

The Two Conformations of Hindered Photochromic 4a,4b-Dihydrophenanthrenes

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Abstract: We analyze conformational stereoisomerism in the sterically hindered 4a,4b-dihydrophenanthrenes of C_2 symmetry. In these labile photointermediates, steric hindrance brought about by disubstitution at the 4 and 5 positions or by benzoannulation at the [c] and [g] bonds allows observation of two interconvertible intermediates denoted as **L** and **S**. In such molecules, theoretical analysis suggests two low-energy structures (**C** and **T**). These differ in the chirality of the polyene perimeter helix for one given configuration of the 4a,4b-ethane unit. **C** and **T** can be distinguished by the position of atom pair H_{4a} , X_4 , or of the equivalent atom pair H_{4b} , X_5 with respect to the mean molecular plane. In **C**, atoms H_{4a} and X_4 are on one side of the mean molecular plane, while in **T** atoms H_{4a} and X_4 are on opposite sides of this plane. The same holds for the atom pair H_{4b} , X_5 . The **C** conformation is assigned to the primary photocyclization product (**L** modification) in which the intersubstituent distance X_4 – X_5 is short and where the angular hydrogens are quasi-antiperiplanar. This is the regular conformation of the unhindered 4a,4b-dihydrophenanthrenes. The **T** conformation is assigned to the secondary conformers (**S** modification) formed spontaneously from the primary **L** product. Here the distances H_{4a} – X_5 and H_{4b} – X_4 are short, and in the case of severe steric hindrance ($X = t$ -Bu) the angular hydrogens are anticlinal. The observed stability order (usually **S** > **L** at around room temperature, except in the 4,5-dimethyl, 4,5-di-*tert*-butyl, and 4,5-dichloro molecules) is the outcome of steric hindrance opposing skeletal deformations. X_4 – X_5 steric interactions are dominant in the **C** forms while the H_{4a} – X_5 and H_{4b} – X_4 interactions (and corresponding interactions in the [c] and [g] dibenzoannulated systems) play a foremost role in the **T** forms. Computed strain energies for **C** and **T** reproduce the observed stability trends of **L** and **S** modifications. Differences in visible absorption band energies are traced to different extents of departure from planarity of the polyene perimeter. The **L** intermediates assigned to the more planar **C** structure are thus predicted to absorb at longer wavelengths. The low intensity of the visible band in the **L** modifications is attributed to symmetry-imposed cancelling-out of one-ethylene-bond transition moments. The present analysis explains also the simultaneous existence and the observed range of values of potential barriers separating the two modifications. The present analysis changes the previous structure assignment for the **S** and **L** modifications of the dibenzo system, leading to full agreement with the observed trend of the electronic spectra of the **S** and **L** modifications. Similar considerations applied to the 4a,4b-dimethyl system suggest that its labile low-temperature intermediate ($\lambda_{\max} = 360$ nm) could have a **T**-like conformation.

Introduction

Photocyclization of *cis*-stilbene (**1a**) gives rise to the colored 4a,4b-dihydrophenanthrene intermediate **2a** (see Scheme 1).^{1–3} This unstable molecule is formed in an allowed conrotatory electrocyclic excited state process.^{3a,4,5} This is an activated

reaction, requiring low activation energies of 1–2 kcal for photoformation of **2a** and of many other unhindered 4a,4b-dihydrophenanthrenes.¹

Molecular models of **2a** and molecular orbital computations suggest an antiperiplanar (trans) conformation of the 4a and 4b angular hydrogens⁴ (Figures 1A and 2) consistent with the experimentally deduced C_2 molecular symmetry^{1,6,7} [for nomenclature, see ref 8].

The excited state ring opening (reverse process, $h\nu_2$, Scheme 1) is also an allowed electrocyclic reaction. No activation energy is required for this process in the unhindered 4a,4b-dihydrophenanthrenes.^{1,3a}

However, the ground state ring opening, while readily observed in these systems, is nevertheless a forbidden electrocyclic process,⁴ observable only because of the significant

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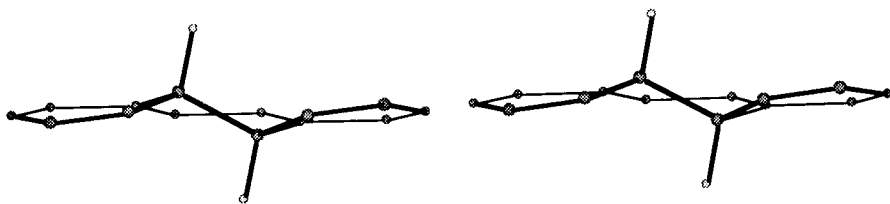
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A : 2a(ap)



B : 2a(ac)

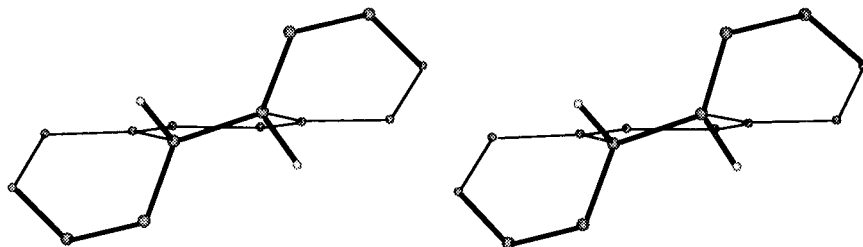


Figure 1. (A) ap canonical structure for systems **2a–2f**. The dihedral angle τ_1 is 180° . Rings A and C are quasiplanar. The distance $X_4–X_5$ is short. X_4 and H_{4a} (as well as X_5 and H_{4b}) are on the same side of the mean molecular plane. The C conformers are derived from the ap structure. (B) ac canonical structure for systems **2a–2f**. The dihedral angle τ_1 is -120° . Bonds $H_{4a}–4a$ and $4b–5$ are eclipsed. Note that ring B is quasiplanar and rings A and C are folded along axes $2–4a$ and $4b–7$. The distance $X_4–X_5$ is large. X_4 and H_{4a} (as well as X_5 and H_{4b}) are on two sides of the mean molecular plane (passing through bond $9–10$ and the midpoint of bond $4a–4b$). The T conformations are derived from the ac structure.

2a(R)

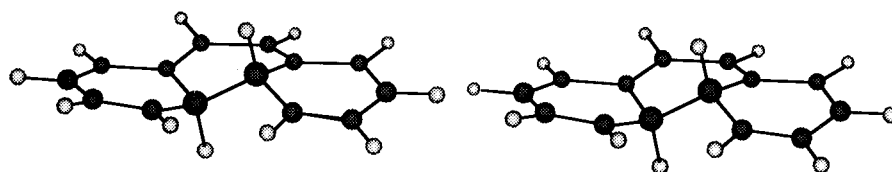
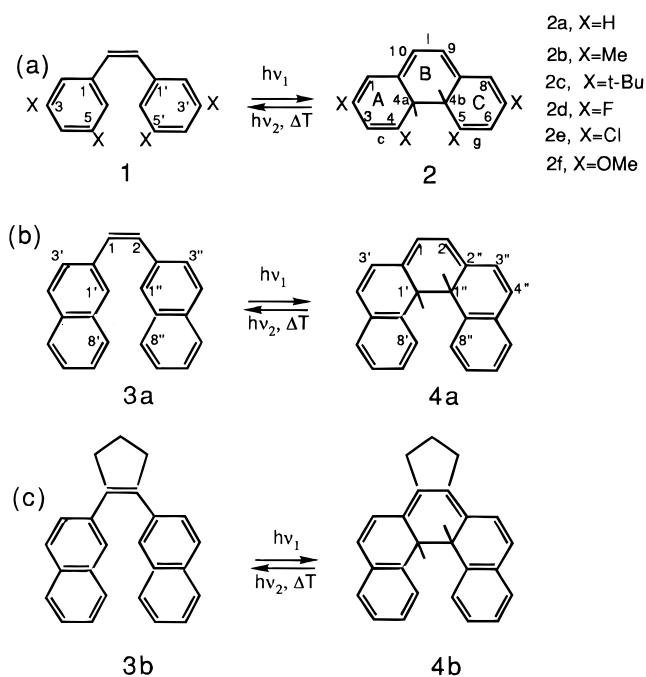


Figure 2. Minimum energy conformation of **2a(R)**.

Scheme 1



destabilization of the ground state of all 4a,4b-dihydrophenanthrenes derived from **2a**, relative to the ground state of their educts.^{1,3a}

Unhindered 4a,4b-dihydrophenanthrenes (*regular*, **R** series,

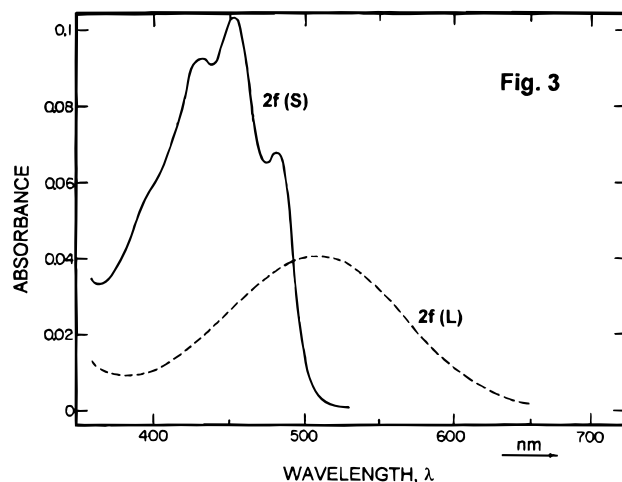


Figure 3. Absorption spectra of the two modifications of **2f** (10^{-3} M) at 133 K in methylcyclopentane–2-methylpentane (1:1). **2f(L)** (broken line) was formed by irradiation with 313 nm light at 133 K. The full line is an extrapolated spectrum of **2f(S)**, obtained by thermal equilibrium at 193 K, recoiling to 133 K, and erasing remnant **2f(L)** by irradiation in the visible. **2f(L)** and **2f(S)** are identified respectively with computed conformers **2f(C)** and **2f(T)**.

listed in Table 1 in ref 1) have a broad but weak visible absorption band [fundamental polyene band, maximum at around 450 nm; $\epsilon \sim 6700$; its shape is similar to curve **2f(L)** in Figure 3].^{1,3a}

4a,4b-Dihydrophenanthrenes can serve as simple models of

Table 1. Tricyclic 4a,4b-Dihydrophenanthrenes of **R**, **L**, and **S** Modifications: Absorption Maxima λ , Extinction Coefficients, ϵ , Activation Energies, E , and Half Life-Time Values, τ , of Ring Opening (RO, LO, and SO), and **L** to **S** Interconversion (LS)^{1,3,10,11}

| | | |
|----|--|--|
| 2a | | R : λ 450nm ϵ 6.7x10 ³ τ_{RO} 96min(300K) E_{RO} 17.5Kcal |
| 2b | | L : ^a λ 525nm τ_{LS} 9ms (293 K); 6min (153 K) E_{LO} 7 Kcal S : τ_{SO} 100ms (293K) |
| 2c | | L : ^b λ 550nm τ_{LO} 6ms (203 K) E_{LO} 5.5 Kcal |
| 2d | | L : λ 480nm S : λ 420nm τ_{SO} 300 μ s (293K) |
| 2e | | L : ^b λ 530nm τ_{LO} 4.1ms (300 K) E_{LO} 13 Kcal |
| 2f | | L : λ 510nm ϵ 4x10 ³ τ_{LS} 50 μ s (300 K) E_{LS} 10 Kcal S : λ 452nm ϵ 9x10 ³ τ_{SO} 50s (300 K) |

^a **L** is more stable than **S** at low temperature. ^b In these systems **L** is more stable than **S**.

an ideal photochromic memory, of a very large scale optical data storage medium, approaching molecular dimension resolution, or of molecular switching devices working in combined photochromic and electrochromic modes.^{1,9} In this context, low temperature operation (~ 100 K) could be a real advantage preventing occurrence of irreversible side reactions. For this reason the study of molecular factors leading to the removal of the potential barrier observed for the concerted photocyclization is of much interest. Several observations made since the early seventies¹⁰ indicate that some molecular factors could indeed abolish this potential barrier and permit photocyclization at low temperatures. Experimentally, the most important factor is steric hindrance introduced into the parent structure by substitution at positions 4 and 5 in the tricyclic systems^{10,11} (see Table 1). Benzoannellation at bonds [c] and [g] (see Scheme 1, and Tables 2 and 3)¹² is another source of steric hindrance removing sometimes (systems **4e** and **4d**) the potential barrier to photocyclization.^{13,14}

However, as its most remarkable effect, steric hindrance was found to give rise to two modifications of 4a,4b-dihydrophenanthrenes.^{1,10,11} [We reserve here the term *modification* for the experimentally observed **R**, **L**, and **S** forms. Conformations **C** and **T** (see below) refer to the computed structures.] These modifications were subsequently termed as **L** and **S**,^{13,14} the absorption maxima of which are shifted to longer and shorter

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Table 2. Pentacyclic 4a,4b-Dihydrophenanthrenes of **L** and **S** Modifications: Spectral and Kinetic Parameters^a

| | | |
|----|--|---|
| 4a | | L : λ 466nm τ_{LS} 10s (293K) E_{LS} 15 Kcal S : λ 422nm ϵ 12x10 ³ stable at 300K E_{SO} 23.3Kcal |
| 4b | | L : λ 490nm τ_{LS} 0.4s (300 K) E_{LS} 15 Kcal S : λ 440nm ϵ 7x10 ³ stable at 300K E_{SO} 29 Kcal |
| 4c | | L : λ 470nm E_{LS} 15 Kcal S : λ 420nm |
| 4d | | L : λ 470nm ϵ 6x10 ³ τ_{LS} 0.7s (323 K) E_{LS} 17 Kcal S : λ 415nm ϵ 13x10 ³ |

^a See caption to Figure 1^{1,12–14}

Table 3. Dimethyl-Substituted Pentacyclic 4a,4b-Dihydrophenanthrenes of **L** and **S** Modifications: Spectral and Kinetic Parameters^a

| | | |
|----|--|---|
| 4e | | L : λ 470nm ϵ 3.6x10 ³ τ_{LS} 2.5s (323 K) stable T<233K. S : λ 410nm ϵ 8.5x10 ³ thermally stable T<300K. |
| 4f | | L : τ_{LS} 0.85s (323K). S : thermally stable at 300K. Both L and S modifications observed by flash photolysis. |
| 4g | | S : thermally stable at 300K. Both L and S modifications observed by flash photolysis. |
| 4h | | L : λ 470nm τ_{LS} 1.8s (323K) S : λ 420nm stable at 300K |

^a See caption to Table 1.¹⁴

wavelengths, respectively, compared with their value in **2a** (cf. values for **2d** in Table 1; for typical spectra see Figure 3). As recently recognized, the **L** modifications are the primary photocyclization products^{13,14} in the majority of systems, and undergo an activated ground-state transformation into the **S** modifications.

The previous studies¹² led to the implicit conclusion that the more stable **S** conformer was traceable to the unhindered (**R**) series of 4a,4b-dihydrophenanthrenes. However, results obtained with **4d** and **4e**, the 3', 3'' disubstituted derivatives of **4a** (Tables 2 and 3), indicate that in fact the **L** series conformers are the primary products in the majority of systems and need to be directly related to the **R** series. This correlation is based on conformational, spectral, and mechanistic considerations.^{13,14}

As details of the photocyclization mechanism emerge from

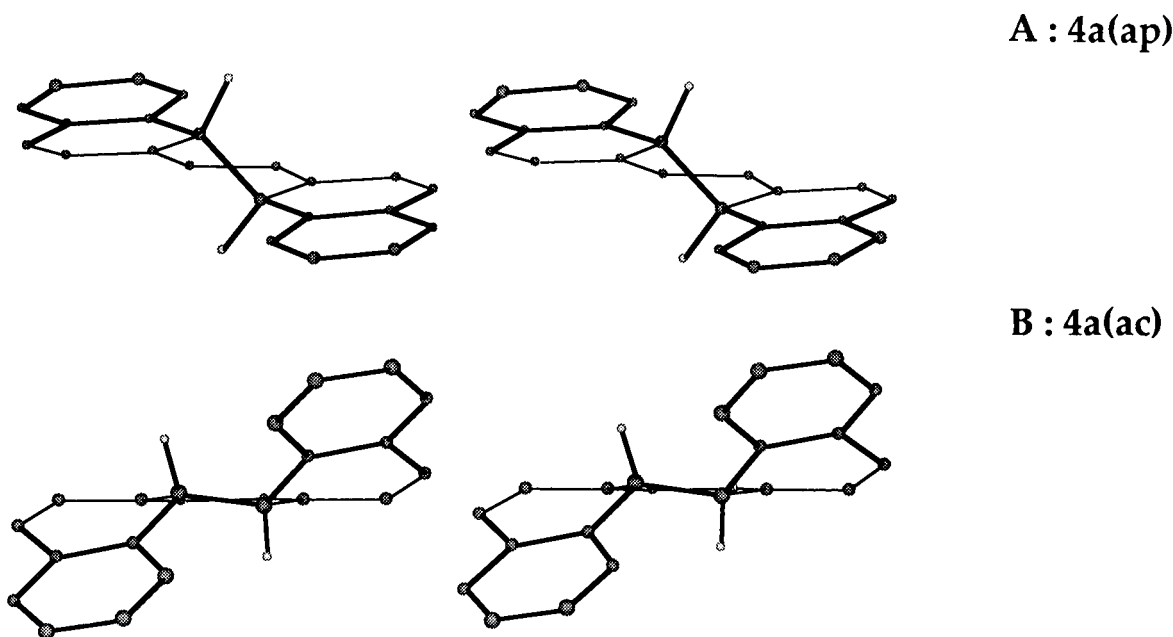


Figure 4. (A) ap Canonical conformation of systems **4a–4h**. (B) ac canonical conformation of systems **4a–4h**.

studies on picosecond and femtosecond time scales^{15–17} and from solvent effect studies,¹⁸ exploration of the conformational space of 4a,4b-dihydrophenanthrenes is warranted to establish if modifications analogous to **L** and **S** of the hindered series (**H**) could be involved in the photocyclization in the **R** series.

In the present work we investigate the conformational space of the 4a,4b-dihydrophenanthrenes of C_2 symmetry to suggest structures and explain stabilities and photochemical characteristics of observed stable and metastable photocyclization intermediates. We applied the MM2 force field,¹⁹ as implemented in MODEL,²⁰ under different steric hindrance regimes. We find in all **H** systems two conformers, **C** and **T**, derived from the canonical forms ap and ac, respectively (Figures 1 and 4), which we identify with the experimentally observed **L** and **S** intermediates (cf. Scheme 2). The computed characteristics of the **C** and **T** conformers such as strain energies and skeletal deformation, as well as the extent of planarity of the polyenic unit, lead to a full understanding of the experimental properties of the observed **L** and **S** modifications. [The first attempt¹² at deducing the structures of the **L** and **S** modifications of **4b** assigned a **T** type structure to the **L** modification and a **C** type structure to the **S** modification. The present, analysis which includes the whole group of hindered 4a,4b-dihydrophenanthrenes, indicates that the early conclusion has to be reversed.]

In particular, we obtain good agreement between experimental and computed stability trends of **S** and **L** modifications. Their main spectral features can now be understood, and a satisfactory model can be obtained for the potential barrier for the **L** → **S** ground state transformation as a function of steric hindrance.

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Scheme 2

Correlation between Experimental, Canonical and Computed Forms

| Experimental Modification | Canonical (Virtual, 4a,4b ethane state) | Computed Conformation |
|---------------------------|---|-----------------------|
| L | ----- ap----- | C |
| S | ----- ac----- | T |

Features of Forms

L - Long wavelength, usually metastable; primary product

S - Short wavelength, usually "stable"; secondary product

ap - H_{4a} - H_{4b} dihedral angle 180° (Staggered, antiperiplanar)

ac - H_{4a} - H_{4b} dihedral angle -120° (Eclipsed, anticlinal)

C - Cis, H_{4a} and X_4 on same side of mean molecular plane

T - Trans, H_{4a} and X_4 on both sides of mean molecular plane

The computed structures of the **C** and **T** conformers suggest that two types of steric interactions control molecular stability in ground and excited states: (a) interactions between substituents at the 4 and 5 positions in **2a–2f** and between rings annelated at bonds [c] and [g] in **4a–4h** and (b) interactions between angular hydrogen H_{4a} and the X group at position 5 in **2a–2f** (and the parallel H_{4b} - X_4 interaction). The corresponding interactions in [c] and [g] benzo annelated system are $H_{1'}-H_{8''}$ and $H_{1''}-H_{8'}$ (for numbering in **4a** see Scheme 1).

As we shall see, these interactions are directly responsible for the greater stability of the **S** modifications, in systems **2f** and **4a–4h**, both in ground and in excited states. In the excited state of the **S** modification, these interactions result in a potential barrier to photochemical ring opening, leading to significant

Table 4. Alignment of Bond Transition Moments \mathbf{m} in Three Lowest Exciton Transitions and Resultant Transition Moment \mathbf{M} in Planar Conformation

| Transition | Transition Moment Diagram | Transition Moment \mathbf{M} (in \mathbf{m} units) |
|--------------|---------------------------|--|
| Fundamental | | 0 |
| 1st Overtone | | 3.46 |
| 2nd Overtone | | 2.0 |

fluorescence intensity. Furthermore, the dependence of such interactions on the nature and size of substituent is also responsible for special situations (**2b**, **2c**, and **2e**) where the **S** modifications (not observed in **2c** and **2e**) are less stable than the **L** modifications. This is also the case in **5**.

Electronic Spectra of **L** and **S** Modifications

We noted before that the **L** modifications (conformation **C**) absorb at longer wavelengths than the **S** modifications of conformation **T**. As the **C** conformations are the more planar, this is the relationship required by considerations of planarity. While the trend of transition energies is thus understandable, the observed intensity relationship of the fundamental (visible) transition, $\epsilon_S > \epsilon_L$ (cf. Tables 1–3 and Figure 3) posed an initial difficulty. Again, from general planarity considerations we would expect $\epsilon_L > \epsilon_S$. The reason for the observed surprising situation became clear once the explicit dependence of the transition moment on the molecular structure of the two modifications was taken into account. Basing our discussion on the exciton model^{23,24} invoked in our previous analyses,^{1,3a} we note that the transition moment \mathbf{M} of polyenes (made up of weakly conjugated chromophore units) can be approximated by a vector sum of oriented ethylene unit transition moments \mathbf{m} . \mathbf{M} adds up to 0 in the case of the fundamental transition of a strictly planar coiled hexaene with the π electron topology of **2a** (see Table 4). These results explain the low intensity of the fundamental transition in the 4a,4b-dihydrophenanthrenes of the **L** modification in the **H** series ($\epsilon \approx 5000$ – 7000 ; Tables 1–3) and in the **R** series (cf. Tables in ref 1). However, in the case of definitely nonplanar systems such as the **S** modifications (C_2 symmetry), the vector sum of the unit moments \mathbf{m} is nonzero, its value depending on the exact conformation. We can thus understand the general trend (cf. Figure 6 in ref 14, Figure 5 in ref 13, and Figures 1 and 2 in ref 10) that $\epsilon_S > \epsilon_L$ for the fundamental transition (in general, $\epsilon_S \approx 2 \epsilon_L$, cf. Tables 1–3). The far-reaching cancelling-out of the one-bond components predicted for the **L** modifications is borne out by the very low values for the extinction coefficients for systems **5**, **6**, and **7**^{25,26} (Table 5). Thus in 1,3,4a,4b,6,8-hexamethyl-4a,4b-dihydrophenanthrene (**5**), $\epsilon_L = 3100$; in the [2.2]metacyclophanenes **6** and **7**, $\epsilon \approx 3000$ – 3500 .²⁵ In these systems the tendency for

Table 5. **L** and **S** Modification of 1,3,4a,4b,6,8-Hexamethyldihydrophenanthrene, **5**, and **L** Modification of [2.2] Metacyclophane, **6**, and of 4,12-Dimethyl[2.2]metacyclophane, **7**^a

| | | |
|----------|--|--|
| 5 | | L : $\lambda 475\text{nm}$ $\epsilon 3100$; $\lambda 320\text{nm}$ $\epsilon 3100$ E_{LO} 22.5Kcal; τ 33hr (298K) S : $\lambda 360\text{nm}$ ($T < 210\text{K}$) |
| 6 | | L : $\lambda 500\text{nm}$ $\epsilon 3500$; $\lambda 319\text{nm}$ $\epsilon 18400$ E_{LO} 20.3Kcal; τ 61hr (298K) |
| 7 | | L : $\lambda 520\text{nm}$ $\epsilon 3000$; $\lambda 323\text{nm}$ $\epsilon 16000$ E_{LO} 15Kcal; τ 916hr (298K) |

^a See footnotes to Tables 1–3.^{1,3,25,26}

planarity is strengthened by the $\text{Me}_{4a}\text{--H}_5$ and $\text{Me}_{4b}\text{--H}_4$ repulsion in **5**, and by the effect of the 4–5 ethane bridge in **6** and **7**. These systems are thus considered to be forced into exaggerated **L** (i.e., **C** type) conformations. In the case of a strictly planar coiled hexaene, the transition moment for the first overtone band obtained by vector addition amounts to $\mathbf{M} = 3.46\mathbf{m}$, explaining why in all modifications of 4a,4b-dihydrophenanthrenes this band is stronger than the fundamental (see Table 4).

Computed Structures

Computation Method. The minimum energy structures, strain energies, and reaction profiles were computed by the program MODEL.²⁰ The MM2 force field developed by Allinger¹⁹ was used in the present study. This force field has been widely tested in ground state studies of conformeric and isomeric aliphatic and cyclic hydrocarbon systems. The computed energies, energy differences, geometries, and conformations usually agree very closely with the experimental data.^{19,21} In particular, the MM2 force field was found to yield good energy estimates for strongly hindered and strained molecules. In another comprehensive study this force field was found to give reliable conformer geometries and conformer energy values very similar to those provided by the *ab initio* computations.²² The computations for **2b**–**2f** were performed on the 4,5-disubstituted molecules.

Definition of Canonical Forms and Classification of Minimum Energy Conformations. The description of the structures of the minimum energy conformers **C** and **T** listed in Table 6 is facilitated by the definition of two canonical conformations, ap and ac (Figures 1A, 1B, 4A, and 4B), originating from the two torsional states of the central ethane unit. Conformation ap (antiperiplanar, 4a,4b-trans) is obtained by requiring that the ethane dihedral angle ($\text{H}_{4a}\text{--}4a\text{--}4b\text{--H}_{4b}$ (τ_1) be 180° [τ_{klmn} is measured *ccw*, from mn to kl]. Conformation ac (anticlinal) is derived by requiring that the same dihedral angle be -120° . Rings A and C are quasiplanar in ap. In ac, ring B is quasiplanar, bonds $\text{H}_{4a}\text{--}4a$ and $4b\text{--}5$ are eclipsed, and the distance $\text{X}_4\text{--X}_5$ is long. We shall apply the mean molecular plane (passing through bond 9–10 and midpoint of bond 4a–4b) to correlate ap and ac with the corresponding minimum energy conformations **C** and **T**. The canonical conformations ap and ac and the minimum energy conformations **C** and **T** can be characterized by the values of the dihedral angle

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Table 6. Molecular Mechanics Computation Results for Conformers of 4a,4b-Dihydrophenanthrenes^a

| conformer | energy, kcal | torsion angles, deg ^b | | | | distances, Å | |
|---------------|--------------|----------------------------------|---|----------------------|-------------------|--------------------------------|---------------------------------|
| | | τ_2 4-4a-4b-5 | τ_1 H _{4a} -4a-4b-H _{4b} | τ_3 8a-9-10-10a | τ_4 7-8-8a-9 | X ₄ -X ₅ | X ₄ -H _{4b} |
| 2a (R) | 14.25 | 64.0 | -173.1 | -16.6 | -165.8 | 2.19 | 2.98 |
| 2b (T) | 25.65 | 88.7 | -152.8 | -5.9 | -155.4 | 3.19 | 2.80 |
| 2b (C) | 24.88 | 35.6 | 157.7 | -26.1 | -177.3 | 3.29 | 4.07 |
| 2c (C) | 51.85 | 130.0 | -97.8 | 11.1 | -137.6 | 5.16 ^c | 2.75 |
| 2c (T) | 46.28 | 27.0 | 145.6 | -27.7 | -178.3 | 4.18 ^c | 4.40 |
| 2d (T) | 18.76 | 80.6 | -158.4 | -10.5 | -158.9 | 2.54 | 2.71 |
| 2d (C) | 18.93 | 45.7 | 168.3 | -23.0 | -174.2 | 2.49 | 3.64 |
| 2f (T) | 28.83 | 83.9 | -153.5 | -7.0 | -157.5 | 2.75 ^d | 2.58 |
| 2f (C) | 30.37 | 35.7 | 160.3 | -25.1 | -176.2 | 2.83 ^d | 3.82 |
| 4a (T) | 40.97 | 88.3 | -151.5 | -4.3 | -155.5 | 3.31 | 2.69 |
| 4a (C) | 41.76 | 37.8 | 161.3 | -24.8 | -177.4 | 2.99 | 3.91 |
| 4e (T) | 41.46 | 90.8 | -147.8 | -4.5 | -176.2 | 3.43 | 2.69 |
| 4e (C) | 43.43 | 34.5 | 160.0 | -26.1 | -176.4 | 3.08 | 4.02 |
| 5 (C) | 30.36 | 73.2 | -168.9 | -18.5 | -176.6 | 2.25 | 3.08 |

^a Conformers **C** and **R** are derived from canonical form **ap** and correspond to the experimentally observed **L** modifications. Conformers **T** (derived from canonical form **ac**) correspond to the experimentally observed **S** modifications. ^b For **4a** and **4e**, the following correspondence of torsional angles applies: τ_2 , 4-4a-4b-5 \equiv 8'a-1'-1''-8''a; τ_1 , H_{4a}-4a-4b-H_{4b} \equiv H_{1'}-1'-1''-H_{1''}; τ_3 , 8a-9-10-10a \equiv 2''-2-1-2'; and τ_4 , 7-8-8a-9 \equiv 4''-3''-2''-2. ^c From quaternary carbon. ^d From etheric oxygen.

τ_1 and the dihedral angles 4-4a-4b-5 (τ_2), 8a-9-10-10a (τ_3), and 7-8-8a-9 (τ_4). Thus τ_2 is 60° in **ap** and 120° in **ac**; τ_3 , which measures the distortion of ring B from planarity, is 0° in both canonical forms **ap** and **ac**. τ_4 is a measure of divergence between planes of ring B and ring A (or ring C).

The computed conformations **C** and **T** (Table 6) are derived from the two canonical forms (**ap** and **ac**, respectively). The **C** as well as **ap** conformations have both H_{4a} and X₄ (and similarly H_{4b} and X₅) on the same side of the mean molecular plane. The **T** conformations (as well as the **ac** canonical forms) have H_{4a} and X₄ on opposite sides of the mean molecular plane. The same obviously holds for H_{4b} and X₅ [cf. Figures 1 and 4].

R Series (Figure 2). These **ap**-like conformations are obtained in all 4a,4b-dihydrophenanthrenes devoid of sterically hindering groups at the strategic positions 4 and 5 (as well as 4a and 4b) and devoid of dibenzoannulation at bonds [c] and [g]. In this study the **R** series is represented by the parent molecule **2a**. Compared to its value in **ap** ($\tau_1 = 180^\circ$), τ_1 in **2a** (-173.1°) is slightly over-extended. This is probably the outcome of the repulsions in the H_{4a}-H₅ and H_{4b}-H₅ pairs. Ring B (formula **2** in Scheme 1) is nonplanar. The H₄-H₅ repulsion can be accommodated without having recourse to an **ac**-type conformation with its inherent H_{4a}-H₅ and H_{4b}-H₄ repulsions. No local minima of **ac**-type [e.g., **2a(T)**] were encountered in the conformational searches.

Slightly hindered 3-Ring ap- and ac-Type Conformers. One such case (the tetrafluoro system **2d**^{10b}) was studied. Both **C** (**ap**-like) and **T** (**ac**-like) conformers are evident in the conformational search (see Figure 1 in the Supporting Information). In **2d(C)** $\tau_1 = 168.3^\circ$ is overextended due to the F₄-F₅ repulsion. Because of the smallness of the H_{4a}-F₅ and H_{4b}-F₄ interactions, τ_1 in **2d(T)**, (-158.4°) is larger than in **ac** ($\tau_1 = -120^\circ$) by 38.4°. The F₄-F₅ distance is slightly smaller in **2d(C)** than in **2d(T)**. The F₄-H_{4b} distance is significantly smaller in **2d(T)** than in **2d(C)**, 2.71 vs 3.64 Å. The τ_2 angle is 45.7° in **2d(C)**, and much larger, 80.6°, in **2d(T)**. This angle increases with the extent of steric hindrance in **2b** and **2c**. In **2d(C)**, the distortion of ring B (**2** in Scheme 1) as measured by τ_3 (-23°) is slightly larger than in **2a**. τ_3 is close to this value in the **C** conformers of all 4a,4b-dihydrophenanthrenes (see Table 6). Ring B in **2d(T)** as well as in other **T** conformers as measured by τ_3 is less distorted than in the **C** conformers (-10.5° vs -23.0°). As judged by the value of τ_4 , ring B and ring A (and ring C) are almost coplanar in **2d(C)** as well as in all **C** conformers. In **2d(T)**, the value of τ_4 (-158.9°) indicates

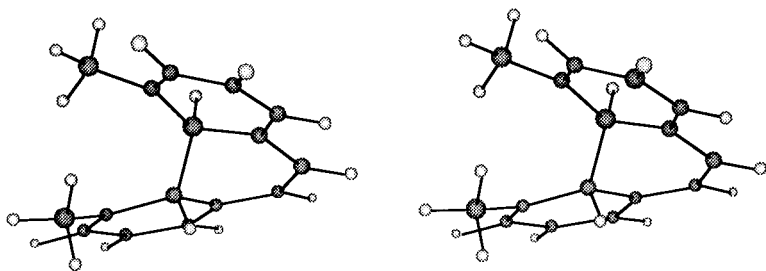
some departure from coplanarity of ring B and ring A or C. The same situation is seen in other **T** conformers, and in **2c(T)**, the distortion is even stronger.

Moderately Hindered 3-Ring ap- and ac-Type Conformers (Figure 5A and B). Two such systems, the tetramethyl (**2b**) and the tetramethoxy (**2f**), were investigated, and clearly show local energy minima corresponding to **ap**- and **ac**-type conformations. The trend of the τ_1 values seen in **2d** continues. In **2b(C)** and **2f(C)** these angles are overextended by 22.3° and 19.7°, respectively. In **2b(T)** and **2f(T)** this angle is still far from its value in **ac** (by 32.8° and 33.5°, respectively). The X₄-H_{4b} distances in **2b(T)** and **2f(T)** are smaller than in the **ap**-type conformers **2b(C)** and **2f(C)**, as this is the dominant close approach distance, going from **C** to **T**. The differences amount to 1.27 Å in **2b** and to 1.24 Å in **2f**. τ_2 is 88.7° in **2b(T)** and 83.8° in **2f(T)**, compared with 80.6° in **2d(T)**. See Figure 2 in Supporting Information for a stereoview of **2f(C)** and **2f(T)**.

Severely Hindered 3-Ring ap- and ac-Type Conformers (Figure 6, A and B). The consequences of the severe hindrance are evident in both **C** and **T** conformers of the tetra *tert*-butyl system **2c**. τ_1 (145.6°) is severely overextended in the **ap**-type form **2c(C)**, by 34.3°, because of the X₄-X₅ repulsion. In the **ac**-type conformer **2c(T)**, τ_1 (-97.6°) is well beyond its canonical form value of -120°. The torsion around the 8-8a bond in this conformer (τ_4 , -137.6°) is large. The X₄-X₅ separation is larger in **2c(T)** than in **2c(C)** [5.16 vs 4.18 Å between methyl carbons]. τ_2 in **2c(T)** is 130.0°, larger than in the canonical **ac** form, and much larger than the values in **2d(T)**, **2b(T)**, and **2f(T)**. This is a consequence of the large X₄-X₅ repulsion in **2c(C)**. In **2c(T)**, the value of τ_4 (-137.6°) is another indication of the severity of the steric hindrance. The value of this angle exceeds by some 20° the values found in the **T** conformers of the other tricyclic 4a,4b-dihydrophenanthrenes.

Five Ring Systems 4a and 4e (Figure 7, A and B). The values of the torsional angle τ_1 of the angular hydrogens (H_{1'}-1'-1''-H_{1''}) in the **T** and **C** conformations indicate moderately hindered systems resembling in this sense systems **2b** and **2f**. In the **C** conformer of **4a** this angle is overextended by 18.7° (compared to **ap**). In **4a(T)** τ_1 is 31.5° short of the value assumed in **ac**. The H_{8'}-H_{8''} distance (corresponding to X₄-X₅ in the tricyclic systems) is decidedly longer in the **T** conformer (3.31 vs 2.99 Å), while the H_{1'}-H_{8''} distance is much longer in the **C** conformer (3.91 vs 2.69 Å). τ_2 in **4a(T)**, 88.3°,

A : 2b(C)



B : 2b(T)

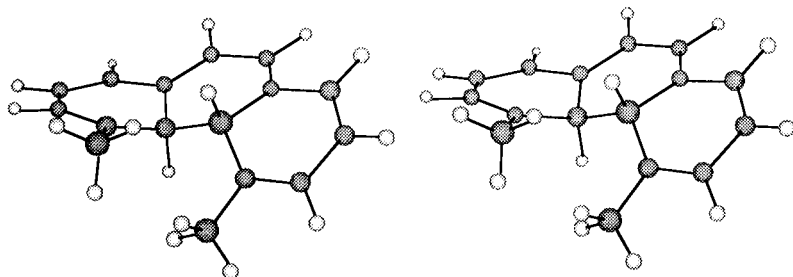
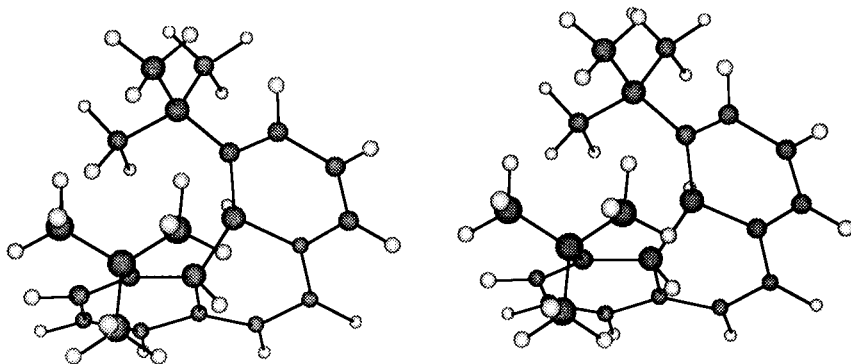


Figure 5. (A) Minimum energy conformation of 2b(C). (B) Minimum energy conformation of 2b(T).

A : 2c(C)



B : 2c(T)

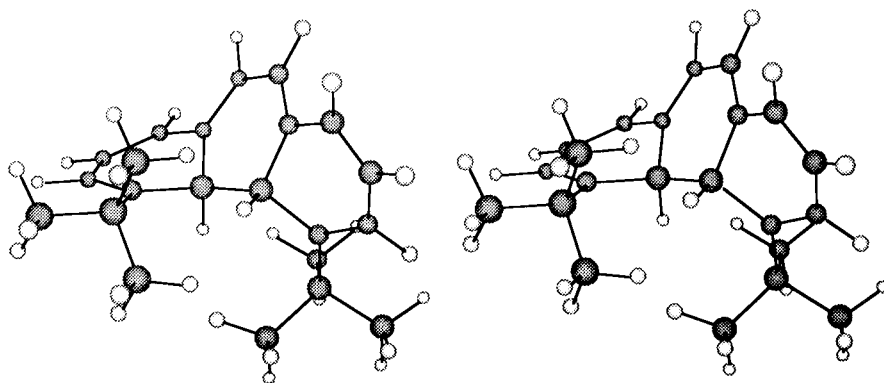
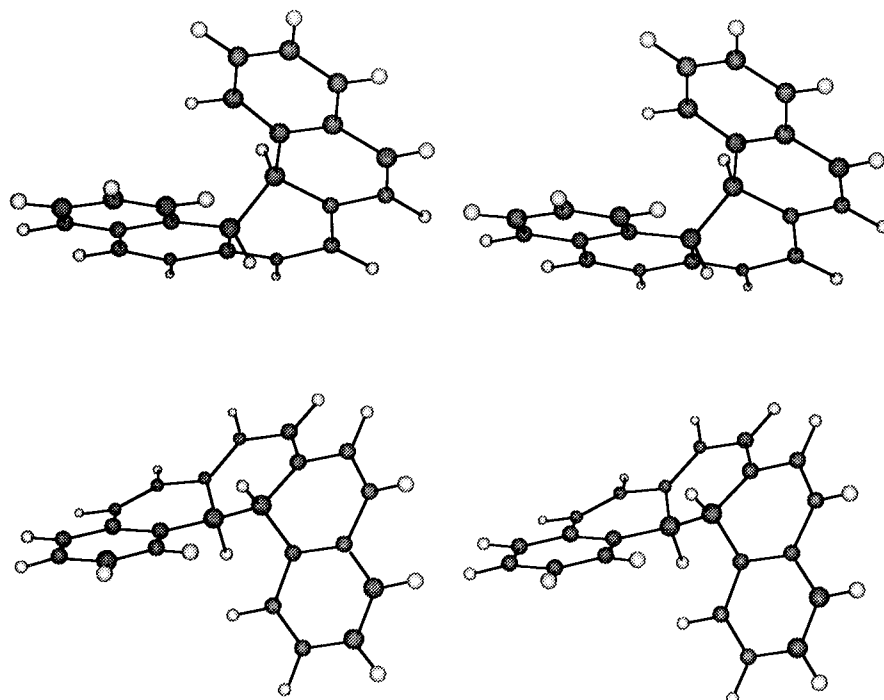


Figure 6. (A) Minimum energy conformation of 2c(C). (B) Minimum energy conformation of 2c(T).

and in 4e(T), 90.8°, is well below the value in the severe hindrance case; $\tau_2 = 130.0^\circ$ in 2c(T). Thus the two benzoan-

related molecules 4a and 4e represent cases of intermediate steric hindrance, together with 2b and 2f.



A : 4a(C)

B : 4a(T)

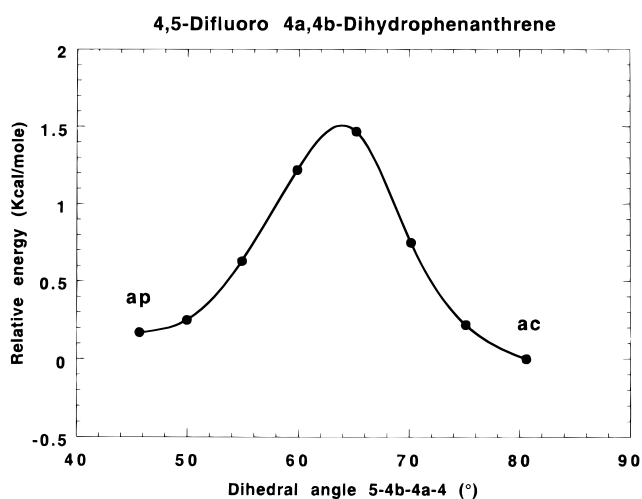
Figure 7. (A) Minimum energy conformation of 4a(C). (B) Minimum energy conformation of 4a(T).**Table 7.** Computed Strain Energy Differences $\Delta E = E(C) - E(T)$ of 4a,4b-Dihydrophenanthrenes (in kcal/mol)

| | 2b | 2c | 2d | 2f | 4a | 4e |
|------------|-------|-------|------|------|------|------|
| ΔE | -0.77 | -5.57 | 0.17 | 1.54 | 0.79 | 1.97 |

4a,4b-Disubstituted Tricyclic System 5. The low-temperature labile photointermediate observed^{3a} ($\lambda_{\max} = 360$ nm) could well be a **T**-type conformer. The MODEL search, however, finds only the regular **C** conformer (Table 6), which corresponds to the room temperature ap-type form.

The Relative Stabilities of C and T Conformers. Comparison with Observed Stabilities of L and S Modifications. Table 6 lists the computed strain energies of the **C** and **T** pairs. The differences $\Delta E = E(C) - E(T)$ listed in Table 7 can be directly correlated with the experimental relative stability data for the **L** and **S** modifications listed in Table 1. Table 7 shows that in system **2b**, and the more so in **2c**, **C** is more stable than **T**. In these systems, **L** is indeed the observed modification. This modification is both the primary product in **2b** and **2c** and the one that is the more stable. Nevertheless, time-resolved experiments indicate some conversion of **L** into **S** at room temperature. In systems **2f**, **4a**, and **4e**, **C** is less stable than **T**. This result explains the observed ground state conversion of **L** (primary modification) into **S** (short wavelength modification). In system **2d** the **T** conformation is slightly the more stable (by 0.17 kcal/mol). Experimentally, **L** and **S** are almost isoenergetic.

Activation Energies for the L \rightarrow S Process. The energy minimizations were carried out pointwise for geometries constrained along an approximate reaction coordinate, allowing rough potential energy barriers estimates for the **L** \rightarrow **S** process. Figures 8 and 9 show such potential energy profiles for two reaction coordinates for the interconversion of **2d**(**C**) and **2d**(**T**) by torsion along τ_2 , and by approach along the F₄-H_{4b} line. Both coordinates indicate activation energies of the order of 1.3–1.7 kcal/mol for the **L** \rightarrow **S** interconversion. Such values are commensurate with the experimental observation of a dynamic equilibrium between the two forms.^{10b} The very small

**Figure 8.** Computed potential energy barrier for interconversion of **2d**(**C**) (ap) to **2d**(**T**) (ac) by torsion along τ_2 .

computed energy difference of 0.17 kcal/mol between **T** and **C** (Table 7) is in agreement with this observation.

Figure 10 shows the potential energy profile for the **C**–**T** interconversion along the τ_2 torsion coordinate of **2b**. This profile indicates an activation energy of approximately 6.5 kcal/mol. Experimentally, the time-resolved study at room temperature indicates a fast ground state **L** \rightarrow **S** interconversion (see Table 1), slowing down completely at low temperatures,¹⁰ as expected of an activated process.

Figure 11 shows the **C**–**T** interconversion profile along the H₁–H_{8'} coordinate in the **4a** system. The activation energy along this coordinate amounts to 6.5 kcal/mol. Experimentally (Tables 2 and 3), the **L** \rightarrow **S** activation energies amount to 15–17 kcal/mol.

Rigidity of S and L Modifications. The **S** modifications show vibrationally resolved visible spectra. One is therefore led to conclude that the **S** modifications are more rigid than the **L** modifications, whose visible spectra are invariably broad and structureless. A typical case illustrating the spectral differences is shown in Figure 3. The same conclusion can be reached by

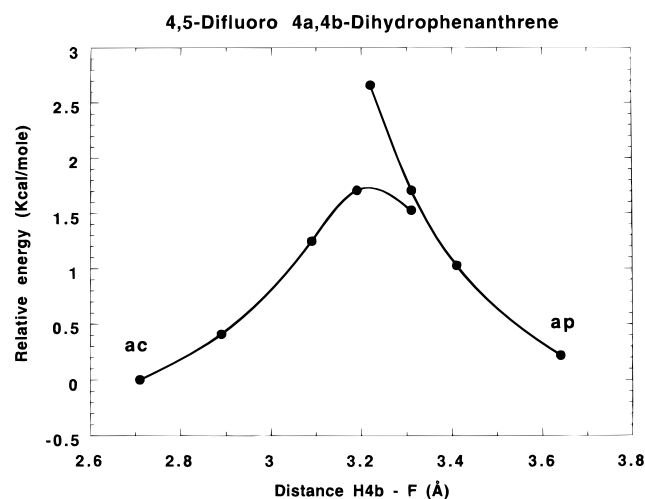


Figure 9. Computed potential energy barrier for interconversion of **2d(C)** (ap) to **2d(T)** (ac) by changing the distance $H_{4b}-F_4$. The rising ap branch is due to constraining the molecule to the ap geometry.

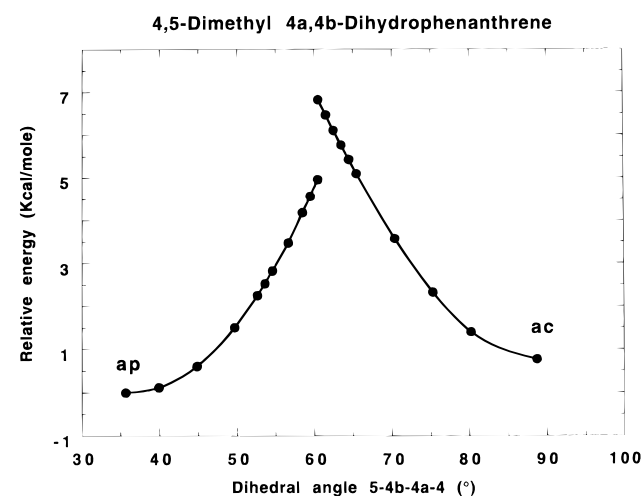


Figure 10. Computed potential energy barrier for interconversion of **2b(C)** (ap) to **2b(T)** (ac) by torsion along τ_2 (4-4a-4b-5).

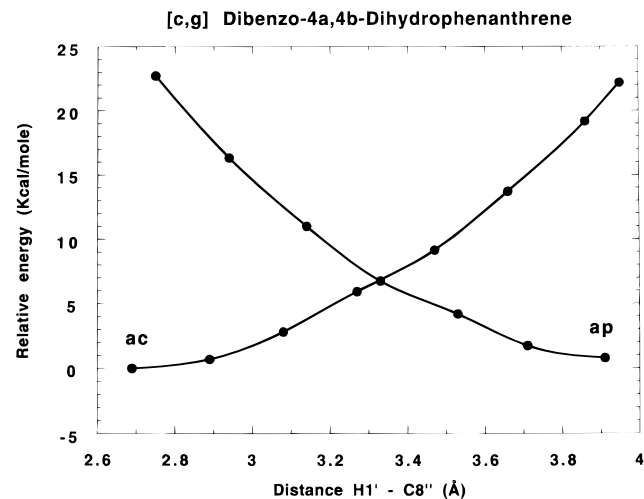


Figure 11. Computed potential energy barrier for interconversion of **4a(C)** (ap) to **4a(T)** (ac) by changing the distance $H_{1'}-C_{8''}$. Both rising branches of ap and ac are shown.

considering the initial values of the slopes of the **C**–**T** interconversion potential energy profiles for deformation about τ_1 or τ_2 (defined in Table 6). These are much larger for the **T** than for the **C** conformers. Thus in **2d** (Figure 8), the initial slopes for deformation along τ_2 are 0.04 kcal/deg for **T** and

Table 8. Strain Energy Components of Conformers of 4a,4b-Dihydrophenanthrenes

| conformer | energies (kcal/mol) ^a | | | | | | |
|--------------|----------------------------------|------|-------|------|-------|-------|------|
| | <i>E</i> | str | bnd | s-b | tor | vdw | dip |
| 2a(R) | 14.25 | 0.64 | 0.93 | 0.07 | 4.42 | 7.14 | 1.05 |
| 2b(T) | 25.65 | 1.77 | 4.86 | 0.35 | 8.36 | 9.22 | 1.08 |
| 2b(C) | 24.88 | 1.04 | 6.72 | 0.03 | 6.95 | 9.15 | 1.00 |
| 2c(T) | 51.85 | 4.14 | 15.23 | 0.62 | 15.41 | 15.37 | 1.07 |
| 2c(C) | 46.28 | 3.41 | 15.34 | 0.34 | 12.86 | 13.35 | 0.99 |
| 2d(T) | 18.76 | 0.79 | 1.59 | 0.14 | 7.97 | 7.19 | 1.07 |
| 2d(C) | 18.93 | 0.77 | 3.21 | 0.06 | 5.85 | 7.81 | 1.24 |
| 2f(T) | 28.83 | 1.84 | 6.44 | 0.23 | 6.89 | 12.64 | 0.78 |
| 2f(C) | 30.37 | 1.48 | 9.35 | 0.15 | 5.90 | 12.93 | 0.56 |
| 4a(T) | 40.97 | 1.50 | 3.80 | 0.18 | 16.28 | 17.72 | 1.49 |
| 4a(C) | 41.76 | 1.33 | 5.42 | 0.08 | 15.04 | 18.46 | 1.44 |

^a *E*: MM2 strain energy. str: stretching. bnd: bending. s-b: improper stretching–bending. tor: torsion. vdw: van der Waals. dip: dipolar electrostatic interaction.

0.02 kcal/deg for **C**. Steric hindrance provides the force opposing the deformation.

Excited State Processes of L and S Modifications. Experimental data on the excited state processes of **L** and **S** modifications of **2f** and **4a** and its derivatives **4b**–**4h** are available,^{10–14} pointing to the following general properties. The **L** modifications (assigned presently to the **C** conformation) undergo excited state ring cleavage to the *cis*-diaryl ethylene educts. Due to this instability they are necessarily devoid of any fluorescence. The immediate reason for the ring-opening reactivity and lack of fluorescence is the X_4-X_5 repulsion (or the equivalent $8'-8''$ repulsion in **4a**–**4h**). This steric hindrance provides a permanent force destabilizing the excited state, and is obviously absent in the **S** modifications (**T** conformation). The **S** modifications require significant activation to undergo excited state ring cleavage. Understandably, their stable but constrained excited state can undergo radiative decay, giving rise to significant fluorescence of their **S** modifications.^{10–14}

The temperature dependence of the excited state ring opening process in the **S** modification can be attributed to the necessity of excited state activated conversion of the more stable **T** conformation to the labile **C** conformation, which can undergo ring opening because of the destabilization due to the X_4-X_5 repulsion (or the equivalent $8'-8''$ repulsion).

Analysis of the Contributions to the Strain Energy. The MM2 strain energy is made up of leading contributions from van der Waals (vdw), torsion (tor), and bending (bnd) terms (see Table 8). Less important terms are contributed by the dipolar electrostatic interactions (dip) and the stretch–bend interaction (s-b). Obviously, the van der Waals term accounts for only part of the strain energy. Nevertheless, the two $E(C)/E(T)$ relationships discussed above, i.e., (A) $E(C) < E(T)$, found for **2b** and **2c**, and (B) $E(C) > E(T)$, found for **2d**, **2f**, and **4a**, are seen to correlate directly with the trends of the van der Waals term. Thus in A, $vdw(T) > vdw(C)$, found for **2b** and **2c**, while in B, $vdw(C) > vdw(T)$, which was found for **2f**, **2d**, and **4a**. Unexpectedly, $vdw(C)$ in **2c** is significantly smaller than $vdw(T)$, probably the effect of $4a-X_5$ and $4b-X_4$ interactions in **2c(T)**.

As seen from Table 8, the stretching, stretching–bending, and torsional terms for the **T** conformers are consistently larger than for the **C** conformers, whereas the bending terms are consistently smaller. The trend of the torsional energies is a consequence of the more planar structure of the **C** conformers.

Correlation of Potential Barrier to Photocyclization with Extent of Steric Hindrance. The possibility that the photocyclization potential barrier is removed by high steric interaction is suggested by the findings that **2b**, **2c**, and **2e**, as well as **4d**,

4e, and **4h**, photocyclize at low temperatures.^{10,11,13,14} Within the simple model of the photocyclization process, the potential barrier arises from the intersection of two harmonic oscillators representing product and educt. Steric hindrance can be taken to correspond to a high vibrational state of the unhindered molecule. In this state part of the potential barrier has already been surmounted and is not required for crossing into product.

Other Systems. The chloro-4a,4b-dihydrophenanthrene **2e** was not included in these computations. Nevertheless, on the basis of the above analyses, its conformeric behavior seems to be well-understood. Thus the long-wave modification **2e(L)** is clearly the sole observable photocyclization product (ref 11, p 224). In this respect, the same conformeric behavior as observed and computed for **2b**, the other moderately hindered 3-ring system, is to be expected. Indeed, on the basis of the similar van der Waals volumes of CH₃ and Cl (13.7 vs 12.0 Å³),²⁷ this is the outcome to be expected. Moreover, in the case of **2e**, the specific stabilizing Cl...Cl interaction²⁸ should exert a stabilizing effect on **2e(C)** (the ap-like conformer)

resulting in the dominance of the **L** modification. Finally, we wish to mention the highly likely possibility that dual conformers similar to **C** and **T** are formed in cyclic photochromic systems of bianthrone and bianthrylidene.^{1,29}

Acknowledgment. M.E. acknowledges the support of the Kimmelman Center for Biomolecular Assembly.

Supporting Information Available: Stereoviews of ap and ac conformers of 4,5-difluoro- and 4,5-dimethoxy-4a,4b-dihydrophenanthrene [**2d(C)**, **2d(T)**, **2f(C)**, and **2f(T)**] (3 pages). See any current masthead page for ordering and Internet access instructions.

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