

Polymorphism Versus Thermochromism: Interrelation of Color and Conformation in Overcrowded Bistricyclic Aromatic Enes

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Abstract: The nature of the thermochromic form of overcrowded bistricyclic aromatic enes (BAEs) has been controversial for a century. We report the single-crystal X-ray structure analysis of the deep-purple and yellow polymorphs of 9-(2,7-dimethyl-9H-fluoren-9-ylidene)-9H-xanthene (**11**), which revealed the molecules in a twisted and a folded conformation, respectively. Therefore, the deeply colored thermochromic form **B** of BAEs is identified as having a twisted conformation and the ambient-temperature form **A** as having a folded conformation. This re-

lationship between the color and the conformation is further supported by the X-ray structures of the deep-purple crystals of the twisted 9-(9H-fluoren-9-ylidene)-9H-xanthene (**10**), and of the yellow crystals of the folded 9-(11H-benzo[*b*]fluoren-11-ylidene)-9H-xanthene (**12**). Based on this conclusive crystallographic evidence, eleven previ-

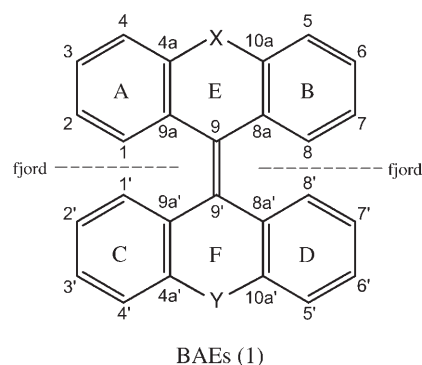
ously proposed rationales of thermochromism in BAEs are refuted. In the twisted structures, the tricyclic moieties are nearly planar and the central double bond is elongated to 1.40 Å and twisted by 42°. In the folded structures, the xanthylidene moieties are folded by 45° and the fluorenylidene moieties by 18–20°. Factors stabilizing the twisted and folded conformations are discussed, including twisting of formal single or double bonds, intramolecular overcrowding, and the significance of a dipolar aromatic “xanthenylium-fluorenone” push–pull structure.

Keywords: aromaticity • conformation analysis • polymorphism • strained molecules • thermochromism

Introduction

The phenomenon of thermochromism^[1–3] in overcrowded bistricyclic aromatic enes (BAEs, **1**; thermochromic ethylenes^[3a]) was discovered almost one hundred years ago.^[4] Meyer reported that the yellow solutions of 9,9'-bi-9(10*H*)-anthracenylidene-10,10'-dione (biantnone, **2**) reversibly

turn dark green upon heating. This change of color may also be triggered by pressure (piezochromism)^[4,5] or by UV irradiation at low temperatures (photochromism).^[2,3,6–9]



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Supporting information for this article is available on the WWW under <http://www.chemurj.org/> or from the author: ORTEP drawings, cell plots, bond lengths, intramolecular nonbonding distances, bond angles, torsion angles, and intermolecular contact distances of the X-ray crystal structures of **10**, purple **11**, yellow **11**, and **12**; ¹H and ¹³C NMR spectra of **11** and **18**.

BAEs have been developed as molecular switches triggered by light.^[10,11] Furthermore, BAEs have been incorporated into calixarenes,^[12] crown ethers,^[13,14] ligands for transition-metal complexation,^[15–17] donor–acceptor systems,^[18] polymers,^[19] liquid crystals,^[11,20] Langmuir films,^[21] and molecular rotors,^[22] with the intention of adding a switchable

functionality and/or an easily observable response. Recently, light-driven unidirectional motors have been discovered that are based on closely related molecules.^[23]

Thermochromism is a reversible, temperature-dependent change of color.^[1] In BAEs, the phenomenon is based on a unimolecular^[24] equilibrium^[25,26] between a colorless or yellow ambient-temperature form **A** and a deep-blue or deep-green high-temperature form **B**:^[27]

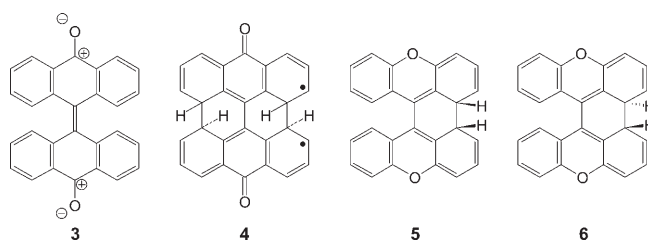


Although **A** absorbs in the UV region (and close to it), the thermochromic form has a new absorption band at $\lambda = 600\text{--}700\text{ nm}$. In thermochromic BAEs, the enthalpy difference ΔH of the two forms is $1\text{--}7\text{ kcal mol}^{-1}$.^[25,26,28] ΔH is independent of the solvent.^[26] The thermochromic, photochromic, and piezochromic **B** forms are identical.^[8,28–31] The reversible formation of color raises the question of the nature of the colored species.^[2,27,32] In fact, the enigma of thermochromism in BAEs has played an important role in the development of the theory of organic chromophores.^[33–35]

Various rationales have been suggested to explain the thermochromic phenomenon in BAEs:

- 1) An aggregation–disaggregation equilibrium in solution.^[36]
- 2) Zwitterionic forms of the molecule with ionoid carbonyl groups (**3**),^[33,37] in accord with Dilthey's theory of organic chromophores.^[38]
- 3) Mesomeric betaine structures that make small contributions to the resonance hybrid at ambient temperatures, but make large contributions at high temperatures.^[39]
- 4) A diradical state in which the central bond linking the planar tricyclic moieties is twisted by 90° and is "not a true double bond".^[24,25,40]
- 5) A "biradikalet": planar molecular halves twisted by less than 90° about the central double bond, the π electrons have parallel spins with a detectable contribution from the triplet state.^[25,41]
- 6) A thermally populated triplet excited state of the molecule.^[26,32,42]
- 7) A coplanar (or nearly planar) conformation with enhanced π delocalization and a stretched central double bond.^[35,43]
- 8) A twisted conformation (singlet state).^[7,29,44]
- 9) A doubly electrocyclic diradical (**4**), as suggested by Woodward and Wassermann.^[45]
- 10) Solid-state effects.^[46]
- 11) 1,1'-Cyclized valence isomers **5**, and/or **6**.^[47]
- 12) A double-chair conformation.^[2,48,49]

Zwitterions and polar mesomeric structures should be stabilized by polar solvents; however, no such solvent dependence of the equilibrium constant and/or the absorption spectrum was observed.^[2,26,27,37,50] Initial reports of "paramagnetic absorption" in connection with thermochromism^[42,51] were later refuted by more careful magnetic measurements



that showed that thermochromism does not lead to increased susceptibility.^[52,53] The ESR spectrum^[42] was attributed to decomposition or photochemical side reactions.^[7,54,55] The 1,1'-cyclized valence isomer **6** has been identified as the photochromic **C** form, which is distinct from the **B** form.^[2,31,56] The photocyclization of BAEs is analogous to that of (*Z*)-stilbene to give 4*a*,4*b*-dihydrophenanthrene.^[8,57]

Substitution with bulky substituents at the 1- and 1'-positions prevents thermochromism.^[2,35,53,58,59] Because substituents in the fjord region would cause prohibitive strain in planar conformations, this has been interpreted as indicating a planar thermochromic **B** form.^[35,59] However, even unsubstituted BAEs have overcrowded fjord regions that would cause prohibitively high strain in a planar conformation, precluding thermal population.^[60–63]

Several nonplanar conformations of BAEs have been characterized by X-ray crystal structure analysis.^[61,64] Representative examples are shown in Figure 1.

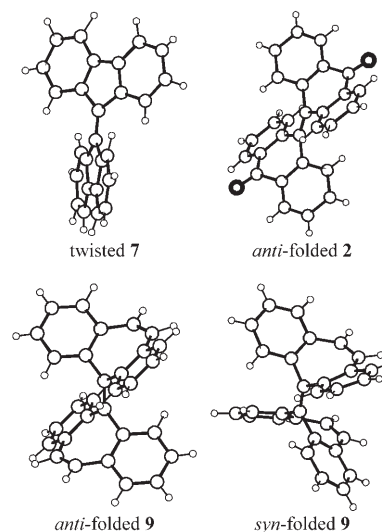
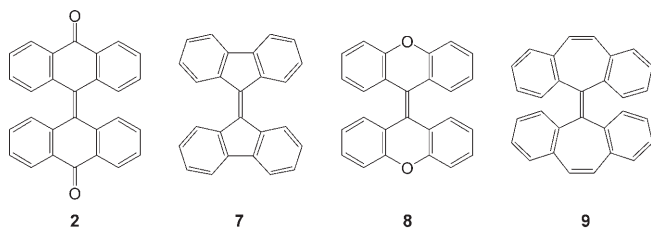


Figure 1. Molecular structures of 9,9'-bi-(9*H*-fluoren-9-ylidene) (**7**), 9,9'-bi-(9(10*H*)-anthracenylidene)-10,10'-dione (**2**), and 5,5'-bi-(5*H*-dibenzo[*a,d*]cyclohept-5-ylidene) (**9**), determined by X-ray crystallography.

The smallest BAE, 9,9'-bi-9*H*-fluoren-9-ylidene (bifluorenylidene, **7**), with central five-membered rings E and F, is bright red and adopts a twisted conformation in the crystal.^[65] The two tricyclic moieties are nearly planar, and the central double bond is twisted by 32° .

BAEs with central six-membered rings, including thermochromic BAEs, such as bianthrone (**2**)^[66] and 9,9'-bi-9*H*-

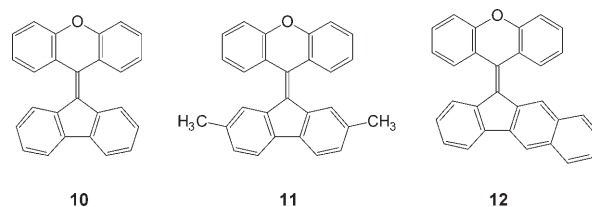


xanthen-9-ylidene (dixanthylene, **8**),^[46] adopt *anti*-folded conformations.^[61,64] The central double bonds are not twisted, but slightly pyramidalized. The rings E and F have boat conformations leading to tricyclic moieties that are folded in opposite directions (*anti*). The dihedral angles of the least-square planes, A–B (and C–D), are 36–55°. Based on these X-ray crystal structures, the ambient-temperature form **A** of BAEs was characterized as the *anti*-folded conformation. In 5,5'-bis-5*H*-dibenzo[*a,d*]cyclohepten-5-ylidene (**9**), which has central seven-membered rings, a metastable *syn*-folded conformation has been found in addition to an *anti*-folded conformation.^[67] In **9**, the degrees of folding are very high: A–B = 55.7° in *anti*-**9** and A–B/C–D = 62.6°/55.5° in *syn*-**9**.

In 1963, Mills and Nyburg reported crystal structures of two polymorphs of dixanthylene (**8**): a yellow β form obtained by slowly cooling an *m*-xylene solution of **8** and a blue–green α form obtained by sublimation at 250°C.^[46] Both polymorphs contain molecules in very similar *anti*-folded conformations.^[46] The authors found that the conformations are identical within the high experimental error (bond lengths ± 0.02 Å, angles $\pm 1.5^\circ$, $R = 20\%$).^[46] They concluded: “We believe the differences in packing cause the differences in color of the crystals, but we are unable to specify what features of the packing are responsible.”^[46] Kortüm and co-workers argued that, at the temperature of sublimation, only 1% of the dixanthylene molecules would be in the thermochromic **B** form, sufficient for the green color of the crystals, but not detectable by X-ray diffraction.^[32,48] As the **B** form has not yet been crystallized and subjected to X-ray structure analysis, one has to rely on indirect and inconclusive arguments regarding its structure.^[2]

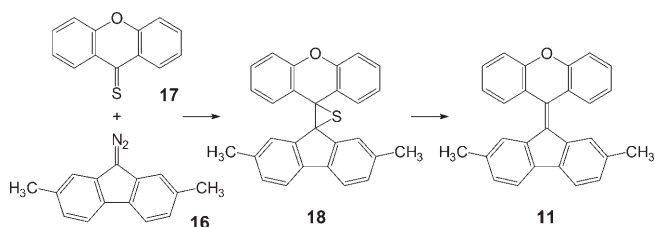
An analysis of the previously reported X-ray structures indicated that BAEs with central five-membered rings E and F have twisted conformations, whereas BAEs with central six-membered rings have *anti*-folded conformations.^[61] In heteromeric BAEs that combine tricyclic moieties with one central five-membered ring and one central six-membered ring, twisted and folded conformations may be expected to have similar energies. This introduces the possibility of crystallizing both conformations in the same BAE or in closely related derivatives. The present study is focused on the heteromeric BAE 9-(9*H*-fluoren-9-ylidene)-9*H*-xanthene (**10**) and its derivatives, whereby a subtle equilibrium of twisted and folded conformations was found in solution.^[68] A comparison of the structures of twisted and folded conformations of closely related BAEs may reveal the factors governing the relative stability of the conformations.

Here, we report the single-crystal X-ray structure analyses of the purple and the yellow polymorphs of 9-(2,7-dimethyl-9*H*-fluoren-9-ylidene)-9*H*-xanthene (**11**). This example of a single BAE with two polymorphs of such widely differing colors reveals the nature of the thermochromic form. Furthermore, we report the X-ray structures of the purple crystals of the parent BAE **10**, and of the yellow crystals of 9-(11*H*-benzo[*b*]fluoren-11-ylidene)-9*H*-xanthene (**12**).



Results

Synthesis: The fluorenylidene-xanthenes **10**, **11**, and **12** have been synthesized by Barton's diazothione addition/twofold extrusion method.^[69] Synthesis and characterization of the parent compound **10**^[68,70–74] and **12**^[68,73] has already been reported. BAE **11** was synthesized by starting from the tricyclic ketones 2,7-dimethyl-9*H*-fluoren-9-one (**13**)^[75] and 9*H*-xanthen-9-one (**14**). Ketone (**13**) was reacted with hydrazine hydrate in ethanol to give 2,7-dimethyl-9*H*-fluoren-9-one hydrazone (**15**), which was oxidized with yellow mercury oxide to 9-diazo-2,7-dimethyl-9*H*-fluorene (**16**).^[76,77] Ketone (**14**) was converted to 9*H*-xanthene-9-thione (**17**)^[78] with Lawesson's reagent, and reacted with (**16**) in boiling benzene to give the intermediate thiirane 2,7-dimethyl-dispiro-(9*H*-fluorene-9,2'-thiirane-3',9'-[9*H*]-xanthene) (**18**). The thiirane sulfur was eliminated with triphenylphosphine^[71] in boiling benzene to give the purple 9-(2,7-dimethyl-9*H*-fluoren-9-ylidene)-9*H*-xanthene (**11**) (Scheme 1), which was purified by chromatography with a yield of 67%. The ¹H NMR spectrum revealed signals for the fjord region hydrogen atoms at $\delta = 8.16$ ppm for H1 and H8 and at 7.71 ppm for H1' and H8'. The carbon atoms of the central double bond appear at $\delta = 131.2$ (C9'), 130.2 ppm (C9).



Scheme 1. Synthesis of 9-(2,7-dimethyl-9*H*-fluoren-9-ylidene)-9*H*-xanthene (**11**).

Crystallization: Single crystals for X-ray crystallography were grown by sublimation of **11** at 180°C under argon (2 Torr). After 2 d, purple crystals formed on the walls of

the tube; m.p. 193–195°C. In addition, a small amount of yellow crystals formed in the cooler regions; m.p. 145°C (purple melt). The yellow crystals gave purple solutions. The NMR spectrum of the yellow crystals dissolved in CDCl_3 was identical to that of solutions of the purple material. Single crystals of the parent compound **10** were grown by recrystallization from a toluene solution;^[74] purple crystals, m.p. 244°C. The same purple-crystal modification was obtained by sublimation at 200°C under 1 Torr argon. Single crystals of 9-(11*H*-benzo[*b*]fluoren-11-ylidene)-9*H*-xanthene (**12**) were grown by sublimation in a sealed glass tube at 180–190°C and 0.05 Torr to afford yellow crystals, m.p. 221–222°C.^[68] In solution, **12** is purple.^[68]

Crystal structure of purple 9-(2,7-dimethyl-9*H*-fluoren-9-ylidene)-9*H*-xanthene (11**):** In the purple polymorph, purple **11**, the molecule adopts a twisted conformation (Figure 2a). The two tricyclic moieties are nearly planar and form a dihedral angle of 50.1°. The ethylenic twist ω of the central double bond, defined as the average of the torsion angles $\tau(\text{C8a-C9-C9'-C8a}')$ and $\tau(\text{C9a-C9-C9'-C9a}')$,^[63,64] is 42.1(3)°.

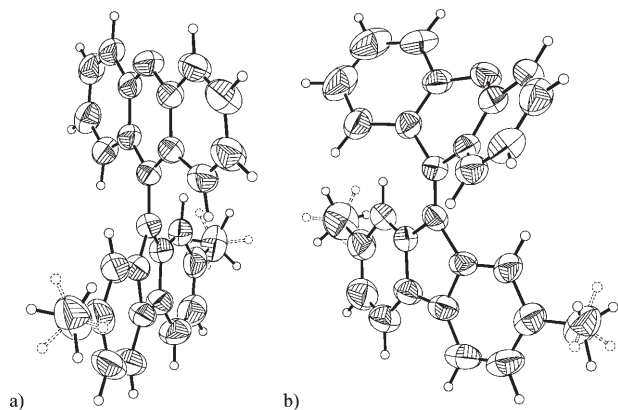


Figure 2. ORTEP drawings of the molecular structures of 9-(2,7-dimethyl-9*H*-fluoren-9-ylidene)-9*H*-xanthene (**11**) in the (a) purple and (b) yellow polymorphs. Anisotropic displacement parameters are drawn at the 50% probability level.

Crystal structure of yellow 9-(2,7-dimethyl-9*H*-fluoren-9-ylidene)-9*H*-xanthene (11**):** In the yellow polymorph, yellow **11**, the conformation is characterized by folded xanthylidene and fluorenylidene moieties (Figure 2b). The dihedral angle of the least-squares planes A–B, defined by the ring carbon atoms, is 44.5(2)°. The fluorenylidene moiety has a smaller folding dihedral angle, C–D = 18.3(1)°, and is folded in the opposite direction (*anti*-folding). The twist of the central double bond is very small, $\omega = -1.9(9)^\circ$; however, there is a substantial *anti*-pyramidalization, $\chi(\text{C9}) = -8(1)^\circ$ and $\chi(\text{C9}') = 5(1)^\circ$. The pyramidalization angles are defined as $\chi(\text{C9}) = [\tau(\text{C9a-C9-C9'-C8a}) \text{ MOD } 360^\circ] - 180^\circ$, and $\chi(\text{C9}') = [\tau(\text{C9a'-C9-C9'-C8a'}) \text{ MOD } 360^\circ] - 180^\circ$.^[63,64]

Crystal structure of 9-(9*H*-fluoren-9-ylidene)-9*H*-xanthene (10**):** In the purple crystals of the parent compound **10**, the

molecules adopt a twisted conformation with nearly planar tricyclic moieties forming a dihedral angle of 52.3° (Figure 3). The central double bond is twisted by $\omega = 42.3(4)^\circ$. Notably, the molecules of **10** are orientationally disordered about a crystallographic C_2 axis that passes through the fjord regions.

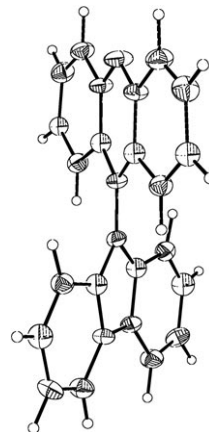


Figure 3. ORTEP drawing of the X-ray crystal structure of 9-(9*H*-fluoren-9-ylidene)-9*H*-xanthene (**10**). Anisotropic displacement parameters are drawn at the 50% probability level (120 K).

Crystal structure of 9-(11*H*-benzo[*b*]fluoren-11-ylidene)-9*H*-xanthene (12**):** In the yellow crystal of **12**, the molecule adopts the *anti*-folded conformation shown in Figure 4. The xanthylidene moiety is folded by A–B = 45.5(1)° and the fluorenylidene moiety is folded by C–D = 19.7(2)°. The two six-membered rings of the naphthalene ring system are almost coplanar: D–G = 2.2(2)°. The ethylenic twist ω of the central double bond is 1.0(5)°. The two carbon atoms of the central double bond are *anti*-pyramidalized: $\chi(\text{C9}) = -5.2(5)^\circ$ and $\chi(\text{C11}') = 4.1(6)^\circ$.

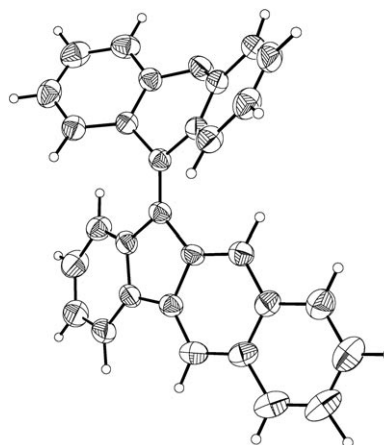


Figure 4. ORTEP drawing of the molecular structure of 9-(11*H*-benzo[*b*]fluoren-11-ylidene)-9*H*-xanthene (**12**) derived from the X-ray structure of the yellow crystals. Anisotropic displacement parameters are drawn at the 50% probability level.

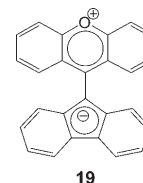
Discussion

Both twisted and folded conformations of the same bonafide BAE (**11**) were characterized for the first time by single-crystal X-ray analysis. Moreover, we report the first twisted conformations of heteromeric BAEs (purple **11** and **10**) that are based on crystal structure determinations. Previously, twisted conformations have been reported for fluorenylidene and its derivatives only.^[13,16,65,79] The purple crystals of 9-(2,7-dimethyl-9H-fluoren-9-ylidene)-9H-xanthene (**11**) comprise twisted molecules and the yellow crystals contain folded molecules, which demonstrates the interrelation of color and conformation. The parent compound 9-(9H-fluoren-9-ylidene)-9H-xanthene (**10**) forms purple crystals with twisted molecules and 9-(11H-benzo[*b*]fluoren-11-ylidene)-9H-xanthene (**12**) forms yellow crystals with folded molecules. In view of the very different crystal-packing motifs found in the four X-ray structures and the lack of any indication of unusual intermolecular interactions (Supporting Information Figures S4–S7 and Tables S5–S8), it is highly unlikely that the purple or yellow colors of the crystals are caused by an intermolecular solid-state effect. This questions the conclusion made by Mills and Nyburg.^[46] In each case, the deep purple crystals revealed a twisted conformation of the molecules, and the yellow crystals revealed a folded conformation. This strongly indicates that color is determined by molecular conformation. The large twist in the central double bond reduces the π overlap, which causes a substantial red shift of the UV-visible absorptions and smaller HOMO–LUMO gaps in the twisted conformations.^[80,81] Therefore, the deeply colored thermochromic **B** form of BAEs may be assigned to a twisted conformation of the molecule, whereas the yellow (or colorless) ambient-temperature form **A** is confirmed to be the (*anti*)-folded conformation.

Selected structural parameters of the X-ray crystal structures of **10**, purple **11**, as well as yellow **11** and **12** are summarized in Table 1 (see also Supporting Information Tables S1–S4). The molecules in purple **11** and **10** have very similar twisted conformations. The tricyclic moieties are

almost planar (RMS deviation from plane <0.07 Å for heavy atoms) and the molecules are twisted about the central double bond. The dihedral angle of the least-squares planes AEB–CFD is 50.1° in **11** and 52.3° in **10**. The main burden of the out-of-plane deformation is on the central double bonds that are highly twisted, $\omega = 42.1(3)^\circ$ (purple **11**), $42.3(4)^\circ$ (**10**), and elongated to $C9=C9' = 1.400(2)$ Å (purple **11**) and $1.401(6)$ Å (**10**).

Similarly, the folded conformations found in yellow **11** and **12** closely resemble each other. The folding dihedral angles of the least-squares planes A–B and C–D are $44.5(2)$ and $18.3(1)^\circ$ (yellow **11**) versus $45.5(1)$ and $19.7(2)^\circ$ (**12**). In both folded conformations, the central double bond is short, $1.353(5)$ Å in yellow **11** and $1.360(4)$ Å in **12**. In the folded structures, the main out-of-plane deformations are in the formal single bonds connecting the central double bond with the peripheral aromatic rings, and in the bridges X and Y. In particular, the $C9-C9a$ and $C9-C8a$ bonds of the xanthylidene moiety are highly twisted with, for example, $\tau(C9'-C9-C9a-C1) = 53.0(8)^\circ$, and $\tau(C9'-C9-C8a-C8) = -49.0(8)^\circ$ in yellow **11**. The formal single bonds of the fluorenylidene-xanthenes are longer in the folded structures than in the twisted structures: in the xanthylidene moieties, $C9-C9a = 1.488$ versus 1.465 Å, $C4a-O10 = 1.389$ versus 1.369 Å, in the fluorenylidene moieties, $C9'-C9a' = 1.497$ versus 1.475 Å (average of equivalent bonds in yellow **11** and **12**, versus average in purple **11**). These changes in the bond lengths indicate that, in the folded conformations, the π systems are more localized in the aromatic rings and the double bond. A priori, twisting of formal single bonds as in the folded conformations may be energetically more favorable than twisting about the central double bond as in the twisted conformation. However, delocalization of the π -electron system because of the more planar tricyclic moieties may stabilize the twisted conformations. Moreover, enhanced contributions of the dipolar aromatic “xanthenylium-fluorenylide” (**19**) push–pull structure may be a significant factor in stabilizing the twisted conformation of fluorenylidene-xanthenes.



In the fjord regions of yellow **11** and **12**, overcrowding is severe for the $C1\cdots H1'$ and $C8\cdots H8'$ distances, which average ≈ 2.40 Å; the overlap of the van der Waals radii (C 1.71, H 1.15 Å)^[82] is 16%. The carbon–carbon contacts are also very short: the $C1\cdots C1'$ and $C8\cdots C8'$ distances are 2.99 – 3.05 Å, corresponding to an overlap of $\approx 12\%$. On the other hand, in the twisted conformation of purple **11**, the above intramolecular contacts of $C1$ and $C8$ with $C1'$, $C8'$, $H1'$, and $H8'$ are longer, indicating considerably less overcrowding (5–9% overlap). However, the very short $H1\cdots C9a'$ and $H8\cdots C8a'$ contacts in twisted **11** (average 2.56 Å, 11% overlap) are not overcrowded in the folded conformations.

In summary, the enhanced delocalization of the π -electron system, the push–pull effect, and the more effective dissipation of intramolecular overcrowding in the fjord regions counterbalance the strain introduced by twisting about the

Table 1. Selected structural parameters of the X-ray crystal structures.

Compound	10	11	11	12
Crystal color	purple	purple	yellow	yellow
Conformation	twisted	twisted	folded	folded
ω [$^\circ$] ^[a]	42.3(4)	42.1(3)	−1.9(9)	1.0(5)
A–B [$^\circ$] ^[b]	0.3(2)	6.01(3)	44.5(2)	45.5(1)
C–D [$^\circ$] ^[b]	5.0(2)	4.9(1)	18.3(1)	19.7(2)
$C9=C9'$ [Å]	1.401(6)	1.400(2)	1.353(5)	1.360(4)
$\chi(C9)$ [$^\circ$] ^[c]	0.6(6)	−1.2(3)	−8(1)	−5.2(5)
$\chi(C9')$ [$^\circ$] ^[c]	−1.3(6)	−2.6(3)	−5(1)	4.1(6)
$C1\cdots C1'$ [Å]	3.144(4)	3.145(3)	3.046(7)	2.996(5)
$C8\cdots C8'$ [Å]	3.125(3)	3.113(3)	2.990(7)	3.051(5)

[a] Ethylenic twist $\omega = \frac{1}{2}[(C9a-C9-C9'-C9a') + \tau(C8a-C9-C9'-C8a')]$. [b] Dihedral angles of the least-squares planes defined by the aromatic ring carbon atoms. [c] Pyramidalization $\chi(C9) = [\tau(C9a-C9-C9'-C8a') \text{ modulus (MOD)} 360^\circ] - 180^\circ$, $\chi(C9') = [\tau(C9a'-C9-C9'-C8a') \text{ MOD } 360^\circ] - 180^\circ$.

central double bond. Therefore, in fluorenylidene-xanthenes, the twisted and folded conformations may be expected to have similar energies. Indeed, an analysis of the NMR chemical shifts of the hydrogen atoms in the fjord regions of fluorenylidene-xanthenes in solution indicates an equilibrium of twisted and folded conformations.^[68] Furthermore, a very low enantiomerization barrier of 6.5 kcal mol⁻¹ was observed in the isopropyl derivative of **10**.^[68] This process also interconverts twisted and folded conformations in solution,^[68] and explains the instantaneous change in color as the yellow crystals of **11** and **12** are dissolved.

Recently, a criterion for thermochromism has been derived from B3LYP/6-31G* DFT calculations of various thermochromic and nonthermochromic BAEs.^[80] B3LYP/6-31G* conformational energies agree with experimental results to within ± 1 kcal mol⁻¹.^[80] Three types of conformational behavior have been distinguished. Thermochromism appears in BAEs with Type 1 conformational behavior that satisfy the following necessary conditions: i) an *anti*-folded global minimum conformation (**a**) corresponding to the ambient-temperature form **A**, and a low-energy local-minimum twisted conformation (**t**) corresponding to the thermochromic form **B**; ii) the energy difference between these two conformations has to be sufficiently small to allow thermal population of **t**, $E(\mathbf{t}) - E(\mathbf{a}) < 8$ kcal mol⁻¹.^[80] Type 3 conformational behavior is displayed by 9-(9*H*-fluoren-9-ylidene)-9*H*-xanthene (**10**): the folded conformation is 1.1 kcal mol⁻¹ higher in energy than the twisted conformation.^[80] Thus, the colored twisted conformation is energetically more stable, and, therefore, dominates in the equilibrium at all temperatures. This is consistent with the observed deep-purple color of the solutions of all fluorenylidene-xanthenes, which show the thermochromic form **B** at room temperature. However, the folded conformation may be substantially populated in thermal equilibrium.^[80] Moreover, owing to the very similar energies, crystal-packing forces may freeze the twisted as well as the folded conformation in the solid state.

The X-ray crystal structures of two fluorenylidene-xanthene derivatives have already been reported: 12-(9*H*-fluoren-9-ylidene)-2-methoxy-12*H*-benzo[*a*]xanthene (**20**), and its 4,5-diazafluorene derivative **21**.^[17] The yellow crystals contained molecules in folded conformations. The benzo[*a*]xanthylidene moieties of the three independent molecules of **20** and of **21** are folded by A–B = 42–47°, the fluorenylidene moieties by C–D = 13–16°. The central double bonds are twisted by $\omega = 1$ –5°. Evidently, little conformational change is required to accommodate a bulky substituent

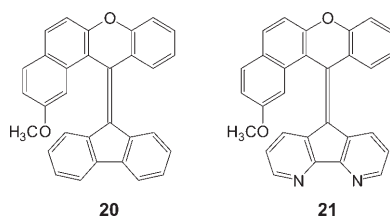
in the 1-position in the folded conformation. H1 and H8 are tilted away from the opposing fluorenylidene moiety (see Figure 2b and Figure 4).

The structures of the heteromeric fluorenylidene-xanthenes may be compared to those of the corresponding homomeric BAEs bifluorenylidene (**7**) and dixanthylene (**8**). The bright red bifluorenylidene has a twisted conformation with $\omega = 32.0^\circ$ and C9=C9' = 1.36 Å (β modification),^[65] which is 8° less twisted and 0.036 Å shorter than the twisted fluorenylidene-xanthenes. Nevertheless, the C...C distances in the nonbonding fjord region are slightly longer in β -bifluorenylidene, namely, 3.17 Å (7% overlap) versus 3.13 Å (8% overlap) in purple **11** (averages). The C9a–C9–C8a bond angle of 115° in the xanthylidene moiety of twisted **11** is larger than the bond angle of $\approx 105^\circ$ imposed by the central five-membered ring of a fluorenylidene moiety. This larger angle pushes the carbon and hydrogen atoms in the 1- and 8-positions deeper into the overcrowded fjord regions. Therefore, a higher twist is required in fluorenylidene-xanthenes to alleviate the intramolecular overcrowding to a permissible level. In the reported (low-resolution) X-ray structures of Mills and Nyburg, dixanthylene (**8**) has an *anti*-folded conformation, with A–B = 40 and 43° in the β and α polymorphs, respectively. This is comparable to the folding of the xanthylidene moieties in yellow **11** (44.5°) and **12** (45.5°). The nonbonding C...C distances of ≈ 3.0 Å are also comparable in the dixanthylene structures as well as in the folded fluorenylidene-xanthenes. Apparently, the small 5-ring bond angle in the fluorenylidene compensates for its lower degree of folding. Several cases have been reported in which overcrowded ethylenes crystallized as two distinctly colored pseudopolymorphs, but with solvent molecules in one of the two crystal structures.^[83] In BAE **11**, both polymorphs^[84] are free of solvent, thus, excluding solvatochromism as a rationale for the different colors.

Conclusion

The yellow and the purple polymorphs of 9-(2,7-dimethyl-9*H*-fluoren-9-ylidene)-9*H*-xanthene (**11**) are the first examples of a bona fide BAE **1** in which a folded as well as a twisted conformation was characterized by single-crystal X-ray structure analysis (Figure 2). In the yellow polymorph, the molecules have a folded conformation with A–B = 44.5(2)° (xanthylidene), and C–D = 18.3(1)° (fluorenylidene). In the purple polymorph, the molecules have a twisted conformation with $\omega = 42.1(3)^\circ$ and nearly planar tricyclic moieties. The interrelation of color and conformation is unambiguously demonstrated. Based on this conclusive crystallographic evidence, the deeply colored purple (or green) thermochromic form **B** of BAEs is identified as the twisted conformation. The assignment of the yellow or colorless ambient-temperature form **A** as (*anti*-)folded conformation is confirmed.

This interrelation of color and molecular conformation is supported further by the purple crystals of the unsubstituted



parent compound **10**, which has a twisted conformation with $\omega = 42.3(4)^\circ$, and the yellow crystals of the benzoannulated derivative **12**, which revealed a folded conformation with $A-B = 45.5(1)^\circ$ and $C-D = 19.7(2)^\circ$.

Enhanced π delocalization in the almost planar tricyclic moieties, the push–pull effect, and reduced overcrowding stabilizes the twisted conformation relative to the *anti*-folded conformation, counterbalancing the high strain of the twisted double bond. In solution, the twisted conformation dominates in fluorenylidene-xanthenes at all temperatures, leading to “thermochromism at room temperature”. Owing to the small energy difference between the twisted and the folded conformations, both conformations could be stabilized as single crystals and, hence, elucidated unambiguously.

Experimental Section

General considerations: Diethyl ether and benzene were dried over sodium wire. Petroleum ether was distilled before use (b.p. $\approx 60^\circ\text{C}$). The NMR spectra were measured in CDCl_3 solution at 295 K by using an AMX or a DRX 400 MHz spectrometer (Bruker Analytical Instruments). Chemical shifts δ are reported relative to $\delta(\text{CHCl}_3) = 7.275$ ppm for ^1H NMR spectra, and relative to $\delta(\text{CDCl}_3) = 77.008$ ppm for ^{13}C NMR spectra. Multiplet shapes are abbreviated as: singlet (s), broad singlet (brs), doublet (d), doublet of doublet of doublets (ddd), and triplet of doublets (td). Assignment of the ^1H and ^{13}C NMR spectra was based on 2D DQF-COSY, 2D long-range ^1H – ^{13}C correlation, and 2D inverse ^{13}C – ^1H correlation spectra. The three-bond ^1H – ^{13}C cross peaks of the xanthyliene carbon atoms C4a, C10a at $\delta \approx 155.0$ ppm with the hydrogen atoms H1, H8 and H3, H6 were used to identify the xanthyliene hydrogen atoms. The aromatic hydrogen atoms of the 2,7-dimethyl-fluorenylidene moiety have characteristic multiplet shapes: H1' and H8' have only small coupling constants (0.7 Hz) with the methyl and *meta* hydrogen atoms; H3' and H6' have one *ortho* coupling constant (7.7 Hz) and small coupling constants with methyl and *meta* hydrogen atoms; H4' and H5' have only one *ortho* coupling constant.

2,7-Dimethyl-9H-fluoren-9-one (13): The sample, prepared according to a literature procedure,^[75] was purified by column chromatography (silica, toluene/petroleum ether (60°C) 20:80–80:20). Orange crystals, m.p. 155–156°C (lit. 157°C^[75]); ^1H NMR (400 MHz CDCl_3 , 295 K): $\delta = 7.456$ (quintet, 0.7 Hz, 2H; H1, H8), 7.369 (d, 7.5 Hz, 2H; H4, H5), 7.270 (dq, 7.6, 0.8 Hz, 2H; H3, H6), 2.378 ppm (s, 6H; CH_3).

2,7-Dimethyl-9H-fluoren-9-one hydrazone (15): Hydrazone **15** was prepared analogously to 9H-fluoren-9-one hydrazone.^[65] Hydrazine hydrate, (98%, $d = 1.032$ g mL $^{-1}$, 1.47 g, 29.3 mmol) was added to 2,7-dimethyl-9H-fluoren-9-one (**13**), 1.222 g, 5.87 mmol) dissolved in hot ethanol (20 mL), and refluxed for 2.5 h. The reaction was monitored by TLC (silica, $R_f(\mathbf{13}) = 0.56$ yellow, $R_f(\mathbf{15}) = 0.25$ yellow (toluene/chloroform 4:1)). The reaction mixture was cooled in an ice bath, and the orange precipitate was filtered off and washed with methanol to afford 2,7-dimethyl-9H-fluoren-9-one hydrazone (**15**) as a yellow powder (0.421 mg 1.90 mmol, 32%), m.p. 165–166°C. Reduction of the filtrate volume to ≈ 5 mL caused precipitation of additional **15** (0.687 mg, 3.09 mmol, 53%), yellow powder, m.p. 164°C (toluene) (lit. 166–167°C (decomp)^[76]); ^1H NMR (400 MHz, CDCl_3 , 295 K): $\delta = 7.734$ (quintet, 0.7 Hz, 1H; H1), 7.604 (d, 7.7 Hz, 1H; H4), 7.531 (quintet, 0.7 Hz, 1H; H8), 7.495 (d, 7.7 Hz, 1H; H5), 7.245 (dq, 7.7, 0.7 Hz, 1H; H3), 7.147 (dq, 7.7, 0.8 Hz, 1H; H6), 6.420 (brs, 2H; NH_2), 2.456 (s, 3H; CH_3), 2.416 ppm (s, 3H; CH_3).

9-Diazo-2,7-dimethyl-9H-fluorene (16): Diazo fluorene **16** was prepared according to a literature procedure.^[76] Anhydrous sodium sulfate (0.511 g, 3.60 mmol), yellow mercury oxide (1.608 g, 7.43 mmol), and 2,7-

dimethyl-9H-fluoren-9-one hydrazone (**15**) (1.000 g, 4.49 mmol) were carefully ground by using a mortar, transferred to a round-bottomed flask equipped with magnetic stirrer and drying tube, and dry diethyl ether (25 mL) was added. Upon dropwise addition of a freshly prepared saturated solution of KOH in ethanol (0.5 mL), the reaction mixture turned deep red. The formation of **16** was monitored by TLC (silica, $R_f(\mathbf{15}) = 0.07$ yellow, $R_f(\mathbf{16}) = 0.78$ orange (petroleum ether/toluene 4:1)). After 3 h of stirring at RT, the reaction was complete. The solution was filtered, and the residue was washed with diethyl ether (3 $\times$ 5 mL). The combined filtrates were evaporated to afford 0.924 g (4.19 mmol, 95%) of 9-diazo-2,7-dimethyl-9H-fluorene (**16**) as orange-red powder, m.p. 119°C (lit. 113.5–115°C^[76]); ^1H NMR (400 MHz, CDCl_3 , 295 K): $\delta = 7.782$ (d, 7.9 Hz, 2H; H4, H5), 7.302 (quintet, 0.7 Hz, 2H; H1, H8), 7.128 (dq, 7.8, 0.7 Hz, 2H; H3, H6), 2.489 ppm (s, 6H; CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 295 K): $\delta = 135.9$ (C), 133.2 (C), 129.3 (C), 125.8 (CH), 120.4 (CH), 119.8 (CH), 62.8 (CN $_2$), 21.7 ppm (CH_3).

9H-Xanthene-9-thione (17): Thione **17** was prepared according to a literature procedure.^[78] 9H-Xanthen-9-one (**14**) (1.57 g, 8.00 mmol) and Lawesson's reagent (1.63 g, 4.04 mmol, 1% excess) were dissolved in dry benzene (15 mL) and refluxed for 1 h in a round-bottomed flask with a magnetic stirrer, a reflux condenser, and a CaCl_2 drying tube. The reaction was monitored by TLC (silica, $R_f(\mathbf{14}) = 0.09$, $R_f(\mathbf{17}) = 0.52$ yellow (petroleum ether/diethyl ether 19:1)). Predried silica (10 g, 120°C/20 Torr) was added to the reaction mixture and the benzene was carefully evaporated under a vacuum. The dry powder was added to the top of a silica column ($l = 12.5$ cm, $\varnothing = 4.5$ cm) and eluted with petroleum ether/diethyl ether (98:2). The blue-green fractions containing pure **17** (TLC) were combined and evaporated under a vacuum to afford 1.36 g (6.39 mmol, 80%) 9H-xanthene-9-thione (**17**) as small black needles with a greenish luster, m.p. 155°C (lit. 157°C^[78]); ^1H NMR (400 MHz, CDCl_3 , 295 K): $\delta = 8.762$ (ddd, 8.2, 1.7, 0.5 Hz, 2H; H1, H8), 7.774 (td, 8.4, 7.0, 1.7 Hz, 2H; H3, H6), 7.518 (ddd, 8.4, 1.2, 0.5 Hz, 2H; H4, H5), 7.389 ppm (td, 8.2, 7.0, 1.2 Hz, 2H; H2, H7); ^{13}C NMR (100 MHz, CDCl_3 , 295 K): $\delta = 205.0$ (C9), 150.5 (C4a, C10a), 134.9 (CH), 129.9 (CH), 129.1 (C8a, C9a), 124.7 (CH), 118.3 ppm (CH).

2,7-Dimethyl-dispiro(9H-fluorene-9,2'-thiirane-3',9''-[9H]-xanthene) (18): Compound **18** was prepared analogously to the parent thiirane dispiro(9H-fluorene-9,2'-thiirane-3',9''-[9H]-xanthene).^[70] 9H-Xanthene-9-thione (**17**, 0.520 g, 2.35 mmol) was dissolved in dry benzene (10 mL), and 9-diazo-2,7-dimethyl-9H-fluorene (**16**, 0.500 g, 2.36 mmol) dissolved in benzene (5 mL) was added. Upon heating, nitrogen evolved and the reaction mixture turned deep purple. After refluxing for 4 h, the reaction was complete (TLC, silica, $R_f(\mathbf{18}) = 0.37$, $R_f(\mathbf{11}) = 0.42$, $R_f(\mathbf{17}) = 0.60$ yellow, $R_f(\mathbf{16}) = 0.70$ orange (petroleum ether/toluene 4:1)). The reaction mixture was cooled to RT and evaporated. The black residue was dissolved in warm benzene (2 mL) and diluted with petroleum ether (3 mL). Upon cooling and standing overnight, crystals of 2,7-dimethyl-dispiro(9H-fluorene-9,2'-thiirane-3',9''-[9H]-xanthene) (**18**, 0.181 g, 0.448 mmol, 19.0%) formed, which were filtered off and washed with petroleum ether. Another crop of **18** (0.121 g, 0.30 mmol, 12.7%) was isolated from the mother liquor by column chromatography (silica, petroleum ether/dichloromethane 95:5–80:20), m.p. 159–162°C; ^1H NMR (400 MHz, CDCl_3 , 295 K): $\delta = 7.977$ –7.953 (m, 2H; H4'', H5''), 7.381 (d, 7.6 Hz, 2H; H4, H5), 7.255–7.193 (m, 4H; H2'', H3'', H6'', H7''), 7.006–6.983 (m, 2H; H1'', H8''), 6.950 (dq, 7.6, 0.7 Hz, 2H; H3, H6), 6.824 (quintet, 0.7 Hz, 2H; H1, H8), 2.121 ppm (s, 6H; CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 295 K): $\delta = 156.6$ (C), 141.7 (C), 138.6 (C), 135.3 (C), 128.7 (CH), 128.5 (CH), 128.3 (CH), 125.7 (CH), 125.0 (C), 122.1 (CH), 118.9 (CH), 116.4 (CH), 58.2 (C), 54.4 (C), 21.3 ppm (CH_3).

9-(2,7-Dimethyl-9H-fluoren-9-ylidene)-9H-xanthene (11): 2,7-Dimethyl-dispiro(9H-fluorene-9,2'-thiirane-3',9''-[9H]-xanthene) (**18**, 0.11 g, 0.26 mmol) was dissolved in dry benzene (8 mL), and triphenylphosphine (0.076 g, 0.29 mmol) in benzene (2 mL) was added. The mixture was refluxed for 3 h. The reaction was monitored by TLC (silica, $R_f(\mathbf{18}) = 0.37$, $R_f(\mathbf{11}) = 0.42$ (petroleum ether/toluene 4:1)). The solvent was evaporated under reduced pressure, and the raw product was washed with methanol and dried (134.8 mg). The black powder was purified by column chromatography (silica, petroleum ether/dichloromethane 95:5–80:20) to give 9-

(2,7-dimethyl-9H-fluoren-9-ylidene)-9H-xanthene (**11**) as a dark-purple powder (64.6 mg, 0.17 mmol, 67%), m.p. 189–191 °C; ^1H NMR (400 MHz, CDCl_3 , 295 K): δ = 8.157 (ddd, 7.9, 1.5, 0.5 Hz, 2H; H1, H8), 7.706 (quintet, 0.7 Hz, 2H; H1', H8'), 7.563 (d, 7.8 Hz, 2H; H4', H5'), 7.391 (td, 8.2, 6.7, 0.5 Hz, 2H; H3, H6), 7.354 (ddd, 8.2, 1.8, 0.5 Hz, 2H; H4, H5), 7.125 (td, 8.0, 6.7, 2.1 Hz, 2H; H2, H7), 7.080 (dq, 7.7, 0.7 Hz, 2H; H3', H6'), 2.277 ppm (s, 6H; CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 295 K): δ = 154.0 (C4a, C10a), 139.6 (C2', C7'), 138.1 (C4a', C4b'), 135.0 (C8a', C9a'), 131.2 (C9'), 130.2 (C9), 130.1 (C1, C8), 129.8 (C3, C6), 128.4 (C3', C6'), 124.9 (C8a, C9a), 124.8 (C1', C8'), 122.5 (C2, C7), 118.8 (C4', C5'), 117.6 (C4, C5), 21.7 ppm (CH_3); HREI-MS: m/z (%) for $\text{C}_{28}\text{H}_{20}\text{O}$: 373.16 (29.8) [$M+1$] $^+$, 372.15 (100) [M] $^+$, 356.12 (8.8) [$M-\text{CH}_3$] $^+$, 342.10 (12.3) [$M-\text{C}_2\text{H}_6$] $^+$, 186.07 (7.2) [M] $^{++}$.

Single crystals for X-ray crystallography were grown by sublimation. A small sample of **11** in a glass vial was inserted into the closed lower end of a quartz glass tube (30 cm long, 10 mm $\varnothing$). The tube was flushed with argon through a glass capillary, and the pressure was adjusted to ≈ 1.5 –1.8 Torr by means of a vacuum system and a valve. The closed end of the glass tube containing the compound was inserted to a depth of ≈ 20 cm into an electrical oven maintained at 180 °C. After 2 d, single purple crystals had formed on the wall of the tube inside the oven, m.p. 193–195 °C. In addition, a small amount of yellow powder and some yellow crystals had formed on the wall of the tube just outside the oven, m.p. 145 °C (purple melt).

X-ray structural analysis, general procedures: Suitable crystals were selected under a microscope and attached to a glass fiber by means of silicone glue or fast-drying acryl acetate glue. Unit-cell dimensions and diffraction intensities were measured with monochromatic $\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ Å, on a four-cycle diffractometer. Intensities were measured with ω scans (unless stated otherwise) at variable scan speeds and were corrected for Lorentz and polarization effects. Three check reflections were measured every 97 reflections and were used to correct for instabilities of the X-ray source and decay of the crystals. No absorption correction was applied. The structures were solved by direct methods with the TREFF routine of the program XS.^[86,87] The structures were refined based on $|F|^2$ by means of the full-matrix least-squares method of the program XL.^[86] The heavy atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located in difference electron-density maps and were added to the refinement either with independent positional parameters and isotropic displacement parameters or as riding on the carbon atoms with isotropic displacement parameters set to $1.2 \times$ that of the carbon atom (see below). CCDC-283156 (purple **11**), CCDC-283157 (yellow **11**), CCDC-283158 (**10**), and CCDC-283159 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Purple 9-(2,7-dimethyl-9H-fluoren-9-ylidene)-9H-xanthene (purple 11): $\text{C}_{28}\text{H}_{20}\text{O}$, $M_r = 372.44$, triclinic, $P\bar{1}$, deep purple, $a = 6.9232(6)$, $b = 11.9501(8)$, $c = 12.3004(8)$ Å, $\alpha = 83.314(5)^\circ$, $\beta = 76.700(6)^\circ$, $\gamma = 82.116(6)^\circ$, $V = 977.3(1)$ Å 3 , $Z = 2$, $\rho_{\text{calcd}} = 1.266$ g cm $^{-3}$, $T = 293$ K, 4364 total reflections, $\theta_{\text{max}} = 25^\circ$, $\omega - 2\theta$ scans, Siemens P4 diffractometer, crystal dimensions $0.45 \times 0.25 \times 0.15$ mm. The aromatic hydrogen atoms were refined with isotropic displacement parameters. The methyl hydrogen atoms were found to be disordered with two orientations corresponding to a 60° rotation about the C–C bond and were refined as riding on the respective carbon atom. The final residual factors are $wR2 = 0.092$, $R1 = 0.041$, and $\text{GOF} = 1.035$ for 327 parameters and 3440 unique reflections, 2302 reflections with $I < 2\sigma(I)$. Residual electron density: $0.11/-0.10$ e Å $^{-3}$ (max/min).

Yellow 9-(2,7-dimethyl-9H-fluoren-9-ylidene)-9H-xanthene (yellow 11): $\text{C}_{28}\text{H}_{18}\text{O}$, $M_r = 372.44$, monoclinic, $P2_1/n$, yellow, $a = 13.678(1)$, $b = 7.600(1)$, $c = 19.373(2)$ Å, $\beta = 94.281(8)^\circ$, $V = 2008.3(4)$ Å 3 , $Z = 4$, $\rho_{\text{calcd}} = 1.232$ g cm $^{-3}$, $T = 293$ K, 3846 total reflections measured, $\theta_{\text{max}} = 22.5^\circ$, Siemens P4 diffractometer, crystal dimensions $0.12 \times 0.06 \times 0.03$ mm. Hydrogen atoms were refined as riding on the respective carbon atoms. The final residual factors are $wR2 = 0.098$, $R1 = 0.067$, and $\text{GOF} = 1.004$ for 267 parameters and 2627 unique reflections, 1153 reflections with $I < 2\sigma(I)$. Residual electron density: $0.14/-0.12$ e Å $^{-3}$ (max/min).

9-(9H-Fluoren-9-ylidene)-9H-xanthene (10): $\text{C}_{26}\text{H}_{16}\text{O}$, $M_r = 344.39$, monoclinic, $C2/c$, deep purple, $a = 21.798(6)$, $b = 7.834(6)$, $c = 10.187(5)$ Å, $\beta = 106.19(4)^\circ$, $V = 1670.7(16)$ Å 3 , $Z = 4$, $\rho_{\text{calcd}} = 1.369$ g cm $^{-3}$, $T = 120$ K, 3880 total reflections, $\theta_{\text{max}} = 35^\circ$, Nicolet P3F diffractometer. The molecules of **10** show an orientational disorder about a crystallographic C_2 axis that runs through the overcrowded fjord regions, perpendicular to the central double bond (Supporting Information Figure S2). Owing to the close superposition, only average positions for the fjord region carbon atoms C1/C1' and C8/C8' could be refined with anisotropic displacement parameters. The atoms C2, C7, C8a, and C9a are separated by less than 0.4 Å from the atoms C2', C7', C8a', and C9a', respectively, of the disordered molecule (optical resolution $0.7\lambda/2 \sin(\theta_{\text{max}}) = 0.43$ Å). Refinement with anisotropic displacement parameters led to a high correlation between the parameters. Therefore, these atoms were refined with isotropic displacement parameters. The remaining heavy atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined as riding on the respective carbon atoms. The final residual factors are $wR2 = 0.221$, $R1 = 0.089$, and $\text{GOF} = 1.023$ for 186 parameters and 3659 unique reflections, 2636 reflections with $I < 2\sigma(I)$. Residual electron density: $0.33/-0.28$ e Å $^{-3}$ (max/min).

9-(11H-Benzo[b]fluoren-11-ylidene)-9H-xanthene (12): $\text{C}_{30}\text{H}_{18}\text{O}$, $M_r = 394.44$, orthorhombic, $Pbca$, yellow, $a = 14.508(2)$, $b = 14.168(2)$, $c = 19.490(3)$ Å, $V = 4006(1)$ Å 3 , $Z = 8$, $\rho_{\text{calcd}} = 1.308$ g cm $^{-3}$, $T = 293$ K, 6455 total reflections, $\theta_{\text{max}} = 30^\circ$, Nicolet P3F diffractometer. Hydrogen atoms were refined with isotropic displacement parameters. The final residual factors are $wR2 = 0.127$, $R1 = 0.115$, and $\text{GOF} = 0.977$ for 355 parameters and 5837 unique reflections, 3388 reflections with $I < 2\sigma(I)$. Residual electron density: $0.21/-0.18$ e Å $^{-3}$ (max/min).

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