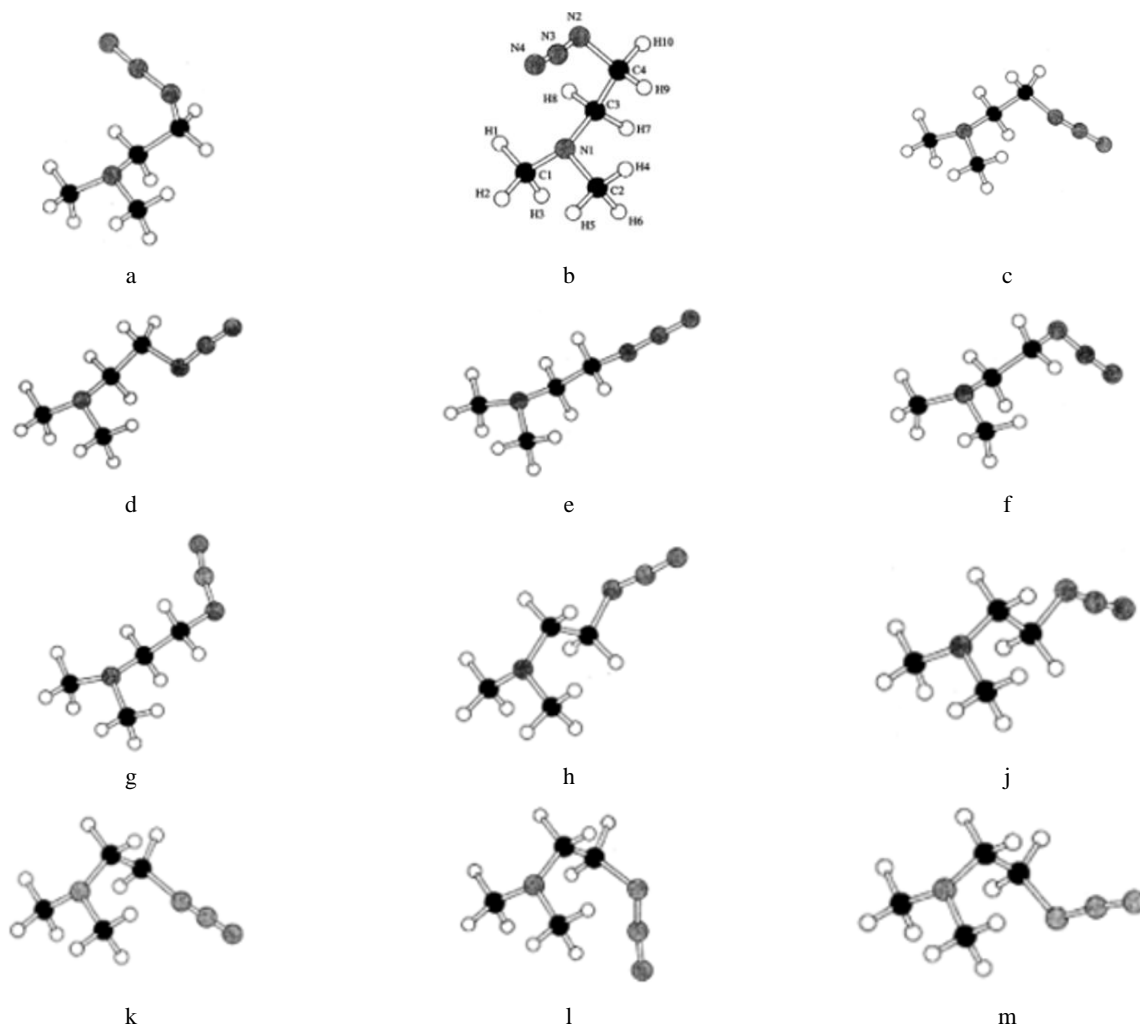


**Fig. 3.** Ignition of DMAZ, N, N, N', N'-tetramethylethylenediamine and their mixture with white fuming nitric acid under different pressures

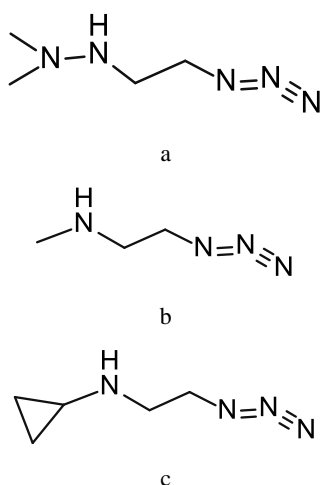
Therefore, it is possible to change the molecular structure so that the amine group N atoms can easily react

while retaining the azide groups. Fig. 4 shows the geometric parameters of 12 equilibrium conformations of DMAZ. The most stable conformation is the central N atoms of azide groups aligned on amine lone pair electrons, as shown in Fig. 4 b. Richman et al. [24] proposed the N,N-dimethyl-2-(2-azidoethyl) hydrazine (DMAEH), which molecular structure is shown in Fig. 5 a. Here, N atoms in the tertiary amine could freely interact with acidic protons, and the adjacent N atoms had unshared electron pairs, enhancing their nucleophilicity.

The molecules with this structure were more conducive to reducing the ignition delay, but no target product has been obtained yet in the actual synthesis process. Researchers from the Air Force Research Laboratory (ARL) [25, 26] investigated azido ethanamines, including N-methyl-2-Azido ethanamine (MMAZ) and N-cyclopropyl-2-Azido ethanamine (CPAZ). Fig. 5 b and c show its molecular structure. Compared with DMAZ, it retained the structure of azidoethyl and modifies the groups connected by amine N atoms. As demonstrated, MMAZ and CPAZ had little effect on the lone pair electrons of amine N atoms.

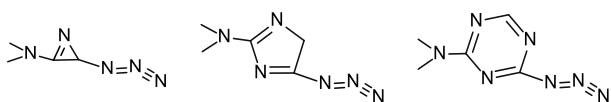


**Fig. 4.** Twelve equilibrium conformations of DMAZ



**Fig. 5.** The structures: a–DMAEH; b–MMAZ; c–CPAZ

Debasis et al. [27] designed a series of novel compounds with the structure of rigid groups by introducing rigid groups between azide groups and amine N atoms. The molecular structure of some compounds is shown in Fig. 6. These compounds were less toxic and had higher density and shorter ignition delay than potential MMH alternatives.



**Fig. 6.** Molecular structure of the proposed compounds

#### 4. CONCLUSIONS

Ignition delay is a key performance indicator of pyrophoric liquid propellant. Substitution of hydrazine by DMAZ as a green high-energy fuel can only be realized if ignition delay is reduced. Adding catalyst, fuel formulation, and tuning molecular structure makes it possible to reduce the ignition delay of DMAZ to hydrazine standard, providing effective support and guidance for developing and applying green fuel DMAZ. However, determining the optimal solution to reduce the ignition delay of DMAZ requires a further in-depth analysis of its mechanism and design of the optimal formulation.

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