# The Chemistry of Polycyclic Arene Imines. VII.
## Reactions of Phenanthrene 9,10-Imine with
## Aromatic Carboxaldehydes, Carboxylic Acids and Acetylenic Esters [1]

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The reactions of phenanthrene 9,10-imine (1) with aromatic aldehydes, benzoic acids and acetylenedicarboxylic esters were investigated. The aldehydes were shown to give 1-[N-(arylmethylidene)-9-phenanthreneamine-10-yl]-1a,9b-dihydrophenanthro[9,10-b]azirine 2. The 'dimeric' structure of these products was established by X-ray diffraction analysis. The carboxylic acids proved to form in the presence of dicyclohexylcarbodiimide, N-aroylphenanthrene 9,10-imines 7, that readily undergo rearrangement to N-aroyl-9-phenanthrenamines 8. Esters of acetylenedicarboxylic acid gave the corresponding esters of (Z)-2-(1a,9b-dihydrophenanthro[9,10-b]azirine-1-yl)-2-butendioic acid 10.

The exceptionally high mutagenic potencies of various polycyclic arene imines [2-4], and the observed correlation between the biological activities of these compounds and of the analogous arene oxides [2] led us to the assumption that aromatic aziridines, like the corresponding epoxides, are active metabolites of polycyclic aromatic hydrocarbons. Consequently, we undertook the investigation of chemical properties of arene imines that may be of biological relevance.

In this paper, we report the reaction of the model compound phenanthrene 9,10-imine (1a,9b-dihydro-1H-phenanthro[9,10-b]azirine) (1) with some aldehydes, carboxylic acids and acetylenic esters.

Unlike aliphatic ethylenimines, compound 1 does not react with aliphatic aldehydes and ketones to give discrete products such as imino alcohols [5] or oxazolidine derivatives [6]. It reacts, however, with *aromatic* aldehydes to form crystalline products according to eq. (1). The

(1)
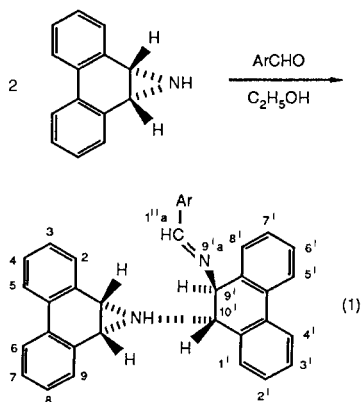
'dimeric' structure of **2** was established by the ei mass spectra (see Experimental) as well as by the X-ray analysis of 1-[N-(4-methylphenylmethylidene)-9-phenanthrene-10-yl]-1a,9b-dihydrophenanthro[9,10-b]azirine (**2**, Ar = 4-CH₃C₆H₄). The crystallographic data for this compound,

Table 1

Crystallographic Data of Compound **2** (Ar = 4-CH₃C₆H₄)

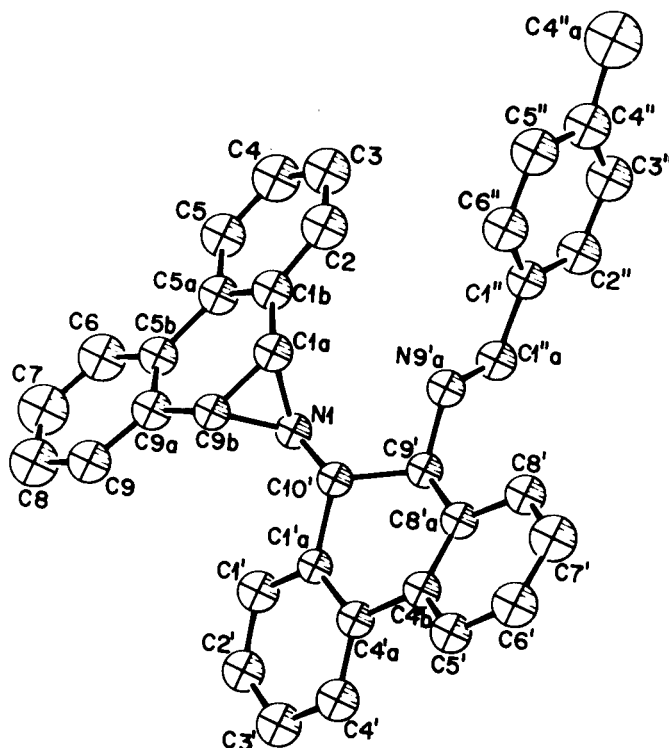| | |
|---|---|
| formula: $C_{36}H_{28}N_2$ | Z = 4 |
| molecular weight = 488.6 | $\rho_{calcd}$ = 1.23 cm⁻³ |
| space group P 2,2,2. | $\mu$(Mo K$_\alpha$) = 0.37 cm⁻¹ |
| a = 14.967 Å | No. of unique reflections 1746 |
| b = 21.816 Å | reflections with I ≥ 2σ(I) 1167 |
| c = 8.075 Å | R = 0.06 |
| V = 2637 Å³ | R$_w$ = 0.082 |

Figure 1. ORTEP drawing of **2** (Ar = 4-CH₃C₆H₄).

## Table 2

Final Positional Parameters for **2** (Ar = 4-CH$_3$C$_6$H$_4$) with Estimated Standard Deviations in Parentheses

| Atom | X | Y | Z |
|------|------|------|------|
| N(1) | 0.8744(4) | 0.2228(3) | 0.6359(8) |
| C(1a) | 0.8432(6) | 0.2715(4) | 0.527(1) |
| C(1b) | 0.9121(6) | 0.3151(4) | 0.466(1) |
| C(2) | 0.9052(7) | 0.3773(5) | 0.508(1) |
| C(3) | 0.9737(7) | 0.4171(5) | 0.460(1) |
| C(4) | 1.0433(7) | 0.3949(5) | 0.368(1) |
| C(5) | 1.0497(7) | 0.3367(5) | 0.319(1) |
| C(5a) | 0.9822(6) | 0.2932(4) | 0.367(1) |
| C(5b) | 0.9840(6) | 0.2298(4) | 0.307(1) |
| C(6) | 1.0491(7) | 0.2094(5) | 0.199(1) |
| C(7) | 1.0440(8) | 0.1526(5) | 0.135(1) |
| C(8) | 0.9749(7) | 0.1122(5) | 0.167(1) |
| C(9) | 0.9079(7) | 0.1318(4) | 0.274(1) |
| C(9a) | 0.9135(6) | 0.1895(4) | 0.346(1) |
| C(9b) | 0.8435(5) | 0.2088(4) | 0.464(1) |
| C(1′a) | 0.8209(5) | 0.1347(4) | 0.801(1) |
| C(1′) | 0.8790(7) | 0.0976(4) | 0.715(1) |
| C(2′) | 0.8842(7) | 0.0367(4) | 0.759(1) |
| C(3′) | 0.8305(6) | 0.0114(4) | 0.875(1) |
| C(4′) | 0.7726(6) | 0.0486(4) | 0.966(1) |
| C(4′a) | 0.7683(6) | 0.1114(4) | 0.927(1) |
| C(4′b) | 0.7149(6) | 0.1548(4) | 1.027(1) |
| C(5′) | 0.6413(6) | 0.1344(4) | 1.122(1) |
| C(6′) | 0.5936(7) | 0.1760(5) | 1.218(1) |
| C(7′) | 0.6202(7) | 0.2354(5) | 1.230(1) |
| C(8′) | 0.6926(6) | 0.2565(4) | 1.136(1) |
| C(8′a) | 0.7393(5) | 0.2160(4) | 1.034(1) |
| C(9′) | 0.8144(6) | 0.2394(4) | 0.921(1) |
| C(10′) | 0.8099(6) | 0.2027(4) | 0.760(1) |
| N(9′a) | 0.8025(5) | 0.3044(3) | 0.8885(9) |
| C(1″a) | 0.8585(6) | 0.3406(4) | 0.957(1) |
| C(1″) | 0.8516(6) | 0.4071(4) | 0.939(1) |
| C(2″) | 0.9170(7) | 0.4434(5) | 1.012(1) |
| C(3″) | 0.9140(7) | 0.5057(5) | 1.001(1) |
| C(4″) | 0.8479(7) | 0.5352(5) | 0.915(1) |
| C(4″a) | 0.8453(9) | 0.6041(5) | 0.886(2) |
| C(5″) | 0.7806(7) | 0.5001(5) | 0.841(1) |
| C(6″) | 0.7815(6) | 0.4363(5) | 0.856(1) |

## Table 3

Selected Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses

### Bond Lengths

| | | | |
|------|--------|------|--------|
| N(1)-C(1a) | 1.46(1) | C(2′)-C(3′) | 1.36(1) |
| N(1)-C(9b) | 1.49(1) | C(3′)-C(4′) | 1.39(1) |
| N(1)-C(10′) | 1.46(1) | C(4′)-C(4′a) | 1.41(1) |
| C(1a)-C(1b) | 1.49(1) | C(4′a)-C(4′b) | 1.48(1) |
| C(1a)-C(9b) | 1.46(1) | C(4′b)-C(5′) | 1.42(1) |
| C(1b)-C(2) | 1.40(1) | C(4′b)-C(8′a) | 1.38(1) |
| C(1b)-C(5a) | 1.40(1) | C(5′)-C(6′) | 1.39(1) |
| C(2)-C(3) | 1.40(1) | C(6′)-C(7′) | 1.36(1) |
| C(3)-C(4) | 1.37(1) | C(7′)-C(8′) | 1.40(1) |
| C(4)-C(5) | 1.33(1) | C(8′)-C(8′a) | 1.40(1) |
| C(5)-C(5a) | 1.44(1) | C(8′a)-C(9′) | 1.53(1) |
| C(5a)-C(5b) | 1.47(1) | C(9′)-C(10′) | 1.53(1) |
| C(5b)-C(6) | 1.38(1) | C(9′)-N(9′a) | 1.45(1) |
| C(5b)-C(9a) | 1.41(1) | N(9′a)-C(1″a) | 1.28(1) |
| C(6)-C(7) | 1.35(1) | C(1″a)-C(1″) | 1.46(1) |
| C(7)-C(8) | 1.38(1) | C(1″)-C(2″) | 1.39(1) |
| C(8)-C(9) | 1.39(1) | C(1″)-C(6″) | 1.40(1) |
| C(9)-C(9a) | 1.39(1) | C(2″)-C(3″) | 1.36(1) |
| C(9a)-C(9b) | 1.48(1) | C(3″)-C(4″) | 1.37(1) |
| C(1′a)-C(1′) | 1.38(1) | C(4″)-C(4″a) | 1.52(1) |
| C(1′a)-C(4′a) | 1.39(1) | C(4″)-C(5″) | 1.40(1) |
| C(1′a)-C(10′) | 1.53(1) | C(5″)-C(6″) | 1.40(1) |
| C(1′)-C(2′) | 1.38(1) | | |

### Bond Angles

| | | | |
|------|--------|------|--------|
| C(1a)-N(1)-C(9b) | 59.3(5) | C(2′)-C(3′)-C(4′) | 119.8(9) |
| C(1a)-N(1)-C(10′) | 114.9(6) | C(3′)-C(4′)-C(4′a) | 118.6(9) |
| C(9b)-N(1)-C(10′) | 111.8(6) | C(1′a)-C(4′)-C(1′) | 119.7(8) |
| N(1)-C(1a)-C(1b) | 116.4(7) | C(1′a)-C(4′a)-C(4′b) | 118.2(8) |
| N(1)-C(1a)-C(9b) | 61.6(5) | C(4′)-C(4′a)-C(4′b) | 121.9(8) |
| C(1b)-C(1a)-C(9b) | 118.8(7) | C(4′a)-C(4′b)-C(5′) | 121.0(8) |
| C(1a)-C(1b)-C(2) | 119.2(8) | C(4′a)-C(4′b)-C(1′a) | 119.9(8) |
| C(1a)-C(1b)-C(5a) | 119.3(8) | C(5′)-C(4′b)-C(8′a) | 119.0(8) |
| C(2)-C(1b)-C(5a) | 121.5(9) | C(4′b)-C(5′)-C(6′) | 119.8(9) |
| C(1b)-C(2)-C(3) | 118.7(9) | C(5′)-C(6′)-C(7′) | 120.7(1) |
| C(2)-C(3)-C(4) | 119(1) | C(6′)-C(7′)-C(8′) | 120.2(1) |
| C(3)-C(4)-C(5) | 123(1) | C(7′)-C(8′)-C(8′a) | 119.9(9) |
| C(4)-C(5)-C(5a) | 119.9(1) | C(4′b)-C(8′a)-C(8′) | 120.2(8) |
| C(1b)-C(5a)-C(5) | 116.9(9) | C(4′b)-C(8′a)-C(9′) | 119.3(7) |
| C(1b)-C(5a)-C(5b) | 121.5(8) | C(8′)-C(8′a)-C(9′) | 120.4(8) |
| C(5)-C(5a)-C(5b) | 121.5(8) | C(8′a)-C(9′)-C(10′) | 107.3(7) |
| C(5a)-C(5b)-C(6) | 121.6(9) | C(8′a)-C(9′)-N(9′a) | 110.2(7) |
| C(5a)-C(5b)-C(9a) | 120.1(8) | C(10′)-C(9′)-N(9′a) | 110.4(7) |
| C(6)-C(5b)-C(9a) | 118.0(9) | N(1)-C(10′)-C(1′a) | 111.6(7) |
| C(5b)-C(6)-C(7) | 120(1) | N(1)-C(10′)-C(9′) | 113.5(7) |
| C(6)-C(7)-C(8) | 124(1) | C(1′a)-C(10′)-C(9′) | 108.6(7) |
| C(7)-C(8)-C(9) | 118.0(1) | C(9′)-N(9′a)-C(1″a) | 116.3(7) |
| C(8)-C(9)-C(9a) | 119.6(9) | N(9′a)-C(1″a)-C(1″) | 121.7(8) |
| C(5b)-C(9a)-C(9) | 121.1(8) | C(1″a)-C(1″)-C(2″) | 118.5(8) |
| C(5b)-C(9a)-C(9b) | 119.8(8) | C(1″a)-C(1″)-C(6″) | 123.4(8) |
| C(9)-C(9a)-C(9b) | 119.1(8) | C(2″)-C(1″)-C(6″) | 118.1(9) |
| N(1)-C(9b)-C(1a) | 59.1(5) | C(1″)-C(2″)-C(3″) | 121.4(9) |
| N(1)-C(9b)-C(9a) | 116.0(7) | C(2″)-C(3″)-C(4″) | 121.6(1) |
| C(1a)-C(9b)-C(9a) | 119.6(7) | C(3″)-C(4″)-C(4″a) | 124.0(1) |
| C(1′)-C(1′a)-C(4′a) | 120.9(8) | C(3″)-C(4″)-C(5″) | 118.6(1) |
| C(1′)-C(1′a)-C(10′) | 122.0(8) | C(4″a)-C(4″)-C(5″) | 117.4(1) |
| C(4′a)-C(1′a)-C(10′) | 117.0(7) | C(4″)-C(5″)-C(6″) | 120.1(9) |
| C(1′a)-C(1′)-C(2′) | 118.3(9) | C(1″)-C(6″)-C(5″) | 120.2(9) |
| C(1′)-C(2′)-C(3′) | 122.5(9) | | |
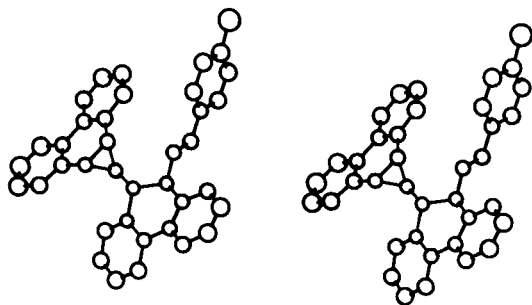


Figure 2. Stereoscopic view of **2** (Ar = 4-CH$_3$C$_6$H$_4$).

the atomic coordinates and selected bond lengths and bond angles are given in Tables 1-3 [7]. The ORTEP drawing and stereoscopic view are presented in Figures 1 and 2, respectively. Table 3 indicates that one of the nitrogen atoms is part of an aziridine moiety [C(1a)-N(1)-C(9b) 59.3°; N(1)-C(1a)-C(9b) 61.6°; N(1)-C(9b)-C(1a) 59.1°] while the other one has the characteristics of a Schiff base nitrogen [C9')-N(9'a)-C(1''a) 116°; bond length of the double bond N(9'a)-C(1''a) is 1.28 Å]. The stereoscopic view shows that the two nitrogen atoms are in a *trans* relationship. Thus, the structure resembles that of the 'dimeric' product obtained from **1** and allyl bromide [1].

The formation of **2** is rationalized by the initial conversion of **1** into an aziridine hydrine **4** which, in turn, is in equilibrium with the aziridinium ion **5**. An alternative route in which **5** is opened by an $S_N1$ mechanism can be ruled out, as such pathway would have given **2** as a mixture of *cis-* and *trans-*isomers.
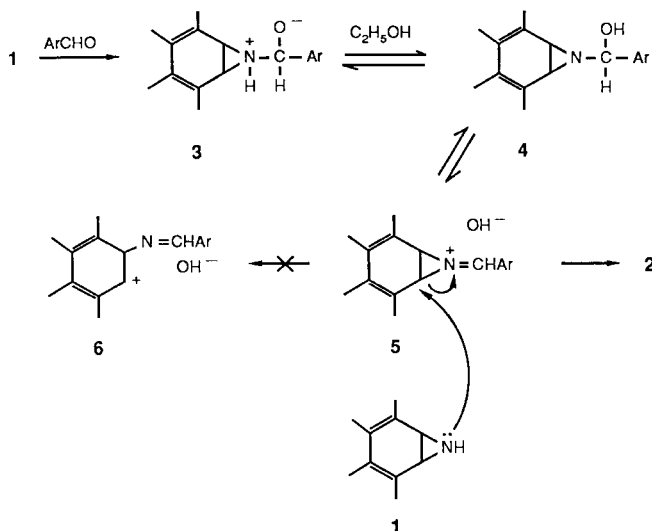
A case of a similar formation of dimers has been reported to take place during the interaction of aliphatic aziridines with benzaldehyde [8]. However, in contrast to the reaction of the nonaromtic ethylenimines, the addition of **1** to benzaldehydes could not be stopped at stage **4** even when carried out at very low temperature (-60°) [9]. Attempts were also made to block the transformation of **5** to **2** by modification of the electronic character of the aldehyde and by introduction of steric factors. Yet benzaldehyde, 4-chlorobenzaldehyde, 4-anisaldehyde, 2,4,6-trimethylbenzaldehyde and 1-naphthaldehyde gave 'dimeric' compounds of type **2** as the only isolable products.

Most aromatic ketones were found to be completely refractory to **1** even upon prolonged refluxing in ethanol.

Benzoic acids reacted with the imine in the presence of dicyclohexylcarbodiimide (DCC) to form unstable *N*-aroylphenanthrene 9,10-imines, **7**. These compounds rearrang-

ed rapidly to *N*-aroyl-9-phenanthrenamines, **8**, (eq. 2) by the mechanism outlined previously [10].

(2)
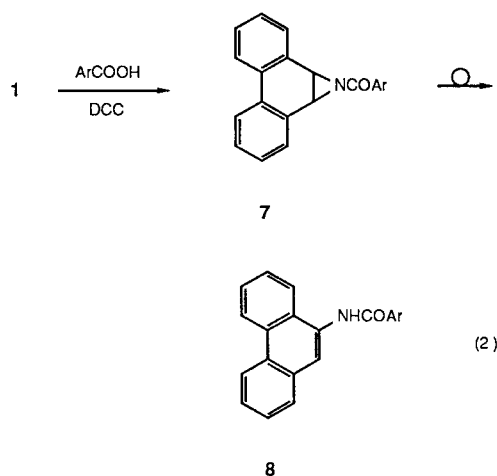
When *e.g.* **1** was treated with equimolar amounts of 4-methoxybenzoic acid and DCC in dichloromethane, characteristic H1a and H9b resonance peaks of **7**, Ar = 4-CH$_3$OC$_6$H$_4$ at 4.235 and 4.279 appeared in the pmr spectrum of the mixture (after work up). The intensities of these peaks increased during the first hour, but then decreased gradually and finally disappeared. After 3 hours the only reaction product present was *N*-4-methoxybenzoyl-9-phenanthrenamine (**8**, Ar = 4-CH$_3$OC$_6$H$_4$).

It should be recalled that previous attempts to prepare *N*-aroylphenanthrene imines from **1** *via* the *N*-trimethylsilyl derivative failed though the analogous unstable *N*-acetyl compound could be prepared by this method [11].

In aprotic solvents (*e.g.* benzene) acetylenedicarboxylic esters were shown to add to **1** *via* their triple bonds to give substituted maleates (eq. 3).

(3)
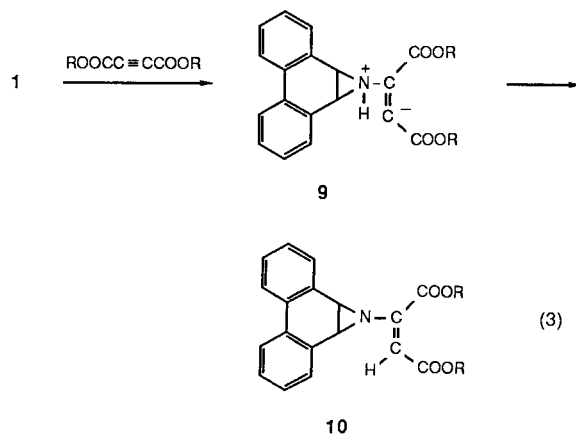
The reaction is assumed to proceed *via* zwitterion **9** which is stabilized by an intramolecular proton shift that predetermines the Z configuration in **10** (*cf.*, reference [12]). In spite of this configuration, the marked steric hin-

drance, extended by the dihydrophenanthroazirinyl substituent, prevents **10** from being hydrogenated and from taking part in 1,3-dipolar Diels Alder reactions.

The addition of the alkyne to **1** proved to proceed equally well with methyl, ethyl and 2-propyl diesters, but neither acetylene-monocarboxylates nor phenylacetylenes could be reacted with phenanthrene-9,10-imine.

## EXPERIMENTAL

1 – [N-(4-Methylphenylmethylidene)-9-phenanthrenamine-10-yl]-1a,9b-dihydrophenanthro[9,10-b]azirine (**2**, Ar = 4-CH₃C₆H₄).

A mixture of 200 mg (1.04 mmoles) of **1**, 0.12 ml (1.04 mmoles) of 4-tolu;aldehyde and 5 ml of absolute ethanol was refluxed under argon for 60 minutes. Upon cooling colorless crystals separated. Recrystallization from a dichloromethane-hexane mixture afforded 141 mg (56%) of **2**, Ar = 4-CH₃C₆H₄, mp 222-224°; 300 MHz pmr (deuteriochloroform): $\delta$ 2.513 (s, 3H, CH₃), 3.177 and 3.769 (ABq, 2H, $J_{AB}$ = 6.3 Hz, H1a, H9b), 3.646 and 4.700 (ABq, 2H, $J_{AB}$ = 11.0 Hz, H9′, H10′), 6.462-8.050 (m, 20H, ArH), 8.267 (s, 1H, CH=N); ms: (70 eV, 220°) m/e (relative intensity) 489 [(M + 1)⁺, 6], 488 (M⁺, 16), 370 ($C_{28}H_{20}N^+$, 28), 369 ($C_{28}H_{19}N^+$, 88), 368 ($C_{28}H_{18}N^+$, 11), 297 ($C_{22}H_{19}N^+$, 22), 296 ($C_{22}H_{18}N^+$, 98), 295 ($C_{22}H_{17}N^+$, 63), 205 ($C_{15}H_{10}N^+$, 23), 193 ($C_{14}H_{11}N^+$, 70), 178 ($C_{14}H_{10}^+$, 100), 165 ($C_{13}H_9^+$, 67).

*Anal* Calcd. for $C_{36}H_{28}N_2$: C, 88.52; H, 5.74; N, 5.74. Found: C, 88.45; H, 5.47; N, 6.01.

X-Ray Crystal Structure of **2**, Ar = 4-CH₃C₆H₄.

Data were measured on an ENRAF-NONIUS CAD-4 automatic diffractometer. Mo $K_\alpha$ ($\lambda$ = 0.71069 A) radiation with a graphite crystal monochromator in the incident beam was used. The standard CAD-4 centering, indexing, and data collection programs were used. The unit cell dimensions were obtained by a least-square fit of 21 centered reflections in the range of $10° > \theta > 12°$. Intensity data were collected using the $\omega$-$2\theta$ technique to a maximum of $2\theta$ of 45°. The scan width, $\Delta\omega$, for each reflection was $1.00 + 0.35 \tan \theta$. An aperture with a height of 4 mm and a variable width, calculated as $(3.0 + \tan \theta)$ mm, was located 173 mm from the crystal. Reflections were first measured with a scan of 10°/minutes. The rate of the final scan was calculated from the preliminary scan results so that the ratio $I/\sigma(I)$ would be at least 30, and the maximum scan time would not exceed 60 seconds. If in a preliminary scan $I/\sigma(I) > 30$, this measurement was used as the datum. Scan rates were verified from 10° to 2°/minutes. Of the 96 steps in the scan, the first and the last 16 steps were considered to be background. During data collection the intensities of three standard reflections were monitored after every hour of X-ray exposure. No decay was observed. In addition, three orientation standards were monitored after every 100 reflections to check the effects of crystal movement. If the standard deviation of the H, K, and L values of any orientation reflection exceeded 0.05, a new orientation matrix was calculated on the basis of the recentering of the 21 reference reflections.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found using the results of the MULTAN direct method analysis [13]. After several cycles of refinements [14] the positions of the hydrogen atoms were calculated, and added with a constant isotropic temperature factor of 0.5 Å², to the refinement process. Refinement proceeded to convergence by minimizing function $\Sigma w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(f)^{-2}$. A final difference Fourier synthesis map showed several peaks less than 0.25 e Å⁻³ scattered about the unit cell without a significant feature.

The discrepancy indices R = $\Sigma \|F_o| - |F_c\|/\Sigma |F_o|$ and Rw = $|\Sigma w(|F_o| - |F_c|)^2/[\Sigma w|F_o|^2]^{1/2}$ are presented with other pertinent crystallographic data in Table 1. Selected positional parameters, bond lengths and angles are given in Tables 2 and 3 [7].

1-(N-Benzylidene-9-phenanthrenamine-10-yl)-1a,9b-dihydrophenanthro-[9,10-b]azirine (**2**, Ar = C₆H₅).

This compound was obtained in 52% yield by the method described above; mp 221-223° (from dichloromethane-hexane); 300 MHz pmr (deuteriochloroform): $\delta$ 3.188 and 3.754 (ABq, 2H, $J_{AB}$ = 6.3 Hz, H1a, H9b), 3.665 and 4.724 (ABq, 2H, $J_{AB}$ = 11.0 Hz, H9′, H10′), 6.438-8.054 (m, 21H, ArH), 8.312 (s, 1H, CH=N); ms: (70 eV, 190°) m/e (relative intensity) 475 [(M + 1)⁺, 17] 474 (M⁺, 43), 370 ($C_{28}H_{20}N^+$, 12), 369 ($C_{28}H_{19}N^+$, 38), 283 ($C_{21}H_{17}N^+$, 22), 282 ($C_{21}H_{16}N^+$, 100), 281 ($C_{21}H_{15}N^+$, 52), 193 ($C_{14}H_{11}N^+$, 53), 178 ($C_{14}H_{10}^+$, 52), 165 ($C_{13}H_9^+$, 3).

*Anal.* Calcd. for $C_{35}H_{26}N_2$: C, 88.61; H, 5.48; N, 5.91. Found: C, 88.42; H, 5.62; N, 5.88.

1-[N-(4-Chlorophenylmethylidene)-9-phenanthrenamine-10-yl]-1a,9b-dihydrophenanthro[9,10-b]azirine (**2**, Ar = 4-ClC₆H₄).

Obtained as above in 65% yield, mp 232-235° (from dichloromethane-hexane); 300 MHz pmr (deuteriochloroform): $\delta$ 3.180 and 3.690 (ABq, 2H, $J_{AB}$ = 6.3 Hz, H1a, H9b), 3.648 and 4.708 (ABq, 2H, $J_{AB}$ = 11.3 Hz, H9′, H10′), 6.510-8.048 (m, 20H, ArH), 8.257 (s, 1H, CH=N); ms: (70 eV, 220°) m/e (relative intensity) 511 and 509 [(M + 1)⁺, 2 and 6], 510 and 508 (M⁺, 6 and 18), 370 ($C_{28}H_{20}N^+$, 31), 369 ($C_{28}H_{19}N^+$, 100), 368 ($C_{28}H_{18}N^+$, 12), 318 ($C_{21}H_{15}^{37}ClN^+$, 17), 317 ($C_{21}H_{14}^{37}ClN^+$, 29), 316 ($C_{21}H_{15}^{35}ClN^+$, 51), 315 ($C_{21}H_{14}^{35}ClN^+$ 87), 204 ($C_{15}H_9N^+$, 15), 193 ($C_{14}H_{11}N^+$, 72), 178 ($C_{14}H_{10}^+$, 90), 165 ($C_{13}H_9^+$, 63).

*Anal.* Calcd. for $C_{35}H_{25}ClN_2$: C, 82.59; H, 4.92; Cl, 6.98; N, 5.51. Found: C, 82.65; H, 5.16; Cl, 6.86; N, 5.05.

1-[N-(4-Methoxyphenylmethylidene)-9-phenanthrenamine-10-yl]-1a,9b-dihydrophenanthro-[9,10-b]azirine (**2**, Ar = 4-CH₃OC₆H₄).

This compound was obtained in a yield of 62%, mp 213-215° (from dichloromethane-hexane); 300 MHz pmr (deuteriochloroform): $\delta$ 3.175 and 3.772 (ABq, 2H, $J_{AB}$ = 6.3 Hz, H1a, H9b), 3.623 and 4.673 (ABq, 2H, $J_{AB}$ = 1.4 Hz, H9′, H10′), 3.946 (s, 3H, OCH₃), 6.506-8.047 (m, 20H, ArH), 8.223 (s, 1H, CH=N); ms: (70 eV, 220°) m/e (relative intensity) 505 [(M + 1)⁺, 6], 504 (M⁺, 15), 370 ($C_{28}H_{20}N^+$, 31), 369 ($C_{28}H_{19}N^+$, 100), 312 ($C_{22}H_{18}NO^+$, 35), 311 ($C_{22}H_{17}NO^+$, 52), 204 ($C_{15}H_9N^+$, 19), 193 ($C_{14}H_{11}N^+$, 46), 178 ($C_{14}H_{10}^+$, 57), 165 ($C_{13}H_9^+$, 44).

*Anal.* Calcd. for $C_{36}H_{28}N_2O$: C, 85.71; H, 5.56; N, 5.56. Found: C, 85.85; H, 5.49; N, 5.30

1-[N-(2,4,6-Trimethylphenylmethylidene)-9-phenanthrenamine-10-yl]-1a,9b-dihydrophenanthro[9,10-b]azirine (**2**, Ar = 2,4,6-(CH₃)₃C₆H₂).

This compound was obtained in a yield of 40%, mp 127-129° (from dichloromethane-hexane); 300 MHz pmr (deuteriochloroform): $\delta$ 1.907 (s, 3H, 4-CH₃), 2.298 (s, 6H, 2,6-CH₃), 3.031 and 3.545 (ABq, 2H, $J_{AB}$ = 6.3 Hz, H1a, H9b), 3.688 and 4.626 (ABq, 2H, $J_{AB}$ = 11.0 Hz, H9′, H10′), 6.469-7.954 (m, 18H, ArH), 8.485 (s, 1H, CH=N); ms: (70 eV, 250°) m/e (relative intensity) 517 [(M + 1)⁺, 3], 516 (M⁺, 5), 369 ($C_{28}H_{19}N^+$, 19), 368 ($C_{28}H_{18}N^+$, 54), 324 ($C_{24}H_{22}N^+$, 11), 323 ($C_{24}H_{21}N^+$, 10), 204 ($C_{15}H_9N^+$, 17), 193 ($C_{14}H_{11}N^+$, 98), 178 ($C_{14}H_{10}^+$, 100), 165 ($C_{13}H_9^+$, 50).

*Anal.* Calcd. for $C_{38}H_{32}N_2$: C, 88.37; H, 6.20; N, 5.43. Found: C, 87.98; H, 6.42; N, 5.51.

1-[N-(1-Naphthylmethylidene)-9-phenanthrenamine-10-yl]-1a,9b-dihydro-[9,10-b]azirine (**2**, Ar = 1-naphthyl).

Prepared as described above, yield 63%; mp 128-130° (from chloroform-hexane); 300 MHz pmr (deuteriochloroform): $\delta$ 3.179 and 3.720 (ABq, 2H, $J_{AB}$ = 6.3 Hz, H1a, H9b), 3.729 and 4.791 (ABq, 2H, $J_{AB}$ = 11.3 Hz, H9′, H10′), 5.862-9.126 (m, 23H, ArH), 8.874 (s, 1H, CH=N); ms: (70 eV, 200°) m/e (relative intensity) 525 [(M + 1)⁺, 11], 524 (M⁺, 27), 370 ($C_{28}H_{20}N^+$, 24), 369 ($C_{28}H_{19}N^+$, 73), 332 ($C_{25}H_{18}N^+$, 44), 331 ($C_{25}H_{17}N^+$, 70), 330 ($C_{25}H_{16}N^+$, 19), 193 ($C_{14}H_{11}N^+$, 85), 178 ($C_{14}H_{10}^+$, 100), 165 ($C_{13}H_9^+$, 10).

*Anal.* Calcd. for $C_{39}H_{26}N_2$: C, 89.32; H, 5.34; N, 5.34. Found: C, 88.98; H, 5.68; N, 5.45.

Reaction of **1** with Benzoic Acids in the Presence of Dicyclohexylcarbodiimide.

In a typical experiment, a mixture of 200 mg (1.04 mmoles) of **1**, 158 mg (1.04 mmoles) of 4-methoxybenzoic acid, 214 mg (1.04 mmoles) of

DCC and 10 ml of dichloromethane was refluxed under argon for 3 hours. The precipitate of dicyclohexylurea was filtered off and the filtrate dried (magnesium sulfate) and concentrated. The residue was recrystallized from ether and hexane to yield 337 mg (99%) of 4-methoxy-N-(phenanthrene-9-yl)benzamide (8, Ar = 4-$CH_3OC_6H_4$), mp 166-167° (lit [15] 166-166.5°).

When the reaction was stopped after 30 minutes and worked up immediately the pmr spectrum of the residue contained two transient singlets at δ 4.235 and 4.279 that correspond to H1a and H9b of 7 (Ar = 4-$CH_3OC_6H_4$).

Dimethyl 2-(1a,9b-Dihydrophenanthro[9,10-b]azirine-1-yl)-2-butenedioate (10, R = $CH_3$).

A mixture of 100 mg (0.52 mmole) of 1, 148 mg (1.04 mmoles) of dimethyl acetylenedicarboxylate and 10 ml of benzene was refluxed under argon for 60 minutes. The solvent was removed under reduced pressure and the residue chromatographed on silica gel (60% ether and 40% hexane as eluent) to yield 118 mg (68%) of the adduct; mp 127-128°; ir (chloroform): 1730, 1700 cm⁻¹ (C = O); 200 MHz pmr (deuteriochloroform): δ 3.677 (s, 3H, CHCOOC$H_3$), 3.764 (s, 3H, CCOOC$H_3$), 4.017 (s, 2H, H1a, H9b), 5.424 (s, 1H, C = C$H$), 7.374 (dt, 2H, $J_{2,3,4}$ = 7.2 Hz, $J_{3,5}$ = 1.2 Hz, H3, H8), 7.445 (ddd, 2H, $J_{2,4}$ = 2.0 Hz, $J_{3,4}$ = 7.2 Hz, $J_{4,5}$ = 7.6 Hz, H2, H9), 8.056 (d, 2H, $J_{4,5}$ = 7.6 Hz, H5, H6); ms: (68 eV, 100°) m/e (relative intensity) 336 [(M+1)⁺, 8], 335 (M⁺, 36), 276 ($C_{18}H_{14}NO_2^+$, 47), 244 ($C_{17}H_{10}NO^+$, 56), 217 ($C_{16}H_{11}N^+$, 37), 216 ($C_{16}H_{10}N^+$, 55), 205 ($C_{15}H_{11}N^+$, 16), 178 ($C_{14}H_{10}^+$, 100), 165 ($C_{13}H_9^+$, 17), 152 ($C_{12}H_8^+$, 15).

*Anal.* Calcd. for $C_{20}H_{17}NO_4$: C, 71.64; H, 5.07; N, 4.18. Found: C, 71.46; H, 5.19; N, 4.23.

Diethyl 2-(1a,9b-Dihydrophenanthro[9,10-b]azirine-1-yl)-2-butenedioate (10, R = $C_2H_5$).

This compound was obtained by the same procedure as above in 79% yield, mp 106-107° (from ether-hexane); ir (chloroform): 1720, 1700 cm⁻¹ (C = O); 300 MHz pmr (deuteriochloroform): δ 1.252 (t, 3H, J = 7.2 Hz, CCOOCH₂C$H_3$), 1.272 (t, 3H, J = 7.2 Hz, CHCOOCH₂C$H_3$), 3.970 (s, 2H, H1a, H9b), 4.143 (q, 2H, J = 7.2 Hz, CCOOC$H_2$CH₃), 4.264 (q, 2H, J = 7.2 Hz, CHCOOC$H_2$CH₃), 5.463 (s, 1H, C = C$H$), 7.299-7.469 (m, 4H, H3, H4, H7, H8), 7.539 (dd, 2H, $J_{2,3}$ = 7.2 Hz, $J_{2,4}$ = 1.5 Hz, H2, H9), 8.039 (d, 2H, $J_{4,5}$ = 7.8 Hz, H5, H6); ms: (70 eV, 50°) m/e (relative intensity) 364 [(M+1)⁺, 8], 363 (M⁺ 29), 318 ($C_{20}H_{16}NO_3^+$, 4), 317 ($C_{20}H_{15}NO_3^+$, 6), 290 ($C_{19}H_{16}NO_2^+$, 23), 244 ($C_{17}H_{10}NO^+$, 27), 217 ($C_{16}H_{11}N^+$, 33), 216 ($C_{16}H_{10}N^+$, 27), 178 ($C_{14}H_{10}^+$, 100), 165 ($C_{13}H_9^+$, 10).

*Anal.* Calcd. for $C_{22}H_{21}NO_4$: C, 72.73; H, 5.79; H, 3.86. Found: C, 73.02; H, 5.82; N, 3.95.

Bis(1-methylethyl) 2-(1a,9b-Dihydrophenanthro[9,10-b]azirine-1-yl)-2-butenediote [10, R = CH(CH₃)₂].

Obtained as above in 72% yield, mp 125-126° (from ether-hexane); ir (chloroform) 1725, 1700 cm⁻¹ (C = O); 200 MHz pmr (deuteriochloroform): δ 1.247 (d, 6H, J = 6.3 Hz, CCOOCH(C$H_3$)₂), 1.296 (d, 6H, J = 6.3 Hz, CHCOOCH(C$H_3$)₂), 3.990 (s, 2H, H1a, H9b), 5.037 (heptet, 1H, J = 6.3 Hz, CCOOC$H$(CH₃₂), 5.021 (heptet, 1H, J = 6.3 Hz, CHCOOC$H$(CH₃)₃), 5.497 (s, 1H, C = C$H$), 7.324 (t, 2H, $J_{2,3,4}$ = 7.3 Hz,

H3, H8), 7.415 (ddd, 2H, $J_{2,4}$ = 1.4 Hz, $J_{3,4}$ = 7.3 Hz, $J_{4,5}$ 7.8 Hz, H4, H7), 7.539 (dd, 2H, $J_{2,3}$ = 7.3 Hz, $J_{2,4}$ = 1.4 Hz, H2, H9), 8.007 (dd, 2H, $J_{3,5}$ = 1.7 Hz, $J_{4,5}$ = 7.8 Hz, H5, H6); ms: (70 eV, 60°) m/e (relative intensity) 392 [(M+1)⁺, 11], 391 (M⁺, 38), 304 ($C_{20}H_{18}NO_2^+$, 47), 289 ($C_{18}H_{11}NO_3^+$, 35), 244 ($C_{17}H_{10}NO^+$, 27), 217 ($C_{16}H_{10}N^+$, 35), 178 ($C_{14}H_{10}^+$, 100), 165 ($C_{13}H_9^+$, 25).

*Anal.* Calcd. for $C_{24}H_{25}NO_4$: C, 73.66; H, 6.39; N, 3.58. Found C. 73.41; H, 6.31; N, 3.82.

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