University of Groningen

Schijnbare symmetrie bij esters van tetrathioorthokiezelzuur

Klasens, Hendrik Anne

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1941

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Klasens, H. A. (1941). *Schijnbare symmetrie bij esters van tetrathioorthokiezelzuur*. Noordhoff Uitgevers.

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 16-07-2023

XII. SUMMARY.

In the introduction we demonstrated theoretically that, by means of X rays, points of the crystal lattice may appear to be equivalent, though in reality they are not. It may also occur that the observed elements of symmetry do not exist, but are found with X rays in consequence of the cooperation of a great number of particles. The observed identical points are statistically identical and the observed elements of symmetry arise from a statistical distribution of particles over points possessing together those elements of symmetry.

Furthermore we pointed out that one has to reckon with such seeming symmetries, when deriving the symmetry of molecules from the X ray analysis of crystals. It is possible that these symmetries do not exist in reality. This is very obvious when the observed elements of symmetry are contradictory to the chemical image of the molecules. It appeared from the examples cited that isomorphism between related compounds of differing symmetry can point to the existence of such seeming symmetries.

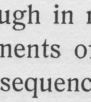
Such an isomorphism has been found to exist between the compounds $Si\{SC(CH_3)_3\}_4$ and $Si\{SC(CH_3)_3\}_3SCH(CH_3)_2$. The crystals of both esters are tetragonal.

The X ray analysis proves that the unit cell contains two molecules and that the space group D_{2d}^4 ($P\,\bar{4}2_1c$) forms the foundation of the crystal lattice. Hence it follows that the molecular symmetry is S_4 (or higher). This symmetry is possible for the tetra-tert. butyl ester but not for the tri-tert.butyl monoisopropyl ester.

In order to know to what extent the fourth alkyl group R in $(BtS)_3SiSR$ may differ from the three tertiary butyl groups Bt, without disturbing the X ray symmetry, we have introduced different groups. The new compounds were prepared according to the scheme:

$$(BtS)_3SiCl + NaSR = (BtS)_3SiSR + NaCl.$$

The following table gives

Tetragonal	
R	m.p.
$-C(CH_3)_3$ *)	160-161°
$-CH(CH_3)_2$ *)	105°
$-CH(CH_3)(C_2H_5)$	79-80°
	104-105°
$-C(CH_3)_2(C_2H_5)$	111-114

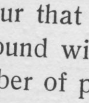
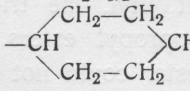
Those esters which cry
the tert. amyl ester) were e
At the same time the te
stannic and -orthogerman
$Si(SBt)_4$, were examined
ments are brought togethe

	p.
$Sn(SBt)_4$	1
$Ge(SBt)_4$	1
$Si(SBt)_4$	1
$(BtS)_3SiCH(CH_3)_2$	1
$(BtS)_3SiCH(CH_3)(C_2H_5)$	1
$(BtS)_3SiSC_5H_9$	1

To examine what influ
tert. butyl group by an i
crystals, the following su
$BtSSi\{SCH(CH_3)_2\}_3$
$(BtS)_2Si\{SCH(CH_3)_2\}_2$
Measurable crystals of
The crystals of the di-i
tetragonal. We also exan
in the length of a_0 and b_0

1) The esters, indicated
H. J. Backer and F. Stienstra

The following table gives a survey of these esters [1]).

Tetragonal		Not tetragonal	
R	m.p.	R	m.p.
$-C(CH_3)_3$ *)	160-161°	$-CH_3$ *)	43-44°
$-CH(CH_3)_2$ *)	105°	$-C_2H_5$ *)	26-27°
$-CH(CH_3)(C_2H_5)$	79-80°	$-C_3H_7$	62-62.5°
	104-105°	$-C_4H_9$	b.p. 153-153.5°/1 mm
		$-CH_2CH(CH_3)_2$	77-77.5°
		$-CH(C_2H_5)_2$	27-29°
$-C(CH_3)_2(C_2H_5)$	111-114°		64-65°

Those esters which crystallise in the tetragonal class (except the tert. amyl ester) were examined both optically and with X rays. At the same time the tetra-tert.butyl esters of tetrathio-orthostannic and -orthogermanic acids, which are isomorphous with $Si(SBt)_4$, were examined with X rays. The results of the measurements are brought together in the following table.

	p.spec.	ε	ω	a_0	c_0
$Sn(SBt)_4$	1.339	1.643 (Na-D)	1.640 (Na-D)	11.3	9.3
$Ge(SBt)_4$	1.210	1.628 („)	1.622 („)	11.3	9.3
$Si(SBt)_4$	1.087	1.615 (Hg_{578})	1.607 (Hg_{578})	11.2	9.2
$(BtS)_3SiCH(CH_3)_2$	1.068	1.600 (Na-D)	1.589 („)	11.2	9.3
$(BtS)_3SiCH(CH_3)(C_2H_5)$	1.080	1.600 („)	1.587 („)	11.4	9.4
$(BtS)_3SiSC_5H_9$	1.098	1.614 („)	1.598 („)	11.3	9.4

To examine what influence the substitution of more than one tert. butyl group by an isopropyl group has on the form of the crystals, the following substances have been synthetised:

$BtSSi\{SCH(CH_3)_2\}_3$ (from $NaSCH(CH_3)_2$ and $BtSSiCl_3$)

$(BtS)_2Si\{SCH(CH_3)_2\}_2$ (out of $NaSCH(CH_3)_2$ and $(BtS)_2SiCl_2$)

Measurable crystals of the tri-isopropyl ester could not be made.

The crystals of the di-isopropyl ester are orthorhombic, pseudotetragonal. We also examined this ester with X rays. A difference in the length of a_0 and b_0 could not be observed. Both are 15.5 Å,

---

[1]) The esters, indicated with *), have already been synthetised by H. J. Backer and F. Stienstra, Rec. trav. chim. **54**, 38 (1935).

c_0 being 9.5 Å. The density is 1.070 and the unit cell contains two molecules.

The space group was found to be D_{2h} (P*nca*). Hence it follows that the molecules possess a twofold axis of rotation.

To compare the esters of orthosilicic acid with those derived from tetrathioorthosilicic acid, some esters of the former acid have been synthetised according to the scheme:

$$SiCl_4 + 4\,RONa = Si(OR)_4 + 4\,NaCl$$

In this way some new esters were obtained, namely the tetra-sec.butyl, the tri-tert.butyl, the tri-tert.butyl monoethyl and the tri-tert.butyl monoisopropyl esters. Owing to steric hindrance, the tetra-tert.butyl ester could not be synthetised. An attempt to obtain this compound gave rise to the formation, among others, of the hexa-tert.butyl ester of disilicic acid, $(BtO)_3SiOSi(OBt)_3$). The tetraalkyl esters of orthosilicic acid are all liquid at room temperature.