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13,13a-Dihydro-13-methoxy-9-methyl-1-benzopyrano[4,3-*i*]dinaphtho[2,1-*c*;1′,2′-*f*]-2,8-dioxabicyclo[3.3.1]nonane

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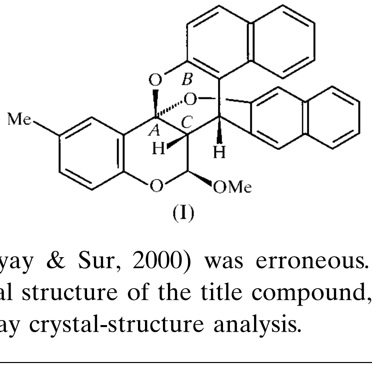
The crystal structure of the title compound, $C_{32}H_{24}O_4$, contains three fused dihydropyran rings (*A*, *B* and *C*); ring *A* is fused with a benzene ring while the other two rings, *B* and *C*, are fused with naphthalene rings. Ring *A* adopts a half-chair conformation with an equatorial methoxy group, whereas ring *B* assumes a distorted half-chair conformation, the *A*/*B* ring junction being *trans*. Ring *C* adopts a distorted half-boat conformation and is nearly orthogonal to ring *B*. Ring *C* is inclined to the best plane of ring *A* at an angle of 112.1 (1)°.

Comment

Recently, some coumarin-based inhibitors of HIV-integrase (Zhao *et al.*, 1997) have been synthesized which have some structural resemblance to the compounds obtained by the reaction of β-naphthol with simple aldehydes (Sirkecioglue *et al.*, 1995), and by the reaction of 4-hydroxycoumarins with vinyl acetate (Balasubramanian *et al.*, 1996) and with isatin (Jain *et al.*, 1997). The synthesis of an analogous chromone-based compound by reacting 6-methyl-4-oxo-4*H*-1-benzopyran-3-carboxaldehyde with β-naphthol was attempted. The present study has revealed that the structure of the compound as determined by spectroscopic analysis and reported earlier (Bandyopadhyay & Sur, 2000) was erroneous. We describe here the actual structure of the title compound, (I), as determined by X-ray crystal-structure analysis.



(I)

The compound contains three fused dihydropyran rings. Two of these dihydropyran rings (*B* and *C*) are attached to naphthalene rings and the third (*A*) is attached to a benzene ring. According to ring-puckering parameters [Q = 0.480 (2) Å, φ = −92.8 (4)° and θ = 131.3 (3)°; Cremer & Pople (1975)] and ring torsion angles (Nashipuri, 1991) (Table 1), the dihydropyran ring *A* adopts a half-chair conformation with atoms C13 and C13a out of the best plane containing the remaining atoms by 0.346 (3) Å and −0.390 (3) Å, respectively. The asymmetry parameter (Nardelli, 1983) ΔC_2(C13—C13a) of 0.008 (1) also reveals the half-chair conformation with a twofold pseudo-axis passing through the midpoints of the C13—C13a and C7b—C11a bonds. The best plane through the fused dihydropyran ring forms a dihedral angle of 5.1 (1)° with the benzene ring.

The half-chair conformation of ring *B* (O20,C19a,C13c,C13b,C13a,C7a) is evident from the ring puckering parameters [Q = 0.544 (2) Å, φ = −101.5 (3)° and θ = 49.0 (2)°] and also from the torsion angles (Table 1). The asymmetry parameter ΔC_2(C13c—C19a) of 0.043 (1) indicates the presence of a twofold pseudo-axis passing through the midpoints of the C13c—C19a and C7a—C13a bonds. The fused naphthalene ring makes a dihedral angle of 5.2 (1)° with the best plane through ring *B*.

Ring *C* adopts a distorted half-boat conformation [ring puckering parameters: Q = 0.556 (2) Å, φ = 147.0 (2)° and θ = 56.7 (2)°]. Atoms C13a and C7a are out of the best plane passing through the remaining atoms of the ring by −0.938 (3) and −0.375 (3) Å, respectively. The asymmetry parameter ΔC_2(O7—C6a) of 0.013 (1) indicates the presence of a twofold pseudo-axis across the O7—C6a and C13a—C13b bonds.

The torsion angle C7b—C7a—C13a—C13b of 171.2 (1)° indicates that the *A*/*B* ring junction is *trans*. The angles between the best planes through rings *A* and *B*, rings *B* and *C*,

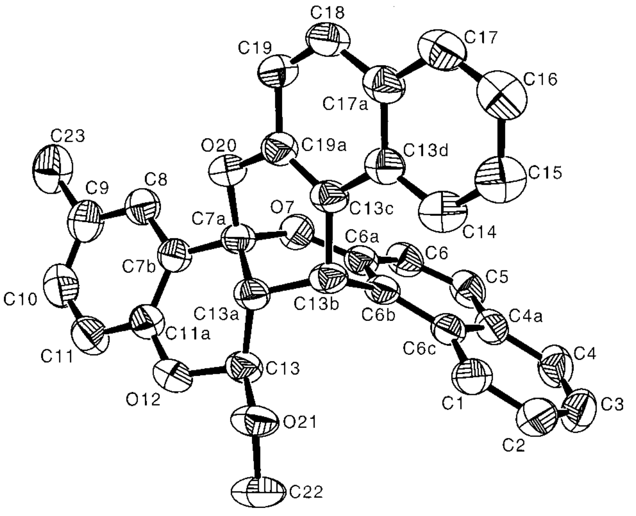


Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids (Farrugia, 1997).

and rings *A* and *C* are 18.0 (1), 94.1 (1) and 112.1 (1)°, respectively.

Experimental

To a stirred solution of β-naphthol (8 mmol) in glacial acetic acid (10 ml) at 333–353 K, concentrated HCl (1 ml) was added dropwise. The mixture was stirred at that temperature for 15 min. A solution of 6-methyl-4-oxo-4*H*-1-benzopyran-3-carboxaldehyde in glacial acetic acid (8 ml) was added dropwise to the reaction mixture which gradually turned red. The deep-red solution solidified on stirring at 333–353 K within 1 h. The whole mass was poured into crushed ice (200 g). The solid obtained was filtered, washed with water, dried in air, and digested with chloroform. The major red insoluble mass obtained after the chloroform extraction was digested with methanol. The methanolic solution produced a white crystalline compound, (I), in more than 50% yield. The compound was recrystallized by slow evaporation at room temperature from a solution in an ethanol/chloroform mixture.

Crystal data

$C_{32}H_{24}O_4$
$M_r = 472.51$
Triclinic, $P\bar{1}$
$a = 10.191\ (7)$ Å
$b = 10.963\ (10)$ Å
$c = 12.6210\ (11)$ Å
$\alpha = 102.23\ (6)°$
$\beta = 114.58\ (3)°$
$\gamma = 100.64\ (6)°$
$V = 1192.7\ (14)$ Å^3
$Z = 2$
$D_x = 1.316$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15$–$20°$
$\mu = 0.689$ mm^{-1}
$T = 293\ (2)$ K
Irregular, colourless
0.35 × 0.27 × 0.23 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
4396 measured reflections
4396 independent reflections
3505 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 69.95°$
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = -15 \rightarrow 15$
2 standard reflections
frequency: 60 min
intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.151$
$S = 1.039$
4396 reflections
328 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0968P)^2 + 0.1715P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.030$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0060 (19)

Table 1
Selected torsion angles (°).

O7—C6a—C6b—C13b	−8.5 (2)
C6b—C6a—O7—C7a	−9.9 (2)
C6a—O7—C7a—C13a	−12.1 (2)
C13a—C7a—C7b—C11a	−17.7 (2)
C7a—C7b—C11a—O12	2.3 (3)
C7b—C11a—O12—C13	−17.6 (3)
C11a—O12—C13—C13a	47.1 (2)
O12—C13—C13a—C7a	−61.24 (18)
C7b—C7a—C13a—C13	45.86 (18)
O20—C7a—C13a—C13b	−69.00 (17)
O7—C7a—C13a—C13b	49.05 (18)
C6a—C6b—C13b—C13a	46.13 (18)
C7a—C13a—C13b—C6b	−65.20 (15)
C7a—C13a—C13b—C13c	53.76 (16)
C13a—C13b—C13c—C19a	−23.28 (19)
C13b—C13c—C19a—O20	2.2 (2)
C13c—C19a—O20—C7a	−14.6 (2)
C13a—C7a—O20—C19a	47.67 (18)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST*93 (Nardelli, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1108). Services for accessing these data are described at the back of the journal.

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