

The increased length of the *b* cell edge (5.81 Å) in ardennite over that found in other aluminum silicates with octahedral chains along *b* (5.45–5.63 in zoisite, 5.57 in kyanite, 5.61–5.64 in epidote, 5.66 in staurolite, 5.75 in allanite) is due to the substitution of the larger Mg and Fe ions for Al in about half of the octahedra that have centers on the mirror planes (001).

As can be seen on Fig. 2, a nearly regular but empty octahedron around the point $\frac{1}{4}00$ shares a face with each of two Al octahedra and an edge with each of two Si tetrahedra. The average length of the remaining four edges is 2.86 Å (Table 7), very comparable to the edge length of the other filled octahedra. The reason that no cation, M, is found at the center is ascribed to the short Al(1)–Al(2) separation, which would lead to M–Al distances of only 2.18 Å.

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The Configuration at C(13) in Labdanolic and Eperuic Acids by an X-ray Crystal Structure Analysis of the *p*-Bromophenacyl Ester of Labdanolic Acid

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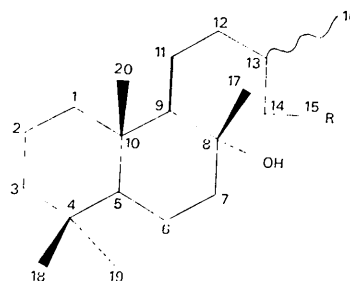
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The crystal structure of the *p*-bromophenacyl ester of labdanolic acid, determined by three-dimensional X-ray analysis, establishes the common configuration for labdanolic and eperuic acids at C(13) as (*S*) (Prelog's notation). The crystals are monoclinic, space group *P2*₁, with two molecules of C₂₈H₄₁O₄Br in a unit cell of dimensions *a* = 11.55, *b* = 6.05, *c* = 19.90 Å; β = 99.0°. The structure has been refined by least-squares methods to a final *R* of 11.4% for 1672 reflexions.

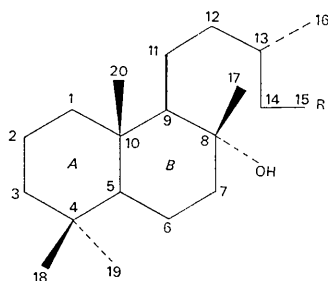
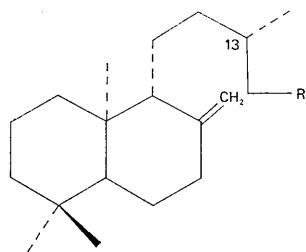
Introduction

Labdanolic acid, C₂₀H₃₆O₃, was first isolated by Cocker, Halsall & Bowers, 1956) from Spanish gum labdanum obtained from *Cistus ladaniferus* (rockrose). The structure of this new bicyclic diterpene hydroxy-acid was determined in a subsequent paper (Cocker & Halsall, 1956) as (I), but the configuration at C(13) remained undetermined.

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(I) R = CO₂H

(II) $R = \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{Br}$ (III) $R = \text{CO}_2\text{H}$ (IV) $R = \text{CO}_2\text{H}$

Bory & Lederer (1957) assigned the (*R*) configuration to C(13) in labdanolic acid. Bigley, Rogers & Barltrop (1960) questioned this as it was based on molecular rotations where hydrogen bonding may be involved, but later accepted it in the mistaken belief that there is no intramolecular hydrogen bonding in methyl labdanolate and methyl 13-epilabdanolate. From subsequent infrared studies (Baker, Eglinton, Gonzalez, Hamilton & Raphael, 1962) with several compounds of the labdane type it is clear that intramolecular hydrogen bonding does occur. The C(13) configuration in labdanolic acid was therefore undefined. Graham & Overton (1964) showed that eperuic and labdanolic acids possess the same C(13) configuration whilst otherwise being antipodal and Overton & Renfrew (1967)* inferred by means of chemical degradation that the C(13) configuration in these acids is (*S*). This *X*-ray analysis was undertaken to establish unambiguously the C(13) configuration and the molecular geometry.

* The configurational designations (*R*) and (*S*) should be interchanged in this paper except in §1.

Crystal data

p-Bromophenacyl labdanolate, $\text{C}_{28}\text{H}_{41}\text{O}_4\text{Br}$, $M = 521.4$, m.p. $124-5^\circ\text{C}$. *Monoclinic*, $a = 11.55 \pm 0.01$, $b = 6.05 \pm 0.01$, $c = 19.90 \pm 0.02 \text{ \AA}$; $\beta = 99.0 \pm 0.2^\circ$. $U = 1373 \text{ \AA}^3$. $D_m = 1.28 \text{ g.cm}^{-3}$ (by flotation in aqueous potassium iodide), $Z = 2$, $D_x = 1.26 \text{ g.cm}^{-3}$. $F(000) = 552$. Space group $P2_1$ (C_2^2 , No. 4). Linear absorption coefficient for *X*-rays (Cu $K\alpha$, $\lambda = 1.542 \text{ \AA}$) $\mu = 24.9 \text{ cm}^{-1}$.

Experimental

Labdanolic acid (44 mg) was esterified with *p*-bromophenacyl bromide (38 mg). The ester was extracted with ether and recrystallized from chloroform-light petroleum as well-formed needles. Elementary analysis gave: C, 64.52; H, 8.25%. $\text{C}_{28}\text{H}_{41}\text{O}_4\text{Br}$ requires C, 64.49; H, 7.89%.

Oscillation, Weissenberg and precession photographs were taken with a crystal mounted along the unique *b* axis with Cu $K\alpha$ radiation. The unit-cell parameters were measured from oscillation, zero-layer Weissenberg and precession photographs. The space group ($P2_1$) was determined from the systematic absences ($0k0$ absent if *k* is odd) and from the knowledge of the molecule being optically active ($[\alpha]_D = -10^\circ$). Non-integrated three-dimensional intensity data were collected along the (needle) *b* axis from a crystal of dimensions $0.13 \times 0.13 \times 3.5 \text{ mm}^3$ with an equi-inclination Weissenberg camera using the multiple-film technique. Layers from $k = 0$ to $k = 5$ were obtained. With a calibrated wedge 1672 reflexions (53% of the 3137 reflexions possible within the copper sphere) were measured visually. The reflexions that were too weak to be measured were not included in any of the calculations. The data were corrected for Lorentz and polarization factors but no absorption corrections were made. In the initial stages of the structure determination the data were put on an approximate absolute scale by making $k\Sigma|F_0| = \Sigma|F_c|$ for each layer. The layer-scale factors were later refined by least-squares methods.

Structure determination

Analysis in the *h0l* projection

The structure was solved by the heavy-atom method; the ratio $\Sigma f_H^2 / \Sigma f_C^2$ being 0.94 at $\sin\theta = 0$. A Patterson

Table 1. Course of the refinement

Parameters refined	Cycle No.	Final ($\Sigma w\Delta^2$)	Final ($R = \Sigma A /\Sigma F_0 $)	Final ($R' = \Sigma w\Delta^2/\Sigma wF_0^2$)
x, y, z, U_{iso} for Br, O, C + layer-scale factors	1-6	1458	20.4%	0.0920
x, y, z, U_{ij} ($i, j = 1, 2, 3$) for Br, O, C, + one overall scale factor	7-15*	211	11.4%	0.0241

* Corrections for $\Delta f'$, $\Delta f''$ for Br were applied.

synthesis was computed with data sharpened to point atom with respect to bromine. From the Harker peak at $(2x, 2z)$ the Br-atom coordinates were deduced as $x=0.218$, $z=0.184$. In a structure-factor calculation with Br alone R was 60% and an electron-density projection calculated with the observed amplitudes and Br phase angles revealed the entire structure. When all the atoms were included in a structure-factor calculation R was 41%. The x and z coordinates for all the atoms were then refined with a minimum-residual program (Bhuiya & Stanley, 1963; Muir, 1967) and in five cycles R was lowered to 23%.

Three-dimensional analysis

In space group $P2_1$ the origin in the y direction is not fixed. Here the bromine atom was put at $y=\frac{1}{4}$ which in a three-dimensional electron-density distribution based on bromine phase angles and observed amplitudes results in pseudo-mirror planes parallel to (010) at $y=\frac{1}{4}, \frac{3}{4}$, etc. Only a few peaks were resolved from the pseudo-mirror planes in the first three-dimensional electron-density distribution, making it difficult to determine the y coordinates of the atoms relative to the Br atom. The two carbon atoms [C(6) and C(7)] from the decalin system which deviated most from $y=\frac{1}{4}$ were first selected and gradually in six further rounds of structure-factors and electron-density calculations all the atoms were resolved. R at this stage was 27%. During the structure determination an overall $U_{iso}=0.05 \text{ \AA}^2$ was assumed.

Refinement

Positional and temperature parameters as well as layer-scale factors were refined by block-diagonal least-squares methods minimizing the expression

$$\sum_{hkl} w (|F_o| - |F_c|)^2.$$

The weighting scheme used was:

$$w = 1/(p_1 + |F_o| + p_2|F_o|^2 + p_3|F_o|^3)$$

where the p -parameters were varied during the refinement in order to minimize the variation of $w\Delta^2$ as a function of $|F_o|$. The final values are: $p_1=4.0$, $p_2=0.05$ and $p_3=0.0005$. In each cycle a shift factor of 0.8 was used. The course of the refinement is outlined in Table 1. After the isotropic refinement the data were put on a common scale using the refined layer-scale factors. Thereafter one overall scale factor was refined. No shifts were greater than 0.1σ in the coordinates and 0.2σ in the thermal parameters after the last cycle of the anisotropic refinement. In the polar space group $P2_1$ an error would be introduced in the y coordinate of the bromine atom unless anomalous-dispersion corrections are applied (Ueki, Zalkin & Templeton, 1966; Cruickshank & McDonald, 1967). The Weissenberg photographs were indexed in a right-handed system according to Peerdeman & Bijvoet (1956). Part of the absolute

configuration of labdanolic acid is already known by synthesis from sclareol of established configuration (Bory & Lederer, 1957) and is the one used here. Anomalous-dispersion corrections were made for the bromine atom during the anisotropic refinement during which the Br-C(26) bond length changed from 1.96 to 1.91 Å.

Atomic form factors and the real and imaginary part of anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1962).

At the conclusion of the refinement a difference Fourier synthesis was calculated; some diffuse maxima occurred in positions stereochemically acceptable for hydrogen atoms but it was not possible to determine their coordinates.

The final coordinates and temperature parameters and their e.s.d.'s (derived from the least-squares normal equations) are listed in Table 2. The thermal parameters are values of U_{ij} in the expression:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)].$$

Observed and calculated structure factors are listed in Table 3.

Superimposed sections parallel to (010) of the three-dimensional electron-density distribution and their interpretation are shown in Fig. 1. Bond lengths and valency angles are shown in Fig. 2., and the mean values of e.s.d.'s in bond lengths and angles are listed

Table 2(a) Fractional coordinates and e.s.d.'s

	x/a	y/b	z/c
Br(1)	0.2116 ± 2	0.2500 ± 0	0.1843 ± 1
O(1)	1.2969 ± 11	0.3726 ± 21	0.6726 ± 5
O(2)	0.8295 ± 9	0.2174 ± 22	0.4405 ± 5
O(3)	0.7617 ± 9	0.4743 ± 18	0.5055 ± 5
O(4)	0.5859 ± 11	0.1923 ± 24	0.4924 ± 7
C(1)	1.0488 ± 10	0.2467 ± 27	0.8517 ± 6
C(2)	1.0354 ± 13	0.2394 ± 31	0.9288 ± 7
C(3)	1.1531 ± 16	0.1681 ± 25	0.9715 ± 7
C(4)	1.2616 ± 12	0.2959 ± 22	0.9612 ± 6
C(5)	1.2660 ± 11	0.3136 ± 18	0.8823 ± 6
C(6)	1.3734 ± 11	0.4362 ± 27	0.8664 ± 7
C(7)	1.3861 ± 13	0.3894 ± 29	0.7886 ± 7
C(8)	1.2807 ± 12	0.4624 ± 21	0.7400 ± 7
C(9)	1.1698 ± 12	0.3495 ± 21	0.7604 ± 6
C(10)	1.1511 ± 11	0.3936 ± 20	0.8368 ± 6
C(11)	1.0569 ± 13	0.3860 ± 25	0.7045 ± 7
C(12)	1.0101 ± 13	0.1687 ± 23	0.6742 ± 7
C(13)	0.9022 ± 12	0.1876 ± 26	0.6159 ± 7
C(14)	0.9411 ± 12	0.3083 ± 27	0.5516 ± 7
C(15)	0.8443 ± 13	0.3170 ± 30	0.4929 ± 7
C(16)	0.8517 ± 16	-0.0374 ± 28	0.5959 ± 8
C(17)	1.2761 ± 15	0.7104 ± 33	0.7333 ± 8
C(18)	1.2651 ± 16	0.5182 ± 27	0.9986 ± 8
C(19)	1.3737 ± 16	0.1694 ± 26	0.9967 ± 8
C(20)	1.1205 ± 14	0.6376 ± 22	0.8460 ± 7
C(21)	0.6679 ± 14	0.5113 ± 30	0.4514 ± 7
C(22)	0.5798 ± 12	0.3318 ± 26	0.4460 ± 7
C(23)	0.4892 ± 11	0.3157 ± 27	0.3831 ± 7
C(24)	0.4193 ± 15	0.1213 ± 33	0.3688 ± 8
C(25)	0.3393 ± 16	0.1043 ± 30	0.3128 ± 8
C(26)	0.3235 ± 11	0.2879 ± 37	0.2649 ± 6
C(27)	0.3891 ± 13	0.4663 ± 36	0.2769 ± 8
C(28)	0.4699 ± 13	0.4891 ± 31	0.3347 ± 8

Table 2(b). Anisotropic temperature parameters and e.s.d.'s(\AA^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Br(1)	0.1071 15	0.1667 28	0.0871 12	0.0213 34	-0.0555 22	-0.0988 37
O(1)	0.1101 91	0.0601 78	0.0597 59	0.0002 107	0.0397 122	-0.0015 134
O(2)	0.0790 66	0.0662 77	0.0614 53	-0.0344 113	-0.0227 94	0.0353 124
O(3)	0.0773 68	0.0415 66	0.0628 56	-0.0321 97	-0.0094 97	0.0146 105
O(4)	0.0887 78	0.0704 90	0.1040 85	0.0623 148	-0.0191 133	-0.0269 139
C(1)	0.0423 63	0.0472 91	0.0617 69	-0.0285 148	0.0103 105	-0.0060 132
C(2)	0.0681 83	0.0504 93	0.0653 77	-0.0069 157	0.0200 128	-0.0242 155
C(3)	0.0995 116	0.0344 94	0.0572 78	0.0031 130	0.0292 157	-0.0053 161
C(4)	0.0745 81	0.0136 73	0.0611 71	0.0020 122	-0.0224 120	-0.0078 128
C(5)	0.0567 68	0.0040 66	0.0549 62	-0.0072 98	0.0029 105	0.0026 105
C(6)	0.0428 71	0.0559 103	0.0641 82	-0.0030 142	-0.0177 122	-0.0035 129
C(7)	0.0532 80	0.0628 106	0.0613 81	0.0040 146	0.0210 133	-0.0251 146
C(8)	0.0593 78	0.0122 75	0.0694 80	-0.0002 117	0.0287 127	0.0036 117
C(9)	0.0592 75	0.0190 76	0.0550 69	0.0053 109	-0.0142 114	0.0072 113
C(10)	0.0468 66	0.0159 68	0.0507 64	-0.0013 104	-0.0097 104	0.0031 101
C(11)	0.0633 84	0.0332 81	0.0576 73	0.0007 123	-0.0062 129	0.0114 128
C(12)	0.0728 87	0.0291 84	0.0542 70	0.0020 116	-0.0024 127	-0.0060 133
C(13)	0.0591 78	0.0453 97	0.0551 70	-0.0118 129	-0.0155 119	-0.0158 134
C(14)	0.0563 76	0.0485 95	0.0585 72	-0.0024 133	0.0035 117	-0.0076 141
C(15)	0.0656 85	0.0614 106	0.0551 73	0.0046 143	0.0142 129	-0.0053 159
C(16)	0.0981 117	0.0403 103	0.0710 90	-0.0022 151	-0.0091 166	-0.0749 183
C(17)	0.0891 110	0.0573 117	0.0724 92	-0.0119 170	0.0478 165	-0.0407 189
C(18)	0.1027 124	0.0238 85	0.0653 84	-0.0251 132	-0.0099 161	-0.0170 161
C(19)	0.1071 128	0.0318 100	0.0703 93	0.0308 145	-0.0119 173	0.0300 171
C(20)	0.0887 100	0.0119 73	0.0561 72	-0.0140 110	-0.0006 137	0.0149 135
C(21)	0.0677 92	0.0568 103	0.0587 78	-0.0071 149	-0.0088 134	-0.0041 160
C(22)	0.0496 70	0.0479 95	0.0646 78	0.0179 137	0.0002 120	0.0125 130
C(23)	0.0503 71	0.0510 99	0.0597 73	0.0059 134	0.0223 115	0.0251 137

Table 2(b) (cont.)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(24)	0.0727 104	0.0729 122	0.0674 92	-0.0015 175	0.0246 159	-0.0069 179
C(25)	0.0691 95	0.0586 104	0.0705 90	-0.0261 163	0.0287 148	-0.0093 164
C(26)	0.0455 68	0.1169 156	0.0431 60	-0.0244 177	-0.0519 106	-0.0033 181
C(27)	0.0495 81	0.0869 138	0.0730 92	0.0317 184	-0.0254 136	-0.0258 166
C(28)	0.0609 89	0.0579 105	0.0727 92	0.0178 158	0.0127 147	-0.0073 164

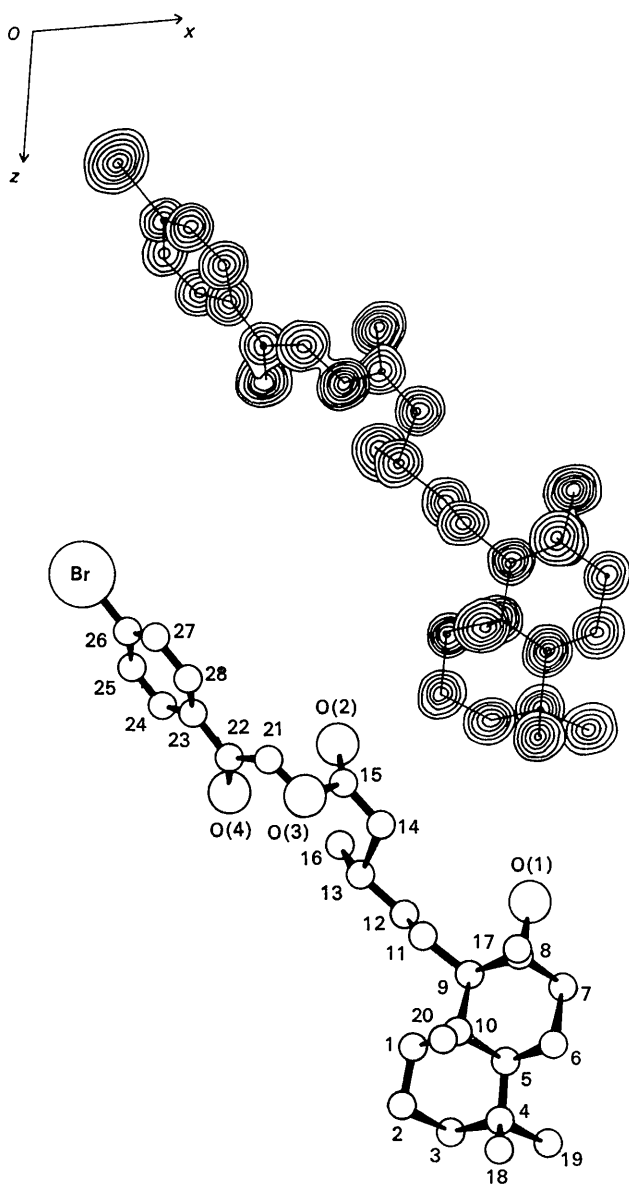


Fig. 1. Superimposed sections parallel to (010) of the three-dimensional electron-density distribution and their interpretation showing the molecular geometry and the numbering scheme. The contours start at $1 \text{ e.}\text{\AA}^{-3}$ and are drawn at intervals of $1 \text{ e.}\text{\AA}^{-3}$ except around the Br atom, where the intervals are $5 \text{ e.}\text{\AA}^{-3}$.

in Table 4. Some intramolecular contacts and intermolecular contacts $< 4.0 \text{ \AA}$ are shown in Tables 5(a) and 5(b).

Discussion

Since part of the absolute configuration is known [by synthesis of labdanolic acid from sclareol of established configuration (Bory & Lederer, 1957)] this X-ray analysis of *p*-bromophenacyl labdanolate unambiguously establishes that the configuration at C(13) is (*S*) (II) (Cahn, Ingold & Prelog, 1956) and consequently it is (*S*) also for labdanolic (III) and eperuic (IV) acids. It also confirms the validity of structure (I) proposed for labdanolic acid by Cocker & Halsall (1956).

The two six-membered rings in the decalin system, *trans*-fused to each other, adopt slightly distorted chair conformations. The four carbon atoms of ring A [C(2), C(3), C(5) and C(10)] are coplanar and the carbon atoms C(1) and C(4) are displaced below and above this plane by 0.66 and 0.61 \AA respectively (Table 6). In a regular cyclohexane chair these two atoms would each have been displaced by 0.73 \AA (calculated value). In ring B the atoms C(5), C(7), C(8) and C(10) are coplanar and the two atoms C(6) and C(9) are respectively above and below this plane by 0.73 and 0.68 \AA (Table 6). These two cyclohexane planes are not parallel but make a dihedral angle of 10° with each other. The distortions are probably mainly due to bending of the axial methyl groups [C(17), C(18) and C(20)] away from each other in order to relieve strain caused by repulsive forces. In a regular cyclohexane chair the non-bonded distances between C(18) and C(20) and between C(17) and C(20) would have been 2.52 \AA ; these distances are here increased to 3.31 and 3.12 respectively (the C(4) \cdots C(10) and C(8) \cdots C(10) non-bonded distances are 2.67 and 2.65 \AA). The van der Waals methyl-methyl distance is 4.0 \AA (Pauling, 1960). A similar distance between two axial methyl groups is observed for instance in a taxadiene-tetraol derivative (3.16 \AA) (Bjåmer, Ferguson & Robertson, 1967). As a consequence of this intramolecular overcrowding, the angles C(5)C(4)C(18) (115°), C(9)C(8)C(17) (116°) and C(5)C(10)C(20) (115°) are significantly greater than tetrahedral while the other angles at C(4), C(8) and C(10) (fully substituted atoms) are tetrahedral or slightly smaller. The increase of the valency angles

Table 3. Observed and calculated structure factors

H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c
0	0	0	23.7	24.7	0	0	8	8.5	9.0	0	1	9	31.5	29.2	7	1	9	8.3	7.6	5	1	15	10.6	9.0
0	0	0	26.6	27.5	0	0	9	16.4	14.4	0	1	10	44.5	42.2	7	1	10	10.0	7.6	5	1	16	16.6	14.5
0	0	0	29.4	35.1	0	0	10	7.4	8.8	0	1	11	4.4	3.1	7	1	11	5.0	4.4	5	1	17	4.5	4.0
0	0	0	22.5	20.3	0	0	11	7.4	8.4	0	1	12	35.3	34.6	7	1	12	5.8	5.6	5	1	18	4.5	3.3
0	0	0	26.9	27.3	0	0	12	10.1	10.3	0	1	13	9.6	7.1	7	1	13	6.8	6.5	6	1	19	16.1	17.6
0	0	0	21.6	19.7	0	0	13	13.3	14.7	0	1	14	9.6	10.2	7	1	14	13.2	13.2	6	1	20	14.6	14.2
0	0	0	28.6	24.4	0	0	14	10.9	10.9	0	1	15	10.9	12.2	7	1	15	18.5	13.2	6	1	21	37.4	39.1
0	0	0	6.6	7.9	0	0	15	7.8	8.1	0	1	16	8.2	8.1	7	1	16	7.4	6.4	6	1	22	6.1	5.6
0	0	0	20.3	20.3	0	0	16	5.8	6.3	0	1	17	5.2	5.2	7	1	17	5.5	5.5	6	1	23	12.4	12.4
0	0	0	11.0	10.8	0	0	17	6.2	6.2	0	1	18	5.0	5.0	7	1	18	3.8	2.8	6	1	24	25.8	23.9
0	0	0	12.6	15.5	0	0	18	7.6	9.1	0	1	19	5.0	4.2	8	1	19	4.0	3.8	6	1	25	5.2	6.3
0	0	0	14.5	13.5	0	0	19	6.1	6.7	0	1	20	10.7	7.6	8	1	20	16.4	16.4	6	1	26	13.4	13.4
0	0	0	16.1	15.5	0	0	20	15.1	28.0	0	1	21	4.3	2.9	8	1	21	18.6	19.2	6	1	27	15.3	13.4
0	0	0	19.5	23.0	0	0	21	16.1	7.1	2	1	0	18.6	10.9	8	1	22	18.4	18.2	6	1	28	9.4	10.0
0	0	0	9.3	10.4	0	0	22	67.7	70.0	2	1	0	45.8	43.7	8	1	23	8.6	8.6	6	1	29	5.6	5.1
0	0	0	9.5	10.4	0	0	23	69.6	60.7	2	1	0	6.0	4.2	8	1	24	12.7	12.6	6	1	30	17.3	16.3
0	0	0	6.6	4.0	0	0	24	59.3	37.0	5	1	0	14.4	13.5	8	1	25	13.1	13.9	6	1	31	6.4	6.1
0	0	0	17.8	10.9	0	0	25	26.0	23.9	5	1	0	13.1	12.8	8	1	26	7.0	7.0	6	1	32	10.7	10.6
0	0	0	89.6	33.0	0	0	26	31.0	25.7	5	1	0	14.1	14.1	8	1	27	16.6	16.6	6	1	33	6.2	6.8
0	0	0	8.4	14.7	0	0	27	69.0	68.6	9	1	0	5.0	4.7	8	1	28	11.4	11.4	6	1	34	18.9	16.3
0	0	0	11.5	6.4	0	0	28	65.4	52.1	10	1	0	12.4	14.0	8	1	29	13.3	10.2	6	1	35	5.6	4.4
0	0	0	34.2	34.2	0	0	29	14.4	12.4	10	1	0	10.5	9.6	8	1	30	10.7	10.7	6	1	36	7.3	7.3
0	0	0	61.3	51.5	0	0	30	17.2	18.2	10	1	0	36.6	36.6	8	1	31	18.7	18.7	6	1	37	16.3	16.3
0	0	0	13.6	14.4	0	0	31	17.2	18.2	10	1	0	36.6	36.6	8	1	32	28.5	28.4	6	1	38	19.0	21.7
0	0	0	19.7	3.9	0	0	32	11.9	11.9	1	1	1	6.4	4.6	9	1	1	9.0	8.3	7	1	39	6.3	6.1
0	0	0	44.3	62.0	0	0	33	7.8	6.9	1	1	2	12.3	13.5	9	1	2	4.4	4.4	7	1	40	6.2	5.6
0	0	0	43.9	45.9	0	0	34	20.9	28.9	1	1	3	38.2	28.3	9	1	3	12.7	12.7	7	1	41	15.4	14.2
0	0	0	32.2	34.6	0	0	35	74.2	76.0	1	1	4	21.1	21.1	9	1	4	6.0	6.0	7	1	42	19.5	17.2
0	0	0	47.9	45.0	0	0	36	105.6	114.2	1	1	5	24.4	19.7	9	1	5	6.0	6.8	7	1	43	6.8	5.4
0	0	0	11.1	15.3	0	0	37	27.1	27.3	1	1	6	27.7	27.3	9	1	6	9.3	7.9	7	1	44	8.3	7.3
0	0	0	10.3	10.3	0	0	38	11.1	9.8	1	1	7	11.0	12.6	9	1	7	4.0	3.1	8	1	45	13.6	13.5
0	0	0	7.4	7.6	0	0	39	4.5	2.2	1	1	8	32.4	34.7	10	1	8	9.9	9.6	8	1	46	12.7	11.2
0	0	0	8.4	9.0	0	0	40	18.4	14.6	1	1	9	13.2	11.8	10	1	9	6.9	6.9	8	1	47	15.0	15.9
0	0	0	13.6	11.7	0	0	41	13.6	5.6	1	1	10	5.2	4.8	10	1	10	7.2	6.8	8	1	48	14.7	14.0
0	0	0	7.4	5.6	0	0	42	7.4	5.3	1	1	11	7.5	6.2	10	1	11	5.1	5.1	8	1	49	6.2	4.9
0	0	0	20.2	6.2	0	0	43	30.4	38.0	1	1	12	5.4	5.4	10	1	12	4.2	4.1	8	1	50	10.2	8.6
0	0	0	6.7	5.2	0	0	44	19.3	13.0	1	1	13	5.6	5.6	10	1	13	5.9	4.9	8	1	51	4.6	4.6
0	0	0	42.0	39.1	0	0	45	8.6	8.1	2	1	1	38.4	30.7	10	1	14	7.9	7.1	9	1	52	5.7	5.0
0	0	0	28.9	28.9	0	0	46	8.6	6.1	2	1	2	7.6	6.3	11	1	1	7.9	8.5	9	1	53	4.4	4.0
0	0	0	23.6	34.0	0	0	47	106.2	85.7	2	1	3	54.3	51.3	11	1	2	7.7	6.9	9	1	54	7.5	6.1
0	0	0	31.6	29.2	0	0	48	67.6	71.9	2	1	4	12.1	24.5	11	1	3	9.2	6.6	9	1	55	17.2	16.0
0	0	0	50.8	51.3	0	0	49	52.3	59.4	2	1	5	28.8	33.2	12	1	4	5.3	3.9	9	1	56	8.9	7.7
0	0	0	11.8	15.3	0	0	50	47.2	45.6	2	1	6	15.2	17.7	12	1	5	6.0	6.0	9	1	57	4.7	3.5
0	0	0	24.9	33.3	0	0	51	28.0	21.0	2	1	7	27.6	34.7	12	1	6	6.0	5.2	9	1	58	4.7	4.7
0	0	0	26.6	32.0	0	0	52	28.0	21.0	2	1	8	9.2	8.7	12	1	7	1.2	1.2	9	1	59	4.8	4.8
0	0	0	14.1	14.3	0	0	53	56.9	51.5	2	1	9	9.9	12.5	13	1	8	4.3	4.3	9	1	60	7.0	7.4
0	0	0	39.1	37.3	0	0	54	6.2	4.7	2	1	10	25.8	26.5	13	1	9	4.4	4.6	9	1	61	3.2	3.2
0	0	0	23.5	24.0	0	0	55	7.1	7.4	2	1	11	11.2	13.9	13	1	10	4.4	4.4	9	1	62	5.3	5.6
0	0	0	26.7	26.7	0	0	56	11.6	6.8	2	1	12	11.6	8.4	13	1	11	19.3	20.1	9	1	63	5.9	5.1
0	0	0	13.1	14.1	0	0	57	9.2	7.9	2	1	13	5.2	5.9	13	1	12	21.3	20.3	9	1	64	4.1	3.4
0	0	0	19.5	20.7	0	0	58	11.4	10.2	2	1	14	17.7	16.5	13	1	13	65.4	60.0	9	1	65	8.3	9.0
0	0	0	8.6	6.3	0	0	59	11.2	13.5	2	1	15	13.9	8.4	13	1	14	6.2	5.3	10	1	66	13.5	12.6
0	0	0	8.6	6.7	0	0	60	11.6	11.7	2	1	16	8.4	8.4	13	1	15	32.4	32.9	10	1	67	6.4	5.8
0	0	0	9.0	5.0	0	0	61	35.3	30.8	2	1	17	4.4	4.4	14	1	1	28.0	28.2	10	1	68	4.4	3.7
0	0	0	22.8	22.8	0	0	62	16.6	21.6	2	1	18	5.6	4.7	14	1	2	11.8	11.8	10	1	69	4.5	4.3
0	0	0	39.2	29.7	0	0	63	10.7	10.7	2	1	19	11.0	11.8	14	1	3	11.8	12.8	10	1	70	10.7	11.2
0	0	0	60.1	60.3	0	0	64	19.3	36.8	2	1	20	4.4	3.4	14	1	4	12.2	12.2	10	1	71	6.2	4.9
0	0	0	41.1	41.1	0	0	65	4.3	3.3	2	1	21	43.3	37.6	14	1	5	11.2	14.2	10	1	72	14.2	12.9
0	0	0	42.1	43.0	0	0	66	39.1	36.4	2	1	22	15.6	15.6	14	1	6	11.4	14.0	10	1	73	14.4	13.1
0	0	0	82.6	82.6	0	0	67	23.9	20.2	2	1	23	21.4	25.9	14	1	7	11.5	10.5	10	1	74	11.4	11.4
0	0	0	17.7	15.0	0	0	68	13.8	13.8	2	1	24	26.6	25.7	14	1	8	9.0	9.0	10	1	75	12.9	12.9
0	0	0	75.1	75.1	0	0	69	27.6	28.3	2	1	25	9.6	34.3	14	1	9	9.0	9.0	10	1	76	4.7	4.7
0	0	0	22.6	29.6	0	0	70	6.9	6.8	2	1	26	28.1	34.3	14	1	10	9.6	9.7	10	1	77	6.0	5.0
0	0	0	16.3	17.0	0	0	71	22.5	21.0	2	1	27	24.8	24.8	14	1	11	4.8	3.9	10	1	78	4.5	3.0
0	0	0	16.3	16.3	0	0	72	10.4	8.3	2	1	28	8.3	8.3	14	1	12	10.7	10.7	10	1	79	4.5	3.0
0	0	0</																						

Table 3 (cont.)

Table with multiple columns of numerical data, organized in groups with headers H, K, L, [Po], [Pc]. The table contains a large volume of numerical values, likely representing experimental or calculated data points.

around the atoms adjacent to C(4), C(8) and C(10) from the tetrahedral angle can also be attributed to the bending of the axial methyl groups.

The carbon atoms C(9), C(11), C(12), C(13) and C(16) form a fully extended and approximately planar carbon chain (Table 6.)

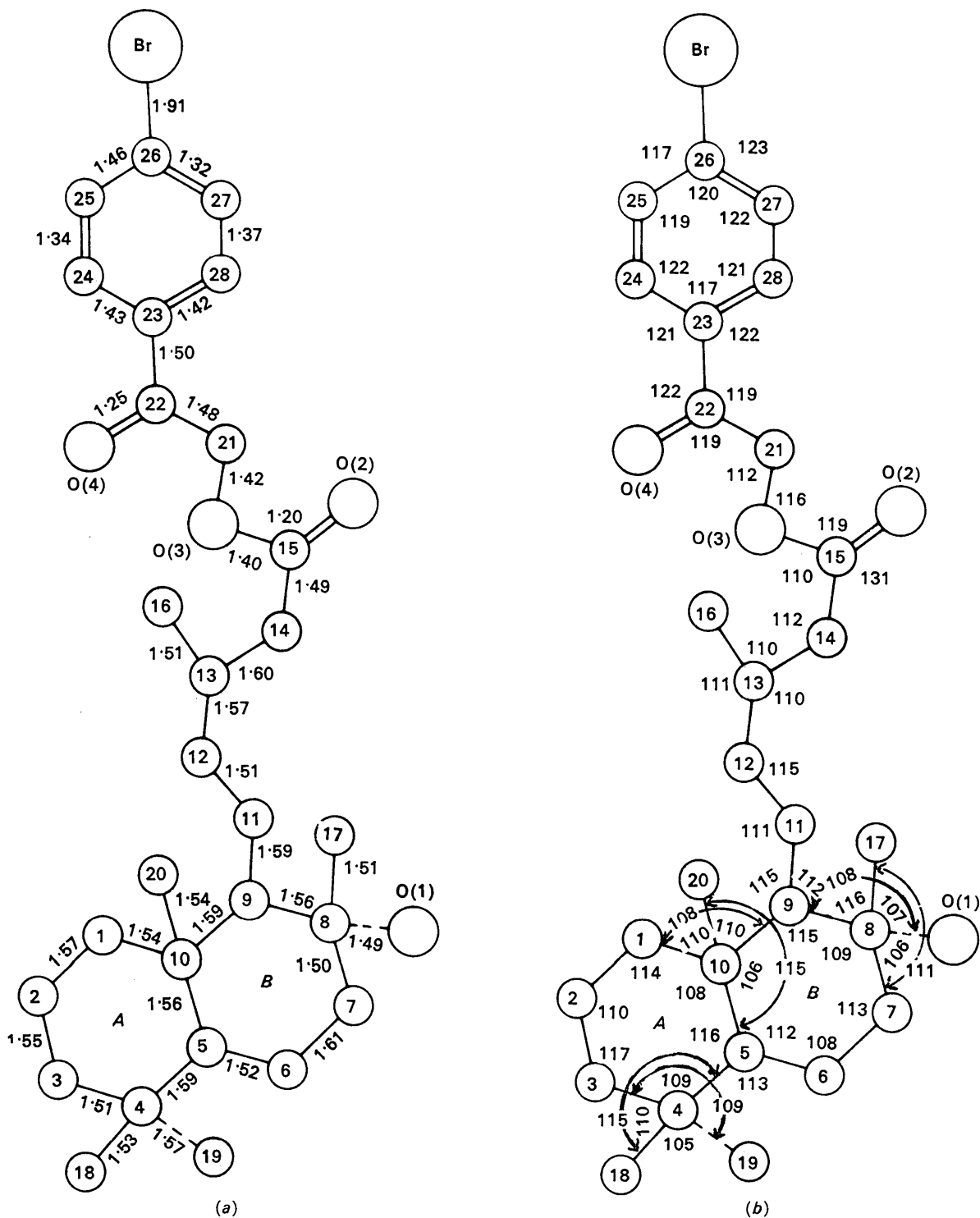


Fig. 2. (a) Bond lengths. (b) Bond angles.

The ester group [O(2),O(3),C(14),C(15)] and carbon atom C(21) are planar within experimental errors (the r.m.s. distance is 0.021 Å) (Table 6). The dihedral angle between the ester group and the extended carbon chain is 41°. A Newman projection down the C(14)–C(13) bond shows that C(12) is *anti* to C(15) (Fig. 3.) The dihedral angles are marked in the Figure. Mathieson (1965), from a survey of a few crystal structures and from energy considerations, has suggested that for

Table 4. Mean values of e.s.d.'s for bond lengths and angles

Bond	e.s.d.
C–C (aromatic)	0.025 Å
C–C (non aromatic)	0.020
C–O	0.019
Br–C	0.013
Angle at	e.s.d.
Aromatic atoms	1.5°
Single-bonded atoms	1.1
Double-bonded non-aromatic atoms	1.3

Table 5(a). Some intramolecular contacts less than 4.0 Å

C(4) ··· C(10)	2.67 Å
C(8) ··· C(10)	2.65
C(20) ··· C(17)	3.12
C(20) ··· C(18)	3.31
C(20) ··· C(1)	2.52
C(20) ··· C(9)	2.57
C(20) ··· C(5)	2.61
C(18) ··· C(3)	2.50
C(18) ··· C(5)	2.63
C(17) ··· C(7)	2.48
C(17) ··· C(9)	2.60
C(18) ··· C(19)	2.46
C(16) ··· C(15)	2.96
C(16) ··· O(2)	3.44
C(16) ··· O(3)	3.65
C(16) ··· O(4)	3.69
C(14) ··· C(11)	3.17
C(14) ··· O(2)	3.61
C(15) ··· C(22)	3.05
C(15) ··· O(4)	3.08
O(4) ··· O(3)	2.63
O(4) ··· O(2)	3.15
O(4) ··· C(24)	2.91
C(21) ··· C(28)	3.00

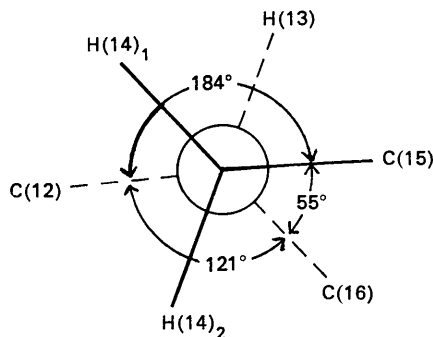


Fig. 3. A Newman projection down the C(14)–C(13) bond with the relevant dihedral angles.

Table 5(b). Intermolecular contacts less than 4.0 Å

Atom A	Atom B	Equivalent position* of atom B	Cell of atom B	Distance
Br	····· C(20)	II	(0, -1, 0)	3.85 Å
O(1)	····· O(2)	II	(1, 0, 0)	3.25
O(1)	····· C(21)	II	(1, -1, 0)	3.37
O(1)	····· C(28)	II	(1, -1, 0)	3.58
O(1)	····· C(24)	II	(1, 0, 0)	3.81
O(1)	····· C(23)	II	(1, 0, 0)	3.92
O(2)	····· C(17)	II	(1, -1, 0)	3.49
O(2)	····· C(14)	II	(1, -1, 0)	3.61
O(2)	····· C(11)	II	(1, -1, 0)	3.91
O(2)	····· C(8)	II	(1, -1, 0)	3.94
O(3)	····· C(16)	I	(0, 1, 0)	3.53
O(3)	····· C(24)	II	(0, 0, 0)	3.62
O(4)	····· C(22)	II	(0, -1, 0)	3.27
O(4)	····· C(21)	II	(0, -1, 0)	3.48
O(4)	····· C(23)	II	(0, -1, 0)	3.58
O(4)	····· O(4)	II	(0, -1, 0)	3.66
O(4)	····· O(4)	II	(0, 0, 0)	3.66
O(4)	····· C(24)	II	(0, 0, 0)	3.80
O(4)	····· C(28)	II	(0, -1, 0)	3.81
C(1)	····· C(20)	I	(0, -1, 0)	3.78
C(16)	····· C(25)	II	(0, -1, 0)	3.76
C(16)	····· C(26)	II	(0, -1, 0)	3.83
C(16)	····· C(24)	II	(0, -1, 0)	3.90
C(17)	····· C(28)	II	(1, 0, 0)	3.81
C(17)	····· C(23)	II	(1, 0, 0)	3.89
C(21)	····· C(24)	II	(0, 0, 0)	3.93
C(25)	····· C(27)	I	(0, -1, 0)	3.99

* The equivalent positions are: I (x, y, z)
II ($1-x, \frac{1}{2}+y, 1-z$).
Atom A is in equivalent position I in the cell (0, 0, 0).

esters involving primary alcohols the two hydrogen atoms of the alcohol α -carbon [here C(21)] are usually in a staggered relation to the double-bonded oxygen of the ester group [here O(2)]. This would have required plane (IV) [defined by the atoms O(2), O(3), C(14), C(15) and C(21)] and plane (V) [defined by the atoms C(21), C(22), C(23) and O(4)] [see Table 6] in this structure to be coplanar. The arrangement is here quite different since the planes make a dihedral angle of 79° with each other and O(2) is approximately *anti* to one of the C(21)–hydrogen atoms.

The phenyl group and carbon atom C(22) are coplanar (Table 6); the bromine atom is out of this plane by 0.055 Å. The atoms C(21), C(22), C(23) and O(4) (Table 6) are in a plane which is rotated about the C(23)–C(22) bond so that the dihedral angle with the aromatic plane is 12°. Non-zero dihedral angles between such planes are not uncommon (e.g. 9° in a *p*-bromobenzoate derivative of taxadiene-tetraol (Bjåmer, Ferguson & Robertson, 1957), 9° in potassium hydrogen di-*p*-chlorobenzoate (Mills & Speakman, 1963) and 3.3° in *p*-nitrobenzoic acid (Sakore & Pant, 1966)).

Most of the bond lengths [Fig. 2(a)] agree within experimental errors with accepted values. However, the Br–C(26) bond (1.912 ± 0.013 Å) is longer than that reported by Sutton (1965) (1.85 ± 0.01 Å). The C(8)–O(1) bond is also long compared with the accepted C–O single bond distance of 1.426 ± 0.005 Å (Sutton, 1965).

located on the line connecting O(1) and O(2) since the angle C(8)O(1)···O(2) is $106.7 \pm 0.8^\circ$. The arrangement of the molecules along the *b* axis can be seen in Fig. 4 and the suggested hydrogen bond is marked with a dotted line. There are no other unusually short intermolecular distances [Table 5(b)].

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Die Röntgenstrukturanalyse des Bullvalens

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(Eingegangen am 28. August 1967)

Tricyclo[3·3·2-0^{4,6}]deca-2,7,9-triene (C₁₀H₁₀), bullvalene, crystallizes in the monoclinic group *P*₂₁/*c*. The unit cell contains four molecules. The X-ray structure analysis was performed by the convolution molecule method. The atomic parameters were refined by three-dimensional Fourier and difference-Fourier syntheses and by least-squares calculations. In contrast to its behaviour in solution, bullvalene shows no valence-isomerization in the crystalline state.

Einleitung

Die Valenzisomerisierung von Bullvalen wurde von Doering & Roth (1963) vorausgesagt. Die Synthese des Bullvalens gelang Schröder (1964) und die NMR-Spektren (Merényi, Oth & Schröder, 1964) bestätigen diese Voraussage.

Bullvalen ist ein extremes Beispiel für Valenzisomerisierung. Jede Cope-Umlagerung (z. B. Ringschluss zwischen den Atomen C(9) und C(3) und Aufheben der Bindung zwischen C(1) und C(7) (Fig. 1) ergibt wieder Bullvalen. Insgesamt sind 1209600 strukturgleiche Isomere möglich. Bei einer Temperatur von 15° in Lösung vollziehen sich die Umlagerungen schon so rasch, dass die NMR-Signale der chemisch ver-

schiedenen Protonen zu einem breiten Signal verschmieren (Merényi, Oth & Schröder, 1964). Das Ziel unserer Arbeit war, durch die Röntgenstrukturanalyse etwas über das Verhalten des Bullvalens im kristallinen Zustand zu erfahren.*

Die Röntgenstrukturanalyse eines Silber-Borfluorid-Bullvalenkomplexes (Newton & Paul, 1966) bei 4° zeigt keine Valenzisomerisierung. Allerdings könnte hierfür die Komplexbindung verantwortlich sein (Allerhand & Gutowsky, 1965).

* Das Ergebnis dieser Strukturanalyse wurde auf der 9. Diskussionstagung der Sektion für Kristallkunde der Deutschen Mineralogischen Gesellschaft in Bonn (24. 4. 1967) vorgetragen (Amit, A., Brandt, F., Brodkerr, N., Gieren, A., Hädicke, E., Hoppe, W., Huber, R. & Röhr, M., Referate, S. 53).