The Molecular Structure of 1,2,4,5-Tetrachlorobenzene Determined by Combined Analysis of Electron Diffraction and Liquid Crystal NMR Data, and by X-Ray Crystallography

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The r_α° molecular structure of 1,2,4,5-tetrachlorobenzene has been determined by combining electron diffraction data with dipolar couplings from ^1H NMR experiments. By assuming overall D_{2h} symmetry, all six independent structural parameters could be determined with high precision. Owing to mutual repulsion, adjacent chlorine atoms are bent away from each other, and in addition the C–C bonds between them are long, 141.2(4) pm. The CCC angles at the chlorinated ring atoms are 119.80(15)°. For comparison, a study was also made of the crystal and molecular structure of the title compound by X-ray diffraction. The structural distortions of the benzene ring in the crystalline phase are similar to those in the gas. The present results are compared with structural parameters reported from previous studies of the compound.

The molecular structure of 1,2,4,5-tetrachlorobenzene was investigated by gas electron diffraction for the first time as early as 1937 by Brockway and Palmer.[1] By assuming that the C_6 skeleton had a regular hexagonal shape with a C–C bond distance of 140 pm, they concluded that the C–Cl vectors did not intersect the centroid of the hexagon, but that interactions between the two neighbouring chlorine atoms resulted in them being bent away from one another. On the basis of an assumed C–Cl bond distance of 172 pm and a distance of 320 pm between the *ortho* chlorine atoms, they estimated the angle between the two adjacent C–Cl bonds to be 63°.

In later years there was discussion as to whether the principal distortions of the strained halogenated benzene rings involved out-of-plane or in-plane bending of the substituents. Bastiansen and Hassel concluded from electron diffraction work with chlorinated and brominated benzene compounds that the out-of-plane distortions were the predominant effect.[2] However, a room-temperature X-ray crystallographic study of hexachlorobenzene, performed in 1958, indicated that the molecule is planar within the error of the experiment.[3] Other crowded halobenzenes were also found to be planar in the crystalline phase, and conformational differences between the solid and gas-phase structures were suggested.[4]

Analysis of nuclear quadrupole resonance data correlated with X-ray data of 1,2,4,5-tetrachlorobenzene indicated that the angle between the two adjacent C–Cl bonds was 63(1)°, but twinning of the crystals prevented the elucidation of further structural details.[5]

In 1966 Strand and Cox obtained new electron diffraction data for hexachlorobenzene and 1,2,4,5-tetrachlorobenzene and found that both molecules were planar: the out-of-plane bending observed by Bastiansen and Hassel 19 years earlier was a consequence of large-amplitude out-of-plane motion of the chlorine atoms (shrinkage).[6] By assuming a regular hexagonal shape for the C_6 ring in the tetrachlorobenzene, the angle between the adjacent C–Cl bonds was found to be 62.8(4)°, in good agreement with the previous results.

Later room-temperature X-ray crystallographic investigations of hexa- and pentachlorobenzene have shown that both molecules are not completely planar, but that the out-of-plane distortions of the chlorines are small. For hexachlorobenzene the chlorine atoms lie alternately above and below the C_6 plane, the distortions from planarity being less than 2 pm.[7] The distortions in pentachlorobenzene show a similar pattern, with the central chlorine atom approximately in the ring plane and the other four alternating above and below the ring plane so as to keep C_2 molecular symmetry.[8] The largest distortion in pentachlorobenzene is 3.9 pm. *Ab initio* Hartree-Fock calculations on all the perhalogenated benzene compounds give no evidence for out-of-plane bending in these compounds, but a flattening of the puckering potential potential curve is obtained as the number of chlorine substituents increases.[9]

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The effects of the chlorine atoms on the bonds and angles of the C_6 skeleton of 1,2,4,5-tetrachlorobenzene were first investigated in a ^1H NMR study of the compound dissolved in anisotropic solvents performed by Diehl *et al.* in 1980.[10] They found that the longest C–C bonds occurred between pairs of carbons bearing chlorine substituents, but unfortunately, owing to high correlation among the parameters, the errors in the derived structural parameters were large, and, as always in a structural analysis based on NMR data alone, the bond distances had to be derived from one assumed distance. In addition, no information on the position of the chlorine atoms could be obtained from such an investigation, since there is no chlorine spin-$\frac{1}{2}$ isotope.

By combining electron diffraction data with dipolar couplings from liquid crystal NMR experiments and, when available, data from rotational spectroscopy, we have recently determined the total molecular structures of a number of chlorinated benzene compounds with no assumptions other than that of the appropriate overall molecular symmetry.[11] In such a structural analysis the electron diffraction data allow scaling of the data from dipolar couplings, while the latter give information about small differences between similar distances that in a structural analysis based on electron diffraction data alone would be so correlated as to be indeterminate. With assumed D_{2h} symmetry, the molecular structure of 1,2,4,5-tetrachlorobenzene is described by only six independent parameters: two different C–C bonds, one C–Cl bond, one C–H bond and two angles, one defining the shape of the C_6 skeleton and one defining the bending of the chlorine atoms. The compound should therefore be an excellent model on which to investigate the structural consequences of having two neighbouring chlorine substituents.

We report here the total molecular structure of 1,2,4,5-tetrachlorobenzene as determined by combined analysis of new electron diffraction data and dipolar couplings from ^1H NMR experiments using liquid-crystal solvents. This is the first structural investigation of this tetrachlorobenzene in which distortions, both of the substituents and of the C_6 skeleton, are analysed simultaneously.

Combined analysis of electron diffraction and liquid crystal NMR data

Materials. The sample of 1,2,4,5-tetrachlorobenzene used in this work was purchased from the Aldrich Chemical Co. and used without further purification.

Electron diffraction. Electron diffraction scattering intensities were recorded photographically on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus,[12] operating at ca. 44.5 kV. During the measurements the sample was maintained at 435 K and the nozzle at 450 K. Three plates were exposed at each of the three camera distances, 257, 201 and 95 mm, and data for benzene were also recorded to provide calibration of the camera distances and electron wavelength (Table 1). The ranges of the data sets and weighting points used in setting up the off-diagonal weight matrix, scale factors and correlation parameters are also listed in Table 1. Optical density data were obtained using a Joyce–Loebl MDM6 microdensitometer at the SERC Laboratory, Daresbury, UK. The scanning program[13] and programs used subsequently for data reduction[13] and least-squares refinements[14] are those described earlier, and make use of standard scattering factors.[15]

Dipolar couplings. The experimental direct dipolar couplings, measured using solutions in Merck liquid crystals ZLI1167 and ZLI1083, were taken from Diehl *et al.*[10]

Vibrational corrections. Since the experimental ED data and LCNMR data are influenced by the molecular vibrations in different ways, parameters derived from both sets of data must be corrected to a common base before they can be meaningfully compared. The required corrections, obtained from a harmonic force-field analysis, allow the determination of a common geometrically consistent r_α° structure. The harmonic force-field analysis for 1,2,4,5-tetrachlorobenzene was performed using the program GAMP.[16] By assuming D_{2h} molecular symmetry, the force field was obtained by least-squares fitting of the calculated vibrational frequencies to the observed frequencies of 1,2,4,5-$C_6H_2Cl_4$ and 1,2,4,5-$C_6D_2Cl_4$ reported by Scherer.[17] The definitions of internal coordinates, symmetry coordinates and calculated frequencies are available from the authors as supplementary material.

The experimental dipolar couplings, D_{exp}, were converted into vibrationally corrected dipolar couplings, D_α, by using the method of Sykora *et al.*[18] The uncertainties in the vibrational corrections were estimated by systematically varying the force field and recalculating the corrections for each new force field. The spread of each correction was then taken as an estimate of the uncertainty of that correction. The total uncertainty in each D_α, which is given in Table 2 and which was used to weight the dipolar cou-

Table 1. Camera heights, electron wavelengths, weighting functions (in nm^{-1}), correlation parameters and scale factors for the ED data.

Camera height/mm	Wave-length/pm	Δs	s_{min}	sw_1	sw_2	s_{max}	Correlation parameter	Scale factor
257.16	5.671	2	20	40	144	164	0.4590	0.887(6)
200.59	5.674	4	40	60	196	220	0.2131	0.827(11)
94.60	5.669	4	148	160	296	348	0.3895	0.811(32)

Table 2. Direct dipolar coupling data (Hz) for 1,2,4,5-tetrachlorobenzene.

	D_{exp}[a]	D_{α}[b]	D_{calc}[c]
$D_{\mathrm{C(6)H(6)}}$[d]	867.96(21)	957.83(800)	957.37
$D_{\mathrm{H(3)H(6)}}$[d]	38.98(20)	39.48(34)	39.63
$D_{\mathrm{C(1)H(6)}}$[d]	165.09(21)	169.75(80)	169.93
$D_{\mathrm{C(2)H(6)}}$[d]	35.17(21)	35.68(33)	35.37
$D_{\mathrm{C(3)H(6)}}$[d]	20.59(29)	20.83(32)	20.87
$D_{\mathrm{C(6)H(6)}}$[e]	−2075.75(29)	−2282.91(1840)	−2274.97
$D_{\mathrm{H(3)H(6)}}$[e]	−92.68(28)	−93.82(85)	−94.18
$D_{\mathrm{C(1)H(6)}}$[e]	−346.46(29)	−356.06(170)	−356.39
$D_{\mathrm{C(2)H(6)}}$[e]	−78.99(29)	−80.10(80)	−79.36
$D_{\mathrm{C(3)H(6)}}$[e]	−48.30(41)	−48.84(80)	−49.58

[a]Observed; taken from Ref. (10). [b]Vibrationally corrected. [c]Calculated from combined analysis. [d]In Merck liquid crystal ZLI1167. [e]In Merck liquid crystal ZLI1083.

pling in the joint structural analysis, is simply the sum of the uncertainty in D_{exp} given in Ref. 10 and the estimated error in the vibrational correction.

From the force field, the perpendicular displacement corrections K_i and the root mean-square amplitudes of vibrations u_i were also determined. These were used to correct the r_a parameters obtained from the ED data to r_α° parameters. Calculated u-values were also used in the joint structural analysis when the values could not be refined.

Molecular model and joint structural analysis. In the joint structural analysis, 1,2,4,5-tetrachlorobenzene was assumed to have D_{2h} symmetry. With this assumption the molecular geometry is described by six geometrical parameters: two different C–C bond distances, one C–Cl bond distance, one C–H bond distance, one angle to define the shape of the C_6 ring, chosen as ∠C(1)C(2)C(3), and one exocyclic angle describing the in-plane bending of the chlorine substituents, chosen as ∠C(2)C(1)Cl. With the assumed D_{2h} symmetry, only two orientation parameters, S_{xx} and S_{yy}, are needed for each set of dipolar couplings. Seven amplitudes of vibration were refined as independent parameters: their values and standard deviations are given in Table 3. The independent parameters were refined by least-squares fitting of a theoretical curve to the three independent experimental intensity curves. The harmonic vibrational analysis and the joint structural analysis were then repeated until the final structure was self-consistent.

Because of the possibility of small out-of-plane distortions of the chlorine atoms, some additional refinements were performed, with the chlorine atoms fixed 4, 8, 12, 16 and 20 pm above and below the C_6 plane, so that the overall symmetry of the molecule was D_2. None of these refinements gave structural parameters significantly different from those presented in Table 4. The fit to the electron diffraction data, however, became poorer when the out-of-plane displacement was larger than 8 pm.

The experimental dipolar couplings, the vibrationally corrected dipolar couplings and the dipolar couplings calculated from the final molecular structure are given in Table 2. In Table 4 the final structural parameters and orientational parameters are given, and in Table 5 the main part of the correlation matrix is shown. The r_a parameters, the refined and calculated r.m.s. amplitudes of vibration (u-values) and the calculated perpendicular displacement corrections (K-values) are given in Table 3. The final coordinates are given in Table 6. The experimental molecular

Table 3. Interatomic distances (r_a), amplitudes of vibration and K-values for 1,2,4,5-tetrachlorobenzene at 450 K.[a]

i	Distance	r_a	u(ED)	u_i(FF)	K_i(FF)
1	C(1)−C(2)	141.5(4)	4.2(3)	4.77	0.47
2	C(2)−C(3)	139.4(2)	4.2 tied to u_1	4.82	0.64
3	C(3)−H	109.8(5)	7.68 fixed	7.68	2.10
4	C(1)−Cl	172.6(1)	4.7(2)	4.86	1.11
5	C(1)···C(3)	242.6(4)	6.12 fixed	6.12	0.42
6	C(1)···C(5)	241.3(4)	8.32 fixed	8.32	0.54
7	C(1)···C(4)	279.6(3)	8.29 fixed	8.29	0.49
8	C(3)···C(6)	279.2(8)	8.84 fixed	8.84	0.25
9	Cl(1)···Cl(2)	317.8(3)	10.8(3)	9.78	0.99
10	Cl(1)···Cl(5)	536.4(2)	10.6(4)	10.49	0.74
11	Cl(1)···Cl(4)	622.8(2)	9.1(3)	9.52	0.29
12	H(3)···H(6)	496.6(15)	13.53 fixed	13.53	1.13
13	C(1)···Cl(2)	273.1(2)	5.9(2)	6.33	0.73
14	C(1)···Cl(4)	451.5(2)	7.2(3)	8.89	0.55
15	C(1)···Cl(5)	398.8(3)	8.6(3)	9.15	0.67
16	C(3)···Cl(2)	269.3(1)	7.1 tied to u_{13}	7.57	0.92
17	C(3)···Cl(1)	401.3(3)	6.2 tied to u_{15}	6.56	0.53
18	H(3)···Cl(2)	283.1(3)	14.58 fixed	14.58	1.50
19	H(3)···Cl(1)	487.4(6)	11.36 fixed	11.36	0.85
20	C(1)···H(6)	215.3(5)	10.19 fixed	10.19	1.39
21	C(2)···H(6)	341.2(8)	9.96 fixed	9.96	1.01
22	C(3)···H(6)	388.0(11)	11.42 fixed	11.42	0.79

[a]ED denotes u-values refined or used in the combined analysis of data from electron diffraction and liquid crystal NMR experiments. FF denotes values from the harmonic force field calculation. All values are in pm.

Table 4. The r_α° structure of 1,2,4,5-tetrachlorobenzene.

Parameters (distances in pm, angles in degrees):		
p_1	mean r(C−C)	139.66(11)
p_2	D_1[a]	2.3(6)
p_3	r(C−Cl)	171.66(12)
p_4	r(C−H)	108.2(5)
p_5	∠C(1)C(2)C(3)	119.80(15)
p_6	∠C(2)C(1)Cl	120.85(10)
Orientation parameters:		
p_7	S_{xx}[b]	−0.0884(12)
p_8	S_{yy}[b]	−0.0402(5)
p_9	S_{xx}[c]	0.1612(24)
p_{10}	S_{yy}[c]	0.0956(11)
Dependent parameters:		
	r[C(1)−C(2)]	141.2(4)
	r[C(2)−C(3)]	138.9(2)
	∠C(2)C(3)C(4)	120.39(29)

[a] The difference r[C(1)–C(2)]−r[C(2)–C(3)]. [b] In Merck liquid crystal ZLI1167. [c] In Merck liquid crystal ZLI1083.

Table 5. Correlation matrix (×100) for the joint analysis of gas electron diffraction data and dipolar couplings from liquid crystal NMR experiments.[a]

	p_6	p_7	p_8	p_{10}	k_2	k_3
p_1	–	–	−50	–	–	–
p_2	76	–	–	–	–	–
p_4	–	–	−86	87	–	–
p_5	–	−52	−52	51	–	–
p_8			100	−80	–	–
u_4					–	54
u_{13}					52	–

[a] Only elements ≧ 50 have been included. p_n is the nth parameter in Table 4, u_i is the ith u-value of Table 3, while k_n is the scale factor of the electron diffraction data set number n in Table 1.

Table 6. Atomic coordinates (in pm) from the combined analysis.

Atom	X	Y	Z
C(1)	120.53	70.59	0.00
C(2)	120.53	−70.59	0.00
C(3)	0.00	−139.63	0.00
C(4)	−120.53	−70.59	0.00
C(5)	−120.53	70.59	0.00
C(6)	0.00	139.63	0.00
Cl(1)	267.91	158.61	0.00
Cl(2)	267.91	−158.61	0.00
H(3)	0.00	−247.87	0.00
Cl(4)	−267.91	−158.61	0.00
Cl(5)	−267.91	158.61	0.00
H(6)	0.00	247.87	0.00

scattering intensities and the difference curve calculated for the final molecular model are shown in Fig. 1, and the corresponding experimental radial distribution curve and difference curve are shown in Fig. 2. Fig. 3 shows the refined molecular structure.

Single-crystal X-ray structure determination for 1,2,4,5-tetrachlorobenzene

Crystal data. The following results were obtained: $C_6H_2Cl_4$, $M = 215.89$, monoclinic, space group $P2_1/n$ (Alt. $P2_1/c$, No. 14), $a = 379.56(12)$, $b = 1051.75(19)$, $c = 956.48(13)$ pm, $\beta = 99.723°$, $V = 376.3\times10^6$ pm^3 [from 2θ-values of 32 reflections measured at $\pm\omega$ ($2\theta = 30.4$–$32.4°$, $\lambda = 71.073$ pm, $T = 173\pm0.1$ K)], $Z = 2$ (implying that each molecule lies across a crystallographic inversion centre), $D_{calc} = 1.905$ g cm^{-3}, $F(000) = 212$, colourless columnar crystal $0.40\times0.50\times0.75$ mm, $\mu = 1.491$ mm^{-1}.

Data collection and processing. A Stoë STADI-4 four-circle diffractometer was employed, equipped with an Oxford Cryosystems low-temperature device,[19] using Mo K_α X-radiation and ω-2θ scans using the learnt-profile method;[20] $T = 173$ K. A total of 1160 reflections ($2\theta_{max} = 60°$, h − 5 →

Table 7. Bond lengths (in pm), angles (in degrees) and torsion angles (in degrees) with standard deviations from the X-ray analysis.[a]

Cl(1)–C(1)	172.5(3)	C(1)–C(3′)	137.9(4)
Cl(2)–C(2)	171.5(3)	C(2)–C(3)	139.1(4)
C(1)–C(2)	139.5(4)	C(3)–H(3)	96.0(3)
Cl(1)–C(1)–C(2)	120.64(20)	C(1)–C(2)–C(3)	119.44(25)
Cl(1)–C(1)–C(3′)	118.71(21)	C(2)–C(3)–H(3)	121.0(20)
C(2)–C(1)–C(3′)	120.65(25)	C(2)–C(3)–C(1′)	119.9(3)
Cl(2)–C(2)–C(1)	121.25(21)	H(3)–C(3)–C(1′)	118.9(20)
Cl(2)–C(2)–C(3)	119.30(21)		
Cl(1)–C(1)–C(2)–Cl(2)	0.8(3)	C(2)–C(1)–C(3′)–H(3′)	176.0(23)
Cl(1)–C(1)–C(2)–C(3)	−179.51(21)	Cl(2)–C(2)–C(3)–H(3)	−4.4(23)
C(3′)–C(1)–C(2)–Cl(2)	−179.50(21)	Cl(2)–C(2)–C(3)–C(1′)	179.50(21)
Cl(1)–C(1)–C(3′)–C(2′)	179.51(21)	C(1)–C(2)–C(3)–H(3)	175.9(23)
Cl(1)–C(1)–C(3′)–H(3′)	−4.3(23)		

[a] Primed atoms are related to their unprimed equivalents by inversion through (0, 1/2, 1/2).

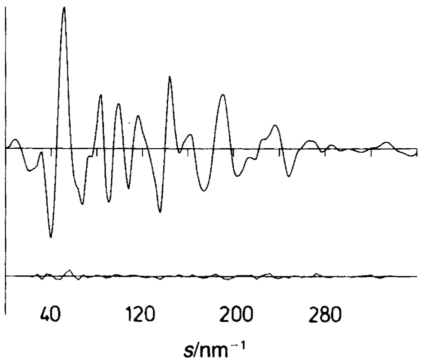

Fig. 1. The combined experimental molecular intensity curve for 1,2,4,5-tetrachlorobenzene. In the lower part of the figure the difference curve (experimental–theoretical) is shown. Theoretical data have been included in the regions for which no experimental data are available.

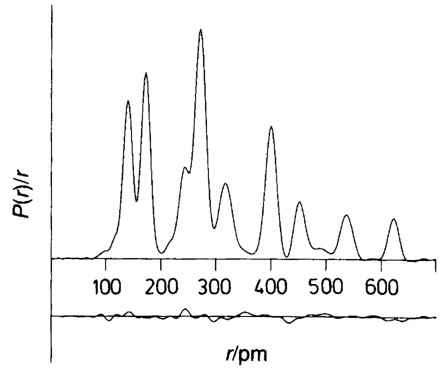

Fig. 2. The experimental radial distribution curve, $P(r)/r$, for 1,2,4,5-tetrachlorobenzene. In the lower part of the figure the difference between experimental and theoretical curves is shown. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.00002s^2)/(Z_C - f_C)(Z_{Cl} - f_{Cl})$.

5, k 0 → 14, l 0 → 13) were collected, of which 1033 were unique ($R_{int} = 0.019$), giving 913 reflections with $F > 6\sigma(F)$ for use in all calculations. There was no significant crystal decay or movement, and no absorption correction was made.

Structure solution and refinement. Automatic direct methods[21] located the two Cl and three C atoms in the asymmetric unit, and a subsequent ΔF synthesis gave the H atom position. The structure was then refined (by least-squares on F)[22] with anisotropic thermal parameters for Cl and C, while the H atom was refined freely with an isotropic thermal parameter. At final convergence R, R_w = 0.0374, 0.0567, S = 1.266 for 50 parameters. Maximum and minimum $\Delta\varrho$ in the final ΔF synthesis were 0.53 and −0.57 e Å^{-3}, respectively, and in the final cycle $(\Delta/\sigma)_{max}$ was 0.005. The weighting scheme $W^{-1} = \sigma^2(F) + 0.0045\,F^2$ gave satisfactory agreement analysis. Scattering factors were inlaid,[22] Fig. 4 was generated using ORTEPII,[23] and molecular geometry calculations utilised CALC.[24] The final structural parameters are given in Table 7, and the final atomic coordinates and thermal parameters are shown in Tables 8 and 9.

Discussion

In Table 10 the bond lengths and valence angles obtained in the combined analysis and in the X-ray analysis are compared with those based on electron diffraction data and dipolar coupling data analysed separately.

All parameters except the C–H bond distance are determined with satisfactory precision by using electron diffraction data alone, together with the u-values obtained from the harmonic force-field calculation. By including the dipolar couplings in the refinement the C–H bond distance can also be determined with high precision. The combined analysis gave a final structure in which all bond distances are determined to within 0.5 pm and all valence angles to within 0.3°.

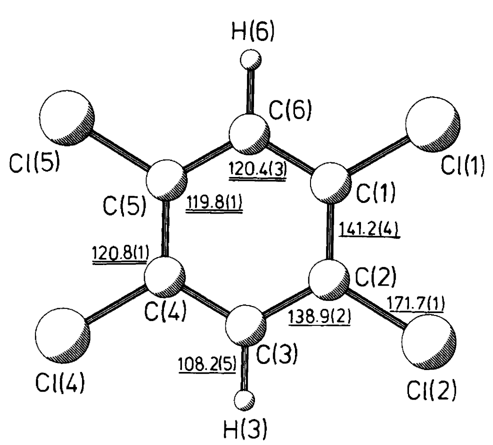

Fig. 3. Final molecular structure of 1,2,4,5-tetrachlorobenzene from the joint analysis of electron diffraction and liquid crystal NMR data. Numbering of the atoms, r_α° bond distances (underlined) and valence angles (doubly underlined) are shown.

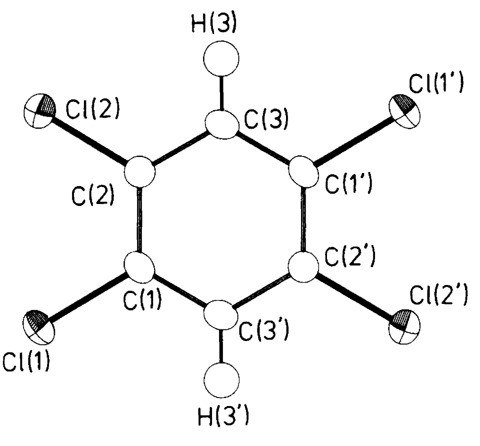

Fig. 4. ORTEP plot of one molecule of 1,2,4,5-tetrachlorobenzene in the crystal at 173 K. Thermal ellipsoids are drawn at the 30 % probability level. Molecules lie across crystallographic inversion centres and therefore possess imposed C_i symmetry.

Table 8. Fractional atomic coordinates from the X-ray analysis.

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
Cl(1)	0.15178(13)	0.42935(5)	0.20000(5)	0.0289(3)
Cl(2)	−0.04184(15)	0.21617(5)	0.40801(5)	0.0310(3)
C(1)	0.0675(5)	0.46741(18)	0.36621(18)	0.0207(8)
C(2)	−0.0190(4)	0.37354(17)	0.45765(20)	0.0208(8)
C(3)	−0.0885(5)	0.40665(18)	0.59159(20)	0.0221(8)
H(3)	−0.164(7)	0.342(3)	0.651(3)	0.028(6)

Crystals of 1,2,4,5-tetrachlorobenzene, whether grown from solution[5] or by sublimation, typically form twins: however, we were able, by screening several candidates, to identify one crystal which was essentially singular, albeit with somewhat greater mosaic spread than normal.

The angles obtained from the X-ray crystallographic analysis are equal to those obtained from the combined analysis to within one standard deviation,. Also, *r*(C–Cl) and *r*[C(2)–C(3)] are insignificantly different in the two structure determinations. However, *r*[C(1)–C(2)] is found to be significantly longer in the combined analysis than in the crystal. Whether this is a real structural difference between the phases investigated or if the difference is due to the physically different kinds of interatomic distances measured by the two techniques used in this study is unknown, but it may be noted here that in most X-ray crystallographic analyses of benzene derivatives the C–C bonds are found to be shorter than in electron diffraction studies. This is due to librational motions in the crystalline state. The discrepancies between the results obtained by the two techniques are larger the higher the temperature of the X-ray experiment: the average C–C bond distance found by an X-ray study of 1,2,4,5-tetrachlorobenzene at room temperature was 137.8 pm, while the average r_α(C–C) from electron diffraction is 139.8 pm. For 1,2,3-trichlorobenzene the average C–C bond distance of 139.1 pm found from an X-ray study at 173 K is only 0.3 pm shorter than the r_α(C–C) from electron diffraction.[11]

The C–C bond lengths in chlorinated benzene compounds vary in a predictable way. If one considers the C–C bond distance of benzene itself (r_α° = 139.59 pm) to be a normal aromatic C–C bond distance, introduction of a chlorine substituent on one of the carbon atoms of the C–C bond tends to decrease the C–C bond distance. On the other hand, if two adjacent chlorine substituents are introduced, the distance between the substituted carbon atoms becomes longer than the normal aromatic C–C bond. The amount by which any particular C–C bond in a highly chlorinated benzene compound is shortened or elongated is dependent on the number and position of other chlorine substituents.

For the valence angles of the C_6 ring, it appears that an electronegative substituent tends to open the CCC angle at the substituted carbon atom, while an electropositive sub-

Table 9. Anisotropic thermal parameters (10^4 pm^2).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	0.0331(3)	0.0320(3)	0.0222(3)	−0.00257(17)	0.01262(19)	0.00016(17)
Cl(2)	0.0394(4)	0.0230(3)	0.0306(3)	−0.00362(17)	0.01155(21)	−0.00191(17)
C(1)	0.0158(8)	0.0269(9)	0.0196(8)	−0.0009(6)	0.0059(5)	0.0016(6)
C(2)	0.0168(8)	0.0221(8)	0.0231(8)	−0.0007(6)	0.0044(6)	0.0003(6)
C(3)	0.0170(7)	0.0266(8)	0.0228(8)	0.0027(7)	0.0063(6)	−0.0006(6)

Table 10. Comparison of the structural parameters obtained from analysis using only LCNMR data, only ED data, and by using both LCNMR and ED data simultaneously. The results from the X-ray crystallographic analysis are shown in the right-hand column.[a]

	ED[b]	LCNMR[c]	ED[d]	ED + LCNMR	XR[e]
r[C(1)–C(2)]	139.5(4)	139.3(14)	141.1(4)	141.2(4)	139.5(4)
r[C(2)–C(3)]		137(14)	138.9(2)	138.9(2)	138.5(8)
r(C–Cl)	172.4(5)	–	171.6(1)	171.7(1)	172.0(7)
r(C–H)	106.0(36)	108.02(4)	110.8(19)	108.2(5)	–
∠C(1)C(2)C(3)	120.0[f]	120.8[g]	119.7(2)	119.8(1)	120.0(9)
∠C(2)C(3)C(4)	120.0[f]	118.4(37)	120.6(3)	120.4(3)	119.9(3)
∠C(2)C(1)Cl	121.4(4)	–	120.9(1)	120.8(1)	120.9(4)
r(H···H)[h]	–	495.86 fixed	–	496.6(15)	–

[a] Distances in pm, angles in degrees. [b] r_g values taken from Ref. 6. [c] Taken from Ref. 10. [d] Results obtained by using the new ED data and a less constrained model. In this refinement the two C–C *u*-values were kept at the values obtained from the harmonic force field calculations. [e] In the crystal there is half a molecule per asymmetric unit, and the parameters are related by molecular, but not crystallographic symmetry. In the cases where for symmetry reasons a parameter has been measured more than once, mean values are given and the estimated standard deviations indicate the spread of the individual distances. [f] Assumed value. [g] Derived from ∠C(2)C(3)C(4). [h] Included because the LCNMR-only results are based upon this assumed distance.

stituent has the opposite effect. At a first glance, therefore, the angle of 119.80(13)° for ∠C(1)C(2)C(3) of 1,2,4,5-tetrachlorobenzene may seem suprising. However, by assuming that the effects upon substitution are additive, the results are not so unreasonable. Domenicano has previously shown that the angle deformations of fluorobenzenes seem to be additive.[25] By taking the angular deformations of the monosubstituted ring as a basis one may predict the ring angles when more chlorine atoms are introduced on the ring. In Table 11 the predicted values for 1,4-$C_6H_4X_2$, 1,3,5-$C_6H_3X_3$ and 1,2,4,5-$C_6H_2X_4$ (X = F or Cl) are shown. As is seen in the table, the predicted ring angles of the compounds 1,4-$C_6H_4X_2$ and 1,3,5-$C_6H_3X_3$ (X = F or Cl) fit well to the observed values. For the 1,2,4,5-$C_6H_2X_4$ compounds, however, the fit is not good: for the tetrafluoro compound ∠C(1)C(2)C(3) is predicted to be 1.1° larger than the experimental value, and for the tetrachloro compound this discrepancy is 0.9°. If this discrepancy from additivity is a result of dipole–dipole interactions in the 1,2,4,5-tetrachlorobenzene, the discrepancy in the tetrachloro compound should be expected to be somewhat smaller than in the analogous tetrafluoro compound, owing to the lower electronegativity of chlorine compared to that of fluorine. This is indeed the case: the discrepancy from the experimental value for the chloro compound is about 75 % of that for the fluoro compound.

Table 11. Predicted ring angles for 1,4-$C_6H_4X_2$, 1,3,5-$C_6H_3X_3$ and 1,2,4,5-$C_6H_2X_4$ (X = F or Cl) derived by assuming that the ring distortions observed for monofluorobenzene and monochlorobenzene are additive when further halogen atoms are substituted to the benzene ring.

	X = F		X = Cl	
Deformation parameters from C_6H_5X:[a]				
$\Delta\alpha_x$	3.4		1.65	
$\Delta\beta_x$	−2.0		−0.95	
$\Delta\gamma_x$	0.3		0.24	
$\Delta\delta_x$	0.0		−0.21	
Predicted and observed angles:				
	Pred.	Obs.	Pred.	Obs.
1,4-$C_6H_4X_2$				
∠C(2)C(1)C(6)	123.4	123.5(1)[b]	121.4	121.1(1)[c]
∠C(1)C(2)C(3)	118.3	118.2[d]	119.2	119.5[d]
1,3,5-$C_6H_3X_3$				
∠C(2)C(1)C(6)	124.0	123.7(2)[e]	122.1	122.4(2)[e]
∠C(1)C(2)C(3)	116.0	116.3[d]	117.9	117.6[d]
1,2,4,5-$C_6H_2X_4$				
∠C(1)C(2)C(3)	121.7	120.6(3)[f]	120.7	119.8(2)[g]
∠C(2)C(3)C(4)	116.6	118.8[d]	118.6	120.4[d]

[a] In degrees: Ref. 25. [b] Ref. 26. [c] Ref. 27. [d] Derived values. [e] Ref. 28. [f] Ref. 29. [g] Present work.

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