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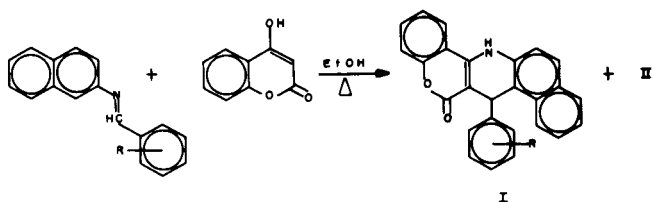
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The reaction of 2-arylidene-naphthylamines with 4-hydroxycoumarin results in Hoffman-Martius type rearrangement yielding 2*H*-benzo[*f*]benzopyrano[4,3-*b*]quinolin-2-ones **I** and the compounds **II**. This work describes the structure elucidation of the compounds **II**. The structure was confirmed using ir, nmr and X-ray spectroscopy.

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After having found [3] that dimedone adds to 2-arylidene-naphthylamines with exclusive formation of tetrahydrobenz[*c*]acridin-8-ones and after having applied this finding to the synthesis of tetrahydrobenz[*a*]acridin-11-ones [4], recently we investigated analogous transformations with 4-hydroxycoumarin [5]. So, from the reaction of 2-arylidene-naphthylamines with 4-hydroxycoumarin we could isolate the 2*H*-benzo[*f*]benzopyrano[4,3-*b*]quinolin-2-ones **I** and the compounds **II**, (Scheme 1). In continuation of this work we now describe the structure elucidation of **II** derivatives.

Scheme 1



Structural assignment of derivatives **II** was made on spectroscopic grounds. The infrared spectrum of compounds **II** displayed absorptions at 3300 and 3200 cm^{-1} which were assigned to -NH and OH stretches, respectively. They showed also two stronger carbonyl absorptions at 1685 (quinolone ring) [6] and 1635 cm^{-1} (*o*-hydroxyphenylketone). The presence of ions at m/z 121 ($\text{C}_7\text{H}_5\text{O}_2$) and $\text{M}-121]^+$ in the mass spectrum of **II** was consistent with the existence of a *o*-hydroxyphenylketone moiety in the framework of **II** derivatives. Likewise, in the ^1H -nmr spectra of **II** the presence of two one-proton singlet at δ 12.5-11.5 and δ 11-10.5, which exchange upon introduction of deuterium oxide, confirmed the above assertion.

The other characteristic ^1H -nmr feature was a pair of broad singlets at δ 5.6-5.1 (1H) and δ 4.78-4.65 (1H) which were assigned to the methine protons attached to C-4 and C-3 [7], respectively. The remaining aromatic protons in **II** were assigned to signal in the region at δ 8.4-6.4 (multiplet) (Table 1).

Definitive evidence for the structure of the compound **II** was obtained by single-crystal X-ray diffraction analysis of compound **IIIh**. Figure 1 shows a perspective view and atom labelling of **IIIh**. The bonds lengths and bond angles are shown in Tables 2 and 3. In the crystal structure **IIIh** adopts an overall cross-like conformation, with the *p*-bromophenyl group at C-4 and the *o*-hydroxyphenyl ketone group at C-3 parallel to each other (angle between planes = 2.9°) and nearly perpendicular (80.7°, 79.5°) and lying in opposite sides of the benzo[*f*]quinolin-2-one ring. The Cremer and Pople [8] parameters indicate that the dihydro-2-pyridinol ring adopts a twisted-boat conformation. The N(1)-C(10a) bond is substantially shorter than C (sp^2)-N (sp^2) single bond of 1.470 (5) Å proposed by Cameron [9] indicating significant π character.

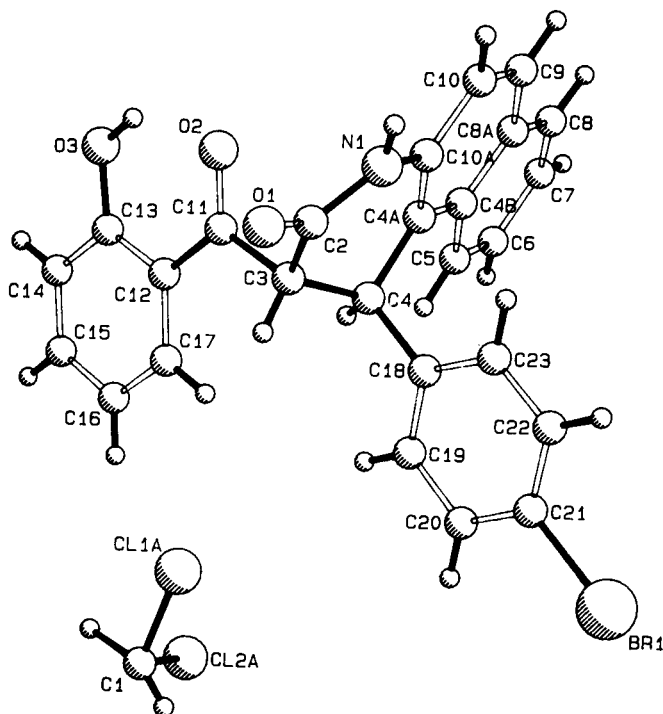


Table 1
Physical, Analytical and Spectral data for Compounds II

Compound No.	R	Mp °C	Yield %	Molecular Formula	Analyses %		Spectral Data
					C	H	
a	H	271-272	12.5	C ₂₆ H ₁₉ NO ₃	79.37 (79.33)	4.87 (4.84)	ir (chloroform): 3308, 1687, 1631 cm ⁻¹ ; ¹ H nmr (DMSO-d ₆): δ 11.45 (s, 1H), 10.41 (s, 1H), 8.13 (bd, 1H), 7.9-6.48 (m, 14H), 5.11 (s, 1H), 4.77 (s, 1H); ms: M ⁺ at m/z 393
b	<i>o</i> -OMe	250-252	16.0	C ₂₇ H ₂₁ NO ₄	76.58 (76.54)	5.00 (4.97)	ir (chloroform): 3400, 1676, 1632 cm ⁻¹ ; ¹ H nmr (DMSO-d ₆): δ 12.5 (s, 1H), 11.5 (s, 1H), 8.4 (bd, 1H), 7.9-6.4 (m, 13H), 5.54 (s, 1H), 4.75 (s, 1H), 4.1 (s, 3H); ms: M ⁺ at m/z 423
c	<i>o</i> -Cl	265-267	15.5	C ₂₆ H ₁₈ ClNO ₃	72.98 (72.96)	4.24 (4.23)	ir (chloroform): 3300, 1685, 1630 cm ⁻¹ ; ¹ H nmr (DMSO-d ₆): δ 12.75 (s, 1H), 11.6 (s, 1H), 8.32 (bd, 1H), 7.9-6.65 (m, 13H), 5.6 (s, 1H), 4.76 (s, 1H); M ⁺ at m/z 427
d	<i>o</i> -Me	273-275	12.0	C ₂₇ H ₂₁ NO ₃	79.59 (79.57)	5.20 (5.18)	ir (chloroform): 3400, 1688, 1634 cm ⁻¹ ; ¹ H nmr (DMSO-d ₆): δ 12.5 (s, 1H), 10.5 (s, 1H), 8.25 (bd, 1H), 7.9-6.5 (m, 13H), 5.35 (s, 1H), 4.65 (s, 1H), 2.58 (s, 3H); ms: M ⁺ at m/z 407
e	<i>o</i> -Br	245-247	14.0	C ₂₆ H ₁₈ BrNO ₃	66.11 (66.08)	3.84 (3.81)	ir (chloroform): 3400, 1687, 1635 cm ⁻¹ ; ¹ H nmr (DMSO-d ₆): δ 12.5 (s, 1H) 11.3 (s, 1H) 8.3 (bs, 1H), 7.9-6.65 (m, 13H), 5.5 (s, 1H), 4.7 (s, 1H); ms: M ⁺ at m/z 471
f	<i>p</i> -OMe	258-260	13.0	C ₂₇ H ₂₁ NO ₄	76.58 (76.56)	5.00 (5.00)	ir (chloroform): 3300, 1676, 1633 cm ⁻¹ ; ¹ H nmr (DMSO-d ₆): δ 12.52 (s, 1H), 11.45 (s, 1H), 8.15 (bd, 1H), 7.9-6.45 (m, 13H), 5.1 (s, 1H), 4.75 (s, 1H), 3.7 (s, 3H); ms: M ⁺ at m/z 423
g	<i>p</i> -Me	261-262	12.5	C ₂₇ H ₂₁ NO ₃	79.59 (79.57)	5.20 (5.18)	ir (chloroform): 3400, 1690, 1633 cm ⁻¹ ; ¹ H nmr (DMSO-d ₆): δ 12.5 (s, 1H), 11.4 (s, 1H) 8.1 (bd, 1H), 7.9-6.45 (m, 13H), 5.1 (s, 1H), 4.7 (s, 1H), 2.55 (s, 3H); ms: M ⁺ at m/z 407
h	<i>p</i> -Br	263-264	25.0	C ₂₆ H ₁₈ BrNO ₃	66.11 (66.07)	3.84 (3.82)	ir (chloroform): 3400, 1689, 1635 cm ⁻¹ ; ¹ H nmr (DMSO-d ₆): δ 12.1 (s, 1H), 11.0 (s, 1H), 8.17 (bd, 1H), 7.95-6.45 (m, 13H), 5.13 (s, 1H), 4.78 (s, 1H); ms: M ⁺ at m/z 471

Table 2

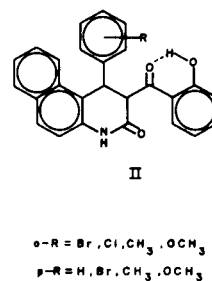
Bond lengths (Å)

Br (1) - C(21)	1.900 (5)	C(4A) - C(4B)	1.421 (7)
Cl (1A) - Cl(1B)	0.820 (1)	C(4B) - C(5)	1.418 (7)
Cl (1A) - C(1)	1.710 (10)	C(4B) - C(8A)	1.428 (7)
Cl (1B) - C(1)	1.780 (1)	C(5) - C(6)	1.375 (8)
Cl (1B) - Cl(2A)	2.210 (3)	C(6) - C(7)	1.40 (1)
Cl (2A) - Cl(2B)	0.800 (4)	C(7) - C(8)	1.331 (9)
Cl (2A) - C(1)	1.710 (2)	C(8) - C(8A)	1.418 (8)
Cl (2B) - H(1A)	1.40 (1)	C(8A) - C(9)	1.420 (7)
Cl (2B) - H(1B)	1.56 (8)	C(9) - C(10)	1.343 (8)
Cl (2B) - C(1)	1.63 (1)	C(10) - C(10A)	1.403 (7)
O (1) - C(2)	1.224 (5)	C(11) - C(12)	1.472 (6)
O (2) - C(11)	1.227 (5)	C(12) - C(13)	1.388 (7)
O (3) - H(3A)	0.940 (7)	C(12) - C(17)	1.392 (7)
O (3) - C(13)	1.359 (7)	C(13) - C(14)	1.396 (8)
N (1) - H(1)	0.800 (6)	C(14) - C(15)	1.346 (9)
N (1) - C(2)	1.344 (6)	C(15) - C(16)	1.380 (1)
N (1) - C(10A)	1.407 (6)	C(16) - C(17)	1.375 (8)
C (1) - H(1A)	0.790 (9)		
C (2) - C(3)	1.519 (6)		
C (3) - C(11)	1.518 (6)		
C (3) - C(4)	1.550 (6)		
C (4) - C(18)	1.509 (6)		
C (4) - C(4A)	1.516 (6)		
C (4A) - C(10A)	1.372 (6)		
C (18) - C(23)	1.375 (7)		
C (18) - C(19)	1.377 (7)		
C (19) - C(20)	1.390 (8)		
C (20) - C(21)	1.370 (1)		
C (21) - C(22)	1.372 (9)		
C (22) - C(23)	1.386 (8)		

One of the most interesting feature obtained from the crystal data of **IIh** was the relationship with the value of the coupling constant (J) between H-3 and H-4.

When the Karplus equation [10] was applied to the solid state conformation τ [H(3)-C(3)-C(4)-H(4)] = 76°, to estimate the vicinal coupling constant expected for these protons, the expected and observed values (J ~ 0 in solution) agree perfectly suggesting a great deal of rigidity in this ring. On other hand, in the unit cell, molecules centrosymmetrically related are linked in pairs by hydrogen bonds (Table 4) forming layers parallel to the $\bar{2}$ 12 plane.

Scheme 2



As shown by investigations of the mechanism of the reaction of 2-arylidene-naphthylamines with 1,3-dicarbonyl compounds [3,4,5] this reaction may take place through a Hoffman-Martius type rearrangement. Therefore, if the assumed intermediate **III** is indeed formed it possess two

Table 3

Bond angles (degrees)

C(5) - C(6) - (7)	121.0 (5)	O(3) - C(13) - C(12)	122.6 (4)
C(8) - C(7) - C(6)	119.8 (5)	O(3) - C(13) - C(14)	116.7 (5)
C(7) - C(8) - C(8A)	122.3 (5)	C(12) - C(13) - C(14)	120.7 (5)
C(8) - C(8A) - C(9)	123.1 (5)	C(15) - C(14) - C(13)	119.7 (5)
C(8) - C(8A) - C(4B)	118.4 (5)	C(14) - C(15) - C(16)	121.2 (5)
C(9) - C(8A) - C(4B)	118.5 (4)	C(17) - C(16) - C(15)	119.5 (5)
C(10) - C(9) - C(8A)	121.1 (4)	C(16) - C(17) - C(12)	121.0 (5)
C(9) - C(10) - C(10A)	120.5 (4)	C(23) - C(18) - C(19)	117.6 (4)
C(4A) - C(10A) - C(10)	121.4 (4)	C(23) - C(18) - C(4)	122.3 (4)
C(4A) - C(10A) - N(1)	120.4 (4)	C(19) - C(18) - C(4)	120.1 (4)
C(10) - C(10A) - N(1)	118.2 (4)	C(18) - C(19) - C(20)	121.7 (5)
O(2) - C(11) - C(12)	120.5 (4)	C(21) - C(20) - C(19)	118.7 (5)
O(2) - C(11) - C(3)	118.9 (4)	C(22) - C(21) - C(20)	121.2 (5)
C(12) - C(11) - C(3)	120.5 (4)	C(22) - C(21) - Br(1)	118.9 (5)
C(13) - C(12) - C(17)	118.0 (4)	Cl(1A) - C(1) - Cl(1B)	27.1 (5)
C(13) - C(12) - C(11)	120.1 (4)	O(1) - C(2) - N(1)	123.4 (4)
C(17) - C(12) - C(11)	121.9 (4)	O(1) - C(2) - C(3)	120.8 (4)
Cl(1B) - Cl(1A) - C(1)	82.0 (1)	N(1) - C(2) - C(3)	115.8 (4)
Cl(1A) - Cl(1B) - C(1)	71.0 (1)	C(11) - C(3) - C(2)	106.7 (3)
Cl(1A) - Cl(1B) - Cl(2A)	116 (2)	C(11) - C(3) - C(4)	110.9 (3)
C(1) - Cl(1B) - Cl(2A)	49.2 (8)	C(2) - C(3) - C(4)	113.4 (3)
Cl(2B) - Cl(2A) - C(1)	71 (1)	C(18) - C(4) - C(4A)	112.2 (4)
Cl(2B) - Cl(2A) - Cl(1B)	123 (2)	C(18) - C(4) - C(3)	112.9 (4)
C(1) - Cl(2A) - Cl(1B)	52.2 (7)	C(4A) - C(4) - C(3)	109.6 (3)
Cl(2A) - Cl(2B) - H(1A)	90 (5)	C(10A) - C(4A) - C(4B)	119.2 (4)
Cl(2A) - Cl(2B) - H(1B)	86 (4)	C(10A) - C(4A) - C(4)	118.3 (4)
Cl(2A) - Cl(2B) - C(1)	82 (1)	C(4B) - C(4A) - C(4)	122.5 (4)
H(1A) - Cl(2B) - H(1B)	77 (5)	C(5) - C(4B) - C(4A)	122.8 (4)
H(1A) - Cl(2B) - C(1)	29 (4)	C(5) - C(4B) - C(8A)	118.0 (4)
H(1B) - Cl(2B) - C(1)	49 (3)	C(4A) - C(4B) - C(8A)	119.2 (4)
H(3A) - O(3) - C(13)	115 (4)	C(6) - C(5) - C(4B)	120.4 (5)
H(1) - N(1) - C(2)	123 (4)		
H(1) - N(1) - C(10A)	110 (4)		
C(2) - N(1) - C(10A)	124.5 (4)		
H(1A) - C(1) - Cl(2B)	58 (8)		
H(1A) - C(1) - Cl(2A)	69 (8)		
H(1A) - C(1) - Cl(1A)	130 (8)		
H(1A) - C(1) - Cl(1B)	110 (8)		
Cl(2B) - C(1) - Cl(2A)	28 (1)		
Cl(2B) - C(1) - Cl(1A)	130.1 (8)		
Cl(2B) - C(1) - Cl(1B)	106.1 (8)		
Cl(2A) - C(1) - Cl(1A)	103 (1)		
Cl(2A) - C(1) - Cl(1B)	79 (1)		
C(20) - C(21) - Br(1)	119.8 (4)		
C(18) - C(23) - C(22)	122.3 (5)		

Table 4

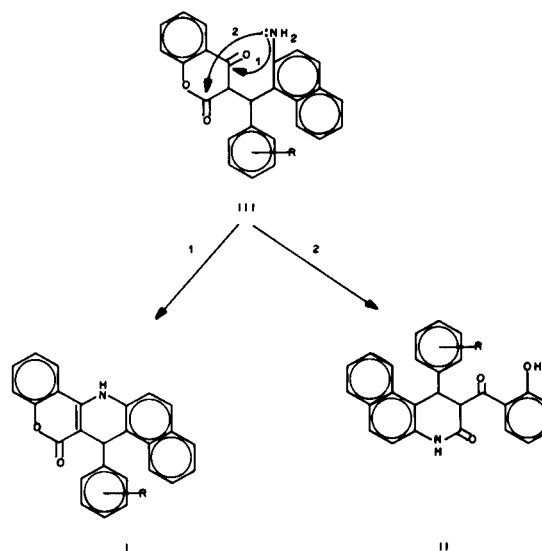
Hydrogen Bond Distances (Å) and Angles (°)

D-H ... A	Position of acceptor atom	D...H	D...A	H...A	< D - H...A
O3-H3a...O2	x,y,z	0.94(6)	2.556(5)	1.81(8)	135(1)
N1-H1...O1	-1 -x, 1-y, 1-z	0.80(5)	2.878(5)	2.10(5)	165(1)

electrophilic centers, *i.e.* the ketone carbonyl and the δ -lactone group. Thus, in principle and in accordance with the general behavior, the nucleophilic 2-naphthylamine

moiety of **III** could interact with either one of these electrophilic centers and give the compounds **I** and **III** (Scheme 3). Further investigation of the reaction of **I** and 2-arylidene-naphthylamines with 1,3-dicarbonyl compounds are presently being carried out.

Scheme 3



EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a Nicolet FT-55X spectrophotometer. The ^1H -nmr spectra were recorded on a Varian FT-80 spectrometer operating at 80 MHz, in hexadeuteriodimethyl sulfoxide solution containing tetramethylsilane as the internal standard with chemical shifts (δ) expressed downfield from TMS. Mass spectra were obtained with a Hewlett Packard 59854-A quadrupole mass spectrometer.

Crystallography.

X-Ray Analysis Data for 3-(2-Hydroxyphenylcarbonyl)-4-(*p*-bromophenyl)-1,2,3,4-Tetrahydro-2*H*-benzo[*f*]quinolin-2-one (**IIh**).

Needle-shape crystals were grown from hexane/dichloromethane, the molecular formula is $\text{C}_{26}\text{H}_{18}\text{NO}_3\text{Br}\cdot\text{CH}_2\text{Cl}_2$, $M_w = 557$, crystal size = 0.14 x 0.14 x 0.44 mm, triclinic, space group, $P\bar{1}$, $Z = 2$, $a = 11.180(3)$, $b = 14.389(3)$, $c = 8.515(2)$ Å, $\alpha = 102.26(2)$, $\beta = 108.88(2)$, $\gamma = 79.19(2)^\circ$, $D_x = 1.47$ g cm $^{-3}$, $F(000) = 564$, μ (Cu $K\alpha$) = 44.85 cm $^{-1}$, L_p and absorption corrections (transmission factors ranged from 0.507 to 1.347) by DIFABS [11], Nicolet P 3/F 4-circle diffractometer with Cu $K\alpha$ radiation (Ni-filtered, $\lambda = 1.54178$ Å), 2θ : ω step scan mode, 3346 reflections measured (2θ max = 110°) of which 3147 were unique and 2500 were considered observed [$I_o > 3\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares (TEXSAN program package [12] on a DEC VAXSTATION II computer). The crystals contained a molecule of rotationally disordered dichloromethane in the asymmetric unit with the carbon atom common to the two orientations (60/40, based on site occupation factors refinement of chlorine atoms). All non-hydrogen atoms were refined with anisotropic thermal parameters and H-atoms with isotropic temperature factors 1.2 Bq those the

bearing atom. Hydrogen fixed at geometrically calculated positions, except for that on N(1), O(3) and those of dichloromethane (major position only) which were located on a difference Fourier map and refined freely. Final R-factors: $R = \Sigma (|F_o| - |F_c|) / \Sigma |F_o| = 0.063$, $R_w = \{ \Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o| \}^{1/2} = 0.103$, $w = (\sigma_{F_o}^2 + 0.12 F_o)$, maximum residual electron density = 0.47 e \AA^{-3} .

The preparation and isolation of compounds **IIa-h** has been described [5]. The physical, analytical and spectra data for synthesized compounds **IIa-h** are recorded on Table 1.

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- [2] Contribution No. 1044 from Instituto de Química, UNAM.
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