The Crystal Structure of 1,2,3-Trichlorobenzene; Neutron Diffraction and Constrained Refinements

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The crystal structure of 1,2,3-trichlorobenzene has been solved using neutron diffraction data. The crystal is monoclinic, $P2_1/c$ with $a=12\cdot66$ (1), $b=8\cdot258$ (3), $c=15\cdot05$ (2) Å and $\beta=114\cdot42$ (5)°. There are two symmetry-unrelated molecules in the asymmetric unit, and these were constrained during refinement to have the same shape and to have the same symmetry, $2mm$, as the molecule in the free state. Relaxing this constraint gave a significant improvement, indicating some distortion of the molecules from the free state shape. The temperature factors were also constrained, assuming the thermal motion to be predominantly of rigid-body character. When the model was extended to take account of the effect of the internal modes on the hydrogen atoms the agreement with experiment was sufficiently good that no significant improvement resulted on removing this constraint. This structure is therefore one of the best examples to date where the rigid-body model is appropriate, and has the added interest of requiring two independent sets of rigid-body motion tensors.

Introduction

At the outset we had two reasons for working on 1,2,3-trichlorobenzene. Certain dichlorobenzenes exhibit plastic crystal phase behaviour but we found no evidence for such behaviour in the present work. Our other reason for interest lies in the fact that small molecules lend themselves well to the technique of constrained refinement. Here we were particularly fortunate as the unit cell contains two sets of molecules with no symmetry relation between them. Consequently this provides a good example for constraining the independent molecules to have identical shapes. Other constraints can be imposed as the molecules have symmetry in the free state which is not used in the crystal space group, and also the molecules can be considered rigid in their thermal motion. We thus get further constraints on positional and thermal parameters.

Experimental

Although the structure had not been solved by X-ray diffraction we decided to attempt the solution using neutron diffraction data only. Large crystals were available from stock, and a sphere of diameter 5·15 mm was cut by hand.

Three-dimensional intensity data were taken from this crystal, using the Hilger and Ferranti automatic four-circle diffractometer at the Danish Atomic Energy Establishment, Risø. The moving crystal, fixed detector method was used with neutrons of wavelength 1·025 Å. The intensities obtained by this method compared well with intensities found by the moving-crystal, moving-detector method for a series of reflexions in the sin θ/λ

range investigated. The crystal was mounted with its b axis along the spindle axis (φ) of the instrument. In order to minimize the possibility of double Bragg scattering we followed the procedure of Duckworth, Willis & Pawley (1970), and rotated the crystal about the scattering vector through one of four angles ($\pm 3°$, $\pm 1\cdot5°$) in sequence. This certainly avoided simultaneous reflexion from (0k0) and (h0l) when (hkl) was being measured.

The monochromatic neutron beam was uniform to 3% over a circle of 6 mm diameter, and the crystal was positioned within this region. 3085 measurements were taken up to sin $\theta/\lambda=0\cdot5$ Å^{-1}. After averaging over symmetry-related reflexions we were left with 1194 observations satisfying the condition

$$F^2 > 2\sigma_s(F^2) .$$

Here the standard deviation $\sigma_s(F^2)$ is based on counting statistics.

After every ten observations a standard reflexion, 004, was measured. This varied in intensity by no more than 4%, and the slow variation was used to correct the observations for drift in the experimental conditions. Step scan measurements were used and counts for each step were recorded. The total scan interval was 3·44°, and two step sizes were employed. Within a central 2·64° the step size was 0·04°, and was 0·08° outside this region. The reflexion profiles were reduced to structure factors by the method of Lehmann & Larsen (1972), in which $\sigma_s(F^2)/F^2$ is minimized by choosing the best division between the peak region and the background.

Finally the structure factors were corrected for absorption using the table for absorption coefficients of a sphere given by Rouse, Cooper, York & Chakera (1970).

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Crystal data

The unit cell dimensions were determined from ten axial reflexions measured on the neutron diffractometer. The absent spectra were $(h0l)$, l odd and $(0k0)$, k odd. Space group: $P2_1/c$

$a = 12 \cdot 66$ (1) Å
$b = 8 \cdot 258$ (3)
$c = 15 \cdot 05$ (2)
$\beta = 114 \cdot 42$ (5)° at 298 °K
$Z = 8$

Density (calculated) $= 1 \cdot 68$ g.cm^{-3}.
Absorption coefficient for neutrons (calculated using 40 barns for the incoherent scattering cross-section for hydrogen) $= 1 \cdot 03$ cm^{-1} for $\lambda = 1 \cdot 025$ Å.
Crystals colourless.
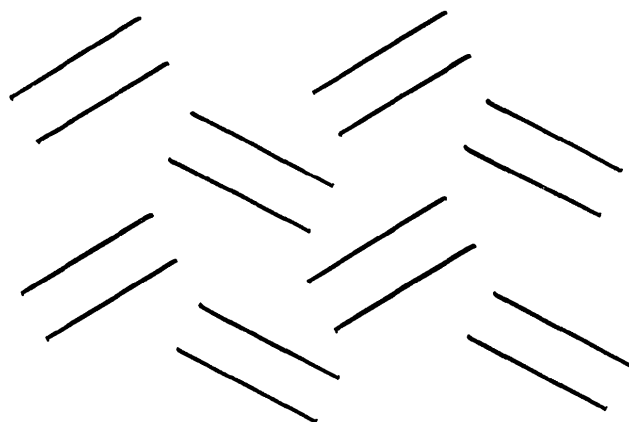

Fig. 3. Molecular parameters for the constrained refinements.

Fig. 1. Schematic arrangement of the molecules as seen in the (001) plane.
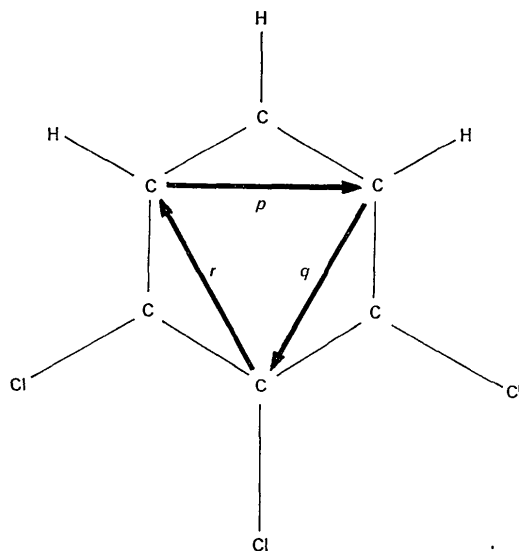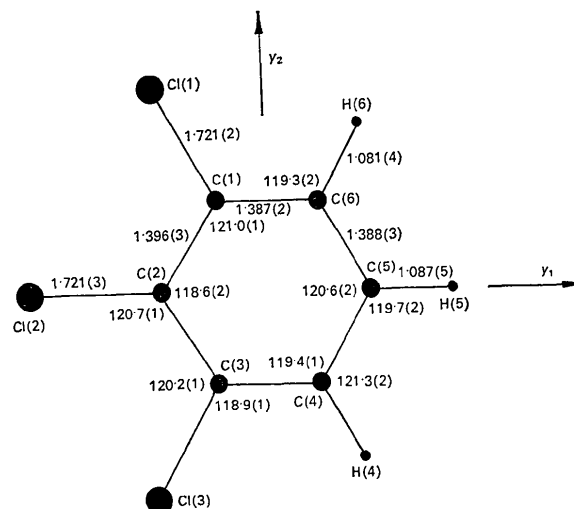

Fig. 2. Interatomic vectors within a molecule.

Solution of the structure

The structure was determined by means of the Patterson method, combined with packing considerations and constrained refinements using low-angle reflexions. Model building indicated a packing as shown schematically in Fig. 1 for a layer parallel to the (001) plane, and this gave approximate coordinates for the centres of the rings.

The negative scattering lengths of the hydrogen nuclei cause Patterson peaks corresponding to intermolecular vectors to be difficult to interpret. However the intramolecular vector pattern is easily recognized. A regular hexagon is expected about the origin with peaks all of the same height, caused by vectors p, q and r of Fig. 2. Further out the Cl–Cl vector parallel to p would give positive peaks defined by $2 \cdot 4$ p, whereas vectors parallel to q and r would give negative regions. The Patterson function showed the two inner hexagons corresponding to the two independent molecules but only one definite Cl–Cl vector. This sufficed to orient one molecule, but two attempts were necessary to orient the other.

Trial structures using molecular centres obtained by packing considerations and the orientations from Patterson maps were the starting points of some constrained refinements. Only the 68 innermost reflexions were used. Besides the overall scale factor only the molecular centres and orientations were allowed to vary. The correct structure refined from $R = 0 \cdot 6$ to $R = 0 \cdot 07$ in six cycles, whereas a trial structure with one molecule misoriented by 60° in its plane refined to $R = 0 \cdot 29$. Poorer trial structures resulted with $R \sim 0 \cdot 4$ to $0 \cdot 6$. The procedure is clearly unable to refine past a false minimum such as occurs for every 60° turn in the molecular plane, although the molecule centres moved by up to $0 \cdot 9$ Å.

Refinement

A number of constrained refinements and a final unconstrained refinement were done on the full data set of 1194 observations. As the course of refinement is not of general interest only the results will be presented.

The philosophy of constrained refinement has been discussed by Pawley (1971a), and we follow the procedure there described. First we dispense with crystal fractional coordinates (x) by transforming to orthogonal Å coordinates (x_i) using equation (P1) (i.e. equation (1) from Pawley, 1971a). The index i ranges over the atoms.

$$x_i = A \ x_i^c \qquad \text{(P1)}$$

$$A = \begin{pmatrix} 12\cdot66 & 0 & -6\cdot217 \\ 0 & 8\cdot258 & 0 \\ 0 & 0 & 13\cdot706 \end{pmatrix}$$

The arrangement of the new axes is shown in Fig. 4. The least-squares program uses this coordinate system for both atomic positions and temperature factors, and so the latter appear in Å² units.

The crystal is composed of molecules which in the free state have symmetry $2mm$.* It is standard practice to refine all the atomic positions and end with a discussion of the molecular symmetry. This would require averaging over bonds related by the molecular symmetry. In our procedure, however, the molecules are constrained to this symmetry and to being identical. The best molecule which results is that of Fig. 3. In this figure the bond lengths and angles have been corrected for the effects of libration.

To construct the crystal structure we proceed as follows. The atomic positions of Table 1 are used to generate the positions of C(3), C(4), Cl(3) and H(4), thus giving coordinates for all atoms of one molecule. Let us call these coordinates y_i. We now rotate these coordinates using a matrix R, which is determined by the Euler angles φ, θ, ψ [see equation (P21)], and translate by a vector x_o. We therefore get the coordinates of one molecule,

$$x_i = R \ y_i + x_o$$

in the crystal (orthogonal) coordinates. A similar transformation positions the second molecule, and the final refined values of the necessary parameters are given in Table 2. Tables 1 and 2 involve 24 parameters which determine the positions of 24 atoms. It is clear that there is one redundancy in these parameters, for if all the y_1 coordinates are allowed to vary the molecule can then move along the y_1 axis, and this variation is already allowed for by having all the molecular positions coordinates variable. Thus we allow only 23 of the parameters to be varied in a least-squares fit of the observations. The molecule is allowed to alter its shape as

* '$2mm$' may not be the standard orientation, but is used here because of the choice of axes for Fig. 3.

the data demand, but the crystallographically independent molecules have the same shape and retain full $2mm$ symmetry. We therefore call this the identical symmetric molecule constraint, (ISM, in Table 5).

Table 1. The final coordinates necessary to define the molecule, uncorrected for the effects of libration

	y_1	y_2
C(1)	−0·700 (*) Å	1·196 (1) Å
C(2)	−1·411 (2)	0
C(5)	1·367 (3)	0
C(6)	0·682 (2)	1·202 (2)
Cl(1)	−1·534 (2)	2·695 (1)
Cl(2)	−3·126 (2)	0
H(5)	2·450 (5)	0
H(6)	1·205 (4)	2·144 (4)

* This parameter was kept fixed during refinement to avoid least-squares matrix singularity. All y_3 coordinates were zero.
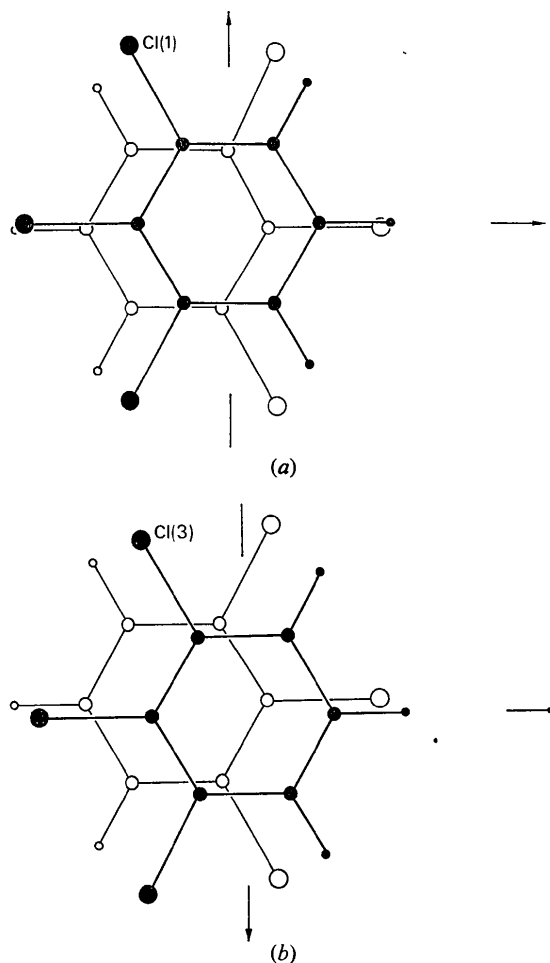

Fig. 4. The arrangement of the molecules about the centres of symmetry, (a) type 1, (b) type 2. The viewpoint is from perpendicular to the molecular planes, and the heavily outlined molecules are uppermost. The axes indicated are for these upper molecules, and correspond to Fig. 3.

Table 2. *Euler angles, in radians, and positions for the origins of the molecules in the crystal structure, in* Å

	Molecule 1	Molecule 2
φ	3·9323 (4)	2·3988 (4)
θ	1·7526 (6)	1·7343 (6)
ψ	−2·4765 (6)	−3·8112 (6)
$(x_0)_1$	5·535 (1)	−0·796 (1)
$(x_0)_2$	2·607 (1)	1·504 (1)
$(x_0)_3$	−0·573 (1)	0·710 (1)

The other major constraint we apply involves the anisotropic temperature factors. For small molecules the assumption that the thermal motion is predominantly of the rigid-body type is very good. We therefore assume that the anisotropic temperature factors for each crystallographically independent molecule are determined by two sets of three tensors, T, L and S. These give respectively the mean-square translational displacement, the mean-square librational displacement, and the screw rotation correlation (Schomaker & Trueblood, 1968). In each set of T, L and S there are 20 parameters, determining the 72 anisotropic temperature factors for each molecule through equation (P31). We call this the TLS constraint.

It has recently been shown that a great improvement in the rigid-body motion model is obtained by giving extra consideration to the hydrogen atoms. These atoms suffer the most displacement in the internal vibrational modes, and although we may neglect the effect of these modes on the heavier atoms we approximate too much by neglecting them altogether. Pawley (1971a) shows how effective an extra isotropic temperature factor contribution for the hydrogen atoms is when the TLS constraint is used. An extra anisotropic contribution is significantly more effective (Pawley, 1971b). Only three extra parameters are needed for the whole of the structure, for we assume that the effect of internal modes is the same for all hydrogen atoms in both molecules. We call this extended model the TLS⁺ constraint, and the values we find for the extra three parameters are: extra mean-square displacement along the C–H bond=0·006 (2) Å², extra mean-square displacement across the C–H bond in the molecular plane= 0·012 (2) Å², extra mean-square displacement out of the molecular plane=0·020 (3) Å². These agree very well with the results previously published.

In using the TLS⁺ constraint we have to decide where to place the origin of coordinates, as the values of T and S depend on this choice. The most convenient origin is the centre of mass of the molecule, because the components of S will then be small. We can therefore start refinement with all the coefficients of S zero, and refinement is smooth. If on the other hand we choose the origin of the unit cell, zero coefficients of S may well not give positive definite temperature factors and refinement may be unstable. The final values for T, L and S and the centres of mass from the fully constrained refinement are given in Table 3.

Table 3. *Final values of* T, L *and* S *for the TLS⁺ model*

The origins chosen for the calculations were the centres of mass.

T, L and S for molecule type 1

$$T = \begin{pmatrix} 0·0408\ (6) & −0·0062\ (7) & 0·0029\ (4) \\ & 0·0412\ (7) & −0·0064\ (5) \\ & & 0·0376\ (6) \end{pmatrix} \text{Å}^2$$

$$L = \begin{pmatrix} 22·7\ (5) & 0·0\ (6) & −1·2\ (5) \\ & 23·7\ (4) & 1·5\ (5) \\ & & 22·5\ (7) \end{pmatrix} (\text{deg})^2$$

$$S = \begin{pmatrix} * & −0·24\ (1) & 0·17\ (1) \\ 0·03\ (1) & * & 0·03\ (1) \\ −0·09\ (1) & −0·10\ (1) & * \end{pmatrix} \text{Å.deg}$$

* $S_{33}-S_{22} = -0·03$ (2), $S_{11}-S_{33} = -0·02$ (2).
Centre of mass: 4·783, 3·003, 0·259 Å.

T, L and S for molecule type 2

$$T = \begin{pmatrix} 0·0399\ (6) & 0·0077\ (7) & 0·0010\ (4) \\ & 0·0434\ (7) & −0·0038\ (5) \\ & & 0·0399\ (6) \end{pmatrix} \text{Å}^2$$

$$L = \begin{pmatrix} 25·6\ (6) & 0·2\ (6) & 0·2\ (5) \\ & 16·2\ (4) & 2·8\ (5) \\ & & 24·8\ (7) \end{pmatrix} (\text{deg})^2$$

$$S = \begin{pmatrix} * & 0·23\ (1) & −0·06\ (1) \\ −0·04\ (1) & * & −0·00\ (1) \\ 0·09\ (1) & −0·18\ (1) & * \end{pmatrix} \text{Å.deg}$$

* $S_{33}-S_{22} = 0·07$ (2), $S_{11}-S_{33} = 0·05$ (2).
Centre of mass: −1·565, 1·064, −0·083 Å.

Besides the overall scale factor one other parameter is used, namely an extinction parameter. We follow Zachariasen's (1967) method, but can take the simple equation (P26) for a spherical sample. The value of the coefficient, appropriate to the scale of the list of F_{obs} in Table 4, is $2·0(3) \times 10^{-8}$.

Discussion

The value of a constrained refinement lies in the ability to make conclusions, either physical or chemical, using a proper statistical test. Hamilton (1965) has discussed the R value ratio test, and gives the statistical distribution for

$$\mathcal{R} = \left[\frac{R_w(\text{constrained})}{R_w(\text{unconstrained})} \right]^{1/2}$$

where R_w is the weighted sum of squared deviations. Percentage points of this distribution appropriate to our refinements are given in Table 5, calculated by the approximation given by Pawley (1970). In this same Table we present the results of the constrained refinements and the final completely unconstrained refinement. The values of the conventional R value $\sum |F_{obs}| - |F_{calc}|/\sum|F_{obs}|$, and R_w for the four refinements considered are:

	ISM & TLS⁺	ISM	TLS⁺	Unconstrained
R	4·4	4·2	4·1	3·9
R_w	3860	3470	3410	3030

Table 4. *Observed and calculated structure factors* × 100 *and the standard deviations used in the weighting scheme*

The model used for the calculated values was the TLS⁺ model, without any positional constraint. The scattering lengths used were 0·66 for C, 0·96 for Cl and −0·374 for H.

h	k	l	Fobs	Fcal	σF
0	0	-2	1270	1249	17
0	0	-4	1458	1457	20
0	0	-6	124	125	6
0	0	-8	434	440	8
0	0	-10	98	65	11
0	0	-12	126	114	11
0	1	-2	83	85	4
0	1	-3	100	95	5
0	1	-5	102	107	6
0	1	-6	85	82	7
0	1	-7	85	65	9
0	1	-10	121	135	8
0	1	-11	297	290	8
0	1	-13	109	110	14
0	2	0	426	401	7
0	2	-1	73	51	6
0	2	-2	134	125	5
0	2	-3	206	208	5
0	2	-4	665	664	10
0	2	-5	767	767	11
0	2	-6	794	795	12
0	2	-7	186	201	6
0	2	-8	240	231	6
0	2	-9	270	271	7
0	2	-10	444	455	9
0	2	-11	975	976	14
0	2	-12	131	134	11
0	2	-13	252	260	8
0	3	-2	85	73	7
0	3	-3	65	19	8
0	3	-5	216	218	6
0	3	-8	79	62	12
0	3	-11	178	168	9
0	4	0	636	634	11
0	4	-1	858	870	13
0	4	-2	167	169	6
0	4	-3	178	163	6
0	4	-5	1071	1083	16
0	4	-6	278	274	7
0	4	-7	502	511	9
0	4	-9	106	47	12
0	4	-10	292	290	8
0	4	-11	226	230	9
0	4	-12	100	80	12
0	5	-4	96	69	10
0	5	-7	76	64	10
0	5	-8	187	185	9
0	5	-9	127	121	10
0	6	0	746	778	13
0	6	-1	178	151	8
0	6	-2	480	490	9
0	6	-3	507	531	9
0	6	-4	279	276	8
0	6	-6	352	358	8
0	6	-7	425	423	9
0	6	-9	102	106	12
0	8	0	135	27	14
0	8	-1	134	129	10
0	8	-3	112	107	10
1	0	12	216	217	8
1	0	10	372	382	8
1	0	8	176	174	6
1	0	6	236	230	6
1	0	4	158	162	4
1	0	2	173	167	4
1	0	-2	76	69	3
1	0	-4	203	207	4
1	0	-6	545	545	9
1	0	-8	374	377	7
1	0	-10	318	322	7
1	0	-12	520	526	10
1	0	-14	277	275	8
1	1	13	118	119	10
1	1	12	223	218	9
1	1	10	353	347	8
1	1	9	168	170	8
1	1	7	330	327	7
1	1	6	897	918	13
1	1	5	441	439	8
1	1	4	218	224	5
1	1	3	230	224	5
1	1	2	104	99	4
1	1	1	721	702	10
1	1	0	224	212	4
1	1	-1	655	628	9
1	1	-2	325	326	5
1	1	-3	401	399	6
1	1	-4	588	595	9
1	1	-5	77	51	8
1	1	-6	449	454	8
1	1	-7	245	244	6
1	1	-8	745	762	11
1	1	-9	187	188	6
1	1	-10	565	562	10
1	1	-11	272	280	7
1	1	-12	467	477	9
1	1	-13	147	128	10
1	2	12	107	48	14
1	2	10	132	58	11
1	2	8	73	44	11
1	2	5	68	62	10
1	2	4	220	221	5
1	2	3	84	88	6
1	2	2	307	299	6
1	2	1	515	509	8
1	2	0	75	73	5
1	2	-1	475	448	7
1	2	-2	190	179	4
1	2	-3	374	368	6
1	2	-4	226	216	5
1	2	-5	177	175	5
1	2	-6	240	237	6
1	2	-8	269	275	6
1	2	-10	254	255	7
1	2	-11	145	164	9
1	2	-12	275	276	8
1	3	12	509	519	10
1	3	11	318	320	9
1	3	10	1200	1192	18
1	3	9	265	258	7
1	3	8	123	116	8
1	3	7	138	142	7
1	3	6	641	654	10
1	3	4	237	234	6
1	3	3	128	131	6
1	3	2	120	119	5
1	3	1	243	242	5
1	3	0	170	165	5
1	3	-1	200	194	5
1	3	-2	333	331	6
1	3	-3	64	75	9
1	3	-4	89	78	8
1	3	-5	271	275	6
1	3	-6	75	57	11
1	3	-8	347	348	7
1	3	-9	178	178	7
1	3	-10	436	450	9
1	3	-11	194	182	9
1	3	-12	325	320	8
1	3	-13	228	228	8
1	4	10	136	112	11
1	4	9	86	26	13
1	4	8	175	168	8
1	4	7	82	77	9
1	4	6	199	208	7
1	4	5	109	95	9
1	4	4	70	20	10
1	4	3	86	80	10
1	4	2	293	294	6
1	4	-1	238	239	6
1	4	-2	205	191	6
1	4	-3	98	73	9
1	4	-4	84	95	10
1	4	-5	150	139	6
1	4	-6	121	128	7
1	4	-7	82	50	12
1	4	-8	93	64	12
1	4	-9	183	196	8
1	4	-10	364	372	8
1	4	-11	158	160	9
1	4	-12	365	358	9
1	5	7	220	232	8
1	5	5	338	341	7
1	5	4	290	295	7
1	5	3	161	163	7
1	5	2	86	69	10
1	5	1	565	580	9
1	5	0	140	149	6
1	5	-1	555	568	9
1	5	-2	91	77	10
1	5	-3	194	205	6
1	5	-4	286	285	7
1	5	-5	198	221	7
1	5	-7	525	520	9
1	5	-8	441	438	9
1	5	-9	151	94	10
1	5	-10	156	141	10
1	5	-11	124	125	12
1	6	8	181	170	10
1	6	6	112	98	12
1	6	5	101	103	9
1	6	4	247	259	8
1	6	3	157	146	9
1	6	2	115	101	10
1	6	0	74	81	10
1	6	-1	191	186	7
1	6	-2	104	64	11
1	6	-4	277	281	8
1	6	-7	401	406	8
1	6	-8	195	186	9
1	7	6	451	459	9
1	7	5	625	634	12
1	7	4	286	277	9
1	7	3	132	120	10
1	7	2	208	205	8
1	7	1	92	32	12
1	7	0	132	114	9
1	7	-1	236	234	7
1	7	-2	111	118	11
1	7	-5	170	193	10
1	7	-6	282	253	9
1	7	-7	325	334	8
1	8	3	121	134	10
1	8	2	206	208	8
1	8	1	151	162	9
1	8	0	92	33	13
1	8	-1	144	111	10
1	8	-3	104	120	10
1	8	-4	236	227	8
2	0	12	112	103	11
2	0	10	249	255	7
2	0	8	878	886	13
2	0	6	534	544	9
2	0	4	737	732	11
2	0	2	168	166	4
2	0	0	257	242	4
2	0	-2	155	127	3
2	0	-4	148	150	4
2	0	-6	878	874	13
2	0	-8	440	437	8
2	0	-10	670	680	11
2	0	-12	276	292	7
2	1	12	90	79	12
2	1	11	325	318	8
2	1	9	447	464	9
2	1	8	451	463	8
2	1	7	113	120	7
2	1	6	193	174	6
2	1	5	175	185	5
2	1	4	213	213	5
2	1	3	121	122	5
2	1	2	59	51	8
2	1	1	227	225	5
2	1	0	1029	1016	14
2	1	-2	1060	1042	14
2	1	-3	239	236	5
2	1	-4	127	125	4
2	1	-6	186	188	5
2	1	-7	329	328	6
2	1	-8	389	403	7
2	1	-9	103	109	8
2	1	-10	563	567	10
2	1	-11	425	432	8
2	1	-12	113	111	7
2	1	-13	334	337	8
2	2	12	327	297	8
2	2	11	153	170	10
2	2	9	185	187	8
2	2	8	281	274	7
2	2	7	78	67	12
2	2	6	236	240	6
2	2	5	881	897	13
2	2	4	469	471	8
2	2	3	254	258	6
2	2	2	378	380	7
2	2	1	945	943	13
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6	7	-5	203	205	8
7	0	6	252	237	8
7	0	2	72	82	11
7	0	0	302	299	6
7	0	-2	657	670	10
7	0	-4	219	233	6
7	0	-6	584	584	10
7	0	-8	121	122	7
7	0	-10	125	113	8
7	0	-12	465	471	8
7	1	7	83	62	14
7	1	6	127	110	10
7	1	5	485	490	8
7	1	4	293	294	8
7	1	3	309	339	7
7	1	2	134	100	9
7	1	1	654	649	11
7	1	0	401	403	8
7	1	-1	261	262	6
7	1	-2	604	619	10
7	1	-3	317	317	7
7	1	-4	307	293	7
7	1	-5	75	71	11
7	1	-6	618	630	10
7	1	-7	480	487	9
7	1	-8	211	219	6
7	1	-10	96	53	10
7	1	-11	461	463	9
7	1	-12	143	136	11
7	2	5	243	250	8
7	2	4	454	462	9
7	2	3	126	134	8
7	2	2	293	299	7
7	2	1	214	121	7
7	2	0	98	55	10
7	2	-1	152	152	6
7	2	-2	271	272	7
7	2	-4	109	119	7
7	2	-5	89	85	9
7	2	-6	260	259	6
7	2	-7	213	205	6
7	2	-8	93	86	9
7	2	-9	152	150	7
7	2	-11	285	288	7
7	2	-12	110	113	9
7	2	-13	178	187	9
7	2	-14	82	127	11
7	3	6	321	334	9
7	3	5	185	134	9
7	3	4	655	649	11
7	3	3	296	303	7
7	3	1	128	141	7
7	3	0	90	67	9
7	3	-1	88	104	10
7	3	-3	133	138	7
7	3	-4	81	25	11
7	3	-5	82	39	12
7	3	-6	70	54	11
7	3	-7	80	25	11
7	3	-9	167	171	8
7	3	-10	396	408	9
7	3	-11	96	80	14
7	3	-12	532	580	11
7	3	-13	159	151	11
7	4	4	273	271	8
7	4	3	108	120	11
7	4	2	162	150	6
7	4	1	173	193	7
7	4	0	176	178	7
7	4	-1	436	449	9
7	4	-2	320	321	7
7	4	-3	135	116	9
7	4	-5	121	143	8
7	4	-6	298	305	7
7	4	-7	458	461	9
7	4	-8	169	175	7
7	4	-9	86	82	10
7	4	-10	204	192	9
7	4	-11	159	137	11
7	5	4	155	146	9
7	5	3	131	102	12
7	5	2	213	222	9
7	5	1	296	282	9
7	5	0	648	646	11
7	5	-1	398	408	7
7	5	-2	856	870	15
7	5	-3	417	425	8
7	5	-4	307	324	8
7	5	-5	395	402	8
7	5	-6	822	835	12
7	5	-7	473	475	9
7	5	-8	165	162	10
7	5	-11	272	271	8
7	6	2	133	135	10
7	6	1	95	42	14
7	6	0	218	214	9
7	6	-1	373	353	9
7	6	-2	85	74	11
7	6	-3	265	269	8
7	6	-4	162	135	10
7	6	-5	285	291	8
7	6	-6	210	226	9
7	6	-7	215	208	9
7	6	-8	86	92	14
8	0	6	433	400	10
8	0	4	190	194	8
8	0	2	102	105	9
8	0	0	174	176	7
8	0	-2	572	580	10
8	0	-4	875	882	13
8	0	-6	567	567	10
8	0	-10	236	198	7
8	0	-12	663	675	11
8	0	-14	733	736	12
8	1	6	286	277	8
8	1	5	125	120	10
8	1	4	494	430	10
8	1	3	100	104	10
8	1	1	79	86	12
8	1	0	91	65	11
8	1	-1	218	229	6
8	1	-2	270	280	7
8	1	-3	243	248	6
8	1	-4	131	140	8
8	1	-5	256	265	6
8	1	-6	172	168	7
8	1	-7	310	317	7
8	1	-9	136	136	7
8	1	-11	363	355	8
8	1	-12	406	412	9
8	1	-13	430	407	10
8	1	-14	126	151	10
8	2	6	133	158	9
8	2	5	431	434	9
8	2	4	420	408	8
8	2	3	239	242	7
8	2	2	275	271	7
8	2	1	233	244	7
8	2	-1	118	106	7
8	2	-2	132	120	8
8	2	-3	255	256	7
8	2	-4	280	278	7
8	2	-5	237	233	7
8	2	-6	82	85	9
8	2	-7	288	287	7
8	2	-8	134	119	8
8	2	-9	184	203	8
8	2	-10	233	232	8
8	2	-12	312	293	8
8	2	-13	256	266	9
8	2	-14	83	90	11
8	3	5	144	137	10
8	3	4	210	193	9
8	3	3	184	175	9
8	3	2	175	187	8
8	3	1	124	111	10
8	3	0	155	156	7
8	3	-1	200	204	7
8	3	-2	280	285	7
8	3	-3	119	115	7
8	3	-6	261	255	7
8	3	-7	272	258	7
8	3	-8	399	393	8
8	3	-10	139	193	8
8	3	-11	163	161	8
8	3	-12	133	128	10
8	4	4	264	265	8
8	4	3	131	98	11
8	4	0	531	548	11
8	4	-2	305	309	7
8	4	-5	122	79	11
8	4	-6	361	370	8
8	4	-7	183	180	6
8	4	-8	634	655	11
8	4	-11	433	413	10
8	4	-12	370	382	9
8	5	1	179	156	9
8	5	-3	90	57	13
8	5	-5	155	147	10
8	5	-7	96	69	12
8	5	-9	142	136	9
8	6	0	174	186	8
8	6	-1	129	114	10
8	6	-4	332	279	9
8	6	-6	115	76	12
9	0	4	660	651	12
9	0	2	451	456	9
9	0	0	252	242	7
9	0	-6	159	160	7
9	0	-8	120	85	10
9	0	-10	149	146	8
9	0	-12	624	631	11
9	0	-14	438	430	9
9	1	5	340	339	8
9	1	2	350	353	8
9	1	1	298	289	7
9	1	0	116	97	11
9	1	-1	281	285	7
9	1	-2	215	236	7
9	1	-3	142	133	8
9	1	-4	153	171	7
9	1	-5	282	292	7
9	1	-6	346	352	7
9	1	-7	149	136	8
9	1	-8	135	124	8
9	1	-9	340	356	6
9	1	-10	172	183	6
9	1	-12	459	429	10
9	1	-13	234	237	9
9	1	-14	96	80	12
9	2	3	156	146	10
9	2	1	104	101	12
9	2	-1	659	675	10
9	2	-2	527	545	10
9	2	-3	430	432	8
9	2	-4	278	286	7
9	2	-5	320	325	7
9	2	-6	522	543	9
9	2	-7	626	643	11
9	2	-8	292	284	6
9	2	-9	548	542	10
9	3	3	122	126	11
9	3	2	114	124	11
9	3	1	200	202	5
9	3	0	84	101	11
9	3	-1	149	155	7
9	3	-2	825	840	13
9	3	-3	246	257	7
9	3	-4	378	391	8
9	3	-5	310	320	7
9	3	-6	770	784	12
9	3	-7	119	112	9
9	3	-8	493	501	9
9	4	2	131	118	11
9	4	0	126	119	11
9	4	-1	95	106	13
9	4	-3	121	87	10
9	4	-6	102	53	12
9	4	-7	134	147	10
9	4	-11	169	188	9
9	5	0	87	74	14
9	5	-1	175	152	9
9	5	-3	215	213	8
9	5	-5	142	151	11
9	5	-6	121	120	10
9	5	-7	180	185	9
9	5	-9	107	114	11
10	0	2	297	301	9
10	0	-2	146	138	8
10	0	-4	418	418	7
10	0	-6	515	504	8
10	0	-8	181	151	8
10	0	-12	393	358	9
10	1	3	185	169	9
10	1	2	217	219	9
10	1	0	124	78	12
10	1	-2	109	73	8
10	1	-3	150	146	8
10	1	-4	209	222	8
10	1	-6	189	172	7
10	1	-7	210	206	7
10	1	-8	123	97	10
10	1	-9	106	116	9
10	1	-11	217	211	8
10	1	-12	143	138	10
10	2	0	195	179	9
10	2	-3	130	133	7
10	2	-4	140	144	7
10	2	-6	152	145	7
10	2	-7	120	117	8
10	2	-8	93	86	12
10	2	-9	149	127	10
10	2	-10	357	346	8
10	3	2	134	141	14
10	3	-2	208	288	8
10	3	-4	415	413	9
10	3	-6	364	358	8
10	3	-8	244	252	8
10	3	-9	91	87	13
10	4	0	93	57	13
10	4	-1	239	254	8
10	4	-2	103	50	13
10	4	-4	85	76	13
10	4	-6	154	154	9
10	4	-7	101	72	13
10	4	-8	118	100	11
10	4	-9	182	188	8
10	5	-3	89	75	13
10	5	-5	92	17	14
11	0	0	333	351	9
11	0	-2	247	235	8
11	0	-4	540	538	10
11	0	-6	201	212	8
11	0	-8	555	555	11
11	0	-12	267	258	8
11	1	1	234	220	8
11	1	0	97	47	14
11	1	-1	252	240	9
11	1	-2	202	200	9
11	1	-3	202	187	8
11	1	-4	543	539	11
11	1	-5	602	583	11
11	1	-6	176	182	8
11	1	-7	438	435	9
11	1	-8	532	545	10
11	1	-11	225	215	8
11	1	-12	121	130	10
11	2	-1	215	181	9
11	2	-2	176	161	9
11	2	-3	210	199	9
11	2	-4	95	95	8
11	2	-5	112	92	11
11	2	-6	91	56	13
11	2	-7	105	91	13
11	2	-9	137	159	10
11	2	-10	205	172	9
11	2	-11	126	92	11
11	3	-1	236	237	8
11	3	-2	81	84	13
11	3	-3	251	241	8
11	3	-4	129	151	10
11	3	-5	108	59	13
11	3	-7	108	86	13
11	3	-8	134	132	11
11	3	-9	379	381	9
11	4	-5	94	97	12
12	0	-2	213	234	8
12	0	-4	209	196	10
12	0	-6	275	269	9
12	0	-8	168	158	10
12	0	-10	333	325	8
12	1	-2	81	65	13
12	1	-4	382	405	9
12	1	-6	683	665	12
12	1	-8	385	406	8
12	1	-10	110	140	9
12	2	-3	123	119	10
12	2	-9	126	82	10

The weighting scheme used estimated standard deviations,

$$\sigma(F) = [\sigma_s(F^2) + 1.025\ F^2]^{1/2} - |F|$$

where $\sigma_s(F^2)$ is derived from counting statistics. This gave values of $||F_{obs}| - |F_{calc}||/\sigma^2(F)$ which were independent of F when divided into classes of F, as expected for a proper weighting scheme.

The difference between constrained and unconstrained models in row (a) of Table 5 is simply that the TLS$^+$ model has been relaxed. This is true also for row (d). In both cases the value for $\mathscr{R}$ lies between the 25% point and the 10% point in the $\mathscr{R}$-distribution. We conclude that the improvement obtained on removing the constraints is not statistically significant. It is therefore probably safe to state that the improvement is not physically significant. If we follow Pawley (1971a), equation (P52), and calculate

$$\mathscr{S}^{TLS+} = (\mathscr{R} - 1)/[\mathscr{R}(1\%) - 1]$$

we get a value 0.88, which is smaller than all the values listed by Pawley (1971a) for molecules such as naphthalene and hexamethylenetetramine. However we must remember that the TLS$^+$ model is a great improvement over the TLS model, and the comparisons cited used the TLS model alone. Nevertheless we can conclude that the present structure is served better by the rigid-body motion than any considered heretofore. Consequently, we do not present the individual atomic anisotropic temperature factors from the unconstrained refinement as these contain no information not included in the TLS$^+$ model parameters. The anisotropic temperature factors corresponding to TLS$^+$ are given in Table 6.
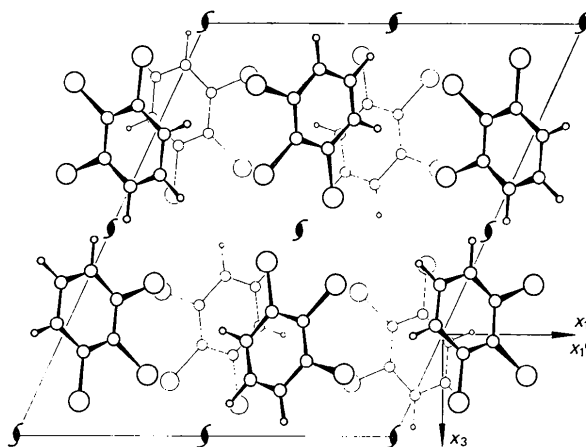

Fig. 5. Projection of the structure down the diad axis. One unit cell is depicted. The origin for all calculations is at a centre of symmetry, and the arrows indicating the directions for the orthogonal coordinates point from this origin.

Table 5. *Comparison of the ratio $\mathscr{R}$ with the percentage points of the $\mathscr{R}$-distribution*

N and n are the number of parameters in the unconstrained and constrained models respectively.

	Constraint used	Model with less constraints	n	N	$\mathscr{R}$	25%	10%	1%	0·1%
(a)	ISM & TLS$^+$	ISM	68	169	1·055	1·053	1·057	1·066	1·073
(b)	ISM	unconstrained	169	218	1·070	1·028	1·032	1·038	1·044
(c)	ISM & TLS$^+$	TLS$^+$	68	117	1·064	1·025	1·029	1·035	1·040
(d)	TLS$^+$	unconstrained	117	218	1·061	1·055	1·060	1·069	1·076
(e)	ISM & TLS$^+$	unconstrained	68	218	1·129	1·080	1·086	1·097	1·105

Table 6. *The anisotropic temperature factors in Å^2 scaled by 10^3, in the crystal orthogonal coordinate system, as derived from the TLS$^+$ model parameters of Table 3 and nuclear positions from Table 7*

The first entry for the hydrogen atoms is without, the second with the extra anisotropic temperature factor.

	Molecule 1							Molecule 2					
u_{11}	u_{22}	u_{33}	u_{23}	u_{31}	u_{12}			u_{11}	u_{22}	u_{33}	u_{23}	u_{31}	u_{12}
45	49	42	−2	0	−3	C(1)		49	47	43	0	2	2
41	43	38	−7	3	−6	C(2)		41	46	40	−5	1	7
53	42	43	−1	0	−5	C(3)		45	50	47	2	5	7
71	54	40	0	11	−10	C(4)		48	54	66	−2	2	−3
63	58	55	−10	22	−5	C(5)		53	62	58	−11	−10	0
48	53	62	−5	8	3	C(6)		59	60	42	−2	−5	5
86	95	50	12	−12	4	Cl(1)		79	78	71	9	13	−22
60	79	56	−19	16	3	Cl(2)		54	86	53	−18	−8	1
82	69	82	10	−16	16	Cl(3)		79	100	54	21	15	6
112	82	42	9	12	−11	H(4)		63	76	97	1	8	−20
88	88	76	−18	42	1	H(5)		70	96	78	−23	−22	−8
60	75	97	−3	5	20	H(6)		87	94	42	4	−8	3
128	99	48	12	12	−8	H(4)		75	90	110	4	9	−26
101	104	86	−19	46	5	H(5)		82	112	88	−24	−26	−13
72	89	110	−1	4	26	H(6)		103	111	49	7	−8	0

Now we turn to rows (*b*) and (*c*) of Table 5, where we have an assessment of the ISM model. Calculating $\mathscr{S}^{ISM}$ as we did above for $\mathscr{S}^{TLS+}$ we obtain from row (*b*) a value 1·84. The improvement is clearly statistically significant but let us compare this improvement with other examples. It is less than that for anthracene, pyrene and ovalene, but more than that for naphthalene (Pawley, 1971*a*). We therefore surmise that the distortion is more important than in the case of the bigger molecule of naphthalene, and if this distortion is physically significant we would expect to find a plausible explanation. The nuclear positions obtained from the unconstrained refinement are listed in Table 7.

Table 7. *Final unconstrained positions of the nuclei in crystal orthogonal Å coordinates*

The standard deviations are 0·0026 for C(1), C(2) and C(3); 0·0033 for C(4), C(5) and C(6); 0·0023 for all Cl; 0·0078 for all H.

Molecule 1

i	$(x_i)_1$	$(x_i)_2$	$(x_i)_3$
C(1)	5·669	2·194	0·739
C(2)	4·641	3·077	0·415
C(3)	4·517	3·485	−0·909
C(4)	5·391	3·025	−1·877
C(5)	6·399	2·149	−1·527
C(6)	6·547	1·732	−0·211
Cl(1)	5·863	1·663	2·363
Cl(2)	3·556	3·650	1·610
Cl(3)	3·265	4·569	−1·362
H(4)	5·272	3·366	−2·897
H(5)	7·081	1·786	−2·292
H(6)	7·328	1·063	0·068

Molecule 2

C(1)	−1·789	0·626	1·110
C(2)	−1·699	0·969	−0·232
C(3)	−0·697	1·855	−0·631
C(4)	0·199	2·375	0·292
C(5)	0·083	2·019	1·624
C(6)	−0·908	1·146	2·039
Cl(1)	−3·018	−0·450	1·643
Cl(2)	−2·822	0·347	−1·370
Cl(3)	−0·556	2·328	−2·270
H(4)	0·965	3·042	−0·048
H(5)	0·771	2·427	2·353
H(6)	−1·004	0·866	3·082

The main difference between the constrained and the unconstrained results came from the shifts of two atoms, C(2) and Cl(2) of molecule type 2. All the molecules are arranged pairwise in centrosymmetrical motifs

and Fig. 4(*a*) and (*b*) show this arrangement for molecules of type 1 and 2 respectively. The molecules in heavy outline are the uppermost, and we view each pair at right angles to the molecular plane. Molecules of type 1 are situated 3·528(2) Å apart whereas those of type 2 are slightly further separated, the distance being 3·534(2) Å. This we would expect from the diagrams as we see that atoms C(1) and C(3) nearly overlap C(3) and C(1) for molecules of type 2. The distortion apparent after lifting the constraints is mainly the movement of C(2) by 0·011 Å towards the neighbouring molecule and into the space provided by the ring, and the movement of Cl(2) by 0·007 Å in the opposite direction. All other shifts are by less than three (least-squares) standard deviations. It is surprising that about 80% of the improvement in R on removing the constraint is due to the variation in the second molecule, whereas the variation in the first molecule is not of statistical significance. The projection of the structure down the diad axis is shown in Fig. 5. No intermolecular contacts have been given as there were none which were surprisingly short.

Conclusion

The best average geometry of the molecules of 1,2,3-trichlorobenzene has been found by constrained refinement. Of the two molecules of independent orientation, one has been shown to be significantly distorted, whereas the other closely retains the free-state symmetry. The thermal motion is excellently described by rigid-body molecular motion, when account is taken of the effect of the internal modes on the hydrogen atoms.

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