



Polymorphism in Energetic Materials

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Polymorphism often occurs in energetic materials. Differences in the forms range from conformational changes in the molecule from one system to another, to conformational equivalents packing in different manners. These differences, whether drastic or subtle, can lead to substantial alterations in stability and performance. The authors recently reported on the crystal structures of five polymorphs of picryl bromide (a common energetic precursor): the previously identified α and β forms, and three new forms, the γ , δ , and ϵ forms. A new type of interaction has been identified between the nitro groups and π -electrons of neighboring phenyl rings. Accurate estimation of the properties of new energetic materials can substantially reduce the development cost of new materials by focusing expensive scale-up and testing on only the most promising candidates. The characterization of this new force involved in crystal packing should greatly improve calculations of packing energy and thus improve predictions of explosive yield.

INTRODUCTION

Polymorphism is defined as the ability to exist in two or more chemically identical, but crystallographically distinct forms. Since the properties of a solid substance are determined by its composition and structure, polymorphs, although chemically identical, can have different properties.¹ This is important in many fields including pharmaceuticals, agrochemicals, pigments, dyestuffs, foods, and explosives. The differences that distinguish polymorphs can lead to substantial alterations in stability and performance. Regardless of the field of application, it is essential to be able to produce materials with consistent properties.

Perhaps the most studied examples of polymorphism occur in the development of pharmaceuticals, as dissolution and absorption rates depend on the exact crystal form of a polymorph. Drugs often receive regulatory approval for only a single crystalline polymorph. Because a single polymorph is described in the patent, competitors may be able to patent and market other polymorphs. In some cases the new preparations are not true polymorphs, as they exist as different hydrates with varying water content or different salts of the parent drug.

It is important to note that not all polymorphs are stable. Although the common drug aspirin (acetylsalicylic acid) was first prepared by Charles Frederic Gerhardt in 1853, a second polymorph of this drug was not discovered until 2005. Studies have shown that this new form is stable only at 100 K and reverts back to the original form at ambient temperature. This may seem like a trivial matter, but there have been cases of

individual laboratories producing one crystal form and later producing a different crystal form. As noted previously, FDA approval may exist for only a single polymorph, thus the new unanticipated polymorph can be disastrous for a drug company.

ENERGETIC MATERIALS

In the production of energetic materials, stability and density are critical properties, and these can vary widely among the polymorphs. Three of the classic cases of polymorphism at ambient conditions in the energetic field are TNT, HMX, and CL20 (Fig. 1). TNT [2,4,6-trinitrotoluene] is known to have two forms with densities of approximately 1.65 Mg/cm³. HMX [1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane] is known to have four forms with densities ranging from 1.76 to 1.903 Mg/cm³; this is a large variation in density, and understanding how to produce the higher density polymorphs allows production of higher energy explosives. CL20 [2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexa-azatetracyclo(5.5.0.0^{5,9}.0^{3,11})dodecane] is known to have five forms with densities ranging from 1.915 to 2.044 Mg/cm³. Differences in the various polymorphs range from conformational changes in the molecule from one system to another, to conformational equivalents packing in different manners.

Picryl bromide (2,4,6-trinitrobromobenzene) also exhibits polymorphism. Picryl bromide is a useful chemical precursor to other energetic materials. The original determinations of picryl bromide date back to the very early days of crystallography and energetic materials research. Two picryl bromide polymorphs

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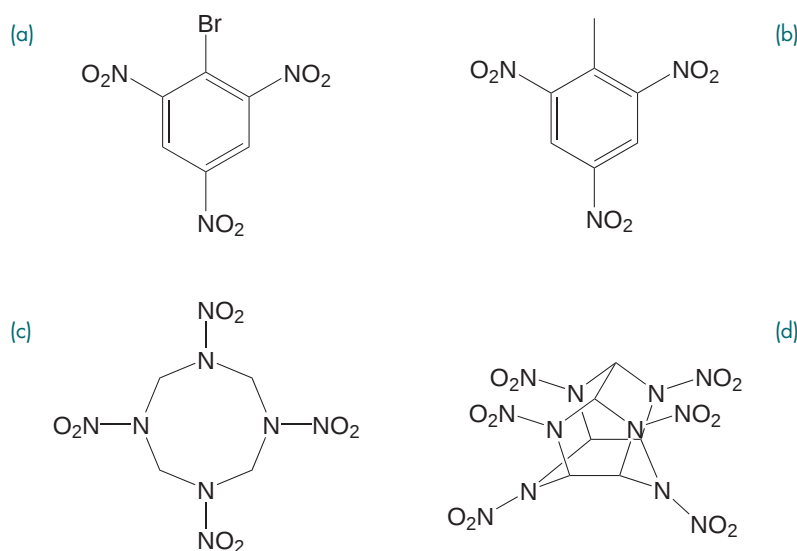


FIGURE 1
Chemical structures of picryl bromide (a), TNT (b), HMX (c), and CL20 (d).

were reported in 1933; however, no X-ray crystal structures were reported at that time. The first structural information was published in 1975 by Herbstein and Kaftory,² who reported on a series of seven co-crystals of picryl bromide with large aromatic ring compounds. Here we discuss the crystal structures of five polymorphs of picryl bromide: the previously identified α and β forms from 1933, and the newly identified γ , δ , and ϵ forms.³

PICRYL BROMIDE ANALYSIS

A vial of picryl bromide was provided to the Naval Research Laboratory by the Naval Surface Warfare Center. The sample was the result of a single synthetic batch. Upon visual examination, the crystals appeared to be consistent in nature. In preparation for data collection, a single crystal was selected for analysis and mounted on a glass fiber, and X-ray diffraction data was collected. First attempts at a structure solution were unsuccessful; the asymmetric unit seemed too large for a molecule as simple as picryl bromide and it was thought that the crystal was twinned. In an attempt to find a non-twinned crystal with the true unit cell, many other crystals were examined. In every case, the experimentally determined unit cells were larger than expected. Once it was accepted that the crystals were not twinned, the various polymorphs were carefully determined and refined. Compounds **1 α** and **1 δ** were collected on a Bruker three-circle platform diffractometer equipped with a SMART 1000 CCD detector using MoK α radiation ($\lambda = 0.71073$ Å), while compounds **1 β** , **1 γ** , and **1 ϵ** were collected on a Bruker three-circle platform diffractometer equipped with a SMART 6000

CCD detector using CuK α radiation ($\lambda = 1.54178$ Å). In all cases, data collection was performed and the unit cell was initially refined using the SMART [v5.625] program. Data reduction was performed using SAINT [v6.36A] and XPREP [v6.12] programs. Corrections were applied for Lorentz and polarization effects. The structure was solved and refined with the aid of the programs in the SHELXTL-Plus [v6.10] system of programs. The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

THE FIVE POLYMORPHS OF PICRYL BROMIDE

The vial of picryl bromide yielded five polymorphs ($\alpha - \epsilon$ in Table 1), the two reported in 1933 plus three new forms. The consistent appearance of the crystal morphologies observed on visual inspection was not indicative of the rich variety of polymorphs eventually discovered in this single sample. This is somewhat unusual, as crystalline polymorphs generally display different crystal morphologies which are obvious upon inspection. A good example of this is the right- and left-hand forms of quartz, in which chains of silicon dioxide can have either a right- or left-hand twist and yield crystal forms that can be distinguished by visual inspection of the crystal faces.

In describing crystal structures, researchers use the symbols Z and Z' to denote the number of molecules in the unit cell and the number of molecules in the asymmetric unit, respectively. Note that for the polymorphs of picryl bromide described in Table 1, Z values range from 12 to 36 while Z' values range from 3 to 18. The

TABLE 1 — Crystallographic Parameters for the Five Polymorphs of Picryl Bromide

Form	α	β	γ	δ	ϵ
Temp. (K)	93(2)	294(2)	294(2)	93(2)	293(2)
γ (Å)	0.71073	1.54178	1.54178	0.71073	1.54178
System	Triclinic	Hexagonal	Triclinic	Trigonal	Triclinic
Space Group	P -1	P 6 ₅	P -1	P 3 ₁	P 1
a (Å)	14.8480(17)	14.8812(1)	14.9166(2)	14.8610(7)	14.9086(1)
b (Å)	14.8614(17)	14.8812(1)	14.9424(2)	14.8610(7)	14.9083(1)
c (Å)	15.3318(17)	22.5449(4)	30.3888(3)	44.007(3)	22.6784(2)
α (°)	72.762(2)	90	94.729(1)	90	95.245(1)
β (°)	80.350(2)	90	93.754(1)	90	90.116(1)
γ (°)	60.225(2)	120	119.925(1)	120	119.896(1)
V (Å ³)	2803.8(6)	4323.69(9)	5805.61(12)	8416.9(8)	4344.89(6)
Z	12	18	24	36	18
Z'	6	3	12	12	18
ρ calc. (Mg/m ³)	2.075	2.019	2.005	2.074	2.009

value of Z is related to Z' and the number of symmetry operations that relate molecules within the unit cell to each other, and is a function of the space group of the crystal. Z' is a function of how molecules pack within the asymmetric unit. Z' values of less than one are quite common. In the most recent release of the Cambridge Structural Database (CSD),⁴ out of 423,756 entries there are 110,194 entries with Z' less than 1; of these, 89,939 have a Z' of 0.5. Only 37,138 entries, fewer than 10%, have a Z' greater than 1. Z' values of 3 or greater are quite uncommon. Fewer than 1% of the structures in the database have a Z' ≥ 3 and aside from the picryl bromide polymorphs, only nine other structures have Z' of 12 and one other has a Z' of 18. Thus the crystal polymorphs of picryl bromide are among a very small group of high Z' structures. A search of the CSD for systems with greater than four polymorphs (using parameters previously defined)⁵ was conducted to determine the rarity of pentamorphic systems. Only two pentamorphic structures were found, along with one heptamorphic structure.

Several attempts were made to re-grow crystals of the various systems reported here, while searching for a simpler system (Z' = 1) as well as more potential polymorphs. Since the crystallization conditions post-synthesis were not recorded, reproducing the conditions resulting in the analyzed sample was not possible. All recrystallization attempts, using slow evaporation techniques while employing a large number of solvents and combinations of solvents, resulted exclusively in the α form.

Despite the variation in Z' and the fact that four space groups and three crystal systems are repre-

sented, there are remarkable consistencies among the five structures. All five polymorphs share a common packing arrangement within layers. There are two types of interactions that stabilize molecules within layers, C-H...O hydrogen bonds, and N-O...Br dipole-induced interactions. These interactions result in the molecules organizing themselves into two different “triad” motifs differing in their intermolecular interactions (Fig. 2). One triad (represented by the red triangle in Fig. 2) is held together by hydrogen bonds involving a C-H moiety from one molecule with a *para* nitro group of an adjacent molecule. C-H...O distances among the various polymorphs range from 3.231(5) to 3.392(5) Å, which is well within the range of expected distances for this type of hydrogen bond.

The second triad (represented by the blue triangle in Fig. 2) is formed through dipole-induced interactions between the Br of one molecule and an *ortho* nitro group from an adjoining molecule. The maximum Br...O distance observed in the five studies, 3.219(6) Å, is well within the combined van der Waals

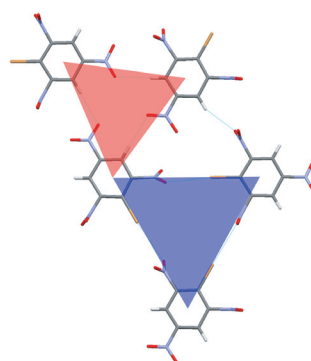


FIGURE 2
Representation of the two triad motifs in picryl bromide. The red triangle represents the hydrogen-bonded triad, the blue triangle represents the induced dipole triad.

radii (3.37 Å), indicating that these are significant stabilizing interactions. Such interactions are known to rival hydrogen bonds in strength.

Within each sheet the triads are arranged such that each dipole-induced triad is surrounded by six hydrogen-bonded triads (Fig. 3). These sheets are found in all five polymorphs. The inter-sheet spacings are also similar and are typically about 4.0 Å. The similar intra-sheet packing (Fig. 3) and spacing between the sheets is reflected in the uniformity in the observed densities of the polymorphs which range from 2.005 to 2.075 Mg/m³.

DISTINGUISHING THE POLYMORPHS

The consistent packing within sheets and spacing between sheets leaves only the relationship between the sheets to produce the subtle differences that result in the formation of the five polymorphs observed. The differences in how the sheets relate to each other is responsible for the differences in crystallographic symmetry that distinguish the polymorphs. Simplifying this somewhat, the five polymorphs can be distinguished by their layer structure. In Fig. 4 the crystallographically equivalent layers are displayed in the same color. Note that in the α form the layers are arranged ABBA where A and B are crystallographically distinct layers and the repeats are crystallographically identical. The β form is even simpler, consisting of only A layers. The γ and δ forms each have four layers; in the δ form the layers are arranged ABCD while in the γ form the layers are arranged ABCDDCBA. Note the “mirror” present in the sequence of both the α and γ forms. The ϵ form has six layers arranged ABCDEF. In addition to different

crystallographically distinct layers in each polymorph, the relationship (molecule to molecule) between layers differs from one polymorph to another. In some cases these differences are distinct and related to crystallographic symmetry, in others the differences are more subtle. In either case these differences are beyond the scope of this review.

A NEW INTERACTION

The interactions within the layers are well known and have been described previously by others. The two unique triads share indices, creating the highly consistent two-dimensional sheets observed in each polymorph. The layers depicted in Fig. 4 are held together by interactions between an *ortho* nitro group from one layer and a phenyl ring in an adjacent layer (Fig. 5). All of the *ortho* nitro groups are twisted out of the phenyl plane due to steric interactions with the Br, while the *para* nitro groups are unaffected and remain in the plane of the aromatic ring. The nitro-O...ring centroid (Cg) distances were calculated and they ranged from 2.899 to 3.215 Å. These distances are within the combined van der Waals radii (3.37 Å) of an oxygen and a carbon. Despite the fact these are O...Cg distances, it is highly likely that there are reasonably strong nitro- π associations present. A survey of the CSD yielded more than 300 structures in which a nitro oxygen is within 3.2 Å of an aromatic ring centroid. Thus there is a general tendency for molecules involving nitro groups to be stabilized in the solid state by such interactions. Despite the occurrence of this interaction in many other structures, this interaction does not appear to have been discussed in the papers reporting their struc-

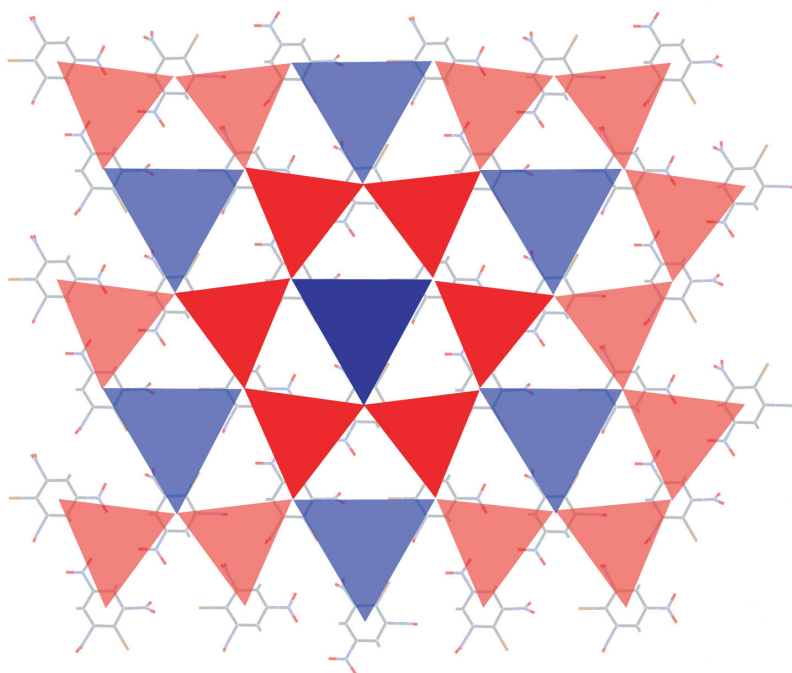
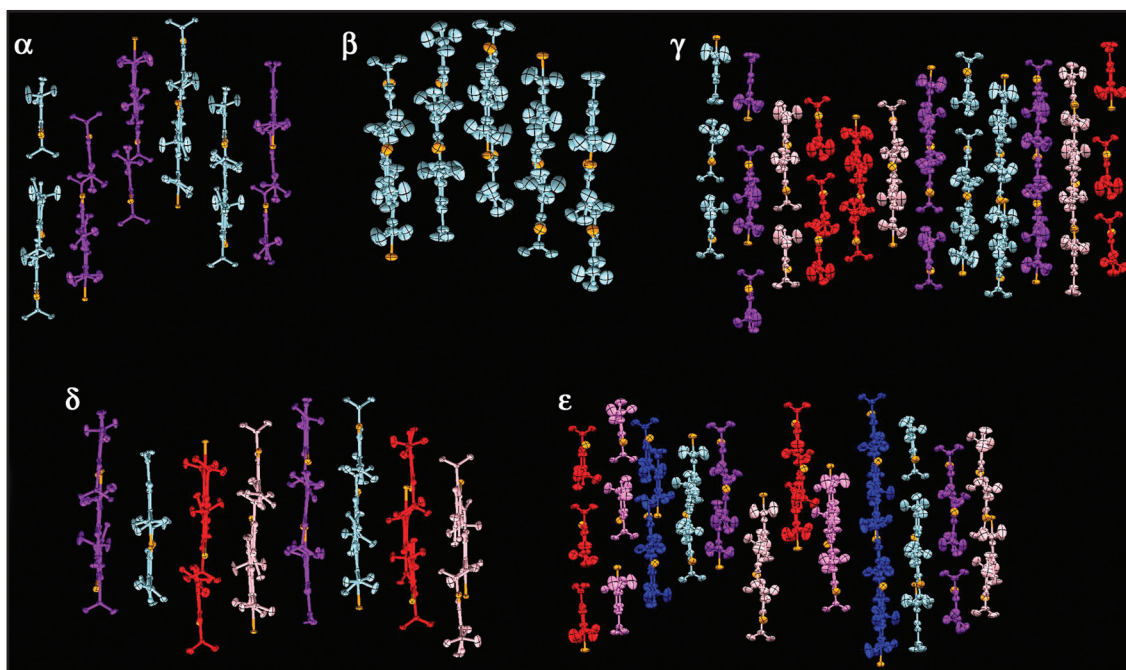
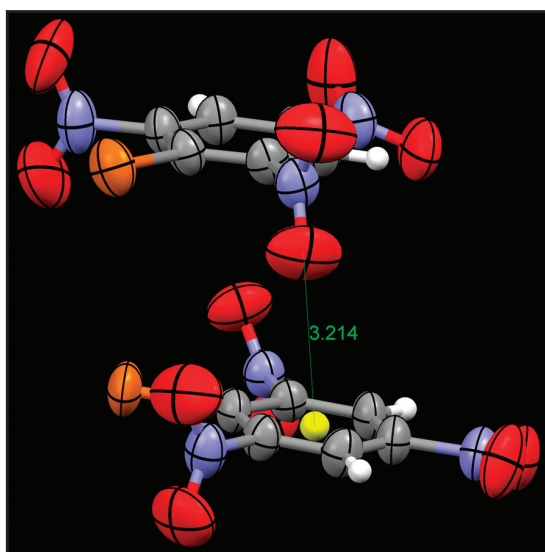


FIGURE 3
Representation of the two-dimensional sheets found in picryl bromide. Note the arrangement of hydrogen-bonded (red) triads surrounding induced dipole triads (blue).

**FIGURE 4**

Relationship between the layers in polymorphs of picryl bromide. In each image, crystallographically unique layers are depicted in a different color. Bromine atoms are shown in orange to help orient the individual molecules.

**FIGURE 5**

Geometry of the nitro- π interactions between adjacent sheets. The center of gravity (Cg) of the aromatic ring in the lower molecule is shown as a yellow sphere; the dotted line represents the O...Cg interaction. Note that the interacting nitro group in the upper molecule is twisted out of the plane of the aromatic ring to an angle of approximately 90° .

tures; however, mention has been made of the potential for π - π interactions between the aromatic ring and the π system of the nitro group. The energies of the nitro- π interactions are currently being studied and may make a significant contribution to packing energies in crystals of picryl bromide.

CONCLUSION

The X-ray structures of five polymorphs of picryl bromide were determined, with Z' values ranging from 3 to 18. Only three other compounds in the current release of the CSD have as many as five polymorphs. The large numbers of crystallographically unique molecules in these polymorphs also makes these structures noteworthy. Three distinct intermolecular interactions are responsible for stabilizing the crystal structures: C-H...O hydrogen bonds, N-O...Br dipole-induced interactions, and finally the N-O... π interactions. Although the N-O... π interactions are present in many other crystal structures, we were the first to note their importance in stabilizing the crystal structure. In all polymorphs the molecules pack into two-dimensional sheets, consisting of two different triad motifs. The relationship between the sheets and packing of equivalent sheets distinguish the polymorphs. Despite the differing orientations, the inter-sheet N-O... π associations are remarkably consistent. This leads to the uniform densities observed and implies that the thermodynamic energy differences from one polymorph to another

are negligible. The knowledge gained in studying these polymorphs can be applied in modeling to aid in the design of new energetic materials with greater stability and increased explosive yields.

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