The Nature of the Long Bond in 3,8-Dichloro-1,1,2,2-tetraphenylcyclobuta[*b*]naphthene

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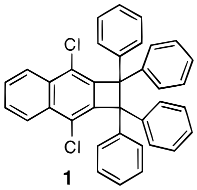
Recent studies involving quantum mechanical computations[2,3] and X-ray crystallographic structure determination[4−6] have dispelled the notion of through-bond coupling as the cause of the long bonds in polyarylethanes. Since the completion of that work, a remarkable bond length of 1.72 Å has been reported for the C(sp^3)−C(sp^3) bond in 1,1,2,2-tetraphenyl-3,8-dichloronaphthenocyclobutene, (**1**).[7] Given the long-standing success of Pauling's bond length/bond order structure correlation,[8] C−C bond lengths greater than 1.70 Å (i.e., bond orders approaching 0.5) deserve special examination and explanation. Variable steric and electronic factors have led to hexaarylethanes with bond lengths ranging from 1.54 Å for 9,9-ditrypticyl (**2**)[9] to 1.67 Å for hexaphenylethane (**3**).[10] In addition, a search of the Cambridge Structural Database (CSD) uncovers ca. 90 examples of C(sp^3)−C(sp^3) benzocyclobutane bonds (Figure 1) that cluster about 1.58 ± 0.5 Å.[11] Thus, the C−C bond length in **1** is a significant outlier no matter what model one takes as "normal." Specifically, the structure report of **1** and cognates raises two important questions:[12] (1) What is the reliability of the reported length? (2) If reliable, what is the origin of the long bond?



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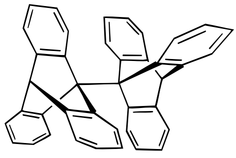

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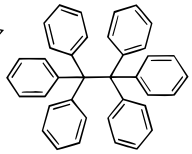

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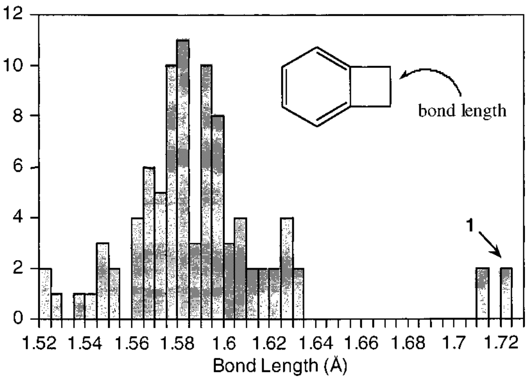

Figure 1. Histogram of C(sp^3)−C(sp^3) benzocyclobutane bond lengths as retrieved from CSD.

Distance (Å)	
C3–C14	1.710(2)
C3–C4	1.535(2)
C14–C13	1.526(2)
C4–C13	1.403(2)
Angle (°)	
C13–C4–C3	95.4(1)
C4–C3–C14	84.2(1)
C3–C14–C13	84.3(1)
C14–C13–C4	96.1(1)

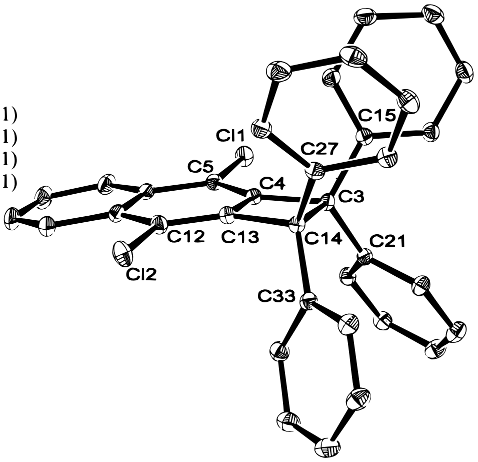

Figure 2. ORTEP plot of **1** (90 K data; ellipsoids shown at the 50% level).

To confirm the experimental bond length in **1**, we redetermined the X-ray crystal structure by collecting data at low temperature (90 K).[13−16] Refinement of this highly accurate data set converged on a C−C bond length of 1.710(2) Å, in excellent agreement with the value determined from room-temperature data.[8] As seen in the ORTEP plot (Figure 2), the thermal ellipsoids of the carbon atoms in the crucial bond are small and almost spherical, supporting the accuracy of the atomic positions found in this structure.

To address the bond length computationally it was necessary to establish a suitable level of theory and model structure.[17−27] Benzocyclobutene (**4**) and naphthocyclobutene (**5**) are reasonable structural cognates, with C(sp^3)−C(sp^3) bond lengths of 1.586 (1.574) Å and 1.586 (1.574) Å, respectively [B3LYP/dz(2d,p)

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(13) Crystallographic data for **1**: $C_{36}H_{24}Cl_2$, MW = 527.45, yellow crystals, monoclinic, space group $P2_1/n$, $Z = 4$, $T = 90$ K, $a = 8.877(3)$, $b = 16.662(3)$, and $c = 17.579(3)$ Å, $\beta = 96.373(19)°$, $V = 2583.9(10)$ Å^3, λ(Mo Kα) = 0.710 73 Å, $\mu = 0.276$ mm^{-1}, Rigaku AFC6A four-circle diffractometer using an Oxford Cryosystem Cooler,[14] $\theta/2\theta$ scans, 7987 measured reflections within $4.6° < 2\theta < 60°$ of which 7548 are independent, 5719 with $I > 2.0\sigma(I)$. The structure at room temperature was used as the initial structure for the refinement which was based on $|F_o|^2$.[15] $R = 0.0386$ for 439 variables. GOF = 1.030. Residual density 0.457/−0.233 eÅ^{-3}. Data reduction and molecular graphics were carried out using Xtal.[16]

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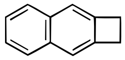
Table 1. Comparison of "Long" Bond Lengths (in Å) for Calculated Structures

molecule	RHF/ dzv(2d,p)	B3LYP/ dz(2d,p)	molecule	RHF/ dzv(2d,p)	B3LYP/ dz(2d,p)
4 (C_{2v})[a]	1.574	1.586	**9** (C_s)	1.609	1.636
5 (C_{2v})[b]	1.574	1.586	**8** (C_2)	1.584	1.598
7 (C_2)	1.587	1.596	**6a** (C_2)		1.708
10 (C_s)	1.588	1.599	**6b** (C_{2v})		1.722

[a] exp = 1.565(2). See: Crawford, J. L.; Marsh, R. E. *Acta Crystallogr. Sect. B* **1973**, *29*, 1238. [b] exp = 1.580(1). See: Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304.

(RHF/DZV(2d,p))] (Table 1). From the similarity of the carbon−carbon bond lengths in **4** and **5**, we assumed that 1,1,2,2-tetraphenylbenzocyclobutene (**6**) would be a suitable model for **1**. Computations (B3LYP/dz(2d,p)) on **6** in a C_2 conformation similar to that found crystallographically for **1** predict a bond length of 1.708 Å *in excellent agreement with the experimental observation* for **1**. Similar computational predictions for **1** have been made in other laboratories.[12b,28] Alternatively, one could imagine a more symmetric C_{2v} conformation and that the C_2 conformation was a result of packing forces. Computations (B3LYP/dz(2d,p)) on **6** in a C_{2v} conformation displayed a yet longer bond (1.722 Å), but this structure was found to be a nonminimum stationary point (1 negative eigenvalue) 8.8 kcal/mol higher in energy than the C_2 form. Given the accurate X-ray analysis and the concurrence of computational bond lengths, it is reasonable to accept the 1.71 Å bond length for **1** as fact and assume the B3LYP/dz(2d,p) is an appropriate computational level.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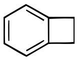
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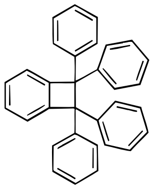
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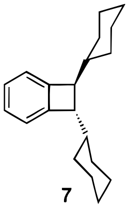
The question of the origin of the bond length can be addressed by comparison of a series of related computationally structures such as **7**−**10**. The pair **7**/**8** allow one to deduce the approximate bond lengthening one might see if through-bond coupling were an important effect. As in previous studies,[3] the control (**7**) and "active" (**8**) compounds have essentially indistinguishable bond lengths (1.596 vs 1.598 Å, respectively). This observation argues against any through-bond coupling effect on the geometry of **8**, and indicates that two generic substitutions on **4** in an anti arrangement might lengthen the bond by ca. 1 pm. The structure of **9** allows one to see the additional steric effects introduced by having two phenyl groups cis to one another. This large through-space coupling (i.e., steric effect) is accompanied by an increased bond length (1.636 Å at B3LYP/dz(2d,p)) of ca. 5 pm compared to **4**. Geminal substitution can also affect bond lengths and must be taken into account in any full analysis. The bond length in **10** (1.599 Å) shows that geminal effects are small in the present system, ca. 1 pm.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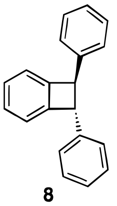
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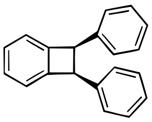
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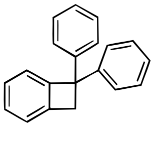
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From the above series of compounds, one can define a series of steric increments for bond lengthening compared to the bond in **4**. Adding together these various empirical lengthening effects, one would predict a bond length in **1** of 1.69−1.73 Å, well within the experimentally determined range. The steric bond lengthening effect in **1** is nonetheless extreme and would indicate a bond order of between 0.5 and 0.6. That such a bond can be faithfully represented by computational methods without CI or MCSCF treatments speaks to the strength of the interaction between the two nuclei.

A full orbital analysis of **6** is complicated by mixing in of the "benzo" orbitals; however, there is nothing striking that would point to a filled−empty through-bond coupling interaction. Indeed, the most exhalted orbital of the C_{2v} conformer of **6** (i.e., the structure with the longest bond and best geometrical arrangement of orbitals) is antisymmetric with respect to both mirror planes. The likely orbitals for filled−empty through-bond coupling are not commensurate enough in energy to show any mixing. Thus, there is no reason to invoke any special orbital interactions such as through-bond coupling to account for the bond length.

On the whole, we conclude that the extraordinary bond length for **1** is reliable and that its origin is primarily explained by a classical steric argument without the need to resort to orbital interactions such as through-bond coupling. Indeed, the distance between ipso carbons of cis-related phenyl groups is only ca. 3.0 Å, significantly shorter than van der Waals' spacing. As such, other larger groups such as *tert*-butyl should be able to push the bond even further, perhaps to exceed 1.75 Å.

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Note Added in Proof: A recent paper (Bettinger, H. F.; Schleyer, P. v. R. S.; Schaefer, H. F. *J. Chem. Soc., Chem. Commun.* **1998**, 769) concluded that through-bond coupling effects are geometrically important in **1**; however, their study (a) does not consider **7** and **9** and (b) predicts a bond length in **8** discrepant to our findings at B3LYP/631-G** (1.600 Å vs 1.622 Å), but coincident with BLYP/631-G**.

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(17) Calculations have been carried out to predict geometric and orbital energy trends using both conventional restricted Hartree−Fock (RHF)[18] and hybrid density functional (HDFT) theories. The ab initio calculations were performed with the aid of analytically determined gradients and the search algorithms contained within GAMESS,[19,20] using the dzv(2d,p)[21] basis set. This basis set includes 2 sets of six d polarization functions on all heavy atoms and 1 set of p functions on hydrogens. The HDFT calculations were performed with the Kohn−Sham formalism[22,23] within GAUSSIAN94,[24] using the Dunning/Huzinaga full double-ζ basis set, again including 2 sets of d functions for heavy atoms and 1 set of p functions for hydrogens.[21] This hybrid method includes a mixture of Hartree−Fock exchange with DFT exchange-correlation, denoted B3LYP. This is Becke's 3-parameter functional,[25] where the correction functional is provided by Lee, Yang, and Parr, and includes both local and nonlocal terms.[26,27] The nature of each stationary point was uniquely characterized by analytically calculating and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies.

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