CRYSTALLOGRAPHIC DATA

1,3,5-Triamino-2,4,6-trinitrobenzene

Howard H. Cady
University of California
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Some of the physical properties and the optical and X-ray crystallography of TATB (1,3,5-triamino-2,4,6-trinitrobenzene) have been investigated at Los Alamos. The following is a summary of the results pertinent to the crystallography.

Crude TATB was prepared by ammonolysis of trichlorotrinitrobenzene. Large crystals of purer TATB, used for the crystallographic studies, were prepared by slow recrystallization from hot nitrobenzene.

X-ray powder patterns and microscopic examination revealed no crystalline impurities.

1. X-Ray Diffraction

Debye-Scherrer diffraction photographs were obtained using filtered copper radiation and a standard Philips 114.6 mm powder camera. The sample was contained in a 0.3 mm Lindemann glass capillary. Observed film readings were corrected for film shrinkage, but not absorption effects. Relative intensities, normalized to give the most intense line a value of 100, were obtained using a Philips X-ray diffractometer and are based on peak heights relative to the base line. The powder pattern is given in Table I.

TABLE I

TATB POWDER PATTERN

d (meas film)		I/I_{100} Diffractometer	hkl	I(precession)	d_{calc} from unit cell
			$1\bar{1}0$	mw	7.697
7.64	u	16.1	100	vs	7.602
7.25		2.1	010	ms	7.213
6.03		3.8	$01\bar{1}$	s	6.026
5.53		2.1	$10\bar{1}$	s	5.511
5.33		5.6	$1\bar{1}1$	s	5.347
			$2\bar{1}0$	m	4.511
4.49	u	3.3	$1\bar{1}\bar{1}$	s	4.491
4.362		2.6	101	s	4.365
			$11\bar{1}$	s	4.276
4.269	u	8.3	$1\bar{2}0$	s	4.268
			$1\bar{2}1$	s	4.229
4.221	u	8.6	110	s	4.219
4.002		3.1	011	s	4.026
3.85		---	$2\bar{2}0$	w	3.848
3.710		3.5	$2\bar{1}1$	s	3.725
--		1.0	201	mw	3.650
3.600		4.4	$2\bar{1}1$	s	3.603
3.385		1.5	$01\bar{2}$	ms	3.397
			$10\bar{2}$	s	3.172
3.138		100.	002	vvs	3.137
			$11\bar{2}$	s	3.100
			$1\bar{2}1$	m	3.091
			$1\bar{2}2$	s	3.047
3.042		2.8	111	m	3.037
			$3\bar{2}0$	ms	2.952
2.942	u	2.5	$1\bar{3}1$	m	2.945
			$21\bar{1}$	ms	2.930
2.833		.90	$2\bar{3}0$	s	2.836
2.791		1.1	210	m	2.798
2.725		1.7	120	ms	2.737
			$2\bar{1}2$	m	2.619
2.609	u	1.0	$12\bar{2}$	ms	2.607
			$30\bar{1}$	ms	2.567
2.556	u	1.5	$3\bar{3}0$	m	2.566
			$3\bar{1}1$	m	2.551
2.534		1.4	300	ms	2.534
2.479		1.1	$2\bar{3}2$	ms	2.480
			$03\bar{2}$	ms	2.411
2.409	u	0.92	030	ms	2.404
2.300		0.41	211	m	2.296
2.242		0.50	$30\bar{2}$	ms	2.244
			$1\bar{2}\bar{2}$	m	2.207
2.205	u	0.55	$3\bar{2}2$	m	2.199
2.172		0.80	112	mw	2.174

TABLE I (Cont.)

d (meas film)		I/I_{100} Diffractometer	hkl	I(precession)	d_{calc} from unit cell
			$4\bar{2}\bar{1}$	s	2.147
2.138	u	6.5	$2\bar{2}\bar{2}$	s	2.138
			$2\bar{4}0$	ms	2.134
			$2\bar{4}2$	s	2.115
			220	s	2.110
2.104	u	6.3	$3\bar{2}\bar{2}$	ms	2.104
			$4\bar{2}1$	s	2.099
2.052	u	0.3	$1\bar{3}3$	w	2.060
			$20\bar{3}$	w	2.045
1.995		0.3	?		
1.928	u	0.42	$1\bar{1}\bar{3}$	w	1.934
			$2\bar{1}\bar{3}$	mw	1.923
---		0.38	$4\bar{1}\bar{2}$	w	1.907
			103	w	1.906
1.877		0.25	$2\bar{1}3$	w	1.872
1.829		0.25	$30\bar{3}$	m	1.837
			013	m	1.828
1.787		0.63	$2\bar{5}1$	m	1.788
			$2\bar{5}2$	w	1.759
1.760	u	0.45	$5\bar{2}1$	w	1.757
			$3\bar{2}\bar{2}$	m	1.753
1.68	u	0.25	diffuse (10 lines m-w in intensity)		
1.613		0.19	$10\bar{4}$	ms	1.613
1.569		2.7	004	vs	1.569
1.548	u	0.67	$22\bar{4}$	ms	1.550
			$2\bar{4}\bar{2}$	ms	1.545
1.521	u	0.5	$2\bar{4}4$	ms	1.523
			222	ms	1.518
1.502		0.48	$4\bar{2}3$	ms	1.507
			$6\bar{3}0$		1.504
1.408		0.13	330		1.406
1.302		1.1	$6\bar{6}1$	m	1.303
1.284		0.13	?		
1.215		0.39	?		
1.203		0.25	?		
1.189		0.41	$7\bar{6}1$	m	1.190
1.170		0.14	?		
1.164		0.12	?		
1.114		0.25	?		
1.110		0.29	?		
1.099		0.16	?		
1.087		0.16	?		
1.072		0.09	?		
1.054		0.09	?		
1.032		0.14	?		
1.027		0.14	?		
1.017		0.12	?		
1.008		0.12	?		
0.983		0.20	?		

u = unresolved
vs = very strong
s = strong
ms = medium strong
m = medium
mw = medium weak
w = weak

Single crystal X-ray diffraction photographs were obtained using a precession camera. Unit cell dimensions and angles were calculated from these photographs. The results of these calculations are summarized below.

Space group:	P_1 or $P_{\bar{1}}$	
Cell dimensions:	a_o = 9.03 Å	α = 108.6°
	b_o = 9.03 Å	β = 91.8°
	c_o = 6.81 Å	γ = 120.0°
Formula weights per cell:	2	
Formula weight:	443.12	
Density	1.935 (calc); 1.93 ± 0.01 (meas)	

2. Optical Crystallography and Other Physical-Chemical Information

The optical crystallography and related information is presented following the outline in Wahlstrom, Optical Crystallography, John Wiley and Sons, Inc., New York (1950), for the examination of nonopaque substances. The relationship between the optical axes and the crystallographic axes are indicated in the figure of a typical TATB crystal. Note that the X optical axis is perpendicular to the $a_o b_o$ plane so that Y and Z lie in the $a_o b_o$ plane.

a. Preliminary Megascopic Examination

Color - Light yellow. TATB is both photosensitive and thermally sensitive in that it turns yellowish green on exposure to light, and dark yellow-brown on exposure to elevated temperature.

Specific gravity - 1.93

Fusibility - Not fusible. TATB begins to sublime at about 300°C and to decompose at a somewhat higher temperature. Decomposition occurs without melting and a solid residue remains. A combination of DTA and pyrolysis indicates an exothermic decomposition starting above 300°C. No endothermic transformations are observed.

b. Microscopic Examination

Lower polar only

(1) Morphology

System - Triclinic, pinakoidal
Habit - Tabular, equant, and occasionally imperfect acicular
Forms - {001}, {100}, {01$\bar{1}$} on all crystals;
{1$\bar{1}$1} on many crystals;
{011}, {$\bar{1}\bar{1}$1} on very few crystals.

(2) Color - Yellow exhibiting strong pleochroism

X = colorless

Y = strong yellow

Z = strong yellow

(3) Luster - Regular reflection off {001} and occasionally off other forms.

(4) Fracture - Uneven or splintery.

(5) Cleavage - Nearly perfect parallel to {001}, and not observed in any other direction.

(6) Refractive indices

Immersion - X = 1.45

Y > 2.11

Z > 2.11

From estimated 2V and X - Y = 2.3

Z = 3.1

(7) Inclusions and alternations - No inclusions, but striations parallel to {001} are common.

Crossed Polars

(1) Anisotropic and biaxial negative

(2) No twinning

(3) Abnormal polarization colors

(4) Dispersion - Rhombic R > B

(5) Optic orientation - see Figure 1

(6) 2E = 62.8°
2V = 26° estimated from centered optic axis figure

Observations on Heating

(1) Sublimes 300°C and above

(2) Decomposes without melting 325-350°C leaving a solid residue

Sublimate

(1) Lower polar only

(a) Morphology

System - Triclinic, pinakoid and pedion faces
Habit - Tabular and pyramidal
Forms - {001}, others not identified

(b) Color - Yellow with strong pleochroism

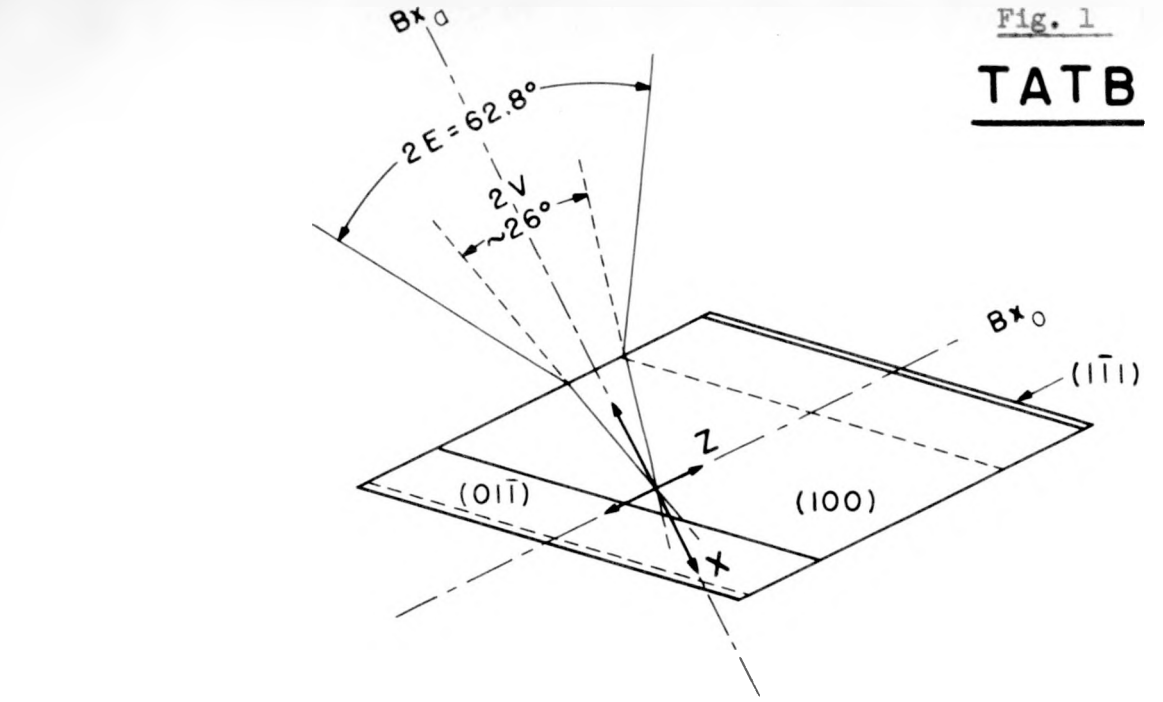
(c) Index of refraction - same as crystals from nitrobenzene

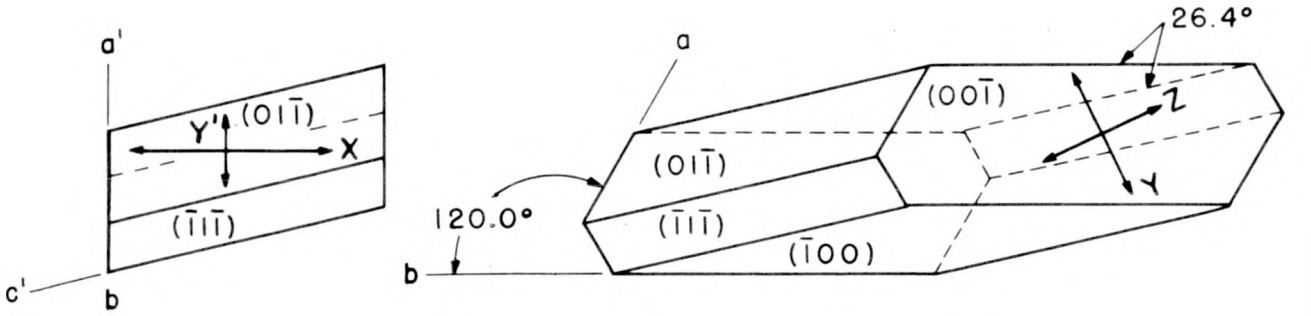
(2) Crossed Polars

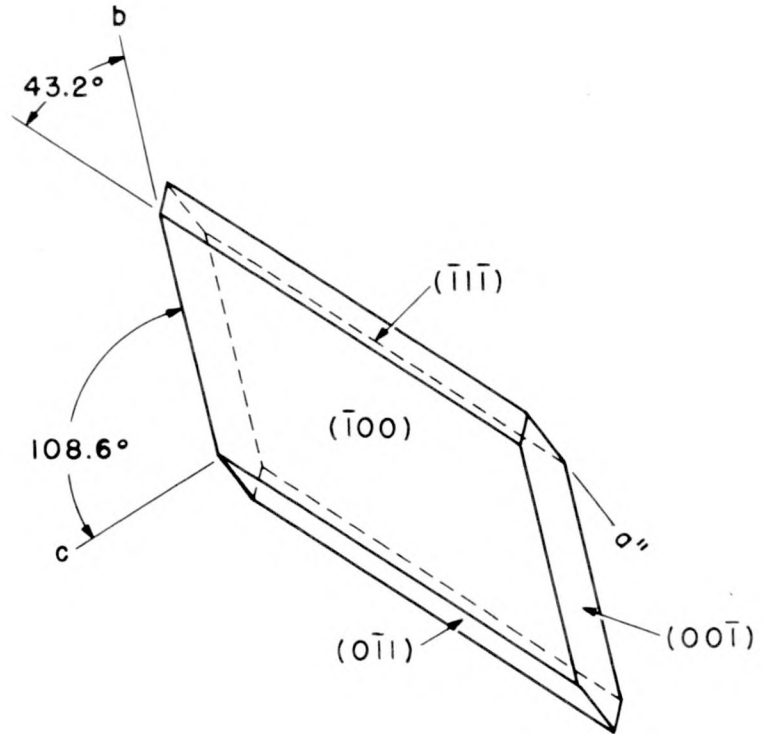
(a) Nearly all crystals highly strained and/or twinned.

Fig. 1

TATB







$a_o = 9.03$ Å $\quad \alpha = 108.6°$

$b_o = 9.03$ Å $\quad \beta = 91.8°$

$c_o = 6.81$ Å $\quad \gamma = 120.0°$

$X_{Na} = 1.45$

$Y_{Na} \cong 2.3$

$Z_{Na} \cong 3.1$

} ESTIMATED FROM CENTERED OPTIC AXIS FIGURE (2V)

Very poor interference figures with 2E varying from 0 to 62.8°.

Optical axial orientation varies from one end of crystal to other.

(b) Anisotropic, biaxial negative in all cases.

This work was performed under the auspices of the U. S. Atomic Energy Commission.