

force constants derived in this way are given in Table 6. A totally independent derivation of bond force constants is possible by means of vibrational spectroscopy. Infrared stretching-force constants can be calculated accurately by complete assignment of the whole spectrum of the compound or approximately from the position of the symmetric stretching frequency of the anion in the compound (preferably in the solid state, although force constants have proved to be characteristic of the bond and fairly independent of the compound). For the compounds under discussion, the infrared force constants are 5.48 ( $K_2CrO_4$ ; Stammreich, Bassi & Sala, 1958), 10.26 ( $K_2SO_4$ ; Rosenthal, 1934), 5.2 ( $K_2MnO_4$ ; from the infrared results of Rocchiccioli, 1963), and 6.1 millidynes/Å ( $K_2SeO_4$ ; from the infrared results of Tarte & Nizet, 1964). Comparison of the force constants derived in these two ways enables the effective charges upon the chemical species in the crystal lattice to be estimated. For potassium chromate, potassium sulphate and possibly potassium manganate, the charges upon A (=Cr, S, Mn respectively), K and O appear to be close to 2.0, 1.0 and -1.0. For the purposes of this calculation, the structure of potassium selenate needs to be redetermined. Force constants derived from the crystallographic results with these values for the charges are rather smaller than those derived from vibrational spectroscopy, but they do show the right trend in going from potassium chromate to potassium sulphate. Closer agreement can be achieved by increasing the charge separation within the anions. However, forces other than electrostatic are important in the solid state and at least the short-range repulsive forces should be included before accurate force constants can be expected. However, several approximations must be

made before these short-range forces can be estimated and much of the value of the electrostatic calculation detailed above would be obscured.

It should be noted that, whilst there are significant differences in the chromium-oxygen bond lengths observed in potassium chromate, there will not necessarily be three observable infrared bands corresponding to the stretching modes. Since equation (2) appears to be valid, the absorption frequency for all three bonds would be expected to be nearly equal. The mere fact that a 'symmetric' stretching frequency is observable in the infrared spectrum is indicative of the fact that the anion is distorted in the solid state.

(iv) If this procedure is valid then any observed deviations must be assigned to specific causes. For example, in ammonium sulphate there should be extra forces due to hydrogen bonding, and calculations on this compound are in progress.

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## The Crystal and Molecular Structure of *cis*-1,3,5-Trichlorocyclohexane

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The crystal and molecular structure of *cis*-1,3,5-trichlorocyclohexane, a cyclic form of polyvinyl chloride, has been determined from X-ray data by direct methods and confirmed by Patterson techniques. The structure was refined by block-diagonal least-squares methods using three-dimensional data. The unit cell is monoclinic, space group  $C2/c$  with  $a=22.131$ ,  $b=8.803$ ,  $c=9.033$  Å,  $\beta=101.3^\circ$  and  $Z=8$ . The final  $R$  value based on 1399 independent observed reflexions is 6.3%.

### Introduction

The crystal and molecular structure of *cis*-1,3,5-trichlorocyclohexane, a cyclic trimer model of polyvinyl chloride, was determined as part of a systematic study of the conformational structure of polyvinyl chloride model compounds (Obereigner, Doskočilová & Štokr, 1968). Colourless crystals, purified in the final stage

by vacuum sublimation, were prepared by Dr B. Obereigner of the Institute of Macromolecular Chemistry, ČSAV, Prague.

### Experimental

The elementary cell parameters were derived by the least-squares technique from rotation and Weissen-

berg photographs calibrated with Si powder lines. Crystal data:

$C_6H_9Cl_3$ , M.W. 187.50, m.p. 61–62°C.

Monoclinic:

$a=22.131$ ,  $b=8.803$ ,  $c=9.033$  Å

$\beta=101.3^\circ$ ,  $V=1726$  Å<sup>3</sup>,  $F(000)=768$

$\lambda(Mo K\alpha)=0.7107$  Å,  $\mu(Mo K\alpha)=9.62$  cm<sup>-1</sup>

$Z=8$ ,  $D_c=1.44$ ,  $D_m=1.42$  (1) g.cm<sup>-3</sup> by flotation in aqueous potassium iodide.

Absent reflexions:  $hkl$  when  $h+k$  odd,  $h0l$  when  $l$  odd. Space group  $Cc$  or  $C2/c$ . The latter was indicated by statistical tests and confirmed by the subsequent refinement.

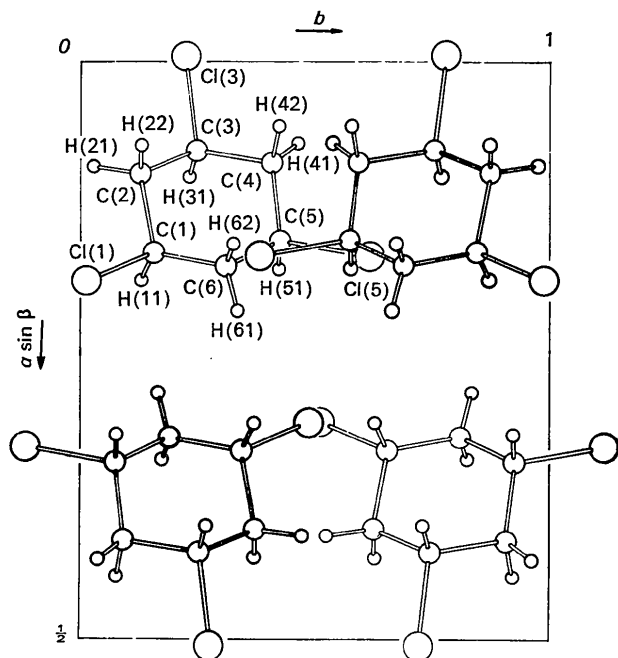


Fig. 1. The structure viewed along  $c$ .

Because of the slow evaporation of crystals in the atmosphere, they were sealed in Lindemann-glass tubes during the X-ray examination. Two independent sets of intensities were collected. The first one, kindly supplied by Professor G. D. Andreotti and Dr P. Sgarabotto (University of Parma) and provided by an automatic Siemens diffractometer on line with a Siemens 304/P computer, was used for the direct methods phase determination. The other set of intensities, measured with a manual Hilger & Watts diffractometer in our laboratory, was used for the Patterson synthesis and the final refinement of the structure. The latter set of intensities was measured by the  $\omega$ -scan method, with a scintillation counter and normal beam arrangement. Zirconium-filtered Mo  $K\alpha$  radiation was used, with pulse-height discrimination and Al attenuation filters. No corrections were made for absorption or extinction. Data were collected for 1803 reflexions, of which 1399 were observed and used for refinement. The absolute scale and approximate overall temperature factors were determined from all three-dimensional data by the Wilson method (Ahmed, Hall, Pippy & Huber, 1966). All the calculations were performed on an IBM 7040 computer.

#### Structure determination and refinement

The structure was determined by the symbolic-addition procedure of Karle & Karle (1966) with the revised programs of Ahmed *et al.* (1966). A Fourier synthesis of 276  $E$  values clearly showed the positions of all the chlorine and carbon atoms. As a check, a three-dimensional Patterson summation was performed and interpreted, giving an orientation of the molecule that was identical with that obtained from the  $E$  map. The  $R$  index ( $\sum ||F_o| - |F_c|| / \sum |F_o|$ , for observed reflexions only) for the trial structure was 33%. Refinement was by block-diagonal least squares, with the use of the pro-

Table 1. Final parameters and *e.s.d.*'s of non-hydrogen atoms

Temperature factor =  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

$B_i$  (Å<sup>2</sup>) are the temperature factors corresponding to the principal radii of the thermal motion ellipsoids.

The other values are all  $\times 10^5$ .

	$x/a$	$y/b$	$z/c$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$B_1$	$B_2$	$B_3$
C(1)	16366	15319	24846	279	1399	1358	-88	192	8	5.35	4.43	4.16
	17	40	39	7	39	38	65	26	27			
C(2)	9555	12735	18001	255	1310	2057	-194	72	-191	5.12	7.00	3.54
	17	39	50	7	40	56	76	32	26			
C(3)	7581	24665	6006	236	1525	1979	-378	-171	-96	4.94	7.69	3.44
	17	44	50	7	42	54	81	30	27			
C(4)	8617	40697	11915	252	1414	2139	18	76	4	4.58	7.22	4.38
	17	42	52	7	42	60	81	33	28			
C(5)	15395	42506	19031	264	1352	1527	-361	251	-119	4.88	5.29	3.78
	16	39	40	7	39	42	68	27	26			
C(6)	17538	31005	31297	283	1522	1448	-258	84	-152	5.94	5.04	3.87
	17	42	41	8	43	42	72	29	29			
Cl(1)	18836	1367	39401	384	1777	2066	1024	-31	-87	4.29	9.29	6.24
	6	13	14	3	13	15	24	10	10			
Cl(3)	-544	22356	-1812	304	2179	3926	184	-809	-203	6.80	16.16	3.83
	6	17	24	3	19	36	40	17	11			
Cl(5)	16700	61556	26210	382	1351	2327	-653	371	-252	7.23	7.73	3.72
	6	11	15	3	11	16	21	11	8			

gram of Ahmed *et al.* (1966). The quantity minimized is  $\sum w(|F_o| - |F_c|)^2$ . The nine hydrogen atoms were located from a difference map which was computed when the *R* index was 12%. Almost all hydrogen atoms were found at or near the expected positions. During the computation procedure their parameters were also refined, with starting thermal motion characteristics assumed to be the mean isotropic values of the adjacent carbon atoms. The initial weighting scheme was chosen arbitrarily, but that used in the final stages was

$$w = (11/|F_o|)^2 \sin^2 \theta \quad \text{for } |F_o| > 11$$

$$w = (|F_o|/11)^2 \sin^2 \theta \quad \text{for } |F_o| \leq 11.$$

This scheme was devised to remove the strong dependence of  $w(|F_o| - |F_c|)^2$  on  $|F_o|$  and  $\theta$ . The scattering factor curves were taken from *International Tables for X-ray Crystallography* (1962). Refinement appeared to be complete when the *R* index was 6.4%. None of the shifts indicated in the final cycle exceeded  $\frac{1}{3}$  of the corresponding e.s.d. Three additional L.S. cycles of the reflexions with  $\sin \theta/\lambda < 0.4 \text{ \AA}^{-1}$  with fixed parameters of Cl and C atoms were used for the further refinement of the hydrogen atoms. The shifts of the H parameters were reasonable and the *R* index from all reflexions decreased to 6.3%. The final atomic parameters with their estimated standard deviations are given in Tables 1 and 2. A three-dimensional final difference synthesis reveals some peaks in the vicinity of the Cl(3) atom and at the mid-points of the *c*-glide symmetrically related Cl(1) and Cl(1'), and Cl(5) and Cl(5') atoms. These peaks are as high as  $0.35 \text{ e.\AA}^{-3}$ . Negative peaks ( $-0.3 \text{ e.\AA}^{-3}$ ) appear in the neighbourhood of the Cl(1) and Cl(5) atoms. Elsewhere, the residual electron density stays between the limits  $\pm 0.2 \text{ e.\AA}^{-3}$ . The e.s.d. of electron density is about  $0.1 \text{ e.\AA}^{-3}$ . However, the agreement between the observed and calculated structure factors (Table 3) leaves no doubt as to the essential correctness of the proposed structure.

Table 2. Final parameters and e.s.d.'s of hydrogen atoms

	Fractional coordinates are $\times 10^4$ .			<i>B</i> ( $\text{\AA}^2$ )
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	
H(11)	1884	1346	1723	4.76
	32	65	74	1.58
H(21)	893	340	1276	2.61
	25	52	61	1.20
H(22)	660	1223	2568	1.65
	25	47	58	1.22
H(31)	972	2320	-212	2.14
	23	52	51	1.10
H(41)	709	4759	188	6.45
	37	69	92	1.71
H(42)	567	4189	1976	2.62
	24	55	62	1.22
H(51)	1767	4213	1218	2.79
	24	57	58	1.29
H(61)	2196	3291	3616	4.92
	31	66	72	1.51
H(62)	1517	3333	3922	3.94
	27	55	61	1.32

### Description of the structure and discussion

A projection of the structure along the *c* axis is shown in Fig. 1. The shortest intermolecular contacts are: C(1')-Cl(1), 3.66; C(5')-H(62), 3.43; Cl(1)-Cl(5''), 3.70; Cl(1')-H(11), 2.83; H(42)-H(42''), 2.85 Å, where a one, two or three-prime superscript to the arabic numerals means an atom related by a *c* glide, a translation by one unit cell in the  $-\mathbf{b}$  direction or a twofold rotation axis. All the intermolecular C-C distances are longer than 4 Å. The thermal motion ellipsoids (program written by Huml & Hlavatá, 1971) of the independent atoms are illustrated in Fig. 2. The molecular geometry of the non-hydrogen atoms is summarized in Fig. 3 and Tables 4 and 5. Valence bonds and angles involving hydrogen atoms are given

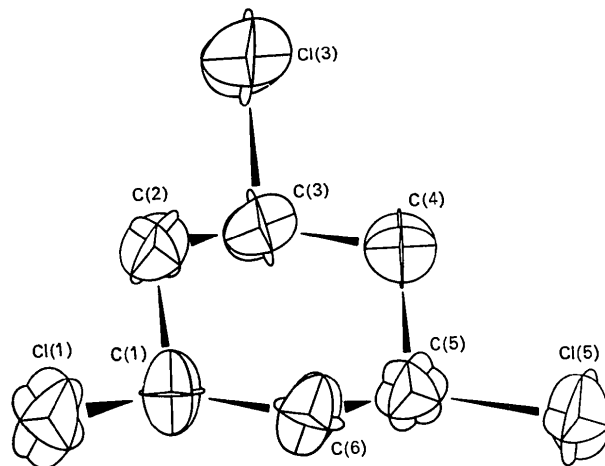


Fig. 2. Thermal-motion ellipsoids of 50% probability. Projection along  $c^*$ .

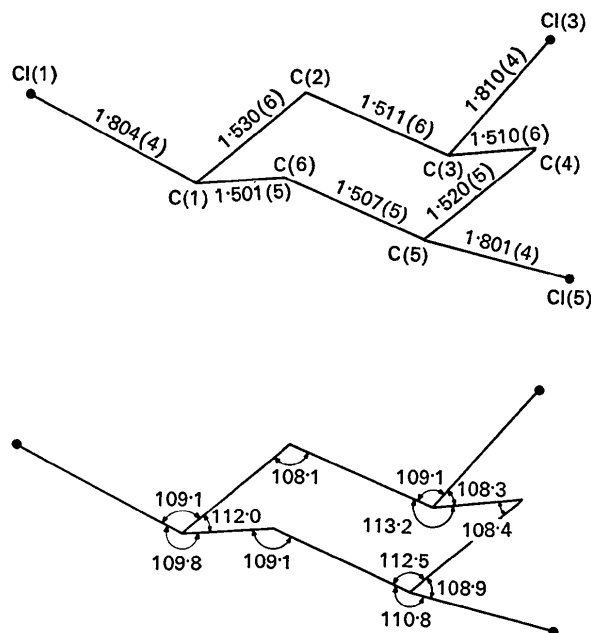


Fig. 3. The bond-lengths ( $\text{\AA}$ ) and valence angles ( $^\circ$ ) of the carbon and chlorine atoms. The e.s.d.'s of the angles are  $0.3^\circ$ .



