The Molecular Structure of 1,2,3,5-Tetrachlorobenzene Determined by Combined Analysis of Data from Gas Electron Diffraction and Liquid Crystal NMR Spectroscopy

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The $r_\alpha{}^\circ$ molecular structure of 1,2,3,5-tetrachlorobenzene has been re-examined by using data from gas electron diffraction experiments and direct dipolar couplings from ^{1}H NMR experiments in a joint structural analysis. The data are consistent with an assumed molecular model of C_{2v} symmetry and 8 of the total number of 11 structural parameters could be refined simultaneously. In the final structure standard deviations for bond distances are between 0.1 and 0.4 pm, and for angles they are between 0.2 and 0.7°. The structural parameters are compared with previous X-ray crystallographic results.

The structural distortions of benzene rings when one hydrogen atom has been substituted have been studied by different methods.[1] One general structural trend is that electronegative substituents tend to make the CCC angle at the substituted carbon atom larger than 120° and shorten the adjacent C–C bonds, while electropositive substituents have the opposite effects. Other systematic deformations of the ring have been harder to detect. Very accurate molecular structures of monochlorobenzene[2] and the dichlorobenzenes[3–5] have recently been determined by combining data from gas electron diffraction (ED), liquid crystal NMR (LC–NMR) and also, when available, rotational spectroscopy. When two or more chlorine atoms are attached to the benzene ring there will in some cases be repulsions between the substituents, in addition to competing electronic effects, which make the interpretation of the deformations not so straightforward.

In order to understand these effects better, we have decided to investigate the more chlorinated benzenes, and in the present paper we present the molecular structure of 1,2,3,5-tetrachlorobenzene as determined by combined analysis of data from ED and LC–NMR experiments. By combining data obtained by these two methods the total molecular structure may be determined with much higher accuracy than is possible using either technique alone, and with fewer assumptions about geometrical parameters. The compound has previously been studied in an analysis based only on LC–NMR data by Dombi *et al.*[6] One shortcoming of such an analysis is that only structural data for carbon and hydrogen atoms can be obtained. In addition, the results must be based on one assumed interatomic distance, and an error in this assumption may cause large systematic errors in the deduced structural parameters. The room-temperature crystal structure of 1,2,3,5-tetrachlorobenzene, determined by X-ray crystallography, has also been reported.[7] The shortcoming of such an investigation in the present context is mainly that the positions of hydrogen atoms are poorly determined. The previous results on 1,2,3,5-tetrachlorobenzene, together with recent results for other chlorinated benzenes, may be used as an indication that our results are accurate, and do not only have high precision.

Experimental and structural analysis

The sample of 1,2,3,5-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[8] operating at ca. 44.5 kV. During the measurements the sample was maintained at 418 K and the nozzle at 449 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

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Table 1. Camera heights, electron wavelengths, weighting functions, 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
		nm^{-1}						
256.59	5.672	2	20	40	144	168	0.4756	0.874(9)
200.56	5.668	4	40	60	188	220	0.1392	0.836(12)
94.60	5.669	4	100	110	296	348	0.4369	0.849(24)

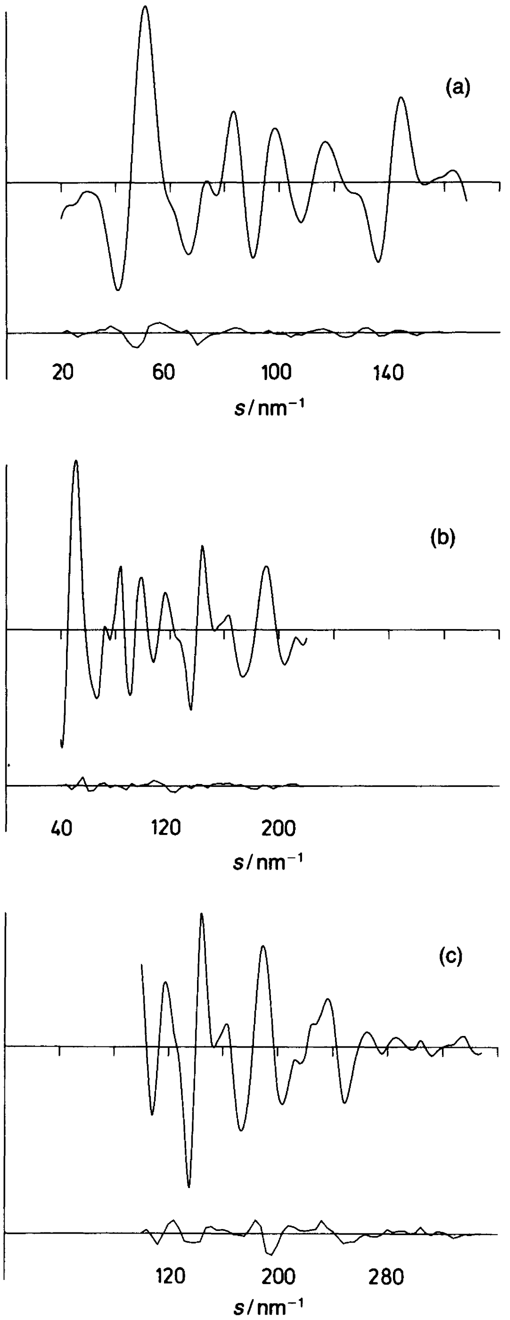

Fig. 1. Experimental molecular scattering intensity curves for 1,2,3,5-tetrachlorobenzene, obtained with camera distances of (a) 257, (b) 201 and (c) 95 mm. The final weighted difference curve (experimental − theoretical) is shown for each curve.

SERC Laboratory, Daresbury, UK. The scanning program[9] and programs used subsequently for data reduction[9] and least-squares refinements[10] are those described earlier. The scattering factors used were those calculated by Schäfer *et al.*[11] The experimental molecular scattering intensity curves are shown in Fig. 1.

Dipolar couplings. The experimental direct dipolar couplings, measured using solutions in Merck liquid crystals ZLI1167 and ZLI1083 at 301 K, were taken from Dombi *et al.*[6]

Vibrational corrections. Since the experimental ED data and LC–NMR data are influenced by the molecular vibrations in different ways, both sorts of data must be corrected to a common base before they can be compared meaningfully. By carrying out a harmonic force field analysis, one can get the corrections needed to determine a common geometrically consistent $r_\alpha{}^\circ$ structure. The harmonic force field analysis for 1,2,3,5-tetrachlorobenzene was performed by using the program GAMP.[12] By assuming C_{2v} molecular symmetry, the force field was obtained by least-squares fitting of the calculated vibrational frequencies to the observed frequencies for 1,2,3,5-$C_6Cl_4H_2$ and 1,2,3,5-$C_6Cl_4D_2$ reported by Scherer.[13] We have decided not to include details of the force field calculations in the present paper, but symmetry coordinates, final force field and frequencies are available from the authors on request.

The experimental dipolar couplings, D_{exp}, were converted to vibrationally corrected dipolar couplings, D_α, by using the method of Sykora *et al.*[14] The uncertainties of the vibrational corrections were estimated by systematically varying the force field and recalculating the corrections for each new force field.[10] The spread of each correction was then taken as an estimate of the uncertainty of that correction, and the total uncertainty of each D_α (given in Table 2), which was used to weight the dipolar coupling in the joint structural analysis, is simply the sum of the uncertainty in D_{exp} given in Ref. 6 and the estimated error in the vibrational correction.

The perpendicular amplitude corrections, K_i, and the root-mean-square amplitudes of vibrations, u_i, were also determined from the force field. These were used to correct the r_a-parameters obtained from the ED data to $r_\alpha{}^\circ$-parameters. Calculated u-values were also used in the joint structural analysis when they could not be refined.

Table 2. Direct dipolar coupling data (in Hz) for 1,2,3,5-tetrachlorobenzene.

	D_{exp}[a]	D_{α}[b]	D_{calc}[c]
D(4,10)[d]	1441.98(14)	1596.28(500)	1596.14
D(5,10)[d]	162.26(14)	167.72(40)	167.71
D(1,10)[d]	265.94(17)	274.01(120)	273.91
D(4,12)[d]	42.61(19)	43.36(30)	43.11
D(2,10)[d]	60.86(14)	61.79(30)	61.82
D(1,12)[d]	33.87(17)	34.41(30)	34.47
D(10,12)[d]	82.06(6)	83.62(20)	83.67
D(4,10)[e]	−2358.06(17)	−2607.38(800)	−2607.45
D(5,10)[e]	−280.93(17)	−289.96(67)	−289.84
D(1,10)[e]	−396.59(18)	−408.66(180)	−408.24
D(4,12)[e]	−72.52(25)	−73.75(49)	−74.12
D(2,10)[e]	−93.23(17)	−94.65(45)	−94.75
D(1,12)[e]	−55.28(18)	−56.14(48)	−56.23
D(10,12)[e]	−142.22(12)	−144.88(50)	−144.78

[a]Observed: taken from Ref. 6. [b]Vibrationally corrected. [c]Calculated from combined analysis. [d]In Merck liquid crystal ZLI1167. [e]In Merck liquid crystal ZLI1083.

Molecular model and joint structural analysis. The experimental radial distribution curve from the electron diffraction data is shown in Fig. 2, and seven experimental direct dipolar couplings in each of two different liquid crystals are listed in Table 2. In the joint structural analysis, 1,2,3,5-tetrachlorobenzene was assumed to have C_{2v} symmetry. With this assumption the molecular geometry is described by 11 geometrical parameters: three different C−C bond distances, three C−Cl bond distances, one C−H bond distance, two angles that describe the shape of the C_6 ring, chosen as ∠C(4)C(5)C(6) and ∠(5)C(6)C(1), and two exocyclic angles, ∠C(5)C(6)H(12) and ∠C(2)C(1)Cl(7). With the assumed C_{2v} symmetry, only two orientation parameters, S_{xx} and S_{zz}, are needed for each of the two sets of dipolar couplings. The parameters were chosen as shown in Table 3. After some trial and error, it was clear that only two parameters could be refined to describe the C−C bond distances, and only one for the C−Cl bond distances. Only eight structural parameters could therefore be refined simultaneously, and p_3, p_5 and p_6 were fixed at, what seem to us, appropriate values: p_3 was fixed at 0.0, since the X-ray results for 1,2,3,5-tetrachlorobenzene[7] indicate no difference in length between the C(3)−C(4) and the C(4)−C(5) bonds. Previous X-ray[15] and neutron diffraction[16] results for 1,2,3-trichlorobenzene and the X-ray results for 1,2,3,5-tetrachlorobenzene strongly indicate that the central C−Cl bond of a C_3Cl_3 fragment is shorter than the two others. The average shortening from the crystal state studies is 0.7 pm. p_5 was fixed at this value. p_6 was fixed at 0.0, since no significant difference in length between the C(1)−Cl and the C(5)−Cl bonds was observed in the crystal phase.

In addition, eight u-values were refined as independent parameters as noted with standard deviations in Table 4. The independent parameters were refined by a least-squares fit 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. The final structural $r_{\alpha}{}^{\circ}$ parameters are given in Table 3. In Table 4 all

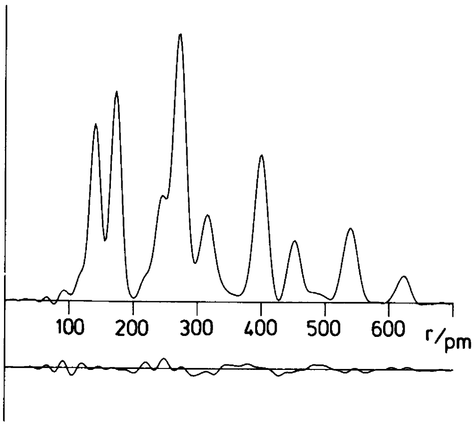

Fig. 2. Experimental radial distribution curve, $P(r)/r$, for 1,2,3,5-tetrachlorobenzene. In the lower part the difference between experimental and theoretical curves is shown. Before Fourier inversion the data were multiplied by $s\exp(-0.00002\,s^2)/(Z_C-f_C)(Z_{Cl}-f_{Cl})$.

Table 3. $r_{\alpha}{}^{\circ}$ Structure of 1,2,3,5-tetrachlorobenzene.

Parameters (distances in pm, angles in °):		
p_1	mean r(C−C)	139.80(8)
p_2	D1[a]	0.8(5)
p_3	D2[b]	0.0 (fixed)
p_4	mean r(C−Cl)	171.80(12)
p_5	D3[c]	0.7 (fixed)
p_6	D4[d]	0.0 (fixed)
p_7	r(C−H)	107.9(3)
p_8	∠C(5)C(6)H(12)	121.8(7)
p_9	∠C(2)C(1)Cl(7)	120.5(3)
p_{10}	∠C(4)C(5)C(6)	122.2(6)
p_{11}	∠C(5)C(6)C(1)	118.3(4)
Orientation parameters:		
p_{12}	S_{xx}[e]	0.1545(11)
p_{13}	S_{zz}[e]	−0.0981(11)
p_{14}	S_{xx}[f]	−0.2405(18)
p_{15}	S_{zz}[f]	0.1429(18)
Dependent parameters:		
	r[C(1)−C(2)]	140.3(4)
	r[C(3)−C(4)]	139.5(2)
	r[C(4)−C(5)]	139.5(2)
	∠C(6)C(1)C(2)	121.3(3)
	∠C(1)C(2)C(3)	118.6(4)

[a]The difference between the mean {r[C(3)−C(4)], r[C(4)−C(5)]} and r[C(1)−C(2)]. [b]The difference between r[C(3)−C(4)] and r[C(4)−C(5)]. [c]The difference between the mean {r[C(1)−Cl(7)], r[C(5)−Cl(11)]} and r[C(2)−Cl(8)]. [d]The difference between r[C(1)−Cl(7)] and r[C(5)−Cl(11)]. [e]In Merck liquid crystal ZLI1167. [f]In Merck liquid crystal ZLI1083.

Table 4. Interatomic distances (r_a), amplitudes of vibration (u_i) and *K*-values, all in pm, for 1,2,3,5-tetrachlorobenzene.[a]

i	Distance	r_a	u_i(ED)	u_i(FF)	K_i(FF)
1	C(1)–C(2)	140.7(4)	4.5(3)	5.09	0.53
2	C(3)–C(4)	140.0(2)	4.2 tied to u_1	4.83	0.63
3	C(4)–C(5)	139.9(2)	4.2 tied to u_1	4.79	0.53
4	C(2)–Cl(8)	172.2(1)	4.5(2)	4.75	1.07
5	C(5)–Cl(11)	172.9(1)	4.7 tied to u_4	4.95	1.08
6	C(1)–Cl(7)	173.0(1)	4.7 tied to u_4	4.91	1.17
7	C(4)–H(10)	109.5(3)	7.69 fixed	7.69	2.20
8	C(1)···C(5)	239.9(5)	5.99 fixed	5.99	0.47
9	C(2)···C(6)	244.2(5)	5.80 fixed	5.80	0.37
10	C(4)···C(6)	244.6(7)	6.18 fixed	6.18	0.47
11	C(1)···C(3)	241.6(6)	6.01 fixed	6.01	0.54
12	C(2)···C(5)	278.8(7)	6.23 fixed	6.23	0.35
13	C(3)···C(6)	280.4(5)	6.41 fixed	6.41	0.55
14	C(5)···H(10)	217.8(9)	10.02 fixed	10.02	1.47
15	C(4)···Cl(11)	269.3(4)	6.4(2)	7.03	0.69
16	C(4)···Cl(9)	268.5(3)	6.3 tied to u_{15}	6.97	0.88
17	C(1)···H(12)	215.8(8)	10.23 fixed	10.23	1.52
18	C(1)···Cl(8)	271.8(5)	6.5 tied to u_{15}	7.16	0.76
19	C(2)···Cl(7)	272.1(3)	6.4 tied to u_{15}	7.09	0.70
20	C(5)···Cl(7)	397.5(2)	7.2(2)	6.82	0.58
21	C(4)···H(12)	343.4(11)	9.89 fixed	9.89	1.19
22	C(4)···Cl(8)	401.9(5)	7.6 tied to u_{20}	7.16	0.51
23	C(1)···Cl(11)	397.9(5)	7.3 tied to u_{20}	6.88	0.36
24	C(1)···Cl(9)	400.9(5)	7.6 tied to u_{20}	7.20	0.46
25	C(2)···H(10)	342.0(9)	9.89 fixed	9.89	1.14
26	C(5)···Cl(8)	450.2(6)	8.0(4)	7.19	0.43
27	C(4)···Cl(7)	452.4(6)	7.3 tied to u_{26}	6.62	0.51
28	C(1)···H(10)	388.9(7)	9.67 fixed	9.67	1.23
29	C(2)···Cl(11)	450.7(6)	7.3 tied to u_{26}	6.58	0.27
30	H(10)···H(12)	433.7(17)	13.37 fixed	13.37	1.62
31	Cl(7)···Cl(11)	535.8(3)	9.9(4)	9.11	0.34
32	Cl(8)···Cl(11)	622.0(6)	8.3(4)	7.23	0.25
33	Cl(7)···Cl(8)	315.9(3)	10.6(4)	11.84	1.24
34	Cl(7)···Cl(9)	542.7(5)	10.1 tied to u_{31}	9.20	0.26
35	Cl(11)···H(10)	286.6(12)	14.36 fixed	14.36	1.16
36	Cl(7)···H(12)	281.6(13)	14.65 fixed	14.65	1.77
37	Cl(7)···H(10)	560.6(8)	9.80 fixed	9.80	0.94
38	Cl(8)···H(10)	486.7(10)	11.83 fixed	11.83	1.00

[a] ED = values obtained or used in the joint analysis of electron diffraction and liquid crystal NMR data. FF = values obtained from the harmonic force field calculation.

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

	p_1	p_2	p_4	p_7	p_8	p_9	p_{10}	p_{11}	p_{12}	p_{13}	p_{14}	p_{15}
p_1	100	–	–	66	–	–	62	−63	67	–	−64	–
p_2		100	–	–	–	70	–	–	–	–	–	–
p_4			100	–	–	–	50	−58	–	–	–	–
p_7				100	–	–	68	−71	93	−72	−93	66
p_8					100	–	–	−54	–	57	–	−65
p_9						100	–	–	–	–	–	–
p_{10}							100	−93	63	–	−61	–
p_{11}								100	−71	–	67	–
p_{12}									100	−81	−91	65
p_{13}										100	77	−89
p_{14}											100	−79
p_{15}												100

[a] Only elements ≥50 have been included. The parameter numbering is given in Table 3.

Table 6. Final atomic coordinates (in pm) for 1,2,3,5-tetrachlorobenzene.

Atom	*X*	*Y*	*Z*
1	0.00	120.63	−69.77
2	0.00	0.00	−141.42
3	0.00	−120.63	−69.77
4	0.00	−122.16	69.77
5	0.00	0.00	137.20
6	0.00	122.16	69.77
7	0.00	271.32	−152.63
8	0.00	0.00	−312.69
9	0.00	−271.32	−152.63
10	0.00	−216.27	122.48
11	0.00	0.00	309.17
12	0.00	216.27	122.48

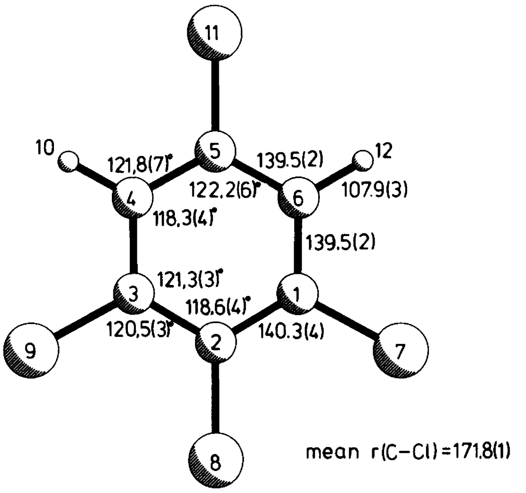

Fig. 3. Final molecular structure of 1,2,3,5-tetrachlorobenzene from the joint analysis of electron diffraction and liquid crystal NMR data. The r_α°-parameters and numbering of the atoms are shown.

interatomic distances (r_a) are listed, together with refined u-values and u- and K-values from the harmonic force field calculation, and principal elements of the least-squares correlation matrix are given in Table 5. Atomic coordinates are listed in Table 6.

Discussion

The geometrical parameters obtained for 1,2,3,5-tetrachlorobenzene in the joint analysis of LC–NMR and ED data are compared in Table 7 with the results from the two sets of data analysed separately and with parameters for the crystalline phase, obtained by X-ray diffraction.[7] The LC–NMR only results are taken directly from Ref. 6. The estimated errors for the parameters in this column do not include any allowance for the uncertainties in the vibrational corrections to the dipolar couplings, and for this reason are probably underestimated. As seen in Table 7, the results obtained from LC–NMR data alone give very precise values for distances and angles involving carbon and hydrogen, but give no information on the position of the chlorine atoms. The bond lengths may also be affected by systematic errors, since they are all based on an assumed parameter, in this case the H(10) · · · H(12) distance, which was taken to be 428.16 pm. On the other hand, the analyses based on ED data only give poor results for the positions of the hydrogen atoms, owing to their low scattering power,

Table 7. Comparison of the structural parameters obtained from analysis using only LC–NMR data, only ED data, and by using both LC–NMR and ED data simultaneously. X-Ray results (XR) are also shown.

	LC–NMR only[a]	ED only	ED + LC–NMR	XR[b]
r[C(1)–C(2)]	139.2(4)	140.0(8)	140.3(4)	138.4(6)
r[C(3)–C(4)]	138.1(11)	139.7(4)	139.5(2)	137.4(5)
r[C(4)–C(5)]	138.5(4)	139.7[c]	139.5[c]	137.5(5)
r[C(1)–Cl]	–	171.8(1)	172.0(1)	173.0(6)
r[C(2)–Cl]	–	171.1[d]	171.3[d]	171.9(4)
r[C(5)–Cl]	–	171.8[e]	172.0[e]	173.6(11)
r[C(4)–H]	107.1(2)	111.6(23)	107.9(3)	–
∠C(6)C(1)C(2)	120.8(2)	121.3(3)	121.3(3)	121.5(3)
∠C(1)C(2)C(3)	119.0(2)	118.8(5)	118.6(4)	118.2(3)
∠C(3)C(4)C(5)	118.9(4)	118.2(4)	118.3(4)	118.6(4)
∠C(4)C(5)C(6)	121.5(3)	122.1(7)	122.2(6)	121.8(4)
∠C(2)C(1)Cl	–	120.7(5)	120.5(3)	120.2(3)
∠C(5)C(6)H	121.2(4)	123.6(50)	121.8(7)	121.9(14)
r(H···H)[f]	428.16 fixed	443.9(104)	433.7(17)	–

[a] Taken from Ref. 6. [b] In the crystal there are two molecules per asymmetric unit, and the parameters are related by molecular, but not crystallographic symmetry. Mean values are given and the estimated standard deviations indicate the spread of the individual distances (Ref. 7). [c] Constrained to be equal to r[C(3)–C(4)]. [d] Constrained to be 0.7 pm shorter than r[C(1)–Cl]. [e] Constrained to be equal to r[C(1)–Cl]. [f] Included since the LC–NMR results are based on this assumed distance.

and also little information on the small differences in the C−C and C−Cl bond distances, which are strongly correlated with one another. The average C−C and C−Cl bond distances and valence angles involving carbon and chlorine atoms only are, however, well determined. By using both LC–NMR and ED data in a joint structural analysis, it was possible to obtain a molecular structure for 1,2,3,5-tetrachlorobenzene in which all refining bond distances and angles were determined with estimated standard deviations smaller than 0.4 pm and 0.7°, respectively, as is seen in the third column of Table 7.

In the fourth column of Table 7 the mean structural parameters from a previous room-temperature X-ray crystallographic study have been included. The C−C bond distances in the crystal are systematically shorter than those obtained in the joint analysis. This is probably a consequence of the libration motion of the ring in the crystalline phase. The differences in length between the different C−C bonds are, however, similar to those from the joint analysis. The C−Cl bond distances from the X-ray study are systematically longer than those from the joint analysis, which is a natural consequence of the C−C bonds being shorter. The mean C−H bond distance has been omitted from the XR column of Table 7 because of the large systematic errors involved in its determination. The valence angles found in the joint analysis are all equal to those found in the crystalline state to within one standard deviation.

We have recently also determined the molecular structure of 1,2,3-trichlorobenzene.[15] The C_3Cl_3 part of 1,2,3,5-tetrachlorobenzene is very similar to the equivalent fragment of 1,2,3-trichlorobenzene: the C−C bond between two chlorine atoms is long, 140.3(4) pm, which we attribute to Cl···Cl repulsion, which also accounts for the two chlorine atoms, Cl(7) and Cl(9), being bent away from Cl(8). The CCC angles at C(1) and C(3) are larger than 120°, which is to be expected at carbon atoms bearing electronegative substituents,[1] while the angle at C(2) is smaller, reduced by the substituents on the neighbouring carbon atoms and by the overall constraints of the carbon hexagon. Introduction of a chlorine atom in the 5-position of the ring leads to the expected distortions: the CCC angle at C(5) widens, to 122.2(6)°, and this opening at the 5-position forces the CCC angles at C(4) and C(6) to be significantly smaller than 120° [118.3(4)]. In 1,2,3-trichlorobenzene the ring angles of the C_3H_3 fragment are all close to 120°.

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