Tetraphenyldihydrocyclobutaarenes—what causes the extremely long 1.72 Å C–C single bond?

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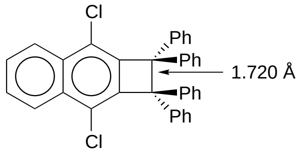
The exceptional 0.19 Å lengthening (to 1.720 *vs.* 1.53 Å in ethane) of the C_{sp^3}–C_{sp^3} bond in tetraphenyldihydrocyclobutaarenes is attributed to a combination of cyclobutene ring strain (0.04 Å), through-bond coupling (0.08 Å) and steric repulsion (0.07 Å) by comparison with model systems.

The 1.720(4) Å C_{sp^3}–C_{sp^3} distance in 3,8-dichloro-1,1,2,2-tetraphenylcyclobuta[*b*]naphthalene **1** is currently the longest known single bond length in hydrocarbons.[1–3] Since semiempirical methods (PM3 and MNDO) underestimate the C_{sp^3}–C_{sp^3} bond length in **1** by as much as 0.05 Å,[3] it was suggested that 'special bonding effects exist'[2] in **1**. Moreover, recent studies concluded that through-bond coupling 'never has more than a 2–3 pm effect'[4] on the length of the mediating single bond.[4,5] Hence, we agree that the extremely long C–C single bonds in 1,1,2,2-tetraphenyldihydrocyclobutaarenes[3] 'are of utmost importance for our understanding of chemical bonding.'[2] Choi and Kertesz recently showed that electron correlation effects have to be included in order to give agreement between quantum mechanical calculations and experiment.[6]



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We computed the geometry of C_2 symmetric **1** at various levels of theory.‡ Since B3LYP/6-31G** gives the best agreement with the X-ray data of **1** (Fig. 1), all subsequent calculations on model systems **2**–**6** were carried out with this hybrid functional.[9,12] Note that at HF/6-31G** the C_{sp^3}–C_{sp^3} bond length of **1** is underestimated by 0.06 Å. The C_{2v} symmetric form of **1** is a transition state at HF/STO-3G (81*i* cm^{-1}) and 9.4 kcal mol^{-1} higher in energy at B3LYP/6-31G** than the C_2 ground state.

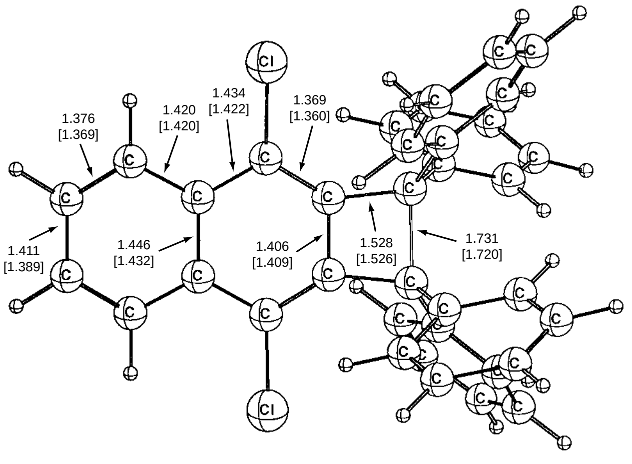

Fig. 1 The structure of 3,8-dichloro-1,1,2,2-tetraphenylcyclobuta[*b*]naphthalene **1** optimized at the B3LYP/6-31G** level of theory. Bond lengths are in Å, experimental bond lengths are given in brackets.

Which effects cause the extremely long bond in **1**? A very similar C_{sp^3}–C_{sp^3} distance (1.718 Å) as for **1** (1.731 Å) is computed for 1,1,2,2-tetraphenylbenzocyclobutene **2** (Fig. 2). Obviously, the two chlorine atoms and the presence of the annelated naphthalene (instead of benzene) ring have only a small influence on the C_{sp^3}–C_{sp^3} bond length. Ring strain in the cyclobutane moiety engenders elongated C_{sp^3}–C_{sp^3} bonds in cyclobutane **3** (1.555 Å),[13] in cyclobutene **4** (1.566 Å, *via* microwave analysis)[14] and in benzocyclobutene **5** (1.580 Å, *via* X-ray analysis)[15] with respect to ethane (1.535 Å; 1.530 Å at B3LYP/6-31G**).[16] the C_{sp^3}–C_{sp^3} bonds in **1** and **2** are 0.14–0.15 Å longer than in the parent compound **5**. However, abnormally long C–C single bonds in the 1.64–1.66 Å range have been observed previously for cyclobutane derivatives with vicinal phenyl groups.[1,2]

The lengthening of a mediating C–C single bond by vicinal phenyl groups has been attributed to through-bond interactions[17] of the favorably aligned π-oribtals of the benzene rings.[1] The benzene rings in **1**, *trans*-1,2-diphenylbenzocyclobutene **6** and **2** are orientated ideally, and due to the low lying σ*(C_{sp^3}–C_{sp^3}) orbital of the cyclobutane ring, the through-bond interaction is expected to be enhanced.[1]

A distance of 1.622 Å between the C_{sp^3} centers is obtained for **6**. Inspection of the MOs reveals an orbital ordering similar to the one reported for *anti*-1,2-diphenylethane.[4] Through-bond coupling is indicated by the reversal of the conventional out-of-phase above in-phase MO ordering,[5] and through-space coupling is not observed due to the 3.72 Å separation of the benzene rings. Thus, the bond elongation of 0.042 Å in **6** with respect to **5** can only be ascribed to through-bond interaction, and is significantly larger than the 0.02–0.03 Å limit of Baldridge *et al.*[4]

Assuming that the elongation effect is additive, a C_{sp^3}–C_{sp^3} bond length of 1.58 + 2 × 0.04 = 1.66 Å, based on through-

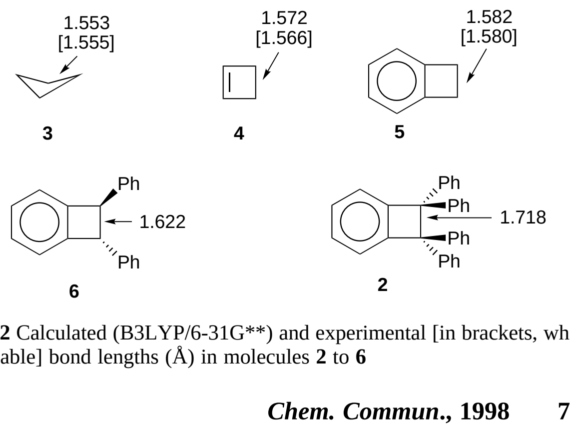

Fig. 2 Calculated (B3LYP/6-31G**) and experimental [in brackets, where available] bond lengths (Å) in molecules **2** to **6**

bond interaction, is expected for **2**. The difference of 0.07 Å with the calculated 1.73 Å length can be ascribed to repulsive steric interactions (and perhaps to through-space interactions) among the phenyl groups.

Indeed, the MM2[18] value for the C_{sp^3}–C_{sp^3} bond length in **2** is 1.651 Å, 0.08 Å shorter than the B3LYP/6-31G** result. As MM2 includes ring strain effects and steric congestion, but not through-bond interactions, our estimate of 0.08 Å as the contribution of the latter effect seems to be reasonable. The C_{sp^3}–C_{sp^3} bond in **1** is 0.18 Å longer than in cyclobutane **3**. Of this, the benzoannelation strain (*i.e.* in **5**) contributes 0.03 Å. Through-bond interaction elongates the bond by an additional 0.08 Å, and repulsion and possible through-space interaction of the phenyl groups contributes another 0.07 Å.

The elongation of a bond is in general associated with the decrease of the corresponding force constant. Thus, a perturbation's effect on the bond length is larger for an already elongated bond than for a 'normal' bond. We conclude that bonds which are weakened (elongated) by other influences are more prone to further bond lengthening by through-bond coupling than concluded recently.[4]

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Notes and References

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‡ The C_{sp^3}–C_{sp^3} bond lengths of **1** are 1.658 Å at AM1 (ref. 7), 1.686 Å at HF/6-31G**, 1.788 Å at BLYP/6-31G** (refs. 8(*a*), 9], 1.757 Å at BP86/6-31G** [refs. 8(*a*), 10], 1.692 Å at BHLYP [ref. 8(*b*)] and 1.731 Å at B3LYP/6-31G** [refs. 8(*c*), 9]. All computations employed GAUSSIAN 94 (ref. 11).

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