Title

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Citation

Chemical Communications, 1999(4): 319-320

Issue Date

1999-01-04

URL

http://hdl.handle.net/10112/5597

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Type

Journal Article

Textversion

publisher
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 π-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 moieties change 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 D2h symmetry vs. 2b and 2c with C5v 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 compound2 were obtained by careful recrystallization from xylene. Five data sets of different crystals of different quality and at various temperatures were collected. All of them showed 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).

Although Schulman and Disch7 predicted unusual structures for 2, all the structural features of 3 are different than those predicted theoretically. The symmetry of the benzo[1,2;4,5]dicyclobutadiene skeleton in 3 is D2h, as in 2a, but the bond lengths are closer to a hybrid of the two theoretical C7h isomers 2b and 2e.8,9 However, the annelated bonds in 3 are shorter than the average of the respective bonds in 2b and 2e. Also, it looked like the more stable isomer was not the one that was experimentally found.8,9 In order to resolve this dichotomy, we decided to study the issue using ab initio calculations on 2 at higher theoretical levels.

GAUSSIAN 949 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.1,10 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 D2h 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.

![Figure 1: Ellipsoid representation (50%) of 3. Important distances (Å) and angles (°): C(1)–C(2) 1.540(5), C(1)–C(3) 1.418(5), C(1)–C(4) 1.407(5), C(2)–C(3) 1.412(5), C(3)–C(4) 1.471(5), C(3)–C(5) 1.524(5), C(4)–C(6) 1.479(5), C(5)–C(6) 1.455(5), C(10)–C(11) 1.382(6), C(11)–C(12) 1.378(5), C(12)–C(13) 1.382(5), C(13)–C(14) 1.364(6), C(14)–C(15) 1.387(5), C(15)–C(16) 1.405(5), C(16)–C(17) 1.388(5), C(17)–C(18) 1.356(5), C(18)–C(19) 1.383(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(3) 126.0(3), C(1)–C(2)–C(5) 88.6(3), C(2)–C(1)–C(4) 88.6(3), C(1)–C(4)–C(3) 91.7(3), C(2)–C(3)–C(5) 91.4(3), C(10)–C(5)–C(4)–C(6) 11.3(6), C(5)–C(2)–C(3)–C(6) –3.18, C(5)–C(4)–C(16)–C(17) –64.5(5), C(4)–C(5)–C(10)–C(11) 136.1(4).]
Both isomers have been shown to be minima on the potential surface by frequency 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 3 is reasonable, we have calculated the structure of the 4,5,9,10-tetraethenyl derivative of 3. Fig. 2 shows the geometries of 4 (at D3h symmetry)\(^\text{11}\) 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,\(^\text{12}\) 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


7 Crystal data for C\(_\text{42}\)H\(_\text{38}\): 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-K\(_\alpha\) radiation at 130 K, \(a = 21.372(15), b = 6.188(10), c = 23.414(46)\) Å, \(\beta = 99.8480(10)\), \(\gamma = 3017.07(7)\) Å\(^3\); monoclinic crystal system, \(Z = 4\), \(D_\text{c} = 1.195 \text{ g cm}^{-3}\), \(\mu = 0.067 \text{ mm}^{-1}\), space group C\(_{2v}\), data collection of 8535 intensities (\(2\theta_\text{max} = 45\), one run 0.3°/0.2°, 120 frames at \(\theta = 0°\), four runs 0.3°/0.2° with 600 frames at angles 135, 143, 156 and 169° in \(\phi\) more than 97% of the data collected), absorption correction with Siemens SADABS \((R_\text{symb} = 0.103)\), 1479 'observed' data \([F_\text{obs} \geq 4\sigma F_\text{obs}]\), structure solution with direct methods (Siemens SHELXS) and refined on \(F^2\) (Siemens SHELXL-Plus, ver. 5.01) (190 parameters), the hydrogen atom positions were calculated and refined asriding groups with 1.2-fold (1.5 for methyl groups) isotropic \(U\) values, \(R_1 = 0.0827, wR_2 = 0.2251, w = 1/(\sigma^2 + 0.003P)^2\), \(P = \left[(\sigma^2 + 0.003P)^2 + 2(\sigma^2 F_\text{c})^2}\right]^{1/2}, \text{max/min residual electron density = 0.264/} -0.246 \text{ e}^{-\text{Å}^{-3}}\), CCDC 1821129.

8 According to Schulerman 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\(^{-1}\).


11 The discussion presented here for 4 regards the tetrathymethyl 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 tetracyclopropyldi-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 \(\sigma\) value (0.005 Å for all the discussed bonds) is considered.