

1-Substituted Perylene Derivatives by Anionic Cyclodehydrogenation: Analysis of the Reaction Mechanism

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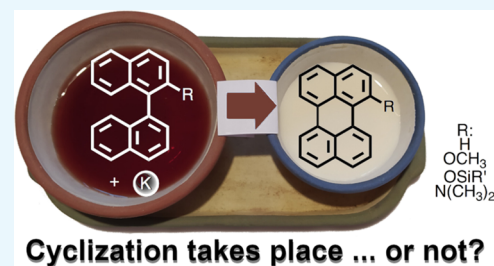


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ABSTRACT: Perylene derivatives constitute a promising class of compounds with technological applications mainly due to their optoelectronic properties. One mechanism proposed to synthesize them, starting from binaphthyl derivatives, is anionic cyclodehydrogenation (under reductive conditions). However, the scope of this reaction is limited. In the present study, we report a theoretical and experimental analysis of this particular reaction mechanism for its use in the synthesis of 1-substituted perylenes. Different substituents at position 2 of 1,1'-binaphthalene were evaluated: $-\text{OCH}_3$, $-\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$, and $-\text{N}(\text{CH}_3)_2$. Based on density functional theory (DFT) calculations on the proposed mechanism, we suggest that the cyclization takes place from binaphthyl dianion instead of its radical anion. This dianion has an open-shell diradical nature, and this could be the species that was detected by EPR in previous studies. The *O*-substituted derivatives could not afford the perylene derivatives since their radical anions fragment and the necessary binaphthyl dianion could not be formed. On the other hand, 49% of *N,N*-dimethylperylene-1-amine was obtained starting from the *N*-substituted 2-binaphthyl derivative as a substrate, employing a simpler experimental methodology.



Cyclization takes place ... or not?

INTRODUCTION

Two hot topics involve new organic compounds with high impact, organic light-emitting diodes (OLEDs) and organic solar cells (OSCs) in photovoltaic devices.¹ At present, OLEDs are employed in the screen of smart devices and in panels for lighting applications and represent an eco-friendly alternative to the traditional systems.² One of the challenges in this field is the generation of efficient pure light emission from the diode with a narrow line. Such an emitter is essential to complete the spectrum for a full-color display based on the principle of additive mixing.³ In addition, it is expected that OSCs could be massively employed within a few years because of their properties. They are potentially flexible, semi-transparent, and lightweight, and their fabrication might be implemented with available and low-cost technologies using eco-friendly materials.^{1a} One of the main goals in this field is to increase the power conversion efficiencies. Historically, OSCs were built with fullerene-based acceptors. However, recent developments propose that other polycyclic compounds could replace fullerene in the next generation of high-performance OSCs.⁴ For these reasons, the search for new industrial processes and molecular systems for these applications is continuously growing.^{1a}

In general, rylenes, perylene included, constitute an important class of compounds that show appropriate optoelectronic properties, fundamental for their application in both OLED and OSC devices.⁵ Perylene shows characteristic fluorescence with high quantum yield, which varies depending on both the nature of the substituents attached to the polycycle and their positions (e.g., the axial or equatorial

regions). Perylene bisimide (PBI) and perylene monoimide are two of the most studied compounds within the rylene family, mainly because of their photophysical properties.

Different strategies have been developed for the synthesis of perylene: condensation of quinone derivatives,⁶ base-induced dimerization of benzoisoquinolinediones,⁷ Cu- or Pd-catalyzed annulation reactions,⁸ cyclodehydrogenation of 1,1'-binaphthyl derivatives (e.g., Scholl reaction),⁹ and decarboxylation of the perylene-3,4,9,10-tetracarboxylic dianhydride under a high temperature and pressure.¹⁰ These strategies are mainly focused on the formation of the perylene ring; however, only two synthetic ways, reported until now, are useful to obtain *bay*-substituted perylene by condensation of the substitute quinolones⁶ and Scholl reaction of a 1,1'-binaphthyl derivative.^{9a,e} Furthermore, most of the reported examples of substituted perylene in the different positions,^{11 bay, 12 ortho, 13 or peri,}¹⁴ discuss the incorporation of functional groups to an already formed perylene nucleus.

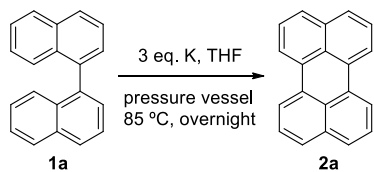
In 1968, Solodovnikov et al. published the synthesis of perylene from 1,1'-binaphthalene (1a) in 1,2-dimethoxyethane with an excess of potassium metal under vacuum at room temperature.¹⁵ More recently, Rickhaus et al. optimized this

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methodology,^{9b} which involves reductive induced cyclization of 1,1'-binaphthalene by the action of three or more equivalents of potassium metal in hot tetrahydrofuran with a quantitative yield (Scheme 1). This anionic cyclodehydroge-

Scheme 1. Anionic Cyclodehydrogenation Reaction for the Synthesis of Perylene^a



^aAdapted with permission from ref 9b.

nation reaction was also employed for the synthesis of 1-azaperylene,^{9c} 13,13'-dibenzo[*b*]perylene derivatives,¹⁶ and heteroaromatic polycyclic compounds, in some cases using a mechanochemical methodology, among others.¹⁷ However, this methodology was not employed for the synthesis of 1-substituted perylene derivatives.

A deeper knowledge of the involved mechanism is essential to extend the scope of the anionic cyclodehydrogenation reaction for the synthesis of *bay*-substituted perylene derivatives. According to this, we carried out a combined experimental and molecular modeling analysis using a selected 2-substituted-1,1'-binaphthalene (Figure 1) to evaluate the application of this reaction mechanism for the preparation of 1-substituted perylenes.

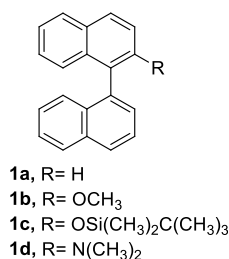


Figure 1. 2-Substituted-1,1'-binaphthalenes employed as substrates in the anionic cyclodehydrogenation reactions.

RESULTS AND DISCUSSION

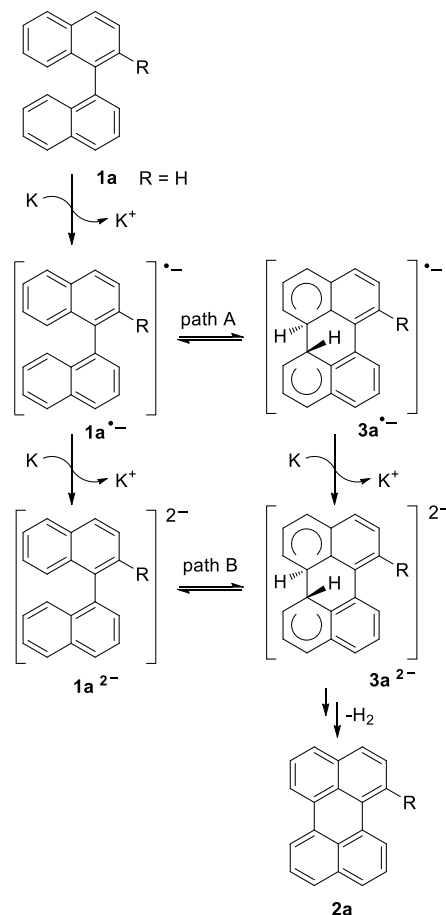
Reactivity of 1,1'-Binaphthalene. The first substrate for the anionic cyclodehydrogenation reactions, 1,1'-binaphthalene (1a), was synthesized following a Suzuki–Miyaura coupling reaction of 1-bromonaphthalene and 1-naphthylboronic acid catalyzed by Pd(0).¹⁸

It is important to mention that the original reaction conditions for the synthesis of perylene, proposed in ref 9b, were slightly modified by changing the solvent from tetrahydrofuran (THF) to toluene (Scheme 1) to replace the use of pressure vessels by simpler Schlenk tube flasks.¹⁹ Within the new reaction conditions, similar yields of perylene (2a) were obtained (90%), starting from 1,1'-binaphthalene (1a), compared with the originally reported yields (higher than 90%).^{9b} This result validates the use of the new reaction conditions.

Rickhaus et al. proposed a reaction mechanism based on previous research and the experimental observations are as follows: the presence of radical species detected by electron

paramagnetic resonance (EPR) and the formation of H₂ bubbles observed at the end of the experiments.^{9b,15} There are two reaction pathways (Scheme 2, paths A and B) by

Scheme 2. Proposed Mechanism for the Anionic Cyclodehydrogenation Reaction^a



^aAdapted with permission from ref 9b.

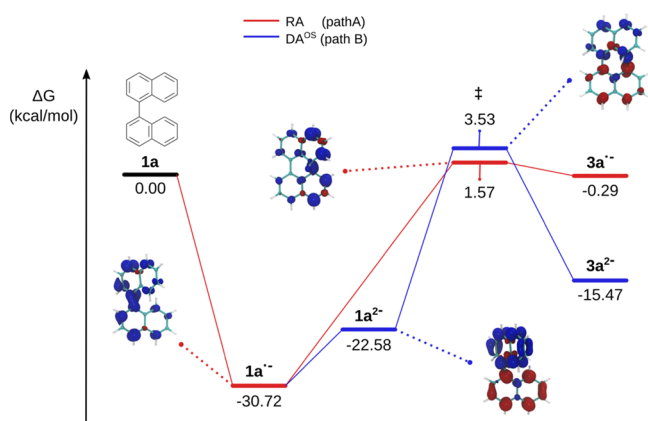
which 1a could be converted into perylene requiring two single-electron reductions, cyclization with C–C bond formation, and two C–H bond-breaking steps to give 2a. The initial anion radical 1a^{•-} can undergo a cyclization to form 3a^{•-} (path A), which takes the second electron to give 3a²⁻; or take a second electron to give the dianion 1a²⁻ which subsequently gives 3a²⁻ (path B); the latter is called the pivotal intermediate for the formation of perylene by Rickhaus et al.

In this study, we carry out the first molecular modeling studies based on the density functional theory (DFT) calculations of the proposed mechanism for the anionic cyclodehydrogenation reaction (Scheme 2). The hybrid-GGA functionals B3LYP²⁰ and ω -B97XD²¹ were employed. All calculations reported here correspond to the B3LYP/6-31+G(d) level of theory, whereas the results with ω -B97XD are included in the Supporting Information (SI). In general, similar tendencies were obtained with both functionals. The polarizable continuum model (IEF-PCM)²² was employed for modeling the solvent used in the reactions (toluene, $\epsilon = 2.37$).

Different electronic states of the dianion 1a²⁻ were modeled concluding that this intermediate has the character of an open-shell (OS) singlet ground state,²³ being a diradical dianion (DA^{OS}). The spin density distribution shows the same

contribution at the two naphthyl rings (Scheme 3, Figure S1, and Tables S1 and S3). Based on these new findings, either

Scheme 3. Profile of Energy for the Ring Closure Reaction of Substrate $1a^a$



^aThe color red is employed to remark path A and blue for path B of Scheme 2. The plots of the total spin density of radical anion ($1a^{\bullet-}$) and open-shell dianion ($1a^{2-}$) and the corresponding transition states were added as an inset. All free energy values are expressed in kcal/mol and adjusted at 363 K.

$1a^{\bullet-}$ or $1a^{2-}$ could be the intermediary species detected by EPR instead of just $1a^{\bullet-}$ as was previously thought.¹⁵

After the electron transfer from K to $1a$ to form $1a^{\bullet-}$ and/or $1a^{2-}$, the next reaction step is the ring closure (path A or B, Scheme 2). Two possibilities were evaluated (Table S3), either from $1a^{\bullet-}$ or from $1a^{2-}$. The energy profile for these reactions is presented in Scheme 3.

In the first place, it should be noted that the barrier (ΔG^\ddagger) for the ring closure from the DA^{OS} $1a^{2-}$ is lower than that from $1a^{\bullet-}$, 26.1 and 32.3 kcal/mol, respectively.²⁴ In addition, ΔG_R is also in favor of the ring closure from $1a^{2-}$ instead of $1a^{\bullet-}$ (7.1 vs 30.4 kcal/mol, respectively). We propose that the main differences are related to electronic rather than geometrical/sterical reasons. In the case of OS $1a^{2-}$, after coupling, a closed-shell intermediary $3a^{2-}$ was obtained. The diradical character of $1a^{2-}$ favors a radical-radical intramolecular recombination reaction,²⁵ as shown by the total spin density at the transition state (see Figure S2). On the other hand, after the coupling of $1a^{\bullet-}$, the product $3a^{\bullet-}$ still presented an unpaired electron.

Finally, the next steps for the formation of perylene include the elimination of two H atoms or an H_2 molecule as revealed

by the bubble formation in the last stages of the experimental reactions. The participation of H^\bullet within the very reductive reaction conditions is not clear at all; hence, DFT studies of that part of the reaction were not carried out.^{17c}

After the molecular modeling analysis of the proposed mechanism, evidence in favor of the participation of the diradical dianion $1a^{2-}$ (barely proposed by Rickhaus et al.^{9b}) as the key intermediary for the ring closure was found. In order to confirm this hypothesis, different 2-substituted-1,1'-binaphthalenes were selected for the experimental studies that were divided into two groups: 2-(O-substituted)-1,1'-binaphthyl derivatives, **1b** and **1c**, in one group and 2-(N-substituted)-1,1'-binaphthalene (**1d**) in the other group (see Figure 1).

Reactivity of 2-(O-Substituted)-1,1'-binaphthalene.

The reactions of radical anions of aromatic ethers have been studied by various authors.²⁶ Azzena et al.²⁷ reported that anisole reacts with potassium in THF to exclusively yield phenol by demethylation through fragmentation of the $PhO-CH_3$ bond, regardless of the temperature. On the other hand, in solvents with a very low dielectric constant (e.g., aliphatic hydrocarbons, toluene, and dioxane), demethoxylation was the main reaction pathway, by breaking of the $Ph-OCH_3$ bond, leading to benzene as the product.

The 1,1'-binaphthyl derivatives **1b** (2-methoxy-1,1'-binaphthalene) and **1c** ([1,1'-binaphthalen]-2-yloxy)(*tert*-butyl)-dimethylsilane) were synthesized in two simple steps. A photoinduced nucleophilic substitution reaction between 1-iodonaphthalene and 2-naphthol was followed by methylation with $(CH_3)_2SO_4$ to give **1b**, in an overall isolated yield of 50%, or followed by silyl protection with *tert*-butylchlorodimethylsilane leading to **1c**.^{28,29}

The anionic cyclodehydrogenation reactions of **1b** and **1c** were carried out. The results are shown in Scheme 4.

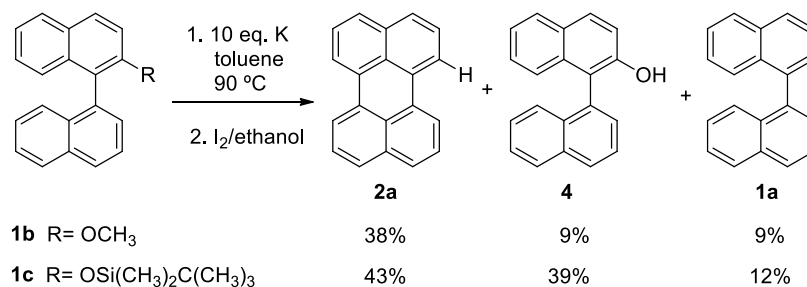
When the reaction of substrate **1b** was carried out, perylene (**2a**) was obtained instead of the substituted 1-methoxyperylene at 38% relative yield. On replacing the methyl group by $-Si(CH_3)_2C(CH_3)_3$, a slightly higher yield of **2a** was obtained (43%), and 39% of product **4**, but none of the 1-substituted perylene, was observed. The anionic cyclodehydrogenation reaction with **4** as a substrate failed too.³⁰

The results are consistent with the participation of radical anions as intermediates in the reactions. In the case of **1b**, fragmentation of the aryl- OCH_3 bond was the main reaction; meanwhile, by replacing the $-CH_3$ group by a better leaving group $-Si(CH_3)_2C(CH_3)_3$, the aryl $O-SiR$ fragmentation was also observed (Scheme 4).

Reactivity of 2-(N-Substituted)-1,1'-binaphthalene.

As in the case of alkyl aryl ethers, there are also a few

Scheme 4. Anionic Cyclodehydrogenation Reactions of **1b** and **1c**^a



^aYields are expressed in relative areas obtained by GC.

N,N-Dimethylperylene-1-amine (**2d**) was obtained in a 14% isolated yield. Traces of perylene were also detected in all reactions (<4%). The yield of **2d** was improved on changing the workup process by exposing the reaction mixture to O₂ overnight, from 14 to 49%.^{17c} However, a perylene isomer, benzo[*j*]fluoranthene (**5**), was the main byproduct in all our reactions. A similar behavior was observed in the pyrolysis of 1,1'-binaphthalene (**1a**) with hexanes as a radical source at 1100 °C. Under these conditions, the cyclodehydrogenation of **1a** forms perylene and the five-membered ring product **5**.³³ For improving the yield of the desired perylene derivative (**2d**), different reaction conditions were assessed by changing the temperature and the equivalents of K (Table S6).

According to these references and our experimental results, the fragmentation, aryl-N(CH₃)₂ or aryl N-(CH₃)₂, of the radical anion of **1d** is not the main reaction pathway followed by this intermediary (since binaphthalene or any demethylated compound was not found). Moreover, experimentally, a wine-red color was also observed in the reaction mixture as it was proposed before for the perylene dianion intermediate.¹⁵ It should be noted that this color was not observed in reactions of **1b** and **1c**. Since **1d**^{•-} did not fragment, we propose that **1d**²⁻ was formed after an electron transfer from the metal to this radical anion. Then, **1d**²⁻ would lead the substituted perylene **2d** after the reaction workup. The ring closure from **1d**^{•-} to **3d**^{•-} and formation of **3d**²⁻ after a second electron transfer could be discarded based on the DFT analysis of the mechanism (Table S4).

The major byproduct observed is benzo[*j*]fluoranthene (**5**), a compound without the dimethylamine group; it must proceed from an intermediary not found in the reactions with **1b** and **1c**. We propose that benzo[*j*]fluoranthene comes from fragmentation of the dianion **1d**²⁻. According to the DFT calculations, this fragmentation is not energetically favored over ring closure of **1d**²⁻ to give **3d**²⁻ (Table S5). However, there would be a competition between an irreversible reaction (cleavage of the aryl-N(CH₃)₂ bond) and an equilibrium reaction (**1d**²⁻ ⇌ **3d**²⁻); thus, relative yields between **2d** and **5** could vary according to the changes in the experimental conditions of the reactions (Table S6).

Finally, to summarize the information about the different analyzed reactions, an extended reaction scheme is shown (Scheme 6) including the possible pathways involved in the formation of the different observed products.

In this mechanism, the reactions of the radical anion (in red) differ from the reactions of the dianion (in blue). In the case of the radical anion, the fragmentations at both the O-aryl and O-alkyl levels are important and there is no formation of the dianion necessary for the cyclization indeed. The reactivity or instability of aryl-O-alkyl rules out the application of this anionic cyclodehydrogenation reaction for the synthesis of *bay* O-substituted perylenes. This scenario would even hold if diaryl ethers were used or if O is replaced by other heteroatoms from group 6, such as S or Se, whose anion radicals are even more fragile.³⁴ If the radical anion is long lived enough to receive a second electron forming a dianion, the chances to form the dihydroperylene derivative increase as it was experimentally found in the case of the *N*-substituted substrate (**1d**), with the formation of fluoranthene derivative as an undesired side reaction.

CONCLUSIONS

Based on the presented results and analyzing the possible reactions of the formed intermediates, radical anions, and dianions, the reactivity of substrates **1b–d** toward the anionic cyclodehydrogenation reaction is explained. Using a simpler reaction condition and toluene as a solvent, 1-N(CH₃)₂ perylene and perylene were obtained in 49 and 90% isolated yields, respectively. We demonstrated the synthetic limitations of this mechanism and could confirm experimentally and with computational modeling that the dianion intermediate **1**²⁻ is necessary as a precursor for perylene formation. Thus, we were able to determine the possibility of an extension of the reaction scope of anionic cyclodehydrogenation to the synthesis of substituted perylene derivatives in the *bay* position with -N(CH₃)₂ as a substituent and not with alkoxy groups due to fragmentation of their radical anions. This methodology could work for 2-C-substituted binaphthalenes in which their radical anion will be stable^{34c} and after the second electron accepting the anionic cyclodehydrogenation could occur.²⁵ This last hypothesis would be the one indicated for future studies about the synthetic usefulness of the anionic cyclodehydrogenation mechanism to obtain new *bay*-perylene compounds.

EXPERIMENTAL SECTION

Computational Modeling. DFT calculations were carried out using Gaussian 09 package Rev.E.01.³⁵ All calculations reported here were carried out with the hybrid-GGA functionals B3LYP²⁰ and ω-B97XD²¹ at the 6-31+G(d) basis set with the polarizable continuum model (IEF-PCM)²² by employing toluene as a solvent (ε = 2.37). Calculations were performed with full geometry optimization. The characterization of stationary points was done by Hessian matrix calculations, with all positive eigenvalues for a minimum and only one negative eigenvalue for the TSs. XYZ coordinates of the optimized geometries are included in Section S4 of the SI.

Experimental Methodologies. Toluene (Carlo Erba) and solvents in general were used after distillation and stored under molecular sieves (4 Å) and an inert atmosphere. ¹H-NMR, ¹³C-NMR, and all 2D NMR spectra were recorded using a 400 MHz Bruker nuclear magnetic resonance spectrometer. HRMS spectra were recorded using a Bruker, MicroTOF-Q II equipment, operated with an ESI source in the positive/negative mode, using nitrogen as a nebulizing and drying gas and 10 mM sodium formate as an internal standard. A gas chromatographic analysis was performed using a Varian GC with a flame ionization detector, which was equipped with a VF-5 MS, 30 m × 0.25 mm × 0.25 mm column. GC-MS analyses were carried out on a Shimadzu GC-MS QP5050 spectrometer, employing a 30 m, 0.12 mm DB-5 MS column.

Synthesis of Substrates. The compounds 1,1'-binaphthalene (**1a**),¹⁸ [1,1'-binaphthalen]-2-ol (**4**),²⁸ [1,1'-binaphthalen]-2-amine,³² 2-methoxy-1,1'-binaphthalene (**1b**),^{9a} and *N,N*-dimethyl-[1,1'-binaphthalen]-2-amine (**1d**)^{9a} were synthesized and purified following previously reported methods.

([1,1'-Binaphthalen]-2-yloxy)(*tert*-butyl)dimethylsilane (**1c**). It was synthesized following a typical *O*-protection reaction by silanes.^{29a} [1,1'-Binaphthalen]-2-ol (**4**) purified by column chromatography from previous synthesis (190 mg, 0.7 mmol ca., 1 equiv), 4-dimethylaminopyridine (8.5 mg, 0.07 mmol, 0.1 equiv), and imidazole (76 mg, 1.12 mmol, 1.6 equiv) were dissolved in dichloromethane (2 mL). The solution was cooled to 0 °C. *tert*-Butyldimethylsilyl chloride

(115.5 mg, 0.77 mmol, 1.1 equiv) was added and the solution was allowed to warm to room temperature. After stirring overnight, the reaction mixture was treated with water (5 mL), HCl (35% in H₂O, 0.2 mL), and ethyl acetate (5 mL). The organic layer was collected, and the aqueous layer was extracted with ethyl acetate twice (2 × 5 mL). The combined organic layers were washed with H₂O, dried over MgSO₄, and filtered. The filtrate was concentrated and purified by column chromatography (hexane/ethyl acetate, 99:1) to provide (**1c**) as a white solid (135 mg, 35% yield referred to the starting material for the synthesis of [1,1'-binaphthalen]-2-ol). M. p.: 139.0–141.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.96–7.89 (m, 4H); 7.63–7.59 (m, 1H); 7.50–7.46 (m, 2H); 7.43–7.25 (m, 6H); 0.48 (s, 9H, 3 × CH₃); –0.09 (s, 3H, Si–CH₃); –0.09 (s, 3H, Si–CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 151.0 (C_q); 135.1 (C_q); 134.7 (C_q); 133.9 (C_q); 133.2 (C_q); 129.4 (C_q); 129.2 (C_{Ar}–H); 129.0 (C_{Ar}–H); 128.1 (C_{Ar}–H); 127.9 (C_{Ar}–H); 127.7 (C_{Ar}–H); 126.7 (C_{Ar}–H); 126.3 (C_{Ar}–H); 125.9 (C_{Ar}–H); 125.8 (C_{Ar}–H); 125.7 (C_{Ar}–H); 125.7 (C_q); 125.7 (C_{Ar}–H); 125.5 (C_{Ar}–H); 123.7 (C_{Ar}–H); 121.1 (C_{Ar}–H); 25.2 (3 × CH₃); 17.7 (C–(CH₃)₃); –4.3 (2 × Si–CH₃). HRMS (ESI-TOF) *m/z* [M + Na]⁺ calcd for C₂₆H₂₈OSiNa: 407.1802; found: 407.1814. MS (EI): *m/z* 384 (15%), 327 (100%), 311 (21%), 252 (17%).

General Procedure for Anionic Cyclodehydrogenation Reactions. Into a previously dried 15 mL Schlenk tube flask equipped with a nitrogen inlet and a magnetic stirrer, 2 mL of a 0.11 M solution of substrate in dried toluene was added. The corresponding equivalents of potassium were added, and the temperature was adjusted according to the experimental setup. The first step of the workup consisted of the dropwise addition of an I₂ (3 equiv) solution in dried toluene. A change in color and bubbles were observed. It was left to stir for 1 h. The second step was the very slow addition of a few mL of ethanol and the system was exposed to the air atmosphere. Finally, 1 mL of 10% of Na₂S₂O₃ solution was added and the suspension was left to stir overnight. Extraction of organic compounds was done with CH₂Cl₂ (3 × 10 mL). The CH₂Cl₂ extract was washed twice. The organic extract thus obtained was dried over MgSO₄. After filtration, the organic solvent was eliminated under a reduced pressure. Purification of the organic crude was carried out by column chromatography employing silica gel and hexane/ethyl acetate as eluents.

1,1'-Binaphthalene (1a). It was purified by column chromatography with hexane/diethyl ether (9.9:0.1) as a white solid (90% yield).³⁶ ¹H NMR (400 MHz, CDCl₃) δ 7.97–7.94 (m, 4H); 7.61–7.58 (m, 2H); 7.51–7.46 (m, 4H); 7.40 (d, *J* = 8.4 Hz, 2H); 7.31–7.27 (m, 2H). MS (EI): *m/z* 254 (86%), 253 (100%), 252 (80%), 239 (18%), 126 (50%), 113 (25%).

Perylene (2a). The product was purified as a pale-yellow solid by semipreparative TLC using hexane/ethyl acetate (90:10) as an eluent.^{9a} ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 7.8 Hz, 4H); 7.68 (d, *J* = 8.0 Hz, 4H); 7.48 (t, *J* = 7.7 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 134.9 (2 × C_q); 131.4 (2 × C_q); 129.0 (4 × C_q); 128.0 (4 × C_{Ar}–H); 126.7 (4 × C_{Ar}–H); 120.4 (4 × C_{Ar}–H). MS (EI): *m/z* 252 (100%), 250 (19%), 125 (18%), 113 (7%).

***N,N*-Dimethylperylene-1-amine (2d).** The compound was purified as an orange oily solid by semipreparative TLC using as eluent a solvent gradient of hexane/ethyl acetate (100:0 → 90:10).^{9a} Isolated yield: 50% (27 mg). ¹H NMR (400 MHz, (CD₃)₂CO) δ 9.21 (dd, ¹*J* = 7.8, ²*J* = 1.0 Hz, 1H); 8.21 (dd, ¹*J*

= 7.5, ²*J* = 1.1 Hz, 2H); 7.73–7.64 (m, 4H); 7.54–7.46 (m, 3H); 7.38 (t, ¹*J* = 7.8 Hz, 1H); 2.85 (s, 6H). ¹³C NMR (100 MHz, (CD₃)₂CO) δ 151.0 (C_q, C–N); 135.6 (C_q); 132.5 (C_q); 132.4 (C_q); 131.9 (C_q); 131.6 (C_q); 131.6 (C_q); 130.8 (C_q); 129.5 (C_{Ar}–H); 128.5 (C_{Ar}–H); 128.2 (C_{Ar}–H); 127.5 (C_{Ar}–H); 127.1 (C_{Ar}–H); 127.0 (C_{Ar}–H); 125.2 (C_{Ar}–H); 124.5 (C_{Ar}–H); 122.1 (C_{Ar}–H); 121.5 (C_{Ar}–H); 120.1 (C_{Ar}–H); 119.6 (C_q); 43.4 (2C, CH₃). MS (EI): *m/z* 295 (100%), 280 (34%), 265 (41%), 264 (23%), 146 (34%), 125 (34%). The 2D NMR spectra are shown in the SI.

[1,1'-Binaphthalen]-2-ol (4). It was purified by column chromatography with hexane/diethyl ether (9:1) as a pale-yellow solid (58% isolated yield).²⁸ ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H, OH); 8.01 (d, *J* = 8.2 Hz, 2H); 7.94 (d, *J* = 8.8 Hz, 1H); 7.89 (d, *J* = 8.2 Hz, 1H); 7.67–7.64 (m, 1H); 7.52–7.47 (m, 2H); 7.38 (d, *J* = 8.8 Hz, 1H); 7.32–7.27 (m, 3H); 7.23–7.19 (m, 1H); 7.01 (d, *J* = 8.4 Hz, 1H). MS (EI): *m/z* 270 (100%), 253 (32%), 239 (43%), 135 (7%), 126 (20%), 113 (11%).

Benzo[*j*]fluoranthene (5). The product was purified as a yellow solid by semipreparative TLC using hexane/ethyl acetate (90:10) as an eluent.³⁷ ¹H NMR (400 MHz, CDCl₃) δ 8.72 (d, *J* = 8.4 Hz, 1H); 8.46 (d, *J* = 7.0 Hz, 1H); 8.06 (d, *J* = 8.2 Hz, 1H); 8.01 (d, *J* = 6.8 Hz, 1H); 7.93 (d, *J* = 8.2 Hz, 1H); 7.88 (d, *J* = 8.2 Hz, 2H); 7.87 (d, *J* = 8.2 Hz, 1H); 7.73–7.60 (m, 3H); 7.49 (t, *J* = 8.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 138.0 (C_q); 137.9 (C_q); 137.3 (C_q); 136.7 (C_q); 134.4 (C_q); 134.2 (C_q); 130.7 (C_q); 129.8 (C_q); 129.5 (C_{Ar}–H); 128.5 (C_{Ar}–H); 128.3 (C_{Ar}–H); 128.0 (C_{Ar}–H); 127.5 (C_{Ar}–H); 127.1 (C_{Ar}–H); 127.1 (C_{Ar}–H); 125.4 (C_{Ar}–H); 124.4 (C_{Ar}–H); 124.3 (C_{Ar}–H); 121.0 (C_{Ar}–H); 120.0 (C_{Ar}–H). MS (EI): *m/z* 252 (100%), 250 (19%), 125 (18%), 113 (7%). The 2D NMR spectra are shown in the SI.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c02017>.

Computational modeling information (determination of electronic state and optimized XYZ coordinates) and experimental description (synthesis and spectroscopic data) (PDF)

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Notes

The authors declare no competing financial interest.

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DEDICATION

In memory of Adriana B. Pierini (1953–2016).

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