J. Phys. Chem. A **1998,** *102,* 9965−9969

Theoretical Thermochemistry of Homolytic C−C and C−Cl Bond Dissociations in Unbranched Perchloroalkanes

Jerzy Cioslowski,* Guanghua Liu, and David Moncrieff

Department of Chemistry and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-3006

Received: July 17, 1998; In Final Form: September 9, 1998

Proper description of the dispersion interactions that attenuate the closed-shell repulsions among chlorine atoms in *n*-perchloroalkanes requires an accurate treatment of long-range electron correlation effects. The presently known density functionals, which do not correctly account for such effects, grossly underestimate thermodynamic stability of these molecules, yielding the standard enthalpy $\Delta H^\circ_{\mathrm{C-C}}$ of C−C bond dissociation in *n*-C_4Cl_{10} as low as 20 kcal/mol. In contrast, the predictions of the CBS-4 scheme fail to reproduce the weakening of the C−C bonds that is experimentally observed in the higher members of the C_nCl_{2n+2} homologous series. For the CCl_4 and C_2Cl_6 the most reliable estimates of $\Delta H^\circ_{\mathrm{C-C}}$ and $\Delta H^\circ_{\mathrm{C-Cl}}$ are provided by the G2 and G2MP2 methods. The MP2/6-311G** level of theory (without ZPEs and finite-temperature corrections) appears at present to be the only viable, though quite inaccurate, theoretical approach to theoretical thermochemistry of larger chlorocarbons. At that level of theory, $\Delta H^\circ_{\mathrm{C-C}}$ is predicted to decrease by ca. 10 kcal/mol upon the addition of each $-CCl_2-$ unit, convincingly explaining the thermal lability of higher *n*-perchloroalkanes. Similar conclusions are reached by examining the estimates of $\Delta H^\circ_{\mathrm{C-C}}$ derived from the CBS-4 standard enthalpies with the E_{CBS} energy term excluded.

Introduction

Chemical properties of *n*-perhalogenoalkanes vary greatly with the size of the halogen atom and the length of the carbon backbone. Thus, whereas *n*-perfluoroalkanes of any chain length are thermally stable and chemically inert,[1] CBr_4 and C_2Br_6 are the only known *n*-perbromoalkanes.[2] This great variation in stability is readily accounted for by steric effects that rapidly rise in importance with the increasing number of the halogen−halogen interactions.

Only the first four members of the C_nCl_{2n+2} homologous series have been characterized thus far[3,4] (the putative synthesis of *n*-C_5Cl_{12}[5] has never been confirmed). Attempts at exhaustive chlorination of higher alkanes are impeded by the intervening C−C bond cleavage and cyclization.[6] Other synthetic approaches, such as addition of chlorine to *n*-perchloroalkadienes, also fail for species with more than four carbons.[3] As expected, higher *n*-perchloroalkanes are thermally less stable than either CCl_4 or C_2Cl_6. Thus, *n*-C_4Cl_{10} rapidly decomposes to C_2Cl_4 and C_2Cl_6 at 200 °C,[3] and pyrolysis of C_3Cl_8 at 350 °C results in its complete conversion to C_2Cl_4 and CCl_4 within 0.5 h,[7] pointing out to the predominance of thermally induced C−C bond cleavage over C−Cl bond scission in both cases. In contrast, thermal decomposition of C_2Cl_6 proceeds through fast dissociation of the C−Cl bond concomitant with slow C−C bond scission.[8] Prolonged heating of chlorocarbons in the absence of oxygen ultimately leads to an equilibrium mixture of CCl_4, C_2Cl_6, and C_6Cl_6 (perchlorobenzene) regardless of the composition of the starting material.[7,9]

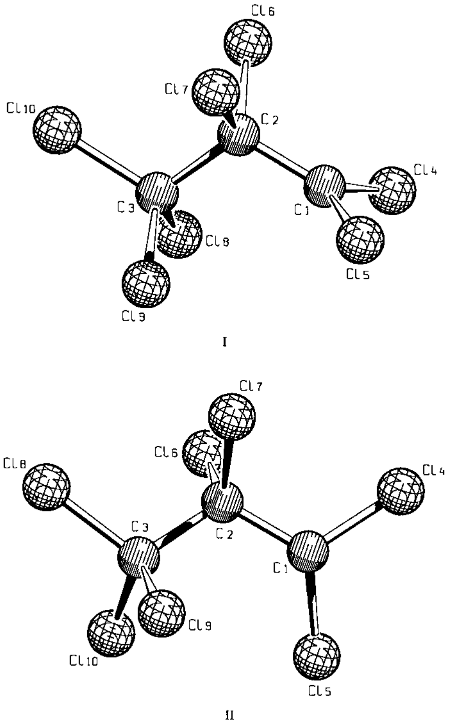


Figure 1. Structures of the two rotamers of the 1-$C_3Cl_7^\bullet$ radical.

Pyrolysis of chlorinated hydrocarbons is of great practical importance to fuel conversion, large-scale synthesis of chemicals, and environmental protection. However, the current understanding of high-temperature chemistry and kinetics of these species is at best fragmentary,[10] the experimentally determined thermochemical properties of *n*-perchloroalkanes and the corresponding radicals being particularly scarce and of poor accuracy (Table 1).[11−16] In light of this lack of data, the need for reliable electronic structure studies of these species is self-

---

* To whom all the correspondence should be addressed. E-mail address: jerzy@kyoko.chem.fsu.edu. Homepage: http://www.scri.fsu.edu/~jerzy.

10.1021/jp9830732 CCC: $15.00

TABLE 1: Summary of the Available Experimental Data on ΔH_f° of the Species Relevant to Homolytic Bond Dissociations in *n*-Perchloroalkanes

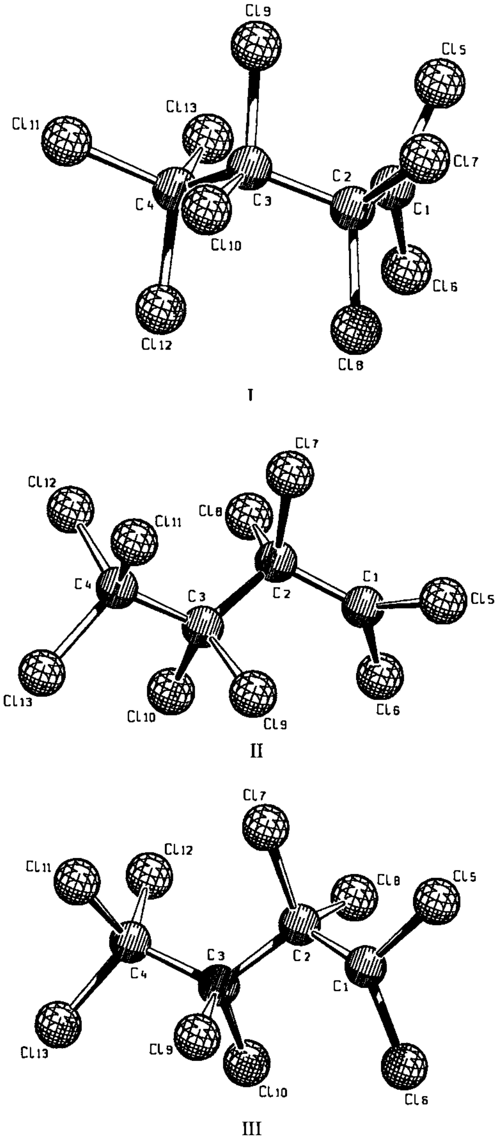
species	ΔH_f° (kcal/mol)	species	ΔH_f° (kcal/mol)
CCl_4	-22.9 ± 0.5[a]	$CCl_3^\bullet$	18.0 ± 2.0,[b] 17.0 ± 0.6[c]
C_2Cl_6	-32.9, -34.7, -33.0, -36.1,[d] -33.7[e]	$C_2Cl_5^\bullet$	7.7 ± 1,[e] 8.4 ± 1.9[f]
$Cl^\bullet$	28.992 ± 0.002[g]		

[a] Reference 11. [b] Reference 12. [c] Reference 13. [d] Reference 14. [e] Reference 8. [f] Reference 15. [g] Reference 16.

TABLE 2: Theoretical and Experimental Standard Enthalpies of Homolytic C−Cl Bond Dissociations in *n*-Perchloroalkanes[a]

	ΔH_{C-Cl}° (kcal/mol)								
species	BLYP[b]	B3LYP[b]	MP2[c]	CBS-4[d]	CBS-q	CBS-Q	G2	G2MP2	expt[e]
CCl_4	58.95	58.48	68.12	72.61 (65.96)	70.46	73.96	71.79	72.81	69.9 ± 2.1
C_2Cl_6	56.44	57.34	71.60	72.72 (68.99)	69.94	78.12	74.53	75.53	71.5 ± 2.8
C_3Cl_8[f]	48.76	48.86	62.45	71.89 (59.09)	n/a	n/a	n/a	n/a	n/a
C_3Cl_8[g]	49.83	51.30	68.76	76.87 (64.73)	n/a	n/a	n/a	n/a	n/a
n-C_4Cl_{10}[h]	45.79	45.83	59.65	71.86 (58.30)	n/a	n/a	n/a	n/a	n/a
n-C_4Cl_{10}[i]	41.71	42.79	60.31	74.46 (57.81)	n/a	n/a	n/a	n/a	n/a

[a] All the computed data pertain to adiabatic (the lowest-energy rotamer → the lowest-energy rotamer) dissociations. [b] Used in conjunction with the 6-311G** basis set. [c] Used in conjunction with the 6-311G** basis set; energy differences at $T = 0$ K, ZPEs not included. [d] Values excluding the E_{CBS} component listed in parentheses. [e] Derived from the data compiled in Table 1. [f] Dissociation into 1-$C_3Cl_7^\bullet + Cl^\bullet$. [g] Dissociation into 2-$C_3Cl_7^\bullet + Cl^\bullet$. [h] Dissociation into 1-$C_4Cl_9^\bullet + Cl^\bullet$. [i] Dissociation into 2-$C_4Cl_9^\bullet + Cl^\bullet$.

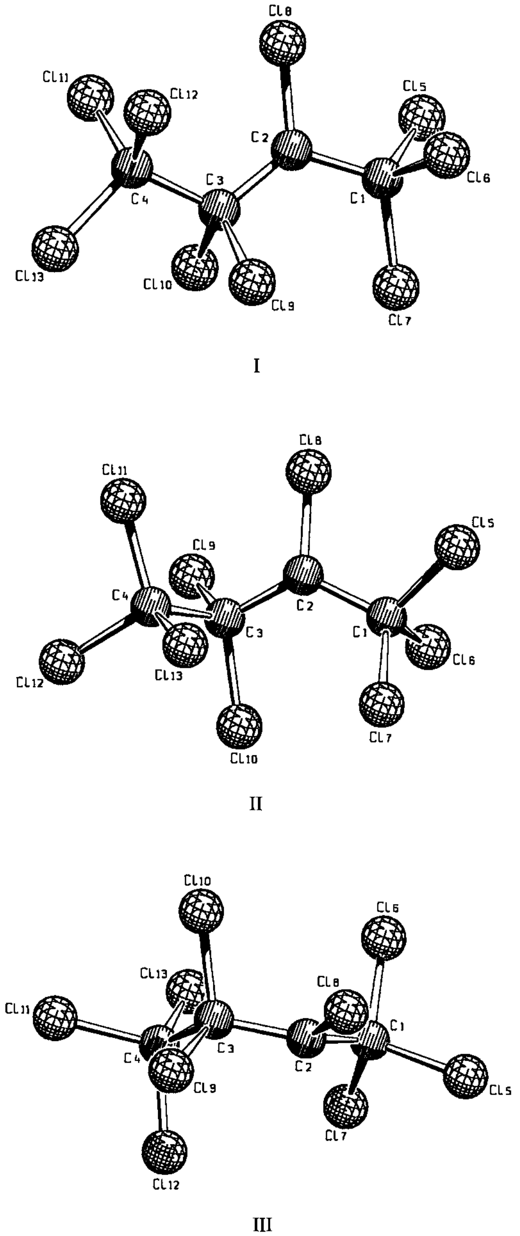


I

II

III

Figure 2. Structures of the three rotamers of the 1-$C_4Cl_9^\bullet$ radical.



I

II

III

Figure 3. Structures of the three rotamers of the 2-$C_4Cl_9^\bullet$ radical.

evident. At present, quantum-chemical calculations involving highly accurate approaches such as G2,[17] G2MP2,[18] CBS-q, and

TABLE 3: Relative Standard Enthalpies of the $C_3Cl_7^\bullet$, n-$C_4Cl_9^\bullet$, and n-C_4Cl_{10} Isomers/Rotamers[a]

			relative standard enthalpy (kcal/mol)			
species	rotamer	symm	BLYP/ 6-311G**	B3LYP/ 6-311G**	MP2/ 6-311G**[b]	CBS-4
1-$C_3Cl_7^\bullet$	I	C_s	0.00	0.00	0.00	0.00
	II	C_1	0.76	1.07	1.13	−4.44
2-$C_3Cl_7^\bullet$		C_1	1.06	2.45	6.31	0.53
1-$C_4Cl_9^\bullet$	I	C_1	0.00	0.00	0.00	0.00
	II	C_1	2.20	2.27	3.22	9.75
	III	C_1	2.47	2.86	3.40	7.34
2-$C_4Cl_9^\bullet$	I	C_1	−4.08	−3.04	0.65	2.85
	II	C_1	−2.74	−1.91	1.22	2.61
	III	C_1	3.34	4.45	7.66	5.06
n-C_4Cl_{10}	I	C_2	0.00	0.00	0.00	0.00
	II	C_2	0.15	0.30	0.92	7.84

[a] See Figures 1−4 for the structures of individual rotamers of 1-$C_3Cl_7^\bullet$, 1-$C_4Cl_9^\bullet$, 2-$C_4Cl_9^\bullet$, and n-C_4Cl_{10}. [b] Energy differences at $T = 0$ K, ZPEs not included.

TABLE 4: Components of the CBS-4 Standard Enthalpies of the Two 1-$C_3Cl_7^\bullet$ Rotamers

quantity	rotamer I (au)	rotamer II (au)	difference (kcal/mol)
E_{HF}	−3330.113 311	−3330.112 058	0.79
E_{therm}	0.035 678	0.035 711	0.02
E_{MP2}	−1.344 057	−1.344 402	−0.22
E_{CBS}	−0.517 012	−0.526 598	−6.02
E_{MP34}	−0.050 307	−0.050 176	0.08
E_{int}	0.119 861	0.122 212	1.48
E_{emp}	−0.382 362	−0.383 283	−0.58
H°_{CBS-4}	−3332.250 567	−3332.257 650	−4.44

CBS-Q[19] are computationally feasible only for chlorocarbons and their radicals with one and two carbon atoms.[20] For larger systems, one has to resort to less accurate methods such as CBS-4.[19] Alternatives to these approaches are offered by the formalisms of the density functional theory (DFT) and the second-order perturbation theory (MP2).

In this paper, results of such calculations are reported. The standard enthalpies of the C−C and C−Cl bond dissociations in the n-C_nCl_{2n+2} ($1 \le n \le 4$) species are computed at several levels of theory, making predictions of thermal fragmentation patterns possible. In addition, the rotamers of both the chlorocarbons and their radicals are identified and their equilibrium geometries are compiled.

Results

Standard enthalpies of the molecules and radicals under study were computed at the BLYP/6-311G**, B3LYP/6-311G**, and CBS-4 levels of theory. For the CCl_4, C_2Cl_6, $CCl_3^\bullet$, $C_2Cl_5^\bullet$, and $Cl^\bullet$ species, CBS-q, CBS-Q, G2, and G2MP2 calculations were also carried out. In addition, optimized geometries and total energies were obtained at the MP2/6-311G** level of theory. In all cases, the Gaussian 94 suite of programs[21] was employed.

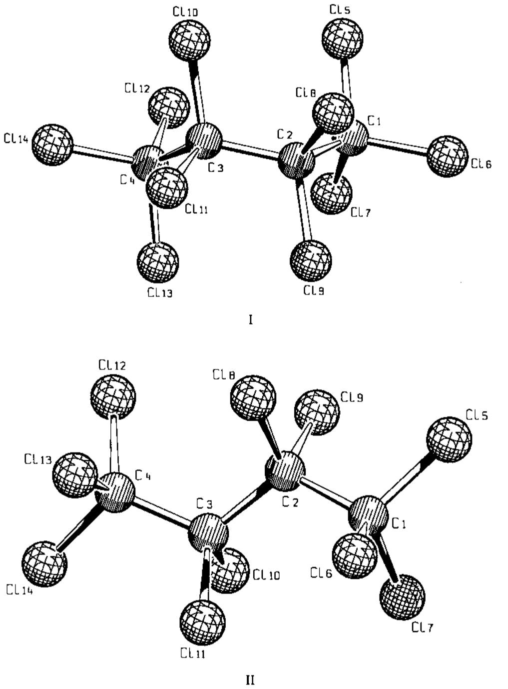


Figure 4. Structures of the two rotamers of the n-C_4Cl_{10} molecule.

The computed standard enthalpies ΔH°_{C-Cl} of the C−C bond dissociation are compiled in Table 2. In agreement with the experimental data,[8] all five methods of the G2 and CBS families predict very similar energetics of the C−Cl bond cleavage in the CCl_4 and C_2Cl_6 molecules. However, the individual enthalpy estimates vary considerably, the largest discrepancies occurring between the data produced by the CBS-q and CBS-Q approaches. Interestingly, despite the neglect of zero-point energies (ZPEs) and finite-temperature contributions, the MP2/6-311G** predictions do not fare much worse than those obtained with the more sophisticated methods. On the other hand, the values of ΔH°_{C-Cl} computed with the BLYP and B3LYP density functionals are very inaccurate, their underestimation stemming from the inability of the contemporary DFT methods to reproduce dispersion (London) interactions among the highly polarizable chloride atoms.[20]

The thermodyamic preference for the C−Cl bond dissociation at the terminal carbon atoms in C_3Cl_8 and n-C_4Cl_{10}, is predicted at both the MP2/6-311G** and CBS-4 levels of theory. However, the MP2/6-311G** standard enthalpies of the C−Cl bond dissociation decrease with the number of carbon atoms, whereas their CBS-4 counterparts stay almost constant. The trends observed among the relative enthalpies of the 1-$C_3Cl_7^\bullet$ (Figure 1), 1-$C_4Cl_9^\bullet$ (Figure 2), 2-$C_4Cl_9^\bullet$ (Figure 3), and n-C_4Cl_{10} (Figure 4) rotamers (Table 3) shed some light on the likely origin of this discrepancy. Whereas the two rotamers of 1-$C_3Cl_7^\bullet$ and n-C_4Cl_{10} are predicted to possess comparable stabilities at the MP2/6-311G** level of theory, unreasonably

TABLE 5: Theoretical and Experimental Standard Enthalpies of Homolytic C−C Bond Dissociations in n-Perchloroalkanes[a]

	ΔH°_{C-C} (kcal/mol)								
species	BLYP[b]	B3LYP[b]	MP2[c]	CBS-4[d]	CBS-q	CBS-Q	G2	G2MP2	expt[e]
C_2Cl_6	50.98	54.34	80.68	72.33 (70.99)	70.09	80.66	77.56	77.72	70.1 ± 3.5
C_3Cl_8	36.24	40.23	70.31	69.34 (60.68)	n/a	n/a	n/a	n/a	n/a
n-C_4Cl_{10}[f]	19.78	24.56	59.96	69.57 (52.88)	n/a	n/a	n/a	n/a	n/a
n-C_4Cl_{10}[g]	26.85	30.18	61.18	71.73 (53.29)	n/a	n/a	n/a	n/a	n/a

[a] All the computed data pertain to adiabatic (the lowest-energy rotamer → the lowest-energy rotamer) dissociations. [b] Used in conjunction with the 6-311G** basis set. [c] Used in conjunction with the 6-311G** basis set; energy differences at $T = 0$ K, ZPEs not included. [d] Values excluding the E_{CBS} component listed in parentheses. [e] Derived from the data compiled in Table 1. [f] Dissociation into $C_2Cl_5^\bullet + C_2Cl_5^\bullet$. [g] Dissociation into $CCl_3^\bullet$ + 1-$C_3Cl_7^\bullet$.

TABLE 6: Selected MP2/6-311G Cl···Cl Nonbonding Distances in $C_2Cl_5^{\bullet}$, C_2Cl_6, $C_3Cl_7^{\bullet}$, and C_3Cl_8**

species	rotamer[a]	nonbonding distance (Å)					
$C_2Cl_5^{\bullet}$		$Cl_3\cdots Cl_6$	3.495	$Cl_3\cdots Cl_7$	3.167		
C_2Cl_6		$Cl_3\cdots Cl_6$	3.229				
1-$C_3Cl_7^{\bullet}$	I	$Cl_4\cdots Cl_6$	3.123	$Cl_4\cdots Cl_8$	3.388	$Cl_6\cdots Cl_8$	3.229
		$Cl_6\cdots Cl_{10}$	3.220				
	II	$Cl_4\cdots Cl_6$	3.386	$Cl_4\cdots Cl_7$	3.120	$Cl_5\cdots Cl_9$	3.447
		$Cl_5\cdots Cl_{10}$	3.178	$Cl_6\cdots Cl_8$	3.321	$Cl_7\cdots Cl_8$	3.092
2-$C_3Cl_7^{\bullet}$		$Cl_4\cdots Cl_7$	3.028	$Cl_5\cdots Cl_{10}$	3.232	$Cl_6\cdots Cl_{10}$	3.262
		$Cl_7\cdots Cl_8$	3.141	$Cl_7\cdots Cl_9$	3.266		
C_3Cl_8		$Cl_4\cdots Cl_7$	3.137	$Cl_5\cdots Cl_7$	3.239	$Cl_5\cdots Cl_9$	3.170

[a] See Figure 1 for atom numbering in the individual rotamers of 1-$C_3Cl_7^{\bullet}$.

TABLE 7: MP2/6-311G C−C Bond Lengths in the Species under Study**

species	rotamer[a]	bond length (Å)		
		C_1-C_2	C_2-C_3	C_3-C_4
$C_2Cl_5^{\bullet}$		1.508		
C_2Cl_6		1.579		
1-$C_3Cl_7^{\bullet}$	I	1.513	1.582	
	II	1.512	1.580	
2-C_3Cl_7		1.510	1.512	
C_3Cl_8		1.600	1.600	
1-$C_4Cl_9^{\bullet}$	I	1.510	1.608	1.589
	II	1.517	1.614	1.597
	III	1.524	1.605	1.605
2-$C_4Cl_9^{\bullet}$	I	1.518	1.507	1.585
	II	1.524	1.532	1.589
	III	1.527	1.541	1.581
n-C_4Cl_{10}	I	1.597	1.639	1.597
	II	1.611	1.628	1.611

[a] See Figures 1−4 for atom numbering in the individual rotamers of 1-$C_3C_7^{\bullet}$, 1-$C_4Cl_9^{\bullet}$, 2-$C_4Cl_9^{\bullet}$, and *n*-C_4Cl_{10}.

large enthalpy differences are produced by the CBS-4 approach. Analysis of the data computed for the 1-$C_3Cl_7^{\bullet}$ radical (Table 4) unequivocally demonstrates that, with the Hartree−Fock (E_{HF}), electron correlation (E_{MP2} and E_{MP34}), finite-temperature (E_{therm}), and empirical-correction (E_{int} and E_{emp}) contributions to the standard enthalpy being very similar for the two rotamers, these differences are almost entirely accounted for by the energy term due to the CBS extrapolation (E_{CBS}). Indeed, the exclusion of this term gives rise to values of ΔH°_{C-Cl} (listed in parentheses in the CBS-4 column of Table 2) that, like their MP2/6-311G** counterparts, steadily decrease with the number of carbon atoms. It is unclear whether this anomalous behavior of the E_{CBS} energy term is inherent to the CBS formalism or stems from the current implementation of the CBS-4 method.[22] In either case, it is prudent to regard the present CBS-4 predictions as less reliable than their MP2/6-311G** counterparts.

The experimentally observed trends in the thermal lability of C−C bonds in *n*-perchloroalkanes with more than two carbon atoms are also well reproduced by the results of MP2/6-311G** calculations (Table 5). The C−C bonds in C_3Cl_8 and *n*-C_4Cl_{10} are predicted to be, respectively, ca. 10 and 20 kcal/mol weaker

TABLE 8: MP2/6-311G C−Cl Bond Lengths in the Species under Study**

species	rotamer[a]	bond length (Å)							
$CCl_3^{\bullet}$		C_1-Cl_2	1.714						
CCl_4		C_1-Cl_2	1.772						
$C_2Cl_5^{\bullet}$		C_1-Cl_3	1.702	C_2-Cl_5	1.773	C_2-Cl_6	1.792		
C_2Cl_6		C_1-Cl_3	1.769						
1-$C_3Cl_7^{\bullet}$	I	C_1-Cl_4	1.695	C_2-Cl_6	1.779	C_2-Cl_8	1.770	C_2-Cl_{10}	1.769
	II	C_1-Cl_4	1.706	C_1-Cl_5	1.700	C_2-Cl_6	1.788	C_2-Cl_7	1.782
		C_3-Cl_8	1.773	C_3-Cl_9	1.772	C_3-Cl_{10}	1.772		
2-$C_3Cl_7^{\bullet}$		C_1-Cl_4	1.773	C_1-Cl_5	1.788	C_1-Cl_6	1.787	C_2-Cl_7	1.691
		C_3-Cl_8	1.787	C_3-Cl_9	1.794	C_3-Cl_{10}	1.767		
C_3Cl_8		C_1-Cl_4	1.784	C_1-Cl_5	1.768	C_2-Cl_7	1.773		
1-$C_4Cl_9^{\bullet}$	I	C_1-Cl_5	1.695	C_1-Cl_6	1.695	C_2-Cl_7	1.796	C_2-Cl_8	1.778
		C_3-Cl_9	1.775	C_3-Cl_{10}	1.770	C_4-Cl_{11}	1.779	C_4-Cl_{12}	1.766
		C_4-Cl_{13}	1.774						
	II	C_1-Cl_5	1.696	C_1-Cl_6	1.696	C_2-Cl_7	1.771	C_2-Cl_8	1.790
		C_3-Cl_9	1.774	C_3-Cl_{10}	1.773	C_4-Cl_{11}	1.774	C_4-Cl_{12}	1.764
		C_4-Cl_{13}	1.782						
	III	C_1-Cl_5	1.706	C_1-Cl_6	1.704	C_2-Cl_7	1.771	C_2-Cl_8	1.795
		C_3-Cl_9	1.774	C_3-Cl_{10}	1.774	C_4-Cl_{11}	1.774	C_4-Cl_{12}	1.764
		C_4-Cl_{13}	1.783						
2-$C_4Cl_9^{\bullet}$	I	C_1-Cl_5	1.788	C_1-Cl_6	1.794	C_1-Cl_7	1.767	C_2-Cl_8	1.693
		C_3-Cl_9	1.788	C_3-Cl_{10}	1.791	C_4-Cl_{11}	1.771	C_4-Cl_{12}	1.771
		C_4-Cl_{13}	1.776						
	II	C_1-Cl_5	1.781	C_1-Cl_6	1.793	C_1-Cl_7	1.773	C_2-Cl_8	1.697
		C_3-Cl_9	1.787	C_3-Cl_{10}	1.774	C_4-Cl_{11}	1.768	C_4-Cl_{12}	1.770
		C_4-Cl_{13}	1.769						
	III	C_1-Cl_5	1.785	C_1-Cl_6	1.791	C_1-Cl_7	1.767	C_2-Cl_8	1.708
		C_3-Cl_9	1.791	C_3-Cl_{10}	1.793	C_4-Cl_{11}	1.781	C_4-Cl_{12}	1.770
		C_4-Cl_{13}	1.767						
n-C_4Cl_{10}	I	C_1-Cl_5	1.765	C_1-Cl_6	1.785	C_1-Cl_7	1.769	C_2-Cl_8	1.782
		C_2-Cl_9	1.776						
	II	C_1-Cl_5	1.782	C_1-Cl_6	1.775	C_1-Cl_7	1.764	C_2-Cl_8	1.769
		C_2-Cl_9	1.778						

[a] See Figures 1−4 for atom numbering in the individual rotamers of 1-$C_3Cl_7^{\bullet}$, 1-$C_4Cl_9^{\bullet}$, 2-$C_4Cl_9^{\bullet}$, and *n*-C_4Cl_{10}.

than that in C_2Cl_6. On the other hand, the CBS-4 approach yields the standard enthalpies ΔH°_{C-C} of C−C bond dissociation that do not vary appreciably with the number of carbon atoms. However, as in the case of the C−Cl bonds, the exclusion of the E_{CBS} energy term affords values of ΔH°_{C-C} that exhibit the same trends as their MP2/6-311G** counterparts. As expected,[20] both the BLYP/6-311G** and B3LYP/6-311G** estimates of ΔH°_{C-C} are markedly too low.

The weakening of the C−C bonds, which is undoubtedly caused by steric overcrowding among the chlorine atoms (Table 6), is reflected in their elongation from 1.579 Å in C_2Cl_6, to 1.600 Å in C_3Cl_8, and to as much as 1.639 Å in the more stable rotamer of *n*-C_4Cl_{10} (Table 7). In contrast, the C−Cl bond lengths in *n*-perchloroalkanes are much less variable (Table 8). The arrangement of atoms linked to the carbons bearing unpaired electrons in the corresponding radicals is pyramidal, with both the C−C and C−Cl bonds being considerably shorter than those in the C_nCl_{2n+2} molecules.

Conclusions

Proper description of the dispersion interactions that attenuate the closed-shell repulsions among chlorine atoms in *n*-perchloroalkanes requires an accurate treatment of long-range electrons correlation effects. The presently known density functionals, which do not correctly account for such effects, grossly underestimate thermodynamic stability of these molecules, yielding the standard enthalpy of C−C bond dissociation in *n*-C_4Cl_{10} as low as 20 kcal/mol. In contrast, the predictions of the CBS-4 scheme fail to reproduce the weakening of the C−C bonds that is experimentally observed in the higher members of the C_nCl_{2n+2} homologous series.

For the CCl_4 and C_2Cl_6 molecules, the most reliable estimates of ΔH°_{C-C} and ΔH°_{C-Cl} are provided by the G2 and G2MP2 methods. The MP2/6-311G** level of theory (without ZPEs and finite-temperature corrections) appears at present to be the only viable, though quite inaccurate, theoretical approach to theoretical thermochemistry of larger chlorocarbons. At that level of theory, ΔH°_{C-C} is predicted to decrease by ca. 10 kcal/mol upon the addition of each $-CCl_2-$ unit, convincingly explaining the thermal lability of higher *n*-perchloroalkanes. Similar conclusions are reached by examining the estimates of ΔH°_{C-C} derived from the CBS-4 standard enthalpies with the E_{CBS} energy term excluded.

Acknowledgment. The research described in this publication was supported by the Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Grant DE-FG02-97ER14758. Support by Florida State University through the allocation of supercomputer resources on the SGI Power Challenge computer is acknowledged.

References and Notes

(1) See for example: Bunn, C. W.; Howells, E. R. *Nature* **1954**, *174*, 549.

(2) Ujhidy, A.; Babos, B.; Marko, L.; Müller, A. *Chem. Ber.* **1965**, *98*, 2197.

(3) Roedig, A. *Ann. Chem.* **1951**, *574*, 122 and the references cited therein.

(4) Miller, W. T. *J. Am. Chem. Soc.* **1940**, *62*, 341.

(5) Motsarev, G. V.; Inshakova, V. T.; Raskina, A. D.; Rozenberg, V. R.; Kolbasov, V. I. *Zh. Obsh. Khimii (Engl. Transl.)* **1990**, *60*, 1623.

(6) Krafft, F. *Chem. Ber.* **1876**, *9*, 1085; **1877**, *10*, 801. Hartmann, E. *Chem. Ber.* **1891**, *24*, 1011.

(7) Aubrey, N. E.; van Wazer, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 4380 and the references cited therein.

(8) Weissman, M.; Benson, S. W. *Int. J. Chem. Kinet.* **1980**, *12*, 403.

(9) Grant, D. *J. Appl. Chem. Biotechnol.* **1974**, *24*, 49.

(10) Taylor, P. H.; Tirey, D. A.; Dellinger, B. *Combust. Flame* **1996**, *104*, 260.

(11) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermodynamical Tables*, 3rd ed. *J. Phys. Chem. Ref. Data* **1985**, *14*, suppl. 1.

(12) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1988**, *110*, 7343.

(13) Hudgens, J. W.; Johnson, R. D., III; Timonen, R. S.; Seetula, J. A.; Gutman, D. *J. Phys. Chem.* **1991**, *95*, 4400.

(14) Kolesov, V. P.; Papina, T. S. *Russ. Chem. Rev.* **1983**, *52*, 425.

(15) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

(16) Cox, J. D., Wagman, D. D., Medvedev, V. A., Eds. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp.: New York, 1989.

(17) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030.

(18) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(19) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

(20) Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Am. Chem. Soc.* **1997**, *119*, 11452.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(22) An unexpectedly large error in the CBS-4 prediction for the standard enthalpy of formation of naphthalene has been recently reported; see: Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; and Stefanov, B. B.; *J. Chem. Phys.* **1988**, *108*, 692. Numerical instabilities in the CBS extrapolation procedure explain this anomaly only partially; see: Montgomery, J. A., Jr.; Frisch, M. J.; Ochtershi, J. W.; Peterson, G. A.; Raghavachari, K.; Zakrzewski, V. G.; *J. Chem. Phys.* **1988**, *109*, 6505.