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# Calculation of the anion and neutral thermochemistry of $c$-$C_5F_6Cl_2$ and $c$-$C_6F_8Cl_2$

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## Abstract

Density functional calculations have been carried out to determine the energetics related to nondissociative and dissociative electron attachment to $c$-$C_5F_6Cl_2$ (1,2-dichlorohexafluorocyclopentene) and $c$-$C_6F_8Cl_2$ (1,2-dichlorooctafluorocyclohexene). Becke's three-parameter functional B3PW91 was used with the 6-311+G(3*df*) basis set to determine total energies of the parent neutrals and anions, and of dissociation fragments, at 0 and 298 K. From these total energies, electron affinities, bond enthalpies, and electron attachment reaction enthalpies were determined. The electron affinities of $c$-$C_5F_6Cl_2$ and $c$-$C_6F_8Cl_2$ were found to be 1.17 and 1.46 eV, respectively. Implications for the experimental results are discussed, notably that dissociative electron attachment to $c$-$C_5F_6Cl_2$ (and probably to $c$-$C_6F_8Cl_2$ as well) is endothermic. (Int J Mass Spectrom 205 (2001) 271–276) © 2001 Elsevier Science B.V.

*Keywords:* Density functional theory; 1,2-Dichlorohexafluorocyclopentene; 1,2-Dichlorooctafluorocyclohexene; Negative ions; Electron attachment; Electron affinity

Recently, we published results of electron attachment experiments with $c$-$C_5F_6Cl_2$ (1,2-dichlorohexafluorocyclopentene) and $c$-$C_6F_8Cl_2$ (1,2-dichlorooctafluorocyclohexene) in the temperature range 300–550 K, carried out in a flowing-afterglow Langmuir probe (FALP) apparatus [1]. These reactions were interesting because of the competition between nondissociative attachment (forming the parent anion) and dissociative attachment (forming $Cl^-$ ion product), and the comparison between attachment for the five-membered and six-membered rings. The overall attachment rate constant was found to be essentially temperature-independent (300–550 K) and close to collisional (in a He buffer gas at 50–150 Pa pressure). The nondissociative channel accounts for essentially 100% of the attachment at room temperature. The dissociative channel was observed at elevated temperatures with a steep temperature dependence and dominates at the highest temperatures.

Interpretation of the experimental results was hampered by a complete lack of literature data on the thermochemistry of neutral and anionic $c$-$C_5F_6Cl_2$ and $c$-$C_6F_8Cl_2$, even on the mere existence of the parent anions. The present calculations were conducted to assist in the understanding of the attachment results. Calculations of the total energies of the parent molecules and fragments were carried out using the GAUSSIAN-98W program package [2]. Density functional theory was used, in particular Becke's three parameter hybrid method denoted by B3PW91,

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Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

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Table 1
Total energies and zero-point energies (ZPEs) for $c$-$C_5F_6Cl_2$ and $c$-$C_6F_8Cl_2$ and dissociation fragments, all in Hartree units.

| Molecule | ZPE[a] | Total energy[b] (0 K) | Enthalpy[c] (298 K) |
|---|---|---|---|
| $c$-$C_5F_6Cl_2$($C_s$ point group, $^1A'$) | 0.048 29 | −1709.842 45 | −1709.829 83 |
| $c$-$C_5F_6Cl_2^-$ ($C_1$ point group, $^2A$) | 0.044 41 | −1709.885 27 | −1709.871 94 |
| $c$-$C_5F_6Cl$($C_1$ point group, $^2A$) | 0.045 23 | −1249.577 03 | −1249.565 76 |
| $c$-$C_6F_8Cl_2$($C_2$ point group, $^1A$) | 0.060 16 | −1947.609 95 | −1947.594 64 |
| $c$-$C_6F_8Cl_2^-$ ($C_2$ point group, $^2A$) | 0.055 93 | −1947.663 69 | −1947.647 57 |
| $c$-$C_6F_8Cl$($C_1$ point group, $^2A$) | 0.057 00 | −1487.354 45 | −1487.340 36 |
| Cl | 0 | −460.111 30 | −460.108 91[d] |
| $Cl^-$ | 0 | −460.245 17 | −460.242 81[d] |
| $e^-$ | 0 | 0 | +0.002 36[d] |

[a] B3PW91/6-311+G($d$) level of theory, and scaled by 0.9316.

[b] B3PW91/6-311+(3$df$)//B3PW91/6-311+G($d$) plus ZPE.

[c] B3PW91/6-311+(3$df$)//B3PW91/6-311+G($d$) plus thermal correction to enthalpy.

[d] Enthalpy correction from JANAF tables (see [5]).

which includes the Perdew and Wang nonlocal correlation functional [3]. We utilized the B3PW91 functional instead of the more commonly used B3LYP because it gave the electron affinity EA(Cl) more accurately for every basis set tried. With our largest basis set, 6-311+G(3$df$), the B3PW91 functional overestimated EA(Cl) by 30 meV, whereas the B3LYP functional overestimated EA(Cl) by 68 meV. The parent and fragment molecules were first geometry optimized by using the B3PW91/6-311+G($d$) functional and basis set with tight convergence of the self-consistent field (SCF) integrals, and a harmonic frequency analysis was performed at the same level of theory to give the zero-point energies (ZPE) and thermal corrections to energies at 298.15 K and 1 atm pressure. The vibrational frequencies were scaled by the empirical factor 0.9613 in calculating both the ZPE and thermal corrections [4]. The thermal correction for the enthalpies of the electron and $Cl^-$ is $5kT/2$, and that for Cl is slightly greater because of spin-orbit splitting [5]. Stability of all wave functions was checked. Next, single-point energies were calculated using the 6-311+G(3$df$) basis set and tight convergence of the SCF integrals. ZPE and thermal energy corrections were then applied to the total energies; all these quantities are given in Table 1. Derived quantities are given in Table 2. Adiabatic EAs were calculated from the difference in 0 K total energies of parent molecules and respective anions. Bond enthalpies were calculated from differences in total energies of parent molecule and the sum of fragment energies. Reaction enthalpies for dissociative electron attachment (yielding $Cl^-$ product ion) were calculated from the total energies given in Table 1. Work by others has shown that thermochemical quantities such as atomization energies, ionization potentials, and proton affinities by using the B3LYP/6-311++G(3$df$,2$p$) functional and basis set (the "2$p$" and second "+" apply to hydrogen atoms, which we do not have in the present work) are good on average to ±0.11 eV, but with a worst-case error of 0.5 eV [6]. As noted earlier, B3PW91/6-311+G(3$df$) gives EA(Cl) within 0.03 eV; this method is less successful with EA($Cl_2$), overestimating it by 0.30 eV, with little change from small to large basis set [7]. The B3LYP

Table 2
Adiabatic electron affinities (EAs), bond enthalpies ($D$), the dissociative attachment reaction enthalpies ($\Delta H_{rxn}$), all in electron volts, calculated from the energies given in Table 1.

| Quantity | 0K value | 298 K value |
|---|---|---|
| EA($c$-$C_5F_6Cl_2$) | 1.17 | . . . |
| $D$($c$-$C_5F_6$Cl–Cl) | 4.19 | 4.22 |
| $D$($c$-$C_5F_6$Cl–$Cl^-$) | 1.72 | 1.72 |
| $\Delta H_{rxn}$ | +0.55 | +0.51 |
| EA($c$-$C_6F_8Cl_2$) | 1.46 | . . . |
| $D$($c$-$C_6F_8$Cl–Cl) | 3.92 | 3.96 |
| $D$($c$-$C_6F_8$Cl–$Cl^-$) | 1.74 | 1.75 |
| $\Delta H_{rxn}$ | +0.28 | +0.25 |

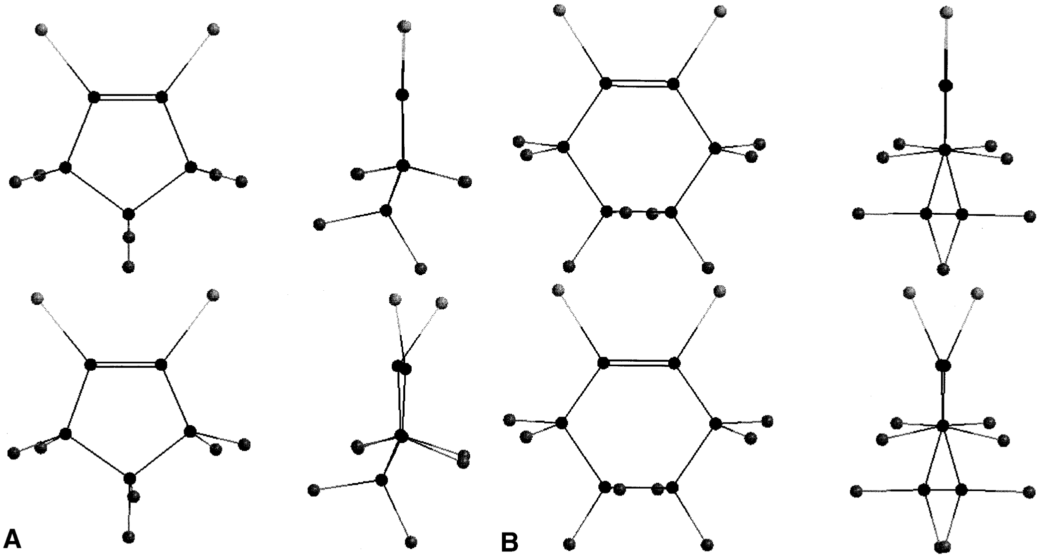

Fig. 1. Optimized geometries from B3PW91/6-311+G(*d*) calculations; views above and to one side of the rings. From top to bottom: (A) $c$-$C_5F_6Cl_2$, $c$-$C_5F_6Cl_2^-$, and (B) $c$-$C_6F_8Cl_2$, and $c$-$C_6F_8Cl_2^-$. The two Cl atoms are at the top of each sketch, bound to C1 and C2. The other C atoms in the rings each have two F atoms bound to them.

functional is worse, overestimating EA($Cl_2$) by 0.47 eV. Since there is not much change in the calculated EA(Cl) and EA($Cl_2$) with basis set or small changes in the Cl–Cl bond length, it seems that the error in EA($Cl_2$) is simply a limitation of the correlation functional. The present EA values for $c$-$C_5F_6Cl_2$ and $c$-$C_6F_8Cl_2$ progress reasonably from small basis set to large basis set: optimization with the 6-31G(*d*) basis set yields EA($c$-$C_5F_6Cl_2$) = 0.69 eV; adding diffuse functions [6-31+G(*d*)] brings this EA up to 1.28 eV. Optimization with the larger basis set 6-311+G(*d*) yields EA($c$-$C_5F_6Cl_2$) = 1.33 eV. Finally, by using the latter geometry and evaluating the total energies with our largest basis set [6-311+G(3*df*)] gives EA($c$-$C_5F_6Cl_2$) = 1.17 eV. Based on this progression, we expect that the present EAs are good to ±0.3 eV. Optimized geometries are shown in Fig. 1.

The results in Table 2 show the similarity of EAs and bond enthalpies for the five-membered and the six-membered ring compounds. These results are not surprising since the molecules are so similar in structure. For both of the subject molecules, the structure most affected by electron attachment involves the double-bonded carbons and their associated chlorine atoms. The rest of the ring and associated F atoms are generally less affected but tend to stabilize the anion. The EA decreases as the ring is made smaller, as seen in going from EA($c$-$C_6F_8Cl_2$) = 1.46 eV to EA($c$-$C_5F_6Cl_2$) = 1.17 eV. Still further decrease is found for $c$-$C_4F_4Cl_2$ (0.93 eV) [8] and for *cis*-$C_2H_2Cl_2$ (-0.006 eV) [9]. Some relevant bond lengths and angles are given in Table 3; a complete specification of the structures of these molecules is available from the authors. As expected, the addition of an electron to these molecules results in reduction of C1–C2 bond order as illustrated by the elongation of the bond and the rotation of the chlorine atoms out of the bond plane. These changes are consistent with the addition of the electron to the $\pi^*$ orbital. However, other changes are significant and suggest that such a simple picture is not sufficient. In particular, the C–Cl bonds lengthen and about two-thirds of the attached electron ends up on C1, C2, and their chlorine partners, suggesting that the electron attachment involves some contribution to the C-Cl $\pi^*$ orbital. Table 4 gives the electronic charge associated

Table 3
A sampling of bond lengths and angles, in angstoms and degrees, with geometries optimized at the B3PW91/6-311+G(*d*) level of theory.

| Bond or angle | $c$-$\mathrm{C_5F_6Cl_2}$ | $c$-$\mathrm{C_5F_6Cl_2^-}$ | $c$-$\mathrm{C_6F_8Cl_2}$ | $c$-$\mathrm{C_6F_8Cl_2^-}$ |
|---|---|---|---|---|
| C1–C2 | 1.338 | 1.406 | 1.341 | 1.391 |
| C2–C3 | 1.504 | 1.471 | 1.512 | 1.452 |
| C1–C5 | 1.504 | 1.451 | · · · | · · · |
| C1–C6 | · · · | · · · | 1.512 | 1.452 |
| C3–C4 | 1.560 | 1.553 | 1.552 | 1.548 |
| C4–C5 | 1.560 | 1.551 | 1.540 | 1.542 |
| C5–C6 | · · · | · · · | 1.552 | 1.548 |
| C1–C1 | 1.698 | 1.749 | 1.713 | 1.790 |
| C2–C2 | 1.698 | 1.811 | 1.713 | 1.790 |
| ∠C1C2C3 | 112.1 | 108.2 | 123.4 | 124.2 |
| ∠C5C1C2 | 112.1 | 113.6 | · · · | · · · |
| ∠C6C1C2 | · · · | · · · | 123.4 | 124.2 |
| ∠C2C3C4 | 103.5 | 103.8 | 113.0 | 111.6 |
| ∠C4C5C1 | 103.5 | 103.1 | · · · | · · · |
| ∠C5C6C1 | · · · | · · · | 113.0 | 111.6 |
| ∠C3C4C5 | 104.5 | 104.7 | 111.5 | 111.3 |
| ∠C4C5C6 | · · · | · · · | 115.5 | 111.3 |
| ∠C2C1C1 | 127.2 | 123.8 | 122.6 | 119.9 |
| ∠C1C2C2 | 127.2 | 121.3 | 122.6 | 119.9 |
| Dihedral[a] | 0.00 | 50.7 | 1.9 | 44.9 |
| Dihedral[b] | 0.00 | −5.6 | −1.1 | 13.2 |

[a] Angle between the C1 and C2 atoms looking along the C1–C2 bond.

[b] Angle between the C1 and C2 atoms looking along a line between the next two carbon atoms on each side (C3 and C5 for $c$-$\mathrm{C_5F_6Cl_2}$ or C3 and C6 for $c$-$\mathrm{C_6F_8Cl_2}$); a measure of the twisting of the ring at the C1–C2 site as shown in Fig. 1.

Table 4
Natural population analysis of charges from electron densities calculated at the B3PW91/6-311+G(*d*) level of theory (geometries optimized at the same level). F31 abd F32 in the table denote the two F atoms bonded to C3, etc.

| Atom | $c$-$\mathrm{C_5F_6Cl_2}$ | $c$-$\mathrm{C_5F_6Cl_2^-}$ | $c$-$\mathrm{C_6F_8Cl_2}$ | $c$-$\mathrm{C_6F_8Cl_2^-}$ |
|---|---|---|---|---|
| C1 | −0.121 | −0.265 | −0.119 | −0.232 |
| C2 | −0.121 | −0.203 | −0.119 | −0.232 |
| C3 | +0.674 | +0.638 | +0.675 | −0.627 |
| C4 | +0.669 | +0.669 | +0.660 | +0.667 |
| C5 | +0.674 | +0.623 | +0.660 | +0.667 |
| C6 | · · · | · · · | +0.675 | +0.627 |
| C1 | +0.120 | −0.035 | +0.115 | −0.091 |
| C2 | +0.120 | −0.173 | −0.115 | −0.091 |
| F31 | −0.340 | −0.376 | −0.336 | −0.379 |
| F32 | −0.336 | −0.381 | −0.335 | −0.386 |
| F41 | −0.333 | −0.360 | −0.334 | −0.349 |
| F42 | −0.328 | −0.363 | −0.326 | −0.326 |
| F51 | −0.340 | −0.396 | −0.334 | −0.349 |
| F52 | −0.336 | −0.379 | −0.326 | −0.357 |
| F61 | · · · | · · · | −0.336 | −0.335 |
| F62 | · · · | · · · | −0.335 | −0.386 |

with each atom of the species under consideration, from a natural population analysis [10]. The calculations reveal some differences between the structural changes in these two molecules upon electron attachment. For the $c$-$\mathrm{C_6F_8Cl_2}$ molecule the extra electron attaches equally to C1 and C2 and to Cl1 and Cl2. For $c$-$\mathrm{C_5F_6Cl_2}$, the attachment is unequal and yields an asymmetrical arrangement of the chlorine atoms in the anion. In Table 5, heat capacities, dipole moments, and polarizabilities are given.

The results of importance to the electron attachment experiments of Ref. [1] are as follows. (1) Dissociative attachment, forming $\mathrm{Cl^-}$ ion product, is endothermic for $c$-$\mathrm{C_5F_6Cl_2}$ and probably for $c$-$\mathrm{C_6F_8Cl_2}$. The calculated dissociative attachment endothermicities are 0.51 ± 0.30 eV and 0.25 ± 0.30 eV, respectively, at 298 K. The FALP experiments [1] yielded activation energies of 0.32 ± 0.05 eV and 0.23 ± 0.05 eV, respectively, for the two compounds. The EAs, endothermicities, and large, relatively temperature-independent rate constants place attachment to these compounds in a class led by the well studied case of $\mathrm{SF_6}$, wherein electron attachment yields both $\mathrm{SF_6}^-$ and $\mathrm{SF_5}^-$ ion products. Španěl et al. have shown that the $\mathrm{SF_5}^-$ channel is endothermic by 0.12 eV [11]. Earlier data had shown that the partial rate constants for dissociative attachment to $\mathrm{SF_6}$, as a function of temperature, give an apparent activation energy of 0.4 eV in 135 Pa He buffer gas, and 0.2 eV in collision-

Table 5
Heat capacities ($C_p$) and average polarizabilities ($\alpha$) calculated by using B3PW91/6-311+G(*d*) functional and basis set; the dipole moments ($\mu_\mathrm{d}$) are from a higher level B3PW91/6-311+G(3*df*) calculation performed with the B3PW91/6-311+G(*d*) geometry.

| Molecule | $C_p$ (cal mol$^{-1}$ K$^{-1}$ | $\mu_d$ (D) | $\alpha$ (Å$^3$) |
|---|---|---|---|
| $c$-$\mathrm{C_5F_6Cl_2}$($^1$A′) | 43.2 | 2.05 | 12.3 |
| $c$-$\mathrm{C_5F_6Cl_2^-}$($^2$A) | 45.3 | · · · | 15.0 |
| $c$-$\mathrm{C_6F_8Cl_2}$($^1$A) | 53.7 | 1.77 | 14.2 |
| $c$-$\mathrm{C_6F_8Cl_2^-}$($^2$A) | 56.2 | · · · | 16.9 |

free experiments [12,13]. The difference is due to collisional stabilization of the initially formed $SF_6^-$ complex in the buffer gas [11]. Thus, agreement between measured activation energies and calculated endothermicities for dissociative electron attachment to $c$-$C_5F_6Cl_2$ and $c$-$C_6F_8Cl_2$ in the present work is not expected to be better than a few tenths of an electron volt, depending on the effectiveness of collisional stabilization of parent anions in the FALP experiments [1]. (2) EA($c$-$C_5F_6Cl_2$) and EA($c$-$C_6F_8Cl_2$) are calculated to be sufficiently large, 1.17 and 1.46 eV, respectively, that the effects of thermal electron detachment would not be detectable in the FALP data even at 550 K. The fact that detachment distortion of the electron density plots in the FALP experiments [1] was not observed, even at 550 K, implies that both EAs must be greater than 1 eV. (3) The calculated anion bond enthalpies $D_{298}$($c$-$C_5F_6Cl$–$Cl^-$) and $D_{298}$($c$-$C_6F_8Cl$–$Cl^-$) are large enough (1.72 and 1.75 eV, respectively) that thermal dissociation of $c$-$C_5F_6Cl_2^-$ and $c$-$C_6F_8Cl_2^-$ products of attachment does not take place to any significant degree in the attachment experiments [1]. (4) The calculated neutral bond enthalpies $D_{298}$($c$-$C_5F_6Cl$–Cl) and $D_{298}$($c$-$C_6F_8Cl$–Cl) are large enough (4.22 and 3.96 eV, respectively) that thermal decomposition of the reactant does not take place in the FALP experiments [1]. (5) A small $Cl_2^-$ signal was observed in the attachment experiments [1], and for various reasons was attributed to impurities and/or secondary ion-molecule reactions. We have calculated the reaction enthalpy for formation of $Cl_2^-$ from $c$-$C_5F_6Cl_2$ and $c$-$C_6F_8Cl_2$ in electron attachment and obtain $\Delta H_{rxn} = +3.4$ and $+1.1$ eV, respectively, at 298 K, assuming only cleavage of the two C-Cl bonds (i.e., no other bond rearrangements) [14]. These results reinforce the experimental evidence that $Cl_2^-$ formation did not arise from electron attachment to these compounds. The authors thank the Air Force Office of Scientific Research for its continued support of this laboratory. One of the authors (J.M.V.D.) is grateful for support from the Research Corporation and the Camille and Henry Dreyfus foundation. Another author (T.M.M.) is under contract (F19628-99-C-0069) to Visidyne, Inc., Burlington, MA.

## References

[1] J.M. Van Doren, D.M. Kerr, M.D. Hargus, W.M. Foley, S.A. McSweeney, T.M. Miller, R.A. Morris, A.A. Viggiano, W.B. Knighton, Int. J. Mass Spectrom. 195/196 (2000) 517.

[2] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98W, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.

[3] A.D. Becke, J. Chem. Phys. 98 (1993) 5648; J.P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 54 (1993) 16533; K. Burke, J.P. Perdew, Y. Wang, Electron Density Functional Theory: Recent Progress and New Directions, J.F. Dobson, G. Vignale, M.P. Das (Eds.), Plenum, New York, 1998.

[4] J.B. Foresman, Æleen Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd ed., Gaussian, Pittsburgh, 1996, p. 64. We used the scaling factor given for B3LYP/6-31G($d$) frequencies. We calculated vibrational frequencies for $c$-$C_5F_6Cl_2$ using both B3LYP/6-31G($d$) and B3PW91/6-311+G($d$), and found those for the latter to be larger than those for the former by 0.05% on average, which would affect quantities in Table 2 by less than 1 meV.

[5] M.W. Chase, C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald, A.N. Syverud, JANAF Thermochemical Tables, 3rd ed., J. Phys. Chem. Ref. Data, Suppl. No. 1, 14 (1986) 718, 720, 1010.

[6] J.B. Foresman, Æleen Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd ed., Gaussian, Pittsburgh, 1996, pp. 146–158.

[7] EA($Cl_2$) calculated using B3PW91/6-311+G(3$df$) (with B3PW91/6-311+G($d$) bond lengths and ZPEs) is 2.682 eV. Using B3PW91/6-311+G(3$df$) bond lengths and ZPEs only improves EA($Cl_2$) by 0.012 eV. By comparison, a GAUSSIAN-2 calculation gives 2.376 eV. Experiment gives 2.38 ± 0.01 eV, from W.A. Chupka, J. Berkowitz, D. Gutmann, J. Chem. Phys. 55 (1971) 2724.

[8] J.M. Van Doren, S.A. McSweeney, M.D. Hargus, W.M. Foley, D.M. Kerr, T.M. Miller, S.T. Arnold, R.A. Morris, A.A. Viggiano, unpublished. A more accurate G2(MP2) calculation was feasible for 1,2-dichlorotetrafluorobutene and yielded EA($c$-$C_4F_4Cl_2$) = 0.72 eV, in good agreement with the B3PW91/6-311+(3$df$) result of 0.92 eV.

[9] The EA value given in the text for $cis$-$C_2H_2Cl_2$ was calculated at the same level of theory as for the other species in this article. The molecule is small enough that accurate GAUSSIAN-2 calculations are feasible, yielding EA($cis$-

$C_2H_2Cl_2) = -0.30$ eV. A bound form of $C_2H_2Cl_2$ anion was found which may be described as $Cl^- \cdot HCCHCl$ and lies 0.024 eV in energy below that of neutral *cis*-$C_2H_2Cl_2$ (GAUSSIAN-2).

[10] P. Španěl, S. Matejcik, D. Smith, J. Phys. B: At. Mol. Opt. Phys. 28 (1995) 2941.

[11] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899; F. Weinhold, J.E. Carpenter, The Structure of Small Molecules and Ions, Plenum, New York, 1988.

[12] T.M. Miller, A.E. S. Miller, J.F. Paulson, X. Liu, J. Chem. Phys. 100 (1994) 8841.

[13] C.L. Chen, P. J. Chantry, J. Chem. Phys. 71 (1979) 3897.

[14] The large difference in $\Delta H_{rxn}$ for $Cl_2^-$ formation between *c*-$C_5F_6Cl_2$ and *c*-$C_6F_8Cl_2$ is due to differences in the presumed neutral products of the attachment reaction, according to the present calculations. We have assumed that the rings are not broken, and that there is no rearrangement of F atoms. The neutral cyclic fragment *c*-$C_5F_6$ was found to possess a triplet ground state and a C1-C2 double bond, whereas the cyclic fragment *c*-$C_6F_8$ has a singlet ground state and a C1-C2 triple bond. This is not surprising since the much larger ring strain in cyclopentenes (i.e. poorer overlap of the orbitals forming the additional $\pi$ bond, resulting in no bond formed and a triplet ground state) compared to cyclohexenes (where the orbital overlap is now sufficient to form the bond and results in the singlet ground state). If the neutral products accompanying $Cl_2^-$ formation happen to be different isomers than assumed, then clearly the reaction enthalpies given in the text would be incorrect. For more discussion of orbital overlap in rings, see A. Greenberg, J.F. Liebman, Strained Organic Molecules, Academic, New York, 1978).