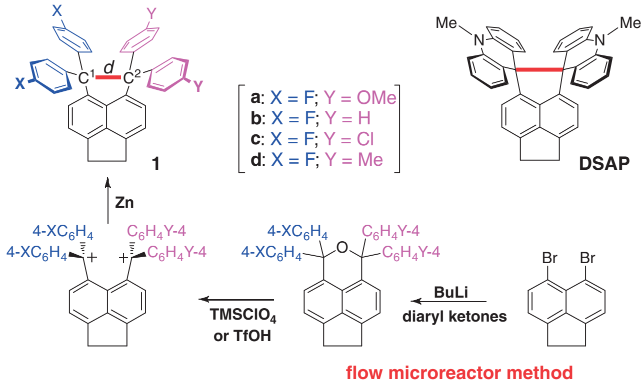
CL-130872 Received: September 21, 2013 | Accepted: September 30, 2013 | Web Released: October 9, 2013

Expandability of Ultralong C–C Bonds: Largely Different C^1–C^2 Bond Lengths Determined by Low-temperature X-ray Structural Analyses on Pseudopolymorphs of 1,1-Bis(4-fluorophenyl)-2,2-bis(4-methoxyphenyl)pyracene

Takanori Suzuki,*[1] Yasuto Uchimura,[1] Fumika Nagasawa,[1] Takashi Takeda,[1,†] Hidetoshi Kawai,[1,††] Ryo Katoono,[1]
Kenshu Fujiwara,[1] Kei Murakoshi,[1] Takanori Fukushima,[2] Aiichiro Nagaki,[3] and Jun-ichi Yoshida[3]
[1]*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-0810*
[2]*Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503*
[3]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering,*
Kyoto University, Kyoto 615-8510

(E-mail: tak@mail.sci.hokudai.ac.jp)

Low-temperature X-ray analyses on several pseudopolymorphs (solvate crystals) revealed that the C^1–C^2 bond length of the highly congested title molecule can adopt quite different values [1.700(6)–1.739(6) Å]. Such an unusual observation indicates that the ultralong covalent bond is endowed with "expandability," thus the prestrained bond can be elongated or shortened very easily accompanied by only a minute change in energy, which can be compensated by intermolecular perturbation in the crystal.



Scheme 1.

Not only from curiosity toward molecules with unusual structural parameters[1] but also from the viewpoint of the development of potential functions,[2,3] considerable recent attention has been focused on ultralong C–C bonds with bond lengths beyond 1.70 Å (standard: 1.54 Å[4]). They are rare but have actually been found in highly congested organic compounds such as condensed hexaphenylethanes[5] or caged-alkane dimers.[6] Based on rational design[7] to stabilize the compounds despite the presence of the C–C bond with a very small bond dissociation energy (BDE), we succeeded in obtaining di(spiroacridan)pyracene (DSAP) with the longest C–C bond,[8] whose bond length [1.791(3) Å at 413 K; 1.771(3) Å at 93 K] is as large as the distance of the shortest nonbonded C$\cdots$C contact [1.80(2) Å].[9]

During the course of our further studies, we have found that a series of 1,1,2,2-tetraarylpyracenes **1** having a common hydrocarbon skeleton with DSAP can serve as an ideal platform for scrutinizing the novel properties of extremely long C–C bonds. The "front strain"[10] among the four aryl groups in **1** is large enough to expand the C^1–C^2 bond beyond 1.70 Å as determined precisely (esd: 0.002–0.004 Å) [e.g., $\mathbf{1F_4}$: $X = Y = F$, $d = 1.761(4)$ Å; $\mathbf{1H_2\text{-}OMe_2}$: $X = H$, $Y = OMe$, $d = 1.714(2)$ Å].[2b,11] Although we did not get any indication that suggests the electronic nature of different aryl groups affecting the C^1–C^2 bond length (d), a wide variation of bond length (Δd: 0.047 Å) was observed for a series of pyracenes **1**, which cannot be explained by considering *intramolecular* factors.

To confirm that the crystallographically determined d value is largely affected by the *intermolecular* perturbation (e.g., crystal packing force), we planned to conduct X-ray analyses of the polymorphs or pseudopolymorphs (solvated crystals) of a certain derivative of **1**, in which only the *intermolecular* factors are responsible for the Δd value, if observed. By considering that fluorinated aromatic compounds often form polymorphs or pseudopolymorphs,[12] bis(4-fluorophenyl) derivatives **1a**–**1d** ($X = F$) were designed in this work. We found here that the title compound **1a** ($X = F$; $Y = OMe$) forms many pseudopolymorphs by incorporating a variety of solvent molecules in the crystal lattice, each of which contains molecule(s) of **1a** with a different C^1–C^2 bond length (Δd: 0.039 Å) as we expected. The details will be shown herein.

By following a procedure we developed previously,[2b,11] sterically hindered tetraarylpyracenes **1a**–**1d**[13] were prepared from 5,6-dibromoacenaphthene and isolated as stable crystalline solids (Schemes 1 and S1[14]). The key step is the selective introduction of two different diarylmethyl groups,[15] which was successfully realized by reaction integration using flow microreactors.[16] Upon recrystallization of **1a**–**1d** from $CHCl_3$–hexane or CH_2Cl_2–hexane, single-crystalline samples suitable for X-ray structural analyses were successfully obtained.[14,17] Absence of any electronic effects of aryl substituents on d was again verified by the nonadditive substituent effects for **1b**–**1d**[18,19] [$d = 1.740(3)$, 1.730(4), and 1.722(4) Å, respectively]. Thus, the d values are quite different from those expected from the corresponding symmetric derivatives [$\mathbf{1H_4}$: $X = Y = H$, $d = 1.754(2)$ Å; $\mathbf{1Cl_4}$: $X = Y = Cl$, $d = 1.730(2)$ Å; $\mathbf{1Me_4}$: $X = Y = Me$, $d = 1.717(4)$ Å][2b,11] (Figure S1).[14]

Different from **1b**–**1d** or $\mathbf{1F_4}$,[2b] **1a** gave pseudopolymorphs by including an equal number of solvent molecules in the unit cell [$\mathbf{1a}\cdot CHCl_3$ and $\mathbf{1a}\cdot CH_2Cl_2$; isomorphous, $P2_1/c$, $Z = 4$]. Not only halogenated solvents but also ether and hexane were found to be incorporated in the crystal lattice [$(\mathbf{1a})_2\cdot$ether and $(\mathbf{1a})_2\cdot$hexane; isomorphous, Cc, $Z = 4$, two independent mole-

Table 1. The d values in the pseudopolymorphs of **1a** determined by X-ray analyses at 123 K along with the crystal data[a]

Solvent	$CHCl_3$	CH_2Cl_2	THF	CCl_4–hexane	Ether	Hexane
Ratio (**1a**:solvent)	1:1	1:1	1:1	2:1 (CCl_4) 4:1 (hexane)	2:1	2:1
C1–C2 bond length (d/Å)	1.718(3)	1.700(6)	1.734(3)	1.735(7) 1.718(7)	1.732(7) 1.706(7)	1.739(6) 1.727(6)
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	Cc	Cc
a/Å	12.624(2)	12.562(11)	11.819(4)	11.976(5)	19.255(9)	19.157(11)
b/Å	22.527(4)	22.28(2)	12.132(3)	12.469(4)	15.420(7)	15.524(8)
c/Å	12.030(2)	12.062(10)	12.210(4)	24.139(9)	22.907(11)	23.456(13)
α/°	90	90	78.759(12)	71.90(3)	90	90
β/°	102.014(2)	102.39(2)	83.352(12)	79.04(3)	109.521(7)	108.802(6)
γ/°	90	90	75.349(10)	78.22(3)	90	90
V/Å^3	3346.1(10)	3297(5)	1657.3(8)	3323(3)	6410(5)	6603(6)
Z	4	4	2	4	8	8

[a] The latter three crystals contain two crystallographically independent molecules in the unit cell.

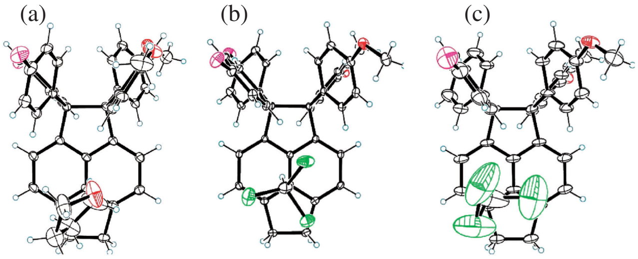


Figure 1. ORTEP drawings of tetraarylpyracene **1a** in (a) THF, (b) $CHCl_3$, and (c) CH_2Cl_2 (1:1) solvate crystals determined by X-ray analyses at 123 K. One chlorine atom in (c) suffers from positional disorder.

cules of **1a**]. The **1a**•THF solvate crystal adopts another space group [$P\bar{1}$, $Z = 2$], whose packing arrangement is similar to $(\mathbf{1a})_2$•CCl_4•$(\text{hexane})_{0.5}$ [$P\bar{1}$, $Z = 2$, two independent molecules of **1a**; hexane on the center of symmetry] but not to others. Differences in the molecular ratio and the space group indicate that the inclusion lattices formed by **1a** in crystal have several variations. Despite facile formation of pseudopolymorphs as above, single crystals of unsolvated **1a** were not obtained.

In accord with our assumption of "bond expandability" that the prestrained bond can be elongated or shortened very easily, structural refinement of the above six pseudopolymorphs of **1a**[14,19] revealed a considerable variation of C^1–C^2 bond length [Δd: 0.039 Å] although there are no direct and/or short contacts between solvent molecules and the C^1/C^2 atom of **1a**. The three crystals including the solvent molecule in a 1:1 ratio (THF, $CHCl_3$, and CH_2Cl_2) have d values of 1.734(3), 1.718(3), and 1.700(6) Å, respectively (Figure 1). It is interesting to note that $CHCl_3$ solvate and CH_2Cl_2 solvate are isomorphous, but the packing force afforded different degrees of perturbation of **1a** to adopt different d values. This is also the case for another pair of $(\mathbf{1a})_2$•ether [d: 1.732(7) and 1.706(7) Å] and $(\mathbf{1a})_2$•hexane [1.739(6) and 1.727(6) Å] (Table 1). Moreover, the two crystallographically independent molecules in $(\mathbf{1a})_2$•ether have the quite different bond lengths (Δd: 0.026 Å) despite being packed in the same crystal.

All the above crystallographic results demonstrate high susceptibility of the d value to the intermolecular perturbation. In general, the covalent bond length is the parameter with a high uniformity since the slight change in length causes considerable loss of BDE. In the case of a prestrained bond[20] with much smaller BDE, further expansion–contraction of the bond would occur with only slight loss of BDE, which accounts for the "expandability" in the ultralong covalent bond such as the C^1–C^2 bond of **1**.

To obtain theoretical support for the "expandability," structural optimization (B3LYP/6-31G*) of tetraphenylpyracene ($\mathbf{1H_4}$: X = Y = H) was conducted under the full-optimization and constrained conditions. The d value in the fully optimized $\mathbf{1H_4}$ was estimated to be 1.763 Å, which is close to the experimental value [1.754(2) Å]. When the geometric optimization processes were performed by constraining d at 13 different values between 1.700–1.820 Å, the scattering plot of the relative energy vs. d suggests a parabolic relationship (Figure 2). The characteristic feature is the very shallow potential curve with the energy difference of 0.35 kcal mol^{-1}. Such a small amount of energy-loss upon deviation of d from that of the optimized structure can be easily compensated by the different crystal packing force among pseudopolymorphs,[21] which rationalizes the observation of a variety of d values in the pseudopolymorphs of **1a**.

Finally, for further validation of the d value determined crystallographically on the ultralong C–C bonds, Raman spectroscopy was applied to the crystalline samples of difluoro (**1b**: X = F, Y = H) and tetrafluoro ($\mathbf{1F_4}$) derivatives. The Raman frequencies for the stretching vibration of the long C^1–C^2 bond were compared with that of unsubstituted compound $\mathbf{1H_4}$ studied before.[2b] The values[22] are 643 (**1b**), 640 ($\mathbf{1H_4}$), and 638 ($\mathbf{1F_4}$) cm^{-1} (Figure S2),[14] which are largely shifted compared with that of ethane itself (995 cm^{-1}). Thus, the C^1–C^2 bond in **1** has a much smaller force constant than the ordinary C–C bonds.

Although the difference in the Raman frequency is not large among **1b**, $\mathbf{1H_4}$, and $\mathbf{1F_4}$, the observed values decrease in the increasing order of the experimental d values [1.740(3), 1.754(2), and 1.761(4) Å, respectively], suggesting that the crystallographically determined bond lengths on the ultralong

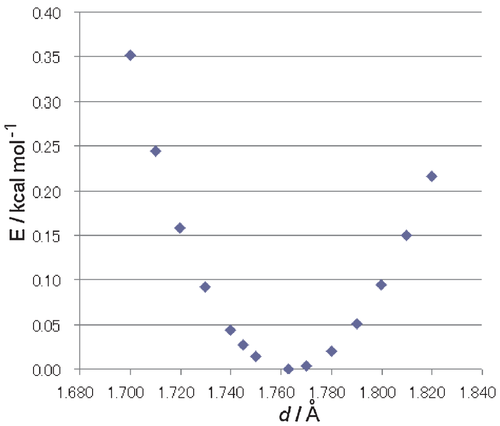


Figure 2. Scattering plot of relative energy (E) of tetraphenylpyracene **1H$_4$** vs. d estimated by DFT calculations (B3LYP/6-31G*).

C–C bond are actually related to the properties of the C–C bond in question (e.g., stretching vibration or force constant).

Studies are now in progress toward noncrystallographic demonstration (e.g., ^{13}C NMR) of the bond expandability as well as proof for facile bond expansion–contraction in solution.

This work was performed by Grant-in-Aid for Scientific Research on Innovative Areas: "Organic Synthesis Based on Reaction Integration" (No. 2105) from MEXT, Japan. TS thanks JSPS Grant-in-Aid for Challenging Exploratory Research on "Maximum Function on Minimum Skeleton (MFMS)" (No. 25620050). This work was also supported by the Cooperative Research Program of "Network Joint Research Center for Materials and Devices."

In memory of Dr. Chizuko Kabuto.

References and Notes

† Present address: Institute for Multidisciplary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-8577

†† Present address: Department of Chemistry, Faculty of Science, Tokyo University of Science, Shinjuku 162-8601

1 a) G. Kaupp, J. Boy, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 48. b) J. S. Siegel, *Nature* **2006**, *439*, 801. c) T. Suzuki, T. Takeda, H. Kawai, K. Fujiwara, in *Strained Hydrocarbons: Beyond the van't Hoff and Le Bel Hypothesis*, ed. by H. Dodziuk, Wiley-VCH, **2009**, Chap. 2.5. doi:10.1002/9783527627134.ch2. d) T. Suzuki, T. Takeda, H. Kawai, K. Fujiwara, *Pure Appl. Chem.* **2008**, *80*, 547. e) T. Takeda, Y. Uchimura, H. Kawai, R. Katoono, K. Fujiwara, T. Suzuki, *Chem. Lett.* **2013**, *42*, 954.

2 a) H. Kawai, T. Takeda, K. Fujiwara, T. Inabe, T. Suzuki, *Cryst. Growth Des.* **2005**, *5*, 2256. b) T. Takeda, H. Kawai, R. Herges, E. Mucke, Y. Sawai, K. Murakoshi, K. Fujiwara, T. Suzuki, *Tetrahedron Lett.* **2009**, *50*, 3693.

3 Y. Morita, S. Suzuki, K. Fukui, S. Nakazawa, H. Kitagawa, H. Kishida, H. Okamoto, A. Naito, A. Sekine, Y. Ohashi, M. Shiro, K. Sasaki, D. Shiomi, K. Sato, T. Takui, K. Nakasuji, *Nat. Mater.* **2008**, *7*, 48.

4 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

5 a) F. Toda, K. Tanaka, Z. Stein, I. Goldberg, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 177. b) F. Toda, K. Tanaka, M. Watanabe, K. Tamura, I. Miyahara, T. Nakai, K. Hirotsu, *J. Org. Chem.* **1999**, *64*, 3102. c) K. Tanaka, N. Takamoto, Y. Tezuka, M. Kato, F. Toda, *Tetrahedron* **2001**, *57*, 3761. d) F. Toda, K. Tanaka, N. Takamoto, *Tetrahedron Lett.* **2001**, *42*, 7979. e) K. K. Baldridge, Y. Kasahara, K. Ogawa, J. S. Siegel, K. Tanaka, F. Toda, *J. Am. Chem. Soc.* **1998**, *120*, 6167.

6 P. R. Schreiner, L. V. Chernish, P. A. Gunchenko, E. Y. Tikhonchuk, H. Hausmann, M. Serafin, S. Schlecht, J. E. P. Dahl, R. M. K. Carlson, A. A. Fokin, *Nature* **2011**, *477*, 308.

7 H. Kawai, T. Takeda, K. Fujiwara, M. Wakeshima, Y. Hinatsu, T. Suzuki, *Chem.—Eur. J.* **2008**, *14*, 5780.

8 The bond of 1.781(15) Å in a silabicyclobutane derivative had previously been the longest among the nonionic organic molecules: G. Fritz, S. Wartanessian, E. Matern, W. Hönle, H. G. V. Schnering, *Z. Anorg. Allg. Chem.* **1981**, *475*, 87.

9 J. L. Adcock, A. A. Gakh, J. L. Pollitte, C. Woods, *J. Am. Chem. Soc.* **1992**, *114*, 3980.

10 B. Kahr, D. Van Engen, K. Mislow, *J. Am. Chem. Soc.* **1986**, *108*, 8305.

11 T. Suzuki, Y. Uchimura, Y. Ishigaki, T. Takeda, R. Katoono, H. Kawai, K. Fujiwara, A. Nagaki, J.-i. Yoshida, *Chem. Lett.* **2012**, *41*, 541.

12 a) S. Terada, K. Katagiri, H. Masu, H. Danjo, Y. Sei, M. Kawahata, M. Tominaga, K. Yamaguchi, I. Azumaya, *Cryst. Growth Des.* **2012**, *12*, 2908. b) G. Kaur, P. Panini, D. Chopra, A. R. Choudhury, *Cryst. Growth Des.* **2012**, *12*, 5096. c) A. Schwarzer, E. Weber, *Cryst. Growth Des.* **2008**, *8*, 2862.

13 Experimental details and physical data for new compounds are given in Supporting Information (ref 14).

14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

15 a) A. Nagaki, N. Takabayashi, Y. Tomida, J.-i. Yoshida, *Org. Lett.* **2008**, *10*, 3937. b) A. Nagaki, N. Takabayashi, Y. Tomida, J.-i. Yoshida, *Beilstein J. Org. Chem.* **2009**, *5*, 16. c) Y. Ishigaki, T. Suzuki, J.-i. Nishida, A. Nagaki, N. Takabayashi, H. Kawai, K. Fujiwara, J.-i. Yoshida, *Materials* **2011**, *4*, 1906.

16 a) H. Usutani, Y. Tomida, A. Nagaki, H. Okamoto, T. Nokami, J.-i. Yoshida, *J. Am. Chem. Soc.* **2007**, *129*, 3046. b) A. Nagaki, Y. Tomida, H. Usutani, H. Kim, N. Takabayashi, T. Nokami, H. Okamoto, J.-i. Yoshida, *Chem.—Asian J.* **2007**, *2*, 1513. c) S. Suga, D. Yamada, J.-i. Yoshida, *Chem. Lett.* **2010**, *39*, 404. d) J.-i. Yoshida, K. Saito, T. Nokami, A. Nagaki, *Synlett* **2011**, 1189.

17 Crystal data and ORTEP drawings are given in Supporting Information (ref 14).

18 X-ray analyses on unsolvated crystals of **1b**–**1d** were conducted at 123 K. They all have an extremely long C^1–C^2 bond, and the ORTEP drawings show no anomalies in thermal ellipsoids of the long C^1–C^2 bond or in electron density maps.

19 Details of crystallographic analyses on pseudopolymorphs of **1a** (THF, CHCl$_3$, CH$_2$Cl$_2$, hexane, CCl$_4$–hexane, and ether) and those of **1b**–**1d** were deposited (CCDC 962022–962030).

20 a) K. Wada, T. Takeda, H. Kawai, R. Katoono, K. Fujiwara, T. Suzuki, *Chem. Lett.* **2013**, *42*, 1194. b) E. Ōsawa, P. M. Ivanov, C. Jaime, *J. Org. Chem.* **1983**, *48*, 3990.

21 J. D. Dunitz, J. Bernstein, *Acc. Chem. Res.* **1995**, *28*, 193.

22 The values were determined by using the same equipment to reduce the machine-dependent errors. The absorption in **1H$_4$** with the highest intensity (expt. 640 cm^{-1}) corresponds to the normal mode with the largest amplitude along the trajectory of the stretching vibration as verified by DFT calculation (B3LYP/6-31G* (ref 2b)).