

Article

An analytical study of the crystal quality of ϵ -Hexanitro-hexaazaisowurtzitane (CL-20) synthesized using several different crystallization techniques and intermediate precursors

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Received: May 27, 2005 Accepted: October 25, 2005

Abstract

ϵ -Hexanitro-hexaazaisowurtzitane (CL-20) was synthesized by various sources using different intermediate precursors (TAIW, TADF and TADA). The nuclear quadrupole resonance (NQR) line widths of the samples were measured to assess their crystal quality and the line widths are compared and correlated with sample purity and density as measured by HPLC and air pycnometry, respectively. The results are discussed and used to predict the shock sensitivity of CL-20 based explosives.

Keywords: Nuclear quadrupole resonance, NQR, CL-20, Hexanitro-hexaazaisowurtzitane, Synthesis, Crystal quality, Crystal morphology

1. Introduction

The hydrodynamic hot spot model is used to explain the difference between shock sensitive and shock insensitive explosives. Among the major factors that influence the shock sensitivity of explosive compounds are the quality and particle size of the energetic crystals used to formulate the explosive composition. The quality of a crystal is determined by its morphology (sharp versus rounded edges or smooth versus rough surfaces) as well the type and quantity of defects it contains¹⁻³. All compounds, such as the energetic compounds RDX, HMX and CL-20, exhibit internal crystal defects the magnitude and type of which depend on the manufacturing process used for synthesis and recrystallization. Several recent papers^{4, 5} have used nuclear quadrupole resonance (NQR) spectroscopy to show that the crystal quality of nitramine compounds such as RDX and HMX affect the shock sensitivity of the formulated explosive. In this paper we use NQR to determine the crystal quality of CL-20 obtained from different manufacturers.

Hexanitrohexaazaisowurtzitane (CL-20) is of great interest to the energetic-materials community because of its high chemical energy, high crystal density and higher oxygen balance than either RDX or HMX. It has four polymorphs (α , β , γ and ϵ) that are stable at room temperature and the structures and densities of each have been established by X-ray crystallography⁶. The ϵ polymorph has the highest density and thermal stability. Because of its superior properties, ϵ -CL-20 based formulations are being developed and evaluated for use in explosives, rocket and gun propellants as well as slapper detonators. The main obstacle to its use, other than its high cost, is the variability of crystal qualities and particle size distributions of batch-to-batch production lots. A number of studies have been conducted to determine the impact, friction and shock sensitivity of CL-20 relative to HMX and to identify the parameters that affect CL-20 sensitivity^{7, 8}.

Nuclear quadrupole resonance (NQR) is a sensitive tool for probing the electronic environment of a quadrupolar nucleus. Crystal imperfections such as dislocations, voids,

stresses and impurities may affect the electric field gradient at enough quadrupolar nuclei to broaden the NQR line in comparison to its width in a more perfect crystal. The various types and amounts of defects found in crystals are a direct result of the manufacturing process used to synthesize and re-crystallize the material. High performance liquid chromatography (HPLC) can identify impurities but cannot distinguish impurities that are embedded in the lattice from those that are not. Only co-crystallized impurities will affect the NQR line width. Optical microscopy can be used to identify and characterize crystalline defects on the microscopic scale. The density of a crystalline material is generally lower if it contains defects and is often used as a measure of the relative defect concentration. But optical microscopy, HPLC and density measurements are performed on milligram sample amounts and several samples must be examined to obtain an accurate representation of the bulk material. Crystal imperfections also affect thermal and mechanical properties and are of great interest to those who manufacture and use energetic materials. The NQR line width is inherently a bulk property and has been used to explain the thermal decomposition of RDX⁹. We are exploring the use of NQR to predict a material's sensitivity to shock and strain.

As part of the Navy CL-20 MANTECH Program, an effort was undertaken to determine whether the sensitivity of neat ϵ -CL-20 to impact and friction stimuli might be affected by changes in precursor type, crystallization method and impurity level. CL-20 samples were prepared by precipitation, evaporation or polymer gel crystallization techniques. Tetraacetyldiamino hexaazaisowurzitane (TADA), tetraacetyldiformyl hexaazaisowurzitane (TADF) or dibenzyltetraacetyl hexaazaisowurzitane (TAIW) was used as a precursor in the preparation of the CL-20 samples. NQR spectroscopy was used to determine the crystal quality of the resultant CL-20 products. The NQR results were then correlated with the densities and HPLC results.

2. Experimental

Three NQR lines are associated with each crystallographic ¹⁴N site and the resonance frequencies are conventionally labeled ν_+ , ν and $\nu_0 = \nu_+ - \nu$. The nitro nitrogen NQR frequencies of CL-20 have not been reported but are expected to lie below 1000 kHz. The tuning range of our NQR probe was 1000 kHz to 6000 kHz and this precluded a study of the nitro nitrogen NQR line widths. The amine nitrogen frequencies of ϵ -CL-20 have been reported elsewhere¹⁰ and are in the regions 5000 kHz – 5500 kHz (ν_+), 3300 kHz – 4000 kHz (ν) and 1400 kHz – 1800 kHz (ν_0). The signal-to-noise ratio is roughly proportional to $\nu^{3/2}$ and this favors the ν_+ amine lines for highest sensitivity. The NQR line at 5242 kHz was chosen for line width comparisons because it was the narrowest ν_+ line that was not part of a doublet and was also free from RF interference. No explosive compositions were available for NQR measurement.

All NQR measurements were performed at room temperature at the US Naval Surface Warfare Center Indian Head

Division (NSWC-IH) with a pulse spectrometer that was designed and constructed at the US Naval Research Laboratory (NRL). The radio frequency field in the 20 ml sample coil was such that the free induction decay (FID) signal from a single pulse applied at thermal equilibrium was largest when the pulse width was 70 μ s. The NQR line widths of ϵ -CL-20 were measured with a spin-locked spin-echo (SLSE) pulse sequence¹¹ in which the pulse interval in the pulse train was 1.0 ms. Scans were repeated 64 – 512 times at intervals of 1 s or 2 s, which proved adequate for detecting the CL-20 lines. (The spin-lattice relaxation times for the ν_+ and ν - lines of ϵ -CL-20 were measured and range from 2 s to 8 s.) The decay times of the SLSE echo envelope under these conditions are longer than 1 s in ϵ -CL-20 and coherent echo addition is quite effective at improving the detectability of the CL-20 NQR lines.

Sample amounts ranged from 1 g to 10 g and the samples were stored in the laboratory for several hours prior to the NQR measurements to ensure thermal equilibration. Each line width measurement lasted from 1 minute to 10 minutes and the temperature indicated by a digital thermometer placed near the probe was generally stable to within less than ± 0.2 °C during each measurement. Our peak-fitting program reported errors ranging from 0.5 % to 3 % for individual line width measurements but repeated measurements for a given CL-20 sample yielded values that varied by ± 10 % due to temperature fluctuations. We assign the larger uncertainty of ± 10 % to all of our line width values.

A Millennium base Waters HPLC system coupled with a Waters 490 E programmable multi-wavelength UV detector was used for the chemical analysis of the CL-20 samples. 4.6 mm \times 250 mm Waters Symmetry C-18 (5 μ m) or Phenomenon Luna C-18 (5 μ m) analytical columns were used for those measurements. CL-20 polymorph compositions were determined by FTIR. Densities were obtained with a Micrometrics AccuPyc 1330 Helium gas displacement pycnometer.

3. Result and discussion

Data from ten CL-20 samples obtained from five domestic and one foreign source are given in Table 1. FTIR analysis determined that only the epsilon polymorph was present in all of the samples. The major difference between each of the samples was in the method of synthesis and re-crystallization of CL-20. Samples #1 and #8 were manufactured on a production scale while the other eight were made in small-scale pilot plants. Samples #6 and #7 have a median particle size of approx. 25 μ m – 30 μ m as determined by scanning electron microscopy (SEM) using software for determining particle size distributions. The remaining eight samples have a median particle size of approximately 150 μ m as determined by Microtrac. However, SEM showed that some of these samples contained a considerable number of agglomerates consisting of individual particles smaller than 50 microns.

The production samples #1 and #8 differ only in precursor (TADA vs. TADF) but NQR and powder X-ray diffraction (XRD) results indicate that the crystal quality of #8 is

Table 1 ^{14}N NQR line widths at 5242 kHz for ϵ -CL-20 from different sources. Sample numbers for production lots are marked with an asterisk.

Sample No.	Density (g/cc)	Impur. (%)	Line width (kHz)	Precursor type	Crystallization method	Solvent system
1*	2.0355	3	2.21	TADF	Crash precip	EtOAc / Heptane
2	2.0226	4	1.95	TADF	Crash precip.	EtOAc / Isopropanol
3	2.0280	2.4	1.71	TADF	Crash precip.	EtOAc / Heptane
4	2.0359	0.5	0.82	TADF	Crash precip.	EtOAc / Heptane
5	2.0191	5	2.45	TADF	Thermo-reversible gel recryst.	Acrylate gel / EtOAc / Dichloromethane
6	2.0394	3	3.5	TADF	Proprietary (from α -hydrate)	Single solvent
7	2.0430	1	1.18	Not given	Proprietary (evaporative)	Solvent / non-solvent
8*	2.0356	0.5	0.69	TADA	Crash precip.	EtOAc / Heptane
9	2.0310	1	1.21	TADA	Crash precip.	EtOAc / Heptane
10	2.0364	1	0.97	TAIW	Proprietary	Single solvent

superior to that of #1. The NQR doublet at 5207.5 kHz shown in Fig. 1 is barely resolvable in sample #1. The SEM photomicrographs in Fig. 2 show that the crystals have a similar morphology but sample #1 consists of smaller particles that have agglomerated. A previous study showed that broadening of the NQR lines of HMX and RDX occurs in very small particles¹⁰ and the same effect might contribute to the broadening of the NQR lines in sample #1.

Samples #6 and #10 were single solvent systems crystallized by proprietary processes. The resultant crystals shown in Fig. 3 have the same morphology but those created from the α -hydrate (#6) were considerably smaller. When only the solvent system is changed (#2 and #3 in

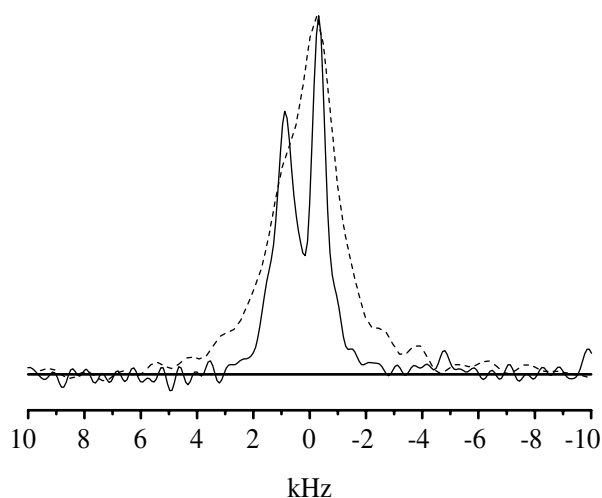
**Fig. 1** NQR doublet at 5207 kHz for CL-20 production lot samples #1 (dashed curve) and #8 (solid curve).

Fig. 4) the crystal habit stays essentially the same with a slight difference in particle size distribution as observed by SEM. Similarly, NQR results show only a slight difference in the quality of the crystals in #2 and #3.

A comparison of XRD and NQR results for all samples showed that NQR was capable of assigning a ranking factor to the crystal quality while XRD could only qualitatively differentiate crystal quality.

Figure 5 shows the dependence of the NQR line width at 5242 kHz on the total impurity level. The rather good linear fit indicates that most of the (unidentified) impurities are in the CL-20 lattice. The deviation of the line width for sample #6 from the fit is probably due to its small particle size. Figure 6 shows that there is also a correlation between sample density and NQR line width and it should be noted that extrapolation of the linear least square fit leads to the ϵ -CL-20 theoretical density (2.045 g cc⁻¹) for a line width of 0 Hz. Of course the NQR line width will always be larger than zero even in a perfect crystal due to thermal motion. The early production lot sample #1 is an outlier and that could be due to its poor crystal quality as well as its small particle size. The deviations of samples #6 and #7 from that fit are most likely due to their small particle sizes. In previous NQR studies on ground and unground RDX samples it was found that grinding large particles to median particle sizes below approximately 15 microns caused an increase in the NQR line width. That indicates that the smaller particles have more strain and other imperfections in their crystal structure. However, shock sensitivity data indicate that these additional imperfections have no affect on the shock sensitivity. The exact nature of these imperfections and at what particle sizes they start to manifest themselves in line broadening is the subject of an ongoing study.

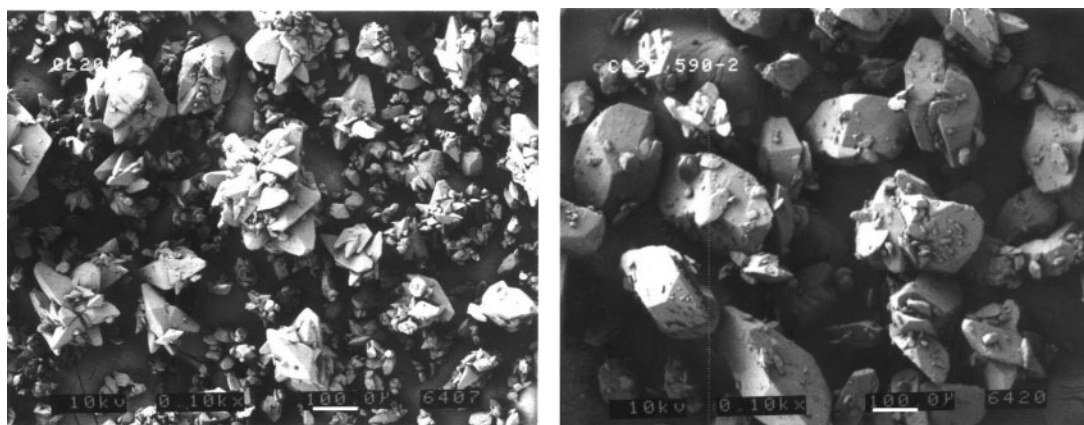


Fig. 2 Crystal morphology of CL-20 production samples manufactured from different precursors: Sample #1, TADF (left) and #8, TADA (right).

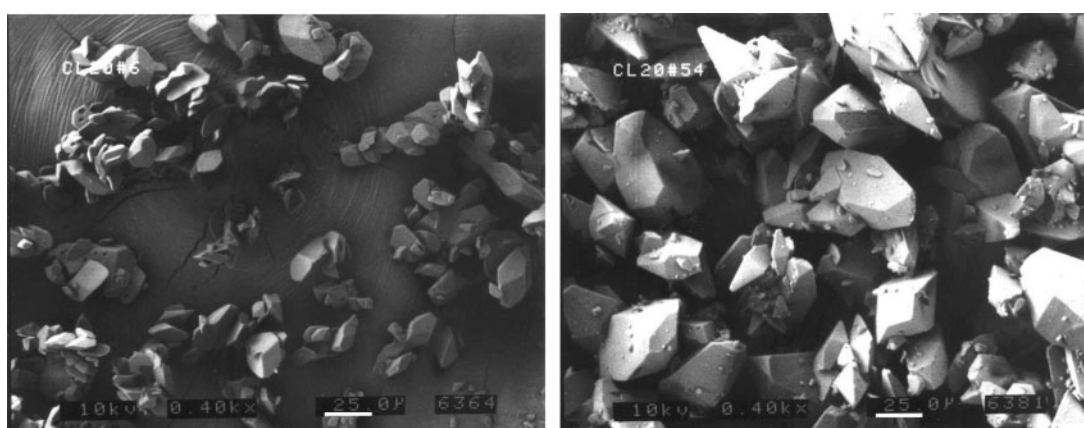


Fig. 3 Crystal morphology of CL-20 samples manufactured using a single solvent but with different precursors: Sample #6, TADF (left) and #10, TAIW (right).

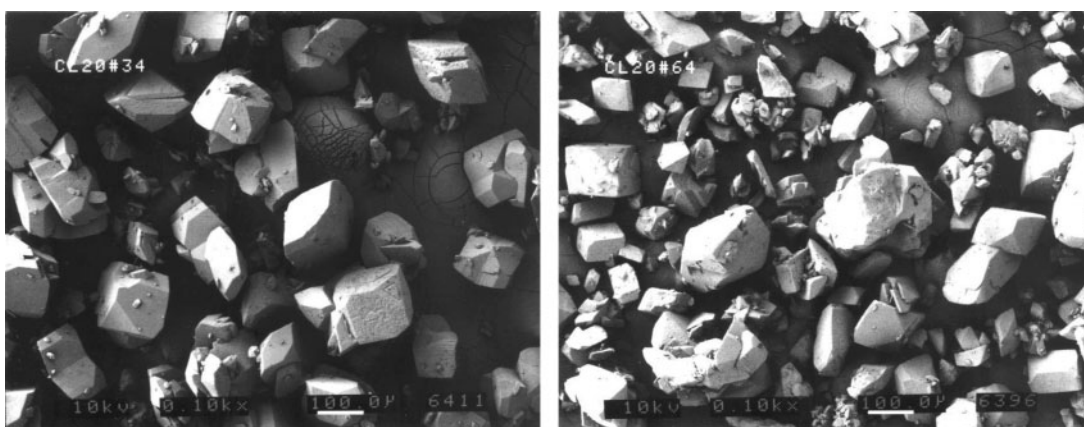


Fig. 4 Crystal morphology of CL-20 samples manufactured with the same precursor (TADF) using different solvent systems: Sample #2, Isopropanol (left) and #3, ETOAc / Heptane (right).

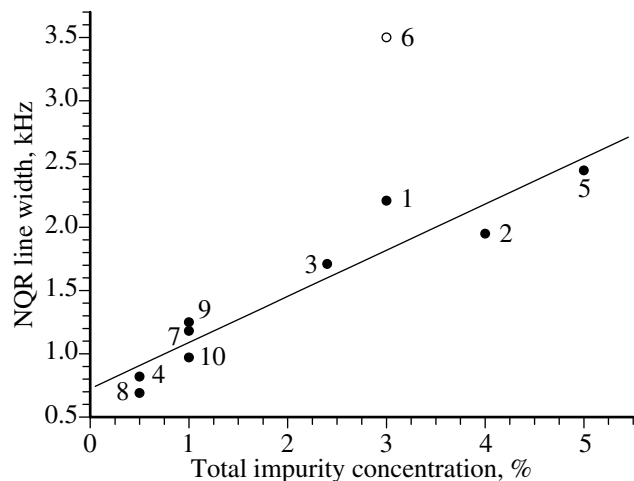


Fig. 5 CL-20 NQR line width at 5242 kHz versus impurity concentration from Table 1. Also shown is the linear least squares fit of the solid data points.

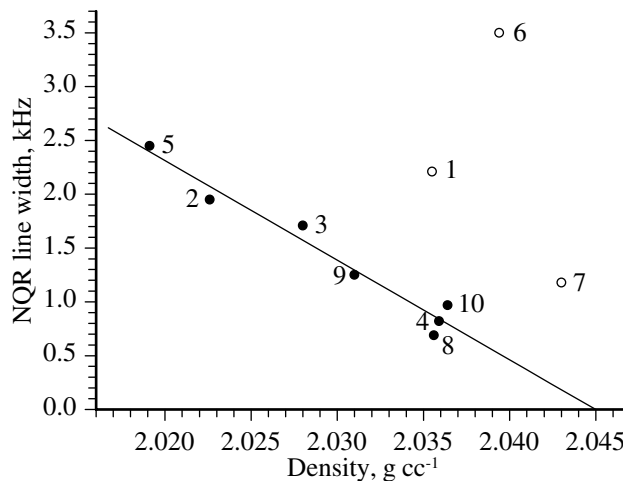


Fig. 6 CL-20 NQR line width at 5242 kHz versus density from Table 1. Also shown is the linear least squares fit of the solid data points.

4. Conclusion

NQR spectroscopy has proven to be a valuable technique for determining the relative defect densities of energetic compounds. Many factors influence the NQR line width and even knowing the manufacturing process used to synthesize a product it may be difficult to predict which factor will dominate. Impurities within the crystal and crystal particle size have been shown to affect the NQR line widths of CL-20. A correlation was found between the density of large CL-20 particles and their NQR line widths. This should allow us to predict on the basis of NQR line widths which explosive compositions containing CL-20 manufactured by various sources will be the least sensitive to a shock stimulus. We are currently determining the NQR line widths of CL-20 formulations for which shock sensitivities will be measured and any correlations will be reported.

Acknowledgements

This work was partially funded by the NSWC MAN-TECH Program.

References

- Borne, L. "Explosive Crystal Microstructure and Shock Sensitivity of Cast Formulations" *Proc. of the 11th Symposium (International) on Detonation*, Snowmass, CO, pp. 653-657, 1995.
- Borne, L. "Microstructure Effect on the Shock Sensitivity of Cast Plastic Bonded Explosives", *Proc. of EUROPYRO 95*, Tours, France, pp. 125-131, 1995.
- C, Spycykerelle, A. Freche, S. Lecume, "I-RDX - Comparative analytical characterization - State of the art", *Reduced Sensitivity RDX Technical Meeting*, Meppen, 17-20 November 2003.
- Caulder, S. M., Buess, M. L., Garroway, A. N. and Miller P. J. : *8th International Pyrotechnic Congress (EUROPYRO 2003)*, St. Malo, France, 28-35 (2003).
- S. M. Caulder, M. L. Buess, A. N. Garroway and P. J. Miller, "NQR Line Broadening Due to Crystal Lattice Imperfections and its Relationship to Shock Sensitivity", *Shock Compression of Condensed Matter-2003*. Proceedings of the Conference of the American Physical Society Topical Group on Shock Compression of Condensed Matter, Portland, Oregon, 929-934, July 20-25, 2003.
- Nielson, A.T., Chafin A. P., Christian S. L., Moore D. W., Nadler M. P., Nissan R. A., Vanderah D. J., Gilardi R. D., George C. F. and Flippen-Anderson J. L. : *Tetrahedron* 54, 11793-11812 (1998).
- "Safety and Hazards of CL-20 and Propellants and Explosives Based on CL-20", *CPIA Publication 668*, November 1997.
- S. Nicolich, M. Mezger, D. Geiss, E. Heider "CL-20 Round Robin Sensitivity Testing Interim Report", *1998 NDIA Insensitive Munitions & Energetic Materials Technology Symposium Proceedings*, November 1998.
- Erofeev L. N., Tarasov Yu. P., Kalmykov Yu. B., Shu Y., Dubikhin V.V. and Nazin G. M. : *Isv. Akad. Nauk. Ser. Khim.* No. 6, 958-960 (2001). [*Russ. Chem. Bull.* 50, 1000-1002 (2001) (Engl. Transl.)].
- M. L. Buess and S. M. Caulder, "Factors Affecting the NQR Line Width in Nitramine Explosives", *Appl. Magn. Reson.* 25, 383-393 (2004).
- Marino R. A. and Klainer S. M. : *J. Chem. Phys.* 67, 3388-3389 (1977).