Table 1. *Selected geometric parameters (Å, °)*

O11—C11	1.217 (5)	O22—C21	1.266 (5)
O12—C11	1.284 (5)	O21—C21	1.228 (5)
C11—C12	1.527 (6)	C21—C22	1.538 (6)
O11—C11—O12	126.2 (4)	O21—C21—O22	127.3 (4)
O11—C11—C12	121.6 (4)	O21—C21—C22	120.3 (4)
O12—C11—C12	112.2 (4)	O22—C21—C22	112.4 (4)
O11—C11—C12—N11	2.5 (5)	O21—C21—C22—N21	2.7 (5)
N11—C12—C13—C14	68.3 (5)	N21—C22—C23—C24	64.8 (5)
C12—C13—C14—C15	−83.8 (5)	C22—C23—C24—C25	−90.6 (5)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O22—HO22···O12^{i}	1.15 (7)	1.31 (7)	2.440 (4)	165 (6)
N11—H1N1···O21^{ii}	0.89	1.911	2.788 (4)	168
N11—H2N1···O1^{ii}	0.89	2.075	2.954 (14)	169
N11—H2N1···O3*^{ii}	0.89	2.235	3.00 (2)	144
N11—H3N1···O3*^{iii}	0.89	2.186	3.070 (17)	172
N11—H3N1···O4^{iii}	0.89	2.253	2.919 (14)	131
N21—H1N2···O2^{ii}	0.89	2.382	3.268 (13)	174
N21—H1N2···O2*^{ii}	0.89	2.178	2.956 (17)	146
N21—H2N2···O11^{iv}	0.89	1.956	2.821 (5)	164
N21—H3N2···O1*^{iii}	0.89	2.132	2.906 (13)	145
N21—H3N2···O2^{iii}	0.89	2.390	3.278 (14)	175

Symmetry codes: (i) $1+x, y-1, z$; (ii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

For H atoms, only the coordinates and isotropic displacement parameters of HO22 were refined. Perchlorate O atoms show disorder over two positions (occupancies of 0.58 and 0.42) corresponding to each atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1040). Services for accessing these data are described at the back of the journal.

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Unusual Substitution of $-SCH_3$ by –OH in 9,10-Dihydrophenanthrene†

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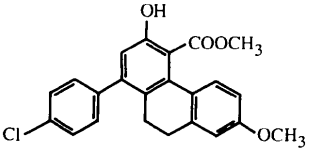
Abstract

The unusual nucleophilic substitution of methylthio by a hydroxyl group in the presence of alkali and dimethylformamide in the synthesis of methyl 1-(4-chlorophenyl)-3-hydroxy-7-methoxy-9,10-dihydrophenanthrene-4-carboxylate, $C_{23}H_{19}ClO_4$, has been confirmed by single-crystal X-ray structure determination.

Comment

Aromatic nuclei and their immediately attached atoms in isolated (*i.e.* not fused) polycyclic systems are generally coplanar and their intramolecular fusion results in inflexible ring skeletons. The electronic character of such systems mainly depends upon the nature of the substituents attached to the ring; these govern the conformation of the molecule (Ram & Goel, 1996), which is an essential factor in biological recognition.

Nucleophilic substitution of $-SCH_3$ by alkoxide is very common, while its displacement by hydroxyl is quite unusual in the presence of alkali in dry dimethylformamide at room temperature. The presence of the unexpected hydroxyl group and its conformation necessitated the X-ray crystallographic study of the title compound, (I).



(I)

The conformation of the title molecule and the atomic numbering scheme are shown in Fig. 1. The molecule contains one phenanthrene ring (fused-ring system *A*/*B*/*C*) to which a phenyl ring (*D*) has been

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attached *via* C1. All the aryl rings (*A*, *C* and *D*) in the molecule are planar as the algebraic sum of torsion angles is approximately zero in each ring. The maximum deviations of individual atoms from the mean plane of the ring are −0.058 (2), 0.018 (2) and −0.006 (2) Å for the C4, C5a and C4′ atoms in rings *A*, *C* and *D*, respectively. In the puckered ring *B*, the deviation of atom C9 from the least-square planes through atoms C10, C1a, C4a, C5a and C9a is −0.676 (4) Å, and this establishes the sofa conformation of the ring. The pendant 4-chlorophenyl ring is twisted with respect to the phenanthrene ring by 57.7 (1)°. The hydroxyl proton is hydrogen bonded to the methoxycarbonyl O atom both intramolecularly [O3″—H···O4″*A* = 2.656 (3) Å] and intermolecularly [O3″—H···O4″*A*(1 − *x*, 2 − *y*, −*z*) = 2.997 (3) Å]. The crystal structure is, therefore, stabilized mainly by hydrogen bonding and van der Waals interactions.

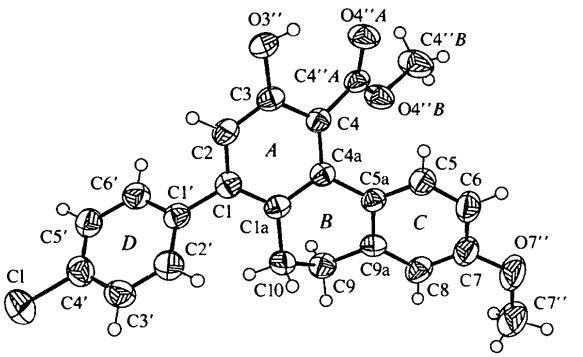

Fig. 1. *ORTEP* (Johnson, 1965) diagram showing displacement ellipsoids at the 50% probability level for the non-H atoms. H atoms are drawn as small spheres of arbitrary radii for clarity.

Experimental

The title compound was prepared through the carbanion-induced ring transformation reaction of 6-aryl-3-methoxycarbonyl-4-methylthio-2*H*-pyran-2-one and 6-methoxy-1-tetralone at room temperature under an inert atmosphere (Ram & Goel, 1997). Diffraction quality crystals were prepared by slow evaporation from acetone solution at room temperature.

Crystal data

$C_{23}H_{19}ClO_4$
M_r = 394.83
Triclinic
$P\bar{1}$
a = 8.9047 (7) Å
b = 9.6102 (13) Å
c = 12.9962 (15) Å
α = 110.332 (12)°
β = 104.167 (8)°
γ = 97.458 (8)°
V = 982.5 (2) Å^3
Z = 2
D_x = 1.335 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 13–22°
μ = 0.221 mm^{-1}
T = 293 (2) K
Block
0.40 × 0.20 × 0.15 mm
Colourless

Data collection

Enraf–Nonius MACH-3 CAD-4 diffractometer
θ–2θ scans
Absorption correction: none
3363 measured reflections
3151 independent reflections
2615 reflections with $I > 2\sigma(I)$
R_{int} = 0.074
θ_{max} = 24.96°
h = 0 → 10
k = −11 → 11
l = −11 → 11
3 standard reflections
every 50 reflections
frequency: 30 min
intensity variation: 1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.223
S = 1.076
3142 reflections
256 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.2045P)^2 + 0.0003P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The structure was solved by direct methods and non-H atoms were refined anisotropically using full-matrix least-squares methods. With the exception of the hydroxyl H atom, which was located from a circular Fourier synthesis and thereafter allowed to rotate on its parent O atom with the O—H distance and C—O—H angle fixed, H atoms were placed in idealized positions and allowed to ride on the parent atom for the final cycles of refinement. Nine of the most disagreeable reflections were suppressed during the later stages of refinement.

Data collection: *MACH3/PC and CAD-4/PC* (Enraf–Nonius, 1996). Cell refinement: *MACH3/PC and CAD-4/PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965) in *NRCVAX*. Software used to prepare material for publication: *SHELXL*93.

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