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# Large PAHs by Reductive *Peri*–*Peri* "Dimerization" of Phenalenones

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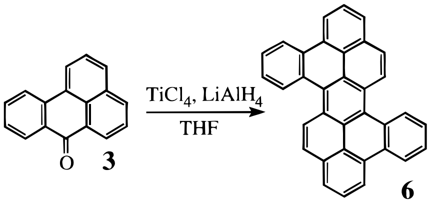
## ABSTRACT



**Reactions of phenalenone (2), benzanthrone (3), and naphthanthrone (4) with a low-valent titanium reagent ($TiCl_4$/$LiAlH_4$/THF) gave peropyrene (1), tetrabenzo[*a*,*cd*,*j*,*lm*]perylene (6), and dibenzo[*jk*,*uv*]dinaphtho[2,1,8,7-*defg*;2′,1′,8′,7′-*opqr*]pentacene (10), respectively. The syntheses of the LPAHs 6 and 10 were regioselective. An unsymmetrical pathway of reductive *peri*–*peri* "dimerization" of the phenalenones leading to peropyrene-type LPAHs was proposed. Ab initio DFT B3LYP/6-311G** calculations indicated that $D_{2h}$-1, the most stable conformation, resembles the Clar picture of 1.**

There has been a growing interest in large polycyclic aromatic hydrocarbons (LPAHs), namely, heptacyclic and higher PAHs, as environmental contaminants, as coal hydrogenation byproducts, and as precursors to fullerenes.[1−3] The earlier expectations that no significant biological impact would result from exposure to LPAHs, which were assumed to be sparingly soluble and therefore not environmentally relevant (e.g., carcinogenic), has been questioned. LPAHs are in fact ubiquitous, from the bottom of the oceans to the dust clouds of interstellar space.[1b,4] It has recently been shown that the majority of PAHs must adopt nonplanar conformations as global minima.[5] The nonplanarity motif is especially frequent in LPAHs.[5] The abundance of overcrowding (e.g., cove and fjord regions) in LPAHs results in a predominance of chiral LPAHs. Peropyrene (dibenzo[*cd*,*lm*]perylene, **1**) and its benzo-annulated homologues provide an interesting series of chiral and achiral pericondensed benzenoid LPAHs. We report here the synthesis of peropyrene-type LPAHs by mild low-valent titanium-induced reductive *peri*−*peri* "dimerization" of phenalenones, a series of novel polycyclic aromatic ketones (PAKs).[6] This method is a variation of the carbonyl coupling reaction by low-valent titanium reagents to produce dimeric alkenes. The prominent reaction was invented in 1973 by Mukaiyama et al.[7] and Tyrlik et al.[8] and is referred to in the chemical literature as the McMurry reaction.[9,10] Previously, the method of choice for syntheses of peropyrene-type LPAHs has been the Clar reaction:[11] a reductive coupling of phenalenone-type PAKs, using zinc dust in a

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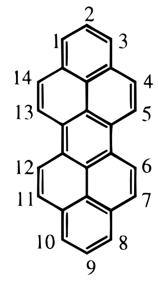

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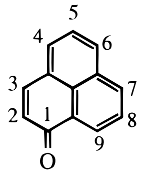

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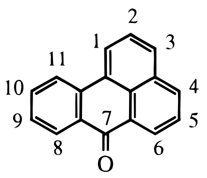

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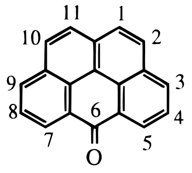

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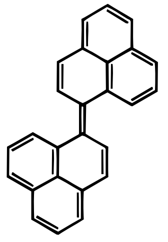

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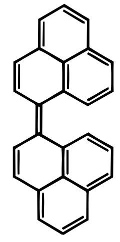

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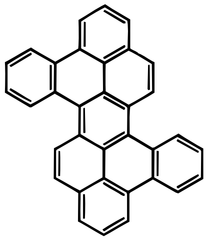

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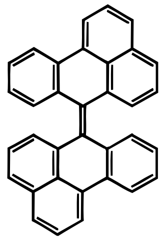

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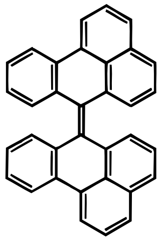

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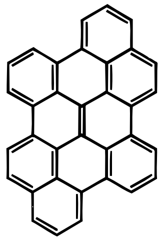

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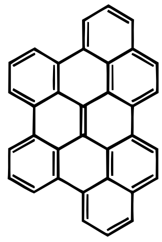

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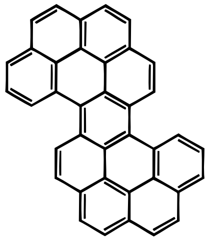

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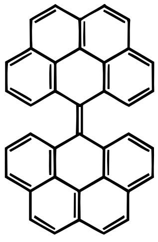

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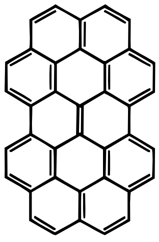

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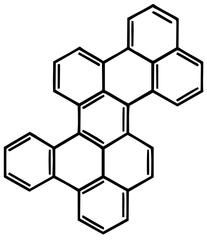

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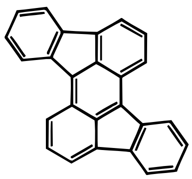

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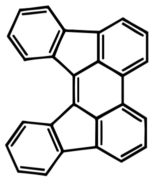

**15**

melt of NaCl and $ZnCl_2$ at elevated temperatures (ca. 300 °C). Thus, 1*H*-phenalen-1-one (**2**) gave peropyrene (**1**).[12] However, the drastic Clar reaction has turned out to be nonregioselective. In the cases of 7*H*-benz[*de*]anthracen-7-one (**3**) and 6*H*-benzo[*cd*]pyren-6-one (**4**), the Clar reaction led to mixtures of $C_{34}$ and $C_{38}$ LPAHs, respectively.[11] A topological approach to this synthesis (which accounts for the PAHs that were formed and the absence of isomeric PAHs) has been outlined.[11]

Treatment of 1*H*-phenalen-1-one (**2**) with low-valent titanium species generated from $TiCl_4$ and $LiAlH_4$ in THF for 120 h gave peropyrene[13] (**1**) in 15% yield. The bistricyclic enes, (*E*)- and (*Z*)-1-(1-phenalenylidene)phenalene ((*E*)-**5** and (*Z*)-**5**), the expected products of the conventional McMurry reaction of **2**, were not found in the reaction mixture. The formation of **1** may be rationalized by two distinct mecha-

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(13) **Low-Valent Titanium Induced Reductive Coupling of 1.** The reaction was carried out under a dry argon atmosphere in a 100-mL three-necked round-bottomed flask equipped with a reflux condenser (protected from moisture), a septum for adding the reagents and sampling the reaction mixture, and an inlet for purging the flask with dried argon. The reaction flask was purged with argon for half an hour, and dry THF (freshly distilled over sodium diphenyl ketyl, 40 mL) was added into it and cooled to 0 °C. Dropwise slow injection of $TiCl_4$ (1.55 mL, 14.4 mmol) using a glass syringe gave a yellow complex. It was stirred for 10 min at 0 °C and treated with $LiAlH_4$ in four portion (0.84 g, 22.2 mmol). The temperature was gradually raised to room temperature, the mixture was stirred for 1.5 h to give a grayish-blue suspension, and then the solution was refluxed for 3 h to give a black suspension. A solution of **1** (2.00 g, 11.1 mmol) in dry THF (20 mL) was added dropwise using a plastic syringe over 3 min at reflux. The resulting mixture was refluxed for 120 h. THF (20 mL) was added during the reflux to keep its volume. After being cooling to room temperature, the mixture was treated with dichloromethane (40 mL), stirred for 15 min, and poured into 100 mL of aqueous HCl (0.1 N) to give two layers. The organic layer was separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic layers was dried ($MgSO_4$), and the solvents were removed in vacuo. Trituration of the crude products by ethanol afforded peropyrene (**2**) as a brown powder, 274 mg, 15%: mp 375−380 °C dec (lit.[12] mp 374−375 °C); $^1H$ NMR ($CHCl_3$, 25 °C, 400.1 MHz, $\delta(CHCl_3) = 7.26$ ppm) $\delta = 9.29$ (d, $J = 9.2$ Hz, $H_5$, $H_6$, $H_{12}$, $H_{13}$), 8.43 (d, $J = 9.2$ Hz, $H_4$, $H_7$, $H_{11}$, $H_{14}$), 8.38 (d, $J = 7.6$ Hz, $H_1$, $H_3$, $H_8$, $H_{10}$), 8.16 (t, $J = 7.9$ Hz, $H_2$, $H_9$) (cf. ref. 14); $^{13}C$ NMR ($CHCl_3$, 25 °C, 100.6 MHz, $\delta(CHCl_3) = 77.01$ ppm) $\delta = 131.30$ ($C_{3a}$, $C_{7a}$, $C_{10a}$, $C_{14a}$), 127.80 ($C_4$, $C_7$, $C_{11}$, $C_{14}$), 126.13 ($C_2$, $C_9$), 125.39 ($C_{5a}$, $C_{5b}$, $C_{12a}$, $C_{12b}$), 125.29 ($C_1$, $C_3$, $C_8$, $C_{10}$), 125.28 ($C_{10b}$, $C_{14b}$), 122.96 ($C_{12b}$, $C_{14c}$), 122.86 ($C_5$, $C_6$, $C_{12}$, $C_{13}$) (cf. ref. 14).

nisms, based on symmetrical and unsymmetrical coupling between two phenalenone radical anions (**2**$^{\bullet-}$):

1. A symmetrical **2**$^{\bullet-}$ + **2**$^{\bullet-}$ carbonyl−carbonyl coupling at $C_1$ and $C_{1'}$ ($C_1$ of another molecule of **2**$^{\bullet-}$), leading to (*Z*)-**5**, followed by a successive 1,3,5-hexatriene → 1,3-cyclohexadiene electrocyclic reaction of (*Z*)-**5** and aromatization. The formation of (*E*)-**5** may lead to **1** only indirectly, via a thermal (*E*)-**5** $\rightleftharpoons$ (*Z*)-**5** isomerization.

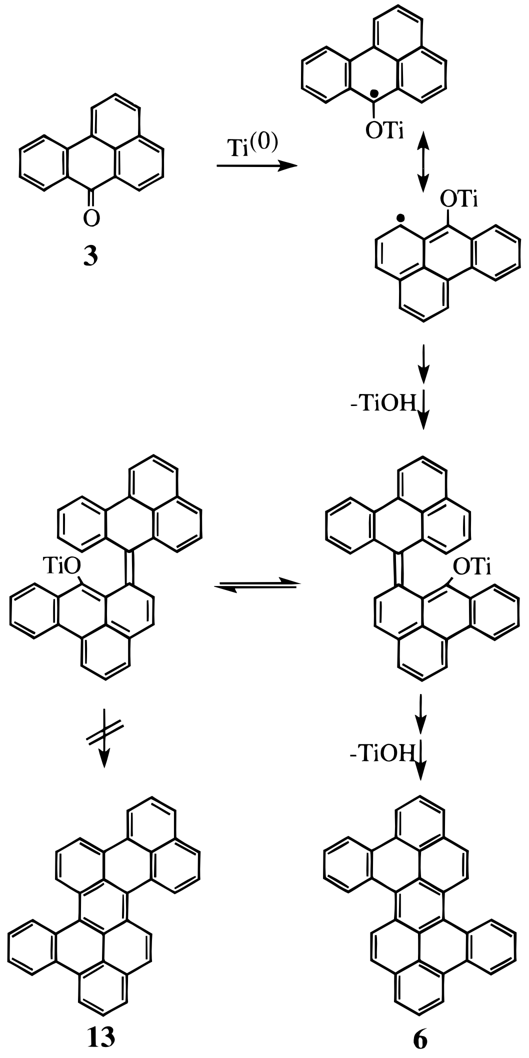
2. An unsymmetrical **2**$^{\bullet-}$ + **2**$^{\bullet-}$ carbonyl−*peri*-aromatic carbonyl coupling at $C_1$ and $C_{9'}$, followed by successive $\beta$-elimination of hydroxytitanium species, 1,3,5-hexatriene → 1,3-cyclohexadiene electrocyclic reaction of (*Z*)-**5**, and aromatization by a second $\beta$-elimination of hydroxytitanium species. This mechanism implies spin densities also at the *peri*-positions in **2**$^{\bullet-}$.

The titanium-induced reductive "dimerizations" of **3** and of **4** may, in principle, distinguish between these two mechanisms.

Treatment of **3** with low-valent titanium species generated from $TiCl_4$ and $LiAlH_4$ in THF for 126 h gave the overcrowded chiral LPAH tetrabenzo[*a*,*cd*,*j*,*lm*]perylene (**6**)[15−17] in 19% yield. Another product of the reaction was 7*H*-benz[*de*]anthracene[18] (21% yield). The reaction was highly regioselective: LPAH **6** was the only isomer among the 12 $C_{34}H_{18}$ nonacyclic LPAHs that could have potentially been formed in such a reductive "dimerization" of **3**.[11] Furthermore, neither the expected conventional McMurry reaction products, (*E*)- and (*Z*)-7-(7*H*-benz[*de*]anthracenylidene)-7*H*-benz[*de*]anthracene ((*E*)-**7** and (*Z*)-**7**),[19] nor their electrocyclization−aromatization $C_{34}H_{16}$ products, dibenzo[*fg*,*ij*]phenanthro[2,1,10,9,8,7-*pqrstuv*]pentaphene (**8**) and perylo[3,2,1,12-*pqrab*]perylene (**9**),[20] were found in the reaction mixture. An analogous low-valent titanium-induced reductive "dimerization" of **4**[21] afforded the overcrowded chiral LPAH dibenzo[*jk*,*uv*]dinaphtho[2,1,8,7-*defg*;2′,1′,8′,7′-*opqr*]pentacene (**10**)[22−24] in 1.3% yield. The major product of the reaction was 6*H*-benzo[*cd*]pyrene[25] (37% yield). LPAH **10** was the only isomer among the eight $C_{38}H_{18}$ undecacyclic LPAHs which potentially could have been formed in such a reductive "dimerization" of **4**.[11] Neither the expected McMurry reaction product 6-(6*H*-benzo[*de*]pyrenylidene)-6*H*-benzo[*de*]pyrene (**11**) nor its electrocyclization−aromatization $C_{38}H_{16}$ product, naphth[2′,1′,8′,7′:4,10,5]anthra[1,9,8-*abcd*]coronene (**12**),[26] were found in the reaction mixture.

The absence of any of the LPAHs related topologically to (*E*)-**7**, (*Z*)-**7**, and **11** among the products of "dimerization" of **3** and of **4** suggests that the reductive coupling reactions of phenalenone-type PAKs leading to LPAHs follow the unsymmetrical route (vide supra) of "dimerization": a coupling between the carbonyl carbon and *peri*-aromatic carbon, $\beta$-elimination of TiOH, 1,3,5-hexatriene-1,3-cyclohexadiene electrocyclic reaction, and aromatization by a second $\beta$-elimination of TiOH (Scheme 1). The alternative symmetrical route would be less favored, due to significant overcrowding (fjord regions) existing in the intermediate alkenes (*E*)-**7**, (*Z*)-**7**, and **11**. It is noted that the regioselectivity revealed in the syntheses of **6** indicates not only a

**Scheme 1**



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(15) A total of 1.61 g of **3** afforded hydrocarbon **6** as yellow needles, 285 mg, 19% (38%, based on consumed **3**): mp 335−340 °C (lit.[16] mp 333−334 °C); $^1$H NMR $\delta = 9.17$ (d, $J = 9.2$ Hz, $H_8$, $H_{17}$), 9.02 (d, $J = 6.9$ Hz, $H_3$, $H_{12}$), 9.01 (d, $J = 7.7$ Hz, $H_7$, $H_{16}$), 8.95 (d, $J = 7.9$ Hz, $H_4$, $H_{13}$), 8.28 (d, $J = 7.8$ Hz, $H_1$, $H_{10}$), 8.15 (d, $J = 10.0$ Hz, $H_9$, $H_{18}$), 8.13 (t, $J = 7.7$ Hz, $H_2$, $H_{11}$), 7.82 (q, $J = 7.1$ Hz, $J = 8.0$ Hz, $H_5$, $H_{14}$), 7.77 (q, $J = 7.0$ Hz, $J = 8.0$ Hz, $H_6$, $H_{15}$) (cf. ref. 14); $^{13}$C NMR $\delta = 131.48$ ($C_{3b}$, $C_{12b}$), 131.14 ($C_{18a}$, $C_{9a}$), 130.95 ($C_7$, $C_{16}$), 130.21 ($C_{7a}$, $C_{16a}$), 129.89 ($C_{3a}$, $C_{12a}$), 127.39 ($C_5$, $C_{14}$), 127.07 ($C_8$, $C_{17}$), 126.65 ($C_9$, $C_{18}$), 126.61 ($C_6$, $C_{15}$), 126.53 ($C_1$, $C_{10}$), 126.46 ($C_2$, $C_{11}$), 125.23 ($C_{7b}$, $C_{16b}$), 125.17 ($C_{7c}$, $C_{16c}$), 123.60 ($C_{9c}$, $C_{18c}$), 123.86 ($C_{9b}$, $C_{18b}$), 123.86 ($C_4$, $C_{13}$), 120.74 ($C_3$, $C_{12}$) (cf. ref. 14).

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(19) The alkenes (*E*)-**7** and (*Z*)-**7** have previously been reported, but their structures have not been characterized.[16]

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selectivity in the initial $\mathbf{3}^{\bullet-} + \mathbf{3}^{\bullet-}$ coupling between the carbonyl $C_7$ and the *peri*-aromatic $C_{6'}$ but also a selectivity in the electrocyclization reaction at $C_6$ and $C_{7'}$. The isomeric LPAH **13**[27] was not found in the reaction mixture.[28]

Ab initio DFT calculations of peropyrene (**1**) at B3LYP/6-311G**// B3LYP/6-311G** showed that the $D_{2h}$ conformation of **1** is the global minimum. The calculated optimized geometry of $D_{2h}$-**1** is depicted in Figure 1a. The calculated bond lengths appear to resemble the Clar picture[29] of **1** (Figure 1b). In PAHs there are approximately three different categories of carbon−carbon bonds: short bonds (ca. 1.36 Å), bonds of intermediate length (ca. 1.39 Å), and long bonds (ca. 1.43 Å). In the Clar representation, these are indicated by double bonds, inscribed circles, and single bonds, respectively. In peropyrene (**1**) there are 32 carbon−carbon bonds, 22 of which are properly represented by the Clar picture. The double-bond character (1.359 Å) of $C_4-C_5$, $C_6-C_7$, $C_{11}-C_{12}$, and $C_{13}-C_{14}$ and the lack of bond length alternation in the central ring (1.423−1.428 Å) are noted. Although the central ring of the Clar picture (Figure 1b) has an inscribed circle, none of its six bonds are in the 1.39 Å range.[30] The results are inconsistent with previous Hückel-type (ef-model) calculations,[31] which concluded that the Clar structure was not sufficient to describe the $\pi$-electron structure of peropyrenes. Peropyrene (**1**) is more stable than its isomers rubicene (**14**)[32] and benz[*e*]indeno[1,2,3,4-*hi*]-acephenanthrylene (**15**),[33] potential *peri*−*peri* coupling products of fluorenone (an isomer of **1**),[34] by 115.0 and 90.3 kJ/mol, respectively. 1*H*-Phenalen-1-one (**2**) is more stable than fluorenone by only 9.6 kJ/mol. A comparison of the isodesmic reactions 2[fluorenone] + $H_2$ → rubicene (**14**) + $2H_2O$ and 2[1*H*-phenalen-1-one (**2**)] + $H_2$ → peropyrene (**1**) + $2H_2O$ at B3LYP/6-311G** indicates that the former reaction is less exothermic than the latter by 95.8 kJ/mol.

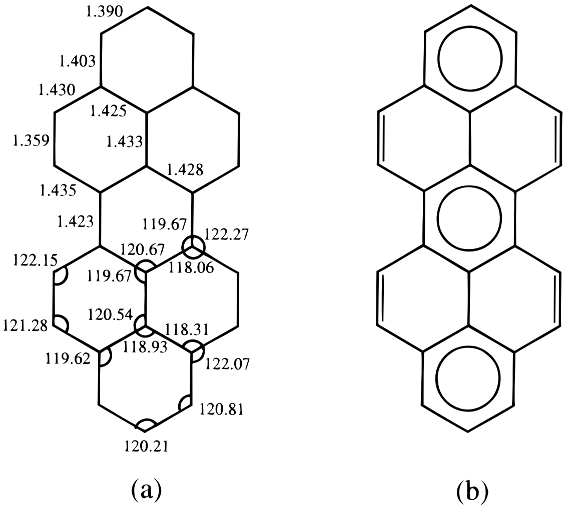

**Figure 1.** (a) DFT calculated optimized geometry of $D_{2h}$-**1** at B3LYP/6-311G**//B3LYP/6-311G**: bond lengths in angstroms (top), bond angles in degrees (bottom); (b) the Clar picture of **1**.

In conclusion, the variation of the low-valent titanium-induced carbonyl coupling reactions of phenalenones provides a direct entry into peropyrene-type LPAHs.

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(23) A total of 1.00 g of **3** afforded hydrocarbon **10** as yellowish-brown powder, 12 mg, 1.3%: mp 330−335 °C (lit.[22] mp 338−339 °C); $^1$H NMR $\delta$ = 9.47 (d, $J$ = 9.1 Hz, $H_8$, $H_{17}$), 9.29 (d, $J$ = 7.8 Hz, $H_7$, $H_{16}$), 8.53 (d, $J$ = 8.2 Hz, $H_1$, $H_{10}$), 8.51 (d, $J$ = 8.3 Hz, $H_2$, $H_{11}$), 8.37 (d, $J$ = 9.1 Hz, $H_9$, $H_{18}$), 8.33 (d, $J$ = 7.1 Hz, $H_5$, $H_{14}$), 8.32 (d, $J$ = 8.7 Hz, $H_3$, $H_{12}$), 8.27 (d, $J$ = 8.8 Hz, $H_4$, $H_{13}$), 8.14 (t, $J$ = 7.8 Hz, $H_6$, $H_{15}$); $^{13}$C NMR $\delta$ = 131.68 ($C_{4a}$, $C_{13a}$), 129.62 ($C_{7a}$, $C_{16a}$), 129.53 ($C_{2a}$, $C_{11a}$), 128.83 ($C_{9a}$, $C_{18a}$), 128.57 ($C_7$, $C_{16}$), 127.97 ($C_9$, $C_{18}$), 127.41 ($C_3$, $C_{12}$), 127.25 ($C_4$, $C_{13}$), 126.74 ($C_8$, $C_{17}$), 126.49 ($C_5$, $C_{14}$), 126.32 ($C_{13b}$, $C_{18d}$), 126.00 ($C_{7c}$, $C_{16c}$), 125.89 ($C_1$, $C_{10}$), 125.89 ($C_6$, $C_{15}$), 125.57 ($C_2$, $C_{11}$), 125.47 ($C_{7b}$, $C_{16b}$), 124.58 ($C_{13e}$, $C_{16d}$), 124.16 ($C_{13c}$, $C_{18c}$), 123.14 ($C_{13d}$, $C_{18b}$).

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(30) The Clar picture is not an ideal representation of **1**. Its shortcomings are reflected in the fact that 10 out of the 32 C−C bond lengths in **1** are not properly represented. We thank a referee for his comments on the shortcomings of the Clar picture of **1**.

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