The Nature of –Cl···Cl– Intermolecular Interactions

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Abstract: The controversy as to whether there is a specific attractive intermolecular force between chlorine atoms, of the charge-transfer or donor–acceptor type, is resolved using various analyses of experimental crystal structure data and theoretical calculations. The occurrence of Cl···Cl intermolecular contacts which are shorter than would be expected from the conventional isotropic van der Waals radius is shown to be most common in the crystal structures of fully or highly chlorinated hydrocarbons, and thus a consequence of close packing of anisotropic atoms, rather than evidence for a specific attractive force. Intermolecular perturbation theory calculations on the Cl···Cl interactions within the chloromethane dimer show that the charge-transfer contribution to the intermolecular energy is negligible, the electrostatic forces are weak, and the repulsive wall is anisotropic. Calculations on the electrostatic interactions between other chlorinated hydrocarbons show that these results will also apply to other Cl···Cl interactions. Thus a realistic anisotropic model for the repulsion, dispersion, and electrostatic forces between chlorinated hydrocarbons should be capable of predicting the observed crystal structures with "short" Cl···Cl intermolecular separations.

1. Introduction

The weak intermolecular interactions between chlorine atoms have been a subject of interest and debate for many decades.[1] Indeed, the earliest use of the term "crystal engineering" followed the discovery by Schmidt and Green[2] that dichloro substitution on aromatic and related molecules tends to produce crystal modifications with short axes around 4 Å. The crystal structures are not governed only by close packing as the substitution of Cl for a methyl group usually changes the crystal structures of aromatics significantly,[3] although the two groups have nearly the same volume. These observations must be closely linked to the common occurrence of shorter Cl···Cl intermolecular contacts than would be expected from the spherical van der Waals radius (as given by Bondi[4]) and the failure of isotropic atom–atom intermolecular potentials to satisfactorily represent these interactions.[5] Thus, if we are to understand and predict the structures of the solid and liquid phases, and van der Waals complexes, of chlorinated molecules, it is essential that we understand the physical origin of the intermolecular forces between chlorine atoms.

Two hypotheses have been put forward to account for the observed crystal structure of Cl_2, which can also account for the short Cl···Cl contacts in the crystal structure of other chlorinated molecules. One explanation[6] is that there is a specific attractive force which produces short contacts in certain directions. This has been variously referred to as a "donor–acceptor", "secondary", or "charge-transfer" interaction, or "incipient electrophilic and nucleophilic attack", involving a weak form of covalent bonding. The alternative hypothesis[7] is that the atomic charge density has a nonspherical shape, producing a decreased repulsion and thus closer Cl···Cl contacts in certain directions.

Although a reduction in the repulsion or an increase in the intermolecular attraction can both account for shorter van der Waals contacts in certain directions, the two are not equivalent and have different implications for the shape of the potential energy surface and how it should be represented. Model intermolecular potentials incorporating anisotropic repulsion have been developed for chlorine which can predict the observed crystal structure[8] and the observed liquid structure[9] using molecular dynamics. A potential where the anisotropy of the repulsion was derived from the *ab initio* monomer wave function[10] has recently been shown to predict many properties of the crystal and liquid states at various temperatures. The alternative viewpoint has been implemented by representing the "weak intermolecular bonding" by a Morse potential and showing that the resulting potential can predict the static structure of solid chlorine.[11] However, since such charge-transfer effects are markedly nonadditive, it is not clear what criteria should be used to include the weak bonding terms when there are more intermolecular Cl···Cl contacts.[12] A more appropriate functional form would need to be developed for modeling chlorinated molecular crystals if the charge-transfer attractive terms were structurally significant.

Desiraju and Parthasarathy[13] have recently claimed that the proportion of Cl···Cl close contacts in the crystal structures of chlorinated hydrocarbons is evidence that there is a specific attractive intermolecular force operating between chlorine atoms. Our response to this issue is 2-fold. First, we believe that the analysis used by Desiraju and Parthasarathy overestimated the prevalence of Cl···Cl contacts. In section 2 we review this analysis, using additional data not available to them, and conclude that their case is very weak for chlorine. Secondly, we take the view

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Table 1. Analysis of Close Cl···Cl Intermolecular Contacts in Crystals of Chlorinated Hydrocarbons[a]

	fully chlorinated C_iCl_k	heavily chlorinated $C_iH_jCl_k$, $k \geq j$	lightly chlorinated $C_iH_jCl_k$, $k < j$	all chlorinated compounds
no. of compds	22	45	87	154
no. of compds with a short Cl···Cl contact	19	35	27	81
no. of unique short Cl···Cl contacts	67	92	38	197
no. of these in double contacts	16	18	4	38
no. of these in triple contacts	3	0	0	3

[a] Short intermolecular contacts correspond to a Cl···Cl separation of less than 3.52 Å. Multiple contacts are defined when one chlorine atom is in "short" contact with more than one other chlorine atom in the crystal structure. Data are taken from Cambridge Crystallographic Database, version 5.1.

that an attractive Cl···Cl interaction does not itself support the notion that charge transfer is important. There are other attractive terms, notably dispersion, and the electrostatic interaction is sufficiently anisotropic that certain geometries can be favored without any contribution from charge transfer. We discuss this in more detail in section 4.

Hence, in the next section, the crystallographic evidence on the nature of the Cl···Cl intermolecular interaction is reanalyzed and reassessed. In addition to scrutinizing the evidence presented by Desiraju and Parthasarathy, the analyses of the preferred relative orientation of the Cl···Cl interaction[6] and the orientation dependence of the effective van der Waals radius[14] are repeated for just the chlorinated hydrocarbons. This subset should show the operation of the Cl···Cl interactions more clearly than crystal structures with strongly polar functional groups and, thus, establish the strength of the experimental evidence for both hypotheses.

The most direct method of assessing the relative importance of anisotropic repulsion and charge transfer is through theoretical calculations. The individual contributions to the intermolecular forces can be identified and evaluated by applying perturbation theory to the *ab initio* wave functions of the isolated molecules. Recent developments in both theory and computer power now make it feasible to perform such calculations on the interactions between two chloromethane molecules, free of the basis set superposition error which has previously plagued such calculations. Such calculations are reported in section 3. The extrapolation of the chloromethane results to other chlorinated hydrocarbons is investigated in section 4, by comparing the multipolar components of the electrostatic interactions for a range of aliphatic and aromatic chlorinated hydrocarbons.

The theoretical calculations show that Cl···Cl intermolecular interactions are quite normal, with the repulsion, dispersion, and electrostatic contributions being the most important, but the nonsphericity of the chlorine charge distribution has a significant effect on these contributions. This picture is compatible with the crystallographic evidence, as discussed in section 5, and thus there is no need to invoke a specific attractive intermolecular force between Cl atoms to explain the crystal structures.

2. Analysis of Crystal Structures of Chlorinated Hydrocarbons

The analysis of molecular crystal structures has formed the major component of the case for significant intermolecular bonding between chlorine atoms. The relative frequency of close Cl···Cl contacts in chlorinated hydrocarbons[13] and the orientation dependence of such contacts[6] have both been cited as evidence for an orientationally specific attractive intermolecular force between chlorine atoms. However, the anisotropy of the effective van der Waals radius of chlorine has also been established from the analysis of crystal structures,[14] supporting the anisotropic repulsion hypothesis. In order to understand these results more fully, we have performed complementary analyses of the crystal structures of the chlorinated hydrocarbons. These were intended firstly to establish whether close intermolecular chlorine contacts were particularly common in any particular subset of the chlorinated hydrocarbons. The second aim was to repeat the analyses of the geometries of such contacts, originally performed on all Cl···Cl van der Waals contacts, on the subgroup found in the chlorinated hydrocarbons. Any orientational preferences should be more apparent in chlorinated hydrocarbons than in crystal structures where the interactions of other heteroatoms, producing, for example, hydrogen bonding, play a major role in determining the structure.

The Cambridge Structural Database[15] (version 5.1, 109 992 entries) was used to retrieve all high-precision ($R \leq 0.075$), fully ordered, diffractometer-based crystal structures of compounds containing only carbon, chlorine, and optionally hydrogen. Structures in which none of the hydrogen atoms had been located were discarded, as were duplicate structures. In the case of duplicates (denoted by the same refcode family), the best resolved room-temperature structure was selected, and in the case where both a compound and its benzene clathrate were present, both were retained.

This set of structures was further analyzed for close Cl···Cl intermolecular contacts, using the nonbonded search procedures introduced in version 5.1 of the database. All unique intermolecular contacts where the Cl···Cl distance was less than 3.52 Å were retrieved, and the distances and C–Cl···Cl angles analyzed. This procedure was repeated on more limited subgroups of chlorinated hydrocarbons $C_iH_jCl_k$, namely, the fully chlorinated compounds ($j = 0$), the heavily chlorinated compounds ($k \geq j$), and the lightly chlorinated compounds ($k < j$).

2.1. Results of Crystal Structure Analysis: Evidence for a Specific Attractive Force. The resulting set of good quality crystal structures of 154 chlorinated hydrocarbons includes almost 200 unique Cl···Cl intermolecular contacts that are shorter than twice the spherical van der Waals radius, i.e. shorter than 3.52 Å. However, as Table 1 shows, the majority of these contacts occur in the crystal structures of the totally or heavily chlorinated molecules. Less than 20% of the close contacts occur in the crystal structures of the molecules with more hydrogen than chlorine atoms, although these comprise more than one-half the compounds analyzed. In contrast, 19 of the 22 fully chlorinated compounds had at least one short intermolecular contact, most structures having several, so that the fully chlorinated compounds account for one-third of the close contacts. Of the three fully chlorinated compounds which did not have a Cl···Cl contact of less than 3.52 Å, all had a closest intermolecular Cl···Cl contact which was only slightly longer (octachloronaphthalene, 3.521 Å; perchloro[4]-radialene, 3.615 Å; hexachloroethane, 3.67 Å), and these longer contacts might be required to pack these nonplanar structures efficiently. There were a significant number of cases where a chlorine atom was involved in two (and in one example, three) close intermolecular contacts. Thus, most of the close intermolecular Cl···Cl contacts occur for molecules where any reasonably dense crystal packing must involve van der Waals contacts between the chlorine atoms.

This observation requires a reassessment of the recent claim

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by Desiraju and Parthasarathy[13] that the frequency of these short contacts is evidence for a specific attractive force between halogen atoms. They calculated an average ratio of halogen to total surface area for each compound and argued that, if the observed number of halogen–halogen contacts greatly exceeded that which would correspond to the proportion of exposed halogen surface area, then this was evidence for a specific attractive force. A major problem with this analysis is the difficulty in estimating accurately the proportion of the exposed surface area which can be attributed to each element. The approximate method they used to calculate the relative probability of halogen being in contact with carbon, hydrogen, or halogen in a molecule was based on the squares of the atomic van der Waals radii, 1.76 Å for Cl, 1.75 Å for C, and 1.2 Å for H. For example, for CCl_4, the relative probabilities would be

$$P(\mathrm{Cl}) = 4(1.76)^2/[4(1.76)^2 + (1.75)^2] = 0.80$$

$$P(\mathrm{C}) = (1.75)^2/[4(1.76)^2 + (1.75)^2] = 0.20$$

$$P(\mathrm{H}) = 0$$

This example highlights the problem with the approximation: there is virtually no exposed carbon van der Waals surface on CCl_4 because this surface almost passes through the Cl nuclei and is almost completely within the overlapping van der Waals surfaces of the chlorine atoms. The method of calculating the relative accessibility of the atoms treats carbon, chlorine, and hydrogen on an equal footing, whereas chlorine and hydrogen, being univalent, are on the surface of the molecule and carbon is normally mainly buried beneath up to four substituents. Hence the method will generally overestimate the probability of halogen–carbon contacts and underestimate the probability of halogen–hydrogen and halogen–halogen contacts.

Our results show that this approximation will have affected the validity of the analysis more than might have been expected because of the high number of fully chlorinated or very heavily chlorinated hydrocarbons in the database. Most of the carbon atoms in the fully chlorinated compounds are sp^2 hybridized and in rings of six atoms or less, so there is only a very restricted region above the ring where a chlorine atom can make van der Waals contact with carbon atoms without also being in contact with a chlorine atom. About 10% of the carbon atoms are sp^3 hybridized and so, by analogy with CCl_4, will not be exposed. Thus the possibilities of forming a crystal structure for the fully chlorinated hydrocarbons without Cl···Cl contacts are negligible. Only when a significant proportion of the carbon substituents are hydrogen rather than chlorine, and suitably distributed, does it become possible for chlorine–chlorine contacts to be avoided. Since over 80% of the close Cl···Cl contacts occur in the crystal structures of fully or heavily chlorinated compounds, these contacts appear to result from normal packing and do not provide any evidence for a specific attractive force.

2.2. Evidence for Preferred Orientations. The geometric preference of close Cl···Cl contacts was also used by Desiraju and Parthasarathy to support the argument for a specific attractive force argument. The idea that there are two preferred geometries, $\theta_1 \approx \theta_2 \approx 160°$ and $\theta_1 \approx 175°$, $\theta_2 \approx 80°$, where θ is a C–Cl···Cl angle (defined in Figure 4), arose from the early observation by Sakurai et al.[16] of a close contact in 2,5-dichloroaniline and a comparison with similar short contacts in seven other compounds. A later survey,[6] using the 1984 version of the Cambridge Crystallographic Database, examined the preferred direction of approach of electrophiles and nucleophiles around the carbon–halogen bond, including halogen–halogen interactions. The authors noted a preference for the expected incipient nucleophile ($\theta \approx 180°$)–electrophile ($\theta \approx 90°$) interaction geometry; the larger angle was more commonly nearer 165°, at least partially reflecting the statistically low probability of exactly head-on orientations. They also noted that many short contacts had $\theta_1 \approx \theta_2$, where the interacting halogen atoms were related by the crystallographic symmetry. These preferences were far more marked for I···I interactions than Cl···Cl interactions.

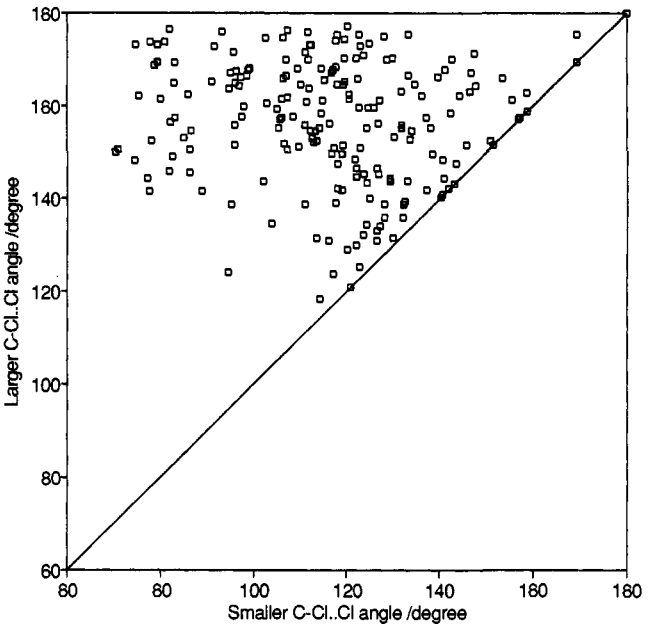

Figure 1. Plot of the angles involved in Cl···Cl intermolecular contacts which are shorter than 3.52 Å in chlorinated hydrocarbon crystal structures.

Our repetition of this analysis (Figure 1) pertains only to the chlorinated hydrocarbons, where one would expect any orientational preferences for the Cl···Cl interaction to be more marked, and yet the distributions are fairly similar, if anything showing less evidence for preferred orientations. The only marked orientational preference for the short Cl contacts (Figure 1) is that, although C–Cl···Cl angles of less than 90° occur, there are no examples where both angles are so small. Such geometries are unlikely to be sterically accessible. There are very few points corresponding to an approximately collinear geometry, though this partially reflects the smaller volumes of configuration space corresponding to such geometries.

2.3. Evidence for Anisotropic van der Waals Radius. According to the anisotropic repulsion hypothesis, the Cl···Cl separation will depend on the C–Cl···Cl angles. Nyburg and Faerman[14] proposed an effective elliptical shape, with a minor radius of 1.58 Å for head-on approach ($\theta = 180°$) and a major radius of 1.78 Å for a side-on approach ($\theta = 90°$). Thus a hard-ellipse model for the Cl···Cl interaction would predict that a polar plot of the Cl···Cl separation against the larger C–Cl···Cl angle should have an elliptical inner surface, corresponding to both angles being equal, and points outside the ellipse displaced by the difference in effective radius between the larger and smaller angles. This plot is given for the short Cl···Cl contacts in chlorinated hydrocarbons in Figure 2, and there is good correspondence to the elliptical model. The elliptical radii of Nyburg and Faerman, which are plotted on Figure 2 for comparison, may be slightly small, but this may reflect stronger packing forces in compounds with other heteroatoms pushing the Cl atoms a little closer together.

It is worth noting that there is a significant change in the number of chlorinated hydrocarbons in the database between the different surveys. At least 40 compounds in our survey were published after the work of Desiraju and Parthasarathy.[13] It would appear that, as the number of compounds has increased, the evidence for the marked orientational preference that would

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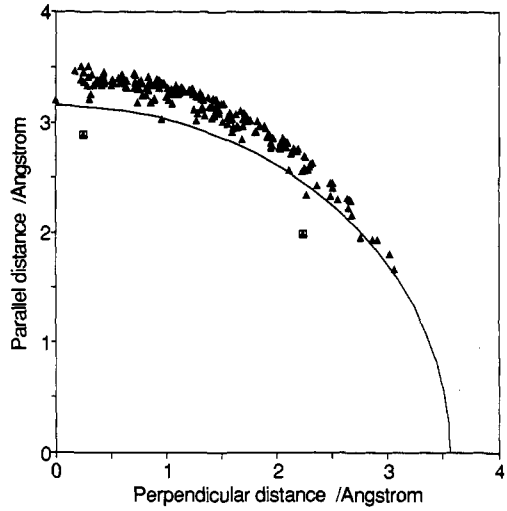

Figure 2. Polar plot of the Cl···Cl intermolecular distance as a function of the larger C–Cl···Cl angle (which corresponds to the smaller elliptical van der Waals radius) for the Cl···Cl contacts less than 3.52 Å in crystal structures of chlorinated hydrocarbons. One Cl atom is at the origin, with the C–Cl bond vertical. The solid line is twice the elliptical van der Waals radius, as determined by Nyburg and Faerman,[14] from a database of all Cl···Cl van der Waals contacts. The plots of contacts enclosed in a square are both to the same Cl atom in a poorly refined CCl_4 of crystallization of $C_{28}Cl_{18}$, which exhibits high thermal motion.[36]

be associated with a specific attractive force has become extremely questionable.

3. Intermolecular Perturbation Theory Calculations of Cl···Cl Interactions within Chloromethane Dimers

The various contributions to the intermolecular forces between small closed-shell molecules can be defined and directly evaluated using intermolecular perturbation theory. The intermolecular Coulombic interaction term $(e_i^A e_j^B/(4\pi\epsilon_0 r_{ij}))$ in the Hamiltonian is the origin of the intermolecular forces and is used as the perturbation operator. The Hartree–Fock (SCF) wave functions of the ground and excited states of the isolated molecules (ψ^A, ψ^B) are used to describe the charge distribution of the interacting complex. At long range, when there is negligible overlap of the molecular wave functions, the product of the SCF ground state isolated molecule wave functions ($\psi_0^A\psi_0^B$) can be used as the zeroth-order wave function. First-order perturbation theory gives the Coulombic interaction between the undistorted charge distributions of the two molecules, which is identified as the electrostatic energy. Second-order theory predicts the additional energy lowering caused by the first-order response of the wave function of molecule A to the field of the undistorted charge distribution of B, which is the polarization or induction energy of A, and also vice versa. The dispersion energy, which arises from the correlation of the instantaneous fluctuations in the electron distribution of the molecules, is also given by the second-order perturbation expression.

Extension of this familiar Rayleigh–Schrödinger perturbation theory treatment to shorter range, where there is overlap of the two molecular charge distributions, is not straightforward, as the wave functions are no longer orthogonal and the exchange of electrons between the molecules is possible. Various methods of overcoming these difficulties have been proposed,[17] which give slightly different mathematical definitions to the additional contributions which appear at short range. These are the exchange–repulsion at first order and the charge-transfer term, arising from the transfer of electron density between the two molecules, at second order. The overlap also modifies the long-range electrostatic, induction, and dispersion effects, producing additional exponentially decaying penetration and damping terms. We use the Hayes–Stone intermolecular perturbation theory (IMPT)[18] method of evaluating all these contributions to the intermolecular potential.

A major problem for all *ab initio* based methods of calculating intermolecular interaction energies is the basis set superposition error, since all practical calculations have to use a basis set that is incomplete for the isolated molecules. The basis set superposition error is the spurious energy lowering that occurs when the basis functions on molecule A act as an extension of the basis set of molecule B and give an energy lowering due to an improved description of the intramolecular electron interactions within molecule B, and vice versa. This effect leads to an overestimate of the depth of the intermolecular potential well and apparent charge transfer. There is an additional complication in partitioning the intermolecular interaction energy into various components in the region of significant overlap, as in IMPT calculations. When large basis sets are used, the same change in the wave function of the interacting complex can be obtained by mixing in orbitals associated with either molecule A or B, and so the distinction between polarization (change within the wave function of A described by orbitals of A) and charge transfer (change within A described by orbitals on B) becomes ill-defined. Stone has recently proposed a method[19] of evaluating charge-transfer energies which eliminates basis set superposition error and gives a reasonably basis set independent division between polarization and charge transfer.

The Hayes–Stone intermolecular perturbation theory has been applied to the intermolecular forces between two chloromethane molecules in orientations involving close Cl···Cl contacts. The calculations were based on the SCF 6-31G* wave functions of the isolated CH_3Cl molecules, except for orientations involving close Cl···H contacts which were done at the 6-31G** level. However, the inclusion of polarization functions on hydrogen changed even these interaction energies by only a few percent. The monomer geometry given by Herzberg[20] (C_{3v}, C–Cl = 1.781 Å, C–H = 1.113 Å, ∠Cl–C–H = 108.42°) was used. Figure 3 shows the variations of the exchange–repulsion, charge-transfer, electrostatic, polarization, and dispersion energies as a function of the Cl···Cl distance for a variety of geometries with antiparallel C–Cl bonds (∠C–Cl···Cl = ∠Cl···Cl–C) (Figure 3a–d), an L-shaped configuration (Figure 3e), and a contrasting geometry with parallel C–Cl bonds and a closer Cl···H interaction (Figure 3f).

3.1. IMPT Results. The clear conclusion from Figure 3 is that the charge-transfer contribution is not significant around the van der Waals region. At a Cl···Cl distance of 3.25 Å, which is approximately the shortest distance observed in crystal structures,[14] the sum of the charge-transfer and polarization terms rarely exceeds 1 kJ/mol, and this rapidly decreases with increasing separation. Thus, even with the uncertainty in the distinction between these two terms, the effect of Cl···Cl charge transfer cannot be structurally important. Note that, although the polarization term may be underestimated because of the basis set limitations, the charge-transfer term is less affected by basis set deficiencies.[19]

The electrostatic contribution can be attractive or repulsive in the range corresponding to van der Waals contact. It is attractive at short range because of the penetration effects, due to the overlap of the charge distributions. Head to head van der Waals contacts are electrostatically unfavorable, whereas the L configuration is somewhat favored by the electrostatic term, though only weakly compared with a Cl···H interaction (Figure 3e,f).

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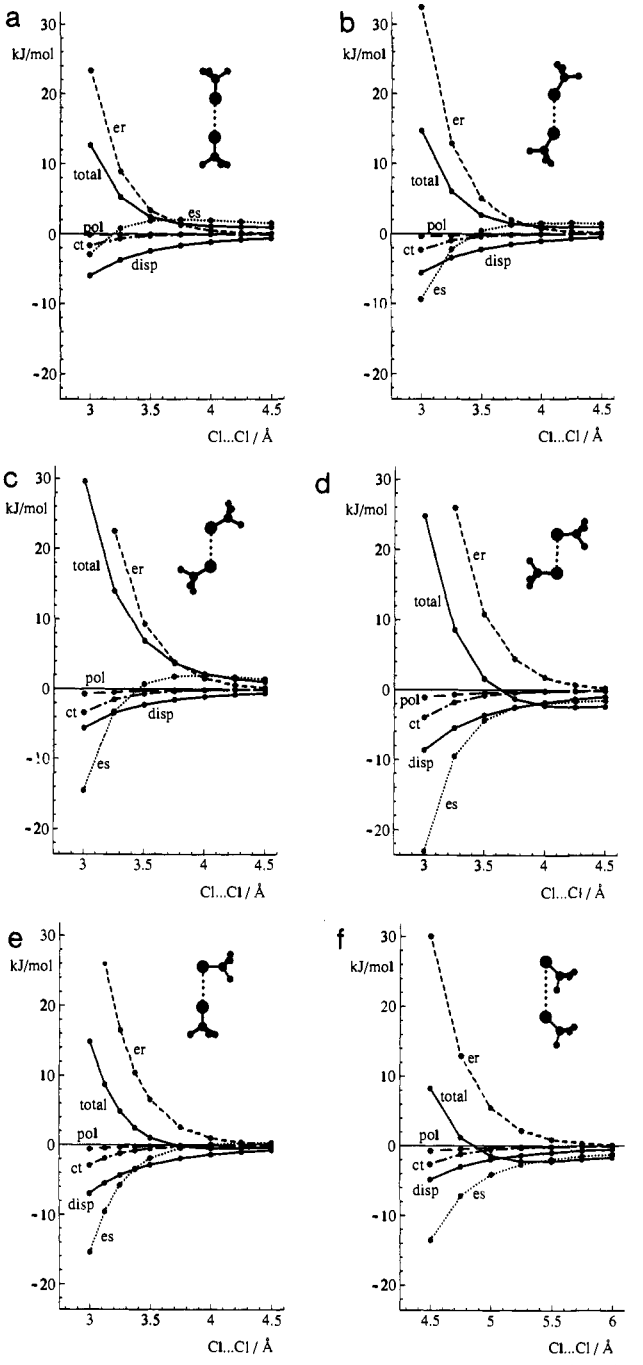

Figure 3. Intermolecular perturbation theory calculations for the contributions to the intermolecular energy of two CH_3Cl molecules, as a function of Cl···Cl separation for various orientations: (a) head-on, linear $\theta_1 = \theta_2 = 180°$, (b) $\theta_1 = \theta_2 = 150°$, (c) $\theta_1 = \theta_2 = 120°$, (d) $\theta_1 = \theta_2 = 90°$, (e) L-shaped $\theta_1 = 180°$, $\theta_2 = 90°$, and (f) close H contacts $\theta_1 = 135°$, $\theta_2 = 45°$. The various components are labeled: er, exchange–repulsion; pol, polarization; ct, charge-transfer; disp, dispersion; es, electrostatic (including penetration effects).

The exchange–repulsion energy is markedly anisotropic and varies exponentially with separation, as Figure 4 shows. An exchange–repulsion energy of 10 kJ/mol is found for Cl···Cl separations varying between 3.2 and 3.6 Å, depending on orientation, consistent with the variation in van der Waals contact distances found by Nyburg and Faerman.[14]

The attractive dispersion energy is only weakly orientation dependent, by comparison, as Figure 5 shows. This term is severely underestimated by these calculations because the 6-31G* basis set is too small to satisfactorily describe the dynamic polarizability that underlies the dispersion interaction. We may quantify this underestimation by noting that the dispersion energy calculated

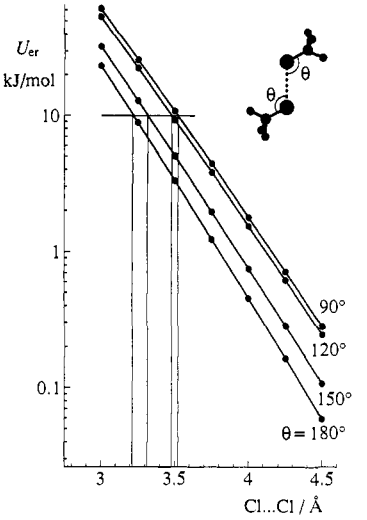

Figure 4. Exchange–repulsion energy as a function of Cl···Cl separation for orientations with $\theta_1 = \theta_2$, as a semilog plot, showing the anisotropy of this exponential contribution. The intercepts with the horizontal bar at 10 kJ/mol show that this anisotropy will lead to a significant variation in the van der Waals contact separation.

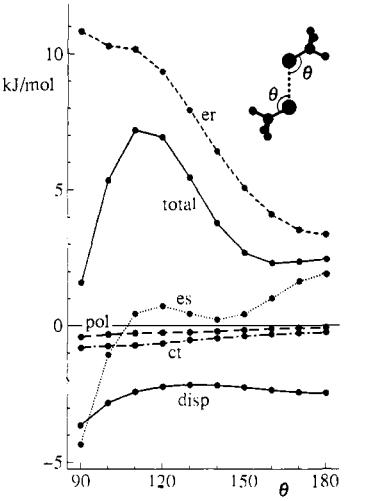

Figure 5. Orientation dependence of the –Cl···Cl– interaction at a Cl···Cl separation of 3.5 Å. The various components are labeled: er, exchange–repulsion; pol, polarization; ct, charge-transfer; disp, dispersion; es, electrostatic. Note that the electrostatic interaction shown here includes the penetration term, so it is different from the multipolar electrostatic interaction shown in Figure 6.

for the CH_3Cl dimer at a given Cl···Cl distance is approximately one-half of the Ar–Ar dispersion at the same distance.

The total energies show that orientations with close Cl···Cl contacts are either mildly attractive or only weakly repulsive for chloromethane. A more realistic representation of the dispersion would probably make them all weakly attractive at the van der Waals separation. However, orientations with Cl···Cl contacts are certainly much less favorable than those with Cl···H contacts.

4. Electrostatic Interactions of Other Chlorinated Hydrocarbons

The IMPT analysis of the intermolecular forces between CH_3-Cl molecules naturally includes contributions from the methyl group, and the methyl group will also affect the charge distribution of the chlorine atom, through short range inductive effects. So, although the IMPT calculations have concentrated on orientations where the intermolecular forces are expected to be dominated by the Cl···Cl interaction, it is necessary to assess whether such interactions could be qualitatively different for other chlorinated hydrocarbons. The full *ab initio* IMPT treatment is computa-

tionally too demanding to be possible for a representative range of molecules. However, the electrostatic interactions can be calculated and compared for a suitable range of chlorinated hydrocarbons, as that requires *ab initio* calculations only on the isolated molecules. Since the electrostatic term is the longest range contribution and is also sensitive to the detailed distribution of the charge in the molecule, if the electrostatic forces for close Cl···Cl contacts are approximately independent of the molecule, then the qualitative picture of -Cl···Cl- interactions derived from the IMPT study of the CH_3Cl dimer is likely to be generally applicable.

The electrostatic interactions were evaluated from a distributed multipole analysis (DMA)[21] of the SCF wave function of each molecule, obtained using the program CADPAC[22] with a 6-31G** basis set.[23] Studies on CH_3Cl with larger basis sets confirmed that this is adequate. The DMA represents the molecular charge distribution as a series of multipoles, in this case, charge, dipole, quadrupole, octopole, and hexadecapole, on every atomic site. Thus, unlike in an atomic point charge electrostatic model, the nonspherical features in the atomic charge distributions, such as lone pair and π electron density, are automatically included. The electrostatic interactions were evaluated from the multipole–multipole interaction formulas[24] for all atom–atom contributions up to R^{-5} (i.e., including quadrupole–quadrupole, dipole–octopole, and hexadecapole-charge terms), using the program ORIENT.[25] This provides the multipolar component of the electrostatic energy and does not include the effects of penetration of the molecular charge densities, but such penetration effects are usually swamped by exchange–repulsion.

The molecules studied were chloromethane, tetrachloromethane, monochlorobenzene, and hexachlorobenzene, to represent Cl atoms bonded to both sp^3 and sp^2 carbon atoms and the extreme possibilities for short-range inductive effects within chlorinated hydrocarbons. The structure for CCl_4 (T_d) with a C–Cl bond length of 1.766 Å was obtained by electron diffraction, and that of C_6Cl_6 (D_{6h}) with a C–C bond length of 1.40 Å and C–Cl bond length of 1.72 Å was taken from the crystal structure.[26] The latter was adapted for C_6H_5Cl by using a C–H bond length of 1.0 Å.

The electrostatic interactions between these molecules were compared for a fixed Cl···Cl distance of 3.52 Å (twice the Bondi isotropic van der Waals radius), as a function of the C–Cl···Cl angle, both for antiparallel C–Cl bonds and with the second Cl···Cl–C angle fixed at 180°. The angle was varied from the smallest compatible with the repulsion from the bonded atoms (assessed assuming the lower limit of 1.58 Å for the Cl van der Waals radius, i.e., R(Cl···Cl) ≥ 3.16 Å, R(Cl···H) ≥ 2.78 Å, and R(Cl···C) ≥ 3.33 Å) to the head to head orientation. The results are given in Figure 6 for various rotations of the molecules around the C–Cl bonds.

4.1. Electrostatic Interactions for Cl···Cl Intermolecular Contacts. The most obvious conclusion from Figure 6 is that the electrostatic interactions for Cl···Cl contacts are remarkably weak and also very similar for this range of chlorinated hydrocarbons. The electrostatic energy for a linear C–Cl···Cl–C configuration in van der Waals contact varies by less than 2 kJ/mol. The

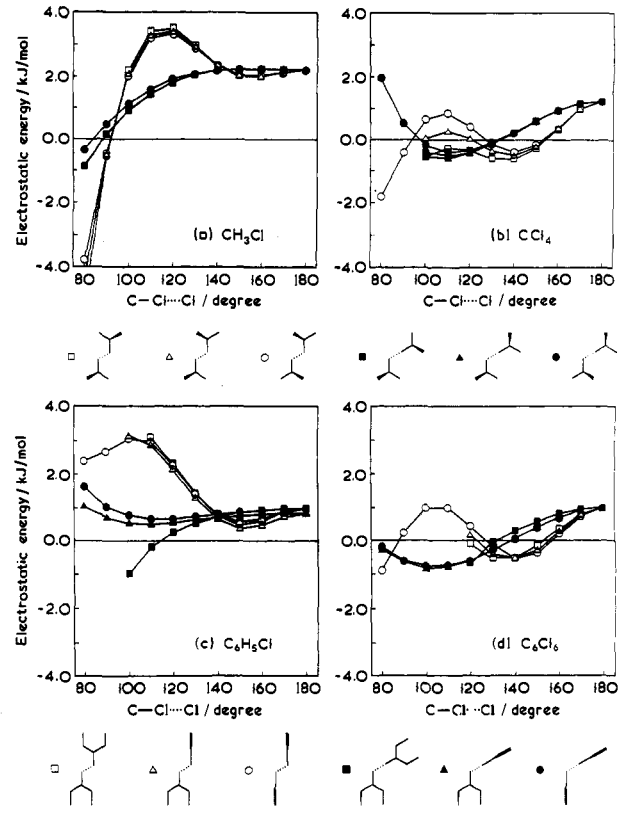

Figure 6. Orientation dependence of the DMA electrostatic energy for various chlorinated molecules. The DMA electrostatic interaction energy for a Cl···Cl distance of 3.52 Å for six types of orientations of (a) chloromethane, (b) carbon tetrachloride, (c) monochlorobenzene, and (d) hexachlorobenzene, three with antiparallel C–Cl bonds and three with Cl···Cl–C collinear, for various orientations of the remainder of the molecules.

variation in the electrostatic energy with orientation is remarkably similar for the four molecules for C–Cl···Cl angles greater than 120°, and the deviations at smaller angles correspond to very close interactions between the differing other atoms in the molecules, and these smaller angles are often sterically inaccessible. The relatively minor contribution from interactions other than the Cl···Cl interaction at larger angles is also shown by the small variation with the orientation of the methyl or aromatic group. The electrostatic interactions are even sometimes slightly attractive in the case of the fully chlorinated molecules.

The two C–Cl···Cl–C geometries have a distinctly different orientation dependence, with the antiparallel C–Cl bonds showing a shallow minimum for angles around 150°. This is caused by the nonspherical features in the chlorine charge distribution, as shown by the disappearance of the minimum if the anisotropic multipoles on Cl are omitted from the calculation.

4.2. Dimer Structures Favored by the Electrostatic Forces. The minima in the electrostatic interaction energy of several dimers of chlorinated hydrocarbons were also located, within sterically accessible orientations, as defined by a pseudo-hard-sphere ($\tanh^{-1}$) potential, using a radius of 1.75 Å for C, 1.2 Å for H, and usually 1.76 Å for Cl. This type of calculation, where the DMA electrostatic energy is minimized subject to a hard-sphere constraint, has been remarkably successful in predicting the structures of van der Waals complexes involving small polyatomics[27] and aromatic molecules.[28] This requires that the orientation dependence of the electrostatic energy mirrors that of the total intermolecular energy. IMPT calculations on several small van der Waals complexes have confirmed that this is

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(28) Price, S. L.; Stone, A. J. *J. Chem. Phys.* **1987**, *86*, 2859–2868.

frequently true because the orientation dependencies of the other contributions to the intermolecular energy tend to cancel.[29] However, the electrostatic interactions are stronger in most of these complexes than within the chlorinated hydrocarbons, so they are more likely to dominate the interactions, and the repulsion forces for chlorine are markedly anisotropic. Nevertheless, the few comparable examples, such as the chlorine and benzene dimers, are predicted by the electrostatic model to have structures which are in agreement with experiment. The model also successfully predicts the structures of HF···Cl_2 and HF···ClF provided the hard-sphere radius used allows the "short" experimental separation to be reproduced.[27] In these calculations, the predicted dimer structures were qualitatively the same when a smaller radius (1.58 Å) was used for chlorine. Hence, we cannot be confident that optimizing the electrostatic energies with a crude isotropic repulsion model will predict the structure corresponding to the van der Waals complex, but it will certainly suggest structures that are likely to be favorable and test whether or not Cl···Cl electrostatic interactions are unfavorable.

For CH_3Cl, the most electrostatically favorable relative orientation has two symmetric H···Cl contacts and a DMA electrostatic energy of –6.8 kJ/mol (Figure 7a). There is another minimum in a less symmetric structure, with a slight elongation of one of the two Cl···H contacts and a shortening of the Cl···Cl separation, at –6.6 kJ/mol, suggesting that there are a range of favorable orientations based on two H···Cl contacts. Monochlorobenzene also has a favorable electrostatic minimum when the molecules are parallel with two equivalent Cl···H contacts (–3.7 kJ/mol), but this is less favorable than another minimum with two hydrogen atoms in contact with a chlorine and the two aromatic rings in a displaced open L shape. Indeed, there is also a series of minima with the two rings perpendicular and the edge of one ring lying almost parallel to the C–Cl bond so that there is one hydrogen in contact with the Cl and another pointing into the aromatic ring (Figure 7d). The electrostatic energies of these minima vary from –3.4 to –4.6 kJ/mol according to the position of the other Cl atom, the structure with antiparallel C–Cl bonds being most stable. The common features between these structures and those of the benzene dimer[28] suggest that the electrostatic interactions between the aromatic rings are of a strength similar to the Cl···H interactions.

The electrostatically favorable relative orientations for the fully chlorinated molecules, carbon tetrachloride and hexachlorobenzene, all involve multiple Cl···Cl close separations. In the most favorable structure of the CCl_4 dimer (Figure 7c), one Cl of each molecule is close to the 3-fold axis of the other, so that there are three short and three slightly longer Cl···Cl contacts, the exact structure being very dependent on the assumed radius for Cl. The short contacts correspond to θ angles in the ranges 130–140° and 85–90°. Another electrostatic minimum occurs with one C–Cl bond symmetrically coordinated to two Cl atoms in the other molecule, but this has approximately one-half the electrostatic stabilization energy of the multiple contact orientation. Again, the exact geometry is very sensitive to the Cl repulsion model, but it is worth noting that these geometries have similar ∠C–Cl···Cl angles, in this case around 155–160° and 85–120°.

The minimum electrostatic energy structures for hexachlorobenzene are noteworthy for all involving two Cl···Cl contacts and few Cl···C contacts, though the minima where the aromatic rings are close are more stable. The favorable relative orientations are shown in Figure 7g and are variants on displaced near parallel or perpendicular aromatic rings. All have two Cl···Cl close contacts, corresponding to C–Cl···Cl angles around 80–90° and around 150°. A point-charge-only electrostatic model predicts a T-shaped minimum, with a Cl atom pointing into the center of the aromatic ring, but this is not a minimum when the realistic distributed multipole electrostatic model is used.

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The minima for molecules with intermediate levels of chlorination show the competition between Cl···H, aromatic–aromatic, aromatic–H, and Cl···Cl electrostatic interactions. The $CHCl_3$ dimer exhibits two minima (Figure 7b) involving the hydrogen of one molecule interacting strongly with two Cl atoms of the other, giving a bifurcated hydrogen bond, with two different orientations of the CCl_3 group, both giving rise to quite close Cl···Cl interactions. (The symmetric structure with four Cl···H bonds does not appear as a minimum.) One minimum (–2.8 kJ/mol) for 1,3,5-trichlorobenzene dimer (Figure 7f) has two H···Cl interactions, with the two molecules twisted from the coplanar configuration. This is not much more stable than another minimum (–2.0 kJ/mol) with just one H···Cl contact and a close Cl···Cl contact. There is also a weak minimum (–0.7 kJ/mol) showing a hydrogen atom interacting with the aromatic ring and a Cl···Cl contact.

It is also noteworthy that a stacked sandwich structure of the 1,3,5-trichlorobenzene dimer (Figure 7f) is electrostatically just attractive (–0.9 kJ/mol) when the two molecules are rotated with respect to each other, so that the Cl···H separation is determined by the aromatic ring repulsion. In contrast, a stacked sandwich structure with an inversion center and six close Cl···H contacts is a very stable structure for 1,2,3-trichlorobenzene (Figure 7e). However, there are also distorted L-shaped minima with two Cl···H contacts which are more stable.

This range of structures, with relatively small electrostatic energies, certainly shows a preference for Cl···H interactions, with the aromatic ring also having a major influence. Chlorine atoms are in van der Waals contact only for the fully chlorinated structures, but there are other examples where the Cl···Cl separation is not much larger, and so the electrostatic forces certainly do not prevent close Cl···Cl intermolecular contacts. This is consistent with our previous findings that the electrostatic forces for chlorinated hydrocarbons with Cl atoms in van der Waals contact were weak, and either attractive or repulsive, depending on the molecule and its orientation. All the structures show multiple van der Waals contacts, implying that any orientational preference for the Cl···H or Cl···Cl electrostatic interaction is either weaker than or compatible with the additional stabilization that can be obtained by having a second van der Waals contact. (The N–H···O=C structures provide an example of where hydrogen bonding in the lone pair direction is often compatible with a second van der Waals contact between the molecules.[30]) These structures confirm that, although Cl···H interactions are the most favorable, the electrostatic interactions certainly allow, and may even favor, close Cl···Cl separations.

5. Discussion

Explicit calculation of the various contributions to the intermolecular forces between two methyl chloride molecules shows that charge transfer between the chlorine atoms is negligible and certainly unlikely to influence the structure of the dimer, liquid or solid. The repulsive wall is certainly sufficiently anisotropic to influence the molecular packing. This will also be the case for other chlorinated hydrocarbons, since the rest of the molecule has little influence on the electrostatic forces when the chlorine atoms are in van der Waals contact, and the variation of the charge associated with the Cl atom is small. Thus the charge-transfer interactions are unlikely to be much larger, or the repulsive wall much more isotropic, in other chlorinated hydrocarbons.

The electrostatic interactions between Cl atoms are fairly weak and can be attractive for Cl atoms in van der Waals contact in some molecules and orientations. The electrostatic effects of the lone pair density are structurally significant. With a realistic description of the electrostatic interactions, there is no need to invoke a specific attractive force, in addition to the dispersion

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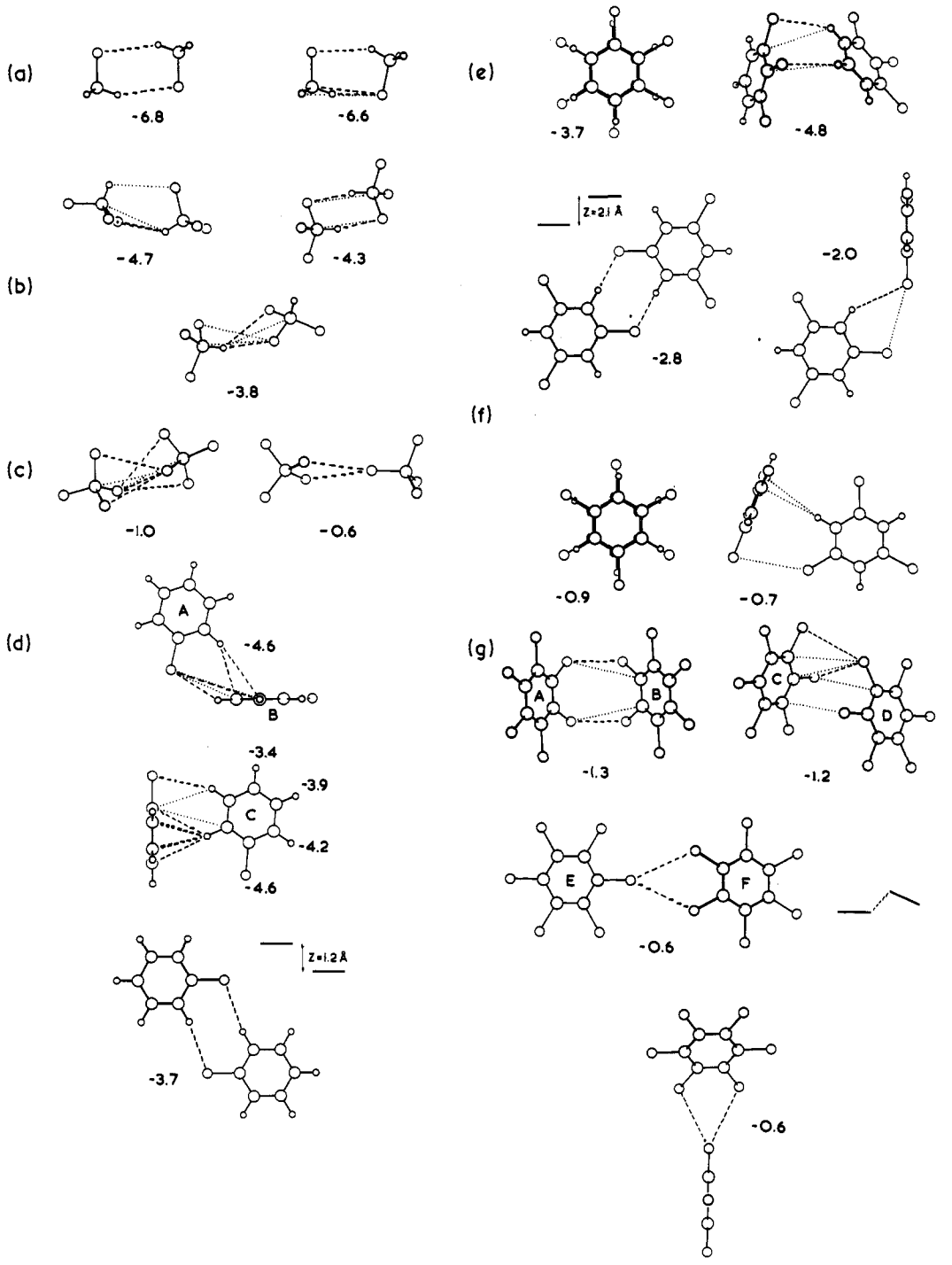

Figure 7. Dimer structures corresponding to minima in the electrostatic energy, within orientations allowed by a pseudo-hard-sphere repulsion model. Electrostatic energy in kJ/mol is given beside each figure. Van der Waals contacts (Cl···H or C···H, <3.25 Å; Cl···Cl, C···Cl, or C···C, <3.75 Å) are denoted by - - -, and other short distances (Cl···H or C···H <3.50 Å; Cl···Cl, C···Cl, or C···C, <4.0 Å), by ···. Some contacts which are just within the upper limit have been omitted for clarity. (a) $(CH_3Cl)_2$. (b) $(CHCl_3)_2$. (c) $(CCl_4)_2$. In (d) $(C_6H_5Cl)_2$, molecule A is 2.0 Å above the perpendicular plane through the symmetry axis of B. There are a series of minima with the aromatic ring in the position of molecule C, with the Cl atoms in the four different positions. The energy is marked beside the Cl position. In (e) $(1,2,3\text{-}C_6H_3Cl_3)_2$, only one of the unsymmetrical structures with two Cl···H contacts is shown. In (f) $(1,3,5\text{-}C_6H_3Cl_3)_2$, the minimum corresponding to an electrostatic energy of 0.7 kJ/mol has the proton in van der Waals contact with the aromatic ring. In (g) $(C_6Cl_6)_2$, A and B are oriented in an open book structure. CD is an unsymmetric structure where C is highly twisted out of the plane of D. F is slightly tilted relative to the plane of E. The monomer structures not given in the text are as follows: CH_3Cl C–H, 1.10 Å; C–Cl, 1.767 Å; ∠H–C–Cl, 109.4 Å; $C_6H_3Cl_3$ C–C, 1.40 Å; C–Cl, 1.72 Å; C–H, 1.10 Å; all angles are 120°. All structures shown were predicted using a pseudo-hard-sphere potential for Cl with a radius of 1.76 Å.

interaction, to account for the van der Waals contacts between Cl atoms being weakly energetically favorable. However, the Cl···Cl interactions will generally be weaker than Cl···H interactions and some interactions involving aromatic rings. Thus structures of van der Waals complexes and molecular crystals will be a compromise between many competing interactions.

This picture is consistent with the known crystal structures of chlorinated hydrocarbons. Chlorine atoms can be in van der Waals contact, and the anisotropy of the repulsive wall results in "short" contacts for head-on orientations. However, such contacts mainly occur in such heavily chlorinated compounds that Cl···Cl contacts are an inevitable consequence of close packing. There is no marked preferred relative orientation for such Cl···Cl contacts, as would be required for a specific attractive donor–

acceptor interaction, and indeed, the anisotropy in the electrostatic forces does not produce a clearly preferred relative orientation. The electrostatic modeling shows that multiple contacts are likely to occur in the van der Waals complexes, giving rise to a range of angles associated with Cl···Cl contacts. This is consistent with the observed range of angles in the crystal structures, suggesting relatively close packing rather than highly directional interactions. Although chlorine atoms involved in more than one Cl···Cl short contact are observed in crystal structures (Table 1), they are not common as such motifs are often not compatible with efficient packing.

Thus, the crystallographic data do not require there to be a specific attractive force between Cl atoms, but the interaction is anisotropic. The charge-transfer hypothesis grew out of the expectation that atoms would pack as spheres (i.e., the van der Waals radius would be spherical) and gained support from early *ab initio* work, as small basis sets lead to a basis set superposition error which can be mistaken for charge transfer, and from the inadequacies of the isotropic atom–atom model intermolecular potential. Inadequate models for intermolecular forces have also led to another argument being put forward for the importance of charge transfer between halogen atoms, namely, that van der Waals complexes, such as $(Cl_2)_2$, probably have a floppy L type structure,[31] as would be expected from HOMO–LUMO interactions. However, such a structure for the chlorine dimer can be predicted[27] by optimizing just the electrostatic interaction between chlorine molecules, within accessible orientations. Indeed, the electrostatic model can also predict[27] the "anti-hydrogen-bonded" structures of HF···ClF[32] and HF···Cl_2,[33] provided that the hard-sphere model, used to define the accessible orientations, uses the experimental separations, which are shorter than the sums of the van der Waals radii. The electrostatic forces and repulsion anisotropy, arising from the lone pair electron density, thus determine the structures of halogen van der Waals complexes, and there is no need to invoke any weak intermolecular bonding.

The charge-transfer contribution is expected to increase with atomic size, and may therefore be larger in bromine and iodine than in chlorine. Nuclear quadrupole resonance studies show evidence for some covalent character in the intermolecular bonding in molecular iodine crystals[34] but not in some compounds with short Cl···Cl contacts.[16] Whether the charge transfer is sufficient to affect the structures of complexes of iodinated hydrocarbons remains a question that cannot be answered from current experimental data or theoretical techniques.

We conclude that the most important contributions to the intermolecular interactions of halogen atoms are the repulsion, electrostatic, and dispersion terms and that the contribution from charge-transfer type interactions is negligible. However, the interactions are anisotropic because the atomic charge distribution is not spherical, and this anisotropy has to be included in the model. The neglect of the anisotropy in the repulsion and electrostatic terms might be empirically compensated for by an intermolecular bonding term, but this has no physical justification. Anisotropic atom–atom potentials, including a distributed multipole electrostatic model, are theoretically well based and are becoming increasingly practical for simulation work. We are developing a crystal structure prediction program[35] which can use such intermolecular potentials and intend to use it to develop a repulsion–dispersion plus electrostatic potential which can quantitatively predict the crystal structures of chlorinated hydrocarbons.

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