rise to two narrow multiplets at δ 4.56 and 4.77; the ring CH_2 group appears likewise as a narrow multiplet at δ 4.16. Double resonance experiments permitted unequivocal assignment of the structure as shown. The structure determination of the unusual PTAD adduct **32** has relied heavily on its ^1H and ^{13}C NMR data. The A_2B_2 pattern at δ 2.25 and 3.18 and the multiplet at δ 0.80 point to a spiro[2.3]hexane derivative; the spectrum is very similar to that of the spiro[2.3]hexan-4-one (**33**) except for the five-proton multiplet at δ 7.48 for the *N*-phenyl group. The symmetry in the molecule manifests itself in the ^{13}C NMR spectrum; four signals appear in the aliphatic region due to the cyclopropyl and cyclobutyl carbon atoms, whereas the quaternary carbon of the 1,2-diaziridine derivative absorbs at δ 87.6.

The major product from the photooxidation of **1** was the epoxide **51**, which was independently prepared from **1** by epoxidation. Its ^1H NMR displays a high symmetry in the molecule, with two sets of multiplets at δ 1.00 and 1.31, both of which appear as parts of an AA'BB' system.

The ^1H NMR spectrum of the ozonolysis product **59** indicates the presence of one spirocyclopropane group only, and shows two CH_2 groups which are adjacent to one another (two triplets with ^3J = 7.2 Hz each). The unusually low-field absorption for one of the CH_2 groups at δ 4.22 testifies to its neighboring an oxygen atom in the ring. The other CH_2 group absorbs at δ 2.71, a little lower than in a cyclopentanone ring. The strong absorption for the carbonyl group in the IR at 1742 cm^{-1} and those corresponding to the C–O stretch at 1090 and 1240 cm^{-1} as well as its mass spectrum confirm the assigned structure.

Registry No. **1**, 27567-82-4; **8**, 24375-17-5; **9**, 542-92-7; **11**, 40459-58-3; **12**, 592-57-4; **12** (dimer), 6143-79-9; **13**, 40459-60-7; **14**, 40459-59-4; **14** (5',6'-dicarboxylic acid), 111407-33-1; **14** (hydrogenated, 5',6'-dicarboxylic acid), 111291-54-4; **15**, 106-99-0; **16**, 40459-57-2; **17**, 24029-73-0; **18**, 73496-17-0; **19**, 73496-18-1; **20**, 73496-19-2; **22**, 73496-21-6; **23**, 73496-22-7; **24**, 73496-20-5; **27b**, 111291-55-5; **31b**, 111291-56-6; **32**, 73496-25-0; **33**, 20571-15-7; **35**, 73506-18-0; **38**, 73496-27-2; **40**, 73496-26-1; **41**, 73506-17-9; **42**, 73496-28-3; **43**, 290-96-0; **46**, 111323-53-6; **47**, 3716-97-0; **49**, 111291-57-7; **51**, 52952-63-3; **59**, 111291-58-8; CSI, 1189-71-5; PTAD, 4233-33-4; TCNE, 670-54-2; trichloroethylene, 79-01-6; acrylonitrile, 107-13-1; *trans*-dicyanoethylene, 764-42-1; trichloroacetyl chloride, 76-02-8; dichloroacetyl chloride, 79-36-7.

Regioselectivity of Nucleophilic Ring Opening in Substituted Phenanthrene 9,10-Imine and 9,10-Oxide. Molecular Orbital Theoretical Predictions and Experimental Results

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Hückel-type calculations of Wheland's π-localization energies were applied to the prediction of product distributions in the reactions of the model nucleophile N_3^- with various unsymmetrically substituted phenanthrene imines **1B** and oxides **1A**. Experimental work with 3-methyl-, 2-methoxy-, 3-methoxy-, and 3-chlorophenanthrene 9,10-imine as well as with the analogous oxides revealed excellent correlation between the observed product distribution and the calculated differences (magnitude and sign) in π-energies of the common ionic precursors of both the isomeric trans-azido alcohols **2Aa** and **2Ab** and the isomeric trans-azido amines **2Ba** and **2Bb**.

The observation that polycyclic arene oxides react with a variety of cellular nucleophiles awoke special interest in the stereo- and regioselectivity associated with the nucleophilic ring opening of these biologically important oxiranes.[1] By application of several model nucleophiles, trans attack has been established both by spectroscopic[2] and by X-ray diffraction analysis,[3] leading to isomeric products in ratios that could be predicted by MO theoretical calculations.[4,5]

Recently, it has been demonstrated that various polycyclic arene imines act in vitro similarly to arene oxides: they were found to bind to DNA[6] and other cellular constituents and to have exceptionally high mutagenic potencies[7-9] that are clearly related to the activities of the corresponding epoxides.[7] Therefore, we found it imperative to undertake a detailed study on the chemical transformations of the imines in the presence of typical nucleophilic reagents.[10]

In this paper we report a theoretical method for predicting the regioselectivity of attack of nucleophiles on both

(1) Harvey, R. G. *Acc. Chem. Res.* **1981**, *14*, 218 and references cited therein.

(2) For example, see: (a) Jefferey, M.; Yeh, H. J. C.; Jerina, D. M.; DeMarinis, R. M.; Foster, C. H.; Piccolo, D. E.; Berchtold, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 6929. (b) Hylarides, M. D.; Lyle, T. A.; Daub, G. H.; Vander Jagt, D. L. *J. Org. Chem.* **1979**, *44*, 4652. (c) Posner, G. H.; Lever, J. R. *J. Org. Chem.* **1984**, *49*, 2029 and references cited therein.

(3) Complete crystallographic data for *trans*-10-azido-9,10-dihydrophenanthren-9-ol (**2**, R = H, X = O), including tables of the positional and thermal parameters, bond lengths, bond angles, and ORTEP and spectroscopic drawings are presented as supplementary material (see paragraph at the end of the paper about supplementary material).

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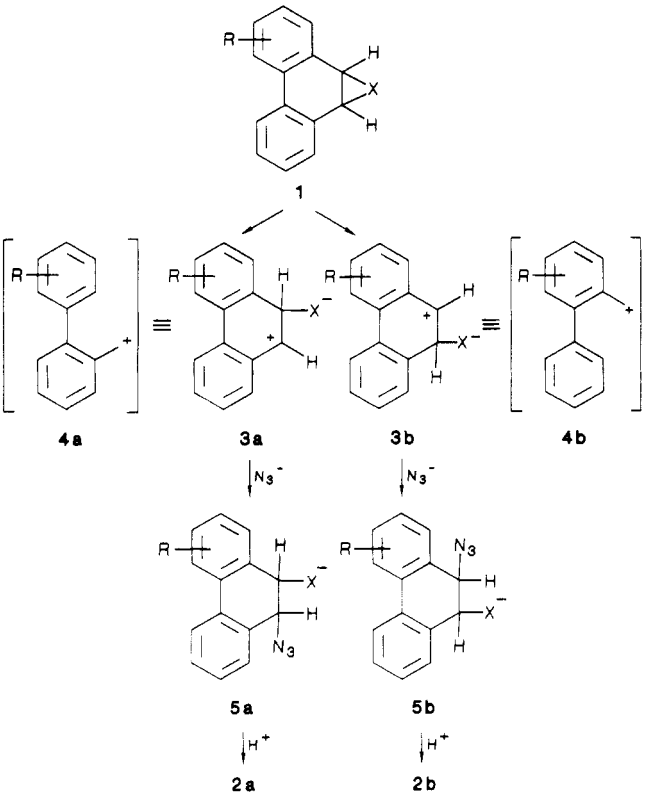
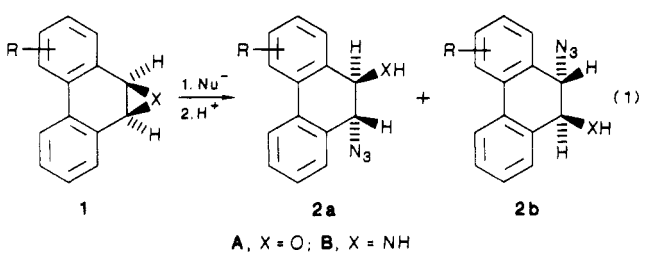
0022-3263/88/1953-0161$01.50/0

Scheme I



asymmetrically substituted phenanthrene 9,10-imines **1B** and phenanthrene oxides **1A**.



A, X = O; B, X = NH

Results and Discussion

The method of Harvey et al. for calculation of the regioselectivity of nucleophilic ring opening in arene oxides[4,5] that employs Dewar reactivity numbers N_t[11] has already been found applicable to various unsubstituted polycyclic systems.[12-14] It proved, however, unsuitable for *substituted* aromatics that differ in their electronic as well as positional nature rather than in the structure of the polycyclic skeleton.

Therefore, we chose for our calculations to revert to Wheland's seminal model[15] and recast it in a form that bears upon the regioselectivity problem at hand. Since Wheland's model of reactivity is static and π-electronic, assumptions and approximations are unavoidable. In the first place we assume that in the transformation of phenanthrene imines **1B** or phenanthrene oxides **1A** to the corresponding amino azides and amino alcohols by the mechanism outlined in Scheme I, bond C–X breaking precedes the C–N_3 bond formation. In other words, **3a** and **3b** are our conceptual equivalents of Wheland's "σ-complexes". Next we assume that the nature of the reaction product is determined at the early stage of the C–X bond breaking: if **3a** is thermodynamically more stable than **3b**, the ultimate product should be enriched with **2a**. Otherwise, **2b** is expected to prevail. Third, the effect of the H–C–X^- grouping on the molecular energy is considered similar in **3a** and **3b**, so that the energy difference ΔE(**3b** – **3a**) is of π-electronic origin and may be equated to ΔE(**4b** – **4a**). This implies that the ring opening of the phenanthrene imines and oxides would show exactly the same regioselectivity. The fourth assumption is that Hückel-type calculations, including parameters to represent atoms and bonds in the substituents R, can furnish the sign of ΔE and classify substituents by the magnitude of their effect.

Chart I

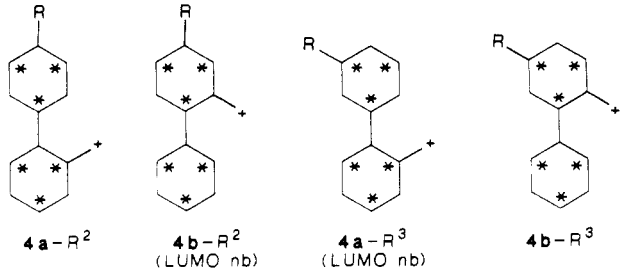


Table I. Results of Computation

R	LUMO of **4a**[a]	LUMO of **4b**[a]	preferred species	ΔE(**4a**;-**4b**) (β units)
2-CN	b	nb	**4a**	0.001
3-CN	nb	b	**4a**	0.001
2-$COOCH_3$	b	nb	**4b**	0.001
3-$COOCH_3$	nb	b	**4a**	0.008
3-Cl	nb	a	**4b**	0.008
2-OCH_3	a	nb	**4a**	0.019
3-CH_3	nb	a	**4b**	0.022
3-OCH_3	nb	a	**4b**	0.068

[a] a, antibonding; b, bonding; nb, nonbonding.

Eight structures of type **1** were examined (making in all 16 calculations). Some of the corresponding arene imines and oxides were actually synthesized and reacted with N_3^- to check the predictions (vide infra).

In the unsubstituted phenanthrene imine (**1B**, R = H) and oxide (**1A**, R = H), the four species shown in Chart I are identical. There are 13 π-levels, of which 6 are occupied. By numbering the molecular orbitals ϕ(i) from the lowest upward, LUMO is ϕ(7) and nonbonding—this being an odd-alternant. In the substituted phenanthrene imines and oxides (R $\neq$ H), the four structures differ one from each other. Let R contain M π-centers and contribute m π-electrons. Then, there are M + 13 π-levels (not necessarily an odd number of levels) and LUMO is $\phi(^1/_2m + 7)$ (not necessarily nonbonding). It is nonbonding (as for R = H) if the exocyclic apex and the substituent-bearing apex belong to the same starring set (**4b**-R^2, **4a**-R^3). Otherwise LUMO is shifted and becomes either bonding or antibonding (**4a**-R^2, **4b**-R^3). Concurrently, the occupied MO's (not all of them) shift by interaction with the substituent and thus modify the total π-energy $[2\sum(\text{occ.})e_i]$. The sense and extent of the change is determined by the

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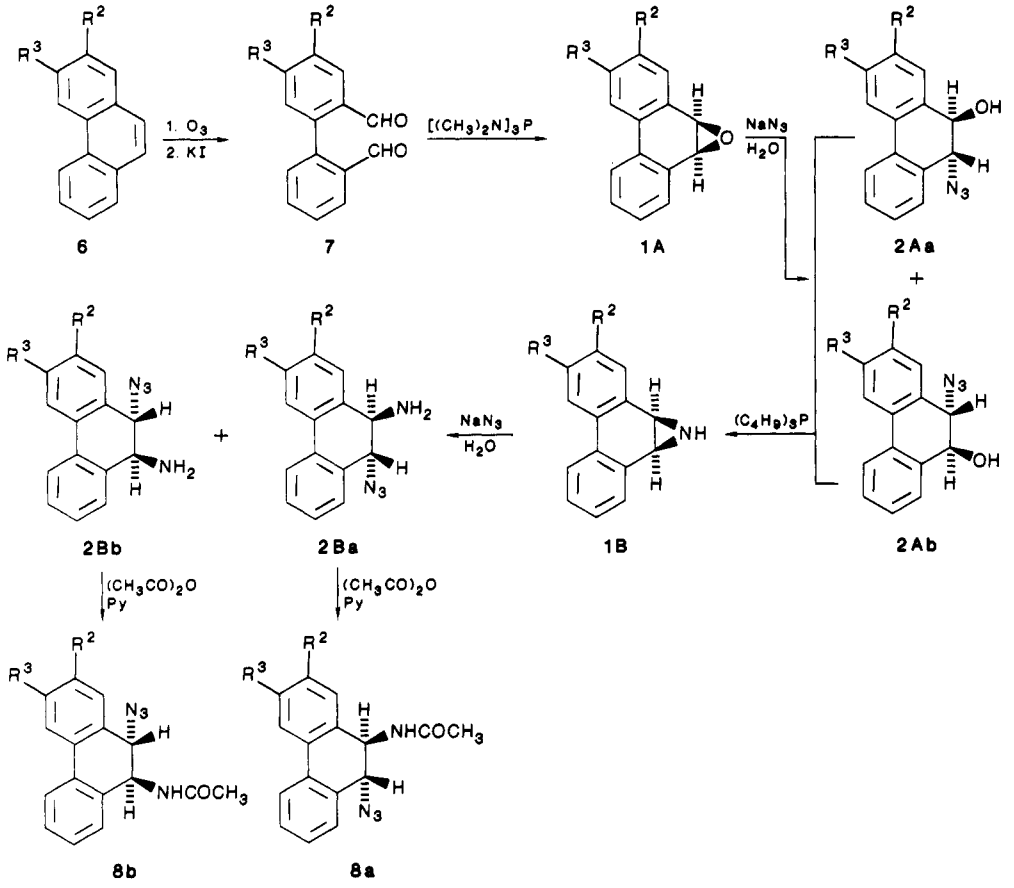
(15) (a) Wheland, G. W. *J. Am. Chem. Soc.* **1942**, *64*, 900. (b) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; Benjamin: New York, 1966; pp 297–305.

Scheme II[a]



[a] I, R^2 = H, R^3 = CH_3; II, R^2 = OCH_3, R^3 = H; III, R^2 = H, R^3 = OCH_3; IV, R^2 = H, R^3 = Cl.

parameters chosen to represent R. We have noticed that when LUMO has become antibonding in **4a**-R^2 or in **4b**-R^3, the species is stabilized with respect to the alternatives **4b**-R^2 and **4a**-R^3, respectively. The opposite was found for a bonding LUMO, except for one case, where R = 2-CN. The parameters for calculation of ΔE(**4a**;**4b**) were taken from previous studies[16,17] without adjustment.[18]

The results of the Hückel calculations are summarized in Table I and can be grouped into three classes. (a) The two computed intermediates **4a** and **4b** have very close energies (R = 2-CN, 3-CN, 2-$COOCH_3$). Therefore, in these cases it is expected that the arene imine and oxides give almost equal amounts of **5a** and **5b**. (b) When the differences in energy are small (R = 2-OCH_3, 3-Cl, 3-CH_3, 3-$COOCH_3$), an excess of one product is expected. (c) A marked difference between the energies of the two intermediates (R = 3-OCH_3) implies the formation of a single product.

Four phenanthrene oxides of type **1A**, where R = 3-Cl, 2-OCH_3, 3-OCH_3, 3-CH_3, and four phenanthrene imines **1B**, with R = 3-Cl, 2-OCH_3, 3-OCH_3, 3-CH_3, were chosen for experimental verification of these predictions. Their syntheses and reactions with N_3^- are outlined in Scheme II.

The substituted phenanthrenes **6** were reacted with ozone and KI to give biphenyldicarboxaldehydes **7**, which, in turn, were transformed into the corresponding phenanthrene oxides **1A** by treatment with Mark's reagent, tris(dimethylamino)phosphine. Reaction with sodium azide in aqueous acetone formed mixtures of the trans-azido alcohols **2Aa** and **2Ab** that cyclized in the presence of tri-*n*-butylphosphine to yield the substituted phenanthrene 9,10-imines **1B**. Conversion of the latter into amino azides **2Ba** and **2Bb** was accomplished with NaN_3 under phase-transfer conditions in the presence of tetrabutylammonium hydrogen sulfate. Since **2Ba** and **2Bb** proved air- and light-sensitive they were immediately acetylated to form stable **8a** and **8b**.

The ratios of the azido alcohols (**2Aa**:**2Ab**) as well as those of the *N*-acetylamino azides (**8a**:**8b**) were determined from the lanthanide shift reagent mediated 200-MHz ^1H NMR spectra. By application of 1–2 equiv of europium(III) tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate), (Eu(fod)), the narrow region of the aromatic proton resonance peaks of <1 ppm extended to 2–3 ppm with sufficiently large peak separations to allow accurate determination of the isomers. In addition, the resonances of the H9 and H10 protons were shifted downfield as far as to δ 16. It should be noted that although both hydroxy and azido functions in **2Aa** and **2Ab**, and both the acetylamino and N_3 groups in **8a** and **8b**, are capable of coordination with the lanthanide shift reagent, the effect of the europium compound on the chemical shifts of H9 and H10 is different. Thus, in the azido alcohols, the C*H*OH

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(18) When δ(Y) is defined by the position α(Y) = α(C) + δ(Y)β(C—C), η(C—Y) by β(C—Y) = η(C—Y)β(C—C), and the δ value of the atom that carries Y is denoted by δ^*(Y), the required parameters are CH_3, δ[C(CH_3)] = 0, η(C≡H_3) = 2, δ(H_3) = –0.2, δ^* = –0.1, η[C(CH_3)—C] = 0.7; —Ō— (in OCH_3, $OCOCH_3$), δ(O) = 2 (1.9 in OCH_3 owing to the CH_3 δ^*), η(C—O) = 0.9; = 0 (in $OCOCH_3$), δ(O) = 0.7, η(C=O) = 2; C≡N, δ(C≡) = 0.1, η(C≡N) = 1.42, δ(≡N) = 0.44; :Cl, δ(Cl) = 2.2, η(C—Cl) = 0.7, δ^* = 0.2.

Table II. Product Distribution in Azide-Mediated Ring Opening in Several Substituted Phenanthrene Oxides 1A[a] and Phenanthrene Imines 1B[a]

	product distribution (%)[b]			product distribution (%)[c]	
starting matl	**2Aa**	**2Ab**	starting matl	**2Ba**	**2Bb**
1A-I	34	66	**1B**-I	34	66
1A-II	68	32	**1B**-II	68	32
1A-III		100	**1B**-III		100
1A-IV	46	54	**1B**-IV	46	54

[a] Under the reaction conditions given in the Experimental Section. [b] Obtained by integration of the ^{1}H NMR spectra of the mixtures of **2Aa** and **2Ab**. [c] Deduced from the ^{1}H NMR spectra of the mixtures of **8a** and **8b**.

signals are the ones that are most affected,[19] and in the acetylamino azides the largest shifts correspond to the C*H*NHCOCH$_3$[20] peaks.

The product distribution in the reaction of N_3^- with the four substituted phenanthrene oxides **1A** and the four phenanthrene imines **1B** are summarized in Table II. The data indicate that the ratios of the isomeric azido alcohols obtained from the arene oxides are *identical* with the ratios of the amino azides formed from the corresponding imines, in spite of the fact that different methods were employed in the ring opening of the aziridines and of the oxides. This observation fully justifies the above assumption that the energy differences ΔE(**3b** - **3a**) represent ΔE(**4b** - **4a**).

Comparison of Tables I and II reveals an excellent correlation between the theoretical predictions and the experimental results. The calculations for ring opening of **1A**-IV and **1B**-IV furnish a slight difference in ΔE(**4b** - **4a**) of 0.008 β. The relative abundances of **2Aa**-IV and **2Ab**-IV (as well as **2Ba**-IV and **2Bb**-IV) were found to be 46% and 54%, respectively. The somewhat greater energy difference for the products of **1A**-I (or **1B**-I) (0.022 β) parallels the relative yield of 34% of **2Aa**-I (or **2Ba**-I) and 66% of **2Ab**-I (or **2Bb**-I). The calculated data for **1A**-I and **1A**-II were of similar magnitude but of opposite signs. Thus, it is understandable that the relative yield of **2Aa**-I resembles that of **2Ab**-II and that the abundance of **2Ab**-I is almost the same as that of **2Aa**-II. The very high energy difference for the 3-methoxyphenanthrene oxide and imine (**1A**-III and **1B**-III, respectively) interpret the exclusive formation of **2Ab**-III from **1A**-III and of **2Bb**-III from **1B**-III.

Finally it should be recalled that the regioselectivity in nucleophilic ring opening of the "linear" analogues of **1A** (i.e., the substituted stilbene oxides) follows different rules than the cleavage of our polycyclic compounds; e.g., the reaction of $LiAlH_4$,[21] as well as of $(C_2H_5)_2Mg$,[22] with *trans*-1-(4-chlorophenyl)-2-phenylethylene oxide and with *trans*-1-phenyl-2-(4-tolyl)ethylene oxide led to products with *opposite* regioselectivities. Furthermore, while in our system the product distribution could be reversed by changing the positional nature of the substituents (as in **1A**-II and **1A**-III), the ratio of isomeric products in nucleophilic ring opening of stilbene oxides was shown to be affected only by the electronic nature and not by the position of the substituents.[23] In conclusion, the few comparative studies on the attack of nucleophiles on nonaromatic ethylene epoxides and imines indicated that unlike the reactions in the phenanthrene series, the ring-opening processes follow completely different steric courses.[24]

Experimental Section

3-Methyl-,[25] 2-methoxy-,[26] 3-methoxy-,[26] and 3-chlorophenanthrene[25] (**6**-I, **6**-II, **6**-III, and **6**-IV), 5-methyl-,[27] 4-methoxy-,[26] and 5-methoxy[1,1′-biphenyl]-2,2′-dicarboxaldehyde[26] (**7**-I, **7**-II, and **7**-III), 1a,9b-dihydro-3-methoxyphenanthro[9,10-*b*]oxirene[26] (**1A**-II), and 1a,9b-dihydro-4-methoxyphenanthro[9,10-*b*]oxirene[26] (**1A**-III) were prepared as described in the literature.

5-Chloro[1,1′-biphenyl]-2,2′-dicarboxaldehyde (7-IV). A stream of ozone was passed at −78 °C through a solution of 1.00 g (4.7 mmol) of **6**-IV in 50 mL of CH_2Cl_2 until the entire starting material disappeared (ca. 60 min). After removal of the excess ozone with a stream of oxygen, the reaction mixture was poured into a stirred solution of 2.2 g of sodium iodide in 3 mL of acetic acid. After 24 h the liberated iodine was reduced with 10% aqueous sodium thiosulfate. Phase separation followed by three successive washings of the organic layer with water afforded a yellow oil which was purified by column chromatography on silica gel (40% ether–hexane as eluent) to give 778 mg (68%) of **7**-IV as a pale yellow oil: IR (neat) 1690 cm^{-1} (C=O); 200-MHz ^{1}H NMR ($CDCl_3$) δ 7.331–7.374 (m, 2, H4, H6′), 7.615 (dt, 1, J_o = 8 Hz, J_m = 2 Hz, H4′, or H5′), 7.645 (s, 1, H6), 7.689 (dt, 1, J_o = 8 Hz, J_m = 2 Hz, H4′ or H5′), 8.005 (d, 1, $J_{3,4}$ = 8 Hz, H3), 8.059 (dd, 1, $J_{3',4'}$ = 8 Hz, $J_{3',5'}$ = 2 Hz, H3′), 9.746 (s, 1, C*H*O), 9.864 (s, 1, C*H*O); mass spectrum (68 eV, 110 °C), *m/z* (rel intensity) 246, 244 ($M^{\bullet+}$, 1;3), 218 ($C_{13}H_9{}^{37}ClO^{\bullet+}$, 5.5), 217 ($C_{13}H_8{}^{37}ClO^+$, 35), 216 ($C_{13}H_9{}^{35}ClO^{\bullet+}$, 17), 215 ($C_{13}H_8{}^{35}ClO^+$, 100), 181 ($C_{13}H_8O^{\bullet+}$, 17), 152 ($C_{12}H_8{}^{\bullet+}$, 51). Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.71; H, 3.68; Cl, 14.52. Found: C, 68.44; H, 3.69; Cl, 14.48.

1a,9b-Dihydro-4-methylphenanthro[9,10-*b*]oxirene (1A-I). To a boiling solution of 1.57 g (7 mmol) of **7**-I in 20 mL of CH_2Cl_2 was added under an Ar atmosphere 2.52 g (15.4 mmol) of hexamethylphosphorous triamide. The mixture was refluxed for 90 min, cooled, and concentrated under reduced pressure. The residue was chromatographed on Woelm alumina (activity III) with a 1:4 mixture of ether–hexane as eluent, to give 0.466 g (32%) of **1A**-I as colorless crystals: mp 93–94 °C; 200-MHz ^{1}H NMR ($CDCl_3$) δ 2.374 (s, 3, C*H*$_3$), 4.467 (s, 2, H1a, H9b), 7.188 (d, 1, $J_{2,3}$ = 8 Hz, H3), 7.377 (dt, 1, $J_{6,8}$ = 1 Hz, $J_{7,8,9}$ = 7.5 Hz, H8), 7.472 (dt, 1, $J_{6,7,8}$ = 7.5 Hz, $J_{7,9}$ = 2 Hz, H7), 7.537 (d, 1, $J_{2,3}$ = 8 Hz, H2), 7.643 (dd, 1, $J_{7,9}$ = 2 Hz, $J_{8,9}$ = 7.5 Hz, H9), 7.919 (s, 1, H5), 8.105 (d, 1, $J_{6,7}$ = 7.5 Hz, H6); mass spectrum (68 eV, 110 °C), *m/z* (rel intensity) 209 [(M + H)$^+$, 35], 208 ($M^{\bullet+}$, 100) 207 [(M − H)$^+$, 29], 192 ($C_{15}H_{12}{}^{\bullet+}$, 4), 191 ($C_{15}H_{11}{}^+$, 5), 180 ($C_{14}H_{12}{}^{\bullet+}$, 39), 179 ($C_{14}H_{11}{}^+$, 47), 165 ($C_{13}H_9{}^+$, 98), 152 ($C_{12}H_8{}^{\bullet+}$, 17). Anal. Calcd for $C_{15}H_{12}O$: C, 86.54; H, 5.77. Found: C, 86.29; H, 6.05.

As partial ring opening occurred during the purification of the epoxide on alumina, the *crude* product was applied in the subsequent step.

4-Chloro-1a,9b-dihydrophenanthro[9,10-*b*]oxirene (1A-IV) was obtained by the procedure described for **1A**-I. Purification by chromatography on Woelm alumina (activity III) with a 2:3 mixture of ether–hexane as eluent afforded 74% of **1A**-IV. Unlike **1A**-I, which underwent partial ring opening during chromatography, the chloro compound was perfectly stable. **1A-IV**: colorless crystals, mp 124–125 °C; 200-MHz ^{1}H NMR ($CDCl_3$) δ 4.538 and

(19) While the H9 NMR signal of unsubstituted *trans*-azido-9,10-dihydrophenanthren-9-ol (**2A**, R = H) at δ 4.747 is shifted downfield by $\Delta\delta_{H9}$ = 0.325, 0.495, and 0.785 ppm, in the presence of 1/30, 1/20, and 1/10 equiv of Eu(fod) (2 h), respectively, the H10 peak at δ 4.645 is shifted only by $\Delta\delta_{H10}$ = 0.229, 0.356 and 0.569 ppm in the presence of the same respective quantities of the lanthanide shift reagent.

(20) The H9 NMR peak of *trans*-9-(acetylamino)-10-azido-9,10-dihydrophenanthrene (**8a**, $R^2 = R^3$ = H) is shifted downfield from δ 5.185 by $\Delta\delta_{H9}$ = 0.487 and 0.759 ppm when 1/30 and 1/20 equiv of Eu(fod) (2 h) are applied, respectively. The H10 signal at δ 4.745 is shifted by 1/30 and 1/20 equiv of the shift reagent by $\Delta\delta_{H10}$ = 0.260 and 0.395 ppm, respectively.

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4.564 (AB q, 2, J_{AB} = 4 Hz, H1a, H9b), 7.349 (dd, 1, $J_{2,3}$ = 8 Hz, $J_{3,5}$ = 2 Hz, H3), 7.399 (dt, 1, J_o = 7 Hz, J_m = 2 Hz, H7 or H8), 7.490 (dt, 1, J_o = 7 Hz, J_m = 2 Hz, H7 or H8), 7.594 (d, 1, $J_{2,3}$ = 8 Hz, H2), 7.676 (dd, 1, $J_{7,9}$ = 2 Hz, $J_{8,9}$ = 8 Hz, H9), 8.053 (d, 1, $J_{6,7}$ = 7 Hz, H6), 8.075 (d, 1, $J_{3,5}$ = 2 Hz, H5); mass spectrum (68 eV, 120 °C), *m/z* (rel intensity) 231, 229 [$(M + H)^+$, 5; 15), 230, 228 ($M^{\bullet+}$, 33, 100), 165 ($C_{13}H_9^+$, 64), 152 ($C_{12}H_8^{\bullet+}$, 11). Anal. Calcd for $C_{14}H_9ClO$: C, 73.52; H, 3.94; Cl, 15.54. Found: C, 73.32; H, 4.08; Cl, 15.55.

Reaction of Phenanthrene Oxides with Sodium Azide. A mixture of 0.44 mmol of the epoxide **1A** in 20 mL of acetone (A.R. grade) and 0.5 g (7.7 mmol) of NaN_3 in 10 mL of triply distilled water was refluxed for 1 h. The solvents were removed under reduced pressure to dryness and the residue was extracted with CH_2Cl_2. The organic solution was washed (3×) with water, dried ($MgSO_4$), and concentrated. Chromatography on silica gel afforded colorless mixtures of the trans-azido alcohols **2Aa** and **2Ab**.

***trans*-10-Azido-9,10-dihydro-6-methyl-9-phenanthrol (2Aa-I) and *trans*-10-azido-9,10-dihydro-3-methyl-9-phenanthrol (2Ab-I)**: overall yield 46% from **7-I**: mp 105–107 °C (from aqueous acetone); IR (Nujol) 3580 (OH), 2100 cm^{-1} (N_3); 200-MHz ^1H NMR (6.7 × 10^{-5} mol of **2Aa-I** + **2Ab-I** and 3.3 × 10^{-5} mol of Eu(fod) in 0.5 mL of $CDCl_3$ after 2 h) data for **2Aa-I** (34% of the mixture) δ 2.917 (s, 3, CH_3), 7.872 (d, 1, $J_{7,8}$ = 7 Hz, H7), 7.962 (t, 1, $J_{1,2,3}$ = 8 Hz, H2), 8.134 (t, 1, $J_{2,3,4}$ = 8 Hz, H3), 8.837 (d, 1, $J_{1,2}$ = 8 Hz, H1), 8.867 (s, 1, H5), 9.079 (d, 1, $J_{3,4}$ = 4 Hz, H4), 9.587 (br s, 1, H10), 9.745 (d, 1, $J_{7,8}$ = 7 Hz, H8), 11.495 (br s, 1, H9), data for **2Ab-I** (66% of the mixture) δ 2.859 (s, 3, CH_3), 7.781 (d, 1, $J_{1,2}$ = 8 Hz, H2), 8.030 (t, 1, $J_{6,7,8}$ = 8 Hz, H7), 8.279 (t, 1, $J_{5,6,7}$ = 8 Hz, H6), 8.742 (d, 1, $J_{1,2}$ = 8 Hz, H1), 8.867 (s, 1, H4), 9.023 (d, 1, $J_{5,6}$ = 8 Hz, H5), 9.565 (br s, 1, H10), 9.788 (d, 1, $J_{7,8}$ = 8 Hz, H8), 11.328 (br s, 1, H9); mass spectrum of **2Aa-I** + **2Ab-I** (70 eV, 100 °C), *m/z* (rel intensity) 252 [$(M + H)^+$, 2], 251 ($M^{\bullet+}$, 11), 223 [$(M - N)^{\bullet+}$, 10], 222 ($C_{15}H_{12}NO^+$, 10), 208 ($C_{15}H_{12}O^{\bullet+}$, 7), 195 ($C_{14}H_{13}N^{\bullet+}$, 20), 194 ($C_{14}H_{12}N^+$, 100), 193 ($C_{15}H_{13}^+$, 7), 180 ($C_{14}H_{12}^{\bullet+}$, 11), 165 ($C_{13}H_9^+$, 20), 152 ($C_{12}H_8^{\bullet+}$, 16). Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.71; H, 5.18. Found: C, 71.77; H, 5.36.

***trans*-10-Azido-9,10-dihydro-7-methoxy-9-phenanthrol (2Aa-II) and *trans*-10-azido-9,10-dihydro-2-methoxy-9-phenanthrol (2Ab-II)**: overall yield of the mixture of isomers was 25% from **7-II**; mp 103–104 °C (from aqueous acetone); IR (Nujol) 3580 (OH), 2097 cm^{-1} (N_3); 200-MHz ^1H NMR (2 × 10^{-5} mol of **2Aa-II** + **2Ab-II** and 4 × 10^{-5} mol of Eu(fod) in 0.5 mL of $CDCl_3$ after 2 h) data for **2Aa-II** (68% of the mixture) δ 4.105 (s, 3, OCH_3), 7.805 (dd, 1, $J_{5,6}$ = 8 Hz, $J_{6,8}$ = 2.5 Hz, H6), 7.858 (d, 1, $J_{1,2}$ = 7 Hz, H1), 7.923 (t, 1, $J_{2,3,4}$ = 7 Hz, H3), 8.071 (t, 1, $J_{1,2,3}$ = 7 Hz, H2), 8.823 (d, 1, $J_{3,4}$ = 7 Hz, H4), 8.892 (d, 1, $J_{5,6}$ = 8 Hz, H5), 9.355 (d, 1, $J_{6,8}$ = 2.5 Hz, H8), 9.628 (br s, 1, H10), 11.216 (br s, 1, H9), data for **2Aa-II** (32% of the mixture) δ 4.105 (s, 3, OCH_3), 7.670 (dd, 1, $J_{1,3}$ = 2.5 Hz, $J_{3,4}$ = 9 Hz, H3), 8.007 (t, 1, $J_{5,6,7}$ = 7 Hz, H6), 8.251 (t, 1, $J_{6,7,8}$ = 7 Hz, H7), 8.425 (d, 1, $J_{1,3}$ = 2.5 Hz, H1), 8.908 (d, 1, $J_{5,6}$ = 7 Hz, H5), 8.965 (d, 1, $J_{3,4}$ = 9 Hz); mass spectrum of **2Aa-II** + **2Ab-II** (68 eV, 110 °C), *m/z* (rel intensity) 268 [$(M + H)^+$, 10], 267 ($M^{\bullet+}$, 46), 239 [$(M - N_2)^{\bullet+}$, 6], 238 ($C_{15}H_{12}NO_2^+$, 9), 225 ($C_{15}H_{13}O_2^+$, 8), 211 ($C_{14}H_{13}NO^{\bullet+}$, 19), 210 ($C_{14}H_{12}NO^+$, 100), 195 ($C_{14}H_{11}O^+$, 13), 167 ($C_{12}H_7O^+$, 38), 165 ($C_{13}H_9^+$, 15), 152 ($C_{12}H_8^{\bullet+}$, 22). Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.42; H, 4.87. Found: C, 67.46; H, 4.81.

***trans*-10-Azido-9,10-dihydro-3-methoxy-9-phenanthrol (2Ab-III)**: overall yield 16% from **7-III**; mp 129–131 °C (from aqueous acetone); IR (Nujol) 3580 (OH), 2094 cm^{-1} (N_3); 200-MHz ^1H NMR (2 × 10^{-5} mol of **2Ab-III** and 2 × 10^{-5} mol of Eu(fod) in 0.5 mL of $CDCl_3$ after 2 h) δ 4.180 (s, 3, OCH_3), 7.405 (dd, 1, $J_{1,2}$ = 8 Hz, $J_{2,4}$ = 2 Hz, H2), 7.937 (t, $J_{6,7,8}$ = 7 Hz, H7), 8.132 (t, 1, $J_{5,6,7}$ = 7 Hz, H6), 8.381 (d, 1, $J_{2,4}$ = 2 Hz, H4), 8.509 (d, 1, $J_{1,2}$ = 8 Hz, H1), 8.614 (br s, 1, H10), 8.776 (d, 1, $J_{5,6}$ = 7 Hz, H5), 9.393 (d, 1, $J_{7,8}$ = 7 Hz, H8), 10.202 (br s, 1, H9); mass spectrum (70 eV, 110 °C), *m/z* (rel intensity) 268 [$(M + H)^+$, 5], 267 ($M^{\bullet+}$, 26), 239 [$(M - N_2)^+$, 16], 238 ($C_{15}H_{12}NO_2^+$, 18), 252 ($C_{15}H_{13}O_2^+$, 51), 211 ($C_{14}H_{13}NO^{\bullet+}$, 22), 210 ($C_{14}H_{12}NO^+$, 100), 195 ($C_{14}H_{11}O^+$, 14), 167 ($C_{12}H_7O^+$, 37), 165 ($C_{13}H_9^+$, 13), 152 ($C_{12}H_8^{\bullet+}$, 19). Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.42; H, 4.87. Found: C, 67.38; H, 5.00.

***trans*-10-Azido-6-chloro-9,10-dihydro-9-phenanthrol (2Aa-IV) and *trans*-10-azido-3-chloro-9,10-dihydro-9-phenanthrol (2Ab-IV)**: yield 77% (from **1A-IV**); mp 138–140 °C; IR (Nujol) 3593 (OH), 2093 cm^{-1} (N_3); 300-MHz ^1H NMR (1.5 × 10^{-5} mol of **2Aa-IV** + **2Ab-IV** and 3 × 10^{-5} mol of Eu(fod) in 0.5 mL of $CDCl_3$ after 2 h) data for **2Aa-IV** (46% of the mixture) δ 7.812 (dt, 1, $J_{1,2,3}$ = 8 Hz, $J_{2,4}$ = 2 Hz, H2), 7.968 (dd, 1, $J_{7,8}$ = 7 Hz, $J_{5,7}$ = 2 Hz, H7), 8.132 (t, 1, $J_{2,3,4}$ = 8 Hz, H3), 8.555 (d, $J_{1,2}$ = 8 Hz, H1), 8.761 (d, 1, $J_{4,3}$ = 8 Hz, H4), 8.767 (s, 1, H5), 8.858 (br s, 1, H10), 9.600 (d, 1, $J_{7,8}$ = 7 Hz, H8), 10.542 (br s, 1, H9), data for **2Ab-IV** (54% of the mixture) δ 7.872 (dt, 1, $J_{6,7,8}$ = 8 Hz, $J_{5,7}$ = 2 Hz, H7), 7.898 (d, 1, $J_{1,2}$ = 7 Hz, H2), 8.014 (t, 1, $J_{5,6,7}$ = 8 Hz, H6), 8.655 (d, 1, $J_{1,2}$ = 7 Hz, H1), 8.736 (s, 1, H4), 8.742 (d, 1, $J_{5,6}$ = 8 Hz, H5), 8.803 (br s, 1, H10), 9.459 (d, 1, $J_{7,8}$ = 8 Hz, H8), 10.490 (br s, 1, H9); mass spectrum of **2Aa-IV** + **2Ab-IV** (68 eV, 120 °C), *m/z* (rel intensity) 245 ($C_{14}H_{10}{}^{37}ClNO^{\bullet+}$, 3), 243 ($C_{14}H_{10}{}^{35}ClNO^{\bullet+}$, 9), 217 ($C_{13}H_{10}{}^{37}ClN^{\bullet+}$, 6), 216 ($C_{13}H_9{}^{37}ClN^+$, 33), 215 ($C_{13}H_{10}{}^{35}ClN^{\bullet+}$, 19), 214 ($C_{13}H_9{}^{35}ClN^+$, 100), 180 ($C_{13}H_8O^{\bullet+}$, 7), 165 ($C_{13}H_9^+$, 7), 152 ($C_{12}H_8^{\bullet+}$, 19). Anal. Calcd for $C_{14}H_{10}ClN_3O$: C, 61.88; H, 3.68; Cl, 13.07. Found: C, 61.69; H, 3.77; Cl, 13.39.

Preparation of Phenanthrene Imines. To a boiling solution of 3.7 mmol of the mixture of azido alcohols **2Aa** and **2Ab** in 100 mL of degassed hexane was added under Ar 1.2 mL of tri-*n*-butylphosphine. The mixture was refluxed for 45 min and cooled and the hexane removed under reduced pressure. The residue was triturated with cold pentane to give colorless crystals of imine.

1a,9b-Dihydro-4-methyl-1*H*-phenanthro[9,10-*b*]azirine (1B-I) was obtained in 75% yield: mp 147–149 °C (from ether–hexane); 200-MHz ^1H NMR ($CDCl_3$) δ 2.428 (s, 3, CH_3), 3.570 (s, 2, H1a, H9b), 7.148 (d, 1, $J_{2,3}$ = 8 Hz, H3), 7.330 (dt, 1, J_o = 7Hz, J_m = 2 Hz, H7 or H8), 7.366 (dt, 1, J_o = 7 Hz, J_m = 2 Hz, H7 or H8), 7.474 (d, $J_{2,3}$ = 8 Hz, H2), 7.579 (dd, 1, $J_{7,9}$ = 2 Hz, $J_{8,9}$ = 7 Hz, H9), 7.871 (s, 1, H5), 8.061 (d, 1, $J_{6,7}$ = 7 Hz, H6); mass spectrum (68 eV, 90 °C), *m/z* (rel intensity) 207 ($M^{\bullet+}$, 100), 206 ($C_{15}H_{12}N^+$, 34), 192 ($C_{15}H_{12}^{\bullet+}$, 13), 179 ($C_{14}H_{11}^+$, 13), 178 ($C_{14}H_{10}^{\bullet+}$, 14), 165 ($C_{13}H_9^+$, 25). Anal. Calcd for $C_{15}H_{13}N$: C, 86.96; H, 6.28; N, 6.76. Found: C, 86.57; H, 6.34; N, 6.26.

1a,9b-Dihydro-3-methoxy-1*H*-phenanthro[9,10-*b*]azirine (1B-II) was obtained in 44% yield: mp 152–153 °C (from ether–hexane); 300-MHz ^1H NMR ($CDCl_3$) δ 3.516 and 3.562 (AB q, 2, J_{AB} = 5 Hz, H1a, H9b), 3.878 (s, 3, OCH_3), 6.934 (dd, 1, $J_{2,4}$ = 2.5 Hz, $J_{4,5}$ = 9 Hz, H4), 7.121 (d, 1, $J_{2,4}$ = 2.5 Hz, H2), 7.297 (t, 1, $J_{7,8,9}$ = 7 Hz, H8), 7.362 (t, 1, $J_{6,7,8}$ = 7 Hz, H7), 7.570 (d, 1, $J_{8,9}$ = 7 Hz, H9), 7.966 (d, 1, $J_{6,7}$ = 7 Hz, H6), 7.797 (d, 1, $J_{4,5}$ = 9 Hz, H5); mass spectrum (68 eV, 90 °C), *m/z* (rel intensity) 223 ($M^{\bullet+}$, 100), 208 ($C_{15}H_{12}O^{\bullet+}$, 11), 194 ($C_{14}H_{10}O^{\bullet+}$, 12), 193 ($C_{14}H_9O^+$, 15), 181 ($C_{13}H_9O^+$, 17), 180 ($C_{13}H_8O^{\bullet+}$, 66), 165 ($C_{13}H_9^+$, 21), 152 ($C_{12}H_8^{\bullet+}$, 42). Anal. Calcd for $C_{15}H_{13}NO$: C, 80.72; H, 5.83; N, 6.28. Found: C, 80.50; H, 5.89; N, 6.16.

4-Chloro-1a,9b-dihydro-1*H*-phenanthro[9,10-*b*]azirine (1B-IV) was obtained in 76% yield: mp 156–157 °C (from ether–hexane); 300-MHz ^1H NMR ($CDCl_3$) δ 3.592 (d, 2, $J_{1a,9b}$ = 4 Hz), 7.298 (dd, 1, $J_{2,3}$ = 8 Hz, $J_{3,5}$ = 2 Hz, H3), 7.375 (dt, 1, J_o = 7 Hz, J_m = 2 Hz, H7 or H8), 7.401 (dt, J_o = 7 Hz, J_m = 2 Hz, H7 or H8), 7.523 (d, 1, $J_{2,3}$ = 8 Hz, H2), 7.606 (t, 1, $J_{7,9}$ = 2 Hz, $J_{8,9}$ = 7 Hz, H9), 7.996 (dd, 1, $J_{6,7}$ = 7 Hz, $J_{6,8}$ = 2 Hz, H6), 8.025 (d, 1, $J_{3,5}$ = 2 Hz, H5); mass spectrum (68 eV, 90 °C), *m/z* (rel intensity) 229, 227 ($M^{\bullet+}$, 33, 100), 192 ($C_{14}H_{10}N^+$, 9), 165 ($C_{13}H_9^+$, 95). Anal. Calcd for $C_{14}H_{10}ClN$: C, 73.85; H, 4.40; Cl, 15.60, N, 6.15. Found: C, 73.97; H, 4.59; Cl, 16.00; N, 5.69.

Reaction of Phenanthrene Imines with Sodium Azide. A mixture of 0.88 mmol of the appropriate imine **1B**, 70 mg (0.2 mmol) of tetrabutylammonium hydrogen sulfate, 5 mL of triply distilled water, 1 g (15.6 mmol) of NaN_3, and 10 mL of CH_2Cl_2 was stirred under an Ar atmosphere at 25 °C for 24 h. After phase separation the aqueous layer was extracted with CH_2Cl_2 and the combined organic solution washed with water, dried, and concentrated. The residue was chromatographed on Woelm alumina-III (ether as eluent) to give a mixture of colorless azidodihydrophenanthrenamines **2Ba** and **2Bb**.

Since the amines were rather air-sensitive they were transformed immediately into the N-acetyl derivatives. Typically, a solution of 0.55 mmol of the amines in 10 mL of CH_2Cl_2 was stirred for 3 h at room temperature with 1 mL of acetic anhydride and 1.5 mL of anhydrous pyridine. The reaction mixture was diluted with 10 mL of CH_2Cl_2, washed with 5% aqueous HCl, water, 3% aqueous NaOH, and again with water, dried ($MgSO_4$), and con-

centrated. Addition of hexane afforded usually a mixture of pure **8a** and **8b**.

***trans*-10-Azido-9,10-dihydro-6-methyl- and *trans*-10-azido-9,10-dihydro-3-methyl-9-phenanthrenamine (2Ba-I and 2Bb-I)**: yield of the mixture 72%; yellow oil; IR (neat) 3360, 3280 (NH_2), 2095 cm^{-1} (N_3); 200-MHz ^1H NMR ($CDCl_3$) δ 2.423, 2.446 (two s, 3, CH_3), 4.012 (d, 1, $J_{9,10}$ = 4 Hz, H9 or H10), 4.514 (d, 1, $J_{9,10}$ = 4 Hz, H9 or H10), 4.790 (s, 2, NH_2), 7.144–7.477 (m, 5, H1, H2, H3, H7, H8 of **2Ba**-I and H1, H2, H6, H7, H8 of **2Ba**-I), 7.638, 7.688 (two s, 1, H5 of **2Ba**-I and H4 of **2Bb**-I), 7.828, 7.867 (two d, 1, $J = J'$ = 8 Hz, H4 of **2Ba**-I and H5 of **2Bb**-I); mass spectrum (68 eV, 105 °C), m/z (rel intensity) 222 [$(M - N_2)^{\cdot+}$, 42], 221 ($C_{15}H_{13}N_2^+$, 42), 207 ($C_{15}H_{13}N^{\cdot+}$, 41), 206 ($C_{15}H_{12}N^+$, 20), 195 ($C_{14}H_{13}N^{\cdot+}$, 42), 194 ($C_{14}H_{12}N^+$, 100), 193 ($C_{15}H_{13}^+$, 28), 180 ($C_{14}H_{12}^{\cdot+}$, 45), 178 ($C_{14}H_{10}^{\cdot+}$, 18), 165 ($C_{13}H_9^+$, 22), 152 ($C_{12}H_8^{\cdot+}$, 16). Anal. Calcd for $C_{15}H_{14}N_4$: C, 72.00; H, 5.60. Found: C, 71.74; H, 5.91. The mixture of the N-acetyl derivatives **8a**-I and **8b**-I was obtained in 90% yield: mp 171–172 °C (from ether–hexane); IR (Nujol) 3420 (NH), 2090 (N_3), 1670 cm^{-1} (C=O); 200-MHz ^1H NMR (2×10^{-5} mol of **8a**-I + **8b**-I, 2×10^{-5} mol of Eu(fod) in 0.5 mL of $CDCl_3$ after 2 h) data for **8a**-I (34% of the mixture) δ 2.952 (s, 3, CH_3), 7.697 (d, 1, $J_{7,8}$ = 7 Hz, H7), 8.090 (t, 1, $J_{1,2,3}$ = 8 Hz, H2), 8.357 (t, 1, $J_{2,3,4}$ = 8 Hz, H3), 8.638 (d, 1, $J_{1,2}$ = 8 Hz, H1), 8.831 (s, 1, H5), 9.169 (d, 1, $J_{3,4}$ = 8 Hz, H4), 10.111 (d, 1, $J_{7,8}$ = 7 Hz, H8), 10.619 (s, 3, $COCH_3$), 11.151–11.308 (m, 2, H9, H10), 16.351 (s, 1, N*H*), data for **8b**-I (66% of the mixture) δ 3.127 (s, 3, CH_3), 7.849 (t, 1, $J_{7,8}$ = 8 Hz, H7), 7.914 (d, 1, $J_{1,2}$ = 7 Hz, H2), 8.193 (t, 1, $J_{5,6,7}$ = 8 Hz, H6), 8.531 (d, 1, $J_{1,2}$ = 7 Hz, H1), 8.985 (s, 1, H4), 9.020 (d, 1, $J_{5,6}$ = 8 Hz, H5), 10.323 (d, 1, $J_{7,8}$ = 8 Hz, H8), 10.576 (s, 3, $COCH_3$), 11.151–11.308 (m, 2, H9, H10), 16.525 (s, 1, N*H*); mass spectrum of **8a**-I + **8b**-I (70 eV, 130 °C), m/z (rel intensity) 264 [$(M - N_2)^{\cdot+}$, 25], 221 ($C_{15}H_{13}N_2^{\cdot+}$, 84), 205 ($C_{15}H_{11}N^+$, 59), 194 ($C_{14}H_{12}N^+$, 100), 190 ($C_{15}H_{10}^{\cdot+}$, 28), 180 ($C_{14}H_{12}^{\cdot+}$, 15), 179 ($C_{14}H_{11}^+$, 14), 165 ($C_{13}H_9^+$, 15), 152 ($C_{12}H_8^{\cdot+}$, 10). Anal. Calcd for $C_{17}H_{16}N_4O$: C, 69.86; H, 5.54; N, 19.18. Found: C, 69.64; H, 5.54; N, 18.80.

***trans*-10-Azido-9,10-dihydro-7-methoxy- and *trans*-10-azido-9,10-dihydro-2-methoxy-9-phenanthrenamine (2Ba-II and 2Bb-II)**: yield of the mixture 74%; IR (neat) 3358, 3293 (NH_2), 2090 cm^{-1} (N_3); 200-MHz ^1H NMR ($CDCl_3$) δ 1.675 (s, 2, NH_2), 3.869 (s, 3 H, OCH_3), 3.966 (d, 1, $J_{9,10}$ = 5 Hz, H9 or H10), 4.506 (d, 1, J = 5 Hz, H9 or H10), 6.907–6.988 (m, 2, H6, H8 of **2Ba**-II and H1, H3 of **2Bb**-II), 7.312–7.497 (m, 3, H1, H2, H3 of **2Ba**-II and H6, H7, H8 of **2Bb**-II), 7.776 (d, 1, J = 7 Hz, H4 or H5), 7.790 (d, 1, J = 7 Hz, H4 or H5); mass spectrum (68 eV, 90 °C), m/z (rel intensity) 266 ($M^{\cdot+}$, 3), 238 [$(M - N_2)^{\cdot+}$, 14], 237 ($C_{15}H_{13}N_2O^+$, 16), 223 ($C_{15}H_{13}NO^{\cdot+}$, 18), 211 ($C_{14}H_{13}NO^{\cdot+}$, 16), 210 ($C_{14}H_{12}NO^+$, 100), 195 ($C_{14}H_{11}O^+$, 11), 180 ($C_{13}H_8O^{\cdot+}$, 19), 167 ($C_{12}H_7O^+$, 25), 165 ($C_{13}H_9^+$, 8), 152 ($C_{12}H_8^{\cdot+}$, 11). The mixture of N-acetyl derivatives **8a**-II and **8b**-II was obtained in 97% yield: mp 139–141 °C (from ether–hexane); IR (Nujol) 3412 (NH), 2088 (N_3), 1662 cm^{-1} (C=O); 200-MHz ^1H NMR (2×10^{-5} mol of **8a**-II + **8b**-II and 3×10^{-5} mol of Eu(fod) in 0.5 mL of $CDCl_3$, after 2 h) data for **8a**-II (68% of the mixture) δ 3.928 (s, 3, OCH_3), 8.013 (dd, 1, $J_{5,6}$ = 9 Hz, $J_{6,8}$ = 2.5 Hz, H6), 8.041 (dt, 1, $J_{1,2,3}$ = 7 Hz, $J_{2,4}$ = 1 Hz, H2), 8.409 (t, 1, $J_{2,3,4}$ = 7 Hz, H3), 8.695 (d, 1, J = 7 Hz, H1), 9.133 (d, 1, $J_{5,6}$ = 9 Hz, H5), 9.262 (d, 1, $J_{3,4}$ = 7 Hz, H4), 10.463 (d, 1, $J_{6,8}$ = 2.5 Hz, H8), 11.306 (s, 3, $COCH_3$), 11.909 (s, 1, H10), 12.043 (br s, 1, H9), data for **8b**-II (32% of the mixture) δ 4.185 (s, 3, OCH_3), 7.925 (t, 1, $J_{6,7,8}$ = 8 Hz, H7), 7.967 (dd, 1, $J_{1,3}$ = 2.5 Hz, $J_{3,4}$ = 9 Hz, H3), 8.300 (t, 1, $J_{5,6,7}$ = 8 Hz, H6), 8.332 (d, 1, $J_{1,3}$ = 2.5 Hz, H1), 9.062 (d, 1, $J_{5,6}$ = 8 Hz, H5), 9.235 (d, 1, $J_{3,4}$ = 9 Hz, H4), 10.469 (d, 1, $J_{7,8}$ = 8 Hz, H8), 11.474 (s, 3, $COCH_3$), 11.750 (br s, 1, H10), 12.043 (br s, 1, H9); mass spectrum of **8a**-II + **8b**-II (68 eV, 150 °C), m/z (rel intensity) 308 ($M^{\cdot+}$, 5), 280 [$(M - N_2)^{\cdot+}$, 30], 266 ($C_{17}H_{16}NO_2^+$, 5), 265 ($C_{17}H_{15}NO_2^{\cdot+}$, 13), 238 ($C_{15}H_{12}NO_2^+$, 29), 237 ($C_{15}H_{13}N_2O^+$, 99), 224 ($C_{15}H_{14}NO^+$, 27), 223 ($C_{15}H_{13}NO^{\cdot+}$, 22), 221 ($C_{15}H_{11}NO^{\cdot+}$, 100), 211 ($C_{19}H_{13}NO^{\cdot+}$, 15), 210 ($C_{14}H_{12}NO^+$, 97), 208 ($C_{15}H_{12}O^{\cdot+}$, 9), 195 ($C_{14}H_{11}O^+$, 20), 167 ($C_{12}H_7O^+$, 37), 165 ($C_{13}H_9^+$, 17), 152 ($C_{12}H_8^{\cdot+}$, 16). Anal. Calcd for $C_{17}H_{16}N_4O_2$: C, 66.23; H, 5.19. Found: C, 66.53; H, 5.44.

***trans*-10-Azido-9,10-dihydro-3-methoxy-9-phenanthrenamine (2Bb-III).** Since 1a,9b-dihydro-4-methoxy-1*H*-phenanthro[9,10-*b*]azirine (**1B**-III) proved to be unstable [δ 3.547 (s, H1a, H9b)], it was employed without purification. **2Bb-III**: overall yield from **2Ab**-III was 9%: IR (neat) 3360, 3290 (NH_2), 2095 cm^{-1} (N_3); 200-MHz ^1H NMR ($CDCl_3$) δ 1.807 (s, 2, NH_2), 3.895 (s, 3, OCH_3), 4.167 (d, 1, $J_{9,10}$ = 4 Hz, H9 or H10), 4.562 (d, 1, $J_{9,10}$ = 4 Hz, H9 or H10), 6.899 (d, 1, $J_{1,2}$ = 7 Hz, H2), 7.266–7.417 (m, 4, H1, H6, H7, H8), 7.645 (d, 1, $J_{2,4}$ = 2 Hz, H4), 7.758 (d, 1, $J_{4,5}$ = 7 Hz, H5); mass spectrum (68 eV, 120 °C), m/z (rel intensity) 238 [$(M - N_2)^{\cdot+}$, 21], 237 ($C_{15}H_{13}N_2O^+$, 19), 223 ($C_{15}H_{13}NO^{\cdot+}$, 23), 211 ($C_{14}H_{13}NO^{\cdot+}$, 27), 210 ($C_{14}H_{12}NO^+$, 100), 208 ($C_{15}H_{12}O^{\cdot+}$, 18), 195 ($C_{14}H_{11}O^+$, 14), 180 ($C_{13}H_8O^{\cdot+}$, 20), 167 ($C_{12}H_7O^+$, 29), 165 ($C_{13}H_9^+$, 10), 152 ($C_{12}H_8^{\cdot+}$, 13). The N-acetyl derivative **8b**-III was obtained in 93% yield: mp 155–156 °C (from ether–hexane); IR (Nujol) 3410 (NH), 2090 (NH), 1660 cm^{-1} (C=O); 200-MHz ^1H NMR (4×10^{-5} mol of **8b**-III and 2×10^{-5} mol of Eu(fod) in 0.5 mL of $CDCl_3$ after 2 h) δ 3.748 ns, 3, OCH_3), 6.754 (d, 1, $J_{1,2}$ = 5 Hz, H1 or H2), 7.574 (d, 1, $J_{1,2}$ = 5 Hz, H1 or H2), 7.786 (t, 1, $J_{5,6,7}$ = 7.5 Hz, H6), 8.006 (t, 1, $J_{6,7,8}$ = 7.5 Hz, H7), 8.270 (d, 1, $J_{5,6}$ = 7.5 Hz, H5), 8.357 (s, 1, H4), 11.836 (br s, 1, H10), 12.266 (d, 1, $J_{7,8}$ = 7.5 Hz, H8), 16.132 (br s, 1, H9), 17.606 (s, 1, N*H*); mass spectrum (68 eV, 150 °C), m/z (rel intensity) 308 ($M^{\cdot+}$, 5), 280 [$(M - N_2)^{\cdot+}$, 53], 266 ($C_{17}H_{16}NO^+$, 24), 265 ($C_{17}H_{15}NO_2^{\cdot+}$, 16); 238 ($C_{15}H_{12}NO_2^+$, 23), 237 ($C_{15}H_{13}N_2O^+$, 100), 224 ($C_{15}H_{14}NO^+$, 54), 223 ($C_{15}H_{13}NO^{\cdot+}$, 14), 211 ($C_{11}H_{13}NO^{\cdot+}$, 17), 210 ($C_{14}H_{12}NO^+$, 94), 208 ($C_{15}H_{12}O^{\cdot+}$, 14), 195 ($C_{14}H_{11}O^+$, 20), 167 ($C_{12}H_7O^+$, 31), 165 ($C_{13}H_9^+$, 16), 152 ($C_{12}H_8^{\cdot+}$, 15). Anal. Calcd for $C_{17}H_{16}N_4O_2$: C, 66.23; H, 5.19. Found: C, 66.51; H, 5.19.

***trans*-10-Azido-6-chloro- and *trans*-10-azido-3-chloro-9,10-dihydro-9-phenanthrenamine (2Ba-IV and 2Bb-IV)**: yield 67%; pale yellow oil; IR (neat) 3360, 3295 cm^{-1} (NH_2), 2095 cm^{-1} (N_3); 200-MHz ^1H NMR ($CDCl_3$) δ 1.735 (s, 2, NH_2), 4.012 (d, 1, $J_{9,10}$ = 5 Hz, H9 or H10), 4.525 (d, 1, J = 5 Hz, H9 or H10), 7.500–7.277 (m, 5, H1, H2, H3, H7, H8 of **2Ba**-IV and H1, H2, H6, H7, H8 of **2Bb**-IV), 7.791 (d, 1, J = 2 Hz, H5 of **2Ba**-IV and H4 of **2Bb**-IV), 7.824 (t, 1, J_o = 8 Hz, J_m = 2 Hz, H4 of **2Ba**-IV and H5 of **2Bb**-IV); mass spectrum (68 eV, 60 °C), m/z (rel intensity) 244, 242 [$(M - N_2)^{\cdot+}$, 6, 18], 229 ($C_{14}H_{10}{}^{37}ClN^{\cdot+}$, 7), 227 ($C_{14}H_{10}{}^{35}ClN^{\cdot+}$, 22), 216 ($C_{19}H_9{}^{37}ClN^+$, 33), 214 ($C_{13}H_9{}^{35}ClN^+$, 100), 180 ($C_{13}H_{10}N^+$, 30), 165 ($C_{13}H_9^+$, 22), 152 ($C_{12}H_8^{\cdot+}$, 13). The mixture of the N-acetyl derivatives was obtained in 96% yield: mp 182–184 °C (from ether–hexane); IR (Nujol) 3420 (NH), 2090 (N_3), 1670 cm^{-1} (C=O); 300-MHz ^1H NMR (2×10^{-5} mol of **8a**-IV + **8b**-IV, 4×10^{-5} mol of Eu(fod) in 0.5 mL of $CDCl_3$ after 2 h) data for **8a**-IV (46% of the mixture) δ 7.705 (dd, 1, $J_{5,7}$ = 1.5 Hz, $J_{7,8}$ = 8 Hz, H7), 8.227 (t, 1, $J_{1,2,3}$ = 7 Hz, H2), 8.443 (t, 1, $J_{2,3,4}$ = 7 Hz, H3), 8.794 (d, 1, $J_{1,2}$ = 7 Hz, H1), 9.190 (d, 1, $J_{3,4}$ = 7 Hz, H4), 9.204 (d, 1, $J_{5,7}$ = 1.5 Hz, H5), 10.587 (d, 1, $J_{7,8}$ = 8 Hz, H8), 11.068 (s, 3, $COCH_3$), 11.319 (br s, 1, H10), 11.810 (br s, 1, H9), data for **8b**-IV (54% of the mixture) δ 7.966 (t, 1, $J_{7,8}$ = 8 Hz, H7), 8.102 (dd, 1, $J_{1,2}$ = 8 Hz, $J_{2,4}$ = 2 Hz, H2), 8.263 (t, 1, $J_{5,6,7}$ = 8 Hz, H6), 8.630 (d, 1, $J_{1,2}$ = 8 Hz, H1), 9.025 (d, 1, $J_{2,4}$ = 2 Hz, H4), 9.034 (d, 1, $J_{5,6}$ = 8 Hz, H5), 10.495 (d, 1, $J_{7,8}$ = 8 Hz, H8), 11.068 (s, 3, $COCH_3$), 11.677 (s, 1, H10), 11.902 (br s, 1, H9); mass spectrum (68 eV, 150 °C), m/z (rel intensity) 286, 284 [$(M - N_2)^{\cdot+}$, 3, 10], 244 ($C_{14}H_9{}^{37}ClNO^+$, 7), 243 ($C_{14}H_{10}{}^{37}ClN_2^+$, 24), 242 ($C_{14}H_9{}^{35}ClNO^+$, 21), 241 ($C_{14}H_{10}{}^{35}ClN_2^+$, 72), 227 ($C_{14}H_8{}^{37}ClN^{\cdot+}$, 16), 225 ($C_{14}H_8{}^{35}ClN^{\cdot+}$, 47), 216 ($C_{13}H_9{}^{37}ClN^+$, 33), 214 ($C_{13}H_9{}^{35}ClN^+$, 100), 190 ($C_{14}H_8N^+$, 68), 180 ($C_{13}H_{10}N^+$, 29), 165 ($C_{13}H_9^+$, 22), 152 ($C_{12}H_8^{\cdot+}$, 31). Anal. Calcd for $C_{16}H_{13}ClN_4O$: C, 61.44; H, 4.16. Found: C, 61.41; H, 4.31.

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Registry No. **1A**-I, 111005-38-0; **1A**-IV, 111005-39-1; **1B**-I, 111005-47-1; **1B**-II, 111005-48-2; **1B**-III, 111005-58-4; **1B**-IV, 111005-49-3; **2A**(R = H, X = O), 53581-32-1; **2Aa**-I, 111005-40-4; **2Aa**-II, 111005-42-6; **2Aa**-IV, 111005-45-9; **2Ab**-I, 111005-41-5; **2Ab**-II, 111005-43-7; **2Ab**-III, 111005-44-8; **2Ab**-IV, 111005-46-0; **2Ba**-I, 111005-50-6; **2Ba**-II, 111005-54-0; **2Ba**-IV, 111025-77-5; **2Bb**-I, 111005-51-7; **2Bb**-II, 111005-55-1; **2Bb**-III, 111005-59-5; **2Bb**-IV, 111005-61-9; **6**-IV, 715-51-5; **7**-I, 109512-68-7; **7**-IV, 111005-37-9; **8a**-I, 111005-52-8; **8a**-II, 111005-56-2; **8a**-IV, 111005-62-0; **8b**-I, 111005-53-9; **8b**-II, 111005-57-3; **8b**-III, 111005-60-8; **8b**-IV, 111005-63-1; NaN_3, 26628-22-8.

Supplementary Material Available: Five tables of crystallographic data and ORTEP and stereoscopic drawings (6 pages). Ordering information is given on any current masthead page.