

04.1-4 QUANTITATIVE RELATIONSHIP BETWEEN ASYMMETRY PARAMETERS IN CYCLOHEXENE RING. By M. L. Główska, Institute of General Chemistry, Technical University, Łódź 90-924, Poland.

Conformation of the medium-size rings arouses wide interest both from theoretical and practical point of view. Quantitatively, the conformation of the rings can be described by torsional angles or by different parameters derived from the angles. Pseudorotation parameters for five-membered and asymmetry parameters for six-membered rings are most often used by crystallographers, though other propositions are occasionally scattered through the literature. All the propositions are based on a hidden assumption that the neighbouring torsional angles are interdependent.

In the cyclohexene ring the difference between  $\Delta C_3^1$  and  $\Delta C_3^2$  parameters (Duax & Norton, Atlas of Steroid Structure, New York, Plenum, 1975) is a simple function of  $\Delta C_2^{12}$ ,

$$\Delta C_2^{12} = A \cdot (|\Delta C_3^1 - \Delta C_3^2|) + B$$

where A and B depend on the number of substituents in the ring and they are equal to 1.390 (A), 0.001 (B) and 1.428 (A), -0.207 (B) for mono and disubstituted cyclohexene derivatives, respectively. The values have been calculated from over 50 data accessible in the literature. There are only four exceptions when the term "deformation of conformation" should be used, as the calculated asymmetry parameters does not satisfy the equation given above. The deformations can be defined by the difference between the calculated and the observed values of  $\Delta C_2$ .

04.1-5 A SECOND-ORDER PHASE TRANSITION OF CALCIUM BROMIDE AND ITS GEOMETRICAL INTERPRETATION. By H. Bärnighausen, W. Bossert, and B. Anselmetti, Institute of Inorganic Chemistry, University of Karlsruhe, D7500 Karlsruhe, Germany.

The structural relationship between the  $\text{CaCl}_2$ -type and rutile-type structure is well-known (see textbooks), but so far the corresponding phase transition has only been found for  $\text{NiF}_2$  as a pressure induced transformation (Jørgensen et al., High Pressure Science and Technology, New York: Plenum, 1979, pp. 152-160). Recently it was shown (Bossert, Thesis, Univ. of Karlsruhe, 1981) that the high-temperature modification of  $\text{CaBr}_2$ ,  $\text{YbBr}_2$ , and  $\text{TmBr}_2$  belongs to the rutile-type (space group  $P4_2/mnm$ ) and that a second-order phase transition to the  $\text{CaCl}_2$ -type (space group  $Pn\bar{3}m$ ) takes place at lower temperatures. This transformation has been studied in greater detail for  $\text{CaBr}_2$  using a high-temperature powder diffraction Guinier camera. By geometrical arguments a simple relationship between the lattice parameters of the orthorhombic unit cell and the tilt-angle  $\omega$  of the cation coordination octahedron with respect to the rutile-type structure has been derived:

$\sin(2\omega) = (b^2 - a^2)/c^2$ . Between  $T_C = 751 \text{ K}$  ( $\omega = 0^\circ$ ) and  $T = 605 \text{ K}$  ( $\omega = 4^\circ$ ), the order parameter  $\omega$  is a linear function of  $|T - T_C|^\beta$  with  $\beta = 1/2$ , as is expected for second-order phase transitions from the classical Landau theory. Probably the transition is associated with a softening of the Raman-active  $B_{1g}$  mode of the rutile-type structure.

The geometrical model which is valid only for small values of  $\omega$ , can be extended to  $\omega \approx 25^\circ$  by introduction of an additional parameter  $f$ . This parameter characterizes small distortions of

the cation coordination octahedron as the result of interactions between the anions by (i) repulsive forces [ $f = 0.90$  for  $\text{CaBr}_2$ ], (ii) covalent chemical bonds [ $f = 1.16$  for marcasite ( $\text{FeS}_2$ ),  $f = 1.12$  for loellingite ( $\text{FeAs}_2$ )] or (iii) hydrogen bonds [ $f = 1.12$  for  $\text{InO}(\text{OH})$ ]. The generalized formula is

$$\tan \omega = [(b-a)/(b+a)] \cdot [(q+1)/(q \cdot f - 1)],$$

whereby  $q = d/\text{SQRT}(d^2 - c^2/4)$  with  $d$  as the mean cation-anion distance. Note that often the sum of ionic radii is an adequate estimation of  $d$ . The formula which is still an approximation works quite well for many rather different compounds. Thus our considerations are useful for a comprehensive survey of rutile-related crystal structures.

For  $\text{CaBr}_2$  an accurate single-crystal structure determination has been carried out at room temperature (4-circle diffractometer,  $\text{MoK}_\alpha$  radiation).  $\text{CaBr}_2$  crystallizes orthorhombic, space group  $Pn\bar{3}m$  (No. 58), with  $a = 6.568(1)$ ,  $b = 6.880(1)$ , and  $c = 4.3428(7) \text{ \AA}$ . From 2836 measured reflections 435 unique structure factors  $F_0$  were obtained (merge R value 1.82%). Based on 389  $F_0$ 's with  $F_0 \geq 3\sigma(F_0)$  the refinement ended in a conventional R value of 2.28%. The results are

Ca at 2(a)  $2/m$  0, 0, 0;  $1/2, 1/2, 1/2$ .  
Br at 4(g)  $m$   $\pm(x, y, 0; 1/2+x, 1/2-y, 1/2)$   
with  $x = 0.26499(4)$  and  $y = 0.33722(4)$ .

The anisotropic temperature factor is given by  $\exp[-2\pi^2(U_{11}h^2/a^2 + U_{22}k^2/b^2 + U_{33}l^2/c^2 + 2U_{12}hk/ab)]$ .

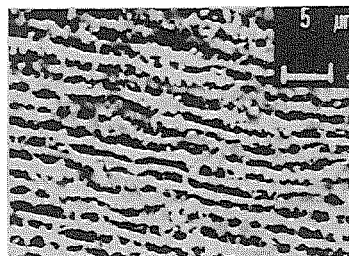
	$U_{11} (\text{\AA}^2)$	$U_{22} (\text{\AA}^2)$	$U_{33} (\text{\AA}^2)$	$U_{12} (\text{\AA}^2)$
Ca	0.0224(3)	0.0229(3)	0.0187(3)	-0.0026(2)
Br	0.0316(2)	0.0329(2)	0.0233(2)	-0.0151(1)

04.1-6 OXIDATION OF TITANIUM BY OXYGEN : STRUCTURE RELATIONS BETWEEN TITANIUM AND RUTILE  $\text{TiO}_2$ . By L. LATAUD\*, D. CIOŚMAK\*, G. BERTRAND\*, J.J. HEIZMANN\*\*\*, A. VADON\*\*\*

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The oxid layer of rutile  $\text{TiO}_2$  appears as a stacking of parallel leaves at the metal-gas interface, separated by empty spaces; the leaves are linked by a few bridges. (K. JARRAYA and all (1982) C.R. ACAD. SCI. II. 294. p. 1365).



To understand that stratification phenomenon, the structure relation existing between the titanium and the rutile formed.

- 1- on the titanium polycrystal sheets,
- 2- on the titanium mono bicrystals

Have been found by means of texture goniometry.

On the polycrystal sample, rutile  $\text{TiO}_2$  has a complete fiber texture with the (110) planes parallel to the surface of the titanium sheet.