Article

Halogen−Halogen Nonbonded Interactions

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ABSTRACT: Halogen−halogen nonbonded interactions were studied for methyl halides and phenyl halides using both B3LYP and MP2 along with 6-311+G* and aug-cc-pVTZ. With the methyl halides, the linear approach was found to lead to little stabilization, whereas the "90°" approach gave 1−2 kcal/mol. This modest stabilization was due to long-range electron correlation effects. The lowest-energy arrangement had the molecules side-by-side, with the major stabilization being derived from halogen−hydrogen interactions. The results for methyl bromide were quite similar. Chlorobenzene dimer with the 90° orientation gave a small stabilization energy, but the best arrangement had the two benzene rings oriented over each other. The meta orientation of the chlorines had a lower energy than ortho or para. The dimerization energy was larger than that for two benzene rings sitting directly above each other, suggesting that whereas Cl···Cl interaction is not very important, the effect of the halogen on the electron distribution does have an effect. This suggests that much of the crystallographic results for these compounds may not be due to halogen−halogen interactions but rather the interaction between the substituted benzene rings along with crystal forces.
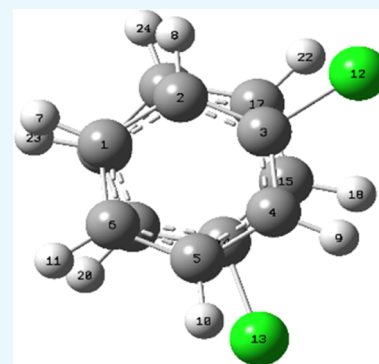
1. INTRODUCTION

There has been much interest in halogen−halogen nonbonded interactions. Wheeler and Colson appear to be the first to suggest that the interaction was anisotropic based on X-ray structures of the three phases of *p*-dichlorobenzene crystals.[1,2] There have been several other studies making use of X-ray crystallographic data.[3,4] There have also been some computational studies.[5,6] Despite all of this work, it is still not clear as to the magnitude of the interactions, and there remains the question of the possible interactions between aromatic rings in determining the crystal structures of aryl halides.

2. RESULTS AND DISCUSSION

2.1. Interaction between Halogens. The halogens themselves are the simplest compounds that might be examined. The Cl₂ dimer has been examined by Prissette and Kochanski[7] and was found to have an **L**-shaped geometry with a **T**-shaped structure having a slightly higher energy. A later study by De Almeida[8] also found a rectangular structure as well as a linear structure. Karim-Jafiri et al.[9] derived a potential energy surface for the Cl₂ dimer that showed the **T** conformation to be a transition state between the **L** conformers. The potential energy surface has also been studied by Thanh-Duoc et al.[10] The earlier calculations were carried out some time ago, and we thought it might be useful to perform calculations at the MP2/aug-cc-pVTZ level and include bromine and mixed dimers. The results of these calculations are shown in Table 1, and the structures are shown in Figure 1.

With the Cl₂ and Br₂ dimers, the lowest-energy structure had the **L** conformation, with **T** as the transition state connecting the two identical **L** conformers. It had an energy slightly greater than

that for **L** and had three imaginary frequencies. The rectangular structure (not shown in the figure) was found to be a transition state connecting the two rhomboid structures (**R**). A linear conformation was studied by enforcing symmetry, and it was found to be a higher-energy transition state that connects the two rhomboid structures. The results for the chlorine dimers and the bromine dimers were similar. In these cases, there is a possibility of a basis set superposition error (BSSE) that was estimated by the counterpoise method.[11] In all cases, this led to a reduction of the dimerization energy.

The dimerization energies are rather small, with Br···Br interactions being a little larger than Cl···Cl. The interaction energies were also calculated using B3LYP/aug-cc-pVTZ, and here, the dimerization energies were very small (−0.27) for the Cl₂···Cl₂ **L** conformers. Since B3LYP does account for much of the short-range electron correlation,[12] we must conclude that it is the long-range electron correlation in MP2 that leads to the larger stabilization energies.

The notable result is that the Cl−Cl···Cl bond angle is very close to 90° for the **L** conformers. When the angle is 180°, there is little stabilization. The reason for this conformation has been studied by Tsirelson et al.,[13] making use of the Laplacian of the electron density that was found to be compressed at chlorine along the bond axis and extended normal to the axis (see Figure

Table 1. MP2/aug-cc-pVTZ Interaction Energies for Chlorine and Bromine Dimers, kcal/mol

A	B	conformer	state	$r(A–B)^a$	angle[b]	ΔE^c	BSSE[d]
Cl−Cl	Cl−Cl	L	GS	3.226	88.36	−2.03	−1.63
		T	TS	3.509	73.45	−1.74	−1.36
		R	GS	3.800	70.17	−1.70	−1.31
		rectangular	TS	3.830	90.00	−1.25	−0.94
		linear	TS	3.382	180.00	−0.66	−0.37
Br−Br	Br−Br	L	GS	3.256	88.32	−4.00	−3.06
		T	TS	3.620	73.64	−3.33	−1.93
		R	GS	3.931	69.40	−3.07	−1.73
		rectangular	TS	4.009	90.00	−2.32	−1.20
		linear	TS	3.102	180.00	−1.77	−0.50
Br−Cl	Br−Cl	L	GS	3.152	92.53	−3.51	−2.45
Br−Cl	Cl−Br	L	GS	3.245	86.95	−2.42	−1.73
Cl−Br	Br−Cl	L	GS	3.213	90.93	−3.66	−2.39

[a]Distances are given in angstrom (Å). [b]The X−X···X angle is in degrees. [c]The difference in energy between two monomers and the dimer; a negative sign indicates that the dimer has lower energy than two monomers. [d]Energies are corrected for the basis set superposition error.
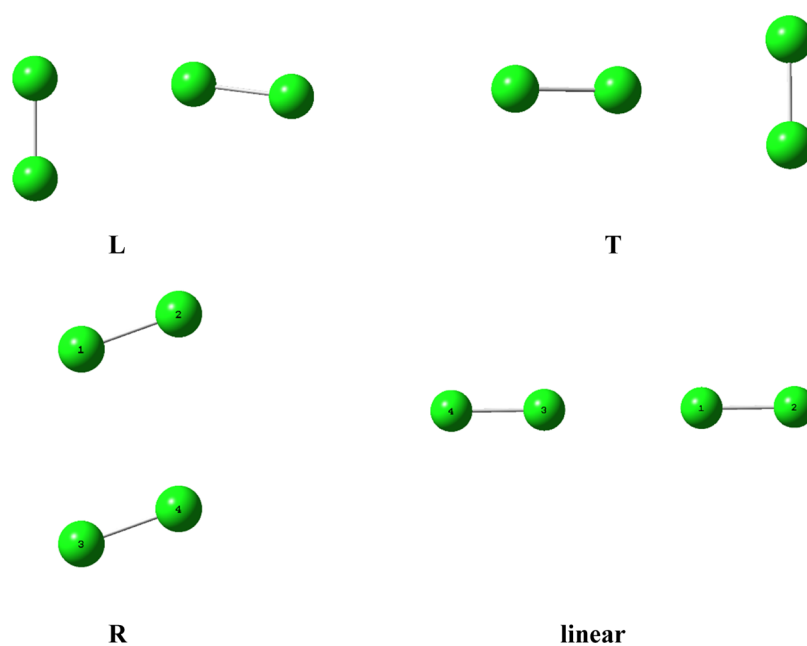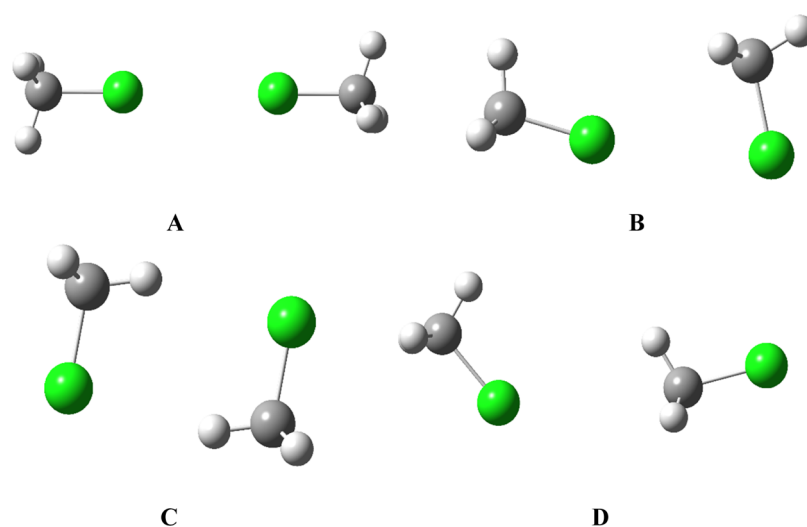

Figure 1. Structures of Cl_2 dimers.

Figure 2. Possible structural arrangements for methyl chloride dimers.

Table 2. Calculated Dimerization Energies for Methyl Chloride and Bromide[a,b]

dimer	conformer	B3LYP/big	LC-wPBE big	MP2/small	MP2/big	with BSSE	r(X–X)
MeCl–Cl–Me	A	−0.01	−0.02	−0.22	−0.57	−0.39	3.484
	B	−0.01	−0.52	−1.33	−1.71	−1.34	3.541
	C	−0.46	−1.25	−3.04	−3.19	−2.55	4.253
	D	−0.14	−0.50	−1.49	−1.37	−1.12	
MeBr–BrMe	A	0.00	−0.02	−0.31	−1.43	−0.65	3.542
	B	−0.06	−0.32	−1.47	−3.12	−1.79	3.581
	C	−1.12	−1.22	−2.82	−4.46	−2.49	4.386
	D	−0.31	−0.43	−1.27	−2.20	−1.22	

[a]The small basis set is 6-311+G*, and the large basis set is aug-cc-pVTZ. [b]Distances are given in angstrom (Å), energies are given in kcal/mol, and negative energies indicate that the dimer is more stable than two monomer molecules.

2 of the reference). Stabilization is found when the extended part of one chlorine interacts with the compressed side of an adjacent chlorine atom.

2.2. Halomethane Interactions. Although the halogen molecules themselves do interact, this is not of a general chemical interest as interactions between molecules with carbon−halogen bonds. The simplest system that might be of interest is the interaction between the halogens of methyl halides. We have carried out calculations using B3LYP and MP2 and using 6-311+G* and aug-cc-pVTZ. The smaller basis set B3LYP calculations led to no significant stabilization and were not further considered. The use of different levels of calculation should provide some information on the role of electron correlation, as well as of the basis set size. The results, of course, are just relative energies, and in the gas phase, the entropy change for forming the dimer is large, and so the concentration of dimers will be small. However, in condensed phases, the entropy effect is markedly reduced.

The structures that were considered are shown in Figure 2. The geometry optimization for the linear approach (**A**) was forced to maintain a C_{3v} symmetry. Releasing this constraint leads to the lower-energy bent conformation **B**.[13] With MeCl, this is a small shoulder on the potential energy curve, which on further optimization leads to the lower-energy parallel structure **C** that has close halogen−hydrogen interactions. These interactions will be stabilizing because chlorine has a negative charge and the hydrogens have a positive charge. This has been reported to be the lowest-energy dimer based on gas-phase studies of methyl chloride clusters.[14] Another structure is **D** that has a Cl···CH$_3$ nonbonded interaction and is less stable than **C**.

The energies associated with these structures are summarized in Table 2. Here, the small basis set is 6-311+G* and the large basis set is aug-cc-pVTZ. The B3LYP aug-cc-pVTZ-calculated stabilization energies for conformer **B** of the methyl chloride and methyl bromide dimers are much smaller than for the MP2 calculations. However, if the stabilization of **B** were electrostatic as found with F$_3$C−Cl,[15] one might expect the energies to be similar. The main difference between B3LYP and MP2 calculations is that the former accounts only for short-range correlation, whereas MP2 accounts for both short- and long-range correlations.[12,16] This leads to the conclusion that interaction is largely due to long-range correlation.

The LC-wPBE functional[12] includes both types of electron correlation and has been found to be useful in the calculation of optical rotations[17] as well as other properties.[18] With LC-wPBE/aug-cc-pVTZ, optimizations for conformer **C** found the stabilization energy for the MeCl dimer to be −1.25 kcal/mol, and for MeBr dimer, it is −2.82 kcal/mol. Although the effect is

not as large as that found with MP2, this finding is in accord with the above suggestion.

The calculated energies of these dimers are probably subject to the basis set superposition effect.[11] It was calculated using the usual counterpoise method, and the corrected energies are also given in Table 2. The small corrected energies indicate that the halogen−halogen attraction is quite weak. The largest dimer stabilization energy was found with conformer **C**, but here, the Cl···Cl distance is long, and the major contributor to the energy is a Coulombic interaction between the negatively charged Cl of one molecule and the nearby positively charged H of the other molecule.

Why are the bent conformers **B** less stabilized than in the 90° halogen dimers? One possible reason is that whereas in the halogen dimers the charge on the halogens will be zero, in the methyl halides, the halogens will have a negative charge and the hydrogens will have a positive charge. The Hirshfeld charges[19] for methyl chloride are H = 0.045 e, C = 0.005 e, and Cl = −0.294 e. Thus, there will be Coulombic repulsion between the halogens of the MeCl dimer, and with a Cl···Cl distance of 3.5 Å, the repulsion will be about 1.5 kcal/mol, making the **B** conformer less stable. It might be noted that the Cl−Cl···Cl angle in the **B** structure is 73.2°.

The interaction between two MeBr molecules was calculated in the same fashion, giving the results shown in Table 2. The effect is somewhat larger than found for the chlorides as expected from its greater polarizability, but after BSSE corrections, the stabilization energies are again quite small. Here, conformer **B** was found to be a true local minimum (i.e., it had no imaginary vibrational frequencies) but with a very small barrier for going to conformer C. It had a C−Br···Br angle of 72.9°.

It was of interest to see if larger effects might be found with methyl iodide where the iodine has a larger polarizability than chlorine or bromine. Unfortunately, the basis sets used in this work are not defined for iodine. To get some information, we made use of the MidiX basis set of Easton et al.[20] The relative energies of MeI dimers **A**−**C** were 0.5, 2.2, and 3.5 kcal/mol, respectively. They are similar to the MeBr dimers.

3. ARYL HALIDE INTERACTIONS

The small halogen−halogen interaction energies for the methyl halides made a study of aryl halide dimers of more interest in that they are related to the X-ray crystallographic studies.[1−5] The interaction between two chlorobenzene molecules was studied at the B3LYP and MP2 levels. The MP2/aug-cc-pVTZ optimizations were too large for our computer facilities, and therefore, the larger basis set was 6-311+G(2df,2p).
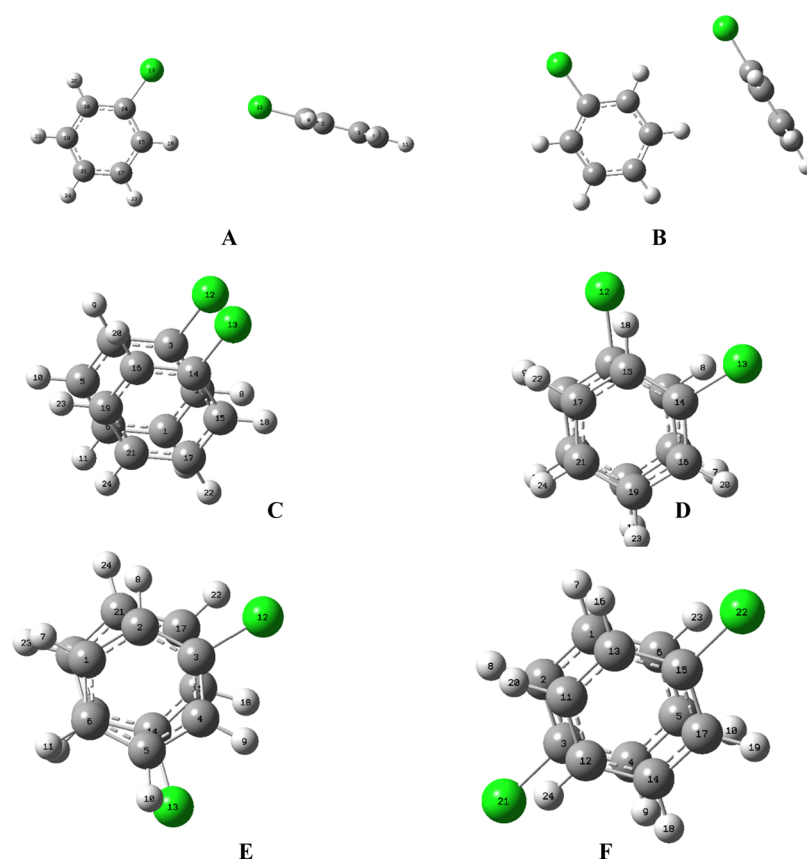
Figure 3. Structures of phenyl chloride dimers.

Table 3. Calculated Stabilization Energies for Aryl Halide Dimers, kcal/mol[a] *The s*

dimer	conformer	B3LYP/big	MP2/small	MP2/big	BSSE[b]	r(X–X)
ArCl–ArCL	**A** 90°	0.00	−3.52	−2.47	−1.36	3.620
	B	−0.22	−7.09	−6.01	−3.90	5.158
	C ipso		−10.40	−8.84	−4.99	3.710
	D ortho	−0.09	−11.50	−9.47	−6.17	5.056
	E meta	0.00	−12.21	−10.26	−6.61	5.078
	F para	0.00	−9.81	−8.08	−5.24	8.106
ArBr–ArBr	**A** 90°	−0.01	−2.59	−2.55	−1.66	3.859
	B	−0.03	−6.70	−6.07	−4.09	5.242
	C ipso		−10.07	−9.03	−5.86	3.917
	D ortho	−0.27	−11.27	−9.81	−6.55	5.285
	E meta		−11.87	−10.54	−7.00	5.307
	F para		−10.05	−8.31	−5.55	8.348

[a] *The s*mall basis set is 6-311G*, and the large basis set is 6-311+G(2df,2p). [b]MP2/6-311+G(2df,2p) is corrected for the basis set superposition error.

They were first studied at the MP2/6-311+G* level starting with a linear approach. This gave essentially no stabilization. A "90°" approach led to structure **A** in Figure 3 as a weak shoulder in the potential energy curve. Here, the Cl···Cl distance was 4.267 Å, considerably larger than the sum of the covalent radii (3.5 Å), and the stabilization energy was only 3.5 kcal/mol (Table 3). Allowing the optimization to proceed for a large number of steps led to a fully optimized structure **B** with a Cl···Cl distance of 5.959 Å and a stabilization energy of 6.0 kcal/mol. The remaining dimers, **C**, **D**, **E**, and **F**, had the two benzene rings over each other, with the two chlorines have either an ipso (**C**), ortho (**D**), meta (**E**), or para (**F**) relationship. These structures are substantially more stable than **A** or **B**, and **E** has the lowest

energy. The **C** conformer was found to be a transition state leading to **D**.

Optimization of these structures at the B3LYP/aug-cc-pVTZ level found negligible stabilization energies. The use of MP2/6-311+G(2df,2p) led to relative energies that were similar to those found with MP2/6-311+G*, and the calculated energy was somewhat reduced at the higher level, suggesting the need for BSSE corrections. The effects of this correction are shown in Table 3 and resulted in significant decreases in stabilization energies.

The stabilization energy of conformer **A** is small with both the ArCl and ArBr dimers and even smaller with the BSSE correction. The energies are somewhat larger than those for

Table 4. Hirschfeld Charges for Chlorobenzene Dimers with H Combined with C[a,b]

	no. ipso	population	no. ortho	population	no. meta	population	no. para	population
				Upper Atom				
ipso	3	0.0377	3	0.0362	3	0.0254	3	0.0221
ortho	4	0.0099	4	0.0013	4	−0.0011	4	−0.0006
meta	5	0.0117	5	0.0107	5	0.0100	5	0.0150
para	6	0.0049	6	0.0027	6	0.0028	6	0.0083
meta'	1	0.0117	1	0.0182	1	0.0154	1	0.0150
ortho'	2	0.0099	2	0.0068	2	0.0028	2	−0.0009
Cl	12	−0.0678	12	−0.0699	12	−0.0439	21	−0.0586
				Lower Atom				
ipso	14	0.0338	14	0.0229	14	0.0224	15	0.0221
ortho	16	0.0006	16	0.0008	16	−0.0023	13	−0.0006
meta	19	0.0142	19	0.0150	19	0.0119	11	0.0150
para	21	0.0006	21	0.0078	21	0.0053	12	0.0083
meta'	17	0.0142	17	0.0170	17	0.0120	14	0.0150
ortho'	15	0.0006	15	0.0016	15	−0.0035	13	−0.0009
Cl	13	−0.0831	13	−0.0810	13	−0.0596	22	−0.0586

[a]Charges were derived from MP2/6-311+G(2df,2p) calculations. [b]The atom numbers correspond to the coordinate given in the Supporting Information.

the corresponding MeCl and MeBr dimers. The sideway interaction as in conformer **B** gives a significant effect but it is only with the benzene rings directly over each other that larger binding energies are found.

Although it is not the lowest-energy dimer of benzene,[21] the one with the benzene rings directly over each other is a stationary state. Its MP2 dimerization energy including BSSE is −4.1 kcal/mol as compared to −5 to −7 kcal/mol for the ArCl and ArBr dimers **C−F**. Thus, the halogens do add to the stabilization of the dimers. However, it is not due to a Cl···Cl interaction since the dimerization energy is larger with the meta arrangement **E** than for ortho as in **D** despite an increase in the nonbonded distance. Apparently, the halogen modifies the electron distribution in the phenyl rings so as to increase the stabilization of the dimers.

To examine the charge distributions, the Hirshfeld charges[19] were calculated and are given in Table 4, with the hydrogen charges combined with the carbon charges. The full set of Hirshfeld populations for these compounds may be found in the Supporting Information. As a reference, it may be noted that chlorobenzene has the charges C(ipso) = 0.0354, C(ortho) = 0.0044, C(meta) = 0.0152, and C(para) = 0.0044. The electronegative chlorine withdraws electron density via the σ-system and returns electron density to the ortho and para positions via the π-system.[22]

The para dimer **F** is unique in that it is symmetrical, and the CH charges are aligned so as to minimize Coulombic repulsion, and there is no charge transfer between the rings. It has a lower energy than dimer **C** despite having a much greater Cl···Cl distance. The **C** conformer would be expected to have a significant Coulombic repulsion between the chlorines. It is difficult to analyze the charge distribution for dimers **D** and **E**.

4. SUMMARY

The dimers of Cl$_2$ and Br$_2$ as well as those of MeCl, MeBr, PhCl, and PhBr have been studied at several levels of theory. A linear approach gave essentially no stabilization, whereas a bent arrangement gave some. For the methyl halides, the lowest-energy conformation had the two molecules arranged side-by-side to give a halogen interaction with the methyl group of the other molecule. With the aryl halides, the bent approach gave

some stabilization but the greatest stabilization was found with the two benzene rings in a parallel arrangement with the halogens in either an ortho, meta, or para orientation. Since meta gave more stabilization than ortho, halogen−halogen interactions are of minor importance, and it is the modification of the charge about the rings that leads to the greater stabilization energies than found with just two benzene rings.

5. CALCULATIONS

All calculations were carried out using Gaussian-16.[23]

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01356.

> Calculated total energies and atomic coordinates of the dimers; and Hirshfeld charges for the chlorobenzene dimers (PDF)

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Notes

The author declares no competing financial interest.

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