Chemical Science

EDGE ARTICLE

Check for updates

Cite this: Chem. Sci., 2018, 9, 2284

Synthesis, structure and aromaticity of carboranefused carbo- and heterocycles[†]

Tek Long Chan D and Zuowei Xie *

Conjugation between a 3-D icosahedral carborane and a fused 2-D π -ring system is ambiguous. To address this issue, we prepared several carborane-fused carbo- and heterocycles. Detailed studies on their molecular structures, NMR data, and NICS (nucleus-independent chemical shift) and ISE (isomerization stabilization energy) values as well as molecular orbital analyses clearly suggest the presence of (1) considerable aromatic character in the exo five-membered ring of carborane-fused carbo- and heterocycles and (2) considerable conjugation between a 3-D carborane and a fused 2-D π -ring system. These results will shed some light on the design of new carborane-based materials.

Received 1st November 2017 Accepted 15th January 2018

rsc.li/chemical-science

DOI: 10.1039/c7sc04722c

Introduction

Icosahedral carboranes are carbon-boron molecular clusters, featuring a fully delocalized system of 26 skeletal electrons via 3c-2e bonding between tangential p orbitals and radial sp orbitals.1 Such clusters are aromatic molecules having 3-D aromaticity (σ -aromaticity),² which are different from classical 2-D aromatic molecules such as benzenes (π -aromaticity).³ On the other hand, both classes of molecules share some common features such as thermal stability and ability to undergo electrophilic substitution reactions.4

Conjugation between a 3-D carborane and an exo-X atom via cage CX vertex (X = atom with π -donor ability) has been evidenced by experimental and theoretical results, and such a unique σ - π conjugation is enhanced as the π -donor ability of X atom increases.⁵ However, conjugation between a 3-D carborane and a fused 2-D π -ring system is ambiguous. No σ - π conjugation is observed between the C₂B₁₀ cage and the diene moiety in benzocarborane (A in Fig. 1), in which the C-C double bonds are localized with the NICS(0) (NICS: nucleusindependent chemical shift) values of -0.7 to -3.4 ppm for exo-C₆H₄ six-membered ring in benzocarborane derivatives.⁶ In contrast, a considerable σ - π conjugation is reported for CB₁₁ cage-fused heterocyclic anion $[1,2-N_3R-1-CB_{11}Cl_{10}]^-$ (B in Fig. 1), leading to an aromatic exo-CBN3 five-membered ring with a NICS(0) value of -7.8 ppm.⁷

In view of wide applications of carboranes as a unique electronic sink and transmitter in optoelectronic materials,8 we initiated a research program to study the σ - π conjugation in *o*-

 $X = CH_2, CH^-, NH, O, S$ $\circ = BH \bullet = BCI \bullet = C$

HEMISTRY

View Article Online

View Journal | View Issue

Fig. 1 Carborane-fused carbo- and heterocycles.

carborane-fused five-membered carbo- and heterocycles, as well as the aromaticity of fused exo five-membered rings (C in Fig. 1). The results of this work would shed some light on the design of new carborane-fused π conjugated materials.

Result and discussion

Synthesis

Scheme 1 outlines the synthetic route to carborane-fused cyclopentadienyl anions. Compound 1 was synthesized



Scheme 1 Synthesis of carborane-fused cyclopentadienyl anions.

Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China. E-mail: zxie@cuhk.edu.hk

[†] Electronic supplementary information (ESI) available: CCDC 1583053-1583058 for 2, 4, 8, 10, 17 and 20. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc04722c



according to the method given in the literature.⁹ Solvent-free dehydration of **1** in the presence of 1 equiv. of *p*-TsOH at 180 °C gave **2** as colorless crystals in 66% yield. Treatment of **2** with 1 equiv. of *n*-BuLi in THF afforded the corresponding lithium salt **3** as a yellow powder in quantitative yield. Recrystallization of **3** from a THF solution containing 12-crown-4 ether produced **4** as yellow crystals in quantitative yield.

Treatment of 1-thio-*o*-carborane¹⁰ (5) with an excess amount of NaH followed by reaction with α -bromoacetone gave **6** as a white solid in 68% yield. Cyclization of **6** in the presence of tetrabutylammonium fluoride (TBAF) generated compound **7** as a white solid in 25% yield. The carborane-fused thiophene (**8**) was synthesized as colorless crystals in 80% yield *via* solventfree dehydration in the presence of 1 equiv. of *p*-TsOH at 180 °C for 4 hours (Scheme 2).

In a similar manner, carborane-fused furan (12) was prepared as a colorless liquid *via* concentrated H_2SO_4 mediated dehydration of 11 in 50% yield (Scheme 3).

The reaction of *o*-carboranyl triflate (13) with lithium *N*allylmethylamide afforded the corresponding amine 14 as a colorless liquid in 53% yield.¹¹ Ruthenium-catalyzed olefin isomerization¹² and cage carbon iodination gave compound 16 as a light yellow solid in 50% yield. UV irradiation of 16 produced carborane-fused pyrrole (17) as colorless crystals in 30% yield (Scheme 4).¹³



Scheme 3 Synthesis of carborane-fused furan (12).



Scheme 4 Synthesis of carborane-fused pyrrole (17).

Similarly, iodination of **18**,¹¹ followed by UV irradiation of **19** generated a carborane-fused indole (**20**) as pale yellow crystals in 50% yield (Scheme 5).¹³

Structural characterization

NMR spectroscopy serves as a useful tool to determine whether a compound has aromatic character.¹⁴ The fused fivemembered ring proton was observed at 6.53 ppm for **3** and 6.10 ppm for **4**, which was shifted downfield compared to that of 5.75 ppm in **2**, suggesting that the fused five-membered ring in **3** and **4** has some aromatic character. On the other hand, the CH proton in carborane-fused heterocycles was observed at 6.27 ppm in **8**, 6.58 ppm in **12** and 6.05 ppm in **17**, which was compared to that of 6.87 ppm in 3-methylthiophene,¹⁵ 7.16 ppm in 3-methylfuran¹⁵ and 6.35 ppm in 3-methyl-*N*-methylpyrrole,¹⁶ respectively. These measured proton chemical shifts were considerably downfield shifted in comparison to those observed in the corresponding dihydrothiophene,¹⁷ dihydrofuran,¹⁸ and dihydropyrrole,¹⁹ indicating that the fused five-membered rings in **8**, **12** and **17** have some aromatic character.

Single-crystal X-ray analyses confirmed the molecular structures of 2, 4, 8, 17 and 20. Their representative structures are



Scheme 5 Synthesis of carborane-fused indole (20).

Chemical Science



Fig. 2 Molecular structures of (a) anion in 4, (b) 8, (c) 17 and (d) 20.

shown in Fig. 2. The results clearly indicate that the fused fivemembered rings in **4**, **8**, **17** and **20** are co-planar with the sum of the internal pentagonal angles being 540°.

As shown in Fig. 3, the bond distances of the fused fivemembered ring in 4 are averaged in comparison with those observed in 2, suggesting the presence of some degree of delocalization within the five-membered ring. Except for the cage C(1)-C(2) distance, the measured distances and angles of the fused five-membered heterocycles in 8, 17 and 20 are comparable to those observed in thiophene,²⁰ pyrrole^{21*a*} and indole.^{21*b*}

The UV-Vis spectra of 2, 4, 8, 12, 17 and 20 in THF were obtained, and they are shown in Fig. S7 and S8 in the ESI.† The UV-Vis spectrum of 4 (see Fig. S7 in the ESI†) displayed a new absorption band centered at 423 nm, which was assigned as $\pi \rightarrow \pi^*$ absorption of the delocalized system of the *exo* five-membered ring.







The UV-Vis spectra of carborane-fused heterocycles (see Fig. S8 in the ESI†) showed absorptions between 287 and 290 nm attributable to $n \rightarrow \sigma^*$ transition and between 306 to 330 nm corresponding to the $\pi \rightarrow \pi^*$ transition of the delocalized *exo* five-membered ring system, which were red-shifted compared to those observed in heteroarenes ($\lambda_{max} = 205-218$ nm)²² and benzene-fused heterocycles ($\lambda_{max} = 282-298$ nm).²³ These assignments were supported by time-dependent DFT (TD-DFT) calculations (see ESI†).

The cyclic voltammograms of **8**, **17**, **20**, indole and benzothiophene obtained from solutions in THF are shown in Fig. S10 (ESI[†]). The absorption edge and reduction potentials of the aforementioned compounds are summarized in Table S1 in the ESI.[†] Based on these data, the energy levels of LUMO (the Lowest Unoccupied Molecular Orbital) and HOMO (the Highest Occupied Molecular Orbital) of these compounds were estimated and are shown in Fig. 4 (also see Table S1 in the ESI[†]). These results indicate that the electron-withdrawing nature of carboranyl moiety decreases the LUMO energy levels of **8**, **17** and **20** compared to those of benzo-fused heterocycles. The DFT-calculated (at the B3LYP/6-311++G(d,p) level of theory) HOMO energy levels are in general agreement with the corresponding experimental values, whereas the DFT-calculated LUMO energy levels are higher than the corresponding



Fig. 3 Selected bond distances (Å) of **2**, **4**, **8**, **17** and **20**. The distances in red are the experimental values (determined by the microwave spectroscopic method) of thiophene, pyrrole and indole.

 $\label{eq:table_$

	NICS(0)		
x	×	$\langle \mathbf{x} \rangle$	×
CH_2	-5.8	-3.3	-0.7
CH^{-}	-9.9	-12.6	-14.0
NH	-9.6	-13.7	-12.5
0	-9.3	-12.0	-10.9
S	-9.0	-14.2	-12.3

Edge Article

Table 2 ISE values (kcal mol⁻¹) of carborane-fused heterocycles and related five-membered heterocycles computed at the B3LYP/6-311+G(d,p) level of theory



experimental values (Table S2 in ESI†). Such differences are often observed in aromatic π systems.²⁴

Computational studies

NICS values have been used extensively for the identification of aromatic properties of molecules.²⁵ In this regard, NICS values of carborane-fused five-membered carbo- and heterocycles were calculated at the B3LYP/6-311++G(d,p) level of theory. For comparison, NICS values of cyclopentadiene, cyclopentadienide, thiophene, furan, pyrrole and their benzo derivatives were also calculated at the same level of theory. The results are compiled in Table 1. The data (-9.0 to -9.9 ppm) suggest that carborane-fused five-membered carbo- and heterocycles have considerable aromatic character. These results are consistent with those obtained from the aforementioned NMR data and structural parameters.

Another parameter used to estimate aromatic stabilization energy is the isomerization stabilization energy (ISE).²⁶ The calculated ISE data for carborane-fused heterocycles and the related systems are summarized in Table 2. The results clearly show that the ISE values of carborane-fused thiophene, furan and pyrrole are about half (-6.4 to -8.8 kcal mol⁻¹) of those calculated for benzo-thiophene, -furan and -pyrrole that are typical aromatic molecules.

To understand the electronic structures of carborane-fused heterocycles, DFT calculations at the B3LYP/6-311++G(d,p) level of theory were performed for both **8** and benzothiophene. The optimized bond distances and angles are in very good agreement with the experimental values of **8** (see Table S5 in the ESI†). Their selected molecular orbitals (MOs) are shown in Fig. 5, revealing the significant mixing between the carborane cage and the fused *exo* ring. It is noteworthy that the five MOs (HOMO–1, HOMO–6, HOMO–10, LUMO+4 and LUMO) in **8** resemble those found in benzothiophene, corresponding to π and π^* MOs. These results again suggest that the carborane



Fig. 5 Plot of the LUMO+4, LUMO, HOMO-1, HOMO-6 and HOMO-10 orbitals in 8 (left) and the LUMO+3, LUMO, HOMO-1, HOMO-2 and HOMO-8 of benzothiophene (right) calculated at the B3LYP/6-311++G(d,p) level of theory, where red and blue indicate different phases of the wave functions.

moiety can utilize its cage carbon p orbitals to participate in the *exo* π bonding interactions, resulting in considerable conjugation between a 3-D cage molecule and a 2-D π system.

Conclusions

Several new carborane-fused cyclopentadienyl anion, furan, thiophene, pyrrole and indole have been prepared. NMR data, X-ray structural parameters, NICS and ISE values as well as molecular orbital analyses prove that the fused five-membered rings in the aforementioned carborane-fused cyclics have considerable aromatic character, and the conjugation between a 3-D cluster and a fused 2-D π system has been realized by the π donation of the *exo* heteroatom/carbanion. These results will shed some light on the design of new carborane-based π molecules for material applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by grants from the Research Grants Council of the Hong Kong Special Administration Region (Project No. 14306114), NSFC/RGC Joint Research Scheme (Project No. N_CUHK442/14) and the incentive fund from the Faculty of Science, CUHK. T. L. C. acknowledges the Tertiary Education Services Office of Macau Special Administration for a postgraduate scholarship. We thank Dr Jiji Zhang for the valuable discussion on DFT calculations and Mr Ruofei Cheng for the measurements of cyclic voltammograms.

Notes and references

- (a) R. N. Grimes, *Carboranes*, 3rd edn, Elsevier, Oxford, 2016;
 (b) N. S. Hosmane, *Boron Science: New Technologies and Applications*, Taylor & Francis Books/CRC, Boca Raton, FL, 2011;
 (c) Z. Qiu, S. Ren and Z. Xie, *Acc. Chem. Res.*, 2011, 44, 299–309;
 (d) J. Zhang and Z. Xie, *Acc. Chem. Res.*, 2014, 47, 1623–1633.
- 2 For selected reviews, see: (a) R. B. King, Chem. Rev., 2001, 101, 1119–1152; (b) Z. Chen and R. B. King, Chem. Rev., 2005, 105, 3613–3642; (c) M. Zhao and B. M. Gimarc, Inorg. Chem., 1993, 32, 4700–4707; (d) P. v. R. Schleyer and K. Najafian, Inorg. Chem., 1998, 37, 3454–3470.
- 3 For selected articles, see: (a) E. Hückel, Z. Phys., 1931, 70, 204–286; (b) E. Hückel, Z. Phys., 1931, 72, 310–337; (c) D. P. Craig and N. L. Paddock, Nature, 1958, 181, 1052–1053; (d) A. T. Balaban, D. C. Oniciu and A. R. Katritzky, Chem. Rev., 2004, 104, 2777–2812; (e) E. Matito, J. Poater, M. Solà and P. v. R. Schleyer, in Chemical Reactivity Theory: A Density Functional View, ed. P. K. Chattaraj, CRC Press, Boca Raton, FL, 2009, ch. 28, pp. 439–449.
- 4 (a) F. A. Carey and R. J. Sundberg, in Advanced Organic Chemistry Part B: Reactions and Synthesis, Springer, New York, 5th edn, 2007, ch. 11, pp. 1003-1062; (b) D. Olid, R. Núñez, C. Viñas and F. Teixidor, Chem. Soc. Rev., 2013, 42, 3318-3336; (c) J. Poater, M. Solà, C. Viñas and F. Teixidor, Angew. Chem., Int. Ed., 2014, 53, 12191-12195; (d) Z. Qiu, Tetrahedron Lett., 2015, 56, 963-971; (e) Z. Xie, Sci. China: Chem., 2014, 57, 1061-1063; (f) Y. Quan and Z. Xie, J. Am. Chem. Soc., 2014, 136, 15513-15516; (g) W.-B. Yu, P.-F. Cui, W.-X. Gao and G.-X. Jin, Coord. Chem. Rev., 2017, 350, 300-319; (h) B. J. Eleazer, M. D. Smith, A. A. Popov and D. V. Peryshkov, J. Am. Chem. Soc., 2016, 138, 10531-10538; (i) B. J. Eleazer, M. D. Smith, A. A. Popov and D. V. Peryshkov, Chem. Sci., 2017, 8, 5399-5407; (j) R. M. Dziedzic, J. L. Martin, J. C. Axtell, L. M. A. Saleh, T.-C. Ong, Y.-F. Yang, M. S. Messina, A. L. Rheingold, K. N. Houk and A. M. Spokoyny, J. Am. Chem. Soc., 2017, 139, 7729-7732; (k) E. A. Qian, A. I. Wixtrom, J. C. Axtell, A. Saebi, D. Jung, P. Rehak, Y. Han, E. H. Moully, D. Mosallaei, S. Chow, M. S. Messina, J.-Y. Wang, A. T. Royappa, A. L. Rheingold, H. D. Maynard, P. Král and A. M. Spokoyny, Nat. Chem., 2017, 9, 333-340; (1) J. C. Axtell, K. O. Kirlikovali, D. Jung, R. M. Dziedzic, A. L. Rheingold and A. M. Spokoyny, Organometallics, 2017, 36, 1204–1210; (m) J. Estrada and V. Lavallo, Angew. Chem., Int. Ed., 2017, 56, 9906–9909; (n) J. F. Kleinsasser, S. P. Fisher, F. S. Tham and V. Lavallo, Eur. J. Inorg. Chem., 2017, 4417-4419; (o) S. G. McArthur, R. Jay, L. Geng, J. Guo and V. Lavallo, Chem. Commun., 2017, 53, 4453-4456.
- 5 (a) S.-h. Wu and M. Jones, *Inorg. Chem.*, 1988, 27, 2005–2008;
 (b) R. Coult, M. A. Fox, W. R. Gill and K. Wade, *Polyhedron*, 1992, 11, 2717–2721;
 (c) L. A. Boyd, W. Clegg, R. C. B. Copley, M. G. Davidson, M. A. Fox, T. G. Hibbert,

J. A. K. Howard, A. Mackinnon, R. J. Peace and K. Wade, Dalton Trans., 2004, 2786–2799; (d) M. A. Fox, C. Nervi, A. Crivello, A. S. Batsanov, J. A. K. Howard, K. Wade and P. J. Low, J. Solid State Electrochem., 2009, **13**, 1483–1495; (e) M. A. Fox, J. A. H. MacBride, R. J. Peace, W. Clegg, M. R. J. Elsegood and K. Wade, Polyhedron, 2009, **28**, 789– 795; (f) J. M. Oliva, N. L. Allan, P. v. R. Schleyer, C. Viñas and F. Teixidor, J. Am. Chem. Soc., 2005, **127**, 13538–13549; (g) T. D. Getman, C. B. Knobler and M. F. Hawthorne, J. Am. Chem. Soc., 1990, **112**, 4593–4594; (h) K. Chui, H.-W. Li and Z. Xie, Organometallics, 2000, **19**, 5447–5453; (i) F. Zhang, J. Zhang, X. Fu and Z. Xie, Chem.–Asian J., 2013, **8**, 1886–1891.

- 6 Although the NICS values of parent benzocarborane are not reported, we use thiophene-fused benzocarboranes, *o*-carborane-based biphenyl and *p*-terphenyl derivatives as examples. (*a*) Y. Morisaki, M. Tominaga and Y. Chujo, *Chem.-Eur. J.*, 2012, **18**, 11251–11257; (*b*) Y. Morisaki, M. Tominaga, T. Ochiai and Y. Chujo, *Chem.-Asian J.*, 2014, **9**, 1247–1251.
- 7 (a) J. H. Wright, C. E. Kefalidis, F. S. Tham, L. Maron and
 V. Lavallo, *Inorg. Chem.*, 2013, 52, 6223-6229; (b)
 A. L. Chan, J. Fajardo, J. H. Wright, M. Asay and V. Lavallo, *Inorg. Chem.*, 2013, 52, 12308-12310; (c) M. Asay,
 C. E. Kefalidis, J. Estrada, D. S. Weinberger, J. Wright,
 C. E. Moore, A. L. Rheingold, L. Maron and V. Lavallo, *Angew. Chem., Int. Ed.*, 2013, 52, 11560-11563.
- 8 For selected examples, see: (a) K. R. Wee, W. S. Han, D. W. Cho, S. Kwon, C. Pac and S. O. Kang, Angew. Chem., Int. Ed., 2012, 51, 2677-2680; (b) K. R. Wee, Y. J. Cho, S. Jeong, S. Kwon, J. D. Lee, I. H. Suh and S. O. Kang, J. Am. Chem. Soc., 2012, 134, 17982-17990; (c) C. Shi, H. Sun, X. Tang, H. Lv, H. Yan, Q. Zhao, J. Wang and W. Huang, Angew. Chem., Int. Ed., 2013, 52, 13434-13438; (d) H. Naito, Y. Morisaki and Y. Chujo, Angew. Chem., Int. Ed., 2015, 54, 5084-5087; (e) N. Tsuboya, M. Lamrani, R. Hamasaki, M. Ito, M. Mitsuishi, T. Miyashita and Y. Yamamoto, J. Mater. Chem., 2002, 12, 2701-2705; (f) J. Guo, D. Liu, J. Zhang, J. Zhang, Q. Miao and Z. Xie, Chem. Commun., 2015, 51, 12004–12007; (g) S. Mukherjee and P. Thilagar, Chem. Commun., 2016, 52, 1070-1093; (h) R. Furue, T. Nishimoto, I. S. Park, J. Lee and T. Yasuda, Angew. Chem., Int. Ed., 2016, 55, 7171-7175; (i) H. Naito, K. Nishino, Y. Morisaki, K. Tanaka and Y. Chujo, Angew. Chem., Int. Ed., 2017, 56, 254-259.
- 9 H. Nakamura, K. Aoyagi and Y. Yamamoto, *J. Am. Chem. Soc.*, 1998, **120**, 1167–1171.
- 10 A.-R. Popescu, A. D. Musteti, A. Ferrer-Ugalde, C. Viñas, R. Núñez and F. Teixidor, *Chem.–Eur. J.*, 2012, **18**, 3174–3184.
- 11 R. Cheng, J. Zhang, J. Zhang, Z. Qiu and Z. Xie, *Angew. Chem., Int. Ed.*, 2016, **55**, 1751–1754.
- 12 S. Xu, F. Haeffner, B. Li, L. N. Zakharov and S.-Y. Liu, *Angew. Chem., Int. Ed.*, 2014, **53**, 6795–6799.
- 13 H. Ni, Z. Qiu and Z. Xie, *Angew. Chem., Int. Ed.*, 2017, **56**, 712–716.
- 14 T. M. Krygowski and M. K. Cyrański, *Chem. Rev.*, 2001, **101**, 1385–1420.

- 15 R. J. Abraham and M. J. Reid, *J. Chem. Soc., Perkin Trans.* 2, 2002, 1081–1091.
- 16 H. McNab and M. E.-A. Murray, J. Chem. Soc., Perkin Trans. 1, 1988, 333–338.
- 17 N. N. Sauer, R. Angelici, Y. C. J. Huang and W. S. J. Trahanovsky, *J. Org. Chem.*, 1986, **51**, 113–114.
- 18 S. H. Hong, D. P. Sanfers, C. W. Lee and R. H. Grubbs, J. Am. Chem. Soc., 2005, 127, 17160–17161.
- 19 G.-H. Hou, J.-H. Xie, P.-C. Yan and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 1366–1367.
- 20 B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, J. Mol. Spectrosc., 1961, 7, 58–63.
- 21 (a) L. Nygaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen and G. O. Sørensen, J. Mol. Struct., 1969, 3, 491–506; (b) N. Sundaraganesan, H. Umamaheswari, B. D. Joshua, C. Meganathan and M. J. Ramalingam, J. Mol. Struct.: THEOCHEM, 2008, 850, 84–93.
- 22 A. R. Chaudhry, R. Ahmed, A. Irfan, A. Shaari and A. Al-Sehemi, *Mater. Chem. Phys.*, 2013, **138**, 468–478.

- 23 (a) A. Muranaka, S. Yasuike, C.-Y. Liu, J. Kurita, N. Kakusawa, T. Tsuchiya, M. Okuda, N. Kobayashi, Y. Matsumoto, K. Yoshida, D. Hashizume and M. Uchiyama, *J. Phys. Chem. A*, 2009, 113, 464–473; (b) N. Singla, V. S. Bhadram, C. Narayana and P. Chowdhury, *J. Phys. Chem. A*, 2013, 117, 2738–2752.
- 24 (a) Z. Liang, Q. Tang, R. Mao, D. Liu, J. Xu and Q. Miao, Adv. Mater., 2011, 23, 5514–5518; (b) X. Gu, B. Shan, Z. He and Q. Miao, ChemPlusChem, 2017, 82, 1034–1038; (c) J.-L. Bredas, Mater. Horiz., 2014, 1, 17–19.
- 25 (a) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842–3888; (b) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Org. Lett.*, 2006, **8**, 863–866; (c) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. E. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317– 6318.
- 26 (a) J. Zhu, K. An and P. v. R. Schleyer, Org. Lett., 2013, 15, 2442–2445; (b) C. Zhu, S. Li, M. Luo, X. Zhou, Y. Niu, M. Lin, J. Zhu, Z. Cao, X. Lu, T. Wen, Z. Xie, P. v. R. Schleyer and H. Xia, Nat. Chem., 2013, 5, 698–703.