Overcoming lability of extremely long alkane carbon-carbon bonds through dispersion forces

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1. Introduction

1.1. Steric effects in chemistry.

• Questions relating to steric chemistry.

    1.   Why are branched alkanes more stable compared to linear alkanes?[1]

    2.   What is the smallest saturated acyclic alkane that cannot be made?[2]

    3.   How long is the C-C single bond length that can be constructed? (this work)

    ⇨ Repulsion forces are usually main focus in these chemistry.

    ⇨ However, consideration of attractive interactions through van der Waals forces

       are necessary to understand chemical bonding and reactivity fully.

• Pauli repulsion

    ➤ The repulsion force to avoid overlap of electron density.

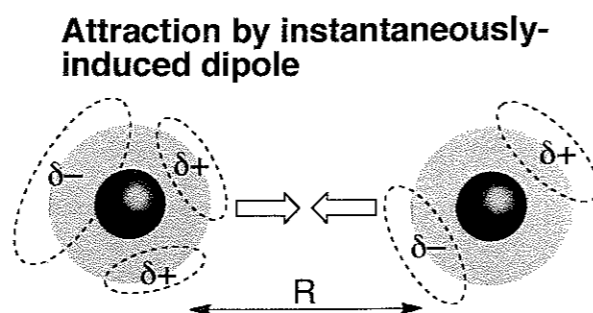**Overlap of electron density**
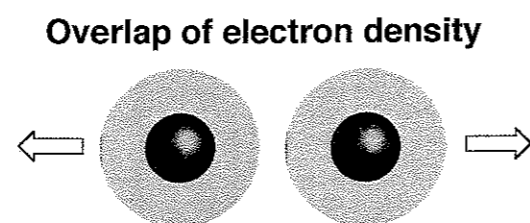
• Van der Waals forces (including London dispersion force)

    ➤ Repulsion and also *attractive* force.

    ➤ Instantaneously-induced (London dispersion force) or permanent dipole causes weak forces.

    ➤ The strength is proportional to R^{-6}, where R is the distance between two moieties concerned.

Attraction by instantaneously-induced dipole

1.2. Long C-C bonds.

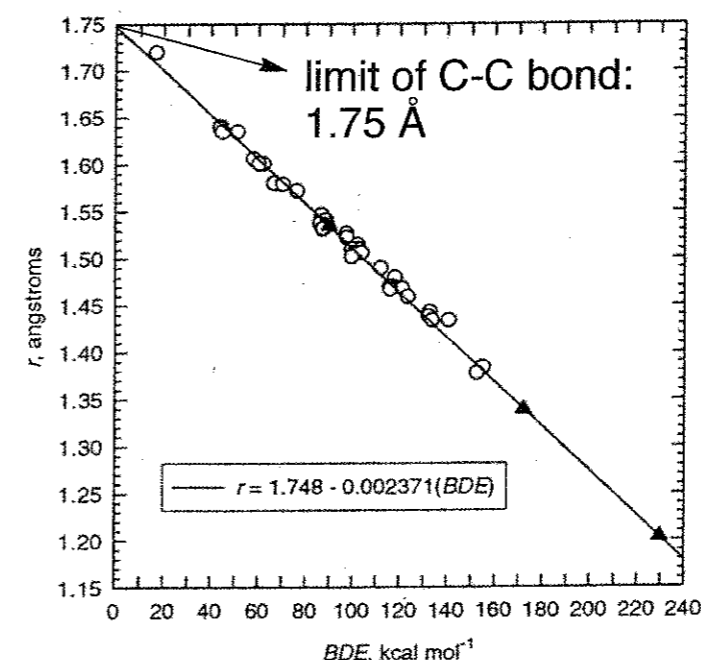• Empirical bond distance/bond strength relationships have been established for C-C bonds[3] (Figure 1).

Figure 1. C-C bond length vs bond dissociation energy (BDE)[3].
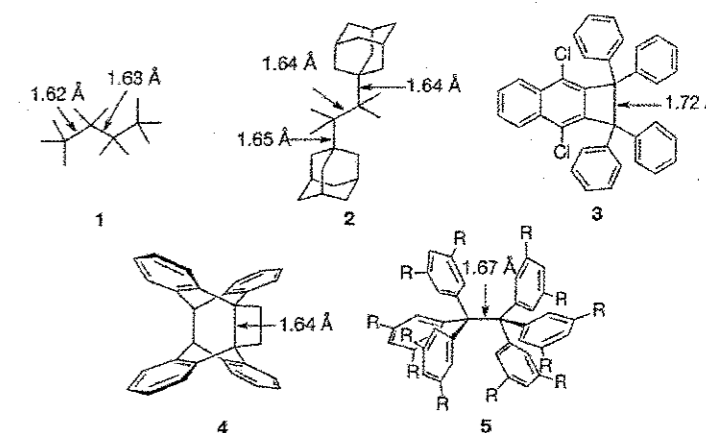
$$r = 1.748 - 0.002371(BDE)$$

Figure 2. Hydrocarbons with exceptionally long C-C bonds.

• Records up to date (see Figure 2, note that normal sp^3C-sp^3C length is 1.54 Å)

    a.   1.64 Å for alkane **2**.

    b.   1.72 Å for naphthocyclobutane derivative **3**.

    c.   1.67 Å for isolated hexaphenylethane derivative **5** (R = *t*-Bu).

    ⇨ All these long bonds are the result of steric crowding.

    ⇨ These bonds are so long that they are thermally labile at room temperature, homolytically cleave to yield corresponding radical species.

    ⇨ How to overcome this bond weakening caused by the repulsions?

1.3. This Work.

• The longest *alkane* C-C bond know to date was constructed.

    ➤ 1.704 Å for **7·8** (Figure 3).

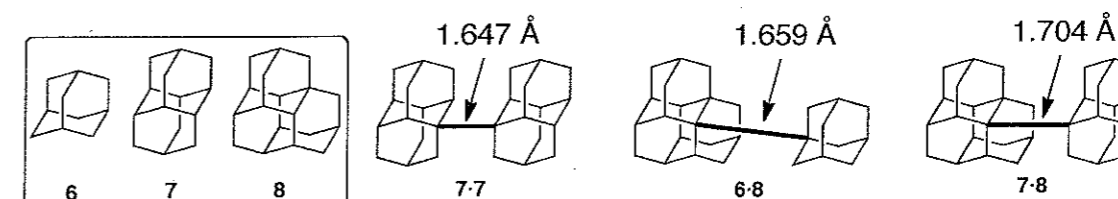   ➤ Use of attractive dispersion forces to suppress bond dissociation.

Figure 3. Structures of newly synthesized alkanes that have exceptionally long C-C bonds.

2. Results and Discussion

2.1. Design strategy for long C-C bonds.

• Repulsive forces are necessary.

• However, elongation of a bond finally leads to bond dissociation.

 ➢ According to the literature[3], empirical BDE of C-C bond become negative beyond bond length of 1.75 Å.

 ➢ Attractive forces to suppress bond dissociation are key to the formation of long C-C bond.

• Diamondoids to construct long C-C bond with attractive forces.

 ➢ Bulky structure for repulsive forces.

 ➢ Hydrogen-hydrogen van der Waals contacts causes attractive dispersion interaction to suppress bond dissociation.

2.2. Synthesis.

• Wurtz coupling of diamondoid bromides gave target compounds.
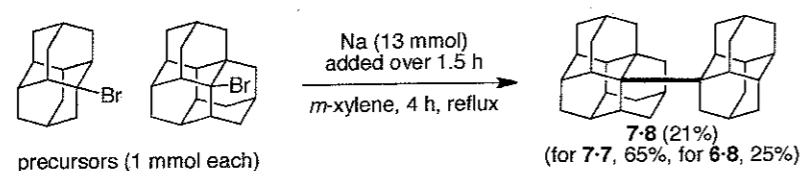
2.3. Properties.

• Extraordinarily long C-C bonds (1.647-1.704 Å) (see Figure 3).

 ➢ 7·8 has the longest C-C bond length (1.704 Å) for alkane up to date.

• High melting temperature and high thermal stability

 ➢ 7·7 is stable up to at least 300 °C (m.p. 360 °C), 6·8 slowly decomposes at 300 °C (m.p. 310 °C) and 7·8 starts decomposition at 220 °C.

• H···H contacts between the two hydrocarbon moieties are mostly between 2.2-2.3 Å, which corresponds well to the value usually found in crystal structure (2.2-2.4 Å).
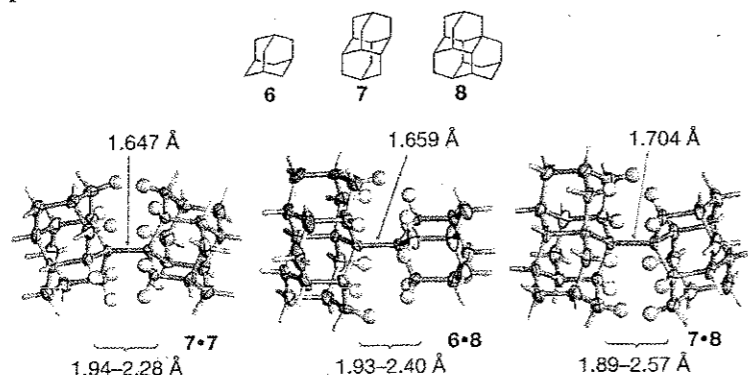

Figure 3. X-ray crystal structures of 7·7, 6·8 and 7·8.

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2.3. Computational study of 7·7 using 5 as the reference.

• Widely used B3LYP method does not reproduce dispersion forces[4].

 ➢ Use of dispersion corrected method, B3LYP-D.

 ➢ Other methods that account for dispersion interactions: B97D and M06-2X.

• For 5 (R = H), inclusion of dispersion corrections increases both BDE and C-C bond length. However, For 7·7, inclusion of dispersion corrections increases BDE, but reduces C-C bond length, which is also the case with 5 (R = t-Bu).

 ⇨ For 5 (R = H), attractive dispersion interactions are not so strong.

 ⇨ For 5 (R = t-Bu), attractive dispersion interactions increased by addition of t-Bu moieties, as is the similar case in 7·7.

Table 1. The BDEs and C-C bond lengths of 7·7 and 5 computed at various level of DFT.

Method/quantity	7·7 BDE (kcal mol⁻¹)	7·7 C-C (Å)	5 (R = H) BDE (kcal mol⁻¹)	5 (R = H) C-C (Å)	5 (R = t-Bu) BDE (kcal mol⁻¹)	5 (R = t-Bu) C-C (Å)
B3LYP/6-31G(d,p)	inc. {43.9	dec. {1.674	inc. {−20.9	inc. {1.730	inc. {−26.1	dec. {1.709
B3LYP-D/6-31G(d,p)	70.7}	1.653}	10.3}	1.735}	44.5}	1.674}
B97D/6-31G(d,p)	64.5	1.668	6.5	1.791	38.8	1.698
M06-2X/6-31G(d,p)	65.8	1.648	12.3	1.702	33.0	1.669
Experiment	―	1.647	―	―	―	1.670(3)

3. Conclusions

• By using attractive dispersion force, alkanes that have exceptionally long C-C bond have isolated and characterized.

• Consideration of attractive interactions including van der Waals forces is necessary for understanding of chemical bonding.

4. References

1) Silva, K. M. N.; Goodman J. M. *J. Inf. Model.* **2005**, *45*, 81.

2) Grimme, S. *Angew. Chem. Int. Ed.* **2006**, *45*, 4460.

3) Zavitsas, A. A. *J. Phys. Chem. A*, **2003**, *107*, 897.

4) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463.

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