# Molecular structure of *rac*-(4R\*,4aS\*,10aS\*)-4-nitro-1,2,3,4,4a,9,10,10a-octahydrophenanthren-4a-ol, an unusual by-product of nitration of a crude 9,10-dihydrophenanthrene

Franco Fernández,<sup>(1)</sup> J. López De Lerma,<sup>(2)</sup> Aurea Perales,<sup>(2)</sup> and Gonzalo Rodríguez<sup>(3),\*</sup>

Received Jul 20, 1993; Accepted March 4, 1994

A new nitro-octahydrophenanthrenol has been isolated by nitration of a crude 9,10-dihydrophenanthrene, which was identified by nmr and X-ray diffraction analysis. Crystallographic and molecular structure confirmed the compound as the *rac*-(4R\*,4aS\*,10aS\*)-4-Nitro-1,2,3,4,4a,9,10,10a-octahydrophenanthren-4a-ol. The crystal was triclinic,  $P\bar{1}$ , a = 10.549(3), b = 8.530(3), c = 7.131(1)Å,  $\alpha = 107.07(3)$ ,  $\beta = 91.62(3)$ ,  $\gamma = 96.27(4)^{\circ}$ . Cyclohexane and cyclohexene rings are *trans*-fused and have chair and half-chair conformations, respectively. The molecules are associated by hydrogen bridge between the hydroxyl oxygen and both nitro oxygens.

KEY WORDS: C14H17NO3, chair, half-chair.

#### Introduction

The preferred site of 9,10-dihydrophenanthrene (1) for typical electrophilic aromatic substitution reactions such as Friedel-Crafts acylation,<sup>1-4</sup> nitration,<sup>5,6</sup> sulfonation,<sup>7</sup> and halogenation<sup>8-10</sup> is position 2, and these reactions are therefore the methods of choice for obtaining 2-substituted (or 2,7-disubstituted) derivatives of 1. Since these derivatives are easily dehydrogenated, they are also useful for preparing 2-substituted (or 2,7-disubstituted) derivatives of phenanthrene,<sup>11,12</sup> which generally cannot be obtained by direct substitution of phenanthrene itself.

We have recently required considerable quantities of 2-nitro-9,10-dihydrophenanthrene (2) as the starting material for the preparation of 7-fluoro-9,10-dihydro-2phenanthrylalkanoic acids.<sup>13</sup> To this end, we have developed a quick, easy method for obtaining multigram



quantities of 1 by Birch reduction of phenanthrene.<sup>14</sup> However, the difficulty of purifying 1 from the crude product obtained (typically 91% of 1, 3-4% phenanthrene and 5-6% polyhydrophenanthrenes) has led us to explore the possibility of obtaining quickly sufficient quantities of 2 by direct nitration of the crude product. We report our findings here.

## Experimental

To optimize the yield of 2, nitration was carried out under various experimental conditions with fuming

<sup>&</sup>lt;sup>(1)</sup>Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Santiago, 15706-Santiago de Compostela, Spain.

<sup>&</sup>lt;sup>(2)</sup>Departamento de Rayos-X, Instituto Rocasolano, C.S.I.C., Serrano, 119, 28006-Madrid, Spain.

<sup>&</sup>lt;sup>(3)</sup> Departamento de Química, C-1, Facultad de Ciencias, Universidad Autónoma de Madrid, Canto Blanco, 28049-Madrid, Spain.

nitric acid in acetic anhydride or glacial acetic acid. Other reagents that have been recommended for the nitration of polycyclic hydrocarbon or non-deactivated aromatic substrates, such as dinitrogen tetroxide,<sup>15</sup> or the complex of fuming nitric acid with tin tetrachloride,<sup>16</sup> were also tried. The most significant results are listed in Table 1. Glc of the crude products showed that the major product, 2, was in all cases accompanied by varying quantities of numerous by-products, and during purification of 2 up to 30% of the crude product was also found to consist of nonvolatile tars that had not been detected by glc. Most tar was removed from the product by column chromatography on silica gel. Recrystallization and/or rechromatography of the fractions separated allowed the isolation of the major product, 2, the known compounds 3-nitrophenanthrene (3) and 2,7-dinitro-9,10-dihydrophenanthrene (4), and two compounds of melting points 179-180°C (5) and 84-85°C (6) for which we found no mention in the literature.

## Elemental and spectral analysis

Microanalysis and m.s. of 5 indicated the molecular formula  $C_{14}H_{10}N_2O_4$ , and the chief m.s. fragments pointed to its being a dinitro-9,10-dihydrophenanthrene, isomer of 4. Its <sup>1</sup>H-nmr spectrum had an AA'BB'-type symmetric multiplet centered at 2.94 ppm that is typical of asymmetrically substituted derivatives of 1, such as 2 and others, <sup>13</sup> when examined at 250 MHz (the spectra of symmetric derivatives such as 4 have a sharp singlet in this region). The chemical shifts and coupling con-

 
 Table 1. Conditions tried for nitration of 9,10-dihydrophenanthrene<sup>a</sup>

	Solvent/ Total volume	Reagent/	Temp.	Time <sup>b</sup>	2
Entry	(ml)	(mmol)	°C	(h)	content <sup>c</sup>
diffra	ction analysis sl	howed 6 to be rac-	(4R*,4aS	*,10aS*)	4-nitro-
					,
1	$Ac_2O/60$	HNO <sub>3</sub> /78	5	24	32
2	AcOH/20	HNO <sub>3</sub> /98	15	2	57
3	AcOH/20	HNO <sub>3</sub> /98	5	6	71
4	CH <sub>2</sub> Cl <sub>2</sub> /1200	N <sub>2</sub> O <sub>4</sub> /44	25	4	30 <sup>d</sup>
5	CH <sub>2</sub> Cl <sub>2</sub> /36	HNO <sub>3</sub> ·SnCl₄/21	25	1	66

<sup>a</sup>Crude product of the reduction of phenanthrene (4.0 g), 91% 1 (20 mmol).

<sup>b</sup>Longer reaction times did not increase the 2 content of the final crude mixture.

<sup>c</sup>Percentage of the total amount of volatile components detected by g.l.c. (UCC, 200°C) in the crude reaction product.

<sup>d</sup>6% of unreacted 1 was also detected.

stants of the other proton signals showed the nitro substituents to occupy positions 2 and 5, 2,5-dinitro-9,10dihydrophenanthrene (5).

Microanalysis and m.s. of **6** yielded the molecular formula  $C_{14}H_{17}NO_3$ , and since its i.r. spectrum clearly reflected the presence of hydroxyl and nitro groups it must be a nitrooctahydrophenanthrenol. Surprisingly, its nmr spectrum had signals for four protons in the  $\delta$  7.10– 7.50 ppm region, so that the nitro group cannot be bound to the aromatic ring. The rest of the nmr spectrum was too complex to allow a reliable structural assignment, but X-ray 1,2,3,4,4a,9,10,10a-octahydrophenanthren-4a-ol **(6).** Given this information, most of the nmr signals can be identified satisfactorily.

(4R\*,4aS\*,10aS\*)-4-Nitro-1,2,3,4,4a,9,10,10aoctahydrophenanthren-4a-ol (6) had m.p. 84-85°C. Anal. Calc. for C<sub>14</sub>H<sub>17</sub>NO<sub>3</sub>: C, 68.00; H, 6.93; N, 5.66. Found: C, 68.21, H, 7.03; N, 5.51. l.r. (KBr, cm<sup>-1</sup>): 3570 (O-H), 3070, 3020, 2930, 2870, 1605, 1535 (N=O), 1490, 1450, 1430, 1370, 1350 (N=O), 1300, 1270, 1255, 1180, 1165, 1120, 1090, 1060, 1000, 950, 935, 870, 820, 785, 760, 720, 690; <sup>1</sup>H-n.m.r. (CDCl<sub>3</sub>, d ppm): 1.59-1.74 (m, 5H, 1eg, 2eg, 2ax, 10eg, 10ax-H), 1.67(s, exchang. with  $D_2O$ , 1H, O-H), 1.85 (virtual qxd, J = 12.8 and 5.6 Hz, 1H, 1ax-H), 2.33 and 2.44 (AB system with J 16.3 Hz, each part additionally splitted as multiplets, 2H, 3eq, 3ax-H), 2.53-2.65 (m, 1H, 10aax-H), 2.83 (A part of a AB system (J 17.3 Hz), additionally splitted as a dd, J 5.6 and 1.7 Hz, 1H, 9weq-H), 2.95 (B part of a AB system (J 17.3 Hz), additionally splitted as a dd, J 12.2 and 5.7 Hz, 1H, 9wax-H), 5.41 (dd, J 4.7 and 2.5 Hz, 1H, 4eq-H), 7.12-7.15 (m, 1H, 5-H or 8-H), 7.19-7.24 (m, 2H, 6,7-H), 7.40-7.43 (m, 1H, 8-H or 5-H). MS (m/z):  $247(M^+, 4\%)$ , 200 (37), 183 (40), 159 (22), 157 (16), 146 (40), 145 (32), 144 (16), 143 (19), 142 (20), 141 (61), 131 (29), 130 (18), 129 (59), 128 (67), 127 (27), 118 (20), 117 (57), 116 (30), 115 (84), 91 (100), 90 (30), 89 (30), 83 (31), 79 (16), 78 (20), 77 (54), 76 (18), 70 (46), 67 (32), 65 (35), 63 (38), 57 (22), 55 (65), 53 (28), 52 (16), 51 (49), 50 (24).

## Structural solution

Crystals for X-ray diffraction were obtained by low evaporation of an ethyl acetate solution of 6. Summary of the X-ray crystal data collection and processing parameters are given in Table 2.

All H-atoms were located in a difference synthesis and included in subsequent refinements as isotropic contribution to  $U = 0.059(5) \text{ Å}^2$ .

 
 Table 2. Crystal data and summary of intensity data collection and structure refinement

Cmpd., rac-(4R*,4aS*,10aS*)-4-Nitro-1,2,3,4,4a,9,10,10a-
octahydrophenanthren-4a-ol,
Color/Shape, colorless/prismatic,
For. wt., C <sub>14</sub> H <sub>17</sub> NO <sub>3</sub> , 247,29,
Space group, triclinic P1
Temp., °C, 20
Cell Constants (# reflections > $\theta$ used) (# 63, within 2 < $\theta$ < 65°)
a, 10.549(3) Å,
b, 8.530(3) Å,
c, 7.131(1) Å,
$\alpha$ , 107.07(3) deg,
$\beta$ , 91.62(3) deg,
$\gamma$ , 96.27(4) deg.
Cell vol, 609.72(3) $Å^3$
Formula units/unit cell, Z, 2.
$D_{\rm calc}$ , 1.347(3) g cm <sup>-3</sup>
$\mu_{\rm calc},  {\rm cm}^{-1},  7.62$
Diffractometer/Scan, Four-circle, Philips PW 1100, $\omega/2\theta$ ,
Radiation, graphite monochromator, $CuK\alpha$ , $\lambda = 1.5418$ Å,
Max crystal dimensions, $0.22 \times 0.25 \times 0.16$ mm
Scan width, 1.5,
Standard reflections, 90 measurements,
Decay of standards, no intensity variation,
Reflections measured, 2066, 1873 observed, with $l > 2\sigma(l)$
criterion,
$2\theta$ range, deg, $2 < \theta < 65$ ,
Range of $h, k, l; 12, \pm 9, \pm 7.$
Corrections applied, Lorenz and polarization,
computer and programs, VAX6410, MULTAN80 <sup>24</sup> , XRay76 <sup>25</sup> ,
PARST.
Source of Structure factors used, International Tables for X-Ray
Crystallography. <sup>26</sup>
Structure solution, direct methods, Least-square in a block.
Treatment of Hydrogen Atoms, difference synthesis, fixed as
isotropic.
No. of parameters varied, 163,
Weights, w-scheme, empirical as to give no trends in $\langle w\Delta F^2 \rangle$
versus $\langle  F_o  \rangle$ and $\langle \sin \theta   \lambda \rangle$ ,
$R = \Sigma[ F_o  -  F_c ]/\Sigma F_o , 0.053$
<i>R</i> <sub>w</sub> , 0.062
Largest feature final diff. map, $\Delta \rho$ (eÅ <sup>3</sup> ), 0.25

# Discussion

# Molecular structure analysis of (6)

Final atomic coordinates and derived bond lengths and angles are given respectively in Tables 3 and 4. Analysis of the bond distances and angles<sup>17</sup> of compound 6 shows the following (see Fig. 1).

a. The  $C(sp^3)-C(sp^3)$  bond distances in rings A and B are unexceptional, ranging between 1.513(3) and 1.533(3)Å, except for C(9)-C(10) (1.537(2)Å) and C(10)-C(11) (1.554(3)Å), which appear to be

	Ta	ble	3.	Atomic	co	ord	lir	iate	s	for	compo	und C <sub>14</sub> F	I <sub>17</sub> NO <sub>3</sub> (6)	
$U_{eq}$	=	1/3	·	Sum[U <sub>ij</sub>	• 6	a*	•	$a_j^*$	•	a <sub>j</sub>	cos (a	$(a_i, a_j)]$	104; (esd's i	n
parentheses)														

Atom	x	v	Ζ.	U.a
				- 64
01	0.2595(1)	0.6405(2)	-0.0177(2)	508(5)
02	0.2871(3)	0.7558(2)	0.6102(2)	896(9)
O3	0.1500(3)	0.5473(4)	0.5403(4)	1272(15)
N	0.2304(2)	0.6356(3)	0.4927(3)	568(7)
Cl	0.0104(2)	0.6986(2)	0.2059(3)	484(7)
C2	-0.1063(2)	0.7583(3)	0.2217(3)	581(8)
C3	-0.1112(2)	0.9251(3)	0.2471(3)	590(8)
C4	0.0000(2)	1.0286(3)	0.2535(3)	537(7)
C5	0.1182(2)	0.9696(2)	0.2364(2)	425(6)
C6	0.1245(2)	0.8019(2)	0.2139(2)	389(6)
C7	0.2363(2)	1.0887(2)	0.2431(3)	506(7)
C8	0.3509(2)	1.0037(2)	0.1647(3)	507(7)
C9	0.3661(2)	0.8658(2)	0.2558(3)	424(6)
C10	0.2511(2)	0.7311(2)	0.1867(2)	371(5)
C11	0.2606(2)	0.5889(2)	0.2796(3)	439(6)
C12	0.3916(2)	0.5258(3)	0.2583(3)	549(8)
C13	0.5043(2)	0.6602(3)	0.3158(4)	623(9)
C14	0.4920(2)	0.7926(3)	0.2144(4)	579(8)

Table 4. Bond distances (Å) and angles (°) for compound  $C_{14}H_{17}NO_3(6)$ 

Bond distances (esd's in parenthesis)							
O1-C10	1.446(2)	C5-C7	1.509(3)				
O2-N	1.202(3)	C6-C10	1.519(3)				
O3-N	1.195(4)	C7-C8	1.513(3)				
N-C11	1.506(3)	C8-C9	1.522(3)				
C1-C2	1.378(3)	C9-C10	1.537(2)				
C1-C6	1.401(3)	C9-C14	1.528(3)				
C2-C3	1.387(4)	C10-C11	1.554(3)				
C3-C4	1.381(3)	C11-C12	1.533(3)				
C4-C5	1.390(3)	C12-C13	1.515(3)				
C5-C6	1.402(3)	C13-C14	1.524(4)				
Bond angles (esd's in parenthesis)							
02-N-03	121.6(2)	C8-C9-C14	113.6(2)				
O3-N-C11	117.5(2)	C8-C9-C10	109.4(2)				
02-N-C11	120.8(2)	C10-C9-C14	111.1(2)				
C2-C1-C6	121.7(2)	C6-C10-C9	112.2(2)				
C1-C2-C3	119.3(2)	O1-C10-C9	109.9(2)				
C2-C3-C4	119.9(3)	O1-C10-C6	109.7(1)				
C3-C4-C5	121.4(2)	C9-C10-C11	111.3(2)				
C4-C5-C7	118.9(2)	C6-C10-C11	ļ13.6(2)				
C4-C5-C6	119.2(2)	01-C10-C11	99.4(1)				
C6-C5-C7	121.9(2)	N-C11-C10	112.9(2)				
C1-C6-C5	118.5(2)	C10-C11-C12	112.3(2)				
C5-C6-C10	120.9(2)	N-C11-C12	109.4(2)				
C1-C6-C10	120.5(2)	C11-C12-C13	114.6(2)				
C5-C7-C8	113.3(2)	C12-C13-C14	111.5(2)				
C7-C8-C9	109.7(2)	C9-C14-C13	111.3(2)				



Fig. 1. Perspective view of the molecular structure of (6), showing the crystallographic numbering of the atoms.

strained. Straining of C(9)-C(10) bond may be due to its being common to both fused rings, and straining of C(10)-C(11) bond to the *trans*-diaxial substitution by the hydroxyl and nitro groups.<sup>18</sup> The  $C(sp^2)-C(sp^3)$ bond distances in ring B, C(5)-C(7) (1.509(3)Å) and C(6)-C(10) (1.519(3)Å) have normal values.

b. Rings A and B are *trans*-fused and have chair and half-chair conformations respectively, their dominant symmetries<sup>19</sup> being respectively  $C_s$  (around C(12)) and  $C_2$  (around C(8)-C(9)).

c. The OH and NO<sub>2</sub> substituents have the expected  $C(sp^3)-O(1)$  and  $C(sp^3)-N$  single bond distances, and the expected angles. Thus O(1)-C(10) = 1.446(2) and C(11)-N = 1.506(3)Å, and N-O(2) (1.202(3)Å) and N-O(3) (1.195(4)Å) are similar to the lengths observed in nitro groups bonded to a tetrahedral carbon atom.<sup>20-23</sup>

d. The bond distances and angles in the aromatic ring are normal, the bond lengths ranging between 1.378(3) and 1.402(3)Å, while the deviations from its mean plane go from 0.001(2)Å to 0.006(2)Å in opposite side of the plane.

e. The molecular packing is shown in Fig. 2. The packing consists of columns of molecules stacked along the c axis through inversion centers, in such a way that there is interaction between H(O1) and the two oxygens O(2) and O(3) of the (-x, -y, -z) and  $\pm(0, 0, n)$  symmetry related molecules. Moreover, these chains are tightened by H-bonds linking O(1), O(2), and O(3) (Fig. 2):

$$A - H \cdot \cdot \cdot B$$
 $A - H(Å)$ 
 $O(1) - H \cdot \cdot \cdot O(2)$ 
 $0.97(1)$ 

$$O(1) - H \cdot \cdot \cdot O(3) = 0.97(1)$$



Fig. 2. A packing diagram of molecules of the compound 6 from the b axis.

The production of 4 and 5 during nitration of our crude 1 is readily explicable. 4 has been reported to be the chief product of the dinitration of 1,<sup>11</sup> and 5 is probably the result of the nitration of 4-nitro-9,10-dihydrophen-anthrene, the major by-product of the mononitration of 1.<sup>5,10</sup>

The presence of 3 is not surprising either, since the crude starting material contained a small proportion of phenanthrene. The most intriguing by-product, **6**, must derive from the addition of the components of nitric acid to one of the polihydrophenanthrenes present in the starting material. The *trans*-diaxial location of its two functional groups on adjacent carbons suggests that it may come about through ionic addition of acetyl nitrate to 1,2,3,9,10,10a-hexahydrophenanthrene (7), followed by hydrolysis of the acetoxyl group during workup in aqueous medium.

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H···B(Ă)	$A \cdot \cdot \cdot B(A)$	AHB(°)	
2.34(1)	3.100(3)	134(1)	
2.56(1)	3.167(3)	120(1)	

#### Structure of rac-(4R\*,4aS\*,10aS\*)-4-nitro-1,2,3,4,4a,9,10,10a-octahydrophenanthren-4a-ol

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