

## Characterization of Hexamine Squarate

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### KEYWORDS

Hexamine squarate, squaric acid, diketocyclobutenediol, hexamine, hexamethylenetetramine, Esbit® tablets, recrystallization, terrorism, explosives, microcrystal test, scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), infrared microspectroscopy, birefringence

### ABSTRACT

Squaric acid has been well characterized as a microcrystal test reagent with a variety of inorganic compounds, however the reaction of squaric acid with organic compounds has not been previously pursued as a microcrystal test. A precursor to military high explosives, hexamine was reacted with squaric acid and the resulting product characterized with polarized light microscopy (PLM), infrared microspectroscopy (IMS), and scanning electron microscopy (SEM).

### INTRODUCTION

#### Squaric Acid

Diketocyclobutenediol (squaric acid), first synthesized by Sidney Cohen in 1959, is a diprotic acid with a  $pK_2$  of approximately 1 (1). Early characterization included molecular orbital calculations, (2) as well as Raman and infrared spectroscopy (3). Complexes with eight divalent and three trivalent metals were also characterized with magnetic studies, powder X-ray diffraction, and infrared spectroscopy (4). Its strong

reducing properties have been exploited in its use as a microcrystal test reagent for a number of inorganic anions; the reaction of squaric acid has been shown with at least 68 different inorganic cations (5). The precipitates of many of these reactions are unique and have been characterized optically and crystallographically (5,6,7).

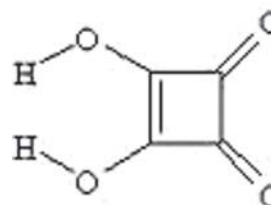


Figure 1. Structure of squaric acid

#### Hexamine

Hexamethylenetetramine (hexamine) is a heterocyclic amine whose synthesis from formaldehyde and ammonia was patented in 1956. It is used as an antimicrobial food additive and as an antibiotic for urinary tract infections. A primary industrial use is as a hardener in a variety of resins (8). When exposed to flame, it burns smokelessly and with little residue. This property led to its use as a chemical fuel tablet for camping and military cooking. It is inexpensive and readily available from camping and military surplus stores as Esbit® tablets (9).

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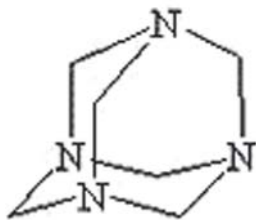


Figure 2. Structure of hexamine

Hexamine is also a precursor to several high explosives mostly used in military applications. A quick search of the internet will yield recipes for these explosive compounds using hexamine (obtained from fuel tablets) and other chemicals that can be obtained by the general public. While the preparation of these compounds is very dangerous, curious individuals as well as those with malicious intent may attempt, to prepare them. Research Department Explosive (RDX) or cyclonite is prepared from hexamine and nitric acid. High-Melting Explosive (HMX) or hexogen was originally seen as a byproduct of the RDX reaction, but its synthesis from hexamine and nitric acid in an acetic acid/acetic anhydride solvent yields greater than 50% HMX (10).

Hexamethylene triperoxide diamine (HMTD) is prepared from hexamine with hydrogen peroxide and citric or sulfuric acid (11). HMTD has been used in several terrorist attacks, including the 2005 London bombings and was reported by *The New York Times* as the explosive planned for use in the 2006 transatlantic aircraft plot. (12) This event was the impetus for the current TSA restrictions on liquids carried onto aircraft. While the legislation varies, many states and federal laws forbid the manufacture or possession of explosives with the intent to use them in an offense or provide them to another with intent to use them in an offense (13). The presence of hexamine residues could be used in investigation of the illicit manufacture of these compounds.

### Microcrystal Tests

Microcrystal tests involving the observation of precipitates of (generally aqueous) reactions have been used for at least three centuries. Books on chemical microscopy have been published in the United States since 1857 (14). Although use of these tests has declined over the past century in favor of more sophisticated technologies, they hold several advantages over newer techniques. They can be performed on very small samples (less than 1 mg), can be performed quickly,

and the instrumentation and reagents are relatively inexpensive.

While some argue that the simplicity of these tests makes them ideal for use in forensic science, the use of microcrystal tests has declined in recent years. One area of forensic science that had relied heavily on microcrystal tests was controlled substances. In initial drafts of the SWGDRUG guidelines, the use of microcrystal tests for identification was not allowed. The current SWGDRUG recommendations classify validated analytical tests as A, B, or C, with category A deemed most discriminating and category C least. Microcrystal tests fall under category B, which allows them to be used as a confirmatory test along with a validated category A test. If a category A test is not performed, three validated tests from categories B and C must be performed. (15) In an article by Walter C. McCrone of the McCrone Research Institute, one of the primary advocates of chemical microscopy in the last 50 years, the need for further optical characterization of the precipitate products of microcrystal tests could go a long way in increasing their acceptance in the courts. (16) While this article addressed the general acceptance requirement of the Frye rule, further characterization of precipitate products, together with published validation of the tests, would help microcrystal tests meet the requirements of the Daubert ruling.

Previous work has focused on the reaction of the squarate ion with inorganic cations. Characterization of the reaction with an organic base has not been studied. The reaction of squaric acid and hexamine was observed in a recent "Microscopy of Explosives" course taught by McCrone Research Institute. The diprotic squaric acid is expected to react with the four nitrogen atoms in hexamine in a 2:1 ratio, forming an insoluble salt. This paper serves to provide further characterization of this reaction for use as a microcrystal test for the presence of hexamine.

### **MATERIALS AND METHODS**

Hexamine and squaric acid were recrystallized from water solutions and as controls for unconsumed recrystallized reactant present in the reaction product. The reaction of hexamine and squaric acid was initially carried out using the two-drop method, described by Chamot and Mason as "Method I," (17) wherein a drop of saturated squaric acid in distilled water is mixed with a drop of water containing dilute hexamine. Squaric acid is sparingly soluble in water, so a saturated solution was prepared by placing an excess of squaric acid crystals in a dropper bottle with

a small amount of distilled water. Optimal reaction speeds were accomplished with solutions of squaric acid which had been prepared and allowed to saturate for at least one day. Hexamine concentrations were less critical, with a few crystals dissolving readily in a drop of water. Once a sufficiently saturated solution of squaric acid was obtained, a few crystals of hexamine were added directly to a drop of saturated squaric acid, and crystals were formed within a few minutes. These preparations and reactions were observed with a Leica MZ16 stereomicroscope and an Olympus BH-2 polarized-light microscope. All photomicrographs were taken with an Olympus DP70 digital camera.

After formation of product crystals, they were removed from the drop with a tungsten needle. The crystals tended to be brittle and stick to the slide if they were allowed to dry undisturbed. Movement of the crystal bundles on the slide during drying produced free crystals and bundles of crystals which were easily manipulated for further analysis.

The reaction was also performed on a larger scale with several drops of saturated solutions of each reagent mixed in the well of a spot plate. These crystals were bigger but maintained the properties of the smaller crystals formed on a slide. Because of their larger size and relative ease of manipulation, these crystals were used for some analyses.

The refractive indices of the crystals were estimated by mounting the crystals in Cargille refractive index liquids and observation of the Becke line with a sodium D-line filter (589 nm). Further determinations were performed using a detent spindle stage, which allows for rotation of the crystal  $180^\circ$  in a plane perpendicular to the rotation axis of the microscope stage.

ExcalibrW software calculated the angle of stage rotation and detent spindle stage for alignment of each optic axis with the polarizer of the microscope as well as the optic axial angle (2V) of the crystal. With the orientation of the optic axes known, the refractive indices can be more accurately determined.

The decomposition and melting of the squarate crystals were observed with a Nikon Optiphot polarized-light microscope with 10x objective and a Mettler FP5 hot stage. The decomposition was observed in air; melting occurred in Dupont 710 silicone oil.

A selection of recrystallized hexamine, recrystallized squaric acid, and product crystals were transferred to a potassium bromide "salt plate" for microinfrared spectroscopy (FTIR) analysis. Analysis was performed using an ATI Mattson ATI Quantmm Infrared microscope.

A selection of recrystallized hexamine, recrystallized squaric acid, and product crystals were transferred to a SEM stub coated with carbon tape for scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS) analysis. These crystals were analyzed using an Amray 1810 SEM with EDAX EDS.

## RESULTS AND DISCUSSION

### Crystal Morphology and Optics

The hexamine squarate product forms highly birefringent acicular crystals with parallel extinction. The crystal dimensions range from approximately  $2\ \mu\text{m} \times 10\ \mu\text{m}$  needles to  $40\ \mu\text{m} \times 1200\ \mu\text{m}$  blades in the orientation most commonly encountered on the microscope slide. When the reaction was performed on a spot plate, larger crystals (up to 0.1 mm by 2 mm)

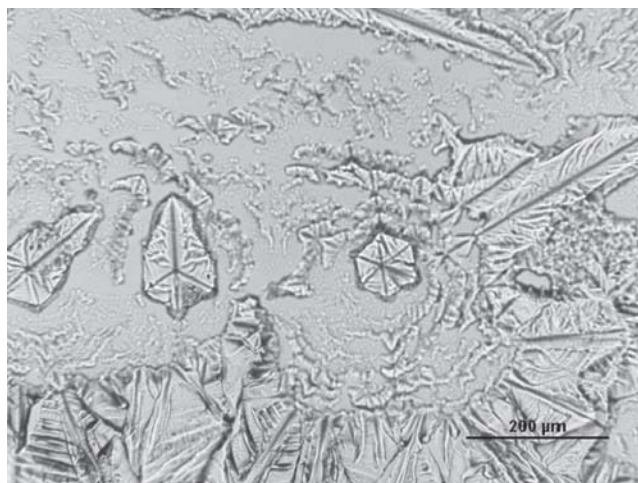


Figure 3. Recrystallized hexamine, plane-polarized light.

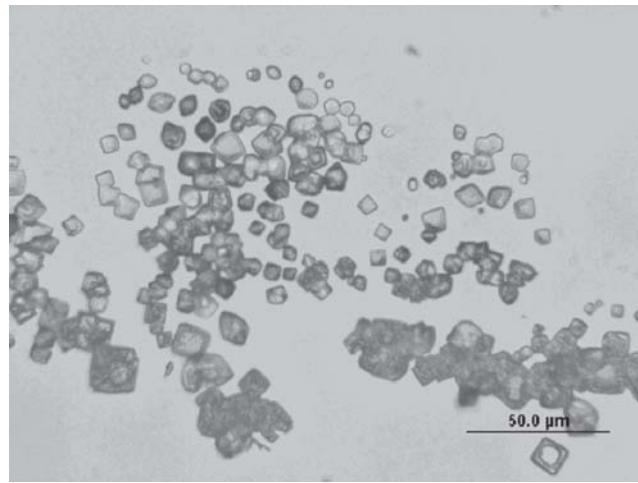


Figure 4. Recrystallized squaric acid, plane-polarized light.

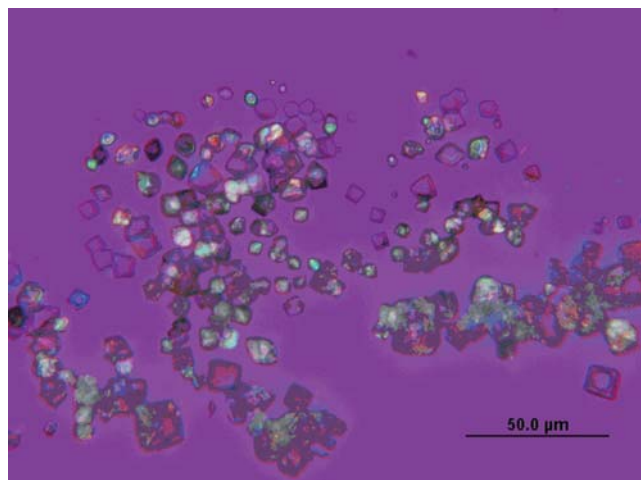


Figure 5. Recrystallized squaric acid, crossed polars and Red I compensator.

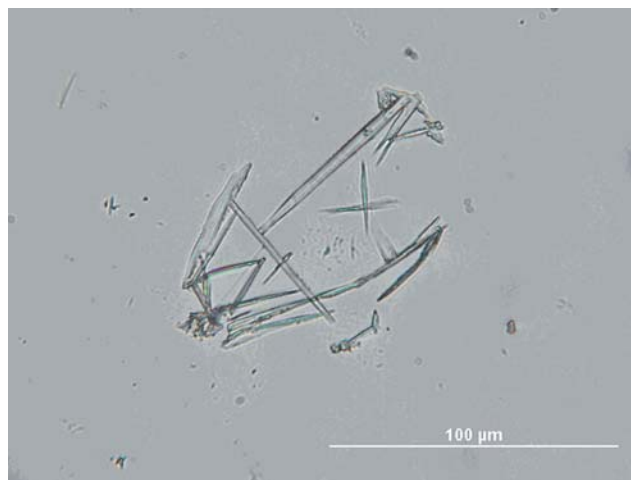


Figure 6. Hexamine squarate crystals, plane-polarized light.

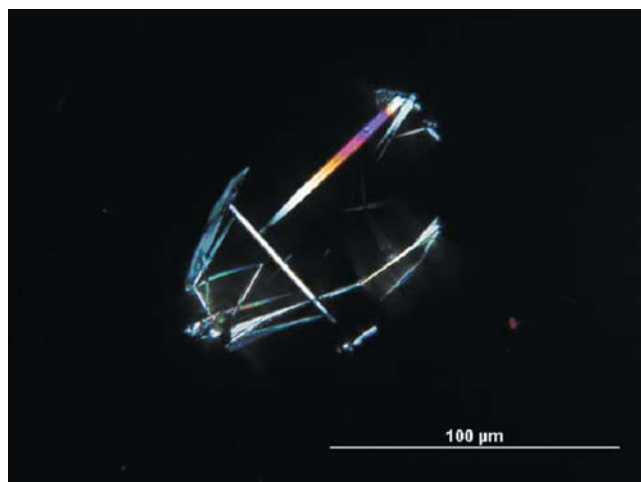


Figure 7. Hexamine squarate crystals, crossed polars.

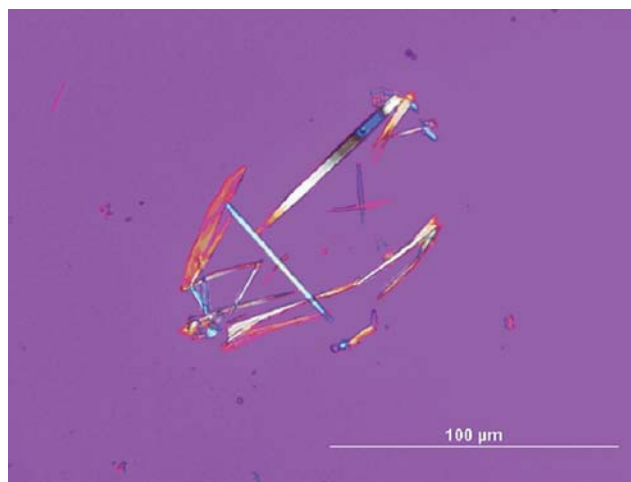


Figure 8. Hexamine squarate crystals, crossed polars and Red I compensator.

were commonly formed. Observation of the ends of these larger crystals with a stereomicroscope shows a flattened hexagonal (six-sided) profile, with the crystals most commonly oriented on the flattened edge. The product crystals were easily distinguished from the anisotropic feathery plates and crosses of hexamine and the isotropic tetrahedra of squaric acid. (See Figures 3-5 for photomicrographs of the reactants, Figures 6-8 for photomicrographs and Figure 9 for a drawing of the product crystals.)

Estimation of birefringence was performed on the smaller crystals. Crystals with a width of approximately 2  $\mu\text{m}$  show maximum retardation colors of red (approximately 550 nm). The thickness of these crys-

tals is likely less than 2  $\mu\text{m}$  due to their flattened profile. This leads to an estimated birefringence near 0.3.

The sign of elongation was determined to be negative using PLM, crossed polars, and the Red I compensator. The refractive indices of the axes parallel to the crystal length were determined to be approximately ( $\alpha$ ) 1.506 and ( $\beta$ ) 1.568. The refractive index perpendicular to the crystal length ( $\gamma$ ) was determined to be greater than 1.700. Further determination of the  $\gamma$  refractive index using immersion in higher index liquids was not pursued. In a refractive index liquid of 1.700, the contrast for the primary parallel orientation and the perpendicular orientation were similar, leading to an estimated refractive index of approximately 1.9.

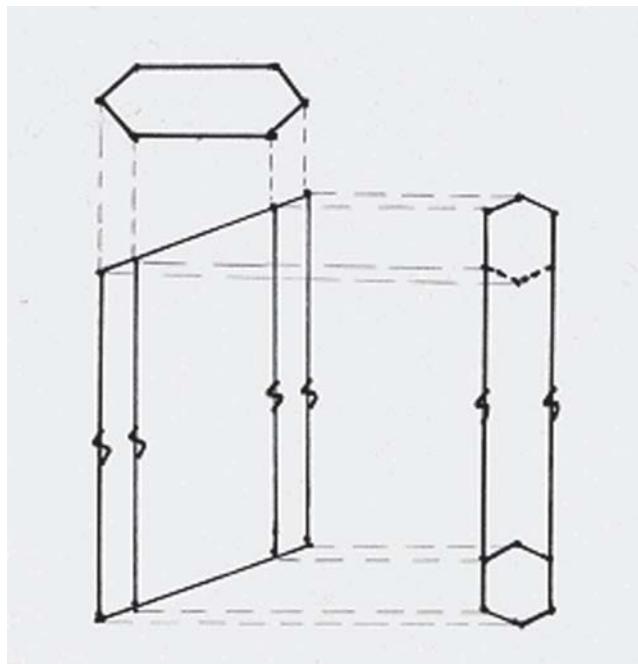


Figure 9. Drawing of hexamine squarate crystals.

This is in keeping with the estimated birefringence of greater than 0.3. The optic sign of the biaxial crystal is positive (+).

Characterization with the spindle stage provided mixed results. Two determinations were performed, each with a single small crystal mounted at the tip of the needle. While the first determination had a high

coefficient of correlation (0.978), the estimated standard error of the calculated optic axial angle ( $2V$ ) was significant (9.018). The second determination had a low coefficient of correlation (-0.194) but smaller estimated standard error of the calculated value of  $2V$  (5.286). In both cases,  $2V$  was approximately  $20^\circ$ . An interference figure was not obtained to confirm this optic axial angle. The estimated standard error of the spindle stage angle for orientation of the crystal to measure each refractive index was large, so confirmation of the  $\alpha$ ,  $\beta$ , and  $\gamma$  refractive indices was not performed. If all three refractive indices are known,  $2V$  can be calculated. Also, if two refractive indices, the optic sign, and  $2V$  are known, the third refractive index can be calculated. Due to the uncertainty in the values of  $\beta$  and  $2V$ , these calculations were not performed.

### Fusion Methods

During determination of the melting point of the hexamine squarate crystals in air, decomposition was observed. When the melting point was observed in DuPont 710 silicone oil, the process began with desolvation at approximately  $175^\circ\text{C}$ , followed by darkening through  $190^\circ\text{C}$ . At approximately  $195^\circ\text{C}$ , a yellow melted residue is present, which continues to darken when heated past  $260^\circ\text{C}$ . Figure 10 shows the progression of these phases.

The decomposition of squaric acid and sublimation of hexamine were also observed. Squaric acid decomposed in air at approximately  $295^\circ\text{C}$ . When observed in silicone oil, desolvation occurred from ap-

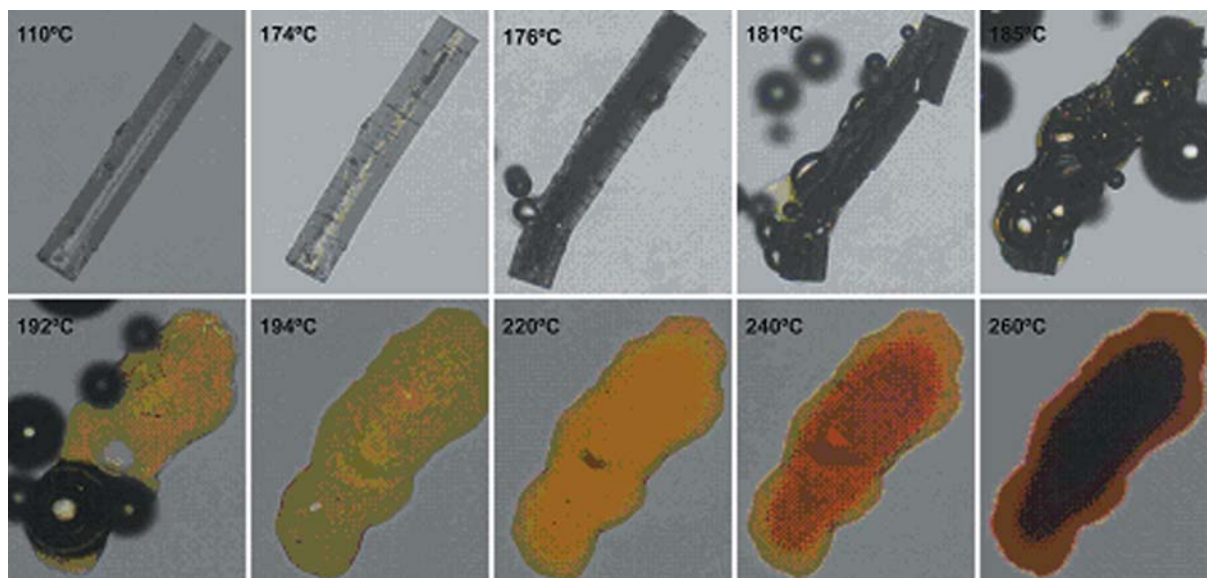


Figure 10. Melting and decomposition of hexamine squarate in Dupont 710 silicone oil.

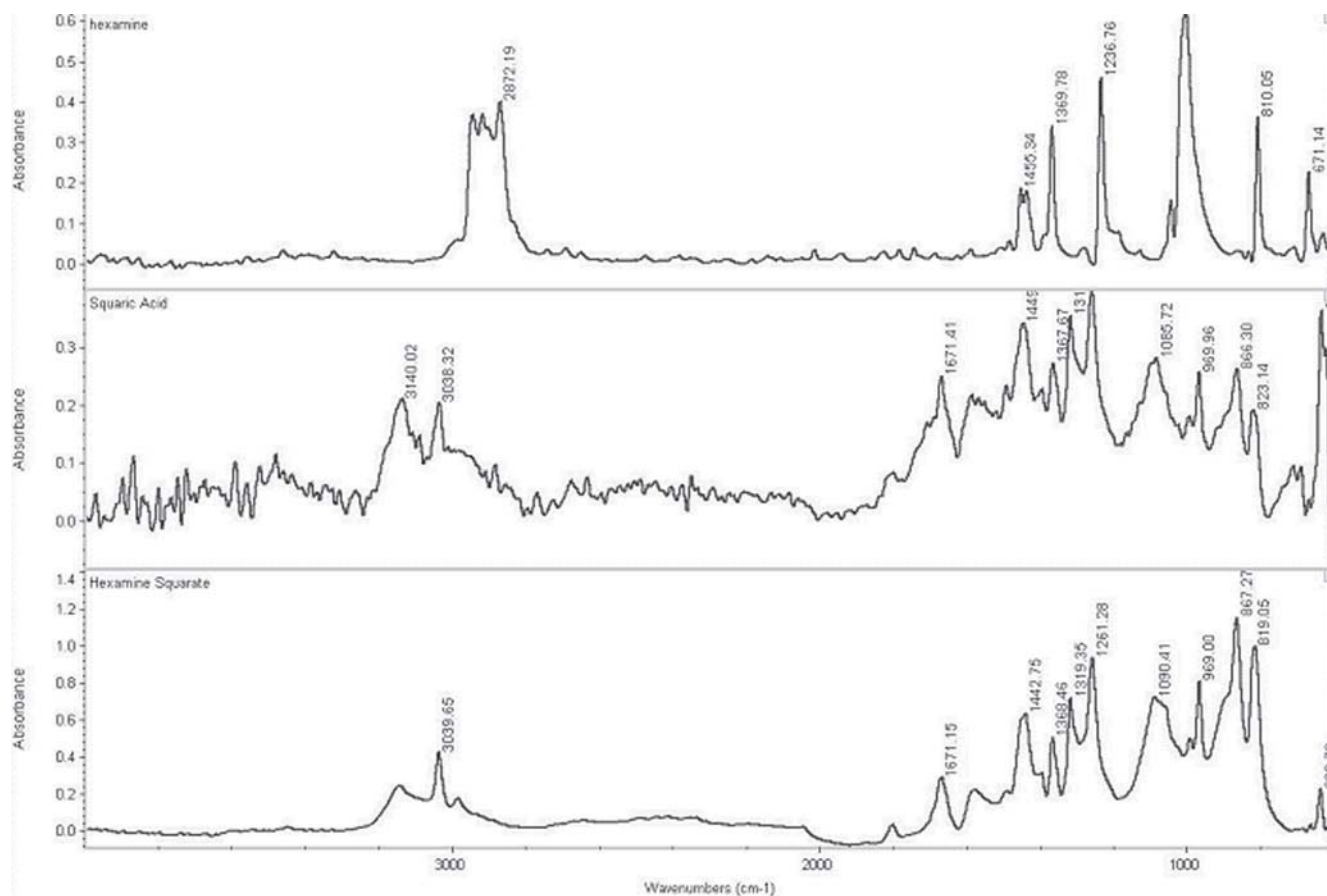


Figure 11. FTIR spectra for hexamine (top), squaric acid (middle), and hexamine squarate (bottom).

proximately 250-275°C, with cracking beginning around 275°C. The crystal shattered into smaller pieces at 296°C, with small unmelted crystals present at 300°C. Hexamine crystals were expected to sublime at 260-280°C.<sup>8</sup> Observation in air showed sublimation from 150-190°C. This lower temperature is likely due to the observation of micro-crystals with increased surface area.

### **Infrared Microspectroscopy**

The transmission infrared spectrum of recrystallized hexamine, recrystallized squaric acid, and hexamine squarate were obtained and compared. The spectra are shown in Figure 11. The hexamine and squaric acid spectra were comparable to commercially available spectra. The hexamine squarate spectrum resembles the squaric acid spectrum. Major peaks corresponding to hexamine are also present in the squaric acid spectrum.

### **Scanning Electron Microscopy**

Scanning electron microscopy was used primarily to confirm the flattened hexagonal (six-sided) profile of the crystals. Electron dispersive spectroscopy was performed but only confirmed the presence of carbon and oxygen. Nitrogen cannot easily be detected by SEM/EDS. See Figures 12 and 13 for photomicrographs of the SEM image of the ends of the crystals.

The crystallographic data collected is summarized:

**Color:** colorless

**Habit:** needles, blades

**Dimensions:** 2 μm x 10 μm to 40 μm x 1200 μm

**Isotropy:** anisotropic

**Extinction:** parallel extinction

**Sign of elongation:** negative

**Optic sign:** positive

**Birefringence:** high, 0.3 (calc)

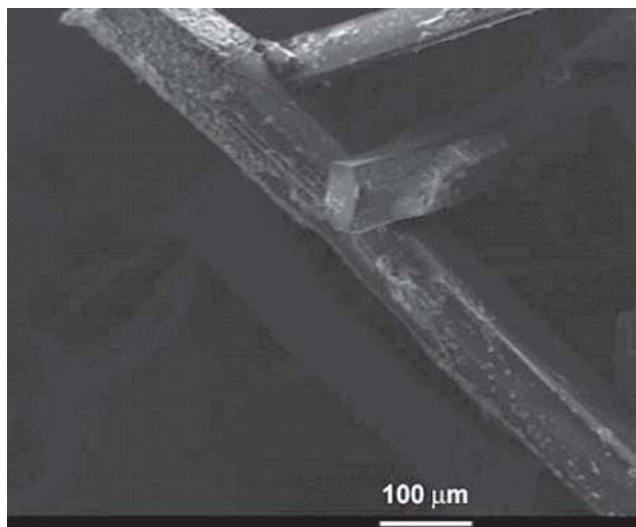


Figure 12. SEM image of hexamine squarate crystal profile.

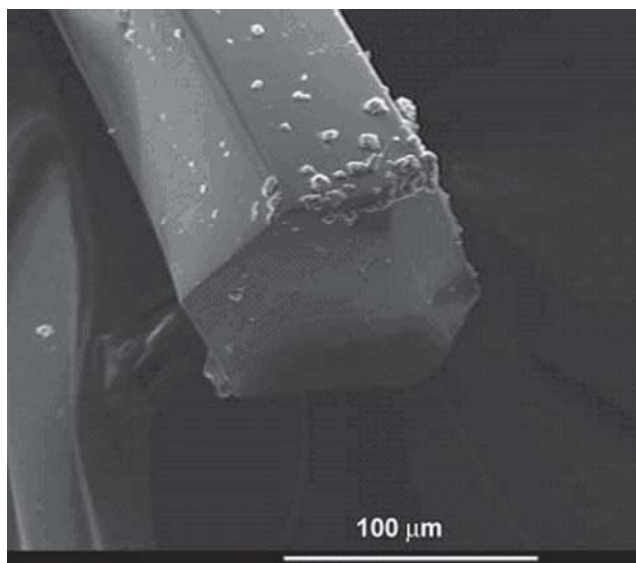


Figure 13. SEM image of hexamine squarate crystal profile.

**Refractive indices**

$\alpha$  – 1.506

$\beta$  – 1.568

$\gamma$  – 1.9 (calc)

**2V:** 20° (calc)

**Melting point (in silicone oil):** approximately 195°C, with decomposition

The optical characteristics determined in this study define this microcrystal test product and allow it to be distinguished from other possible squarates. It

also shows that squaric acid has potential as a microcrystal test reagent with other basic organic molecules in addition to the inorganic cations previously studied. Further work in the characterization of this product could involve confirmation of the 2V angle and  $\beta$  refractive index, measurement of the interfacial angles, and assignment of Miller indices in addition to other spectroscopic methods.

**CONCLUSIONS**

The reaction of hexamine and squaric acid was performed in a reproducible manner, and the hexamine squarate product was optically characterized. While the infrared spectrum of hexamine squarate does not differ significantly from that of squaric acid, the large difference in melting and decomposition behavior indicates that the product crystals are probably not simply a polymorph of squaric acid. The use of squaric acid as a microcrystal test reagent had previously been limited to inorganic cations. The optical characterization of the highly birefringent needles and blades of hexamine squarate allows squaric acid to be used as a microcrystal reagent for detection of hexamine, and opens the door for its use with other organic bases.

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