The Molecular Structure of *ortho*-Dichlorobenzene, Determined by the Combined Analysis of Data Obtained by Electron Diffraction, Rotational Spectroscopy and Liquid Crystal NMR Spectroscopy

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The molecular structure of *ortho*-dichlorobenzene has been determined by the simultaneous analysis of gas-phase electron diffraction scattering data, rotation constants for two isotopic species, and dipolar couplings, measured using solutions in a nematic liquid crystal phase. All eleven parameters (seven bond lengths and four angles) needed to define the structure were refined simultaneously. The estimated standard deviations in distances are between 0.19 and 0.79 pm, and errors in angles are in the range 0.14 to 0.25°. Deviations of the ring from regular hexagonal symmetry are very small, with the total scatter of C–C distances about 1 pm, and the greatest deviation from 120° angles 0.43±0.25° within the ring, and 0.77±0.18° for an external angle.

Dedicated to Professor Otto Bastiansen on his 70th birthday

In the determination of molecular structures using electron diffraction data, one is frequently faced with the problems caused by the limitations of the method. In particular, the resolution of several similar distances, and the location of light atoms, especially hydrogen, may be difficult or impossible. In such circumstances, additional structural data obtained by some other physical technique may be invaluable, and where these are available they should be used. Direct dipole-dipole coupling constants, measured by NMR spectroscopy for solutions in liquid crystal solvents, can provide such structural data, and complement electron diffraction data to a remarkable degree. Many independent couplings can be observed, each corresponding to a different interatomic distance in the molecule. As the data are most easily obtained for hydrogen, and the couplings are essentially independent of one another, both the problems inherent in using diffraction data are circumvented. Moreover, any errors in the measurement or interpretation of the couplings tend to cancel each other out. The major problems are the uncertainty in the orientation parameters, which translates into uncertainty in an overall scaling factor, or the size of the molecule, and the restriction of the data to nuclei with a spin of 1/2.

Using rotation constants to supplement electron diffraction is also beneficial, but there are other problems here. It is only possible to obtain at the most three independent data for any one molecule, and isotopic substitution may prove to be prohibitively expensive or time-consuming. Also, isotopic substitution changes bond lengths by small but significant amounts, and neglect of these changes can lead to major errors in the derived structure, as errors tend to propagate themselves. However, rotation constants do provide excellent indicators of the overall size of the molecule, and so the ideal procedure should be to use electron diffraction, rotation constants, and

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dipolar coupling data together, when they are available.

We are currently using this procedure, to see whether it is a useful and reliable method for determining precise structures. Our first results, for pyrazine,[1] pyrimidine[1] and thiophene,[2] suggest that it is. However, if we determine a structure with greater precision than was possible earlier, how can we tell whether the results are correct? One possibility is to look at a series of structures which are chemically related, but which present different procedural problems, and then see whether the results form a consistent pattern. We are therefore studying chlorine-substituted benzenes. Some of these are extremely simple. For example, the structure of 1,3,5-trichlorobenzene is described by just four parameters. In contrast, 1,2,4-trichlorobenzene requires 21 geometrical parameters. In this paper we present results for *ortho*-dichlorobenzene. This molecule has two different C–H bond lengths, four C–C lengths, and requires definition of two CCH angles, as well as one angle within the ring. It is therefore impossible to study fully by electron diffraction, for all of these reasons. In principle, a full structure could be determined by rotational spectroscopy but the isotopic substitutions required are too many and complicated for this to be countenanced. In practice, data are available for just two isotopic species, containing

$^{35}Cl_2$ and $^{37}Cl^{35}Cl$.[3] Finally, liquid crystal NMR cannot give information on the chlorine atom position, and some distance must be assumed in order to provide an overall scale factor.[4]

Table 1 shows the best results that can be obtained with the available data for each method. Nevertheless, using all the data together does give a complete structure, with reasonable precision for each parameter.

Experimental

ortho-Dichlorobenzene (99 % spectrophotometric grade) was obtained from the Aldrich Chemical Co. Ltd. and was used without further purification.

Electron diffraction scattering intensity data were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus,[5] operating at ca. 44 kV. The sample temperature was 359 K and the nozzle temperature was 378 K. Three plates were obtained at each of two camera distances, 258 and 93 mm, and plates for benzene were also run to provide calibration of the electron wavelength and camera distances. The plates were traced using a Joyce Loebl Microdensitometer 6 at the S.E.R.C. Laboratory, Daresbury, using a scanning program described previously.[6] Calculations were carried out using standard data-reduction[6] and least-squares

Table 1. Geometrical parameters for *ortho*-dichlorobenzene. Distances in pm, angles in °. Errors are given (in parentheses) as e.s.d.'s obtained in the least-squares refinements.

	Electron diffraction r_α	Rotational spectroscopy[a] r_0	Liquid crystal NMR spectroscopy[b]
$rC(1)–C(2)$	138.4(3)		140.8(15)
$rC(2)–C(3)$	138.7[c]	139.7(2)	138.5(13)
$rC(3)–C(4)$	140.8(4)		137.6(7)
$rC(4)–C(5)$			139.6(assumed)
$rC(3)–H$	111.5(9)	108.4(assumed)	108.7(5)
$rC(4)–H$		108.4(assumed)	108.4(1)
$rC(1)–Cl$	173.5(2)	172.3(3)	–
$\angle C(1)C(2)C(3)$	120.1(3)	120.0(2)	119.8(6)
$\angle C(2)C(3)C(4)$	120.8(7)	120.0(2)	119.9(6)
$\angle C(3)C(4)C(5)$	119.1(4)	120.0(2)	120.3(2)
$\angle C(3)C(4)H$	120.3(assumed)	120.0(assumed)	120.3(1)
$\angle C(4)C(3)H$	119.7(assumed)	120.0(assumed)	119.7(2)
$\angle C(1)C(2)Cl$	121.3(1)	121.0(2)	–

[a]Ref. 3. [b]Ref. 4. [c]Constrained to be 0.3 pm greater than $rC(1)–C(2)$.

Table 2. Weighting functions, correlation parameters and scale factors.

Camera height / mm	Wavelength / pm	Δs^a	s_{min}^a	sw_1^a	sw_2^a	s_{max}^a	Correlation parameter	Scale factor
93.17	5.673	4	80	100	260	328	0.426	0.654(24)
258.05	5.672	2	20	40	140	164	0.493	0.845(17)

^{a} In nm^{-1}.

refinement[7] programs. The weighting points used in setting up the off-diagonal weight matrices for the refinements are given in Table 2, together with other experimental data. In all calculations the complex scattering factors of Schäfer *et al.*[8] were used.

Rotation constants for $^{12}C_6{}^{1}H_4{}^{35}Cl_2$ and $^{12}C_6{}^{1}H_4{}^{35}Cl^{37}Cl$ were taken from Ref. 3, and dipolar coupling constants measured for a 15 mol % solution of *ortho*-dichlorobenzene in Merck Phase IV, a nematic liquid crystal solvent, at 301 K, were taken from Ref. 4.

Vibrational analysis

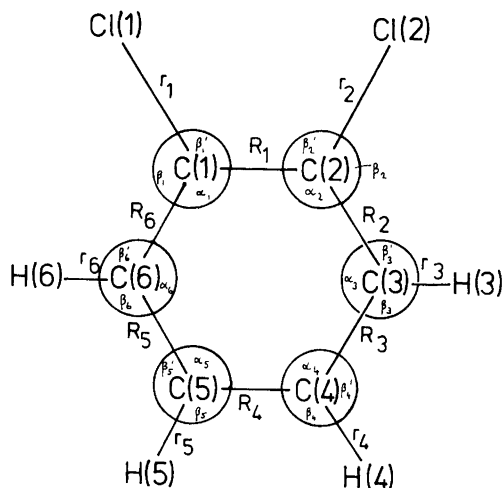So that all the experimental data can be related to a common structure, various vibrational correc-

tion terms must be calculated. Analysis of the normal modes of *ortho*-dichlorobenzene was performed using the program GAMP,[9] assuming C_{2v} symmetry. A force field was obtained, giving the optimum fit to the observed vibrational frequencies for $C_6H_4Cl_2$ and $C_6D_4Cl_2$.[10,11] Details of the atom numbering and internal coordinates used in

Table 3. Symmetry coordinates for *ortho*-dichlorobenzene.

A_1: $S_1 = (1/\sqrt{2})[r_3 + r_6]$
$S_2 = (1/\sqrt{2})[r_4 + r_5]$
$S_3 = R_1$
$S_4 = R_4$
$S_5 = (1/\sqrt{2})[R_2 + R_6]$
$S_6 = (1/\sqrt{2})[R_3 + R_5]$
$S_7 = (1/\sqrt{2})[r_1 + r_2]$
$S_8 = (1/2)[\beta_{3'} - \beta_3 + \beta_{6'} - \beta_6]$
$S_9 = (1/2)[\beta_{4'} - \beta_4 + \beta_{5'} - \beta_5]$
$S_{10} = (1/\sqrt{3})[(1/2)(\alpha_1 + \alpha_2 + \alpha_4 + \alpha_5) - (\alpha_3 + \alpha_6)]$
$S_{11} = (1/2)[\beta_{1'} - \beta_1 + \beta_{2'} - \beta_2]$

A_2: $S_1 = (1/\sqrt{2})[\gamma_6 - \gamma_3]$
$S_2 = (1/\sqrt{2})[\gamma_5 - \gamma_4]$
$S_3 = (1/\sqrt{2})[\tau_4 - \tau_1]$
$S_4 = (1/\sqrt{2})[\tau_4 + \tau_1]$
$S_5 = (1/\sqrt{2})[\gamma_1 - \gamma_2]$

B_1: $S_1 = (1/\sqrt{2})[\gamma_3 + \gamma_6]$
$S_2 = (1/\sqrt{2})[\gamma_4 + \gamma_5]$
$S_3 = (1/2)[\tau_2 - \tau_3 + \tau_5 - \tau_6]$
$S_4 = (1/\sqrt{2})[\gamma_1 + \gamma_2]$

B_2: $S_1 = (1/\sqrt{2})[r_6 - r_3]$
$S_2 = (1/\sqrt{2})[r_5 - r_4]$
$S_3 = (1/\sqrt{2})[R_6 - R_2]$
$S_4 = (1/\sqrt{2})[R_5 - R_3]$
$S_5 = (1/\sqrt{2})[r_1 - r_2]$
$S_6 = (1/2)[\beta_3 - \beta_{3'} - \beta_6 + \beta_{6'}]$
$S_7 = (1/2)[\beta_4 - \beta_{4'} - \beta_5 + \beta_{5'}]$
$S_8 = (1/\sqrt{6})[\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6]$
$S_9 = (1/2)[\alpha_1 - \alpha_2 + \alpha_4 - \alpha_5]$
$S_{10} = (1/2)[\beta_{1'} - \beta_1 - \beta_{2'} + \beta_2]$

Fig. 1. Atom numbering and definition of internal coordinates. γ_1 is the out-of-plane motion of carbon atom 1, with the hydrogen or chlorine atom defined first. τ_1 is the torsion of ring bond 1, defined by the atom string C(6)C(1)C(2)C(3).

Table 4. Force field for *ortho*-dichlorobenzene.

A_1

5.113										
0.	5.102									
0.	0.	5.871								
0.	0.	0.267	7.746							
0.	0.	0.442	0.242	5.716						
0.	0.	−0.153	2.536	1.632	5.885					
0.	0.	0.650	−0.107	0.671	−0.003	6.906				
0.	0.	0.	0.	0.293	−0.347	−0.155	0.461			
0.	0.	0.	−0.105	0.	−0.107	0.	0.004	0.480		
0.	0.	−0.110	0.	−0.185	0.	0.	0.	0.	1.112	
0.	0.	0.601	0.	0.	0.	−0.115	0.	0.	0	1.231

A_2

0.392				
0.023	0.512			
0.082	−0.380	0.660		
−0.049	−0.426	0.080	1.303	
−0.026	−0.039	−0.023	0.478	0.586

B_1

0.346			
0.088	0.396		
−0.039	0.131	0.225	
0.003	−0.001	0.101	0.696

B_2

5.120									
0.	5.135								
0.	0.	7.652							
0.	0.	0.606	6.539						
0.	0.	1.806	0.	6.967					
0.	0.	0.029	−0.310	−0.022	0.529				
0.	0.	0.	0.110	0.	0.	0.477			
0.	0.	0.	0.	−0.542	0.	0.	0.866		
0.	0.	0.	−0.153	−0.974	0.	0.	0.	1.256	
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.732

this work are shown in Fig. 1, and the definitions of symmetry coordinates are given in Table 3. The elements of the force field are listed in Table 4.

This force field was then used to calculate r.m.s. amplitudes of vibration and K-values, which were used in the conversion of r_a distances obtained in analysis of the electron diffraction data to the geometrically consistent r_α distances. In the refinements based on electron diffraction data, whether alone or with other data, some amplitudes of vibration were fixed at the values calculated from this force field. Others were free to refine, either separately or constrained in groups, with the ratios of various amplitudes fixed at the calculated values. So far as geometrical parameters and their e.s.d.'s were concerned, it made no significant difference whether or not vibrational amplitudes were refined. The calculated amplitudes and K-values used in the final refinement based on diffraction data, dipolar couplings and rotation constants are listed in Table 5, together with the interatomic distances in that final structure.

Table 5. Interatomic distances, amplitudes of vibration and *K*-values (pm).

Atoms	Distance, r_a	Amplitude[a] of vibration	K^a
C(1)C(2)	140.2(8)	4.68	0.36
C(2)C(3)	139.4(7)	4.66	0.39
C(3)C(4)	139.5(4)	4.81	0.53
C(4)C(5)	140.5(3)	4.50	0.39
C(1)Cl(1)	173.7(2)	4.19	0.41
C(3)H(3)	108.5(4)	7.69	2.20
C(4)H(4)	109.6(2)	7.69	1.84
C(1)C(3)	242.2(3)	5.85	0.36
C(1)C(5)	240.5(4)	5.74	0.27
C(3)C(5)	242.4(4)	5.54	0.46
C(1)Cl(2)	272.8(4)	5.87	0.18
C(3)Cl(2)	270.0(3)	6.07	0.40
C(1)H(6)	214.7(6)	9.90	1.49
C(3)H(4)	214.9(4)	10.22	1.10
C(4)H(3)	215.3(6)	9.86	1.66
C(4)H(5)	216.8(4)	10.05	1.07
C(1)C(4)	278.3(3)	6.18	0.28
C(3)C(6)	280.3(5)	6.34	0.49
C(3)Cl(1)	401.9(3)	6.00	0.10
C(5)Cl(1)	399.1(2)	6.12	0.13
Cl(1)Cl(2)	317.0(2)	9.77	0.12
C(1)H(3)	339.5(4)	9.75	1.10
C(1)H(5)	338.9(4)	9.72	0.77
C(3)H(5)	341.0(6)	9.62	0.96
C(4)H(6)	340.2(6)	9.59	1.22
Cl(1)H(6)	283.3(5)	13.85	1.32
H(3)H(4)	247.6(5)	15.88	1.96
H(4)H(5)	249.9(8)	16.03	1.44
C(4)Cl(1)	451.4(2)	5.95	0.07
C(1)H(4)	387.1(3)	9.50	0.74
C(3)H(6)	387.9(6)	9.61	1.17
Cl(1)H(3)	486.7(2)	10.89	0.59
Cl(1)H(5)	484.2(2)	11.06	0.48
H(3)H(5)	430.2(9)	13.16	1.55
Cl(1)H(4)	560.0(2)	9.36	0.36
H(3)H(6)	495.1(8)	12.02	1.56

[a]Calculated from the force field in Table 4, at 300 K.

The force field was also used to calculate corrections to the dipolar coupling constants,[12] to give D_α couplings, which relate directly to the r_α structure, and also to give the correction terms which convert the B_0 rotation constants to B_z. The structure given by the B_z constants is strictly r_α^0, but the differences between this and the r_α structure are extremely small. However, the corrections to dipolar couplings and rotation constants

are fairly large, and uncertainties in these corrections should be reflected in the weights assigned to the associated observations. We therefore performed a series of refinements of the force field, starting with a range of different but reasonable values for the various elements. Because the force field is underdetermined, this procedure gave final force fields with somewhat different values for the elements and a consequent scatter in the calculated correction terms. This scatter was used to give an estimate of the uncertainty of each correction term, and this was combined with the error of the observation to give an estimated error for the corrected observation, used in the refinements. Each such extra observation is given a weight inversely proportional to the square of its uncertainty.[7] The dipolar couplings and rotation constants, as observed and vibrationally corrected, are given in Table 6. This table also lists the uncertainties in these quantities, and the values calculated from the final structural model. It should be noted that the corrections to dipolar couplings for bonded C–H atom pairs are large, and that the uncertainties in these corrections are particularly significant.

Structure analysis

For all least-squares refinements of the structure of *ortho*-dichlorobenzene it was assumed that the molecule was planar, with C_{2v} symmetry. It has been suggested[13] that the chlorine atoms could lie out of the plane of the rest of the molecule, but the very small inertia defect noted in a microwave study[3] indicates that the molecule is planar. Making only this assumption, the structure is defined by 11 geometrical parameters. The independent parameters chosen for our analyses are listed in the first column of Table 1, together with two dependent parameters, viz. the ring angles C(1)C(2)C(3) and C(2)C(3)C(4).

Using electron diffraction data alone, it was necessary to assume that the two different C–H distances were equal and the angles defining the hydrogen atoms were fixed; this was due to the fact that when they were free to refine, their estimated standard deviations were 5 to 10°. It was also necessary to reduce the number of independent C–C distances, because these were very strongly correlated with one another. Knowing that electronegative substituents on benzene rings tend to shorten the C–C bonds adjacent to

Table 6. Dipolar coupling constants (Hz) and rotation constants (MHz).

	Observed	Vibrationally corrected	Calculated from final structural model
DH(3)H(4)	−572.94(4)	−591.45(41)	−591.44
DH(3)H(5)	−54.58(5)	−56.01(6)	−56.02
DH(3)H(6)	−17.78(18)	−18.40(18)	−18.46
DH(4)H(5)	−137.54(18)	−143.22(19)	−143.21
DC(1)H(3)	−20.3(9)	−20.9(9)	−21.5
DC(2)H(3)	−122.2(17)	−128.2(17)	−128.7
DC(3)H(3)	−382.3(7)	−457.4(12)	−457.4
DC(4)H(3)	−121.7(2)	−128.8(2)	−128.8
DC(5)H(3)	−20.9(6)	−21.6(6)	−21.5
DC(6)H(3)	−9.1(7)	−9.4(7)	−9.7
DC(1)H(4)	−38.4(9)	−38.7(9)	−38.3
DC(2)H(4)	−69.0(17)	−69.7(17)	−70.1
DC(3)H(4)	−275.5(7)	−280.9(7)	−280.9
DC(4)H(4)	−1596.2(2)	−1737.4(18)	−1737.4
DC(5)H(4)	−94.6(6)	−96.6(6)	−96.5
DC(6)H(4)	−36.2(7)	−36.8(7)	−36.4
AC$_6$H$_4$^{35}Cl$_2$	1930.02(13)	1929.23(13)	1929.24
BC$_6$H$_4$^{35}Cl$_2$	1431.16(7)	1430.92(7)	1430.90
CC$_6$H$_4$^{35}Cl$_2$	821.670(4)	821.558(4)	821.558
AC$_6$H$_4$^{35}Cl^{37}Cl	1895.87(18)	1895.09(20)	1895.02
BC$_6$H$_4$^{35}C^{37}Cl	1414.10(14)	1413.86(15)	1413.90
CC$_6$H$_4$^{35}Cl^{37}Cl	809.846(8)	809.735(10)	809.743

the substituents,[14] we assumed that the bond lengths C(3)–C(4) and C(4)–C(5) were equal, and that C(2)–C(3) was 0.3 pm longer than C(1)–C(2). Under these conditions, and refining also 10 amplitudes of vibration or groups of amplitudes, the structure described in Table 1 was obtained. Only six geometrical parameters could be refined, of the 11 that are needed.

The second structure in Table 1 is that determined from rotation constants for two isotopic species.[3] We repeated the analysis and found that the four parameters that can be refined are very sensitive to the assumed positions of the hydrogen atoms. With these atoms fixed in the positions found in our final, combined analysis, the C–Cl distance increased to 174.7 pm, while the mean C–C distance decreased to 139.0 pm.

The third structure in Table 1 is that based only on dipolar coupling constants.[4] It should be noted that the quoted errors are underestimates, as no allowance has been made for uncertainty in the vibrational corrections, or for possible error in the assumed C(4)–C(5) distance. Although only

eight parameters can be refined in this case, the most useful information relates to the hydrogen atom positions, and the four parameters defining these positions are all well determined.

Further refinements were then performed using the electron diffraction data, plus the 16 dipolar coupling constants and 6 rotation constants listed in Table 6. It was now possible to refine all 11 geometrical parameters, as well as vibrational amplitude parameters. Allowing the amplitudes of vibration to refine made no significant difference to bond lengths and angles (the maximum change was 0.1 pm) or to their estimated standard deviations, so the distances listed in Table 5 are those for a refinement in which all vibrational parameters were fixed at the values calculated from the force field. After the structure had been determined by this combined analysis, the whole force field was redetermined, using the new geometry, and all vibrational terms and corrections were recalculated. The structural refinement was then repeated, to give the results listed in Table 7. This structure is consistent with all the available

Table 7. Geometrical parameters (r_α) for *ortho*-dichlorobenzene, obtained by combined analysis of electron diffraction data, rotation constants and dipolar coupling constants. Distances in pm, angles in °. Errors (in parentheses) are e.s.d.'s obtained in the least-squares refinement.

	All parameters refined independently	C–C distances defined by 2 parameters only (see text)
rC(1)–C(2)	139.9(8)	139.0(4)[a]
rC(2)–C(3)	139.1(7)	139.3(1)[a]
rC(3)–C(4)	139.0(4)	139.6(2)[a]
rC(4)–C(5)	140.2(3)	139.6(2)[a]
rC(3)–H	106.9(4)	107.0(3)
rC(4)–H	108.4(2)	108.2(2)
rC(1)–Cl	173.3(2)	173.2(2)
∠C(1)C(2)C(3)[a]	120.24(18)	120.27(18)
∠C(2)C(3)C(4)[a]	119.57(25)	119.67(22)
∠C(3)C(4)C(5)	120.19(15)	120.06(11)
∠C(3)C(4)H	120.48(14)	120.49(14)
∠C(4)C(3)H	120.28(25)	120.66(16)
∠C(1)C(2)Cl	120.77(18)	121.05(6)
S_{zz}[b]	0.09197(45)	0.09193(42)
S_{yy}[b]	0.01853(18)	0.01860(14)

[a]Dependent parameter. [b]Orientation parameters for the liquid crystal solution.

data, as can be seen from the observed and calculated values in Table 6, and the molecular scattering curves (Fig. 2) and radial distribution curves (Fig. 3).

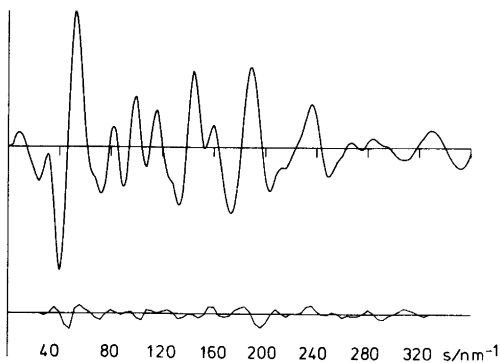The results described above are the best that

Fig. 2. Combined observed and final weighted difference molecular scattering intensity curves for *ortho*-dichlorobenzene.
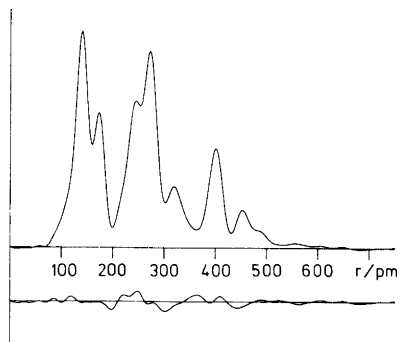
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Fig. 3. Observed and final difference radial distribution curves, $P(r)/r$, for *ortho*-dichlorobenzene. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002\ s^2)/(Z_C-f_C)(Z_{Cl}-f_{Cl})$.

can be obtained from the existing data without making assumptions about the structure. Unfortunately, the differences between the four C–C distances are small, and the standard deviations for the individual distances are comparable with the differences. We therefore carried out one more refinement, making the assumption that the effect of the chlorine substituents was to change the adjacent C–C bond lengths by equal amounts, with the effects being additive for the bond C(1)–C(2). This reduced the number of refining parameters to nine, and the longest C–C distance now refined to 139.6(2) pm, with a shortening of 0.3(3) pm attributable to chlorine substitution. The results of this refinement are also given in Table 7.

Discussion

It is clear from the results given in Tables 1 and 7 that the simultaneous analysis of data obtained by three distinct experimental techniques gives a structure of precision and completeness far exceeding those given by any one data set alone. The question then remains: does the accuracy match up to the precision? Our purpose in studying chlorine-substituted benzenes is to compare the structures with one another, and as this is the first structure to be completed we cannot make many comments. However, it is satisfying to note that the distortions of the ring from regular hexagonal symmetry are small. The effects of chlorine substituents in adjacent positions may be expected to cancel each other out to some extent.

Thus, widening of the CCC angle at the carbon atom bound to the substituent will be partially negated by narrowing of the angles adjacent to the other substituted carbon atom. The major distortions involve displacement of the chlorine atoms away from each other, and slight movement of H(3) and H(6) towards the chlorine atoms. Variations in C–C bond lengths are not significant, but the total spread is only 1 pm and the evidence of the final refinement is that a chlorine substituent contracts neighbouring C–C bonds by about 0.3 pm.

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