

Communication

London Dispersion Enables the Shortest Intermolecular Hydrocarbon H•••H Contact

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J. Am. Chem. Soc., Just Accepted Manuscript • Publication Date (Web): 13 May 2017 Downloaded from http://pubs.acs.org on May 14, 2017

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London Dispersion Enables the Shortest Intermolecular Hydrocarbon H•••H Contact

Sören Rösel,[#] Henrik Quanz,[#] Christian Logemann,[‡] Jonathan Becker,[‡] Estelle Mossou,^{§,¶} Laura Cañadillas-Delgado,^{§,¤} Eike Caldeweyher,⁺ Stefan Grimme,⁺ and Peter R. Schreiner^{#,*}

[#] Institut für Organische Chemie, Justus-Liebig Universität, Heinrich-Buff-Ring 17, 35392 Giessen (Germany)

[‡] Institut für Anorganische und Analytische Chemie, Justus-Liebig Universität, Heinrich-Buff-Ring 17, 35392 Giessen (Germany)

[§] Institute Laue-Langevin, Rue Jules Horowitz 6, BP 156, 38042 Grenoble Cedex 9 (France)

^a Centro Universitario de la Defensa de Zaragoza. Ctra Huesca s/n, 50090 Zaragoza (Spain)

[¶] Faculty of Natural Sciences, Keele University, Staffordshire, ST₅ 5BG, United Kingdom

⁺ Mulliken Center for Theoretical Chemistry, Institute of Physical and Theoretical Chemistry, University Bonn, Beringstraße 4, 53115 Bonn (Germany)

Supporting Information Placeholder

ABSTRACT: Neutron diffraction of tri(3,5-*tert*-butylphenyl)methane at 20 K reveals an intermolecular C–H…H–C distance of only 1.566(5) Å, which is the shortest reported to date. The compound crystallizes as a C_3 -symmetric dimer in an unusual head-to-head fashion. Quantum chemical computations of the solid state at the HSE-3c level of theory reproduce the structure and the close contact very well (1.555 Å at o K) and emphasize the significance of packing effects; the gas-phase dimer structure at the same level shows a 1.634 Å C–H…H–C distance. Intermolecular London dispersion interactions between contacting *tert*butyl substituents surrounding the central contact deliver the decisive energetic contributions to enable this remarkable bonding situation.

Continuously probing the limits of chemical bonding helps improve our current understanding and sophistication of molecular structure theories. Many of us are enthralled by the notion of going beyond carbon-carbon triple bonds,¹ inorganic quadruple and higher bond orders,²⁻³ twisted double bonds,⁴⁻⁶ compressed⁷⁻⁸ and stretched covalent bonds⁹⁻¹¹ and non-covalent interactions such as extremely short C···C contacts,¹²⁻¹³ and many more. To the best of our knowledge, we report here the shortest *intermolecular* H···H contact in a hydrocarbon as evident from the exceptional congruence of both neutron and X-ray diffraction experimental data with sophisticated quantum chemical crystal structure computations.

Impressive examples for very short *intramolecular* C-H····H-C contacts are some bowl-like structures such as *exo,exo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane **3** derivatives with $R_{\text{H····H}}$ down to 1.713(3) Å¹⁴ (neutron diffraction data, NRD) and the famous current record holder "half-cage" pentachloro-pentacyclododecane **4** with a short H···H contact of 1.617(3) Å (NRD), thereby significantly undercutting the sum of the van-der-Waals (vdW) radii of 2.40 Å¹⁵ by $\Delta R_{vdW} = -$ 0.78 Å (Figure 1).¹⁶ Such compressions are not uncommon in heteroatomic polycycles, with Pascal's record holder **5** that displays an intramolecular Si–H···H–Si contact of roughly 1.56 Å, as judged from quantum chemical computations and the Si···Si distance of 4.433(2) Å derived from X-ray single crystal diffraction (XRD) data; unfortunately, no NRD study of **5** has been published.¹⁷⁻¹⁸



Figure 1. The very short *intermolecular* H···H contact in all*meta* ^tBu-triphenylmethane dimer 1_2 and the very long R_{C-C} in LD stabilized all*-meta* ^tBu-hexaphenylethane **2**. Polycyclic structures with very short intramolecular H···H contacts: *exo,exo*-tetracyclododecane **3** (NRD), "half-cage" **4** (NRD) and *in,in*-bis(hydrosilane) **5** (XRD; $R_{H\cdots H} \sim 1.56$ Å by computations and 1.531(8), NRD¹⁸).

Structures **3–5** share very tight transannular H…H contacts within a sterically confined environment, and at first glance

such short contacts would not be expected *inter*molecularly because of the energetic penalty associated with bringing atoms much within their comfortable vdW-radii.¹⁹⁻²² Here we demonstrate not only that this energetic drawback can be overcome in an intermolecular bonding situation *via* highly attractive London dispersion²³⁻²⁵ (LD) interactions, but also that such short nonbonding distances can be compressed even more than in the shortest published intramolecular case.

In molecular design large alkyl groups are used to introduce bulk and sterically shield reactive moieties. The fact that bulky groups are highly polarizable -thereby increasing their ability to engage in non-negligible, stabilizing LD interactions- is often disregarded. Such groups are appropriately termed "dispersion energy donors", DEDs.²⁶ This thermodynamic stabilization can be utilized to isolate otherwise highly reactive molecular entities within an LD shell,²⁷ as demonstrated recently for bulky NHC coordinated main group compounds²⁸ and the exceedingly crowded hexaphenylethane derivatives such as all-meta ^tBuhexaphenylethane (2).29-30

While hexaphenylethane is experimentally unknown, sterically much more crowded **2** is isolable and was characterized *via* XRD³¹ and NMR-spectroscopy.³² The origin of the stabilization was traced back to LD interactions between the ^tBugroups, which are deemed excellent DEDs.²⁹⁻³⁰ The otherwise delicate organic peroxide functionality³³ is also highly stabilized when embedded in the all-*meta* ^tBu-trityl motive leading to a m.p. (decomp.) of 253 °C in bis(tri(3,5-di-*tert*-butylphenyl)methyl) peroxide.³⁴ These peripheral LD interactions also give rise to an all-*meta* ^tBu-triphenylmethane dimer **1**₂ [Bis(tri(3,5-di-*tert*-butylphenyl)methane)], featuring the shortest C–H···H–C contact reported to date.



Figure 2. ORTEP representation of 1_2 derived from neutron diffraction data with ellipsoids drawn at 50% probability.

Hydrocarbon **1** crystallizes in the cubic space group $Pa\overline{3}$ as determined by XRD at 100 K. The asymmetric unit consists of one 3,5-di-⁶Bu-phenyl group attached to the central C_{α} -H_{α} moiety. Application of the S_6 symmetry operation present in $Pa\overline{3}$ along the C_{α} -H_{α} axis result in dimer **1**₂ with a $R_{C\alpha\cdots C\alpha}$ of 3.780(7) Å. As the XRD C–H bond length of $R_{C-H} = 1.00(4)$ Å already revealed a remarkably short C–H···H–C distance of 1.77(7) Å, we reckoned that the true distance must be significantly shorter because of the well known underestimation of XRD C-H bond distances.

Using NRD at the lowest achievable temperature of 20 K utilizing a large crystal with 2 mm edges, we determined the cubic, yet less symmetric space group $P_{2,3}$.³⁵ The new asymmetric unit consists of two distinguishable fragments, lowering the symmetry in the dimer to C_3 . While the C_{α} -H_{α} bond lengths are ordinary³⁶ (Table 1) with 1.088(5) Å and 1.098(5) Å the extremely short intermolecular H_{α}···H_{α}' contact of only 1.566(5) Å is the shortest reported to date.

To allow such short contacts well below their vdW radii,^{15,} ³⁷ the overall stabilization must derive from other parts of the molecule, which, based on the measured NRD data, do not suffer from significant deformations: The sp³ angles around the central carbon C_{α} amounts to 106.0° (H_{α} - C_{α} - C_i) and 112.7° (C_i - C_{α} - C_i); the C–C bonds are ordinary.³⁶ More importantly, there are 33 contacts within the attractive vdW-range below the sum of the atom radii (3.08 Å)³⁸ down to 2.39 Å. NRD measurements at higher temperatures (Table 1) reveal the expected structural temperature dependence resulting in an H···H distance change of $\Delta R_{H···H}$ (20 K \rightarrow 200 K) = 0.03 Å; linear extrapolation leads to a minimum $R_{H···H}$ of 1.563 Å at o K.

Table 1. Structural data of 1₂ determined by NRD and DFT computations.

	NRD		HSE-3c ^b		
T [K]	20	100	200	0	0
(state)				(<i>s</i>)	(<i>g</i>)
<i>R</i> -value	0.031	0.054	0.096		
Volume [ų]	7833.1(4)	7901.4(4)	8040.4(4	7676.	
)	9	
$H_{\alpha} \cdots H_{\alpha}'$	1.566(5)	1.577(6)	1.594(9)	1.555	1.634
	1.093(5) ^{c,}				
C_{α} - H_{α}	a	1.093(3)	1.091(5)	1.088	1.092
Ave. C _{alk} -H	1.090(7)	1.078(29)	1.068(45)	1.091	1.091
Ave. C _{arom} -	1.085(6)	1.085(2)	1.076(4)	1.082	1.082
Н					
C_{α} - C_{i}	1.515(1) ^c	1.515(1)	1.515(2)	1.509	1.513
H_{α} - C_{α} - C_{i}	106.0(1) ^c	106.0(1)	105.9(1)	105.9	104.8
$C_i - C_\alpha - C_i$	112.7(1) ^c	112.7(1)	112.8(1)	112.8	113.7
$\begin{array}{c} H_{\alpha}\text{-}C_{\alpha}\text{-}C_{i}\text{-}\\ C_{o} \end{array}$	39.8	39.8	40.1	39.8	45.3
$H_o \cdots Ph^a$	3.632	3.639	3.654	3.613	3.637
$H_o \cdots C_o'$	2.927(1)	2.958(1)	2.978(1)	2.917	3.062
^t Bu…Ph' ^a	5.192	5.136	5.140	5.025	4.982
^t Bu… ^t Bu' ^a	6.166	6.115	6.113	6.037	5.889

^aGroup centroid distances; ^bBasis set: def2-mSVP; ^cAve. of both molecules in $\mathbf{1}_2$ (*cf.* SI); ^dC_{α}-H_{α} = 1.088(5) Å; C'_{α}-H'_{α} = 1.098(5) Å.

To rationalize the structural peculiarities of 1_2 we employed DFT computations within the CRYSTAL14 software suite³⁹

utilizing the recently developed screened Fock exchange density functional composite scheme termed HSE-3c.⁴⁰ This efficient method includes the D₃ correction⁴¹ and a geometrical counterpoise correction scheme⁴² accounting for the basis set superposition error (BSSE) and improving the description of LD interactions. The primitive cell starting from the 20 K NRD data ($P2_13$) was fully optimized featuring relaxation of all atom positions as well as cell parameters. Due to the high symmetry of the molecular crystal we were able to reduce the atom count within the primitive cell from 856 reducible to 74 irreducible atoms.

The HSE-3c computed solid state structure is in good agreement with the NRD structure of 1, (Table 1). The H…H distance of 1.555 Å at o K reproduces the NRD extrapolated value within the error bounds. The volume of the primitive cell is 2% smaller than observed experimentally. This equals a thermal density gradient of $\approx 1 \text{ mg cm}^{-3} \text{ K}^{-1}$ (cf. SI), which deviates from the experimental value ($0.1 \text{ mg cm}^{-3} \text{ K}^{-1}$) but is in the typical range for organic crystals.⁴³ To estimate packing effects, 1, was computed in the gas phase at the same level of theory. This elongates the central H…H contact to 1.634 Å. Crystal packing therefore provides some nonnegligible stabilization to the tight H…H contact. Note that the often employed approximation of using molecularly (non-periodic) optimized structures as substitute for periodic crystal data is insufficient in our case and would lead to inconsistencies between theory and experiment of about 0.07 Å.

Closely related unsubstituted triphenylmethane 6^{44} and the all-*meta* methyl derivative 7 (*cf.* SI) crystallize in space groups different from $\mathbf{1}_2$, namely in *Pna2*₁ and *P* $\overline{1}$, respectively, and no linear head-to-head dimers can be discerned.

An energy decomposition analysis (EDA, Figure 3 and *cf*. SI)⁴⁵ of $\mathbf{1}_2$ at the B₃LYP-D₃^{ATM}(BJ)/def2-TZVPP level is instructive in understanding the roles of the various (arguably arbitrary) energy contributions to the overall stability of $\mathbf{1}_2$; the trends are mirrored by an SAPT(o) analysis (Figure S23). Of course, the steric bulk of the ^tBu-groups increase the overall Pauli exchange repulsion between the monomers significantly. However, all other contributions including electrostatics stabilize the dimer interactions, with the dispersion component being by far the most important.



Figure 3. The energy decomposition analysis of 1_2 at B3LYP-D3^{ATM}(BJ)/def2-TZVPP.

To estimate the overall stabilizing energy contributions of the ^tBu groups, the dissociation energy of 1_2 was computed by optimization at B₃LYP-D₃^{ATM}(BJ)/def2-TZVPP including thermostatistical corrections at PBEh-3c and compared to the unsubstituted symmetric triphenylmethane dimer 6_2 . Structure 1_2 is bound by 48.9 kcal mol⁻¹ of LD, dissociation

therefore is unfavored by $\Delta G_d^{298} = 7.7$ kcal mol^{-1.46} By omitting the ^tBu moieties the head-to-head arrangement of G_2 becomes unstable and about 77% of LD interaction is lost resulting in $\Delta G_d^{298} = -8.5$ kcal mol⁻¹. Solvation free energy contributions computed with BP86-COSMO-RS⁴⁷⁻⁴⁹ for CHCl₃ destabilize the dimerization of $\mathbf{1}_2$ by $\Delta \Delta G_d^{298} = -8.1$ kcal mol⁻¹. In addition we note a relatively large contribution of the (often repulsive) three-body Axilrod-Teller-Muto (ATM) dispersion terms^{46, 50-51} that enlarge the H…H distance by about 0.01 to 0.02 Å while decreasing the D_e from 30.9 to 27.7 kcal mol⁻¹.

Dimer 1, is formally the hydrogenation product of 2. Upon dissociation of 2 a second, local minimum was predicted to occur along the intrinsic reaction coordinate.²⁹ Such radical "van-der-Waals-complexes" -better termed LD-complexesare related to the "cage-effect".⁵² The bis(all-meta ^tButriphenylmethyl radical) LD-complex $\mathbf{8}_2$ with a C···C distance of 5.28 Å can be taken as a hydrocarbon analogue of structures with frustrated Lewis pairs (FLPs),⁵³ where the split central C-C bond corresponds to the unsaturated dative $D \rightarrow A$ bond. This analogy was recognized in the very first appearance of FLPs, where the authors depicted HPE derivatives as structures analogous to FLPs.⁵⁴ As FLPs are able to split H_{21}^{55} it seemed plausible to assume $\mathbf{8}_{2}$ may be able to split H_2 with I_2 being the formal product. Unfortunately, all experimental attempts to split dihydrogen with the corresponding radical 8. were unsuccessful, as solutions of 8. eventually hydrolyze over a period of one month to all-meta ^tBu-triphenylmethanol and all-*meta* ^tBu-triphenylmethane 1 when pressurized with H, or D, (for ease of identification by NMR, for details see SI). We attributed this finding to the fact that the barrier for H, cleavage is the highest when there is no polarization as is the case for 8.

From a different viewpoint, 12 may perhaps also be viewed as a "frozen early transition state" because of the very close contact of the H_{α} 's. Indeed, our computational analysis of the contact between the close hydrogens using the quantum theory of atoms in molecules (QTAIM)⁵⁶ reveals a bond critical point (Fig. S25) and the non-covalent interaction (NCI) plot⁵⁷ displays a strongly attractive region (Fig. S28). Such computed attractions in tight H…H contacts were also found in a study of 5.58 As such arrangements are far off equilibrium, an interpretation of the analysis of the density gradient is delicate and might lead to contradictory results. A bonding interaction between the H_{α} 's should weaken the respective C_{α} -H_{α} bond, measurable by a red-shifted C-H bond stretching frequency. However, experimentally the stretching vibration frequency of, e.g., 5 increases.¹⁶ Unfortunately, the central C-H IR absorptions are buried under other vibrational bands for 1_2 . Deuteration at the central methine carbon red-shifts the corresponding C-²H bond stretching frequency into the uncongested region around 2100 to 2300 cm⁻¹ but we did not observe additional absorptions (cf. Figure S15). The PBEh-3c computed central asymmetric (IR active) $v(C_{\alpha}$ -H···H-C_{α}) is about 56 cm⁻¹ blueshifted as compared to $v(C_{\alpha}$ -H) of the monomer, similar to what was found for 5.

Table 2. B3LYP-D3^{ATM}(BJ)/def2-TZVPP//PBEh-3c computations of the dimeric structures of unsubstituted triphenylmethane 6 and all-*meta* ^tBu-substituted 1. Distances in Å, energies in kcal mol⁻¹.

	1_2	6 ₂
$D_{\rm e}$	27.8	8.2
$\Delta H_{\rm d}^{298}$	26.6	8.7
$T\Delta S_{\rm d}^{298}$	18.9	17.2
$\Delta G_{ m d}^{298}$	7.7	-8.5 ^b
$\Delta G_{ m d;solv}^{298}$	-0.4 ^c	-8.3°
$E_{ m disp}$	48.9	11.3
$\Delta R_{\rm C-H}^{a}$	-0.007	-0.005
R _{CH···HC}	1.601	1.717

^aDifference to monomer; ^b ΔG < o means dissociation; ^cafter solvent correction [BP86-COSMO-RS:CHCl₃].

In summary, we have experimentally identified the shortest intermolecular H···H contact (1.566(5) Å) reported to date in the crystal structure of the all-*meta* ^tBu-triphenylmethane dimer 1₂, as analyzed by NRD at temperatures as low as 20 K. Solid state DFT computations reveal that crystal packing does affect this distance but is not chiefly responsible for this short H···H contact. Rather, large LD interactions exerted *via* the ^tBu-groups surrounding the compressed H···H contact stabilize 1₂. The ^tBu-groups act as DEDs and counter the otherwise energetically unfavorable head-to-head arrangement of H_α's.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details, NMR, IR, XRD and NRD data as well as computational details (coordinates, NCI Plot, QTAIM) (PDF)

AUTHOR INFORMATION

Corresponding Author

*prs@org.chemie.uni-giessen.de

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the Priority Program "Dispersion" (www.spp1807.de) of the Deutsche Forschungsgemeinschaft.

REFERENCES

- (1) Shaik, S.; Danovich, D.; Wu, W.; Su, P.; Rzepa, H. S.; Hiberty, P. C., *Nat. Chem.* **2012**, *4*, 195.
- (2) Roos, B. O.; Borin, A. C.; Gagliardi, L., Angew. Chem. Int. Ed. 2007, 46, 1469.
- (3) Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettinger, J. C.; Long, G. J.; Power, P. P., *Science* **2005**, *310*, 844.
- (4) Molins, E.; Miravitlles, C.; Espinosa, E.; Ballester, M., J. Org. Chem. 2002, 67, 7175.

- (5) Lenoir, D.; Wattenbach, C.; Liebman, J. F., *Struct. Chem.* 2006, *17*, 419.
- (6) Krebs, A.; Kaletta, B.; Nickel, W.-U.; Rüger, W.; Tikwe, L., *Tetrahedron* **1986**, *42*, 1693.
- (7) Huntley, D. R.; Markopoulos, G.; Donovan, P. M.; Scott, L. T.; Hoffmann, R., *Angew. Chem.* **2005**, *117*, 7721.
- (8) Irngartinger, H.; Lukas, K. L., Angew. Chem. Int. Ed. Engl. 1979, 18, 694.
- (9) Schreiner, P. R.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Schlecht, S.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A., *Nature* **2011**, *477*, 308.
- (10) Fokin, A. A.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E.
- Y.; Hausmann, H.; Serafin, M.; Dahl, J. E. P.; Carlson, R. M. K.; Schreiner, P. R., J. Am. Chem. Soc. **2012**, *134*, 13641.
- (11) F. Bettinger, H.; v. R. Schleyer, P.; F. Schaefer Iii, H., *Chem. Commun.* **1998**, 769.
- (12) Adcock, J. L.; Gakh, A. A.; Pollitte, J. L.; Woods, C., *J. Am. Chem. Soc.* **1992**, *114*, 3980.
- (13) Wu, W.; Gu, J.; Song, J.; Shaik, S.; Hiberty, P. C., Angew. Chem. Int. Ed. 2009, 48, 1407.
- (14) Ermer, O.; Mason, S. A., J. Chem. Soc., Chem. Commun. 1983, 105, 53.
- (15) Alvarez, S., Dalton Trans. 2013, 42, 8617.
- (16) Ermer, O.; Mason, S. A.; Anet, F. A. L.; Miura, S. S., J. Am. Chem. Soc. **1985**, 107, 2330.
- (17) Zong, J.; Mague, J. T.; Pascal, R. A., J. Am. Chem. Soc. 2013, 135, 13235.
- (18) There is an unpublished neutron diffraction study available for 5 that gives an H \cdots H distance of 1.531(8) Å for the central head-tohead Si-H bonds. Personal communication from Robert A. Pascal, Jr., March 26, 2017
- (19) Berstis, L.; Siegel, J. S.; Baldridge, K. K., PCCP 2014, 16, 1379.
- (20) Baldridge, K. K.; Siegel, J. S., J. Phys. Org. Chem. 2015, 28, 223.
- (21) Firouzi, R.; Shahbazian, S., Struct. Chem. 2014, 25, 1297.
- (22) Firouzi, R.; Shahbazian, S., *ChemPhysChem* **2016**, *17*, 51.
- (23) Eisenschitz, R.; London, F., Z. Phys. A **1930**, 60, 491.
- (24) London, F., Z. Phys. A **1930**, 63, 245.
- (25) London, F., Trans. Faraday Soc. 1937, 33, 8.
- (26) Grimme, S.; Huenerbein, R.; Ehrlich, S., *Chem. Phys. Chem.* 2011, *12*, 1258.
- (27) Wagner, J. P.; Schreiner, P. R., Angew. Chem. Int. Ed. 2015, 54, 12274.
- (28) Wagner, J. P.; Schreiner, P. R., J. Chem. Theory Comput. 2016, 12, 231.
- (29) Grimme, S.; Schreiner, P. R., Angew. Chem. Int. Ed. 2011, 50, 12639.
- (30) Rösel, S.; Balestrieri, C.; Schreiner, P. R., *Chem. Sci.* 2017, *8*, 405.
- (31) Kahr, B.; Engen, D. v.; Mislow, K., J. Am. Chem. Soc. 1986, 108, 8305.
- (32) Yannoni, N.; Kahr, B.; Mislow, K., J. Am. Chem. Soc. 1988, 110, 6670.
- (33) Lv, J.; Chen, W.; Chen, L.; Tian, Y.; Yan, J., *Thermochim. Acta* **2014**, 589, 11.

(34) Khuong, T.-A. V.; Zepeda, G.; Sanrame, C. N.; Dang, H.; Bartberger, M. D.; Houk, K. N.; Garcia-Garibay, M. A., *J. Am. Chem. Soc.* **2004**, *126*, 14778.

(35) Rösel, S.; Cañadillas-Delgado, L.; Logeman, C.; Mason, S. A.; Mossou, E.; Schreiner, P. R. *Exact determination of hydrogen positions in tris*(3,5-*di-tert-butyl phenyl)methane could reveal the shortest intermolecular CH*•••*HC contact*; 10.5291/ILL-DATA.5-12-321; Institut Laue-Langevin: Grenoble, 2016.

- (36) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R., *J. Chem. Soc., Perkin Trans.* 2 1987, S1.
- (37) Rowland, R. S.; Taylor, R., J. Phys. Chem. 1996, 100, 7384.
- (38) Rahm, M.; Hoffmann, R.; Ashcroft, N. W., Chem. Eur. J. 2016, 22, 14625.
- (39) Dovesi, R.; Orlando, R.; Erba, A.; Zicovich-Wilson, C. M.; Civalleri, B.; Casassa, S.; Maschio, L.; Ferrabone, M.; De La Pierre, M.;

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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	 Arco, P.; Noël, Y.; Caush, M.; Rérat, M.; Kittman, B., Int. J., and there is a standard strain Chem soc., <i>inp.</i>, 1997. (9) Brandenburg, J. G.; Caldeweyher, E.; Grimme, S., <i>PCCP</i> 2006, 1997. (9) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., <i>J. Chem. Poys.</i>, 2007. (9) Brann, A.; Whorn, S.; 2007. (9) Brann, A.; Whorn, Sci. 2007., 030, 100. (9) Alinold, B., Teller, E., J. Chem. Phys. 2009., 189, 0410. (9) Stant, A., <i>WRES:</i> Comput. Mol. Sci. 2019., 1690. (9) Kant, A., <i>WRES:</i> Comput. Mol. Sci. 2019., 1690. (9) Mato, Y., <i>J. PhysMath. Soc. Japan.</i>, 1993., 17, 629. (9) Mato, Y., <i>J. PhysMath. Soc. Japan.</i>, 1993., 17, 629. 				

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