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A note on the elastic properties of pentaerythritol. By R. C. SRIVASTAVA*, *Physics Department, University of Allahabad, Allahabad, India*

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Srivastava & Chakraborty (1960) published theoretical relationships connecting the rekha constants (using the nomenclature of Ramachandran & Wooster, 1951) corresponding to simple and elementary directions of reciprocal lattice and the thermal wave vector in terms of the elastic constants for crystals belonging to tetragonal crystal classes 4 , $\bar{4}$ and $4/m$. They also suggested a method of 'successive approximations' to obviate the difficulty arising in the evaluation of the elastic constants due to the presence of the constant C_{16} in the elastic matrix of the above crystals. It may be mentioned here that the elastic constants of any crystal belonging to 4 , $\bar{4}$, or $4/m$ class have not yet been determined. It is expected, therefore, that the elastic constants of such crystals may prove to be of interest.

Pentaerythritol belongs to $\bar{4}$ crystal class. Its (200), (020) and (004) diffuse reflections with [010] axis and, (200) and (220) with [001] axis perpendicular to the direction of incidence of X-rays have been studied. The choice of the reflections was made according to the criterion given by Ramachandran & Wooster (1951). For evaluating the elastic constants from the experimentally determined rekha constants the method suggested by Srivastava & Chakraborty (1960) has been employed.

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The value of the constants is given below in units of 10^{10} dynes/cm.²:

$$C_{11} = 6.1, C_{33} = 8.0, C_{44} = 3.5, C_{66} = 4.6, \\ C_{16} = -0.39, C_{13} = 0.50, C_{12} = -2.50.$$

The discussion of the accuracy of the method has been done in detail by Ramachandran & Wooster (1951) and Chakraborty & Sen (1958). The accuracy of the determination of the constants C_{11} , C_{33} , C_{44} , C_{66} , C_{16} is estimated to be $\pm 4\%$ whereas that of C_{12} and $C_{13} \pm 6\%$.

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The morphology and space groups of some halogen substituted derivatives of 5 α -cholestane.

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In connection with investigations in one of our laboratories (L.O.C.), concerning the stereochemical features of 1,2 dihalogenocyclohexane and dioxane compounds (Kwestroo, Meyer & Havinga, 1954; Altona, Romers & Havinga, 1959; Van der Linden, 1958; Wessels, 1960) and of steroids (Van Moorselaar, 1962), a morphological survey and an X-ray analysis of some dihalogenosteroids was undertaken.

Single crystals of

- I 2β , 3α [a , a] dibromo-cholestane
 II 2β , 3α [a , a] chloro-bromo-cholestane
 III 2β , 3α [a , a] dichloro-cholestane (two forms α and β)
 IV 2α , 3β [e , e] dibromo-cholestane
 V 2α , 3β [e , e] dichloro-cholestane

were obtained by slow crystallization from ethylacetate.

Morphology and optics

I. 2, 3 [a , a] Br, Br

$$a:b:c = 4.214:1.05810; \beta = 90^\circ; \text{orthorhombic.}$$

Crystals are tablets {100} of varying thickness and with a rectangular outline. In the zone [010] the form {101} is always present and sometimes {001}. In [001] occur

{110}, {210} and {310} of which the latter is always very small.

Barker angles, omitting {310}:

$$cr = 82^\circ 9', am = 30^\circ 9', bq = 13^\circ 21'.$$

Transformations: old \rightarrow new 001/010/ $\bar{1}$ 00; new \rightarrow old 00 $\bar{1}$ /010/100.

Barker angles for combinations without {110}, but with {210} present:

$$cr = 16^\circ 12', am = 25^\circ 23', bq = 82^\circ 9'.$$

Transformations: old \rightarrow new 020/ $\bar{1}$ 00/001; new \rightarrow old 0 $\bar{2}$ 0/100/002.

II. 2, 3 [a , a] Cl, Br

$$a:b:c = 1.285:1.0949; \beta = 112^\circ 26'; \text{monoclinic.}$$

Crystals are tablets {100}, elongated along the c -axis.

Observed forms: {100} large, {110} and { $\bar{1}$ 10} small; sometimes {010} and {0 $\bar{1}$ 0}. The tablets are terminated by {001}, {101}, {0 $\bar{1}$ 1}, {011}, { $\bar{1}$ 11} and {111}. Of these {0 $\bar{1}$ 1} is always larger than {011}, while {111} is always larger than { $\bar{1}$ 11}. The latter six forms are not always all present, but various combinations occur.

Table 1. *X-ray data*

Compound	Space group	<i>Z</i>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β	<i>T</i>	<i>d</i> (exp.) (g.ml. ⁻¹)
2, 3 [e, e] Br, Br	<i>P</i> ₂ ₁	2	15.05	7.72	11.50	104° 30'	20	1.33
2, 3 [e, e] Cl, Cl	<i>P</i> ₂ ₁	2	14.88	7.74	11.44	105°	20	1.14
2, 3 [a, a] Br, Br	<i>P</i> ₂ ₁ 2 ₁ 2	4	43.3	10.25	5.95	90°	20	1.30
2, 3 [a, a] Cl, Br	<i>P</i> ₂ ₁	2	13.56	10.59	10.08	112° 30'	20	1.21
idem	<i>P</i> ₂ ₁	2	13.36	10.45	9.97	112° 23'	-120	
2, 3 [a, a] Cl, Cl (α -mod.)	<i>P</i> ₂ ₁	2	16.48	6.70	12.72	108° 56'	20	
Cl, Cl (β -mod.)	<i>P</i> ₂ ₁	2	13.56	10.54	10.07	113° 09'	20	1.12
idem	<i>P</i> ₂ ₁	2	13.31	10.47	9.88	113° 22'	-120	

Barker angles:

$$am = 49^\circ 54', \quad bq = 48^\circ 45', \quad cr = 28^\circ 2', \quad ra = 39^\circ 22', \\ ca = 67^\circ 34'.$$

Optical properties: plane of optic axes is perpendicular to (010); through (100) an isogyre can be seen; the optic sign is negative.

III. 2, 3 [a, a] Cl, Cl modification α

$$a:b:c = 2.438:1:1.899; \quad \beta = 108^\circ 55'; \quad \text{monoclinic.}$$

Crystals are elongated parallel to the *b*-axis. Observed forms: {001} and {100} large; $\{\bar{1}01\}$ small. Terminations by $\{11\bar{1}\}$.

Barker angles:

$$am = 66^\circ 33', \quad bq = 30^\circ 18', \quad cr = 26^\circ 51', \quad ra = 37^\circ 29', \\ ca = 64^\circ 20'.$$

Transformations old \rightarrow new 101/010/ $\bar{1}00$, new \rightarrow old $00\bar{1}/010/101$.

Optical properties: no optic axes are observed on (001) or on (100).

Modification β

$$a:b:c = 1.273:1:0.950; \quad \beta = 112^\circ 59'; \quad \text{monoclinic.}$$

Crystals are tablets {100}, elongated along the *c*-axis. Observed forms {100} large, {110} intermediate and {010} very small; terminations by {001}, {011} and {111} of which the latter is always small; {101} is sometimes observed.

Barker angles:

$$am = 49^\circ 31', \quad bq = 48^\circ 50', \quad cr = 28^\circ 1', \quad ra = 39^\circ 0', \\ ca = 67^\circ 1'.$$

Optical properties: plane of optic axes is perpendicular to (010); through (100) an isogyre can be seen; the optic sign is negative.

IV. 2, 3 [e, e] Br, Br

$$a:b:c = 1.938:1:1.481; \quad \beta = 104^\circ 11'; \quad \text{monoclinic.}$$

Crystals are elongated parallel to the *b*-axis. Observed forms: {100}, {001} large, $\{\bar{1}01\}$ small, sometimes {201} is observed.

Terminations by {110}, {011} and {111}.

Barker angles:

$$am = 61^\circ 59', \quad bq = 34^\circ 51', \quad cr = 31^\circ 58', \quad ra = 43^\circ 51', \\ ca = 75^\circ 49'.$$

Optical properties: (010) is plane of optic axes, one

of the optic axes is nearly perpendicular to (100); $2V$ is close to 90° .

V. 2, 3 [e, e] Cl, Cl

$$a:b:c = 1.907:1:1.475; \quad \beta = 104^\circ 33'; \quad \text{monoclinic.}$$

Crystals are elongated parallel to the *b*-axis. Observed forms: {100}, {001} large and $\{10\bar{1}\}$ small. Terminations by {011}, {110} and {111}.

Barker angles:

$$am = 61^\circ 33', \quad bq = 35^\circ 1', \quad cr = 32^\circ 5', \quad ra = 43^\circ 22', \\ ca = 75^\circ 27'.$$

Optical properties: (010) is plane of optic axes; one of the optic axes is nearly perpendicular to (100); $2V$ is close to 90° .

X-ray analysis

Space groups and lattice constants were determined from Weissenberg photographs about [010] and [001]; densities were measured using the flotation method. Table 1 gives the experimental results.

The compounds II and III mod. β as well as IV and V form isomorphous pairs.

Patterson projections along [010] and [001] proved—as was concluded by Alt & Barton (1954) from dehalogenation rates—that in I, II and III the halogen atoms are in axial positions, and that they are equatorially bound in IV and V.

There seem to be exceptions to the statement of Alt & Barton that corresponding pairs of 2:3 dihalogenocholestanes are isomorphous.

A three-dimensional analysis of the compounds III and V is in progress.

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