

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 ΔC_3^1 and ΔC_3^2 parameters (Duax & Norton, Atlas of Steroid Structure, New York, Plenum, 1975) is a simple function of ΔC_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 ΔC_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 CaCl_2 -type and rutile-type structure is well-known (see textbooks), but so far the corresponding phase transition has only been found for 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 CaBr_2 , YbBr_2 , and TmBr_2 belongs to the rutile-type (space group $P4_2/mnm$) and that a second-order phase transition to the CaCl_2 -type (space group $Pn\bar{m}$) takes place at lower temperatures. This transformation has been studied in greater detail for 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 ω 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 ω 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 ω , 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 CaBr_2], (ii) covalent chemical bonds [$f = 1.16$ for marcasite (FeS_2), $f = 1.12$ for loellingite (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 CaBr_2 an accurate single-crystal structure determination has been carried out at room temperature (4-circle diffractometer, MoK_α radiation). CaBr_2 crystallizes orthorhombic, space group $Pn\bar{m}$ (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 $\exp[-2\pi^2(U_{11}h^2/a^2 + U_{22}k^2/b^2 + U_{33}l^2/c^2 + 2U_{12}hk/ab)]$.

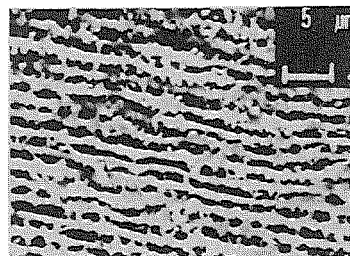
	$U_{11} (\text{\AA}^2)$	$U_{22} (\text{\AA}^2)$	$U_{33} (\text{\AA}^2)$	$U_{12} (\text{\AA}^2)$
Ca	0.0224(3)	0.0229(3)	0.0187(3)	-0.0026(2)
Br	0.0316(2)	0.0329(2)	0.0233(2)	-0.0151(1)

04.1-6 OXIDATION OF TITANIUM BY OXYGEN: STRUCTURE RELATIONS BETWEEN TITANIUM AND RUTILE TiO_2 . By L. LATAUD*, D. CIOSEK*, G. BERTRAND*, J.J. HEIZMANN***, A. VADON***

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The oxid layer of rutile 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 TiO_2 has a complete fiber texture with the (110) planes parallel to the surface of the titanium sheet.

On the monocrystal, rutile has a sharp texture of topotactic type, with the (110) plane remaining nevertheless parallel to the monocrystal face.

The macroscopic geometry of the metal seems to play as important a part as its crystal orientations.

Results are given in the table below. The values obtained from (I) and (II) agree to within 3σ in all but three cases. More interesting, but not surprising, the standard distances to oxygen obtained here mainly from organic molecular compounds with mixed coordinative environments agree with those obtained by Brown and Shannon from oxides and inorganic oxyacid salts.

Table: Standard bond lengths d_{iO} ($CN_O = 4$); values for other CN's may be obtained from (I), (II), c and N.

	Mg	Al	Si	P	
C		2.032(3)	1.872(1)	1.788(1)	a)
		2.032(3)	1.872(1)	1.786(1)	b)
N		1.851(10)	1.721(5)	1.616(1)	a)
		1.850(9)	1.718(4)	1.615(1)	b)
O	1.885(14)	1.701(7)	1.610(4)	1.534(1)	a)
	1.898(11)	1.715(6)	1.613(4)	1.534(1)	b)
F			1.500(6)	1.402(3)	a)
			1.520(5)	1.418(3)	b)
Si(-Si)			2.391(11)	2.168(22)	a)
P(-P)			2.391(15)	2.145(26)	b)
Cl	2.297(17)	2.131(3)	2.026(8)	1.935(5)	a)
	2.281(17)	2.131(3)	2.022(8)	1.913(5)	b)
c	0.501(37)	0.466(19)	0.455(13)	0.484(6)	a)
N	4.31(30)	4.25(16)	4.01(11)	3.41(4)	b)
σ^2	0.0858	0.0195	0.0099	0.0067	a) c)
	0.0785	0.0182	0.0099	0.0065	b) c)
m	504	522	826	1878	c)
N _{obs}	89	117	189	441	c)

a) (I); b) (II); c) m=number of distances used in refinement; N_{obs}=number of structures in data set; p=number of standard bond lengths refined $\sigma^2 = (\sum N_{obs} - \sum N_{calc})^2 / N_{obs} - (p + 1)$

04.1-7 STANDARD BOND LENGTHS IN MOLECULAR COMPOUNDS FROM EMPIRICAL BOND LENGTH-BOND STRENGTH RELATIONSHIPS (Mg,Al,Si,P-C,N,O,F,Cl) By G. Klebe, H.B. Bürgli, Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern, Freiestr. 3, CH-3012 Bern, Switzerland

Standard bond lengths are a prerequisite for interpretations and comparisons of interatomic distances. Such distances (d_O) are given here for bonds from Mg,Al,Si,P to C,N,O,F,Cl. They are based on least squares analysis using two empirical bond strength (n)-bond length(d) relationships: (I) $n_i/n_O = \exp[-(d_i/d_{iO})/c]$ (L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, (1940)); (II) $n_i/n_O = (d_i/d_{iO})^{-N}$ (G. Donnay and R. Allmann, Amer. Min. (1970), 55, 1003; I.D. Brown and R.D. Shannon, Acta Cryst. (1973), A29,266). The data for Al,Si,P with coordination numbers (CN) 4,5,6 were taken from the Cambridge Structural Data Base and supplemented with gas phase electron diffraction data; the data for Mg were taken from J.C.J. Bart and P. Vitarelli (Inorg. Chim. Acta (1983), 73, 215). The data include molecules with up to 4 different ligand atoms around the central atom. Details will be given in a future, full account of the work. Values of d_{iO} , c and N, respectively, were determined by minimizing the expression

$$(CN_O - \sum_{i=1}^{CN} n_i)^2$$

for Mg,Al,Si,P separately, but considering all coordination numbers simultaneously; CN_O is a reference coordination number, n_O is taken as 1.

04.1-8 CONTRIBUTION TO THE CRYSTAL CHEMISTRY OF SODIUM HEXACHLOROANTIMONATE, -NIOBATE, AND -TANTALATE. By Henning Henke, Institut für Anorg. Chemie der Universität Karlsruhe (TH), D 7500 Karlsruhe, Bundesrepublik Deutschland.

From single-crystal X-ray data collected at room temperature the individual structures of three sodium salts can be established:

	a [Å]	b [Å]	c [Å]	β [°]
NaSbCl ₆	6.393(2)	6.393	10.717(4)	--
NaNbCl ₆	6.398(2)	6.850(2)	19.012(4)	90.72(2)
NaTaCl ₆	6.449(2)	6.880(2)	18.989(6)	90.87(2)

While NaSbCl₆ is tetragonal with space group $P4_2/m$ and $Z=2$, the niobium and tantalum analogues crystallize both in the monoclinic space group $P2_1/c$; since there is a doubling of the c-axis the unit cell has $Z=4$. Parameter refinement includes absorption and extinction corrections; the final R-values are 0.018 (NaSbCl₆, 611 obs.refl.), 0.018 (NaNbCl₆, 2214 obs.refl.), and 0.024 (NaTaCl₆, 2341 obs.refl.). All three compounds contain discrete MCl_6^- ions arranged with their centres like $PtCl_6^{2-}$ in cubic K_2PtCl_6 . The same applies to the cations