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Conformational Flexibility of Fused Tetracenedione Propellers Obtained from One-Pot Reductive Dimerization of Acetylenic Quinones

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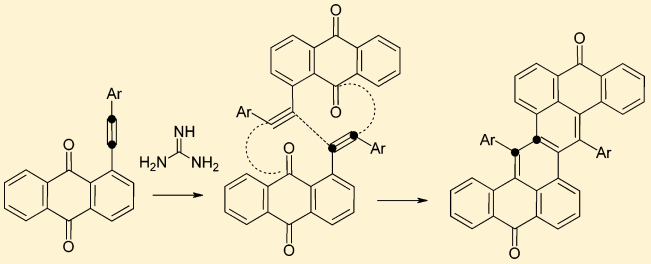
Supporting Information

ABSTRACT: Reductive dimerization of acetylenic anthraquinones provides synthetic access to flexible nonplanar polyaromatics with a tetracenedione core. In solution, these nonplanar, contorted polycycles exist as equilibrating mixtures of two symmetric conformers. The fused tetracenediones are easily reduced and exhibit rich electrochemical behavior.



INTRODUCTION

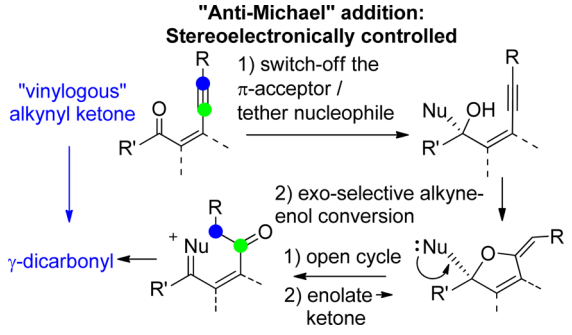
Diverse transformations of polyfunctional arylacetylenes open new avenues in chemistry and material science.[1] Due to the high carbon content of alkynes, this functionality is an attractive entry point for the preparation of carbon-rich structures.[2] The renewed interest in such compounds stems from their structural relation to fullerenes, carbon nanotubes, and graphene.[3]

Furthermore, cyclizations of vicinally substituted acetylenyl arenes and heteroarenes provide a direct synthetic route toward condensed heterocycles with many promising features in drug design.[4] Additionally, such cyclizations assist in developing and testing the general rules for the formation of cyclic structures.[5] Because cascade transformations can produce multiple cycles in a coordinated and efficient manner, they offer a particularly attractive approach to the construction of polycyclic aromatic molecules.[6,7]

Because alkynes have the same oxidation state as carbonyl compounds, one can design crossover transformations where an initial alkyne reaction uncovers a reactive carbonyl derivative (Scheme 1). Although the largest body of such transformations is mediated by Au catalysis,[8] metal-free approaches are also known. For example, nucleophilic additions to alkynes lead to regioselective formation of enol and enamine derivatives via the use of either polarization effects[9] or stereleoelectronic factors, such as the preference for *exo-dig* cyclizations[10] (Scheme 1).

Earlier,[11] we had reported the formation of products of three cascade transformations in the reaction of periphenylethynyl-

Scheme 1. Stereoelectronic Approach to Regioselective Alkyne/Carbonyl Transformations Based on Intramolecular Constraints



9,10-anthraquinone (**1**) with guanidine in refluxing *n*-butanol:[11] 2-phenyl-7*H*-dibenzo[*de*,*h*]quinolin-7-one, 2-amino-3-benzoyl-7*H*-dibenzo[*de*,*h*]-quinolin-7-one, and 1-phenyl-*H*-dibenzo-[*de*,*h*]isoquinoline-3,7-dione. The two first condensed systems—the products of cascades initiated by N-6-*endo-dig* and N-6-*exo-dig* attack, respectively—are close analogues of aporphinoid alkaloids, natural compounds with anticancer[12] and antiacetylcholine esterase[13] activity. These cascade transformations were found to be quite sensitive to the nature of

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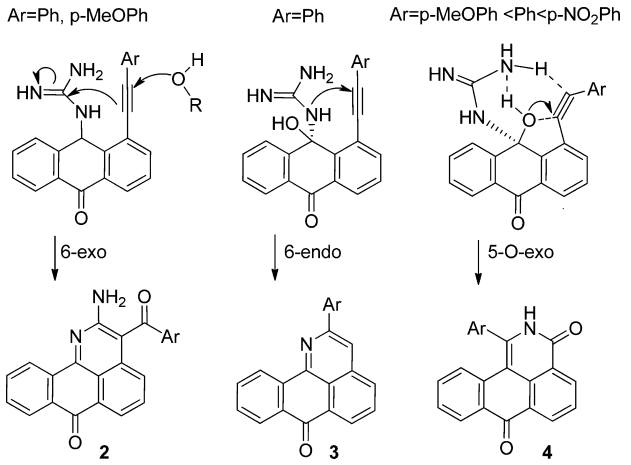
alkyne substitution, because the triple bond polarization is reflected in the ratio of three cyclization products formed via N-6-*endo-dig*, N-6-*exo-dig*, and O-5-*exo-dig* attacks. Electron-donating Ar groups favor the formation of 6-*exo-dig* products,[14] whereas the electron-withdrawing *p*-nitrophenyl directs the reaction toward the heterocyclic amides via the 5-*exo-dig* step (Scheme 2).

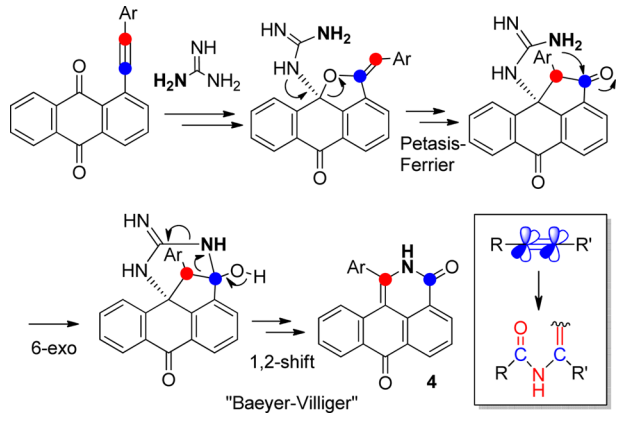
Scheme 2. Diverse Products Formed in Nucleophilic Cyclizations of Acetylenic Anthraquinones[a]



[a]See Scheme 3 for additional details on the formation of product **4**.

Formation of isoquinoline-3,7-dione is particularly intriguing from a mechanistic perspective, since this process involves insertion of nitrogen atom between the two alkyne carbons with the concomitant formation of *six* new bonds.[15] In this case, the "anchored" nucleophile initiates a cascade that inserts a nitrogen atom between the two alkyne carbons. This transformation is mediated by classic carbonyl chemistry; i.e., the fragmentation–recyclization sequence is similar to the Petasis–Ferrier rearrangement, whereas the 1,2-shift to a heteroatom with a good leaving group that converts the cyclic heminal intermediate into the final lactam product is analogous to the 1,2-shift terminating the Baeyer–Villiger oxidation (Scheme 3).

Scheme 3. "Carbonyl Chemistry" of an Alkyne Reactant Mediated by Selective Intramolecular Attack at the Alkyne Moiety and Leading to Nitrogen Insertion between Alkyne Carbons



Considering the unusual features of these reactions and their sensitivity toward the nature of alkyne substitution, we expanded our studies toward additional activated acetylenic anthraquinones. This work reports transformations enabled by the presence of an electron-withdrawing Ar group at the alkyne moiety and intriguing conformational properties of their twisted polyaromatic products.

RESULTS AND DISCUSSION

Experimental Observations. Reaction of alkynes **1a–c** with guanidine was carried out in refluxing *n*-butanol. As expected, we observed the formation of O-5-*exo-dig*- and N-6-*exo-dig*-products **2** and **3** with the greater yield of isoquinoline-3,7-diones **2** for the more electron withdrawing substituents. This is consistent with our earlier findings where dibenzo-[*de,h*]quinolin-7-ones **3** were found to be favored by the electron-donating substitution.

However, we also observed the formation of 9,18-diaryl tetrabenzo[*a,de,j,mn*]tetracene-4,13-diones **5a–c**, the highly unusual products of a new reductive polycondensation, which yielded a carbocyclic polyaromatic moiety rather than the previously reported heterocyclic products (Scheme 4).

Overall, the yields for the formation of tetracenes **5a–c** ranged from 12 to 24%. The structure of tetracenediones **5a–c** was reliably established using NMR methods, mass spectrometry, and X-ray crystallography (for **5a** and **5c**).

Structural Analysis. All cycles in the tetracene-2,8-dione moiety of compounds **5a** and **5c** deviate from planarity and display folding at the C4–C8B, C8b–C18A, C9A–C17B, and C17B–C13 lines with the respective dihedral angles of 17°–21°. As a result, the overall angle between the anthracen-9-one planes is in the range of 61°–63°, the molecules are strongly twisted, adopting a propeller shape. The bond lengths are similar to those reported for 2,5,10,13-tetra-*tert*-butyldibenzo-[*a,o*]perylene-7,16-dione.[16] The CH_2Cl_2 molecule in the crystal lattice is involved in a C–H···O H-bond (H···O, 2.31 Å; C–H···O, 176°) with the carbonyl group of **5a**. Crystal packing of **5a** (Figure 1) involves π-stacking between the cycles (i.e., C13A and C14–C17A with centroid–centroid and interplane distances of 3.91 and 3.55 Å), along with a number of C–H···π interactions with the H···centroid distances of 2.57–2.72 Å and a slightly shortened Br1···Cl2 contact of 3.509 Å [see the Supporting Information (SI)]. Crystal packing of **5c** also involves π-stacking (distances of 4.20 and 3.21 Å) and C–H···π interactions, with the H···centroid distances of 2.56–2.77 Å, and a C–H···N interaction (H···N, 2.61 Å; C–H···N, 155°).

Considering the significant interest in the properties of contorted nonplanar polyaromatic systems,[17] we decided to investigate conformational flexibility of this new family of polycyclic molecules.

NMR Analysis of Conformational Flexibility. The conformational mobility of the tetracenedione products was indicated by the presence of two sets of NMR signals that suggested that the pairs of ortho and meta protons in these compounds are nonequivalent but undergo interconversion (Figure 2). The measured rate constants for this conversion of ortho and meta protons of the Br–Ph in tetracene **5a** in the 245–304 K temperature range provided the activation enthalpy of 11.2 kcal/mol (see the SI for experimental details). A similar activation enthalpy of 11.8 kcal/mol was found for the rotation of the aryl group in dione **5b** (see the SI).

These experimental data qualitatively agree with the activation enthalpies of 18.3 and 17.5 kcal/mol calculated

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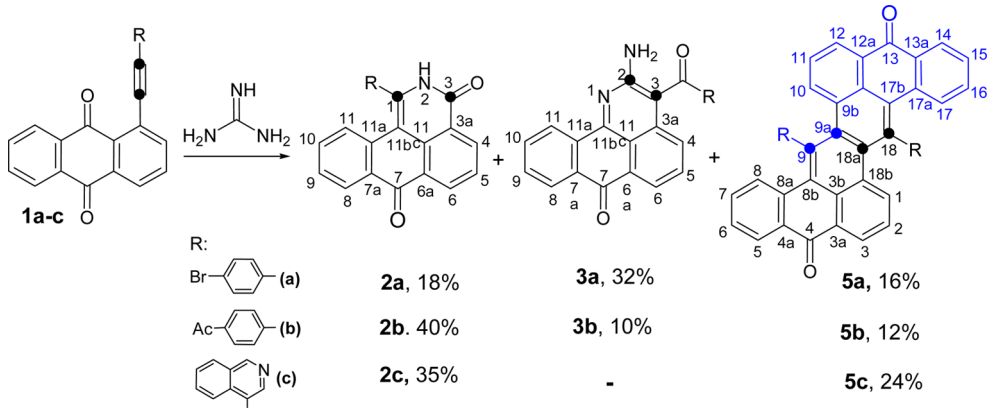
Scheme 4. Effect of Terminal Aromatic Substituent at the Selectivity of Guanidine Interaction with Acetylenic Anthraquinones



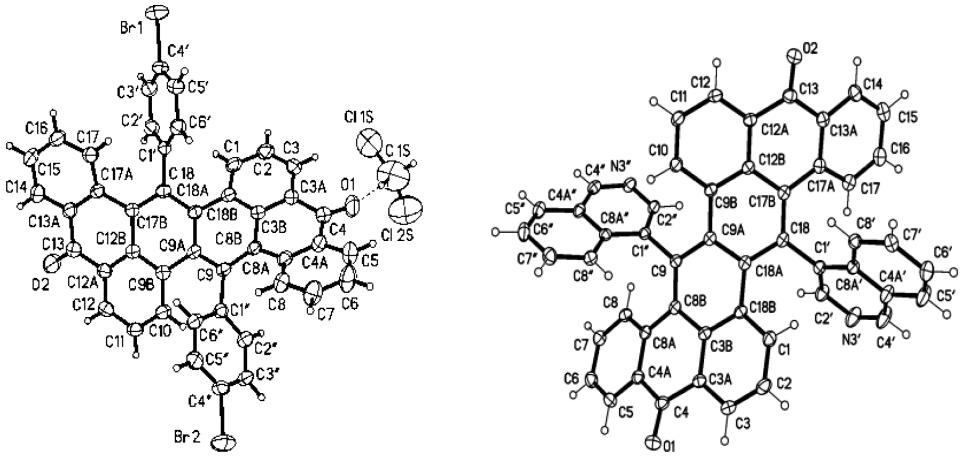


Figure 1. ORTEP of compound **5a** (left, with CH_2Cl_2 molecule included in the crystal lattice) and compound **5c** (right).

with the DFT approach at the PBE/L22 level of theory[18] for the synchronous enantiomerization of the whole molecule, where rotations of the aryl rings are correlated with each other (Scheme 5), rather than the independent rotation of the aryl ring.

In the case of compound **5c**, the DFT calculations found three structures (with their respective enantiomers) corresponding to the local energy minima (see the SI). The isoquinoline substituents can be positioned either on the same side of the tetracene core or on the opposite sides. The conformer C with substituents on the opposite sides is nonsymmetric. On the other hand, the two structures A and B with substituents projected to the same side have C_{2v} symmetry and are expected to show the correspondingly decreased number of signals in the NMR spectra. The X-ray analysis (Figure 1) corresponds to the conformation where the isoquinoline substituents in **5c** are on the same side of the tetracyclic core.

The six possible structures **A** (**M**), **A** (**P**), **B** (**M**), **B** (**P**), **C** (**M**), and **C** (**P**) are shown in Scheme 5. **A** (**M**), **B** (**M**), and **C** (**M**) are enantiomers for **A** (**P**), **B** (**P**), and **C** (**P**), respectively. **C** (**M**) and **C** (**P**) can interconvert, unlike **A** (**M**) and **A** (**P**) [or **B** (**M**) and **B** (**P**)]. On the other hand, **A** (**M**) can be in dynamic equilibrium with **B** (**P**), whereas **A** (**P**) can interconvert to **B** (**M**).

According to the NMR spectra, only the two symmetric structures exist in solution in the **A**:**B** ratio of 1:2.5 at 223 K (Figures 1.6 and 1.7 in the SI). The ratio is not changed significantly at different temperatures, but the rate of this interconversion is. Measurement of this rate in the 223−304 K temperature range (Figure 3) allowed us to determine the magnitude of the enthalpy of activation (10.9 kcal/mol; see the SI for the full analysis and additional data).

The NOESY experiment had indicated that the interatomic distance H2′−H1 (H2″−H10) is smaller than H2′−H17 (H2″−H8) in conformer **A**.[19] Comparison of these results with the calculated geometric parameters of the energetically favorable conformations and with the X-ray data confirm that structure **A** corresponds to a less energetically favorable conformation in comparison to **B**. The measured NMR ratios of the two conformations are fully consistent with the small (0.3 kcal) difference in calculated energies. Again, the calculated activation energy (∼17.0 kcal/mol) for the conformational transition is slightly larger than the experimental value.

The available NMR data suggest that, at the room temperature, the symmetric structures **A** and **B** do not convert into the nonsymmetric structures with the opposite orientation of the isoquinoline substituents relative to the averaged molecular plane. It is unclear, at the moment, why only the symmetric structures are detected, whereas the nonsymmetric structures **C** with energies similar to **A** and **B** are not.

Mechanistic Possibilities and Additional Exploratory Synthetic Studies. Mechanistic scenarios involved in this transformation are complex, but it is clear that they have to involve a redox stage that leads to deoxygenation of the intermediate products (Scheme 6). The relative timing of this

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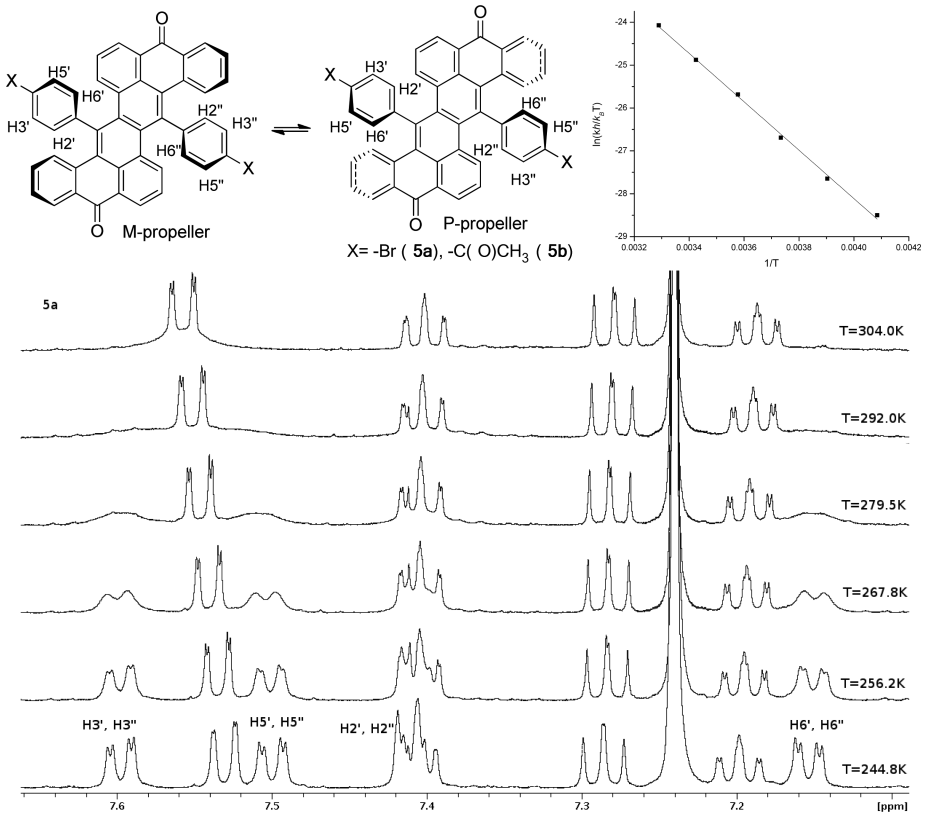
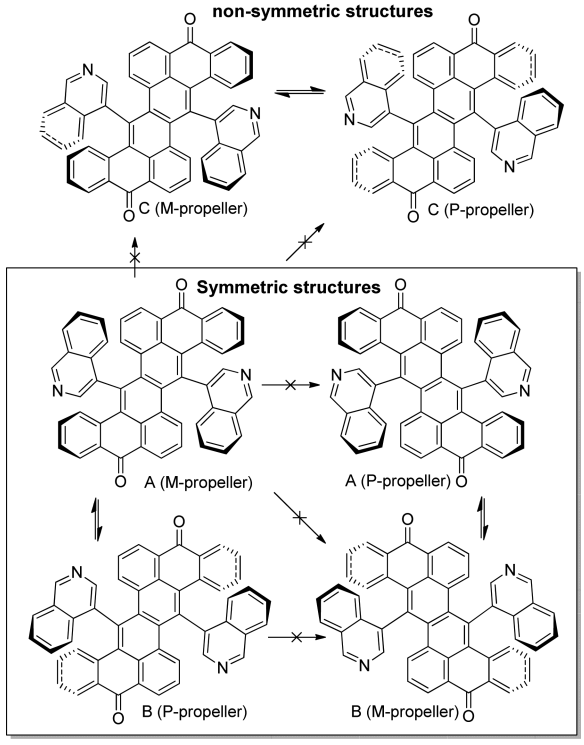


Figure 2. Conformational equilibrium for **5a**/**5b** and Eyring plot for **5a** (top). Temperature-dependent ^{1}H NMR spectra of **5a** (bottom).

Scheme 5. Conformational Equilibrium for 5c



step in relation to the multiple cyclization reactions is, at this time, unclear, and in fact, it is possible that parallel pathways exist and more than one mechanism converge on a common product. We outline several possibilities below to provide a possible framework for understanding the inherent mechanistic complexity of this transformation. More work is needed in the future for evaluating and refining these preliminary mechanistic ideas and for increasing the product yields.

In the first mechanistic possibility, all of the new cycles, but one, are created via transition from alkynes into carbonyls and subsequent aldol condensation. Guanidine may play the dual role. First, it can assist in achieving the correct regioselectivity of alkyne/enamine conversion (as outlined in Scheme 1), setting up the initial cyclizations. Analogous intramolecular delivery from a hemiacetal can explain the opposite regiochemistry of nucleophilic attack at the second alkyne due to intramolecular constraints associated with the transient formation of a medium-sized cycle. Second, guanidine may be capable of serving as a reducing agent that, similar to hydrazine in the Wolff–Kishner reaction, participates in deoxygenation (possibly coupled with the final ring formation, Scheme 7). Guanidine is a relatively strong base, only slightly less basic than KOH (pK_a of guanidinium ion is 13.6).

Alternatively, one can start with the reductive step that leads to partial or full reduction at one of the carbonyl positions followed by intermolecular attack at the activated alkyne of antraquinone followed by the cascade of 6-*exo*-*dig* and 6-*exo*-*trig* cyclizations (Scheme 8). Again, this mechanism depends on the viability of Wolff–Kishner-like reduction of carbonyls, where guanidine serves as a putative reducing agent that is transformed into products with the higher oxidation state of nitrogen (e.g., nitrogen and HCN). Similar reduction of antrones into anthrolates has been reported,[20] and the exoselectivity of cyclizations would be consistent with the known stereoelectronic preferences for these types of reactions.[5,10]

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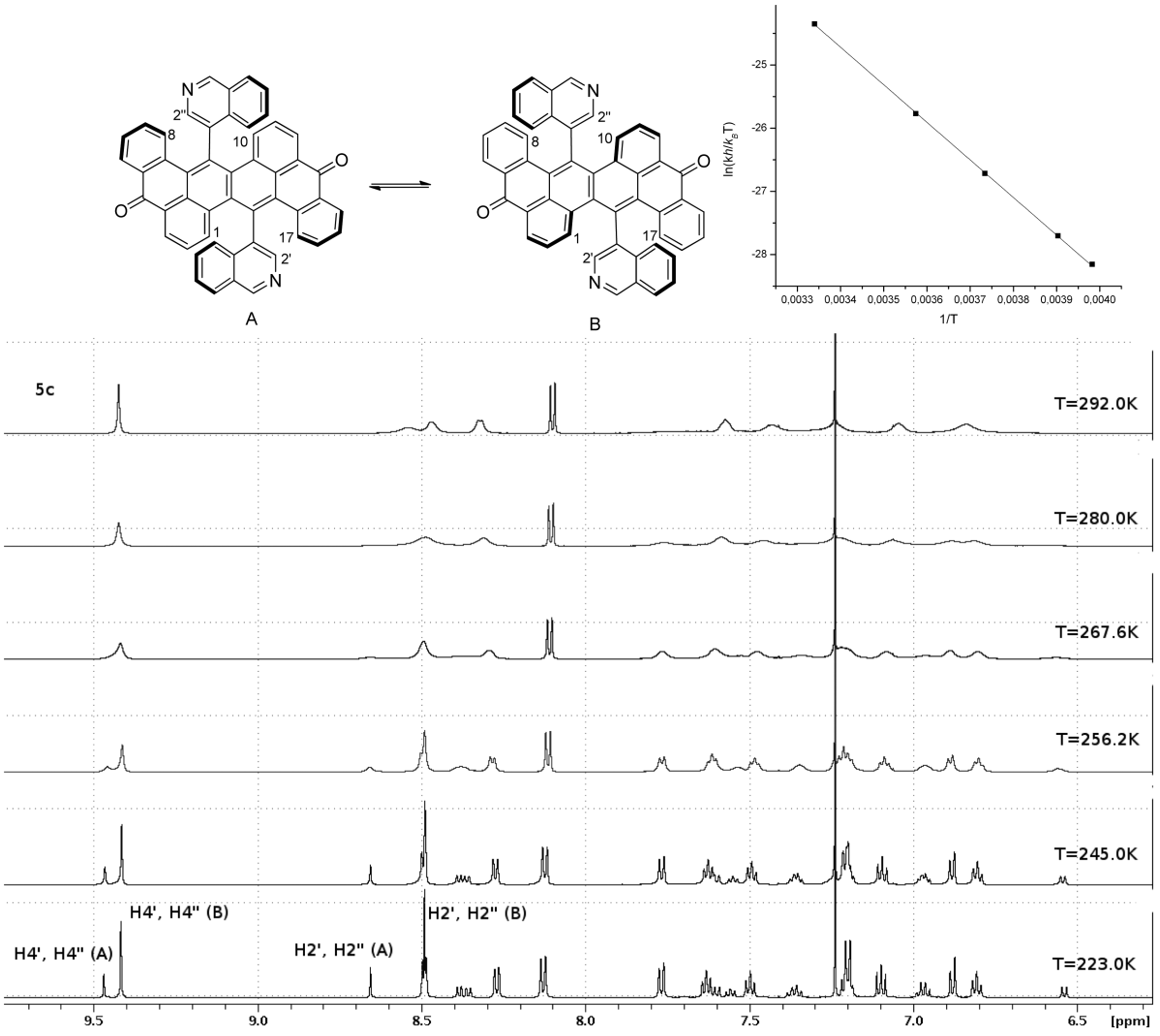
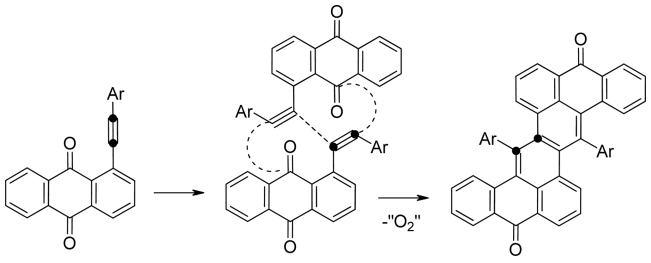


Figure 3. Eyring plot and temperature-dependent ^{1}H NMR spectra of **5c**.

Scheme 6. General Scheme for the Reductive Dimerization of Acetylenic Anthraquinones



Finally, one can picture the possibility of carbenoid coupling illustrated in Scheme 9. In this scenario, which takes advantage of the bifunctional nature of guanidine, the initial formation of imines/or azacarbinols from two quinones and a single guanidine molecule sets up a cyclization sequence. Subsequent transformation of the "guanidine" bridge into two stable fragments (N_2 and HCN) leads to coordinatively unsaturated carbon reactive intermediates that can form the final cycle. One can consider either a concerted or a stepwise version of such fragmentations, but they are likely to be disfavored by the strained nature of possible intermediates.

Again, one can arrive to the observed reaction products by changing the order of steps in each of the above mechanistic scenarios, but it is clear that the overall transformation should include a combination of cyclizations, condensations, and reductive fragmentations.

Because compounds **5a−c** do not contain nitrogen, we tested whether oxygen-containing nucleophiles/bases can promote these transformations using reactions of alkynes **1a,b** in refluxing butanol with KOH. Despite the formation of a large amount of polymeric products, we were able to isolate 1-(2-aryl-2-butoxyvinyl)-9,10-anthraquinones **6a,b** and tetracenediones **5a,b** (Scheme 10). The latter compounds were obtained in yields comparable to the guanidine-mediated cyclizations, suggesting that the reductive dimerization can proceed via a mechanistic path that does not involve N-containing intermediates of the Wolff−Kishner-like processes. The relevance of these observations to the mechanistic scenarios discussed earlier is under investigation.

The double bond stereochemistry was assigned on the basis of the NOESY data for the *Z*-isomer. In the latter case, the spatial proximity of the H−C═C with the H2 and H2′,6′ protons is supported by the presence of the respective cross-peak. In the *E*-isomer, the observed NOESY cross-peaks (see the SI) indicate the proximity of H2 and H2′,6′, as well as that

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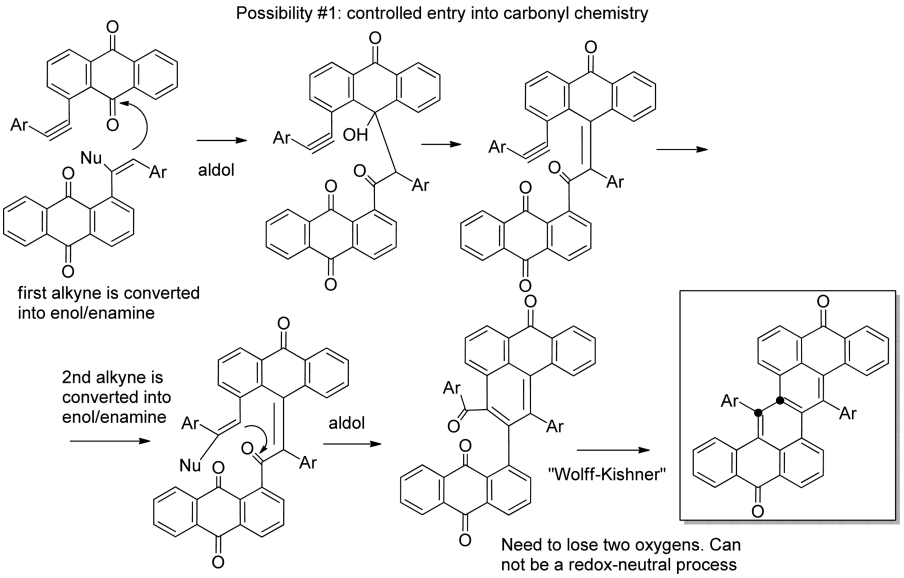
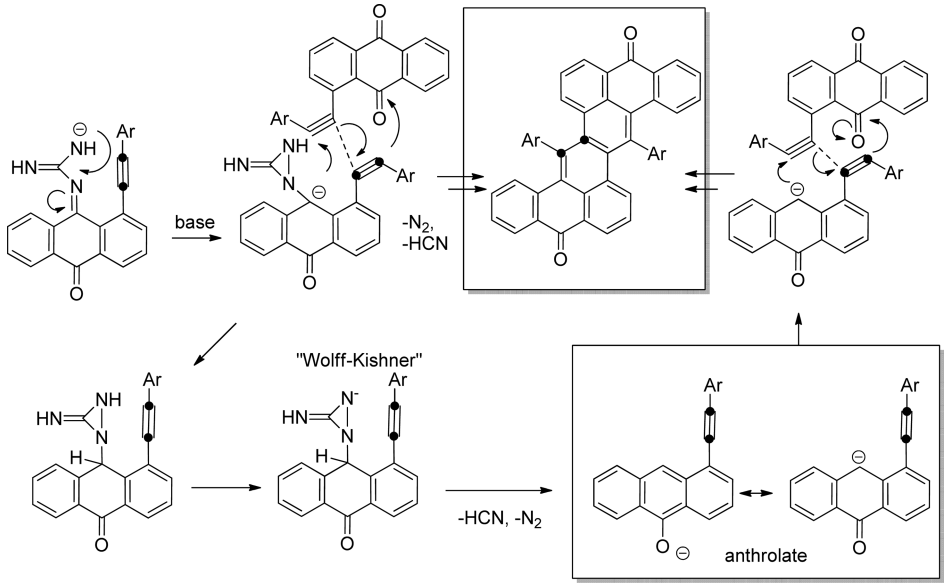
Scheme 7. Possible Mechanism for Reductive Dimerization of Acetylenic Anthraquinones in the Presence of Guanidine: (a) Conversion of Alkyne to Activated Carbon Nucleophile, (b) Aldol Cyclization/Condensation Cascade, and (c) Reductive Deoxygenation



Scheme 8. Possible Mechanisms Initiated by Partial or Full Reduction at One of the Carbonyl Positions Followed by Intermolecular Attack at the Activated Alkyne



for the vinyl proton and protons from the −O−CH_2−Pr moiety. The regioselelectivity of nucleophlic addition is determined from HMBC spectra, where protons from the O−CH_2−Pr group interact with the carbons from the C1−CH═C moiety.

Further substituent effects were explored by introducing nonaromatic substituents at the acetylenic terminus. In the reaction of guanidine with 1-alkylethynyl-9,10-anthraquinones **1d,e**, the formation of heterocyclic products was not observed as well (Scheme 11). Despite the presence of the relatively acidic methylene group, direct 6-*exo-trig* cyclization of a propargylic anion is unlikely, due to the significant strain in the product. The observed formation of 2-hydroxy-1-alkyl-7*H*-benzo[*d*,*e*]anthracen-7-ones **7d,e** (~30%) is likely to proceed via transformation of alkyne into an enolate followed by aldol condensation. The overall process provides another interesting example for the use of alkynes as synthetic equivalents of ketones.[1f,8]

The two possible scenarios for the formation of six-membered carbocycle involve 6-exocyclization of propargylic anion followed by (or concomitant with) hydration of the strained alkyne bond. In a more likely scenario, which avoids the formation of a highly strained intermediate, initiation via intermolecular nucleophilic attack at the polarized triple bond of compound **1d,e** sets up formation of the final carbocycle **7** via alkyne/carbonyl conversion followed by aldol cyclization.

The structure of compounds **7d,e** was established using NMR methods, mass-spectrometry, and (for **7d**) X-ray crystallography (Figure 4). Bond lengths in compound **7d** are similar to those in the analogous cycles of *N*-pyrrolidinoben-

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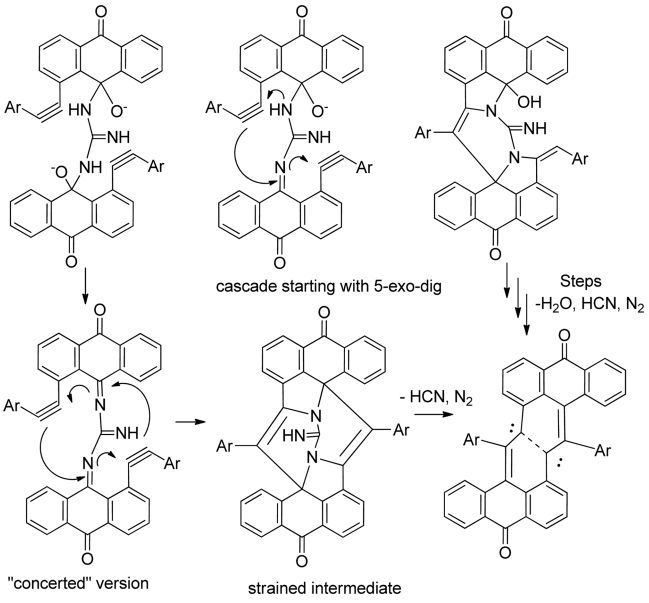
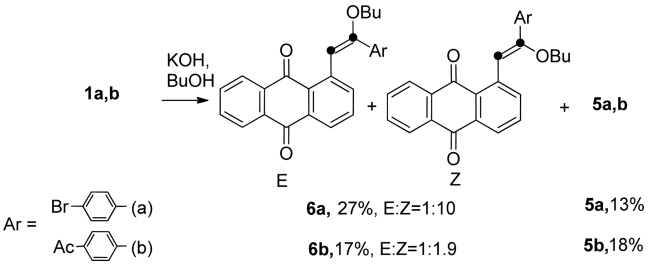
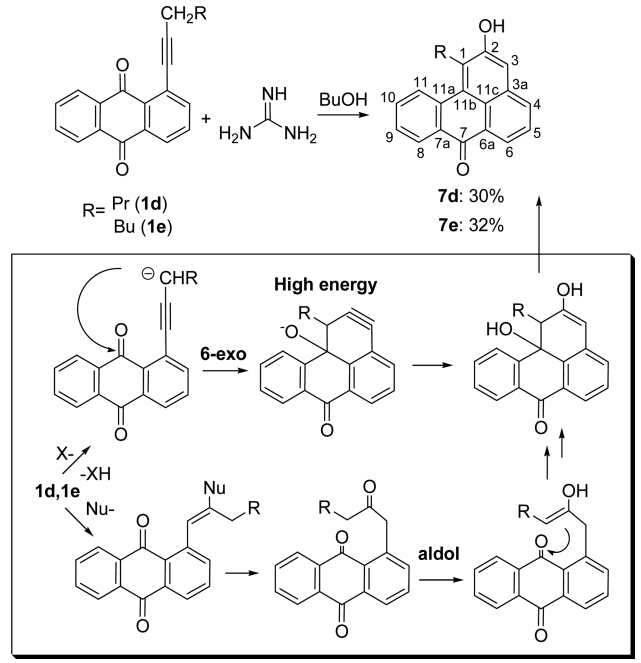
Scheme 9. A Possible Way To Take Advantage of Bifunctional Nucleophile (Guanidine)



Scheme 10. Reactions of Alkynes 1a,b in Refluxing Butanol/KOH Mixture



Scheme 11. Reaction of Guanidine with 1-Alkylethynyl-9,10-anthraquinones 1d,e



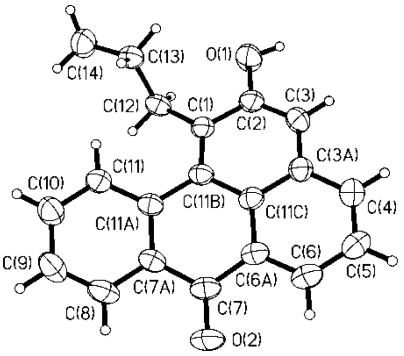
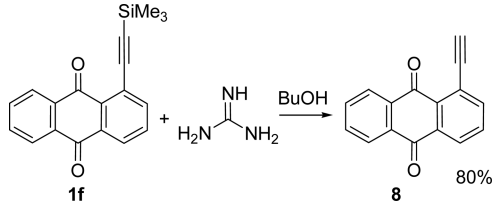


Figure 4. X-ray geometry for compound **7d**.

zanthrone[21] and 3-*N*,*N*-diacetylaminobenzanthrone.[22] Molecule **7d** is not flat—the angle between the C(3A)−C(6A),C(11B) and C(7a)−C(11A) planes is 18.14(9)°. In the crystal, molecules of **7d** form chains along the *b* axis by means of H-bonds O(1)−H(1)···O(2) [H···O, 1.90(4) Å; O−H···O, 176(3)°] and C(3)−H(3)···O(2) (H···O, 2.60 Å; C−H···O, 132°). π-Stacking between C(1)−C(3A),C(11C),C(11B) and C(7A)−C(11A) rings can be noted (centroid−centroid and interplane distances of 3.88 and 3.7 Å, respectively).

In the presence of guanidine in refluxing *n*-butanol (Scheme 12), TMS-substituted alkyne **1f** underwent desilylation with the formation of terminal alkyne **8**.

Scheme 12. Reaction of Guanidine with TMS-Substituted Alkyne 1f



We had also investigated the interaction of the terminal alkyne **8** with guanidine. However, this reaction led to a complex multicomponent mixture, most likely due to the insufficient stability of the alkyne and/or its transformation into an acetylide anion inert toward the nucleophilic attack.

Properties of the Diones. Zethrenes (or Z-shaped quinoidal hydrocarbons), the reduced polyaromatic version of quinones **5a−c**,[23] are known to possess unusual optical, electronic, and magnetic properties due to the significant biradical[24] character in the ground state. Such compounds provide valuable insights in understanding the interplay between spin pairing and aromaticity as well as the validity of the Clar's aromatic sextet rule in these expanded polyaromatics (Scheme 13).

To lay the groundwork for the future detailed study, we had briefly forayed into the electrochemical behavior of this new type of zethrene and their photophysical properties.

Cyclic voltammogram (CV) of **5b** in CH_3CN−0.1 M TEAP is characterized by three reduction peaks, 1C, 2C, and 3C, within the potential sweep range 0 > *E* > −2.10 V [Figure 5; $E_p^{1C} \sim E_p^{2C} \sim -1.04$ V (vide infra), $E_p^{3C} = -1.97$ V]. The shape of the first peak in Figure 5 suggests that there are two overlapping, reversible peaks with close reduction potentials. Double differentiation of the voltammogram gives two well-

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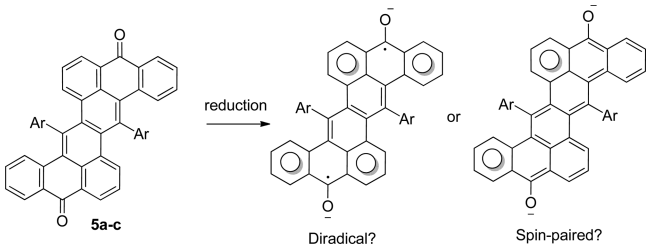
Scheme 13. Interplay between Spin Pairing and Aromaticity in Reduced Tetracenediones Described in This Work[a]



[a]The Clar's aromatic sextets are shown with circles.

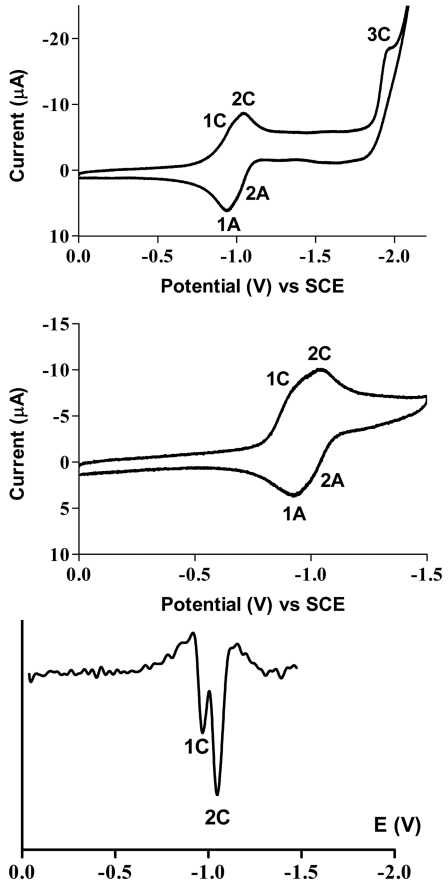


Figure 5. (Top) CV of **5b** within the potential sweep range from 0 to −2.10 V, ν = 0.1 V·s^{-1}. (Center) CV of **5b** within the potential sweep range from 0 to −1.50 V, ν = 0.1 V·s^{-1}. (Bottom) Double differentiation of the CV from the central panel (cathodic branch).

defined peaks, 1C and 2C, in the cathodic branch and two well-defined peaks, 1A and 2A, in the anodic branch, which clearly indicates the presence of two reversible, overlapping peaks. The third reduction peak (3C) of **5b** is irreversible at all studied potential sweep rates.

Similar cyclic voltammograms with the closely spaced peaks were observed earlier in the electrochemical reduction of β-carotene,[25] electrochemical oxidation of 3,3′-dimethoxybianthrone,[26] and a few other examples.[27] Two well-separated, one-electron, reversible reductive peaks usually correspond to the formation of radical anion and dianion, respectively. The potential difference of the first and second stages of a two-electron transfer depends on many factors.[25,27,28]

The peak potential E_p^{1C} can be estimated only approximately from the voltammograms. If the peak 1C corresponds to one-electron transfer, the estimated value for E_p^{1C} based on the E_p^{1A} value is ≈ −0.99 V. In the case of two-electron transfer, the estimated value of E_p^{1C} at the potential peak 1C is −0.96 V. In any case, the potential difference of the first and second reduction peaks (0.05−0.08 V) is close to the minimum possible value of 35 mV.[27,28]

Estimation of peak potentials 1C and 1A from voltammograms shown in Figure 5 by double differentiation gives the following values of the potentials: E_p^{1C} = −0.95 V, E_p^{1A} = −0.92 V. The estimated value of the potential difference between these peaks is sufficiently small (0.03 V) and may indicate a two-electron transfer at the potential of the first reduction peak 1C.

Furthermore, the literature data suggest that in this case one should not eliminate the possibility of potential inversion,[27] when the two-electron transfer takes place more easily than one-electron transfer. The answer to the question whether there is an inversion of the first and second reduction process for **5b** requires further investigation.

Comparison of reduction potentials of **5b** and standard quinone: 1,4-benzoquinone (E_p^{1C} = −0.53 V) and 9,10-anthraquinone (E_p^{1C} = −0.97 V) under the same conditions shows that compound **5b** has very similar reduction potential to 9,10-anthraquinone (E_p^{1C} ≈ −0.96 to −0.99 V). Benzoquinone, on the other hand, should be a stronger oxidant than the tetracenediones.

Electrochemical oxidation of **5b** in the 0 < E < 2.20 V range (Figure 6) is, at least, a four-stage process (E_p^{1Ox} = 1.53 V; E_p^{2Ox} = 1.72 V; E_p^{3Ox} ≈ 1.92 V; E_p^{4Ox} ≈ 2.08 V).

The first oxidation peak 1Ox is quasi-reversible (E_p^{1Ox} = 1.51 V, E_p^{1Red} = 1.45 V; $E_p^{1Ox} - E_p^{1Red}$ = 0.06 V, $E_p^{1Ox} - E_{p/2}^{1Ox}$ = 0.06 V) and obviously corresponds to the one-electron transfer with the formation of the radical cation of **5b**.

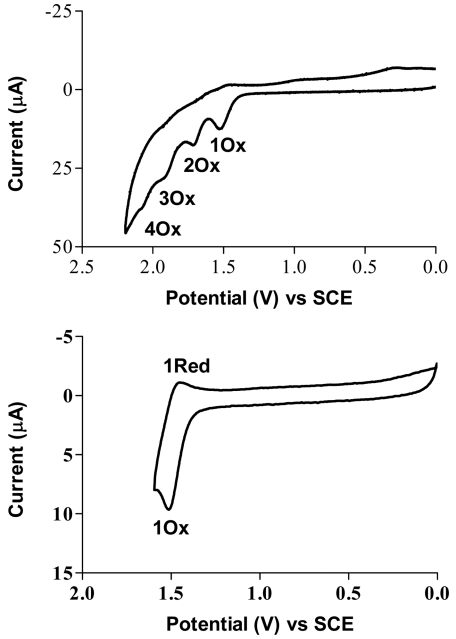


Figure 6. (Top) CV of **5b** within the potential sweep range from 0 to 2.20 V, ν = 0.1 V·s^{-1}. (Bottom) CV of **5b** within the potential sweep range from 0 to 1.60 V, ν = 0.1 V·s^{-1}.

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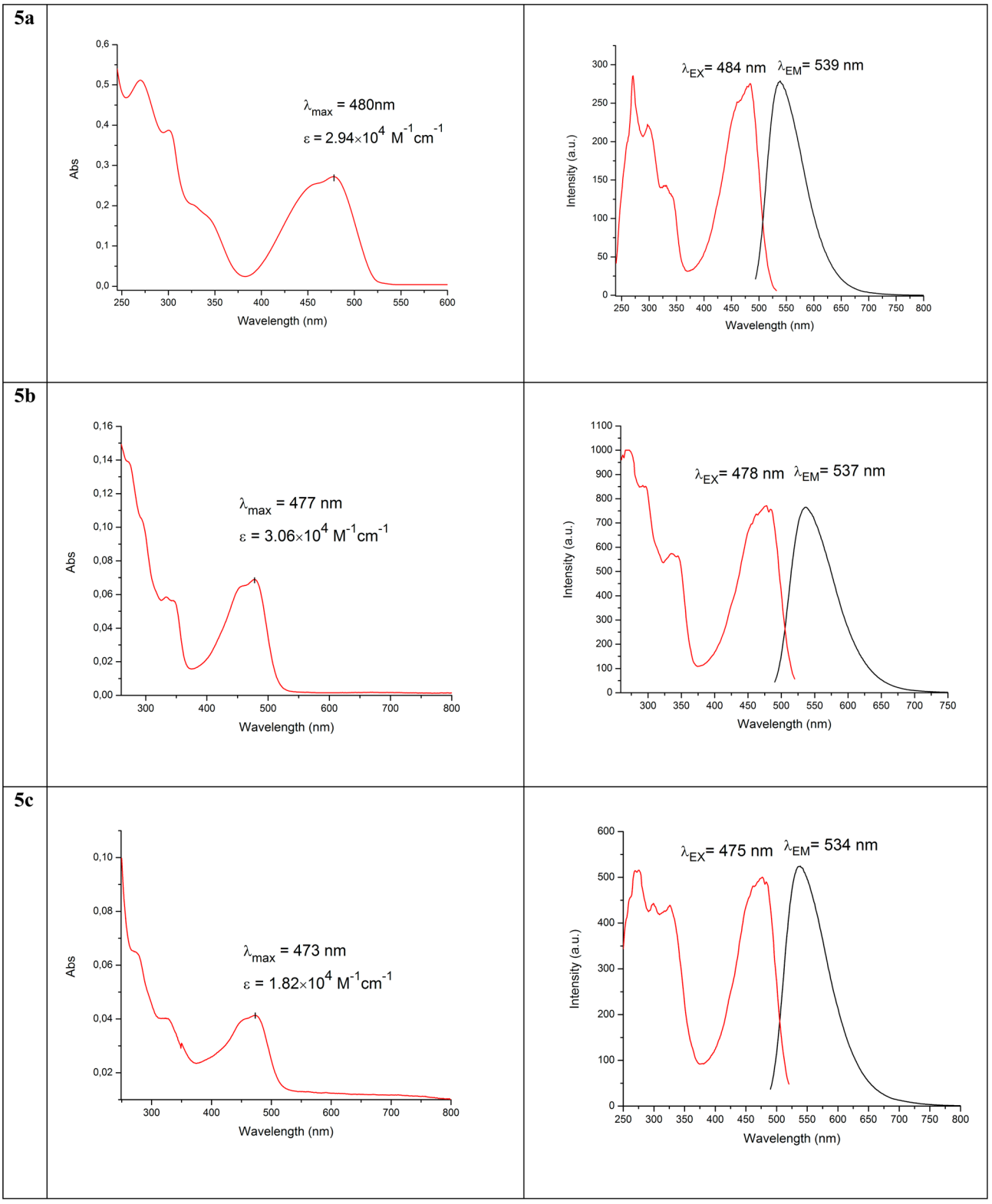

Figure 7. UV−vis absorption (left panels) and fluorescence (excitation and emission, right panels) spectra of compounds **5a−c**.

The presence of the cathodic peak 1Red even at relatively low potential sweep rates (ν = 0.05 V·s^{-1}) indicates the relative stability of the resulting radical cation. This fact is interesting, since the molecule has four electron-withdrawing C = O moieties. Other oxidation peaks are irreversible.

Absorption, excitation, and fluorescence spectra of 2 × 10^{-6} M solutions of the tetracenediones in $CHCl_3$ are shown in Figure 7. The lowest energy absorption peaks are located in the blue region. The fluorescence spectra for compounds **5a−c** display Stokes shifts of 55−59 nm.

The HOMO−LUMO gap for compound **5b** derived from cyclic voltammetry (2.40 eV) corresponds well to the average of UV−vis and fluorescence values (2.45 eV), especially taking

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into account the differences in solvents and in the basic physical principles of these methods.

CONCLUSIONS

In summary, reductive dimerization of acetylenic anthraquinones under strongly basic conditions provides quick synthetic access to flexible nonplanar polyaromatic products with a tetracenedione core. The mechanistic scenarios involved in this multistep process are complex, and a detailed experimental and theoretical study is required in the future for unraveling this complexity. In solution, the nonplanar contorted polyaromatic products exist as an equilibrating mixture of two symmetric conformers, suggesting that distortion of the opposite sides of the polycyclic core are coupled. The tetracenediones **5a–c** are easily reduced and show interesting electrochemical behavior.

EXPERIMENTAL SECTION

Column chromatography was performed on silica (0.063–0.2 mm) or Al_2O_3. UV-254 plates were used for TLC analysis. All the organic solvents were of analytical quality. The IR spectra were recorded in KBr pellets, and fluorescence spectra were recorded of 2×10^{-6} M solutions in $CHCl_3$ in 10 mm cuvettes. Fluorescence spectra for compounds **5a**, **5b**, and **5c** were recorded with the excitation wavelengths λ = 484, 478, and 475 nm, respectively. Combustion analysis was performed with a CHN analyzer. NMR spectra were recorded with 400 MHz (^{1}H, 400 MHz; ^{13}C, 100 MHz) and 600 MHz (^{1}H, 600 MHz; ^{13}C, 150 MHz) spectrometers. Chemical shifts (δ) are given in ppm with reference to the residual signals of chloroform-d_1 (^{1}H, δ = 7.24 ppm; ^{13}C, δ = 76.90 ppm) or DMSO-d_6 (^{1}H, δ = 2.50 ppm; ^{13}C, δ = 39.51 ppm). Kinetic studies of interconversion of **5a–c** were carried out with the DNMR technique in $CDCl_3$ using the DNMR line shape fitting module implemented in the gNMR 5.0 computer program (http://home.cc.umanitoba.ca/~budzelaa/gNMR/gNMR.html). Compounds **5a** and **5b** were investigated in the temperature interval of 245–304 K and broadening of H5′↔H3′ (H5″↔H3″) and H6′↔H2′ (H6″↔H2″) proton signals were taken in consideration. In the case of **5c**, the kinetic investigation was performed in the temperature interval of 223–304 K and H2′(**A**)↔H2′(**B**) [H2″(**A**)↔H2″(**B**)] and H4′(**A**)↔H4′(**B**) [H4″(**A**)↔H4″(**B**)] proton signals were measured. NMR temperature calibration was performed with reference to a standard sample of methanol. Due to the low solubility of **5a**, the ^{13}C spectrum for this compound was obtained from two-dimensional ^{1}H–^{13}C HSQC and HMBC experiments. Peak assignments of ^{1}H NMR spectra for compounds **1a–c**, **2a–c**, **3a,b**, and **7e,d** were performed by analysis of spin–spin coupling constants and line shape fitting of simulated spectra to experimental spectra. Compounds **3b**, **5a–c**, and **6b** were analyzed with application of two-dimensional ^{1}H–^{1}H NOESY, COSY and ^{1}H–^{13}C HSQC, HMBC experiments. The mass spectra (high resolution GC/MS) were measured using a double-focusing system with electron ionization and the direct injection method (the temperature of the ionization chamber was 220–270 °C and the ionization voltage was 70 eV). The Priroda program package was used for ab initio energy calculations and geometry optimization. Details of computational analysis are given in ref 18.

The cyclic voltammetric measurements of **5b** (concentration of the depolarizer was 0.3 mM) were performed at 295 K in an argon atmosphere in acetonitrile (MeCN) purified by a standard procedure (MeCN was distilled over $KMnO_4$ and twice over P_2O_5) at a stationary Pt spherical electrode (S = 0.08 cm^2) with 0.1 M Et_4NClO_4 as a supporting electrolyte with potential sweep rates of $0.05 < \nu < 2.1$ V·s^{-1}. The PG 310 USB potentiostat was used for cyclic voltammetric measurements. A standard electrochemical cell (the volume of solution was 5 mL) connected to the potentiostat with a three-electrode scheme was used. Peak potentials are quoted with reference to a saturated calomel electrode (SCE).

Typical Procedure for the Preparation of 1-*R*-Ethynyl-9,10-anthraquinones 1a–c,f. A mixture of the 1-iodo-9,10-antraquinone (6 mmol), Et_3N (3 mL, 20 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol), CuI (0.04 mmol), and corresponding 1-alkyne (6.5 mmol) in 60 mL of toluene was stirred under argon stream at 60 °C (1–9 h) until iodide is consumed (TLC control). The reaction mixture was cooled and chromatographed on Al_2O_3 (25 × 40 mm^2, elution with toluene). Then solvents were evaporated, and subsequent recrystallization gave pure compounds.

*1-(4-Bromophenylethynyl)anthracene-9,10-dione (**1a**).* Time of reaction 1 h, 60 °C. The yield is 2.07 g (89%), mp 206.5–207.5 °C (from toluene). ^{1}H NMR ($CDCl_3$, J/Hz): δ 7.51–7.59 (4H, m, H(2′), H(3′), H(5′), H(6′)), 7.73 (1H, dd, H(3), J = 7.9, 7.9), 7.77 (1H, ddd, H(6), J = 1.4, 7.4, 7.8), 7.80 (1H, ddd, H(7), J = 1.4, 7.4, 7.7), 7.94 (1H, dd, H(2) J = 1.4, 7.9), 8.27 (1H, ddd, H(5), J = 0.5, 1.4, 7.8), 8.32 (1H, dd, H(4), J = 1.4, 7.9), 8.33 (1H, ddd, H(8), J = 1.4, 7.4, 7.7). ^{13}C NMR ($CDCl_3$): δ 90.3, 94.6, 122.3, 123.4, 123.4, 127.0, 127.6, 127.7, 131.8, 132.8, 133.0, 133.4, 133.6, 134.0, 134.2, 134.5, 134.6, 140.2, 182.1, 182.8. HRMS: m/z calcd for $C_{22}H_{11}O_2Br$ 385.9937, found 385.9974. Anal. Calcd for $C_{22}H_{11}O_2Br$: C, 68.24; H, 2.86; Br, 20.64. Found: C, 68.52; H, 3.23; Br, 20.42. IR: cm^{-1}, ν 1675 (C═O); 2200 (C≡C).

*1-(4-Acetylphenylethynyl)anthracene-9,10-dione (**1b**).* Time of reaction 2.5 h, 60 °C. The yield is 1.93 g (78%), mp 217–218 °C (from toluene–ethyl acetate). ^{1}H NMR ($CDCl_3$, J/Hz): δ 2.62 (3H, s, Me), 7.75 (1H, dd, H(3), J = 7.7, 7.7), 7.77 (1H, ddd, H(6), J = 2.0, 7.3, 7.8), 7.78 (2H, dd, H(2′), H(6′), J = 2.0, 8.2), 7.80 (1H, ddd, H(7), J = 1.3, 7.3, 7.7), 7.97 (1H, dd, H(2), J = 1.4, 7.7), 7.98 (2H, H(3′), H(5′), J = 2.0, 8.2), 8.27 (1H, ddd, H(5), J = 0.4, 1.3, 7.8), 8.34 (1H, ddd, H(8), J = 0.4, 2.0, 7.7), 8.34 (1H, dd, H(4), J = 1.4, 7.7). ^{13}C NMR ($CDCl_3$): δ 26.4, 91.9, 94.4, 122.8, 126.8, 127.3, 127.7, 127.9, 128.1, 132.0, 132.6, 132.7, 133.3, 133.7, 133.9, 134.2, 134.4, 136.5, 140.0, 181.7, 182.5, 197.2. HRMS: m/z calcd for $C_{24}H_{14}O_3$ 350.0938, found 350.0940. Anal. Calcd for $C_{24}H_{14}O_3$: C, 82.27; H, 4.03. Found: C, 82.27; H, 3.98. IR: cm^{-1}, ν 1674, 1700 (C═O); 2198 (C≡C).

*1-(Isoquinolin-3-ylethynyl)anthracene-9,10-dione (**1c**).* Time of reaction 9 h, 60 °C. The yield is 1.5 g (82%), mp 223–224 °C (from benzene–ethanol). ^{1}H NMR ($CDCl_3$, J/Hz): δ 7.69 (1H, ddd, H(5′), J = 1.1, 7.0, 8.2), 7.77 (1H, dd, H(3), J = 7.7, 7.8), 7.78 (1H, ddd, H(7), J = 1.3, 7.4, 7.9), 7.81 (1H, ddd, H(6), J = 1.3, 7.4, 7.9), 7.90 (1H, ddd, H(6′), J = 1.1, 7.0, 8.3), 8.01 (1H, ddd, H(4′), J = 0.8, 1.1, 8.2), 8.05 (1H, dd, H(2), J = 1.4, 7.7), 8.26 (1H, ddd, H(5), J = 0.5, 1.3, 7.6), 8.33 (1H, dd, H(4), J = 1.3, 7.7), 8.37 (1H, ddd, H(8), J = 0.5, 1.4, 7.6), 8.85 (1H, dddd, H(7′), J = 0.6, 0.8, 1.1, 8.3), 8.87 (1H, s, H(2′)), 9.23 (1H, d, H(8′), J = 0.6). ^{13}C NMR ($CDCl_3$): δ 90.9, 95.9, 115.9, 123.0, 125.6, 126.8, 127.4, 127.62, 127.67, 127.7, 127.8, 131.3, 132.6, 132.8, 133.1, 133.7, 133.5, 134.2, 134.4, 135.9, 140.2, 147.1, 152.4, 181.7, 182.5. HRMS: m/z calcd for $C_{25}H_{12}NO_2$ 358.0863, found 358.0863 [M − H]$^+$. Anal. Calcd for $C_{25}H_{13}NO_2$: C, 83.55; H, 3.65; N, 3.90. Found: C, 83.50; H, 3.59; N, 3.91. IR: cm^{-1}, ν 1675 (C═O); 2191 (C≡C).

*1-(Trimethylsilylethynyl)anthracene-9,10-dione (**1f**).* Time of reaction 2.5 h, 40 °C.The yield is 1.25 g (90%), mp 142–143 °C (from hexane–benzene). ^{1}H NMR ($CDCl_3$, J/Hz): δ 0.33 (9H, s, Me), 7.67 (1H, dd, J = 7.7, 7.8), 7.71–7.81 (2H, m), 7.90 (1H, dd, J = 1.4, 7.7), 8.23 (1H, dd, J = 1.6, 7.6) 8.28 (1H, J = 1.4, 7.8), 8.31 (1H, dd, J = 1.5, 7.6). ^{13}C NMR ($CDCl_3$): δ 0.0, 102.3, 104.0, 123.4, 126.8, 127.6, 127.7, 132.80, 132.81, 133.8, 134.13, 134.17, 134.4, 135.9, 141.2, 181.8, 182.8. HRMS: m/z calcd for $C_{19}H_{16}O_2Si$ 304.0914, found 304.0920 [M]$^+$. IR: cm^{-1}, ν 1677 (C═O); 2157 (C≡C).

Synthesis of 1-*R*-ethynyanthracene-9,10-diones (**1d,e**) was carried out as previously described.[29]

Reaction 1-R-Ethynyl-9,10-anthraquinones with Guanidine. A mixture of the 1-*R*-ethynyl-9,10-anthraquinone **1** (3.25 mmol) and 27 mL of 1 M solution of guanidine in methanol (27 mmol) boiled in 60 mL of 1-butanol (9–19 h) (TLC control). The reaction mixture was cooled. The solvent was removed in vacuo, and the residue was purified by column chromatography (toluene, ethyl acetate). Subsequent recrystallization gave pure compounds **2–5**.

*1-(4-Bromophenyl)-2H-dibenzo[de,h]isoquinoline-3,7-dione (**2a**).* Time of reaction 10 h. The yield is 22%, mp 336–337 °C (from ethanol–ethyl acetate). TLC (methylene chloride/ethyl acetate, 1:1):

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R_f = 0.65. ^{1}H NMR (DMSO-d_6, J/Hz): δ 6.92 (1H, d, H(11), J = 0.4, 1.0, 8.5), 7.33 (1H, ddd, H(10), J = 1.6, 7.2, 8.5), 7.39 (1H, ddd, H(9), J = 1.0, 7.2, 7.9), 7.57 (2H, dd, H(2′), H(6′), J = 1.9, 8.3), 7.81 (2H, dd, H(3′), H(5′), J = 1.9, 8.3), 7.89 (1H, dd, H(5), J = 7.7, 7.7), 8.27 (1H, ddd, H(8), J = 0.4, 1.6, 7.9), 8.68 (dd, 1H, H(4), J = 1.6, 7.7), 8.71 (dd, 1H, H(6), J = 1.6, 7.7), 12.09 (1H, s, NH). ^{13}C NMR (DMSO-d_6): δ 104.4, 123.8, 124.7, 126.6, 126.9, 127.1, 127.2, 127.6, 130.0, 131.6, 132.0, 132.4, 132.6, 132.9, 134.5, 134.7, 134.9, 144.4, 160.8, 181.6. HRMS: m/z calcd for $C_{22}H_{12}NO_2Br$ 401.0046, found 401.0045 $[M]^+$. Anal. Calcd for $C_{22}H_{12}NO_2Br$: C, 65.69; H, 3.01; N, 3.48; Br, 19.86. Found: C, 65.86; H, 2.91; N, 3.48; Br, 19.66. IR: cm^{-1}, ν 1642, 1668 (C═O); 3029 (NH).

*2-Amino-3-(4-bromobenzoyl)-7H-dibenzo[de,h]quinolin-7-one (**3a**).* Time of reaction 10 h. The yield is 32%, mp 241−242 °C (from benzene−ethyl acetate). TLC (toluene): R_f = 0.42. ^{1}H NMR ($CDCl_3$, J/Hz): δ 6.03 (2H, s, NH_2), 7.49 (1H, dd, H(4), J = 1.1, 8.6), 7.50 (1H, dd, H(5), J = 7.2, 8.6), 7.56 (4H, m, H(2′), H(3′), H(5′), H(6′)), 7.68 (1H, ddd, H(9), J = 1.3, 7.6, 7.8), 7.80 (1H, ddd, H(10), J = 1.4, 7.6, 7.8), 8.26 (1H, dd, H(6), J = 1.1, 7.2), 8.39 (1H, ddd, H(8), J = 0.5, 1.4, 7.6), 8.82 (1H, ddd, H(11), J = 0.5, 1.3, 7.6). ^{13}C NMR ($CDCl_3$): δ 105.6, 118.0, 125.7, 126.0, 127.7, 128.4, 129.4, 130.80, 130.88, 131.2, 131.4, 132.3, 132.8, 134.0, 137.7, 136.6, 138.8, 151.8, 155.5, 183.5, 196.1. Anal. Calcd for $C_{23}H_{13}N_2O_2Br$: C, 64.35; H, 3.05; N, 6.53; Br, 18.61. Found: C, 64.73; H, 3.25; N, 6.52; Br, 18.50. IR: cm^{-1}, ν 1671 (C═O); 3462 (NH_2).

*9,18-Di(4-Bromophenyl)tetrabenzo[a,de,j,mn]tetracene-4,13-dione (**5a**).* Time of reaction 10 h. The yield is 16%, mp >360 °C (dec 300 °C) (from ethyl acetate). TLC (toluene): R_f = 0.60. ^{1}H NMR (T = 245 K, $CDCl_3$, J/Hz): δ 6.88 (2H, dd, H(8), H(17), J = 0.7, 8.3), 7.15 (2H, dd, H(6′), H(6″) J = 1.4, 8.2), 7.20 (2H, ddd, H(7), H(16), J = 1.5, 7.2, 8.3), 7.29 (2H, dd, H(2), H(11), J = 7.4, 8.3), 7.41 (2H, ddd, H(6), H(15), J = 0.7, 7.2, 8.0), 7.41 (2H, dd, H(2′), H(2″) J = 1.4, 8.2), 7.50 (2H, dd, H(5′), H(5″), J = 2.2, 8.2), 7.53 (2H, dd, H(1), H(10), J = 1.0, 8.3), 7.60 (2H, dd, H(3′), H(3″), J = 2.2, 8.2), 8.38 (2H, dd, H(5), H(14), J = 1.5, 8.0), 8.52 (2H, dd, H(3), H(12), J = 1.0, 7.4). ^{13}C NMR (T = 245 K, $CDCl_3$): δ 124.49 (C2, C11), 127.05 (C5, C14), 127.66 (C3, C12), 127.77 (C6, C15), 128.81 (C8, C17), 129.59 (C3b, C12b), 131.06 (C7, C16), 132.57 (C5′, C5″), 132.68 (C4a, C13a), 133.10 (C3′, C3″), 133.28 (C1, C10), 133.36 (C6′, C6″), 133.96 (C2′, C2″), 136.34 (C8a, C17a), 141.0 (C1′, C1″), 184.30 (C4, C13). HRMS: m/z calcd for $C_{44}H_{22}O_2Br_2$ 739.9982, found 739.9968 $[M]^+$. IR: cm^{-1}, ν 1656 (C═O). UV−vis spectra (2 × 10 $^{-6}$ M solution in $CHCl_3$): λ_{max} = 480 nm, ε = 2.94 × 10^4 M^{-1} cm^{-1}.

*1-(4-Acetylphenyl)-2H-dibenzo[de,h]isoquinoline-3,7-dione (**2b**).* Time of reaction 17 h. The yield is 40%, mp 355−356 °C (from 1,4-dioxane). TLC (methylene chloride/ethyl acetate, 1:1): R_f = 0.63. ^{1}H NMR (T = 313 K, DMSO-d_6, J/Hz): δ 2.70 (3H, s, Me), 6.89 (1H, ddd, H(11), J = 0.4, 1.1, 8.5), 7.25 (1H, ddd, H(10), J = 1.6, 7.1, 8.5), 7.38 (1H, ddd, H(9), J = 1.1, 7.1, 7.9), 7.75 (2H, dd, H(2′), H(6′), J = 1.9, 8.2), 7.89 (1H, dd, H(5), J = 7.7, 7.7), 8.14 (2H, dd, H(3′), H(5′), J = 1.9, 8.2), 8.29 (1H, dd, H(8), J = 1.6, 7.9), 8.69 (1H, dd, H(4), J = 1.6, 7.7), 8.72 (1H, dd, H(6), J = 1.6, 7.7), 11.97 (1H, s, NH). ^{13}C NMR (DMSO-d_6): δ 26.6, 104.3, 124.6, 126.3, 126.7, 126.96, 126.97, 127.5, 128.8, 129.7, 129.8, 131.6, 132.3, 132.6, 134.3, 134.5, 137.7, 139.7, 144.2, 160.5, 181.4, 197.3. HRMS: m/z calcd for $C_{24}H_{15}NO_3$ 365.1046, found 365.1045 $[M]^+$. IR: cm^{-1}, ν 1644, 1662, 1685 (C═O); 3031 (NH).

*2-Amino-3-(4-acetylbenzoyl)-7H-dibenzo[de,h]quinolin-7-one (**3b**).* Time of reaction 17 h. The yield is 10%, mp 223−224 °C (from ethyl acetate). TLC (methylene chloride/ethyl acetate, 20:1): R_f = 0.64. ^{1}H NMR (600.3 MHz, $CDCl_3$, J/Hz): δ 2.63 (3H, s, Me), 6.29 (2H, br.s, NH_2), 7.43 (1H, dd, H(4), J = 1.0, 8.6), 7.45 (1H, dd, H(5), J = 7.2, 8.6), 7.70 (1H, ddd, H(9), J = 1.3, 7.6, 7.8), 7.75 (2H, ddd, H(2′), H(6′), J = 1.7, 2.0, 8.3), 7.81 (1H, ddd, H(10), J = 1.4, 7.6, 7.8), 7.98 (2H, ddd, H(3′), H(5′), J = 1.7, 2.0, 8.3), 8.25 (1H, dd, H(6), J = 1.0, 7.2), 8.39 (1H, ddd, H(8), J = 0.5, 1.4, 7.6), 8.83 (1H, ddd, H(11), J = 0.5, 1.3, 7.6). ^{13}C NMR (151.0 MHz, $CDCl_3$): δ 26.80 (CH_3C(O)), 104.84 (C3), 117.89 (C11c), 125.40 (C6), 125.86 (C11), 127.48 (C8), 128.59 (C3′, C5′), 129.23 (C6a), 129.50 (C2′, C6′), 130.62 and 130.66 (C4, C5), 131.42 (C9), 132.65 (C7a), 133.89 (C10), 135.37 (C11a), 136.49 (C3a), 139.82 (C4′), 143.91 (C1′), 152.21 (C11b), 155.88 (C2), 183.30 (C7), 196.26 (C(O)C3), 197.30 (CH_3C(O)). HRMS: m/z calcd for $C_{25}H_{16}N_2O_3$ 392.1155, found 392.1156 $[M]^+$. IR: cm^{-1}, ν 1613, 1659, 1685 (C═O); 3355, 3460 (NH_2).

*9,18-Di(4-acetylphenyl)tetrabenzo[a,de,j,mn]tetracene-4,13-dione (**5b**).* Time of reaction 17 h. The yield is 11.5%, mp >360 °C (dec 300 °C) (from ethyl acetate). TLC (methylene chloride/ethyl acetate, 20:1): R_f = 0.28. ^{1}H NMR (T = 245 K, $CDCl_3$, J/Hz): δ 2.72 (6H, s, CH_3C(O), CH_3C(O)), 6.82 (2H, dd, H(8), H(17), J = 0.7, 8.3), 7.11 (2H, ddd, H(7), H(16), J = 1.5, 7.2, 8.3), 7.21 (2H, dd, H(2), H(11), J = 7.4, 8.4), 7.40 (2H, ddd, H(6), H(15), J = 0.7, 7.2, 8.0), 7.43 (2H, dd, H(6′), H(6″) J = 1.8, 8.0), 7.46 (2H, dd, H(1), H(10), J = 1.2, 8.4), 7.68 (2H, dd, H(2′), H(2″) J = 1.8, 8.0), 7.98 (2H, dd, H(5′), H(5″) J = 1.8, 8.0), 8.07 (2H, dd, H(3′), H(3″) J = 1.8, 8.0), 8.38 (2H, dd, H(5), H(14), J = 1.5, 8.0), 8.51 (2H, dd, H(3), H(12), J = 1.2, 7.4). ^{13}C NMR (T = 245 K, $CDCl_3$): δ 27.01 (CH_3C(O)), 124.80 (C2, C11), 126.65, 127.27, 127.33 (C5, C14), 127.88 (C3, C12), 128.05 (C6, C15), 128.77, 129.26 (C3′, C3″), 129.77 (C3b, C12b), 129.85 (C5′, C5″), 130.09 (C8, C17), 131.20 (C7, C16), 131.80, 132.38 (C2′, C2″), 132.80 (C4a, C13a), 132.85 (C6′, C6″), 133.45 (C1, C10), 136.02 (C4′, C4″), 136.34 (C8a, C17a), 147.18 (C1′, C1″), 184.53 (C4, C13), 198.10 (CH_3C(O)). HRMS: m/z calcd for $C_{48}H_{28}O_4$ 668.1982, found 668.1977 $[M]^+$. UV−vis (2 × 10^{-6} M solution in $CHCl_3$): λ_{max} = 477 nm, ε = 3.06 × 10^4 M^{-1} cm^{-1}.

*1-(Isoquinolin-3-yl)-2H-dibenzo[de,h]isoquinoline-3,7-dione (**2c**).* Time of reaction 19 h. The yield is 35%, mp >360 °C (from ethanol). TLC (toluene/ethyl acetate, 1:1): R_f = 0.10. ^{1}H NMR (DMSO-d_6, J/Hz): δ 6.70 (1H, dd, H(11), J = 0.8, 8.5), 7.05 (1H, ddd, H(10), J = 1.6, 7.2, 8.5), 7.29 (1H, ddd, H(9), J = 0.8, 7.2, 7.9), 7.72−7.85 (3H, m, H(4′), H(5′), H(6′)), 7.94 (1H, dd, H(5), J = 7.6, 7.9), 8.27 (1H, dd, H(8), J = 1.6, 7.9), 8.34 (1H, m, H(7′), J = 0.6, 1.2, 8.4), 8.70 (1H, s, H(2′)), 8.74 (1H, dd, H(4), J = 1.5, 7.6), 8.76 (1H, dd, H(6), J = 1.5, 7.9), 9.60 (1H, s, H(8′)), 12.21 (1H, br s, NH). ^{13}C NMR (DMSO-d_6): δ 106.4, 123.8, 125.2, 125.5, 126.7, 127.32, 127.33, 127.4, 127.7, 128.0, 128.4, 128.5, 129.6, 132.1, 132.4, 132.7, 133.0, 133.1, 134.52, 134.53, 140.6, 143.0, 154.4, 160.8, 181.6. HRMS: m/z calcd for $C_{25}H_{13}N_2O_2$ 373.0972, found 373.0968 $[M - H]^+$. IR: cm^{-1}, ν 1643, 1678 (C═O); 3067 (NH).

*9,18-Di(isoquinolin-3-yl)tetrabenzo[a,de,j,mn]tetracene-4,13-dione (**5c**).* Time of reaction 19 h. The yield is 24%, mp >360 °C (dec 300 °C) (from ethyl acetate). TLC (toluene/ethyl acetate, 1:1): R_f = 0.25. HRMS: m/z calcd for $C_{50}H_{26}N_2O_2$ 686.1989, found 686.1968 $[M]^+$. IR: cm^{-1}, ν 1634 (C═O). UV−vis (2 × 10 $^{-6}$ M solution in $CHCl_3$): λ_{max} = 473 nm, ε = 1.82 × 10 ^{4} M^{-1} cm^{-1}.

Compound **A** (24%): ^{1}H NMR (T = 223 K, $CDCl_3$, J/Hz): δ 6.54 (2H, dd, H(8), H(17), J = 0.9, 8.42), 6.97 (2H, dd, H(2), H(11), J = 7.3, 8.5), 6.98 (2H, ddd, H(7), H(16), J = 1.4, 7.2, 8.4), 7.19 (2H, ddd, H(4′), H(4″), J = 0.1, 0.7, 8.6), 7.36 (2H, ddd, H(6), H(15), J = 0.9, 7.2, 8.0), 7.37 (2H, ddd, H(5′), H(5″), J = 1.1, 6.9, 8.6), 7.56 (2H, ddd, H(6′), H(6″), J = 0.7, 6.9, 8.2), 7.60 (2H, dd, H(1), H(10), J = 1.2, 8.5), 8.13 (2H, dddd, H(7′), H(7″), J = 0.1, 0.7, 1.1, 8.2), 8.36 (2H, dd, H(5), H(14), J = 1.4, 8.0), 8.39 (2H, dd, H(3), H(12), J = 1.2, 7.3), 8.66 (2H, dd, H(2′), H(2″)), 9.47 (2H, d, H(8′), H(8″), J = 0.7). ^{13}C NMR (T = 223 K, $CDCl_3$): δ 123.82 (C4′, C4″), 125.15 (C2, C11), 126.82 (C3a, C12a), 127.41 (C5, C14), 128.00 (C3, C12), 128.00 (C6′, C6″), 128.30 (C6, C15), 128.30 (C7′, C7″), 129.05 (C3b, C12b), 129.15 (C9b, C18b), 129.75 (C8, C17), 130.96 (C1, C10), 131.23 (C7, C16), 131.70 (C4a, C13a), 131.84 (C5′, C5″), 132.15 (C9, C18), 133.87 (C3′, C3″), 134.17 (C3a′, C3a″), 136.30 (C8a, C17a), 145.98 (C2′, C2″), 153.21 (C8′, C8″), 184.28 (C4, C13).

Compound **B** (76%): ^{1}H NMR (600.3 MHz, T = 223 K, $CDCl_3$, J/Hz): δ 6.81 (2H, ddd, H(7), H(16), J = 1.5, 6.9, 8.4), 6.88 (2H, dd, H(8), H(17), J = 0.9, 8.4), 7.10 (2H, dd, H(2), H(11), J = 7.3, 8.5), 7.20 (2H, dd, H(1), H(10), J = 1.2, 8.5), 7.21 (2H, ddd, H(6), H(15), J = 0.9, 6.9, 7.9), 7.50 (2H, ddd, H(5′), H(5″), J = 1.2, 6.9, 8.4), 7.63 (2H, ddd, H(6′), H(6″), J = 1.3, 6.9, 8.3), 7.77 (2H, ddd, H(4′),

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H(4″), J = 0.5, 1.3, 8.4), 8.13 (2H, dddd, H(7′), H(7″), J = 0.5, 0.7, 1.2, 8.3), 8.27 (2H, dd, H(5), H(14), J = 1.5, 7.9), 8.49 (2H, dd, H(3), H(12), J = 1.2, 7.3), 8.49 (2H, s, H(2′), H(2″)), 9.42 (2H, d, H(8′), H(8″), J = 0.7). ^{13}C NMR (151.0 MHz, T = 223 K, $CDCl_3$): δ 123.71 (C4′, C4″), 125.21 (C2, C11), 127.18 (C3a, C12a), 127.29 (C5, C14), 127.71 (C8, C17), 128.20 (C3, C12), 128.20 (C6′, C6″), 128.30 (C6, C15), 128.30 (C7′, C7″), 128.98 (C9b, C18b), 129.23 (C3b, C12b), 131.02 (C9, C18), 131.53 (C7, C16), 131.70 (C4a, C13a), 131.84 (C5′, C5″), 133.36 (C1, C10), 133.87 (C3′, C3″), 134.27 (C3a′, C3a″), 136.20 (C8a, C17a), 145.86 (C2′, C2″), 152.82 (C8′, C8″), 184.69 (C4, C13).

*2-Hydroxy-1-propyl-7H-benzo[d,e]anthracen-7-one (**7d**).* Time of reaction 18.5 h. The yield is 30%, mp 219−220 °C (from ethyl acetate−methylene chloride). ^{1}H NMR ($CDCl_3$, J/Hz): δ 1.18 (3H, t, Me, J = 7.3), 2.07 (2H, m, CH_2Me), 3.21 (2H, m, CH_2Et), 5.54 (1H, s, OH), 7.25 (1H, s, H(3)), 7.55 (1H, ddd, H(9), J = 1.1, 7.3, 7.8), 7.61 (1H, dd, H(5), J = 7.4, 8.0), 7.70 (1H, ddd, H(10), J = 1.5, 7.3, 8.3), 7.94 (1H, dd, H(4), J = 1.4, 8.0), 8.10 (1H, ddd, H(11), J = 0.6, 1.1, 8.3), 8.51 (1H, dd, H(6), J = 1.4, 7.4), 8.51 (1H, ddd, H(8), J = 0.6, 1.5, 7.8). ^{13}C NMR ($CDCl_3$): δ 14.5, 22.4, 32.6, 111.3, 124.9, 126.2, 127.1, 127.9, 128.1, 128.30, 128.35, 128.4, 132.3, 132.4, 132.8, 132.9, 134.2, 137.4, 154.3, 184.7. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C,83.42; H, 5.69. HRMS: m/z calcd for $C_{20}H_{16}O_2$ 288.1145, found 288.1145 $[M]^+$. IR: cm^{-1}, ν 1634 (C═O); 3299 (OH).

*2-Hydroxy-1-butyl-7H-benzo[d,e]anthracen-7-one (**7e**).* Time of reaction 19 h. The yield is 32%, mp 189−190 °C (from ethyl acetate−methylene chloride). ^{1}H NMR ($CDCl_3$, J/Hz): δ 1.07 (3H, t, Me, J = 7.3), 1.60 (2H, m, CH_2Me), 2.03 (2H, m, CH_2Et), 3.24 (2H, m, CH_2Pr), 5.38 (1H, s, OH), 7.25 (1H, s, H(3)), 7.54 (1H, ddd, H(9), J = 1.2, 7.3, 7.8), 7.62 (1H, dd, H(5), J = 7.4, 8.0), 7.69 (1H, ddd, H(10), J = 1.6, 7.3, 8.3), 7.95 (1H, dd, H(4), J = 1.4, 8.0), 8.14 (1H, ddd, (11), J = 0.6, 1.2, 8.3), 8.51 (1H, ddd, H(6), J = 1.4, 7.4), 8.51 (1H, ddd, H(8), J = 0.6, 1.6, 7.8). ^{13}C NMR ($CDCl_3$): δ 14.0, 23.2, 30.3, 31.1, 111.3, 125.0, 126.2, 127.11, 127.16, 127.9, 128.1, 128.30, 128.38, 128.5, 132.3, 132.8, 132.9, 134.3, 137.3, 154.3, 184.7. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.90; H, 5.91. HRMS: m/z calcd for $C_{21}H_{18}O_2$ 302.1301, found 302.1299 $[M]^+$. IR: cm^{-1}, ν 1633 (C═O); 2870, 2953 (Bu); 3335 (OH).

*1-Ethynyl-9,10-anthraquinone (**8**).* Time of reaction 0.5 h. The yield is 80%, mp 218−220 °C (from toluene) (lit.[30] mp 222−225 °C).

Reaction 1-*R*-Ethynyl-9,10-anthraquinones with KOH in 1-Butanol. A mixture of the 1-*R*-ethynyl-9,10-anthraquinone (2.6 mmol) and 0.1 g KOH in 70 mL of *n*-butanol boiled 2.5−14 h (TLC control). Then solvents were evaporated. Crude product was chromatographed on Al_2O_3 (d = 30 mm, h = 200 mm, elution with toluene). Then solvents were evaporated and subsequent recrystallization gave pure compounds **5a,b** and **6a,b**.

*1-[2-(4-Bromophenyl)-2-butoxyvinyl]-9,10-anthraquinone (**6a**).* Time of reaction 2.5 h. The yield is 27%, mp 141−142 °C (from benzene−hexane). *Z*-isomer (91%): ^{1}H NMR ($CDCl_3$, J/Hz): δ 0.76 (3H, t, Me, J = 7.3), 1.24 (2H, m, CH_2Me), 1.50 (2H, m, CH_2Et), 3.60 (2H, t, CH_2Pr), 7.31 (1H, s, H(Vi)), 7.58 (4H, m), 7.70−7.81 (3H, m), 8.22−8.32 (4H, m). ^{13}C NMR ($CDCl_3$): δ 13.8, 19.2, 32.0, 71.4, 113.0, 122.7, 126.6, 126.9, 127.4, 128.4, 129.9, 131.3, 131.8, 132.9, 133.7, 134.3, 134.8, 134.9, 135.9, 137.7, 138.1, 155.2, 183.7, 185.0. HRMS: m/z calcd for $C_{26}H_{21}O_3Br$ 460.0669, found 460.0655 $[M]^+$. IR: cm^{-1}, ν 1668 (C═O); 2870, 2928, 2957 (Bu).

*9,18-Di(4-Bromophenyl)tetrabenzo[a,de,j,mn]tetracene-4,13-dione (**5a**).* . The yield is 12%, mp >360 °C (from ethyl acetate).

*1-[2-(4-Acetylphenyl)-2-butoxyvinyl]-9,10-anthraquinone (**6b**).* Time of reaction 14 h. The yield is 17%, mp 137−138 °C (from benzene−hexane). HRMS: m/z calcd for $C_{28}H_{24}O_4$ 424.1669, found 424.1672 $[M]^+$. *E*-isomer (34%): ^{1}H NMR ($CDCl_3$, J/Hz): δ 1.02 (3H, Me, J = 7.4), 1.57 (2H, CH_2Me), 1.87 (2H, CH_2Et), 2.52 (3H, C(O)CH_3), 4.15 (2H, CH_2Pr), 6.87 (1H, H(Vi), J = 0.7), 7.12 (1H, H(2), J = 0.7, 1.2, 8.5), 7.30 (1H, H(3), J = 7.3, 8.5), 7.33 (2H, H(2′), H(6′), J = 0.3, 1.4, 8.3), 7.73−7.82 (4H, H(3′), H(5′), H(6), H(7)), 8.13 (1H, H(4), J = 1.2, 7.3), 8.25−8.31 (2H, H(5), H(8)). ^{13}C NMR ($CDCl_3$): δ 13.85 (Me), 19.39 (CH_2Me), 26.45 (C(O)CH_3), 31.22 (CH_2Et), 68.41 (CH_2Pr), 105.00 (C1−CH═C), 126.05 (C4), 126.63 and 127.22 (C5 and C8), 127.88 (C3′, C5′), 129.67 (C2′, C6′), 129.87 (C9a), 132.41 (C3), 133.55 and 134.09 (C6 and C7), 134.64, 136.64 (C4′), 138.91 (C2), 139.99 (C1), 140.77 (C1′), 155.91 (C1−CH═C), 183.34 (C10), 184.46 (C9), 197.51 (C(O)CH_3).

Z-isomer (66%): ^{1}H NMR ($CDCl_3$, J/Hz): δ 0.76 (3H, t, Me, J = 7.3), 1.25 (2H, m, CH_2Me), 1.52 (2H, m, CH_2Et), 2.63 (3H, s, C(O)CH_3), 3.61 (2H, t, CH_2Pr, J = 6.5), 7.44 (1H, d, H(Vi), J = 0.7), 7.73−7.82 (3H, m, H(3), H(6), H(7)), 7.83 (2H, ddd, H(2′), H(6′), J = 0.3, 1.4, 8.3), 8.02 (2H, ddd, H(3′), H(5′), J = 0.3, 2.3, 8.3), 8.25−8.31 (4H, m, H(2), H(4), H(5), H(8)). ^{13}C NMR ($CDCl_3$): δ 13.56 (Me), 18.99 (CH_2Me), 26.55 (C(O)CH_3), 31.83 (CH_2Et), 71.39 (CH_2Pr), 114.48 (C1−CH═C), 126.60 (C4), 126.60 (C2′, C6′), 126.63 and 127.22 (C5 and C8), 128.53 (C3′, C5′), 129.67 (C9a), 132.67 (C3), 133.55 and 134.09 (C6 and C7), 134.64, 136.79 (C4′), 137.48 (C2), 137.66 (C1), 141.41 (C1′), 154.79 (C1−CH═C), 183.45 (C10), 184.82 (C9), 197.51 (C(O)CH_3).

*9,18-Di(4-acetylphenyl)tetrabenzo[a,de,j,mn]tetracene-4,13-dione (**5b**).* The yield is 18%, mp >360 °C (from ethyl acetate).

X-ray Diffraction. The X-ray diffraction data for **5a**, **5c**, and **7d** were obtained at room temperature (for **5a** and **7d**). Crystals were grown by recrystallization from the dichloromethane−acetyl acetate solutions. Absorption corrections were applied empirically using the SADABS program. All structures were solved by direct methods, using the SHELXS-97 program and refined by anisotropic full-matrix least-squares method against all F^2 reflections using the SHELXL-97 program. The H atom of OH group in **7d** was located from the difference Fourier map and refined isotropically. Other H atoms were refined isotropically with a riding model. The partial site occupation (0.797) of the solvate dichloromethane molecule in crystal **5a** should be noted. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre.

*Crystal Data for Compound **5a**.* Crystal system triclinic, space group $P\bar{1}$, a = 9.5559(5) Å, b = 13.1086(7) Å, c = 15.3621(8) Å, α = 105.124(2)°, β = 102.639(2)°, γ = 103.148(2)°, V = 1727.97(16) Å^3, $C_{44}H_{22}Br_2O_2{\cdot}0.797CH_2Cl_2$, Z = 2, formula weight 810.12, d_{calc} = 1.557 g·cm^{-3}, μ = 2.509 mm^{-1}, crystal size 0.09 × 0.20 × 0.24 mm^3, 24 523 reflections measured, 6664 unique reflections, θ < 26°, transmission 0.72−0.86, wR_2 = 0.1228, S = 1.015 for all data (R = 0.0425 for 4299 reflections with $F > 4\sigma(F)$), CCDC 823559.

*Crystal Data for Compound **5c**.* Crystal system monoclinic, space group $P2_1/c$, temperature 150 K, a = 11.5675(5) Å, b = 24.356(1) Å, c = 12.0597(5) Å, β = 98.503(2)°, V = 3360.4(3) Å^3, $C_{50}H_{26}N_2O_2$, Z = 4, formula weight 686.73, d_{calc} = 1.357 g·cm^{-3}, μ = 0.083 mm^{-1}, crystal size 0.05 × 0.09 × 0.22 mm^3, reflections measured 50396, unique reflections 5946, θ < 25°, transmission 0.93−0.99, wR_2 = 0.1377, S = 1.104 for all data (R = 0.0478 for 4032 reflections with $F > 4\sigma(F)$), CCDC 1022500.

*Crystal Data for Compound **7d**.* Crystal system monoclinic, space group $P2_1/c$, a = 9.275(2) Å, b = 18.499(4) Å, c = 8.4499(19) Å, β = 97.966(8)°, V = 1435.9(6) Å^3, $C_{20}H_{16}O_2$, Z = 4, formula weight 288.33, d_{calc} = 1.334 g·cm^{-3}, μ = 0.085 mm^{-1}, crystal size 0.03 × 0.10 × 0.54 mm^3, reflections measured 9388, unique reflections 2541, θ < 25°, transmission 0.79−0.94, wR_2 = 0.1308, S = 0.985 for all data (R = 0.0503 for 1412 reflections with $F > 4\sigma(F)$), CCDC 823560.

■ ASSOCIATED CONTENT

Supporting Information

Full details of kinetic experiments; ^{1}H NMR, ^{13}C NMR, and 2D NMR spectra for all of the compounds prepared; X-ray crystallographic data; computational details and Cartesian coordinates for the calculated structures, and a CIF file containing data for **5a**, **5c**, and **7d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) The intensity of NOESY peaks is inversely proportional to r^6. This property can be used for evaluating the distance between interacting nuclei. It is especially straightforward to compare two distances. Because all protons in the analyzed triads (H2′−H1−H17 and H2″−H10−H8) have similar relaxation times, one only needs to compare the intensity of peaks for each pair (compare the H2′−H1 cross-peak with H2′−H17 cross-peak. A greater intensity corresponds to a shorter distance.

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