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Structure of Long-Lived Alkynyl-Substituted Carbocations of the Phenanthrene Series and Their Precursors

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Abstract—According to the NMR data, 9-(R-ethynyl)-9-hydroxy-10,10-dimethyl-9,10-dihydrophenanthrenes (R = H, Me, Ph) in superacid medium (HSO_3F–SO_2ClF) at low temperature undergo dehydroxylation with formation of the corresponding long-lived 10,10-dimethyl-9-(R-ethynyl)-9,10-dihydrophenanthren-9-yl cations which do not isomerize to 10-(R-ethynyl)-9,10-dimethyl-9,10-dihydrophenanthren-9-ylium. In contrast, long-lived 10,10-dimethyl-9-(3,3,3-trifluoroprop-1-yn-1-yl)-9,10-dihydrophenanthren-9-yl cation derived from 9-(3,3,3-trifluoroprop-1-yn-1-yl)-10,10-dimethyl-9,10-dihydrophenanthren-9-ol undergoes partial isomerization to 10-(3,3,3-trifluoroprop-1-yn-1-yl)-9,10-dimethyl-9,10-dihydrophenanthren-9-yl cation.

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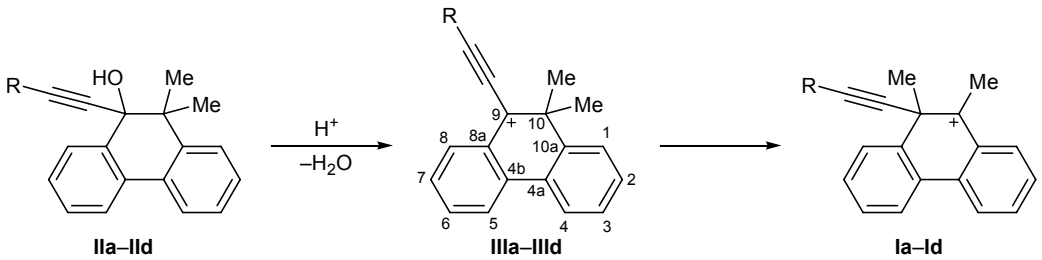
Carbocation-mediated molecular rearrangements widely occur in organic chemistry. Migration of an atom or group to a carbocationic center is nothing else than intramolecular electrophilic substitution reaction. Up to now, a lot of data on alkyl group migrations in long-lived carbocations have been published, whereas no analogous migrations of ethynyl groups have been reported [1]. However, such electrophilic substitution reactions are classed with processes underlying the structural–kinetic theory of organic reactions. Therefore, relevant studies constitute an important problem.

We previously found that long-lived 9-R-9,10-dimethyl-9,10-dihydrophenanthren-9-yl cations (R = alkyl, cyclopropyl, aryl, vinyl) are convenient models for studying intramolecular electrophilic substitution reactions [1, 2]. These cations are capable of undergoing degenerate rearrangements via 1,2-shift of the R group at a rate measurable by dynamic NMR methods.

The goal of the present work was to generate long-lived 9-(R-ethynyl)-9,10-dimethyl-9,10-dihydrophenanthren-9-yl cations **Ia**–**Id** by dehydroxylation of the corresponding 9-(R-ethynyl)-10,10-dimethyl-9,10-dihydrophenanthren-9-ols **IIa**–**IId** in superacid medium, followed by isomerization of initially formed 10,10-dimethyl-9-(R-ethynyl)-9,10-dihydrophenanthren-9-yliums **IIIa**–**IIId** (Scheme 1).

Initial alcohols **IIa**–**IId** were synthesized by reaction of the corresponding alkynylmagnesium bromides or alkynyllithiums with 10,10-dimethyl-9,10-dihydrophenanthren-9-one. According to the ^1H NMR data, dissolution of **IIa**–**IId** in the superacid system HSO_3F–SO_2ClF at –95°C was accompanied by formation of 10,10-dimethyl-9-(R-ethynyl)-9,10-dihydrophenan-

Scheme 1.

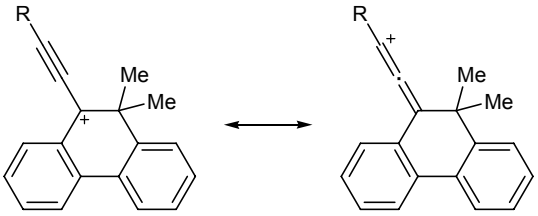


IIa–IId **IIIa–IIId** **Ia–Id**

R = H (**a**), Me (**b**), Ph (**c**), CF_3 (**d**).

thren-9-yl cations **IIIa**–**IIId**. No signals assignable to isomeric cations **Ia**–**Ic** were detected in the ^{1}H NMR spectra at –95°C; cations **Ia**–**Ic** did not appear when the temperature was raised to –20°C. Taking into account that 1,2-shifts of methyl group in structurally related phenanthrenyl cations occur at a high rate even at low temperature [3, 4] and that the calculated energy barrier to the migration of methyl group in **IIIa**–**IIIc** does not exceed 49 kJ/mol, the equilibrium between cations **Ia**–**Ic** and **IIIa**–**IIIc** is obviously displaced toward the latter almost completely. This means that generation of long-lived cations **Ia**–**Ic** is hardly probable. The higher stability of **IIIa**–**IIIc** relative to **Ia**–**Ic** is likely to be determined by participation of the triple C≡C bond in delocalization of the positive charge (Scheme 2; cf. [5]).

Scheme 2.



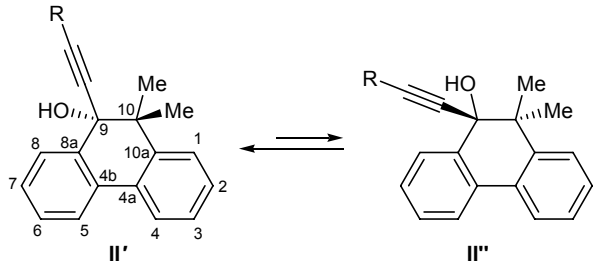
Unlike **IIIa**–**IIIc**, long-lived cation **IIId** partly isomerizes into **Id**. Evidently, the electron-donor effect of the ethynyl group weakens in going from R = H, Me, Ph to R = CF_3. The isomerization process is likely to involve migration of one methyl group (cf. [3, 4]). The equilibrium ratio **Id**/**IIId** is equal to 1.8 at –83°C, and it decreases to 1.3 as the temperature rises to –16°C. Specific structural features and chemical behavior of cation **Id** will be the subject of separate publication.

The equilibria between 10,10-dimethyl-9-R- and 10-R-9,10-dimethyl-9,10-dihydrophenanthren-9-yl cations, where R = C(Me)=CH_2 [4], *cis*-C(Me)=CHMe [6], and *trans*-C(Me)=CHMe [4], are displaced toward the latter; when R = CH=CH_2 [3], the isomeric cations are comparable in their stability. A probable reason for the observed differences in the equilibrium compositions of isomeric cations with ethynyl and ethenyl groups is that the ethenyl group in 10,10-dimethyl-9-R-9,10-dihydrophenanthren-9-yliums [R = CH=CH_2, C(Me)=CH_2, *cis*-C(Me)=CHMe, *trans*-C(Me)=CHMe] is forced out of the plane of the phenanthrene skeleton due to steric factor [7], so that its electron-donor effect is reduced; by contrast, there are no steric hindrances to the in-plane orientation of ethynyl group, and its effective participation in delocalization of the positive charge ensures higher stability of cations **IIIa**–**IIIc** as compared to isomeric cations **Ia**–**Ic**.

The results of DFT quantum-chemical calculations confirmed the experimental data indicating strong prevalence of **IIIa**–**IIIc** in the equilibrium mixtures with **Ia**–**Ic**: the corresponding energy differences are 28.4, 44.8, and 61.8 kJ/mol, respectively. As applied to the trifluoromethylethynyl-substituted cations, comparison of the experimental and calculation data for cations **IIId** and **Id** suggests that the calculated relative stability of **IIId** is overestimated (the energy difference is 20.9 kJ/mol).

Specific features of the steric structure of acetylenic alcohols **II** should be considered. As might be expected (cf. [3, 8]), compounds **II** exist as mixtures of conformers with pseudoaxial and pseudoequatorial orientation of the ethynyl group. Their ^{1}H and ^{13}C NMR spectra recorded at room temperature display broadened signals, presumably due to conformational exchange (Scheme 3); as a result, averaged signals from the pseudoaxial and pseudoequatorial groups are observed. Lowering the temperature reduces the rate of conformational exchange, and the spectra contain two sets of signals with an intensity ratio of 3:1 to 5:1 (Fig. 1).

Scheme 3.



The results of quantum-chemical calculations of the chemical shifts of protons in **II** allowed us to deduce two criteria for the assignment of signals to conformers like **II′** and **II″**. First, protons in a pseudoequatorial group resonate in a weaker field relative to those of the corresponding pseudoaxial group (obviously, due to magnetic anisotropy of the aromatic rings in the phenanthrene core). Second, protons in the geminal methyl groups in conformers with pseudoequatorial C≡CR substituent are less shielded than in conformers with pseudoaxial orientation of the alkynyl group (Fig. 2). Therefore, the major set of signals was assigned to conformers **II′**; the equilibrium conformer ratios

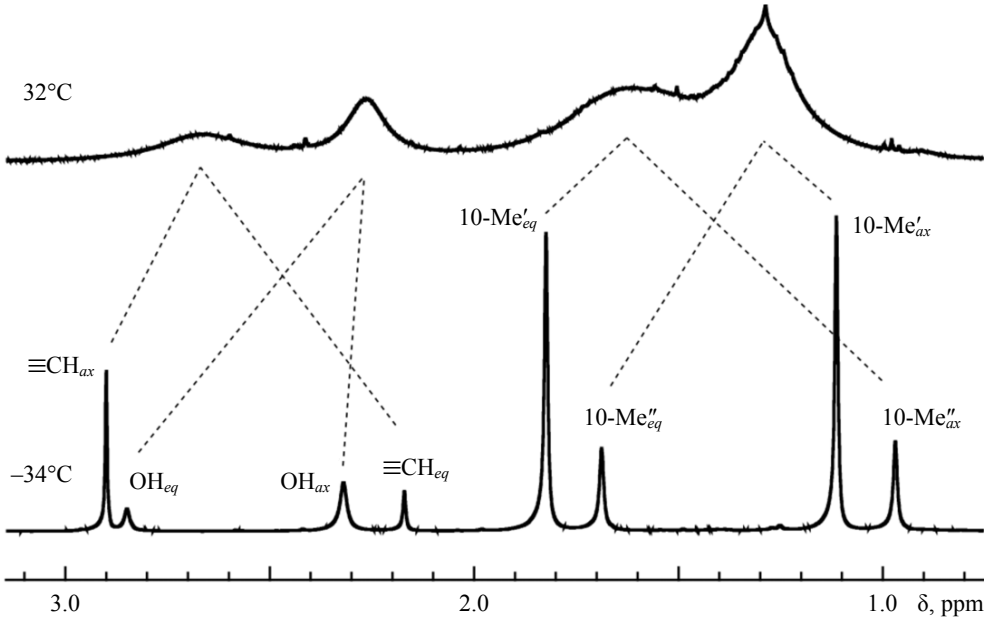
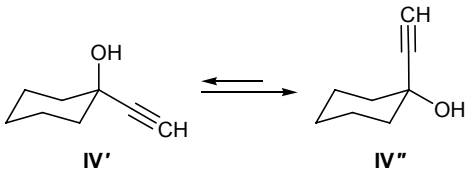


Fig. 1. [1]H NMR spectra of 9-ethynyl-10,10-dimethyl-9,10-dihydrophenanthren-9-ol (**IIa**) in $CDCl_3$.

(Scheme 3) in $CDCl_3$ at –34°C are 1:3 (**IIa**), 1:4 (**IIb**), 1:5 (**IIc**), and 1:4 (**IId**).

Unlike carbinols **II**, conformational equilibria of carbinols **IV** (Scheme 4) are displaced toward structures with axial orientation of the ethynyl group [9]. Presumably, intramolecular interaction between the axial hydroxy group and the aromatic ring in **II** (cf. [10]) is responsible for the higher stability of conformers with equatorial ethynyl substituent.

Scheme 4.



The rate constants of conformational exchange **II′** ↔ **II″** were estimated by dynamic NMR at –9°C and were 28, 13, 22, and 48 s^{-1} for compounds **IIa**–**IId**, respectively; the Gibbs energies of activation calculated by the Eyring equation were $\Delta G^{\neq}$ = 57.1±0.9, 58.9±1.1, 57.6±1.0, and 55.9±0.9 kJ/mol, respectively.*

In the [1]H NMR spectra of conformers **IIa′**–**IIc′**, the 8-H proton characteristically resonated even in a weaker field (by ~0.2 ppm) than 4-H and 5-H which are deshielded due to the effect of the neighboring aromatic ring. The 8-H proton in **IIa′**–**IIc′** appears in the vicinity of the C≡C bond, and it could be presumed that anisotropic effect of that bond is responsible for the downfield position of the 8-H signal. The triple bond in **IIa″**–**IId″** is more distant from 8-H, and no such downfield shift of the latter is observed. However, it is not observed for conformer **IId′**, where the position of the triple bond is the same as in **IIa′**–**IIc′**. Obviously, the reason is steric effect rather than magnetic anisotropy of the triple bond (cf. [11]). This steric effect in conformer **IId′** is weaker due to lower electron density on the triple bond. Quantum-chemical

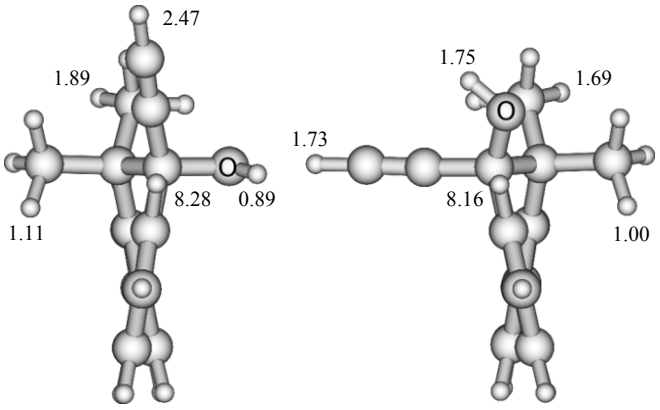


Fig. 2. Calculated structures of conformers of 9-ethynyl-10,10-dimethyl-9,10-dihydrophenanthren-9-ol (**IIa**); calculated chemical shifts (δ, ppm) of some protons are given.

* Mean-square deviations are given. The mean-square deviations for the temperature and rate constants were assumed to be 4°C and 3 s^{-1}, respectively.

calculations reproduce well both the downfield shift of 8-H in **IIa′**–**IIc′** and its absence in the ^{1}H NMR spectra of **IId′** and **IIa″**–**IId″**.

EXPERIMENTAL

The spectral and analytical studies were performed at the Chemical Service Center, Siberian Branch, Russian Academy of Sciences. The IR spectra were recorded on a Bruker Verctor-22 spectrometer. The ^{1}H, ^{13}C, and ^{19}F NMR spectra of neutral compounds in $CDCl_3$ and of cationic species in HSO_3F–SO_2ClF–CD_2Cl_2 were measured on a Bruker AV-400 spectrometer. The ^{1}H and ^{13}C chemical shifts for neutral compounds were determined relative to $CDCl_3$ (δ 7.24, δ_C 76.9 ppm), and for cations, relative to CD_2Cl_2 (δ 5.33, δ_C 53.3 ppm); $CFCl_3$ was used as external reference in ^{19}F NMR measurements. The temperature of NMR probes was calibrated against standard methanol sample. Signals in the NMR spectra were assigned on the basis of comparison of the experimental chemical shifts with calculated values. NOESY experiments were additionally performed for cations **Id** and **IIId**. If necessary, spin system simulation was applied. The high-resolution mass spectra were obtained on a DFS Thermo Electron Corporation instrument.

Carbocations were generated using doubly distilled HSO_3F (bp 158–161°C), SO_2ClF [12] dried by passing its vapor through concentrated sulfuric acid, and CD_2Cl_2 dried over 4-Å molecular sieves. Tetrahydrofuran was purified by heating under reflux over metallic sodium in a stream of argon, followed by distillation. 10,10-Dimethyl-9,10-dihydrophenanthren-9-one was synthesized according to [13].

The geometric parameters of carbocations and their precursors were optimized in terms of the density functional theory using PBE functional [14] and L1 basis set (Λ01 [15], an analog of cc-pVDZ) with the aid of PRIRODA program [16]. Conformers of **II** were preliminarily localized with the aid of ChemAxon Marvin (*conformers* plugin) [17] and VeraChem Vconf [18]. The chemical shifts were calculated by the GIAO/DFT/PBE method with L22 basis set (Λ22, an analog of cc-pCVTZ) using PRIRODA program. The calculations were performed at the Information and Computation Center, Novosibirsk State University (*http://www.nusc.ru/*). Carbocation structure visualizations and their Cartesian coordinates and chemical shifts are available at *http://limor1.nioch. nsc.ru/quant/phen-CC/*.

Exchange dynamic NMR spectra were analyzed using MEX program [19], and the spin system parameters were determined using NUMMRIT program [20], which were accessed through *xsim* interface (*ftp://nmr.nioch.nsc.ru/pub/nmr/*).

9-Ethynyl-10,10-dimethyl-9,10-dihydrophenanthren-9-ol (IIa). A solution of 0.50 g (2.25 mmol) 10,10-dimethyl-9,10-dihydrophenanthren-9-one in 10 ml of THF was added dropwise over a period of 5 min under stirring at 0°C in an argon atmosphere to 7.5 ml of a 0.5 M solution of ethynylmagnesium bromide in THF (3.75 mmol, Aldrich). The mixture was stirred for 45 min at 0°C and for 2 h at room temperature, and 18 ml of a saturated solution of ammonium chloride was added dropwise, maintaining the temperature below 10°C. The upper yellowish organic layer was separated, the aqueous layer was extracted with diethyl ether (2×10 ml), and the extracts were combined with the organic phase, washed with water (3×10 ml), and dried over magnesium sulfate. Removal of the solvent left alcohol **IIa** as a thick yellowish nontransparent oily substance (0.56 g), which was purified by passing it through a thin layer of silica gel, followed by elution with a mixture of hexane and chloroform (1:1 by volume). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3590 (OH), 2118 (C≡C), 3305, 637 (H–C≡C). Found: *m*/*z* 248.1204 $[M]^+$. $C_{18}H_{16}O$. Calculated: *M* 248.1201.

Conformer **IIa′**. ^{1}H NMR spectrum (–34°C), δ, ppm: 1.11 s (10-Me$_{ax}$), 1.82 s (10-Me$_{eq}$), 2.32 s (9-OH$_{ax}$), 2.90 s (HC≡C), 7.33–7.61 m (1-H, 2-H, 3-H, 6-H, 7-H), 7.80–7.89 m (4-H, 5-H), 8.04 d (8-H, *J* = 7.5 Hz). ^{13}C NMR spectrum (–34°C), δ_C, ppm: 21.1 (10-Me$_{ax}$), 26.7 (10-Me$_{eq}$), 42.9 (C^{10}), 73.2 (H**C**≡C), 76.5 (C^9), 82.8 (HC≡**C**); 123.9, 124.0, 125.9, 127.0, 127.4, 127.9, 128.6, 129.4 (C^1–C^8)**; 131.0, 131.6, 135.1, 141.1 (C^{4a}, C^{4b}, C^{8a}, C^{10a}).**

Conformer **IIa″**. ^{1}H NMR spectrum (–34°C), δ, ppm: 0.97 s (10-Me$_{ax}$), 1.69 s (10-Me$_{eq}$), 2.17 s (HC≡C), 2.85 s (9-OH$_{eq}$), 7.33–7.61 m (1-H, 2-H, 3-H, 6-H, 7-H), 7.74–7.89 (4-H, 5-H, 8-H). ^{13}C NMR spectrum (–34°C), δ_C, ppm: 20.5 (10-Me$_{ax}$), 22.3 (10-Me$_{eq}$), 43.2 (C^{10}), 72.0 (H**C**≡C), 76.9 (C^9), 84.6 (HC≡**C**), 123.7–128.2 (C^1–C^8); 131.8, 132.0, 137.8, 142.5 (C^{4a}, C^{4b}, C^{8a}, C^{10a}).**

10,10-Dimethyl-9-(prop-1-yn-1-yl)-9,10-dihydrophenanthren-9-ol (IIb). *a. Preparation of prop-1-yn-*

** Hereinafter, signals assigned by comparing the experimental chemical shifts with calculated ones are marked with a double asterisk.

1-yllithium and its activation (cf. [21]). A solution of 0.945 g of a mixture of (*Z*)- and (*E*)-1-bromoprop-1-ene (Aldrich, 98%) in 5 ml of THF was cooled to –75°C, 8.4 ml (17.05 mmol) of a 2.05 N solution of butyllithium in hexane was added dropwise under stirring over a period of 10 min, and the mixture was stirred for 2 h at –75°C. The resulting white suspension was added in one portion at –75°C to 1.91 g (7.75 mmol) of $CeCl_3$ (Aldrich, 99.9%), and the mixture was stirred for 1 h at that temperature.

b. Reaction of prop-1-yn-1-yllithium with 10,10-dimethyl-9,10-dihydrophenanthren-9-one. A solution of 1.1 g (5 mmol) of 10,10-dimethyl-9,10-dihydrophenanthren-9-one in 25 ml of THF was added dropwise over a period of 30 min under stirring at –75°C in an argon atmosphere to the suspension of prop-1-yn-1-yllithium prepared as described in *a*. The mixture was stirred for 1 h at –75°C (it turned yellowish), allowed to warm up to room temperature, treated first with 5 ml and then with 7 ml of a saturated aqueous solution of ammonium chloride, and left overnight under argon. The colorless organic layer was separated, the aqueous layer was extracted with diethyl ether (2×20 ml), and the extracts were combined with the organic phase, washed with brine (2×20 ml), dried over $MgSO_4$, and evaporated. The residue was a yellowish oily substance (1.33 g) which was subjected to column chromatography on Al_2O_3 (10×3.5 cm, 105 g). Elution with hexane–diethyl ether (2:1 by volume) removed almost all impurities, and the subsequent elution with diethyl ether afforded compound **IIb**. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3595 (OH), 2240 (C≡C). Found: *m*/*z* 262.1353 $[M]^+$. $C_{19}N_{18}O$. Calculated: *M* 262.1352.

Conformer **IIb′**. ^{1}H NMR spectrum (–34°C), δ, ppm: 1.06 s (10-Me$_{ax}$), 1.78 s (10-Me$_{eq}$), 2.07 s (MeC≡C), 2.18 s (9-OH$_{ax}$), 7.30–7.55 m (1-H, 2-H, 3-H, 6-H, 7-H), 7.77–7.84 m (4-H, 5-H), 8.02 d (8-H, *J* = 7.5 Hz). ^{13}C NMR spectrum (–34°C), δ_C, ppm: 4.0 (**Me**C≡C), 21.2 (10-Me$_{eq}$), 26.8 (10-Me$_{ax}$), 43.1 (C^{10}); 76.6, 78.0, 84.8 (C^9, C≡C); 123.86, 123.89, 125.9, 126.9, 127.5, 127.8, 128.5, 129.2 (C^1–C^8)**; 131.1, 131.6, 136.2, 141.5 (C^{4a}, C^{4b}, C^{8a}, C^{10a}).**

Conformer **IIb″**. ^{1}H NMR spectrum (–34°C), δ, ppm: 0.94 s (10-Me$_{ax}$), 1.65 s (10-Me$_{eq}$), 1.54 s (MeC≡C), 2.59 s (9-OH$_{eq}$), 7.30–7.55 m (1-H, 2-H, 3-H, 6-H, 7-H), 7.71–7.84 (4-H, 5-H, 8-H). ^{13}C NMR spectrum (–34°C), δ_C, ppm: 3.8 (MeC≡C), 20.6 (10-Me$_{eq}$), 22.6 (10-Me$_{ax}$), 43.2 (C^{10}); 73.4, 79.9, 80.2 (C^9, C≡C); 123.6, 123.7, 123.8, 124.6, 126.7, 127.9, 128.0, 128.1 (C^1–C^8)**; 131.90, 131.93, 138.9, 143.0 (C^{4a}, C^{4b}, C^{8a}, C^{10a}).**

10,10-Dimethyl-9-phenylethynyl-9,10-dihydrophenanthren-9-ol (IIc) was synthesized by reaction of phenylethynyllithium (4 mmol, 10 ml of a 1.0 M solution in THF; Aldrich) with a solution of 0.505 g (2.27 mmol) of 10,10-dimethyl-9,10-dihydrophenanthren-9-one in 5 ml in THF under the conditions described above for the synthesis of **IIa**, but the mixture was stirred at 0°C for 25 min. The mixture was treated with 20 ml of a saturated aqueous solution of ammonium chloride, and the subsequent treatment (as in the isolation of **IIa**) gave 0.735 g (quantitative yield) of alcohol **IIc** as a yellow viscous oily substance which solidified on storage. The product was purified by recrystallization from a mixture of 20 ml of hexane and 3.5 ml of chloroform. Slightly colored crystals were filtered off and washed with hexane. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3306 (≡C–H), 2228 (C≡C), 3590 (OH). Found: *m*/*z* 324.1516 $[M]^+$. $C_{24}N_{20}O$. Calculated: *M* 324.1514.

Conformer **IIc′**. ^{1}H NMR spectrum (–34°C), δ, ppm: 1.18 s (10-Me$_{ax}$), 1.88 s (10-Me$_{eq}$), 2.35 s (9-OH$_{ax}$), 7.32–7.69 m (1-H, 2-H, 3-H, 6-H, 7-H, Ph), 7.82–7.91 m (4-H, 5-H), 8.10 d (8-H, *J* = 7.5 Hz). ^{13}C NMR spectrum (–40°C), δ_C, ppm: 21.4 (10-Me$_{eq}$), 27.0 (10-Me$_{ax}$), 43.3 (C^{10}), 77.0 (C^9), 88.1 and 88.2 (C≡C), 122.0 (C^i); 123.9, 124.0, 125.9, 127.0, 127.5, 127.9, 128.5, 128.6, 129.4 (C^1–C^8, C^p)**; 128.2 and 131.6 (C^m, C^o)**; 131.1, 131.6, 135.7, 141.4 (C^{4a}, C^{4b}, C^{8a}, C^{10a}).**

Conformer **IIc″**. ^{1}H NMR spectrum (–34°C), δ, ppm: 1.02 s (10-Me$_{ax}$), 1.74 s (10-Me$_{eq}$), 2.78 s (9-OH$_{eq}$), 7.03 d (*o*-H, *J* = 7 Hz), 7.14 t (*m*-H, *J* = 7 Hz), 7.19 t (*p*-H, *J* = 7 Hz), 7.32–7.69 m (1-H, 2-H, 3-H, 6-H, 7-H), 7.72–7.91 (4-H, 5-H, 8-H). ^{13}C NMR spectrum (–34°C), δ_C, ppm: 20.7 (10-Me$_{eq}$), 22.4 (10-Me$_{ax}$), 43.7 (C^{10}), 73.8 (C^9), 83.4 and 89.9 (C≡C), 121.8 (C^i), 123.8–131.6 (C^1–C^8, C^o, C^m, C^p); 132.1, 132.4, 138.2, 142.8 (C^{4a}, C^{4b}, C^{8a}, C^{10a}).**

10,10-Dimethyl-9-(3,3,3-trifluoroprop-1-yn-1-yl)-9,10-dihydrophenanthren-9-ol (IId). Gaseous 3,3,3-trifluoroprop-1-yne (Aldrich) was passed over a period of 25 min at a flow rate of no less than 7 ml/min through a solution of ethylmagnesium bromide [prepared from 0.204 g (8.4 mmol) of magnesium turnings and 1.02 g (9.36 mmol) of ethyl bromide in 10 ml of diethyl ether] maintained at room temperature under argon. The resulting dark solution of 3,3,3-trifluoroprop-1-yn-1-ylmagnesium bromide was cooled to 0°C, a solution of 1.00 g (4.5 mmol) of 10,10-dimethyl-9,10-dihydrophenanthren-9-one in

30 ml of diethyl ether was added dropwise under stirring over a period of 30 min, and the mixture was stirred for 2 h at room temperature and left overnight. After appropriate treatment, a dark oily material was isolated, and it rapidly crystallized to form fine crystals (1.4 g, 98.4%). The product was dissolved on heating in 100 ml of hexane, the solution was clarified with charcoal and filtered, and the filtrate was evaporated by half. After cooling in an ice bath, colorless crystals separated (0.26 g). The mother liquor was evaporated to a volume of 20 ml to isolate an additional portion (0.74 g) of slightly colored crystals. Further evaporation gave the third portion, 0.32 g of **IId** as light brown crystals. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3586 (OH), 2259 (C≡C). Found: *m/z* 316.1066 $[M]^+$. $C_{19}H_{15}F_3O$. Calculated: *M* 316.1070.

Conformer **IId′**. ^{1}H NMR spectrum (–34°C), δ, ppm: 1.10 s (10-Me$_{ax}$), 1.78 s (10-Me$_{eq}$), 2.36 s (9-OH$_{ax}$), 7.32–7.56 m (1-H, 2-H, 3-H, 6-H, 7-H), 7.78–7.88 m (4-H, 5-H, 8-H). ^{13}C NMR spectrum (–34°C), δ_C, ppm: 21.1 and 26.7 (10-Me), 43.1 (C^{10}), 76.6 (C^9); 124.0, 124.3, 125.8, 127.0, 127.3, 128.2, 128.9, 130.1 (C^1–C^8)**; 130.6, 131.6, 133.5, 140.2 (C^{4a}, C^{4b}, C^{8a}, C^{10a})**; 86.9 q (CF_3C≡**C**, J_{CF} = 6 Hz), 75.1 q (CF_3**C**≡C, J_{CF} = 53 Hz), 113.7 q (CF_3, J_{CF} = 258 Hz). ^{19}F NMR spectrum (–34°C): δ_F –49.6 ppm, s.

Conformer **IId″**. ^{1}H NMR spectrum (–34°C), δ, ppm: 0.94 s (10-Me$_{ax}$), 1.66 s (10-Me$_{eq}$), 2.83 s (9-OH$_{eq}$), 7.32–7.56 m (1-H, 2-H, 3-H, 6-H, 7-H), 7.68–7.88 m (4-H, 5-H, 8-H). ^{19}F NMR spectrum (–34°C): δ_F –49.8 ppm, s.

Generation of carbocations in superacid medium. A 5-mm NMR ampule was charged with 0.13 ml of HSO_3F and cooled to –30 to –50°C, and a triple volume of SO_2ClF was condensed thereto. The mixture was stirred and cooled to –95°C, a solution of 20–30 mg of compound **IIa**–**IId** in 0.15 ml of CD_2Cl_2 was carefully added, and the mixture was stirred with a glass rod (cooled with liquid nitrogen) until a colored solution was obtained.

Cation IIIa. ^{1}H NMR spectrum (–47°C), δ, ppm: 2.03 s (6H, 9-Me, J_{CH} = 134 Hz), 6.39 s (1H, HC≡C, J_{CH} = 265 Hz), 7.85 t (1H, 6-H, *J* = 7 Hz), 7.93 t (1H, 2-H, *J* = 7 Hz), 8.02 t (1H, 7-H, *J* = 7 Hz), 8.10 d (1H, 8-H, *J* = 8 Hz), 8.65 t (1H, 3-H, *J* = 7 Hz), 8.71 d (1H, 1-H, *J* = 8 Hz), 8.75 d (1H, 4-H, *J* = 8 Hz), 8.83 d (1H, 5-H, *J* = 8 Hz). ^{13}C NMR spectrum (–57°C), δ_C, ppm: 30.7 (9-Me), 53.2 (C^9); 126.4, 128.1, 128.3, 130.1, 132.4, 135.9, 140.5, 155.1 (C^1–C^8)**; 126.9, 137.8, 150.7, 151.8 (C^{4a}, C^{4b}, C^{8a}, C^{10a})**; 198.6 (C^{10}), 84.2 (HC≡**C**), 127.7 (H**C**≡C).

Cation IIIb. ^{1}H NMR spectrum (–40°C), δ, ppm: 1.98 s (6H, 9-Me, J_{CH} = 134 Hz), 2.88 s (3H, MeC≡C, J_{CH} = 135 Hz), 7.78 t (1H, 6-H, *J* = 7 Hz), 7.87 t (1H, 2-H, *J* = 7 Hz), 7.93 t (1H, 7-H, *J* = 7 Hz), 8.02 d (1H, 8-H, *J* = 8 Hz), 8.54 t (1H, 3-H, *J* = 7 Hz), 8.62 d (1H, 1-H, *J* = 8 Hz), 8.67 d (1H, 4-H, *J* = 8 Hz), 8.75 d (1H, 5-H, *J* = 8 Hz). ^{13}C NMR spectrum (–52°C), δ_C, ppm: 31.6 (9-Me), 53.5 (C^9); 125.9, 127.4, 128.0, 129.7, 131.7, 134.7, 140.3, 152.4 (C^1–C^8)**; 136.8, 126.7, 149.2, 149.4 (C^{4a}, C^{4b}, C^{8a}, C^{10a})**; 203.2 (C^{10}), 88.3 (MeC≡**C**), 152.9 (Me**C**≡C), 8.7 (**Me**C≡C).

Cation IIIc. ^{1}H NMR spectrum (–42°C), δ, ppm: 2.09 s (6H, 9-Me, J_{CH} = 133 Hz), 7.78 t (1H, 6-H, *J* = 7 Hz), 7.78 t (2H, *m*-H, *J* = 7 Hz), 7.86–8.00 m (3H, 2-H, 7-H, *p*-H), 8.04 d (1H, 8-H, *J* = 8 Hz), 8.14 d (2H, *o*-H, *J* = 8 Hz), 8.50 t (1H, 3-H, *J* = 7 Hz), 8.61 d (1H, 1-H, *J* = 8 Hz), 8.67 d (1H, 4-H, *J* = 8 Hz), 8.84 d (1H, 5-H, *J* = 8 Hz). ^{13}C NMR spectrum (–12°C), δ_C, ppm: 32.4 (9-Me), 52.4 (C^9); 126.2, 127.4, 128.1, 129.9, 131.9, 134.6, 139.0, 150.7 (C^1–C^8)**; 127.3, 136.1, 148.0, 148.5 (C^{4a}, C^{4b}, C^{8a}, C^{10a})**; 198.6 (C^{10}), 101.3 (PhC≡**C**), 151.9 (Ph**C**≡C), 120.4 (C^i), 130.8 (C^m), 137.1 (C^o), 138.4 (C^p).

Cation IIId. ^{1}H NMR spectrum (–47°C), δ, ppm: 2.03 s (9-Me, J_{CH} = 135 Hz), 7.92 t (6-H, *J* = 7.6 Hz), 7.95–8.03 (2-H), 8.12 t (7-H, *J* = 7.5 Hz), 8.17 d (8-H, *J* = 8.0 Hz), 8.68 d (1-H, *J* = 8.4 Hz), 8.70–8.85 (3-H, 4-H, 5-H). ^{13}C NMR spectrum (–83°C), δ_C, ppm: 29.4 (9-Me), 52.4 (C^9), 80.9 q (CF_3C≡**C**, J_{CF} = 6 Hz), 108.6 q (CF_3**C**≡C, J_{CF} = 56 Hz), 114.1 q (CF_3, J_{CF} = 261 Hz), 126–158 (C^1–C^8, C^{4a}, C^{4b}, C^{8a}, C^{10a}), 188.9 (C^{10}). ^{19}F NMR spectrum (–47°C): δ_F –53.0 ppm, s.

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