Photoswitching of Local (Anti)Aromaticity in Biphenylene-Based Diarylethene Molecular Switches

Péter Pál Kalapos, Péter J. Mayer, Tamás Gazdag, Attila Demeter, Baswanth Oruganti,* Bo Durbeej,* and Gábor London*

Cite This: J. Org. Chem. 2022, 87, 9532−9542

ABSTRACT: Photoinduced tuning of (anti)aromaticity and associated molecular properties is currently in the focus of attention for both tailoring photochemical reactivity and designing new materials. Here, we report on the synthesis and spectroscopic characterization of diarylethene-based molecular switches embedded in a biphenylene structure composed of rings with different levels of local (anti)aromaticity. We show that it is possible to modulate and control the (anti)aromatic character of each ring through reversible photoswitching of the aryl units of the system between open and closed forms. Remarkably, it is shown that the irreversible formation of an annulated bis(dihydro-thiopyran) side-product that hampers the photoswitching can be efficiently suppressed when the aryl core formed by thienyl groups in one switch is replaced by thiazolyl groups in another.

INTRODUCTION

Aromaticity and antiaromaticity are two fundamental physical organic chemistry concepts that underlie several molecular properties of polycyclic conjugated systems.1−6 Hence, a widely used approach to design such molecules with novel functions is to tune their electronic structure on the aromatic−nonaromatic−antiaromatic scale.7,8 Apart from structure and reactivity, properties that are influenced by (anti)aromaticity such as molecular stacking or conductance have recently been the subject of major interest. For example, aromatic systems assemble in a manner to minimize π-orbital repulsion,9,10 while antiaromatic rings are predicted to prefer face-to-face stacking due to the emergence of transannular delocalization.11−15 Furthermore, the increment in conductivity within aromatic, nonaromatic, and antiaromatic molecular wires has been rationalized based on their decreasing resistance to redistribute their π-electron systems upon charge transport.16−22 As of now, the best approach to probe the effects of (anti)aromaticity on molecular properties is to design and synthesize new compounds with different conjugation patterns,23−35 among which reversible control of (anti)aromaticity has rarely been reported.26,36,37

To reversibly control the (anti)aromatic character of individual rings in polycyclic conjugated systems, photochemical mechanisms for rearranging their π-systems are particularly desirable, as electronic excitation circumvents the need to overcome thermal barriers inducible by losses in aromaticity. Photochromic switching that provides opportunities to create dynamic molecular systems can be considered such a mechanism.38 Among the established molecular photoswitches, diarylenes39 are of particular interest, as these molecules significantly alter their electronic structure upon photoinduced electrocyclization, which could potentially be exploited in (anti)aromaticity control. A further advantage of this class of molecules is that they can switch also in the solid state, which makes them suitable for thin-film- or single-crystal-based applications.40

To construct functional diarylethene switches that are interfaced with benzenoid conjugated systems, one common approach in the literature has been to lower the aromaticity of the ethylene bridge by embedding it in a heteroaromatic unit or a six-membered benzenoid ring with strongly electron-withdrawing substituents.41−46 The assumption underlying this approach is that the low aromaticity of the bridge that facilitates thermal electrocyclization (by reducing the associated barriers) is preserved also in the photoactive excited state of the switch. Notably, our groups have recently shown that electronically unperturbed diarylethene switches with an aromatic benzene bridge connecting two thienyl units undergo photoinduced electrocyclization47 driven by excited-state antiaromaticity,48−50 in accordance with Baird’s rules51 (which are the reverse of Hückel’s rules for ground-state aromaticity).

The goal of this work is to elucidate whether the local ground-state (anti)aromaticity of all monocyclic units in a polycyclic bridge fused to a diarylethene framework can be modulated through the ensuing photoswitching. In this regard,
bridges that contain both aromatic and antiaromatic subunits are an interesting prospect. To this end, we envisioned a system where the aromatic benzene bridge of dithienylbenzene switches is extended with an antiaromatic benzocyclobutadiene unit, resulting in a dithienylbenzene molecule. The open and closed isomers of this molecule, hereafter referred to as 1o (or 1, for simplicity) and 1c, respectively, are shown in Scheme 1.

Scheme 1. Design of a Dithienylbiphenylene Molecule and the Expected Changes in (Anti)aromaticity of Its A, B, and C Rings Upon Photocyclization of the Open Isomer (1o) into the Closed Isomer (1c)\(^\text{a}\)

\[
\begin{array}{ccc}
\text{A} & \text{B} & \text{C} \\
\text{WA} & \text{AA} & \text{NA} \\
\end{array}
\]

\(\text{A}: \text{aromatic}; \text{WA}: \text{weakly aromatic}; \text{AA}: \text{antiaromatic}; \text{NA}: \text{nonaromatic.}

In the biphenylene bridge of 1, the two conjugated six-membered rings A and C are only weakly aromatic, as a means to minimize the antiaromatic contribution of the central cyclobutadiene ring B.\(^\text{52}\) If 1 is able to undergo photocyclization, the ensuing electronic rearrangement should change the (anti)aromatic character of all three rings A, B, and C, as illustrated in Scheme 1. Additionally, the initially aromatic thienyl moieties would become nonaromatic upon ring closing, which is a characteristic change of dithienylethene photoswitches.\(^\text{53}\) However, besides asserting that photocyclization does indeed promote all of these changes in (anti)aromaticity, it is also desirable to verify that the changes can be reverted back by photocycloreversion of 1c into 1o, and that reversible photoswitching between 1o and 1c can be achieved for multiple cycles under ambient conditions. In this work, combining organic synthesis, spectroscopic characterization, and quantum chemical calculations, we report on how diarylethene switches can be made to realize all of these goals.

Finally, as for facilitating applications of diarylethene switches, the incorporation of a polycyclic bridge where all monocyclic units change the (anti)aromatic character between the open and closed isomers has a particular potential key advantage. Specifically, such a design might afford high-free-energy barriers for both thermal electrocyclization and thermal cycloreversion if both reactions are impeded by a loss of aromaticity in at least one of the monocyclic units. This characteristic would be appealing for the possibility to use diarylethenes as molecular solar thermal energy (MOST) storage systems\(^\text{54−57}\) that first absorb solar energy through the parent, open form, and then store it as chemical energy in the photoisomerized, closed form.\(^\text{58}\) In particular, a high barrier for the thermal cycloreversion is advantageous in allowing the absorbed solar energy to be stored for a long time, which is one of the main desirable features of MOST systems,\(^\text{59}\) and a high barrier for the thermal electrocyclization is naturally required for the overall efficiency of this technique.

**RESULTS AND DISCUSSION**

In the following, we first present the synthesis of 1 and characterize its photoswitching by means of UV–vis and proton nuclear magnetic resonance (\(^1\)H NMR) spectroscopy methods. Next, we describe a computational assessment of how the photoswitching changes the local (anti)aromatic character of the individual rings (A, B, and C) of the biphenylene moiety of 1. Noting that the photoswitching is hampered by low fatigue resistance due to the occurrence of a competing, irreversible side-reaction, we then explore different strategies to circumvent this problem. Among these, replacing the thiienyl groups of 1 by thiazolyl groups is found to be of particular value.

**Synthesis and Spectroscopic Characterization of the Photoswitching of Compound 1.** The synthesis of compound 1 was achieved by a \([2 + 2 + 2]\) cycloaddition of dialkyne 4 and monoalkyne 8 (Scheme 2). Dialkyne 4 was prepared according to a literature procedure\(^\text{59}\) in two steps (Scheme 2a). 1,2-Diodobenzene was reacted with TMS-acetylene under Sonogashira-coupling conditions, which provided compound 3 in excellent yield. The TMS-protecting groups were removed in a quantitative reaction to obtain the desired dialkyne 4. Monoalkyne 8, in turn, was prepared according to a literature procedure\(^\text{60}\) in three steps (Scheme 2b). First, 2,5-dimethylthiophene was reacted with oxallyl-
chloride (5) in a double Friedel-Crafts reaction leading to diketone 6 in moderate yield (42%). Compound 6 was then condensed with hydrazine hydrate to afford dihydrazone 7, followed by a Cu(I) mediated aerobic oxidation/elimination sequence to obtain the desired dithienylacetylene derivative 8 in reasonable yield (53%). Finally, compound 1 was synthesized in modest yield by a CpCo(I)-catalyzed [2 + 2 + 2] cycloaddition under light irradiation (white LED) according to a modified literature procedure.61 (Scheme 2c). The product was characterized by 1H and 13C NMR spectroscopy. Thereby, 1H NMR chemical shifts of protons directly attached to the biphenylene motif (6.61, 6.67, 6.77 ppm, CDCl3) suggest that the product has a modest Hückel-aromatic character. The parallel and antiparallel conformers of the dithienylbiphenylene were not distinguishable by NMR spectroscopy at 30 °C, indicating free rotation around the carbon–carbon bonds that connect the biphenylene to the thiophene moieties.

The UV–vis absorption spectrum of 1o in toluene displays a sharp band at 260 nm and two less intense bands at 353 and 372 nm (Figure 1a). Recording the spectrum in different aprotic solvents showed little effect on the bands (Figure S1 in the Supporting Information (SI)). Upon irradiation of a sample of 1o in toluene with UV light (365 nm), the intensity of the bands at 353 and 372 nm increased, while a new band appeared at 550 nm (Figure 1a). Similar changes were observed upon irradiation in CH3CN (Figure S2 in the SI). A closer look at the spectra obtained after 30 and 60 s of irradiation revealed that the two bands at 353 and 372 nm increased independently. Furthermore, when the resulting solution was irradiated with visible light (590 nm), the intensity of the peaks at 353, 372, and 550 nm decreased, but the initial spectrum could not be regenerated completely. These observations prompted us to speculate on the existence of two distinct photochemical processes driven by UV irradiation. In particular, the occurrence of a side-reaction that transforms the closed isomer 1c into an annulated bis(dihydro-thiopyran) side-product (9 in Figure 1b) could be confirmed by 1H NMR spectroscopy (Figure 2). Furthermore, this species, which is a well-known source of fatigue within dithienylethene-type molecular switches,62–65 could be isolated and characterized (Section S3 in the SI). Although the side-reaction clearly hampers the reversible photoswitching of I, the process is not fully inhibited (Figures 1a and S7 and S8 in the SI).
To monitor the changes in aromaticity resulting from the photocyclization of compound 1o, a detailed 1H NMR spectrum of the aromatic region of 1 was recorded in a CD2CN solvent (Figures 2 and S8 in the SI). Thereby, resonances of protons attached to ring A and the thiophenes (H\textsubscript{A} and H\textsubscript{B}) shifted upfield, whereas signals from protons attached to ring C (H\textsubscript{C} and H\textsubscript{D}) shifted significantly downfield (Figure 2). This suggests that the photocyclization disrupts the π-electron system of the biphenylene, making ring A nonaromatic, while the outer benzene ring C attains a more pronounced aromatic character. In the next section, the extent to which this picture of a gain (loss) in the aromaticity of ring C (A) is consistent with the results from quantum chemical calculations will be analyzed.

Quantum Chemical Calculations. To further assess the effect of photocyclization of 1o on the local (anti)aromatic character of rings A, B, and C, nucleus-independent chemical shift (NICS) index\textsuperscript{66,67} were calculated with density functional theory (DFT) methods, as fully detailed in Section S7 of the SI. Briefly, providing a magnetic measure of (anti)aromaticity by probing ring currents resulting from circulating π-electrons, these indices were calculated by using gauge-including atomic orbitals and an NICS-scan procedure.\textsuperscript{68,69} Thereby, so-called NICS\textsubscript{zz} values were obtained for each ring of the biphenylene at distances 1.50/1.60/1.70/1.80/1.90/2.00 Å above the geometric center of the ring in question. The NICS-scan procedure was adopted to alleviate the arbitrariness associated with single-point NICS\textsubscript{zz} calculations and to reduce π-electron contaminations of the induced magnetic field,\textsuperscript{65,69} as further described in Section S7 of the SI. For ease of analysis, the discussion of these results below focuses on the NICS\textsubscript{zz} values obtained at 1.70 Å, which is the distance that Gershoni-Poranee and Stanger\textsuperscript{69} recommend for calculations of this kind. All calculations were carried out with the B3LYP hybrid density functional in combination with the cc-pVTZ basis set and the SMD continuum solvation model\textsuperscript{70} to describe a toluene solvent (this solvent was used in the UV−vis irradiation experiments summarized in Figure 1).

The NICS\textsubscript{zz} values calculated for 1o and 1c at 1.70 Å are summarized in Figure 3, whereas the full set of NICS\textsubscript{zz} values is provided in Table S3 of the SI. Noting that negative/positive values indicate aromaticity/antiaromaticity and values close to zero indicate nonaromaticity,\textsuperscript{66} it can first be seen that ring A upon photocyclization loses the weak aromaticity that it shows in 1o (NICS\textsubscript{zz} = −8.7 ppm) by becoming nonaromatic in 1c (NICS\textsubscript{zz} = −2.1 ppm). Ring B, in turn, also becomes nonaromatic in 1c, but rather by relief of antiaromaticity, as can be inferred from the change in the NICS\textsubscript{zz} value from 7.3 ppm in 1o to −3.3 ppm in 1c. At the same time, ring C experiences a gain in aromaticity upon photocyclization, going from being quite weakly aromatic in 1o (NICS\textsubscript{zz} = −11.0 ppm) to being more distinctly aromatic in 1c (NICS\textsubscript{zz} = −17.3 ppm). Overall, these results suggest that the local (anti)aromatic character of each ring of the biphenylene can indeed be controlled through the photocyclization of 1o.

To further corroborate this conclusion and complement the magnetic NICS indices, geometric harmonic oscillator model of aromaticity (HOMA)\textsuperscript{71,72} and electronic Shannon aromaticity (SA)\textsuperscript{73,74} indices were also calculated, as detailed in Section S7 of the SI. The corresponding results are given in Table S4 of the SI. The HOMA index probes the deviation of the carbon−carbon bond lengths of the conjugated ring system in question from an ideal value associated with the fully aromatic benzene molecule. In particular, this index is designed to approach 1, 0, and −1 for an aromatic, nonaromatic, and antiaromatic system, respectively.\textsuperscript{71,72} The SA index, in turn, probes the variation in electron density at bond critical points of the conjugated ring, with aromatic/antiaromatic systems typically showing SA values below/above 0.003/0.005.\textsuperscript{3,74} From Table S4, the changes in HOMA and SA values upon photocyclization are consistent with those in NICS\textsubscript{zz} values described above. Accordingly, ring A loses aromaticity (the HOMA/SA value goes from 0.76/0.0013 in 1o to −0.32/0.0065 in 1c), ring B is relieved of antiaromaticity (the HOMA/SA value goes from −0.85/0.0062 in 1o to −0.60/0.0024 in 1c), and ring C gains some aromaticity (the HOMA/SA value goes from 0.87/0.0006 in 1o to 0.93/0.0002 in 1c).

DFT calculations were also performed to estimate the relative free energies of 1o and 1c, as well as the free-energy barriers for their thermal electrolycycloadition and cycloreversion reactions. These results, which are summarized in Table S5 of the SI, indicate that systems of this kind are an interesting prospect for the development of MOST applications. In particular, as mentioned as a possibility in Introduction, both reactions have a high barrier, amounting to ∼206 (electrocyclization) and ∼105 kJ mol\textsuperscript{−1} (cycloreversion). Furthermore, the fact that 1c lies ∼101 kJ mol\textsuperscript{−1} higher in energy than 1o suggests that a reasonably high energy-storage density can be achieved by this system upon photocyclization. In fact, with a molecular weight of ∼373 g mol\textsuperscript{−1}, the value of 101/373 ≈ 0.27 MJ kg\textsuperscript{−1} attained by 1 comes quite close to the oft-quoted target value of 0.30 MJ kg\textsuperscript{−1} for MOST applications.\textsuperscript{75}

**Strategies To Improve the Reversible Photoswitching through Improved Fatigue Resistance.** Overall, the UV−vis and NMR spectroscopic data reveal that the photocyclization of 1o into 1c occurs readily. Furthermore, the experimental and computational results show that this reaction modulates the local (anti)aromaticity of all monocyclic units of the biphenylene moiety. However, exploiting such modulation for the realization of reversible tuning of (anti)aromaticity and associated material properties (such as conductance) in future molecular electronic devices would require that the fatigue resistance of the system is improved. Indeed, ideally one would like to achieve reversible photoswitching between 1o and 1c for multiple cycles under ambient conditions. In this regard, photoswitching in the solid state is an appealing prospect, because this has been shown to suppress the formation of the

![Figure 3. NICS\textsubscript{zz} values for rings A−C of 1o and 1c calculated 1.70 Å above the geometric ring centers. (A: aromatic; WA: weakly aromatic; AA: antiaromatic; NA: nonaromatic).](https://doi.org/10.1021/acs.joc.2c00504)
annulated side-product and is desirable for thin-film- and single-crystal-based applications. Unfortunately, however, solid-state irradiation of a film of 1o with 365 nm light produced absorption bands at ~600 nm characteristic of the side-product (Figure S5 in the SI). Moreover, when the sample subsequently was irradiated with visible light, only minor reversibility was observed, suggesting that most of 1c rearranged to side-product 9 during the initial UV irradiation.

Turning to other possible strategies to suppress the formation of 9, we then performed triplet-sensitization experiments. Irradiation of 1o with 445 nm light in the presence of diacetyl (~100 equiv) produced a red-shifted absorption between 400 and 450 nm, as well as a weak-intensity band at 550 nm (Figure 4). The visible absorption is consistent with the initial absorption changes when 1o was irradiated with 365 nm light in the absence of diacetyl (Figure 1a), indicating that this band (at 550 nm) corresponds to 1c. Prolonged irradiation (>30 s) resulted in intensity loss of all bands, which suggests that all species undergo degradation in the presence of the sensitizer. A similar degradation of a unprotected sample (Figure S19 in the SI). Similar to the situation for 1, the UV−vis spectrum of 10 showed only moderate solvent dependence (Figure S16 in the SI).

Irradiation experiments with 10o to generate 10c were performed in CH3CN using 356 nm light (Figure 6a). Upon UV irradiation, the appearance of a blue color (Figure 6c) along with new absorption bands around 400 and 600 nm is indicative of the formation of 10c. Based on 1H NMR spectroscopy (Figure S10 in the SI). As the solid-state irradiation and triplet-sensitization experiments achieved only limited success in improving the fatigue resistance of 1, we then turned to synthetic modifications of its aryl core. In particular, retaining the biphenylene bridge, we decided to replace the thienyl groups of 1 with thiazolyl groups. To this end, and because of the straightforward synthetic access to its components and the previously reported reliable photochemistry of dithiazolylarenes, we synthesized compound 10, a 2,3-dithiazolylbiphenylene (Scheme 3), via a Suzuki−Miyaura cross-coupling between 2,3-diiodobiphenylene (13) and thiazolylboronic acid derivative 18. Both 13 and 18 were prepared according to literature procedures. Briefly, 13 was synthesized via a CpCo(I)-catalyzed [2 + 2 + 2] trimerization between diacetylene 4 and bis(trimethylsilyl)acetylene 11, followed by an iododesilylation (Scheme 3a). 18, in turn, was prepared via the condensation of thiobenzamide 14 and 2-chloroacetaldehyde followed by the bromination of the resulting heterocycle 15 using NBS. The brominated compound 16 was reacted with LDA and iodomethane to yield 17 in excellent yield. Compound 17 was subjected to n-butyllithium, and the resulting lithiated heterocycle was quenched with isopropylpinacol-borate to obtain 18 in moderate yield (Scheme 3b).

The UV−vis spectrum of 10 in CH3CN shows two distinct absorption maxima (at 251 and 276 nm) below 300 nm compared to the single band (at 254 nm) that 1 displays in this region (Figure 5). Furthermore, in the visible region of the UV−vis spectrum of 10, a band centered around 600 nm could be observed that is characteristic of the closed form of the molecule, which suggests that 10 is sensitive to ambient light. Indeed, this band disappeared when the solution was irradiated with visible (620 nm) light (Figures 5 and S18 in the SI).

Irradiation experiments with 10o to generate 10c were performed in CH3CN using 356 nm light (Figure 6a). Upon UV irradiation, the appearance of a blue color (Figure 6c) along with new absorption bands around 400 and 600 nm is indicative of the formation of 10c. Based on 1H NMR spectroscopy (Figure S10 in the SI). As the solid-state irradiation and triplet-sensitization experiments achieved only limited success in improving the fatigue resistance of 1, we then turned to synthetic modifications of its aryl core. In particular, retaining the biphenylene bridge, we decided to replace the thienyl groups of 1 with thiazoyl groups. To this end, and because of the straightforward synthetic access to its components and the previously reported reliable photochemistry of dithiazolylarenes, we synthesized compound 10, a 2,3-dithiazolylbiphenylene (Scheme 3), via a Suzuki−Miyaura cross-coupling between 2,3-diiodobiphenylene (13) and thiazolylboronic acid derivative 18. Both 13 and 18 were prepared according to literature procedures. Briefly, 13 was synthesized via a CpCo(I)-catalyzed [2 + 2 + 2] trimerization between diacetylene 4 and bis(trimethylsilyl)acetylene 11, followed by an iododesilylation (Scheme 3a). 18, in turn, was prepared via the condensation of thiobenzamide 14 and 2-chloroacetaldehyde followed by the bromination of the resulting heterocycle 15 using NBS. The brominated compound 16 was reacted with LDA and iodomethane to yield 17 in excellent yield. Compound 17 was subjected to n-butyllithium, and the resulting lithiated heterocycle was quenched with isopropylpinacol-borate to obtain 18 in moderate yield (Scheme 3b).

The UV−vis spectrum of 10 in CH3CN shows two distinct absorption maxima (at 251 and 276 nm) below 300 nm compared to the single band (at 254 nm) that 1 displays in this region (Figure 5). Furthermore, in the visible region of the UV−vis spectrum of 10, a band centered around 600 nm could be observed that is characteristic of the closed form of the molecule, which suggests that 10 is sensitive to ambient light. Indeed, this band disappeared when the solution was irradiated with visible (620 nm) light (Figures 5 and S18 in the SI). Moreover, the formation of a trace amount of 10c from 10o under ambient light is confirmed by the observed color change of unprotected samples (Figure S19 in the SI). Similar to the situation for 1, the UV−vis spectrum of 10 showed only moderate solvent dependence (Figure S16 in the SI).

Irradiation experiments with 10o to generate 10c were performed in CH3CN using 356 nm light (Figure 6a). Upon UV irradiation, the appearance of a blue color (Figure 6c) along with new absorption bands around 400 and 600 nm is indicative of the formation of 10c. Based on 1H NMR spectroscopy (Figure S10 in the SI). As the solid-state irradiation and triplet-sensitization experiments achieved only limited success in improving the fatigue resistance of 1, we then turned to synthetic modifications of its aryl core. In particular, retaining the biphenylene bridge, we decided to replace the thienyl groups of 1 with thiazoyl groups. To this end, and because of the straightforward synthetic access to its components and the previously reported reliable photochemistry of dithiazolylarenes, we synthesized compound 10, a 2,3-dithiazolylbiphenylene (Scheme 3), via a Suzuki−Miyaura cross-coupling between 2,3-diiodobiphenylene (13) and thiazolylboronic acid derivative 18. Both 13 and 18 were prepared according to literature procedures. Briefly, 13 was synthesized via a CpCo(I)-catalyzed [2 + 2 + 2] trimerization between diacetylene 4 and bis(trimethylsilyl)acetylene 11, followed by an iododesilylation (Scheme 3a). 18, in turn, was prepared via the condensation of thiobenzamide 14 and 2-chloroacetaldehyde followed by the bromination of the resulting heterocycle 15 using NBS. The brominated compound 16 was reacted with LDA and iodomethane to yield 17 in excellent yield. Compound 17 was subjected to n-butyllithium, and the resulting lithiated heterocycle was quenched with isopropylpinacol-borate to obtain 18 in moderate yield (Scheme 3b).

The UV−vis spectrum of 10 in CH3CN shows two distinct absorption maxima (at 251 and 276 nm) below 300 nm compared to the single band (at 254 nm) that 1 displays in this region (Figure 5). Furthermore, in the visible region of the UV−vis spectrum of 10, a band centered around 600 nm could be observed that is characteristic of the closed form of the molecule, which suggests that 10 is sensitive to ambient light. Indeed, this band disappeared when the solution was irradiated with visible (620 nm) light (Figures 5 and S18 in the SI). Moreover, the formation of a trace amount of 10c from 10o under ambient light is confirmed by the observed color change of unprotected samples (Figure S19 in the SI). Similar to the situation for 1, the UV−vis spectrum of 10 showed only moderate solvent dependence (Figure S16 in the SI).
spectroscopy, a composition of 1:1.6 (10a/10c) at the photostationary state was reached in dichloromethane after 95 min of irradiation, while an improved composition of 1:4.8 was reached in C₆D₆ after 160 min of irradiation (Figures S20 and S22 in the SI). Satisfyingly, the original spectrum could be regenerated by irradiating the solution with visible light (620 nm). This latter observation confirms that replacing the thiophene units in 1 with thiazole moieties in 10 is sufficient to efficiently suppress the formation of the annulated side-product of type 9. Furthermore, repeated UV and visible irradiation cycles did not lead to observable degradation or side-product formation (Figure 6b). Reversible switching of 10 was also demonstrated in dichloromethane and methanol solutions (Figure S18 in the SI). Moreover, the photostability of 10 is also considerably higher than that of 1. In particular, while the irradiation experiments of 1 had to be performed under oxygen-free conditions to avoid degradation, in the case of 10 this was not necessary for reversible switching (Figure S18 in the SI). It is noted, however, that prolonged exposure to UV light in CH₃CN led to the degradation of 10.

In addition to probing its photostability, we also assessed the thermal stability of 10c (Section S6 in the SI). Measurements by UV–vis spectroscopy in toluene revealed that, at 110 °C, most of 10c isomerizes back to 10a within 1 h. Furthermore, we conducted kinetics measurements of the thermal cycloreversion in C₆D₆ at 70 and 90 °C using ¹H NMR spectroscopy. These measurements revealed that, at 70 °C, the half-life for the process is about 54 h, while it is about 5.7 h at 90 °C. Based on these results, the activation energy for the cycloreversion was estimated to be 117 kJ mol⁻¹, which is quite close to the calculated value of 104.8 kJ mol⁻¹ (Table S5). Notably, no thermal decomposition or side-product formation was observed in these experiments.

Finally, regarding the structural changes made to 1 that resulted in improved fatigue resistance in 10, it should be noted that these do not affect the modulation of the local (anti)aromaticity of each ring of the biphenylene achieved by 1 upon photoswitching. In particular, NICS₃₉₀, HOMA, and SA values calculated for both the open and closed forms of 10 predict changes in local (anti)aromaticity that are very similar to those that were predicted for 1 by analogous calculations. The corresponding results are summarized in Figure S28 and Tables S3 and S4 of the SI.

Overall, then, we have shown that reversible photoswitching of diarylbiphenylenes is readily achievable under ambient conditions and that this process can be exploited to reversibly tune the local (anti)aromaticity of all three monocyclic units of the biphenylene moiety. For future research, and clearly beyond the scope of the present work, it will be of interest to also investigate aromaticity changes in the excited state during the photoswitching and gain a mechanistic understanding of why 10 exhibits better fatigue resistance than 1. From a computational point of view, exploring these problems poses a
considerable but worthwhile challenge in photochemical modeling.

**CONCLUSIONS**

In summary, we have demonstrated efficient and reversible photoswitching by diarylethenes featuring a bipyrenene group as the ethene bridge between the two aryl units. Starting with a compound (1) for which the aryl core is constituted by thienyl groups, the photoswitching is assessed experimentally using UV–vis and NMR spectroscopy methods. Probing changes in the local (anti)aromaticity of the individual rings of the bipyrenene in terms of experimental $^1$H NMR chemical shifts and calculated NICS, HOMA, and SA aromaticity indices, it is found that the character of each ring is altered through the photoswitching. Although 1 is found to undergo reversible photoswitching, the process is hampered by the irreversible formation of an annulated bis(di-hydro-thiopyran) side-product (9).

Next, to bypass this problem and improve the fatigue resistance of the switch, which is a prerequisite for its potential use in applications, the thienyl groups in the aryl core of 1 were replaced by thiazolyl groups. This structural change resulted in a switch (10) capable of reversible operation under ambient conditions without considerable degradation even after multiple switching cycles. Overall, we conclude that the photoswitching can be used to control the local (anti)aromatic character of each ring of the bipyrenene in a reversible fashion. In future research, we plan to investigate whether other diarylethenene switches can be made to control the local (anti)aromatic character of other polycyclic conjugated systems in a similar fashion.

**EXPERIMENTAL SECTION**

**General Information.** Commercial reagents, solvents, and catalysts (Aldrich, Fluorochem, VWR) were purchased as reagent grade and used without further purification. Solvents for extraction or sample treatment, opti-grade quality solvents were used. Organic grade and used without further purification. Solvents for extraction or catalysts (Aldrich, Fluorochem, VWR) were purchased as reagent.

**Synthesis of 1,2-Bis(trimethylsilyl)ethynyl]benzene (3).** A round-bottom flask was charged with Pd(PPh$_3$)$_2$Cl$_2$ (298 mg, 0.424 mmol) and Cul (40.4 mg, 0.212 mmol) and purged with N$_2$. 1,2-Diodobenzene (14.0 g 42.44 mmol) and ethynyltrimethylsilane (18.2 mL, 131.6 mmol) dissolved in triethylamine (100 mL) were added, and the mixture was heated in an oil bath and refluxed at 60 °C for 6 h. After completion, the reaction mixture was filtered through a Celite pad. The solvent was evaporated in vacuo, and the crude product was further purified by column chromatography ($SiO$_2, n-hexane) to yield the product (10.6 g, 92%) as a yellow oil, which solidified in the freezer. $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 7.45$ (dd, $J = 5.8, 3.4$ Hz, 2H), 7.23 (dd, $J = 5.8, 3.4$ Hz, 2H), 0.27 ppm (s, 18H); $1^3$C(H) NMR (126 MHz, CDCl$_3$) $\delta = 132.5$ (2), 129.2 (2), 126.0 (2), 103.4 (2), 98.6 (2), 0.2 (6) ppm.

**Synthesis of 1,2-Diethynylbenzene (4).** Compound 3 (10.00 g, 14.8 mmol) and K$_2$CO$_3$ (25.5 g, 73.9 mmol) were dissolved in a mixture of methanol (200 mL) and THF (200 mL) at 0 °C. The mixture was stirred at 0 °C in an ice bath for 2 h. After completion, the solvent was evaporated in vacuo, the crude product was redissolved in EtOAc (100 mL) and washed with water (3 x 50 mL), and the organic layer was dried over MgSO$_4$. Removal of the solvent gave compound 4 (4.38 g, 94%) as a crimson oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 7.52$ (dd, $J = 5.7, 3.4$ Hz, 2H), 7.31 (dd, $J = 5.8, 3.4$ Hz, 2H), 3.33 ppm (s, 2H); $1^3$C(H) NMR (126 MHz, CDCl$_3$) $\delta = 132.8$ (2), 128.6 (2), 125.2 (2), 82.0 (2), 81.3 (2) ppm.

**Synthesis of 1,2-Bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione (6).** A three-necked flask equipped with a thermometer was charged with AcCl (6.0 g, 44.9 mmol) and purged with N$_2$. CH$_2$Cl$_2$ (50 mL) was added, and the suspension formed upon stirring was cooled to −15 °C using an NaCl/ice bath. Pyridine (1.8 mL, 22.3 mmol) dissolved in CH$_2$Cl$_2$ (10 mL) and 2,5-dimethylthiophene (5.0 g, 44.6 mmol) dissolved in CH$_2$Cl$_2$ (25 mL) were added followed by the dropwise addition of oxalyl chloride (2.3 mL, 26.8 mmol) dissolved in CH$_2$Cl$_2$ (25 mL) in ~90 min at −15 °C. After the addition was complete, the reaction was allowed to warm to 5 °C in 60 min. The mixture was poured on ice cold water (200 mL), and the organic phase was separated. The aqueous layer was extracted with CHCl$_3$ (3 x 200 mL) and the combined organic layer was washed with water and saturated Na$_2$CO$_3$ solution and dried over MgSO$_4$. The solvent was evaporated under reduced pressure, and the dark residue was further purified by column chromatography ($SiO$_2, n-hexane/EtOAc 9:1) to obtain the product as a red oil (2.6 g, 43%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 6.91$ (s, 2H), 2.72 (s, 6H), 2.38 ppm (s, 6H); $1^3$C(H) NMR (126 MHz, CDCl$_3$) $\delta = 189.2$ (2), 151.5 (2), 136.2 (2), 131.8 (2), 126.9 (2), 15.9 (2), 14.8 (2) ppm.

**Synthesis of 1,2-Bis(2,5-dimethylthiophen-3-yl)-1,2-diethynoethane (7).** Compound 6 (4.0 g, 14.32 mmol) and p-toluenesulfonic acid (150 mg, 0.77 mmol) were dissolved in EtOH (30 mL), and hydrazine hydrate was added (7.0 mL, 144 mmol). The reaction was heated in an oil bath and refluxed for 20 h. After completion, the reaction mixture was cooled to 0 °C, and filtered, and the solid was washed with ice cold EtOH and allowed to dry on air. Compound 7 was obtained as a white/pale yellow solid (2.91 g, 65%). $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta = 6.45$ (s, 2H), 6.05 (s, 4H), 2.38 (s, 6H), 2.15 ppm (s, 6H); $1^3$C(H) NMR (126 MHz, DMSO-d$_6$) $\delta = 143.1$ (2), 135.6 (2), 133.6 (2), 129.8 (2), 126.3 (2), 14.8 (2), 13.8 (2) ppm.

**Synthesis of 1,2-Bis(2,5-dimethylthiophen-3-yl)ethene (8).** CuCl (653 mg, 6.6 mmol) was dissolved in pyridine (25 mL) and stirred vigorously in an open flask for 30 min. Compound 7 (1.0 g, 3.26 mmol) was added in four equal portions in 2 h, and then the reaction mixture was stirred for 22 h on air. After completion, 3 M HCl was added, and the mixture was extracted with Et$_2$O three times. The combined organic layer was washed with water and brine and dried over MgSO$_4$. The crude product was further purified by column chromatography ($SiO$_2, n-hexane) to obtain compound 8 as a white solid (403 mg, 53%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 6.66$ (s, 2H), 2.50 (s, 6H), 2.40 ppm (s, 6H); $1^3$C(H) NMR (126 MHz, CDCl$_3$) $\delta = 140.6$ (2), 135.8 (2), 127.3 (2), 119.8 (2), 86.2 (2), 15.3 (2), 14.5 (2) ppm.
Synthesis of 2,3-Bis(2,5-dimethylthiophen-3-yl)biphenylene (1). Compound 4 (100 mg, 0.79 mmol), compound 8 (205 mg, 0.83 mmol), and cyclopentadienylcobalt dicarbonyl (14.3 mg, 10.6 µL, 0.08 mmol) were dissolved in xylene (1.5 mL, mixture of isomers) in a glove box. The solution was transferred to a syringe and added to xylene (5.0 mL, mixture of isomers, under an N₂ atmosphere) in 8 h at 150 °C (the reaction was heated in an oil bath), under visible light irradiation. After the addition was complete, the reaction mixture was refluxed and irradiated for an additional ~60 h under an N₂ atmosphere. After completion, the reaction mixture was quenched with water and diluted with EtOAc. The organic layer was washed with water, and filtered, and the solvent was evaporated under reduced pressure. The crude product was further purified by column chromatography (SiO₂, n-hexane/EtOAc 12:1) to obtain a pale-yellow oil (60 mg, 20%), which solidified in the freezer.¹ H NMR (500 MHz, CDCl₃) δ = 6.77 (dd, δ = 4.9, 2.8 Hz, 2H), 6.67 (dd, δ = 4.8, 2.8 Hz, 2H), 6.61 (s, 2H), 6.23 (s, 2H), 2.32 (s, 6H), 2.05 ppm (s, 6H);¹³C¹H NMR (126 MHz, CDCl₃) δ = 150.9 (2), 149.4 (2), 138.0 (2), 135.9 (2), 134.5 (2), 132.5 (2), 128.3 (2), 127.5 (2), 119.9 (2), 117.5 (2), 15.0 (2), 13.8 (2) ppm. HRMS (APCI) m/z: [M + H]⁺ calcd for C₁₅H₁₀Si₂: 373.1079; found 373.1081.

Synthesis of 2,3-Bis(trimethylsilyl)biphenylene (12). Compound 4 (240 mg, 1.83 mmol) was dissolved in bis(trimethylsilyl)acetylene (3 mL), and the solution was transferred to a glove box.¹³C¹H NMR (500 MHz, CDCl₃) δ = 6.96 (s, 2H), 6.73 (dd, δ = 4.9, 2.9 Hz, 2H), 6.66 (dd, δ = 4.9, 2.9 Hz, 1H), 0.33 ppm (s, 18H);¹³C¹H NMR (126 MHz, CDCl₃) δ = 152.7 (2), 150.7 (2), 147.9 (2), 128.3 (2), 122.9 (2), 117.8 (2), 2.3 (6) ppm.

Synthesis of 3,4-Diiodobiphenylene (13). Compound 12 (300 mg, 1.01 mmol) was dissolved in dichloromethane (15 mL), and 11C (411 mg, 2.53 mmol) was added at 0 °C. The reaction was allowed to warm to rt. in 2 h, and then the mixture was stirred at rt. for 72 h. After the reaction was complete, most of the solvent was evaporated at reduced pressure, and the residue was dissolved in Et₂O. The organic layer was washed with Na₂SO₄ solution (2x) and brine, and the combined aqueous layer was extracted with Et₂O. The combined organic layer was dried over MgSO₄, concentrated, and purified by column chromatography (SiO₂, n-hexane) to obtain the pure product as a brownish yellow solid (256 mg, 63%).¹ H NMR (500 MHz, CDCl₃) δ = 7.15 (s, 2H), 6.81 (dd, δ = 4.9, 2.9 Hz, 2H), 6.69 ppm (dd, δ = 4.9, 2.9 Hz, 2H);¹³C¹H NMR (126 MHz, CDCl₃) δ = 151.8 (2), 149.9 (2), 129.3 (2), 127.8 (2), 119.0 (2), 106.4 (2) ppm.

Synthesis of 2-Phenylthiazole (15). Thiobenzamide (4.0 g, 39.0 mmol, 1.0 eq.) was dissolved in diethyl ether (20 mL, 1 M), and the solution was cooled to −78 °C. The solution was allowed to warm to rt overnight. Subsequently, water and EtOAc were added and the organic layer was separated. The organic phase was washed with water and brine, dried over MgSO₄, and further purified by column chromatography (SiO₂, n-hexane/EtOAc 12:1) to obtain compound 17 as a white crystalline solid (2.7 g, 10.7 mmol, 89%).¹ H NMR (500 MHz, CDCl₃) δ = 7.93–7.79 (m, 2H), 7.48–7.38 (m, 3H), 2.44 ppm (s, 3H);¹³C¹H NMR (126 MHz, CDCl₃) δ = 166.5, 132.9, 130.2, 128.9 (2), 128.7, 126.0 (2), 125.4, 13.0 ppm.

Synthesis of 5-Methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-di-oxaborolan-2-yl)thiazole (18). Compound 17 (254 mg, 1.0 mmol, 1.0 eq.) was dissolved in Et₂O (10 mL, 0.1 M) in a round-bottom flask under an N₂ atmosphere. The solution was cooled to −78 °C, and n-BuLi (0.44 mL, 1.1 mmol, 1.10 eq., 2.5 M solution in hexanes) was added dropwise in 15 min. The reaction mixture was stirred for 1 h followed by the addition of 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.30 mL, 1.5 mmol, 1.5 eq.). The reaction mixture was allowed to warm to rt overnight. Subsequently, water and EtOAc were added and the organic layer was separated. The organic phase was washed with water and brine and concentrated under reduced pressure. The crude product was further purified by column chromatography (SiO₂, n-hexane/EtOAc 2:1) to obtain compound 18 as a yellow oil (132 mg, 0.54 mmol, 53%), which solidified in the freezer.¹ H NMR (500 MHz, CDCl₃) δ = 7.94 (dd, δ = 7.9, 1.8 Hz, 2H), 7.40–7.31 (m, 3H), 2.72 (s, 3H), 1.37 ppm (s, 12H);¹³C¹H NMR (126 MHz, CDCl₃) δ = 166.0, 148.3, 133.8, 129.5, 126.8 (2), 126.2 (2), 83.9, 75.0, 24.8 ppm. The crude product was further purified by column chromatography (SiO₂, n-hexane/ETOA 2:1) to obtain compound 12 as a blue colored waxy solid (the blue color is caused by the presence of a trace amount of 10c) (7 mg, 10%). An analytically pure sample of 10c was obtained by subliming a sample of compound 10c to visible light irradiation (620 nm). Pure 10c is a yellow waxy solid.¹ H NMR (500 MHz, CDCl₃) δ = 7.88–7.82 (m, 4H), 7.42–7.38 (m, 6H), 6.94 (s, 2H), 6.88 (dd, δ = 4.9, 2.9 Hz, 2H), 6.80 (dd, δ = 4.9, 2.9 Hz, 2H), 2.10 ppm (s, 6H);¹³C¹H NMR (126 MHz, CDCl₃) δ = 163.4 (2), 152.1 (2), 150.7 (2), 150.6 (2), 134.8 (2), 133.9 (2), 129.9 (2), 129.4 (2), 128.7 (2), 128.7 (2), 126.0 (2), 119.5 (2), 117.9 (2), 11.8 (2) ppm. HRMS (APCI) m/z: [M + H]⁺ calcd for C₉H₈N₂S₂: 499.1308; found 499.1320.

The ¹H NMR characterization of compound 10c is based on the PSS mixture following the irradiation of 10c (Figure S21 in the SI).
1H NMR of 10c (500 MHz, CD$_2$Cl$_2$) δ = 7.99 (dd, J = 7.6, 1.8 Hz, 4H), 7.60–7.49 (m, 6H), 7.38–7.29 (m, 4H), 7.23 (s, 2H), 2.06 ppm (s, 6H).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.2c00504.

UV–vis spectroscopic characterization of 1 and 10, 1H NMR spectroscopic characterization of the photochemical transformations of 1 and 10, isolation and characterization of side-product 9, thermal stability assessment of 10c, computational details and complementary computational results, NMR spectra of reported compounds, HRMS of 1 and 10, LED emission spectra, and Cartesian coordinates and electronic energies of 1 and 10 (PDF)

**REFERENCES**

(1) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. Aromaticity and Antiaromaticity: John Wiley and Sons: New York, 1994.

(2) Gleieter, R.; Haberhauer, G. Aromaticity and Other Conjugation Effects; Wiley-VCH: Weinheim, Germany, 2012.

(3) Breslow, R. Antiaromaticity. *Acc. Chem. Res.* 1973, 6, 393–398.

(4) Krygowski, T. M.; Cyrański, M. K.; Czarnocki, Z.; Häfeling, G.; Katrićzyk, A. R. Aromaticity: a Theoretical Concept of Immense Practical Importance. *Tetrahedron* 2000, 56, 1783–1796.

(5) Randic, M. Aromaticity of Polycyclic Conjugated Hydrocarbons. *Chem. Rev.* 2003, 103, 3449–3605.

(6) Fernandez, I.; Ed.; Aromaticity: Modern Computational Methods and Applications; Elsevier: Amsterdam, Netherlands, 2021.

(7) Frederickson, C. K.; Rose, B. D.; Haley, M. M. Explorations of the Indeno[1,2-b]fluorenes and Expanded Quinoidal Analogues. *Acc. Chem. Res.* 2017, 50, 977–987.

(8) Wang, X.-Y.; Yao, X.; Müllen, K. Polycyclic Aromatic Hydrocarbons in the Graphene Era. *Sci. China Chem.* 2019, 62, 1099–1144.

(9) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. Aromatic Interactions. *J. Chem. Soc., Perkin Trans. 2001*, 2, 651–669.

(10) Mas-Torrent, M.; Rovira, C. Role of Molecular Order and Solid-State Structure in Organic Field-Effect Transistors. *Chem. Rev.* 2011, 111, 4833–4856.

(11) Corminboeuf, C.; Schleyer, P. V. R.; Warner, P. Are Antiaromatic Rings Stacked Face-to-Face Aromatic? *Org. Lett.* 2007, 9, 3263–3266.

(12) Bean, D. E.; Fowler, P. W. Stacked-Ring Aromaticity: an Orbital Model. *Org. Lett.* 2008, 10, 5573–5576.

(13) Ahara, J.-I. Origin of Stacked-Ring Aromaticity. *J. Phys. Chem. A* 2009, 113, 7945–7952.

(14) Nozawa, R.; Tanaka, H.; Cha, W.-Y.; Hong, Y.; Hisaki, I.; Shimizu, S.; Shin, J.-Y.; Kowalczyk, T.; Irie, S.; Kim, D.; Shinokubo, H. Stacked Antiaromatic Porphyrins. *Nat. Commun.* 2016, 7, 13620.

(15) Kawashima, H.; Ukai, S.; Nozawa, R.; Fukui, N.; Fitzsimmons, G.; Kowalczyk, T.; Fliegè, H.; Shinokubo, H. Determinant Factors of Three-Dimensional Aromaticity in Antiaromatic Cyclophanes. *J. Am. Chem. Soc.* 2021, 143, 10676–10685.

(16) Breslow, R.; Foss, F. W., Jr. Charge Transport in Nanoscale Aromatic and Antiaromatic Systems. *J. Phys.: Condens. Matter* 2008, 20, No. 374104.

(17) Schneebeli, S.; Kamenskaja, S.; Foss, F.; Vazquez, H.; Skoua, R.; Hybertsen, M.; Venkataraman, L.; Breslow, R. The Electrical Properties of Biphenylenes. *Org. Lett.* 2010, 12, 4114–4117.

(18) Chen, W.; Li, H.; Widawsky, J. R.; Appayee, C.; Venkataraman, L.; Breslow, R. Aromaticity Decreases Single-Molecule Junction Conductance. *J. Am. Chem. Soc.* 2014, 136, 918–920.

(19) Fujii, S.; Marquéz-González, S.; Shin, J.-Y.; Shinokubo, H.; Masuda, T.; Nishino, T.; Arasu, N. P.; Vázquez, H.; Kiguchi, M.
Highly-Exciting Molecular Circuits Based on Antiaromaticity. Nat. Commun. 2017, 8, 15984.

(20) Yin, X.; Zang, Y.; Zhu, L.; Low, J. Z.; Liu, Z.-F.; Cui, J.; Neaton, J. B.; Venkataraman, L.; Campos, L. M. A Reversible Single-Molecule Switch Based on Activated Antiaromaticity. Sci. Adv. 2017, 3, No. eaa02615.

(21) Gantenbein, M.; Li, X.; Sangtarash, S.; Bai, J.; Olsen, G.; Alqorashi, A.; Hong, W.; Lambert, C. J.; Bryce, M. R. Exploring Antiaromaticity in Single-Molecule Junctions Formed from Biphenylene Derivatives. Nanoscale 2019, 11, 20659−20666.

(22) Schmidt, M.; Wassy, D.; Hermann, M.; Gonzalez, M. T.; Aigrat, N.; Zotti, L. A.; Esser, B.; Leary, E. Single-Molecule Conductance of Dibenzopentalenes: Antiaromaticity and Quantum Interference. Chem. Commun. 2021, 57, 745−748.

(23) Frederickson, C. K.; Zakhvorob'ev, L. N.; Haley, M. M. Modulating Paratropicity Strength in Diareno-Fused Antiaromatics. J. Am. Chem. Soc. 2016, 138, 16827−16838.

(24) Warren, G. I.; Barker, J. E.; Zakhvorob'ev, L. N.; Haley, M. M. Enhancing the Antiaromaticity of s-Indacene through Naphthophinophene Fusion. Org. Lett. 2023, 23, 5012−5017.

(25) Barker, J. E.; Price, T. W.; Karas, L. J.; Kishi, R.; MacMillan, S. N.; Zakhvorob'ev, L. N.; Gómez-García, C. J.; Wu, J. I.; Nakano, M.; Haley, M. M. A Tale of Two Isomers: Enhanced Antiaromaticity/Diradical Character versus Deleterious Ring-Opening of Benzofuran-fused s-Indacenes and Dicyclopenta[b,g]naphthalenes. Angew. Chem., Int. Ed. 2021, 60, 22385−22392.

(26) London, G.; von Wantoch Rekowski, M.; Dumele, O.; Schweizer, W. B.; Gisselbrecht, J.-P.; Boudon, C.; Diedrich, F. Pentalenes with Novel Topologies: Exploiting the Cascade Carboxylation Reaction Between Allenyls and gem-Dibromomolecules. Chem. Sci. 2014, 5, 965−972.

(27) Cao, J.; London, G.; Dumele, O.; von Wantoch Rekowski, M.; Trapp, N.; Ruhlmann, L.; Boudon, C.; Stanger, A.; Diedrich, F. The Impact of Antiaromatic Subunits in [4n+2]-π-Systems: Bis-pentalenes with [4n+2]-π-Electron Perimeters and Antiaromatic Character. J. Am. Chem. Soc. 2015, 137, 7178−7188.

(28) Kawase, T.; Fujiwara, T.; Kitamura, C.; Konishi, A.; Hiroa, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Shinamura, S.; Mori, H.; Miyazaki, E.; Takimai, K. Dinaphthenogenes: Pentalene Derivatives for Organic Thin-Film Transistors. Angew. Chem., Int. Ed. 2010, 49, 7728−7732.

(29) Konishi, A.; Fujitawa, T.; Ogawa, N.; Hiroa, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Kitamura, C.; Kawase, T. Pentaleno[1,2-c:4,5-c']dithiophene Derivatives: First Synthesis, Properties, and a Molecular Structure. Chem. Lett. 2010, 39, 300−301.

(30) Konishi, A.; Okada, Y.; Nakano, M.; Sugisaki, K.; Sato, K.; Takui, T.; Yasuda, M. Synthesis and Characterization of Dibenzo[α,α']pentalene: Harmonization of the Antiaromatic and Singlet Biradical Character. J. Am. Chem. Soc. 2017, 139, 15284−15287.

(31) Konishi, A.; Okada, Y.; Kishi, R.; Nakano, M.; Yasuda, M. Enhancement of Antiaromatic Character via Additional Benzonucleation into Dibenzo[α,α']pentalene: Syntheses and Properties of Benzo[α]naptho[2,3-f]pentalene and Dibenzothiophene[2,3-f][1,2-c,5-c']pentalene. J. Am. Chem. Soc. 2019, 141, 560−571.

(32) Usuda, J.; Hayakawa, M.; Yamaguchi, S.; Fukazawa, A. Dithieno[5,6-c,d]'pentalenes: Highly Antiaromatic Yet Stable π-Electron Systems without Bulky Substituents. Chem. − Eur. J. 2021, 27, 1638−1647.

(33) Dai, G.; Chang, J.; Luo, J.; Dong, S.; Aratani, N.; Zheng, B.; Huang, K.-W.; Yamada, H.; Chi, C. Z-Shaped Pentaleno-Acene Dimers with High Stability and Small Band Gap. Angew. Chem., Int. Ed. 2016, 55, 2693−2696.

(34) Kato, S.-I.; Kuwako, S.; Takahashi, N.; Kijima, T.; Nakamura, Y. Benzo- and Naphthenogenes: Syntheses, Structures, and Properties. J. Org. Chem. 2016, 81, 7700−7710.

(35) Jin, Z.; Teo, Y. C.; Teat, S. J.; Xia, Y. Regioselective Synthesis of [3]Naphthenylene and Tuning of their Antiaromaticity. J. Am. Chem. Soc. 2017, 139, 15933−15937.
