VIP Antiaromaticity Very Important Paper

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Tetracyclopenta[*def,jkl,pqr,vwx*]tetraphenylene: A Potential Tetraradicaloid Hydrocarbon**

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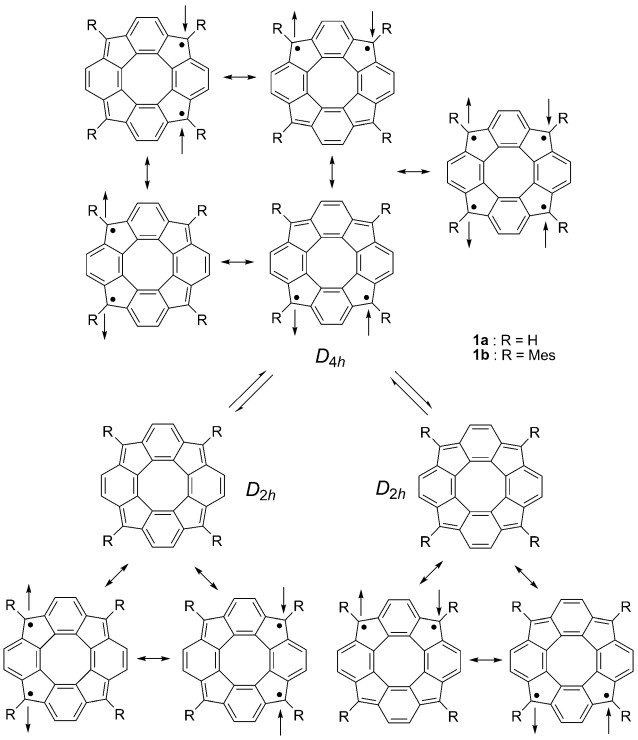
Abstract: *A tetramesityl derivative of hitherto unknown tetracyclopenta[def,jkl,pqr,vwx]tetraphenylene (TCPTP), which is a potential tetraradicaloid hydrocarbon, was synthesized. Theoretical calculations based on spin-flip time-dependent density functional theory predict that the closed-shell D_{2h} form of TCPTP is more stable than the open-shell D_{4h} form with its slightly tetraradical character. The tetramesityl derivative $(Mes)_4$-TCPTP exhibits remarkable antiaromaticity as a result of the peripheral 20-π-electron circuit, which causes an absorption maximum at a long wavelength and a small HOMO–LUMO gap. In solution, $(Mes)_4$-TCPTP most likely adopts rapidly equilibrating D_{2h} structures that interconvert via the D_{4h} transition state. X-ray crystallographic analysis showed $(Mes)_4$-TCPTP as an approximate D_{2h} structure.*

We report the synthesis, structure, and fundamental physical properties of compound **1b**, a tetramesityl derivative of hitherto unknown tetracyclopenta[*def*,*jkl*,*pqr*,*vwx*]tetraphenylene (TCPTP, **1a**). Particularly noteworthy aspects of compound **1a** include:

1) Closed-shell D_{2h} and open-shell D_{4h} structures exist, and their mutual interconversion (Scheme 1) is similar to that observed for cyclobutadiene (CBD). For CBD, the valence tautomerization that interconverts the two rectangular D_{2h} isomers via the square D_{4h} transition state of diradical character has been the topic of controversy for more than thirty years, even after numerous experimental and theoretical investigations have been done.[1,2]



Scheme 1. Valence tautomerization of **1a** and **1b** with closed-shell D_{2h} isomers (bottom) with a small diradical character via a D_{4h} isomer (top) with open-shell diradical and tetraradical characters.

2) **1a** contains 28 π electrons distributed over an inner 8-π-electron system and an outer 20-π-electron system, both of which can be antiaromatic in their highest symmetry forms. The inner 8-π-electron system is fixed in a planar geometry and has relevance to planar cyclooctatetraenes (COTs), which also attracted substantial interest from synthetic and theoretical chemists.[3] For example, a few derivatives were synthesized in which a COT core was forced to adopt a planar geometry.[3] Moreover, the D_{8h} transition state of the bond shifting between D_{4h} COTs

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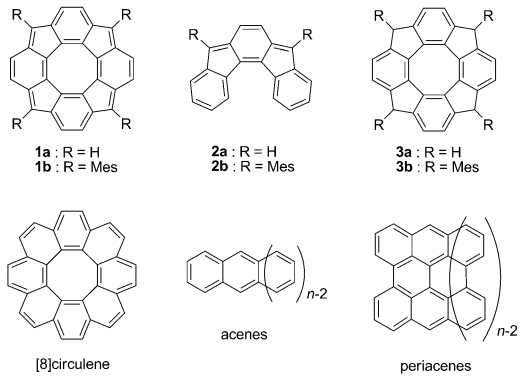
was experimentally shown to violate the Hund's rule in a strictest sense.[4]

3) **1a** is a cyclic congener of indeno[2,1-*c*]fluorene (**2a**),[5] one of the indenofluorene isomers, which have attracted keen interest because of their semiconducting character, resulting from small band gaps, and their nonlinear optical properties, arising from their singlet diradical characters.[6,7] It should be emphasized that **1a** represents a potential singlet tetraradicaloid compound with a hydrocarbon framework (Scheme 1, the top right canonical structure). A stable tetraradical consisting of two diboradiphosphinocyclobutane rings linked by a *meta*-phenylene has been reported previously.[8] Although large polycyclic aromatic hydrocarbons, such as an acene with 20 rings (icosacene: $n=20$) and periacenes with more than 8 zigzag-edge rings (perioctacene, $n=8$), are expected to have tetraradical ground states, such materials have not yet been prepared.[9]
4) Compound **1a** can be regarded as a member of the corannulene family, according to the corannulene concept proposed by Hellwinkel,[10] and as a smaller analogue of [8]circulene, whose derivatives, including its tetrabenzo homologues, have been prepared recently.[11] Although Hellwinkel and Reiff reported the generation of a dicationic species of **1a** (with 26 π electrons) from its tetrahydro derivative **3a** in a mass spectrometry sample chamber,[12] isolation and characterization of **1a** or its derivatives have not been reported.



Herein we report the theoretical investigation of the relationship between the open-shell singlet character and the structures of these compounds. The optimized geometries of these antiaromatic molecules, which are composed of five- and six-membered rings, often depend significantly on the calculation methods, as shown for *s*-indacene.[13] We thus applied the unrestricted natural orbital complete active space method,[14] UNO-CAS(4,4)/6-311G(d,p), and the spin-flip time-dependent density functional theory (SF-TD-BHHLYP/6-311G(d,p)) methods, which reproduced the experimental structures of such molecules very well.[15] These two methods provided similar structures for the present systems (Figure S12 and S13), so that the geometries optimized with SF-TD-BHHLYP/6-311G(d,p) were employed for later discussion. We first investigated the diradical characters, which are determined by the occupation numbers y_0 and y_1 of the lowest and second lowest unoccupied natural orbital (LUNO and LUNO + 1, respectively). These were obtained by the long-range-corrected LC-UBLYP/6-311 + G(d,p) method,[16] which is known to semiquantitatively reproduce the open-shell characters obtained by highly-electron-correlated methods.[17] The y_0 and y_1 values ranged from 0 to 1 ($y_0 \geq y_1$), thus indicating the diradical and tetraradical characters, that is, $(y_0, y_1) = (1, 0)$ indicates a purely diradical character, while $(y_0, y_1) = (1, 1)$ indicates a purely tetraradical character.

Table 1 lists the calculated y_0 and y_1 values for three model systems, that is, model A (with the structure of **1a** optimized under the constraint of D_{2h} symmetry) and model B (with the structure of **1a** optimized under the constraint of D_{4h} symmetry). We also examined model C with the structure of the TCPTP part of **1b** experimentally obtained by X-ray crystallographic analysis (described below). Table 2 shows the bond lengths of the peripheral bonds *a*–*j*, internal bonds *k*–*n*, and spoke bonds *o*–*r* of models A–C (Figure 1). The structure of the D_{2h} symmetric model A is similar to that of the experimental model C (Table 2, and Figure S12 in the Supporting Information) and shows a relatively small diradical character ($y_0 = 0.095$ for model A and 0.258 for model C). On the other hand, the D_{4h} symmetric model B, which had a higher energy (34.7 kJ mol^{-1} at the SF-TD-BHHLYP/6-311G(d,p) level of approximation) than model A, featured a significant y_0 value (1.000) together with a small y_1 value

Table 1: Occupation numbers y_0 and y_1 of the lowest and second lowest unoccupied natural orbitals (LUNO and LUNO + 1, respectively) obtained by LC-UBLYP/6-311 + G(d,p) for models A–C of **1a**.

Occupation number	Model A	Model B	Model C
y_0	0.095	1.000	0.258
y_1	0.032	0.166	0.085

Table 2: Calculated (models A and B) and experimental (model C) bond lengths for the TCPTP core.

Bond[a]	Model A[b]	Model B[b]	Model C[c]
a	1.447	1.397	1.460(6)
b	1.350	1.397	1.371(6)
c	1.437	1.403	1.433(6)
d	1.339	1.366	1.349(6)
e	1.437	1.403	1.440(5)
f	1.350	1.397	1.373(5)
g	1.447	1.397	1.452(6)
h	1.378	1.403	1.391(6)
i	1.390	1.366	1.390(6)
j	1.378	1.403	1.380(6)
k	1.476	1.477	1.479(5)
l	1.344	1.359	1.359(5)
m	1.476	1.477	1.487(5)
n	1.373	1.359	1.379(6)
o	1.469	1.442	1.481(5)
p	1.469	1.442	1.476(6)
q	1.420	1.442	1.433(5)
r	1.420	1.442	1.435(5)

[a] Bond positions are shown in Figure 1. [b] Calculated at the SF-TD-BHHLYP/6-311G(d,p) level. [c] Data obtained from X-ray analysis of **1b**.

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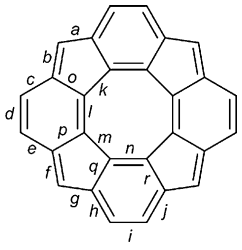


Figure 1. Bond numbering for models A–C of **1a**.

(0.166). The relationship between the open-shell characters and the structures can be explained with the resonance structures for closed-shell (D_{2h} symmetric), diradical (C_{2v} symmetric), and tetraradical (D_{4h} symmetric) forms (Scheme 1). Indeed, the bond-length alternation (BLA) for the outer-ring region (bonds *a–j* in Figure 1) is reduced in model B compared with models A and C (Figure S12). This alteration coincides with that observed in the diradical and tetraradical resonance structures (Scheme 1). These results indicate that the D_{2h} structure exhibits a slightly diradical nature, while the D_{4h} structure exhibits a significantly diradical nature together with a slightly tetraradical nature. In order to investigate the spatial contribution of unpaired electrons to the diradical characters, we calculated the odd-electron-density distributions for models B and C (Figure 2),[17] which are divided into contributions from y_0 and y_1. The odd-electron densities of y_0 have much larger amplitudes than those of y_1. Moreover, their distributions are largest on the carbon atoms in the five-membered rings for both y_0 and y_1, which can be explained with the diradical and tetraradical resonance structures (Scheme 1).

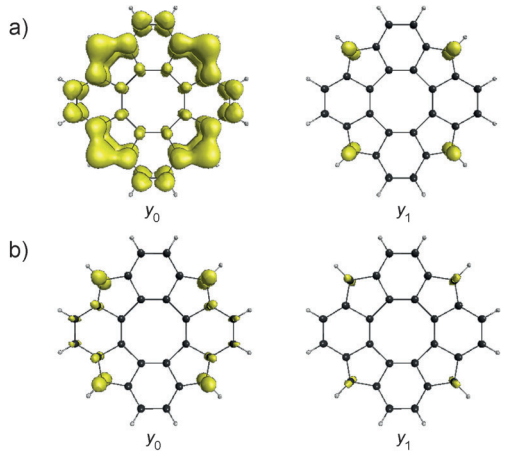
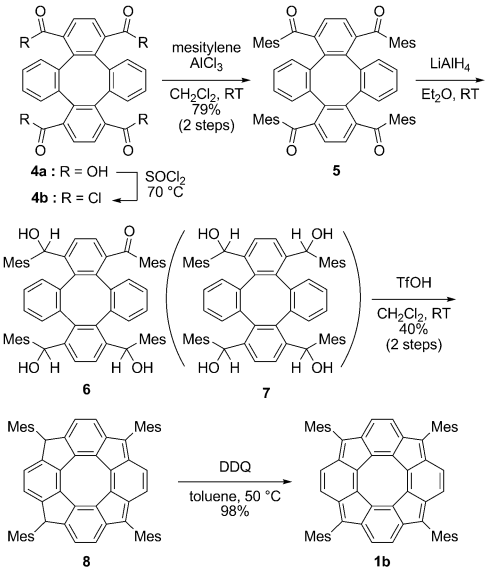


Figure 2. Odd-electron-density distributions of y_0 and y_1 of models B (a) and C (b) calculated at the LC-UBLYP/6-311+G(d,p) level [contour value of 0.0025 a.u.; 1 a.u. = 27.21 eV].

We started the synthesis of **1b** from the known tetracarboxylic acid **4a**[18] (Scheme 2). A Friedel–Crafts reaction of acid chloride **4b** with mesitylene gave tetraketone **5**. After treatment of **5** with $LiAlH_4$, the crude product was subjected without purification to an intramolecular alkylation by treatment with trifluoromethanesulfonic acid. However, the product of the alkylation was not the expected tetrahydro derivative **3b**, but dihydro-TCPTP **8**. We assumed that the reduction of **5** was not complete because of the low solubility of the alkoxide intermediates, which precipitated out from the reaction mixture, giving triol **6** instead of tetraol **7**.[19]



Scheme 2. Synthesis of **1b**.

Dehydrogenation of **8** with DDQ gave product **1b** as a dark brown solid that was stable in air for at least a few months.

The ^{1}H NMR spectrum of **1b** measured in [D$_8$]toluene at 30 °C exhibits a singlet at 2.85 ppm for the core "aromatic" proton (Figure S3), which is remarkably upfield shifted compared to the corresponding proton of hemicircular hydrocarbon **2b**[5] and dihydro derivative **8** (6.13 and 5.84 ppm in $CDCl_3$, respectively). The nucleus-independent chemical shift (NICS(1)) values (LC-UBLYP/6-311+G(d,p)) calculated for the observed TCPTP core (model C) and D_{2h} symmetric **1a** (model A) indicate that the six-membered rings are either weakly aromatic or antiaromatic (Figure 3), thus suggesting that the "aromatic" proton would exhibit an averaged chemical shift in a nonaromatic region. The remarkable upfield shift is therefore ascribed to the paramagnetic shielding effect of the outer 20-π-electron system. At higher temperatures (50 °C), the signals start to broaden, thus indicating the population of the thermally excited triplet state (Figure S4). Theoretically estimated vertical singlet–triplet energy gaps (81 and 69 kJ mol^{-1} for models A and C, respectively) at the SF-TD-PBE0/6-311G(d,p) level of theory,[20] are however relatively large. The appearance of a single signal for the core proton indicates that **1b** adopts the

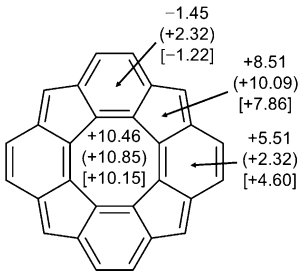


Figure 3. NICS(1) values of **1a** in models A, B (in round brackets), and C [in square brackets] calculated at the LC-UBLYP/6-311+G(d,p) level.

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D_{4h} structure or exists in a rapid equilibrium between the D_{2h} structures. However, no peak separation was observed when the solution was cooled to −80 °C (Figure S5). Similarly, the ^{13}C NMR spectrum showed the four signals that were expected for the TCPTP core carbon atoms of D_{4h} symmetric **1b** at 30 °C (Figure S6). Cooling to −60 °C barely showed line broadening indicating that the rates of conversion between the D_{2h} structures became slow on the NMR time scale (Scheme 1). Based on the calculated chemical shifts for the peripheral protons of **1a** (4.86 and 5.38 ppm) by the LC-UBLYP method for the D_{2h} structure, the energy barrier for the $D_{2h} \rightleftharpoons D_{2h}$ valence tautomerization is estimated to be smaller than around 10 kJ mol^{-1}, which is substantially smaller than the theoretically estimated value (34.7 kJ mol^{-1}).

Crystals suitable for X-ray structure analysis were obtained by recrystallization from chloroform.[21] As shown in Figure 4, the TCPTP core of **1b** adopts a planar geometry

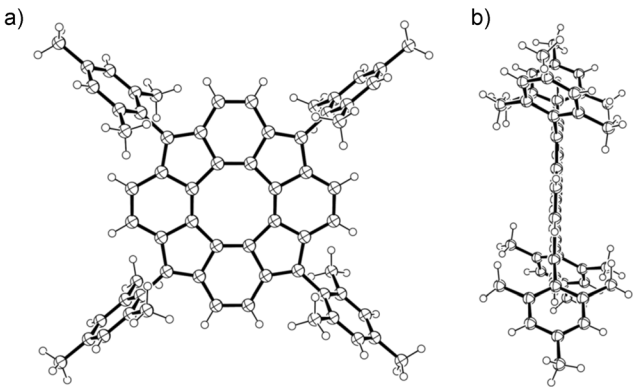

Figure 4. a) Top-view and b) side-view ORTEP drawings of **1b** at the 50% probability level. Disordered solvent molecules are omitted for clarity.

with deviations from the mean square plane of less than 0.0034 Å. The mesityl groups are oriented nearly perpendicular to the TCPTP plane with dihedral angles of 72.3–88.3°. The most important feature of the structure of **1b** is that it adopts an approximate D_{2h} structure, which is evident from the presence of a crystallographic center of inversion. The observed bond lengths at the TCPTP core (model C) are listed in Table 2 together with those of theoretically optimized D_{2h} model A and D_{4h} model B. The relatively short bonds *b* (1.371 Å), *d* (1.349 Å), *f* (1.373 Å), and *l* (1.359 Å), and relatively long bonds *a* (1.460 Å), *c* (1.433 Å), *e* (1.440 Å), and *g* (1.452 Å) indicate the presence of a *p*-quinodimethane substructure. On the other hand, the bonds *h*, *i*, *j*, and *n* in the other six-membered ring are more homogeneous (1.379–1.391 Å), thus suggesting its benzenoid structure. The inner COT ring adopts an approximate D_{2h} structure with remarkable bond-length alternation: bonds *l* (1.359 Å) and *n* (1.379 Å), which are part of the six-membered rings, are shorter than bonds *k* (1.479 Å) and *m* (1.487 Å), which are part of the five-membered rings. The data in Table 2 show again that the present SF-TD-DFT calculations at the BHHLYP/6-311G(d,p) level of theory reasonably reproduce the structure of **1b**.

Figure 5 shows UV-Vis-NIR spectra of **1b** and its dihydro derivative **8**. Compound **1b** exhibits an intense absorption maximum at 475 nm ($\varepsilon = 10\,100\,M^{-1}cm^{-1}$) together with a broad band centered at 909 nm ($\varepsilon = 1210\,M^{-1}cm^{-1}$) with

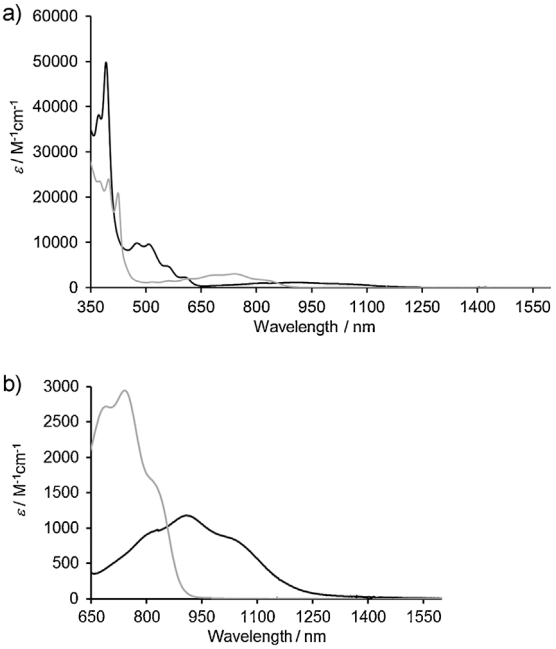

Figure 5. a) UV-Vis-NIR spectra of **1b** (black) and dihydro derivative **8** (gray) in CH_2Cl_2. b) NIR region with expanded longitudinal axis.

a low oscillator strength. The lowest energy absorption band is shifted to much longer wavelengths compared to indeno-[2,1-*c*]fluorene derivative **2b** ($\lambda_{max} = 603$ nm)[5] and dihydro derivative **8** ($\lambda_{max} = 740$ nm) because of the extended conjugation. Time-dependent density functional theory calculations[22] (TD-UB3LYP/6-311 + G(d,p) level: Tables S1 and S2) indicate the lowest energy band for model A at 1079 nm ($f = 0.0053$). The small HOMO–LUMO gap of **1b** was also characterized by cyclic voltammetry and exhibited two reversible oxidation and reduction waves ($E_1^{ox} = +0.08$, $E_2^{ox} = +0.47$, $E_1^{red} = -1.39$, and $E_2^{red} = -1.68$ V vs. Fc/Fc$^+$, see Figure S11 in Supporting Information).

In conclusion, we succeeded in the synthesis of a tetramesityl derivative (**1b**) of hitherto unknown tetracyclopenta-[*def*,*jkl*,*pqr*,*vwx*]tetraphenylene (**1a**). Regarding its molecular structure, that is, an open-shell D_{4h} or a closed-shell D_{2h} structure, results of an NMR study suggested the existence of **1b** as rapidly equilibrating D_{2h} structures through valence tautomerization in solution. In crystals containing a chloroform solvate molecule, it adopts an approximate D_{2h} structure. Studies are under way to force **1b** and other derivatives of **1a** to adopt the D_{4h} structure by establishing electronic and/or steric perturbations arising from external factors, including substituents.[23]

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[1] For reviews of earlier works, see: a) T. Bally, S. Masamune, *Tetrahedron* **1980**, *36*, 343 – 370; b) G. Maier, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309 – 332; *Angew. Chem.* **1988**, *100*, 317 – 341; c) B. R. Arnold, J. Michl in *Kinetics and Spectroscopy of Carbenes and Biradicals* (Ed.: M. S. Platz), Plenum, New York, **1990**, pp. 1 – 35.

[2] See for example: a) B. R. Arnold, J. Michl, *J. Phys. Chem.* **1993**, *97*, 13348 – 13354; b) M. Eckert-Maksić, M. Vazdar, M. Barbatti, H. Lischka, Z. B. Maksić, *J. Chem. Phys.* **2006**, *125*, 064310; c) T. Saito, S. Nishihara, Y. Kitagawa, T. Kawakami, S. Yamanaka, M. Okumura, K. Yamaguchi, *Chem. Phys. Lett.* **2010**, *498*, 253 – 258.

[3] a) K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **2001**, *123*, 1755 – 1759; b) A. Matsuura, K. Komatsu, *J. Am. Chem. Soc.* **2001**, *123*, 1768 – 1769; c) Y. Nakamura, N. Aratani, H. Shinokubo, A. Takagi, T. Kawai, T. Matsumoto, Z. S. Yoon, D. Y. Kim, T. K. Ahn, D. Kim, A. Muranaka, N. Kobayashi, A. Osuka, *J. Am. Chem. Soc.* **2006**, *128*, 4119 – 4127; for reviews: d) J. F. M. Oth, *Pure Appl. Chem.* **1971**, *25*, 573 – 622; e) T. Nishinaga, T. Ohmae, M. Iyoda, *Symmetry* **2010**, *2*, 76 – 97.

[4] P. G. Wenthold, D. A. Hrovat, W. T. Borden, W. C. Lineberger, *Science* **1996**, *272*, 1456 – 1459.

[5] A. G. Fix, P. E. Deal, C. L. Vonnegut, B. D. Rose, L. N. Zakharov, M. M. Haley, *Org. Lett.* **2013**, *15*, 1362 – 1365.

[6] a) D. T. Chase, B. D. Rose, S. P. McClintock, L. N. Zakharov, M. M. Haley, *Angew. Chem. Int. Ed.* **2011**, *50*, 1127 – 1130; *Angew. Chem.* **2011**, *123*, 1159 – 1162; b) D. T. Chase, A. G. Fix, S. J. Kang, B. D. Rose, C. D. Weber, Y. Zhong, L. N. Zakharov, M. C. Lonergan, C. Nuckolls, M. M. Haley, *J. Am. Chem. Soc.* **2012**, *134*, 10349 – 10352; c) A. Shimizu, Y. Tobe, *Angew. Chem. Int. Ed.* **2011**, *50*, 6906 – 6910; *Angew. Chem.* **2011**, *123*, 7038 – 7042; d) A. Shimizu, R. Kishi, M. Nakano, D. Shiomi, K. Sato, T. Takui, I. Hisaki, M. Miyata, Y. Tobe, *Angew. Chem. Int. Ed.* **2013**, *52*, 6076 – 6079; *Angew. Chem.* **2013**, *125*, 6192 – 6195; for recent reviews, see: e) A. G. Fix, D. T. Chase, M. M. Haley, *Top. Curr. Chem.* **2014**, *349*, 159 – 195; f) A. Shimizu, S. Nobusue, H. Miyoshi, Y. Tobe, *Pure Appl. Chem.* **2014**, *86*, 517 – 528.

[7] For recent reviews on singlet diradical hydrocarbons, see: a) Z. Sun, Q. Ye, C. Chi, J. Wu, *Chem. Soc. Rev.* **2012**, *41*, 7857 – 7889; b) M. Abe, *Chem. Rev.* **2013**, *113*, 7011 – 7088; c) Z. Sun, Z. Zeng, J. Wu, *Acc. Chem. Res.* **2014**, *47*, 2582 – 2591; d) Z. Sun, J. Wu, *Top. Curr. Chem.* **2014**, *349*, 197 – 248; e) T. Kubo, *Chem. Lett.* **2014**, DOI: 10.1246/cl.140997.

[8] A. Rodriguez, F. S. Tham, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2004**, *43*, 4876 – 4880; *Angew. Chem.* **2004**, *116*, 4984 – 4988.

[9] a) D. Jiang, S. Dai, *J. Phys. Chem. A* **2008**, *112*, 332 – 335; b) W. Mizukami, Y. Kurashige, T. Yanai, *J. Chem. Theory Comput.* **2013**, *9*, 401 – 407.

[10] According to the corannulene concept, corannulenes are defined as compounds possessing an inner annulene system that is connected through all its radial valences with an outer annulene system. Using this nomenclature, **1a** is named [8,20^{2,1,2,1,2,1,2,1}]corannulene: D. Hellwinkel, *Chem.-Ztg.* **1970**, *94*, 715 – 718.

[11] a) C.-N. Feng, M.-Y. Kuo, Y.-T. Wu, *Angew. Chem. Int. Ed.* **2013**, *52*, 7791 – 7794; *Angew. Chem.* **2013**, *125*, 7945 – 7948; b) Y. Sakamoto, T. Suzuki, *J. Am. Chem. Soc.* **2013**, *135*, 14074 – 14077; c) R. W. Miller, A. K. Duncan, S. T. Schneebeli, D. L. Gray, A. C. Whalley, *Chem. Eur. J.* **2014**, *20*, 3705 – 3711.

[12] D. Hellwinkel, G. Reiff, *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 527 – 528; *Angew. Chem.* **1970**, *82*, 516 – 517.

[13] a) R. H. Hertwig, M. C. Holthausen, W. Koch, Z. B. Maksić, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1192 – 1194; *Angew. Chem.* **1994**, *106*, 1252 – 1254; b) M. Nendel, B. Goldfuss, K. N. Houk, K. Hafner, *J. Mol. Chem. Struct. (THEOCHEM)* **1999**, *461 – 462*, 23 – 28.

[14] a) K. Yamaguchi, *Int. J. Quantum. Chem. Symp.* **1980**, *18*, 269 – 284; b) J. M. Bofill, P. Pulay, *J. Chem. Phys.* **1989**, *90*, 3637 – 3646.

[15] R. Kishi, M. Nakano, S. Ohta, A. Takebe, M. Nate, H. Takahashi, T. Kubo, K. Kamada, K. Ohta, B. Champagne, E. Botek, *J. Chem. Theory Comput.* **2007**, *3*, 1699 – 1707.

[16] H. Iikura, T. Tsuneda, T. Yanai, K. Hirao, *J. Chem. Phys.* **2001**, *115*, 3540 – 3544.

[17] M. Nakano, H. Fukui, T. Minami, K. Yoneda, Y. Shigeta, R. Kishi, B. Chempagne, E. Botek, T. Kubo, K. Ohta, K. Kamada, *Theor. Chem. Acc.* **2011**, *130*, 711 – 724; Erratum: M. Nakano, H. Fukui, T. Minami, K. Yoneda, Y. Shigeta, R. Kishi, B. Champagne, E. Botek, T. Kubo, K. Ohta, K. Kamada, *Theor. Chem. Acc.* **2011**, *130*, 725.

[18] D. Hellwinkel, G. Reiff, V. Nykodym, *Justus Liebigs Ann. Chem.* **1977**, 1013 – 1025.

[19] We are grateful to Prof. Dietmar Kuck (University of Bielefeld) for pointing out this possibility.

[20] Y. A. Bernard, Y. Shao, A. I. Krylov, *J. Chem. Phys.* **2012**, *136*, 204103.

[21] CCDC-1016787 (**1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[22] a) E. Runge, E. K. U. Gross, *Phys. Rev. Lett.* **1984**, *52*, 997 – 1000; b) E. K. U. Gross, W. Kohn, *Adv. Quant. Chem.* **1990**, *21*, 255 – 291.

[23] For example, tetra-*tert*-butyl-*s*-indacene was reported to adopt an approximate D_{2h} structure in crystals. This structure is a transition-state of valence tautomerization of C_{2h}-symmetric isomers: J. D. Dunitz, C. Krüger, H. Irngartinger, E. F. Maverick, Y. Wang, M. Nixdorf, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 387 – 389; *Angew. Chem.* **1988**, *100*, 415 – 418.

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