

## The Crystal and Molecular Structure of Cembrene\*

BY MICHAEL G. B. DREW, DAVID H. TEMPLETON AND ALLAN ZALKIN

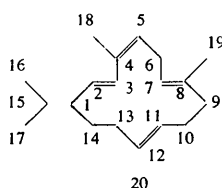
Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.

(Received 27 September 1967 and in revised form 25 March 1968)

A hydrocarbon  $C_{20}H_{32}$ , called cembrene or thunbergene, is confirmed to be 1-isopropyl-4,8,12-trimethyl-2,4,7,11-cyclotetradecatetraene by X-ray diffraction. The crystals are orthorhombic, spacegroup  $P2_12_12_1$ ,  $a=6.224(4)$ ,  $b=21.517(8)$ ,  $c=13.794(6)$  Å,  $Z=4$ . The structure was determined by a statistical method. The structure was refined to an  $R$  of 0.088 for 2045 reflections. Average bond distances are C-C=1.33 Å (double bond), 1.48 Å (single bond between two double bonds), 1.49 Å (single bond adjacent to one double bond), and 1.54 Å (single bond not adjacent to a double bond), with maximum deviation 0.02 Å. Bond distances were different by as much as 0.05 Å before hydrogen atoms were included in the calculations. The molecular structure is consistent with the hypothesis of biosynthesis from geranylgeraniol.

### Introduction

A crystalline diterpene ( $C_{20}H_{32}$ ) called cembrene (Mirov, 1961) or thunbergene (Akiyoshi, 1937) has been isolated from the turpentine oil of *Pinus ablicaulus*, *Pinus thunbergii*, and several other species of pine trees. Two independent investigations by Dauben, Thiessen & Resnick (1962, 1965) and by Kobayashi & Akiyoshi (1962, 1963) have shown by systematic degradation and spectroscopic evidence that this hydrocarbon is 1-isopropyl-4,8,12-trimethyl-2,4,7,11-cyclotetradecatetraene, but failed to establish the stereochemistry of the double bonds. We have determined the crystal structure of this compound by X-ray diffraction, confirming the molecular structure and showing that the ring is *trans* at three double bonds and *cis* only at the 4-ene. We designate the carbon atoms as follows:



### Experimental

Crystals were kindly provided by Professor W. G. Dauben of this University. Preliminary photographs by the Weissenberg technique showed an orthorhombic lattice. The cell dimensions measured with a General Electric quarter-circle goniostat ( $\lambda=0.70926$  Å for  $Mo K\alpha_1$ ) are:  $a=6.224(4)$ ,  $b=21.517(8)$ ,  $c=13.794(6)$  Å. The errors in the last digits (in parentheses) are subjective estimates of the standard deviations. These dimensions agree with those reported by Ibers (1961)

within the accuracy that he stated. With  $Z=4$ , the calculated density  $0.980$  g.cm $^{-3}$  agrees with the value observed by flotation,  $0.98$  g.cm $^{-3}$ , again in accord with Ibers (1961). Reflections are absent for  $h00$  if  $h=2n+1$ , for  $0k0$  if  $k=2n+1$ , and for  $00l$  if  $l=2n+1$ . These rules are characteristic of space group  $P2_12_12_1$ , and this choice is confirmed by the structure determination. All atoms are in the general set of positions:

$$4(a) \quad x, y, z; \frac{1}{2} - x, -y, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} - y, -z; \\ -x, \frac{1}{2} + y, \frac{1}{2} - z.$$

Intensities were measured for 2045 independent reflections. Two crystals of approximately the same size ( $0.1 \times 0.3 \times 0.2$  mm) were used in the experiment. Each reflection was integrated by the  $\theta$ ,  $2\theta$  technique with  $Cu K\alpha$  radiation filtered through Ni, at 35 kV and 20 mA. Each scan extended from  $0.5^\circ$  (of  $2\theta$ ) below the  $\alpha_1$  peak to  $0.5^\circ$  above the  $\alpha_2$  peak, at a rate of  $1^\circ/\text{min}$ . The background was measured for 10 seconds at each end of the scan with crystal and counter stationary. The background was assumed to be a linear function of  $2\theta$  between these two points. The net intensity  $I$  is

$$I = C - (B_1 + B_2)(t_c/2t_b),$$

where  $C$  is the total counts recorded during the scan time  $t_c$ , and  $B_1$  and  $B_2$  are the background counts each in time  $t_b$ . The standard deviation of the intensity was assumed to be:

$$\sigma(I) = [C + (t_c/2t_b)^2(B_1 + B_2) + (0.05 I)^2]^{1/2}.$$

The first crystal was used to collect data for reflections for which  $2\theta < 110^\circ$ . During the data collection, the intensity of the four standard reflections had uniformly dropped by approximately 15% and the crystal was discarded. A second and slightly larger crystal was used for data in the range  $100^\circ$ – $140^\circ$ . At the end of this data collection, the standard reflections for this crystal had also dropped by 15%. The two sets of data were put on a common scale by comparing intensities

\* Work done under the auspices of the U.S. Atomic Energy Commission.

in the region  $100^{\circ}$ – $110^{\circ}$ . The ratio was 1.60. No correction was made for absorption or for decomposition in the crystals.

In the calculation of structure factors, atomic scattering factors for neutral C and H were taken from *International Tables for X-ray Crystallography* (1962). The isotropic temperature factor was defined as  $\exp(-B \sin^2 \theta / \lambda^2)$ . Calculations were made with the CDC-6600 computer with our unpublished programs for Fourier series and interatomic distances and angles, and our modified (unpublished) version of the Gantzel-Sparks-Trueblood full-matrix least-squares program, which minimizes  $\sum w | \Delta F |^2 / \sum w | F_o |^2$ . The anisotropic temperature factors used have the form:

$\exp(-0.25 \sum_i \sum_j h_i h_j b_i b_j B_{ij})$ ,  $i, j = 1, 2, 3$ , and where  $b_i$  is the  $i$ th reciprocal cell length.

### Determination and refinement of the structure

The structure of cembrene was solved by a statistical method using the general principles laid down for non-centrosymmetric structures by Karle & Karle (1966). We calculated the normalized structure factor magnitudes  $|E|$  using an unpublished program written by Maddox & Maddox (1965), and we used 98 reflections with  $|E|$  values greater than 1.67 in subsequent calculations.

In  $P2_12_12_1$ , there are eight possible origins and two enantiomorphs giving sixteen equivalent combinations of phases. It is possible to isolate an origin and enantiomorph by fixing the phases of four two-dimensional reflections. We could find only three two-dimensional reflections of suitable parity among the larger  $|E|$  values, 0 19 5, 0 11 10 and 1 18 0, and assigned to them the phase of  $\pi/2$ . Arbitrary restriction of the phase of 1 3 2 to the range  $0 - \pi$  completed the choice of origin and enantiomorph. The phases of this reflection and three others were assigned symbols. These initial assignments are listed in Table 1.

Table 1. *Initial phase assignments*

	h		$ E_h $	$\varphi_h$	
	0	19	5	2.40	$\pi/2$
	0	11	10	1.95	$\pi/2$
	1	18	0	1.99	$\pi/2$
	0	2	12	2.86	<i>a</i>
	3	9	6	2.59	<i>b</i>
	1	3	2	1.99	<i>c</i>
	1	10	10	2.45	<i>d</i>

Symbol *a* was deduced to be zero from the  $\Sigma_1$  relationship. Next we used the formula (Karle & Karle, 1966):

$$\varphi_h \simeq \langle \varphi_k + \varphi_{h-k} \rangle_k \quad (1)$$

We required the value of the triple product  $|E_h E_k E_{h-k}|$  to exceed 9.0 if a single phase indication was to be accepted. As new phases  $\varphi_h$  were calculated from combinations  $(\varphi_k + \varphi_{h-k})$ , they were added to the list of

known phases and subsequently used to determine other phases. This programmed technique resulted in a set of 25 self-consistent phases. For the remaining reflections, the contributing sums  $(\varphi_k + \varphi_{h-k})$  to a particular  $\varphi_h$  were sometimes different. Relationships between the symbols were derived from these differences. The most frequently occurring relationships were  $2d=0$ ,  $2b+2c=0$  and  $2b+2c=\pi$ . In view of this inconsistency, we decided to make no assumptions about the values of *b*, *c* and *d*,\* and to use a different approach with the tangent formula (Karle & Hauptman, 1956):

$$\tan \varphi_h \simeq A/B, \quad (2)$$

where

$$A = \sum_k |E_k E_{h-k}| \sin(\varphi_k + \varphi_{h-k}),$$

$$B = \sum_k |E_k E_{h-k}| \cos(\varphi_k + \varphi_{h-k}).$$

In order to apply the tangent formula, numerical phases were assigned to the symbols. Symbol *c* was phased from 0 to  $\pi$  in steps of  $\pi/4$  and *b*, *d* from 0 to  $7\pi/4$ , also in steps of  $\pi/4$ . The interval of  $\pi/4$  is arbitrary. There are 320 ( $=8 \times 5 \times 8$ ) combinations of possible values for these three symbols, and for each of these, the following procedure was adopted.

The 25 reflections, whose phases were determined by use of equation (1) were given numerical phases. The tangent formula was only applied to these reflections and to those with  $|E|$  values above 2.0. The consistency of a phase determined from the tangent formula can be judged from the value of the parameter  $t_h$ , where

$$t_h = (A^2 + B^2)^{1/2} / \sum_k |E_k E_{h-k}|.$$

We required this parameter  $t_h$  to be greater than an arbitrary value of 0.4. If this criterion was satisfied, a phase determined by the tangent formula was subsequently used in the next cycle. No changes were made to the phase of a reflection until the conclusion of a cycle, when the tangent formula had been applied to all the reflections. After ten cycles, all 98 reflections were introduced into the procedure. Although forty more cycles were carried out in the way described, most of the phases were determined after five cycles.

For each of the 320 starting sets, a final list of refined phases were printed, together with a consistency index, *Q*, for each set. This consistency index *Q* is

\* As this was our first attempt at solving a structure by this method, we employed an over-cautions approach. Later experience with other problems suggest that we would have been justified in assuming that  $d=0$  or  $\pi$  and that  $2b+2c=\pm\pi/2$ .

Table 2. *The most consistent sets of phases*

Phases given in millicycles, so 500 represents  $\pi$ .

3 9 6	1 3 2	1 10 10	<i>Q</i>
-444	307	-3	0.22
-487	-488	-1	0.27
189	206	8	0.31
-295	335	15	0.31

defined as\*:

$$Q = \frac{\sum_h |E_h - t_h E_h|}{\sum_h |E_h|}$$

\* The  $Q$  value is equivalent to the  $R$  value of Karle & Karle (1966). We have changed the name to avoid confusion with the  $R$  value calculated from the observed and calculated structure factors.

Table 2 shows the phases of the 3 9 6, 1 3 2 and 1 10 10 reflections and the  $Q$  values for the four most consistent sets.

An  $E$  map was calculated using 98 reflections with the phases in the most consistent set ( $Q=0.22$ ). A least-squares refinement confirmed that 19 of the top 20 peaks were carbon atoms. The remaining carbon atom

Table 3. *Final coordinates* ( $\times 10^4$ ) *and thermal parameters* ( $\times 10^2$ ) *for the carbon atoms in cembrene*

Standard deviations estimated by least squares for the least significant digit are given in parentheses.

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	1958 (6)	4701 (2)	8296 (2)	461 (18)	351 (13)	350 (14)	37 (15)	01 (13)	-33 (12)
C(2)	0792 (6)	4548 (2)	7371 (3)	423 (18)	367 (14)	383 (15)	71 (14)	09 (14)	-29 (12)
C(3)	1356 (6)	4100 (2)	6765 (3)	443 (17)	359 (14)	325 (13)	48 (14)	-00 (14)	-02 (12)
C(4)	0186 (7)	3924 (2)	5876 (3)	557 (20)	415 (16)	327 (14)	-09 (16)	-29 (15)	46 (13)
C(5)	0893 (9)	3445 (2)	5330 (3)	719 (28)	512 (20)	327 (15)	-40 (20)	-59 (17)	-11 (15)
C(6)	2746 (9)	3034 (2)	5519 (3)	718 (27)	512 (19)	385 (16)	54 (22)	70 (19)	-105 (15)
C(7)	2452 (8)	2620 (2)	6396 (3)	535 (21)	363 (16)	472 (17)	55 (17)	10 (17)	-113 (14)
C(8)	3808 (7)	2531 (2)	7121 (3)	431 (18)	376 (14)	535 (19)	79 (15)	15 (16)	-97 (14)
C(9)	3149 (10)	2130 (2)	7972 (3)	715 (29)	327 (15)	590 (21)	112 (19)	-77 (21)	03 (15)
C(10)	3044 (10)	2501 (2)	8929 (3)	696 (28)	489 (20)	461 (19)	69 (21)	-67 (20)	65 (15)
C(11)	1441 (8)	3018 (2)	8891 (3)	533 (21)	458 (18)	383 (16)	44 (17)	-13 (17)	73 (13)
C(12)	1347 (8)	3504 (2)	9466 (3)	661 (23)	439 (17)	349 (14)	-27 (18)	81 (16)	58 (13)
C(13)	-0366 (8)	3983 (2)	9361 (4)	562 (23)	507 (20)	505 (20)	18 (18)	207 (20)	01 (17)
C(14)	0459 (9)	4646 (2)	9173 (3)	718 (28)	460 (18)	395 (18)	52 (21)	133 (20)	-40 (16)
C(15)	3041 (8)	5351 (2)	8264 (3)	606 (23)	370 (16)	515 (19)	-33 (17)	-104 (19)	-21 (15)
C(16)	1505 (12)	5884 (2)	8076 (4)	893 (40)	366 (18)	693 (29)	91 (23)	109 (30)	03 (19)
C(17)	4877 (11)	5349 (3)	7527 (6)	570 (25)	586 (26)	995 (39)	-57 (24)	100 (28)	162 (28)
C(18)	-1733 (10)	4296 (3)	5601 (4)	738 (32)	598 (25)	516 (22)	36 (23)	-200 (25)	16 (20)
C(19)	5943 (10)	2826 (3)	7187 (5)	499 (27)	912 (37)	757 (34)	39 (26)	-62 (26)	40 (31)
C(20)	2920 (17)	3600 (3)	10281 (4)	957 (48)	790 (33)	457 (23)	76 (36)	-142 (29)	-81 (23)

Table 4. *Final coordinates* ( $\times 10^3$ ) *and thermal parameters* ( $\times 10$ ) *for the hydrogen atoms in cembrene*

Also given are the C-H distances in Å

	$x$	$y$	$z$	$B$	C-H (Å)
H(1)	321 (6)	437 (1)	836 (2)	13 (7)	1.06 (4)
H(2)	-057 (5)	479 (1)	723 (2)	3 (6)	1.01 (3)
H(3)	280 (6)	388 (1)	694 (2)	13 (7)	1.04 (4)
H(5)	-008 (7)	339 (2)	482 (3)	26 (9)	0.94 (4)
H(6-1)	416 (8)	331 (2)	562 (3)	32 (10)	1.08 (5)
H(6-2)	314 (9)	277 (2)	491 (4)	50 (12)	1.05 (5)
H(7)	093 (7)	244 (2)	645 (3)	23 (9)	1.02 (5)
H(9-1)	432 (8)	185 (2)	807 (3)	47 (12)	0.95 (5)
H(9-2)	156 (8)	195 (2)	785 (3)	30 (9)	1.08 (5)
H(10-1)	463 (8)	265 (2)	905 (3)	24 (9)	1.05 (5)
H(10-2)	227 (10)	220 (3)	940 (4)	73 (16)	1.04 (6)
H(11)	023 (6)	295 (2)	849 (3)	17 (7)	0.95 (4)
H(13-1)	-132 (8)	386 (2)	885 (14)	41 (12)	0.96 (5)
H(13-2)	-131 (8)	405 (2)	996 (3)	33 (9)	1.03 (5)
H(14-1)	-079 (7)	496 (2)	906 (3)	27 (9)	1.03 (4)
H(14-2)	138 (9)	476 (2)	973 (4)	57 (13)	0.99 (5)
H(15)	400 (8)	540 (2)	880 (3)	33 (11)	0.96 (5)
H(16-1)	075 (8)	584 (2)	738 (4)	49 (13)	1.07 (5)
H(16-2)	230 (13)	623 (3)	806 (5)	94 (21)	0.90 (8)
H(16-3)	038 (10)	592 (3)	842 (4)	50 (16)	0.85 (6)
H(17-1)	597 (10)	569 (3)	757 (4)	62 (15)	1.00 (6)
H(17-2)	563 (11)	502 (3)	793 (4)	71 (16)	1.03 (6)
H(17-3)	414 (14)	522 (3)	686 (5)	104 (23)	1.06 (8)
H(18-1)	-300 (9)	430 (2)	609 (4)	40 (12)	1.04 (5)
H(18-2)	-239 (8)	413 (3)	505 (4)	41 (12)	0.93 (5)
H(18-3)	-120 (8)	476 (2)	550 (3)	41 (16)	1.06 (5)
H(19-1)	672 (12)	296 (3)	662 (4)	101 (25)	0.97 (8)
H(19-2)	705 (13)	267 (3)	745 (4)	55 (16)	0.85 (7)
H(19-3)	601 (13)	317 (4)	774 (6)	113 (24)	1.06 (8)
H(20-1)	391 (15)	319 (4)	1041 (5)	122 (26)	1.09 (9)
H(20-2)	210 (19)	376 (5)	1065 (8)	152 (40)	0.80 (11)
H(20-3)	421 (13)	373 (4)	1009 (5)	71 (24)	0.89 (8)



Table 6. Observed and calculated structure factors ( $\times 3.0$ ) for cembrene  $C_{20}H_{32}$

Reflections marked with an asterisk were assigned zero weight in the least-squares refinement.  $F_{000} (\times 3.0) = 1824$ .

Table with multiple columns of reflection indices (h, k, l) and corresponding observed and calculated structure factor values. The table is organized into several sections based on reflection indices.

C(7)–C(8) and C(11)–C(12) are both *trans*. In an analysis of the bond distances and angles in the molecule, it is convenient to group particular values together. We do not claim that the environments of atoms making up the bonds and angles in these categories are exactly equivalent, but the similarity of the values is striking. The distribution of bond distances and internal ring angles is shown in Table 7.

The difference in bond distance between the two categories =C–C– and –C–C– is significant from the standpoint of either the standard deviations from least-squares refinement or from the deviations shown in Table 7. Such a difference in single C–C bond lengths has often been found but the exact cause is still under active debate (Dewar, 1962; Alden, Kraut & Traylor, 1968). It is interesting to note that after the refinement of the carbon atoms alone, such a pattern was not discernible. With the inclusion of the hydrogen atoms in the refinement, some of the C–C bond distances changed by as much as 0.05 Å.

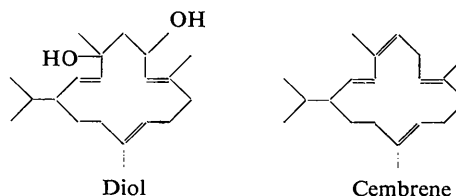
The four categories of angles in the ring follow a similar pattern: the C–C–C angles are larger when the central carbon atom is bonded to hydrogen(s) than when it is bonded to carbon(s). This is true both for the unsaturated carbon atom (in Table 7, categories 7,8 have average values of 126.5° for H and 120.4° for C) and for the saturated carbon atom (categories 5,6 have average values 113.4° for H and 111.0° for C as compared with the tetrahedral angle of 109.5°).

The average bond distance for the C–H bonds is 1.01 Å (maximum deviation 0.07 Å) for the non-methyl hydrogen atoms and 0.98 Å (maximum deviation 0.18 Å) for the methyl hydrogen atoms. These values are somewhat shorter than the standard C–H bond lengths, as is typical for X-ray diffraction work. The consistency of the C–H bond distances for the non-methyl hydrogen atoms agrees well with the standard deviations of the bonds (~0.05 Å) calculated

from the least-squares refinement. All angles involving ring carbon atoms and hydrogen atoms are between 102 and 124°, but there is no obvious grouping between angles of similar type.

Some of the methyl hydrogen atoms show large thermal parameters, thus suggesting that some of the positions are not well defined. There is also a larger variation in C–H bond distance for the methyl hydrogen atoms than for the non-methyl hydrogen atoms. The average deviation from the tetrahedral angle is 7° for the C–C–H angles and 12° for the H–C–H angles. The standard deviations calculated from least-squares for such angles are approximately 4° and 6°.

Hydroxylated derivatives of cembrene have been found in tobacco leaves and cigarette smoke (Roberts & Rowland, 1962; Rowland & Roberts, 1963; Rowland, Rodgman, Schumacher, Roberts, Cook & Walker, 1964; Kinzer, Page & Johnson, 1966; Courtney & McDonald, 1967). Most of these various compounds have been related to 12-isopropyl-1,5,9-trimethyl-4,8,12-cyclotetradecatriene-1,3-diol. This compound is shown below and compared to cembrene.

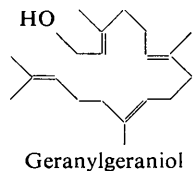


Nuclear magnetic resonance and degradation studies (Roberts & Rowland, 1962; Courtney & Macdonald, 1967), have shown that all three double bonds in the diol are probably *trans*. This structure determination of cembrene has confirmed the close similarity between these two compounds, for in cembrene the same double bonds are also *trans*. Such a configuration for both compounds is compatible with the proposed bio-

Table 7. Distribution of bond distances and internal ring angles in cembrene

Category	Contributing atoms (bonds)	Average	Average deviation	Maximum deviation	
1	–C=C–	C(2)–C(3), C(4)–C(5), C(7)–C(8), C(11)–C(12)	1.328 Å	0.012 Å	0.023 Å
2	=C=C=	C(3)–C(4)	1.476	—	—
3	=C–C–	C(1)–C(2), C(4)–C(18), C(5)–C(6), C(6)–C(7), C(8)–C(9), C(10)–C(11), C(12)–C(13), C(8)–C(19), C(12)–C(20)	1.493	0.011	0.021
4	–C–C–	C(9)–C(10), C(13)–C(14), C(14)–C(1), C(1)–C(15), C(15)–C(16), C(15)–C(17)	1.536	0.010	0.021
Central atom (angles)					
5	$\begin{array}{c} X \\   \\ C-C-C \\   \\ H \end{array}$	with X=H C(6), C(9), C(10), C(13), C(14)	113.4°	0.8°	1.5°
6		X=C C(1)	111.0	—	—
7	$\begin{array}{c} C=C-C \\   \\ X \end{array}$	with X=H C(2), C(3), C(5), C(7), C(11)	126.5	1.2	2.0
8		X=C C(4), C(8), C(12)	120.4	0.8	1.2

syntheses from geranylgeraniol (Rowland & Roberts, 1963; Dauben, Thiessen & Resnick, 1965; and Courtney & McDonald, 1967), which can be drawn as:



#### References

- AKIYOSHI, S. (1937). *Rep. Osaka Ind. Res. Inst.* **17**, No. 10.  
 ALDEN, R., KRAUT, J. & TRAYLOR, T. G. (1968). *J. Amer. Chem. Soc.* **90**, 74.  
 COURTNEY, J. L. & McDONALD, S. (1967). *Tetrahedron Letters*, 459.  
 DAUBEN, W. G., THIESSEN, W. E. & RESNICK, P. R. (1962). *J. Amer. Chem. Soc.* **84**, 205.  
 DAUBEN, W. G., THIESSEN, W. E. & RESNICK, P. R. (1965). *J. Org. Chem.* **30**, 1693.  
 DEWAR, M. J. S. (1962). *Hyperconjugation*, p 63. New York: Ronald Press.  
 IBERS, J. A. (1961). *Acta Cryst.* **14**, 1001.  
*International Tables for X-ray Crystallography* (1962). Vol. III, p. 201. Birmingham: Kynoch Press.  
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.  
 KARLE, J. & HAUPTMANN, H. (1956). *Acta Cryst.* **9**, 635.  
 KOBAYASHI, H. & AKIYOSHI, S. (1962). *Bull. Chem. Soc. Japan*, **35**, 1044.  
 KOBAYASHI, H. & AKIYOSHI, S. (1963). *Bull. Chem. Soc. Japan*, **36**, 823.  
 KINZER, G. W., PAGE, T. F. & JOHNSON, R. R. (1966). *J. Org. Chem.* **31**, 1797.  
 MADDOX, H. S. & MADDOX, M. L. (1965). Private communication.  
 MIROV, N. T. (1961). U.S. Dept. Agr. Tech. Bull. No. 1239.  
 ROBERTS, D. L. & ROWLAND, R. L. (1962). *J. Org. Chem.* **27**, 3989.  
 ROWLAND, R. L. & ROBERTS, D. L. (1963). *J. Org. Chem.* **28**, 1165.  
 ROWLAND, R. L., RODGMAN, A., SCHUMACHER, J. N., ROBERTS, D. L., COOK, L. C. & WALKER, W. (1964). *J. Org. Chem.* **29**, 16.

*Acta Cryst.* (1969). B25, 267

## Die Kristall- und Molekülstruktur von Thioacetanilid-S-Oxid

VON O. H. JARCHOW

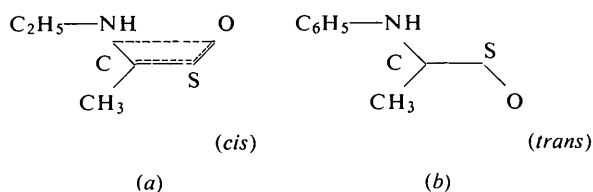
*Mineralogisch-Petrographisches Institut der Universität Hamburg, Deutschland*

(Eingegangen am 12. Januar 1968)

Thioacetanilid-S-Oxid kristallisiert in der Raumgruppe *Pbca* mit den Zellabmessungen (bei Raumtemperatur)  $a = 18.58$ ,  $b = 10.57$ ,  $c = 8.21$  Å. Die Struktur wurde durch zweidimensionale Patterson- und Vektorverschiebungsverfahren bestimmt. Die ungefähren atomaren Koordinaten wurden durch Verwendung der vollständigen Matrix-Least-Squares-Methoden auf einen  $R$ -Wert von 6% verfeinert. Die Moleküle sind paarweise über zwei  $\text{NH} \cdots \text{O}$  (2.86 Å) Wasserstoffbrückenbindungen verknüpft. Die Moleküle sind durch ein Symmetriezentrum miteinander verknüpft. Alle Atome, außer Wasserstoff, liegen in zwei Ebenen, einer Ebene des Anilinderivs und der anderen Ebene des Thioacetyl-S-Oxid-Gruppen. Der Winkel der beiden sich schneidenden Ebenen beträgt  $45^\circ$ . Diese Verzerrungen können durch sterische Hindernisse erklärt werden.

### Einführung

Im Rahmen der Untersuchungen an Thioamiden durch Walter und Mitarbeiter (Walter & Maerten, 1963; Walter, Maerten & Rose, 1966) ist das Thioacetanilid-S-Oxid (TASO) von besonderem Interesse. Aus spektroskopischen (NMR-Spektren) Untersuchungen des Stoffes in Lösung waren einige Fragen offengeblieben, die erst nach einer Röntgenstrukturanalyse beantwortet werden konnten, z. B. die Frage, ob im kristallinen Zustand die *cis*- oder *trans*-Konfiguration vorliegt:



In der *cis*-Stellung (a) befinden sich NH und O auf der gleichen Seite bezüglich einer zentralen C-S-Gruppe, während sie in der *trans*-Stellung (b) wechselseitig angeordnet sind. Daneben ist interessant, ob das H-Atom am Stickstoff in Form einer Amido ( $\text{NH} \cdots \text{O}$ ) oder Imidol ( $\text{N} \cdots \text{HO}$ ) Bindung vorliegt und ob es eine intra- oder intermolekulare Bindungsaufgabe erfüllt. Aus den Arbeiten von Brown & Corbridge (1948, 1954) und Brown (1966) am Acetanilid sowie von Pedersen & Pedersen (1965) am *N*-Methylacetanilid konnten nur Vermutungen für die Verhältnisse im Thioacetanilid-S-Oxid angestellt werden. Danach liegen der Benzolring und die Amidgruppe jeweils in verschiedenen Ebenen. Der Winkel, den die beiden Ebenen miteinander bilden, lässt sich vor allem auf sterische Effekte zwischen der Amidgruppe und dem Benzolring zurückführen. Im Zusammenhang hiermit verdient der sterische Einfluss der  $\text{CH}_3$ -Gruppe im Thioacetanilid-S-Oxid ebenfalls besondere Aufmerksamkeit.