

Tabelle 1. Beobachtete und berechnete Strukturaktoren

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
020	133	-176	210	26	-25	340	70	-80	460	19	-23	630	55	-66
040	260	+287	220	240	+274	350	220	-219	470	129	-133	640	98	-99
060	114	+112	230	42	+33	360	32	+33	510	31	-33	650	28	-41
080	77	-66	240	58	-77	370	14	-14	520	18	-16	710	29	+27
120	12	-27	250	84	-80	380	72	-66	530	33	+59	720	109	+110
130	74	+83	260	160	-162	410	269	-269	540	43	+46	730	144	-154
140	196	+185	270	94	+70	420	231	+225	550	89	-109	740	29	-23
150	120	+118	280	11	+3	430	31	+30	560	56	-57	810	45	+43
160	192	-196	310	168	-142	440	58	+65	610	51	+51	820	106	+102
170	85	+90	320	179	+206	450	38	-40	620	98	+120	830	108	-112
180	65	-73	330	58	-60									

Die vorliegende Untersuchung zeigt, dass die Struktur des Tetraargentotellurperchlorates das gleiche komplexe Gerüstskation enthält wie das  $\beta$ -Tetraargentotellurnitrat (Schultze-Rhonhof, 1969). Offenbar ist die Struktur dieses Gerüstskations von der Art des eingebauten Gegenanions weitgehend unabhängig. Aufgrund dieses Befundes wurde auf dreidimensionales Arbeiten und weitere Verfeinerung verzichtet.

Die notwendigen Rechnungen wurden mit Hilfe der Programmkette *BN-X-64* (Schultze-Rhonhof, 1966) auf der IBM 7090 der GMD in Bonn ausgeführt.

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**On certain structural relations between racemic and optically active crystal structures.** By C. PEDONE and E. BENEDETTI, *Istituto Chimico, Università di Napoli, Via Mezzocannone 4, 80134 Napoli, Italy*

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The occurrence of certain structural relations between racemic and optically active pairs is pointed out for some structures. When these relations occur, the determination of the structure of an optically active form can be derived from that of the racemic one or *vice versa*. Usually it is possible to recognize for such a pair of structures a conservative plane of close-packed isomorphous molecules whose repetitions by the appropriate symmetry elements generate the two structures.

Many cases of polymorphism consist of a different packing of identical molecular layers. This occurs whenever different crystalline modifications with nearly the same lattice energy can be generated by repetition of one plane of molecules through the operation of different symmetry elements; the conservative plane of molecules is one in which the molecules are close-packed with respect to each other. It is obvious that, when this phenomenon is recognized, the determination of the structure of a second form can be directly derived from that of the first one. It is interesting to note that this phenomenon may occur in the crystal structures of racemic and optically active pairs. Therefore, as mentioned above, the crystal structure of an optically active form can be derived from that of the racemic one or *vice versa*, as we shall see in the following. Simpson & Marsh (1966) have determined the crystal structure of L-alanine. Surprisingly they found that the L-form and DL-form (Donohue, 1950) show nearly the same structure as far as the molecular packing is concerned. On the basis of the solved structures, those authors showed that it was possible to derive the structure of the L-form by reversing sense and direction of a column of D molecules. The similarity of the two structures was clearly indicated by the fact that

the unit-cell parameters (see Table 1) were nearly identical. Furthermore the zero-level Weissenberg photographs taken along the *c* axes were only slightly different for the two compounds. From the packing of the racemic form we recognized one plane (*bc*) of close-packed isomorphous molecules related by a screw symmetry axis contained in the plane. Then we were able to generate the L-alanine crystal structure assuming as conservative the *bc* plane of the racemic structure. A good trial model for the optically active structure is obtained simply using the fractional coordinates of the crystallographically independent molecule of the racemic form, taking into account the proper shift of the origin due to the change in space group. Incidentally, the assumption of the existence of a conservative plane of molecules in the two structures allows the *a priori* prediction of the possible space groups and the unit-cell parameters for the optically active form once those of the racemic form are known and *vice versa*. In the case of the L-alanine structures for example, without taking into account packing considerations, we should expect as probable the  $P2_1$ ,  $P2_12_1$  or  $P2_12_12$  space group and simple relations with the unit-cell parameters of the DL-alanine structure.

The same phenomenon occurs also for the ( $\pm$ ) and (+)

Table 1. *Crystal data of racemic and optically active pairs*

	Crystal system	Space group	Mols per cell <i>Z</i>	<i>a</i>	<i>b</i>	<i>c</i>	$\alpha$	$\beta$	$\gamma$	Reference†
DL-Alanine	Ortho.	<i>Pna</i> 2 <sub>1</sub>	4	12.05	6.05	5.82	—	—	—	1
L-Alanine	Ortho.	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> * 4	4	12.343	6.032	5.784	—	—	—	2
(±)- <i>trans</i> -1,2-Cyclohexanedicarboxylic acid	Mono.	<i>C</i> 2/ <i>c</i>	4	5.65	13.94	11.04	—	113°16'	—	3
(+)- <i>trans</i> -1,2-Cyclohexanedicarboxylic acid	Mono.	<i>C</i> 2 <sub>1</sub>	4	5.58	13.94	10.25	—	—	95°	4
(±)- <i>trans</i> -1,2-Cyclopentanedicarboxylic acid	Mono.	<i>C</i> 2/ <i>c</i>	4	9.25	6.65	12.18	—	100°38'	—	5
(+)- <i>trans</i> -1,2-Cyclopentanedicarboxylic acid	Mono.	<i>C</i> 2 <sub>1</sub>	4	9.24	6.64	12.04	—	—	96°	5

\* The *a* and *b* unit cell dimensions have been interchanged.

† References: 1 Donohue (1950), 2 Simpson & Marsh (1966), 3 Benedetti, Coradini, Pedone & Post (1969), 4 Benedetti, Corradini & Pedone (1969), 5 Benedetti, Corradini & Pedone (1972).

forms of *trans*-1,2-cyclohexanedicarboxylic acid (Benedetti, Corradini, Pedone & B. Post, 1969; Benedetti, Corradini & Pedone, 1969). In this case it is possible to generate the structure of the optically active form assuming as conservative the *ab* plane of the racemic compound (containing isomorphous molecules) in the *C*2/*c* space group. The space group of the (+) form becomes *C*2<sub>1</sub> (see Table 1). The parameters of the conservative plane are only slightly modified in the (+) form as compared to the (±) ( $\gamma_{\text{rac}} = 90^\circ$ ,  $\gamma_{\text{op.act}} = 95^\circ$ ) but the fractional coordinates of the independent unit in the racemic compound are still very close to those of the refined optically active model.

By application of analogous considerations we have been able to solve the crystal structure of the optically active form of (+)-*trans*-1,2-cyclopentanedicarboxylic acid, once that of the (±) form was known.

A feature indicating the presence of a conservative layer of molecules in the two structures was that the parameters of the *ab* plane of a *C*2<sub>1</sub> space group (*c* unique axis) of the optically active form nearly coincide with the corresponding parameters of the *ab* plane of the racemic one (space group *C*2/*c*) (see Table 1) and the *0kl* reflexions were almost identical for the two compounds in the *C*-centered space groups. As a consequence, we expected no appreci-

able change in the fractional coordinates of the independent unit of the optically active structure as compared with those of the racemic one. This was verified and the resulting refined crystal structures of both forms will be published in detail elsewhere (Benedetti, Corradini & Pedone, 1972).

The study of the occurrence of this phenomenon in the structures of optically active and racemic forms is under further investigation in our laboratory.

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**High pressure Mn<sub>2</sub>As with Fe<sub>2</sub>P-type structure.** By W. JEITSCHKO and VANCLIFF JOHNSON, *Central Research Department,\* E.I. du Pont de Nemours and Company Experimental Station, Wilmington, Delaware 19898, U.S.A.*

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Mn<sub>2</sub>As has been prepared in a tetrahedral anvil high-pressure device at 65 kb. It has an Fe<sub>2</sub>P-type structure with lattice constants *a* = 6.3627 (4) and *c* = 3.6784 (5) Å, space group *P*6<sub>2</sub>*m*. The structure has been refined from single-crystal X-ray counter data. High-pressure Mn<sub>2</sub>As is antiferromagnetic with Néel temperature 50 ± 10°K. Fe<sub>2</sub>P-type Cr<sub>2</sub>As is confirmed to be a high-temperature phase.

#### Introduction

Both Cr<sub>2</sub>As (Nowotny & Årstad, 1938; Yuzuri, 1960) and Mn<sub>2</sub>As (Nowotny & Halla, 1937; Yuzuri & Yamada,

1960) have been reported with the Cu<sub>2</sub>Sb-type structure. Recently, Cr<sub>2</sub>As was found with the Fe<sub>2</sub>P-type structure at high temperature (Wolfsgruber, Boller & Nowotny, 1968). We also have prepared Fe<sub>2</sub>P-type Cr<sub>2</sub>As by quenching from high temperatures. We were not able to prepare Fe<sub>2</sub>P-type Mn<sub>2</sub>As in this way, but have found it at high pressures.

\* Contribution No. 1890.