



## Negligible diradical character for the ultralong C–C bond in 1,1,2,2-tetraarylpyracene derivatives at room temperature

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### ABSTRACT

There is evidence that the crystalline-state thermochromic behavior of dispiropyracene **acr-1** with an ultralong C–C bond [1.791(3) Å at 413 K, 1.771(3) Å at 93 K] might be due to thermal generation of a bond-dissociated triplet diradical. The C<sub>1</sub>–C<sub>2</sub> bond lengths (*d*) in the newly prepared 1,1,2,2-tetraarylpyracenes **1a–e** [1.717(4)–1.761(4) Å at 113/123/153 K] are also much larger than the standard value for C(sp<sup>3</sup>)–C(sp<sup>3</sup>) (1.54 Å). The fact that there is no correlation between *d* and the radical-stabilizing parameter ( $\sigma^*$ ) provides evidence that there is no contribution from a crystallographic artifact caused by contamination of the diradical in the crystal of **1** at room temperature or below. Further indication for the covalent nature of the ultralong C–C bond in tetraphenylpyracene **1c** was attained by Raman spectroscopy, showing the far red-shifted C<sub>1</sub>–C<sub>2</sub> stretching vibration (638 cm<sup>-1</sup>) and by the theoretical prediction of very large vertical singlet–triplet energy gap (58.3 kcal mol<sup>-1</sup> at the UB3LYP/6-31G<sup>+</sup> level). However, at elevated temperatures bond dissociation might occur forming a triplet diradical.

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The C–C bond length (*d*) is one of the most fundamental parameters in organic chemistry,<sup>1</sup> and a *d* value of 1.54 Å is assumed as the standard length of a C(sp<sup>3</sup>)–C(sp<sup>3</sup>) single bond. This explains why the experimentally determined *d* can be used to assess the  $\pi$ -bond order in combination with other standard values [1.33 Å for C(sp<sup>2</sup>)=C(sp<sup>2</sup>); 1.20 Å for C(sp)≡C(sp)]. On the other hand, there have been several reports in which the C–C single bond is shortened or elongated independent of the bond order,<sup>2</sup> and such elongation is often accompanied by a strained molecular structure and/or severe steric hindrance.<sup>3</sup>

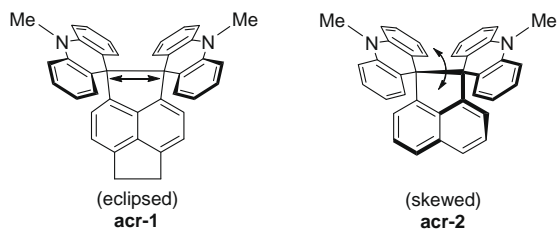
Hexaphenylethane (HPE) is a good example of this phenomenon; its central C–C bond is elongated [1.67(3) Å]<sup>4</sup> primarily due to steric repulsion among six aryl substituents. According to the proposed linear relationship between *d* and bond-dissociation energy (BDE),<sup>5</sup> a smaller BDE is expected for a longer C–C bond. In fact, some isolable HPE derivatives exist as equilibrated mixtures containing bond-dissociated trityl radicals in solution. On the other hand, ‘cross-clamped’ or ‘condensed’ derivatives of HPE show higher thermodynamic stability because dimeriza-

tion is switched from an intermolecular to an intramolecular process. Thus, the HPEs with an even longer C–C bond (*d* > 1.70 Å) could be isolated [1.712(5)–1.734(5) Å for 3,8-dihalo-1,1,2,2-tetraphenyl-naphthocyclobutenes by Toda's group<sup>6</sup> and 1.713(2) Å for a multi-benzannulated caged hydrocarbon by one of us<sup>7</sup>].

Recently, we also reported<sup>8a,b</sup> that a pyracene-based HPE derivative **acr-1** with two spiro(10-methylacridan) units has an ultralong C–C bond [*d* = 1.771(3) Å at 93 K], which is one of the longest ever reported<sup>9</sup> [the *d* values for other crystallographically independent molecules of **acr-1** are 1.758(3), 1.712(2), and 1.707(2) Å]. The above X-ray analysis was carried out with special care, however, there still remains some possibility that the concomitant presence of a bond-dissociated diradical might have led to the assignment of a larger *d* than the intrinsic value.<sup>10,13</sup> Our major concern in this Letter is to shed light on the following points: (a) does a bond-dissociated diradical exist or can it be generated in the crystal of HPEs with an ultralong C–C bond; and (b) is the crystallographically determined very large *d* (> 1.75 Å) be intrinsic or an artifact by the concomitant presence of a bond-dissociated diradical (or diradicaloid) in the crystal.

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Here we found the reversible thermochromic behavior<sup>14</sup> of **acr-1** in the single-crystalline state, which might be related to the bond dissociation of the ultralong bond forming the corresponding diradical in the crystal, as shown in the first part of this Letter. Next, we have conducted the X-ray analyses of **acr-1** at several elevated temperatures to see if generation/increased contribution of the diradical at higher temperatures expands the experimentally determined  $d$  value of **acr-1**. Since the marginal expansion of 0.020 Å over a temperature difference of 320° does not provide decisive support for the diradical contribution, we have then turned our attention to the studies on a new series of HPEs, 1,1,2,2-tetraarylpyracenes **1**. The experimentally assigned  $d$  value should change with the attachment of radical-stabilizing/non-stabilizing substituents when the coexistence of a bond-dissociated diradicals affects the apparent bond lengths determined by X-ray analyses (Scheme 1). If the corresponding diradicals exist in equilibrium with HPEs in the crystal,<sup>14</sup> compounds with radical-stabilizing substituents would exhibit a larger value of  $d$  than those with non-stabilizing or radical-destabilizing substituents. The low-temperature X-ray structures of the corresponding compounds do not reveal such a relationship. The details of our results will be shown in the last part of this Letter.

First, we noticed a color change of crystalline samples of **acr-1** when they were heated in an ESR tube sealed with Ar. Similar thermochromic behavior was observed by heating the single crystalline sample on a glass fiber (Fig. 1), where temperature control was carried out by a N<sub>2</sub> gas flow. At 273 K, the sample is pale yellow, whose color gradually turned to dark red (413 K) via orange (333 K). This observation is not accompanied by decomposition of **acr-1** because the crystal returned to pale yellow upon cooling to room temperature or 123 K, which still gave X-ray diffraction data identical to those obtained before the heat treatment. A reversible phase transition or bond fission to generate a certain population of diradicals upon heating might be responsible for the observed thermochromic behavior. Thus, the X-ray analysis of **acr-1** was carried out at several temperatures above 273 K.<sup>15,16</sup> No phase transition occurs in the range between 273 K and 413 K, thus the observed thermochromic behavior is not related to a phase transition.

The X-ray structure at 413 K is quite similar to those obtained at lower temperatures except for the enlarged thermal ellipsoids at

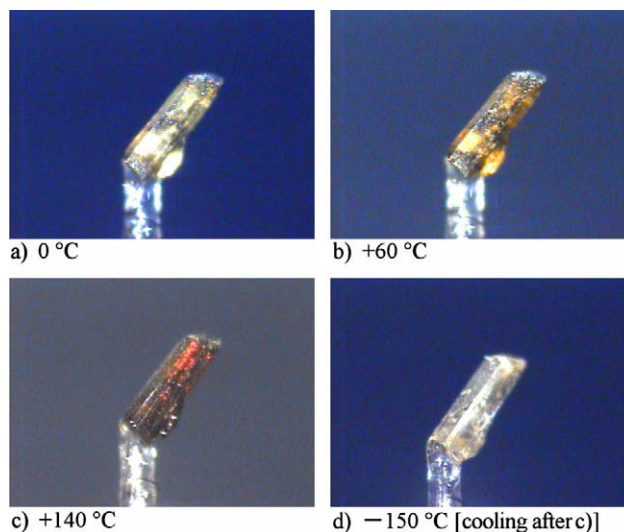
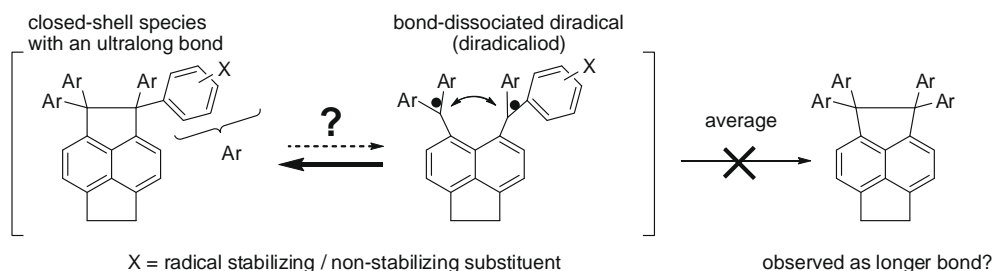


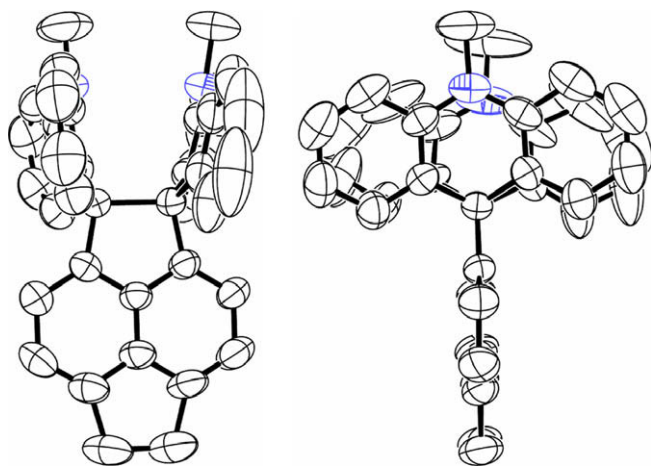
Figure 1. Single-crystalline thermochromic behavior of **acr-1**.

most atoms. It is noteworthy that those for C<sub>1</sub> and C<sub>2</sub> are still small and round shaped (Fig. 2). The difference electron density map indicates the presence of bonding electron between C<sub>1</sub> and C<sub>2</sub>, (Fig. S2) as in the case of the X-ray analysis at 93 K.<sup>8a</sup> The  $d$  value for the bond in question is 1.791(3) Å, which is only 0.020 Å longer than that measured at 93 K.<sup>17</sup> The X-ray analyses at 333 K and 373 K gave the results with the intermediary structures with the  $d$  value of 1.776(3) Å and 1.786(3) Å, respectively. As shown by Toda's and Siegel's groups, 3,8-dichloro-1,1,2,2-tetraphenylnaphthocyclobutene exhibits a similar degree of bond expansion [1.710(2) Å at 90 K,<sup>6e</sup> 1.720(4) at 298 K<sup>6a</sup>].

The vertical singlet-triplet energy gap ( $\Delta E_{S-T}$ ) is a frequently used indicator to evaluate the diradical character of molecules.<sup>18</sup> We performed calculations at the UB3LYP/6-31G\* level of DFT based on the X-ray geometry of **acr-1** at 413 K (fixed  $d$  of 1.7922 Å) and obtained the  $\Delta E_{S-T}$  value of 58.99 kcal mol<sup>-1</sup>. A quite similar value (59.04 kcal mol<sup>-1</sup>) was obtained for the crystallographically independent molecule with the shortest C<sub>1</sub>–C<sub>2</sub> bond measured at 93 K ( $d = 1.7062$  Å). The very large  $\Delta E_{S-T}$  values indicate that the diradical contribution to the overall wavefunction of **acr-1** is negligible at lower temperatures (compare with the  $\Delta E_{S-T}$  of *o*-, *m*-, and *p*-benzynes: 37.5, 21.0, 3.8 kcal/mol).<sup>19</sup> On the other hand, we found a triplet minimum structure with a very large bond distance  $d$  of 3.110 Å which energetically is only 8.14 kcal mol<sup>-1</sup> above the singlet structure (UB3LYP/6-31G\*, Fig. S3). This species could explain the observed thermochromism on a theoretical basis. According to TD DFT calculations the longest wavelength absorption of the singlet state is 362 nm which is in agreement with the fact that the crystals are almost colorless at low temperatures. By contrast the triplet state exhibits several



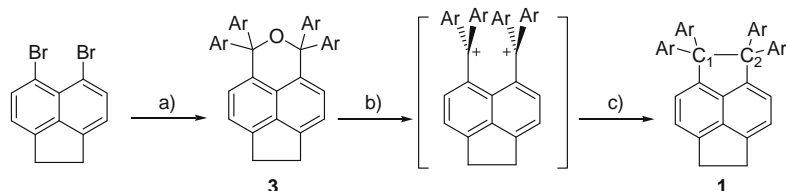
Scheme 1.



**Figure 2.** ORTEP drawings of **acr-1** (top view and side view) at 413 K. Note the small and round-shaped ellipsoids for C<sub>1</sub> and C<sub>2</sub>.

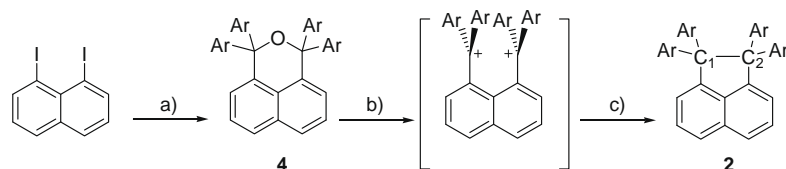
absorptions within the visible range (strongest bands at 450 and 475 nm; Table S1) which explain the red color of the crystals at higher temperatures at which the triplet state will be increasingly populated. Thus, it is clear that the ultralong C–C bond in **acr-1** at room temperature and below is intrinsic and that the concomitant presence of bond-dissociated triplet diradical becomes important only at higher temperatures.

To gain further insight into the nature of the ultralong bonds we set out to crystallographically measure the bond length  $d$  in HPEs other than **acr-1**. For this purpose, we designed 1,1,2,2-tetraarylpyracene derivatives **1a–e** as suitable HPE derivatives from the following viewpoints: first, the pyracene skeleton should act as a scaffold to induce enough ‘front strain’<sup>4</sup> to ensure the presence of an extremely long C<sub>1</sub>–C<sub>2</sub> bond ( $d > 1.70$  Å), as shown by **acr-1**; second, the system should be designed in such a way that the bond-dissociated species is a diradical and not (as, e.g., in the case of the benzocyclobutenes-type HPEs) a closed shell structure (*o*-quinodimethane),<sup>20</sup> and third, a series of compounds with various substituents on aryl groups should be accessible via the corresponding dicationic precursors.<sup>21</sup>



**a** : Ar = 4-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>; **b** : Ar = 4-MeC<sub>6</sub>H<sub>4</sub>; **c** : Ar = C<sub>6</sub>H<sub>5</sub>; **d** : Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; **e** : Ar = 4-FC<sub>6</sub>H<sub>4</sub>

**Scheme 2.** Preparation of tetraarylpyracenes **1a–e**. Reagents: (a) (1) *n*-BuLi, then Ar<sub>2</sub>CO, ether; (2) trifluoroacetic acid, CH<sub>2</sub>Cl<sub>2</sub>; (b) TMSClO<sub>4</sub>, 1,1,1,3,3,3-hexafluoro-2-propanol; (c) Zn, MeCN.



**a** : Ar = 4-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>; **b** : Ar = 4-MeC<sub>6</sub>H<sub>4</sub>; **c** : Ar = C<sub>6</sub>H<sub>5</sub>; **d** : Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; **e** : Ar = 4-FC<sub>6</sub>H<sub>4</sub>

**Scheme 3.** Preparation of tetraarylacenaphthenes **2a,b,d,e**. Reagents: (a) (1) *n*-BuLi, then Ar<sub>2</sub>CO, ether; (2) trifluoroacetic acid, CH<sub>2</sub>Cl<sub>2</sub>; (b) TMSClO<sub>4</sub>, 1,1,1,3,3,3-hexafluoro-2-propanol for **4a,b,d**; TFOH, 1,1,1,3,3,3-hexafluoro-2-propanol for **4e**; (c) Zn, MeCN.

We have prepared here the parent tetraphenylpyracene (**1c**)<sup>22</sup> from 5,6-dibromoacenaphthene and benzophenone in three steps via pyran **3c**, as shown in Scheme 2. By starting with the substituted benzophenones, HPEs with benzyl radical-stabilizing substituents on phenyl rings such as 4-<sup>t</sup>Bu (**1a**), and 4-Me (**1b**) could be similarly prepared along with those with non-stabilizing [3,5-Me<sub>2</sub> (**1d**)] and destabilizing [4-F (**1e**)] substituents. The desired HPEs (**1**) were isolated as surprisingly stable colorless/pale yellow solids despite the very large  $d$  value for the C<sub>1</sub>–C<sub>2</sub> bond (vide infra). Another series of HPEs **2** with an acenaphthene  $\pi$ -framework was also designed to further support the conclusion obtained from **1**. The structurally related acenaphthene derivative **acr-2**<sup>8a,8c</sup> has a shorter bond length [1.696(3) Å] than **acr-1** because it adopts a skewed arylene framework to relieve steric repulsion between two acridan units. Yet, the skeleton might be still suitable enough to test the validity of our approach adopted here. So, 1,1,2,2-tetraarylacenaphthenes **2a**(4-<sup>t</sup>Bu), **b**(4-Me), **d**(3,5-Me<sub>2</sub>), **e**(4-F) were prepared over three steps from 1,8-diodonaphthalene and the corresponding benzophenones via pyrans **4** (Scheme 3).<sup>22</sup> The preparation and X-ray structure of tetraphenylacenaphthene (**2c**) were reported previously by Gabbai and coworker.<sup>23</sup>

After considerable effort, we finally obtained a single-crystal specimen of high quality for all nine kinds of HPEs **1a–e/2a,b,d,e**.<sup>16</sup> Low-temperature X-ray analyses revealed that all of them have an extremely long C<sub>1</sub>–C<sub>2</sub> bond [1.717(4)–1.761(4) Å for **1** and 1.694(3)–1.708(4) Å for **2**] (Tables 1 and 2).<sup>24</sup> No structural disorder around the C<sub>1</sub>–C<sub>2</sub> bond was found in any case. As represented by 4-Me derivative **1b** [ $d = 1.717(4)$  Å: the smallest among **1a–e**] and 4-F derivative **1e** [ $d = 1.761(4)$  Å: the largest] (Fig. 3), the ORTEP drawings show no anomalies in thermal ellipsoids of the long C<sub>1</sub>–C<sub>2</sub> bond or in electron density maps. The radical-stabilizing parameters ( $\sigma^*$ )<sup>25</sup> are also summarized in Table 1, which quantify the thermodynamic stability of the benzyl radicals attached with a various substituent on the benzene nucleus. As shown by these data, HPEs with radical-stabilizing groups (**1a,b/2a,b**;  $\sigma^* > 0$ ) do not necessarily have larger  $d$  values than the parent compound (**1c/2c**;  $\sigma^* < 0$ ) or those with non-stabilizing/destabilizing groups (**1d,e/2d,e**;  $\sigma^* < 0$ ). Thus, the radical-stabilizing substituents do not increase the apparent bond length determined by X-ray, which leads us to conclude that the contribution from the bond-dissociated diradical is negligible for the present HPEs **1/2**

**Table 1**

Structural parameters of pyracene-type HPEs **1** determined by low-temperature X-ray analyses and the radical-stabilizing parameters  $\sigma^*$

Compound	<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b>	<b>1e</b>
X	4- <sup>t</sup> Bu	4-Me	H	3,5-Me <sub>2</sub>	4-F
<i>d</i> (Å)	1.749(4)	1.717(4)	1.754(2)	1.743(2)	1.761(4)
$\sigma^*$	0.036	0.015	0.000	-0.002	-0.011

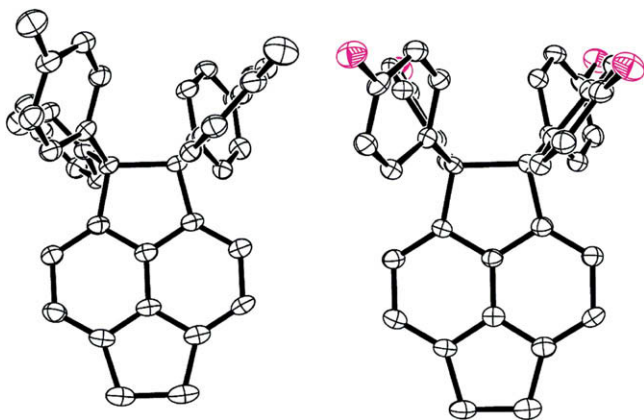
**Table 2**

Structural parameters of acenaphthene-type HPEs **2** determined by low-temperature X-ray analyses

Compound	<b>2a</b>	<b>2b</b>	<b>2c<sup>a</sup></b>	<b>2d</b>	<b>2e<sup>b</sup></b>
X	4- <sup>t</sup> Bu	4-Me	H	3,5-Me <sub>2</sub>	4-F
<i>d</i> (Å)	1.708(4)	1.694(3)	1.701(3)	1.701(2)	1.707(2) 1.705(2)

<sup>a</sup> Ref. 23.

<sup>b</sup> Two crystallographically independent molecules.

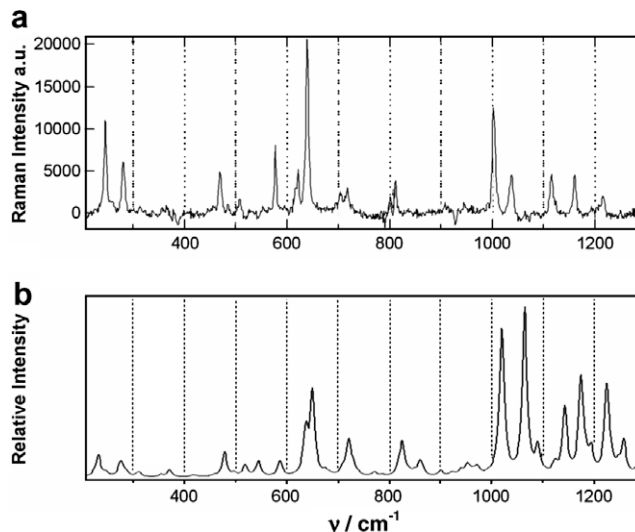


**Figure 3.** ORTEP drawings of **1b** (left) and **1e** (right) at 123 K.

in the crystal state even for derivatives with an ultralong C–C bond with a *d* value as large as 1.76 Å.

For further validation of the crystallographically determined extremely long C–C bond, Raman spectroscopy was applied on the crystalline samples of tetraphenyl derivatives (**1c/2c**). The stretching vibration of the long C<sub>1</sub>–C<sub>2</sub> bond studied by Raman spectroscopy at 298 K gives direct information on the force constant of the bond. The absorption in pyracene derivative **1c** with the highest intensity (expt. 638 cm<sup>-1</sup>) in **Figure 4a** corresponds to the normal mode with the largest amplitude along the trajectory of the stretching vibration as verified by DFT calculation (B3LYP/6-31G\*: calcd 650 cm<sup>-1</sup>). There are other absorptions assigned as normal modes that include C<sub>1</sub>–C<sub>2</sub> stretching vibration (470, 621, 718, 812 cm<sup>-1</sup>), for which the calculation well reproduced the frequencies (478, 637, 720, 825 cm<sup>-1</sup>) (**Fig. 4b**). The observed red-shifted value compared to the C–C stretching vibration of ethane itself (995 cm<sup>-1</sup>) clearly shows that the ultralong C–C bond [*d*<sub>expt</sub> = 1.754(2) Å; *d*<sub>calcd</sub> = 1.759 Å] in **1c** has a very small force constant.

Not only the frequencies of the C<sub>1</sub>–C<sub>2</sub> stretching bands but also the other experimental spectral lines were well reproduced by the calculation. In contrast to the X-ray analysis and NMR, Raman is a very fast spectroscopic method. In a hypothetical equilibrium of a closed shell species with a large *d* value and a diradical, both species should appear with separate absorption bands and not as a time-averaged spectrum like in NMR. The agreement of the experimental and theoretical Raman spectrum is very good, and there are no additional lines in the experimental spectrum, which could



**Figure 4.** Experimental (a) and calculated (b) Raman spectra of **1c**.

not be assigned to the closed shell structure. Therefore, at room temperature or below a diradical structure can either be completely excluded or, if there is an equilibrium, it must be present in very little concentration in the crystalline sample of **1c**.<sup>26</sup> Raman investigations at higher temperatures are in progress.

In conclusion, we have no reason to assume that the extremely long (*d* > 1.70 Å) or ultralong (*d* > 1.75 Å) C–C bond in the present HPEs gives rise to a noticeable diradical character of the corresponding compounds. However, there is indication that there is a triplet diradical in a thermal equilibrium with the closed shell structure at higher temperatures in crystalline **acr-1**. Despite the large expansion that may lower the BDE, the present HPEs exhibit surprising chemical stability: For example, the parent **1c** [*d* = 1.754(2) Å] can be purified by chromatography using aerated solvents and can be stored infinitely as solids. It remains intact upon treatment with Et<sub>3</sub>SiH or Bu<sub>3</sub>SnH. Based on our results, studies to achieve further elongated C–C bonds are warranted with a *d* value even longer than the shortest nonbonded C–C contact (1.80 Å).<sup>27</sup>

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## Supplementary data

Crystallographic data (excluding structure factors) for the structures in this Letter has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 704958–704964, 715129, 715130, 715701–715703). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. Spectral data of new HPEs (**1a–e/2a,b,d,e**), ORTEP drawings of **1a,c,d/2a,b,d,e** (**Fig. S1**), the *D* map of **acr-1** at 413 K (**Fig. S2**), plots of singlet (*d* = 1.776 Å) and triplet (*d* = 3.110 Å) species obtained by DT-DFT calculation on **acr-1** (**Fig. S3**), and calculated absorption bands of both singlet and triplet species of **acr-1** (**Table S1**). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.202.

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- The bond of 1.781(15) Å in a silabicyclobutane derivative had been the longest among the non-ionic organic molecules before this Letter: Fritz, G.; Wartanessian, S.; Matern, E.; Hönle, W.; Schnering, H. G. v. Z. *Anorg. Allg. Chem.* **1981**, 475, 87–108.
- In some earlier examples, the coexistence of a bond-dissociated valence isomer caused the misassignment of a too-large *d* value (Ref. 11), since X-ray structure only gives the time- and position-averaged geometry of molecules in the crystal. The true value of those cases was later proven to be much smaller by low-temperature data collection and the careful examination of thermal ellipsoids (Ref. 12).
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- Crystal data and details on crystallographic studies of **1a-e/2a,b,d,e** (at 113/123/153 K) were given in [Supplementary data](#).
- In another crystallographically independent molecule, the C<sub>1</sub>–C<sub>2</sub> bond length is 1.719(3) Å; whose expansion degree (0.012 Å) over 320° is similar to the one with the ultralong C–C bond.
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