

in the bond lengths, the maximum change being 0.012 Å, and the mean 0.007 Å. The revised values of the bond lengths are given in Table 7. The mean C-C distance in the benzene ring is thus 1.398 Å, compared with 1.391 Å for the uncorrected coordinates.

We wish to thank Prof. Dame Kathleen Lonsdale, F.R.S. for her valuable suggestions and advice in this work, and one of us (R. S.) thanks the British Council for the award of a scholarship in 1952-3 when the initial part of this work was carried out. The completion of the work was made possible by means of a grant from the Department of Scientific and Industrial Research. Funds for the computing facilities were provided by the Wellcome Trust, and the tape preparation was carried out on apparatus provided by the University of London Central Research Fund.

References

- ALLEN, N. C. B. (1927). *Phil. Mag.* **3**, 1037.
 BECKER, K. & ROSE, H. (1923). *Z. Phys.* **14**, 369.
 BUJOSA, A. & CRUICKSHANK, D. W. J. (1961). *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*. p. 73. Oxford: Pergamon Press.
 DES CLOIZEAUX, A. (1869). *C. R. Acad. Sci., Paris*, **68**, 308.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
 CRUICKSHANK, D. W. J. & PILLING, D. E. (1961). *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*. p. 32. Oxford: Pergamon Press.
 GROTH, P. (1919). *Chemische Kristallographie*, **5**, 188. Leipzig: Engelmann.
 JEFFREY, G. A. (1947). *Proc. Roy. Soc., A*, **188**, 222.
 KNAGGS, I. E. & LONSDALE, K. (1939). *Nature, Lond.* **143**, 1023.
 LONSDALE, K. & SMITH, H. (1941). *Proc. Roy. Soc. A*, **179**, 8.
 TROTTER, J. (1960). *Acta Cryst.* **13**, 86.
 WOLFF, P. M. DE (1948). *Acta Cryst.* **1**, 207.

Acta Cryst. (1965). **18**, 164

The Conformation of Non-Aromatic Ring Compounds. XIV.* The Crystal Structure of *trans*-2,3-Dichloro-1,4-dithiane at -180°C

BY H. T. KALFF AND C. ROMERS

Laboratory of Organic Chemistry, University of Leiden, The Netherlands

(Received 6 March 1964)

The structure of *trans*-2,3-dichloro-1,4-dithiane has been determined from projections along [100], [010], and $[\bar{1}01]$ by means of data obtained at about -180°C with molybdenum radiation. The space group is Pn with

$$a = 7.174, b = 7.511, c = 6.726 \text{ \AA}, \beta = 93.93^{\circ}, \text{ and } Z = 2.$$

The dithiane ring has the chair form with the chlorine atoms in axial positions. A comparison is made with similarly substituted 1,4-dioxanes.

Introduction

The present study is an extension of the studies made in this laboratory on substituted cyclohexanes (Kwestroo, Meijer & Havinga, 1954; Wessels, 1960; van Dort, 1963), dioxanes (Altona & Romers, 1963*a, b*; Altona, Knobler & Romers, 1963*a, b*) and dithianes (Kalff & Havinga, 1962).

We have been able to synthesize some 2,3-disubstituted (dichloro-, chlorobromo-, and dibromo-) and one 2,5-disubstituted (dibromo-) 1,4-dithiane (Kalff, 1964). Since the unit cell of the dichloro compound contains only two molecules and its absorption coefficient is the lowest, this compound was chosen for structure determination.

Experimental

trans-2,3-Dichloro-1,4-dithiane was prepared by addition of chlorine to 1,4-dithiane in chloroform (Kalff, 1964). The compound crystallizes from hexane in small needles, elongated along the a axis and twinned on the plane (001). A specimen used for collecting $0kl$ data was obtained by cutting a twinned crystal. Crystals of a different habit were obtained by slowly evaporating a solution in chloroform. The crystals from the latter solvent appeared in the form of plates with (010) as main face and again twinned according to (001). These crystals were used for collecting $h0l$ and hkh data. All specimens were sealed in dry Lindemann capillaries.

Unit-cell dimensions (Table 1) were measured from zero level Weissenberg photographs about [100] and

* Part XIII: Mossel & Romers (1964).

Table 1. Unit-cell dimensions and standard derivations, densities (g.cm^{-3}), and space groups of some 2,3-dihalogeno-1,4-dithianes

Compound	a	b	c	β ($^\circ$)	d_{exp}	d_{calc}	T ($^\circ\text{C}$)	Z	Space group
Di-Cl	7.174 ± 0.004	7.511 ± 0.003	6.726 ± 0.004	93.93 ± 0.07	—	1.75	-180	2	Pn
Di-Cl	7.30	7.60	6.88	93.67	1.68	1.66	+20	2	Pn
ClBr	7.40	7.60	6.96	93.50	2.03	1.99	+20	2	Pn
Di-Br	14.54	7.52	7.60	90	2.20	2.19	+20	4	$Pnam$ or $Pna2_1$

[010], taken with unfiltered Cu radiation ($\lambda = 1.5418 \text{ \AA}$) at -180°C . The photographs were superposed with Al powder lines ($a = 4.9089 \text{ \AA}$ at 20°C) at room temperature. Unit-cell dimensions and standard deviations calculated from 64 measured glancing angles θ were refined with a least-squares procedure. Included in Table 1 are the unit-cell dimensions at room temperature of the 2,3-dichloro, the 2-chloro-3-bromo, and the 2,3-dibromo compound. The room temperature data are less accurate since no calibration with Al powder lines and no least-squares procedures were applied.

Zero layer Weissenberg photographs about [100] and $[\bar{1}01]$ (non-integrated photographs) and about [010] (integrated photographs) were taken with $\text{MoK}\alpha$ radiation at -180°C by means of the liquid-nitrogen adaptor designed by Altona (Altona, 1964a). The intensities of $0kl$ and hkh reflexions were estimated visually. The $h0l$ data were measured partly with a photometer and partly visually (the weaker spots). The six strongest reflexions were correlated from corresponding spots on a different set of $h0l$ data that had been taken at a slightly higher temperature. The intensities were reduced to structure factor moduli (Geise, 1964) and the usual Lorentz and polarization corrections were made. The chosen crystals were sufficiently small (largest dimension 0.5 mm) to permit the absorption effects ($\mu \leq 13.3$) to be neglected.

The absence of reflexions with $h+l$ odd indicates that Pn or $P2/n$ are possible space groups. The density (1.68 g.cm^{-3}) was determined by the flotation method. It follows that the unit cell contains two molecules. Inspection of Table 1 shows that the dibromo compound is orthorhombic. The chlorobromo compound, however, is isomorphous with the dichloro compound.

Patterson functions

Since the unit cell of the dichloro compound contains only two molecules, it follows that the asymmetric unit consists of one molecule if the space group is Pn , and of half a molecule if the true space group is $P2/n$.

A distinction between the alternatives was made by a successful interpretation of the Patterson projections along [010], $[\bar{1}01]$, and [100]. All Patterson functions were calculated with Fourier coefficients $F^2 (\sin^2 \theta / \lambda^2) \exp(-0.60 \sin^2 \theta / \lambda^2)$. The $P(uw)$ function was analysed first.

Keeping in mind that the scattering power of sulphur and chlorine atoms is about the same, and

neglecting the contributions of the carbon and hydrogen atoms, there are two peaks with double weight and two with single weight if the space group is $P2/n$, and six peaks of about equal weight if the space group is Pn . The latter requirement was met in our analysis and we concluded that the asymmetric space group was the true one. Approximate x and z parameters of three heavy atoms were found. The x and z parameters of the fourth atom (Cl(1)) (cf. Fig. 2 for the numbering of the atoms) were arbitrarily fixed at zero. The y parameters of these four atoms were found from the Patterson projection along $[\bar{1}01]$ and checked with those from the projection along [100].

Structure factors with the heavy atom contributions were calculated for the three projections mentioned. The reliability index R was 0.24, 0.19, and 0.21 for the $h0l$, hkh , and $0kl$ reflexions respectively. The positions of the carbon atoms were found from subsequent electron density projections (see Fig. 1).

Refinement

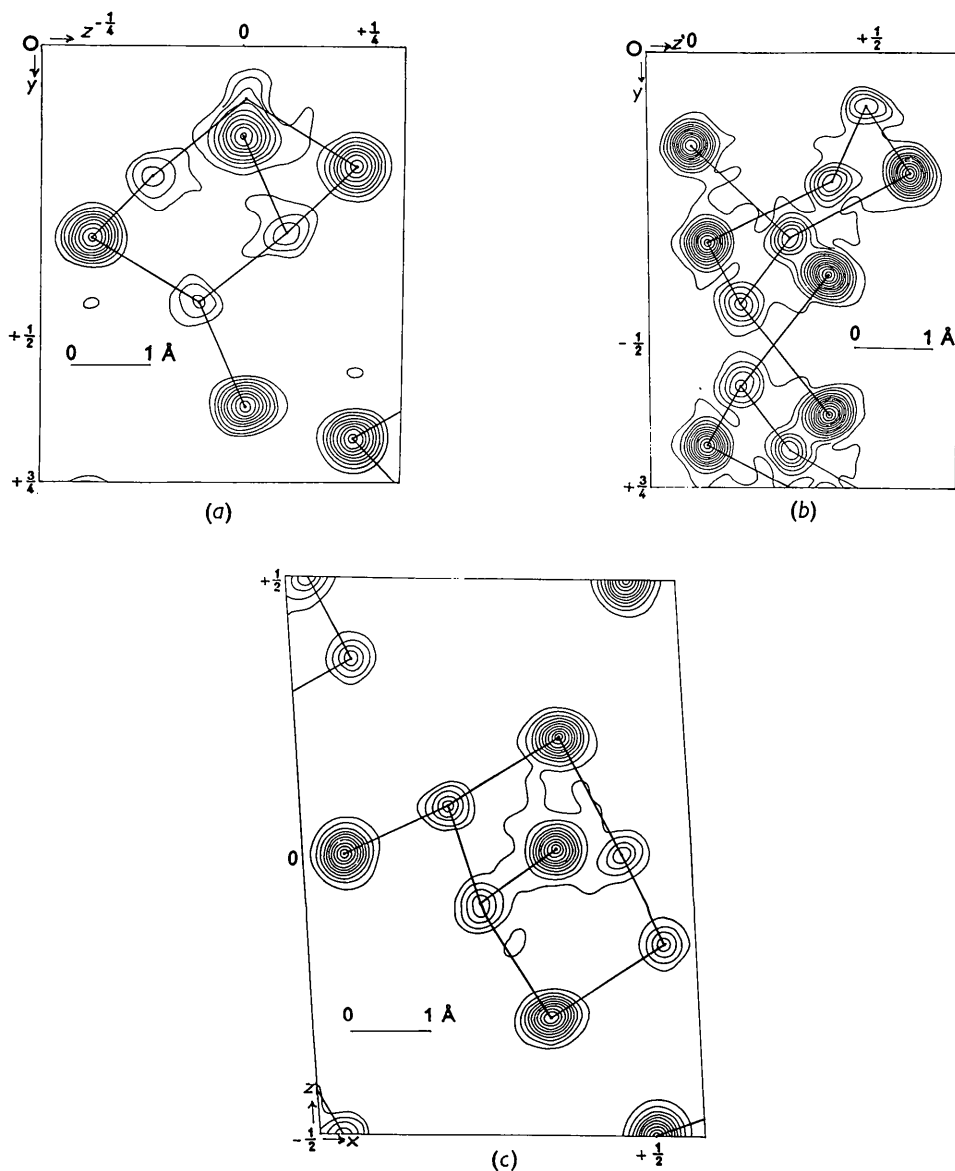
The refinement of the structure was carried out by several cycles of calculated structure factors, electron density projections and difference Fourier maps. At a later stage a least-squares method was used for the refinement (minimizing $\sum w(F_o - F_c)^2$, and taking $w = 1$ during all cycles). The refinement was stopped when the shifts were within the standard deviations. The heavy atoms were refined with anisotropic temperature factors in all projections. All atoms in the [010] projection showed some anisotropy in the difference maps. Therefore we introduced anisotropic temperature factors for the carbon atoms also in this projection. No hydrogen atoms were introduced in the calculations, because only in the $[\bar{1}01]$ difference map, calculated with reflexions with $\sin \theta < 0.35$, could

Table 2. Final atomic coordinates (in fractions of cell edges) and standard deviations (10^{-3} \AA units)

Atom	x	y	z
S(1)	0.3749 (6)	0.2037 (6)	0.2124 (6)
S(2)	0.3302 (6)	0.3241 (6)	-0.2880 (5)
Cl(1)	0.0000 (5)	0.1575 (6)	0.0000 (5)
Cl(2)	0.3563 (6)	0.6200 (6)	0.0090 (6)
C(1)	0.1778 (19)	0.3159 (24)	0.0886 (18)
C(2)	0.2238 (20)	0.4327 (22)	-0.0894 (19)
C(3)	0.4709 (20)	0.0933 (26)	-0.0020 (19)
C(4)	0.5320 (20)	0.2172 (22)	-0.1537 (19)

Table 3. *Temperature factors* B (\AA^2) and *peak electron densities* ρ_0 ($\text{e} \cdot \text{\AA}^{-2}$)

Atom	[010]				[100]					[101]				
	B_{11}	B_{33}	$2B_{13}$	ρ_0	B_{iso}	B_{22}	B_{33}	$2B_{23}$	ρ_0	B_{iso}	B_{22}	B_{33}'	$2B_{23}'$	ρ_0
S(1)	1.63	1.20	0.17	49		0.89	1.33	0.14	45		0.98	0.97	0.34	54
S(2)	1.72	1.02	0.36	48		0.81	1.42	0.04	42		1.13	0.97	-0.15	56
Cl(1)	1.42	1.56	0.44	50		0.98	1.47	-0.20	44		1.00	1.05	-0.21	58
Cl(2)	1.49	1.52	0.06	50		0.88	1.48	0.10	45		0.89	1.21	-0.71	60*
C(1)	1.29	1.09	0.37	15	1.16				12	1.02				19*
C(2)	1.57	1.32	0.55	15	1.25				10	1.02				15
C(3)	1.69	1.56	1.44	14	1.28				†	1.05				14
C(4)	1.53	1.41	0.22	14	1.13				11	1.02				17

* In projection $[\bar{1}01]$ atoms Cl(2) and C(1) partially overlap.† In projection $[100]$ atoms Cl(1) and C(3) show heavy overlap.Fig. 1. Electron density projections along (a) $[100]$, (b) $[\bar{1}01]$, and (c) $[010]$. Contours are drawn at 5, 10, 15, ... $\text{e} \cdot \text{\AA}^{-2}$ for the sulphur and chlorine atoms and at 5, 7.5, 10, ... $\text{e} \cdot \text{\AA}^{-2}$ for the carbon atoms. The coordinate $z' = x + z$ in (b).

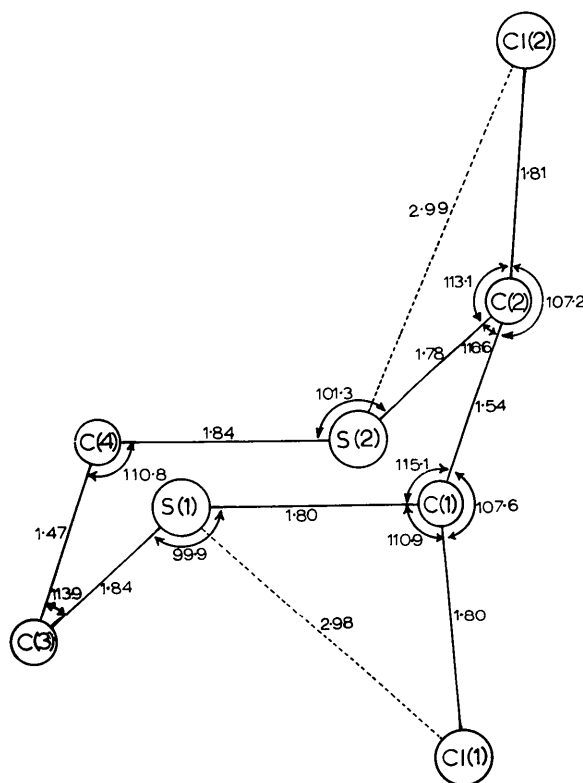


Fig. 2. Atomic distances and bond angles in *trans*-2,3-dichloro-1,4-dithiane.

three or four peaks possibly be assigned to hydrogen. The final R values, defined in the usual way (observed structure factors only) were 0.069, 0.061, and 0.081 for the [010], $[\bar{1}01]$ and [100] projections respectively. As can be seen from Fig. 1, only the [100] projection has two overlapping atoms (Cl(1) and C(3)). The final atomic positions are shown in Table 2.

In Table 3 the temperature factors for the three projections and the peak electron densities ρ_0 are given.

Discussion of the structure

The electron density projection along $[\bar{1}01]$ demonstrates that the dithiane ring has the chair form; the chlorine atoms occupy axial positions. Fig. 2 shows the distances and angles in the molecule. From a comparison of the corresponding bond distances and bond angles it follows that the molecular symmetry is C_2 , a twofold axis running through the midpoints of C(1)–C(2) and C(3)–C(4). Therefore averaged bond distances and bond angles are cited in the discussion of the structure. The distances and angles found are listed in Table 4.

The distances S(2)–C(4) and S(1)–C(3) with an average value of 1.84 Å are possibly longer than the distances S(1)–C(1) and S(2)–C(2) with an average value of 1.79 Å. The distance C(3)–C(4) (1.47 Å) is

Table 4. Intramolecular distances (Å), angles (°) and estimated standard deviations

Bond	Distance	e.s.d. 10^{-3}
C(1)–Cl(1)	1.81	22
C(2)–Cl(2)	1.80	22
C(1)–C(2)	1.54	28
C(3)–C(4)	1.47	31
C(1)–S(1)	1.80	21
C(2)–S(2)	1.78	21
C(3)–S(1)	1.84	22
C(4)–S(2)	1.84	21
Non-bonded		
S(1)···Cl(1)	2.98	8
S(2)···Cl(2)	2.99	8
S(1)···S(2)	3.48	8
Bonds		
C(1)–C(2)–S(2)	116.6	1.4
C(2)–C(1)–S(1)	115.1	1.4
C(1)–S(1)–C(3)	99.9	0.9
C(2)–S(2)–C(4)	101.3	0.9
C(3)–C(4)–S(2)	110.8	1.4
C(4)–C(3)–S(1)	113.9	1.4
C(1)–C(2)–Cl(2)	107.2	1.4
C(2)–C(1)–Cl(1)	107.6	1.4
S(1)–C(1)–Cl(1)	110.9	1.2
S(2)–C(2)–Cl(2)	113.1	1.2

not significantly shorter than the 'normal' value of C(1)–C(2) (1.54 Å). A smaller value (1.49 Å) was also found for the corresponding C–C distance in 1,4-dithiane (Marsh, 1955). The carbon–chlorine bonds (average value 1.805 Å) do not deviate from the accepted value for this type of bond distance.

The C–S–C angle (100.6°) has the expected value for divalent sulphur linked to two atoms (Abrahams, 1956).

The S–C–C angles (112.3°) belonging to carbon atoms without chlorine atoms are significantly smaller than the corresponding S–C–C angles (115.8°) belonging to carbon atoms attached to the axial chlorine atoms. A comparison with 1,4-dithiane shows that the dihedral angle between the planes S(1)–C(3)–C(4) and S(2)–C(4)–C(3) has the 'normal' value of 70.9°. The corresponding dihedral angle between the planes S(2)–C(2)–C(1) and C(2)–C(1)–S(1) amounts to 58.7° and is about 10° lower than the dihedral angle in 1,4-dithiane which is 68.9°. The C(1)–Cl(1) and C(2)–Cl(2) vectors make an angle of 12.7°, and account, at least partially, for the observed dipole moment of 1.63 D (Kalff, 1964). The atoms Cl(1)–C(1)–C(2)–Cl(2) are non-planar. The dihedral angle between the planes Cl(1)–C(1)–C(2) and C(1)–C(2)–Cl(2) is 13.3°.

The conformational features of this molecule closely resemble those of *trans*-2,3-dichloro-1,4-dioxane and the corresponding dibromo compound (Altona & Romers, 1963*b*; Altona, Knobler & Romers, 1963*b*). A detailed account of these phenomena is given elsewhere (Altona, 1964*b*).

In Fig. 3 a view of the structure is given along [001]. Only half the intermolecular distances are shown.

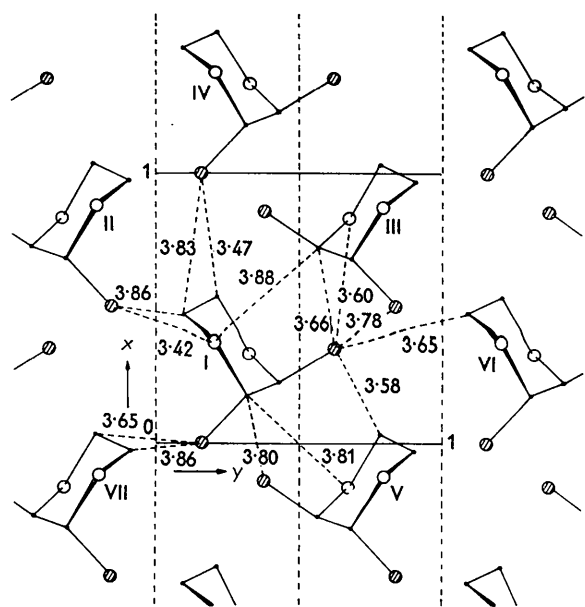


Fig. 3. A view of the structure along $[001]$. Only half the distances are given for the sake of clearness. Not showing is the distance $S(1)-S(2)$ (3.52 \AA) of the molecules with parameters x, y, z , and $x, y, z-1$, respectively.

Parameters of the molecules:

I	x	y	z
II	$x + \frac{1}{2}$	\bar{y}	$z + \frac{1}{2}$
III	$x + \frac{1}{2}$	$1 - y$	$z + \frac{1}{2}$
IV	$x + 1$	y	z
V	$x - \frac{1}{2}$	$1 - y$	$z + \frac{1}{2}$
VI	x	$y + 1$	z
VII	$x - \frac{1}{2}$	\bar{y}	$z + \frac{1}{2}$

No hydrogen atoms were drawn. The only distance not showing in the figure is that between $S(1)$ and $S(2)$ (3.52 \AA) of the molecules with parameters x, y, z and $x, y, z-1$ respectively.

According to Kitaigorodskii (1960) the space group Pn will occur with close packing only when certain spatial conditions are fulfilled. Apparently this is the case in this structure. As can be seen from Fig. 3 the molecule is surrounded by 14 neighbours.

We wish to express our thanks to Prof. E. Havinga who suggested this investigation, to Mrs E. V. M. Rutten-Keulemans, Dr H. J. V. H. Geise and Mr B. Hesper for help with the calculations and to Mr E. van Heijkoop for technical assistance.

The program used for calculation of unit-cell dimensions was developed by Miss J. van der Berg.

All calculations were carried out on the X1 computer of the University of Leiden.

References

ABRAHAM, S. C. (1956). *Quart. Rev. Chem. Soc., Lond.* **10**, 414.

Table 5. Calculated and observed structure factors

h k l	Pcalc	Pobs	h k l	Pcalc	Pobs
001	27.4	29.5	+7	27.4	29.5
010	35.1	37.6	+8	35.1	37.6
020	32.3	31.0	+9	32.3	31.0
030	17.5	16.8	+10	17.5	16.8
+10	20.5	20.6	+11	20.5	20.6
+20	40.6	39.6	+12	40.6	39.6
+30	59.0	58.2	+13	59.0	58.2
+40	75.5	75.0	+14	75.5	75.0
+50	89.5	89.1	+15	89.5	89.1
+60	100.0	99.7	+16	100.0	99.7
+70	107.5	107.0	+17	107.5	107.0
+80	112.0	111.5	+18	112.0	111.5
+90	113.5	113.0	+19	113.5	113.0
+100	111.5	111.0	+20	111.5	111.0
+110	94.4	93.8	+21	94.4	93.8
+120	69.9	69.2	+22	69.9	69.2
+130	49.2	48.5	+23	49.2	48.5
+140	28.0	27.3	+24	28.0	27.3
+150	16.9	16.2	+25	16.9	16.2
+160	6.4	6.1	+26	6.4	6.1
+170	1.7	1.5	+27	1.7	1.5
+180	0.0	0.0	+28	0.0	0.0
+190	0.0	0.0	+29	0.0	0.0
+200	0.0	0.0	+30	0.0	0.0
+210	15.1	14.4	+31	15.1	14.4
+220	29.4	28.6	+32	29.4	28.6
+230	42.8	42.0	+33	42.8	42.0
+240	54.3	53.5	+34	54.3	53.5
+250	63.1	62.2	+35	63.1	62.2
+260	68.8	68.0	+36	68.8	68.0
+270	71.1	70.3	+37	71.1	70.3
+280	70.1	69.3	+38	70.1	69.3
+290	66.1	65.3	+39	66.1	65.3
+300	59.1	58.3	+40	59.1	58.3
+310	49.1	48.3	+41	49.1	48.3
+320	37.1	36.3	+42	37.1	36.3
+330	24.1	23.3	+43	24.1	23.3
+340	11.1	10.3	+44	11.1	10.3
+350	0.0	0.0	+45	0.0	0.0
+360	0.0	0.0	+46	0.0	0.0
+370	0.0	0.0	+47	0.0	0.0
+380	0.0	0.0	+48	0.0	0.0
+390	0.0	0.0	+49	0.0	0.0
+400	0.0	0.0	+50	0.0	0.0
+410	17.4	16.7	+51	17.4	16.7
+420	34.8	34.1	+52	34.8	34.1
+430	51.2	50.5	+53	51.2	50.5
+440	66.6	65.9	+54	66.6	65.9
+450	80.0	79.3	+55	80.0	79.3
+460	91.4	90.7	+56	91.4	90.7
+470	100.8	100.1	+57	100.8	100.1
+480	108.2	107.5	+58	108.2	107.5
+490	113.6	112.9	+59	113.6	112.9
+500	116.0	115.3	+60	116.0	115.3
+510	115.4	114.7	+61	115.4	114.7
+520	111.8	111.1	+62	111.8	111.1
+530	95.2	94.5	+63	95.2	94.5
+540	69.6	68.9	+64	69.6	68.9
+550	44.0	43.3	+65	44.0	43.3
+560	18.4	17.7	+66	18.4	17.7
+570	2.8	2.1	+67	2.8	2.1
+580	0.0	0.0	+68	0.0	0.0
+590	0.0	0.0	+69	0.0	0.0
+600	0.0	0.0	+70	0.0	0.0
+610	15.6	14.9	+71	15.6	14.9
+620	31.2	30.5	+72	31.2	30.5
+630	46.8	46.1	+73	46.8	46.1
+640	62.4	61.7	+74	62.4	61.7
+650	78.0	77.3	+75	78.0	77.3
+660	93.6	92.9	+76	93.6	92.9
+670	109.2	108.5	+77	109.2	108.5
+680	124.8	124.1	+78	124.8	124.1
+690	140.4	139.7	+79	140.4	139.7
+700	156.0	155.3	+80	156.0	155.3
+710	171.6	170.9	+81	171.6	170.9
+720	187.2	186.5	+82	187.2	186.5
+730	202.8	202.1	+83	202.8	202.1
+740	218.4	217.7	+84	218.4	217.7
+750	234.0	233.3	+85	234.0	233.3
+760	249.6	248.9	+86	249.6	248.9
+770	265.2	264.5	+87	265.2	264.5
+780	280.8	280.1	+88	280.8	280.1
+790	296.4	295.7	+89	296.4	295.7
+800	312.0	311.3	+90	312.0	311.3
+810	327.6	326.9	+91	327.6	326.9
+820	343.2	342.5	+92	343.2	342.5
+830	358.8	358.1	+93	358.8	358.1
+840	374.4	373.7	+94	374.4	373.7
+850	390.0	389.3	+95	390.0	389.3
+860	405.6	404.9	+96	405.6	404.9
+870	421.2	420.5	+97	421.2	420.5
+880	436.8	436.1	+98	436.8	436.1
+890	452.4	451.7	+99	452.4	451.7
+900	468.0	467.3	+100	468.0	467.3

ALTONA, C. (1964a). *Acta Cryst.* **17**, 1282.
ALTONA, C. (1964b). Thesis, University of Leiden.
ALTONA, C., KNOBLER, C. & ROMERS, C. (1963a). *Acta Cryst.* **16**, 1217.
ALTONA, C., KNOBLER, C. & ROMERS, C. (1963b). *Trav. chim. Pays-Bas*, **82**, 1089.
ALTONA, C. & ROMERS, C. (1963a). *Acta Cryst.* **16**, 1225.
ALTONA, C. & ROMERS, C. (1963b). *Rec. Trav. chim. Pays-Bas*, **82**, 1080.
DORT, H. M. VAN (1963). Thesis, University of Leiden.
GEISE, H. J. V. H. (1964). Thesis, University of Leiden.
KALFF, H. T. & HAVINGA, E. (1962). *Rec. Trav. chim. Pays-Bas*, **81**, 282.
KALFF, H. T. (1964). Thesis, University of Leiden.
KITAIGORODSKII, A. J. (1960). *X-ray Crystallography of Organic Compounds*. Chapter 3, p. 95. New York: Consultants Bureau.
KWESTROO, W., MEYER, F. A. & HAVINGA, E. (1954). *Rec. Trav. chim. Pays-Bas*, **73**, 717.
MARSH, R. E. (1955). *Acta Cryst.* **8**, 91.
MOSSER, A. & ROMERS, C. (1964). *Acta Cryst.* **17**, 1217.
WESSELS, E. C. (1960). Thesis, University of Leiden.