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Nonadditive Substituent Effects on Expanding Prestrained C–C Bond in Crystal: X-ray Analyses on Unsymmetrically Substituted Tetraarylpyracenes Prepared by a Flow Microreactor Method

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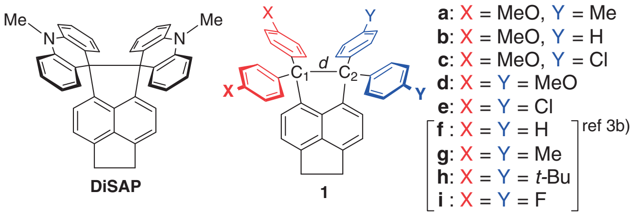
Based on space integration using a flow microreactor system, the title unsymmetrically substituted pyracenes with an extremely long C–C bond [1.714(2)–1.739(4) Å] are readily accessible, whose structures demonstrate nonadditive substituent effects on expanding the polyarylated C_1–C_2 bond in crystal. The bond lengths rather exhibit correlation with the eclipsing degree of the C_{sp^3}–C_{sp^3} bond, which is more affected by the intermolecular factors such as crystal packing.

Recently, considerable attention has been focused on the extremely long C–C bond[1] (>1.70 Å; standard: 1.54 Å[2]) found in highly congested organic compounds. The central topics are precise determination of the greater C–C bond length than ever as well as the special properties (e.g., thermochromism) derived therefrom.[3,4] The challenge in molecular design is how to stabilize the compound despite the presence of a C–C bond with a very small bond dissociation energy (BDE), for which reliable concepts have been proposed to date.[5,6] Hexaphenylethane derivatives[7–9] with a condensed carbon skeleton have often served as promising motif for the study. The major advantage in them is that the weakened C–C bond is prevented from dissociation by being framed in a rigid structure, which also allowed us to discover the nonionic longest C–C bond[10,11] [1.791(3) Å at 413 K; 1.771(3) Å at 93 K] in a crystal of DiSAP[3,5] with spiroacridan units on the pyracene framework (Chart 1).



a: X = MeO, Y = Me
b: X = MeO, Y = H
c: X = MeO, Y = Cl
d: X = Y = MeO
e: X = Y = Cl
f : X = Y = H
g: X = Y = Me
h: X = Y = *t*-Bu
i : X = Y = F

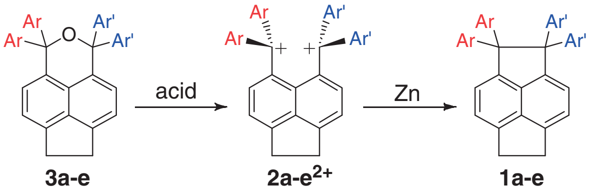
Chart 1.

In further X-ray studies on the 1,1,2,2-tetraarylpyracenes, not only DiSAP but also several substituted derivatives **1f**–**1i** have an extremely long C–C bond, and the considerable variation in the C_1–C_2 bond length (*d*) [**1f**: 1.754(2), **1g**: 1.717(4), **1h**: 1.749(4), and **1i**: 1.761(4) Å] comes with the substituents at the 4-position of aryl groups (H, Me, *t*-Bu, or F).[3b] Although the major factor to expand the C_1–C_2 bond in **1f**–**1i** should be the steric repulsion among the four aryl groups at C_1 and C_2, it is unlikely that the direct spatial interaction between the substituents at the 4-position produces the difference in steric congestion. The longest bond was found in **1i** with electron-withdrawing F groups, yet the electron-donating groups such as OMe are expected to cause bond elongation based on the (π–σ^*)-type through-bond interaction. Thus, it is still unclear how the substituent on the aryl rings causes variation on *d*. To shed light on the ambiguous substituent effects on expanding the prestrained bond, we have designed here unsymmetrically substituted derivatives of **1** in the anticipation that *d* in the unsymmetric compounds would exhibit the intermediary value of those in two symmetric counterparts if the electronic effects of the substituents are working as the major factor in changing *d*.

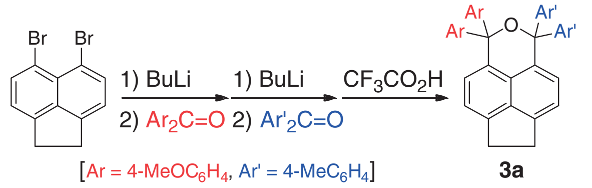
Here we report preparation and X-ray structural analyses of three unsymmetric compounds **1a** (X = MeO, Y = Me), **1b** (X = MeO, Y = H), and **1c** (X = MeO, Y = Cl). Two newly prepared symmetric compounds are also included in the paper as references: **1d** (X = Y = MeO) and **1e** (X = Y = Cl).

As in the previous study,[3b] the largely congested molecules **1a**–**1e** would be obtained from the less hindered dicationic precursors $\mathbf{2a}^{2+}$–$\mathbf{2e}^{2+}$ upon two-electron reduction,[13] which in turn would be generated from pyrans **3a**–**3e** under the acidic dehydrating conditions (Scheme 1). Pyrans **3d** and **3e**[14] with the same aryl groups on C_1 and C_2 were easily obtained from 5,6-dibromoacenaphthene by the successive treatment with BuLi (2.5 equiv) and the diarylketone (2.5 equiv) followed by treatment with TFA. They were isolated in respective yields of 80% and 70% with no need of chromatography for separation.

However, this is not the case of unsymmetric pyrans with two different aryl groups. Even under the careful execution by sequential addition of BuLi (1.0 equiv), $Ar_2C{=}O$ (1.0 equiv), BuLi (1.2 equiv), and $Ar'_2C{=}O$ (1.2 equiv), the yield of **3a** was only 49% after chromatographic separation (Scheme 2). On the other hand, we have recently demonstrated that monolithiation of arylenedibromide can be successfully conducted under the flow microreactor conditions.[16] By taking advantage of this



Scheme 1.



Scheme 2.

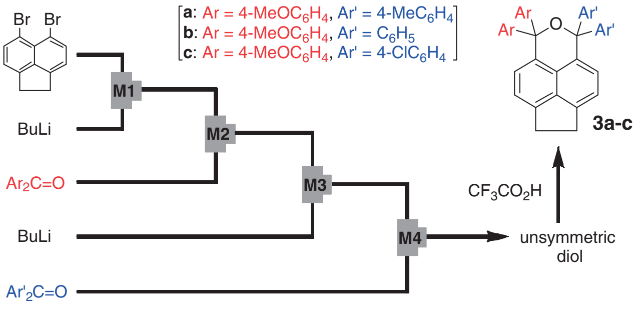


Figure 1. An integrated flow microreactor system for the sequential introduction of two different diarylmethanol units.

process, we also succeeded in the sequential introduction of two diarylmethanol units[17] on the 2,2′-positions of biphenyl by reaction integration using flow microreactors.[18]

It has been found here that the flow method works effectively in selective production of unsymmetric pyrans **3a**–**3c**[14] (Figure 1). Thus, 0.1 M 5,6-dibromoacenaphthene in THF (flow rate 6.0 mL min^{-1}) was reacted with 0.5 M BuLi in hexane (1.2 mL min^{-1}) at 24 °C to generate 5-bromo-6-lithioacenaphthene, which was sequentially reacted with 4,4′-dimethoxybenzophenone (0.2 M in THF, 3.0 mL min^{-1}), BuLi (0.5 M in hexane, 1.44 mL min^{-1}), and 4,4′-dimethylbenzophenone (0.2 M in THF, 3.6 mL min^{-1}). After treatment with TFA, **3a** was obtained as a sole product and isolated in 68% yield. Similarly, by using parent benzophenone or 4,4′-dichlorobenzophenone as the second electrophile, pyrans **3b** and **3c** were also obtained in respective yields of 69% and 71%.

With pyrans **3a**–**3e** in hand, new members of tetraarylpyracenes **1a**–**1e**[14] were prepared according to Scheme 1. In the cases of **1a** and **1d** with four electron-donating aryl groups, the precursor dications **2a**$^{2+}$ and **2d**$^{2+}$ were generated by using $HBF_4/(CF_3CO)_2O$ and isolated as stable BF_4^- salts.[14] Dications **2b**$^{2+}$ and **2c**$^{2+}$ generated with $TMSClO_4$[19] were not isolated but directly reduced with Zn dust to furnish **1b** and **1c**. The stronger acidic treatment [$TfOH/(CF_3)_2CHOH$] is necessary on **3e** for dehydration. Despite the different acidic conditions applied on **3a**–**3e**, the target compounds **1a**–**1e** were isolated in high yields (y. 72%, 81%, 75%, 84%, and 91%, respectively, based on **3a**–**3e**) as stable pale yellow crystalline materials.

By the vapor diffusion method ($CH_2Cl_2/CHCl_3$–hexane), we successfully obtained a single-crystalline specimen of high quality of tetraarylpyracenes **1a**, **1b**, **1d**, and **1e**, as well as **1b**•CH_2Cl_2 (1:1 solvate) for precise determination of the *d* value.[20] Low-temperature X-ray analyses[21] at 123 K showed that all of the molecules in these five crystals have an extremely long C_1–C_2 bond [$d > 1.70$ Å], whose bond lengths were determined with high accuracy [esd: 0.002–0.004 Å]. As represented by

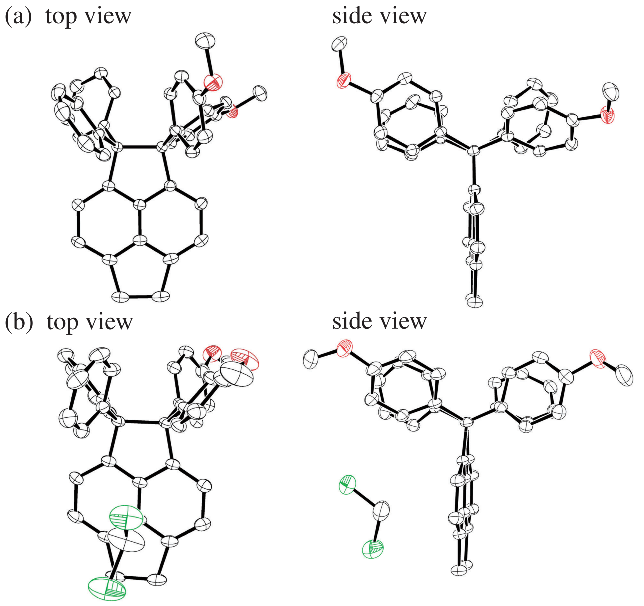


Figure 2. ORTEP drawings of tetraarylpyracene molecule in (a) unsolvated **1b** [1.714(2) Å] and in (b) **1b**•CH_2Cl_2 [1.739(4) Å] determined by X-ray analyses at 123 K.

unsolvated **1b** and **1b**•CH_2Cl_2 (Figure 2), the ORTEP drawings show no anomalies in thermal ellipsoids of the long C_1–C_2 bond or in electron density maps for all cases.

The significant finding is that the *d* value in the unsymmetric derivative **1a** (X = MeO, Y = Me) [1.738(3) Å] is greater than either of those in two symmetric counterparts: **1d** (X = Y = MeO) [1.726(3) Å] and **1g**[3b] (X = Y = Me) [1.717(4) Å]. Furthermore, in another unsymmetric derivative **1b** (X = MeO, Y = H), the bond length [1.714(2) Å] is smaller than in both of the corresponding symmetric counterparts: **1d** (X = Y = MeO) [1.726(3) Å] and **1f**[3b] (X = Y = H) [1.754(2) Å], thus demonstrating nonadditive substituent effects on expanding the C_1–C_2 bond of **1** in crystal. Another important finding is that the *d* value of **1b** in the unsolvated crystal [1.714(2) Å] and that in CH_2Cl_2 solvate [1.739(4) Å] differs considerably even though there are no special interaction with the solvent and aryls groups in **1b**•CH_2Cl_2, showing that the expansion of C_1–C_2 (Δd: 0.025 Å) can be induced only by the small energy supplied from the different crystal packing.

It can be concluded that the electronic nature of substituents is not the major determinant of the *d* values in the crystals of **1** despite the fact that the wide variation of bond length (Δd: 0.047 Å) was observed for a series of **1** with different aryl groups. The *d* values rather correlate with the eclipsing degree (χ)[22] of C_1–C_2 (Figure 3): the *d* value becomes greater by larger steric repulsion among aryl groups as the C_1–C_2 bond becomes closer to the perfect eclipsed conformation ($\chi = 100$). The χ value in **1** is difficult to predict without analyzing the X-ray structure since it is largely affected by the intermolecular contacts among aryl groups in a certain crystal packing. Due to the small BDE[23] for the extremely long C_1–C_2, change in BDE upon further expansion of the prestrained bond would be only marginal ("bond expandability"), which results in wide variation of *d* in response to the small perturbation in χ.

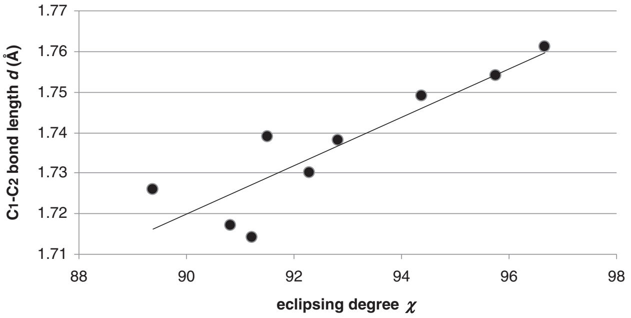


Figure 3. Scattering plot of d versus the eclipsing degree (χ) of C_1–C_2 for **1a**, **1b**, **1d**–**1i**, and **1b**$\cdot CH_2Cl_2$ determined by X-ray analyses. Full listing of geometric parameters are given in the Supporting Information.[15]

The expandability of the extremely long C–C bond would be the key to future developing novel function (e.g., chromism), since the enough energy for changing the bond length is easily supplied by external stimuli. At the same time, by further increment of steric repulsion with keeping the eclipsed conformation, there is high possibility to discover much longer C–C bond, whose length is greater than the value for the shortest nonbonded C···C contact (1.80 Å).[25] Studies in this vein are now in progress.

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References and Notes

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20 We have not so far succeeded in obtaining suitable specimen of **1c** for precise determination of d in crystal. Probably due to the similar spatial requirement of MeO and Cl groups, two kinds of aryls groups occupy the same positions both in the crystals of unsolvated **1c** (ccdc: 870493; isomorphous to **1d**) and **1c**$\cdot CH_2Cl_2$ (1:1) solvate. Only the d value with a large esd was obtained in the former [1.712(8) Å]. The structural refinement could not be converged sufficiently in the latter due to additional positional disorder of solvent. Thus, these two crystals of **1c** are not included in the discussion in this paper.

21 Crystal data of **1a**, **1b**, **1d**, **1e**, and **1b**$\cdot CH_2Cl_2$ (CCDC 870491, 870493, 870495, 870496, and 870492) and details of crystallographic work are given in Supporting Information (ref. 15).

22 The eclipsing degree (χ) of the C_{sp^3}–C_{sp^3} bond is defined by the smallest three torsion angles (α, β, and γ) over the bond in question as follows: $\chi\ (\%) = [1 - (|\alpha| + |\beta| + |\gamma|)/180] \times 100$. The χ value is 100 for the completely eclipsed C–C bond whereas it is 0 for the perfectly staggered conformation. Each of α, β, and γ in **1** is defined by the two eclipsing C_{sp^2} atoms over the C_1–C_2 bond.

23 By assuming the linear relationship between BDE and the C–C bond length (ref. 24), BDE was predicted to be very small when the length becomes beyond 1.70 Å. For the bond of the length beyond 1.75 Å, BDE was thought to be zero.

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