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STUDIES IN THE FIELD OF CHEMISTRY OF NITRO COMPOUNDS (TO 100TH BIRTHDAY ANNIVERSARY OF S. S. NOVIKOV)

Polymorphic Transformations of Hexanitrohexaazaisowurtzitane

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Abstract—Conditions of recrystallization of hexanitrohexaazawurtcitane from one polymorphic state into another were examined. Techniques for preparations of various polymorphic modifications of product were developed.

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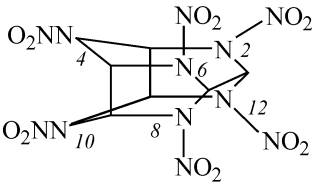
Synthesis of new high power substances are one of the priority trends in development of defense and space technologies. Thus, hexanitrohexaazawurtcitane, polycyclic nitramine (HNIW, CL-20) is the urgent and promising subject of studies. It was for the first time synthesized in 1987 in Naval Air Wifave Center (USA). It possesses the combination of unique power properties and can have the widest field of application [1]:



Under the normal conditions there are four stable polymorphous modifications of the product: α, β, γ and ε, which distinguish by conformations, by a nature of packing of molecules in a crystal, by density and other physical properties (Table 1) [1–3].

There exists labile ξ- polymorphous modification under the increased pressure [2, 4]. ε- Polymorph is the most high-density (the commodity product is HNIW).

Literature data shows that many studies of polymorphous regroupings in the solid product under the action of the increased temperatures and pressure were conducted [4, 5]. Nine transformations between five known polymorphous modifications: γ-α, γ-β, γ-ε, γ-ξ, ξ > ε, β > ε, β > α, ε > α, ξ > α were described. It was

Table 1. The properties of the polymorphic modifications of HNIW

Properties	Polymorphic modification			
	α	γ	β	ε
N_{10}–N_4 orientation	*exo–exo*	*exo–exo*	*exo–exo*	*exo–endo*
Nimber of molecules in a cell	8	4	4	4
Spatial group	Pbca	$P2_1/n$	$Pb2_1a$	$P2_1/n$
Cristalline form	orthrhombic	monoclinic	orthrhombic	monoclinic
Temperature and nature of melting, °C	– 250 (decomp.)	– 250 (decomp.)	$114_{\beta>\gamma}$ 250 (decomp.)	$164_{\varepsilon>\gamma}$ 250 (decomp.)
Density, g cm^{-3}	1.961 (2.001)[a]	1.916	1.985	2.04

[a] The value for a semihydrate of α-modefecation.

shown that the thermal treatment of product in different plasticizers and polymers also can be accompanied by the partial or complete polymorphous transformation [6].

Sufficiently many recent studies, IR and Raman spectroscopy [2, 4, 6], RFC [7], DTA/TGA analysis [5], are devoted to the identification of polymorphous belonging HNIW. The analysis of polymorphous mixtures presents the greatest complexity, although in practice even cleanest samples can contain trace quantities of polymorphous admixtures.

Literature data about preparation of different polymorphous modifications from the solutions of the substance are small and often badly reproduced. Cooling the saturated solution in the individual solvent in [8], precipitation in [9–12], and the evaporation [11, 13–15] were recommended to use.

In the case of the crystallization from the individual solvent the expressed dependence of the solubility of substance on the temperature is necessary. The selection of a solvent for the recrystallization of HNIW is hampered since this dependence is weak (Table. 2).

At least two constituents are used for the precipitation and evaporation techniques: one of them are used as solvent of HNIW (solubility of more than 20%), and another, as a precipitating agent (solubility of less than 5%). Besides these constituents must miscible and be chemically compatible.

In the course of this study a solubility of HNIW was determined in some binary systems (the mixing with 150 rpm for 7 h) (Table 3).

The greatest dependence of the solubility on the temperature was observed for the systems ethylacetate–dichloroethane, ethylacetate–ethanol.

The order of the mixing of the constituents of the crystallization system played important role. In the start time at addition of the precipitating agent to the saturated solution of HNIW the concentration of latter was maximum (Fig. 1, curve *1*).

On the contrary at the low addition of the saturated solution of HNIW to the precipitating agent in the start time the HNIW concentration was zero (Fig. 1, curve *2*).

In the course of a dosage the weight of the crystallization system increased and as a result the HNIW concentration in the solution changed. Gradually the HNIW concentration in the solution reached the critical value, which corresponds to the beginning of the crystal formation. Thereby a part of HNIW transferred from the solution in the solid state with decrease in HNIW concentration in the solution. In certain time the equilibrium between the HNIW concentration in the solution and in the solid was reached and then the crystal formation damped.

In the regime of the precipitation (Fig. 1, curves *1, 2*) for the completion of the formation of crystals was required a long-term maintenance. The dynamics of the crystal growth was investigated in the three-component

Table 2. HNIW solubility in various solvents

Solvent	HNIW solubility, g/100 g of a solvent		References
	at 20–25°C	at solvent boiling temperature	
Aceton	94.6–97.1	–	[16]
Acetinitrile	47.5–49.3	–	[16]
Ethyl acetate	42.97–45	–	[16]
Nitroplastizide	1.46–2.3	–	[16]
Trimethylol trinitrate	0.73–1.61	–	[16]
Ethanol	0.63–0.87	1.57	[16]
Water	<0.005–0.0095	–	[16]
1,2-Dichloroethane	0.24	0.52	–
Tetrahydrofuran	–	27.66	–
DMFA	65–67	–	–
ε-Caprolactam	–	55.7 (at 100°C)	–

Table 3. HNIW solubility in binary systems

System	System composition, %	Temperature, °C	HNIW solubility, %	Δ,%
Aceton/tetrachloromathane	6.81/93.19	40	1.3–1.6	0.76
		25	0.7–0.8	
Aceton/water	79.2/20.8	30	21.9–22.6	0.40
		25	21.4–22.2	
Ethyl acetate/ethanol	58.8/41.2	50	19.5–20.7	7.20
		25	13.1–13.5	
Ethyl acetate /1,2-dichloroethane	50.4/49.6	70	17.6–18.3	9.80
		25	7.9–8.5	
Ethyl acetate / tetrachloromathane	20.1/79.9	45	3.9–4.3	2.20
		25	1.7–2.1	
tetrachloromathane /toluene	49.0/51.0	60	41.4–44.8	2.10
		40	41.2–44.4	
		20	40.6-43.9	
Acetonitrile/1,2-dichloroethane	13.5/86.5	22	0.4–0.55	4.75
		82	5.0–5.3	
Tetrahydrofuran/tetrachloromathane	14.3/85.7	–8	0.92–0.95	1.85
		25	2.3–2.8	

system: HNIW 2.5%, the solvent 5.8%, the precipitating agent 91.7%. The precipitating agent was drop by drop added to the HNIW saturated solution being stirred in the solvent during 2 h at temperature 17°C (Fig. 2).

First probing of the product (Fig. 2a) was made in the crystal formation onset. On the snapshot made in the transmitted light it is apparent that the crystal seeds were grouped into the agglomerates of rounded form (Fig. 2a). The size of agglomerates was 150–200 μm. For 3 h from the crystallization onset upon the seed growth made we could see distinct flat and rectangular single crystals with the size of 120–160 μm (Fig. 2b). For 24 h in the crystallization system the crystals of two dimensional fractions: of 250–300 m with regular rounded form, and of 120–150 μm with elongated oval irregular form, were formed (Fig. 2c). The growth in the fine crystal fraction was observed for 48 h to 150–200 μm with formation of more regular crystals (Fig. 2d). For 72 h a number of the large particles (300–350 μm) was notable increase compared to the small ones.

The form of the crystals became even more rounded (Fig. 2e). For 144 h the large rounded particles with the flat surface were formed (300–350 μm). In the sample there were an insignificant number of the particles with the size 150–200 μm of oval form (Fig. 2f). The output of the product at the end of the crystallization was 70%.

The evaporation technique of crystallization is the most optimum in our estimation. From the three-component crystallization system HNIW–solvent–precipitating agent with the aid of the simple or vacuum distillation the part of the solvent was gradually removed (Fig. 1, curve *3*). Namely, under these conditions the largest crystals optimum for the morphology can be obtained in short time with the high output.

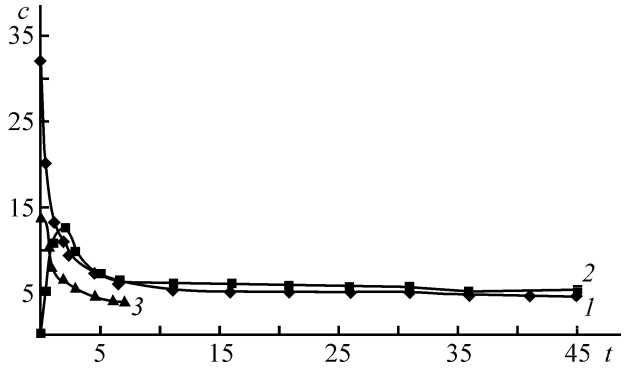


Fig. 1. A change in HNIW concentration *c* (%) in the solution of the crystallization system vs. the crystallization time *t* (h). (*1*) Addition of a solvent to HNIW saturated solution; (*2*) Addition of HNIW saturated solution to a precipitating agent; (*3*) Distillation of a solvent from a three-component system.

In some works it is asserted that the applied precipitating agent and solvent (density, polarity) determine the polymorphous belonging of the obtained product [8]. Our study showed that this assertion was not correct entirely.

The same system of solvents under the varied conditions can provide relatively stable preparation of different polymorphous modifications of HNIW. Seemingly the formation of one or other polymorph of HNIW is of the random and unpredictable nature. However, the selectivity of the preparation of the required polymorphous modification can be attained selecting such technological parameters as temperature and composition of the crystallization system, and also introducing the additionally prepared inoculum of the required polymorph.

As shown in the studies two factors promote formation of γ-polymorphous modification of HNIW: a temperature increase and an absence of water in the crystallization system. The crystals of γ-polymorph can be bulk rectangular parallelepipeds as well as flat square or rectangular plains in correspondence with the solvent type (Fig. 3).

The samples of γ- polymorphous modification possess larger sensitivity to shock than ε-polymorph.

For the crystallization systems, which consist of different solvent-precipitating agents, there exists an distinct lower temperature threshold of the formation of γ-polymorphous modification (Table. 4).

α-Polymorphous modification of HNIW (Fig. 4) can be both as the distinct compound and as the admixture but only in the form of hydrate. An anhydrous compound was not hitherto described. Thus, the key factor in preparation of α-polymorph is the presence of water in the crystallization system. Therefore the solvent and precipitating agent for crystallizing the α-polymorphous modification should be selected in a number of the

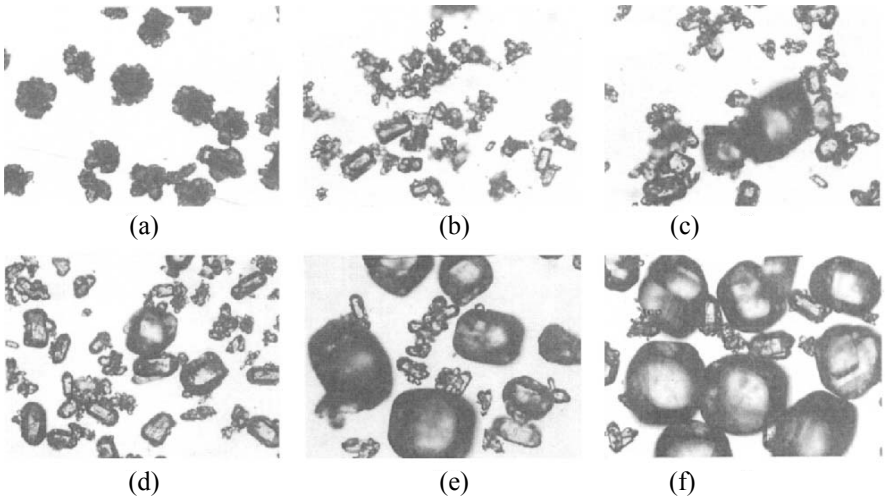


Fig. 2. A dynamics of the HNIW crystal growth vs. the crystallization time *t*. Crystallization time (h): (a) 2, (b) 3, (c) 24, (d) 48, (e) 72, (f) 144.

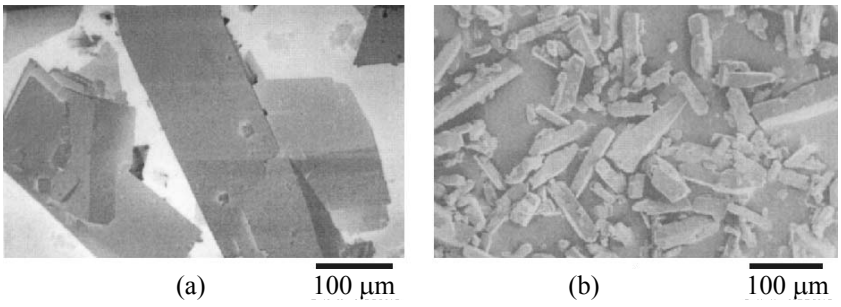


Fig. 3. Micro snapshots of γ-polymorph. (a) Precipitation of 1,2-dichloroethane without polymorphous admixtures, (b) The evaporation crystallization in system ethyl acetate–toluene at 90°C (an amount of ε-polymorph is 5%, an amount of α-polymorph, 3%).

Table 4. Lower temperature threshold of formation of γ-polymorphic modification

Crystallization system		Lower temperature threshold of formation of γ-polymorphic modification,°C
Solvent	precipitating agent	
Mixture nitrous and acetic acids, 50/50	–	55–60
Ethyl acetate	toluene	85–90
1,2-Dichloroethane	–	80
Tetrahydrofuran	methylene chloride	30

polar solvents, which contain the hydrated water (water, alcohols, acid, aqueous acetone, acetonitrile).

System tetrahydrofuran–methylene chloride] [17] and dimethylcarbonate [8] was suggested for preparation of β- polymorphous modification.

The single crystals of β-polymorph of the complex irregular form were obtained as a result of a sharp cooling of the HNIW saturated solution in 1,2-dichloroethane

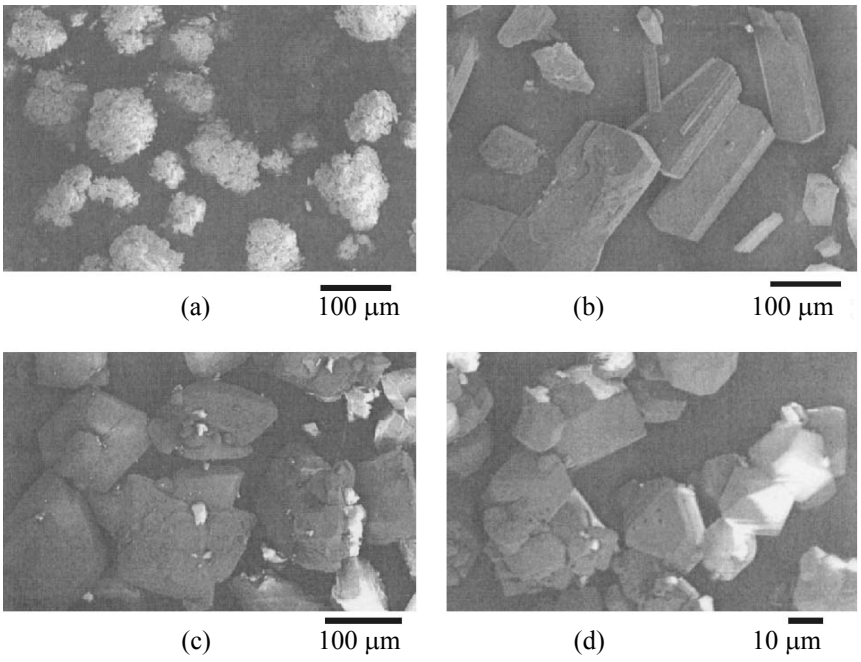


Fig. 4. Micro snapshots of α-polymorph. (a) Precipitation from solution in tetrahydrofuran by tetrachloromethane(an amount of ε-polymorph is 5%); (b) from acetonitrile solution by tetrachloromethane without polymorphous admixture; (c) from solution in acetone by water (an amount of ε-polymorph is 8%); (d) from ethyl acetate solution by tetrachloromethane (an amount of ε-polymorph is 10 %).

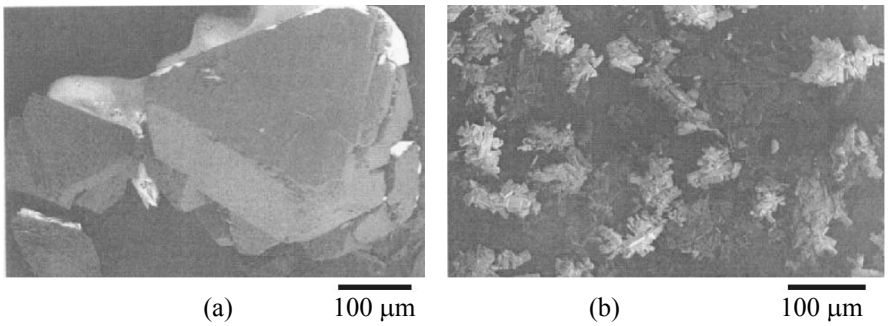


Fig. 5. Micro snapshots of β-polymorph. (a) Cooling of the saturated solution in 1,2-dichloroethane (amount of ε-polymorph 5–10%); (b) precipitation in tetrahydrofuran by clorinated carbon (an amount of ε-polymorph is 25–30%).

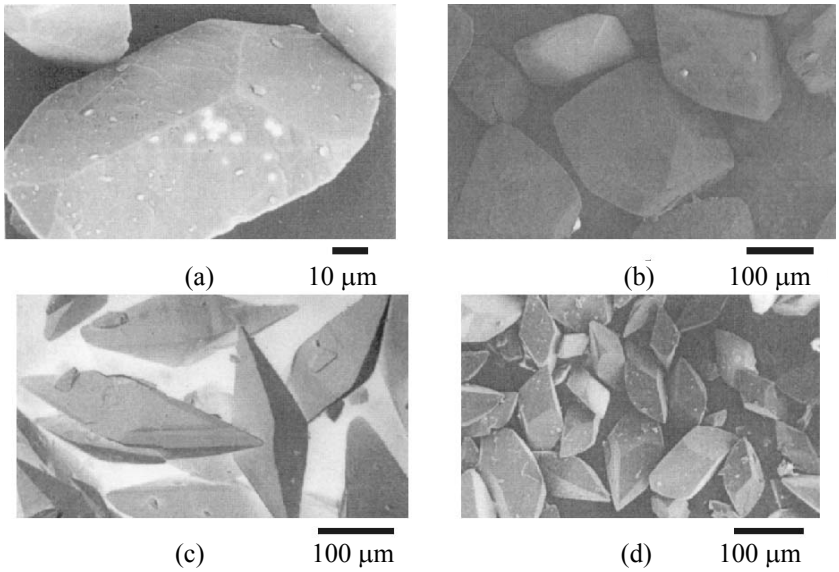


Fig. 6. Micro snapshots of ε-polymorph. (a) Addition of toluene in ethylacetate solution; (b) Precipitation of the ethylacetate solution by benzyl alcohol; (c) Ethylacetate–toluene at an increased temperature; (d) Ethylacetate–toluene at room temperature;

(Fig. 5a). We established that the upper temperature boundary of β-polymorph formation in tetrahydrofu ran–chloroform was 30°C, thereby we obtained the crystals with thin needles assembled in fanciful bunches (Fig. 5b).

The crystals of ε-polymorph have complex octahedral form. Depending on the type of crystallization system and the preparation conditions they can be rounded, rectangular, elongated along one axis or pointed (Fig. 6).

In the course of the crystallization from the solutions of ε-caprolactam was isolated HNIW crystalline complex. On IR spectrum of complex the absorption band in the region 1420–1490 cm^{-1} is observed. This band is absent on the spectrum of pure HNIW but characteristic for the spectrum of ε- caprolactam.

EXPERIMENTAL

Purity and polymorphic belonging were determined by IR and Raman spectrocropy (double-beam IR spectrometer Specord 75 IR and double-beam IR spectrometer Perkin–Elmer-684), and by X-ray phase analysis with DRON-2 diffractometer. Melting point was measure by a heating table of Boetius type, electron-microscopic examinations were conducted with the aid of optical and scanning electron microscope. The crystal density was measured by helium densimeter Accu Rus 1340. We used chemicals of pure and chemically pure grades.

γ-Polymorphous modification of HNIW. The solution of HNIW (50 g) in 125 ml of ethyl acetate was added to 360 ml of heated (95°C) toluene being stirred. This mixture kept an hour at 90°C. Then with the aid of a water-jet pump a flask with the crystallization system was evacuated up to 0.08–0.4 kgs cm^{-2}. A distillate was condensed in the Liebig condenser and gathered into receiver. For 6 h the obtained product was filtered off, washed on the filter in toluene, and dried. Yield was 85%; $\rho = 1.92$ g cm^{-3}.

IR spectrum: 1628.1, 1608.5, 1553.8, 1332.1, 1278.0, 1265.9, 1220.7, 1179.7, 1152.3, 1106.2, 1080.2, 1042.5, 958.0, 937.7, 909.5, 892.2, 878.5, 858.3, 830.4, 754.7, 718.8, 668.3 cm^{-1}.

Raman spectrum: 3038.0, 3022.9, 1620.1, 1618.2, 1613.8, 1611.7, 1609.6, 1607.0, 1605.2, 1603.4, 1579.1, 1577.2, 1555.5, 1329.7, 1289.4, 1287.9, 1265.4, 1263.9, 1227.7, 1052.8, 905.7, 878.9, 750.0, 716.7, 656.3 cm^{-1}.

β-Polymorphous modification. To heated up to the boiling 1,2-dichloroethame (360 ml) being stirred 1.53g of fine-crystalline HNIW preliminarily purified by recrystallization were gradually added. The mixture was maintained at a temperature 95°C during 30 min. Then additionally 45 ml of 1,2-dichloroethane were added. The mixture was cooled to 17°C for 1 h. The obtained product was filtered off, and dried. Yield was

22%; ρ = 1.99 g cm^{-3}.

IR spectrum: 1605.9, 1569.1, 1555.7, 1329.6, 1266.4, 1169.3, 1094.4, 1051.9, 990.4, 944.0, 904.7, 880.8, 834.9, 764.9, 751.1, 718.0 cm^{-1}.

Raman spectrum: 3038.3, 3033.6, 3023.3, 1620.0, 1618.2, 1616.1, 1613.7, 1611.6, 1609.4, 1605.2, 1576.8, 1569.8, 1568.2, 1555.0, 1328.8, 1290.5, 1267.2, 1265.6, 1227.2, 1093.6, 1051.1, 989.4, 950.7, 943.2, 903.8, 880.0, 834.0, 764.1, 750.1, 744.8, 742.2, 740.1, 737.4, 716.8, 654.1 cm^{-1}.

α-Polymorphous modification. Tetracloromethane was drop by drop added to the solution of HNIW (11.75 g) in 50 ml of acetonitril at 22 °C during 10 min. After 30 min keeping 50 ml of tetrachloroethame were added. For 4 hour the product was filtered off, washed on the filter by tetrachloromethane, and dried. Yield was 33.5%; ρ = 2.001 g cm^{-3}.

IR spectrum: 1619.2, 1556.1, 1330.6, 1266.3, 1228.5, 1166.9, 1095.4, 1053.8, 988.7, 951.8, 903.4, 879.8, 834.9, 825.1, 764.2, 751.0, 717.6, 687.92 см$^{-1}$.

Raman spectrum: 3038.0, 3022.9, 1620.1, 1618.2, 1613.8, 1611.7, 1609.6, 1607.0, 1605.2, 1603.4, 1579.1, 1577.2, 1555.5, 1329.7, 1289.4, 1287.9, 1265.4, 1263.9, 1227.7, 1052.8, 950.7, 878.9, 750.0, 716.7, 656.3 см$^{-1}$.

ε-Polymorphous modification. Toluene (360 ml) was added to the stirred solution of HNIW (55 g) in 125 ml of ethylacetate at 25 °C during 2 hours. After ending the dosage in the crystallization system 0.5 g of inoculum crystals of ε-polymorph were added. The mixture was heated up to 60°C and kept for an hour. Then with the aid of water-jet pump the flask with the crystallization system was evacuated up to 0.08–0.4 kg s cm^{-2}. Distillate was condensed in the Liebig condenser and gathered into receiver. For 6 h the product was filtered off, washed with toluene on the filter, and dried. Yield was 80%; ρ = 2.04 g cm^{-3}.

IR spectrum: 1632.7, 1607.7, 1588.5, 1566.8, 1328.9, 1283.9, 1130.1, 1123.8, 1087.0, 1045.5, 943.6, 882.8, 854.5, 830.6, 819.3, 757.4, 750.7, 737.8, 722.6, 659.3 cm^{-1}.

Raman spectrum: 3043.7, 3041.0, 3035.7, 3030.9, 3015.9, 1649.1, 1631.9, 1606.8, 1587.8, 1566.0, 1537.1, 1347.3, 1328.1, 1298.1, 1283.2, 1263.9, 1255.0, 1217.0, 1191.0, 1180.1, 1048.4, 1046.4, 1044.7, 1022.1, 1020.1, 942.8, 935.9, 923.3, 882.0, 853.5, 829.6, 818.2, 756.5, 749.8, 742.7, 736.8, 721.7, 658.4, 647.3, 642.9, 622.4 cm^{-1}.

The complex of HNIW and ε-caprolactam. To a stirred melt of 5 g of ε-caprolactam at 80°C 2.15 g of HNIW was added by portion. To the prepared solution 13.5 ml of toluene was added. The flask content was gradually cooled up to room temperature and kept a day. The crystals were filtered off, washed with toluene, and dried. Yield of the crystal complex was 2.35 g, mp 87.3, 150.6, temperature of decomposition was 260°C.

IR spectrum: 1660.3, 1596.5, 1483.2, 1436.1, 1414.2, 1332.6, 1273.3, 1198.3, 1121.6, 1038.6, 958.2, 878.5, 827.6, 716.7, 667.3 cm^{-1}.

CONCLUSIONS

1. The limits of the hexanitrohaxaazawurtzitane solubility in different district solvents and binary mixture were established.

2. The methods of obtaining four polymorphous modifications of the compound were developed. It was shown that an increase in the temperature under the anhydrous conditions enables formation of γ-polymorth.

3. The crystalline complex of initial compound with ε-caprolactam was for the first time isolated.

4. The conducted investigations made it possible to develop and to implement the methods of preparation of the pure ε-polymorph of hexanitrohexaazaisowurtzitane in the experimental-industrial production.

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