

# Studies in the Cycloproparene Series:<sup>1</sup> An Experimental and Theoretical Investigation of Polar Dyes Derived from Cyclopropa[*b*]naphthalene

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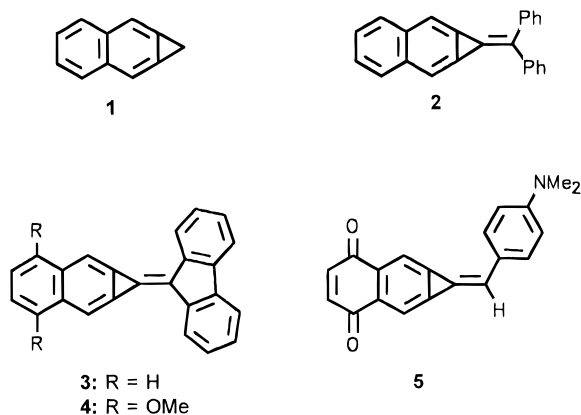
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1*H*-Cyclopropa[*b*]naphthalene is converted into novel polar olefins **15**–**19** via reaction of the 1,1-disilyl with anthrone-like ketones. The alkenes so formed are crystalline, polar compounds that range in color from yellow to magenta. Solutions of the 10,10-dimethylanthyrylidene **15**, the xanthenylidene **16**, and *N*-methylacrydinylidene **18** fluoresce; parent anthrone **19** likely phosphoresces. X-ray crystal structure determinations are reported for **15**, **18**, and the thioxanthyrylidene **17**. Theoretical studies using ab initio calculations at the HF/6-31G\* level have been performed to provide assessments of the structures, charge distributions, and dipole moments of **15**–**19**.

## 1. Introduction

Despite wide interest<sup>2</sup> in the strained cycloproparenes, e.g., **1**, and their novel methylidene derivatives, e.g., **2**,<sup>3–5</sup> the number of compounds available that carry substituents in the aromatic frame are remarkably few.<sup>6</sup> Following our earlier studies<sup>7</sup> involving polar methylidenecycloproparenes, e.g., **3**, and the observation that certain members of this class are exceptionally fluorescent,<sup>4,8,9</sup> we became attracted to extended polar systems that incorporate electron-donating or electron-withdrawing functionality within the cycloproparenyl component of the methylidene derivatives as illustrated by **4** and **5**.<sup>6,10</sup>



When coupled with the classical route to the linear cycloproparene hydrocarbons,<sup>11</sup> the incorporation of an

exocyclic double bond at C1 proved<sup>4,12</sup> to be a comparatively uncomplicated process from transformation into the corresponding 1,1-bis(trimethylsilyl) derivative, e.g., **9**, and subsequent Peterson olefination (Scheme 1). While this path leads to electron-donating cyclopropa[naphthalenyl] diethers **4**, the procedure has been singularly unsuccessful in providing the corresponding electron withdrawing methylidenequinones, e.g. **5**, either directly, by way of the 1,1-disilyl-3,6-quinone, or by oxidative demethylation of **4**.<sup>6</sup> An appealing alternative for polar derivatives of potential use appeared possible by using the known<sup>7</sup> amphiphilic nature of the cyclopropa[naphthalenyl] moiety and carrying out the Peterson olefination sequence employing ketones formally derived from anthrone. We report here the synthesis and properties of the anthronylidene dye derivatives **15**–**18** and anthrylidene **19** that includes X-ray crystal structure analyses of **15**, **17**, and **18** and a theoretical assessment of the structures, polarity, and charge distributions within this family of compounds.

## Results and Discussion

The attachment of aromatic substituents to the exocyclic C8 carbon center of **2** results in a conformation that is markedly closer to planarity than is the case for traditional penta- and heptafulvenes.<sup>3,4</sup> This stems from an appropriate volume of free space between C2 and C8 because of the 1,6-didehydroheptafulvene nature of **2**. In fact, the twist angle between an aromatic ring and the (essentially) planar cycloproparenyl moiety is close to the angles recorded for a range of (*E*)-stilbenes.<sup>4,13</sup> The impact of the close planarity is to allow for mesomerism

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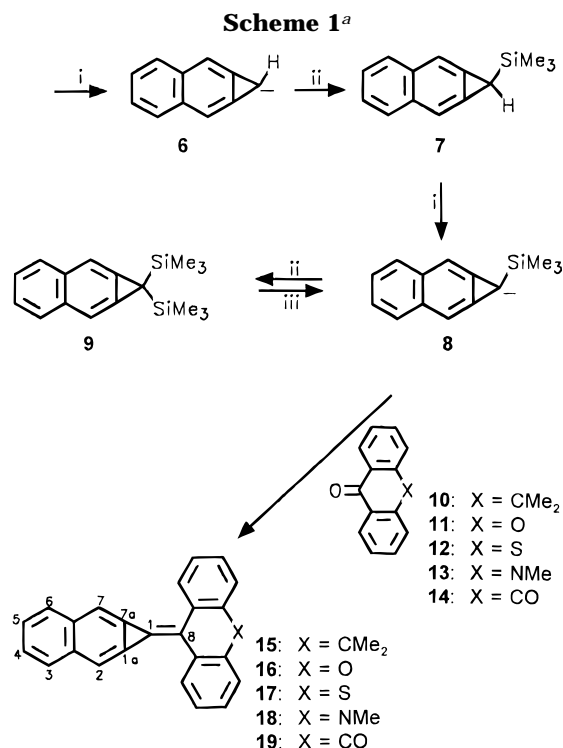
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<sup>a</sup> Reagents: (i) BuLi, THF; (ii) Me<sub>3</sub>SiCl; (iii) *t*-BuOK, THF.

throughout the carbon frame rather than require the polarization that is necessary in analogous heptafulvenes.<sup>14</sup> In light of this, the synthesis of a range of mesomerically stabilized methylenecyclopropenes **15**–**19** from carbonyl compounds structured on the anthrone skeleton, viz. **10**–**14**, became attractive not only because of their expected extended polar conjugation and dye-like characteristics but also because of the reversal of polarity from the amino **18** to the carbonyl-containing **19**.

**(a) Experimental Study.** The requisite ketones **10**–**14** were obtained as commercial samples or by application of literatures procedures (Experimental Section), and reaction of each of these with the  $\alpha$ -silyl anion **8** (generated from **9** by the revised procedure<sup>4</sup>) provided the sought-after extended alkenes **15**–**19** as crystalline compounds in yields ranging from 22 to 81%. The compounds vary in color from yellow (**15**) to orange (**16**) to red (**17** and **19**) and to magenta (**18**), and the spectroscopic properties are fully compatible with the assigned structures. In particular, the typically<sup>2,3</sup> shielded <sup>13</sup>C NMR signals for C2/7 appear from 102 to 110 ppm and C1 and C8 resonate between 100 and 113 ppm; the H2/7 protons are a singlet in the range 7.2–7.9 ppm. The compounds show molecular ions in the mass spectrum. Like the cyclopropa[*b*]naphthalene analogue<sup>9</sup> of **5**, cyclohexane and acetonitrile solutions of **15**, **16**, and **18** fluoresce (Experimental Section), but the Stokes shifts (80–20 nm) are moderate to small and the efficiency is markedly less.<sup>9</sup> With carbonyl **19** phosphorescence from

**Table 1. Experimental Data for Structure Analyses of 15, 17, and 18**

	<b>15</b>	<b>17</b>	<b>18</b>
chemical formula	C <sub>27</sub> H <sub>20</sub>	C <sub>24</sub> H <sub>14</sub> S	C <sub>25</sub> H <sub>17</sub> N
<i>M</i>	344.4	334.4	331.4
Crystal size (mm <sup>3</sup> )	0.13 × 0.09 × 0.23	0.53 × 0.13 × 0.11	0.43 × 0.37 × 0.17
Temperature (K)	ambient	ambient	130
space group	<i>Pbca</i>	<i>C2/c</i>	<i>P2<sub>1</sub>/c</i>
space group no.	61	15	14
<i>Z</i>	8	8	4
<i>a</i> (Å)	41.357(11)	32.081(8)	10.901(2)
<i>b</i> (Å)	12.651(3)	3.9461(11)	17.816(5)
<i>c</i> (Å)	7.1672(13)	27.865(8)	8.607(2)
$\alpha$ (deg)	90.00	90.00	90.00
$\beta$ (deg)	90.00	113.18(2)	95.97(2)
$\gamma$ (deg)	90.00	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	3750.1(15)	3243.1(15)	1662.5(7)
<i>d</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.220	1.370	1.324
$\mu$ (mm <sup>-1</sup> )	0.07	0.20	0.08
$2\theta$ range (deg)	3 ≤ 2( $\theta$ ) ≤ 45	3 ≤ 2( $\theta$ ) ≤ 50	3 ≤ 2( $\theta$ ) ≤ 55
unique reflectns	2455	2839	3820
obsd reflectns	1529	1543	2906
[ <i>F</i> <sub>o</sub> ≤ 4 $\sigma$ ( <i>F</i> )]			
parameters	245	226	249
refined			
<i>g</i> and <i>d</i> for weighted scheme	0.096/0	0.068/0	0.091/0.34
R1, wR2	0.0670, 0.1778	0.0637, 0.1939	0.0539, 0.1514

the triplet state appears likely, while for the thioxanthenyliene **17** the emission collapses to a single strong emission at 511 nm in acetonitrile. The limited solubilities of the compounds in benzene have precluded dipole moment measurements<sup>4</sup> for all but the dimethylanthrone derivative (**15**) and this gives a value of 1.7 D. This value is notably higher than that recorded<sup>15</sup> for the diphenylmethylidene **2** (0.4 D) and attributable to a decrease in the twist angle of the substituent rings because of fusion of the two phenyl substituents of **2** through the CMe<sub>2</sub> connector in **15**. The polarity in **15**, and that which can be reasonably assumed for carbonyl **19**, is presumed to involve electron donation by the cyclopropene moiety. The heteroatom-substituted derivatives **16**–**18** are likewise presumed polar, and intuition suggests that the dipole will lie in the opposite direction, viz. with the cyclopropene acting as the electron acceptor from donation by the electron rich heteroatom. However, as has been pointed out for cycloheptatrienyliene derivatives of the cyclopropenes,<sup>8,16</sup> intuitive expectation based upon simple principles can conflict with the outcome of detailed ab initio calculations that provide not only the magnitude but also the direction of the dipole moment (see below)!

**(b) Structural Study.** Of the range of cyclopropenes that carry an exocyclic double bond, four fulvenes<sup>4</sup> and three fulvalene derivatives<sup>16</sup> have had their structures confirmed by X-ray crystallographic analysis. The six-membered fulvalenes prepared in the present study provide the first examples of anthrone-like compounds fused to the cyclopropene framework via an exocyclic double bond; the crystal structures of hydrocarbon **15** and sulfur **17** and nitrogen-containing **18** are presented here. Relevant crystal data are provided in Table 1, and selected bond lengths and angles appear in Tables 2 and

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**Table 2.** Selected Experimental and Calculated [HF/6-31G\*] Bond Lengths (Å) for 15–19<sup>a</sup>

bond lengths	15	16	17	18	19
C1–C2	1.352(3) [1.349]	[1.348]	1.354(4) [1.350]	1.355(1) [1.347]	[1.354]
C1–C10	1.388(4) [1.377]	[1.379]	1.384(5) [1.376]	1.400(2) [1.381]	[1.371]
C1–C11	1.431(3) [1.431]	[1.430]	1.433(5) [1.430]	1.429(2) [1.430]	[1.426]
C2–C3	1.425(4) [1.431]	[1.434]	1.431(4) [1.430]	1.439(2) [1.435]	[1.425]
C3–C8	1.445(4) [1.428]	[1.427]	1.445(6) [1.429]	1.444(2) [1.427]	[1.432]
C11–C12	1.352(4) [1.330]	[1.332]	1.354(5) [1.330]	1.362(2) [1.331]	[1.337]
C12–C13	1.470(4) [1.479]	[1.476]	1.473(5) [1.483]	1.459(3) [1.474]	[1.478]
C13–C18	1.405(4) [1.399]	[1.388]	1.406(4) [1.394]	1.413(1) [1.401]	[1.396]
C18–X <sup>b</sup>	1.531(6) [1.538]	[1.356]	1.741(4) [1.774]	1.393(3) [1.396]	[1.486]
X–Y <sup>c</sup>	1.541(5) 1.545(6) [1.537] [1.550]			1.456(2) [1.446]	[1.201]

<sup>a</sup>Experimental values are librational corrected and averaged with  $C_s$  symmetry; standard deviations in parentheses. <sup>b</sup>Atom X: **15**, C25; **16**, O; **17**, S1; **18**, N1; **19**, C=O. <sup>c</sup>X–Y: **15**, C–Me(C26/27); **18**, N–Me(C25); **19**, C=O.

**Table 3.** Selected Experimental and Calculated [HF/6-31G\*] Bond and Dihedral Angles (deg) for 15–19

bond angle <sup>a</sup>	15	16	17	18	19
C1–C2–C3	114.8(4) [114.1]	[114.2]	114.3(3) [114.0]	114.5(1) [114.2]	[113.9]
C2–C1–C10	124.3(7) [124.7]	[124.7]	124.7(3) [124.7]	124.4(2) [124.6]	[124.7]
C2–C1–C11	174.3(7) [174.1]	[174.2]	174.2(3) [174.1]	174.0(2) [174.2]	[174.0]
C2–C3–C8	120.9(2) [121.2]	[121.2]	121.1(3) [121.3]	121.1(1) [121.2]	[121.3]
C1–C10–C11	61.0(1) [61.2]	[61.2]	61.2(3) [61.2]	60.7(1) [61.1]	[61.3]
C1–C11–C10	58.0(2) [57.5]	[57.6]	57.7(3) [57.5]	58.6(1) [57.7]	[57.5]
C1–C11–C12	150.7(9) [151.2]	[151.2]	151.1(5) [151.2]	150.5(5) [151.1]	[151.2]
C11–C12–C13	121.3(10) [122.1]	[122.3]	119.2(3) [120.9]	121.5(2) [122.3]	[120.7]
C13–C12–C19	117.2(3) [115.9]	[115.3]	121.6(3) [118.3]	117.0(1) [115.4]	[118.5]
C18–X–C24 <sup>b</sup>	110.5(3) [109.5]	[120.3]	103.9(2) [100.9]	120.9(1) [119.5]	[117.2]
dihedral angle					
$\theta_1$ C11–C12–C13–C18 and C11–C12–C19–C24	$\pm 154.3(4)$ [150.2]	[165.5]	$\pm 172.2(10)$ [145.6]	$\pm 171.7(3)$ [154.8]	[162.1]
$\theta_2$ C13–C18–X–C24 and C19–C24–X–C18	$\pm 30.5(7)$ [37.6]	[12.1]	$\pm 4.0(9)$ [31.0]	$\pm 13.6(6)$ [25.8]	[8.0]

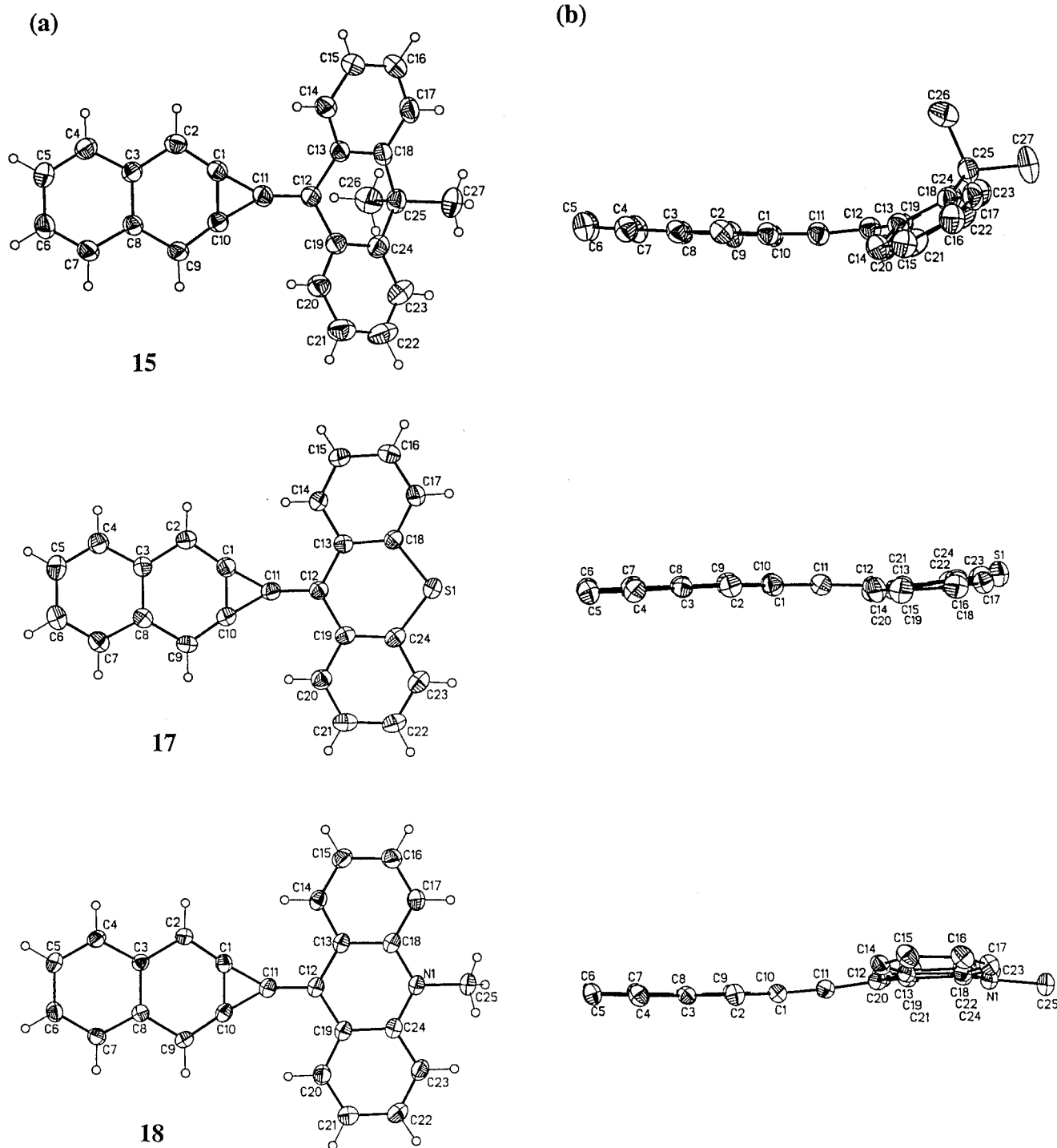
<sup>a</sup>Experimental values are averaged on  $C_s$  symmetry with standard deviations in parentheses. <sup>b</sup>Atom X: **15**, C25; **16**, O; **17**, S1; **18**, N1; **19**, C=O.

3, respectively, that also show the calculated parameters from the theoretical study (see below). The structural analyses confirm the identity of the compounds as shown by the ellipsoid plots of Figure 1a that have the crystallographic numbering appended; approximately orthogonal views appear as Figure 1b and these show the cyclopropenyl moiety to be almost planar. For convenience, the discussion of the X-ray and calculated structures that follows uses crystallographic numbering rather than systematic numbering of Scheme 1.

The bond distances in the naphthalene moieties of **15** and **17** and those of their exocyclic double bonds compare very well even though the methylenide fragment of **15** is markedly bent while that of **17** is almost planar. Both structures also exhibit features similar to those of the five-membered fluorenylidene<sup>16</sup> analogue as well as the methylenecyclopropanaphthalene with one or two *p*-dimethylanilino substituents at the methylenide center,<sup>4</sup>

*cf.* **5**. For **18**, however, there are significant differences: the exocyclic double bond C11–C12 (1.362 Å) and the bridge bond of the cyclopropene moiety C1–C10 (1.400 Å) are longer. This indicates that the electron distribution in **18** is different than that in **15** and **17**, and this is supported by the theoretical studies (see below).

The packing mode of the bent dimethylanthrone **15** is quite different from that of the almost planar **17** and **18**. In **15** parallel stacks are found in which the cyclopropenyl moieties lie almost on top of one another with a separation of 3.58 Å (half of the *c* axis), but with a rotation of one with respect to the other of 101°. In contrast to this, thioxanthonylidene **17** has its molecules stacked at an incline along the *b* axis (3.95 Å) and adjacent stacks are antiparallel to compensate the dipoles. In acridinylidene **18**, however, we find the typical herringbone pattern that has the molecules arranged along a 2-fold screw axis that passes through the exocy-

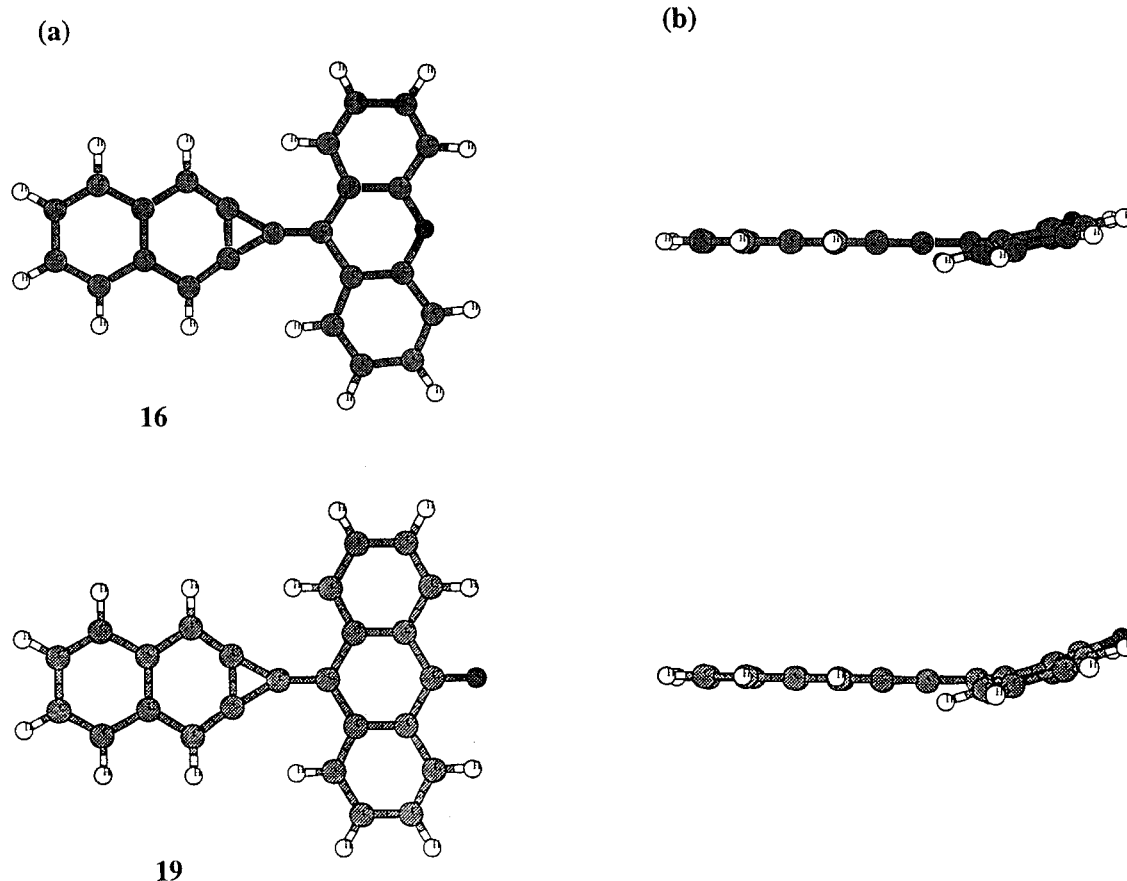


**Figure 1.** X-ray structures of compounds **15**, **17**, and **18** (a) top view with crystallographic labeling of the atoms and (b) side view from an approximately orthogonal plane showing the bending in the molecules.

clic double bond. Thus the molecules are arranged antiparallel in the stacks at a distance of 3.49 Å. The patterns for both **17** and **18** form the closest contacts for flat molecules—for **18**, which is expected to have the highest dipole moment of **15**–**18** (see below), the compensation of intermolecular charges is found within the stacks while for **17**, with its lower dipole, the compensation occurs between the stacks. In **15**, where the dipole is the lowest, the molecules are rotated within the stacks, thereby allowing them to adopt the bent conformation—the compensation occurs in the centrosymmetric structure on antiparallel stacks.

**(c) Theoretical Study.** Each of the cyclopropanaphthalenes **15**–**19** has been optimized at the ab initio RHF/6-31G\* level of theory utilizing the programs Gaussian 94<sup>17</sup> and Spartan 4.0<sup>18</sup> imposing  $C_s$  symmetry with a mirror plane along C11–C12 and orthogonal to the naphthalene fragment. In addition, the RHF/STO-3G energy calculations have been performed using the RHF/

(17) Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala,



**Figure 2.** Calculated [HF/6-31G\*] structures of **16** and **19** (a) top view and (b) side view from an approximately orthogonal plane showing the bending in the molecules.

6-31G\* optimized geometries. This has been done because we recognized in previous cases that the split valence basis set is appropriate for the geometry optimization, but the minimal basis set performs better for estimation of the dipole moment.<sup>16</sup>

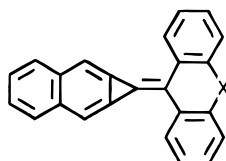
The RHF/6-31G\* optimized geometries of **15**–**19** are given in Tables 2 and 3 as selected distances, angles, and dihedral angles. Top and side views of **16** and **19** are shown in Figure 2 to complement the experimental X-ray structures of **15**, **17**, and **18** displayed in Figure 1. The calculated bond lengths are in good agreement with the symmetry-averaged experimental data and the mean values of deviation are 0.008 (**15**), 0.013 (**17**), and 0.012 Å (**18**). However, there are larger deviations that are noteworthy. It is obvious that difficulties are encountered in describing adequately the length of the exocyclic (C11–C12) bond that connects the two ring systems at this level of theory. The deviations for this bond are 0.022 (**15**), 0.024 (**17**), and 0.031 Å (**18**), and in each case the calculated distance is *shorter* than that determined experimentally in the solid state. Similar differences are also noted for the bridge bond (C1–C10) of the naphthalene fragment. Additionally, the experimental and calculated distance for the C–S bond in **17** differ by 0.033 Å. Comparison of the calculated bond distances for **15**–

**19** (Table 2) shows remarkable similarities except for ketone **19**. Here the small differences calculated are best explained by the influence of the carbonyl group on the electron distribution as illustrated by the significantly larger dipole moment (see below).

The calculated angles are in very good agreement with the experimentally measured ones with deviations of less than 1° in the majority of cases. The dihedral angles about the exocyclic double bond show very little twisting of the fused anthrone-like rings, and the substituent atoms bonded to the exocyclic linkage are held close to planarity. The dihedral angle C11–C12–C13(**19**)–C18–(24) ( $\theta_1$ ) reflects the bending of the anthronylidene fragment with respect to the cyclopropa[*b*]naphthalene ring system and C13(**19**)–C18(24)–X–C24(18) ( $\theta_2$ ) the shape of the six-membered ring fused to the exocyclic double bond (Table 3). In **15** these two parameters are similar (X-ray,  $\theta_1 \pm 154.3(4)^\circ$ ;  $\theta_2 \pm 30.5(7)^\circ$ ; HF/6-31G\*,  $\theta_1 150.2^\circ$ ;  $37.6^\circ$ ) (Table 3 and Figure 1), but in **17** and **18** the differences are remarkable. Compounds **17** and **18** are found to be almost planar in the solid state ( $\theta_1 \pm 172.2(10)$  and  $\pm 171.7(3)^\circ$ ;  $\theta_2 \pm 4.0(9)$  and  $\pm 13.6(6)^\circ$ , respectively) whereas the calculations predict there to be significant bending ( $\theta_1 145.6$  and  $154.8^\circ$ ;  $\theta_2 31.0$  and  $25.8^\circ$ ) (Table 3). On the basis of the fact that both the PM3 and HF/6-31G\* levels of theory predict a bent structure for the dyes, it can be assumed that at least in a vacuum and in nonpolar solvents this is a distinct feature of these molecules. The energy differences between the planar and the bent conformation at the

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(18) Spartan 4.0: Wavefunction Inc., 18401 Von Karman Suit 370, Irvine, CA.

**Table 4.** Calculated Electronic Properties of Compounds 15–19

	15 (X = CMe <sub>2</sub> )	16 (X = O)	17 (X = S)	18 (X = NMe)	19 (X = CO)
$\mu^a$	→	→	→	←	→
$\mu$ (HF/STO-3G//HF6-31G*)	0.54 <sup>b</sup>	0.91	1.18	1.26	3.69
$\mu$ (HF/6-31G*)	0.84 <sup>b</sup>	1.23	2.54	1.17	6.15
$q_{C11}$	0.08	0.04	0.08	0.05	0.07
$q_{C12}$	-0.23	0.02	-0.14	0.00	-0.06
$\Sigma_{CPN}^c$	0.06	-0.03	0.08	-0.01	0.08

<sup>a</sup> The arrow shows the direction of the dipole referred to the structure above and points toward the negative pole; values are in debye units. <sup>b</sup> Measured as 1.7 D, see Experimental Section. <sup>c</sup> Sum of total Mulliken charges on the cyclopropa[b]naphthalenyl (CPN) fragment.

PM3 level are 1.8 (**15**), 0.0 (**16**), 1.6 (**17**), 1.3 (**18**), and 0.8 (**19**) kcal mol<sup>-1</sup>, respectively, in favor of the bent structure. Moreover, the PM3 frequency calculations of the planar structures reveal that the lowest frequency is the vibration from one to the other identical bent form. This vibration is imaginary for all except **16** and thus indicates a transition state for **15** and **17–19**. The small values reveal that the potential energy surfaces are shallow with respect to the corresponding dihedral angles  $\theta_1$  and  $\theta_2$ . The higher value for **15** compared to **17** and **18** indicates why it is the last two that are more easily distorted toward a planar conformation in the solid state where intermolecular interactions and a polar environment can influence the equilibrium geometry. It is reasonable to assume that xanthenylidene **16** and anthrylidene **19** (Figure 2) (for which crystallographic data are not available) prefer an almost planar structure in the solid state.

To gain more insight into the electronic structure of the dyes, the Mulliken charges and the molecular dipole moments have been determined at different levels of theory. The values are given in Table 4, and they show a remarkable difference depending on the basis set used. As mentioned above, we have found it desirable to use dipole moments based on the RHF/STO-3G density but with RHF/6-31G\* optimized geometry.<sup>16</sup> In general the value of the dipole moment is smaller using the RHF/STO-3G//RHF/6-31G\* level of theory. However, the calculated dipole moments for **15** (0.54 and 0.84 D) are both quite different from that experimentally recorded (1.7 D). It is known<sup>19</sup> that CI methods are needed for reliably calculating dipole moments but these methods are too time-consuming for the comparatively large molecules examined in the present study. Thus the magnitude of the dipole moments calculated herein provides the *trend* for compounds **15–19** and the results also reveal the direction of the dipole moments which are not accessible by experiment. It is especially noteworthy that it is only the *N*-methyl derivative **18** that has the negative end of its dipole directed toward the cycloproparene fragment!

The Mulliken population analysis based on atomic charges ( $q$ ) of C11, C12 and the sum of the total charges in the cyclopropanaphthalenyl (CPN) moiety ( $\Sigma_{CPN}$ ) are given in Table 4. The atomic charges of C11 and C12 are considered because it can be assumed that the partial

charges of the exocyclic double bond atoms may reflect the electron distribution, i.e., they may show whether the compound in question is "normal" with the CPN fragment carrying a partial positive charge or in the reverse situation (Table 4).<sup>16</sup> However, there is no obvious correlation between the charges on C11 and C12 and the dipole moment. Most interestingly, the  $\Sigma_{CPN}$  values indicate that it is not only *N*-methyl **18** that has a negative charge in the CPN fragment. The oxygen-containing **16** has an even higher partial negative charge in this subunit despite a dipole moment in the opposite direction! This probably results from the different position of the center of mass that is the reference point for estimation of the dipole moment. On the basis of this, the dipole moment cannot be used to determine whether the cycloproparene moiety of a given compound is positively or negatively charged. Thus both **16** and **18** carry a small partial negative charge in the CPN fragment. According to the present ab initio investigation and to our previous studies at the same level of theory, the charge distribution of the CPN fragment of the cycloproparenes and the corresponding reactivity seem unpredictable. However, the theoretical results do support the experimental findings that the cyclopropa[b]naphthalene moiety can behave as an electron sink when appropriately strong electron donating groups are attached to the exocyclic double bond.<sup>4,5,16</sup>

## Experimental Section

General procedures have appeared previously.<sup>6</sup> NMR spectra were recorded for (D)chloroform solutions at 300 (<sup>1</sup>H) and 75 (<sup>13</sup>C) MHz unless otherwise stated with assignments based on <sup>1</sup>H–<sup>1</sup>H and <sup>1</sup>H–<sup>13</sup>C COSY experiments. Ketones **11–14** were commercial samples while dimethylanthrone (**10**) was prepared as detailed below:

**10,10-Dimethylanthrone (10).** The ketone was synthesized in three steps from phthalic anhydride according to the method of Leung and Curtin.<sup>20</sup> The final step involving treatment of 3,3-dimethyl-1-hydroxy-1-phenylphthalan (1.05 g, 4.33 mmol) was improved upon by subjecting the slow-moving (major) column fraction to radial chromatography (1:1 dichloromethane/light petroleum elution) and collecting the only band visible at 254 nm.

Yield: 213 mg, 22%, mp 101–102 °C (lit.<sup>20</sup> 10%, mp 101.5–102 °C); <sup>1</sup>H NMR  $\delta$  8.43–8.30 (m, 2H), 7.70–7.31 (m, 6H), 1.74 (s, 6H); <sup>13</sup>C NMR  $\delta$  179.8 (CO), 150.5, 130.1, 37.84 (all quaternary), 133.3, 127.5, 126.6 (all CH), 32.9 (2xMe); GC/

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MS *m/z* (rel intensity) 222 (M, 9), 207 (M-15, 98), 178 (80), 152 (38), 89 (98), 88 (50), 76 (100%).

**The 1-Alkylidene-1*H*-cyclopropa[b]naphthalenes 15–19.** The methylenecyclopropa[b]naphthalenes **15–18** were prepared from disilyl **9**<sup>4</sup> employing a large excess of KOBu-*t* with minor variations to the published<sup>4</sup> procedure whereas the synthesis of **19** employed stoichiometric base and addition of **14** to anion **8** preformed from **9**.

**A. 1-(10,10-Dimethyl-9-anthrylidene)-1*H*-cyclopropa[b]naphthalene (15):** from anthrone **10** (165 mg, 0.74 mmol), **9** (150 mg, 0.53 mmol), and KOBu-*t* (131 mg, 1.17 mmol). Addition of the first drops of *tert*-butoxide solution turned the colorless solution yellow. The cold bath was allowed to warm to room temperature overnight with continuous stirring. The reaction mixture was poured into 50 mL of water and subjected to conventional workup.<sup>4</sup> Purification (radial chromatography; 10:1 light petroleum/dichloromethane elution) and recrystallization (dichloromethane/light petroleum) gave *anthrylidene 15* (116 mg, 63%) as small bright yellow needles; mp 153–155 °C; IR 3050, 2971, 2956, 2914, 1775, 1598, 1511, 1471, 1450, 1421, 1354, 1345, 1246, 1139 (s), 838 (s), 758 (s), 737 cm<sup>-1</sup> (s); <sup>1</sup>H NMR δ 8.40 (m, H9/17), 7.91 (AA' of AA'BB', H3/6), 7.66 (s, H2/7), 7.66–7.62 (m, H12/14), 7.48 (BB' of AA'BB', H4/5), 7.45–7.23 (m, H10/16 and H11/15), 1.69 (s, 2 × Me); <sup>13</sup>C NMR δ 143.55 (C12a/13a), 138.97 (C2a/6a), 132.74 (C8a/17a), 128.73 (C3/6), 127.51 (C11/15), 126.90 (C1a/7a), 126.78 (C4/5), 126.38 (C10/16), 125.27 (C12/14), 124.22 (C9/17), 112.75 (C8), 107.80 (C1), 106.99 (C2/7), 39.24 (C13), 32.12 (C18); UV (cyclohexane) λ<sub>max</sub> (log ε) 216 (sh, 4.04), 230 (4.73), 263 (4.56), 278 (sh, 4.49), 294 (sh, 4.34), 406 (sh, 4.34), 431 (4.54), 464 nm (4.62); UV (acetonitrile) λ<sub>max</sub> (log ε) 228 (4.44), 265 (3.88), 277 (sh, 3.75), 405 (sh, 4.31), 427 (4.62), 459 nm (4.72); λ<sub>max</sub><sup>Ex</sup> (cyclohexane) 270 (31), 409.5 (35), 443 (33), 470 (33); λ<sub>max</sub><sup>470</sup> 480 (33), 509.5 nm (27); λ<sub>max</sub><sup>Ex</sup> (acetonitrile) 323 (10), 477.5 (6.5), 487.5 nm (10); λ<sub>max</sub><sup>477</sup> 478 (6), 507 (7) nm; MS *m/z* (rel intensity) 345 (M + 1, 6), 344 (M, 20), 330 (17), 329 (63), 328 (M - 15, 29), 327 (24), 326 (23), 314 (15), 313 (28), 172 (10), 165 (57), 164 (72), 163 (86), 162 (57), 157 (100), 156 (49), 150 (52), 144 (21), 137 (21). Anal. Calcd for C<sub>27</sub>H<sub>20</sub>: C, 94.15; H, 5.85. Found: C, 94.27; H, 5.98. [Emission data (Em) from specified excitation (Ex) are preceded by the excitation (absorption) data recorded on the fluorescence spectrometer.]

**B. 1-Xanthenylidene-1*H*-cyclopropa[b]naphthalene (16):** from xanthone **11** (145 mg, 0.74 mmol), **9** (150 mg, 0.53 mmol), and KOBu-*t* (131 mg, 1.17 mmol). Addition of the first drops of *tert*-butoxide solution turned the colorless solution fluorescent yellow. The solution was stirred for 3 h at -78 °C and then allowed to warm to room-temperature overnight with continued stirring. Normal workup<sup>4</sup> (radial chromatography; chloroform elution) and crystallization (chloroform) gave *xanthenylidene 16* (100 mg, 59%) as small bright orange needles; mp 219–221 °C; IR 3066 (vw), 3031 (vw), 1594, 1510, 1477, 1452, 1314, 1260, 1216, 1146, 1120, 1104, 848, 758, 739 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 8.27 (m, H9/17), 7.88 (AA' of AA'BB', H3/6), 7.53 (s, H2/7), 7.47 (BB' of AA'BB', H4/5), 7.33–7.20 (m, H10/16 and H11/15), 7.14–7.11 (m, H12/14); <sup>13</sup>C NMR δ 150.82 (C12a/13a), 138.87 (C2a/6a), 128.97 (C10/16), 128.55 (C3/6), 126.64 (C4/5), 125.82 (C1a/7a), 124.24 (C9/17), 123.69 (C11/15), 121.63 (C8a/8a'), 116.84 (C12/14), 107.19 (C8), 105.75 (C2/7), 102.00 (C1); UV (cyclohexane) λ<sub>max</sub> (log ε) 272 (5.64), 444 (4.71), 481 nm (5.11); UV (acetonitrile) λ<sub>max</sub> (log ε) 234 (4.70), 256 (4.25), 322 (3.31), 339 (3.18), 440 (4.03), 475 nm (4.37); λ<sub>max</sub><sup>Ex</sup> (cyclohexane) 260 (59), 284 (56), 346.5 (15), 416.5 (55), 444.5 (289), 481 nm (455); λ<sub>max</sub><sup>481</sup> 485 (447), 528.5 nm (119); λ<sub>max</sub><sup>Ex</sup> (acetonitrile) 284.5 (30), 295.5 (30), 413.5 (66), 440.5 (187), 475 nm (328); λ<sub>max</sub><sup>475</sup> 483 (332), 522 nm (109); MS *m/z* (rel intensity) 319 (M + 1, 13), 318 (M, 53), 289 (25), 287 (16), 158 (23), 144 (43), 143 (100), 130 (43). Anal. Calcd for C<sub>24</sub>H<sub>14</sub>O: C, 90.54; H, 4.43. Found: C, 90.48; H, 4.14.

**C. 1-Thioxanthenylidene-1*H*-cyclopropa[b]naphthalene (17):** from thioxanthone **12** (296 mg, 1.40 mmol), **9** (285 mg, 1.00 mmol), and KOBu-*t* (245 mg, 2.2 mmol). Addition of the first drops of *tert*-butoxide solution turned the colorless solution fluorescent green. The cold bath was warmed to 0

°C over ca. 2 h and the product mixture worked up as normal.<sup>4</sup> Dry column chromatography (1:1 light petroleum/dichloromethane elution) and recrystallization (acetone/dichloromethane) gave *thioxanthenylidene 17* (270 mg, 81%) as small bright red needles; mp 171–172.5 °C; IR 3043 (w, br), 1644, 1591, 1500, 1465, 1437, 1321, 1162, 1145, 1084, 1046, 834, 759, 734, 718 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 8.25 (m, H9/17), 7.86 (AA' of AA'BB', H3/6), 7.54 (s, H2/7), 7.46 (BB' of AA'BB', H4/5), 7.36–7.29 (m, H11/15 and H12/14), 7.25–7.20 (m, H10/16); <sup>13</sup>C NMR δ 138.98 (C2a/6a), 132.62 (C12a/13a), 130.75 (C8a/17a), 128.69 (C3/6), 127.35 (C10/16), 126.82 (C4/5), 126.67 (C1a/7a), 126.48 (C12/14), 125.73 (C11/15), 125.54 (C9/17), 112.82 (C8), 109.51 (C1), 106.66 (C2/7); UV (cyclohexane) λ<sub>max</sub> (log ε) 211 (4.00), 233 (4.54), 251 (4.59), 295 (3.72), 368 (3.90), 468 (sh, 4.54), 486 nm (4.60); UV (acetonitrile) λ<sub>max</sub> (log ε) 208 (4.19), 231 (4.55), 249 (4.54), 292 (3.47), 366 (3.62), 458 (4.45), 472 nm (sh, 4.44); λ<sub>max</sub><sup>Ex</sup> (cyclohexane) 293 (18), 367 (11), 468 (41) 489 nm (45); λ<sub>max</sub><sup>489</sup> 510 nm (595); MS *m/z* (rel intensity) 336 (M + 2, 4.8), 335 (M + 1, 17), 334 (M, 65), 302 (21), 300 (13), 287 (6), 166 (100), 165 (44), 153 (26), 150 (27), 143 (26), 130 (23). Anal. Calcd for C<sub>24</sub>H<sub>14</sub>S: C, 86.19; H, 4.22. Found: C, 86.12; H, 4.32.

**D. 1-(10-Methyl-9(10*H*)-9-acridinylidene)-1*H*-cyclopropa[b]naphthalene (18):** from acridone **13** (293 mg, 1.40 mmol), **9** (285 mg, 1.00 mmol), and KOBu-*t* (245 mg, 2.2 mmol) at -70 °C. The colorless solution became red-orange as the addition proceeded. The cold bath was allowed to warm to -20 °C over 1.75 h whereupon the undissolved starting material dissolved and the color darkened to crimson. Conventional workup<sup>4</sup> afforded crude material that was dissolved in 1:1 dichloromethane/light petroleum (ca. 20 mL) and quickly filtered, with suction, through a pad of silica gel (70 mm depth) on a glass frit (55 mm i.d.) using the same solvent. The dark orange eluate contained product while unchanged **13** and a yellowish decomposition product remained behind. The filtrate was concentrated under reduced pressure to a crimson solid which contained traces of cyclopropa[b]naphthalene (**1**). Recrystallization (dichloromethane/light petroleum) gave *acridinylidene 18* (70 mg, 22%) as small crimson needles; crystallization (dichloromethane/chloroform, 3:1) provided a sample for structure determination; mp 178–179 °C; IR 3025 (w), 1762 (w), 1736 (w), 1591, 1510, 1469, 1423, 1362, 1328, 1296, 1269, 1201, 1172, 1138, 828, 737 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 8.35 (m, H9/17), 7.82 (AA' of AA'BB', H3/6), 7.42 (BB' of AA'BB', H4/5), 7.38 (s, H2/7), 7.33–7.20 (m, H10/16 and H11/15), 7.14–7.11 (m, H12/14); <sup>13</sup>C NMR δ 150.82 (C12a/13a), 138.87 (C2a/6a), 128.97 (C10/16), 128.55 (C3/6), 126.64 (C4/5), 125.82 (C1a/7a), 124.24 (C9/17), 123.69 (C11/15), 121.63 (C8a/8a'), 116.84 (C12/14), 107.19 (C8), 105.75 (C2/7), 102.00 (C1); UV (cyclohexane) λ<sub>max</sub> (log ε) 229 (4.76, sh), 243 (4.71), 370 (3.95), 404 (3.89), 434 (3.98), 492 (4.12), 537 nm (4.58); UV (acetonitrile) λ<sub>max</sub> (log ε) 207 (3.99), 244 (4.54), 372 (3.73), 398 (3.16), 536 nm (4.66); λ<sub>max</sub><sup>Ex</sup> (cyclohexane) 337.5 (78), 352 (76), 372 (28), 400.5 (57), 521.5 nm (2); λ<sub>max</sub><sup>400</sup> 400.5 (70), 438.5 (43), 473.5 (35), 544.5 nm (11); MS *m/z* (rel intensity) 332 (M + 1, 28), 331 (M, 100), 316 (M - 15, 65), 314 (M - 17), 194 (17), 166 (20), 158 (23). Anal. Calcd for C<sub>25</sub>H<sub>17</sub>N C, 90.60; H, 5.17; N, 4.23. Found: C, 90.62; H, 4.96; N, 4.30%.

**E. 1-Anthronylidene-1*H*-cyclopropa[b]naphthalene (19).** To the anion **8** generated from disilyl **9** (300 mg, 1.05 mmol) and KOBu-*t* (120 mg, 1.06 mmol) at -78 °C was added 9,10-anthracenedione (**14**) (220 mg, 1.06 mmol) in THF (120 mL). The mixture was then stirred at -40 °C for 4 h and worked up conventionally<sup>4</sup> (radial chromatography, 1:1 dichloromethane/light petroleum elution) to give *carbonyl-containing 19* (124 mg, 35%) as bright red needles (chloroform); mp 248–250 °C; IR 2924 (w), 2853 (w), 1759, 1651, 1593, 1537, 1470, 1348, 1307, 1142, 851, 772 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 8.64–8.62 (m, H9/17), 8.51–8.47 (m, H12/14), 8.02–7.98 (AA' of AA'BB', H3/6), 7.91 (s, H2/7), 7.79–7.73 (m, H11/15), 7.61–7.57 (m, BB' of AA'BB', H4/5), 7.55–7.50 (m, H10/16); <sup>13</sup>C NMR δ 183.27 (CO), 140.13 (C2a/6a), 132.73 (C10/16), 129.50 (C12a/13a), 129.26 (C3/6), 128.04 (C4/5), 127.68 (C9/17), 127.23 (C11/15), 125.94 (C1a/7a), 123.98 (C12/14), 114.48 (C1), 109.89 (C2/7), 107.26

(C8); UV (cyclohexane)  $\lambda_{\max}$  (log  $\epsilon$ ) 212 (4.06), 242 (4.27), 260 (4.36), 280 (4.03), 298 (3.97), 434 sh (3.80), 458 (4.11), 494 nm (4.24); UV (acetonitrile)  $\lambda_{\max}$  (log  $\epsilon$ ) 204 (4.56), 252 (4.76), 274 (4.34), 436 (4.67), 464 (4.95), 496 nm (4.99);  $\lambda_{\max}^{\text{Ex}}/\lambda_{\max}^{\text{Em}}$ , **19** does not fluoresce, rather phosphorescence is implied; MS  $m/z$  (rel intensity) 331 (M + 1, 28), 330 (M, 100), 302 (M - CO, 20), 300 (M - CH<sub>2</sub>O, 34). Anal. Calcd for C<sub>25</sub>H<sub>14</sub>O:  $M$  330.10446. Found:  $M$  330.10447.

**Single-Crystal X-ray Diffraction Analyses.** **Crystal Data.** Data for **15**, **17**, and **18** are collected in Table 1.

**Data Collection and Processing.**<sup>21</sup> Siemens P4 (**15** and **17**) and R3 (**18**) four-circle diffractometers, Wyckoff scan modes, graphite-monochromated Mo K $\alpha$  radiation, data collection, and unique reflections as specified in Table 1.

**Structure Analysis and Refinement.** Direct methods with full matrix least squares refinement on  $F^2$  with SHELX93 (SGI IRIS Indigo) using the implemented atomic scattering factors. All non-hydrogen atoms were given anisotropic and hydrogen atoms isotropic temperature parameters and the latter were treated as riding groups. The weighting schemes are  $w^{-1} = [\sigma^2(F_o^2) + (gP) + dP]$  where  $P = [(\max F_o^2) + (2F_c^2)]/$

3 with  $g$  and  $d$  listed in Table 1 as well as the final R1 [ $I > 2\sigma(I)$ ] and wR2 (all data) values.

Atomic coordinates, bond lengths and interbond angles, and thermal parameters for each of **15**, **17** and **18** have been deposited with the Cambridge Crystallographic Data Centre (see Instructions for Authors, Issue No. 1).

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**Supporting Information Available:** Details of the X-ray analyses of **15**, **17**, and **18** (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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