Consistencies between experiments and quantum calculations of strained C–C single bond lengths

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Modern electron correlated methods can accurately predict the unusually stretched C–C single bond lengths substantiating experimental structural information.

Typical covalent bond lengths, such as 1.54 Å for C–C single bonds[1] have been one of the fundamental parameters in chemistry. At the same time, the possibility of unusually long C–C bond lengths has attracted much attention for its challenging nature raising the questions: is there an upper limit to the length of a stretched C–C single bond?

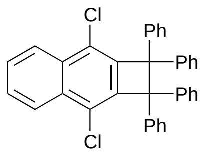
Recently, Toda *et al.*[2] have reported unusually long C–C bond lengths such as 1.720(4) Å in **1**, and 1.710(5) as well as 1.724(5) Å in **2**. They are considered the longest C–C single bonds accurately determined to date.[3] However, semiempirical methods have underestimated the length of the long bond in **1** by about 0.05 Å showing that special bonding effects exist that are not suitably covered by the current semiempirical parameters.[2]

In order to resolve these discrepancies between experiments and theories, full geometry optimizations[4] based on Hartree–Fock (HF) and density functional theory (DFT)[5] have been performed on **1**, as well as on other representative molecules (**3**, **4**, **5**) having strained long C–C bonds. Becke's 1988 (B)[6] and his three parameter hybrid (B3)[7] functionals incorporating exact exchange were used as gradient-corrected density functionals in combination with the Lee, Yang, and Parr (LYP)[8] correlation functional in the calculations.

Hagler *et al.*[9] have shown that high-level quantum calculations, including HF and DFT in combination with available gas electron diffraction data, can assign a unique structure of **3** in which C–C bond length between the center methane carbon and that of a *tert*-butyl group is as long as 1.622(6) Å[10] (see Table 1). It can be seen that while HF slightly underestimates and BLYP overestimates the stretched bond length in **3**, our B3LYP/6-31G* calculation agrees perfectly with experiment.

The crystal structure of **4** has been refined by Choi and Marinkas[11] at room temperature and by Abboud *et al.*[12] at 198 K. They have shown that its two bridge bonds connecting the two anthracene components are 1.624[11] and 1.618(3)[12] Å, respectively. MNDO calculations[13] underestimate this long single bond by 0.04 Å. Again, while the B3LYP value is in perfect agreement with the experimental long C–C single bond length, HF underestimates and BLYP overestimates it. The same trend can also be found in the calculations for **5**. The C–C bond length, 1.77 Å for the two bridging bonds of **5** determined by Ehrenberg[14] has been disputed by several studies.[13,15] They have concluded that Ehrenberg had investigated a mixture of two photodimers[13] and found the bond lengths to be 1.663(4)[15a] and 1.648(3)[15b] in their X-ray diffraction studies. Our B3LYP/6-31G* calculation as well as the earlier two DFT calculations are in excellent agreement with Harata *et al.*'s experiment. However, BLYP/6-31G* calculation overestimates it by 0.035 Å.

The overlong C–C bond length in **1** as calculated with B3LYP/6-31G* is in very good agreement with experiment showing excellent consistency between experiment and modern quantum calculations. The fact that HF systematically underestimates the stretched single C–C bond lengths indicates that



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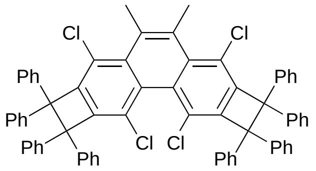

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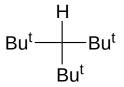

$HC(Bu^t)_3$

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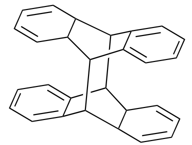

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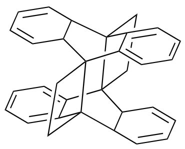

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Table 1 Experimental and theoretical long C–C bond lengths (Å)

Tris(*tert*-butyl)methane **3**					
Exptl.	HF/6-13G*[b]	DFT/BLYP[b]	DFT/ACM[b]	B3LYP/6-31G*[c]	
1.622(6)[a]	1.616	1.639	1.609	1.621	
Bis(9,10-dihydro-9,10-anthracenediyl) **4**					
Exptl.	MNDO[f]	HF/6-31G*[c]	BLYP/6-31G*[c]	B3LYP/6-31G*[c]	
1.618(3)[d],1.624[e]	1.585	1.605	1.645	1.623	
Bis(anthracene-9,10-dimethylene) **5**					
Exptl.	HF/6-31G*[g]	DF/Local[g]	DF/Non-Local[g]	BLYP/6-31G*[c]	B3LYP/6-31G*[c]
1.648(3)[g], 1.663(4)[h]	1.635	1.661	1.673	1.698	1.667
1,1,2,2-Tetraphenylcyclobutaarenes: 3,8-dichloro-1,1,2,2-tetraphenylcyclobuta[b]naphthalene **1**					
Exptl.	MNDO[i]	HF/6-31G*[c]	BLYP/6-31G*[c]	B3LYP/6-31G*[c]	
1.720(4)	1.676	1.686	1.789	1.732	

[a] Ref. 10. [b] Ref. 9. [c] This work. [d] Ref. 12. [e] Ref. 11. [f] Ref. 13. [g] Ref. 15(*b*). [h] Ref. 15(*a*). [i] Ref. 12.

electron correlation effects in describing the lengthened bonds are essential. Since extreme bond lengthening is accompanied by large changes in electron correlation at the beginning of bond breaking, the underestimation of the bond length by HF is not surprising. Furthermore, our results show that incorporating the exact exchange term *via* Becke's three parameter methods (B3) is also very important to obtain accurate results in these kinds of chemical bonds.

In summary, on the basis of first principle calculations, the existence of the unusually long bond length of **1** has been further substantiated. The consistencies between experiments and modern quantum calculations have been demonstrated by comparing four representative molecules. It is clearly seen that electron correlation effects have to be included in the calculations to correctly describe lengthened bonds.[16]

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Footnote and References

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16 Fully optimized geometry is available upon request.

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