

Communication

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Synthesis and Characterization of Dibenzo[*a*,*f*]pentalene: Harmonization of the Antiaromatic and Singlet Biradical Character

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Supporting Information Placeholder

ABSTRACT: Mesityl derivatives of the hitherto unknown dibenzopentalene isomer, dibenzo[a,f]pentalene, were synthesized. The molecular geometry and physical properties of dibenzo[a,f]pentalene were experimentally investigated. Dibenzo[a,f]pentalene combines a large antiaromatic and appreciable singlet open-shell character, properties that are not shared by the well-known isomer, dibenzo[a,e]pentalene.

Non-benzenoid polycyclic hydrocarbons with antiaromaticity have been the subject of extensive synthetic, structural, and electronic studies.^{1–8} Unlike aromaticity, antiaromaticity leads to distinct destabilization, π -bond localization, a paratropic current, and a decrease in the HOMO–LUMO energy gap.⁹ These unique electronic properties have attracted tremendous interest for their utility in advanced optoelectronic materials.^{10–16} One of the most interesting topics of study in connection with the structure–property relationships of antiaromatic hydrocarbons involves the position and/or direction of the π -extension on the periphery of an antiaromatic system, which can dramatically shift the electronic structure between closed- and open-shell ground states.^{17–22}

The dibenzopentalenes constitute an intriguing family of compounds consisting of the antiaromatic 8π -electron pentalene 1 and two aromatic 6π -electron benzenoid rings. Since the first synthesis of the stable isomer, dibenzo[*a*,*e*]pentalene 2, by Brand in 1912,²³ related compounds have attracted attention^{24,25} as probes of aromaticity/antiaromaticity^{26,27} as well as potential scaffolds for use in organic optoelectronic materials.^{28–31} In the dibenzo[a,e]pentalene 2, the two fused benzene rings remarkably stabilize the pentalene core through the aromaticity of the fused benzene rings, which negates the antiaromatic character of pentalene and furnishes the pentagonal rings with olefinic properties. Recent progress in the synthesis of dibenzo[a,e]pentalene,³²⁻⁴⁸ including monoannulated⁴⁹⁻⁵¹ and π -extended derivatives, ^{52–56} has advanced our understanding of fascinating dibenzo[a,e]pentalene-based materials.^{57,58} Dibenzopentalene has another structural isomer, dibenzo[a, f] pentalene 3, which has not been extensively explored except in its dianion form, 3a^{2-.59,60} Recently, Diederich's group described synthetic attempts

toward the π -extended pentalenes with an [*a*,*f*]-type fusion pattern that readily gave the Diels–Alder adducts and failed to provide the fully conjugated products that were hypothesized to have significant antiaromaticity based on theoretical calculations.⁵⁰ The pioneering synthetic⁶¹ and theoretical^{62,63} studies of **3** suggested that the position of the benzene fusion on the pentalene core played a critical role in the electronic properties and chemical stability of the compound.



Figure 1. (A) Molecular structures of pentalene **1**, dibenzo[*a*,*e*]pentalene **2**, and dibenzo[*a*,*f*]pentalene **3**. Mes = 2,4,6-trimethylphenyl. (B) Resonance structures of **2a** and **3a**. The hexagonal rings in gray denote benzenoid rings, and the trimethylenemethane (TMM) subunits in the open-shell structures are highlighted by two unpaired electrons (dots).

The effects of the [a,f]-type dibenzoannulation at the pentalene core on the electronic properties of the structure were investigated by performing the first synthesis and characterization of the dibenzo[a,f]pentalene derivatives **3b** and **3c**. The non-alternant hydrocarbons of the peripheral 16π -electron system provided large antiaromaticity and appreciable singlet biradical character. Dibenzo[a,f]pentalene **3a** is expected to provide larger antiaromaticity than the [a,e]-isomer **2a**. The single fused hexagonal ring of **3a** inevitably adopts an *o*-quinoidal form in the closed-shell resonance structure of **3a**, which loses the aromatic stabilization and enhances the $4n\pi$ -electron antiaromatic character. These results contrast starkly with the case of **2a**, in which the two aromatic rings remain stable (Figure 1B).⁶² The π -conjugated systems that incorporate the *o*-quinodimethane subunit often provide a singlet openshell character.^{64–66} **3a** includes a TMM biradical subunit typical of non-Kekulé molecules, with a triplet ground state⁶⁷ and two aromatic rings in the biradical form, which would stabilize the biradical structure and provide an open-shell character (Figure 1B). These intriguing estimations prompted us to synthesize **3** and investigate the electronic structures of **3**.

Scheme 1. Synthesis of dibenzo[a,f]pentalenes 3b and 3c^a



a DIBAL = diisobutylaluminum hydride, Mes = 2,4,6-trimethylphenyl, PPA = polyphosphoric acid.

The syntheses of 3b and 3c, in which bulky mesityl groups were introduced to kinetically protect the reactive sites, are shown in Scheme 1. Considering that 3 is aromatically stabilized to only a small degree, the selection of the precursor for the fully conjugated system 3 is important. Thus, we designed a synthetic route via the aromatic dianion 3^{2-} , which enjoys aromatic stability and is readily oxidized to the neutral hydrocarbon 3 under mild conditions. The dianion 3^{2-} was accessed via the dihydrogenated hydrocarbon 9, which was a suitable precursor because the two cyclopentadiene structures enabled the conversion to 3^{2-} . The treatment of the benzophenone dimethylacetal derivative 4 and dimethyl malonate with catalytic amounts of InBr3 gave the diaryl methylenated products 5 in moderate yields.68 The direct C-C double bond formation provided a starting material that was sufficiently unsaturated that it could transform the dihydrogenated precursor 9. The reduction of the ester groups of 5 with DIBAL afforded the diol 6, and subsequent oxidation gave the dialdehydes 7. The treatment of 7 with mesitylmagnesium bromide afforded the diols 8. The intramolecular cyclization of 8 was carried out under acidic conditions⁶⁹ to afford the dihydrogenated hydrocarbon 9. The dianion 3^{2-} was quantitatively generated by the treatment of 9 with *n*BuLi in THF at -35°C, according to Kitahara's procedure.⁵⁹ The molecular geometry of **3b**²⁻ determined by X-ray analysis was nearly identical to that of the dibenzo [a,e] pentalene dianion, 32,70 in which the 10 π -electron pentalenide moiety was the dominant structure (see Figures S2 and S6). The subsequent two-electron oxidation of 3^{2-} with *p*-chloranil furnished the mesityl derivatives of dibenzo[a,f]pentalene **3b** and 3c as brown solids. Under ambient conditions, the obtained dibenzo[a, f] pentalene 3 was immediately oxidized to give the oxygen-adduct, as confirmed by mass spectroscopy. As a reference compound, the dibenzo[*a*,*e*]pentalene derivative **2b** with the same substituents as **3c** was prepared according to Itami's procedure.⁴¹

Careful recrystallization from a hexane/dichloromethane solution in a degassed sealed tube gave a single crystal of **3c** that was suitable for X-ray crystallographic analysis.⁷¹ Two crystallographically independent molecules (hereafter, molecules A and B) were present in the asymmetric unit, one of which is shown in Figure 2. The X-ray crystallographic analysis of **3c** illustrated that the main core of **3c** assumed a planar structure and the two mesityl groups formed a large dihedral angle (~70°) with the main core (Figure 2B). Between the molecules A and B, the difference in the bond lengths was observed; while the bond lengths in molecule A adopts an approximate C_s symmetry, those in molecular B comes closer to a $C_{2\nu}$ symmetry (Figure S5). We believe that the observed geometry of **3c** is either an equilibrium $C_{2\nu}$ structure that is stabilized by crystal pacing forces or a pair of C_s structures that equilibrate over a lower energy barrier during the time of the X-ray data collection.

The molecular geometry of **3c** reflected the contribution of the singlet biradical character to the ground state electronic configuration. The molecular structure of 2b (Figure S4), a typical closedshell molecule, exhibited a large bond length alternation (BLA) in the pentalene core (1.345(5)-1.501(6) Å).^{32,34} On the other hand, the degree of BLA of 3c in the pentagonal rings was significantly relieved (1.409(3)–1.458(3) Å), and the values were intermediate between the lengths of the $C(sp^2)-C(sp^2)$ bond in benzene (1.390) Å) and a $C(sp^2)$ – $C(sp^2)$ single bond (1.467 Å). Considering the relatively large single bond character of the bond a (1.458(3) Å) in the 5-5 ring fusion of 3c (Figure 2), the open-shell canonical structures of 3a-B rather than 3a-C moderately contributed to the ground state electronic structure of 3c (Figure 1B). The experimental bond lengths analyses illustrated that 3 should be represented as a resonance mixture between the o-quinoidal canonical structure and a biradical structure involving the TMM subunit (Figure 1B). The harmonic oscillator model of aromaticity (HOMA) values,72,73 which are an index of the assessment of the degree of bond alternation, also supported the observed features, illustrating greater π bond delocalization on the pentagonal rings of 3c (0.29) than of 2b (-0.62) (Figure 2C). Furthermore, the extent of π -delocalization on the hexagonal rings of 3c (HOMA values; 0.75) confirmed the resonance structures of 3c, as represented by Figure 1B.



Figure 2. ORTEP drawing of 3c, measured at 123 K at the 50% probability level: (A) top view and (B) side view, (C) HOMA values for 3c and 2b, and NICS(1) values for 3a and 2a.

The experimentally determined physical properties of 3c supported the moderate singlet biradical character of 3. Powder samples of **3c** displayed signals typical of triplet species. The observed zero field splitting parameters (|D| = 0.0561 cm⁻¹ and |E| = 0.0056 cm^{-1}) agreed well with the theoretical estimates ($D = +0.0461 cm^{-1}$) ¹ and E = 0.0052 cm⁻¹, obtained using UNO-BLYP/6-31G* calculations) of the optimized molecular geometry of 3c in the triplet state (Figure S10A). The spin density map of **3c** shows that the C4b, C9, and C10 carbons displayed the largest unpaired electron density, supporting the presence of a TMM subunit (Figure S17). The ESR signal intensities of 3c decreased with the temperature decreasing, indicating the occurrence of a singlet ground state in 3c (Figure S10B). The Bleaney-Bower's fit to the intensity change in the forbidden $\Delta M = \pm 2$ half-field signal of **3c** as a function of temperature in the solid state gave a singlet-triplet energy gap (ΔE_{S-T}) of -2160 K (-18.0 kJ/mol) (Figure 3A). Superconducting quantum interfering device (SQUID) measurements confirmed the presence of a singlet ground state in 3c. The magnetic susceptibility decreased when cooled to low temperature (Figures S13).

The ¹H NMR spectrum of **3c**, recorded at 30°C in THF-*d*₈, showed severe line broadening. Cooling to -100°C was accompanied by progressive line sharpening, indicating that the ground state of **3c** was the singlet state, and the signal broadening at room temperature arose from the thermally excited triplet species (Figure S7). In the ¹³C NMR measurement of **3c**, the interconversion of the *C*_s structures was not observed; no significant signal in the aromatic region was observed at 25°C, illustrating that the line broadening

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was caused by the triplet species rather than the structural interconversion (Figure S9). This phenomenon has been observed among singlet biradical compounds^{64,66} and was consistent with the variable temperature ESR measurements. The 1H NMR signals were assigned to the structure of 3c with the help of 2D-NOESY NMR spectroscopy. It is noteworthy that the protons of 3c on the main core appeared significantly upfield (4.49, 5.20, and 5.33 ppm) compared to those of **2b** (6.22, 6.32, and 6.47 ppm) and $3c^{2-}$ (6.30, 6.48, and 7.67 ppm) (Figure 3B). Pronounced paratropic ring current effects in the dibenzo[a,f]pentalene 3 were clearly observed, in agreement with positive nucleus-independent chemical shift (NICS) calculations. The averaged NICS(1) values of 3a calculated at the GIAO-B3LYP/6-31G** level were +25.5 and +7.48 for the pentagonal and hexagonal rings, respectively (Figure 2C). The paratropicity of the pentalene core significantly increased compared to that of the pentalene 1 (+18.4 calculated at the same level of theory, Figure S19). Furthermore, antiaromaticity expanded toward the hexagonal rings, suggesting an enhancement in the formally peripheral 16π -electron character of **3c**. These results indicated that the [a,f]-type dibenzoannulation on the pentalene core heightened the $4n\pi$ antiaromatic character,⁶³ which was more effective compared with the other non-alternant antiaromatic hydrocarbon¹⁹ and would lead to the symmetry reduction of the molecular structure in the singlet ground state (see below).74



Figure 3. (A) The change in the ESR signal intensity with temperature (\bigcirc) and the Bleaney-Bower's fit (\neg). Inset: the ESR spectra of the forbidden half-field signal of **3c**. (B) Partial ¹H NMR spectra (400 MHz, THF-*d*₈) of **3c**²⁻ (rt), **2b** (rt), and **3c** (-100° C).

Although planar $4n\pi$ -electron systems commonly exhibit π -bond localization to avoid instabilities associated with antiaromaticity, a resonance or bond shift of the o-quinoidal structure of 3 compelled the π -electrons to delocalize, leading to strong antiaromaticity and destabilization of the closed-shell singlet state. In the meantime, a TMM subunit observed in the open-shell structure of 3 in association with the recovery of two benzene rings effectively stabilized the triplet state, which gave a small value of ΔE_{S-T} for 3, consisting of only a 16π -electron system. The molecular geometry and magnetic properties of 3c indicated that the singlet biradical features of 3 accompanied its antiaromaticity. The UB3LYP/6-31G** optimized geometries of 3a indicated that the lowest singlet had a C_s structure and the triplet state adopted a $C_{2\nu}$ structure. According to the frequency analysis, the singlet $C_{2\nu}$ structure had an imaginary frequency, which suggested that the singlet $C_{2\nu}$ structure was a transition structure for interconversion of two equivalent C_s structures (Table S3 and Figure S22). It is possible that the $4n\pi$ character of 3 leads to the structural deformation toward a low symmetric structure in the singlet ground state by a pseudo Jahn–Teller effect.⁷⁴ The estimated $\langle S^2 \rangle$ values ($\langle 1 \rangle$) for the singlet C_s and $C_{2\nu}$ structures implied that the open-shell character of 3 would not be large (Table S3). The detailed molecular geometry together with open-shell character in the singlet state of 3 will be the subject of future investigations.

The small HOMO–LUMO energy gap is a characteristic feature of both singlet biradicaloids and antiaromatic compounds. The cyclic voltammogram of **3c** displays two reversible and two irreversible redox waves ($E_2^{\text{ox}, \text{pa}} = +0.77$, $E_1^{\text{ox}} = 0.0$, $E_1^{\text{red}} = -1.34$, and E_2^{red} ,

 $p^c = -2.28$ V vs. Fc/Fc⁺; Figure S14). The difference between the first oxidation and reduction potentials was used to determine the electrochemical HOMO–LUMO gap of 1.34 eV, which was 1.45 eV smaller than that of **2b** (Figure S14). The electronic absorption spectrum of **3c** in CH₂Cl₂ exhibited a moderate absorption band at 500 nm, together with a weak broad band centered at 965 nm and having a long tail that extended up to 2000 nm. These features are characteristic of $4n\pi$ -electron systems (Figure 4).^{27,34,51} The longest wavelength absorption band was significantly red-shifted compared to that of **2b** ($\lambda_{max} = 490$ nm). The observation of a smaller HOMO–LUMO energy gap in **3c** than in **2b** again supported the antiaromaticity and singlet biradical character of **3c**.



Figure 4. UV/Vis/NIR absorption spectra of 3c (red) and 2b (black) in CH₂Cl₂. The inset shows a magnified view. The background signals at 1700 nm arose from an overtone of the C-H vibrations of the solvent.

In conclusion, we achieved a first synthesis and characterization of the dibenzo[a,f]pentalene derivatives **3**. The obtained dibenzo[a,f]pentalene exhibited enhanced antiaromatic character and possessed singlet biradical features. The molecular magnetism observed in the dibenzo[a,f]pentalene system has not been observed among other well-known dibenzo[a,e]pentalenes. The unusual electronic structures of **3** induced by [a,f]-type dibenzoannulation to form a pentalene core could potentially be exploited in optoelectronic devices and organometallics ligands. Further experimental studies of dibenzo[a,f]pentalene-based molecules as well as detailed theoretical investigations are ongoing in our group.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXX. Crystallographic data for **2b**, **3b**^{2–}, **3c** and **9b** (CIF).⁷⁵ Experimental details of the preparations and characterizations of **2b**, **3–9**, Cartesian coordinates and energies of all calculated structures, and details of computational methods (PDF).

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Hafner, K. Angew. Chem. Int. Ed. Engl. 1964, 3, 165.
- (2) Nozoe, T. *Topics in Nonbenzenoid Aromatic Chemistry*; Wiley, 1973.
- (3) Parkhurst, R. R.; Swager, T. M. In *Polyarenes II*; Siegel, J. S., Wu, Y.-T., Eds.; Springer International Publishing: Cham, 2014; pp 141–175.
- (4) Tobe, Y. Chem. Rec. 2015, 15, 86.
- (5) Breslow, R. Chem. Rec. 2014, 14, 1174.
- (6) Frederickson, C. K.; Rose, B. D.; Haley, M. M. Acc. Chem. Res. 2017, 50, 977.
- (7) Nozawa, R.; Tanaka, H.; Cha, W.-Y.; Hong, Y.; Hisaki, I.; Shimizu, S.; Shin, J.-Y.; Kowalczyk, T.; Irle, S.; Kim, D.; Shinokubo, H. *Nat. Commun.* 2016, 7, 13620.
- (8) Liu, J.; Ma, J.; Zhang, K.; Ravat, P.; Machata, P.; Avdoshenko, S.; Hennersdorf, F.; Komber, H.; Pisula, W.; Weigand, J. J.; Popov, A. A.; Berger, R.; Müllen, K.; Feng, X. J. Am. Chem. Soc. 2017, 139, 7513.
- (9) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. I. A. Aromaticity and antiaromaticity: electronic and structural aspects; Wiley-Interscience publication; J. Wiley & Sons, 1994.
- (10) Parkhurst, R. R.; Swager, T. M. J. Am. Chem. Soc. 2012, 134, 15351.
- Chase, D. T.; Fix, A. G.; Kang, S. J.; Rose, B. D.; Weber, C. D.; Zhong,
 Y.; Zakharov, L. N.; Lonergan, M. C.; Nuckolls, C.; Haley, M. M. J. Am.
 Chem. Soc. 2012, 134, 10349.
- Rudebusch, G. E.; Espejo, G. L.; Zafra, J. L.; Peña-Alvarez, M.; Spisak, S. N.; Fukuda, K.; Wei, Z.; Nakano, M.; Petrukhina, M. A.; Casado, J.; Haley, M. M. J. Am. Chem. Soc. 2016, 138, 12648.
- (13) Zeng, Z.; Shi, X.; Chi, C.; López Navarrete, J. T.; Casado, J.; Wu, J. Chem. Soc. Rev. 2015, 44, 6578.
- (14) Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ponce Ortiz, R.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Ottosson, H.; Casado, J.; Haley, M. M. *Nat. Chem.* **2016**, *8*, 753.
- (15) Marshall, J. L.; Uchida, K.; Frederickson, C. K.; Schütt, C.; Zeidell, A. M.; Goetz, K. P.; Finn, T. W.; Jarolimek, K.; Zakharov, L. N.; Risko, C.; Herges, R.; Jurchescu, O. D.; Haley, M. M. Chem. Sci. 2016, 7, 5547.
- (16) Nishida, J.; Tsukaguchi, S.; Yamashita, Y. Chem. Eur. J. 2012, 18, 8964.
- Chase, D. T.; Rose, B. D.; McClintock, S. P.; Zakharov, L. N.; Haley, M. M. Angew. Chem. Int. Ed. 2011, 50, 1127.
- (18) Chase, D. T.; Fix, A. G.; Rose, B. D.; Weber, C. D.; Nobusue, S.; Stockwell, C. E.; Zakharov, L. N.; Lonergan, M. C.; Haley, M. M. Angew. Chem. Int. Ed. 2011, 50, 11103.
- (19) In the case of indeno[2,1-b]fluorine, the antiaromatic character of the sindacene core is less than that of the parent s-indacene. Shimizu, A.; Kishi, R.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Hisaki, I.; Miyata, M.; Tobe, Y. Angew. Chem. Int. Ed. **2013**, 52, 6076.
- (20) Shimizu, A.; Tobe, Y. Angew. Chem. Int. Ed. 2011, 50, 6906.
- Fix, A. G.; Deal, P. E.; Vonnegut, C. L.; Rose, B. D.; Zakharov, L. N.;
 Haley, M. M. Org. Lett. 2013, 15, 1362.
- (22) Miyoshi, H.; Miki, M.; Hirano, S.; Shimizu, A.; Kishi, R.; Fukuda, K.; Shiomi, D.; Sato, K.; Takui, T.; Hisaki, I.; Nakano, M.; Tobe, Y. J. Org. Chem. 2017, 82, 1380.
- (23) Brand, K. Ber. Dtsch. Chem. Ges. 1912, 45, 3071.
- (24) Saito, M. Symmetry **2010**, *2*, 950.
- (25) Kawase, T.; Nishida, J. Chem. Rec. 2015, 15, 1045.
- (26) Frederickson, C. K.; Zakharov, L. N.; Haley, M. M. J. Am. Chem. Soc. 2016, 138, 16827.
- (27) Oshima, H.; Fukazawa, A.; Yamaguchi, S. Angew. Chem. Int. Ed. 2017, 56, 3270.
- Kawase, T.; Fujiwara, T.; Kitamura, C.; Konishi, A.; Hirao, Y.; Matsumoto,
 K.; Kurata, H.; Kubo, T.; Shinamura, S.; Mori, H.; Miyazaki, E.; Takimiya,
 K. Angew. Chem. Int. Ed. 2010, 49, 7728.
- (29) Nakano, M.; Osaka, I.; Takimiya, K.; Koganezawa, T. J. Mater. Chem. C 2014, 2, 64.
- (30) Dai, G.; Chang, J.; Zhang, W.; Bai, S.; Huang, K.-W.; Xu, J.; Chi, C. Chem. Commun. 2015, 51, 503.
- Liu, C.; Xu, S.; Zhu, W.; Zhu, X.; Hu, W.; Li, Z.; Wang, Z. Chem. Eur. J. 2015, 21, 17016.
- (32) Saito, M.; Nakamura, M.; Tajima, T.; Yoshioka, M. Angew. Chem. Int. Ed. 2007, 46, 1504.
- (33) Babu, G.; Orita, A.; Otera, J. Chem. Lett. 2008, 37, 1296.
- (34) Kawase, T.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *Chem. Eur. J.* **2009**, *15*, 2653.
 - (35) Zhang, H.; Karasawa, T.; Yamada, H.; Wakamiya, A.; Yamaguchi, S. Org. Lett. 2009, 11, 3076.
- (36) Levi, Z. U.; Tilley, T. D. J. Am. Chem. Soc. 2009, 131, 2796.
- Konishi, A.; Fujiwara, T.; Ogawa, N.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Kitamura, C.; Kawase, T. *Chem. Lett.* **2010**, *39*, 300.

- (38) Yin, X.; Li, Y.; Zhu, Y.; Kan, Y.; Li, Y.; Zhu, D. *Org. Lett.* **2011**, *13*, 1520.
- (39) Hashmi, A. S. K.; Wieteck, M.; Braun, I.; Nösel, P.; Jongbloed, L.; Rudolph, M.; Rominger, F. Adv. Synth. Catal. 2012, 354, 555.
- (40) Chen, C.; Harhausen, M.; Liedtke, R.; Bussmann, K.; Fukazawa, A.; Yamaguchi, S.; Petersen, J. L.; Daniliuc, C. G.; Fröhlich, R.; Kehr, G.; Erker, G. Angew. Chem. Int. Ed. 2013, 52, 5992.
- (41) Maekawa, T.; Segawa, Y.; Itami, K. Chem. Sci. 2013, 4, 2369.
- (42) Zhao, J.; Oniwa, K.; Asao, N.; Yamamoto, Y.; Jin, T. J. Am. Chem. Soc. 2013, 135, 10222.
- (43) Hu, C.; Zhang, Q. Chinese J. Chem. 2013, 31, 1404.
- (44) Chen, C.; Harhausen, M.; Fukazawa, A.; Yamaguchi, S.; Fröhlich, R.; Daniliuc, C. G.; Petersen, J. L.; Kehr, G.; Erker, G. *Chem. Asian J.* 2014, 9, 1671.
- (45) Li, H.; Wang, X.-Y.; Wei, B.; Xu, L.; Zhang, W.-X.; Pei, J.; Xi, Z. Nat. Commun. 2014, 5, 4508.
- Shen, J.; Yuan, D.; Qiao, Y.; Shen, X.; Zhang, Z.; Zhong, Y.; Yi, Y.; Zhu, X. Org. Lett. 2014, 16, 4924.
- (47) Takahashi, K.; Ito, S.; Shintani, R.; Nozaki, K. Chem. Sci. 2017, 8, 101.
- Wurm, T.; Bucher, J.; Duckworth, S. B.; Rudolph, M.; Rominger, F.;
 Hashmi, A. S. K. Angew. Chem. Int. Ed. 2017, 56, 3364.
- (49) Rivera-Fuentes, P.; Rekowski, M. v. W.; Schweizer, W. B.; Gisselbrecht, J.-P.; Boudon, C.; Diederich, F. Org. Lett. 2012, 14, 4066.
- (50) London, G.; Rekowski, M. v. W.; Dumele, O.; Schweizer, W. B.; Gisselbrecht, J.-P.; Boudon, C.; Diederich, F. Chem. Sci. 2014, 5, 965.
- (51) Kato, S.; Kuwako, S.; Takahashi, N.; Kijima, T.; Nakamura, Y. J. Org. Chem. 2016, 81, 7700.
- (52) Levi, Z. U.; Tilley, T. D. J. Am. Chem. Soc. 2010, 132, 11012.
- (53) Xu, F.; Peng, L.; Orita, A.; Otera, J. Org. Lett. 2012, 14, 3970.
- (54) Cao, J.; London, G.; Dumele, O.; Rekowski, M. v. W.; Trapp, N.; Ruhlmann, L.; Boudon, C.; Stanger, A.; Diederich, F. J. Am. Chem. Soc. 2015, 137, 7178.
- (55) Xu, F.; Peng, L.; Shinohara, K.; Nishida, T.; Wakamatsu, K.; Uejima, M.; Sato, T.; Tanaka, K.; Machida, N.; Akashi, H.; Orita, A.; Otera, J. Org. Lett. 2015, 17, 3014.
- (56) Maekawa, T.; Ueno, H.; Segawa, Y.; Haley, M. M.; Itami, K. Chem. Sci. 2016, 7, 650.
- (57) Dai, G.; Chang, J.; Shi, X.; Zhang, W.; Zheng, B.; Huang, K.-W.; Chi, C. *Chem. Eur. J.* **2015**, *21*, 2019.
- (58) Dai, G.; Chang, J.; Luo, J.; Dong, S.; Aratani, N.; Zheng, B.; Huang, K.; Yamada, H.; Chi, C. Angew. Chem. Int. Ed. 2016, 55, 2693.
- (59) Uyehara, T.; Honda, T.; Kitahara, Y. Chem. Lett. 1977, 6, 1233.
- (60) Cristol, S. J.; Whittle, P. R.; Dahl, A. R. J. Org. Chem. **1970**, 35, 3172.
- (61) Baker, W.; McOmie, J. F. W.; Parfitt, S. D.; Watkins, D. A. M. J. Chem. Soc. 1957, 4026.
- (62) Randić, M. Chem. Rev. 2003, 103, 3449.
- (63) Fowler, P. W.; Steiner, E.; Havenith, R. W. A.; Jenneskens, L. W. Magn. Reson. Chem. 2004, 42, S68.
- (64) Kubo, T. Chem. Lett. 2015, 44, 111.
- (65) Abe, M. Chem. Rev. 2013, 113, 7011.
- (66) Sun, Z.; Ye, Q.; Chi, C.; Wu, J. Chem. Soc. Rev. 2012, 41, 7857.
- (67) Borden, W. T. Diradicals; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982.
- (68) Yasuda, M.; Somyo, T.; Baba, A. Angew. Chem. Int. Ed. 2006, 45, 793.
- (69) Markopoulos, G.; Henneicke, L.; Shen, J.; Okamoto, Y.; Jones, P. G.; Hopf, H. Angew. Chem. Int. Ed. 2012, 51, 12884.
- (70) Kuwabara, T.; Ishimura, K.; Sasamori, T.; Tokitoh, N.; Saito, M. Chem. Eur. J. 2014, 20, 7571.
- (71) Despite many trials, a single crystal of 3b was not obtained for use in X-ray analysis or other physical measurements. Thus, the following physical measurements were conducted using recrystallized 3c.
- (72) Kruszewski, J.; Krygowski, T. M. *Tetrahedron Lett.* **1972**, *13*, 3839.
- (73) Krygowski, T. M. J. Chem. Inf. Model. 1993, 33, 70.
- (74) The symmetry reduction of antiaromatic molecules in the singlet ground state is known as a pseudo Jahn–Teller effect. On the other hand, the high symmetric geometry is recoverd in the thermally excited triplet state. (a) Kostenko, A.; Tumanskii, B.; Kobayashi, Y.; Nakamoto, M.; Sekiguchi, A.; Apeloig, Y. Angew. Chem. Int. Ed. 2017, 56, 10183. (b) Toyota, A.; Koseki, S. J. Phys. Chem. 1996, 100, 2100. (c) Bearpark, M. J.; Blancafort, L.; Robb, M. A. Mol. Phys. 2002, 100, 1735. (d) Kozuch, S. RSC Adv. 2014, 4, 21650.
- (75) CCDC 1550838 (2b), 1550839 (3b²), 1550840 (3c), and 1550841 (9b) contain supplementary crystallographic data associated with 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.

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