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Preparation and Performance of a HNIW/TNT Cocrystal Explosive

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Abstract: A novel cocrystal explosive composed of 2,4,6,8,10,12-hexanitrohexaazaiso-wurtzitane (HNIW) and 2,4,6-trinitrotoluene (TNT) in a 1:1 molar ratio was effectively prepared by solvent/nonsolvent cocrystallization adopting dextrin as modified additive. The structure, thermal behavior, sensitivity, and detonation properties of HNIW/TNT cocrystal were studied. The morphology and structure of the cocrystal were characterized by scanning electron microscopy (SEM) and single crystal X-ray diffraction (SXRD). SEM images showed that the cocrystal has a prism type morphology with an average size of 270 μm. SXRD revealed that the cocrystal crystallizes in the orthorhombic system, space group *Pbca*, and is formed by hydrogen bonding interactions. The properties of the cocrystal including sensitivity, thermal decomposition, and detonation performances were discussed in detail. Sensitivity studies showed that the cocrystal exhibits low impact and friction sensitivity, and largely reduces the mechanical sensitivity of HNIW. DSC and TG tests indicated that the heterogeneous exothermic decomposition of the cocrystal occurs in the temperature range from 170 °C to 265 °C with peak maxima at 220 °C and 250 °C and significantly increases the melting point of TNT by 54 °C. The cocrystal has excellent detonation properties with a detonation velocity of 8426 $m\,s^{-1}$ and a calculated detonation pressure of 32.3 MPa at a charge density of 1.76 $g\,cm^{-3}$, respectively. Moreover, the results suggested that the HNIW/TNT cocrystal not only has unique performance itself, but also effectively alters the properties of TNT and HNIW. Therefore, the cocrystal formed by HNIW and TNT could provide a new and effective method to modify the properties of certain compounds to yield enhanced explosives for further application.

Keywords: Cocrystal explosive · HINW · TNT · Preparation · Performance

1 Introduction

The unprecedented aim for improving the safety and effective destructibility of modern weapons led to the development of insensitive high explosives (IHE) in the field of energetic materials [1, 2]. Unfortunately, the existing explosives having good thermal stability and excellent mechanical sensitivity usually exhibit poor explosive performances and vice versa. For instance, HNIW (Figure 1) is considered as an important high energy density compound with high detonation velocity, but it is more sensitive to impact and shock [3, 4]. On the contrary, TNT (Figure 1) features low sensitivity to impact with poor explosion performances [5]. Briefly, the demands from military weapons for explosives having good thermal stability, excellent safety and better performance could not be met with existing explosives. Hence, the main drawbacks for existing explosives in terms of sensitivity and power limit their further applications and the developments of modern weapons.

In view of the above, it is not devious to take an intensive study on the synthesis of new energetic materials and the modifications of existing explosives. However, the development of new explosives is a complex and time consuming process that requires a comprehensive consideration about property and cost for finally military applications [6–8]. On the other hand, researchers at different study groups have adopted recrystallizing and coating technologies to desensitize the existing explosives [9–14]. In fact, these traditional methods can't markedly reduce the sensitivity of existing explosives, only modify morphology or dilute power, due to without changing the inherent structures of explosive molecules. However, in the pharmaceutical industry, currently cocrystal technology is emerging as a potential method for offering improvements in solubil-

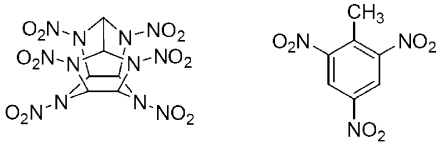

Figure 1. Molecular structures of HNIW and TNT.

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ity, stability, bioavailability, and mechanical property of drugs [15–18].

Cocrystals are single crystalline homogeneous phases consisting of two or more components assembled via noncovalent interactions such as hydrogen bonds, π–π or van der Waals interactions [19, 20]. Thus, cocrystals have different compositions and structures compared with pure components. Likewise, it is implied that cocrystal explosives may provide an opportunity to tune the properties of existing energetic materials. Nevertheless, literatures about cocrystal explosive are currently very limited. Michael first reported the HMX/AP (ammonium perchlorate) cocrystal [21]. Recently, two types of cocrystal explosives based on TNT have been obtained by slow evaporation solvent [22, 23]. Duan et al. simulated and obtained a HMX/TATB cocrystal explosive without crystal structure data [24, 25]. Research results indicated that cocrystal explosives could effectively modify the properties of single pure explosives. However, the preparation of cocrystal explosive by reported methods suffers from main drawbacks like, (a) difficulty of scale-up, (b) consuming more time, and (c) low yield. Besides, detailed information about performance changes for cocrystal explosives, are not readily available in open literature, especially detonation and safety properties. Therefore, with this in mind, we have undertaken efforts to develop an effective preparation method, which can favor scale-up preparation of cocrystal explosive being available to allow detailed performance evaluation studies for further applications.

In this work, a HNIW/TNT cocrystal explosive was prepared by cocrystallization. The process was carried out by adding water (as nonsolvent) to ethyl acetate (as solvent) solution of HNIW and TNT in the presence of dextrin (as additive). The paper also presents a multifaceted study on HNIW/TNT cocrystal explosive including structure characterization, thermolysis, sensitivity, and detonation properties in detail.

2 Experimental Section

2.1 Materials

HNIW was provided by Liaoning Qing Yang Chemical Industry Co., Ltd. TNT was obtained by East Chemical Industry Company. The other chemicals and reagents used in the present study were purchased from trade without further purification.

2.2 Preparation of HNIW/TNT Cocrystal Explosive with Additive

Ethyl acetate (150 mL) was put into a crystallizer fitted with a stirrer and a thermometer. HNIW (43.8 g), TNT (22.7 g), and dextrin (1.5 g) were added to the ethyl acetate solution, and the mixtures were stirred to dissolve at 50 °C. Afterwards distilled water (120 mL) was added to the crystallizer by constant flow pump within 60 min. The temperature was kept at 50 °C during the addition of water. After completion of addition, stirring was continued for another 10 min at the same temperature. At last, the precipitate was filtered, washed, and dried in air to give 56.5 g of HNIW/TNT cocrystal explosive as colorless particles with a yield of 85 %. Elemental analysis for HNIW/TNT cocrystal (confirmed by Vario EL III elemental analyzer): calcd. C 23.46; H 1.65; N 31.58 %; found: C 23.52; H 1.62; N 31.55 %. Results suggested that the HNIW/TNT cocrystal contains no dextrin after crystallization.

2.3 Morphology Characterization

The morphologies of the HNIW/TNT cocrystal explosive and raw materials were examined with a LE0438 VP scanning electron microscope (SEM) instrument made in Britain at 12 kV and 10 μA.

2.4 Structure Characterization

The structural features of the HNIW/TNT cocrystal explosive was investigated with a Xcalibur Eos diffractometer, using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å) at 50 kV and 30 mA. A total of 12659 diffraction data were collected at 293 K in the 2θ range 6.08–52.74°. Among them, 4892 data were unique with $R_{int} = 0.0298$ and 4468 observed data were used in the refinement.

The crystal structure was solved by direct methods using SHELXS and refined by least squares minimization using SHELXL [26].

2.5 Sensitivity Test

The impact sensitivity test was conducted with a WL-1 type impact sensitivity instrument according to the GJB-772A-97 standard method 601.2 [27]. The test conditions were: drop weight, 2 kg; sample mass, 30 mg. The impact sensitivity of each test sample was expressed by the drop height of 50 % explosion probability (H_{50}).

The friction sensitivity test was determined with a WM-1 type friction sensitivity instrument according to GJB-772A-97 standard method 602.1 [27]. The test conditions were: relative pressure, 3.92 MPa; sample mass: 20 mg, pendulum weight: 1.5 kg; pendulum angle: 90°. The fraction sensitivity of each test sample was expressed by explosion probability (P).

In addition, the physical mixtures of HNIW and TNT at 1 : 1 molar ratio were used as a reference.

2.6 Thermal Analysis

The differential scanning calorimeter (DSC) test was recorded with a TA Q100 instrument by heating 1–2 mg of HNIW/TNT cocrystal explosive at a rate of 10 K min^{-1} in a nitrogen atmosphere (50 mL min^{-1}).

The thermogravimetry (TG) test was recorded with a TA Q600 instrument by heating about 2 mg of HNIW/TNT cocrystal explosive at a rate of 10 K min^{-1} in a nitrogen atmosphere (50 mL min^{-1}).

In addition, the physical mixtures of HNIW and TNT at 1:1 molar ratio were used as a reference.

2.7 Detonation Properties Test

The detonation velocity of the sample was tested by probes based on GJB-772A-97 standard method 702.1 [27]. The HNIW/TNT cocrystal explosive sample was molded at room temperature under 180 MPa pressure with a dwell time of 15–20 s to obtain an explosive cylinder with a dimension of 10×10 mm. When the explosive cylinder was initiated by the detonator, the propagation time of detonation wave across the distance between two probes was recorded. The detonation velocity was calculated from the probe distance and measured time of propagation.

Besides, the physical mixtures of HNIW and TNT at 1:1 molar ratio were used as a reference.

3 Results and Discussions

3.1 Morphology

The SEM images of HNIW, TNT, and the HNIW/TNT cocrystal explosive are shown in Figure 2. The differences in morphology among them are obvious. The HNIW exhibits a spindle-like shape, and the TNT has an irregular block type glomerocryst microstructure with very coarse surfaces. However, the HNIW/TNT cocrystal explosive presents a prism type crystal morphology with smooth and integrated particle surface. Besides, the cocrystal explosive has an average particle size of about 270 μm with good flowability. Therefore, the SEM results reveal that the cocrystal provides a useful method for controlling the morphology and particle size of energetic materials. In addition, dextrin was used as a modified additive to enhance crystal quality of the HNIW/TNT cocrystal. Experiments showed that cocrystals become more compact and smooth as the dextrin increases, i.e. bulk density and flowability of cocrystals increase with increasing the dextrin.

3.2 Structure of the Cocrystal Explosive

A HNIW/TNT cocrystal explosive with suitable size was selected for single-crystal X-ray diffraction (SXRD) to determine the crystal structure of the cocrystal. The crystallographic data of the cocrystal are reported in Table 1 with molecular and 3D structures shown in Figure 3 and Figure 4, respectively.

The obtained results indicate that the HNIW/TNT cocrystal consists of HNIW and TNT in a 1:1 molar ratio, belonging to the orthorhombic system with space group *Pbca*. SXRD analysis shows that the HNIW and TNT molecules are arranged as linear tapes, mainly assembled by a series of C–H···O hydrogen bonds. For instance, as shown in Figure 5, one C–H···O intermolecular hydrogen bond (H···O 231 pm, C–H···O 146°) occurs between the O_{HNIW} atom O(3)

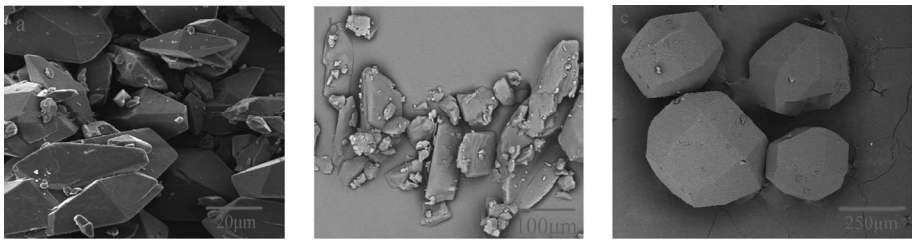

Figure 2. SEM images of explosives, (a) HNIW; (b) TNT; (c) HNIW/TNT cocrystal explosive.

Table 1. Crystallographic data for HNIW/TNT cocrystal explosive.

HNIW/TNT cocrystal explosive			
Formula	$C_{13}H_{11}N_{15}O_{18}$	β/°	90.00
MW/g mol^{-1}	665.37	γ/°	90.00
Stoichiometry	1:1	Cell volume/pm^3	478720(10)
Color	colorless	Z	8
Morphology	prism	ρ_{calc}/g cm^{-3}	1.846
Temperature/K	293.15	Crystal size/mm^3	0.35×0.30×0.30
Crystal system	orthorhombic	No. of all data	12659
Space group	*Pbca*	No.of unique data	4892
a/pm	973.52(2)	No. of observed data	4468
b/pm	1991.21(6)	GOF	1.023
c/pm	2469.55(6)	R_1 [$I > 2\sigma$]	0.0489
α/°	90.00	wR_2 [all data]	0.1166

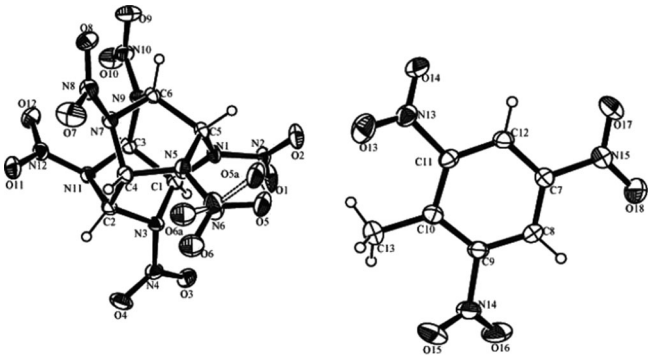

Figure 3. Molecular structure of HNIW/TNT cocrystal.

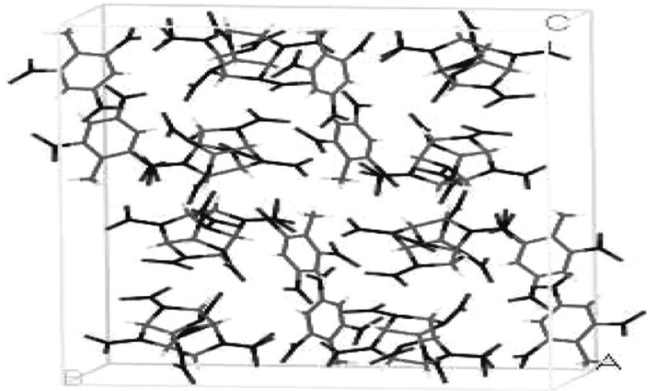

Figure 4. 3D packing of HNIW/TNT cocrystal.

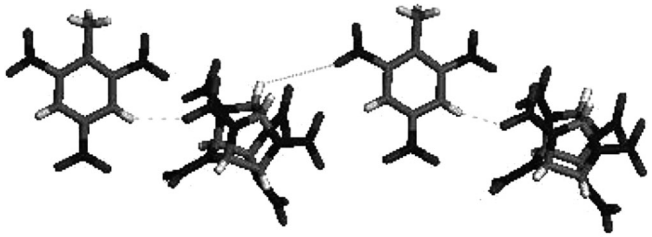

Figure 5. Hydrogen bonds between HNIW and TNT molecules.

and the H_{TNT} atom H(8), another hydrogen bond (H···O 262 pm, C–H···O 161°) interaction lies between the H_{HNIW} atom H(5) and the O_{TNT} atom O(13). The observed distances are in the region for hydrogen bonds of this type [28]. These hydrogen bond interactions connect HNIW and TNT molecules, form the zigzag chains and propagate through crystal, resulting in formation of the cocrystal.

3.3 Sensitivity

The HNIW, TNT, HNIW/TNT mixtures, and the HNIW/TNT cocrystales all having similar crystal sizes and surface roughness, were subject to sensitivity tests and the results are given in Table 2.

The impact and friction sensitivity of the HNIW/TNT cocrystal are 30 cm and 58%, respectively, which are higher than those of TNT, but evidently lower than those of HNIW and HNIW/TNT mixtures. It indicated that the cocrystal is more insensitive to mechanical stimuli due to its unique crystal structure formed by cocrystallization. As known to all, the mixtures were formed only by simple accumulation of HNIW and TNT particles at a macroscopic scale without changing inherent structure and component of pure component crystal. Whereas for the cocrystal, HNIW and TNT molecules are packed close through intermolecular interactions by cocrystallization, which can decrease the volume and number of cavity in cocrystal crystalline, therefore leading to a reduction in the probability of formation hot spots [29]. Furthermore, the stability of the cocrystal is improved by hydrogen bond interactions [30]. As a result, the cocrystal can significantly reduce the sensitivity of HNIW compared to the mixtures. Besides, experiments showed that the impact sensitivity of HNIW, TNT, the mixtures, and the cocrystal reduce with decreasing crystal sizes and surface roughness, and the friction sensitivity of them increase as crystal sizes decrease and surface roughness increases. However, the cocrystal brings greater changes in sensitivity than those of crystal size, surface roughness, and the mixtures. The results proved that cocrystallization provides to be an effective method to alter the sensitivity for sensitive explosives. Consequently, we can cocrystallize a sensitive explosive with an insensitive explosive, such as TATB, LLM-105, to reduce the sensitivity of the sensitive explosive so as to obtain more insensitive cocrystal explosives.

3.4 Thermal Analysis

The DSC and TG curves of HNIW/TNT cocrystal and HNIW/TNT mixture are depicted in Figure 6 and Figure 7, respectively. In the DSC curve, the cocrystal has a narrow endothermic peak with onset at 134 °C, which is denoted as the melting point of the cocrystal. It showed that the melting

Table 2. Results of sensitivity for explosive samples.

Samples	Average particle size, d_{50}/μm	Surface roughness	Impact sensitivity, H_{50}/cm	Fraction sensitivity *P*/%
TNT	98	smooth	103	0
HNIW	99	smooth	13	100
HNIW/TNT mixture	98	smooth	19	89
HNIW/TNT cocrystal	100	smooth	30	58

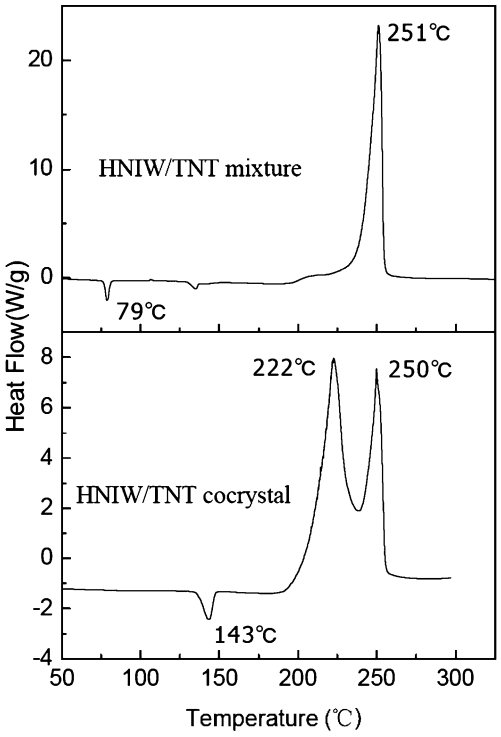

Figure 6. DSC curves of HNIW/TNT cocrystal and HNIW/TNT mixture.

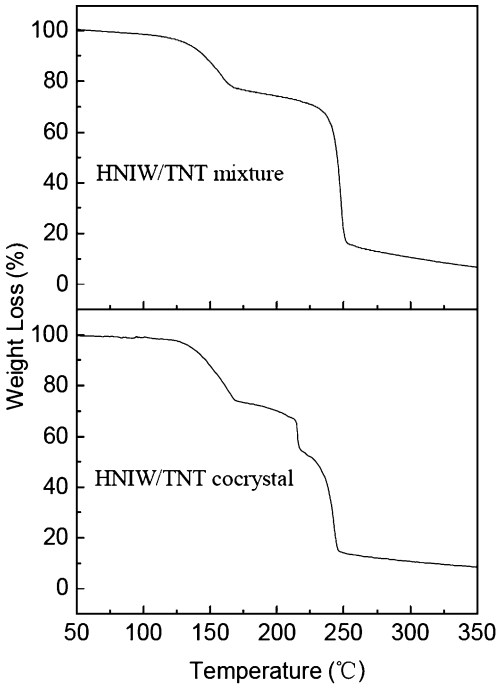

Figure 7. TG curves of HNIW/TNT cocrystal and HNIW/TNT mixture.

point of the cocrystal is higher than that of TNT (melting point 79–80 °C [31]), whereas for the HNIW/TNT mixture, a narrow endothermic peak appears at 79 °C corresponding to the melting point of TNT. Thus, the result indicated that the melting point can be tuned by cocrystallization. Surprisingly, unlike many of pharmaceutical cocrystals, the cocrystal presents two exothermic peaks in the temperature range of 170–265 °C. It may be explained by the assumption that the structure of the cocrystal is destroyed with increasing temperature and is converted to liquid TNT and HNIW, leading to heterogeneous decomposition [32]. In consequence, the decomposition peak maxima (T_{max} = 222 °C, T_{max} = 250 °C) of the cocrystals have a shift in contrast to TNT (T_{max} = 320 °C [31]) and HNIW (T_{max} = 249 °C [31]). For the mixture, it has an intense exothermic decomposition peak similar to pure HNIW. So the results also revealed that cocrystallization can change the decomposition temperature of explosives. The results obtained above demonstrated the potential ability of cocrystallization to alter thermal behaviors of explosives.

In addition, the TG curves of the HNIW/TNT cocrystal and HNIW/TNT mixture exhibit four and three weight loss steps, respectively, reflecting a heterogeneous decomposition process. A stable weight loss starts at 117 °C due to evaporation loss of TNT in the mixture, but for cocrystal, it starts at 134 °C due to evaporation loss of the cocrystal, indicating that the cocrystal may have higher thermal stability than simple mixtures. Two obvious and rapid weight losses occur in the temperature ranges of 214–221 °C and 238–249 °C for the cocrystal, respectively, suggesting intense thermal decomposition, whereas for the mixture, a rapid weight loss appears between 236 and 251 °C.

3.5 Detonation Properties

The detonation velocity of each explosive sample was measured by standard method and the results are listed in Table 3. The detonation pressure of these samples were calculated based on charge density and measured detonation velocity by the following equation [33].

$$P = \rho_0 D^2 (1-0.713\rho_0^{0.07})$$

where P is the detonation pressure of an explosive in GPa, ρ_0 the initial density of unreacted explosive in g cm^{-3}, and D is the detonation velocity in km s^{-1}. When substituting the charge density and measured detonation velocity into

Table 3. Results of measured detonation velocity and calculated detonation pressure for explosive samples.

Samples	Charge density/g cm^{-3}	Measured detonation velocity/m s^{-1}	Calculated detonation pressure/MPa
TNT	1.61	6712	19.1
HNIW	1.83	8770	36.1
HNIW/TNT mixture	1.70	8058	28.7
HNIW/TNT cocrystal	1.76	8426	32.3

above equation, calculated detonation pressure can be obtained easily. The results are shown in Table 3.

From Table 3, it can be seen that the measured detonation velocity and calculated detonation pressure of HNIW/TNT cocrystal are higher than those of both samples except for pure HNIW. It suggested that the cocrystal exhibits better detonation properties than pure TNT and the mixtures. It can be explained by the fact that the cocrystal has higher crystal density due to increasing packing coefficient by cocrystallizing HNIW with TNT, and thus it presents higher pressed density under the same pressure. Moreover, the results showed that the cocrystal brings larger improvements on the detonation properties for pure TNT than the mixtures. For example, the cocrystal increases the detonation velocity of pure TNT as much as 25.5 %. In short, cocrystallization can offer a means of tuning the detonation performances and achieving higher density explosives with enhanced property.

4 Conclusion

A novel HNIW/TNT cocrystal explosive was prepared by solvent/nonsolvent cocrystallization using dextrin as additive in a high yield of 85 %. SEM images and SXRD results showed that the cocrystal with prism shaped morphology belongs to the orthorhombic system with space group *Pbca*. Sensitivity tests indicated that the cocrystal has lower impact and friction sensitivity, and significantly reduces mechanical sensitivity of HNIW. DSC and TG curves revealed that the exothermic decomposition of the cocrystal occurs in the temperature range of 170–265 °C with a melting point at 134 °C, meanwhile, the cocrystal alter the thermal behaviors of TNT and HNIW. Moreover, detonation performance studies revealed that the measured detonation velocity and calculated detonation pressure for the cocrystal are 8426 m s^{-1} and 32.3 MPa at a charge density of 1.76 g cm^{-3}, respectively, showing that the cocrystal has an excellent detonation performance. The HNIW/TNT cocrystal exhibits lower sensitivity with good power by cocrystallization, which offers a potential opportunity to tune performances of existing explosives to offer explosives with enhanced properties. The investigation on the other properties of HNIW/TNT cocrystal and searching for other cocrystal explosives are undergoing.

Acknowledgments

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