ChemComm

The crystal and molecular structure of 2,7-di-*tert*-butyl-4,5,9,10-tetraphenylbenzo[1,2,:4,5]dicyclobutadiene: an exceptionally long C–C aromatic bond

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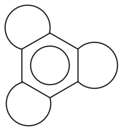
Received (in Cambridge, UK) 23rd December 1998, Accepted 4th January 1999

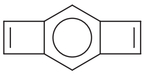
The X-ray determined structure of the title compound is reported; it was found that the annelated bonds are the longest observed in a benzene derivative [1.540(5) Å]; *ab initio* calculations (at the B3LYP/6-31G* and MP2/6-31G* levels of theory) were used in order to understand the electronic and structural properties of the compound.

Strain imposed on aromatic compounds alters the properties of the aromatic systems. Of particular interest is strain that is imposed in the σ-plane, namely, perpendicular to the π-system. When the strain is imposed in an angular manner (schematically shown in **1**) it causes the localization of the aromatic bonds.[1] When imposed in a linear manner (as in the title compound) the aromatic moiety changes dramatically.[2] However, in the particular case of benzo[1,2:4,5]dicyclobutadiene **2** it was predicted that this system should show two types of isomerism:[3] bond-stretch isomerism (**2a** with D_{2h} symmetry *vs.* **2b** and **2c** with C_{2v} symmetry) and Kekulé isomerism (*i.e.* **2b** *vs.* **2c**). As the title derivative of **2** was prepared some years ago,[4] and the study of its chemical and physical properties has not yielded conclusive answers,[5] and in light of the controversial issue of bond-stretch isomerism,[6] it was decided to characterize the structure crystallographically.

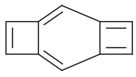
The title compound **3** was made as previously published.[4] Crystals suitable for X-ray analysis of this highly sensitive compound[4] were obtained by careful recrystallization from *p*-xylene. Five data sets of different crystals of different quality and at various temperatures were collected. All of them showed the same features that are presented in Fig. 1 (the essential bonding parameters can be found in the figure caption). In the monoclinic system (space group $C2/c$, a = 21.3735(5), b = 6.11890(10), c = 23.4144(6) Å, β = 99.8480(10)°, Z = 4),[7] the molecular structure was found to possess C_2 symmetry with some unexpected bond distances, especially in the central ring. To the best of our knowledge, the C(1)C(2) distance is the longest distance ever found in a benzene ring. The geometry is not expected to be essentially influenced by intermolecular contacts, which are mostly beyond van der Waals contacts; the closest are at H(9B) and H(12A) with 2.22 Å (C–H distances expanded to 1.08 Å).



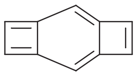
1



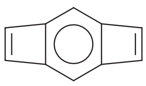
2a



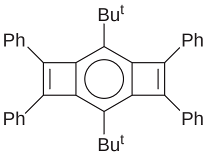
2b



2c



2d



3

Although Schulman and Disch[3] predicted unusual structures for **2**, all the structural features of **3** are different than those predicted theoretically. The symmetry of the benzobicyclobutadiene skeleton in **3** is D_{2h}, as in **2a**, but the bond lengths are closer to a hybrid of the two theoretical C_{2v} *isomers* **2b** and **2c**.[8a] However, the annelated bonds in **3** are shorter than the average of the respective bonds in **2b** and **2c**. Also, it looked like the more stable isomer was not the one that was experimentally found.[8b] In order to resolve this dichotomy, we decided to study the issue using *ab initio* calculations on **2** at higher theoretical levels.

GAUSSIAN 94[9] was used. The systems under study were optimized at the B3LYP/6-31G* and MP2/6-31G* theoretical levels, which have been shown to produce reliable structures for small-ring annelated benzene systems.[1c,10] Table 1 summarizes the geometry of the systems obtained at these levels of theory. It was found that there are only two bond-stretch isomers, both possessing D_{2h} symmetry. One is similar to **2a**, and the second one, **2d**, does not correspond to **2b** (or **2c**) but is similar that one found in the crystal structure of **3**. Furthermore, **2d** is theoretically predicted to be 2.4 and 3.7 kcal mol^{-1} (at B3LYP/6-31G* and MP2/6-31G*, respectively) more stable than **2a**.

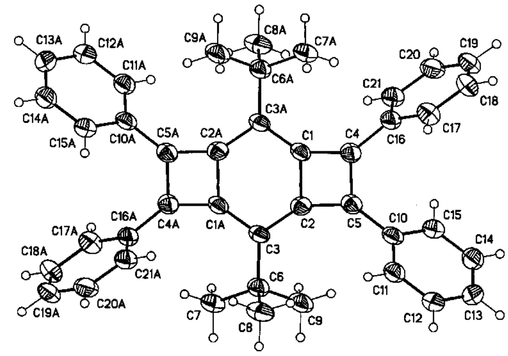


Fig. 1 Ellipsoid representation (50%) of **3**. Important distances (Å) and angles (°): C(1)–C(2) 1.540(5), C(2)–C(3) 1.416(5), C(1A)–C(3) 1.407(5), C(1)–C(4) 1.402(5), C(2)–C(5) 1.412(5), C(4)–C(5) 1.471(5), C(3)–C(6) 1.524(5), C(4)–C(16) 1.479(5), C(5)–C(10) 1.455(5), C(10)–C(11) 1.397(6), C(11)–C(12) 1.378(5), C(12)–C(13) 1.382(6), C(13)–C(14) 1.364(6), C(14)–C(15) 1.387(6), C(10)–C(15) 1.405(6), C(16)–C(17) 1.388(6), C(17)–C(18) 1.385(6), C(18)–C(19) 1.362(6), C(19)–C(20) 1.374(6), C(20)–C(21) 1.397(6), C(16)–C(21) 1.394(6), H(15)···H(17) 3.34; C(2)–C(3)–C(1A) 109.7(3), C(1)–C(2)–C(3) 123.7(3), C(2)–C(1)–C(3A) 126.0(3), C(1)–C(2)–C(5) 88.5(3), C(2)–C(1)–C(4) 88.6(3), C(1)–C(4)–C(5) 91.7(3), C(2)–C(5)–C(4) 91.0(3), C(10)–C(5)–C(4)–C(16) 11.3(6), C(5)–C(2)–C(3)–C(6) −3.1(8), C(5)–C(4)–C(16)–C(17) −64.5(5), C(4)–C(5)–C(10)–C(11) 136.1(4).

Table 1 Calculated (B3LYP/6-31G* and MP2/6-31G*) geometries and relative energies of the two isomers of **2**

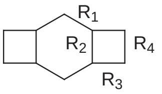
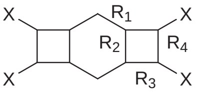
	Isomer	Level	R_1	R_2	R_3	R_4	ΔE/kcal mol^{-1}
	**2d**	B3LYP/6-31G*	1.3888	1.5641	1.3916	1.4583	−2.4
	2a	B3LYP/6-31G*	1.3944	1.4026	1.5430	1.3456	0
	2d	MP2/6-31G*	1.3898	1.5545	1.3921	1.4587	−3.7
	2a	MP2/6-31G*	1.3943	1.4082	1.5361	1.3456	00

Table 2 Bond-length differences between the calculated geometries of **2d** (at B3LYP/6-31G* and MP2/6-31G*) and **4** and **3**

	X	Level	ΔR_1	ΔR_2	ΔR_3	ΔR_4	Average error
	H (**2d**)	B3LYP/6-316*	−0.023	+0.024	−0.016	−0.013	0.019
	H (**2d**)	MP2/6-31G*	−0.023	+0.015	−0.016	−0.015	0.018
	Vinyl (**4**)	B3LYP/6-31G*	−0.021	−0.011	−0.001	+0.014	0.012

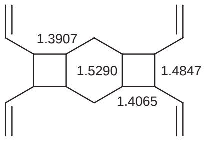


Fig. 2 B3LYP/6-31G* structure of **4** at D_{2d} symmetry (the experimentally found isomer).

Both isomers have been shown to be minima on the potential surface by frequencies calculations.

Although the agreement between the calculated and observed structures is reasonable, we have calculated the structure of the 4,5,9,10-tetraethenyl derivative of **2** (**4**), to see if the alkenyl substitution (that mimics the phenyl substitution in **3**) is responsible for (at least some) of the geometrical differences between the calculated and measured structures. Fig. 2 shows the geometry of **4** (at D_{2h} symmetry)[11] and Table 2 presents an error survey of the studied systems. The numbers in Table 2 suggest that (i) B3LYP/6-31G* and MP2/6-31G* describe the system with about the same accuracy,[12] and (ii) that at least a part of the discrepancy between the measured and calculated structures is due to the substitution. This can be concluded from the fact that the average error values for **4** are 37% smaller than for **2**, and that the sign of the error for different bonds is different.

We are currently studying the issue of interconversion between the two isomers theoretically, and are trying to prepare other derivatives of the title compound that may yield the other bond-shift isomer.

We thank The American – Israeli Binational Science Foundation, the Lise-Meitner-Minerva Center for Computational Quantum Chemistry, the VPR fund at the Technion and the Fonds der Chemischen Industrie for financial support.

Notes and references

1 (*a*) R. Boese, D. Bläser, W. E. Billups, M. M. Haley, A. H. Maulitz, D. L. Mohler and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 313; (*b*) N. L. Frank and J. S. Siegel, in *Advances in Theoretical Interesting Molecules*, JAI Press, London 1995, vol. 3, p. 209; (*c*) A. Stanger, *J. Am. Chem. Soc.*, 1991, **113**, 8277; (*d*) A. Stanger, *J. Am. Chem. Soc.*, 1998, **120**, 12 034.

2 J. M. Schulman, R. L. Disch, H. Jiuo and P. v. R. Schleyer, *J. Phys. Chem.*, in the press and references therein; K. P. C. Vollhardt and D. B. Mohler, in *Advances in Strain in Organic Chemistry*, ed. B. Halton, JAI Press, London, 1996, vol. 5, p. 121.

3 J. M. Schulman and R. L. Disch, *J. Am. Chem. Soc.*, 1993, **115**, 11 153.

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5 F. Toda, N. Dann, K. Tanaka and Y. Tekehira, *J. Am. Chem. Soc.*, 1977, **99**, 4529; F. Toda and P. Garratt, *Chem. Rev.*, 1992, **92**, 1685.

6 See, for example, A. Bashall, V. C, Gibson, T. P. Kee, M. McPartlin, O. B. Robinson and A. Shaw, *Angew. Chem.*, 1991, **103**, 1021; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 980; G. Parkin, *Acc. Chem. Res.*, 1992, **25**, 455; G. Parkin, *Chem. Rev.*, 1993, **93**, 887; K. Yoon, G. Parkin and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **114**, 2210.

7 *Crystal data* for **2**: $C_{42}H_{38}$, crystal dimensions 0.13 × 0.11 × 0.07 mm^3, green, mounted with polyfluorinated oil and measured on a Siemens SMART-CCD diffractometer (three-axis platform) with Mo-Kα-radiation at 130 K; a = 21.3735(5), b = 6.11890(10), c = 23.4144(6) Å, β = 99.8480(10)°, V = 3017.07(7) Å^3; monoclinic crystal system, Z = 4, D_c = 1.195 g cm^{-3}, μ = 0.067 mm^{-1}, space group $C2/c$, data collection of 8535 intensities ($2\Theta_{max}$ = 45°, one run 0.3° ω-scans, 120 frames at ϕ = 0°, four runs 0.3° ϕ-scans with 600 frames at angles 135, 143, 156 and 169° in ω, more than 97% of the data covered), absorption correction with Siemens SADABS (R_{merg} before/after = 0.115/0.063, max/min equivalent transmission = 1.00/0.60), 1910 independent intensities (R_{merg} = 0.103), 1479 'observed' data [$F_o \geqslant 4\sigma(F)$], structure solution with direct methods (Siemens SHELXS) and refined on F^2 (Siemens SHELXTL-Plus, ver. 5.01) (190 parameters), the hydrogen atom positions were calculated and refined as riding groups with 1.2-fold (1.5 for methyl groups) isotropic U values. $R1$ = 0.0827, $wR2$ = 0.2251, $w^{-1} = \sigma^2(F_o^2) + (0.103P)^2 + 6.50P$, where $P = [(\max F_o^2) + (2F_c^2)]/3$, max/min residual electron density = 0.264/−0.246 eÅ^{-3}. CCDC 182/1129.

8 According to Schulman and Disch (ref. 4): (*a*) the experimentally obtained structure is a transition state between the two Kekulé isomers **2b** and **2c**, and (*b*) **2a** was predicted to be more stable than **2b** by 17.9–20 kcal mol^{-1}.

9 GAUSSIAN 94, Revision E.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.

10 N. L. Frank, K. K. Baldridge and J. A. Siegel, *J. Am. Chem. Soc.*, 1995, **117**, 2102.

11 The discussion presented here for **4** regards the tetraethenyl derivative of isomer **2d**. However, **2a** also has a stable tetravinyl derivative. The two bond-shift isomers (*i.e.* **2a** and **2d**) also have other stable derivatives that show this isomerism, such as the tetrahydroxy and tetracyano derivatives (A. Stanger, unpublished results). These are, however, beyond the scope of this paper.

12 The agreement between the experimental and calculated structures is even better if the experimental σ value (0.005 Å for all the discussed bonds) is considered.

Communication 8/09116A