Semi-empirical Parameters in π-Electron Systems

IV. Heteroatomic Molecules Containing Chlorine Atoms

BARBRO GRABE

Institute of Theoretical Physics, University of Stockholm, Stockholm, Sweden

A modification of the Pariser-Parr-Pople method has been extended to chloroethylenes and chlorobenzenes. The method has been applied in calculations of ionization potentials, electronic transitions, and bond lengths. The overall agreement between calculated values and measurements is satisfactory.

The semi-empirical method by Pariser-Parr-Pople is widely used in calculations on π-electron systems. The value of the method depends, however, on the possibility to give a scheme for the determination of the semi-empirical parameters of the method in such a manner, that they can be used in arbitrary molecules. The present series is an attempt to give such a scheme. In previous papers parameters are suggested for unsaturated hydrocarbons [1] as well as methyl substituted ones [2] by Roos and Skancke and for nitrogen containing molecules by Fischer-Hjalmars and Sundbom.[3] In the present paper the scheme is extended to molecules containing chlorine.

Calculations have been made on a set of small molecules, *viz.* vinyl chloride, *cis*-dichloroethylene and monochlorobenzene. The parameters have been adapted so that the calculated values on ionization potentials and singlet transitions of the chosen molecules coincide as well as possible with empirical data. Then these parameter values have been tested on a set of other molecules.

METHOD

The method used is a SCF—MO—LCAO—CI method in the Pariser-Parr-Pople approximation. This implies zero-differential overlap approximation (ZDO) and semi-empirical estimation of some integrals. The following approximations and notations are used.

$$S_{\mu\nu} = (\mu|S|\nu) = \delta_{\mu\nu} \tag{1}$$

$$\alpha_\mu = (\mu|H^{\text{core}}|\mu) \neq 0 \tag{2}$$

$$\beta_{\mu\nu} = (\mu|H^{\text{core}}|\nu) \quad \begin{cases} \neq 0, \text{ when } \mu \text{ and } \nu \text{ are neighbours} & (3a) \\ = 0, \text{ when } \mu \text{ and } \nu \text{ are non-neighbours} & (3b) \end{cases}$$

$$(\alpha\beta|1/r_{12}|\mu\nu) = \delta_{\alpha\mu}\ \delta_{\beta\nu}\ \gamma_{\mu\nu} \tag{4}$$

Fischer-Hjalmars [4] has examined the grounds for the ZDO-approximation and showed that it can be described as a second order theory in the overlap integral, $S_{\mu\nu}$, between neighbouring AO's. The resonance integral, $\beta_{\mu\nu}$, and the Coulomb integral, $\gamma_{\mu\nu}$, were shown to be transferable from one molecule to another, *i.e.* the contribution from other centres than μ and ν are of third order and thus these integrals can be considered in this approximation as dependent only on the kind of atoms μ and ν and of the distance between them. The core integral, α_μ, is non-local and can according to Goeppert-Mayer and Sklar [5] be written

$$\alpha_\mu = W_\mu - (n_\mu - 1)\ \gamma_{\mu\mu} - \sum_{\nu \neq \mu} n_\nu\ \gamma_{\mu\nu} \tag{5}$$

where n_ν is the number of electrons contributed to the delocalized π system by the ν orbital. W_μ is local to the first order in the overlap integral only. The second order terms include contributions from the nearest neighbours and therefore Roos and Skancke [1] have introduced a term ΔW_μ in W_μ which is dependent on the kind of neighbours and the distances to them.

The scheme given in Refs. 1, 2, and 3 for the determination of the semi-empirical parameters implies the suggestion of linear dependence of $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ on the distance between μ and ν, if they are nearest neighbours, and the dependence of W_μ on all the nearest neighbours and on the distances to them. For the justification of these suggestions see Ref. 1. Thus it is suggested that

$$\beta_{\mu\nu} = \beta_{\mu\nu}° + \delta_{\mu\nu}{}^\beta(R_{\mu\nu} - R_{\mu\nu}°) \tag{6}$$

$$\gamma_{\mu\nu} = \gamma_{\mu\nu}° + \delta_{\mu\nu}{}^\gamma(R_{\mu\nu} - R_{\mu\nu}°) \tag{7}$$

$$W_\mu(\text{P,Q}, \ldots) = W_\mu° + \sum[\Delta W_\mu°(\text{P}) + \delta_{\mu\text{P}}{}^W(R_{\mu\text{P}} - R_{\mu\text{P}}°)] \tag{8}$$
$$\text{P over all}$$
$$\text{bonded atoms}$$

$R_{\mu\nu}$ and $R_{\mu\text{P}}$ are the distances between the atoms and $R°$ are standard values, chosen so that $R_{\text{CC}}° = 1.397$ Å (the C—C distance in benzene) and $R_{\text{CCl}}° = 1.718$ Å. P,Q, $\ldots$ are atoms bound to μ.

The parameter values $\beta_{\text{CC}}°$, $\delta_{\text{CC}}{}^\beta$, $\gamma_{\text{CC}}°$, $\delta_{\text{CC}}{}^\gamma$, $W_{\text{C}}°$, $\Delta W_{\text{C}}°(\text{C})$, and $\delta_{\text{CC}}{}^W$ have been chosen in accordance with Ref. 2. $W_{\text{C}}°$ is the ionization potential for the π-orbital in the planar CH_3 radical and $\Delta W_{\text{C}}(\text{C})$ is the correction when a hydrogen atom is replaced by an sp^2 hybridized carbon atom. The values are given in Table 2.

The parameter values $\beta_{\text{CCl}}°$, $\gamma_{\text{CCl}}°$, $\Delta W_{\text{C}}°(\text{Cl})$ and $W_{\text{Cl}}(\text{C}) = W_{\text{Cl}}° + \Delta W_{\text{Cl}}°(\text{C})$ have been determined through a least square fit to experimental values on ionization potentials and singlet transitions for three standard molecules, *viz.* vinyl chloride, *cis*-dichloroethylene and chlorobenzene. The choice of experimental data is discussed in a subsequent paragraph. Since the chlorine

is single valued and bounded to a sp^2 hybridized carbon at the same distance in all the molecules, no more parameters of (6)—(8) have been determined. The parameter values are given in Table 2.

For the calculation of the γ-integrals for non-neighbours the ball approximation has been used.

The one-center integrals γ_{CC} and γ_{ClCl} are determined from atomic spectral data. For the values, see Table 2.

The SCF—MO's have been evaluated by means of a data machine programme written by P. Eisenberger, T. Alm and B. Roos. This programme also calculates the energy levels of excited states by mixing all configurations obtained from single excitations. Oscillator strengths for the dipole transitions and eigenvectors for the multi-configurational problem are also obtained directly from the computer. The CDC 3600 machine at Uppsala University has been used for the present calculations.

EXPERIMENTAL DATA FOR BOTH STANDARD MOLECULES AND TEST MOLECULES USED IN THE PRESENT PAPER

The parameters have been adapted by a least squares method so that six calculated values coincide as well as possible with experimental data, viz. the first ionization potential for vinyl chloride, cis-dichloroethylene, and chlorobenzene, the lowest singlet-singlet transition for the chloroethylenes and the three lowest transitions for chlorobenzene. However, for the chloro-substituted benzenes it is not the absolute values of the calculated transitions but the shifts of the transitions in relation to unsubstituted benzene that are compared with the corresponding experimental data.

Then the parameter values obtained are tested on trans-dichloroethylene, tetrachloroethylene, the three dichlorobenzenes, 1,2,4,5-tetrachlorobenzene, and hexachlorobenzene.

All the experimental data used in this program, in the calculations or for testing the results, are given in Tables 1, 3, 4, and 5: in Table 1 the geometry of the molecules, in Table 3 ionization potentials, and in Tables 4 and 5 singlet-singlet transitions. In Tables 3, 4, and 5 the corresponding values obtained
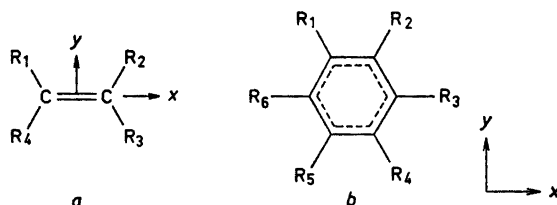

Fig. 1. The figure shows the direction of x and y in Tables 4 and 5 in column "Polarization". The places where Cl is substituted for H in ethylene and benzene are the following:
a. Vinyl chloride $R_1=Cl$; cis-dichloroethylene $R_1=R_2=Cl$; trans-dichloroethylene $R_1=R_3=Cl$; tetrachloroethylene $R_1=R_2=R_3=R_4=Cl$.
b. Chlorobenzene $R_3=Cl$; o-dichlorobenzene $R_1=R_2=Cl$; m-dichlorobenzene $R_2=R_4=Cl$; p-dichlorobenzene $R_3=R_6=Cl$; 1,2,4,5-tetrachlorobenzene $R_1=R_2=R_4=R_5=Cl$; hexachlorobenzene $R_1=R_2=R_3=R_4=R_5=R_6=Cl$.

Table 1. Distances (Å) between nearest neighbours and bond angles (°), used in the calculations.

	r_{C-C}	r_{C-Cl}		
Ethylene	1.337			Ref. 6.
Vinyl chloride	1.33	1.718 [a]	$\angle CCCl = 122$	See Ref. 7.
cis-Dichloroethylene ⎫	1.354	1.718	$\angle CCCl = 123.8$	The values for
trans-Dichloroethylene ⎭				cis-dichloro-ethylene given in Ref. 8.
Tetrachloroethylene	1.354	1.718	$\angle ClCCl = 115.7$	Ref. 9.

m-Dichlorobenzene ⎫
p-Dichlorobenzene
Hexachlorobenzene
o-Dichlorobenzene
1,2,4,5-Tetrachlorobenzene ⎭

$1.397 \qquad 1.718 \qquad \angle CCC = 120$

The angle between the *ortho* carbon-chlorine bonds is distorted in tetrachlorobenzene and equal to 62.8° (Ref. 10). The same value is used in o-dichlorobenzene.

[a] In Ref. 7 the value 1.72_6 Å is given but in the present calculation the same C—Cl distance is used in all the molecules.

by the calculations are given. The parameters used in these calculations are given in Table 2.

In the following paragraphs a short review is given of the experimental data taken from literature for adaption and testing of the parameter values.

The geometry of the molecules (see Table 1 and Fig. 1). The geometry of vinyl chloride has been determined by Kivelson, Wilson and Lide [7] from microwave spectroscopy and that of cis-dichloroethylene by Davis and Hanson [8] from gas phase electron diffraction. The same distances and angles have been used for the *trans* form as for the *cis* form. The geometry of tetrachloroethylene, and of 1,2,4,5-tetrachlorobenzene and hexachlorobenzene have been determined by Strand [9] and by Strand and Cox [10] by the gas electron

Table 2.

Carbon parameters used in the calculations, the same as those given in Ref. 2.				Chlorine and carbon-chlorine parameters determined in the present paper and used in the calculations.			
R_{CC}°	$=$	1.397	Å	R_{CCl}°	$=$	1.718	Å
$\gamma_{\pi\pi}$	$=$	11.97	eV	$\gamma_{\pi\pi}$	$=$	12.28	eV
γ_{CC}°	$=$	6.91	eV	γ_{CCl}°	$=$	5.52	eV
δ_{CC}^{γ}	$= -$	3.99	eV/Å				
β_{CC}°	$= -$	2.42	eV	β_{CCl}°	$= -$	1.35	eV
δ_{CC}^{β}	$=$	3.05	eV/Å·				
W_C°	$= -$	9.84	eV				
$\Delta \bar{W}_C^{\circ}(C) =$		0.07	eV	$W_{Cl}(C)$	$= W_{Cl}^{\circ} + \Delta W_{Cl}^{\circ}(C) = -11.24$ eV		
δ_{CC}^{W}	$=$	9.21	eV/Å	$\Delta W_C(Cl)$	$= -$	0.76	eV

Table 3. Ionization potentials, eV.

Molecule	Calc.	Exptl.	Experimental method
Ethylene	10.52	10.52 [a][12,15]	Photo-ionization cross-section
Vinyl chloride	10.14	10.00 [b][13]	Photo-ionization and spectr.
		9.95 [14]	Spectr.
		9.995 [16]	Photo-ionization
	12.22		
cis-Dichloro-	9.68	9.61 [b][14]	Spectr.
ethylene		9.65 [16]	Photo-ionization
	11.58		
	12.48		
trans-Dichloro-	9.66	9.6 [17]	Spectr.
ethylene		9.63 [18]	
		9.66 [16]	Photo-ionization
	11.56		
	12.46		
Tetrachloro-	9.35	9.33 [19]	Spectr.
ethylene		9.32 [16]	Photo-ionization
	11.22		
	11.26		
	11.81		
	13.26		
Benzene	9.25	9.39 [b][11a] 9.40 [11b] vert.	Photoelectron spectra
		9.25 [a][12,11a] adiab.	Spectr.a.photoelectron spectr.
		9.245 [15,16]	Photo-ionization
	12.36	11.91 [11a] 11.86 [11b] vert.	Photoelectron spectra
		11.49 [12] adiab.	Spectr.a.photoelectron spectr.
Chlorobenzene	9.12	9.35 [b][11a] 9.31 [11b] vert.	Photoelectron spectra
		8.99 [11a,12] adiab.	» »
		9.07 [15,16]	Photo-ionization
	9.22	9.68 [11a] 9.71 [11b] vert.	Photoelectron spectra
		9.60 [12] adiab.	» »
	11.40	11.76 [11b]	» »
	12.75	12.38 [11a] vert.	» »
		11.88 [12] 12.2 [11b] adiab.	» »
o-Dichlorobenzene	9.04	9.06 [18]	
		9.07 [16]	Photo-ionization
	9.13		
	11.24		
	11.59		
	13.01		
m-Dichlorobenzene	9.06	9.12 [16]	Photo-ionization
	9.14		
	11.10		
	11.87		
	12.96		
p-Dichlorobenzene	9.02	9.17 [11b] vert.	Photoelectron spectra
		8.94 [16] 8.95 [18]	Photo-ionization
	9.19	10.01 [11b] vert.	Photoelectron spectra
	11.02		
	11.95		
	12.95	12.7 [11b] adiab.	Photoelectron spectra
1,2,4,5-Tetra-	8.90		
chlorobenzene	9.03		
	10.71		
Hexachloro-	8.83		
benzene	10.47		

[a] Used in Ref. 1 for the determination of carbon parameters.
[b] Used in the present paper for the determination of chlorine and carbon-chlorine parameters.

diffraction method. The deviation in the C—C distances in the chlorine substituted benzenes from those of benzene are so small that they are not taken into consideration. Similarly the differences in C—Cl distances from that in cis-dichloroethylene is within the limits of the method so the same C—Cl distance has been used in all the molecules. The angle between the ortho carbon-chlorine bonds for 1,2,4,5-tetrachlorobenzene is according to Ref. 10 62.8° and this value has also been used in o-dichlorobenzene.

Ionization potentials (see Table 3). In the calculations the vertical ionization potentials have been determined by Koopmans' theorem. Since vertical ionization potentials are very difficult to determine experimentally, most of the accurate values in the literature are adiabatic IP's. However, for benzene and chlorobenzene Turner et al.[11 a,b] have determined both adiabatic and vertical ionization potentials by photoelectron spectroscopy. The vertical IP's are 9.40 eV for benzene and 9.31 eV for chlorobenzene.[11 b] These values can be compared with the adiabatic values 9.25 for benzene and 8.99 for chlorobenzene.

As is seen from Table 3 we have used data determined by Turner[12] for ethylene, by Sood and Watanabe[13] for vinyl chloride, and by Walsh[14] for cis-dichloroethylene. The values given by Walsh are taken as limits of Rydberg series. All the values for these molecules seem to be adiabatic ionization potentials.

Singlet-singlet transitions (see Tables 4 and 5). The calculated singlet-singlet transitions correspond to vertical transitions in the gas phase and thus the values should be compared with experimental values of the energy of the absorption maxima in the gas phase. Unfortunately it is difficult to find such values in the literature and therefore it has been necessary in some cases to use experimental values, where only one of these conditions is fulfilled, i.e. 0—0 transitions in gas phase or absorption maxima in non-polar solutions. The calculated values are given in Tables 4 and 5 together with experimental data.

RESULTS AND DISCUSSION

As is mentioned above the parameter values obtained by the calculation on the standard molecules and used in all the calculations are given in Table 2. The values obtained on ionization potentials are given in Table 3, the electronic transitions in Tables 4 and 5, and the π-electron densities and bond orders in Table 6.

Ionization potentials (Table 3). As is mentioned above the calculated values on ionization potentials should be compared with experimental vertical IP's. Unfortunately it has been difficult to find accurate values of this kind in the literature, but values given for both vertical and adiabatic IP's by Turner et al.[11] for some molecules give a certain idea of the differences between the two types of IP. The results of the calculations seem to be satisfactory and it is especially encouraging that the results on higher IP's agree reasonably well with experiments in spite of the fact that no such value is used for the determination of the parameters.

Electronic spectra (Tables 4 and 5). The electronic transitions calculated for the chlorine substituted ethylenes seem to be in relatively good agreement

Table 4. Calculated and experimental electronic singlet-singlet transitions.

	Transition, cm^{-1} × 10^{-3} (kK)		Oscillator strength		Polarisation [a]
	calc.	experimental	$f_{calc.}$	$f_{exp.}$	calc.
		ν_{max} in vapour			
Ethylene	61.5	61.7 [b][20,21]	0.60	0.34 [21]	x
Vinyl chloride	55.3	54.3 [c][13] 54.1 [14]	0.47		169°
	70.7		0.17		23°
cis-Dichloro-ethylene	51.5	52.6 [c][14]	0.50		x
	64.6		0.09		y
	72.6		0.12		x
trans-Dichloro-ethylene	51.5	51.3 [14,17]	0.54		165°
	64.4		forb.		
	72.6		0.17		33°
Tetrachloro-ethylene	46.2	50.8 [14,19]	0.54		x
	58.6		forb.		
	58.9		0.18		y

[a] The directions x and y are in the molecular plane according to Fig. 1 and the angles given are the angles with the x-axis.

[b] The value 61.5 has been used in Ref. 1 for the determination of carbon parameters.

[c] Used in the present paper for the determination of chlorine and carbon-chlorine parameters.

with experimental data, with the largest discrepancy for tetrachloroethylene. For the substituted benzenes it is difficult to find experimental data in literature which correspond to the calculated ones, *i.e.* values for ν_{max} in gas phase. The shifts in the spectra, when chlorine is substituted for hydrogen are in all cases smaller than the experimental ones, also in the cases where ν_{max} in gas phase are given. However, if the shifts of a certain level in different molecules are compared, the calculated sequences are in all cases the same as those obtained from experiments. The same is true also if the shifts of the different levels of a single molecule are compared with experimental data, the only exception being the sequence of the shifts of the two highest levels of hexachlorobenzene given in Table 5.

Bond orders and bond lengths (Table 6). π-Electron densities and bond orders are given in Table 6. To test the values of bond orders the carbon-carbon bond lengths have been calculated from the bond orders by means of the following relation [28]

$$R_{\mu\nu} = 1.517 - 0.18 p_{\mu\nu} \qquad (9)$$

where $p_{\mu\nu}$ is the mobile bond order and $R_{\mu\nu}$ is the distance in Å between the atoms μ and ν. These bond lengths should be compared with those given in Table 1 and used in the calculations.

The carbon-carbon length used in the calculations is for vinyl chloride 1.33 Å and for the other substituted ethylenes 1.354 Å. The values obtained

Table 5. Calculated and experimental electronic singlet-singlet transitions.

| Transitions, cm⁻¹ × 10⁻³ (kK) | | Shift from unsubst. benzene cm⁻¹ × 10⁻³ (kK) | | | Oscillator strength | | Polarization |
calc.	exptl.	calc.	exptl.		$f_{calc.}$	$f_{exp.}$	calc.
	ν_{max} in vapour		0—0 in vapour	ν_{max} in solution			
			Benzene				
39.2	39.5 [b] [22]				forb.	0.002 [a] [23,24]	
50.6	49.8 [22] 50.6 [b] [26]				»	0.10 [a] [24]	
56.1	56.3 [22] 55.9 [b] [26]				1.19	0.69 [a] [24]	
	56.5 [30]					0.86 [30]	
			Chlorobenzene				
38.8	38.0 [22]				0.002	0.005 [22]	y
49.5	48.0 [22]				0.04	0.195 [22]	x
55.3	54.2 [22] 53.7 [30]				1.19	0.471 [22]0.60 [30]	x
55.4	55.5 [22] 55.2 [30]				1.13	0.732 [22]0.46 [30]	y
		−0.4	−1.04 [c] [23]	−1.4 [25]		0.003 [22]	
		−1.1		−2.9 [25]			
				−2.5 [c] [27]			
		−0.8		−1.7 [c] [25]			
			o-Dichlorobenzene				
38.4		−0.8	−1.8 [23]		0.002	0.004 [23]	y
48.4		−2.2		−3.8? [25]	0.04		x
54.3		−1.8		−3.2 [25]	1.22		y
			m-Dichlorobenzene				
38.4		−0.7	−1.9 [23]		0.002	0.004 [23]	y
48.7		−1.9		−3.7? [25]	0.03		x
54.4		−1.8		−3.4 [25]	1.22		y
			p-Dichlorobenzene				
38.4		−0.8	−2.3 [23]		0.006	~0.007 [23]	y
48.3		−2.3		−5.1 [25]	0.12		x
54.8		−1.3		−2.6 [25]	1.09		y
			1,2,4,5-Tetrachlorobenzene				
37.7		−1.5			0.008		y
46.7		−3.9			0.09		x
53.0		−3.1			1.29		y
			Hexachlorobenzene				
36.9		−2.2		−5.3 [25]	forb.		
45.4		−5.2		−7.0? [25]	forb.		
51.8		−4.4		−8.4 [25]	1.21		

[a] Ref. 24 in heptane.
[b] Used in Ref. 1 for determination of carbon parameters. [c] Used in the present paper for determination of chlorine and carbon-chlorine parameters.

Table 6. Calculated π-electron densities and bond orders. The carbon atoms are denoted 1 to 6. The Cl atoms are denoted Cl_i where the index i indicates that it is bounded to the carbon numbered i.

Molecule	Atom No.	π-Electron density	Bond	Bond order
Vinyl chloride	1	1.067	1—2	0.984
	2	0.962	1—Cl_1	0.165
	Cl_1	1.971		
cis-Dichloroethylene	1	1.031	1—2	0.969
	Cl_1	1.969	1—Cl_1	0.173
trans-Dichloroethylene	1	1.031	1—2	0.969
	Cl_1	1.969	1—Cl_1	0.173
Tetrachloroethylene	1	1.066	1—2	0.934
	Cl_1	1.967	1—Cl_1	0.176
Chlorobenzene	1	1.067	1—2	0.658
	2	0.980	2—3	0.668
	3	1.001	3—4	0.666
	4	0.993	1—Cl_1	0.145
	Cl_1	1.977		
o-Dichlorobenzene (1,2)	1	1.048	1—2	0.649
	3	0.981	2—3	0.660
	4	0.994	3—4	0.666
	Cl_1	1.976	4—5	0.666
			1—Cl_1	0.150
m-Dichlorobenzene (1,3)	1	1.068	1—2	0.659
	2	0.960	3—4	0.657
	4	0.974	4—5	0.667
	5	1.002	1—Cl_1	0.144
	Cl_1	1.977		
p-Dichlorobenzene (1,4)	1	1.061	1—2	0.658
	2	0.981	2—3	0.669
	Cl_1	1.977	1—Cl_1	0.147
1,2,4,5-Tetrachlorobenzene	1	1.043	1—2	0.649
	3	0.962	2—3	0.660
	Cl_1	1.976	1—Cl_1	0.150
Hexachlorobenzene	1	1.025	1—2	0.651
	Cl_1	1.975	1—Cl_1	0.154

from (9) are 1.340 for vinyl chloride, 1.343 for both *cis*- and *trans*-dichloroethylene, and 1.349 Å for tetrachloroethylene. The largest difference is thus 0.011 Å, which is quite satisfactory. It may be mentioned that a calculation with the carbon-carbon distance 1.354 Å for vinyl chloride gave nearly the same results for all values except that for IP which changed from 10.14 to 9.91 eV, showing that the influence of the detailed structure is comparatively weak.

In the chlorine substituted benzenes the carbon-carbon distance 1.397 Å has been used in all cases. The values obtained from (9) varied between 1.397 and 1.400 Å in complete agreement with experiments.

The chlorine-carbon distance 1.718 Å has been used in all the molecules. The bond orders vary between 0.144 and 0.176. It is not possible to determine the constants in a relation similar to (9) for C—Cl. If we use the constant 0.2 (compare the values for C—C, C—N, and C—O in Ref. 29) the difference in bond length for the extreme bond orders should be only 0.006 Å. This small difference is consistent with the use of the same C—Cl bond length in all the molecules.

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