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Influence of ring size on the strength of carbon bonding complexes between anions and perfluorocycloalkanes

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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In this manuscript we combine high level theoretical calculations (RI-MP2/def2-TZVP) with the Cambridge Structural Database (CSD) analysis to demonstrate the importance of carbon bonding in cyclobutane rings. The higher ability of four-membered rings to interact with electron rich molecules is rationalized using several computational tools, including molecular electrostatic potential surfaces, energetic and geometric features of the complexes and “atoms in molecules” analysis. We have found strong support to the theoretical calculations from the solid state architectures of several X-ray structures retrieved from the CSD searches. Particularly, carbon bonding interactions are quite common in nitro-substituted cubanes.

Introduction

Non-covalent interactions dictate many aspects of modern chemistry and biology. At the present time the assembly of any receptor to bind essentially any substrate is conceivable thanks to modern synthetic chemistry methods even in competitive media.¹ The understanding of many biological functions and drug design grows mostly due to the chemical and physics insights acquired from the study of synthetic host-guest complexes² and the development of supramolecular chemistry. Clear examples are cation- π ³ and anion- π ⁴ interactions that previously to the demonstration of their prominent role in living systems⁵ they first became apparent in artificial systems. This also applies for other noncovalent interactions involving aromatic moieties,⁶ weak C-H hydrogen bonds⁷ or the interaction between halogen atoms and Lewis bases.⁸ Unquestionably the most important aspect of host-guest chemistry is the possibility of elucidating the mechanism of all contributions to molecular recognition and clarifying geometric constraints and to assign discrete energy values to them.⁹ In addition, this also contributes to develop energy scoring functions for many purposes like drug design, catalysis and crystal engineering.

Interactions between a covalently-bonded atom of groups IV-VII acting as a Lewis acid and a Lewis base centre are an important and emerging class of noncovalent interactions. They are classified as σ -hole bonds.¹⁰ The Lewis acid center is generated as a consequence of the loss of the electronic charge on the extension of one of the covalent bonds causing a positive electrostatic potential.¹¹ Halogen,¹² chalcogen¹³ and pnicogen¹⁴ interactions are the most studied σ -hole bonds both theoretically and experimentally, where atom of groups VII, VI

and V, respectively, act as Lewis acid centres.^{9,10,14,15} More recently the atoms of group IV have been also considered as Lewis acid centres forming σ -hole bonds.¹⁶ More particularly the carbon-Lewis base interactions, named as the carbon bonds, were analyzed and compared with the hydrogen bond.¹⁷ It was pointed out that the carbon bond could play a stabilizing role in S_N2 reaction intermediates.¹⁷ The σ -hole bond formed by the group IV elements has been named as a tetrel bond by two research groups almost simultaneously.¹⁸ More recently, single-electron tetrel bonding interaction with radical species as electron donors has been studied.¹⁹ Although only recently this special type of interaction has been classified as a σ -hole bond, previous theoretical and experimental studies have already recognized and described this type of interaction. For example Alkorta *et al.*²⁰ studied molecular complexes between silicon derivatives (SiX_4 , X = halogen) and electron-rich groups (NH_3 , H_2O , etc.). Moreover, they have also analyzed this interaction in aminopropylsilanes.²¹ Furthermore other groups have described this type of complexes in studies on the S_N2 processes for the elements of group IV.²²

In this manuscript we analyze the characteristics of the carbon bond in perfluorocycloalkanes in an effort to analyze the effect of the ring size on the strength of the interaction. In addition, we have also used perfluorocubane as a carbon bond donor because we have learned from the Cambridge Structural Database²³ that cubanes substituted with electron withdrawing groups (e.g. $-NO_2$) present significant carbon bonds ($O\cdots C$) that have a critical influence on their solid state architecture. Moreover, we have studied if multiple carbon bonding interactions could induce planarity in larger rings (6R and 5R) as has been previously observed in similar silicon rings.²⁴ For

this purpose, we have used compounds **1–5** (see Figure 1) and we have analyzed theoretically (RI-MP2/def2-TZVP) multiple carbon bonding interactions where the anion interacts simultaneously with all carbon atoms of the ring. In the last part of the manuscript we analyze the CSD and describe some relevant examples to illustrate the importance of the carbon bonding interaction in cubane derivatives.

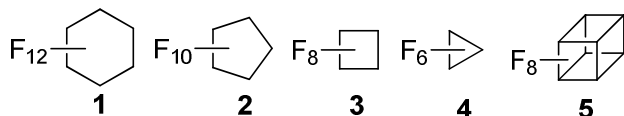


Figure 1. Compounds **1–5** used in this work.

Results and Discussion

Preliminary considerations and MEP analysis

It has been recently reported an interesting theoretical study²⁵ devoted to explain the formation of “inverse sandwich” complexes in perhalogenated cyclohexasilanes²⁶ interacting with anions or lone pair donor molecules (see Fig. 2). A similar behaviour has been also observed in perchlorocyclopentasilane.²⁷ In these systems, the ring becomes planar upon complexation due to the formation of six/five concurrent tetrel bonds.

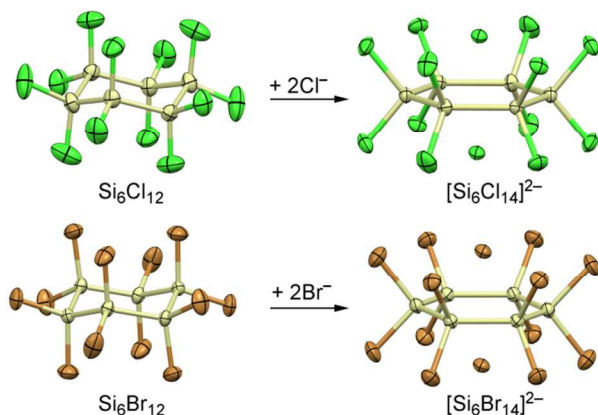


Figure 2. X-ray structures of perhalogenated cyclohexasilanes and their “inverse sandwich” complexes with anions.

Inspired by the behaviour of perhalogenated cyclohexasilanes in the solid state, we have analysed how the carbon bond donor ability of perfluorocyclohexane and perfluorocyclopentane (**1** and **2**, respectively) changes by imposing planarity of the ring. We have computed the molecular electrostatic potential (MEP) surfaces of **1** (D_{3d} and D_{6h}) and **2** (C_1 and D_{5h}) and compared the electrostatic potential at the σ -holes. The results are gathered in Figure 3. Interestingly the six-membered ring only presents a σ -hole over the ring centroid in its D_{6h} conformation, which is 35.8 kcal/mol higher in energy than the D_{3d} one. Therefore, to accomplish the formation of carbon bonding complexes of **1** with anions, the interaction energy must compensate the conformational changing cost. The initial

approximation of the electron rich molecule to the D_{3d} conformer of **1** is difficult because the electrostatic potential energy is small and the σ -hole is not accessible due to the proximity of the negative electrostatic potential belts of the three fluorine atoms (see Figure 3, bottom left), surrounding the σ -hole. For compound **2**, the energetic difference between the C_1 and the D_{5h} conformers is small (7.3 kcal/mol) and consequently a complete planarity of the five-membered ring is expected upon complexation. Similarly to compound **1**, the initial approximation of the anion is not easy due to the low accessibility of the σ -hole.

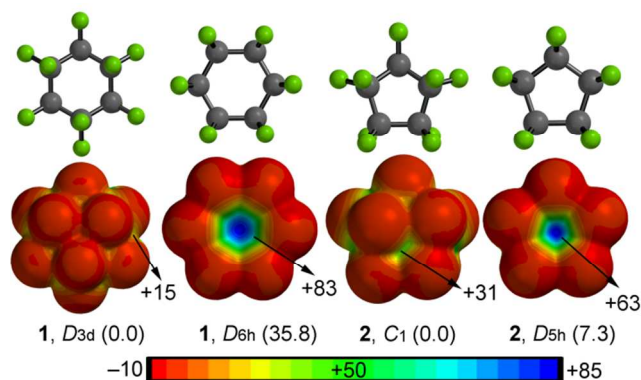


Figure 3. MEP surfaces of compounds **1** and **2** using different symmetries. The MEP energies at selected points are indicated in parenthesis (kcal/mol). The relative energies are also indicated in parenthesis (kcal/mol).

We have also computed the MEP surfaces of the smaller rings (compounds **3** and **4**), which are conformationally more rigid. The results are shown in Fig. 4. Interestingly, in the four membered ring the σ -hole is more exposed and the energetic difference between the both conformers is very small. In three membered rings, the positive region (σ -hole) over the ring center is very narrow and the approximation of the anion to that region is not favoured due to the repulsion with the three negative belts of the F atoms. Therefore the most promising ring to participate in multiple carbon bonding interactions is the four membered ring.

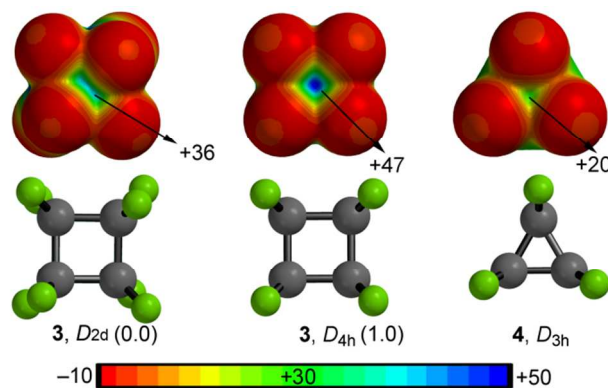


Fig. 4 MEP surfaces of compounds **3** and **4** represented in two orientations (on-top and edge views). The MEP energies at selected points are indicated in kcal/mol.

Geometric and energetic study of carbon bonding complexes

We have optimized the carbon bonding complexes **6–20**, which are represented in Fig. 5. For perfluorocyclohexane (**1**) complexes **6–8**, the interaction energy is only favourable for the OH⁻ anion, which is the best nucleophile. For CN⁻ complexes in any of both orientations (**7**, **8**) the interaction energies are positive. The geometries of the complexes and some geometric features are shown in Fig. 6. In complex **6** the cyclohexane ring has significantly changed its conformation to facilitate the formation of the six O...C carbon bonding interactions, thus explaining the favourable interaction energy. The other two complexes the planarity of the ring is not reached and only three weak carbon bonds are formed that do not compensate the X(-)...F repulsion and the deformation cost of the cyclohexane chair.

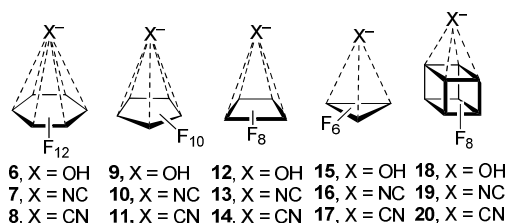


Fig. 5. Complexes **6–20** studied in this work.

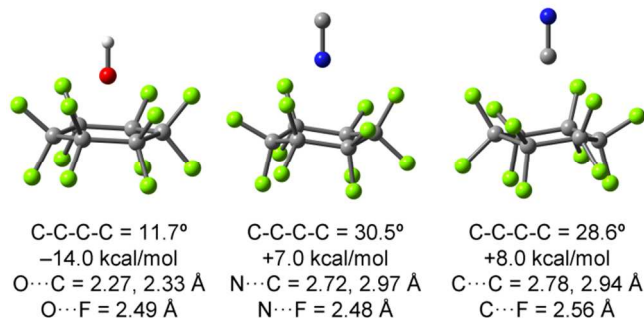


Fig. 6. RI-MP2/def2-TZVP optimized geometries of anion...**1** complexes **6–8**.

The rest of complexes involving five, four and three membered rings present favourable interaction energies in all cases. As expected the OH⁻ complexes are considerably more favourable than the CN⁻ ones and present shorter equilibrium distances. Regarding the influence of the ring size on the interaction energies, the five membered ring is the best carbon bond donor because it is able to provide five simultaneous carbon bonds with a small conformational cost. In fact, the five-membered ring is completely planar in complexes **9–11** (see Fig. 7 for **9** as representative complex). The complexes involving four and especially the three-membered rings have more modest interaction energies apart from complex **12** between perfluorocyclobutane and OH⁻ (DE = -11 kcal/mol) and short equilibrium.

In Table 1 we have also summarized the interaction energies of perfluorocubane **5**, and they are large and negative indicating a higher ability of cubane with respect to perfluorocyclobutane to participate in carbon bonding interactions. This issue is further

analysed below and it is related to the magnitude and availability of the σ-hole.

Table 1. Interaction energies with the BSSE correction (E_{BSSE} , kcal/mol) and equilibrium distances (R_e , Å) at the RI-MP2/def2-TZVP level of theory

Complex	E_{BSSE}	R_e	Symmetry
6	-14.0	1.685	C _{3v}
7	+7.0	2.375	C _{3v}
8	+8.0	2.404	C _{3v}
9	-20.9	1.838	C _s
10	-6.0	2.342	C _s
11	-5.1	2.386	C _s
12	-11.0	2.020	C _{4v}
13	-4.8	2.954	C _{4v}
14	-3.8	3.384	C _{4v}
15	-3.8	3.059	C _{3v}
16	-2.1	3.636	C _{3v}
17	-1.6	3.988	C _{3v}
18	-28.9	2.104	C _{4v}
19	-17.8	2.394	C _{4v}
20	-18.2	2.468	C _{4v}

^aMeasured from the anion to the ring centroid

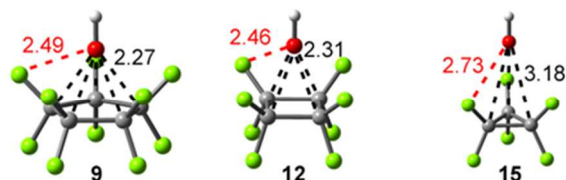


Fig. 7. RI-MP2/def2-TZVP optimized geometries of several carbon bonding complexes. Distances in Å.

Atoms-in-molecules characterization of carbon bonding complexes

We have performed the atoms-in-molecules²⁸ (AIM) analysis of all complexes included in this study. In general the complexes are characterized by the presence of several bond, ring and cage critical points. In particular we are interested in investigating the nature of the interaction by analysing the bond paths connecting the anions with the perfluorinated rings. The distribution of bond critical points and bond paths are depicted in Fig. 8 for a representative set of complexes. For perfluorocyclohexane we represent the distribution for the three complexes (**6–8**) and for the rest we have limited the discussion to the OH⁻ complexes for simplicity. Regarding the perfluorocyclohexane complexes, in **6** the bond paths connect the anion with three carbon atoms thus forming three simultaneous carbon bonds. For **7** and **8** the interaction is basically with three F atoms in agreement with the unfavourable interaction energies and long distances observed in these complexes (see Table 1). For the rest of OH⁻ complexes, it is observed that for five- and four-membered rings the bond paths connect the anion with the carbon atoms (or the middle of the CC bond), which is an indication of carbon bond formation. Conversely, in complex **15** the bond paths connect the anion with the F atoms, in agreement with the modest interaction energy and large HO...C distance obtained for this complex (see Table 1). Conversely to complexes **7** and **8**, the interaction energy in complex **15** is favourable regardless

of the bond paths connect the anion with the F atoms. This is likely due to the longer anion \cdots F distance in **15** than in either **7** or **8** and, moreover, there is not any conformational cost of the ring upon complexation in **15** because of its rigidity.

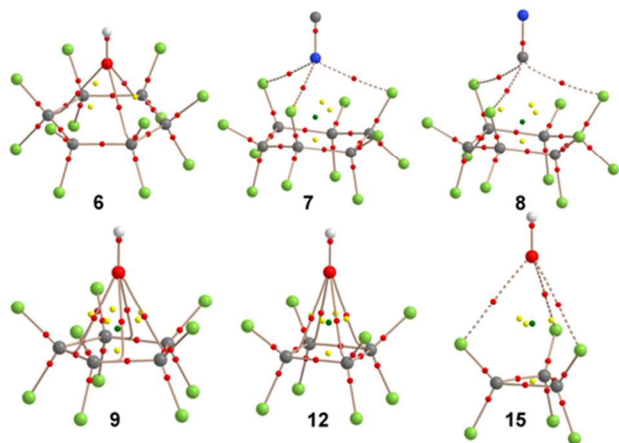


Fig. 8 Representation of bond (red), ring (yellow) and cage (green) critical points in several complexes. The bond paths connecting (3,-1) critical points are also represented.

CSD analysis

We have performed several searches in the Cambridge Structural Database (CSD) in order to provide experimental support to the ability of the small carbocycles to form carbon bonds with electron rich atoms (Lewis bases) by means of the σ -hole. It is well-known that the CSD is a convenient and reliable tool for analysing geometrical parameters and often reveals aspects that have not been noticed by the original authors. We have performed several searches of cycloalkanes establishing short contacts (distance \leq than the van der Waals radii sum) with electron rich atoms (N, O, F, Cl, Br). For six and five membered rings we have not found hits due to the lack of poly-substituted cycloalkanes with either fluorine or any other electron withdrawing group. For three-membered rings we have not found hits likely due to the reduced availability of the σ -hole and electrostatic repulsion with the substituents.

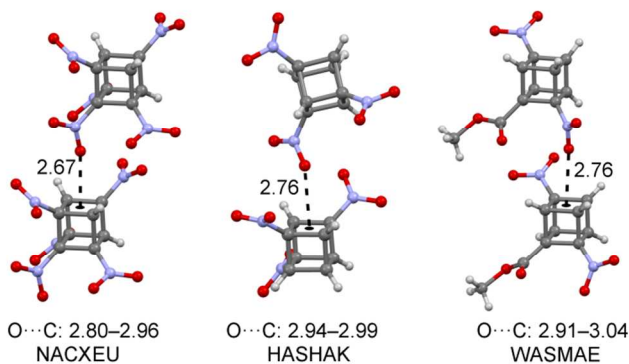


Fig. 9 Partial view of nitrocubane structures and their CSD codes. Distances in Å.

Remarkably, in the search of multiple carbon bonding interactions in four membered rings, we have found a series of

nitro substituted cubanes that present great number of O \cdots C carbon bonds. Interestingly, the four membered rings of cubane are conformationally rigid and the σ -hole is maximally exposed. Some interesting examples are represented in Fig. 9 and it can be observed that the oxygen atom of the nitro group is pointing to the middle of one face of the cubane forming four simultaneous carbon bonds. It is worth mentioning the short O \cdots C distances appreciated in the three structures that are considerably shorter than the sum of van der Waals radii (3.22 Å). In fact the distance decreases as the number of nitro group increases. Interestingly, the crystal packing of these structures in the solid state is governed by carbon bonding interactions instead of the more common C–H \cdots O interactions.

The CSD analysis has revealed that nitrocubanes are ideal compounds to form carbon bonding complexes. We have further analysed theoretically this issue by computing and comparing the MEP surfaces of perfluorocubane and tetrafluorotetra-nitrocubane (**21**), which are shown in Figure 10. Perfluorocubane presents six identical sigma-holes located at the middle of the six four-membered rings of the cube. For compound **21**, where four fluorine atoms have been replaced by nitro groups, a significantly more positive σ -hole is observed, due to the higher electron withdrawing ability of the nitro group. The MEP surface analysis also reveals that some faces of the cube do not have σ -hole (see Fig. 10) due to the influence of the oxygen atoms of the nitro groups. The interaction energies and equilibrium distances of the nitrocubane complexes are gathered in Table 2. The binding energies are very favourable for OH $^-$ and cyanide in any of both orientations and the equilibrium distances are shorter than those previously shown in Table 1 for perfluorocubane. The AIM analyses of two cubane complexes are also shown in Fig. 10. Even for the less nucleophilic anion the bond paths connect the anion with the carbon atoms (or the middle of the CC bond), revealing that they are characterized by carbon bonding interactions. In addition, for complex **21** \cdots CN $^-$ the bond paths connect the carbon atom of the anion with the two carbon atoms of cubane that are bonded to the nitro groups.

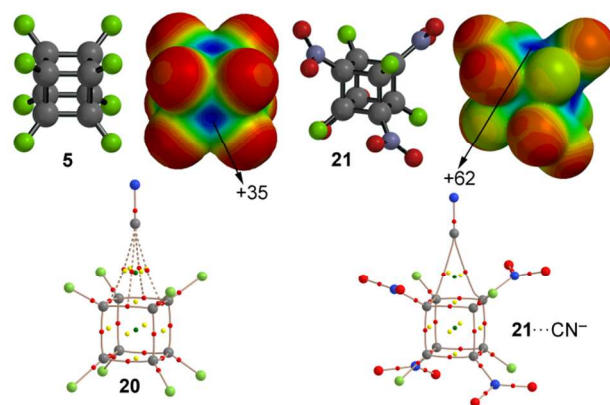


Fig. 10 Top: MEP surfaces of compounds **5** and **21** are represented. The MEP energies at selected points are indicated in kcal/mol. Bottom: Representation of bond (red), ring (yellow) and cage (green) critical points in cubane complexes. The bond paths connecting (3,-1) critical points are also represented.

Table 2. Interaction energies with the BSSE correction (E_{BSSE} , kcal/mol) and equilibrium distances (R_c , Å) at the RI-MP2/def2-TZVP level of theory

Complex	E_{BSSE}	R_c	Symmetry
21...OH ⁻	-61.2	2.049	C_{2v}
21...NC ⁻	-39.9	2.296	C_{2v}
21...CN ⁻	-41.2	2.353	C_{2v}

^aMeasured from the anion to the ring centroid

Conclusions

We have studied how that carbon bonding interactions are influenced by the ring size in perfluorocycloalkanes. Combining high level theoretical calculations and the CSD analysis we have evidenced the importance of carbon bonding in the smaller cyclobutane ring. The ability of cubane to form four simultaneous carbon bonds carbon bonds is remarkable. To date, carbon bonds have been proposed in the stabilization of intermediates to the S_N2 reaction; however the present study clearly contributes to expand its importance in crystal engineering and supramolecular chemistry fields.

Acknowledgements

We thank the DGICYT of Spain (projects CTQ2011-27512/BQU and CONSOLIDER INGENIO 2010 CSD2010-00065, FEDER funds) and the Direcció General de Recerca i Innovació del Govern Balear (project 23/2011, FEDER funds) for financial support.

Theoretical methods

The geometries of all complexes were optimized at the RI-MP2/def2-TZVP level of theory by means of the Turbomole 6.4 software.²⁹ The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys-Bernardi counterpoise technique.³⁰ The symmetry constrain imposed in the optimizations of the complexes is indicated in the tables. The Bader's "Atoms in molecules" theory has been used to study the carbon bonding interactions discussed herein by means of the AIMall calculation package.³¹ The MEP surface analysis was performed at the RI-MP2/6-31+G* level of theory by using the Spartan'10 package.

Notes and references

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† Electronic Supplementary Information (ESI) available: Cartesian coordinates of all optimized complexes and CSD search details. See DOI: 10.1039/b000000x/

- G. V. Oshovsky, D. N. Reinhoudt and W. Verboom, *Angew. Chem. Int. Ed.*, 2007, **46**, 2366–2393; J. M. Zayed, N. Nouvel, U. Rauwald and O. A. Scherman, *Chem. Soc. Rev.*, 2010, **39**, 2806–2816
- M. Zürcher and F. Diederich, *J. Org. Chem.*, 2008, **73**, 4345–4361; D. K. Smith, *J. Chem. Educ.*, 2005, **82**, 393–400; D. A. Uhlenheuer, K. Petkau and L. Brunsveld, *Chem. Soc. Rev.*, 2010, **39**, 2817–2826.

- J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303–1324; N. Zacharias and D. A. Dougherty, *Trends Pharmacol. Sci.*, 2002, **23**, 281–287.
- A. Frontera, P. Gamez, M. Mascal, T. J. Mooibroek and J. Reedijk, *Angew. Chem. Int. Ed.*, 2011, **50**, 9564–9583; A. Frontera, *Coord. Chem. Rev.* 2013, **257**, 1716–1727.
- C. Estarellas, A. Frontera, D. Quiñonero and P. M. Deyà, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 415–418;
- E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem. Int. Ed. Engl.*, 2003, **42**, 1210–1250; L. M. Salonen, M. Ellermann, F. Diederich, *Angew. Chem. Int. Ed.*, 2011, **50**, 4808–4842.
- G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*; Oxford University Press, Oxford, 1999; T. Steiner, *Angew. Chem. Int. Ed.*, 2002, **41**, 48.
- A. C. Legon, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7736–7747; M.R. Scholfield, C. M. Vander Zanden, M. Carter and P. S. Ho, *Prot. Sci.*, 2013, **22**, 139–152; M. Erdelyi, *Chem. Soc. Rev.*, 2012, **41**, 3547–3557; E. Parisini, P. Metrangolo, T. Pilati, G. Resnati and G. Terraneo, *Chem. Soc. Rev.*, 2010, **40**, 2267–2278.
- H.-J. Schneider, *Angew. Chem. Int. Ed. Engl.*, 2009, **48**, 3924–3977.
- J. S. Murray, K. E. Riley, P. Politzer and T. Clark, *Aust. J. Chem.*, 2010, **63**, 1598–1607; P. Politzer, J.S. Murray and T. Clark, *Phys. Chem. Chem. Phys.*, 2013, **15**, 11178–11189.
- T. Clark, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2013, **3**, 13–20.
- P. Metrangolo and G. Resnati, *Chem.–Eur. J.*, 2001, **7**, 2511–2519; G. Cavallo, P. Metrangolo, T. Pilati, G. Resnati, M. Sansotera and G. Terraneo, *Chem. Soc. Rev.* 2010, **39**, 3772–3783; S. J. Grabowski, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7249–7259.
- P. Sanz, M. Yáñez and O. Mó, *Chem. Eur. J.*, 2002, **8**, 3999–4007; P. Sanz, M. Yáñez and O. Mó, *New J. Chem.*, 2002, **26**, 1747–1752; P. Sanz, M. Yáñez and O. Mó, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2003 2942–2947.
- M. R. Sundberg, R. Uggla, C. Viñas, F. Teixidor, S. Paavola and R. Kivekäs, *Inorg. Chem. Commun.*, 2007, **10**, 713–716; S. Scheiner, *Acc. Chem. Res.*, 2013, **46**, 280–288; A. Bauzá, R. Ramis and A. Frontera, *J. Phys. Chem. A*, 2014, **118**, 2827–2834
- P. Politzer, J.S. Murray and T. Clark, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7748–7757.
- A. Bundhun, P. Ramasami, J.S. Murray and P. Politzer, *J. Mol. Model.*, 2013, **19**, 2739–2746.
- D. Mani and E. Arunan, *Phys. Chem. Chem. Phys.*, 2013, **15**, 14377–14383.
- A. Bauzá, T. J. Mooibroek and A. Frontera, *Angew. Chem. Int. Ed.*, 2013, **52**, 12317–12321; S. J. Grabowski, *Phys. Chem. Chem. Phys.*, 2014, **16**, 1824–1834; A. Bauzá, R. Ramis and A. Frontera, *Comput. Theor. Chem.*, 2014, **1038**, 67–70; A. Bauzá, T. J. Mooibroek and A. Frontera, *Chem Eur. J.*, 2014, accepted.
- Q. Li, X. Guo, X. Yang, W. Li, J. Cheng and H.-B. Li, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11617–11625.
- I. Rozas, I. Alkorta and J. Elguero, *J. Phys. Chem. A*, 2001, **105**, 743–749.
- I. Alkorta, J. Elguero, A. Fruchier, D. J. Macquarrie and A. Virgili, *J. Organomet. Chem.*, 2001, **625**, 148–153
- C. J. Levy, R. J. Puddephatt, *J. Am. Chem. Soc.*, 1997, **119**, 10127–10136; J. Langer, S. Matejcek and E. Illenberger, *Phys. Chem. Chem.*

- Phys.*, 2000, **2**, 1001–1005; J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lauderaj, J. X. Zhang, W. L. Hase, M. Weidemüller and R. Wester, *Science*, 2008, **319**, 2008, 183; M. Sohail, R. Panisch, A. Bowden, A.R. Bassindale, P. G. Taylor, A. A. Korlyukov, D. E. Arkhipov, L. Male, S. Callear, S. J. Coles, M. B. Hursthouse, R. W. Harrington and W. Clegg, *Dalton Trans.*, 2013, **42**, 10971–10981.
- 23 F. H. Allen, *Acta Cryst.*, 2002, **B58**, 380–388.
- 24 J. Tillmann, L. Meyer, J. I. Schweizer, M. Bolte, H.-W. Lerner, M. Wagner and M. C. Holthausen, *Chem. Eur. J.*, 2014, 10.1002/chem.201402655.
- 25 A. Robertazzi, J. A. Platts and P. Gamez, *ChemPhysChem.*, 2014, **15**, 912–917.
- 26 X. Dai, D. L. Schulz, C. W. Braun, A. Ugrinov and P. Boudjouk *Organometallics*, 2010, **29**, 2203–2205; X. Dai, S.-B. Choi, C. W. Braun, P. Vaidya, S. Kilina, A. Ugrinov, D. L. Schulz and P. Boudjouk, *Inorg. Chem.*, 2011, **50**, 4047–4053
- 27 J. Tillmann, F. Meyer-Wegner, A. Nadj, J. Becker-Baldus, T. Sinke, M. Bolte, M. C. Holthausen, M. Wagner and H.-W. Lerner, *Inorg. Chem.*, 2012, **51**, 8599–8606
- 28 R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893–928; R. F. W. Bader, *Atoms in Molecules, A Quantum Theory*; Oxford, University Press: Oxford, UK, 1990; P. L. A. Popelier, *Atoms In Molecules. An Introduction*; Prentice Hall: Harlow, England, 2000.
- 29 R. Ahlrichs, M. Bär, M. Hacer, H. Horn and C. Kömel, *Chem. Phys. Lett.*, 1989, **162**, 165–169.
- 30 S. B. Boys, F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.
- 31 AIMAll (Version 13.05.06), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2013.

Table of contents/Graphical Abstract

High level ab initio calculations and the Cambridge Structural Database analysis demonstrate the importance of carbon bonding in cyclobutane rings.

