Steric Overcrowding in Perhalogenated Cyclohexanes, Dodecahedranes, and [60]Fulleranes

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Received May 5, 1995[⊗]

Abstract: Results of *ab initio* electronic structure calculations on ethane, cyclohexane, dodecahedrane, [60]fullerane, and their perhalogenated analogs, i.e. molecules with the compositions C_2X_6, C_6X_{12}, $C_{20}X_{20}$, and $C_{60}X_{60}$, where X = H, F, Cl, and Br, are presented. Analysis of energies, geometries, and electron densities computed at the Hartree−Fock level of theory with basis sets of the TZP quality indicates that steric overcrowding in these molecules ranges from minor to severe. The destabilization due to steric overcrowding, assessed with the help of isodesmic transhalogenation reactions, is particularly large in the $C_{20}X_{20}$ and $C_{60}X_{60}$ species, putting the recent claims of the synthesis of $C_{20}Br_{20}$ in some doubt. No energy minimum is found for the hypothetical $C_{60}Br_{60}$ system. In molecules with severe steric repulsions attractor interaction lines that connect nonbonded halogen atoms were found. In the C_6Cl_{12} and C_6Br_{12} species, these lines extend between axial halogens in accordance with the commonly accepted notions of organic chemistry but in variance with the expectations based on the distance between spherically symmetrical atoms, thus confirming the usefulness of the attractor interaction lines as indicators of steric overcrowding.

Introduction

Perhalogenation of saturated hydrocarbons produces species with varying degrees of steric overcrowding. The extent to which this overcrowding affects the stability of a given perhalogenated hydrocarbon is determined by several factors, the main ones being the number and the size of the halogen atoms. Steric effects are cumulative, quickly rising in importance with the increasing number of halogen−halogen interactions—a phenomenon that is nicely illustrated by the example of perhalogenated linear alkanes. Among the isolable members of the homologous C_nX_{2n+2} series, there is apparently no upper limit to the chain length for X = F,[1] whereas bonding is sustainable only up to $n = 4$[2] or 5[3] for X = Cl and up to a mere $n = 2$[4] for X = Br.

Steric effects in perhalogenated hydrocarbons are particularly pronounced in molecules that, for geometrical reasons, possess halogens in eclipsed positions. This unfavorable arrangement of atoms is present in derivatives of cage hydrocarbons in which all of the C−X bonds are exohedral, i.e. protrude outwards from the cage surface. In light of these considerations, the recent reports claiming isolation of such species come as a surprise. The initial observation of the icosahedral perfluoro[60]fullerane ($C_{60}F_{60}$) being formed upon exhaustive fluorination of the C_{60} fullerene[5] has never been confirmed, and the subsequent experimental studies have shown that the isolable compound with the largest number of fluorine atoms is actually $C_{60}F_{48}$.[6] On the other hand, the recent claim of perbromododecahedrane ($C_{20}Br_{20}$) being found among the products of "extreme" bromination of dodecahedrane ($C_{20}H_{20}$) appears to be supported by the published mass spectra.[7] Reportedly, the analogous $C_{20}F_{20}$ and $C_{20}Cl_{20}$ compounds have been obtained by respective perhalogenations of $C_{20}H_{20}$.[8]

Prompted by these unexpected experimental finidngs, in this paper we report results of *ab initio* electronic structure calculations on perfluoro, perchloro, and perbromo derivatives of ethane, cyclohexane, dodecahedrane, and [60]fullerane. A two-pronged interpretation of these results is presented. First, the effects of steric overcrowding on molecular geometries and energetics are discussed. Second, topological analysis of electron densities in the molecules under study is employed to reveal the predominant steric interactions.

Details of Calculations

The calculations were performed at the Hartree−Fock level of theory on a Cray Y-MP4/6 supercomputer and on various RISC workstations with the TURBOMOLE[9] and Gaussian 92[10] suites of programs. The standard 6-311G** basis set[11] was used for the hydrogen, carbon, and fluorine atoms, whereas for chlorine and bromine the TZVP basis set of Ahlrichs et al.[12] was employed. Geometry optimizations were carried out within the D_{3d} point group for the C_2X_6 and C_6X_{12} (X = H, F, Cl, and Br) species and the I_h point group for the $C_{20}X_{20}$ and $C_{60}X_{60}$ systems. The optimized geometries of the C_2X_6 and C_6X_{12} molecules were confirmed as local minima by calculations of vibrational frequencies. Although analogous calculations were not feasible for the $C_{20}X_{20}$ and $C_{60}X_{60}$ species, the possibility of symmetry breaking/lowering can

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1995.

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Table 1. Total Hartree–Fock Energies (au) of the Molecules under Study

X	C_2X_6	C_6X_{12}	$C_{20}X_{20}$	$C_{60}X_{60}$
H	−79.251 708	−234.263 577	−769.193 263	−2 306.764 736
F	−672.565 121	−1 420.816 199	−2 746.612 907	−8 238.266 911
Cl	−2 832.715 279	−5 741.107 671	−9 947.123 078	−29 835.507 179
Br	−15 510.091 907	−31 095.822 458	−52 204.850 095	n/a

Table 2. Bond Lengths (Å) and Angles (deg) in the C_2X_6 Molecules

parameter	C_2H_6	C_2F_6	C_2Cl_6	C_2Br_6
C−C	1.527	1.529	1.576	1.573
C−X	1.086	1.306	1.775	1.944
C−C−X	111.19	109.80	110.22	111.02
X−X[a]	2.524	2.709	3.261	3.479

[a] Distances between nonbonded atoms.

Table 3. Bond Lengths (Å) and Angles (deg) in the C_6X_{12} Molecules[a]

parameter	C_6H_{12}	C_6F_{12}	C_6Cl_{12}	C_6Br_{12}
C−X_a	1.090	1.321	1.789	1.975
C−C	1.531	1.540	1.600	1.606
C−X_e	1.087	1.317	1.785	1.964
C−C−C	111.50	112.86	113.46	113.70
C−C−X_a	109.17	108.86	109.37	110.00
C−C−X_e	110.13	108.65	110.04	110.65
X_{a1}−X_{e2}[b]	2.463	2.619	3.112	3.311
X_{e1}−X_{e2}[b]	2.499	2.764	3.342	3.546
X_{a1}−X_{a3}[b]	2.654	2.797	3.228	3.417
X_{a1}−X_{a2}[b]	3.045	3.450	4.356	4.705
X_{a1}−X_{e3}[b]	3.802	4.193	5.067	5.396
X_{e1}−X_{e3}[b]	4.298	4.640	5.490	5.811

[a] See Figure 1 for atom numbering. [b] Distances between nonbonded atoms.

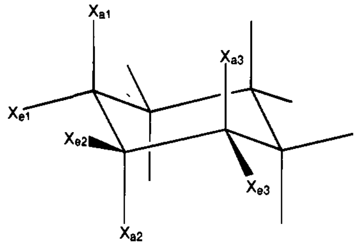

Figure 1. Atom numbering in the C_6X_{12} molecules.

Table 4. Bond Lengths (Å) in the $C_{20}X_{20}$ Molecules

parameter	$C_{20}H_{20}$	$C_{20}F_{20}$	$C_{20}Cl_{20}$	$C_{20}Br_{20}$
C−C	1.548	1.551	1.592	1.606
C−X	1.084	1.327	1.781	1.974
X−X[a]	2.321	2.499	2.863	3.015

[a] Distances between nonbonded atoms.

almost certainly be ruled out in these cases. The critical points in the Hartree–Fock electron densities were located with a previously published algorithm.[13] The total Hartree–Fock energies of the molecules under study are listed in Table 1. One should also mention that the present computations on the $C_{60}Cl_{60}$ and $C_{60}Br_{60}$ molecules (which involved 2520 and 2940 basis functions, respectively) constitute the largest Hartree–Fock calculations ever reported in chemical literature.

Results and Discussion

Geometries and Energetics. The optimized geometries of the C_2X_6 molecules are presented in Table 2. As expected, the computed lengths of the C−C and C−H bonds in C_2H_6 are slightly smaller than their experimental counterparts (1.536 and 1.091 Å, respectively[14]) due to the neglect of electron correlation effects. Since the available experimental data for the higher hexahalogenoethanes are far less accurate, the agreement between the predicted and the measured geometries of C_2Cl_6 (exp bond lengths: 1.550 and 1.740 Å[15]) and C_2Br_6 (exp bond lengths: 1.526 and 1.944 Å[16]) is not as good as in the case of C_2H_6.

The present calculations accurately reproduce the experimentally determined geometry of C_6H_{12} (Table 3). The predicted C−C bond length of 1.531 Å is in excellent agreement with both the value of 1.536 Å obtained from the electron diffraction data[17] and that of 1.5300 Å recently measured with the pulsed microwave Fourier transform spectrometry.[18] The superior accuracy of the latter experimental technique has made it possible to determine that bonds between carbon atoms and the axial hydrogens (C−H_a, Figure 1) are slightly longer than those involving the equatorial hydrogens (C−H_e, Figure 1). This difference in bond lengths is qualitatively reproduced by our calculations and also found at other levels of theory.[19,20] However, the theoretical prediction for this phenomenon persisting in perhalogenated cyclohexanes (Table 3) cannot be presently confirmed because of the scarcity of experimental data on the C_6X_{12} species. An electron diffraction study of C_6F_{12}, in which no distinction has been made between the lengths of the C−F_a and C−F_e bonds, has yielded the values of 1.551 and 1.337 Å for the C−C and C−F bond lengths, respectively.[21] These values are in rather poor agreement with the results of present calculations. Nevertheless, the same qualitative trends are observed in both the experimental and theoretical geometries. In particular, comparisons between C_2F_6 and C_6F_{12} reveal a substantial lengthening of all bonds in the latter molecule. This lengthening, which becomes even more prominent in the perchloro and perbromo derivatives of cyclohexane, indicates the presence of significant steric repulsions among halogen atoms in the C_6X_{12} species.

Geometries of the $C_{20}X_{20}$ molecules (Table 4) are strongly influenced by two factors. First of all, the strain associated with the curvature of the dodecahedral cage gives rise to a partial rehybridization at the carbon atoms. Second, the all-eclipsed orientation of the substituents produces a significant increase in steric overcrowding. Indeed, the C−C bond in $C_{20}H_{20}$ is calculated to be markedly longer than that in either C_2H_6 or C_6H_{12}, in apparent agreement with the limited experimental X-ray data on dodecahedrane and its alkyl derivatives.[22−24]

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Table 5. Bond Lengths (Å) and Angles (deg) in the $C_{60}X_{60}$ Molecules

parameter[a]	$C_{60}H_{60}$	$C_{60}F_{60}$	$C_{60}Cl_{60}$
C−C (h-h)	1.553	1.604	1.879
C−C (h-p)	1.561	1.603	1.767
C−X	1.080	1.330	1.788
C−C−X (h-h)	101.13	101.19	100.07
C−C−X (h-p)	101.93	101.89	102.52
X−X (h-h)[b]	1.970	2.120	2.504
X−X (h-p)[b]	2.007	2.151	2.542

[a] See Figure 2 for bond labeling. [b] Distances between nonbonded atoms.

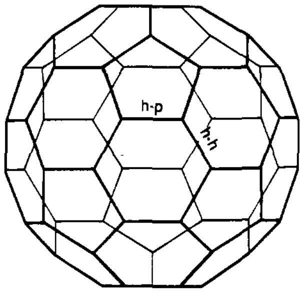

Figure 2. Labeling of the C−C bonds in the $C_{60}X_{60}$ molecules.

Although this bond elongation is also present in the optimized geometry of $C_{20}F_{20}$, it becomes less pronounced in $C_{20}Cl_{20}$ and $C_{20}Br_{20}$, both of which possess C−C bonds with lengths very similar to those in the respective perhalogenated cyclohexanes. Notably, the calculations predict only minor differences between the lengths of the analogous C−X bonds in all of the $C_{20}X_{20}$ and C_6X_{12} molecules under study.

Comparing with those in $C_{20}X_{20}$, halogen atoms in the $C_{60}X_{60}$ species experience dramatically increased steric repulsions. In the presently unknown $C_{60}H_{60}$, $C_{60}F_{60}$, and $C_{60}Cl_{60}$ molecules, this repulsion is partially relieved by a substantial lengthening of the C−C bonds (Table 5). In $C_{60}H_{60}$, the C−C bonds that fuse two hexagons [C−C (h-h), Figure 2] are found to be somewhat shorter than those fusing a hexagon with a pentagon [C−C (h-p), Figure 2], in agreement with the previously published results of *ab initio* electronic structure calculations.[25,26] These two kinds of bonds are of about the same length in $C_{60}F_{60}$, whereas in $C_{60}Cl_{60}$ the ordering of bond lengths is reversed. In the latter species, all of the C−C bonds are predicted to be extremely elongated. As in the case of perhalogenated dodecahedranes, the increased steric overcrowding has almost no effect on the lengths of the C−X bonds in $C_{60}H_{60}$, $C_{60}F_{60}$, and $C_{60}Cl_{60}$. However, no C−Br bonding was observed in our calculations on the hypothetical $C_{60}Br_{60}$ species, for which all attempts at geometry optimization inevitably resulted in the dissociation into C_{60} fullerene and bromine atoms.

The effect of varying degrees of steric overcrowding on the stabilities of perhalogenated hydrocarbons can be readily quantified by considering the following transhalogenation reactions:[25]

$$(1/6)C_2X_6 + (1/m)C_nH_m \rightarrow (1/6)C_2H_6 + (1/m)C_nX_m \qquad (1)$$

The energies of the isodesmic reactions 1 measure the destabilization per C−X bond caused by the increase in steric repulsions that occurs upon the substitution of the hydrogen atom by the respective halogen. In the cyclohexane derivatives, this destabilization is relatively small for all halogen substituents (Table 6). In contrast, the energetic effects of steric overcrowding are quite large in the $C_{20}X_{20}$ series. In particular, the steric destabilization per C−X bond in $C_{20}Br_{20}$ is comparable to that calculated for the unisolable $C_{60}F_{60}$, putting the recent claims concerning the synthesis of the former compound[7,8] in some doubt.

Table 6. Energies of the Transhalogenation Reactions 1 (kcal/mol)[a]

X	C_2X_6	C_6X_{12}	$C_{20}X_{20}$	$C_{60}X_{60}$
F	0.00	3.88	9.15	17.07
Cl	0.00	4.34	8.85	61.63
Br	0.00	6.35	14.97	n/a

[a] At 0 K, ZPEs not included.

The loss of stability due to steric effects is even greater in derivatives of the unknown [60]fullerane ($C_{60}H_{60}$). At first glance, the larger size of the C_{60} cage might lead to a mistaken expectation of steric repulsions among the halogens being smaller in the $C_{60}X_{60}$ systems than in the analogous $C_{20}X_{20}$ molecules. However, it turns out that the greater curvatures of small cages translate into larger angles of inclination between the adjacent exohedral C−X bonds, resulting in increased X−X distances and, in turn, reduced repulsive interactions. In light of these observations, the huge destabilization of the $C_{60}Cl_{60}$ species and the nonexistence of the $C_{60}Br_{60}$ molecule come as no surprise. One should mention here that quantitative estimates of the standard heats of formation may necessitate the inclusion of electron correlation effects in the case of extremely congested systems.[2]17 However, the qualitative conclusions drawn from the data presented in Table 6 are expected to remain unaltered upon going to higher levels of theoretical treatment.

Attractor Interaction Lines between Nonbonded Atoms. Topological analysis of the electron density provides a rigorous tool for uncovering predominant interactions among atoms in molecules.[28] Among the various types of critical points at which the density gradient vanishes, the bond points are of particular interest. Each of these points is associated with an attractor interaction line (AIL), i.e. a pair of gradient paths that connect the bond point with a pair of nuclei or nonnuclear attractors. Originally, the presence of an attractor interaction line (also called a bond path) had been believed to indicate the existence of a chemical bond between two atoms.[28] However, subsequent investigations have determined that attractor interaction lines also occur between atoms engaged in strong repulsive interactions.[25,29,30]

Attractor interaction lines between nonbonded atoms are absent in the C_2H_6, C_2F_6, C_2Cl_6, C_2Br_6, C_6H_{12}, and C_6F_{12} molecules. On the other hand, steric interactions among the axial halogens in the C_6Cl_{12} and C_6Br_{12} species are sufficiently strong to precipitate six slightly curved attractor interaction lines in each molecule (Figure 3) whose appearance supports the well-established paradigm of the predominance of repulsions between the 1,3-diaxial substituents in derivatives of cyclohexane.[31] It

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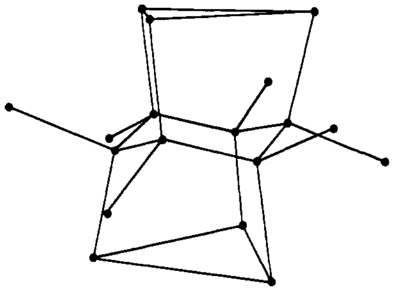

Figure 3. Attractor interaction lines in the C_6Cl_{12} and C_6Br_{12} molecules. Note the six attractor interaction lines extending between the 1,3-diaxial halogen atoms.

is of interest to note that this paradigm is *not* supported by simple geometrical considerations that invoke distances between spherically symmetrical "atoms". In fact, the *gauche* $X_{a1}-X_{e2}$ distances in both C_6Cl_{12} and C_6Br_{12} (Figure 1) are substantially *shorter* than those between halogen atoms in the 1,3-diaxial positions (Table 3). In C_6H_{12} and C_6F_{12}, not only the $X_{a1}-X_{e2}$ but also the *gauche* $X_{e1}-X_{e2}$ distances are shorter, the predicted ordering being confirmed for the latter molecule by electron diffraction experiments that yield the values of 2.64, 2.79, and 2.83 Å for the $F_{a1}-F_{e2}$, $F_{e1}-F_{e2}$, and $F_{a1}-F_{a3}$ interatomic separations, respectively.[21] The observation that the topology of the electron density reflects the well-known features of steric effects in substituted cyclohexanes while simple geometrical criteria fail to do so once again confirms the superiority of the AIL-based criterion for the presence of steric overcrowding over approaches that employ the van der Waals atomic radii.[30]

As expected, attractor interaction lines between halogens are also present in the $C_{60}F_{60}$, $C_{20}Cl_{20}$, $C_{60}Cl_{60}$, and $C_{20}Br_{20}$ molecules. Properties of bond critical points associated with these AILs exhibit interesting regularities within each type of interaction (Table 7). Predictably, the values of the electron density and its Laplacian at these bond points decrease with the distance between the nonbonded atoms. In general, the same is true about the bond ellipticities, except for the case of the two different types of F−F interactions occuring in the $C_{60}F_{60}$ molecule.

Table 7. Properties of Bond Critical Points on the Halogen−Halogen Attractor Interaction Lines in the Molecules Under Study

line	molecule	attractor−attractor distance (Å)	density (au)	density Laplacian (au)	ellipticity
F−F	$C_{60}F_{60}$	2.120	0.0392	0.296	0.511
		2.151	0.0366	0.271	0.850
Cl−Cl	$C_{60}Cl_{60}$	2.504	0.0513	0.185	0.238
		2.542	0.0472	0.176	0.206
	$C_{20}Cl_{20}$	2.863	0.0248	0.103	0.114
	C_6Cl_{12}	3.228	0.0129	0.052	0.025
Br−Br	$C_{20}Br_{20}$	3.015	0.0252	0.085	0.046
	C_6Br_{12}	3.417	0.0133	0.043	0.037

Conclusions

Steric overcrowding in the perhalogenated hydrocarbons under study range from minor to very substantial. Its severity can be readily assessed for a given molecule by computing the energy of the transhalogenation reaction 1 and then confirmed by searching for the presence of attractor interaction lines between the halogen atoms. Both of these criteria lead to the conclusion that $C_{60}Cl_{60}$ is too congested to be isolable. The destabilization due to steric repulsion per C−X bond in $C_{20}Br_{20}$ is very close to that predicted for $C_{60}F_{60}$. The magnitudes of destabilization per C−C bond are also very similar, as the connectivity of the carbon atoms (1 C−X bond and 1.5 C−C bonds per carbon) is the same in both molecules. Since the reactivity of fluorine greatly exceeds that of bromine and $C_{60}F_{60}$ has never been isolated, the possibility of a successful synthesis of $C_{20}Br_{20}$ appears to be remote. These findings are in variance with the recent reports on perbromination of dodecahedrane.[7,8] Significant destabilization due to steric effects is also present in the C_6Br_{12}, $C_{20}F_{20}$, and $C_{20}Cl_{20}$ molecules. On the other hand, steric repulsions in the experimentally known C_6F_{12} and C_6Cl_{12} species can be characterized as relatively small, though not negligible.

Analysis of the optimized geometries leads to the conclusion that the overcrowding is partially relieved by an initial lengthening of all bonds, followed in highly congested molecules by a preferential elongation of the C−C bonds. Contrary to the expectations based on the ordering of distances between the halogen atoms, steric interactions in perhalogenated cyclohexanes are dominated by the 1,3-diaxial repulsions, in accordance with the commonly accepted notions of structural organic chemistry. The fact that the attractor interaction lines occur between the *second* nearest halogens in C_6C_{12} and C_6Br_{12} implies a strong anisotropy of steric interactions in these molecules.

Acknowledgment. This work was partially supported by the National Science Foundation under Grant No. CHE-9224806, the Florida State University through time granted on their Cray Y-MP digital computers, and the US DOE through its Supercomputer Computations Research Institute.

JA951457P